9th International Symposium On Photochromism

ISOP’ 2019

September 23-27, 2019
Institut Pasteur - Paris, France

Abstract Book

www.isop2019.conferences-pasteur.org
Conference Prizes will be awarded at the end of the conference, during the Conclusion.
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Dear Participants, Dear Friends and Colleagues,

Welcome to Paris. The organizing committee is pleased and honored to be your host for a week.

For regular participants to ISOP, it is a pleasure to meet again, after the very successful and memorable edition in Shanghai in 2016, perfectly organized by He Tian and his coworkers, and very timely to celebrate Ben Feringa’s Nobel Prize.

The topic of photochromism has grown continuously during the last decades. Concomitantly, ISOP became the place shared by an increasing number of experts of the field. Although most of us are aware of recent scientific results of colleagues through publications, the symposium will be the occasion to hear viva voce some of them, to discuss and to brainstorm face-to-face.

At the same time, any scientific field needs constant renewal. We always expect to meet new comers, from specialties next to us, and also the young generation. This time, the venue is in the world famous Institut Pasteur, and we want to take advantage of this opportunity to open new connections for photochromism.

France hosts ISOP for the third time: in Paris for this ninth edition, in Arcachon in 2004, organized by Jean-Luc Pozzo, and on the island Les Embiez, near Marseille, in 1993 for the first one. It was organized by Robert Guglielmetti, a leading figure of photochromism. Unfortunately he passed away last year, and we will pay a tribute to him.

Finally, Paris is also called the City of Light, and has many attractions. We hope that you can spare some time to enjoy Paris during your stay, especially for those of you who traveled for many hours to share your precious time with us.

Prof Keitaro Nakatani
Scientific Chair of ISOP’2019
In the 1980’s, as professor of organic chemistry, Robert Guglielmetti founded the department of chemistry of the University of the Mediterranean, Marseille (France). Over more than 20 years, until his retirement in 2003, he has been strongly committed to the development of teaching and research in organic chemistry.

His contribution led to the creation of the Organic Chemistry and Molecular Materials Group (GCOM2), a laboratory that gained international recognition for its pioneering work in the field of photochromic molecules and materials. Robert Guglielmetti and his co-workers developed the design and the synthesis of broad ranges of photochromic systems, such as spiropyran, spirooxazine and chromene derivatives and studied their optical properties in collaboration with French and foreign teams. This work has led to important industrial applications, in particular by Essilor.

Concerning his international activity, this period also marks his early initiative to establish close scientific collaborations with Russian chemists. This led to the International Research Network "GDRI PHENICS (PHoto-switchable orgaNIC molecular systems and deviceS)", supported by CNRS, involving scientists from France, China, Japan, Russia and Germany.

In 1993, he organized the first edition of the International Symposium on Organic Photochromism (ISOP) on Les Embiez island in the South of France. This major event fostered the international collaboration on photochromism. The book, which Robert Guglielmetti edited with John C. Crano (PPG Industries) in 1999, "Organic Photochromic and Thermochromic Compounds - Main Photochromic Families", remains a reference in the field. Robert Guglielmetti published more than 220 publications and filled several patents.

Robert Guglielmetti passed away on July 12th, 2018 at the age of 81.

Group photo taken at PHENICS Symposium 2015 in Cargèse (Corsica island, France). Robert Guglielmetti used to live in Corsica since his retirement. He kindly joined the symposium and gave a lecture.
Conference prizes design: VRC

and Céline Khy
(khyceline@gmail.com)

ISOP logo design:

Antoine Ren
(renantoinez@gmail.com)
THANKS TO OUR SPONSORS AND PARTNERS
Chiara Bertarelli received her M.S. in Industrial Chemistry from Università degli Studi di Milano, a post-laurea specialization degree in Polymer Science and Ph.D. in Materials Engineering from Politecnico di Milano, where she is presently Professor in Materials Science and Technology and team leader of the Laboratory of Synthesis of Organic Functional and Nanostructured Materials. Her research interests focus on the design, synthesis and development of new functional materials for smart optics, optoelectronics and flexible electronics. She is principal investigator or local coordinator of several funded projects, including EU Projects in the 6thFP, 7thFP and H2020.

Masahiro Irie received his B.S. and M.S. from Kyoto University and his Ph.D. in radiation chemistry from Osaka University. In 1968, he joined the Faculty of Engineering, Hokkaido University, as a research associate and started his research on photochemistry. He was the faculty member at Osaka University, Kyushu University and Rikkyo University. He has been conducting research on molecular photoswitches for the last 40 years. In the middle of the 1980s he discovered a new class of photochromic molecules, diarylethenes, which undergo thermally irreversible and fatigue resistant photochromic reactions. At present, these derivatives are widely used in functional molecular systems as key elements of photoswitches. His current interest focuses on the development of light-driven molecular crystal actuators and turn-on mode fluorescent diarylethenes for super-resolution fluorescence microscopies.
Ehud Isacoff obtained his B.S. in biology and Ph.D. (1987) in physiology at McGill University (Montreal). He was a postdoctoral fellow (1988-1993) at U.C. San Francisco, and has been a professor at U.C. Berkeley since 1993, where he is currently Evan Rauch Professor of Neurobiology and Director of the Helen Wills Neuroscience Institute. His research interests include the mechanisms of ion channel and neurotransmitter receptor function, the molecular basis of synaptic transmission and plasticity, and the development of neural circuits. He has strongly contributed to open a novel branch of optogenetics that enables synaptic connections to be probed in real time in intact circuits at multiple scales, and has led to an effort to create a treatment for blindness by installing light sensitivity into surviving retinal layers following photoreceptor cell degeneration.

He Tian received his Ph.D. degree from ECUST in 1989. He is an appointed Cheung Kong Distinguished Professor by the Education Ministry of China in 1999. He is a member of the Chinese Academy of Science and a Fellow of the World Academy of Sciences (TWAS) for the advancement of science in developing countries. He serves as Vice President of Chinese Chemical Society since 2019. His current research interests focus on the development of interdisciplinary materials science that determines the electronic and optical properties of materials.
Invited Speakers

Pr. Tsuyoshi ASAHI
Ehime University, Japan
Photochromism of diarylethene nanoparticles under cw-light and nanosecond pulse laser excitation

Dr. David BLÉGER
Evonik Creavis GmbH, Germany
Visible-light-activated polymer networks

Dr. Martial BOGGIO-PASQUA
Paul Sabatier University, France
Towards rationalization and design of improved dihydropyrene photochromism: interplay between theory and experiment

Pr. Olga FEDOROVA
Russian Academy of Sciences, Russia
A multi-state molecular switch based on hetarylphenylethene derivatives

Pr. Cristina FLORS
IMDEA Nanoscience Madrid, Spain
Switchable and selective photodynamic damage of amyloid aggregates: a nanoscale view

Pr. Silvia GIORDANI
Dublin City University, Ireland
From molecular switches to functional nanomaterials

Pr. Gerrit GROENHOF
University of Jyväskylä, Finland
Manipulating molecular photo-chromism with confined light

Dr. Thomas GRUTTER
Strasbourg University, France
Optical control of ATP-gated P2X receptors
**Pr. Hiroshi MIYASAKA**
Osaka University, Japan
*Photosynergetic responses of cycloreversion reaction in 6 \( \pi \) electron systems*

**Dr. Takuya NAKASHIMA**
Nara Institute of Science and Technology (NAIST), Japan
*Control of chiral geometry in bifluorophoric systems with light*

**Dr. Pierre PAOLETTI**
École Normale Supérieure Paris, France
*Illuminating glutamate receptor structure and function using optogenetic pharmacology*

**Pr. Guy ROYAL**
Grenoble Alpes University, France
*Storage and Production of Singlet Oxygen using Photochromic Dimethyldihydropyrene Derivatives*

**Pr. Karola RÜCK-BRAUN**
Technische Universität Berlin, Germany
*Light-controlled interactions of BODIPY-DAE conjugates in solution and linked to the surface of titanium dioxide*

**Dr. Wiktor SZYMANSKI**
University of Groningen, The Netherlands
*Photopharmacology and imaging: towards a theranostic approach*

**Pr. Yanlei YU**
Fudan University, China
*Photodeformable Liquid Crystal Polymers and Bioinspired Soft Actuators*
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<td>Sergey ALDOSHIN</td>
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<td>Ben FERINGA</td>
<td>University of Groningen</td>
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<td>Norbert HAMPP</td>
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<td>Tsuyoshi KAWAI</td>
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<td>Rafał KLAJN</td>
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<td>Alexander Dequan LI</td>
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<td>Keitaro NAKATANI</td>
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<td>Fausto ORTICA</td>
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<td>Jean-Luc POZZO</td>
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<td>He TIAN</td>
<td>ECUST</td>
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<td>Kingo UCHIDA</td>
<td>Ryukoku University</td>
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<tr>
<td>Itamar WILLNER</td>
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<td>Vivian W.W. YAM</td>
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<tr>
<td>Yasushi YOKOYAMA</td>
<td>Yokohama National University</td>
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NATIONAL SCIENTIFIC COMMITTEE

Nicolas BOGLIOTTI  ENS Paris-Saclay
Pierre-Jean CORRINGER  Institut Pasteur
Christophe COUDRET  Université Paul Sabatier
Eléna ISHOW  Université de Nantes
Guillaume LAURENT  ENS Paris-Saclay
Stéphane MAISONNEUVE  ENS Paris-Saclay
François MAUREL  Université Paris Diderot
Rémi MÉTIVIER  ENS Paris-Saclay
Keitaro NAKATANI  ENS Paris-Saclay
Stéphane RIGAUT  Université de Rennes 1
Michel SLIWA  Université de Lille
Joanne XIE  ENS Paris-Saclay
Pei YU  Université Paris-Sud

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Rémi MÉTIVIER  ENS Paris-Saclay
Keitaro NAKATANI  ENS Paris-Saclay
Joanne XIE  ENS Paris-Saclay
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On the Institut Pasteur campus, the "Plan Vigipirate Attentats" is on, so please make sure to have an official ID or passport to enter the campus.

If your registration is fully covered, you will receive your complete congress kit including your badge, the certificate of attendance, the conference programme. Please wear your badge at all time.

If registration was not fully covered, please come directly to the registration desk "on site payment". We accept only payment by cash.

All conference activities except Wednesday afternoon (cultural afternoon and conference dinner) will take place at the Scientific Information Center Auditorium (CIS) on Institut Pasteur campus.

For any query, please contact the conference staff (isop2019@conferences-pasteur.org) or the local organizing committee (isop2019@ens-paris-saclay.fr)

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**REGISTRATION**

**Registration desk opens at 12.30 pm on September 23rd, 2019** in the hall of the CIS Auditorium.

- Opening hours other days: 8.15 am to 10.00 am.
- Congress staff assistance also during coffee breaks, lunches and cocktails.
- A cloakroom is available on registration level. We ask you not to leave any personal belongings unattended in the auditorium.

---

**PLENARY SESSIONS**

Scientific sessions are taking place in the auditorium of the CIS.
Two posters sessions are scheduled during the conference:

- Poster session 1: Tuesday, 24th, 06:45 pm #1 to #45
- Poster session 2: Thursday, 26th, 06:30 pm #46 to #97

NB: Poster numbers are in the program book. Magnets are available on board panel to fix the poster.

All Coffee breaks, lunches buffet and poster-session snacks will be served in the hall of CIS. Access to lunches is limited to participants who are registered.

All attendees are invited to the Welcome Reception which will be held on Monday 23rd, at 7 pm in the hall of the CIS auditorium.

Sponsors and partners will have the pleasure of meeting participants around their stands to discuss and demonstrate their innovative scientific equipment.
Wednesday September 25th is kept free, to enjoy a cultural afternoon in Paris. Three different tours around Paris will be proposed to the participants, organized by the students themselves from PPSM laboratory. They will be pleased to accompany you during these pleasant moments together. Each tour, departing from Institut Pasteur, will last approximatively two hours (3 PM to 5 PM).

**CULTURAL AFTERNOON**

**TOUR n°1 : EIFFEL TOWER**

The iconic symbol of Paris, if not of France: see the Parisian skyline and look at the Parisian suburbs from the top of this architectural masterpiece!

**TOUR n°2 : OPÉRA**

One of the most well-known opera houses in the world since 1661! Discover the majestic architecture and sumptuous interiors of one of the most luxurious buildings in Paris and enjoy the vibrant commercial neighbourhood of Opéra.

**TOUR n°3 : MONTMARTRE**

Picasso, van Gogh, Monet. These are just some of the artists that lived in the artist's district of Paris: Montmartre. Retrace their steps around the neighborhood of Basilica de Sacré Cœur, Moulin Rouge and Pigalle!
Conference dinner on “Le Paris” boat - Port Debilly
Wednesday September 25th, 2019 at 8:00 pm

Entrance in front of 26 avenue de New York, Paris 16 district

**Metro:** Line 9, Iéna station or Alma Marceau (20 minutes from Institut Pasteur)

**Bus:** n°82 Stop Varsovie; n°72 stop Musée Art Moderne Palais de Tokyo

**Public car park:** 10 avenue George V, Paris 8 district

Participants who have registered to this conference dinner will find their voucher together with their name badge in the registration envelope.
Hall of CIS
Welcome Desk, Posters and Sponsors exhibitions, Cocktail, Lunches and Coffee breaks
## Programme at a Glance

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<th>Date</th>
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<th>Event</th>
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<tr>
<td>23-Sep-19</td>
<td>10:00</td>
<td>Introduction</td>
<td>Reception</td>
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<tr>
<td></td>
<td>11:45</td>
<td>H. Miyakawa</td>
<td>G. Berdnikov &amp; C.</td>
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<td></td>
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<td>L. Bernini, K. Nagayama &amp; A. Hricovics</td>
<td>P. Kallay &amp; G.</td>
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<td>14:20</td>
<td>G. Koeppe, R. Castagna, F. Domanin</td>
<td>G. Mariet &amp; A. J.</td>
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<td>15:10</td>
<td>F. Oreadi, A. J., &amp; A. Hricovics</td>
<td>P. Kallay &amp; G.</td>
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<td>G. Mariet &amp; A. J.</td>
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<td>17:00</td>
<td>Closing</td>
<td>Reception</td>
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<tr>
<td>24-Sep-19</td>
<td>10:00</td>
<td>Lunch</td>
<td>Coffee Break</td>
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<td></td>
<td>12:30</td>
<td>Lunch</td>
<td>Lunch - sandwiches</td>
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<td>14:00</td>
<td>Welcome</td>
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<td></td>
<td>14:45</td>
<td>P. Biondi, A. Mammarella, J. Delporte</td>
<td>G. Berdnikov &amp; C.</td>
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<tr>
<td>25-Sep-19</td>
<td>10:00</td>
<td>Lunch</td>
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<tr>
<td>26-Sep-19</td>
<td>10:00</td>
<td>Lunch</td>
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<td>G. Berdnikov &amp; C.</td>
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**Conference Banquet**

19:00 - 21:15

**Poster Session + Snacks**

18:30 - 21:30

**Coffee Break**

19:30 - 20:00

**Poster Session + Wine & Cheese**

19:30 - 21:30
### Session 1

**Chair:** Tsuyoshi Kawai, Nara Institute of Science and Technology, Japan

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<th>Session</th>
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<th>Speaker</th>
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<tr>
<td>1.45 pm</td>
<td><strong>Introduction</strong></td>
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<tr>
<td>2.00 pm</td>
<td>1-IL</td>
<td>Photosynergetic responses of cycloreversion reaction in 6 π electron systems</td>
<td>Hiroshi Miyasaka</td>
<td>Graduate school of Engineering Science, Osaka University, Toyonaka, Japan</td>
</tr>
<tr>
<td>2.20 pm</td>
<td>2-OC</td>
<td>New strategies for photomodulation of Single Molecule Magnets</td>
<td>Lucie Norel</td>
<td>UMR 6226 - CNRS Université de Rennes 1, ISCR, Rennes, France</td>
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<tr>
<td>2.35 pm</td>
<td>3-OC</td>
<td>Enhancing classic indigoid photochromic motifs: from structure-property relationships to pH modulators and back</td>
<td>Benjamin Koeppe</td>
<td>Humboldt-Universität zu Berlin, Germany</td>
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<td>2.50 pm</td>
<td>4-OC</td>
<td>A novel GABA$_\alpha$ receptor ligand derivative that photoswitches with red light</td>
<td>Rossella Castagna</td>
<td>Nanoprobes and Nanoswitches, IBEC - Institute for Bioengineering of Catalonia, Barcelona, Spain</td>
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<tr>
<td>3.05 pm</td>
<td>5-OC</td>
<td>Photoswitching of indolyl fulgimide monolayers on silicon surfaces</td>
<td>François Ozanam</td>
<td>Laboratoire PMC, Ecole Polytechnique-CNRS-IP Paris, Palaiseau, France</td>
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<td>3.20 pm</td>
<td>6-OC</td>
<td>Crawling motion of various azobenzene crystals on surfaces by light irradiation</td>
<td>Yasuo Norikane</td>
<td>National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan</td>
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<tr>
<td>3.35 pm</td>
<td>7-OC</td>
<td>Nanomolar affinity dithienylethene-CB8 host-guest pairs</td>
<td>A. Jorge Parola</td>
<td>Dep. Chemistry, FCT-UNL, Photochemistry and Supramolecular Chemistry Lab., Universidade NOVA de Lisboa, Caparica, Portugal</td>
</tr>
<tr>
<td>3.50 pm</td>
<td>8-IL</td>
<td>A multi-state molecular switch based on hetarylphenylethene derivatives</td>
<td>Olga Fedorova</td>
<td>Laboratory of photoactive supramolecular systems, A. N. Nesmeyanov Institute of Organoelement compounds, Moscow, Russia</td>
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**Coffee Break**

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<td>4.10 pm</td>
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**MONDAY, SEPTEMBER 23$^{\text{TH}}$, 2019**
# Session dedicated to Robert Guglielmetti

**Chairperson:** Jean-Claude Micheau, University Toulouse III, France  
Jean Aubard, Université Paris Diderot, France

## 9 - oc 4.50 pm
**Polychromogenic molecular systems with spiropyran photochromic core**  
Anatoly Metelitsa  
*Institute of Physical Organic Chemistry, Southern Federal University, Rostov On Don, Russia*

## 10 - oc 5.05 pm
**Joining high coloration and fast color fading with photochromic fused-naphthopyrans**  
Paulo Coelho  
*Chemistry, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal*

## 11 - oc 5.20 pm
**Photochromic Core-Shell Nanoparticles**  
Valery Barachevsky  
*Interdepartmental Center of Analytical Researches of the Russian Academy of Sciences, Moscow, Russia Photochemistry Centre, Lab for Photochromic Systems, FSRC «Crystallography and Photonics» RAS, Moscow, Russia*

## 12 - oc 5.35 pm
**Photochromism of new benzopyrans bearing pyridine units**  
Fausto Ortica  
*Department of Chemistry, Biology and Biotechnology, University of Perugia/INFN Perugia, Italy*

## 13 - oc 5.50 pm
**Correct determination of the value and sign of magnetic anisotropy of monomolecular magnets based on Co(II) Kramer’s ions and possibility of their photoinduced change**  
Sergey Aldoshin  
*Institute of Problems of Chemical Physics, Russian Academy of Science, Chernogolovka, Russia*

## 6.10 pm
**Tribute to Robert Guglielmetti**

---

**Welcome reception**  
**7.00 pm - 9.30 pm**
Session 2 (Part 1)  8.30 am - 10.20 pm

Chair: Weihong Zhu, East China University of Science and Technology, China

8.30 am  Welcome

14-KL  Diarelethene Molecular Photoswitches: Recent Progress and Future Prospects
8.45 am  Masahiro Irie
         Research Center for Smart Molecules, Rikkyo University, Tokyo, Japan

15-IL  From molecular switches to functional nanomaterials
9.30 am  Silvia Giordani
         School of Chemical Sciences, Dublin City University, Dublin, Ireland

16-OC  Hemi-indigo photoswitch: ON-OFF fluorescent binder for HIV-1 RNA
9.50 am  Daria Berdnikova
         Universität Siegen, Germany

17-OC  Control of Basic Photochromic Nature of Diarylethenes by Acid
10.05 am  Yasushi Yokoyama
         Graduate School of Engineering Science, Yokohama National University, Japan

Coffee Break  10.20 am - 11.00 am

Session 2 (Part 2)  11.00 am - 12.40 pm

Chair: Denis Jacquemin, University of Nantes, France

18-IL  Towards Rationalization and Design of Improved Dihydropyrene Photochromism: Interplay between Theory and Experiment
11.00 am  Martial Boggio-Pasqua
         Laboratoire de Chimie et Physique Quantiques, IRSAMC, Université Toulouse III – Paul Sabatier, Toulouse, France

11.20 am  Sponsor Presentation
         PPG Industries

19-OC  Photochromic Radical Dimers that Show Heterolytic Bond Clevage
11.25 am  Yoichi Kobayashi
         Department of Applied Chemistry, Ritsumeikan University, Kusatsu, Japan

20-OC  An Innovative approach based on diarelethene film for tailoring the patterns in soft lithography
11.40 am  Andrea Bianco
         Osservatorio Astronomico di Brera, INAF, Merate, Italy

21-OC  Photochromic and Water-soluble Diarylethenes enable Reversible Fluorescent Modulation and Optical Superresolution
11.55 am  Kakishi Uno
         Department of NanoBiophotonics, Max Planck Institute for Biophysical Chemistry, Göttingen, Germany
### Session 3 (Part 1)

**Chair:** Eléna Ishow, Université de Nantes, France

#### 24-IL

**2.00 pm**

**Photodeformable Liquid Crystal Polymers and Bioinspired Soft Actuators**

Yanlei Yu  
*Department of Materials Science and State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai, China*

#### 25-YC

**2.20 pm**

**Donor-Acceptor Dihydropyrenes as Direct One-Photon NIR Photoswitches**

Kristin Klaue  
*Laboratory of Organic Chemistry and Functional Materials, Department of Chemistry, Humboldt Universität zu Berlin, Germany*

#### 26-YC

**2.30 pm**

**Molecular and Supramolecular Tuning of Photochromism**

Lorenzo Casimiro  
*Department of Chemistry, University of Bologna, Italy*

#### 27-YC

**2.40 pm**

**Acceleration of glassy dynamics with azobenzene as a new tool to study the glass transition problem**

Paul Datin  
*NIMBE UMR 3685, CEA, CNRS, Université Paris-Saclay, Gif Sur Yvette Cedex, France*

#### 28-IL

**2.50 pm**

**Photochromism of diarylethene nanoparticles under cw-light and nanosecond pulse laser excitation**

Tsuyoshi Asahi  
*Ehime University, Japan*

#### 29-OC

**3.10 pm**

**Functional Switchable PolyAromatics: a little flexibility in Molecular Cages**

Brigitte Bibal  
*Institut des Sciences Moléculaires, UMR CNRS 5255, Université de Bordeaux, Talence, France*

#### 30-OC

**3.25 pm**

**Theoretical approaches for the modeling of photoactive systems**

Frederic Labat  
*i-CLeHS, Chimie ParisTech, Paris, France*
### Session 3 (Part 2)

**Chair:** Jiro Abe, Aoyama Gakuin University, Japan

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
<th>Speaker</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.20 pm</td>
<td>31-IL</td>
<td><strong>Storage and Production of Singlet Oxygen using Photochromic Dimethylmonohydropyrene Derivatives</strong></td>
<td>Guy Royal</td>
<td>DCM, Grenoble Alpes University, France</td>
</tr>
<tr>
<td>4.40 pm</td>
<td></td>
<td><strong>Sponsor Presentation</strong></td>
<td><strong>IDIL Fibres Optiques</strong></td>
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</tr>
<tr>
<td>4.45 pm</td>
<td>32-YC</td>
<td><strong>A versatile platform for holography based on diarylethenes</strong></td>
<td>Maria Chiara Mantero</td>
<td>Osservatorio Astronomico di Brera, INAF, Merate, Lecco, Italy</td>
</tr>
<tr>
<td>4.55 pm</td>
<td>33-YC</td>
<td><strong>Study of the effect of cocrysalization on a N-salicylideneaniline switch using a combination of periodic and embedded quantum theory methods</strong></td>
<td>Jean Quertinmont</td>
<td>Unité de Chimie Physique Théorique et Structurale, Namur Institute of Structured Matter, University of Namur, Belgium</td>
</tr>
<tr>
<td>5.05 pm</td>
<td>34-YC</td>
<td><strong>Preparation and photochemistry of gold nanoparticles decorated with azobenzene derivative with lipoic acid</strong></td>
<td>Nina Tarnowicz-Staniak</td>
<td>Advanced Materials Engineering and Modelling Group, University of Science and Technology, Wroclaw, Poland</td>
</tr>
<tr>
<td>5.15 pm</td>
<td>35-OC</td>
<td><strong>Photoswitching of glass transition temperatures of azopolymers induces reversible solid-to-liquid transitions</strong></td>
<td>Si Wu</td>
<td>Max Planck Institute for Polymer Research, University of Science and Technology of China, Hefei, China</td>
</tr>
<tr>
<td>5.30 pm</td>
<td>36-OC</td>
<td><strong>Oxygen Evolving Complex in Photosynthesis II, Is it a Photochromic System in Nature? A Theoretical Study</strong></td>
<td>Shinichiro Nakamura</td>
<td>RIKEN, Wako, Japan</td>
</tr>
<tr>
<td>5.45 pm</td>
<td>37-OC</td>
<td><strong>Hydrazone-Based PhotoSwitches and Functional Materials</strong></td>
<td>Ivan Aprahamian</td>
<td>Dartmouth College, Hanover, United States</td>
</tr>
<tr>
<td>6.00 pm</td>
<td>38-OC</td>
<td><strong>DTE-based Cyclometalated Platinum(II) Complexes: Efficient Optical PhotoSwitches</strong></td>
<td>Julien Boixel</td>
<td>Institut des Sciences Chimiques de Rennes, France</td>
</tr>
<tr>
<td>6.15 pm</td>
<td>39-OC</td>
<td><strong>Analysis of vibrational and electronic transitions recorded simultaneously for 3H-naphthopyrans</strong></td>
<td>Gotard Burdzinski</td>
<td>Adam Mickiewicz University in Poznan, Poland</td>
</tr>
<tr>
<td>6.30 pm</td>
<td>40-OC</td>
<td><strong>A “building-block” design for enhanced visible-light switching of diarylethenes</strong></td>
<td>Junji Zhang</td>
<td>NO.130 Meilong Road, East China University of Science and Technology, Shanghai, China</td>
</tr>
</tbody>
</table>

**Poster session 1 - wine and cheese**

6.45 pm - 9.30 pm
### Session 4 (Part 1)

**Chair:** Pierre-Jean Corringer, Institut Pasteur, Paris, France

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>8.30 am</td>
<td><strong>Welcome</strong></td>
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</tbody>
</table>
| 8.45 am | **41-KL** Light-gated synaptic receptors  
Ehud Isacoff  
*University of California Berkeley, United States* |
| 9.30 am | **42-IL** Illuminating glutamate receptor structure and function using optogenetic pharmacology  
Pierre Paoletti  
*Institut de Biologie de l’Ecole Normale Supérieure (IBENS), Ecole Normale Supérieure, Université PSL, CNRS, INSERM, Paris, France* |
| 9.50 am | **43-OC** Covalent hybrid polyoxometalates with optical properties  
Olivier Oms  
*Institut Lavoisier de Versailles, Université de Versailles Saint-Quentin, Université Paris-Saclay, Versailles, France* |
| 10.05 am | **44-OC** Unravelling photoswitching in the confinement of surfaces, thin films and metal organic frameworks with Raman spectroscopy  
Wesley Browne  
*University of Groningen, The Netherlands* |

**Coffee Break**  
10.20 am – 11 am

### Session 4 (Part 2)

**Chair:** Wesley Browne, University of Groningen, The Netherlands

<table>
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<tr>
<th>Time</th>
<th>Event</th>
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</table>
| 11.00 am | **45-IL** Control of chiral geometry in bifluorophoric systems with light  
Takuya Nakashima  
*Division of Materials Science, Nara Institute of Science and Technology (NAIST), Nara, Japan* |
| 11.20 am | Sponsor Presentation  
Safas |
| 11.25 am | **46-OC** Solid materials with tunable reverse photochromism  
Claudio Roscini  
*Nanostructured Functional Materials, Catalan Institute of Nanoscience and Nanotechnology, Barcelona, Spain* |
| 11.40 am | **47-OC** Investigation of photochromic systems under continuous irradiation using soft and hard modelling approaches  
Olivier Devos  
*LASIR, Univ. Lille, CNRS, Villeneuve D’ascq, France* |
| 11.55 am | **48-OC** Photoisomerization Force Moves Matter  
Zouheir Sekkat  
*Rabat design center, University Mohamed V in Rabat; & MAScIR, Rabat, Morocco* |
<table>
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<tr>
<th>Time</th>
<th>Event</th>
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</table>
| 12.10 pm | **Turn-on mode photoswitchable fluorescent diarylethenes: Substituent effect on photoswitching performance**  
Masakazu Morimoto  
*Department of Chemistry, Rikkyo University, Tokyo, Japan* |
| 12.25 pm | **Nonlinear Optical Responses of Photoswitchable Self-Assembled Monolayers: A Computational Approach**  
Frederic Castet  
*Institut des Sciences Moléculaires, University of Bordeaux, Talence, France* |
| 12.40 pm | **Sponsor Conference: Reaxys - or how leveraging chemical knowledge into creativity and innovation**  
Carine Culot Rypens  
*Life Sciences, ELSEVIER, R&D Solutions, Paris, France* |

### Lunch - sandwiches
1.20 pm - 2.00 pm

### Free / Cultural afternoon
2.00 pm - 6.00 pm

### Conference banquet
8.00 pm - 09.30 pm
### Session 5 (Part 1)  
8.30 am - 10.20 pm

**Chair:** Stefan Hecht, Humboldt-Universität zu Berlin, Germany

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Presenter</th>
<th>Affiliation</th>
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<tbody>
<tr>
<td>8.30 am</td>
<td>Welcome</td>
<td></td>
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<tr>
<td>8.45 am</td>
<td>Dynamic Molecular Assembling Photoswitches</td>
<td>He Tian</td>
<td><em>Institute of Fine Chemicals, School of Chemistry &amp; Molecular Engineering, East China University of Science &amp; Technology, Shanghai, China</em></td>
</tr>
<tr>
<td>9.30 am</td>
<td>Manipulating molecular photo-chromism with confined light</td>
<td>Gerrit Groenhof</td>
<td><em>University of Jyväskylä, Finland</em></td>
</tr>
<tr>
<td>9.50 am</td>
<td>Reversible Valence Photoisomerization between Quinoidal and Biradical Forms of Photochromic Phenoxyl-Imidazolyl Radical Complex</td>
<td>Jiro Abe</td>
<td><em>Department of Chemistry, Aoyama Gakuin University, Kanagawa, Japan</em></td>
</tr>
<tr>
<td>10.05 am</td>
<td>Azobenzene derivatives as components of artificial supramolecular pumps</td>
<td>Serena Silvi</td>
<td><em>Dipartimento di Chimica &quot;G. Ciamician&quot;, Università di Bologna, Italy</em></td>
</tr>
</tbody>
</table>

**Coffee Break**  
10.20 am – 11.00 am

### Session 5 (Part 2)  
11.00 am - 12.40 pm

**Chair:** Sergey Aldoshin, Russian Academy of Science, Russia

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Presenter</th>
<th>Affiliation</th>
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</thead>
<tbody>
<tr>
<td>11.00 am</td>
<td>Visible-light-activated polymer networks</td>
<td>David Bléger</td>
<td><em>Evonik Creavis GmbH, Germany</em></td>
</tr>
<tr>
<td>11.20 am</td>
<td>Sponsor Presentation</td>
<td></td>
<td><em>Hamamatsu</em></td>
</tr>
<tr>
<td>11.25 am</td>
<td>Robust norbornadiene-quadricyclane-based molecular photoswitch</td>
<td>Behabitu Tebikachew</td>
<td><em>Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden</em></td>
</tr>
<tr>
<td>11.40 am</td>
<td>Spiro-functionalized diarylethenes and their photoreactivities</td>
<td>Tetsuya Nakagawa</td>
<td><em>Graduate School of Engineering, Yokohama National University, Yokohama, Japan</em></td>
</tr>
<tr>
<td>11.55 am</td>
<td>Manipulating photoblinking in red fluorescent proteins: localization microscopy with ordinary labels and longer tracks in single-particle tracking</td>
<td>Peter Dedecker</td>
<td><em>Chemistry, KU Leuven, Heverlee, Belgium</em></td>
</tr>
<tr>
<td>12.10 pm</td>
<td>Hybrid organic-inorganic polyoxometalates for photoactive switching devices</td>
<td>Rémi Dessapt</td>
<td><em>Institut des Matériaux Jean Rouxel (IMN), University of Nantes - CNRS, Nantes, France</em></td>
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<tr>
<td>Time</td>
<td>Title</td>
<td>Speaker</td>
<td>Institution</td>
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<tr>
<td>12.25 pm</td>
<td>Bidirectional light-induced conductance switching in molecular wires containing a dimethyldihydropyrene unit</td>
<td>Saioa Cobo</td>
<td>DMC, Université Grenoble Alpes, Grenoble, France</td>
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<tr>
<td>12.40 pm - 2.00 pm</td>
<td>Lunch - buffet</td>
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<tr>
<td>2.00 pm - 3.45 pm</td>
<td>Session 6 (Part 1)</td>
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</tr>
<tr>
<td>2.00 pm</td>
<td>Photopharmacology and Imaging: towards a theranostic approach</td>
<td>Wiktor Szymanski</td>
<td>Medical Imaging Center, University of Groningen, University Medical Center Groningen, The Netherlands Stratingh Institute for Chemistry, Faculty of Science and Engineering, University of Groningen, The Netherlands</td>
</tr>
<tr>
<td>2.20 pm</td>
<td>Photochromism in complex environments: theoretical insights</td>
<td>Laura Le Bras</td>
<td>Chimie ParisTech, Institute of chemistry for life and health sciences, PSL university, Paris, France</td>
</tr>
<tr>
<td>2.30 pm</td>
<td>Iminothioindoxyl: a new molecular photoswitch with 100 nm band separation in the visible range</td>
<td>Mark Hoorens</td>
<td>Department of Radiology, Medical Imaging Center, Univeristy Medical Center Groningen, Groningen, The Netherlands</td>
</tr>
<tr>
<td>2.40 pm</td>
<td>Double functional switching from photochromic molecules on surface</td>
<td>Imen Hnid</td>
<td>Université Paris Diderot, Sorbonne Paris Cité, ITODYS, CNRS UMR 7086, Paris, France</td>
</tr>
<tr>
<td>2.50 pm</td>
<td>Covalent Photoswitchable Ligands to Investigate G Protein Coupled Receptor Dynamics</td>
<td>Ranit Lahmy</td>
<td>Institute of Organic Chemistry, University of Regensburg, Germany</td>
</tr>
<tr>
<td>3.00 pm</td>
<td>Irradiation method dependence of photoinduced shape change of diarylethene crystals</td>
<td>Seiya Kobatake</td>
<td>Graduate School of Engineering, Osaka City University, Osaka, Japan</td>
</tr>
<tr>
<td>3.15 pm</td>
<td>Sensitized Photoswitching by Ultrafast Electronic Energy Transfer in a Benzimidazole-Naphthopyran Donor-Acceptor Dyad</td>
<td>Falk Renth</td>
<td>Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Germany</td>
</tr>
<tr>
<td>3.30 pm</td>
<td>An all-photonic full color RGB system based on molecular photoswitches</td>
<td>Joakim Andréasson</td>
<td>Chemistry and Chemical Engineering, Chalmers University of Technology, Goteborg, Sweden</td>
</tr>
</tbody>
</table>
### Coffee Break

3.45 pm – 4.25 pm

### Session 6 (Part 2)

Chair: Anil Kumar, PPG Industries, United States

<table>
<thead>
<tr>
<th>70-IL</th>
<th>4.25 pm</th>
<th>Light-controlled interactions of BODIPY-DAE conjugates in solution and linked to the surface of titanium dioxide</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Karola Rück-Braun</td>
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<tr>
<td></td>
<td></td>
<td>Department of Chemistry, Technische Universität Berlin, Germany</td>
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<thead>
<tr>
<th>71-YC</th>
<th>4.45 pm</th>
<th>Sponsor Presentation</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Malvern</td>
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<table>
<thead>
<tr>
<th>72-YC</th>
<th>4.50 pm</th>
<th>Chiral and achiral azobenzene derivatives bound to DNA template</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Marta Dudek</td>
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<td></td>
<td></td>
<td>Wrocław University of Science and Technology, Wrocław, Poland</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>73-YC</th>
<th>5.00 pm</th>
<th>Photodegradation of diarylethenes: from Photochromic molecules to Combretastatin A-4 analogues</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Anthony Yadykov</td>
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<tr>
<td></td>
<td></td>
<td>Zelinsky Institute of Organic Chemistry, Moscow, Russia</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>74-YC</th>
<th>5.10 pm</th>
<th>Dynamic contrast for micro- and macro-scale multiplexed fluorescence imaging against autofluorescence and ambient light</th>
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<tbody>
<tr>
<td></td>
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<td>Raja Chouket</td>
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<td></td>
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<td>Institut Pasteur, DÉpartement de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, Paris, France</td>
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<thead>
<tr>
<th>75-OC</th>
<th>5.20 pm</th>
<th>Stepwise commutation of multi-modal and multi-level molecular systems based on indolinooxazolidine (BOX) units</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Youssef Aidibi</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Laboratory of Moltech-Anjou, Universite d'Angers, France</td>
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<tr>
<th>76-OC</th>
<th>5.30 pm</th>
<th>Microscopic photomechanical motion of single particles achieved by switching of photon force through photochromic reactions</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Syoji Ito</td>
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<tr>
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<td></td>
<td>Osaka University, Toyonaka, Japan</td>
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</tbody>
</table>

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<thead>
<tr>
<th>77-OC</th>
<th>5.45 pm</th>
<th>Efficient fluorescence photoswitching in photochromic nanoparticles and single crystals</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Tsuyoshi Fukaminato</td>
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<td></td>
<td></td>
<td>Department of Applied Chemistry &amp; Biochemistry, Kumamoto University, Kumamoto, Japan</td>
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<thead>
<tr>
<th>78-OC</th>
<th>6.00 pm</th>
<th>Light-Driven Chiral Switching of Supramolecular Metallacycles with Photoreversibility</th>
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<tbody>
<tr>
<td></td>
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<td>Weihong Zhu</td>
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<td></td>
<td></td>
<td>Institute of Fine Chemicals, East China University of Science and Technology, Shanghai, China</td>
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<tr>
<th>78-OC</th>
<th>6.15 pm</th>
<th>When 2D materials meet photochromic molecules</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Sara Bonacchi</td>
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<tr>
<td></td>
<td></td>
<td>Dept of Chemical Sciences, University of Padova, Italy</td>
</tr>
</tbody>
</table>

### Poster session 2 + snacks

6.30 pm - 9.30 pm
## Session 7 (Part 1)

**Chair:** Kingo Uchida, Ryukoku University, Japan

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<td>8.30 am</td>
<td><strong>Welcome</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.45 am</td>
<td><strong>Rule material properties through photochromism: towards optical elements and concept devices</strong></td>
<td>Chiara Bertarelli</td>
<td>Politecnico di Milano, Italy</td>
</tr>
<tr>
<td>9.30 am</td>
<td><strong>Switchable and selective photodynamic damage of amyloid aggregates: a nanoscale view</strong></td>
<td>Cristina Flors</td>
<td>Madrid Institute for Advanced Studies in Nanoscience (IMDEA Nanoscience), Madrid, Spain</td>
</tr>
<tr>
<td>9.50 am</td>
<td><strong>Photoinduced Macroscopic Motion of Diarylethene Assembly by Combination of Photochromism and Lower Critical Solution Temperature (LCST) Behavior</strong></td>
<td>Kenji Matsuda</td>
<td>Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan</td>
</tr>
<tr>
<td>10.05 am</td>
<td><strong>New All-Visible Azo Photoswitches for Use in Aqueous Media</strong></td>
<td>Yves Garmshausen</td>
<td>Laboratory of Organic Chemistry and Functional Materials, Department of Chemistry, Humboldt-Universität zu Berlin, Germany</td>
</tr>
</tbody>
</table>

### Coffee Break

10.20 am - 11.00 am

## Session 7 (Part 2)

**Chair:** Fausto Ortica, University of Perugia/INFN Perugia, Italy

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</thead>
<tbody>
<tr>
<td>11.00 am</td>
<td><strong>Ion-modulated photochromic rearrangements of spirobenzopyrans bearing azole moiety</strong></td>
<td>Anatoly Chernyshev</td>
<td>Laboratory of photochemistry and luminescence, Institute of Physical and Organic Chemistry at Southern Federal University, Rostov On Don, Russia</td>
</tr>
<tr>
<td>11.15 am</td>
<td><strong>Reversible photoisomerization within a 2D self-assembled layer of diarylethene molecules</strong></td>
<td>Marion Cranney</td>
<td>Institut de Science des Matériaux de Mulhouse IS2M, CNRS, Mulhouse, France</td>
</tr>
<tr>
<td>11.30 am</td>
<td><strong>Highly Efficient Electrocatalytic Synthesis of Azobenzenes from Nitroaromatic Derivatives Using Sml₂</strong></td>
<td>Mohamed Mellah</td>
<td>ICMMO, Université Paris Sud/Paris Saclay, Orsay, France</td>
</tr>
<tr>
<td>11.45 am</td>
<td><strong>Photo-Switchable Photocytotoxicity of Diarylethenes</strong></td>
<td>Kingo Uchida</td>
<td>Department of Materials Chemistry, Ryukoku University, Otsu, Japan</td>
</tr>
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9th International Symposium On Photochromism, Institut Pasteur, Paris - 2019
## Spectroscopic applications of quantum cascade laser frequency combs

**Andreas Hugi**  
IRsweep AG, Stäfa, Switzerland

**Optical control of ATP-gated P2X receptors**

**Thomas Grutter**  
Conception et application de molécules bioactives, University of Strasbourg, UMR 7199 CNRS, France

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**Conclusion**

**Conference Prizes**

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### Lunch - sandwiches

12.50 pm - 2.00 pm

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### Satellite workshop on NANOSYNERGETICS (Part 1)

2.00 pm - 3.45 pm

**Chair:** Christophe Coudret, Université Paul Sabatier, France

#### Synthesis and electro-induced isomerization of terarylene 7-mer on a beta-cyclodextrin as a photo- and nano-synergetic molecular system

**Tsuyoshi Kawai**  
Division of Materials Science, Nara Institute of Science and Technology, Nara, Japan

#### Luminescence of lanthanide(III) beta-diketonate complexes under mechanical stimulation

**Yuichi Hirai**  
PPSM, ENS Paris-Saclay, Paris, France

#### Photoinduced Reentrant Transition and Thermal Stepwise Transition of Supramolecular Assembly Composed of Amphiphilic Diarylethene

**Yasunobu Kotani**  
Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan

#### NIR Light-Responsive Negative Photochromic Compounds Based on 1,1’-Binaphtyl-Bridged Imidazole Dimer

**Yuki Inagaki**  
Department of Chemistry, Aoyama Gakuin University, Kanagawa, Japan

#### Fluorescence modulation and uncommon photokinetics with photochromic-fluorescent nanosystems

**Nicolas Fabre**  
PPSM, ENS Paris-Saclay, Cachan, France

#### Real-time Imaging of evaporative crystallization process of dibenzooylmethanato boron difluoride complexes by hyperspectral camera

**Fuyuki Ito**  
Department of Chemistry, Institute of Education, Shinshu University, Nagano, Japan

#### Multimodal time-resolved spectroscopy of ultra-small upconverting nanoparticles

**Aude Bouchet**  
LASIR, Université de Lille, Villeneuve D’ascq, France
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<th>Time</th>
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<td>96-oc 3.30 pm</td>
<td>Photo/Redox Control of π-Dimerization as a Trigger for Molecular and Supramolecular Metamorphism</td>
<td>Denis Frath</td>
<td>Laboratoire de Chimie, ENS Lyon, CNRS UMR 5182, Lyon, France</td>
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<td>3.45 pm</td>
<td>Coffee Break</td>
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<td>4.25 pm</td>
<td>Satellite workshop on NANOSYNERGETICS (Part 2)</td>
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<td>Chair: Kenji Matsuda, Kyoto University, Japan</td>
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<td>97-oc 4.25 pm</td>
<td>Cyclization reaction dynamics of an inverse type diarylethene derivative in solution and solid phases</td>
<td>Hikaru Sotome</td>
<td>Department of Engineering Science, Osaka University, Toyonaka, Osaka, Japan</td>
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<tr>
<td>98-oc 4.40 pm</td>
<td>Recent evolutions in terarylene scaffolds using thienothiophene and benzothiazole substituents</td>
<td>Colin Martin</td>
<td>International Collaborative Laboratory for Supraphotoactive Systems, NAIST-CEMES, Toulouse, France</td>
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<tr>
<td>99-yc 4.55 pm</td>
<td>Photochromic molecules and plasmonic materials for new reversible switchable devices</td>
<td>Céline Jégat</td>
<td>PPSM Laboratory, Cachan, France</td>
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<tr>
<td>100-yc 5.05 pm</td>
<td>Specific electrocyclic reaction dynamics of a dithiazolylarylene derivative</td>
<td>Tatsuhiko Nagasaka</td>
<td>Graduate school of Engineering Science, Osaka University, Toyonaka, Japan</td>
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<td>101-yc 5.15 pm</td>
<td>Irreversible photo-isomerisation of arene-Ru complexes bearing azobipyridine-derived ligands</td>
<td>Jonathan Long</td>
<td>PPSM, ENS Paris-Saclay, Cachan, France</td>
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<td>102-yc 5.25 pm</td>
<td>Red-Light Driven Photochromic Molecule by Using Triplet Fusion</td>
<td>Ayako Tokunaga</td>
<td>School of Science and Engineering, Aoyama Gakuin University, Sagamihara, Japan</td>
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<td>103-yc 5.35 pm</td>
<td>First study of the photodynamics of a hydrozoan photo-switchable fluorescent protein: existence of different switching mechanisms</td>
<td>Lucas Martinez Uriarte</td>
<td>LASIR, CNRS Univ Lille UMR 8516, Villeneuve D'ascq, France</td>
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<td>104-yc 5.45 pm</td>
<td>Fluorescent response to forces at the nanoscale of photo-polymerized polydiacetylenes</td>
<td>Luca Polacchi</td>
<td>PPSM - ENS Paris Saclay, Cachan, France</td>
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<td>105-oc 5.55 pm</td>
<td>Photo- and Electrochromic Molecular Switch Based on Aryl-Bridged Radical Complexes</td>
<td>Katsuya Mutoh</td>
<td>Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, Tokyo, Japan</td>
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<tr>
<td>106-oc 6.10 pm</td>
<td>Photo- and Electro-Control of NIR Luminescence</td>
<td>Stéphane Rigaut</td>
<td>Institut des Sciences Chimiques de Rennes, Université de Rennes 1, France</td>
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ABSTRACTS: ORAL SESSIONS
Photosynergetic responses of cycloreversion reaction in 6 π electron systems

H. Miyasaka
Graduate school of Engineering Science, Osaka University, Toyonaka, Japan

Molecules in the electronic excited state take important roles in various photo-functional systems. Three general restrictions, however, limit the efficient utilization of light energies. First, large molecules in higher excited states with more than 10–20 atoms usually very rapidly relax to lower electronic states (Kasha’s rule) and subsequent vibrational relaxation leads to the formation of the thermally equilibrated S1 state in the condensed phase. During these relaxation pathways, some portion of the absorbed photon energy is diminished. Second, a large number of the molecules excited in assemblies undergo fast annihilation and only a small number of excited state molecules can remain, leading to the loss of the number of photons absorbed in the system. In addition, the electronic state accessible through the one-photon absorption is limited by the optical selection rule and we cannot access to various dark electronic excited states of molecules. These three restrictions have been limiting the photochemistry in “one-photon one-molecule responses in the lowest electronic state”. Research outcomes beyond these restrictions have been recently reported by several groups including us in the field of photochemistry, such as specific photochemical reactions in higher excited state attained by multiple excitation and multiphoton absorption, cooperative responses of multiple excitons/excited states in molecular assemblies, modulation of electronic states via the strong-coupling between light and matters, and so on. Based on these backgrounds, we have been conducting the project “Photosynergetics", as a research program supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan, since 2014, through the collaborative investigations so as to develop and advance excitation methods and molecules/molecular assemblies that can overcome these three restrictions.

In the present talk, we will introduce several topics on photochromic systems relating to Photosynergetic project, such as multiple and multiphoton excitation responses in photochromic molecules, one-color control of both reactions in photochromic systems, and so forth.
New strategies for photomodulation of Single Molecule Magnets

L. Norel, B. Le Guennic, K. Bernot, S. Rigaut

1UMR 6226 - CNRS Université de Rennes 1, ISCR, Rennes, France 2Université de Rennes 1, Rennes, France

For potential applications in information storage devices, Single Molecule Magnets (SMM) are remarkable candidates because they are able to retain magnetic information at the level of one molecule, the smallest imaginable magnetic domain. The switching of such SMM through an external stimulus is extremely promising for the preparation of tristable or even multistable systems, then providing new paradigms for information storage with enhanced density. For this switching, the use of a redox input has already been explored, unlike light switching that remains largely untapped and mostly limited to very few transition metal based systems showing spin crossover behavior.[1]

Our strategy rely on the incorporation of precisely designed photochromic ligands into lanthanide based complexes, nowadays recognized as the best systems in the field of SMM, with record magnetic blocking temperatures close to liquid nitrogen temperature. In this presentation, we will show dysprosium(III) complexes with strong magnetic anisotropy in the merocyanine form [2] and original partial (trans to cis) isomerization under visible light.[3] We will also introduce a supramolecular approach to photoswitchable SMM in which ligands possessing a robust photochromic behavior are assembled with dysprosium(III) fluoride complexes with very high magnetic anisotropy [4], as shown in the figure below.

References:


Enhancing classic indigoid photochromic motifs: from structure-property relationships to pH modulators and back

B. Koeppe, V. Schröder, S. Rühl, F. Römpp
Humboldt-Universität zu Berlin, Germany

Close indigo derivatives, such as thioindigos and N-substituted indigos are visible light $trans\leftrightarrow cis$ isomerizing photoswitches with excellent spatial control characteristics: they are especially well suited to dictate the distance and relative orientation of attached molecular fragments,\cite{1} i.e. to enforce or prevent intra- and/or intermolecular interaction of such fragments and other species (Fig. 1).

Functional molecules with such features could be interesting e.g. for applications in solution state biological systems. Nonetheless, the classic thioindigo motif has rarely found inclusion in functional molecules, apparently due to issues of low solubility and sensitivity to quenching by protic media. Beginning in the mid 1960’s, the phototropic properties of these motifs were studied quite intensively by several groups for at least two decades. But systematic efforts towards performance enhancements aiming at the design of functional molecules were rather limited. We could show rather recently that appropriate electronic tuning and solubilizing groups may lead to thioindigos soluble and efficiently operating in aqueous media.\cite{1} As a demonstration of the concept of steric control, we also developed a photoswitch forming a strong intramolecular hydrogen bond specifically in one isomer and found it to be a prototype for an unusually effective pH modulator that, unfortunately suffers from poor photochemical performance in protic media (Fig. 2).\cite{2}

In contrast, particularly fast and robust switching has been found in $N,N'$-di-tert-Boc-indigos which also served as a model class for which substituent and medium effects on spectral and photochemical behavior as well as thermal reversion have been studied experimentally and computationally.\cite{3} Thus, several clear structure-property relationships could be established (Fig. 3).

References:

A novel GABA<sub>A</sub> receptor ligand derivative that photoswitches with red light

R. Castagna<sup>1,2</sup>, C. Matera<sup>1,2</sup>, H. Lee<sup>1</sup>, G. Maleeva<sup>1</sup>, P. Bregestovski<sup>3</sup>, P. Gorostiza<sup>1,4</sup>

<sup>1</sup>Nanoprobes and Nanoswitches, IBEC - Institute for Bioengineering of Catalonia, Barcelona, Spain
<sup>2</sup>CIBER-BBN, Network Biomedical Research Center in Bioengineering, Biomaterials, and Nanomedicine, Madrid, Spain
<sup>3</sup>Institut de Neurosciences des Systèmes, Aix-Marseille Université, Marseille, France
<sup>4</sup>Catalan Institution for Research and Advanced Studies, Barcelona, Spain

A balance between excitatory and inhibitory neurotransmission occurs in the central nervous system of mammals. Inhibition is mediated by two fast transmitters, glycine and gamma-aminobutyric acid (GABA). GABA released from presynaptic terminals activates ligand-gated ion channel receptors (GABA<sub>A</sub>R), which are present in all organisms with a neurons system. GABA<sub>A</sub>Rs constitute a key target for pharmacology since many neurodegenerative and age-related diseases result in changes in pre- and post-synaptic GABAergic and glycinergic inhibitory neurotransmission.

Drugs acting as positive allosteric modulators (PAM) or agonists of GABA<sub>A</sub>R have been effectively used as sedatives, anxiolytics, hypnotics and anticonvulsants to treat the symptoms of epilepsy, migraines and used for anesthesia during surgery. However, when applied systemically, these drugs give rise to numerous side effects and cause addiction.

The possibility to spatiotemporally control neuronal activity with light-regulated drugs is a powerful capacity of photopharmacology. This emerging field of pharmacology allows mimicking the complex activity patterns of cell-to-cell communication thanks to the use of photoswitchable drugs and controlled light stimulation.

A key step forward in the field is the possibility to address the photochromic conversion in the drug molecule with a low energy light, which is less scattered in tissue and can penetrate deeper in the body, and in the brain in particular. In this regard, a proper molecular structure should be designed to ensure a photoconversion with light in the region of red and infrared light, that effectively enabling remote photoswitching by non-invasive illumination. Here, we will present the molecular design of a novel GABA<sub>A</sub>R ligand derivative displaying photochromic properties with red light, and will discuss the synthetic procedure, the characterization of its chemical and photoisomerization properties in polar and aqueous solvents, and its photopharmacological properties.
Photoswitching of indolyl fulgimide monolayers on silicon surfaces

S. Klaes¹, C. Henry-De-Villeneuve¹, F. Ozanam¹, C. Barta², K. Rück-Braun², R. Métivier³, P. Allongue¹

¹Laboratoire PMC, Ecole Polytechnique-CNRS-IP Paris, Palaiseau, France ²Institut für Chemie, Technische Universität Berlin, Germany ³PPSM, ENS Cachan-CNRS-Université Paris-Saclay, Cachan, France

Photochromic molecules change their conformation upon absorption of electromagnetic radiation. Grafting them at a solid surface opens attractive possibilities for designing (multi)functional surfaces, but may also have a significant impact on the switching kinetics. Here, this impact is quantitatively assessed by comparing photo-stationary states, photo-isomerization cross section and quantum yield of indolyl fulgimide compounds dispersed in solution to those of the same compounds covalently immobilized as a monolayer on a functionalized Si(111) surfaces. The photo isomerization kinetics of fulgimide compounds in solution is monitored using UV-Vis spectroscopy and that of monolayers by quantitative FTIR spectroscopy [1]. For monolayers, polarized photoexcitation has been used in order to separate local-field effects from other surface effects [2].

The isomeric composition at photo-stationary states is found to be similar in solution and at surfaces and reproducible for successive photoswitching cycles. It is also independent on the fulgimide surface concentration in the monolayer when the latter is lower than \( \sim10^{14} \text{ cm}^{-2} \). On the opposite, a strong influence of the polarization of the excitation light (s-polarized or p-polarized) is found on the photo-isomerization cross section \( \sigma (\sigma_s \ll \sigma_p < \sigma_{sol}) \), evidencing surface effects on the photoswitching kinetics. Accounting for the local excitation electromagnetic field indicates that the fulgimide groups adopt a preferential tilt angle with respect to the surface normal and that their transition dipole is almost parallel to the surface plane for either C or E/Z isomers. DFT indicates that this orientation corresponds to photochromic groups lying in contact with the underlying monolayer. The close similarity of the orientation between the open and closed form of the molecules indicates that the majority open form is the E form. The interaction between the photochromic groups and the underlying monolayer plausibly explains why the photo-isomerization quantum yield is found nearly twice lower at the surface than in the solution.

2. Klaes, S. et al., Influence of Light Polarization on Photocommutation of Fulgimide Monolayers on Surfaces, J. Phys. Chem. C, Just Accepted Manuscript (DOI: 10.1021/acs.jpcc.9b00836).
Crawling motion of various azobenzene crystals on surfaces by light irradiation

Y. Norikane¹², K. Saito¹, M. Hayashino²¹, M.I.O. Ohnuma¹, M. Nakano¹, N. Takada¹
¹National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan ²Department of Chemistry, University of Tsukuba, Tsukuba, Japan

Nature has developed fascinating molecular systems that exhibit various type of motion such as translational, rotational, and deformational motions. Among these motion, the translational motion has been of interest to researchers, because this motion is essential for living organisms for finding food and escaping from an enemy. For example, amoeba exhibits a crawling type of motion that involves the formation of semisolid (gel) in the front, while the gel becomes sol at the opposite end of the cell. The motion of natural objects has inspired scientists to attempt the design and fabrication of novel mimicking systems that produce externally powered or self-propelling motion. Molecular-sized to centimeter-sized objects have been proposed, whose motion is produced by diverse energy sources, such as chemical, thermal, electric, electromagnetic, and light energy. Light is a powerful energy source and an excellent tool for triggering and controlling the direction of motion.

Recently, we found the crawling motion of crystals of simple azobenzenes such as azobenzene and 3,3'-dimethylazobenzene on a glass surface (Figure). The motion is directional and continuous when irradiated simultaneously with two different wavelengths (365 and 465 nm) [1]. This method is simple as crystals move on a solid surface using a light-emitting diodes or Hg lamp as light sources in a fixed position. It is presumed that the motion is driven by crystallization and melting at the front and rear edges of the crystal, respectively, via photochemical conversion between the crystal and liquid phases induced by the trans-cis isomerization of azobenzenes. Here we would like to report the overview of the crawling motion of crystals and our recent results in two topics: 1) The effect of various solid surfaces upon the motion of the crystals [2], 2) The motion of azobenzenes, having short lifetime of the cis-isomer, induced by a single visible light source [3].

Nanomolar affinity dithienylethene-CB8 host-guest pairs

P. Ferreira, P. Máximo, N. Basílio, A. Parola
Dep. Chemistry, FCT-UNL, Photochemistry and Supramolecular Chemistry Lab., Universidade NOVA de Lisboa, LAQV-REQUIMTE, Caparica, Portugal

Diarylethenes (DAE) have attracted considerable interest owing to their outstanding photochromic properties and photoswitching ability. [1] On the other hand, cucurbit[n]urils (CBn) are macrocyclic receptors that display high affinity for complementary guest molecules in aqueous solution. In particular, CB8 has the ability to form ternary complexes with applications in catalysis and supramolecular polymers. [2] On our search for photorheological fluids, [3,4] we have engaged in the design of supramolecular polymers based on diarylethenes containing terminal donor-acceptor moieties to be polymerized through CB8-assisted ternary complexes. In previously reported CBn:DAE complexes, the macrocycle binds to peripheral groups rather than the photoactive unit, precluding significant differences in the stability of the complexes upon switching between the open and closed forms. [5]

In this communication, a series of DAE-CB8 host-guest pairs with 1:1 association constants close to \(10^{10}\text{M}^{-1}\) will be reported. A first example of these systems has recently been published. [6] A water-soluble photochromic bis(pyridinium)dithienylethene derivative, 1, forms 1:1 host:guest complexes with CB8. The closed isomer 1c shows nanomolar affinity for the macrocyclic receptor while the open isomer 1o shows a binding constant that decreases by two orders of magnitude. This differential binding affinity together with the photoswitchable properties of diarylethenes confers light-responsive properties to the host-guest system allowing remote control over the association/dissociation process in the nanomolar concentration range. It can also be employed in ternary systems to photoregulate the complexation of high-affinity guests 2-8 through competitive binding and assembly/disassembly of supramolecular polymers.

FCT-MCTES is acknowledged though project PTDC/QUI-QFI/30951/2017.

2. H. Zou, J. Liu, X. Li, X. Li, X. Wang, Small 2018, 14, 1802234
A multi-state molecular switch based on hetarylphenylethene derivatives

O. Fedorova\textsuperscript{1,2}, D. Berdnikova\textsuperscript{3}, P. Panchenko\textsuperscript{1,2}, Y. Fedorov\textsuperscript{1}

\textsuperscript{1}Laboratory of photoactive supramolecular systems, A. N. Nesmeyanov Institute of Organoelement compounds, Moscow, Russia
\textsuperscript{2}D. Mendeleev University of Chemical Technology of Russia, Moscow, Russia
\textsuperscript{3}Department Chemie-Biologie, Organische Chemie, Universität Siegen, Germany

Multiphotochromic systems represent an emerging field of photoactive compounds possessing high practical importance for creation of miniature molecular devices, logic gates, and high-density optical memory. Stilbenes and their substituted derivatives have attracted significant attention for their wide range of useful properties. Combination of stilbene with functional molecules results in the obtaining of hybrid multistate molecular systems. For example chromene–styryl dye hybrid (exists in two different modes. In the free state, the molecule undergoes efficient photoinduced energy and electron transfer between chromophores and, for this reason, exhibits virtually no photochromism (the “transfer” mode). Protonation switches the hybrid to the dual photochromic mode, in which both units demonstrate characteristic photochemical trans-formations, i.e. ring opening/closure reaction of the chromene residue and reversible E-Z-isomerization of the styryl dye fragment.

In the report the hybrid photoactive compounds on the basis of heterostibenes linked to the fluorophores, photochromes are presented. For these systems the analysis of the possible photoinduced processes competing with the photochromic reaction is performed.

Acknowledgment: OAF thanks Russian Science Foundation, grant № 17-73-30036.
Polychromogenic molecular systems with spiropyran photochromic core

A. Metelitsa, A. Chernyshev, N. Voloshin
Institute of Physical Organic Chemistry, Southern Federal University, Rostov On Don, Russia

Photochromic transformations is limited mainly to a few reaction mechanisms. The principal ones include cis-trans isomerization, excited-state intramolecular proton transfer (ESIPT) or electron (charge) transfer, and $2p + 2p + 2p$ pericyclic reactions. The latter mechanism (1,6-electrocyclization) is at the root of photo- and thermochromic behavior of spiropyrans [1]. The scheme of SPPs photochromic reactions includes the stages related to the reversible processes of Cspiro-O bond rupture in cyclic forms (A) and cis-trans isomerizations to the merocyanine forms (B) [2]. Cyclic and merocyanine isomers have significantly different physicochemical properties and, in particular, absorption spectra.

On the other hand, the reaction of opening of the pyran cycle is very sensitive to various external influences such as light, temperature, pressure, etc. allowing them to exhibit a variety of chromogenic properties. Polychromogenic media possessing two or more chromogenic properties open new perspectives for application of the smart materials constructed on their basis. In particular, photochromic properties and fluorescence have allowed proposing reversible media for 3D data storage. Presence of photochromic and ionochromic properties of the medium predetermines obtaining of photodriven chemosnsors for metal ions. The spiropyrans are promising for development of a polychromogenic medium.

The study was carried out at the expense of the grant of the Russian Science Foundation (project No.19-13-00185).

Joining high coloration and fast color fading with photochromic fused-naphthopyrans

C. Sousa, P. Coelho
1Chemistry Center - Vila Real, Portugal 2Chemistry, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal

Naphthopyrans are the main photosensitive compounds used to create photochromic lenses that darken under sunlight. UV irradiation of common uncolored naphthopyrans for less than 1 minute, at room temperature, generates two thermally unstable colored species (TC and TT) that fade with different speed to the initial uncolored state. The formation of a variable amount of the slow fading TT isomer ensures a high color intensity, under UV, but originates a globally slow color fading in the dark, with a persistent residual color that can extend the complete discoloration of the lens to near 8 min.

The linkage of the naphthalene core to the pyran double bond provides photochromic fused-naphthopyrans that can only form the fast fading TC isomer, under UV, and thus affords a fast and complete color fading in the dark. This structural change is very effective to suppress the undesired residual color but it also confers strain to the molecule which can lead to a too fast color fading affording a very slow concentration of the colored species and thus a weak coloration.

We present a new uncolored photochromic fused-naphthopyran that can be easily prepared from naphthols and but-2-yn-1,4-diols, in one step, can be dispersed in soft polymers (0.8%), provide an intense orange coloration under UV irradiation (or sunlight) (Abs=0.7) and return completely to the uncolored state in just 2 min, at room temperature. The use of this compound allows a faster adaptation of the material’s coloration to the surrounding UV-light intensity, without compromising the color intensity, an important feature to create high performance photochromic ophthalmic lenses.

Acknowledgment:
The authors acknowledge FCT (Portugal’s Foundation for Science and Technology) and COMPETE for financial support through the research project PTDC/QUI-QOR/28532/2017.
Photochromic Core-Shell Nanoparticles

V. Barachevsky
Interdepartmental Center of Analytical Researches of the Russian Academy of Sciences, Moscow, Russia
Photochemistry Centre, Lab for Photochromic Systems, FSRC «Crystallography and Photonics» RAS, Moscow, Russia

The results of own spectral-kinetic studies in the field of nanophotochromism of hybrid compounds of the core–shell type are generalized. Properties of photochromic nanoparticles of this type based on photochromic spirocompounds (spiropyans and spirooxazines), chromenes as well as diarylethenes, using nanoparticles of noble metals (Ag and Au), diamonds, graphene and its oxide, fullerenes, and quantum dots, are considered. Preparation methods of photochromic nanoparticles have been developed.

Comparative spectral-kinetic study of their photochromic properties in solution, polymer and solid-phase layers has been carried out. The dependence of the nature of the interaction (chemical or physical) of molecules of photochromic compounds with inorganic nanoparticles, depending on their functionalization, has been found. It is shown that the interaction of spiropyran molecules with the surfaces groups of silica and diamonds nanoparticles leads to the formation of the proton complexes. The surfaces of nanoparticles of graphene and its oxide in the presence of photochromic compounds from the class of diarylethenes and spirooxazines are functionalized by thiol-substituted photochromic molecules. The differences in the properties of photochromic nanoparticles based on fullerene with chemically bound spiropyran molecules containing substituents of different nature have been revealed. Using quantum chemical methods, the presence of photochromism was explained only for nanoparticles with nitro-substituted spiropyran fragments.

The phenomenon of inductive-resonant energy transfer (the FRET-effect) in photochromic nanoparticles has been investigated. Using this phenomenon, the possibility of creating devices that provide photo-induced reversible modulation of the emission of quantum dots is shown.

Solid-phase nanostructured optical elements that can simultaneously reversibly change their absorption, luminescent, and electric properties during photoinduced transformations of photochromic fragments have been designed for the first time using diarylethenes, organic fluorophores (oxazine, phenalenon in the presence of Ag nanoparticles), and inorganic fluorophores (CdSe/ZnS quantum dots).

Acknowledgments: The study was performed under support of Russian Foundation for Basic Research (project No. 18-53-00010 and No. 18-03-00650).
Photochromism of new benzopyrans bearing pyidine units

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1Department of Chemistry, Biology and Biotechnology, University of Perugia, Italy 2INFN Perugia, Perugia, Italy 3Institut Lavoisier de Versailles, UMR CNRS 8180, UVSQ, Université Paris-Saclay, Versailles, France

The photochromism of a series of newly synthesized benzopyrans bearing a pyridine unit (Fig.1) has been studied in n-hexane, toluene and acetonitrile solutions.

![Fig. 1. Structures of the benzopyrans investigated.](image)

The four compounds exhibit a similar mechanism of reaction upon UV irradiation, that involves consecutive transformation of the benzopyran into the thermally labile transoid-cis (TC) and thermally stable transoid-trans (TT) coloured isomers. However, while the naphthopyran-based molecules show a relatively fast thermal decay of the TT forms, in the case of the CN-Me compounds the TT isomers are by far the most abundant coloured species produced upon UV photocolouration and exhibit a notable long-term stability in the dark.

Spectrokinetic analyses allowed quantitative absorption spectra, quantum yields for visible photobleaching and rate constants of thermal bleaching to be determined. For NaPy and NaPhPy a systematic study as a function of temperature also enabled measuring the activation parameters of the thermal bleaching process for TC. In the cases of CN-Me-Py and CN-Me-PhPy, the long-term stability of the TT isomers allowed their separation by HPLC and selective visible photobleaching and thermal bleaching analyses of the various coloured species to be performed.

As a general behavior observed for the two series, the most promising results were found with the molecules bearing a simple pyridine moiety, namely NaPy and CN-Me-Py. These compounds exhibited the highest colourability in the two series and, for CN-Me-Py in toluene, a very high percentage of conversion of the initial benzopyran into the TT forms, equal to 80%.
Correct determination of the value and sign of magnetic anisotropy of monomolecular magnets based on Co(II) Kramer's ions and possibility of their photoinduced change

S. Aldoshin*, D.V. Korchagin¹, A.V. Palii¹-², K.V. Bozhenko¹, E. YA. Misochko¹
¹Institute of Problems of Chemical Physics, RAS, Chernogolovka, Russia ²Institute of Applied Physics, Chisinau, Moldova

The structure and magnetic properties of single ion magnets (SIM) related to Co(II) complexes have been considered. Specific features of the structure and magnetic anisotropy of Co complexes and the influence of reversible switching of the ligand surrounding on Co coordination and slow magnetic molecule relaxation are under consideration.

Particular attention has been paid to the results of experiments and theoretical modeling of hexacoordinated complexes of Co(II) with negative and positive magnetic anisotropy. To analyze magnetic anisotropy of these complexes, additional experimental techniques, such as SQUID magnetometry, Multi High Frequency EPR Spectroscopy, and Frequency-Domain Fourier-Transform THz-EPR Spectroscopy have been used, as well as theoretical modeling using parametrized Griffith's Hamiltonian with parameters obtained from ab initio calculations. As follows from the analysis, magnetic anisotropy of these complexes is mainly triaxial, with different signs of axial components. Independently on the sign of the axial anisotropy, Co(II) complexes exhibit a slow paramagnetic relaxation in the constant magnetic (DC) field, i.e., belong to the class of field induced non-monoaxial single ion magnets (FI-SIMs). Such type of SIM behavior is due to Kramer's character of Co(II) ion.

The possibility of reversible varying of the value and sign of magnetic anisotropy due to photoinitiated change of the metal coordination has been shown.

Possibility to produce new photomagnetic materials based on these compounds is being discussed.

This work was performed in accordance with the state task, state registration No 0089-2019-0011. The work was financially supported by the Ministry of Education and Science of Russian Federation (Agreement No. 14.W03.31.0001-Institute of Problems of Chemical Physics of RAS, Chernogolovka).
Diarylethene Molecular Photoswitches: Recent Progress and Future Prospects

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“Diarylethene” was serendipitously discovered during the course of study on photoresponsive polymers 30 years ago.[1] The first report was presented in 1987 at the annual meeting of Chemical Society of Japan [2] and then published in 1988 in J. Org. Chem.[3] Theoretical analysis of the photoswitching reactions revealed that introduction of aryl groups with low aromatic stabilization energy is essential to provide the thermal irreversibility to the diarylenes. Since then, tremendous efforts have been made to improve the photoswitching performance and explore their applications.[4] The well-designed diarylethene derivatives exhibit the following photoswitching performance; both isomers are thermally stable, photoinduced colouration/decolouration can be repeated more than $10^4$ cycles, the quantum yield of cyclization reaction is close to 1 and the response times of the reactions are less than 10 ps.

Although the diarylenes undergo unprecedented photoswitching reactions, there is still room for improvement. Recently we focus on developing light-driven actuators [5-7] and also turn-on mode fluorescent diarylenes. Molecular design strategies for increasing the fluorescence quantum yield, improving the fatigue resistance and controlling the photoswitching response have been pursued for super-resolution microscopies.[8-10] The outstanding photoswitching performance of diarylethene derivatives, which has already been gained and will be fulfilled in future, would offer great potential for advancing photoresponsive materials and photonic devices, and also certain promise for applications in biological science and technologies.

1. Irie, M. Pure Appl. Chem. 2015, 87, 617.
From molecular switches to functional nanomaterials

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The long-term goal of my research program is to develop a library of “smart” nanomaterials incorporating molecular components that can be interchanged and thus tailored for the development of nanosized sensors, probes, delivery vehicles and diagnostic tools.

We have synthesized a library of spiropyran-based photo switchable molecules that can act as sensors for biologically important cations and subsequently utilized it as a basis for zinc (II) selective sensor and for light activated delivery of small therapeutic molecules.¹

The spiropyran molecules were coupled to carbon nanotubes (CNTs), resulting in light-modulated continuous on-off switching of the nanomaterial in solution and light controllable uptake and release of zinc ions.² We have expanded the library of smart nanotubes by functionalizing CNTs with a switchable boron azadipyrromethene (aza-BODIPY) dye. We demonstrated the ability to reversibly switch on and off the fluorescence by modulation of pH.³

We have recently shown that multi-shell fullerenes, known as carbon nano-onions (CNOs) are particularly attractive platforms for biomedical applications due to their small size (diameter ≈ 5 nm), high cellular uptake and biocompatibility.⁴ We have developed intracellular imaging systems based on functionalized CNOs with pH sensitive BODIPY derivatives. The on/off emission of the fluorescent CNOs is fast and reversible both in solution and in vitro, making this nanomaterial suitable as pH-dependent probes for diagnostic applications.⁵ We are now investigating the ability of these nanoconstructs to act as drug-delivery systems.

Figure 1 Chemical structures and confocal fluorescence images of HeLa cells treated for 1 h with 20 μg mL⁻¹ of fluo-CNOs. (a) PBS, pH 7.4; (b) acid buffer, pH 4.5.


Hemi-indigo photoswitch: ON-OFF fluorescent binder for HIV-1 RNA

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Application of organic photoswitches as “smart” binders for nucleic acids is an emerging research area in the interdisciplinary field between chemistry, biology and medicine [1,2]. However, the reported examples are mainly confined to the covalent integration of photoswitches into nucleic acids that interfere with the native structures of the latters. At the same time, the examples of photoactive noncovalent binders are focused on DNA, whereas RNA as a target has been almost neglected. Except for a single example [3], no studies on noncovalent interactions of organic photoswitches with naturally occurring RNA are available up to date. This fact is surprising because RNA represents an important target for the therapy of viral and bacterial infections and several genetic diseases [4].

The aim of this work was to explore the field of noncovalent photoactive binders for naturally occurring RNAs and adopt for this a new photochromic scaffold. As a result, a proof-of-principle for the application of hemi-indigo derivatives as photoswitchable RNA binders, specifically for the human immunodeficiency virus type 1 (HIV-1) RNA, is described. Notably, hemi-indigo has not been used for the nucleic acids studies previously, and there are no previous examples of the interaction of photoswitches with HIV-1 RNA. Binding of the Z-form of the hemi-indigo ligand to the regulatory elements of HIV-1 RNA produces a remarkable light-up effect of the emission (ON). Switching of the RNA-bound ligand to the E-form by irradiation with blue light (470 nm) results in the fluorescence quenching (OFF). Subsequent irradiation with amber light (590 nm) leads to the restoration of the fluorescent state (ON). ON-OFF photoinduced switching of the ligand can be performed several times without destroying the ligand–RNA associates. The obtained results is a starting point for the application of hemi-indigo photoswitches in the nucleic acids field.

Control of Basic Photochromic Nature of Diarylenes by Acid

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Photochromism is induced by the alternate irradiation of light with different wavelengths. If the photochromic reaction itself is locked or unlocked by irradiation of a third light, it is the “all-optical control of on/off switching of photochromic phenomena”. We have realized it by the combination of a spiropyran 1mc and a diarylethene 2o. 1 The spiropyran 1mc, a thermally more stable merocyanine form, generates a strong Brønsted acid 1sp, a thermally less stable spiropyran form, upon irradiation of visible light. While 2o does not show photochromism in polar solvents due to the twisted intramolecular charge transfer (TICT), 2oH shows typical thermally irreversible photochromism. 1

Of interest is whether similar behavior may occur with a Lewis acid. In this presentation, the peculiar photochromic behavior of 2o in the presence of Lewis acids will be disclosed. We will also show another characteristic function of 1mc which is the change in the thermal stability for the closed form of diarylethene 2o.

Towards Rationalization and Design of Improved Dihydropyrene Photochromism: Interplay between Theory and Experiment

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Photochromism represents an increasing area of research in photochemistry because of its applications in nanosciences, biology, and photonic or optoelectronic devices.[1] Light-activated organic molecular switches are most often used as photochromic systems. One of the largest groups of photochromic switches is based on the ring-opening/ring-closure reactions in photoinduced electrocyclic reactions of p-conjugated systems. This is the case of the dimethyldihydropyrene (DHP) derivatives, which can be reversibly isomerized to their corresponding cyclophanediene (CPD) forms (Figure 1).[2][3] Interestingly, DHPs are negative photochromes (i.e., the thermally stable DHP isomer is the colored one), whereas most of the photochromic compounds are positive (their stable form is colorless). This feature makes DHPs compatible for many applications since their activation can be achieved by visible light at low energy.

However, the photoswitching mechanism of the DHP/CPD photochromic couple is still not fully understood.³ Computational photochemistry is a powerful tool that can provide critical mechanistic information in order to rationalize the excited-state behavior of such systems.[4] Here, I will present some results of our theoretical contribution [5] in the study of the photoisomerization of DHPs and how the interplay with experiment has help us to improve our understanding of these systems and will possibly lead to the design of new improved DHPs.

Figure 1. The dimethyldihydropyrene (DHP) / cyclophanediene (CPD) photochromic couple.

Acknowledgments. The authors thank the French ANR for the financial support through grant No. ANR-18-CE29-0012.

Photochromic Radical Dimers that Show Heterolytic Bond Cleavage

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Radical-dissociation-type photochromic molecules have been extensively studied based on imidazole dimers because of their fascinating properties such as initiators for radical polymerizations, wide range of rate-tunable photochromic properties, and broad absorption over visible and near infrared regions. Recent research advancement enabled to develop novel photochromic radical complex called phenoxyl imidazolyl radical complex (PIC).¹ PIC is the first example of radical-dissociation-type photochromic molecule which forms two heterogeneous radical moieties in a molecule. The PIC framework can be used as a molecular platform for further novel photochromic compounds by replacing radical moieties. If we could introduce radical moieties which have other functions to the PIC framework, it is expected that various advanced photochromic materials can be developed over conventional photochromic reactions. As a candidate for other radical moieties for photochromic radical complexes, we came up with a phenothiazine framework. A phenothiazine has been widely applied as electron donors, triplet sensitizers, and pharmacological applications such as tranquilizers and Insecticides. A phenothiazine shows the similar oxidation reaction to that of phenol. This similarity suggests that phenothiazine can be incorporated to the PIC framework as similar to phenol of PIC.

In this study, we synthesized novel photochromic radical complexes composed of an imidazolyl radical and a phenothiazine or a phenoxazine radical. These compounds show durable photochromic reactions upon irradiation of visible light and the photoinduced absorption were observed even in the near infrared region. Femtosecond transient absorption spectroscopy revealed that these molecules show the photoinduced heterolytic bond cleavage with a time scale of sub picoseconds and generate the charge transfer (CT) state, while conventional PIC and other radical-dissociation-type photochromic compounds show the photoinduced homolytic bond cleavage. The generated CT state is converted to the neutral ring-opening form by back electron transfer with a time scale of picoseconds. This study may suggest that further novel photofunctional materials which generate zwitterion-like photogenerated transient species could be developed with the framework of photochromic radical complex by increasing the donor and acceptor properties in each radical moieties.

Reference:

An Innovative approach based on diarylethene film for tailoring the patterns in soft lithography

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Photochromic diarylethenes are versatile systems that have been found to be of great interest in many applications. The capability to tune finely the optical properties makes them suitable for the development of tunable filters and masks. In this framework, a versatile and easy customizable mould platform for the Micro-Contact printing of 1D and 2D patterns of fluorescent dyes is developed. The mould is obtained by Absorbance Modulation Optical Lithography (AMOL) applied to a stack of a crosslinked polyurethane photochromic layer and a photoresist. The process is optimized to have a fast process with high quality features on wide areas. Supported by a kinetic and an electro-magnetic model, 1D and 2D patterns are designed and successfully transferred on the photoresist layer and finally copied with PDMS to fabricate stamps to be used in the printing process. Fluorescence patterning by means of PDMS stamp is validated and compared with the stamp structure.
Photochromic and Water-soluble Diarylethenes enable Reversible Fluorescent Modulation and Optical Superresolution

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Superresolution fluorescence microscopy revolutionized optical imaging in the life and material sciences. RESOLFT (REversible Saturable Optical Fluorescence Transitions) microscopy is based on reversible photo-switching of labels between non-fluorescent (dark) and fluorescent (bright) states, and enables to observe (sub)cellular structures and dynamics at nano-meter level using relatively low power lasers.[1] Fluorescent labels for the biology-related RESOLFT microscopy are required to be photo-switched on and off several hundreds times in aqueous medium. While reversibly photo-switchable (green) fluorescent proteins (Dreiklang, rsGFP) have been employed in RESOLFT microscopy as benchmark labels,[2] synthetic fluorescent labels comparable to rsGFP are still rare.[3] Here we report design, synthesis and photo-physical characterization of new photoswitchable fluorescent diarylethenes, which exhibit good water-solubility and, most importantly, excellent fatigue resistance. Several hundreds switching cycles can be repeated in aqueous solution maintaining adequate fluorescence switching ability. As illustrations, we present the superresolution RESOLFT images of cytoskeleton and silica nanoparticles with extended recording time.

References:

Density Functional Theory to Evaluate the Mechanism of DASA Photochromes

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The majority of organic photochromic materials employ azobenzenes (AZ), spiropyrans (SP), or diarylethenes (DA) due to their excellent performances (large conformational changes and high fatigue resistance). However, they are often triggered by high-energy irradiation, which can cause photodamage of healthy cells or photodegradation of the studied materials. Within that framework, donor–acceptor Stenhouse adducts (DASA) have recently highlighted and display highly interesting photochemical properties (1-4).

In the present work, we will present recent investigations on DASA photochrome, i.e. photomechanism and, more particulary, how theoretical tools succeed to get deeper insights into ultrafast time-resolved pump-probe spectroscopy in both the visible and IR regions.


Towards understanding photochromicity of bacteriophytochromes using multi-scale molecular modelling

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Phytochromes are a class of photoreceptor proteins found in various plants, fungi and bacteria, in which a biological response is mediated by interconversion between distinct photo-active states following photon absorption. Therefore, phytochromes are a promising platform for optogenetics [1].

The initial step in the photocycle is the photo-isomerization of a covalently-bound biliverdin chromophore. This event is followed by structural rearrangements of the protein matrix that ultimately result in the biological response. To understand how the protein has evolved to mediate this photobiological process and characterize the pathway in atomic detail we have used multiscale QM/MM (quantum mechanics/molecular mechanics) simulations to identify the effect of protonation form of chromophore [2] and further to follow the dynamics of the chromophore upon photo-excitation. The results of our excited-state ab initio molecular dynamics simulations, suggest that that the chromophore undergoes ultra-fast isomerization on the excited state potential energy surface, followed by slower structural re-arrangements between various intermediates on in the ground-state potential energy surface.

Photodeformable Liquid Crystal Polymers and Bioinspired Soft Actuators

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Photodeformable liquid crystal polymers (LCPs) can generate sophisticated 3D motions such as bending, twisting, oscillation and rotation, thus they have been processed into various bioinspired actuators, such as walking worm, winding ribbons and artery like tubes. Especially with the application of novel fabrication techniques like lithography, reactive ion etching and direct laser writing, diverse photodeformable LCP actuators on micrometer are prepared, which are promising for applications as stimuli-responsive surfaces, microrobots, and optofluidic microchips.
Donor-Acceptor Dihydropyrenes as Direct One-Photon NIR Photoswitches

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The incorporation of photochromic moieties in complex molecular systems enables a wide variety of applications in materials and life sciences. For most of these applications, visible or near-infrared (NIR) light is more suitable than UV light due to its greater penetration depth and non-damaging character. However, the isomerization of photoswitches usually requires high-energy photons in at least one direction, which limits their utilization especially in biological applications.\(^1\) Employing negative photochromic T-type photoswitches opens up the opportunity to utilize visible or NIR light exclusively. Such systems benefit from the selective lower energy light-induced isomerization of the thermodynamically more stable state in combination with the quantitative thermal reversion of the metastable isomer. One class of negative photochromic T-type switches are dihydropyrenes (DHP), pioneered by Boekelheide and Mitchell, which undergo a photoinduced 6π electrocyclization.\(^2\)

Here we show a general design strategy for direct one-photon NIR photoswitches based on strong donor-acceptor DHPs, which display strongly bathochromic charge-transfer bands and exhibit a pronounced positive solvatochromism. In the closed DHP isomers the donor and acceptor substituents are π-conjugated and hence the DHPs exhibit a partial quinoid character, giving rise to a long-wavelength transition depending on the donor-acceptor strength. Upon photo-induced ring-opening with far-red or NIR light the cross-conjugated meta-cyclophanediene (MCD) isomer is formed, which in turn decouples the donor and acceptor substituents (Figure). The thermal half-lives of the metastable MCDs range from seconds to hours depending on the polarity of the environment. The utilization of these donor-acceptor DHPs allows efficient and nearly quantitative switching induced by invisible NIR light, which renders them attractive for various applications.\(^3\)

References:
Molecular and Supramolecular Tuning of Photochromism

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The most interesting features in a photochromic species are the high stability and good performances in terms of photoconversion, thermal processes and fatigue resistance.\textsuperscript{1} In this regard, an appealing perspective is the possibility to tune or improve such properties. Herewith we report two examples of molecular and supramolecular tuning of photochromism.

In the first case, two azobenzenes, each bearing two ethylmalonate groups in \textit{p,p'} or \textit{m,m'} position, show the typical \textit{E/Z} photoisomerization. These molecules can react with fullerene through the malonates, to give bis-equatorial adducts.\textsuperscript{2} In the \textit{p,p'} adduct, the \textit{Z} isomer becomes the thermodynamically most stable form, with a poor photoconversion to the \textit{E} form upon visible irradiation, and a fast \textit{E} to \textit{Z} thermal isomerization. On the contrary, the \textit{m,m'} derivative can be linked to the fullerene exclusively in its \textit{E} form, regardless of the reacting isomer. In this latter case, the molecular locking on the fullerene prevents the photoisomerization.

A second example is given by threadlike imidazolium-based terarylenes, where the imidazolium bridging unit acts as a recognition site for crown ethers to form pseudorotaxanes.\textsuperscript{3} If irradiated in the UV region, the isolated threads show very high thermal photocycloreversion rates, that, in some cases, do not allow the accumulation of the photoproduct. In suitable non-protic solvent, these molecules yield very stable [2]pseudorotaxanes, that are photochromic as well, but with improved features. Indeed, in the supramolecular adducts, the photoinduced cyclization and the thermal cycloreversion reactions are strongly affected, in terms of mechanisms, rates and quantum yields.

References:


Financial support from the EU (H2020 ERC AdG “Leaps” no. 692981) is gratefully acknowledged.
Acceleration of glassy dynamics with azobenzene as a new tool to study the glass transition problem

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Keywords: Azobenzene, Dielectric Spectroscopy, Glass transition

Explaining the slowing down of dynamics in glassy liquids during the glass transition is a long-standing problem, which still awaits for its conclusion. Glassy dynamics can be studied using photochromic probes such as azobenzene molecules, monitoring relaxations of cis isomers and of light-induced anisotropy [1]. Among other techniques, this led to the discovery of the heterogeneous nature of dynamics in the glassy phase, a key concept in glass transition theories nowadays. But azobenzene probes can also modify the glassy properties of their host under illumination, as used for photo-induced mass transport in glassy polymers [2]. More specifically, modifying the structural relaxation time of a glass with photochromic molecules could provide a new tool to study the glass transition.

Here, by using dielectric spectroscopy on an azobenzene-doped molecular glass, we quantitatively measure a light-induced acceleration of the dynamics of the glassy matrix. We simultaneously measure the behavior of chromophores through polarized UV-Visible spectroscopy. We find that illuminating our molecular glass reduces the structural relaxation time by a factor as large as 2 at low temperature, despite the concentration of the azobenzene-grafted glassy molecules we synthetized being as low as 2%. This effect is far beyond what the small heating due to the light absorption would cause. It is not related to the volume variations linked to the production of cis isomers during illumination, but to the flux of azobenzene isomerizations.

Our results confirm simulations results on the effect of isomerizations of azobenzene in a molecular glass [3]. In addition, we link this effect to the SWAP algorithm used to simulate glasses, which, by allowing the equilibration of glassy systems at very low temperatures, allowed breakthrough discoveries on the putative underlying “glassy” thermodynamic transition [4]. Therefore, we believe that the use of photochromic compounds opens a new avenue to study the glass transition.

\begin{itemize}
  \item[1.] Richert, \textit{Journal of Physics: Condensed Matter} 14, 23 (2002)
\end{itemize}
Photochromism of diaryethene nanoparticles under cw-light and nanosecond pulse laser excitation

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We have investigated photochromic properties of aqueous nanocolloids of diarylethene derivatives by means of steady-state and time-resolved absorption spectroscopies, and have compared the conversion yield and reaction dynamics to those of the solutions. In this presentation, we will focus on the effects of dense excitation of nanoparticles on the ring-opening (cycloreversion) reaction. We found the nonlinear enhancement of the cycloreversion reaction induced by excitation with single-shot of ns-laser pulse and demonstrated that the mechanism can be explained well on the bases of the effect of transient laser heating in a ns-time scale, i.e. single ns-pulse plays two roles: one is ultra-fast heating of the nanoparticles through the efficient photo-thermal conversion and another is to induce the cycloreversion reaction of molecules in the “hot” nanoparticle. We will discuss a novel type of photo-synergetic effect that a number of photons and molecules cause in densely photo-excited organic solids.
Functional Switchable PolyAromatics: a little flexibility in Molecular Cages

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Molecular cages represent a versatile class of molecules that possess unique abilities for guest encapsulation, detection, transport or transformation.¹

Our research aims to design polyaromatic compounds devoted to adjustable molecular recognition using singlet oxygen.²

Molecular cages 1a and 2a incorporating a 9,10-diphenylanthracene (DPA) chromophore were synthesized through a templated ring-closure metathesis approach that allows substantial variation in cavity size through the introduction of up to three different pillars.

Reversible Diels–Alder reaction between the DPA moiety and photogenerated singlet oxygen smoothly converted 1a and 2a to the corresponding endoperoxide cages 1b and 2b. In the presence of Na+ and Cs+ ions, cages 1a and 2a form 1 : 2 and 1 : 1 complexes whose association constants increase 6- to 100-fold upon conversion to 1b and 2b.

DFT calculations show that a different mode of cation binding is responsible for such impact on molecular recognition.

References:

Theoretical approaches for the modeling of photoactive systems

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The interest recently garnered by the field of materials chemistry can be attributed to the vast range of chemical functionality that has been demonstrated in a great number of cases as well as the practicality of materials for the creation of devices. Within this field, photo-responsive materials are gaining ever-increasing attention thanks to their fast and often dramatic response and the relatively non-invasive nature of light as a stimulus [1].

However, understanding the excited state mechanisms at play in these materials remains difficult. In particular, from a theoretical standpoint, it is only recently that the study of excited state phenomena for periodic crystalline systems has become feasible [2-4] and certain tasks, such as the study of excited state reactivity, mechanochromism or photoemission remain a significant challenge.

We present our contribution to the modeling of some of these phenomena, combining different theoretical tools ranging from classical to quantum approaches in either molecular or periodic formalisms [5-8]. We demonstrate that by choosing, developing and combining suitable theoretical tools, such phenomena can be qualitatively (or even quantitatively) described and that mechanisms at play can then be rationalized.

Storage and Production of Singlet Oxygen using Photochromic Dimethyldihydropyrene Derivatives

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The dimethyldihydropyrene (DHP) compound is a polycyclic π-conjugated unit that can be isomerized under visible light irradiation into its corresponding cyclophanediene (CPD) form (See Figure). Compared to other well-known photochromic systems such as spiropyrans, diarylethenes or azobenzenes, dimethyldihydropyrene derivatives have been the subject of much less attention. However, recent results show that, upon suitable chemical functionalizations, this photochrome is a very attractive system for several applications such as for the preparation of multi-functional optically and redox-active materials, for molecular electronics,[1-3] or for biological purposes.

In particular, we show that DHPs may exhibit an unusual reactivity towards dioxygen. Indeed, this small organic molecule can act as O₂ photosentitizer, but it can also store (under an endoperoxide form) and release singlet oxygen.[4-5] These properties can be used in PhotoDynamic Therapy (PDT).

![Dimethyldihydropyrene (DHP) and Cyclophanediene (CPD) photochromic system](image)

The DHP/CPD photochromic system

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A versatile platform for holography based on diarylethenes.

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Photochromic materials are attractive for the development of Computer Generated Holograms (CGHs). Indeed, they show a modulation of the complex refractive index; hence, they are suitable for both amplitude and phase holograms; moreover, they do not require any chemical process after the light exposure to have the final hologram, so the manufacturing process is easy. Finally, thanks to the reversibility of the transformation, the holograms are rewritable. Therefore, photochromic films can be considered as a versatile and reconfigurable platform for such diffractive optical elements. Here, we will show the features of photochromic diarylethenes in terms of modulation of the transparency in the visible spectral range and the refractive index in the near infrared region as function of their chemical structure. We also report the strategies for writing binary and grayscale holograms, both Fresnel and Fourier, highlighting the achieved results in terms of reconstruction fidelity of the images and the corresponding efficiency.
Study of the effect of cocrystallization on a N-salicylideneaniline switch using a combination of periodic and embedded quantum theory methods

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Cocrystallization is being developed as a strategy to tune the thermochromic and photochromic properties of molecular switches. As this grows into a powerful tool, quantum chemistry methods can provide insights on the effects of cocrystallization on the switching process as well as on the accompanying changes of properties. In this presentation, we focus on a single N-salicylideneaniline derivative, which tautomerizes between an enol and a keto form, and on its cocrystals where it forms intermolecular hydrogen bonds or halogen bonds with a variety of coformers. First, using periodic boundary conditions density functional theory, the enol and keto forms are characterized (their relative energies, bond lengths, and electronic distributions) and are discussed at the light of the interactions between the N-salicylideneaniline switch and the conformer. In particular, we discuss the impact of co-crystallization on the keto/enol equilibrium and its relationship with the modifications of thermochromism observed experimentally. Then, using embedding methods combined with the second-order approximate coupled cluster singles and doubles model, CC2, the optical properties (UV/vis absorption spectra) are simulated and analyzed, highlighting the effect of the geometry and of the environment of the switch.
Preparation and photochemistry of gold nanoparticles decorated with azobenzene derivative with lipoic acid

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Design and preparation of smart materials able to convert external stimuli in a microscale into a desired response in the macroscale belong to one of the most popular research topics in Materials Engineering [1]. Smart materials in a form of superstructured assemblies [2] play a key role as functional materials thanks to their versatility [3], hence their precise control is a current scientific challenge.

Probably the best stimulus that can be used to manipulate smart materials is light. Its tunable parameters such as wavelength, intensity and exposure time can be broadly adjusted [3]. Light is also noninvasive, ultrafast, environment-friendly and able to induce remotely and control spatiotemporally an action with high precision [4].

Nanostructured, light-responsive systems are economical and very easy to manipulate. Within this group functionalized nanoparticles are of special interest due to their unique shape- and size-dependent optical and chemical properties that make them useful in nanoelectronics, cancer therapies or smart materials development [5]. Decoration of nanoparticles with proper photochromic ligands may lead to highly-ordered superstructures and, moreover, to innovative solutions crucial for problems related to energy, environment, and health [3]. From a photochemical point of view, in case of metallic nanoparticles, their interactions with photochromes may lead to electron density variations in a metallic core, influencing also absorption of the photochromic ligand and plasmonic properties of the nanoparticles themselves [5].

Within scope of the presented studies, functionalization of gold nanorods with azobenzene derivative with lipoic acid has been performed. First, functionalization protocol consisting in either nanoparticles incubation or washing has been established. Second, kinetics of photoisomerization of obtained systems has been examined and reaction rate constants have been determined. Influence of other parameters such as presence of different ligands (e.g. nanocellulose) and plasmonic properties of the metallic core have also been investigated.

Photoswitching of glass transition temperatures of azopolymers induces reversible solid-to-liquid transitions

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The development of polymers with switchable glass transition temperatures (Tg) can address scientific challenges, including the healing of cracks in high-Tg polymers and the processing of hard polymers at room temperature without using plasticizing solvents. In this talk, I will show you that light can switch the Tg of azobenzene-containing polymers (azopolymers) and induce reversible solid-to-liquid transitions of the polymers.[1] The azobenzene groups in the polymers exhibit reversible cis-trans photoisomerization. Trans azopolymers are solids with Tg above room temperature, while cis azopolymers are liquids with Tg below room temperature. Because of the photoinduced solid-to-liquid transitions of these polymers, light can reduce the surface roughness of azopolymer films, repeatedly heal cracks in azopolymers, and control the adhesion of azopolymers for transfer printing. The photoswitching of Tg provides a new strategy for designing healable polymers with high Tg and allow for control over the mechanical properties of polymers with high spatiotemporal resolution.

References:
Oxygen Evolving Complex in Photosynthesis II, Is it a Photochromic System in Nature?
A Theoretical Study

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The protein complex known as photosystem II splits water molecules to release oxygen using sunlight. At the heart of photosystem II is a cluster of manganese, calcium and oxygen atoms, known as the oxygen-evolving complex (OEC), that catalyses the water-splitting reaction. It is very difficult to mimic the efficient natural process, because of an incomplete understanding of the water oxidation mechanism of photosystem II. We have carried out a theoretical study to reveal the hidden pathways of water molecules inside photosystem II.

To the eyes of researcher who has studied diarylethene for a long time through quantum chemical methods, it looks like a photochromic system, since this is an intelligent photo-switching system in nature.

Recent high-resolution x-ray crystallography studies have yielded important structural clues into photosynthetic water oxidation, the movements of water, oxygen and protons and the details of electronic states within the protein complex are still the subject of much speculation. To resolve this problem, we carried out a total MD simulation, without any truncation of the protein or simplification, on an exact model of photosystem II inside a thylakoid—a lipid and fatty-acid membrane-bound compartment found in the chloroplasts of plant cells.

A rigorous MD simulation of the protein—membrane system in the presence of more than 300,000 water molecules indicated that water, oxygen and protons move through photosystem II not randomly but via distinct pathways that are not obviously visible. The pathways revealed by the simulations are delicately coupled to the dynamic motions of the photosystem II protein residues.

We then focused on the electronic structure of Mn-cluster by quantum chemical method. We elucidated the mechanism of spin chemistry to produce the triplet oxygen from singlet waters. In parallel, in an attempt to mimic the process in nature, we studied inorganic electrodes (MnO₂, NiOOH and FeOOH) by first principles calculations.
Hydrazone-Based PhotoSwitches and Functional Materials

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For the past few years we have been developing structurally simple, easy to make, modular, and tunable hydrazone-based functional materials (e.g., switches, sensors and fluorophores). This presentation will deal with our recent advances with these systems, with an emphasis on newly developed photochromic compounds that exhibit many interesting properties, including emission ON/OFF toggling in solution and the solid-state. The integration of these photochromic compounds into liquid crystals and liquid crystalline elastomers will also be discussed.

Representative references:

DTE-based Cyclometalated Platinum(II) Complexes: Efficient Optical Photo-Switches

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Organometallic systems with commutable optical responses (e.g. nonlinear optics (NLO) and luminescence) are of growing interest due to their potential application in photonics technologies. In the course of finding new strategies for quadratic NLO metallo-switches, our group has been investigating dithienylethene-based cyclometalated platinum complexes with the aim of combining the optical properties of cyclometalated Pt(II) complexes[1] with the photochromic performances of dithienylethene (DTE)[2].

We have designed and synthetized various mono- and di-nuclear DTE-based Pt(II) complexes.[3] Here, the influence of the design (i.e., the position and the number of Pt(II) fragments) on the photochromic reactivity will be discussed.

Quantitative to inhibited photo-isomerization have been observed depending on the position of the platinum(II) moiety. In case of efficient photochromism a significant NLO photo-modulation, both in solution and in thin films have been recorded. In case of inhibited photo-isomerization, a contrasted behavior leads to NIR luminescence. A better insight on the electronic and optical behaviors have been obtained by crystallographic studies of several complexes in both open and closed forms, together with theoretical calculations.

References:

   d) Boixel, J. et al., Inorg. Chem. 2018, 57, 7051-7063
Analysis of vibrational and electronic transitions recorded simultaneously for 3H-naphthopyrans

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The photochromic reaction mechanism for a model compound 3H-naphthopyran (3,3-diphenyl-3H-naphtho[2,1-b]pyran, NP) has been studied in details using NMR spectroscopy [1, 2]. UV photolysis of NP generates the short-lived transoid-cis (TC) form and the long-lived transoid-trans (TT) form. Getting structural information on the species involved in photoreaction using FT-IR spectroscopy at room temperature should give a clear advantage over NMR studies requiring low-temperature conditions to stabilize TC form. The application of both, time-resolved vibrational and electronic spectroscopies allows detection of various intermediates involved in photoreaction of 3H-naphthopyrans.

We equipped an FTIR spectrometer with an extra UV-vis spectrometer. UV LED (λ_{exc} = 365 nm) light was used for NP photolysis. The changes in mid-IR and UV-vis absorption spectra were simultaneously probed with temporal resolution of 0.87 s to elucidate the reaction paths and yields. The characteristic C=O vibrational stretching band of TC form is observed at 1644 cm⁻¹, while that of TT form at 1655 cm⁻¹ in cyclohexane. Carbonyl groups serve as an excellent selective probe for getting structural information on colored isomeric species nascent in the photoreaction [3]. In solution and in the polymer matrix phase, the colored TC species is formed after a single-photon excitation process, while TT is a secondary long-lived photoproduct generated after a two-step excitation involving two photons.

A “building-block” design for enhanced visible-light switching of diarylenes

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Current development of light-responsive materials and technologies imposes an urgent demand on visible-light photoswitching on account of its mild excitation with high penetration ability and low photo-toxicity. However, complicated molecular design and laborious synthesis are often required for visible-light photoswitch, especially for diarylenes.1 Worse still, a dilemma is encountered as the visible-light excitation of the diarylethene is often achieved at the expense of photochromic performances.2 To tackle these setbacks, we introduce a building-block design strategy to achieve all-visible-light photochromism with the triplet-sensitization mechanism.3 The simply designed diarylethene system is constructed by either employing a novel sensitizer building-block with narrow singlet-triplet energy gap to a diarylethene building-block or simply mixing the diarylenes with corresponding sensitizers.3 The wavelength of the visible excitation light can be easily modulated (from 405 to 470 nm) by elaborate selection of diarylethene-sensitizer couples with matched triplet energy levels. A significant improvement on the photochromic efficiency is obtained as well as an enhanced photo-fatigue resistance over those under UV irradiation. The balance between the visible-light excitation and decent photochromism is thus realized, promoting a novel guiding principle for the visible-light photochromism. Based on this strategy, the all-visible-light write-and-erase and patterning applications in polymer films and filtering papers are further demonstrated. This smart strategy may fulfill the requirements for further development and modulation of visible-light photoswitches in both molecular structure designs and corresponding applications. First, The building-block strategy can facilitate the bespoke construction of DAE-sensitizer systems with demanded visible-light excitation wavelengths, by appropriately selecting sensitizer and diarylethene building blocks from the database. Second, the modular building of DAE-sensitizer system can also be directed by various means, e.g. supramolecular self-assembly and polymer chemistry, further broadening the visible-light DAE system design.

References:
Light-gated synaptic receptors

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A major goal of neuroscience is to understand how neuromodulatory systems regulate core processes of brain and behavior, from motor function and learning to reward, aversion, attention, and sleep. These systems go awry in schizophrenia and disorders of mood, motor control and cognition. Treatment for these conditions often turns to pharmacological manipulation of neuromodulators and their receptors. Understanding of neuromodulatory circuits has advanced considerably thanks to optogenetics and chemogenetics. But neuromodulation is difficult to crack. A major obstacle is that a single neuromodulator may play many diverse roles. There are several reasons for this complexity: i) each neuromodulator has multiple receptor subtypes, and these may couple to distinct G proteins, and, even when coupled to the same G protein, may activate distinct effectors, ii) a receptor may have different functions in different cell locations (e.g. axons versus dendrites, and different micro-domain signaling complexes), and iii) a receptor may have different functions in different cells within a circuit. The problem is that the classical approaches of pharmacology and gene manipulation cannot be targeted to specific cells or cell location, may can lead to compensation and cannot be turned on and off rapidly, reversibly or with spatial precision. I will describe a new approach that overcomes these limitations by controlling native neuromodulatory receptors at their natural cellular locations with photoswitchable that provide precise, receptor-, cell type- and brain region-selective switchable pharmacology. The approach works for AMPA receptors and both Class C and Class A G protein coupled receptors (GPCRs): metabotropic glutamate receptors (mGluRs) and dopamine receptors (DRs).
Illuminating glutamate receptor structure and function using optogenetic pharmacology

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Reprogramming receptors and channels to artificially respond to light has wide-ranging applications in molecular studies and interrogation of biological functions. Light confers high temporal and spatial resolution and, combined with genetics, provides unique control on the cellular and molecular level. Recently, we set out to develop a set of NMDA receptor (NMDAR) subunits that can be precisely controlled by light using a variation of receptor engineering methodologies. NMDARs are glutamate-gated ion channels that play crucial roles in brain development and function. NMDARs exert control over many forms of synaptic plasticity that underlie learning and memory. They are also targets of therapeutic interest since their dysfunction is associated to numerous neurological and psychiatric disorders such as schizophrenia, mental retardation and epilepsy. Light sensitivity was successfully endowed to GluN1 and GluN2 subunits by either attaching photoswitchable ligands or by directly encoding light-sensitive amino acids by means of the genetic code expansion technology. Optically-controlled two-electrode voltage-clamp (TEVC) and patch-clamp recordings revealed robust photoresponses combining high temporal precision, bi-directionality (photopotentiation or photoinhibition) and molecular (subunit) specificity. Photocontrol of key receptor properties including channel open probability, agonist sensitivity and ion permeation was achieved. Our results demonstrate the feasibility and utility of these approaches to probe the structure and biophysics of an important neurotransmitter receptor. They also bear general applicability to other membrane receptors and ion channels. We are now aiming at implementing these innovative optochemical tools in more native situations for in vivo optogenetic exploration of specific neuronal receptor functions.
Covalent hybrid polyoxometalates with optical properties

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Polyoxometalates (POMs) can be viewed as large metallic molecular oxides mainly based on molybdenum, tungsten or vanadium cations in high oxidation state.¹ Due to their huge versatility, POM-based systems have found applications in various areas of research. For example, when associated with organo-ammonium cations, POMs may exhibit photochromic properties.²

In this field, we have been developing since 2010 a new family of hybrid compounds combining through covalent bonds POMs and spiropyran (SP) or spironaphthoxazine (SN) entities.³ Under soft UV-irradiation, these assemblies show enhanced solid-state photochromic properties which can be tuned both by the nature of the inorganic platform and the photoactive group. Moreover, multifunctional molecular materials such as the biphotochromic POM-based compound (SP-POM-SN)³ and the fluorescent photoswitch (SP-POM-BODIPY)³ have been fully characterized. In addition, these molecular systems can be incorporated into matrices, with noticeable effects on their optical properties.³

Lastly, this family of photoactive POM-based materials has been recently extended with the covalent grafting of a DASA (Donor Acceptor Stenhouse Adducts) derivative, an original reverse photochrome,⁴ onto an Anderson-type POM, leading to the original anionic DASA-POM-DASA hybrid. Here, the crucial role of the the counter-ions on the optical properties will be especially discussed.

References:
Unravelling photoswitching in the confinement of surfaces, thin films and metal organic frameworks with Raman spectroscopy

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The move from solution to interfaces and the concentrated enviroments of polymer films and metal organic frameworks has opened up many new applications for photochromic switching. At the same time it has placed increasing demands on conventional techniques to characterise the function of molecular switches[1] and motors and demonstrate their proper operation - not least due to inner filter and other optical effects. Over the last decade our group has focused on the confinement of molecular switches as self-assembled monolayers,[2] thin polymer films[3] and more recently in metal organic frameworks.[4] These environments have presented excellent challenges to push the limits of our ability to characterise their function and in particular good use of Raman spectroscopy, as well as resonance and surface enhanced Raman spectroscopies. In this presentation I will focus on the challenges that laser based spectroscopies bring with them, in particular, heat dissipation management and inner filter effects, to show that we can confidently distinguish between purely photoinduced events from thermal induction of changes.

Control of chiral geometry in bifluorophoric systems with light

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Chiroptical photoswitches are of interest in terms of advanced informational technologies. The stereoselective photo-isomerization of chiroptical switches often lead to changes in optical rotatory dispersion (ORD), circular dichroism (CD) and circularly polarized luminescence (CPL). Molecules having multiple fluorophores (chromophores) arranged in a chiral manner often exhibit CD and CPL activity based on the exciton coupling theory. We have been making efforts to control the chiral arrangement of fluorophores by exploiting photochromic scaffolds which change the arrangement and distance between the fluorophores (Figure 1). We first introduced two pyrene units bridged by a 6p-based photo-responsive tetrathiazole whose chiral geometry was controlled in a one-handed manner. The pyrene-bearing photoswitch exhibited CPL activity in the excimer region, which was quenched by the photoisomerization of tetrathiazole moiety. The emergence and control of chiroptical property were explained by the exciton coupling theory. Then, the pyrene units were replaced by lanthanide complexes to form binuclear complexes. The dinuclear photoresponsive Eu(III)-complex exhibited strong CPL activity derived from the chiral Eu(III) complexes. The origin of chiroptical activity was different from the pyrene derivative but attributed to the intrinsic chirality arising in the local coordination structure in the Eu(III) complex sites, which could be modulated by the control of inter-distance between the complex sites. Finally, two metal nanoclusters exhibiting photoluminescence were bridged by chiral photoresponsive linkers. The photo-reaction of linker moiety led to a change in the chiroptical activity emerging in the metal nanoclusters.

![Figure 1. Molecular design of chiroptical photoswitch](image)

References:

Solid materials with tunable reverse photochromism

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Organic photochromic dyes are receiving an increasing interest from the academic and industrial sectors for the preparation of color-changing materials and devices. Researchers have dedicated lots of efforts to develop strategies to finely tune the photochromic performances (e.g. color, activation wavelength and colouration/fading rates) of these materials. The broad variety of T-Type photochromic dyes, which undergo UV-induced colouration and subsequent fading in the dark (i.e. direct photochromism), has been exploited for their employment in the industrial manufacturing of photoprotective coatings (e.g. smart windows, ophthalmic lenses, etc.). On the other hand, more research has to be done to develop straightforward strategies to achieve tunable reverse photochromism (i.e., photoinduced colour fading followed by thermal colouration after irradiation) in the solid state, which not only would allow the photoinduced colour changing with the less energetic visible light, but also grant the access to other applications, such as anti-counterfeiting technologies and rewritable displays. In spite of this, functional solid devices based on reverse T-type photochromes are still very scarce and only started to be reported recently (e.g., in multicolored light-responsive rewritable devices).

Herein, we report a novel, straightforward, and universal strategy to achieve solid materials with highly tunable reverse photochromism.¹,² This was accomplished by means of commercially available spiropyran dyes, which can produce different types of stable merocyanine states (i.e., non-protonated and protonated forms) displaying distinct colours and coloration rates. To finely control the concentration ratio of these species and the corresponding optical performance of the photochromes, we exploited their differential interaction with surrounding media of distinctive nature (i.e., non-volatile protic and aprotic polar solvents). In this way, mixtures displaying different photochromic responses were prepared for individual spiropyrans without requiring chemical derivatization, with distinct acid–base properties. To transfer this behavior to the solid state, core–shell capsules of these solutions were prepared, which were then used as ink materials for the fabrication of flexible polymeric films with unprecedented tunability of their photochromic properties that can be employed as rewritable multicolored devices.

1. ACS Appl. Mater. Interfaces 2019, 11, 12, 11884-11892
Investigation of photochromic systems under continuous irradiation using soft and hard modelling approaches.

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Photochemical processes are chemical processes occurring in the excited state and induced by light absorption. The dynamic of photochemical systems is usually investigated with UV-Visible spectroscopy under continuous monochromatic irradiation. The point is the determination of the main photochromic parameters, quantum yields of the reactions and pure spectra of the different species. These can be obtained fitting the data to the photochemical model (hard-modelling). Nevertheless, the use of hard-modelling requires a complete knowledge of the reactions mechanism and kinetics.

The incorporation of hard-models constraints in soft-modelling methods [1] is known to drastically decrease the rotational ambiguity and allowed to extract kinetic parameters in situations where a complete knowledge of the system is not available (other absorbing species, instrumental artifact...).

In this work, MCR-ALS using “photochemical” hard-modeling constraints has been applied to the study of CMTE (Cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene) under continuous irradiation at different wavelengths in a multi-experiment approach. For irradiation at 405 nm the system is known [2]: CMTE can undergo photoreversible photoisomerization and photocyclization leading to three possible forms: 2 open forms (cis/trans) and one closed-ring form. For irradiation at 365 nm the formation of a new product is suspected. The model at 405 nm still holds but with the addition of new photochemical process(es) (possibly reversible) that has not been identified. Therefore for this irradiation no complete model can be postulated and only soft-constraints will be used.

Finally, the use of MCR with hard-modelling constraints allows to extract the quantum yields for the "known processes" with the spectra of the three "known" CMTE forms and the concentration and spectral profiles of a new product obtained under irradiation at 365nm [3].

References:
Photoisomerization Force Moves Matter

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In this talk, I will discuss the concept of the photoisomerization force (PF) for moving matter. PF occurs when chromophores are isomerized in gradients of light intensity. I will discuss photoselection effects and vectorial motion of matter, containing such chromophores, in different gradients of actinic light intensities. The chromophores are high-rate, reversibly isomerizing, molecular machines which are fueled by light absorption and transform photon energy into mechanical energy. I will discuss experimental works of photo-induced motion of photoactive nanoparticles in viscous solutions and azo-polymers. Perspectives of the use of the PF in materials tweezing and structuring will be discussed as well.
Turn-on mode photoswitchable fluorescent diarylethenes: Substituent effect on photoswitching performance

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Photochromic diarylethene derivatives having benzothiophene S,S-dioxide groups undergo turn-on mode fluorescence switching upon photoirradiation. Upon irradiation with ultraviolet light, the open-ring isomers undergo cyclization reactions to form the highly fluorescent closed-ring isomers. Such photoswitchable fluorescent molecules can be applied to super-resolution fluorescence microscopies, such as PALM, STORM, and RESOLFT microscopy. For practical applications, it is essential to rationally control photoswitching performance of the fluorescent diarylethenes. Here, we report on substituent effect on photoswitching performance of fluorescent diarylethene derivatives [1,2].

PALM and STORM require the cycloreversion (switching off) quantum yield in the order of $10^{-4}$ or less, while a yield in the order of $10^{-2}$–$10^{-3}$ is claimed in RESOLFT microscopy. We found that introducing ortho-methyl substituents into phenyl groups at 6- and 6'-positions of the benzothiophene rings or introducing bulky isobutyl substituents at the reacting carbon atoms increases the cycloreversion quantum yield without significant decrease of the fluorescence quantum yield. Based on such appropriate chemical modifications, the photoswitching properties can be tuned to meet the requirements for the microscopies.

A diarylethene derivative having electron-donating thiophene rings at 6- and 6’-positions exhibited solvatochromism of fluorescence in the closed-ring form. The photogenerated closed-ring isomer dramatically changed its fluorescent color in response to solvent polarity, such as green in hexane, yellow in tetrachloromethane, orange in dichloromethane, and red in dimethyl sulfoxide. The closed-ring isomer shows high fluorescence quantum yields around 0.8 in less polar solvents and the yields remain relatively high (> 0.6) even in polar solvents. Such a solvatochromic fluorophore with photoswitching ability can be applied to super-resolution fluorescence imaging of microscopic polarity in biological cells and materials.

Nonlinear Optical Responses of Photoswitchable Self-Assembled Monolayers: A Computational Approach

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Photochromic materials that exhibit switchable second-order nonlinear optical (NLO) responses are of particular interest for optical data storage or chemical sensing applications. Indeed, NLO responses being measured using low energy near-infrared wavelengths, they can be exploited to probe the electronic states of a light-responsive system without triggering uncontrolled photoconversions. NLO switchable materials thus offer a unique way for designing molecular-scale memory devices with multiple storage and nondestructive readout capacity. [1]

The suitability of a material for practical use as photo-responsive NLO device is mainly conditioned by two requirements. First, the constitutive molecules must exhibit a large first hyperpolarizability in one of their state, as well as a large hyperpolarizability contrast upon switching. Second, the constitutive molecules must adopt a non-centrosymmetric spatial organization that preserves their switching ability. By constraining the alignment of the molecular units within controlled concentrations, surface coating with self-assembled monolayers (SAMs) constitutes the most effective strategy for introducing NLO chromophores into a device in view of maximizing its macroscopic second-order susceptibility. Such 2D functional materials were recently designed by anchoring azobenzene or fulgimide NLO switches at silicon or gold solid surfaces. [2]

In complement to chemical engineering, the rational design of NLO devices and optimization of their performances requires the development of computational strategies that provide a microscopic description of the relationships linking the interfacial molecular organization to the NLO properties of the material. In this contribution, we present a sequential computational approach combining molecular dynamic (MD) simulations and DFT calculations to evaluate the dynamical behavior and second harmonic generation (SHG) responses of azobenzene-based photoresponsive SAMs. [3]

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C. Culot Rypens
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Dynamic Molecular Assembling Photoswitches

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Self-assembly has become an efficient strategy in constructing well-ordered nanostructures using a bottom-up way in material science and has also shown its great potential in biological applications. Introducing some photo-switchable & responsive core units into self-assembling systems endows the dynamic molecular nanostructures or materials with intriguing responsive behavior to light, which can be conveniently orthogonal to other stimuli. From another perspective, the well-ordered supramolecular structures with complexity and stimuli-responsive properties have the capability to “amplify” the light-controlled conformation changes, thus producing more sophisticated functions. This lecture mainly highlights the recent advances achieved in our laboratory in fabricating artificial dynamic-assembling systems for tuning emission colors and selective sensing biomarkers. We report the supramolecular host-guest inclusion of a “glycosylated” photoswitch to a serum protein forms the protein sensor capable of fluorescence-activatable sensing of a glycosidase activity in different cell models based on photochromic protein sensors. Importantly, we demonstrate that the sensor can be used to monitor glycosidase activity in cancer cells and during cell aging with super-resolution microscopy thanks to its enhanced intracellular photochromic activity. We also developed a visible light-driven diarylethene system by introducing a D-A type sensitizer to the DAE core. Taking advantages of the unique features of the D-A type sensitizer and the intramolecular TTET process, the DAE-sensitizer dyad was endowed with a remarkable visible light photochromism of high efficiency and robust fatigue resistance. This strategy may fulfill the requirements for further development of visible light-triggered photoswitches. By appropriately designing donor-acceptor structures and adjusting the energy level matching between sensitizers and diarylenes, DAE-sensitizer systems excited via visible light of variable and longer wavelengths are foreseeable.

References:

Manipulating molecular photo-chromism with confined light

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Molecular photo-switches can be reversibly photo-converted between states with different chemical or optical properties. While photo-switching has so far been controlled through careful engineering of the molecular structure, recent experiments on photo-switches inside optical cavities suggest that photo-switching can also be controlled by modifying the electro-magnetic vacuum field [1]. By confining light to smaller volumes, optical cavities, plasmonic particles or propagating surface plasmons enhance the light-matter interaction, which can become strong enough for the photonic and molecular degrees of freedom to hybridize into new light-matter states, known as polaritons. The hybridization between light and matter into polaritons not only delocalizes the excitation over many molecules but also changes their potential energy surface, and thus provides a new way to control photo-chromism. However, despite a relatively easy fabrication of structures for confining light, exploiting strong light-matter coupling to control photo-chromism requires a theoretical model with which the effect of the light-matter coupling on the molecular dynamics can be predicted accurately. Therefore, we have developed a multi-scale quantum mechanics/molecular mechanics (QM/MM) molecular dynamics simulation model for photoactive molecules strongly coupled to confined light in optical cavities [2]. After presenting our model, I will discuss recent all-atom simulations of thousands of photo-switchable molecules inside optical cavities. These simulations illustrate how interaction with confined light affects the outcome of ultra-fast photo-switching reactions.

Reversible Valence Photoisomerization between Quinoidal and Biradical Forms of Photochromic Phenoxyl-Imidazolyl Radical Complex

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Phenoxyl-imidazolyl radical complex (PIC) is one of the T-type photochromic compounds which generates a colored biradical form upon UV light irradiation, and the generated biradical thermally reverts to the initial colorless closed form\(^1\). One of the PIC derivatives, RPIC, shows a sequential photochromic reaction\(^2\). The photochromic reaction of RPIC is consisted of three processes: (i) photochemical bond breaking of the C–N bond affording the colored open-shell biradical form, (ii) a thermal equilibrium process by valence isomerization to form the closed-shell quinoidal form, and (iii) thermal back reaction to reproduce the initial colorless closed form while keeping the equilibrium between the biradical and the quinoidal form in the microsecond time region.

We report here a kinetic study on the thermal equilibrium process between the biradical form and the quinoidal form starting from the singlet biradical form alone of the RPIC system. The thermodynamic parameters for the equilibrium process were determined for the first time by nanosecond laser flash photolysis\(^3\). We also found that the visible-light excitation to the equilibrium state causes the valence photoisomerization from the quinoidal to the biradical form, that returns thermally to the quinoidal form.

References:

Azobenzene derivatives as components of artificial supramolecular pumps

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Azobenzene derivatives as components of artificial supramolecular pumps

Molecular machines and motors are assemblies of a discrete number of molecular components, designed to be set in motion relative to one another. In particular, a molecular motor can perform work on its environment in a progressive fashion, and this result is achieved by using an energy source to cyclically repeat directionally controlled movements. Light is the most valuable energy source to operate a molecular device, because it can be controlled in terms of space, time and energy, it is clean, and it can be used both to "read" and "write" the state of the system. The integration of photochromic moieties within the components of a molecular motor has proven a successful strategy for tuning the thermodynamic and kinetic parameters at the basis of the operation of the device. Indeed, we reported a pseudorotaxane system that performs the unidirectional relative transit of the wheel and axle components under continuous light irradiation.[i] The cis-trans isomerization of an azobenzene moiety at the extremity of the axle is responsible for the control of the threading and dethreading directions, and of the stability of the supramolecular system. With the aim of improving the performance of the supramolecular pump,[ii] we are currently investigating how different azobenzene derivatives can affect the rates of threading and the relative stabilities of the trans and cis adducts.

Financial support from the EU (H2020 ERC AdG “Leaps” no. 692981) is gratefully acknowledged.

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Visible-light-activated polymer networks

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The possibility to control materials via external stimuli is highly attractive for a variety of applications and motivate the preparation of macromolecular architectures that are responsive or even adaptive, meaning that a change in their environment is accompanied by an autonomous (and beneficial!) variation in the materials properties. Such systems can be obtained by incorporating isomerizable molecules, e.g. molecular photoswitches, whose structural modification is leveraged to control advanced functions and harness macroscopic responses of the interfaced materials.[1]

In that context, and in order to overcome the limitations inherent to UV light irradiation, the development of molecular switches that can be activated by visible light is crucial.[2] Those allow for increasing penetration length, enhancing fatigue and selectivity, efficiently harvesting sunlight, and developing biomaterials. In that presentation, the design of red-shifted fluorinated azobenzenes[3] and their integration into polymer networks, from soft hydrogels[4] and liquid crystalline elastomers[5] to (micro)crystalline metal-organic frameworks,[6] will be presented.

References:

Robust norbornadiene-quadricyclane-based molecular photoswitch

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Photoswitch molecules are molecules that can interconvert between two stable isomers using light as a stimuli. Such molecules find application in areas such as solar energy storage, single molecule electronics, and bioimaging. In this context, we synthesized various norbornadiene-based molecular photoswitch to explore their potential towards single molecule electronics. Our norbornadiene-based photoswitch has two ethynylphenyl units terminated with thioacetate groups on both sides of the norbornadiene for anchorage. In the photo-excited state the π-bonds in norbornadiene rearrange to σ-bonds. Thus, the norbornadiene form is expected to be more conductive than the quadricyclane form. The photoswitching was followed in solution by NMR as well as UV-visible spectroscopy. STM-break junction conductance measurement showed that indeed the norbornadiene form (NB-1) is more conductive than the quadricyclane form (QC-2) as anticipated. This result was further corroborated by quantum chemical calculation using the non-equilibrium Green’s function (NEGF). Furthermore, some norbornadiene-derivatives were found to be emissive with fluorescence quantum yields (Fₜ) as high as 49%, the highest value recorded for norbornadiene derivatives to date.

References:
Spiro-functionalized diarylethenes and their photoreactivities

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Spiro derivatives have been attached much attention in the research field of organic electronics¹ owing to their intrinsic characteristics such as an excellent amorphous thin film forming capability and an orthogonal π-conjugation system. In addition, they have been widely studied as a promising organic semiconductor because of their easiness of chemical modification. With this in mind, photochromic diarylethenes² having an orthogonal π-conjugation system assembled in a spiro ring system were synthesized and their photochromic as well as fluorescent properties were studied. The spiro-functionalized photochromic diarylethene showed reversible photochromic reaction in ethyl acetate solution with a photon-quantitative photocyclization reactivity. Furthermore, the fluorescence colors of the diarylethene derivative changed from blue to red upon photochromic reaction. This result indicates that the both open- and closed-ring isomers show the multi-color fluorescence modulation.³

References:
Manipulating photoblinking in red fluorescent proteins: localization microscopy with ordinary labels and longer tracks in single-particle tracking

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Fluorescent proteins are essential tools in the life sciences, yet are also known for their varied and rich photochemistry, including the presence of short- and long-lived intermittencies (‘blinking’). This blinking can be detrimental but also essential for the imaging: in localization microscopy, for example, one desires long-lived blinking to ensure emitter sparseness, while in single-particle tracking these intermittencies limit the length of the tracks that can be required, restricting the available information.

In this talk I will discuss two recent investigations into the structural changes underlying long-lived intermittencies in red fluorescent proteins, and how these can be manipulated to enhance the performance of advanced imaging. In the first investigation, we discovered that the fluorescence of mCherry can be reversibly caged using addition of beta-mercapto ethanol. We investigated the mechanism underlying this caging using ensemble spectroscopy and crystallography, and found that it arises from a direct reduction of the chromophore as well as a reversible Michael addition of beta-mercapto ethanol onto the chromophore. We then showed how this caging could be used to perform localization microscopy in samples labeled with unmodified mCherry.

The second study investigated long-lived intermittencies in the red state of a popular photo-activable fluorescent protein, mEos4b. We identified a long-lived dark state in this protein using immobilized single-molecule spectroscopy, measured the absorption and emission spectra of this state, and determined its crystal structure. Based on this structure, we rationalized that weak illumination with 488 nm light would likely revert it back to the emissive state, and indeed found recovery of the red fluorescence. We demonstrated how this can be used to achieve considerably longer and more informative tracks in SPT-PALM. Our blinking suppression strategy should be similarly useful in increasing the accuracy of molecular counting in quantitative SMLM imaging.
Hybrid organic-inorganic polyoxometalates for photoactive switching devices

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Polyoxometalates (POMs) are an unique class of redox and optically active metal-oxide anionic clusters that can be used as cofactors to improve or tune the optical properties of photoactive molecules in the solid state. Firstly, photoswitchable systems¹,² have been designed by coupling POMs with cationic spiropyans (SP) and spirooxazines (SN) into crystallized supramolecular assemblies. The nature of the POM together with the design of the frameworks govern the SP or SN photoisomerization, and some of these bistable hybrids exhibit remarkable photoresponses in the crystalline state. Secondly, new supramolecular assemblies combining for the first time phosphorescent cationic cyclometalated iridium (III) complexes and POMs have been recently obtained. From this innovative coupling, the solid-state phosphorescence of an orange-emitter iridium complex was successfully modulated from green to red without any preliminary functionalization, but only by playing with the nature of the POMs and the crystal packing.³ These new chemosensors show remarkable reversible vapoluminescent properties for detection of volatile organic compounds (VOCs) in the environment or workplace, even in presence of moisture.

References:

Bidirectional light-induced conductance switching in molecular wires containing a dimethyldihydropyrene unit

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The use of photochromic couples as key component in light-powered molecular switches has been shown to be one of the most attractive and straightforward strategy towards the development of useful molecules or materials in molecular electronics. In this context, photochromic coordination polymers, based on zinc(II) bis-terpyridine-appended dimethyldihydropyrene building block, have been built following a stepwise synthesis on a surface yielding photo-switchable molecular junctions. Under irradiation, reversible structural changes occur by isomerization of the photosensitive units thus inducing a conductance switching of the molecular junctions with a good reproducibility. These molecular wires represent, to our knowledge, the first example of multilayer thin films of coordination polymers that display photochromic character. Of additional importance is the fact that these functional architectures show a conductance switching with light irradiation. These results provide a promising alternative for exploring optical and electrical properties of photochromic materials as well as a novel platform for the construction of devices.
Photopharmacology and Imaging: towards a theranostic approach

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Light offers unparalleled advantages in regulation of compound bioactivity (photopharmacology) and as an input/output signal in medical (mostly optical) imaging. Combination of those two paradigms along the principles of theranostics (“treat what you see, see what you treat”) requires light-responsive tools that, preferably in combination, enable both therapy and imaging.

I will present our efforts towards the discovery of such tools, focusing on new (i) photopharmacological agents, (ii) molecular photoresponsive tools and (iii) new light-responsive, MRI-active liposomal drug delivery agents.

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Acknowledgements:
The financial support of the Dutch Scientific Organisation (NWO VIDI grant 723.014.001 for WS) is gratefully acknowledged.
Photochromism in complex environments: theoretical insights

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Photochromism consists in the reversible transformation of a chemical species between two isomers, induced in one or both directions by the absorption of electromagnetic radiation. We propose here to study a dithienylethene (DTE) photochromic compound, functionalized by ureidopyrimidinone (Upy) moieties (Figure 1.a), which enable the formation of a block of 4 hydrogen bonds (Figure 1.b). DTE-Upy molecules present two isomers, an open form (OF) that can be isomerized into a closed form (CF) upon UV light excitation (the cycloreversion reaction being triggered by visible light). In addition to the modification of the absorption spectrum due to the reorganization of the π electron cloud, the photoisomerization reaction induces a strong structural reorganization. It has been demonstrated that only the CF can form supramolecular assemblies (involving Upy-Upy interactions) in solution¹-³. Moreover, for CF isomers embedded in a polymer matrix (Figure 1.c), the morphology of the film is modified upon visible light irradiation (Figure 1.d). This macroscopic optomechanical effect is attributed to a molecular-scale phenomenon, i.e., the photochromic reaction. Aiming to participate to the design of efficient photoactuators, we propose to rationalize, thanks to Molecular Dynamics (MD) and TD(DFT), the behavior of DTE-Upy molecules in these complex environments, more precisely:

i. in solution, to investigate the properties of both OF and CF that can justify the supramolecular assembly for the CF only

ii. in a polymer matrix, to explore the interactions between both DTE-Upy and polymer chains that can justify the optomechanical behavior. The MD « STAMP » code developed by the CEA-DAM will allow us to perform in situ polymerization around the photochromic molecule.
Iminothioindoxyl: a new molecular photoswitch with 100 nm band separation in the visible range

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Light is an exceptional external stimulus for establishing precise control over the properties and functions of chemical and biological systems, which is enabled through the use of molecular photoswitches.1-4 Ideal photoswitches are operated with visible light only5-9, show large separation of absorption bands, and are functional in various solvents including water. However, especially for biological applications such as photopharmacology, the repertoire of stable full visible light switches that can operate in aqueous solutions is very limited.

Recently, we reported a class of fully-visible-light-operated molecular photoswitches, Iminothioindoxyls (ITI)10, which are a fusion of photochromic dyes thioindigo and azobenzene. ITI is a full visible-light-operated photoswitch that shows an impressive band separation of over 100 nm between both photo-isomers. Photoswitching of ITIs has been observed in solvents with a wide variety of polarities from cyclohexane till even aqueous solutions. Photo-isomerization from Z to E is a process occurring on a picosecond time scale and thermal re-isomerization from E to Z occurs on a millisecond time scale.

The presentation will describe the preparation and structure - photochemical properties relation of ITI. First, the synthetic routes towards ITIs will be discussed. Secondly, the influence of structural modifications and environment on the photochemical properties of ITIs will be shown. Thirdly, using a combination of advanced spectroscopic and computational techniques, a rationale for mechanisms of photo-isomerization and thermal re-isomerization of ITIs will be presented. Altogether, this interdisciplinary approach resulted in understanding of ITIs and how to tune the photophysical properties, which paves the way for the development of improved photo-controlled systems for a wide variety of applications that require fast responsive functions, including applications in photopharmacology in aqueous solutions.

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7. Dong M et al., JACS, 2017,139,13483-13486
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Double functional switching from photochromic molecules on surface

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Molecules can be switched between different states by different stimuli, including heating, light, and pH. Among these molecules, azobenzenes are excellent candidates as photochromic molecular switches since they can exist in two forms, the AZO-cis and the AZO-trans isomers [1]. We introduce here two different molecules incorporating an azobenzene group as a central photochromic unit bridging two different terminal groups: bipyridine for the first [Bipy-Azo-Bipy] and terpyridine for the second [Tpy-Azo-Tpy]. The organizations of these molecules on a surface have been investigated by Scanning Tunneling Microscopy (STM). Both molecules self-assemble on surfaces and various supramolecular networks can be observed with a sub-molecular resolution, thanks to the intermolecular interactions of the terminals moieties.

Hence, we studied by STM the different phase transitions induced by the protonation of the bipyridine terminal moieties and by the photo-switching of the photochromic central bridge. Indeed, a multiscale irreversible phase transition upon protonation was already observed on similar molecules consisting of a central bifluorene bridge and bipyridine terminal groups [Bipy-Fl-Bipy] [2-3]. Using [Bipy-Azo-Bipy], a similar, protonation induced, phase transition involving the switching from a cis-like to a trans-like isomer is also observed as depicted in the figure below. Next we studied the effect of irradiation on the system. The photo-switching transition from the Azo-trans bridge to the Azo-cis can be triggered by UV light and reversed back to its initial state by visible light [4]. The photo-effect on the central photochromes was firstly confirmed in solution by UV-visible absorption spectroscopy and the organization of the Azo-cis isomers on surfaces will be presented [5].

References:
Covalent Photoswitchable Ligands to Investigate G Protein Coupled Receptor Dynamics

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There is a current need to further understand the kinetics and dynamics of G Protein Coupled Receptors (GPCRs) for novel modes of disease treatment. Enhanced tools are required to facilitate these investigations. Photoswitchable ligands exemplify these advanced tools due to their ability to be activated and deactivated when desired. Generation of covalent photoswitchable ligands may enhance these mechanistic investigations. In this project, covalent photoswitchable ligands that target the clinically significant \textit{μ}-opioid receptor will be designed and synthesized. Following generation, radioligand-based binding studies and activation assays will be conducted. Covalent binding will be evaluated, as the ability of ligands to covalently bind their cognate receptor is central to this investigation. In order to attain dynamic information on receptor interactions, Single Molecule Fluorescence Spectroscopy will be employed. The development of novel photoswitchable ligands will expand the biological ‘toolbox’ to study the functional significance of GPCRs.
Irradiation method dependence of photoinduced shape change of diarylethene crystals

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Photochromic compounds undergo a photochemically reversible transformation reaction between two isomers. Such molecules in organic crystals, which are regularly oriented and fixed in the crystal lattice, may be potentially useful for optoelectronic devices. We have so far reported various types of photoresponsive crystal shape changes in diarylethene crystals, such as contraction, expansion, bending, twisting, fragmentation, and curling. In this paper, we have focused on irradiation method dependence of photoinduced shape change of diarylethene crystals.

The photoinduced bending behavior of rod-like crystals of 1,2-bis(2-methyl-5-(4-(1-naphthoyloxymethyl)phenyl)-3-thienyl)perfluorocyclopentene (1) and 1,2-bis(2-methyl-5-p-methoxyphenyl-3-thienyl)perfluorocyclopentene (2) was observed upon irradiation with polarized UV light [1]. The rod-like crystal of 1 bends away from the light source, and the crystal of 2 bends toward the light source. The bending speed depended on the polarization angle. The polarization angle showing the maximum bending speed was paralleled to the short axis of diarylethene molecules. The absorption anisotropy of the open-ring isomers in the crystals was well consistent with the anisotropy of the bending speed. This result indicates that the reaction depth from the crystal surface played an important role in controlling the bending speed. These results would provide not only the potential use of polarized light to tune photomechanical crystal deformations but also an advantage of changing the irradiation conditions to control the photomechanical material deformations.

The photoinduced crystal twisting, cylindrical helix, and bending for the crystal of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (3) were observed by tuning the irradiation direction upon irradiation with UV light [2]. The different twisting modes are ascribed to the two different-oriented diarylethene molecules, which show different reactivities by the irradiation direction. Moreover, the crystal twisting takes place in both a left-handed helix and a right-handed helix. The direction of the twisting depends on the face irradiated with UV light. The control of photomechanical crystal deformation by illumination direction provides a convenient and useful way to generate a variety of photomechanical motions from a single crystal.

References:
Sensitized Photoswitching by Ultrafast Electronic Energy Transfer in a Benzimidazole-Naphthopyran Donor-Acceptor Dyad

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Photo-induced electronic energy transfer (EET) is a key step, e.g., for natural and artificial photosynthetic energy conversion, or in data and signal processing applications based on molecular donor-acceptor dyads involving photochromic molecules as optical switches. For the rational design of EET-based functional devices, however, a quantitative understanding of the underlying photo-induced processes is crucial.

We have studied the excited-state dynamics of a model donor–acceptor dyad consisting of 1-propyl-2-pyridinyl-benzimidazole (PPBI) as donor linked via an ester bridge to the photochromic switch diphenylnaphthopyran (DPNP) as acceptor using static and femtosecond time-resolved spectroscopies and quantum chemical calculations [1]. The computed electronic transitions and the static absorption spectrum of the dyad, which is virtually identical to the sum of the spectra of its constituents, indicate only weak electronic coupling between the donor and acceptor in the electronic ground state. After selective photoexcitation of the PPBI subunit in the dyad at 310 nm, a strong quenching of its fluorescence, which has a quantum yield of 0.36 in the free PPBI molecule, was observed. The corresponding spectro-temporal transient absorption maps for the dyad and its building blocks gave evidence for a fast and practically quantitative electronic energy transfer from the PPBI*–DPNP donor-excited state to the PPBI–DPNP* acceptor-excited state in the dyad, by which the lifetime of the normally long-lived excited state of PPBI (1.4 ns) was reduced to a few ps. Enabled by the EET, the acceptor switches from its ring-closed naphtopyran form to its ring-opened merocyanine form. The EET time constant of 2.90 ± 0.60 ps was determined by singular value decomposition-based global analyses of the transient absorption data and confirmed by measurements of the transient absorption anisotropy decay. For comparison, a quantitative prediction assuming Förster resonance energy transfer provided an EET time estimate of 1.2 − 4.2 ps, in good agreement with our experimental results. The obtained quantitative insight should aid future developments of devices utilizing EET for sensitized photoswitching.

An all-photonic full color RGB system based on molecular photoswitches

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A tri-component “cocktail” consisting of a fluorescent donor molecule and two photochromic acceptor molecules encapsulated in polymer micelles has been devised. We show that the color of the emitted fluorescence can be continuously changed from blue-to-green and from blue-to-red upon selective light-induced isomerization of the photochromic acceptors to the fluorescent forms. Interestingly, isomerization of both acceptors to different degrees allows for the generation of all emission colors within the red-green-blue (RGB) color system. The function relies on orthogonally controlled FRET reactions between the blue emitting donor and the green and red emitting acceptors, respectively.
Light-controlled interactions of BODIPY-DAE conjugates in solution and linked to the surface of titanium dioxide

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Energy and electron transfer processes in photoswitchable conjugates are being intensively studied for applications in material and life sciences. So far, reversible light modulation of intramolecular and interfacial electron and energy transfer processes on semiconductor surfaces remains challenging. We have developed a series of BODIPY-DAE-conjugates designed for reversible light modulation of electron- and energy transfer processes on titanium dioxide surfaces.¹² My talk will present our newly developed systems, and I will discuss results from solution and surface studies.

Chiral and achiral azobenzene derivatives bound to DNA template

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There has been recent interest in using biopolymers as templates to construct well-organized nanostructures. Unquestionably, the most important biopolymer for such an application is DNA, which is an astounding nano-scale scaffold for assembly of light-responsive moieties. A particularly important group of compounds in this case are azobenzenes, well-known photochromic switches. Azobenzene derivatives can occur in either cis (Z) or trans (E) conformation. Irradiation with light of proper wavelength induces a molecular geometry change leading to the cis isomer, which can revert back to the trans state thermally or upon irradiation. Due to the fact that these isomers have different geometries, their properties differ significantly, the unsubstituted trans isomer being almost flat and having no dipole moment, whereas the cis form presents an angular geometry and a dipole moment of 3.0 D. Against this background, incorporation of the azobenzene motif into DNA matrix is a very attractive approach, photoswitching between different conformational states of the molecule providing an easy means to reversibly control with a spatiotemporal precision functions/structures/properties of the resulting hybrid system.¹

Herein, we present the facile preparation of photoswitchable chiroptical DNA assemblies obtained through the noncovalent incorporation of water-soluble chiral azobenzene units into right- and left-handed canonical and noncanonical DNA structures, in which the amplified induced chirooptical response of the resulting hybrid DNA nanostructures can be driven and controlled by light.²

Furthermore, we incorporated water-soluble ortho-fluorinated azobenzene derivatives that are tailored to undergo trans-cis and trans-cis isomerization with visible light, into canonical and noncanonical DNA structures. We found that the use of those photochromic molecules provided photocontrol of the DNA melting transition of long and short duplexes. This discovery allows straightforward DNA regulation by visible-light stimulation and offers new insights into the design of new hybrid and addressable photoresponsive DNA-based nanomaterials.³

Literature:

Photodegradation of diarylethenes: from Photochromic molecules to Combretastatin A-4 analogues

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Diarylethenes (stilbenes) are an important class of photoactive compounds of interest for photonics and optoelectronics. Among them, photochromic diarylethenes occupy an important place, which has been actively studied for the development of optical memory elements and molecular switches over the last 30 years. Another important class of diarylethenes are analogues of combretastatin A-4 (cis-stilbene), which have a high anti-proliferative activity. Heterocyclic analogues of combretastatin A-4, comprising the 3,4,5-trimethoxyphenyl fragment as one of the aryl residues, are being actively studied to design new effective antitumor drugs.

However, one of the important factors limiting the practical application of diarylethenes is their photodegradation. The basis of most of the side processes leading to photodegradation are irreversible photocyclization of diarylethenes.

The aim of this work is to study the irreversible photoreactions of diarylethenes (photocyclization / oxidation, photocyclization / elimination and photocyclization / rearrangement).

Much attention in this work will be paid to the light resistance of combretastatin A-4 analogues and photochromic diarylethenes under the action of UV irradiation and daylight.

This work was supported by Russian Science Foundation (RSF grant 18-13-00308).
Dynamic contrast for micro- and macro-scale multiplexed fluorescence imaging against autofluorescence and ambient light

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We introduced Out-of-Phase Imaging after Optical Modulation (OPIOM), which exploits reversible photoswitchable fluorophores (RSFs) as labels and combines optimized periodic illumination with phase-sensitive detection to specifically retrieve the label signal.¹⁻⁶ OPIOM can extract the fluorescence emission from a targeted label in the presence of spectrally interfering fluorophores and autofluorescence¹⁻³,⁶ and image biological processes in real time.³ First implemented in fluorescence microscopy,¹³ OPIOM discriminated in cells up to four fluorescent proteins exhibiting a same green fluorescence either sequentially or in parallel.³

More recently we demonstrated that OPIOM is not limited to microscopy but is relevant as well for other modalities of fluorescence imaging. We first built a fluorescence macroscope for RSF imaging against detrimental autofluorescence and ambient light.⁴ OPIOM strongly enhanced sensitivity and signal-to-noise ratio for fluorescence detection in blot assays over direct fluorescence observation under constant illumination. It successfully overcame the strong autofluorescence of growth media currently used in microbiology and achieved multiplexed fluorescence observation of colonies of spectrally similar fluorescent bacteria. Finally it easily discriminated RSFs from the autofluorescent and reflective background in labeled leaves, even under interference of incident light at sunlight intensities.

We also transposed OPIOM to wide-field fluorescence microendoscopy with one-photon excitation.⁶ It provided intrinsic optical sectioning, which facilitated the observation of RSFs at targeted positions within the sample. It was efficient to eliminate the interference of autofluorescence arising from both the fiber bundle and the specimen when observing targeted RSFs in several biological samples. Finally, it enabled multiplexed observations of two spectrally similar RSFs, which differed by their photoswitching dynamics.

Compatible with multiple imaging modalities, and simple and cheap instrumentation, OPIOM is expected to find numerous applications in fluorescence micro- and macro-imaging ranging from biological assays, bioprocessing, clinical diagnostics, to outdoor observations of plants and surfaces.

References:

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Stepwise commutation of multi-modal and multi-level molecular systems based on indolino-oxazolidine (BOX) units

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Over the past decade many efforts have been focused on the synthesis, modification and application of multi-responsive molecular systems. Up to now, two main strategies have been conducted to elaborate such systems: either by connecting different molecular switches through covalent links or by mixing them within supramolecular assemblies to obtain multi-responsiveness through the combination of various stimulations (i.e., photon, electron, proton, magnetic field, etc…).[1] In this communication, we present a different approach based on the employment of identical indolino-oxazolidine (BOX) unit as multi-modal switch. Indeed, the opening of the oxazolidine ring can be reversibly and selectively achieved either under UV irradiation, electrochemical stimulation or acidity changes. [2] According to our first attempt, the condensation of two BOX connected around a pi conjugated core was already done with an observation of stepwise commutation with all kinds of stimulations (proton, photon and electron). [3] Going further, in order to promote the metastable states possibilities, we tried to increase the number of BOX by connecting three of them on more elaborated pi systems, such as various trisaryl amine or simple benzene moiety in order to obtain a C3v symmetric or full dissymmetric molecular systems. The influence of the nature of the interactions between BOX units as well as the redox properties of the central core on multimodal switching abilities were studied in details and presented in this communication.

Figure 1: Switching features of tri-BOX conjugated system as multilevel and multimodal molecular system.

References
Microscopic photomechanical motion of single particles achieved by switching of photon force through photochromic reactions

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Micromechanical motion of molecular systems triggered by photo-absorption is attracting considerable attention because of its possible applications of remote light-driven soft-actuators. Morphological changes of molecular aggregates/crystals under photoirradiation have been intensively investigated as representative studies, where flexible micromechanical motions were successfully demonstrated. However, precise control of the motion of organic systems is relatively difficult compared with inorganic solid devices.

Here we propose a combined approach of optical tweezer and photochromic reactions for achieving controllable nanomechanical motions of organic particles in solution. In general, a photo-irradiated particle experiences three photon forces, i.e., gradient, scattering, and absorption ones. To achieve precise manipulation of target particles by controlling these three forces, photo-irradiation condition is normally optimized. On the other hand, photon forces acting on a particle can be controlled also by changing the photo-response of the target particle by using chemical reactions. Along this line, we have employed in the present study P-type and T-type photochromic reactions for photo-switching of radiation forces acting on small polymer particles.[1,2]

As samples, we prepared 300-nm PMMA particles including a diarylethene derivative and those including a pyranoquinazoline derivative. One of the PMMA particles was optically trapped in water by using a CW 532-nm laser at a point where the gradient force balanced with the scattering force. At this stage, the absorption force was negligible because most of the photochromic molecules in the particle were in the colorless form. UV irradiation to the particle induced the photoisomerization of the included photochromic compounds, resulting in the increase in mainly the absorption force and, the position of particle shifted towards the light propagation direction by 50 - 500 nm depending on experimental condition. After turning the UV light off, the particle moved back to the original position. The trapped particle thus underwent reciprocal motion along the optical axis of the trapping beam synchronizing with the color change due to the photochromic reaction.

References

Efficient fluorescence photoswitching in photochromic nanoparticles and single crystals

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The field of advanced photoactive nanomaterials, with photoswitching capabilities, is extremely active and has been attracting ever-growing interest in recent years for their various potential applications in biological sensors, targeted medicine, high-resolution fluorescence imaging, and innovative materials science. In this scope, we have been studying novel fluorescent photoswitchable organic molecules to produce efficient light-triggered nanomaterials [1].

Recently, we successfully prepared highly efficient fluorescent photoswitchable nanoparticle (NP) and single crystal, in which a photochromic molecule is combining with a highly fluorescent molecule [2,3]. In this presentation, we describe the design, synthesis, and photoswitching properties of these materials. Both materials represent a state-of-the-art system, showing bright fluorescence, reversible fluorescence photoswitching upon UV-visible irradiation, complete ON-OFF photoswitching with a high contrast, excellent photostability and fatigue-resistance (> 100 switching cycles). Most interestingly, upon UV irradiation, both materials exhibit a complete fluorescence quenching even at very low conversion yield of the photochromic unit. This “giant amplification of fluorescence quenching” evidenced for both materials, originates from a long-range intermolecular Förster resonance energy transfer (FRET) within each nanosystem, leading to the quenching of a large amount of fluorescent molecules, for only one converted photochromic molecule. Such efficient amplification of fluorescence quenching in both materials compared to solution enables “photon-saving” during the switching procedure. These results represent an extremely promising and challenging step towards smart photo-controllable nanodevices, and pave the way to a new generation of nanomaterials for innovative technologies on multicolor display, optical data storage, organic electronics, or bio-imaging [4].

References:
Light-Driven Chiral Switching of Supramolecular Metallacycles with Photoreversibility

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The construction of artificial chiral self-assembled systems has evolved to be one of the most attractive topics within supramolecular chemistry and materials science. However, the stimuli-responsive chirality transcription with the enantiospecific photoreversibility still remains challenging for chiral metallosupramolecular structures because of the lack of appropriate building blocks. Herein we present a novel chiral photoresponsive family of diarylethene-containing dipyridyl donors and their coordination-driven self-assembly behavior with 120° di-platinum (II) acceptor. The photochromic trimer units in the assembled metallacycles exhibited an unprecedented concerted photoconversion process without observing the step-by-step transformation. By taking advantage of the full-separated photoactive dipyridyl donor enantiomers based on the sterically hindered system, we have successfully achieved the photo-triggered chirality transformation in supramolecular multi-dithienylethene metallacycles arising from the axial helicity and central asymmetry, and established light-driven control in circular dichroism (CD). Such unique photoreversible self-assembled metallacycles with photo-induced enantiospecificity enables the potential chemical version to bistable chiroptical switches and nondestructive information encoding.

When 2D materials meet photochromic molecules

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Van der Waals heterostructures, composed of vertically stacked inorganic 2D materials, represent an ideal platform to demonstrate novel device architectures and to fabricate on-demand materials.[1] The incorporation of photochromic molecules within these systems holds an immense potential, since an almost infinite variety of molecules can be designed and synthesized with photo-switchable functionalities.[2]

Herein, we demonstrate how the photo-responsive nature of photochromic molecules can be conferred to the charge transport properties of 2D materials.[3] For achieving this goal, we have designed a spiropyran derivative with a long alkyl chain enable the formation of ordered and atomically precise superlattices on graphene and MoS₂: the light-induced reorganization of the spiropyran to merocyanine promotes a controllable tuning of the superlattice structure, thus a control over the local charge carrier density. The nanoscale molecular ordering and the effect of the light has been investigated by combining scanning tunneling microscope (STM), atomic force microscopy (AFM) in air with optical and electrical characterization (figure). Novel device functionalities are demonstrated, including the photo-modulation of the threshold voltage in MoS₂ and the use of spatially confined light irradiation to define reversible lateral heterojunctions.

These experiments provide a glimpse of the potential of combining 2D materials with photo-switchable monolayers to build up novel multifunctional materials with unique properties.


Figure: Photo-switchable molecular crystals in two dimensions. a Schematic representation of our approach. A spiropyran (SP) derivative forms ordered crystalline structures when deposited on different van der Waals substrates. Photo-induced isomerization induces a structural rearrangement. (e, f) STM image of the molecular assemblies obtained (e) after spin-coating the SP solution, (f) immediately after UV irradiation (i.e., merocianyne, MC) on highly oriented pyrolitic graphite.
Rule material properties through photochromism: towards optical elements and concept devices

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The colour change is the eye-sighted consequence of the molecular isomerization in photochromic materials. Nevertheless, the photochromic process is accompanied by significant modifications of other features such as dipole moment, refractive index, redox potential, conductivity, luminescence etc.. Certainly, these switching properties can be exploited for a number of applications in imaging, life science or pharmacology, and to develop optical and optoelectronic devices. Here, we highlight opportunities to apply photochromism in smart optics, where the light-triggered switching in UV–vis absorption and in the refractive index of 1,2-diarylethenes is exploited to develop rewritable optical elements, specifically tunable masks, amplitude and phase holograms and volume gratings. We show that the description of the configuration and the theoretical efficiency of the devices is a relevant issue to be considered in the material design and selection, to provide the required modulation of the properties for a convenient functioning of the device. Worth noting, the light-induced modulation of properties achieves different values for liquid or solid state systems. At the solid state, including dyes in the crystalline or amorphous state and polymer-dispersed dyes, the situation is complex since the light-induced process proceeds from the outer layer to the inner layer. We show a kinetic model that allows to predict or monitor the degree of conversion through the volume of a photochromic layer, and to determine whether a penetration depth of the radiation exists or not. We pointed out that the actual coloration of a photochromic material at the solid state depends not only on the intrinsic capability of absorbing visible light by the colored form, but also on its absorption at the illumination wavelength. The conversion kinetics in a photochromic system can be described even under complex illumination conditions, and applied to lithography. We determined the influence of the material characteristics on the confinement to subdiffraction dimensions of the transmitted dose, to finally produce patterned surfaces through in Absorbance Modulation Optical Lithography (AMOL) and Patterning via Optical Saturable Transition (POST).

Finally, we rationalize how the illumination conditions specifically affect the fatigue resistance in 1,2-diarylethenes.
Switchable and selective photodynamic damage of amyloid aggregates: a nanoscale view

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The misfolding and aggregation of proteins into amyloid fibers is at the origin of many neurodegenerative disorders. In recent years, photochemical tools for blocking amyloid aggregation have been developed. Of particular interest is a thioflavin T derivative that selectively photo-oxidizes pathogenic aggregates in the presence of functional non-aggregated proteins [1]. The mechanism for selective photo-oxidation involves the enhancement of the excited-state lifetime and singlet oxygen production upon binding to specific features of amyloid aggregates due to rotational restriction. We investigate the photodynamic damage induced by this compound on model amyloid fibers using a combination of spectroscopic tools and correlative fluorescence and atomic force microscopy. Our results provide a nanoscale view of light-induced amyloid breakage, and are relevant to improve phototherapeutical strategies for amyloid-related disorders.

Photoinduced Macroscopic Motion of Diarylethene Assembly by Combination of Photochromism and Lower Critical Solution Temperature (LCST) Behavior

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In order to apply photochromic compound in practical use, especially in molecular electronics, assembly and arrangement of the molecules are very important. We have recently found that self-assembled microstructures of an amphiphilic diarylethene showed a photoinduced reversible morphological change in water [1-5]. Photoisomerization of the core diarylethene gave rise to a morphological transformation between colorless microspheres and colored fibers. This system showed reversible morphological change also by temperature change. Synchronization of the molecular structural change between open- and closed-ring isomers, and LCST phase transition between high- and low-temperature phases is the key of the macroscopic transformation. Supramolecular nanofibers composed of the closed-ring isomer formed bundles in methylcellulose aqueous solution by depletion force while the spheres composed of the open-ring isomer were not coagulated [6]. Upon irradiation with UV light to the suspension of the open-ring isomer, the fibers were found to be generated and the formed submillimeter-sized bundles showed photoinduced shrinking over than 100 μm by the visible light irradiation. New results for the mixture of diarylenes are also presented [7].

New All-Visible Azo Photoswitches for Use in Aqueous Media

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During the last decade azo-containing switches and their performance have been largely improved,[1] by exploring the effect of functional groups, especially in the ortho positions, heteroaromatic substituents, as well as coordination and protonation of the N=N bond. However, several problems remain. To avoid the use of harmful UV-light via irradiation of the allowed and thus intense π-π* transition, typically the red-shifted yet much less intense n,π* bands are being excited, requiring long irradiation times and/or high light intensities. Moreover, the limited separation of the E and Z isomers’ n,π* bands in the visible region limits the compositional differences of the photostationary states, i.e. achievable E:Z isomer ratios. Last but not least, in order to render azobenzenes photoswitchable in aqueous media solubilizing groups have to be incorporated and aggregation must be avoided.

To overcome the aforementioned drawbacks, we here report on a new design for azobenzenes based on the tetracyanocyclopentadienide (TCCp) substituent. It allows for broad structural variation, including electron-rich or electron-poor benzene derivatives as well as heterocycles. The TCCp unit provides a handle to overcome the problem of the poorly separated n,π* bands in the visible region, where band separations up to 80 nm have been observed. The combination of absorption maxima with high extinction coefficients (ε > 20000 L mol⁻¹ cm⁻¹) for the E isomer together with the absorption gap of the corresponding Z isomer at almost the same wavelength grants access to highly E or Z enriched photostationary states, utilizing solely visible light for both isomerization directions. Given the anionic nature of the TCCp unit, the solubility of the same switch can be tuned from non-polar to polar solvents, which is accompanied by a shortened thermal half-life in more polar solvents. By covalent attachment of the cation to the aryl unit, a photochromic zwitterion is obtained, which switches efficiently between both isomers using visible light. Furthermore, the TCCp unit stabilizes the Z isomer of the corresponding azonium species in acidic media, giving rise to azo-based pKa switches, which do not suffer from an ultrafast thermal back reaction.

References:

Ion-modulated photochromic rearrangements of spirobenzopyrans bearing azole moiety

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Spiropyrans (SPP) are widely known organic photochromic dyes. The colorless cyclic form of SPP can be transformed into the colored merocyanine as a result of valence photo- or thermal isomerization, thus demonstrating positive photochromism [1]. Presence of the oxygen atom acquiring partial negative charge in the merocyanine structure makes SPP a powerful ligand in the complexation reaction with metal ions [2]. This provides for ionochromic effect. Introduction of additional fragments bearing donor atoms ortho-positioned to the pyran oxygen significantly increases stability of complexes. Such effect can be provided by the azole fragment in the 8′-position of the benzopyran part. In this work, using the example of a wide range of spiropyran derivatives, the influence of the azole moiety and the substituents in the indoline, pyran fragments on the photo- and ionochromic properties is considered. Photochromic properties demonstrate variability of spectral kinetic characteristics in the wide range depending on structural features. 8′-Positioned azole fragment is a key factor providing prominent ionochromic properties. Effective chromogenic complexation has been observed upon addition of transition metal ions to a solution of azole containing SPP. Mn²⁺, Cd²⁺ and Zn²⁺ ions form 1:1 complexes displaying fluorescence, while Co²⁺, Ni²⁺, Cu²⁺ ions coordinate two merocyanine ligands to form the non-fluorescent complexes. Stability of complexes rises upon increasing of basicity of the azole cycle nitrogen atom. Introduction of withdrawing groups in the indoline fragment leads to significant decrease of complex stability. Upon irradiation with visible light colored solutions of complexes exhibiting negative photochromism, undergo reversible discoloration as a result of photodissociation characterized by the quantum yields reaching 46%. The obtained data demonstrate the possibility to realize controlled by light cation induced isomerizations towards merocyanine complexes. A system where the direction of photochromic transformations can be driven by transition metal ions can be constructed.

This work was financially supported by Russian Foundation for Basic Research, project No. 19-03-01029A

Reversible photoisomerization within a 2D self-assembled layer of diarylethene molecules

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This study comes within the framework of design and study of smart surfaces. They are based on the self-assembly of functionalized molecules on a substrate, that will respond in a defined way to an external stimulus. As the use of light to control smart surfaces seems to hold promising prospects [1], diarylethenes [2] are one of the most appropriate functionalized molecules for the achievement and study of smart surfaces.

In this study, we report an in situ reversible photoisomerization within a self-assembled layer of diarylethene molecules on a graphite surface at the solid-liquid interface. To achieve this aim, a new diarylperfluorocyclopentene derivative has been designed and synthesized, bearing benzothiophene groups in order to improve its fatigue resistance compared to diarylethenes with thiophenes [2]. Its photophysical properties have been investigated by a UV-visible study in solution, confirming its interesting properties. A submolecularly resolved scanning tunneling microscopy study shows that both open and closed isomers form a self-assembled layer on HOPG at the solid-liquid interface, with markedly different organizations. In situ UV and visible light irradiations lead to reversible isomerizations of the molecular self-assembled layer. This photoisomerization is proven to occur within the self-assembled layer and not in solvent coupled to a molecular desorption-readsorption process, which should have hindered dramatically the use of these diarylethenes for potential applications. We do not observe any photodegradation of the adsorbed molecules after prolonged UV light irradiation. Moreover, it is possible to attain conversion ratio on the HOPG surface of 100%, both for cycloreversion and cyclization reactions. Furthermore, the self-assembly of the closed molecules is improvable by light irradiation, leading to expanding closed domains without thermal treatment of the sample. Using these newly synthetized molecules, we should then be able to obtain photoresponsive supramolecular 2D self-assemblies on large scale that isomerize within the molecular layer with thermal stability and good photorobustness, and where STM might be used as a non-destructive readout tool.

Highly Efficient Electrocatalytic Synthesis of Azobenzenes from Nitroaromatic Derivatives Using SmI₂

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The application of samarium diiodide (SmI₂) as reducing agents in organic synthesis found remarkable developments since the pioneering works by Kagan. [1] Recently, we have developed new electrochemical synthesis of SmI₂ by direct oxidation of samarium anode. [2] The procedure offers the possibility to synthesize various well characterized Sm(II) complexes. [3] This alternative route for the in situ synthesis of Sm(II) is particularly efficient and can be carried out under simple control of electrochemical intensity. The beneficial effects in terms of reactivity and solvent economy have been highlighted in various C-C bond forming reactions mediated by SmI₂ as catalytic reducing reagent [4].

Aromatic azo compounds are a common functionality in dyes and pigments. [5a] Recently, it is grown rapidly in their next-generation applications as photoresponsive soft materials, [5b] photochromic ligands for photochemical genetics [5c] and photoswitches in biological systems [5d]. The challenge in this chemistry is to synthesize non-symmetric azo compounds which generally need several steps and harsh conditions (high pressure & temperature).

Herein, we report that the catalytic use of electrogenerated samarium diiodide (SmI₂) could promote, in one-step synthesis, the reduction of nitrobenzenes into azobenzenes in high yields under mild reaction conditions. [6] The absence of precious metals, bases, and nonhazardous substances, already makes our catalytic procedure a serious alternative to currently available methods. This is a promising method for the efficient synthesis of both symmetrical and asymmetrical azo compounds with a high functional group tolerance.

References:
Diarylethenes are photoswitchable molecules and have been applied for optical memory and devices. On the other hand, photo-manipulation of biosystem has been examined actively and photo-responsive molecules have attracted attention as possible means for these utilities. In these situations, we have investigated several diarylethenes, which have been well-known photochromic molecules with high chemical stability, as molecular machines to manipulate biosystems by light. In the examinations of their bio-application, we happened to observe that the culture cells dosed with small amount of compound of 1 (dithiazoylperfluorocyclopentene) were killed very effectively by the irradiation of light with 436 nm wavelength. We investigated the feature in detail and found that this photoinduced cytotoxicity was inherent only in its closed-ring isomer 1c; the same irradiation had no impact on the cell with open-ring isomer 1o at much higher dosage, indicating that the photoinduced cytotoxicity was switchable by light. In practice, we demonstrated that the culture cells, which had been dosed with 1o, were killed by 436 nm irradiation only if the cells had a 365 nm irradiation before and to isomerize 1o to 1c.

According to cell bioassay, it was indicated that the process was apoptotic involving caspase cascade. The results of molecular-biological analysis, double strand break of the DNA was suggested strongly as an elementary step of the photoinduced cell death. Then we investigated DNA intercalation based on the competitive binding of ethidium bromide, and obtained the results suggesting that the photoinduced action of 1c intercalated in the cell DNA triggered the cell death. Further, we examined the intercalation ability and photocytotoxicity of fifteen diarylethene derivatives and studied the relation of the properties and the molecular structures systematically. The results were basically consistent with the photocytotoxicity observed in the experiments using cell cultures indicating that the derivatives having N atoms in the molecular structures were effective to induce the cytotoxicity and only closed-ring isomers showed the toxicity. These finding suggested a direction to apply the photoisomerization of diarylethenes to new biomedical utilities.
Spectroscopic applications of quantum cascade laser frequency combs

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Fast infrared spectroscopy is an important tool for research and industrial applications, giving insight into chemical kinetics on many timescales, biological processes, as well as providing an important tool for routine process monitoring and quality control. Quantum cascade laser frequency comb infrared spectroscopy has recently emerged as a new method for obtaining fast continuous measurements, enabling the parallel acquisition of many mid-infrared wavelengths with microsecond time resolution. In addition, laser-based IR spectroscopy breaks the fundamental size vs resolution barrier that is a limiting factor for interferometric techniques, allowing for spectral resolutions of <1x10⁻⁴cm⁻¹.

This contribution presents pump-probe experiments conducted on the transmembrane protein bacteriorhodopsin using a frequency comb spectrometer, which enables spectral information of three different light-activated states to be obtained after a single 10 ns excitation pulse, representing a total experimental time of 16 ms[1]. Combustion monitoring and chemical kinetics are other important applications where single-shot measurements are essential, as relatively variable reaction conditions complicate acquisition averaging. Preliminary results show the evolution of multiple species on a microsecond timescale in a gas-phase reaction at high temperature and pressure[2]. Frequency comb spectroscopy is unique in its ability to simultaneously detect and quantify these species on a single-shot basis in the mid-infrared spectral region.

References:


Optical control of ATP-gated P2X receptors

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P2X receptors are ligand-gated ion channels activated by extracellular ATP. There are seven P2X receptor subunits in mammals (from P2X1 to P2X7) that assemble to form functional homo or hetero trimeric cation-selective channels. P2X receptors contribute to many important physiological processes, including the modulation of neurotransmitter release, hearing protection, male fertility, the response to inflammation and pain sensation. They are also involved in severe disorders, such as neuropathic pain and are thus recognized as important therapeutic targets. Recent X-ray structures of P2X receptors solved in resting, open-channel, and desensitized states have greatly advanced our understanding of agonist binding and channel gating. However, despite these significant biophysical advances, there is still a lack of specific pharmacological tools targeting P2X receptors. Recent developments of optogenetics offer great opportunities for the optical control of channel activation, with exquisite temporal and spatial resolution. Inspired by these achievements, we have developed new and versatile approaches, called optogating and opto-tweezers, in which the gating machinery of P2X receptors was reprogrammed to respond to light. We demonstrated photocontrol of neuronal activity by a light-gated P2X receptor, in which the natural sensitivity to ATP was genetically removed. We also uncovered part of the gating mechanism and ion permeation of P2X receptors using these optical actuators. Engineered light-gated purinergic receptors represent valuable tools for investigating P2X signaling in native tissues.

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Synthesis and electro-induced isomerization of terarylene 7-mer on a beta-cyclodextrin as a photo- and nano-synergetic molecular system

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We have reported highly efficient electro-isomerization reaction of photochromic triangle terarylenes [1-2], where electro-generated cation radical of C-form isomer converts into radical cation of O-form isomer. Since the cation-radical of O-form has enough strong oxidation power, inter-molecular electron transfer with neutral C-form re-generates cation-radical of C-form. With these successive intra-molecular isomerization and inter-molecular electron transfer, many of C-forms convert into the O-form. We have also reported specific substituent effect on this chain-like reaction.

We further synthesized a dimer and polymers of terarylenes by connecting terarylenes with flexible alkyl linkages and studied their capability of chain-like electro-cycloreversion reactivity. Interestingly, they showed rather suppressed ring-opening reactivity, which is possibly because of unexpected stabilization of cation-radicals in the pair-stacked dimers. In the present study, we here synthesized 7-mer of triangle terarylene based on a beta-cyclodextrin, which is accomplished by efficient collaboration between PPMS/ENS-Paris Saclay and NAIST teams. The new compounds were well characterized with NMR and MS and exhibited reversible photochromic nature. Efficient oxidation-induced cycloreversion reaction was successfully demonstrated.

The study was supported by the CNRS-LIA program, “NANO-SYNERGETICS” and JSPS KAKENHI Grant Number JP26107006 in Scientific Research on Innovative Areas “PHOTOSYNERGETICS”.

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Luminescence of lanthanide(III) beta-diketonate complexes under mechanical stimulation

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The relationship between luminescence and mechanical stimuli has been of great interest in the field of photophysics and crystallography. Triboluminescence (TL) and mechanofluorochromism (MFC) are well-known examples due to their characteristic photon release without light source and emission color change upon mechanical grinding, and potential applications to visualize damage and stress of solid materials have been introduced. [1-4] However, the molecular designs to induce mechanical responsivity are not elucidated, and the general characterization methods to obtain well-defined photophysical/mechanical quantities have not been established.

In this study, we focused on lanthanide(III)-beta-diketonate complexes composed of lanthanide(III) ions, beta-diketonate ligands and phosphine oxide bridging ligands due to their sharp and bright 4f-4f transitions and their potential as mechanical responsivity. [5] The TL properties were monitored by using shock waves and a mechanical stirrer, and the PL properties under mechanical force was also recorded using a force and torque sensor equipped with a color camera. The photophysical properties with and without mechanical force are discussed on the basis of spectra and lifetimes.

Photoinduced Reentrant Transition and Thermal Stepwise Transition of Supramolecular Assembly Composed of Amphiphilic Diarylethene

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Amphiphilic molecules aggregate with each other and form supramolecular assembly in aqueous media due to hydrophobic interaction. Morphology of the nanometer-sized assembly is determined by the volume ratio of hydrophilic and hydrophobic moieties and the geometrical shape of amphiphiles. Therefore, the supramolecular assembly composed of stimuli-responsive amphiphiles show morphological change along with the change in the molecular structure. Meanwhile, the oligo(ethylene glycol) unit, often used as a hydrophilic unit, is known to exhibit lower critical solution temperature (LCST) behavior. When a photochromic unit is incorporated into an oligo(ethylene glycol) derivative, the LCST temperature would change with the photochromic reaction, because the transition temperatures of the isomers are different. Therefore, the LCST transition might be triggered by change in conversion ratio upon photoirradiation.

Some amphiphilic diarylethenes having two hydrophilic tri(ethylene glycol)s and a hydrophobic alkyl chain have been found to form supramolecular assemblies in water. Rod-like micelles and bilayer sheets are generated from the closed-ring isomers having ridged triangular plate-shapes at room temperature. In contrast, the open-ring isomers scarcely form the ordered supramolecular assemblies because the LCST temperatures are lower than room temperature. Therefore, the reported photoinduced LCST transitions are one step-change between dehydrated state of the open-ring isomer and hydrated closed-ring isomer.

In this work, we found that the supramolecular assembly composed of amphiphilic diarylethene having two hydrophilic and two hydrophobic chains underwent two-step transition. Both the open- and closed-ring isomers formed the ordered supramolecular assemblies at room temperature. In contrast, mixture of the both isomers underwent LCST transition at lower than room temperature. As a result, micrometer-sized structure showed morphological change from hydrated to another hydrated via dehydrated states upon photoirradiation under optical microscope. The open-ring isomer formed multiple folded nanorod. On the other hand, the closed-ring isomer showed time-evolution change from nanofiber to sheet at room temperature. Additionally, the suspension containing the closed-ring isomer showed two-step spectral shift corresponding to the time-evolution change, i.e., bathochromic and subsequent hypsochromic shift. In conclusion, the supramolecular assembly showed complicated change in nanometer- and micrometer-sized structures, and absorption spectra.
NIR Light-Responsive Negative Photochromic Compounds Based on 1,1'-Binaphtyl-Bridged Imidazole Dimer

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The development of novel photo-responsive materials is an intense research area because their photophysical and photochemical properties can be controlled temporally and spatially. Among them, near-infrared (NIR) light-activatable photoswitches are significantly important for especially biological applications, because NIR light can penetrate deeper into the inside of the biological tissue in contrast to ultra-violet (UV) and visible light. While red- or NIR light-activatable photoswitches induced by multi-photon absorption process have extensively explored, one-photon NIR photoswitching has been still limited and challenging.  

Recently, negative photochromism, in which the compound shows the decoloration upon light irradiation, has been attracted due to the advantages in the applications for photoswitching materials. 1,1'-Binaphtyl-bridged imidazole dimer (BN-ImD) shows the unique negative photochromism where the thermally stable colored form photochemically transforms into the metastable colorless form via a short-lived radical. Here, we present a strategy of the molecular design for red- and NIR-light-induced negative photochromism of BN-ImD derivative. The introduction of electron donating substituents brings about the appearance of a new absorption band attributable to a charge transfer transition at visible-NIR light region. This absorption band shows red-shift with increasing the electron-donating ability of the substituent. Some BN-ImD derivatives have the absorption tail at more than 700 nm. We have succeeded to induce their photochromic reaction by using NIR light (ca. 790 nm). Therefore, this molecular design will be a good candidate for the application of photoswiching molecule to the biological field such as control of biological activities.

References:
Fluorescence modulation and uncommon photokinetics with photochromic-fluorescent nanosystems

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Combination of photochromic molecules with fluorescent dyes leads to photoswitchable emissive systems.¹ The fluorescence signal is observed when the photochromic unit is colorless, and the fluorescence quenching occurs by energy transfer when the photochromic part is converted into its colored form. If the two moieties are covalently linked and studied in solution, a linear relationship is expected between the fluorescence signal and the conversion yield. But when the molecules are gathered into nanoparticles, a nonlinear effect is observed: the fluorescence is totally quenched with few photons by multiple intermolecular energy transfer processes, even if a small number of molecules are converted in the colored form.² New dyad diarylethene / perylene-diimide compounds showing these properties are presented. Interestingly, the combination of such dyads into nanoparticles leads to uncommon photokinetic behavior and a pseudo zero order can be obtained for the ring-opening reaction upon irradiation in a specific absorption range.

Figure 1 a) Representation of a diarylethene compound with two perylene-diimide fluorophores. b) Typical photokinetics of a simple diarylethene compound (ring-closure and ring-opening reactions).

Real-time Imaging of evaporative crystallization process of dibenzoylmethanato boron difluoride complexes by hyperspectral camera

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We have achieved the fluorescence visualization of the two-step nucleation mechanism proposed by organic crystal formation processes as a result of solvent evaporative crystallization of dibenzoylmethanato boron difluoride (BF$_2$DBM) complex. The fluorescence of the droplet was purple just after the dropping. The emission color changed to purple to blue via orange. Orange emission is not observed even at high concentration, which exhibited only from a supersaturated solution. Crystal of BF$_2$DBM can be formed from monomer species via an amorphous state, which is presumed to show hierarchical change like a consecutive reaction. A transient amorphous state is formed prior to crystal formation. The fluorescence detection during the solvent evaporative crystallization is also useful to assess the material properties of the mechanofluorochromism based on the amorphous-crystal phase transformation. These findings indicate that amorphous-like aggregated species with orange emission (Am1) was transiently generated during the solvent evaporation, which supports the two-step nucleation model proposed for the crystallization mechanism. Recently we have observed the different emissive amorphous aggregated with bluish-green (Am2) depending on the initial solution concentration. The schematic representation of the molecular dynamics of the evaporative crystallization is shown in Figure 1.

In this paper, to evaluate the heterogeneity of the evaporation process and to confirm the existence of Am2 phase, we performed the real-time imaging of the evaporative crystallization process by a hyperspectral camera which combines the digital imaging and spectroscopy. We will discuss on the dynamics of crystallization process analyzed by the spectral changes and the space imaging of the crystal, Am1, and Am2, depending on initial concentration, speed of evaporation, and observed regions.

Figure 1. Schematic representation of the evaporative crystallization process of BF$_2$DBMb based on the concentration-dependent fluorescence
Multimodal time-resolved spectroscopy of ultra-small upconverting nanoparticles

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Lanthanide-doped inorganic nanoparticles present the unique feature of being able to emit light up to the blue region of the visible spectrum (depending on the nature of the dopants) while being excited by near infrared (NIR) light. Because biological samples have limited absorption in the NIR, these so-called Up-Converting NanoParticles (UCNPs) are attractive candidates for biological applications.

UCNPs can be functionalized with photochromic dyes which absorb light emitted by one UCNP emission channel. These nanohybrids represent promising probes allowing, at the same time, single particle tracking using one emission channel and, super-resolution microscopy with a second emission channel. Indeed, Förster Resonance Energy Transfer (FRET) switching between photochromic dye and UCNP will induce blinking of the particles that can be used for super-resolution fluorescence microscopy (STORM, SOFI). In order to optimize their design, the blinking properties and emission lifetimes of such inorganic luminescent UCNPs grafted with organic photochromic quenchers have to be thoroughly described.

The behavior of ultrasmall bare NaYF\(_4\)-based UCNPs as a function of the excitation power (time-resolved emission dependence vs. excitation power) is investigated in solution and at the single particle level in order to extract their photophysical properties (lifetime, brightness). Luminescence spectra are recorded using the 976 nm light of a pulsed diode laser through a confocal microscope allowing for collecting spatial and time-resolved information on the power-dependent fluorescence of single UCNPs.

We will discuss the properties of single UCNPs and nanohybrid particles grafted with a fast photochromic dye. Their blinking dynamics will be especially detailed to prepare new ultra-small UCNPs for super-resolved fluctuation fluorescence microscopy.
Photo/Redox Control of π-Dimerization as a Trigger for Molecular and Supramolecular Metamorphism

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One of the keys to the development of nanoscience is to observe, modify and control matter at the nanoscale. One strategy proposed to meet these immense challenges is to develop responsive molecular or supramolecular systems that can trigger a structural reorganization when exposed to an external stimulus: this phenomenon is known as “metamorphism”. Systems with controllable architectures are of great interest in different fields such as molecular electronics, capture and controlled release of guest molecules, or molecular machines. The strategy developed at the Chemistry Laboratory of ENS Lyon is to exploit the switching and assembly properties of π-conjugated organic radicals that can be generated in-situ by electrical or light excitation.¹,² This concept is based on molecular or supramolecular engineering strategies aiming at promoting the formation of π-dimers in solution under usual conditions of temperature and concentration. A first approach consists in connecting viologen subunits with mobile covalent bond in order to guide and facilitate an electron-transfer triggered switching from an open conformation, imposed by intramolecular charge repulsion, to a folded form stabilized by the formation of an intramolecular π-dimer between two cationic radicals. Another approach consists in favoring the formation of π-dimers inside cavitands molecules such as cucurbituril in order to control the reversible association/dissociation of molecular building blocks into 2D-supramolecular assembly. These strategies are very promising for the development of new soft-materials with switchable properties.

Cyclization reaction dynamics of an inverse type diarylethene derivative in solution and solid phases

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Diarylethene derivatives undergo a reversible photochromic reaction between the closed- and open-ring isomers. A series of the compounds have been attracting continuous attention due to their excellent molecular properties, leading to realization of the advanced photofunctions in the field of material science. With respect to the orientation of two heterorings, diaylethene derivatives can be categorized into two groups, normal type and inverse type. The inverse type derivatives have a great advantage for designing photofunctional materials with higher reactivity than normal derivatives. In addition, from the fundamental viewpoint, it is crucially important to investigate the relation between shapes of potential energy surfaces and chemical reactivity in the excited state. In the present study, we have investigated the cyclization reaction dynamics of a typical inverse derivative, iDAE in solution and solid states by means of time-resolved absorption and fluorescence spectroscopies.

In solution phase, steady-state and time-resolved fluorescence spectroscopy with the aid of quantum chemical calculations revealed that there exist three kinds of conformers, one parallel and two anti-parallel forms in the ground state. Femtosecond transient absorption spectroscopy showed that one of the anti-parallel form undergoes the cyclization reaction with a time constant of 36 ps, which is significantly slower than that of normal type derivatives. The other two forms are nonreactive species and their major relaxation processes are the radiative decay and intersystem crossing into the triplet states.

To investigate the reactivity in the solid state, we applied ultrafast spectroscopies to iDAE nanoparticles in water. Transient absorption spectroscopy showed that the S1 state formed by photoexcitation is relaxed into another transient species on a few tens picosecond timescale. A similar time constant was observed in time-resolved fluorescence measurements. By considering that iDAE nanoparticles show red-shifted fluorescence, we assigned this time constant to the relaxation from the S1 state into the species such as charge transfer states. No absorption of the closed-ring isomer remains after the decay of transient absorption, indicating that iDAE does not undergo the cyclization reaction in the solid state. This distinct reactivity between in solution and in solid states is probably due to change of viscosity in surrounding environments.
Recent evolutions in terarylene scaffolds using thienothiophene and benzothiazole substituents

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We have, in the last few years reported highly sensitive, neutral terarylenes containing photoexchangeable open and closed forms, with uses in areas including in situ acid generation and on/off fluorescence [1-2]. Here we present recent synthetic, computational and photophysical investigations into the development of new members of this extended family containing thienothiophene and benzothiazole synthetic moieties.

The incorporation of benzothiazole permits the directed photogeneration of a closed form state that spontaneously undergoes hydride loss in the presence of suitable acceptor molecules. This has allowed for the development of a light initiated hydride donor, which has successfully been used to generate silver nanoparticles in situ [3]. Detailed photophysical analysis comparing these systems to existing non-light induced hydride donors has been carried out and will also be presented.

Recent investigations have also allowed for the development of new thieno[3,2-b]thiophene systems, the extended aromatic character of which makes them excellent targets for the absorption of higher energy photons, including X-Rays. This offers up the possibility of new uses for our terarylene frameworks in particle detection and energy storage.

References:
Photochromic molecules and plasmonic materials for new reversible switchable devices

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Using metallic nanoparticles (NPs) for electronic devices show many advantages due to their specific optical and electric properties that can be driven by light. This owes to the surface plasmon resonance that gives rise to a great enhancement of the local electromagnetic field. As surface plasmon resonance is very sensitive to their direct environment, it is possible to use photochromic molecules as a local photoswitch to reversibly modify these photophysical properties. [1] The goal is to develop a hybrid material combining molecular and plasmonic components which by action of an external stimulus – here a light excitation - shows a reversible change of its electrical - conductance - and optical properties at the millimeter scale. [2,3]

In this communication we present hybrid nanomaterials made of (i) gold nanorods as the plasmonic unit [4] and (ii) charged diarylethene as photochromic unit. A polyelectrolyte is used as a linker between them thanks to electrostatic interactions, limiting the quenching of the photochromic molecules. Steady state absorption experiments highlight the fact that using polyelectrolyte as linker avoids the quenching of the photochromic reactions. Furthermore, transient absorption experiments clearly show that the hybrid nanomaterial behaves differently from the single gold nanorod or diarylethene.

References:

Specific electrocyclic reaction dynamics of a dithiazolylarylene derivative

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Photoinduced 6π-electrocyclic reaction is one of the basic processes leading to various photofunctions and photoresponses. For the development of advanced photofunctional materials, it is important to elucidate its reaction dynamics and mechanism. In actual, a lot of experimental and theoretical studies have been so far reported on this reaction mechanism and it has been regarded, as a general scheme, that the photoinduced cyclization and cycloreversion reactions in 6π-electron systems take place on the 2A potential energy surface (PES) and the same conical intersection (CI) mediates the 2A and 1A (ground state) PESs in both the reactions. However, we recently found the 6π-electron system showing the reaction dynamics different from the above conventional scheme in a dithiazolylarylene derivative (DTA). In the present work, the origin of the difference will be discussed on the basis of the experimental results by femtosecond transient absorption and fluorescence spectroscopies.

First, the cyclization and cycloreversion reaction dynamics of DTA in n-hexane solution was elucidated by femtosecond transient absorption measurements. After spectral evolution on a sub-picosecond timescale, transient absorption signals appearing in the excited state of the closed- and open-ring isomers decayed with a time constant of ca. 23 ps. In addition, spectral band shapes of the transient species in both cases are quite similar with each other. These results strongly suggest that the cyclization and cycloreversion of DTA occur via the common intermediate. From the detailed studies of the fluorescence spectroscopy, this common species was assigned to the excited state of DTA(c). That is, the excitation of the open-ring isomer leads to the formation of the excited state of the closed ring isomer, although the typical ring-closing reaction in the 6π-electron system results in the formation of the ground state of the closed ring isomer. It should be noted that the geometry of DTA is rather planar owing to the intramolecular hydrogen bond and S-N interaction, leading to the suppression of the rotation of the aryl moieties. By integrating these geometrical features with the experimental results on the solvent polarity dependencies, we will discuss the factors responsible for the specific reaction mechanism.
Irreversible photo-isomerisation of arene-Ru complexes bearing azobipyridine-derived ligands

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The external manipulation of molecular systems with light is being increasingly exploited for the control of events at various scales, eventually giving rise to “smart” systems. [1,2] In particular, metal centers bearing photochromic ligands have attracted attention in recent years for applications in biology and medicine, but also in the field of molecular machines and catalysis. [3]

In this context, we have synthesized novel azobipyridine derivatives and studied their behavior as ligands for ruthenium. Spectroscopic studies of the resulting organometallic complexes, allied with structural analysis by DFT and X-Ray diffraction revealed a new coordination pattern of the Z complex that lead to its irreversible photo-isomerisation.

References:
Red-Light Driven Photochromic Molecule by Using Triplet Fusion

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Photochromic molecule driven by red or near-infrared light has a potential for application in biological and material chemistry because it has several advantages such as a high efficiency of the reaction inside of biological tissues or organic media and no requirement of UV light which damages materials and cells. Many visible-light-sensitive photochromic molecules are investigated based on the molecular structure of azobenzene, spiropyran, diarylethene, DASA, and so on. However, introduction of substituent into a molecule in order to extend the absorption band to the long-wavelength region sometimes occurs several problems such as decrement of the conversion efficiency or destabilization of the photogenerated species.

Herein, we demonstrate a photochromic reaction under red light irradiation by using triplet fusion upconversion (also refer to triplet-triplet annihilation), which is a methodology that converts lower-energy photons into higher-energy photons. We synthesized a phenoxy-imidazolyl radical complex derivative connected with a perylene (Pery-RPIC) working as an energy acceptor. Radical complex generates a colored biradical upon light irradiation and thermally returns to the initial closed form by the recombination of the radical pair. We report the photochromic reaction of Pery-RPIC can be induced with 635 nm light irradiation via the triplet fusion of itself sensitized by Pd(II) mesotetraphenyltetraphenoporphyrin in toluene. Ultrafast transient absorption and fluorescence measurements revealed that the bond-dissociation reaction of Pery-RPIC can be efficiently occurred at the excitation to the perylene unit with almost no emission while perylene is well-known as a highly fluorescent molecule. We also confirmed that the reaction can be proceeded from only the singlet-excited state of Pery-RPIC generated by the intermolecular collision, not from the triplet-excited state. We anticipate that the method of direct utilization of the excited state generated by triplet fusion can be applied to design of valuable photochemical reactions beyond photochromic reaction.

References:
First study of the photodynamics of a hydrozoan photo-switchable fluorescent protein: existence of different switching mechanisms

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Recently, reversibly photoswitchable fluorescent proteins (RSFPs) have been widely applied in super-resolved fluorescence microscopy. Even though photo-physical parameters (switching and fluorescence quantum yields) are linked to the resolution and image acquisition speed, the switching mechanism that controls these parameters is still a matter of debate. The most studied RSFP is Dronpa, a negative RSFP from Anthozoa. The majority of studies have focused on the switching dynamics from the non-fluorescent (off) to the fluorescent (on) state. It has been reported that a trans-to-cis isomerization occurs within a few picoseconds in the excited state, followed by chromophore deprotonation in the ground state on the microsecond time scale (Warren et al. Nat. Comm. 2013). On the contrary, a recent report suggested that protein cage rearrangements play an important role for the isomerization process and provided evidence for both isomerization and deprotonation occurring in the ground state (Laptenok et al. Nat. Chem 2018). Here, we share results on another RSFP, rsEGFP2, an RSFP from Hydrozoa which is a protein used in super-resolved microscopies (Grotjohann et al. elife 2012). Time-resolved serial femtosecond crystallography at an X-ray free electron laser, combined with UV-visible transient absorption (TA) spectroscopy, showed the existence of a twisted chromophore configuration on the picosecond time-scale, with the two cyclic moieties perpendicular to each other and a dynamically restricted by the close proximity to the V151 side chain (Coquelle et al. Nat. Chem 2018). Accordingly, mutation of the latter to alanine (V151A) doubles the off-to-on switching quantum yield.

Using optical time-resolved TA spectroscopy from the femtosecond to the millisecond time scale we studied the mechanism of off-to-on photoswitching in WT and mutant rsEGFP2 with various off-to-on switching quantum yields. We found that different isomerization mechanisms for the trans-to-cis isomerization can explain the variation in switching quantum yields. The increase of off-to-on switching quantum yield for V151A mutant is rationalized by a sub-picosecond isomerization without any intermediate in the excited state. We also characterized a 100-picosecond intermediate in the ground state that does not exist in the WT protein. We will discuss how the protein cage controls the off-to-on dynamics in rsEGFP2.
Fluorescent response to forces at the nanoscale of photo-polymerized polydiacetylenes

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Mechanofluorochromic materials change their fluorescent properties when subjected to external mechanical stimulation. [1] This mechanical force affects their supramolecular structure, resulting in different emitted light. Polydiacetylenes (PDA) are ordered π-conjugated systems that undergo topochemical polymerization under UV (254 nm). [2] According to the molecular arrangement, such polymerization may produce a non-fluorescent “blue” form and a weakly fluorescent “red” form. [3] Upon external stimulation, the blue form is converted to the red form.

We study the fluorescent properties of PDA-based materials when subjected to nN-range forces by means of an atomic force microscope (AFM) coupled with a fluorescence microscope. We aim at providing a mechanical fluorescent sensor with a well-defined correlation force-fluorescence recovery. We present here the photo-polymerization properties, morphology, and photophysical response to nanoscale shears of three PDA-derived compounds. DA1 is a simple diacetylene with urethane moiety as self-assembling group; TzDA1 is a derivative covalently attached to a tetrazine fluorophore; TzDA2 has a modified urethane moiety. Tetrazine is not fluorescent when PDA is blue (OFF) due to energy transfer, while it is fluorescent when PDA is converted to the red form (ON). [4] Vacuum evaporation of the monomer followed by UV irradiation produced blue PDA thin films. Upon mechanical stimulation using AFM in contact mode, fluorescence was recovered by conversion to the red form. Comparing DA1 vs TzDA1, a better fluorescence contrast was found in the latter, demonstrating the importance of the tetrazine fluorophore. To test the role of the self-assembling group, we modified the urethane moiety in TzDA2. We found that the simple urethane moiety in TzDA1 was more optimal for nano-mechanical stimulation. Thus, TzDA1 showed the clearest correlation between applied force vs fluorescence recovery. Therefore, in this work, we show the importance of the fluorophore and the self-assembling unit in making a nanoscale mechanical force sensor.

Fluorescence image (left) and morphology image (right) of mechanically stimulated TzDA1 thin film.

Photo- and Electrochromic Molecular Switch Based on Aryl-Bridged Radical Complexes

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The development of a single molecular switch showing multi-way response to various external stimuli has been demanded for the development and the versatility of the design of attractive switching materials. Photochromic molecules are a well-known class of photo-switching molecules that undergo the reversible isomerization between the colorless and the colored isomers. It has been reported that some of them respond to the other stimuli, and therefore, such photochromic molecules have been accepted as a good candidate for a multi-responsive molecular component. Pentaarylbiimidazole (PABI) and phenoxyl–imidazolyl radical complex (PIC) are one of the fast photochromic molecules based on imidazolyl radicals.1,2 Because the photochromic reaction of these fast photochromic molecules proceeds from the optically forbidden $S_1$ state, it is difficult to estimate the excitation energy to induce the photochromic reactions by spectroscopic techniques. In this study, we performed the electrochemical measurements of PABI and PIC to investigate the electronic properties and to estimate the $S_0$–$S_1$ transition energies.3 In addition, we also revealed that the electrochemical reductions of PABI and PIC generate the radical anion which spontaneously shows the C–N bond breaking reaction to form the radical species. The initial photochromic dimer is reproduced by the reversible oxidation of the anion species. We also investigated the electrochemical oxidation processes of PABI and PIC, and revealed for the first time that they reversibly generate the highly stable radical cations with accompanying the color change from colorless to green.4 These characteristic photochromic and electrochromic properties can be applicable to the photo-addressable electrochromic devices with high spatial resolution.

References:

Photo- and Electro-Control of NIR Luminescence

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Lanthanide ion complexes display unique long lived and narrow bandwidth luminescence ranging from the visible up to the near infra-red spectral range, with high emission efficiency, and a large (pseudo)-Stokes shift.\(^1\) Therefore, remote control of this luminescence is attractive for the development of optical materials.

Ruthenium (II) acetylide complexes are relevant redox active moieties as they promote a very efficient communication between carbon chains and the metal atoms. They can be incorporated in 4d-4f bimetallic complexes to achieve excellent redox-switching behavior for the ON/OFF switching of NIR emission in the case of Ytterbium(III).\(^2\)

On the other hand, photochromic ligands, such as dithienylethene units, are easily isomerized between two isomers with different electronic structures, and they are ideal optically triggered candidates for also switching lanthanide luminescence.\(^3\)

In this work, we combine, for the first time, the two approaches to achieve efficient switching of NIR luminescence with two types of orthogonal stimuli: light and electron transfer.

ABSTRACTS: POSTERS SESSION 1
Reactivity of Photo-Lewis-Acid Generator Based on Photochromic Terarylene

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Photo-Acid Generators, PAGs, generate Brønsted acid upon photo-irradiation, which is widely used in photopolymer systems such as photoresists. Expansion of PAGs to a Photo-Lewis acid generating system may expand their application to various Lewis acids catalytic reactions such as Friedel-Crafts reaction and Mukaiyama-aldol reaction. We herein propose the Photo-Lewis-Acid Generator (PLAG) based on a photochromic terarylene.

We designed PLAG based on terarylene aiming for formation of a carbocation as a Lewis acid after the elimination of a leaving group from the reactive carbon atoms, the compound is composed of three electron-donative groups such as benzo[b]thiophene, phenylthiophene and naphthalene units to promote stable carbocation. Two kinds of leaving units, the methoxy group (PLAG-1a) and the triflate group (PLAG-2a), are introduced at the naphthalene unit. PLAG-1a showed reversible photochromism upon UV and visible light irradiation in acetonitrile with the absorption band at 576 nm which is typical for ring-closed form isomers of terarylene derivatives. In the case of PLAG-2a, we observed a progression of absorption bands at 396, 526 and 694 nm by UV light irradiation, irreversibly with typical isosbestic point (308 nm). $^{13}$C-NMR showed 24-new peaks including two characteristic peaks at around 200 ppm after UV light irradiation, which are typical for carbocation compounds. The triflate unit is considered to eliminate spontaneously after ring-cyclization reaction to give a carbocation form, which is also supported by HRMS and DFT calculation. We examined the reactivity of PLAG-2a in Lewis acid catalytic reactions. Photo-triggered epoxy polymerization of cyclohexene oxide was confirmed with PLAG2a as a photo-triggered catalyst. Mukaiyama aldol reaction of benzaldehyde with silyl enol ether derivatives was also catalyzed by the photo irradiation of PLAG-2a.

In summary, we synthesized PLAG-2a based on a photochromic terarylene as a new photo-Lewis-acid generator. PLAG-2a formed a carbocation through 6-p electro-cyclization by photo-irradiation, which triggers Lewis acid catalytic reactions such as cationic polymerization reaction and Mukaiyama aldol reaction.
Synthesis and Photochromism of the Spiro[2H-indole-2,2'-[2H]phenanthro[9,10-b][1,4]oxazine] system

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Photochromic 1,4-oxazine systems have attracted commercial success for many years in ophthalmic sun lenses. The 1,4-oxazine system is typified by intense red – green hue development upon sunlight activation and good reversibility with readily controllable rates of fade combined with robust performance. There has also been interest in the negative photochromism of oxazines and their use as active constituents in switching systems.

Our present work focuses on the exploration of the chemistry and photochromic performance of the spiro[2H-indole-2,2'-[2H]phenanthro[9,10-b][1,4]oxazine] system 1 (Figure 1). Whilst substituent effects have been explored concerning the indole moiety of 1 there is a dearth of information concerning the introduction and influence of substituents on the phenanthrene moiety. Our present study describes the regiospecific synthesis of some dibromo-substituted oxazines 2 and 3, and examines their behaviour towards transition metal-mediated functionalisation with aryl, phenylethenyl and phenylethylnyl substituents. The influence of the location and the electronic characteristics of the foregoing substituents upon the photochromism of the new 1,4-oxazines 4 is discussed.

Figure 1

References and Notes:
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2. B. M. Heron et al., Dyes Pigm., 2018, 149, 92-121.
Correlation between Aromaticity and Photochromic Properties of Fast Photochromic Pentaarylbimidazole

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Delocalized biradicals have been extensively studied because of fundamental interests to singlet biradicals and several potential applications to such as two-photon absorption materials, leading to the demand to evaluate the biradical character. Recently, we have developed fast photochromic pentaarylbimidazole (PABI). PABI undergoes the homolytic cleavage of the C-N bond between the two imidazole rings to generate the open-ring isomer upon UV light irradiation. The open-ring isomer of PABI is described as a resonance hybrid of the open-shell biradical and closed-shell quinoidal structures. It is expected that the contribution of the biradical character to the open-ring isomer of PABI derivatives can be controlled by changing the aromaticity of the bridging unit. In this study, we designed and synthesized PABI derivatives bridged by a naphthalene (1) and a benzothiophene (2) unit to control the biradical character of the open-ring isomer.

The transient absorption spectrum of 1 is in good agreement with the calculated absorption spectrum of the open-ring biradical form, indicating the large aromaticity in the bridging unit increases the contribution of the biradical character to the open-ring isomer. In addition, the thermal back reaction of the open-ring isomer is accelerated (185 ns), compared with that of PABI. In contrast, the transient species of 2 shows the similar absorption band with that of the closed-shell quinoidal form, and the thermal back reaction is decelerated to the second time scales (22 s). These results suggest the large contribution of the open-shell biradical form increases the reactivity between the radicals to form the C-N bond. Therefore, we succeeded to establish the efficient strategy to control the biradical character of the transient colored form, and to experimentally determine the biradical character of the singlet biradicals by measuring the thermal back reaction rates.

References:

Red-Light-Responsive Fast Photochromic Reaction of Phenoxyl-Imidazolyl Radical Complex

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Thermally reversible photochromic molecules offer the opportunity to change the molecular properties by simply turning a light source on and off, and have attracted great attention due to their potential applications. Although UV light has been frequently used to induce the photochromic reactions of conventional artificial photochromic molecules, visible light has been utilized in photoreceptors in nature, such as the cis–trans isomerization of retinal in rhodopsin proteins. Visible light has several advantages over UV light, reduction of degradation in devices and mutagenesis of cells and the ability to penetrate into the inside of the sample. Therefore, development of visible light sensitive photochromic molecules has been recently received much attention. We previously succeeded to develop the green-light-responsive fast photochromic molecule by using a zinc tetraphenylporphyrin (ZnTPP) as a photosensitizer. While conventional bridged imidazole dimer (ImD) shows the photochromic reaction upon UV light irradiation, the ZnTPP-substituted ImD demonstrated the visible light responsive photochromic reaction involving a stepwise two photon absorption process.

In this study, we developed a red-light-responsive photochromic compound (1) by combining a red light sensitizer to a phenoxyl-imidazolyl radical complex (PIC) derivative. The steady-state absorption spectrum of 1 is the superposition of those of the photochromic unit and the sensitizer. Upon red light irradiation (670 nm), the two transient components, fast and slow decay components, were observed. The fast and slow decay components can be attributed to the thermal equilibrium process from the biradical to the quinoidal form and the thermal back reaction from equilibrated two forms to the initial form, respectively. Because the amount of the photo-induced transient species is proportional to the square of the excitation light intensity, this photochromic reaction is sensitized by the two photon absorption process.

References:
Cooperative Switching Processes in Dihydropyrene Dimers

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For systems composed of multiple photochromic units the coupling of the individual switching events is hard to predict and the bridging moiety has shown to be a crucial factor. Typically, the loss of photochromism or diminished quantum yields are observed for the second switching event.[1] In contrast dihydropyrenes, pioneered by Mitchell and Boekelheide, are negative T-type photoswitches exhibiting great potential for the use in multiphotochromic systems.[2,3]

Here we present symmetrical bis-photochromes consisting of two dihydropyrenes conjugated either through a suitable acceptor or donor bridge, resulting in three accessible states (closed-closed vs. closed-open vs. open-open). In some derivatives we have been able to uncover a cooperative switching behavior in which the second ring-opening event is more efficient than the first one.[4]

Based on our insights into the mechanism of information transfer we aim to design multiphotochromic systems with enhanced switching efficiencies.

References:
Photochromic properties of nitroaryl (or hetaryl)-methyl derivatives of nitrogen heterocycles

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The spectral-kinetic characteristics of the 2 - and 4-(2',4'-dinitronaphthyl-1'-methyl)-pyridine (1,2) and -quinoline (3,4); 2 - and 4-(5',7'-dinitroquinolin-8'-methyl)-pyridine (5,6) and -quinoline (7,8) in comparison with the 2 - and 4-(2',4'-dinitrobenzyl)-pyridine (9,10) and -quinoline (11,12) was investigated. Absorption spectra photoinduced forms of these compounds and constant of the rate back reaction \( k_f \) dependent on the pH. Numerically constant speed reaction bleaching of colored forms naphthylmethyl derivatives (1,2) is more than an order of magnitude less than the benzyl analogue (9,10) at the same pH. This difference, as obtained by the method of flash photolysis value of the equilibrium constant between azamerocyanine and anion (pK_a 6.1) for the naphthyl derivative (1) was almost an order of magnitude greater than that of the benzyl analog (9) (6.9), due to the delocalization of the charge for a more extended \( \pi \)-system. The simultaneous presence of photoactive dinitroquinoline and basic quinoline fragment (7,8) leads to an increase in the lifetime of an order of magnitude compared with naphthylmethyl derivatives (1-4) and 3 orders of magnitude - compared with benzyl derivatives (9,10). Photoinduced form 4-quinoline derivative (8) in ethanol at room temperature has a record in this series of compounds lifetime (4000 s). Annelation of the benzene ring to the two fragments dinitrobenzylpyridine (3,4) leads to a deepening of color photoinduced azamerocyanine and increases the color of the anion. In the record, a maximum - for 4-(2',4'-dinitronaphthylmethyl)-quinoline (4) - this range is 160 nm (480 nm in an alkaline medium, 640 nm in an acid). The quantum yields of photocoloration increase only upon anellation to the nitrobenzyl fragment and decrease upon attachment to the heterocyclic fragment. It is shown that the lifetime of photoinduced azamerocyanines, anions and range of color - substantially increases by the extension of chain conjugation electrons in the heterocyclic and in dinitroaryl fragments, i.e. at the transition from the pyridine to quinoline derivatives and from a nitrobenzyl to nitronaphthylmethyl derivatives.

The work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (4.4697.2017/6.7) and the Russian Foundation for Basic Research (grant 19-08-01232).
Electrochemical Switching of Spiropyrans

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The elucidation of the mechanisms of redox driven organic reactions, although fundamental research, is central to the study of the redox behaviour of natural products, especially organic antioxidants such as tocopherol, and the performance of redox responsive molecular based materials. Recently we have explored the redox chemistry of spiropyrans and found that the well-known nitro-spiropyran undergoes aryl-aryl radical – radical coupling upon (electro)chemical oxidation. In this presentation, our recent studies of the redox driven switching of a spiropyran derivative, that cannot engage in aryl-aryl coupling, allows for redox driven ring opening and switching of localisation of oxidation from the indoline to the phenol moiety. The reactivity of the radical (protonated) phenol moiety is investigated both photo- and electrochemically.
Visible-light driven molecular motors based on oxindole

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Overcrowded alkene-based molecular motors have proven to be valuable in many fields, however a major challenge in their use is to drive their rotation with benign visible-light rather than harsh UV-light. This poster highlights recent advances in the synthesis of oxindole-based molecular motors that can be powered with visible light.
Dynamic Covalent Assembly of Diarylethene Photoswitches

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Dynamic bond formation is a prerequisite for adaptive systems.\[1\] These systems are under thermodynamic control and react to external stimuli as they strive to reach global energetic minima. Depending on the design, they can thus function as dynamic combinatorial libraries to identify chemical compounds with desired features.\[2\]

Depicted below in Figure 1, we found that Knoevenagel products (A1 and A2) are interconvertible upon addition of corresponding nitriles and that they represent an interesting class of non-bridged diarylethene photoswitches. The here presented dynamic covalent access to such chromophores serves hence as a methodological approach for rapidly screening for a large range of novel photoswitches.

Figure 1: Dynamic equilibrium between Knoevenagel products A1 and A2 (top) and their potential photoisomerization reactions (bottom).

In a recently reported study, we showed that diarylethenes can be selectively pumped into or out of an equilibrium reaction, thereby gaining perfect control of the latter.\[3\] Here, we want to develop this concept further and will discuss the potential of dynamic covalent chemistry to form light-activatable intermediate chromophores. Those act as conventional catalyst substrate complexes that dissociate again after substrate-to-product conversion.

References:
Influence of Carbonyl Substituents on the Photochromic Properties of Naphthopyrans without Residual Color

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Naphthopyrans, as a kind of thermally reversible (T-type) photochromic molecules, attracted more and more interest in the past decades. The synthesis and photochromic properties of differently substituted naphthopyrans have been reported in recent years.[1, 2] When applied on silicon (111) surface studies, naphthopyrans will have a broad use in photovoltaic devices, molecular electronics and chemical and biological sensing.[3-6] However, the residual color and thermal bleaching rate limits their fast-photo switching applications.

Herein, we introduced substituents on the naphthopyran ring and the aryl groups, resulting in the disappearance of residual color, because the thermal rate of TT form was improved. Interestingly, we find that different substituents on the 8-position had a different impact on the thermal back rates of both TC and TT forms at the same time. (Figure 1) With the help of different measurements, such as UV-Vis, in-situ NMR and IR, the details of ring-opening and ring-closure reaction of 1-4 will be discussed.

To be published:

Fast color switching with photochromic fused-naphthopyran

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Naphthopyrans are one of the most important classes of photochromic systems with excellent photochromic activity that have met considerable success in the production of variable-transmission optical materials, namely photochromic plastic ophthalmic lenses. The UV light promotes the cleavage of the pyran C(sp³)-O bond affording a mixture of two coloured photoisomers named TC and TT which have different thermal stability. Thus, when the light source is removed, the major photoisomer (TC) fades quickly to the initial uncolored form but the minor one (TT, responsible for 10-20% of the coloration) in thermally more stable and returns slowly to the uncolored form. As a result a residual colouration due to the long-lived photoisomer is observed [1,2].

One way to prevent the formation of the unwanted TT photoisomer is to connect the pyran double bond to the naphthalene core and create a fused-naphthopyran. Unlike common photochromic naphthopyrans, the opening of the pyran ring in such compound, leads to only one coloured photoisomer that exhibit a fast mono-exponential decay to the initial uncoloured state [3,4].

In this communication we describe a short synthesis (3 steps) of a new polycyclic photochromic fused-naphthopyran that shows this behavior. An uncolored polymeric film doped with this dye (0.8 %) can be activated in 30 s with UV light and loses 90% of the coloration in 1 min, in the dark, at room temperature. The use of this compound allows a faster adaptation of the material’s coloration to the surrounding UV-light intensity.

Figure 1. Photochromic equilibrium for a fused-naphtho[1,2-b]pyran and a photo of a polymeric film half exposed to the UV light.

Acknowledgments:

The authors acknowledge FCT (Portugal's Foundation for Science and Technology) for financial support through the research project PTDC/QUI-QOR/28532/2017

References:

Highly Enantioselective Photochromic Ring Closure of Bisthienylenethenes and Their Absolute Stereochemistry

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We have previously reported the enantioselective photochromic ring closure of bisthienylenethenes (BTEs) 1o-3o incorporated in Human Serum Albumin (HSA).¹² The BTEs have the connection of thiophene rings to the ethene bridge at their C-3 positions. BTEs 2o and especially 3o showed highly enantioselective photochromic reactions.² We determined their absolute stereochemistry of the major enantiomers photochemically generated in HSA to be (R,R)-2c and (S,S)-3c by X-ray crystallographic analysis³ and the transformation of (R,R)-2c to (R,R)-3c.²

In the present study we employed BTEs 4o-6o having the connections at their C-2 (Scheme 1). BTEs 5o and 6o showed highly enantioselective photochromic reactions. We determined the absolute stereochemistry of the major 5c to be (S,S) by the comparison of the CD spectrum of optically resolved 5c with the predicted CD spectrum by DFT calculations, and the docking simulations between HSA and 5o. Transformation of (S,S)-5c to (S,S)-6c proved that the major 6c photochemically generated in HSA was (R,R).

![Diagram](image)

Scheme 1. Stereochemistry of closed forms of BTEs

Tripodal N-Functionalized Arylazo-3,5-dimethylpyrazole Derivatives of Trimesic Acid: Photochromic Materials for Rewritable Imaging Applications

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Solid state photochromic materials find potential application in photoactive devices such as sensors and optical switches and memories. We report the development of tripodal N-functionalized arylazo-3,5-dimethylpyrazole derivatives of trimesic acid as a new class of photochromic materials which show reversible photochromic properties in solid state upon light irradiation. Because of contrasting colour changes shown by most of the compounds after UV light irradiation in the solid state, these compounds can be extremely useful for rewritable imaging applications. While in most of the cases, the image printed with known solid state photochromic compounds requires thermal conditions for erasing, these compounds allow reversible erasing and printing with light only.
Synthesis and photochromism of 5H-chromeno[3,2-j]carbazole derivatives

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Photochromic compounds are of great interest for many fields of technologies and development of new photochromic systems is continuously growing [1]. Previously we have demonstrated that 2,3,3’,4’-tetrahydroindolino spiropyrans are ultrafast photochromic substances and they can be applied in cyanide detection [2].

Here we present synthesis and study of photochromic properties of constrained 2,3,3’,4’-tetrahydroindolino spiropyran derivatives 2. Alkylation of 4aH-carbazole methylene bases 1 with 2-chloromethyl-4-nitrophenol in acetonitrile yielded formation of racemic 4b,14-dimethyl-10-nitro-4b,6,7,7a,8,14-hexahydro-5H-chromeno[3,2-j]carbazoles 2 (Scheme 1). X-ray diffraction data analysis of monocrystal confirmed structure 2.

When solution of 2 in acetonitrile is irradiated with UV pulses (355 nm, 4 mJ, 5 ns) cleavage of C-O bond of pyrane ring appears and colored zwitterionic compound 3 with maximum absorption band at 450 nm forms. It reverts back to uncolored ground state in few tens of ns.

Literature:

Towards novel hydrazone-based light-driven rotary molecular motors

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Switches and molecular motors hold great promise in the field of nanotechnology and photo pharmacology.\textsuperscript{1,2} Nowadays, the majority of light-activated molecular switches and motors operates under the influence of UV-light. In order to fully exploit their potential in soft materials and biomedical applications, it is crucial to move away from the usage of these high-energetic and damaging excitation wavelengths. One of the approaches to shift the absorption maximum of photoactive compounds into the visible light range of the electromagnetic spectrum involves metal complexation to photochromic cores.\textsuperscript{3} Taking inspiration from the azo-BF\textsubscript{2} visible light operative switches described by Aprahamian et al.\textsuperscript{4} and the earlier work of Lehn and co-workers on photochemical C=N isomerization\textsuperscript{5}, we envision novel designs of hydrazone-like molecular motors which may be fueled by visible light.

The presence of a nitrogen coordination site in the central rotary axle makes imines and hydrazones interesting for metal complexation, as nitrogen atoms are widely used in coordination chemistry. By combining this imino nitrogen with an additional anionic coordination site in the upper halves of these imine-like systems, truly LX-type ligands are created. The incorporation of a (semi)-metal center should influence the optical properties of the hydrazone ligands, thereby shifting the absorption maximum into visible light without compromising the expected switching ability.\textsuperscript{4} Furthermore, different chiral bidentate ligands can be attached to the metal in order to add chirality to the system.

In our continuous endeavor for molecular machinery, we present the design of potential hydrazone rotary motors fueled by visible light.

References:

NIR-Light Responsive Negative Photochromism of Bipyrenyl-Bridged Imidazole Dimer

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Photoswitches have received much attention because of their ability to change the molecular and the electronic structures by light. Several applications of photoswitches have been reported in both chemical and biological research fields for switching macroscopic bending, surface polarity, electric conductivity, catalytic activity and biological functions. In particular, for biological applications, the photoswitching molecule is required to have a photosensitivity to red or NIR light within the first biological window ($\lambda = 650–950 \text{ nm}$), while UV light is frequently used for conventional photochromic molecules. Recently, we developed binaphthyl-bridged imidazole dimer (BN-ImD) showing negative photochromism in which the stable colored isomer of BN-ImD isomerizes to the metastable colorless isomer via the short-lived biradical upon visible light irradiation.\(^1\) The negative photochromic reaction can be easily induced at the inside of materials because the photogenerated colorless species does not reabsorb the excitation visible light. In addition, visible light is energetically acceptable to avoid undesired reactions. On the other hand, 1-phenylnaphthalene-bridged imidazole dimer (PN-ImD) shows multistate photochromism.\(^2\) The stable colorless 1,2'-isomer photochemically isomerizes to the colorless 2,2'-isomer via the biradical upon light irradiation. The 2,2'-isomer thermally returns to the 1,2'-isomer via the colored isomer. However, these negative photochromic molecules are not responsive to the red and NIR light.

Herein, we designed a novel negative photochromic molecule, bipyrenyl-bridged imidazole dimer (BPy-ImD), to increase the photosensitivity to red and NIR light. The colored isomer of BPy-ImD has an absorption band at 640 nm which is largely red-shifted relative to that of BN-ImD by extending the conjugation of the diazafulvene chromophore. The colored blue isomer of BPy-ImD isomerizes to the yellow isomer via the short-lived biradical upon NIR light irradiation. The color of the solution thermally returns to blue at room temperature. These results will give an attractive insight for the development of novel NIR-light responsive negative photochromic molecules.
Visible-light photochromism of a perylenebisimide-diarylethene dyad

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Photochromic molecules have been used as key components of optical memories, molecular electronics, and molecular machines. In particular, their applications to biological systems such as super-resolution imaging, biological markers, and bioactivity control, have recently attracted extensive attention. Among a wide variety of photochromic molecules, a family of diarylethene (DAE) derivatives is one of the most attractive molecules because of their excellent thermal stability of both open- and closed-ring isomers, rapid photoresponse, and high fatigue resistance. In the photochromism of most of DAEs, ultra-violet (UV) light with high-photon energy is required to induce the reactions in at least one direction. UV light, however, has drawbacks such as low transparency for commonly used optical components as well as mutagenesis of cells. Therefore, it is desired to develop photochromic DAEs, which undergo reversible photoisomerization reactions upon only visible light irradiation.

Figure 1. Photochromism and molecular structure of a diarylethene-perylenebisimide dyad 1.

In this presentation, we report an unexpected photochromic reaction of a perylenebisimide-diarylethene (PBI-DAE) dyad. We prepared several PBI-DAE dyads to develop highly fluorescent photo switchable molecules with non-destructive fluorescence readout capability [1,2]. Some of them, for example PBI-DAE dyad 1 (Figure 1), showed an unexpected photocyclization reaction induced by irradiating with visible (>500 nm) light, where the DAE unit has no absorption band. Very interestingly, the photocyclization reactivity strongly enhanced in a solvent containing the heavy atom, such as carbon tetrachloride (CCl₄). This result indicated the contribution of triplet state for this unexpected photoreaction. The detailed mechanism will be discussed based on the results of theoretical calculations, solvent dependence, and molecular structure dependence.

References:
Rapid Negative Photochromism of Naphthalene-Bridged Phenoxy-Imidazolyl Radical Complex Derivatives

H. Ito, A. Tokunaga, K. Mutoh, J. Abe
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Negative photochromism, in which the thermally stable colored isomer photoisomerizes to the transient colorless isomer upon visible light irradiation, has increased attention as a light-switch for functional materials. The use of visible light has some advantages compared with that of UV light, such as the less damage to cells and high conversion efficiency at the inside of materials. In addition, the development of fast photochromic molecules has been also expected because the rapid thermal back reaction within a millisecond time scale is useful for real-time switching. Although several negative photochromic compounds have been reported, the acceleration of thermal back reactions is one of the challenges to be solved. Recently, we developed a naphthalene-bridged phenoxy-imidazolyl radical complex (Np-PIC),\(^1\) which shows stealth negative photochromism in UVA light region and the rapid thermal back reaction in the millisecond time region.

Here, we synthesized Np-PIC derivatives to increase the visible light sensitivity and to control the thermal back reaction rates. It is expected that one of the derivatives, acenaphthylene-bridged phenoxy-imidazolyl radical complex (AcNp-PIC) shows the red-shift of the absorption band of the thermally stable isomer by changing the bridging unit from naphthalene to acenaphthylene because the conjugation of the isomer was extended. In addition, the acceleration of the thermal back reaction is also suggested due to the destabilization of the transient colorless isomer by the longer distance between the bridging carbons of acenaphthylene than those of naphthalene. These results indicate that the change in the bridging unit is an efficient strategy to increase the visible light sensitivity of negative photochromic molecules and to accelerate the thermal back reaction rate.

References

Development of Multi-State Negative Photochromic Compounds Based on 1,1-Binaphthyl-bridged Imidazole Dimers

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Photochromic molecules, which are capable of reversibly transforming between a colored and a colorless isomer upon light irradiation, are attractive light-driven molecular switches applicable to research fields of materials and life sciences. Among the various artificial multiple photoresponsive systems, multi-photochromic materials incorporating more than two photochromic units in a molecule have been extensively studied. However, many of the reported multi-photochromic systems still rely on UV light to induce at least a part of the photochromic reaction. In contrast, most of the photo-responsive biochemical processes are regulated by visible light because visible light is energetically acceptable to avoid undesired reactions. The negative photochromism, the reversible color change induced by visible light irradiation, are attractive candidates to achieve the visible-light-driven molecular switch.1,2 Recently, we have developed T-type negative photochromic 1,1'-Binaphthyl-bridged imidazole dimers (BN-ImD).3 BN-ImD shows three states negative photochromism, where the initial colored isomer reversibly converts to the metastable colorless isomer via the short-lived radical upon light irradiation. In this study, we designed a novel biphotochromic compound (bisBN-ImD) which has a couple of BN-ImD moieties in a molecule. The absorption spectrum of bisBN-ImD shows a bathochromic shift that is approximately 100 nm larger than BN-ImD. This characteristic bathochromic shift of bisBN-ImD is attributable to the exciton coupling of the binaphthyl moieties. This molecular design will provide a strategy for the development of advanced photoresponsive molecules such as wavelength-selective photoswitches.

References:

Bimetallic gold complexes of photoswitchable diphosphines

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In organometallic catalysis, photoswitch phenomena have been investigated in processes involving monometallic complexes with photoswitchable ligands, while bimetallic catalysts haven’t been considered so far. Our studies proceed from the assumption that ligands photoswitch might have a particularly marked effect in catalytic reactions which involve cooperative effects between two metals. In these reactions indeed, the catalytic activity should increase when a light-induced switch between different spatial arrangements of the catalyst will bring the metals closer to each other.

The first photoresponsive bimetallic gold catalysts based on an azobenzene backbone have been prepared, their photochromic properties have been studied and the catalytic behavior has been investigated notably in an intramolecular hydroamination reaction. The reaction rate proved to be dependent on the $E$- or $Z$-configuration of the catalyst, with the $Z$-isomer being significantly more active.

These preliminary results suggest that cooperative effects between the two metals might operate here, e.g. double activation of the substrate by coordination of gold(I) to both the olefin and the carbonyl groups.

The experiments above as well as additional examples of bimetallic photoswitch catalysis will be discussed.

References:


Synthesis of cationic azobenzenes and study of photoisomerization by experiments of in situ irradiation by NMR spectroscopy

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A new series of cationic probes derived from azobenzene were synthesized and the photoisomerization cis-trans was studied. These photochromic molecules were covalently bonded to organic cationic moieties, through an aliphatic chain. These new molecular "cationic organic switches" show reversible photoisomerization trans to cis, which is inherent to the azobenzene group and negligible retro thermal conversion cis to trans. The behavior of these new photoswitches was monitored by NMR spectroscopy and UV-vis. The irradiation of the trans probes with UV light shows an increase of the cis absorption of isomer absorbing around 450 nm, but overlapped with the trans absorption. Similarly, the same process was monitored at real time by NMR with a new LED-fiber optic system but with in situ irradiation. In this case, a decreasing of the trans isomer protons was clearly observed with the corresponding increase of the cis isomer protons. The mean goal of this type of experiments, based on diodes light emitters optic fiber coupled, was the photoswitching behavior yield a clear picture of the variation of the trans and cis protons (concentration) due to the non-overlapped signals, which represents a promising advance in the study of photoactive systems.
A terthiazole-based bidirectional photo- and electro-chemical switch

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Owing to their good photochromic features (thermal stability, high photo-resistance, readily tunable optical properties etc.) photochromic diarylethenes have been attracting much interest over last decades and extensively investigated as molecular switches for potential applications in various fields.¹ Moreover, some of them are also known to undergo redox-triggered ring-opening or/and ring-closing reaction in addition to light.²³⁴⁵ Such a dual stimuli sensitive behavior is much sought after as it offers an additional and convenient way to address the system.

In this work, we have designed and fully characterized a new terthiazole-based molecular switch which can be driven in both directions either photo-chemically or electro-chemically. DFT and TD-DFT calculations have also been performed in order to better understand such a behavior.
Synthesis, photochromic properties and spectral modulation of para-S-azobenzene conjugates

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Azobenzene is one of the most popular photoswitch as it exhibits good photochromic properties associated with a large geometrical change upon trans/cis isomerization about the azo bond. This feature has been extensively exploited for the photocontrol of conformation in molecular architectures such as polymers, supramolecular assemblies or bioactive compounds, for instance.\(^1\)

In the context of our research on shape-switchable glycomacrocycles\(^2\) and photoswitchable lectin ligands,\(^3\) we have started to investigate the conjugation of azobenzene in para position (relative to the azo bond) with glycosyl thiols. Using a palladium-catalyzed reaction,\(^4\) we readily prepared azobenzene glycoconjugates using 1- or 6-thiol carbohydrate and para-iodoazobenzene derivatives, including red-shifted ortho-fluoro motifs (Figure 1). Interestingly, the coupling is also effective with other types of thiols. Like para-oxygenated counterparts, para-S-azobenzene conjugates present favorable photo switching properties. In addition, their spectral addressability can be easily modified by oxidation of the sulfide linkage to a sulfone, resulting in a large blue-shift of the band corresponding to the \(\pi\pi^*\) transition (Figure 1). According to this modification, it was possible to obtain conjugates for which the trans-cis isomerization is achieved solely with visible light while the backswitching occurs under UV- or blue-light irradiation. With such a photoswitch in hand, it is therefore possible to build up molecular systems comprising two distinct azobenzene derivatives that can be independently addressed.

![Figure 1](image-url)  
**Figure 1.** Synthesis (a) of para-S-azobenzene glycoconjugates and photochromic properties before (b) and after (c) oxidation of the sulfide bond.

A "zero-to-eight" shape-switchable glycoazobenzene macrocycle

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Chiral dynamic architectures are omnipresent in nature for example in cells where they fulfil eminently important tasks in molecular recognition processes, catalysis or signal transduction.[1] Hence, the precise control over conformation and chirality in a small molecular system opens up different promising fields of applications such as drug delivery systems, asymmetric catalysts or optical devices.[2]

We synthesized a nano-sized chiral macrocycle based on carbohydrate units and two azobenzene photoswitches. First, the rigid carbohydrate blocks and the inflexible linkages of our structure ensure a well-defined and constrained geometry to the macrocycle.[3] Second, the azobenzene hinges drive a reversible conformational switching between two distinct forms upon cis/trans photoisomerization with UV- or green-light.[4] Third, the chiral information of the sugar units is transferred onto the azobenzene switch which thereby shows axial chirality in both trans,trans and cis,cis states. As supported by circular dichroism spectroscopy and molecular modeling, the title macrocycle switches its shape between a square "figure-of-zero", in the trans,trans configuration, and a figure-of-eight in the cis,cis state (Figure 1). This is what we call a "zero-to-eight" molecular switch. Interestingly, the helical conformation of the cis,cis-isomer is opposite in DMSO and water, suggesting that the difference in interaction between the carbohydrates and the solvent may induce an overall conformational change in the macrocycle.

This works highlights the reciprocal transmission of information between carbohydrate and photoswitch through a cyclic framework and therefore delineates a new approach for the conception of smart photoresponsive molecular systems.

![Figure 1. Solvent-dependent "zero-to-eight" shape switching of the title macrocycle.](image)

Electro-induced modification of coordination pattern in arene-Ru complexes bearing azobipyridine ligands

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While the redox behavior of metallic complexes containing ligands derived from azopyridine has been well documented [1,2], the use of electrochemical inputs to target modification of coordination pattern in organometallic compounds has been much less explored.

We have synthesized arene-Ru complexes of type 1 and 2, bearing azobipyridine ligand in E and Z configuration, respectively, and studied their behavior upon electrochemical stimulation by cyclic voltammetry, spectro-electrochemistry and DFT modeling.

The results provided evidence for reversible redox processes occurring in 1, whilst complex 2 undergoes electron-induced irreversible conversion to 1 through Z→E isomerization of the azobipyridine ligand.

References:
Photochromic molecules have attracted more and more interest not only for reversibly photomodulating various properties of molecules, but also for remote-controlling chemical reactivity and catalytic activities.\(^1\) Photoswitchable glycoconjugates have also been developed for light-controlled various applications in biology and material sciences.\(^2\) As a continuing interest in the development of glycomacrocycles,\(^3\) we are developing an intramolecular glycosylation method to access to photoswitchable glycomacrocycles. The principle is to use a photochromic molecule for linking together glycosyl donor and acceptor via non-reacting centers. It’s expected that photoisomerization of the photochromic template will change the disposition between the glycosyl donor and glycosyl acceptor, and consequently influence the efficiency and the stereoselectivity of the reaction by stereoelectronic and conformational effects (Scheme). It is to be noticed that the carbohydrate anomeric configuration has an important influence on the properties and biological functions of carbohydrates, so stereoselective glycosylation is very important for the glycoscience. We will report the results by using azobenene as photochromic template to realize the intramolecular glycosylation. The photoswitching properties as well as the chiroptical properties of azobenzene-based glycomacrocycles will also be presented.

Scheme 1: Intramolecular glycosylation with photochromic template.

References:


Photoswitchable Fluorescence of DCM-based Multichromophoric Systems

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Dicyanomethylene-4H-pyran (DCM) is a chromophore of typical donor-π-acceptor type, with bright long wavelength emission. Its E/Z type photoisomerization contributes to the photoswitchable characteristics, which is still not fully clarified yet. Here we aim at linking together several DCM units, allowing intramolecular interactions (such as energy transfer).

Through copper (I)-catalyzed alkyne-azide cycloaddition (CuAAC) click reaction,[1][2] multiple DCM chromophores were synthesized to dendrimeric linkers for previewing their specific photophysics. By comparing of 1, 2, 3-DCM multichromophoric structures, the fluorescence quantum yields (Φ_f), lifetimes (τ_f), the extinction coefficient values and E/Z photoisomerization characteristics of DCMs are prone to be affected by the number of DCM units.

In order to highlight the role of energy transfer processes within these systems, DFT calculations and anisotropy experiments will be performed.

References:
Synthesis and characterization of photochromic azobenzene-based dyes for dye-sensitized solar cells

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Azobenzene and its derivatives containing an azo moiety (–N=N–) have the ability to alter their geometries via photochemical or thermal trans-cis isomerization. Recently, we computationally investigated the trans-cis isomerization of the azobenzene-based dyes and their optical and electronic properties [1]. Accordingly, we designed and synthesized metal-free organic dyes featuring the azobenzene spacer for dye-sensitized solar cells (DSSCs). The azobenzene was used for a bridge between a donor unit (dimethylamine and diphenylamine) and an acceptor unit (cyanoacrylic acid) and thus the two dyes (DMAC and DPAC) were successfully synthesized. In agreement with density functional theory (DFT) calculations, they exhibited two ultraviolet/visible absorption bands. The transformation from trans-isomer to cis-isomer was performed by ultraviolet exposure, while trans-isomer gradually recovered from cis-isomer in the dark. We also investigated their photovoltaic performance under various irradiation conditions. The trans-cis photoisomerization resulted in different behaviors in the DSSCs.

NIR Light-Responsive Negative Photochromic Compounds Based on 1,1'-Binaphtyl-Bridged Imidazole Dimer

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The development of novel photo-responsive materials is an intense research area because their photophysical and photochemical properties can be controlled temporally and spatially. Among them, near-infrared (NIR) light-activatable photoswitches are significantly important for especially biological applications, because NIR light can penetrate deeper into the inside of the biological tissue in contrast to ultra-violet (UV) and visible light. While red- or NIR light-activatable photoswitches induced by multi-photon absorption process have extensively explored, one-photon NIR photoswitching has been still limited and challenging.1, 2

Recently, negative photochromism, in which the compound shows the decoloration upon light irradiation, has been attracted due to the advantages in the applications for photoswitching materials. 1,1'-Binaphthyl-bridged imidazole dimer (BN-ImD) shows the unique negative photochromism where the thermally stable colored form photochemically transforms into the metastable colorless form via a short-lived radical.3 Here, we present a strategy of the molecular design for red- and NIR-light-induced negative photochromism of BN-ImD derivative. The introduction of electron donating substituents brings about the appearance of a new absorption band attributable to a charge transfer transition at visible-NIR light region. This absorption band shows red-shift with increasing the electron-donating ability of the substituent. Some BN-ImD derivatives have the absorption tail at more than 700 nm. We have succeeded to induce their photochromic reaction by using NIR light (ca. 790 nm). Therefore, this molecular design will be a good candidate for the application of photoswitching molecule to the biological field such as control of biological activities.

References:
Recent evolutions in terarylene scaffolds using thienothiophene and benzothiazole substituents

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We have, in the last few years reported highly sensitive, neutral terarylenes containing photoexchangeable open and closed forms, with uses in areas including \textit{in situ} acid generation and on/off fluorescence [1-2]. Here we present recent synthetic, computational and photophysical investigations into the development of new members of this extended family containing thienothiophene and benzothiazole synthetic moieties.

The incorporation of benzothiazole permits the directed photogeneration of a closed form state that spontaneously undergoes hydride loss in the presence of suitable acceptor molecules. This has allowed for the development of a light initiated hydride donor, which has successfully been used to generate silver nanoparticles \textit{in situ} [3]. Detailed photophysical analysis comparing these systems to existing non-light induced hydride donors has been carried out and will also be presented.

Recent investigations have also allowed for the development of new thieno[3,2-b]thiophene systems, the extended aromatic character of which makes them excellent targets for the absorption of higher energy photons, including X-Rays. This offers up the possibility of new uses for our terarylene frameworks in particle detection and energy storage.

References:

Red-Light Driven Photochromic Molecule by Using Triplet Fusion

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Photochromic molecule driven by red or near-infrared light has a potential for application in biological and material chemistry because it has several advantages such as a high efficiency of the reaction inside of biological tissues or organic media and no requirement of UV light which damages materials and cells. Many visible-light-sensitive photochromic molecules are investigated based on the molecular structure of azobenzene, spiropyran, diarylethene, DASA, and so on. However, introduction of substituent into a molecule in order to extend the absorption band to the long-wavelength region sometimes occurs several problems such as decrement of the conversion efficiency or destabilization of the photogenerated species.

Herein, we demonstrate a photochromic reaction under red light irradiation by using triplet fusion upconversion (also refer to triplet-triplet annihilation), which is a methodology that converts lower-energy photons into higher-energy photons. We synthesized a phenoxyl-imidazolyl radical complex derivative connected with a perylene (Pery-RPIC) working as an energy acceptor. Radical complex generates a colored biradical upon light irradiation and thermally returns to the initial closed form by the recombination of the radical pair. We report the photochromic reaction of Pery-RPIC can be induced with 635 nm light irradiation via the triplet fusion of itself sensitized by Pd(II) mesotetraphenyltetrabenzo[porphyrin in toluene. Ultrafast transient absorption and fluorescence measurements revealed that the bond-dissociation reaction of Pery-RPIC can be efficiently occurred at the excitation to the perylene unit with almost no emission while perylene is well-known as a highly fluorescent molecule. We also confirmed that the reaction can be proceeded from only the singlet-excited state of Pery-RPIC generated by the intermolecular collision, not from the triplet-excited state. We anticipate that the method of direct utilization of the excited state generated by triplet fusion can be applied to design of valuable photochemical reactions beyond photochromic reaction.

References:

Irreversible photo-isomerisation of arene-Ru complexes bearing azobipyridine-derived ligands

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The external manipulation of molecular systems with light is being increasingly exploited for the control of events at various scales, eventually giving rise to “smart” systems.[1,2] In particular, metal centers bearing photochromic ligand have attracted attention in recent years for applications in biology and medicine, but also in the field of molecular machines and catalysis.[3]

In this context, we have synthesized novel azobipyridine derivatives and studied their behavior as ligands for ruthenium. Spectroscopic studies of the resulting organometallic complexes, allied with structural analysis by DFT and X-Ray diffraction revealed a new coordination pattern of the Z complex that lead to its irreversible photo-isomerisation.

References:
Photo- and Electrochromic Molecular Switch Based on Aryl-Bridged Radical Complexes

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The development of a single molecular switch showing multi-way response to various external stimuli has been demanded for the development and the versatility of the design of attractive switching materials. Photochromic molecules are a well-known class of photo-switching molecules that undergo the reversible isomerization between the colorless and the colored isomers. It has been reported that some of them respond to the other stimuli, and therefore, such photochromic molecules have been accepted as a good candidate for a multi-responsive molecular component. Pentaarylbiimidazole (PABI) and phenoxyl–imidazolyl radical complex (PIC) are one of the fast photochromic molecules based on imidazolyl radicals.\(^1,2\) Because the photochromic reaction of these fast photochromic molecules proceeds from the optically forbidden S\(_{1}\) state, it is difficult to estimate the excitation energy to induce the photochromic reactions by spectroscopic techniques. In this study, we performed the electrochemical measurements of PABI and PIC to investigate the electronic properties and to estimate the S\(_{0}\)--S\(_{1}\) transition energies.\(^3\) In addition, we also revealed that the electrochemical reductions of PABI and PIC generate the radical anion which spontaneously shows the C–N bond breaking reaction to form the radical species. The initial photochromic dimer is reproduced by the reversible oxidation of the anion species. We also investigated the electrochemical oxidation processes of PABI and PIC, and revealed for the first time that they reversibly generate the highly stable radical cations with accompanying the color change from colorless to green.\(^4\) These characteristic photochromic and electrochromic properties can be applicable to the photo-addressable electrochromic devices with high spatial resolution.

References:

Effects of electron donating and accepting substituents on the photochromism of indigo derivatives

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Indigo is a dye with trans-molecular configuration fixed with double intramolecular hydrogen bonds (H-bonds). When the hydrogen of the amino moiety of indigo is replaced by substituents so as to break the H-bonds, the derivatives exhibit trans→cis photoisomerization reaction. Computational study suggests prompt deactivation of the excited state induced by proton transfer mediated by the H-bonds inhibits the isomerization of indigo. We have been utilizing femtosecond time-resolved transient absorption spectroscopy to investigated the photoisomerization dynamics of indigo derivatives to elucidate the effect of the substituents. So far, we have studied three derivatives with an electron accepting substituent, N,N'-diacetylindigo (DAI) and electron donating ones, N,N'-dimethylindigo (DMI) and t-butylesterlmethylindigo (tBMI). Excited state lifetime of DAI was 3.3 ± 0.3 ns in ethyl acetate (EtAc) and the isomerization was a slow and inefficient process which could be easily prevented by rapid nonradiative decay induced by weak intermolecular H-bond with solvent molecules. On the other hand, the lifetime of DMI was much shorter, 52 ± 3 ps in EtAc, which suggests rapid photoisomerization. However, accumulation of the cis-form of DMI was difficult due to the short lifetime of the cis-form (30 s in benzene). On the other hand, cis-form of tBMI can be easily accumulated and the excited state lifetime was also as short as 46 ± 2 ps in acetonitrile. These results suggests that electron donating substituent on the amino moiety induces, while electron accepting one inhibits the photoisomerization. The color of indigo is due to the charge transfer (CT) type chromophore with amino and carbonyl groups being the electron donating and accepting moieties. Electron donating and accepting substituents on the amino group either assists or disturbs the CT. Thus, electron donating substituent causes red-shift of the absorption spectrum while accepting ones causes blue-shift. We conclude that the rapid photoisomerization of DMI and tBMI is prompted by twisting of the central C=C double bond induced by the CT. The slow isomerization of DAI is due to inhibition of the CT by the additional acetyl group which hinders twisting of the central C=C bond.
Stepwise Two-Photon-Induced Photochromic Reaction of Rhodamine Derivatives

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Photochromic molecules are important to construct photoresponsive systems in material science and life science because they reversibly convert multiple states by light irradiation. In conventional photochromic molecules, the photochemical reactions proceed even with weak light source. Therefore, it is difficult to exclude the influence of background light. If nonlinear photoresponsive properties are combined with photochromic molecules, they could show photochromism which depends on the excitation intensity. Therefore, the photochromic reaction hardly proceeds when the incident light intensity is weak, but it efficiently proceeds with the increase in the incident light intensity. Recently, stepwise two-photon absorption processes, which is defined as an absorption of another photon from a photogenerated transient state, have been received particular attention because of their low power thresholds and drastic enhancements of photochemical reaction yields in some systems.¹,² However, these reactions were reported only in specific molecules such as diarylethene, fulgide, and bridged-imidazole dimer, and these systems still require high power pulse lasers to induce the nonlinear processes.

In this study, we developed a novel stepwise two-photon-induced photochromic material based on the rhodamine framework. The molecule dissolved in THF gives the blue emission upon excitation with continuous wave (CW) UV LED (365 nm, 500 mW cm⁻² for 20 sec) and the photochromic reaction did not proceed. On the other hand, the photochromic reaction efficiently proceeded upon excitation with the nanosecond pulse laser (355 nm, 3.3 mJ pulse⁻¹). The excitation power to induce the nonlinear reaction (< 1 MW cm⁻²) is much smaller than those of conventional two-photon absorption systems. The low power threshold enables to induce the reaction by a CW laser under microscope. Wide ranges of time-resolved spectroscopies revealed that this nonlinear photochromic reaction proceeds via a higher triple excited state produced by the stepwise two-photon absorption process.

References:

Excited State Dynamics of Photogenerated Biradicals of Phenoxy Imidazolyl Radical Complex Derivatives

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Excited states of organic radicals have been received particular attention because of their sensitivity to the near infrared light and high oxidation potentials for super oxidant and photocatalyst. However, radicals are usually highly reactive and unstable in both the ground state and the excited state, and they often induce unwanted side reactions. Therefore, radical-dissociation-type photochromic compounds such as phenoxy-imidazolyl radical complex (PIC) are promising candidates for above radical based novel photofunctional materials because the formation of their radicals can be spatiotemporally controlled by light. However, excited state dynamics of these biradicals still remain elusive.

In this study, we investigated excited state dynamics of photogenerated biradicals of thiophene-substituted PIC (TPIC) derivatives. TPIC generates a biradical form upon UV light irradiation and the generated biradical form thermally reverts to the initial closed form with a half-life of 1.1 second in benzene solution at room temperature. We applied femtosecond transient absorption spectroscopy to photogenerated biradicals of TPIC under continuous irradiation of 365-nm continuous wave (CW) light. Upon excitation with 740 nm of a femtosecond laser pulse, a bleach signal was observed at 700 nm, and transient absorption signals were observed at 500 nm and 850 nm. Since the initial closed form does not have any sensitivities to near infrared light, the observed transient absorption signals can be safely assigned to the photogenerated biradicals. The generated transient signals quickly decay within 30 ps. The excitation of TPIC at 520 nm gave very similar transient absorption spectra to those excited at 740 nm, indicating the excited states of the biradical form of TPIC follow Kasha’s rule. On the other hand, in the case of a pyrenyl group-substituted TPIC (Py-TPIC), while the excitation at 740 nm gave the similar spectra to those of TPIC excited at 740 nm, the excitation at 520 nm gave different transient absorption spectra as compared to those excited at 740 nm. It suggests that the excited states of the biradical form of Py-TPIC do not follow the conventional Kasha’s rule.

Reference:
A practical view of the fatigue resistance in diarylethenes

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Photochromic diarylethenes are suitable for the production of photosensitive films with high response. In the design of devices, the fatigue resistance is crucial and it differs from application to application.

We investigated the fatigue behaviour of diarylethenes in solution by developing a measuring protocol and the necessary theory to calculate the fraction of active molecules during illumination. For two series of thiazole and thienyl based derivatives of 1,2-diarylethenes, with no electroactive substituents, it turns out that the fatigue resistance ultimately depends on the dose of light absorbed by the colored form rather than on the specific molecular structure. Accordingly, beyond the chemical structure of the diarylethene, the switching conditions, namely, the wavelength used to induce the photoreaction and the exposure dose, strongly affect the resistance performances. This finding is of great importance for the practical use of photochromic materials, giving an estimation of their fatigue resistance based on their absorption spectra, or, alternatively, allowing for the selection of the conversion wavelength to provide the largest absorption modulation and the best fatigue performances.
Evaluation microscopic phase-separation in a polymer alloy by means of long-time single-molecule tracking based on the one-color fluorescence switching

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Phase separation of polymer alloys in mesoscopic scales is closely related to physical properties of these materials. It is crucially important to elucidate the relation between the property and the structure of the microphase separation in the polymer alloy. Compared to conventional methods such as electron microscopy and scanning probe microscopy, super-resolution fluorescence microscopy is a powerful tool to investigate the internal structures of polymeric materials owing to the deep penetration depth of the light. In the present study, we have applied single-molecule tracking (SMT) with a fluorescent diarylethene derivative (DAE) to elucidate nano/macro-structures of a polymer alloy showing mesoscopic phase separation. We tracked lateral motions of many DAEs in the polymer alloy in the time period > 60 min by employing the one-color fluorescence activation, excitation, and deactivation (OF-AED) method that we recently developed for fluorescent DAEs.

A thin polymer alloy film of poly(2-hydroxyethyl acrylate) and a hyper-branched silicone polymer was prepared by spin-casting from 1,4-dioxane solution containing a fluorescent DAE. The optical transmission micrograph confirmed the phase separation in mesoscopic scales as a contrast in the transmission image, while such contrast was not detected for neat films of poly(2-hydroxyethyl acrylate) or hyper-branched silicone polymer. To obtain higher spatial resolution in micropase separation in the alloy, we measured the translational diffusion of the single DAEs in the film by using the OF-AED method with a 532-nm CW laser. Because the fluorescent DAEs were soluble only in the area of poly(2-hydroxyethyl acrylate) in the polymer alloy, the trajectories of single DAEs clearly visualized nanometer sized phase-separation structure. Detailed analysis of the translational diffusion behavior of the DAEs also provide a spatial mapping of the diffusion coefficient of the guest molecules in the polymer alloy depending on the distance from the interface of the two polymers. At the conference site, we will discuss the spatial resolution of the visualization and the correlation between lateral diffusion coefficient of the guest molecule and the phase-separation structure.
Looking for LOV: Investigating the Chromophore in a Photoswitchable Protein by Spectral Watermarking of Femtosecond Stimulated Raman Spectroscopy

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ELI (Extreme Light Infrastructure) Beamlines is an EU-supported user facility being commissioned near Prague in the Czech Republic. One of the techniques available is femtosecond stimulated Raman spectroscopy (FSRS), a time-resolved vibrational spectroscopy technique. The FSRS setup belongs to an experimental setting that also includes other spectroscopical methods – time-resolved UV–visible and IR spectroscopy and ellipsometry, as well as laser-driven femtosecond VUV and X-ray sources for complementary diffraction, imaging and spectroscopy measurements.

The light–oxygen–voltage-sensing (LOV) domain is a photochromic domain in many proteins. (Mathes et al. in Weber & Schleicher, 2014) Its chromophore is the cofactor flavin mononucleotide (FMN). As a precursor to a study of LOV, we have measured FMN with FSRS. Due to the sub-100-fs time resolution of the technique, together with transient UV–visible spectroscopy and global fitting, we can identify Raman signals from the ground (S₀), S₁ and T₁ electronic states. By varying the solvent, we observe effects from hydrogen bonding, solvent polarity and the protonation state of FMN.

In conjunction, we have developed the experimental setup and data analysis methodology. Our setup mainly uses spectral watermarking to extract time-resolved Raman spectra with high fidelity. (Kloz et al., 2011; Kloz et al., 2016) In contrast to other FSRS processing methods, spectral watermarking collects the information from a series of measurements with different Raman shifts, called modulations. Convolution of the modulations with spectral watermarks allows extraction of the Raman signal separate from the background and fixed-pattern noise. Compared to previous watermark FSRS setups, our setup uses more modulations and two detectors, and a white light probe generated by the output of a nonlinear optical parametric amplifier. These differences create opportunities for improved data quality and range of frequencies detected but also present certain challenges. On the data analysis side, we have developed several Matlab scripts to accelerate and automatize the extraction of the Raman signals from large datasets, for example by removing artifacts from scattered light, the ground state sample signal and the transient absorption signal. Finally, since ELI Beamlines is a user facility, we have developed scripts for packaging the data in appropriate formats for the users.
Ultrafast structural study in photoreaction of dicyanoaurate oligomers with an X-ray free electron laser

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Direct "observation" of the bond making, through a chemical reaction including a photochromism, has been longstanding dream for chemists. However, the distance between atoms is very small, at about 100 picometer, and the bonding is completed very quickly, taking less than one picosecond (ps). In this study, we demonstrate that it is possible to track in detail and in real time the structural changes that occur during a chemical reaction in solution. In the femtosecond time-resolved x-ray solution scattering experiment using an X-ray free-electron laser, we focused on the process of photoinduced bond formation between gold ions in dicyanoaurate oligomers dissolved in water[1]. In the ground state (S0 state) Au ions that are weakly bound to each other by an electron affinity and aligned in a bent geometry. Upon a photoexcitation, the S0 state rapidly converts into a 1st intermediate state (I1) where Au-Au covalent bonds are formed among Au ions aligned in a linear geometry. Subsequently, the I1 state transforms to a 2nd intermediate state (I2 state) in 1.6 ps while accompanying further contraction of Au-Au bonds by 0.1 Å. Later, the I2 state of the trimer converts to a tetramer (tetramer state) on nanosecond time scale. Finally, the Au ions returned to their original loosely interacting bent structure.

Surface Enhanced Raman Scattering signal of photochromic isomers on isolated Gold Nanorods particles

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Thanks to the fingerprint offered by such a vibrational spectroscopy, SERS is a technique of choice to monitor chemical reactions. Because of the high enhancement factor attainable, short acquisition times of hundreds of ms are possible, and the macroscopic averaging effect could be avoided by working at the few/single objects level. The first step is to identify unequivocally the reactants and products, and if possible select a specific fingerprint of each of them. Here, we are interested in the study of photochromic species, i.e. molecules switching between 2 isomers of distinct photophysical properties under resonant absorption of light. We focus more specifically on species of the diarylethene family whose large spectral change and bi-stability make them excellent candidates for optical switching and coupling to plasmonic structures [1].

We report on a SERS study of the B2629 photochromic species (Fig.1) combining experimental microscopy, spectroscopy and calculations [2].

The molecules were deposited on synthetized gold nanorods (GNR) with a 672nm longitudinal plasmon resonance (inset fig.2) drop casted on glass. The density of GNR allows for the SERS signal to arise from isolated particles composed of single or few GNR, as shown by dark-field scattering imaging and spectroscopy.

The SERS spectra of the open and closed form were obtained (Fig.2), and compared to the theoretical spectra obtained by Density Functional Theory calculation to allow for a qualitative assignment of the bands.

References:
Correlated fluorescence and AFM microscopy to probe nanomaterials with photochromic or mechanofluorochromic properties

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The study of photo- or mechano-responsive nanosystems requires measuring several parameters (size, shape, fluorescence, energy transfer) under external stimulation (light or mechanical stress). For this purpose, we designed dedicated microscopy instrumentation in order to measure these parameters at the level of single nanoparticles. We propose to show here two kinds of nanosystems. The first ones were designed in order to show giant amplification of fluorescence photoswitching. The second ones were synthesized for their mechanofluorochromic properties in the sub-microscale range.

The first experimental system is based on a confocal microscope with three different lasers focalized at the same point to activate the photochromic-fluorescent organic nanoparticle at 561 nm, probe the emission at 445 nm and reset the system at 375 nm. By a proper synchronization of the laser sources, the fluorescence intensity of single nanoparticles could be tuned and, taking advantage of a non-linear effect in the multichromophoric nanosystems, led to an improvement of the optical resolution of the confocal setup.

The second home-built setup is dedicated to probe the mechanofluorochromic properties of nanoparticles. The set up is composed of an optical microscope, an AFM, a spectrograph and an excitation light source (405 nm). Fluorescence properties (intensity and spectra) were recorded before and after mechanical stimulation driven by the AFM, showing spectral shifts under shearing stress.

![Figure 1. Correlation between fluorescence microscopy and AFM, applied to photochromic and fluorescent molecular nanoparticles.](image)

280 nm Picosecond Laser for High Speed Lifetime Measurement of Proteins like Human Serum Albumin

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Laser pulses from diode based laser systems in the UV range are of great interest in the fields of microscopy and spectroscopy. Of particular interest is the wavelength range between 280 and 300 nm where the fluorescence of aromatic amino acids such as tryptophane / thryrosine can be excited. Up to now this spectral range was only accessible through an expensive combination of amplified Ti:Sapphire laser with an OPO, with power inefficient pulsed LED or frequency doubled supercontinuum lasers (with optical output levels in µW range at MHz repetition rate).

The approach we present here is based on a freely triggerable distributed feedback (DFB) laser diode that enables generation of sub-100 ps seed pulses. After passing through a two-stage fiber amplifier, pulses with an energy of 30 nJ and peak power of 0.5 kW are fed into a commercial PM-Raman fiber which then outputs light at 1120 and 1180 nm, respectively. The spectral line width and central wavelength of these Raman signals were controlled and optimized by co-propagating CW signals from a FBG-stabilized laser diode at 1122 or 1178 nm.

The Raman-shifted pulses are separated from residual fundamental light and then frequency doubled twice in a single pass cascade consisting of MgPPLN and beta-BBO crystals with optimized focal conditions and spectral filtering. Fundamental light background was removed from the UV signal by a high dynamic range clean-up filter. The optical output achieved average power levels of more than 1 mW at 80 MHz, which is more than enough for a broad range of life science applications, such as fluorescence spectroscopy and time-resolved confocal microscopy.

Fig 1. Fluorescence decay of the Human Serum Albumin (HSA) in water collected on a FluoTime 300. A) using a 280 nm LED as excitation source. B) using the new VisUV-280 picosecond pulsed laser with 280 nm emission wavelength.

To demonstrate the advantages of this new UV laser light source for time-resolved spectroscopy, the fluorescence lifetime of Human Serum Albumin (HSA, an important protein for many pharmaceutical and biomedical applications) were measured with a FluoTime 300 spectrometer (PicoQuant GmbH, Germany), using either a 280 nm pulsed LED or our new picosecond pulsed UV laser (VisUV-280, PicoQuant GmbH, Germany). The acquired fluorescence decays and fitted functions are shown in Fig. 1, where one can easily see that excitation with the VisUV-280 results in a much shorter instrument response function. Furthermore, the overall acquisition time for the full decay was about 35 times faster with the laser (from 10 min to 20 s).
Specific electrocyclic reaction dynamics of a dithiazolylarylene derivative

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Photoinduced 6π-electrocyclic reaction is one of the basic processes leading to various photofunctions and photoresponses. For the development of advanced photofunctional materials, it is important to elucidate its reaction dynamics and mechanism. In actual, a lot of experimental and theoretical studies have been so far reported on this reaction mechanism and it has been regarded, as a general scheme, that the photoinduced cyclization and cycloreversion reactions in 6π-electron systems take place on the 2A potential energy surface (PES) and the same conical intersection (CI) mediates the 2A and 1A (ground state) PESs in both the reactions. However, we recently found the 6π-electron system showing the reaction dynamics different from the above conventional scheme in a dithiazolylarylene derivative (DTA). In the present work, the origin of the difference will be discussed on the basis of the experimental results by femtosecond transient absorption and fluorescence spectroscopies.

First, the cyclization and cycloreversion reaction dynamics of DTA in n-hexane solution was elucidated by femtosecond transient absorption measurements. After spectral evolution on a sub-picosecond timescale, transient absorption signals appearing in the excited state of the closed- and open-ring isomers decayed with a time constant of ca. 23 ps. In addition, spectral band shapes of the transient species in both cases are quite similar with each other. These results strongly suggest that the cyclization and cycloreversion of DTA occur via the common intermediate. From the detailed studies of the fluorescence spectroscopy, this common species was assigned to the excited state of DTA(c). That is, the excitation of the open-ring isomer leads to the formation of the excited state of the closed ring isomer, although the typical ring-closing reaction in the 6π-electron system results in the formation of the ground state of the closed ring isomer. It should be noted that the geometry of DTA is rather planar owing to the intramolecular hydrogen bond and S-N interaction, leading to the suppression of the rotation of the aryl moieties. By integrating these geometrical features with the experimental results on the solvent polarity dependencies, we will discuss the factors responsible for the specific reaction mechanism.
Cyclization reaction dynamics of an inverse type diarylethene derivative in solution and solid phases

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Diarylethene derivatives undergo a reversible photochromic reaction between the closed- and open-ring isomers. A series of the compounds have been attracting continuous attention due to their excellent molecular properties, leading to realization of the advanced photofunctions in the field of material science. With respect to the orientation of two heterorings, diarylethene derivatives can be categorized into two groups, normal type and inverse type. The inverse type derivatives have a great advantage for designing photofunctional materials with higher reactivity than normal derivatives. In addition, from the fundamental viewpoint, it is crucially important to investigate the relation between shapes of potential energy surfaces and chemical reactivity in the excited state. In the present study, we have investigated the cyclization reaction dynamics of a typical inverse derivative, iDAE in solution and solid states by means of time-resolved absorption and fluorescence spectroscopies.

In solution phase, steady-state and time-resolved fluorescence spectroscopy with the aid of quantum chemical calculations revealed that there exist three kinds of conformers, one parallel and two anti-parallel forms in the ground state. Femtosecond transient absorption spectroscopy showed that one of the anti-parallel form undergoes the cyclization reaction with a time constant of 36 ps, which is significantly slower than that of normal type derivatives. The other two forms are nonreactive species and their major relaxation processes are the radiative decay and intersystem crossing into the triplet states.

To investigate the reactivity in the solid state, we applied ultrafast spectroscopies to iDAE nanoparticles in water. Transient absorption spectroscopy showed that the S1 state formed by photoexcitation is relaxed into another transient species on a few tens picosecond timescale. A similar time constant was observed in time-resolved fluorescence measurements. By considering that iDAE nanoparticles show red-shifted fluorescence, we assigned this time constant to the relaxation from the S1 state into the species such as charge transfer states. No absorption of the closed-ring isomer remains after the decay of transient absorption, indicating that iDAE does not undergo the cyclization reaction in the solid state. This distinct reactivity between in solution and in solid states is probably due to change of viscosity in surrounding environments.
ABSTRACTS: POSTERS SESSION 2
Modulation of Enzyme Activity by Photochromism of Dicarboxy Dithienylethene

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Artificial control of enzyme reactions is useful for analysis of their mechanism, and design of biomimetic functional materials. Photochromic compounds have a function for effective regulation, because their chemical and physical properties change reversibly with their structural change by photo irradiation.

In this study, hen egg white lysozyme (EC 3.2.1.17) was chosen as a model enzyme, and dicarboxyl dithienylethenes; 1,2-bis (5-carboxy-2-methyl-3-thenyl) cyclopentene (DAE) was prepared as a photo-switching molecule. The interaction of lysozyme with DAE, and the influence of DAE on lysozyme activity were studied. DAE showed good photochromic properties upon irradiation with 313 nm light and subsequent 530 nm light in 20 mM sodium phosphate buffer solution (3% DMSO, pH = 6.8) in the presence of lysozyme and/or substrate. Enzyme reactions were assayed using peptidoglycan as a substrate and the kinetic parameter were analyzed according to Michaelis–Menten kinetic model. The enzyme activity was modulated reversibly according to photochromism. The catalytic efficiency of lysozyme at photo stationary state (313 nm) lowered to 10% of that in sample solution containing open form. The binding constants (K) of DAE to lysozyme, which were estimated by fluorescence quenching, also enhanced by isomerization open form to closed form. Moreover the molecular docking simulation results suggested that DAE located in near the substrate binding subsite B, and the closed form had stronger inhibitory effects than the open form.
Light-Triggered Activation of Photoswitchable Kinase Inhibitors

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Protein kinases are the key signaling enzymes which are involved in almost all physiological processes. Hence, it is of great importance to elucidate signaling pathways mediated by kinases to understand how human diseases arise from their malfunction.[1]

An important method for this investigation is the analog-sensitive (AS) kinase approach based on a mutation of the gatekeeper residue leading to AS kinases targeted by an orthogonal inhibitor which does not interfere with wild-type (WT) kinases (see Figure 1).

However, most pharmacological tools lack specificity caused by the inability to precisely control the drug activity with spatiotemporal resolution. Incorporation of a photosensitive unit into the inhibitor scaffold allows for an external and reversible control of the enzyme inhibition which results in advantages over classical small molecule inhibitors.[2]

The photoswitchable orthogonal inhibitor is converted to its active state by irradiation with light leading to the inhibition of the AS kinase. Irradiation with light of a different wavelength converts the photoswitchable inhibitor to its inactive form while regaining the initial active kinase (see Figure 2).

References:
Structural Basis for the Optical Control of c-Jun N-terminal Kinase 3

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Kinase pharmacology of ATP-binding pocket inhibitors suffers from poor selectivity¹, increasingly addressed by covalent kinase inhibitors². Optogenetics and photopharmacology offer an orthogonal approach to selectively target kinases. Here we present structural insight into optical control of kinases using synthetic small molecules. c-Jun N-terminal kinase 3 (JNK3), a key signaling enzyme in cellular stress response and promising target for the treatment of neurodegenerative diseases³, is targeted by cyclic azobenzene based, photoswitchable inhibitors, thereby introducing the combination of covalent inhibition and photopharmacology. X-ray crystal structure determination of JNK3 resolving both azobenzene isomers provides insight into the underlying binding characteristics responsible for the kinase activity difference upon photoisomerization. This approach of enabling spatiotemporal control of JNK3 lays the foundation for other covalent inhibitors and kinases.

References:

DNA liquid crystals doped with azobenzene derivative

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Over the last decades, experimental studies have shown that DNA in highly concentrated aqueous solutions, tends to self-organize into lyotropic liquid crystals (LCs), which mimic in-vivo conditions of DNA packing [1-2]. Among different dopants of DNA LCs, azobenzene derivatives, which are able to change their molecular geometry, offer a possibility to modify an adjustment to mesophases under the influence of electromagnetic irradiation. Hence, photochromic compounds could be used to perform light-induced phase transition in liquid crystalline DNA.

In the present work, the formation of DNA mesophases doped with photochromic dyes has been observed and compared with pure DNA LCs. Furthermore, phase transitions triggered by trans-cis isomerization were investigated by polarized light microscopy equipped with the mercury lamp and the hot-stage.

Fig.1. Cholesteric texture of liquid crystalline DNA doped with photochromic compound.
Scale bar: 20µm.

Photopharmaceuticals for microtubule stabilization

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Microtubules play crucial roles in a multitude of vital cellular processes, including trafficking, structural plasticity, and cell division, and there is an eminent need for understanding the regulatory basis of these many functions.[1] Conventional small molecule probes (inhibitors such as colchicine, nocodazole, paclitaxel, and vinca alkaloids) have limited utility for this, given the plethora of contemporaneous microtubule-dependent functions they suppress. Deeper insights could be gained with tools allowing spatiotemporally specific manipulations of subsets of microtubules. Photopharmaceuticals—light-responsive small molecule inhibitors that act as an optically-controlled interface between a researcher and their protein of interest—have recently shown promise in this field.[2,3] Their inhibitory activity can be non-invasively controlled with high spatiotemporal precision, and the approach may have easier and wider applicability than optogenetics (that is not applicable for manipulating cytoskeleton structure).

In particular, photocontrolled microtubule depolymerizers have been used extensively in a variety of different model systems e.g. cancer cell lines,[2] early mouse embryos[4] and Drosophila;[5] and they have proven valuable tools for the exploration of microtubule functionalities. However, microtubules only exert their functions in their polymerized state. Therefore, spatiotemporal control over microtubule polymerization would allow for far deeper investigations into microtubule-dependent processes. We present ongoing work aiming to solve this unmet need for photocontrolled microtubule stabilizers, that would allow for high precision activation of microtubule functions in a range of biological systems, and so would significantly expand the reagent toolbox for cell biology investigations.

2. M. Borowiak et al., Cell 2015, 162, 403.
Despite the rapid development of imaging techniques, precise probe localization and manipulation in living cells is still a challenging task. Photochromism offers an alternative opportunity to enhance the precision of bioimaging because photochromophores can be light-controlled to reversibly emit fluorescence. This enables the probe’s signal to be differentiated from auto-biofluorescence. We have demonstrated a spiropyran based glycoprobe could be used in targeted photoswitchable living cell imaging and precise endogenous sulfite detection.\textsuperscript{[1]} Although fluorescent diarylethene derivatives have been employed in high-resolution bioimaging,\textsuperscript{[2]} the majority of current photochromophores are non-emissive because of the low fluorescence quantum yields and molecular aggregation in aqueous solutions and in cells. Here, we show that the simple hybridization between a photochromic fluorescent glycoprobe and human serum albumin (HSA) enables a unique fluorescence “double-check” mechanism for precisely localizing and manipulating probe molecules in living cells. Docking of a carbohydrate-modified naphthalimide (Naph)-spiropyran (SP) dyad to a hydrophobic pocket of HSA produces the glycoprobe-protein hybrid, causing the protein conformation to fold as determined by small-angle X-ray scattering. We show that the Naph and merocyanine (the photoisomer of SP) fluorescence of the resulting hybrid can be reversibly switched by light in buffer solution and in target cells overexpressing the carbohydrate receptor.\textsuperscript{[3]}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Scheme1.png}
\caption{Scheme 1. Top: Molecular structures and photoswitching of the Naph-SP sensor. Bottom: Photoswitching of Naph-SP/HSA hybrid and duplexed cell imaging.}
\end{figure}

Reference:
Synthesis and Structural Optimization of Diarylethene-based Photochromic Nucleosides and their Application to regulate Transcription

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Diarylenethenes (DAE’s) are a prominent class of photochromic molecules that undergo a cyclization and cycloreversion reaction upon irradiation with UV or VIS light, respectively. Desired properties of such photochromic molecules are thermal stability of the closed isomer, fatigue resistance, rapid response, high quantum yields and a high switching yield [1]. DAE’s basic structure as a derivate of stilbene has changed significantly as a result of many year’s studies with the aim to optimize the above mentioned properties. Our group developed photochromic nucleosides based on DAE’s and focuses on improving their performance to match those of the classic dithienyl DAE’s [2]. We showed that the replacement of one of the thiophene rings with the nucleobase of a nucleoside does not interfere with the DAE’s classic photochromism and offers interesting applications in the biological realm, where those photochromic nucleosides can be incorporated in short oligonucleotides by chemical solid phase synthesis [3]. Recently we were able to synthesize photochromic uridines with an additional methyl group at position 6 of the nucleobase, which significantly improves the cyclization quantum yield and switching efficiency.

Ideally, in a biological application a photochromic oligonucleotide generates an on/off situation, which can be remotely controlled by applying light as an external signal. For the realization of such an on/off situation the yield of the cyclization reaction is of great importance. Recently, we successfully executed the first proof of principle experiments in which the transcription activity of a T7 polymerase was modulated and measured in real time with a 5-fold turn on/off-factor.

3. D.L. Kellis et al., ACS Nano, 2019, 133, 2986-2994

Figure 1. A: Absorption spectra of a photochromic T7 promotor sequence recorded at various time points during irradiation with 340 nm UV light. B: Real-time measurement of the transcription-activity of a photochromic T7 promotor sequence.
Synthesis of photoswitchable fluorescent diarylethene based nucleosides

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In recent years the concept of regulating processes with light has attracted considerable interest because light is a powerful, noninvasive and bio-orthogonal trigger to control and investigate a wide range of biological processes.\(^1\) Especially DNA offers great opportunities for light triggering due to its well-defined structure and its ability to bind small molecules.\(^2\) Reversible switching of DNA requires the introduction of a photoswitching-moiety and for this purpose we introduced nucleoside-based diarylenes.\(^3\) The photochromism of the nucleosides is based on the reversible photocyclization reaction of diarylenes. They are well known to undergo an electrocyclic ring closure upon irradiation with UV-light and exhibit promising photophysical properties such as high reversibility and thermostability. These properties make this class of photoswitches interesting candidates for the use in reversible DNA switching. Therefore, the nucleosides are introduced as part of the photoswitch and participate in the electrocyclic reaction. The first generation of our photochromic nucleosides contain a cyclopentene bridge and thiophene as the second aryl-unit.\(^4\)

For the second generation we synthesized new photoswitchable nucleosides, which show promising fluorescence properties combined with high fatigue resistance, thermostability and bleaching stability. For this purpose, we exchanged the bridge by a benzofurane moiety and the thiophene by benzothiophene. Also first approaches to introduce our first-generation nucleoside-based diarylethene photoswitches into biological systems were investigated. Therefore, the photoswitches were incorporated in the double stranded promoter region of a T7-RNA-Polymerase transcription template and by the measurement of melting temperatures the impact of electronic and structural changes of the photochromic-unit were investigated.


Revealing the ultrafast dynamics of Orange Carotenoid Protein

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Orange Carotenoid Protein (OCP) is a water-soluble pigment protein responsible for dissipation of excited state energy harvested by cyanobacterial antenna complexes, phycobilisomes. OCP performs its photoprotective function in a selective way: in the dark it occurs in inactive form (OCP₀), but after illumination with a blue-green light it undergoes photoconversion with a low quantum yield (< 1%) to quenching-capable form called OCP red (OCPₚ). OCPₚ interacts with the phycobilisome, causes a decrease of the phycobilisome fluorescence emission intensity and prevents the excitation energy reaching the reaction centers (Kirilovsky, D. & Kerfeld, C. A. Nat. Plants, 2016). The exact mechanism that control the photoconversion of OCP₀ to OCPₚ is still not fully understood, and it is essential to obtain a complete picture of of light-cyanobacteria interaction.

To distinguish different excited states and clarify the deactivation of OCP₀ we employed femtosecond transient absorption spectroscopy in the NIR region (750-1400 nm). We observed a short living species (less than 0.2 ps) absorbing at 1050 nm, which is presumably S₂ state. After its decay, a stimulated emission around 1200 nm is growing and disappearing within 1 ps. The fused analysis of NIR and visible region with two different excitations (470 and 540 nm) allows us to separate the contribution of S₁, ICT and S* states and obtain their spectra and dynamics (formation and decay). We found that quantum yield and dynamics in the ground state strongly depend on method used to produce the OCP. Based on these results, we can build an improved scheme of early OCP photoconversion dynamics.
Turn-on azo-based fluorescent nanoprobes to unveil the fate and endocytosis of organic nanoparticles

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Photoactive organic nanoparticles, exclusively composed of small fluorescent dyes, have been stirring tremendous attraction for a decade for their ability to serve as bright labels for bioimaging [1] and carry drugs with poor natural biodisponibility [2]. The emergence of photochrome-based nanoparticles is by contrast much more recent and has unveiled strong interactions between the self-assembled dyes due to strong spatial confinement effects.[3] We have thus combined fluorescent and photochromic dyes within the same nano-objects to decipher the fate of organic nanoparticles after cell endocytosis and trigger instantaneous cell apoptosis upon pulse light irradiation. The targeted systems were made out of azo dyes and benzothiadiazole (BDZ) red emitters forming well-defined nanospheres with large colloidal stability in biological media (Fig. 1a).

We found that exergonic photoinduced electron transfer was responsible for the quantitative emission quenching observed with only a 0.2:1 azo:BDZ ratio thanks to the close vicinity between the photoactive dyes within the nanoparticles. Immunofluorescence staining of cancer cells demonstrated a non receptor-dependent endocytosis pathway for the cellular uptake of the hybrid azo-BDZ organic nanoparticles that readily disassemble after endosomal entrapment. Ulterior treatment with mefloquine, causing endosomal/lysosomal disruption, revealed homogeneous distribution of the dyes within the cytoplasm, thereby indicating that part of the BDZ emission, still quenched within the endocytosis vesicles, actually originated from the high spatial confinement of BDZ and azo chromophores induced by the organelles (Fig. 1b-c). Finally, the presence within each endocytosed nanoparticle of a high payload of photoswitchable entities, amenable to large photoinduced motions, was harnessed to induce extensive blebbing, causing cellular death of HeLa cancer cells within only a few seconds (Fig. 1d).

Figure 1. a) TEM images of hybrid azo-BDZ nanoparticles. Endocytosed nanoparticles in mesothelioma cancer cells before b) and after c) mefloquine treatment. d) Irradiation of HeLa cancer cells after uptake of azo-BDZ nanoparticles (λexc = 488 nm).

References:
First study of the photodynamics of a hydrozoan photo-switchable fluorescent protein: existence of different switching mechanisms


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Recently, reversibly photoswitchable fluorescent proteins (RSFPs) have been widely applied in super-resolved fluorescence microscopy. Even though photo-physical parameters (switching and fluorescence quantum yields) are linked to the resolution and image acquisition speed, the switching mechanism that controls these parameters is still a matter of debate. The most studied RSFP is Dronpa, a negative RSFP from Anthozoa. The majority of studies have focused on the switching dynamics from the non-fluorescent (off) to the fluorescent (on) state. It has been reported that a trans-to-cis isomerization occurs within a few picoseconds in the excited state, followed by chromophore deprotonation in the ground state on the microsecond time scale (Warren et al. Nat. Comm. 2013). On the contrary, a recent report suggested that protein cage rearrangements play an important role for the isomerization process and provided evidence for both isomerization and deprotonation occurring in the ground state (Laptenok et al. Nat. Chem 2018). Here, we share results on another RSFP, rsEGFP2, an RSFP from Hydrozoa which is a protein used in super-resolved microscopies (Grotjohann et al. elife 2012). Time-resolved serial femtosecond crystallography at an X-ray free electron laser, combined with UV-visible transient absorption (TA) spectroscopy, showed the existence of a twisted chromophore configuration on the picosecond time-scale, with the two cyclic moieties perpendicular to each other and a dynamically restricted by the close proximity to the V151 side chain (Coquelle et al. Nat. Chem 2018). Accordingly, mutation of the latter to alanine (V151A) doubles the off-to-on switching quantum yield.

Using optical time-resolved TA spectroscopy from the femtosecond to the millisecond time scale we studied the mechanism of off-to-on photoswitching in WT and mutant rsEGFP2 with various off-to-on switching quantum yields. We found that different isomerization mechanisms for the trans-to-cis isomerization can explain the variation in switching quantum yields. The increase of off-to-on switching quantum yield for V151A mutant is rationalized by a sub-picosecond isomerization without any intermediate in the excited state. We also characterized a 100-picosecond intermediate in the ground state that does not exist in the WT protein. We will discuss how the protein cage controls the off-to-on dynamics in rsEGFP2.
Influence of the aggregation of metallic nanoparticles when coupled to photochromic molecules in hybrid systems

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Hybrid materials showing multiple photophysical properties have attracted considerable interest in the last few decades in the field of molecular electronics and photonic devices. Coupling plasmonics nanoparticles with photochromic molecules show many advantages such as enhanced optical and electromagnetic properties and molecular light switch control. Coupling these two units could lead to modulation of the surface plasmon resonance resonance under light irradiation [1] and an improvement of the photoswitching efficiency [2] at the same time due to crossed interactions between the plasmonic and the photochromic units. Such interactions can be increased when considering aggregated nanoparticles instead of isolated ones. [3]

Here we present hybrid nanosystems that highlight these crossed interactions. Moreover we will see how the aggregation state of gold nanoparticles could enhance these intercations. The enhancement of the local electromagnetic field induced by the aggregation process is studied using photo-emission electron microscopy (PEEM). This powerfull technic allows to map the near field intensity and localize it respect to the nanoparticles’ organisation. [4]

Figure 1 Images show the topography of aggregated gold nanorods and the localization of bright spots detected in photo-emission electron microscopy. Circular diagrams show the modulation of the photo-emission intensity when the polarization of the incident excitation laser is changed.

References:
Dual Wettability on Diarylethene Microcrystalline Surface Mimicking a Termite Wing

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Termite wing of Nasutiermes sp. has specific properties of wetting to water droplets. It adsorbs water mist, while larger water droplets were bounced on the surface. This is due to the survival strategy of termites (Nasutiermes sp.). We report here the study of the novel structure of the wing, through reproducing the dual wettability surface by photoinduced crystal growth technique. Diarylethenes 1o and 2o were reported to form rough surfaces covered with needle crystals of 1c and 2c upon irradiation with UV light on the microcrystalline surfaces of 1o and 2o, respectively. This time, we prepared microcrystalline surface of the mixture of 1o and 2o, then UV light was irradiated to form two types of needle shaped crystals; larger sized crystals of 1c and smaller sized ones of 2c on the surfaces simultaneously. The surface showed superhydrophobicity, on which the contact angle of water droplets was 163.7°. However, we found different wettability for different sized-water droplets as follows: the surface showed repellence to a larger water droplet (several hundred um-diameter), while it showed adhesive property for a smaller water mist (several tens um-diameter). To understand the difference, the results were compared with the bouncing phenomena of water droplets on two microcrystalline homo surfaces consisting of 1c and 2c. It was found that the different bouncing ability for different sized water droplets on the mixed surface is attributed to the smaller sized needle crystals of 2c, while adhesive property is due to the larger sized ones of 1c. Furthermore, by spraying the microdroplets to the mixed surface, we observed the specific wetting properties of the termite wing in nature. The smaller microdroplets impacting to the surface were adsorbed, its size was classified as fog. On the other hand, the larger microdroplet were bounced off from the surface, its size was classified as drizzle and rain. By mixing the different sizes of the crystals, the surface having specific dual wetting properties was reproduced. The bouncing ability of microdroplets is explained theoretically based on the experimental results in terms of adhesion energy, viscous friction of water, and restitution coefficient.
Antibacterial photocatalytic thin films: from light absorption to bacterial inactivation

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Antibacterial thin films provide an ideal alternative to current chemical sterilization methods. These photo-catalytic films are flexible, biologically resistant, made out of non-toxic earth abundant elements and only require typical UV light exposure to perform. Their potential application is tremendous and ranges from infrastructures to chirurgical devices.

In this presentation, we are reporting about the different mechanisms involved in the catalytic properties of iron and copper oxides thin films, from the early charge dynamics that follows light absorption up to bacterial inactivation.

Early carrier dynamics are investigated by means of ultrafast transient spectroscopy and the actual antibacterial properties are evaluated by means of flow cytometry. Composition and structure of the films are determined by X-ray Photo-electron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM). While, in each film, the full inactivation of bacterial colonies takes place within hours of UV exposure, the difference in efficiency seems to be related to overall absorbance of the films rather than composition or electronic structure.
Photochemical release of electrochemically deposited polymers

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Recently, Abe et al have reported several examples of an imidazole dimer that shows rapid switchable negative photochromism through photochemically induced bond-breaking to form two imidazolyl radical monomers.

The imidazole dimers mentioned above are synthesised by oxidation of the imidazole monomer precursors. In this presentation we utilise the chemistry of the imidazole to prepare polymer films on electrode surfaces through electrochemical oxidation of the monomer. The polymer can be unmasked by light releasing the blocking layer on the electrode and restoring electrochemical activity to exposed regions.
Designing ortho-fluoroazobenzenes for cyclodextrin soft materials

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Hydrogels represent an important class of soft materials, which have received much attention in recent years, especially in medicine, due to their unique mechanical properties and biocompatibility.[1] They can be described as 3D networks that are formed by self-assembly through either covalent bonds or noncovalent interactions, such as H-bonding, π-stacking, metal-ligand coordination, hydrophobic contacts, and host-guest complexation. For the design of photoresponsive hydrogels, the complexation of cyclodextrin (CD) hosts by azobenzene guests has been proven very valuable since the binding constants of the E and Z isomers to the CD's hydrophobic cavity differ significantly.[2] There are many examples of supramolecular systems in the literature based on this azobenzene-CD interaction.[3] However, in most of these systems the need of UV light for the photoisomerization can be considered as a major drawback due to limited penetration into biological tissue and radiation damage.

We herein describe a series of novel ortho-fluorinated azobenzenes[4] as photoswitchable guests for CD hosts that respond to visible light irradiation (Figure 1). Both molecular assemblies in aqueous solution as well as integration into bulk materials are presented.

References:

Molecular Design of Photochromic Terarylene for Solar Thermal Fuels

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New solutions for efficient solar energy conversion and storage are crucial for the development of a sustainable society. Current technologies rely on silicon-based photovoltaic solar cells that convert solar energy to electric power which is stored in batteries. One potential alternative is Solar Thermal Fuel (STF) which can store solar energy and release it as thermal energy. The solar energy is, therefore, stored within the chemical energy of photochromic molecules, which is so-called Molecular Solar Thermal Storage (MOST). The storage efficiency of these systems is defined by the ratio of released energy on-demand to input energy. For high efficiency, the molecules must have a high isomerization quantum yield, a large enthalpy change upon isomerization, high storage lifetime of their quasi-stable state, and easily stimulated isomerization to release stored heat. Although considerable interest has been focused on MOST compounds based on azobenzene, fulvalene, fulvalene-diruthenium, and norbonadiene systems, most of these materials do not adequately satisfy the requirements for efficient MOST systems. For example, in typical azobenzene systems, the low trans-to-cis isomerization quantum yield limits the storage efficiency to 0.3\%. We here focus on diarylethenes and their derivatives due to their excellent photoswitching properties. The standard enthalpy change is enhanced by aromatic rings of diarylethene with specific aromatic stabilization energy which is lost upon photoisomerization. It is thus rationally improved in terarylenes, because three aromatic rings are involved in each photoisomerization. In addition, terarylenes undergo a highly efficient cycloreversion, through the oxidation-induced chain-like reaction which displays overall electron efficiencies of up to 100,000\%. We here propose to use this highly efficient system as a controllable stimuli for energy release.
Mechanism of photochemical oxidative dimerization of tyrosine based hydrogelators

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Hydrogelation with low molecular weight compounds is an emerging technology in the fields as diverse as soft-robotics and drug delivery. Functional gelators, i.e. gelators that respond to external stimuli such as light are especially interesting. Building in functionality to the gelator compounds directly is a key challenge due to the fine balance of supramolecular interactions required to achieve anisotropic fiber growth to form the gel fiber network. Recently we have demonstrated that a tyrosine based hydrogelator can engage in photochemical oxidation both in the solution and gelated state, however, the low concentrations preclude facile analysis of the products, either dopamine or biphenol expected. In this presentation we will explore this reaction by UV/Vis absorption, and emission, and resonance Raman spectroscopy to identify the nature of the photoproduct and its application in controlling gel properties.
Synthesis and fluorescence switching of hyper-branched polymers having diarylethene at branching point

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We designed and synthesized hyperbranched polymers (HBP) having diarylethene (DE) at branching point and fluorene derivative (FL) between branching points in order to investigate the effect of polymer structure to fluorescence on/off switching efficiency accompanied with photochromic reaction of DE. HBP were synthesized by copolymerization of FL monomer and diarylethene monomer with reversible addition-fragmentation chain transfer (RAFT) unit in the feed ratio of [FL]/[DE] = 10. Fluorescence intensity of the resulting HBP decreased linearly accompanied with increasing photocyclization conversion of DE. As a result of simulation for fluorescence intensity changes, it is estimated that one DE closed-ring isomer can quench 13 FL moieties. However, the switching speed and on/off contrast were very low. This is possibly because the number of FL is much higher than DE in the polymer chain. Moreover, we synthesized two types of HBP having DE in not only branching points but also between them with different branching degree in the feed ratio of [FL]/[DE] = 1. Fluorescence intensity of polymer with few branches (HBP1) and polymer with more branches (HBP2) decreased non-linearly accompanied with the photocyclization conversion, and the significant decrease in low conversion and high on/off contrast were observed. It is estimated that one DE closed-ring isomer can quench 5.2 and 6.2 FL moieties, respectively, and their values were similar to that for linear polymer (LP) we previously reported [1]. However, fluorescence quantum yield in “on” state and Förster distance (Φₜ, R₀/nm) were determined to be HBP1 (0.16, 3.34), HBP2 (0.14, 3.26), and LP (0.35, 3.80), respectively. Here, in spite of low R₀ for HBP1 and HBP2, their quenching number did not decrease and the quenching number of HBP2 was more than that of HBP1. Taking these results into consideration, the utility of branching structure and high branching degree to fluorescence switching efficiency could be demonstrated.

Luminescence kinetics of up-converting nanoparticles for near-infrared photochromism

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Lanthanide-doped up-converting nanoparticles (UCNPs) can emit UV, visible and/or near-infrared (NIR) light upon NIR excitation via a multiphoton process. In order to optimize the luminescence of these “nanolamps” and to get ultrasmall upconverting nanoparticles (UCNPs), a MW assisted thermal coprecipitation pathway has been carried-out. Thus, hexagonal, Tm-doped (1% Tm) 2.5-nm UCNPs with an unusual Na(Yb–Gd)F₄ matrix with 57% Yb were produced. A NaGdF₄ shell for removing surface quenching gives a final 5.5nm size [1].

Photoemissive properties were examined using a 976nm pulsed NIR laser. The pulse duration (400µs) was triggered by a signal generator and the incident power was varied using calibrated neutral filters.

A multi-wavelengths, multi-experiments kinetic analysis based on the translation of the energy level diagram into differential rate equation model has been performed. Parameters values were harvested from an extensive literature data mining and refined numerically.

The assessment of the upconversion quantum yields is classically addressed using physical measurements [2]. Compared to physical radiometry, DAE photochromism actinometry is adapted to turbid mixtures, and can be extended to polychromatic sources in biology-relevant conditions such as drug uncaging, photodynamic therapy or optogenetics. The “NIR photochemistry”, based on the up-conversion phenomenon can find attractive biological applications since the use of sub-10 nm nano-objects promote fast renal excretion.

Metallic Nano-graphing by Direct Laser Writing

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Conventional methods for depositing and patterning metals on substrate require metal evaporation/sputtering, photolithography or electron beam lithography on photoresist, lift-off and etching processes. It involves multiple steps and requiring high-tech equipment. Meanwhile, these processes normally leave behind contamination (for instance, from resist polymer). Therefore, it is of significant importance to develop a simple and practical method for the nanopatterned deposition of metals without the use of a sacrificial resist.

In this work, we demonstrate a practical and low-cost optical technique for the direct deposition of metal nano-patterned structures without the need of a sacrificial lift-off resist. The technique relies on the laser induced reduction of metal ions on a graphene film. We investigate the mechanism of the metal deposition on graphene and show that this deposition is optically driven. The spatial resolution is limited only by the diffraction limit of the light source being used. Patterned metal features as small as 270 nm are deposited by focusing light with a wavelength of 532 nm on graphene with an objective (a numerical aperture of 1.25). Deposition of different metals such as Au, Ag, Pd, Pb and Pt is shown.

The method here presented enables the deposition of patterned metal structures without the need for lift-off like processes, thereby reducing contamination and opening a new way for metal nano-graphing. The concept of electron-hole production could also be useful for other functionalization protocols of graphene where ionization of the surface is required such as molecular grafting.
Photochromic reactions in supramolecular assemblies of stilbene derivatives

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Hetarylphenylethenes (heterostilbenes) like stilbenes exhibit a diverse photochemical behavior in solution such as reversible trans-cis isomerization, cyclization of cis-heterostilbene to dihydrophenanthrene derivative and further oxidation to the phenanthrene heteroanalogue, and dimerization of trans-heterostilbene to yield cyclobutane products.

The photochemical reactions of heterostilbenes are important from synthetic viewpoint. Thus, (E)-2-(3,4-dimethoxystyryl)quinoxaline in acetonitrile solution demonstrates the reversible regioselective and stereospecific formation of cyclobutane derivative upon the irradiation with light. Cyclobutanes are important synthetic intermediates providing atom-economic one-step transitions from simple to complex structures that is especially important in the total synthesis of natural products and other intricate molecules.

It is demonstrated that the regiospecific C–N bond formation is a general feature of the photoinduced electrocyclization of ortho-staryl substituted N-heterocycles comprising one and two nitrogen atoms. This phototransformation provides a straightforward synthesis of pharmaceutically important benzo[c]quinolizinium cation and its aza-analogues.

Generally the two alkene stereoisomers of a particular E/Z stilbenoid pair exhibit meaningfully different physiochemical properties. The main problems lead to the limitation of the applying of photochromic isomerization process in practice are connected with low stability of Z-izomer and low effectiveness of isomerization due to occurrence of competitive photoinduced processes.

The presented researches showed that the supramolecular organization of stilbene molecules can provide the formation of system demonstrating the photoinduced promising characteristics.

Acknowledgements: The research was supported by Russian Scientific Foundation, grant № 19-43-04127.
Photoresponsive Supramolecular Gels for Controlling Crystal Growth

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Low molecular weight supramolecular gels are ideal candidates in various areas, such as drug delivery, self-healing materials, and chemo-sensing. They can also offer a number of advantages as crystal growth media. For example, the ease of disrupting non-covalent interactions between supramolecular gelators provides the possibility to recover crystals with great convenience, and synthetic and structural versatility of gelators offers the potential to match the chemical structure of the crystallization substrate and hence provide an active nucleation surface. However, the potential of responsive supramolecular gels as mediums for crystal growth remains largely unexplored, especially for crystal growth of organic compounds. Among the external stimuli available to control the physical properties of a supramolecular gel, light offers unparalleled advantages, as it is a remote stimulus that can be controlled spatially and temporally.

In this study, a series of stiff-stilbene based bis-urea supramolecular gelators with different end groups and varying solubility were investigated to demonstrate their potential as crystallization media for organic compounds. Their trans isomers were expected to form an intermolecular urea hydrogen bonded network, while the cis isomers may form an intramolecular urea hydrogen bonding. Based on these different hydrogen bonding patterns, a poorer gelation ability was observed for the cis isomers than for the trans isomers offering the possibility of photo-inducing gel–sol transition which can be used for recovery of crystals. Moreover, different polymorphic forms and morphologies were observed when crystals grew in the supramolecular gel media.
Reversible fluorescence photoswitching based on the cooperative orientation in a dye-doped liquid crystalline azobenzene polymer

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Fluorescent photoswitchable molecular systems have attracted increasing interest because of their potential applications in optical memories, molecular switches, and fluorescent biological markers. We have been developed several fluorescence photoswitchable molecules based on a photochromic energy transfer or electron transfer process and successfully demonstrated reversible fluorescence photoswitching with non-destructive readout capability even at the single-molecule level [1-3]. In this study, as the new method to achieve reversible fluorescence photoswitching and non-destructive fluorescence readout, we focused on the stimuli-responsive orientation behavior of a liquid crystalline polymer (LCP) containing a photochromic azobenzene unit.

Figure 1 Molecular structures of an azobenzene liquid crystal polymer (PMAz6Ac) and a doped fluorescent dye (terrylenediimide).

Some LCPs containing an azobenzene unit in the side chain or the main chain are well known to show thermal and polarized-light induced out-of-plane and/or in-plane molecular orientation. We attempted to cooperatively control the molecular orientation of a fluorescent dye by doping into an azobenzene LCP (PMAz6Ac) film and reversibly switch the fluorescence intensity along with the orientation of PMAz6Ac induced by the polarized-light irradiation or the thermal annealing process. We successfully observed a cooperative orientation behavior of a doped fluorescent dye along with the orientation of PMAz6Ac by choosing an appropriate fluorescent dye. This cooperative orientation allows us to demonstrate the reversible modulation of fluorescence intensity with non-destructive readout capability under irradiating with the polarized excitation light. The results obtained in this study clearly indicated that PMAz6Ac thin film containing a fluorescent dye is a promising candidate for the ultra-high density optical memory media with the non-destructive fluorescence readout capability because the strategy enables to downsize by the single molecule level in principle.

References:

Quantum Rod Orientation Microscopy to Reveal Deca-Nanometer Features of Nano-Fibers of an Organogel

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Soft materials are, in a variety of cases, constituted of nano-structures of self-organized small organic molecules and a solvent (organic solvent, oil, water), and can be found in many industrial and technological applications, as well as in bio-materials. It is of major importance to control the molecular packing and the objects’ nano-structures, being at the origin of their properties. However, their development requires nowadays imaging techniques that are more evolved and provide deca-nanometer resolution in solvated materials, and potentially dynamically. In this presentation, we will discuss fluorescence polarimetric approaches used to characterize organic nano-fibers which present several constraints that inhibit the application of current super-resolution reconstruction imaging based on single molecule detection: the nanostructures are 100% made of fluorescent chromophores (thus impossible to switch off enough to see isolated single molecule blinking); and the soft materials are based on organic solvents and not water (most of commercial dyes are not appropriate). We used anisotropic core-shell CdSe/CdS quantum-rods (QRs) (~5-6 nm wide, ~50-60 nm long) to probe the nanostructured surface of the fluorescent nanofibers (NFs) constituting an organogel of DDOA (2,3-didecyloxyanthracene). The QR’s were modified with an appropriate molecular outer shell so that they were dispersible into the same solvent than the organogel, allowing the preparation of hybrid organogels containing NFs and QRs. TEM microscopy of desolvated samples reveals that QRs align along the long axis of the NFs. QROM imaging of solvated gels exploits the linearly polarized emission of the QRs to establish an orientation map of each individual QR interacting with NFs. This indirectly reveals the orientation of the underlying nanofibers’ structure probed at the deca-nanometer scale. This fluorescence microscopy technique provides a much wider wide-field of view as compared to TEM, and opens up perspectives for dynamic imaging in solvated materials. In addition, the hybrid material shows interesting emission properties, such as two-color orthogonal linearly polarized emission. \cite{1}

Crawling motion of azobenzene crystals by a single visible light source

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The motion of living systems are of great interest to researchers. Natural systems such as motor proteins within a cell are essential to the whole organism, and animals locomote constantly in search of food. Over the last few decades, self-propelling nano-to-micrometer sized objects have been research topics for fabricating artificial systems with various type of motion. Their motions are induced by chemical reaction or external stimuli, such as heat and light. Light is a useful external stimulus because it enables motion to be remotely and reversibly controlled. In this viewpoint, photochromic reaction is a powerful molecular engine to induce and to control the motion of artificial objects.

We have reported that the crawling motion of the crystal of 3,3'-dimethylazobenzene on a glass surface when the crystals are irradiated simultaneously with two different light sources (365 and 465 nm) [1]. Two light sources are required, since irradiation with 365 nm induces melting of the crystals, while irradiation with 465 nm induces recrystallization of the melted state. On the other hand, it is well known that a substitution of a functional group may cause shortening the lifetime of cis isomer of azobenzene. Thus, we anticipated a rapid recrystallization from the melted cis-rich state without light. Here, we wish to report that the crystals of 4-(methylamino)azobenzene exhibits crawling motion with a single light source of visible light (405 or 465 nm) [2]. The crystals exhibited the negative phototactic behavior, i.e., the direction is away from the light source. In addition, the crystal motion was observed by using a commercial white LED. This behavior resembles that of an amoeba, whose motion is induced by self-assembly of cytoplasm.

Self-Reporting Micro-Fibers from Polymer Blends: A Study on Photochromic and Mechanochromic Sensitivity

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Stimuli responsive polymers processed into micro-fibers bear the potential to be fabricated as systems detecting stress-induced failures. We report the high-throughput preparation of photochromic and mechanochromic micro-fibers from a blend of poly(methyl acrylate) (PMA) functionalized with spiropyran (SP) and poly(methyl methacrylate) (PMMA) via centrifugal force spinning (CFS). The micro-fibers showed reversible photochromism on irradiation with ultraviolet (UV) light (360-370 nm) and green light (520-530 nm) with negligible photodegradation, making it suitable for sensing history of light exposure. To obtain mechanochromic fibers, the applied force must be sufficient to isomerize the colorless SP to the purple merocyanine (MC) form. For an effective translation of the force from the polymer chains to activate the mechanophore, bead free, non-fused, and uniformly aligned fibers were desired. PMMA was added (1 to 5 wt %) to improve structural stability, i.e. the shape of the micro-fibers. It emerged that a blend solution constituting 3 wt % PMMA with an overall concentration of 28%, gave high-throughput fibers with an average diameter of 8.0 µm ± 2.3 µm. Furthermore, during mechanical testing, the polymer chains aligned in the direction of the applied force switching SP into MC, indicated by a visible color change. These fibers detected high strain deformations in real-time, before material failure and retained the mechanochromic response after unloading. The outstanding benefit of processing high quantities of fibers from polymer blends is the development of stress detectors tuned to respond within the desired strain range. Such tunable mechanochromic micro-fibers may have exceptional applications as components in composite materials for active stress monitoring.
Light-responsive ligands controlling bimetallic catalyst formation

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Bimetallic nanoparticles are characterized by a high catalytic activity that is attributable to the synergistic effect between the two metals that are involved. Amongst other bimetallic particles, core-shell catalysts are particularly efficient because the electron charge transfer in the over layer is enhanced due to their specific architecture. However, the control of the composition, the size and the shape of these core-shell nanoparticles remains challenging. Here, we propose a supramolecular approach that involves light as an external and versatile control parameter to control the thickness of the shell. I will report on the synthesis of the photochromic ligands, the functionalization of palladium nanoparticles by ligand exchange, and on the formation of the core-shell systems.
Mechanochromic luminescence of tricarbonylrhenium complexes

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Molecular solids that respond to mechanical stimuli by a change in photophysical properties have attracted attention in recent years not only from a basic point of view but also for their promising applications (in optics, optoelectronics, bio-imaging, etc.).\textsuperscript{1} We report here the mechanochromic luminescence properties of tricarbonyl rhenium(1) complexes incorporating a pyridyl-triazole (pyta) ligand with appended 2-phenylbenzoxazole (PBO) moiety. Previously, it was demonstrated that varied photophysical properties could arise from simple structural isomerism of the pyta moiety for ReL\textsubscript{1} and ReL\textsubscript{2} (Fig. 1a).\textsuperscript{2} Here, we report the changes in luminescence properties of compounds ReL\textsubscript{3} and ReL\textsubscript{4} (Fig. 1a), optimized for their spectroscopic properties\textsuperscript{3}, upon application of mechanical stimulus. As-synthesized pristine powders of ReL\textsubscript{3} and ReL\textsubscript{4} were shown to be luminescent with maximum $\lambda_{\text{em}}$ at 565 nm and 542 nm, respectively. Upon grinding, these peaks shifted to 595 nm and 600 nm, respectively. This shift was accompanied by major variations of the photoluminescence quantum yields and lifetimes. This effect was reversible upon solvent fuming. This could be due to changes in structure brought about by a transition from a crystalline to an amorphous phase, and vice versa. To the best of our knowledge, this is the first report of changes in luminescences properties of rhenium complexes as response to mechanical stimulation.

![Figure 1](image)

\textbf{Figure 1.} (a) Structure of compounds. (b-c) Emission and excitation spectra of pristine and ground samples of (b) ReL\textsubscript{3} and (c) ReL\textsubscript{4}.

\textbf{References:}

Multifunctional Self-Assembled Macrocycles with Enhanced Emission and Reversible Photochromic Behaviour

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Nature has wide range of species (cephalopods, chameleons, insects, and bacteria) that reversibly change their color or structure in response to various environmental stimuli. By mimicking such stimuli responsive behavior in artificial systems, sophisticated architectures with tunable functionality can be achieved. What is even more important is to make those systems multifunctional. To achieve new multifunctional systems, diverse types of non-covalent but stronger supramolecular interactions have been utilized. Having these in mind it will be fascinating to generate an AIE active and stimuli responsive bifunctional advanced material. As external stimuli, light is always the best choice.

To incorporate dual functions in a single coordination architecture, we have designed an AIE active Pt(II) 120° acceptor and a spiropyran decorated triarylamine based photochromic dipyridyl donor with a complementary bite angle of 120° as well. A series of self-assembled functional Pt(II) molecular hexagons (M1-M3) has been developed. Hexagons M1 and M2 were found to be aggregation induced emissive and photochromic respectively; while macrocycle M3 is bifunctional, containing both the kinds of building units. Also these macrocycles showed acidochromic behaviour. These macrocycles have been characterized and established using multinuclear NMR, ESI-MS and DFT optimization. Macrocyle M3 represents the first example of a multifunctional self-assembled Pt(II) architecture, with aggregation-induced emission (AIE), photochromic, and acidochromic properties. Our present approach of incorporating multiple functions into a single self-assembled structure with enhanced functionality compared to the starting building blocks via coordination self-assembly is noteworthy and has huge potential for the development of multifunctional materials.
Mechanofluorochromic dyes: quantification of their response to mechanical stimuli and incorporation into polymers

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A compound is said to be mechanofluorochromic when its fluorescence properties are modified under an external mechanical force [1]. When incorporated into polymer matrices, such compounds give mechanofluorochromic behavior to the resulting composite material [2]. The opportunity to follow fluorescence modifications by non-invasive spectroscopic measurements (Figure 1c) makes them good candidates for mechanical stress probes [3]: such functional materials could be used to monitor fatigue phenomena on machine components exposed to repeated strains or to control undesired opening of a package.

Boron diketone complexes (DFB – Figure 1a) and triphenylamine derivatives (TPA) are well known for their mechanofluorochromism as molecular materials. However, to the best of our knowledge, the mechanofluorochromism of polymers doped with these compounds has never been investigated. Furthermore, like for most of the mechanofluorochromic molecular materials, the type and intensity of force that has to be applied to these compounds to observe a fluorescence response remains unknown.

This poster presents a setup which is able to apply a shearing force on a molecular material under illumination and to simultaneously record fluorescence pictures as well as force and torque values. The procedure developed to process these data and to quantify the shearing threshold required to observe mechanofluorochromism will be described. Finally, our ongoing work on the incorporation of mechanofluorochromic molecules into different polymer matrices (figure 1 b and c) in order to test their sensitivity to different mechanical forces will be described.

**Figure 1.** (a) DFB-H structure, (b) Picture of a TPU polymer doped by DFB-H (2 wt%) and submitted to a scratching and a compression ($\lambda_{ex} = 370$ nm) and (c) corresponding normalized emission spectra (457 nm)

**References:**

Mechano-responsive circularly polarized luminescence of chiral Difluoroboron-ß-diketonate complexes

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Difluoro-boron-diketonate (DFB) complexes have emerged as a leading class of mechano-responsive luminescent materials for their versatile synthesis, high fluorescence quantum yields in the solid state and marked fluorescence emission changes upon force application. The diversity of known mechano-responsive luminescent materials is rapidly expanding due to their potential applications in mechanical stress sensors, memory chips and security inks. In this context, materials displaying not only a change in the emission wavelength but also in the circularly polarized luminescence (CPL) signal upon mechanical stimulation will be highly desirable. CPL is not only a powerful tool for structural information of the involved excited states but also it has shown potential applications in several fields such as spintronic based devices, biological probes and enantioselective CPL sensors.

The new diketonate DFB-Hex-amide compound (Figure 1a) display a yellow fluorescence upon deposited (AD) on a paper substrate, known to be amorphous and rapidly transform into crystalline state upon thermal annealing (TA) with bright blue-green emission. The mechanofluorochromic property was probed by smearing (SM) the thermally annealed samples and a bathochromic shift in emission was observed in response to mechanical stress (Figure 1b). The CPL active fluorescent DFB complexes showed a significant CPL signal in the crystalline state (\(|\mathbf{g}_{\text{lum}}|\) value = \(2.4 \times 10^{-2}\)) (Figure 1c). Interestingly, sign inversion and wavelength shift of the CPL signal was observed upon application of a shearing stress (“mechano-CPL effect”), which can be rationalized by a switching between monomer and excimer emission.

Figure 1 (a) (Top) chemical structure of (S)-enantiomer of DFB-Hex-amide and (bottom) photographs of the samples after deposition (AD), thermal annealing (TA) and smearing (SM) under UV illumination 365nm and their associated (b) fluorescence and (c) CPL spectra. (R)-isomers are plotted as solid lines and (S)-isomers as dashed lines.

References:
Hybrid nanostructured thin films, optically tunable

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Nowadays, micro- and nanopatterning of surfaces, thin films or multilayer structures via lithography-based technologies are widely used to design optical devices. However, they are based on complex processes and suffer from several drawbacks in terms of cost, material compatibility and device tunability. Recently, alternative approaches are proposed which exploit the properties of azobenzene-containing photoactive soft materials [1,2]. These materials are compatible with simple low-cost deposition and patterning processes and their mechanical response to light excitation allows one to envisage devices with tunable properties that can be controlled by a contactless optical stimulus [3].

We will present simple routes to elaborate micro- and nanopatterned metal / dielectric structures that exploit the photo-mechanical response of azobenzene-containing materials for controlling the shape of the structure pattern at the microscopic scale by illumination in the chromophore absorption band. The optical properties of the device are shown to exhibit spectacular changes related to the photo-induced modifications of the pattern shape (Figure 1).

Figure 1  PMMA-DR1/gold micro-pillar array obtained by a combination of soft micromolding and metal evaporation, before (a) and after (b) 120 mins of illumination with 25 mW/cm² of p-polarized light in the absorption band of the azobenzene derivative (488nm). c) Evolution of the optical reflexion spectrum of the structure as a function of illumination time.

References:

Mechanofluorochromic molecular materials: insights into the origins of the mechanically induced fluorescence change

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Fluorescent materials, designed through appropriate molecular engineering, are able to signal different stimuli with a high sensitivity. In particular, a material is called “mechanofluorochromic” when its fluorescence emission changes upon mechanical stimulation (pressure, shearing force…). Mechanofluorochromic compounds have attracted a rapidly growing interest for the last five to six years, in particular for their possible use as mechanical sensors\textsuperscript{[1]} and several series of new molecules have been synthesized\textsuperscript{[2]}. We are interested in a multiscale study of this phenomenon, in order to relate the molecular structure of a mechanofluorochromic dye to its sensitivity to different mechanical stimuli.

We synthesized a short series of difluoroboron b-diketone derivatives \textsuperscript{[3]} bearing carbonyl substituents, which all demonstrate mechanofluorochromic behavior (Fig. 1). The photophysical properties of those novel compounds, in solution as well as in bulk solid, in thin films and in nanoparticles will be presented, along with studies by AFM coupled to fluorescence microscopy, which allow simultaneously following the changes of morphology of these materials and the changes of their fluorescence emission.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{compound.png}
\caption{compounds synthesized and mechanofluorochromic behavior of the compound DFB-amide.}
\end{figure}

Funding: Mission pour l’Interdisciplinarité (CNRS), ERC StG-2016-715757 (MECHANO-FLUO)

References:

Photoswitchable multi-emissive materials and nanosystems

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Design of photoswitchable emissive systems still represents a challenge, in order to develop fluorescence-based devices for nanotechnologies. In the last decade, excitation energy transfer processes have been advantageously employed to design photoswitchable fluorescent molecular systems between a photochromic dye and an appropriate fluorescent molecule as shown in Figure 1a.[1] More recently, diarylethenes of particular interest, showing no emission in the open-form (P-FO) but a strong emission signal in the closed-form (P-FF), have been developed.[2] Such molecules allow multi-emission photoswitching when combined with fluorescent dyes (Figure 1b).[3]

We describe here the design of materials combining Bodipy fluorophores with diarylethene-sulfone photochromic compounds, inducing the change of the emission color from green to orange along with the photocyclization reaction of the photochromic units. Several systems have been prepared, based on polymer matrices or silica nanoparticles embedding fluorescent and photochromic dyes, and fully characterized by spectroscopy methods. Collective effects, such as enhanced colorimetric transitions due to multiple energy transfer processes, have been demonstrated (Figure 1c).

Figure 1. Schematic representation of (a) “ON/OFF” and (b) “multi-emissive” principles of fluorescence photoswitching. (c) Silica-doped nanomaterials with enhanced multi-emissive photoswitching behaviour.

References:

The relation between mechanofluorochromic properties and evaporative crystallization process for dibenzoylmethane difluoride complexes

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Fluorescence switching in response to external stimuli, namely mechanofluorochromism, is highly interesting as this phenomenon can potentially be exploited for a sensor, memory, security ink applications, etc. Furthermore, fundamental information regarding intermolecular interactions can be garnered from the fluorescence properties of the organic molecular solids that exhibit this phenomenon. The dibenzoylmethane boron difluoride (BF$_2$DBM) derivative exhibits mechanofluorochromism in response to perturbation by a mechanical force. The phase transition of BF$_2$DBM from the amorphous to crystal due to mechanofluorochromism is ascribable to the dynamic hydrogen-bonding formation depending on substituent.

We have achieved the fluorescence visualization of the two-step nucleation mechanism proposed by organic crystal formation processes as a result of solvent evaporative crystallization of BF$_2$DBM complex. The fluorescence of the droplet was purple just after the dropping. The emission color changed to purple to blue via orange. Orange emission is not observed even at high concentration, which exhibited only from supersaturated solution. Crystals of BF$_2$DBM can be formed from monomer species via an amorphous state, which are presumed to show hierarchical change like a consecutive reaction. A transient amorphous state is formed prior to crystal formation. In the present case, the observed orange emission originating from an amorphous species demonstrated the existence of a liquid-like cluster before crystallization. The fluorescence detection during the solvent evaporative crystallization is also useful to assess the material properties of the mechanofluorochromism based on the amorphous-crystal phase transformation.

In this paper, to clarify the effects on the intermolecular interaction concerning both mechanofluorochromic properties and the evaporative crystallization process, especially intermolecular hydrogen-bonding formation, we synthesized the alpha-substituted BF$_2$DBM derivatives of the dioxaborin ring and measured the changes of the fluorescence color and spectra as a function time during the evaporative crystallization from solutions. We will discuss on the phase stability and the crystallization ability of BF$_2$DBM derivatives.
The present poster reports on the formation and on the electrochemical/spectroscopic characterization of inclusion complexes formed in aqueous media between cucurbit[7 or 8]urils cavitands (CB[7], CB[8]) and a rigid four-pointed star-shaped viologen-appended porphyrin tecton. The formation of discrete 4:1 pseudo-rotaxane-like caviplexes, involving threading of CB[n] rings on the rigid viologen-based star's branches has been demonstrated by nuclear magnetic resonance and mass spectrometry measurements. Then, the photo- and redox-triggered formation of 2D supramolecular assemblies involving CB[8]s and the four electron reduced tectons as key building elements, has been established on the ground of in-depth electrochemical and spectroscopic analyses supported by quantum calculations. The CB[8]-promoted intermolecular p-dimerization of the viologen cation radicals introduced at the meso positions of the porphyrin platform has been brought to light through the diagnostic signatures of the 1:2 host-guest ternary caviplexes formed between viologen and CB[8] and by spectroscopic data collected after electrochemical, chemical or photochemical reduction of the viologen-based tectons. The CB[8] hosts not only proved useful to promote the redox-triggered formation of supramolecular assemblies, it was also found to prevent the chemical reduction of the porphyrin ring in aqueous media and its subsequent conversion into phlorin products.

Multimodal time-resolved spectroscopy of ultra-small upconverting nanoparticles

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Lanthanide-doped inorganic nanoparticles present the unique feature of being able to emit light up to the blue region of the visible spectrum (depending on the nature of the dopants) while being excited by near infrared (NIR) light. Because biological samples have limited absorption in the NIR, these so-called Up-Conversion NanoParticles (UCNPs) are attractive candidates for biological applications.

UCNPs can be functionalized with photochromic dyes which absorb light emitted by one UCNP emission channel. These nanohybrids represent promising probes allowing, at the same time, single particle tracking using one emission channel and, super-resolution microscopy with a second emission channel. Indeed, Förster Resonance Energy Transfer (FRET) switching between photochromic dye and UCNP will induce blinking of the particles that can be used for super-resolution fluorescence microscopy (STORM, SOFI). In order to optimize their design, the blinking properties and emission lifetimes of such inorganic luminescent UCNPs grafted with organic photochromic quenchers have to be thoroughly described.

The behavior of ultrasmall bare NaYF₄-based UCNPs as a function of the excitation power (time-resolved emission dependence vs. excitation power) is investigated in solution and at the single particle level in order to extract their photophysical properties (lifetime, brightness). Luminescence spectra are recorded using the 976 nm light of a pulsed diode laser through a confocal microscope allowing for collecting spatial and time-resolved information on the power-dependent fluorescence of single UCNPs.

We will discuss the properties of single UCNPs and nanohybrid particles grafted with a fast photochromic dye. Their blinking dynamics will be especially detailed to prepare new ultra-small UCNPs for super-resolved fluctuation fluorescence microscopy.
Photoinduced Reentrant Transition and Thermal Stepwise Transition of Supramolecular Assembly Composed of Amphiphilic Diarylethene

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Amphiphilic molecules aggregate with each other and form supramolecular assembly in aqueous media due to hydrophobic interaction. Morphology of the nanometer-sized assembly is determined by the volume ratio of hydrophilic and hydrophobic moieties and the geometrical shape of amphiphiles. Therefore, the supramolecular assembly composed of stimuli-responsive amphiphiles show morphological change along with the change in the molecular structure. Meanwhile, the oligo(ethylene glycol) unit, often used as a hydrophilic unit, is known to exhibit lower critical solution temperature (LCST) behavior. When a photochromic unit is incorporated into an oligo(ethylene glycol) derivative, the LCST temperature would change with the photochromic reaction, because the transition temperatures of the isomers are different. Therefore, the LCST transition might be triggered by change in conversion ratio upon photoirradiation.

Some amphiphilic diarylethenes having two hydrophilic tri(ethylene glycol)s and a hydrophobic alkyl chain have been found to form supramolecular assemblies in water. Rod-like micelles and bilayer sheets are generated from the closed-ring isomers having ridged triangular plate-shapes at room temperature. In contrast, the open-ring isomers scarcely form the ordered supramolecular assemblies because the LCST temperatures are lower than room temperature. Therefore, the reported photoinduced LCST transitions are one step-change between dehydrated state of the open-ring isomer and hydrated closed-ring isomer.

In this work, we found that the supramolecular assembly composed of amphiphilic diarylethene having two hydrophilic and two hydrophobic chains underwent two-step transition. Both the open-and closed-ring isomers formed the ordered supramolecular assemblies at room temperature. In contrast, mixture of the both isomers underwent LCST transition at lower than room temperature. As a result, micrometer-sized structure showed morphological change from hydrated to another hydrated via dehydrated states upon photoirradiation under optical microscope. The open-ring isomer formed multiple folded nanorod. On the other hand, the closed-ring isomer showed time-evolution change from nanofiber to sheet at room temperature. Additionally, the suspension containing the closed-ring isomer showed two-step spectral shift corresponding to the time-evolution change, i.e., bathochromic and subsequent hypsochromic shift. In conclusion, the supramolecular assembly showed complicated change in nanometer- and micrometer-sized structures, and absorption spectra.
Fluorescent response to forces at the nanoscale of photo-polymerized polydiacetylenes

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Mechanofluorochromic materials change their fluorescent properties when subjected to external mechanical stimulation. [1] This mechanical force affects their supramolecular structure, resulting in different emitted light. Polydiacetylenes (PDA) are ordered π-conjugated systems that undergo topochemical polymerization under UV (254 nm). [2] According to the molecular arrangement, such polymerization may produce a non-fluorescent “blue” form and a weakly fluorescent “red” form. [3] Upon external stimulation, the blue form is converted to the red form.

We study the fluorescent properties of PDA-based materials when subjected to nN-range forces by means of an atomic force microscope (AFM) coupled with a fluorescence microscope. We aim at providing a mechanical fluorescent sensor with a well-defined correlation force-fluorescence recovery. We present here the photo-polymerization properties, morphology, and photophysical response to nanoscale shears of three PDA-derived compounds. DA1 is a simple diacetylene with urethane moiety as self-assembling group; TzDA1 is a derivative covalently attached to a tetrazine fluorophore; TzDA2 has a modified urethane moiety. Tetrazine is not fluorescent when PDA is blue (OFF) due to energy transfer, while it is fluorescent when PDA is converted to the red form (ON). [4] Vacuum evaporation of the monomer followed by UV irradiation produced blue PDA thin films. Upon mechanical stimulation using AFM in contact mode, fluorescence was recovered by conversion to the red form. Comparing DA1 vs TzDA1, a better fluorescence contrast was found in the latter, demonstrating the importance of the tetrazine fluorophore. To test the role of the self-assembling group, we modified the urethane moiety in TzDA2. We found that the simple urethane moiety in TzDA1 was more optimal for nano-mechanical stimulation. Thus, TzDA1 showed the clearest correlation between applied force vs fluorescence recovery. Therefore, in this work, we show the importance of the fluorophore and the self-assembling unit in making a nanoscale mechanical force sensor.

Fluorescence image (left) and morphology image (right) of mechanically stimulated TzDA1 thin film

Photochromic molecules and plasmonic materials for new reversible switchable devices

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Using metallic nanoparticles (NPs) for electronic devices show many advantages due to their specific optical and electric properties that can be driven by light. This owes to the surface plasmon resonance that gives rise to a great enhancement of the local electromagnetic field. As surface plasmon resonance is very sensitive to their direct environment, it is possible to use photochromic molecules as a local photoswitch to reversibly modify these photophysical properties. [1] The goal is to develop a hybrid material combining molecular and plasmonic components which by action of an external stimulus – here a light excitation - shows a reversible change of its electrical - conductance - and optical properties at the millimeter scale. [2,3]

In this communication we present hybrid nanomaterials made of (i) gold nanorods as the plasmonic unit [4] and (ii) charged diarylethene as photochromic unit. A polyelectrolyte is used as a linker between them thanks to electrostatic interactions, limiting the quenching of the photochromic molecules. Steady state absorption experiments highlight the fact that using polyelectrolyte as linker avoids the quenching of the photochromic reactions. Furthermore, transient absorption experiments clearly show that the hybrid nanomaterial behaves differently from the single gold nanorod or diarylethene.

References:

Polymorphism and mechanofluorochromism of pyrene derivatives with and without tert-butyl groups

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Mechanofluorochromism (MFC) refers to the solid-state emission color change upon mechanical stimuli, and has attracted increasing attention in recent years.¹ In general, the molecular arrangements or intermolecular interactions are forced to be altered by mechanical shearing, and crystal-to-amorphous or crystal-to-crystal phase change induce emission color change.² Growing numbers of MFC molecules have been developed and potential applications have been demonstrated as well; however, study on MFC is still in the early stage from the viewpoint of correlation among mechanical, photophysical and crystallographic properties.

In this study, we focused on pyrene-based compounds to develop a new series of organic solid-state emitters with MFC properties. In order to control the solid-state steric structures, pyrene derivatives w/ and w/o tert-butyl groups in 2,7-position were prepared. Two types of polymorphic powders were identified for each molecule, and they were found to show a pair of bathochromic and hypsochromic MFC upon grinding (Figure 1). Two forms of crystals (longer-λ_em and shorter-λ_em form) were successfully prepared by recrystallization, and the MFC spectral range of polymorphic powders fell within that of polymorphic crystals. Photophysical parameters including emission spectra and lifetimes were evaluated for pristine/ground samples, and structure-property relationships were discussed on the basis of crystallography.

Figure 1. MFC of two polymorphic powders of 4-acetyl-2,7-di-tert-butylpyrene (λ_ex = 365 nm).

Fluorescence modulation with photochromic-fluorescent nanosystems

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Combination of photochromic molecules with fluorescent dyes leads to photoswitchable emissive systems.¹ The fluorescence signal is observed when the photochromic unit is colourless, and the fluorescence quenching occurs by energy transfer when the photochromic part is converted into its coloured form. If the two moieties are covalently linked and studied in solution, a linear relationship is expected between the fluorescence signal and the conversion yield. But when the molecules are gathered into nanoparticles, a nonlinear effect is observed: the fluorescence is totally quenched with few photons by multiple intermolecular energy transfer processes, even if a small number of molecules are converted in the coloured form.² New compounds showing these properties are presented. Microscopy studies of a diarylethene molecule linked to two fluorescent perylene-diimide moieties were performed to investigate the photoswitching of isolated nanoparticles. Besides, negative photochromic compounds³ (phenoxy-imidazole complex and HABI derivative) were combined non covalently with suitable fluorophore in polymer matrix or silica nanoparticles, in order to induce efficient “OFF-ON” fluorescence photoswitching.⁴

Figure 1 a) Representation of a diarylethene compound with two perylene-diimide fluorophores studied by b) confocal microscopy showing c) “ON-OFF” fluorescence photoswitching. d) Scheme of a phenoxy-imidazole negative photochromic molecule with e) “OFF-ON” fluorescence photoswitching when combined to a fluorophore.

Photo-activated room-temperature phosphorescence and thermally activated delayed emission in phenanthroline-based derivatives

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Recently the field of pure-organic luminescent materials displaying room-temperature phosphorescence and/or thermally activated delayed phosphorescence (TADF) has attracted an ever-growing attention giving access to a wide range of exciting novel applications. Amongst these, our attention was more specifically turned to the development of phosphorescent programmable luminescent tags (PLTs) under aerated conditions which remains a key challenge. Indeed, the few existing examples suffer from the mandatory use of UV-light to trigger the luminescence response

Here, we report the design and synthesis of a wide range of phenanthroline-based derivatives displaying long-lived room temperature phosphorescence sometimes combined with TADF. Their spectroscopic properties (absorption, emission, lifetimes…) will be compared, analyzed and discussed. The most promising targets are used to realize photo-programmable PLTs. A simple host/guest system top coated with an oxygen barrier layer enables a definite local photo-control of the oxygen concentration inside the films leading to the precise blue-light activation of the phosphorescence to encrypt information on their surfaces with a very high resolution (>700 dpi).

Taking advantage of the combined TADF and phosphorescence abilities of some derivatives, and through a carefully chosen additional emitter, white phosphorescent PLTs could be obtained.

Figure 1: A. Chemical structure of one promising target: PhenTpa. B. a. Photo-activation of the phosphorescence with high intensity blue LED. Enables localized consumption of the oxygen triplet contained inside the film. b. Reading with low intensity blue LED. High luminescence contrast is obtained by phosphorescence on previously photo-activated area. c. Heating the sample by exposing it to IR radiations leads to diffusion of oxygen in the sample and erase the programming. C. Different phosphorescent patterns successively obtained on the same sample. λ_{exc} = 420 nm.

Single-molecule fluorescence microscopy coupled to resampling statistics: a novel approach for the identification of microbial species based on DNA optical mapping

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In the last decade, single molecule fluorescence microscopy has gotten enormous success in many different research fields especially in biology and medicine [1]. One of its most recent applications is the characterization of the composition of the gut microbiome for monitoring the development and progression of particular disorders such as Alzheimer’s disease [2, 3]. In this specific case, gut content is sampled and the extracted cells are subjected to an induced lysis process for the collection of their DNA. DNA is afterwards enzymatically labelled with a fluorophore (e.g. Rhodamine B) at specific nucleotide substrings of its double-helix (e.g. TCGA, when TaqI Methyltransferase is concerned) and stretched on a coated surface which is imaged by a single molecule fluorescence microscopy setup. From the captured images, characteristic signal patterns – giving an idea of the sequences of fluorophores on a single DNA chain and thus of the sequences of its nitrogenous bases – are extracted. However, as DNA naturally shears off during sample preparation, such signal patterns do not span the full genome of a single species, but just fragments of it. Then, how is it possible to identify which microbial species the concerned fragments come from? In this study, a novel approach to achieve this goal is proposed and tested in several simulated and real scenarios.

References:

Photoinitiated polymerization using Donor-Acceptor Stenhouse Adducts under near-infrared light

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In recent years, a new family of organic photochromic molecules working with visible light have been reported, namely the Donor-acceptors Stenhouse adducts (DASAs)¹. The synthesis of these photochromic molecules is made in two steps, using commercially available starting materials and a biomass derivative i.e. furfural. Photochromic properties provide a possible answer to the current limitations of other photo-switch classes in the visible and NIR regions. Since their discovery in 2014, the first successful examples of applications demonstrate the full potential of this new family of photochromes.

Parallel to this, photopolymerization has witnessed intense research effort due to the constant growth of industrial applications associated with the synthesis of new photoinitiators PI and monomers. The development of NIR photoinitiators allowing to simultaneously initiate a thermal and photochemical polymerization have been developed, addressing these different issues.²

In this presentation, the possible use of these DASA as efficient photoinitiators for a polymerization under infrared light will be presented.

References:
Light-induced switching effects in metal halide perovskite and perovskite-like materials for thin film electronics applications

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Perovskite-type semiconductors have attracted tremendous attention of the research community since they demonstrate exciting physical, optical and electronic properties. In particular, the efficiency of solution-processed perovskite solar cells surpassed 24% in 2019, thus offering a real third generation photovoltaic technology with a bright market potential. One of the main obstacles for commercialization of perovskite photovoltaics is related to their complex behavior under solar illumination, which is still poorly understood.

In this presentation, we will discuss the results of our recent studies of the light-triggered phenomena in complex metal halides with perovskite and perovskite-like crystal structure. Particular attention will be paid to the light-induced ion motion and halide phase separation as well as photochemical aging effects in different types of materials. Some revealed fundamental correlations between the photochemical stability of the perovskite semiconductors and their stability will be presented.

We will also show a number of useful applications of light-switching and electrical switching effects in metal halide perovskites featuring the design of multiplication-type photodetectors and optical memory elements. The enhancement of the light response and/or the film healing effects were achieved in some systems using photochromic materials such as spiroxazines, spiropyans, photochromic dyes and metal complexes. The proposed new approaches might speed up the commercialization of the perovskite photovoltaics and hybrid thin film electronics in a broader context.

This work was supported by RSF (grant No. 19-73-30020).
Photoswitchable organic field-effect transistors and memory devices using light sensitive porphyrin monolayers

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Organic electronics is one of the most rapidly developing fields of science and technology. A considerable attention has been paid recently to the exploration of memory devices based on bistable organic field-effect transistors.

Here we report for the first time the application of the self-assembled monolayers of donor-acceptor dyads with porphyrin moieties as light-sensitive components integrated at the semiconductor/dielectric interface in OFET-based optical memory elements. The designed devices operated at low voltages (<15 V), showed wide memory windows and reliable switching between multiple quasi-stable electrical states characterized by Ids current ratios of 10^2-10^4 when measured at the same Vgs voltage. The operation mechanism of the designed light-switchable transistors has been revealed and will be discussed in the presentation.

Exploring a series of porphyrin-based dyads with appended acceptor units based on [60]fullerene or ruthenium pyridyl complexes allowed us to establish some important molecular structure – electrical performance relationships, which should facilitate future design of advanced organic memory devices possessing all the advantages of organic electronics while being cheap, flexible, biodegradable and hence more environmentally friendly.

This work was supported by RFBR (project № 18-33-00904).
Light-induced switching effects in metal halide perovskite and perovskite-like materials for thin film electronics applications

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Perovskite-type semiconductors have attracted tremendous attention of the research community since they demonstrate exciting physical, optical and electronic properties. In particular, the efficiency of solution-processed perovskite solar cells surpassed 24% in 2019, thus offering a real third generation photovoltaic technology with a bright market potential. One of the main obstacles for commercialization of perovskite photovoltaics is related to their complex behavior under solar illumination, which is still poorly understood.

In this presentation, we will discuss the results of our recent studies of the light-triggered phenomena in complex metal halides with perovskite and perovskite-like crystal structure. Particular attention will be paid to the light-induced ion motion and halide phase separation as well as photochemical aging effects in different types of materials. Some revealed fundamental correlations between the photochemical stability of the perovskite semiconductors and their stability will be presented.

We will also show a number of useful applications of light-switching and electrical switching effects in metal halide perovskites featuring the design of multiplication-type photodetectors and optical memory elements. The enhancement of the light response and/or the film healing effects were achieved in some systems using photochromic materials such as spiroxazines, spiropyrans, photochromic dyes and metal complexes. The proposed new approaches might speed up the commercialization of the perovskite photovoltaics and hybrid thin film electronics in a broader context.

This work was supported by RSF (grant No. 19-73-30020).
Surface quasi random structures on thin films based on nanomotor lithography for light trapping

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Disordered photonics has experienced a burst of activity in the last two decades. The fabrication of nanostructured materials for the control of light-matter interactions becomes particularly important for the improvement of different phenomena involving a highly scattering of light. Different techniques have been explored as photonic crystals, self-assembly of particles, or randomly distributed voids. However, the strategy which proposes easy fabrication method, good reproducibility, wide area fabrication and cheap materials would be appreciated.

We propose in this study the use of azopolymer to the fabrication of 2D quasi random structures. The technology is based on a new azopolymer. We show the fabrication of quasi-random and Gaussian random structures (2D random structures) with a photo-induced nanostructured material for the control of light-matter interactions. This material offers a novel approach for the design of richer Fourier spectra by using a pattern with different periodic structures and sub-structures that allow the control of the Fourier components at will. These structures can be used to achieve highly efficient omni-directional light coupling in thin films.

Two types of gratings inscribed randomly on the surface with two different directions can be obtained. The pitch of the gratings is about 0.9 mm and the angle between the two gratings is about 45°. The diffraction obtained after illumination of the patterned structures on the surface corresponds to the Fourier transform and we have observed a circular configuration of the spatial frequencies. These configuration allows the light to be spatially diffracted in an omni-directional way.

We have also observed light coupled to the surface grating. Four gratings have been inscribed in the same angle direction that the two different grating inscribed on the surface of the azopolymer. A red light was send to the central grating in order to observe the diffracted light coupled into the thin film. The thin film thickness is 500 nm.

In conclusion, we have presented a cheap method for the fabrication of 2D random structures able to couple light into a thin film with an omni-direction. This organic material can be suitable for energy harvesting of organic solar cells or OLEDs.
Direct laser writing of crystallized TiO$_2$ and TiO$_2$/carbon microstructures with tunable conductive properties

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Metal oxides (MOs) are an important class of materials for optoelectronic applications. Developing simple and versatile processes for integrating these materials at the microscale and nanoscale has become increasingly important. Solution-based processes have gained much attention during the last years due to their simplicity, cost effectiveness, vacuum-free processes, and high versatility. However, in solution-based processes, thermal annealing is required to eliminate the solvent and organic ligands that are complexed on metal ions and to obtain material and phase compositions with suitable properties. This step is typically conducted at temperatures ranging from 300 to 1000 °C. Thus, such a fabrication strategy can be difficult to apply in the case of multistep integration processes involving different materials. In this context, laser processing of MOs presents many advantages due to the control of the laser-matter interaction in space and time. Laser curing allows a fast treatment that can be confined to a limited volume by focusing the laser beam. In the present work, near-infrared femtosecond laser irradiation was successfully used to prepare amorphous or crystallized TiO$_2$ microstructures in a single step using a direct laser writing (DLW) approach from a TiO$_2$ precursor thin film doped with a suitable dye. The laser-induced chemical modification was investigated by coupling photostructuration experiments and Raman microspectroscopy. When laser writing is conducted under a nitrogen atmosphere, simultaneous to the crosslinking of the Ti oxide precursor, the graphitization of the organic species embedded in the initial film is observed. In this case, a carbon network is generated within the TiO$_2$ matrix, which significantly increases the conductivity. Since the TiO$_2$/C nanocomposite exhibits piezoresistive behavior, a miniaturized pressure microsensor has been realized as a proof of concept.
Formation of robust photochromic patterns on cellulose paper

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Cellulose is an organic compound, and more precisely a polysaccharide which represents the main part of wood, paper and cotton. Many different methods were invented to modify cellulose such as the use of wax or oil, polymerization in solution at the surface of the cellulose or even by chemical vapor deposition.

Through the grafting of single molecules under the surface of the cellulose, it could be possible to make a modification of the cellulose properties. Indeed, previous research in our laboratory at the University of Nantes has shown that the grafting of some compounds enables the modification of cellulose from a hydrophilic to a hydrophobic state, with a spatial control, by the grafting of dithiodiglycolic acid onto cellulose in a first step and then, a thiol-ene or thiol-yne reaction which permits the grafting of hydrophobic molecules. This reaction could also be useful for the grafting of photochromic molecules. Therefore, we have made the synthesis of dibenzothienylethenes with alkyne moieties and the grafting spatially controlled of these molecules onto cellulose paper. The pattern is robust even after several washing steps and the photochromic behaviour is the same even after 18 write-erase cycles.

Such systems could be used for the creation of robust microfluidic devices or in anti-counterfeiting of bills. These reactions were made onto cellulose paper but could also be used in textile industry.
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