

Molecules and Light 2017



IV Autumn Meeting of the Polish Photochemistry Group
Zakopane, 25 - 29 September 2017

Book of Abstracts

Institute of Physics, Polish Academy of Sciences, Warsaw
Jagiellonian University, Kraków

<http://www.ifpan.edu.pl/ml2017/>

Official conference web site:
<http://www.ifpan.edu.pl/ml2017/>

Important Information

Conference venue: **Hotel *Bel-Ami***, Zakopane, ul. Goszczyńskiego 24
Tel.: +48 18 20 155 75, <http://belami-zakopane.pl/>
(all lectures, communications, panel discussion and poster session)

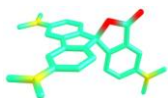
Welcome Dinner: **Hotel *Bel-Ami***, Zakopane, ul. Goszczyńskiego 24
25 September 2017

Excursion: **Niedzica castle or Białego Valley (mountain walk)**
27 September 2017 (alternatively, 2 groups depending on weather)

Conference Dinner: ***Karczma Czarczi Jar***, Zakopane, ul. Małe
28 September 2017 Żywczańskie 11a, Tel.: +48 18 20 641 78,
www.czarcijar.pl

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Molecules and Light 2017



IV Autumn Meeting of the Polish Photochemistry Group
Zakopane, 25 - 29 September 2017

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Welcome

Dear Colleagues and Friends,

It has been slowly becoming a tradition that at the onset of autumn the Polish Section of the European Photochemistry Association (EPA) has a honour and pleasure to invite the researchers working in photophysics, photochemistry, photocatalysis and molecular spectroscopy to present and discuss recent developments in interactions between light and matter. After three successful past Molecules and Light editions (2011, 2013, and 2015) I can say with conviction that our biannual Meeting has become a permanent fixture in the calendar of scientific conferences in Poland.

The passage of time is not only marked by progress, advance and development, but unfortunately also by passing away. Early this year we bid farewell to Prof. Zbigniew R. Grabowski, a great scientist, researcher and man, who in 1970's founded the Polish Section of the EPA. Because of his age and health condition he was not able to attend our meetings, but he was always with us with his heart and soul, interested in program, lectures and discussions. Moving forward in science is much more efficient, when we remember and recall our past and those who were among us.

In line with the profile of the three past editions, also this year's Meeting will aim at reviewing, in an international context, current research conducted in Poland in the field of photochemistry and photophysics. I believe that especially for younger researchers the Molecules and Light meetings are an excellent platform for promoting and presentation of results of their research, as usually we offer invited lectures for talented scientists just before or after the doctor of science (habilitation) degree. I hope also that ML meetings are a good opportunity for establishing and strengthening scientific and personal contacts between the members of our community. I am sure that beautiful surrounding of the Polish Tatra Mountains (and hopefully nice weather) will provide additional stimulation and inspiration for creative and imaginative concepts and ideas.

The present meeting is organised jointly by the Institute of Physics, Polish Academy of Sciences, and the Jagiellonian University, and we sincerely acknowledge their support. We thank also our exhibitors and sponsors.

I wish you a pleasant, enjoyable and inspiring stay in Zakopane, and a fruitful conference.

Jerzy Karpiuk
Chairman ML2017

Conference Program

Conference Program

Monday, 25 September, 2017

| Monday, 25 September, 2017: | |
|---|---|
| 14.00-19.00 | Registration |
| Monday, 25 September 2017 Evening Session: 19.00-23.00 | Light-molecule interactions - lessons learned from Nature Chair: Jerzy Karpiuk |
| 19.00-19.15 | Welcome address and conference opening |
| 19.15-20.15 OL | Opening lecture Wiesław Gruszecki , Faculty of Mathematics, Physics and Information Science, Maria Curie-Skłodowska University, Lublin <i>Regulation of light harvesting and excitation energy transfer in the photosynthetic apparatus of plants</i> |
| 20.15-23.00 | Welcome dinner |

Tuesday, 26 September 2017

| Tuesday, 26 September 2017 Morning Session: 9.00-13.00 | | Water, light and photocatalysis Chair: Marek Sikorski |
|---|---|---|
| 9.00-10.00 PL1 | Andrzej Sobolewski , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Burning water with sunlight: insights from computational chemistry</i> | |
| 10.00-10.30 OC1 | Olaf Morawski , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Photocatalytic water oxidation – the new approach to water splitting</i> | |
| 10.30-11.00 | Coffee break | |
| 11.00-11.30 OC2 | Wojciech Macyk , Faculty of Chemistry, Jagiellonian University, Kraków <i>Self-sensitized photocatalytic degradation of colorless organic pollutants forming surface Ti(IV) complexes</i> | |
| 11.30-12.00 OC3 | Marcin Kobielski , Faculty of Chemistry, Jagiellonian University, Kraków <i>Spectroelectrochemical method of surface states characterization and DOS determination for titanium dioxide</i> | |
| 12.00-12.20 OC4 | Magdalena Mikrut , Faculty of Chemistry, Jagiellonian University, Kraków <i>Photoinduced reactive oxygen species generation by particulate matter standard material SRM1648a</i> | |
| 12.20-12.50 OC5 | Joanna Kunciewicz , Faculty of Chemistry, Jagiellonian University, Kraków <i>Spectroelectrochemical approach to estimation of bands position and density of introduced electronic states in rhodium-doped titania</i> | |
| 13.00-14.30 | Lunch | |

Molecules and Light 2017, Zakopane 25 - 29 September 2017

Conference Program

Tuesday, 26 September 2017

| | | |
|---------------------------------------|---|---|
| Tuesday, 26 September 2017 | | Photochemistry and information processing with light |
| Afternoon Session: 14.30-19.00 | | Chair: Wojciech Macyk |
| 14.30-15.30 PL2 | Radek Cibulka , University of Chemistry and Technology, Prague <i>Flavins: from yellow cofactors to useful tools in photocatalysis</i> | |
| 15.30-16.00 OC6 | Konrad Szaciłowski , AGH University of Science and Technology, Kraków <i>Photoelectrochemical sensors, neuromimetic devices and reservoir computers</i> | |
| 16.00-16.30 OC7 | Karol Krzysiński , Faculty of Chemistry, University of Gdańsk, Gdańsk <i>Acridinium chemiluminescent salts – physicochemistry and examples of application</i> | |
| 16.30-17.00 | Coffee break | |
| 19.00-20.00 | Dinner | |
| Tuesday, 26 September 2017 | | Poster session |
| Evening Session: 20.00-21.00 | | |

Wednesday, 27 September 2017

| | | |
|--------------------------------------|--|--|
| Wednesday, 27 September 2017 | | Photophysics in various time and space scales |
| Afternoon Session: 9.00-13.00 | | Chair: Gotard Burdziński |
| 9.00-10.00 PL3 | Michel Sliwa , University of Lille, CNRS <i>Synergy between serial femtosecond crystallography & transient absorption spectroscopy to reveal the dynamics of photo-switchable fluorescent proteins</i> | |
| 10.00-10.30 OC8 | Marek Sikorski , Faculty of Chemistry, Adam Mickiewicz University, Poznań <i>Fluorescence excitation-emission spectroscopy: principles and applications</i> | |
| 10.30-11.00 | Coffee break | |
| 11.00-11.45 IL1 | Michał Gil , Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw <i>Supersonic jet spectroscopy of aza-aromatic molecules with intra- and intermolecular hydrogen bonds</i> | |
| 11.45-12.15 OC9 | Bolesław Kozankiewicz , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Vibronic structure of single terylene molecules in crystalline matrices</i> | |
| 12.15-12.45 OC10 | Marcin Andrzejak , Faculty of Chemistry, Jagiellonian University, Kraków <i>Missing states and irregularities in excited states manifold of 2,2'-bithiophene – what basis set is large enough?</i> | |
| 13.00-14.00 | Lunch | |
| Wednesday, 27 September 2017 | | Excursion |
| 14.00-19.00 | | |
| 19.00-20.30 | Dinner | |

Conference Program

Thursday, 28 September 2017

| | | | |
|------------------------------------|--|------------------------------------|--|
| Thursday, 28 September 2017 | | Photodynamics and electrons | |
| Morning Session: 9.00-13.00 | | Chair: Piotr Skurski | |
| 9.00-10.00 PL4 | Stefan Lochbrunner , Institute of Physics, University of Rostock, Rostock <i>Electron transfer pathways from time resolved spectroscopy</i> | | |
| 10.00-10.45 IL2 | Janina Kopyra , Faculty of Sciences, Siedlce University, Siedlce <i>Decomposition of biologically relevant molecules by electron impact</i> | | |
| 10.45-11.15 | Coffee break | | |
| 11.15-11.45 OC11 | Gotard Burdziński , Faculty of Physics, Adam Mickiewicz University, Poznań <i>Photochromic reactions of 3H-naphthopyrans</i> | | |
| 11.45-12.15 OC12 | Michał Rode , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Excited state relaxation pathways in substituted phthalides</i> | | |
| 12.15-12.45 OC13 | Iwona Grądzka , Faculty of Physics, Adam Mickiewicz University, Poznań <i>Photodynamics of ruthenium dyes interacting with titania nanoparticles for solar cells and water splitting systems</i> | | |
| 13.00-14.30 | Lunch | | |

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|---------------------------------------|--|--|--|
| Thursday, 28 September 2017 | | Panel Discussion: Problems, dilemmas and predictions - the future of science on Molecules and Light | |
| Afternoon Session: 15.00-18.00 | | | |
| 15.00-16.15 Part 1 | Jerzy Karpiuk , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Chair and Introduction</i> | | |
| | Andrzej Sobolewski , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Organic photovoltaics with p-f-n junctions: A computational suggestion</i> | | |
| | Stefan Lochbrunner , Institute of Physics, University of Rostock, Rostock <i>Molecular nanostructures for photonics: some challenges</i> | | |
| | Wojciech Macyk , Faculty of Chemistry, Jagiellonian University, Kraków <i>Bandgap determination: shall we rely on DRS measurements?</i> | | |
| | Open discussion | | |
| 16.15-16.45 | Coffee break | | |
| 16.45-18.00 Part 2 | Marek Sikorski , Faculty of Chemistry, Adam Mickiewicz University, Poznań <i>Between success and failure: The history of Singlet Oxygen</i> | | |
| | Piotr Skurski , Faculty of Chemistry, University of Gdańsk, Gdańsk <i>Novel aspects of the key process in the Fischer-Tropsch synthesis: transition-metal-free catalysis of carbon monoxide hydrogenation reaction</i> | | |
| | Jerzy Karpiuk , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Charge transfer triplet states - still elusive or yet promising?</i> | | |
| | Open discussion | | |

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|------------------------------------|--|--------------------------|--|
| Thursday, 28 September 2017 | | Conference Dinner | |
| Evening, 19.00 – 23.00 | | | |

Molecules and Light 2017, Zakopane 25 - 29 September 2017

Conference Program

Friday, 29 September 2017

| Friday, 29 September 2017 | | Proton and electron transfer |
|------------------------------------|--|-------------------------------------|
| Morning Session: 9.00-12.00 | | Chair: Andrzej Sobolewski |
| 9.30-10.15 IL3 | Leszek Łapiński , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Solid H₂ versus solid noble-gases: Matrix-environment effect on photoinduced hydrogen-atom transfer in heterocyclic compounds</i> | |
| 10.15-10.45 OC14 | Cristina Barboza , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Revealing the dynamics of the excited proton transfer of a π-conjugated salicylidene compound</i> | |
| 10.45-11.15 | Coffee break | |
| 11.15-11.45 OC15 | Jerzy Karpiuk , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Intramolecular electron transfer in solid hosts</i> | |
| 11.45-12.00 | Closing remarks | |
| 12.30-13.30 | Lunch | |

List of Posters

Posters:

| | |
|-----|---|
| P1 | Iwona Anusiewicz, Piotr Skurski , Faculty of Chemistry, University of Gdańsk, Gdańsk <i>Formation of H_3O^+ cations due to aluminum fluoride</i> |
| P2 | Paweł Gawryś , Institute of Physics, Polish Academy of Sciences, Warsaw <i>Synthesis and photophysics of phthalide-based white fluorophores</i> |
| P3 | Hanna Grajek , Department of Physics and Biophysics, University of Warmia and Mazury in Olsztyn, Olsztyn <i>The effect of temperature and light on tetracycline degradation by $Na[Fe(EDTA)]$ and $Fe(III)$ citrate</i> |
| P4 | Agnieszka Jarosz , Faculty of Chemistry, Jagiellonian University, Kraków <i>Two synthetic approaches for the preparation of core-shell upconverting nanoparticles</i> |
| P5 | Paulina Majewska , Faculty of Chemistry, Jagiellonian University, Kraków <i>Core-shell upconverting nanoparticles coated with surface-modified titania for photocatalytic applications</i> |
| P6 | Paweł Mikrut , Faculty of Chemistry, Jagiellonian University, Kraków <i>Photocatalysis at shaped TiO_2 crystals</i> |
| P7 | Dorota Prukala , Faculty of Chemistry, Adam Mickiewicz University, Poznań <i>Photophysical properties of E-hydroxystilbazols in dependence of pH</i> |
| P8 | Mateusz Trochowski , Faculty of Chemistry, Jagiellonian University, Kraków <i>Hydroxy derivatives of anthraquinone as TiO_2 sensitizers</i> |
| P9 | Olena Vakuliuk , Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw <i>Isoindolo[5,8]diones - structurally unique fluorescent dyes</i> |
| P10 | Jacek Wierzchowski , Department of Physics and Biophysics, University of Warmia and Mazury in Olsztyn, Olsztyn <i>Excited-state proton transfer in purine analogues: kinetic analysis</i> |

Plenary Lectures

Opening Lecture

Regulation of Light Harvesting and Excitation Energy Transfer in the Photosynthetic Apparatus of Plants

Gruszecki W. I.

Institute of Physics, Maria Curie-Skłodowska University, Lublin, wieslaw.gruszecki@umcs.pl

Life on our planet is powered by sunlight and photosynthesis is practically a sole process able to convert energy of electromagnetic radiation to the forms which can be directly utilized to drive biochemical reactions. In the photosynthetic apparatus of plants, light quanta are collected by numerous chlorophyll and carotenoid molecules, embedded in the pigment-protein complexes called light-harvesting antenna, and energy is transferred non-radiatively towards the reaction centers where primary charge separation takes place. The major pigment-protein antenna complex of plants, referred to LHCII, comprises virtually half of the chlorophyll molecules in the biosphere and is responsible for deep green color of plants. The results of intensive studies, carried out in numerous photo-physical laboratories worldwide, revealed that this complex is not only responsible for collecting energy of light but also for protective excitation quenching, operating under high light conditions leading to over-excitation of the photosynthetic apparatus and photo-damage. According to the research results from several laboratories, including those reported recently by our group, one of the key processes responsible for mechanistic control of such a regulatory mechanism is light-driven formation of supramolecular structures of LHCII, characterized by high rate of thermal de-excitation. The results leading to such a concept will be presented and discussed during my talk.

Burning water with sunlight: insights from computational chemistry

Sobolewski Andrzej L.

Institute of Physics, Polish Academy of Sciences, Warsaw, sobola@ifpan.edu.pl

Impressive progress has recently been achieved in water-splitting photocatalysis with so-called graphitic carbon nitride materials consisting of heptazine (tri-s-triazine) building blocks. In addition to efficient hydrogen evolution in the presence of sacrificial electron donors, stoichiometric splitting of pure water with doped C_3N_4 materials has been reported [1]. The mechanism of the photoinduced water-splitting reaction catalyzed by C_3N_4 is generally discussed in terms of the band structure of the amorphous or crystalline materials and the mobility of photoinduced electrons and holes which are supposed to eventually drive the reduction of protons and the oxidation of water, respectively. However, the fundamental mechanistic principles of the photoinduced reaction and the catalytic cycle are currently not understood.

In this contribution, I provide first-principles computational evidence that water splitting with heptazine-based materials [2], as well as in other azines [3,4] and TiO-porphyrines [5,6] is a molecular photochemical process taking place in hydrogen-bonded chromophore-water complexes. The water splitting occurs homolytically via an electronically driven nonadiabatic proton-transfer reaction from water to chromophore, resulting in ground-state hydrogenated molecular radicals and OH radicals. The long-lived hypervalent molecular radicals can recombine to yield H_2 in a dark reaction when a suitable catalyzer (colloidal platinum) is present. The OH radicals can be recombined to H_2O_2 with suitable catalyzers (carbon or metal-oxide nano dots).

- [1] Wang, Y., Wang, X., Antonietti, M, *Angew. Chem. Int. Ed.* **2012**, 51, 68.
- [2] Ehrmaier J., Karsili T.N.V., Sobolewski A.L., Domcke W., *J. Phys. Chem. A*, **2017**, 121, 4754
- [3] Liu, X., Sobolewski, A. L., Borrelli, R., Domcke W., *Phys. Chem. Chem. Phys.* **2013**, 15, 5957.
- [4] Liu, X; Karsili T.N.V., Sobolewski A.L., Domcke W., *Chem. Phys.*, **2016**, 464, 78.
- [5] Morawski O., Izdebska K., Karpiuk E., Suchocki A., Zhydachevskii Y., Sobolewski A.L., *Phys. Chem. Chem. Phys.*, **2014**, 16, 15256
- [6] Morawski O., Izdebska K., Karpiuk E., Suchocki A., Zhydachevskii Y., Sobolewski A.L., *J. Phys. Chem. C*, **2015**, 119, 14085

Flavins: from yellow cofactors to useful tools in photocatalysis

Cibulka R.

University of Chemistry and Technology, Prague, Czech Republic, cibulka@vscht.cz

Photoexcitation allows chemical transformations that are not accessible by conventional methods. Use of visible light combined with a photocatalyst even improves classical photochemical methodologies avoiding side reactions of functionalities sensitive to UV light and making photochemistry available for most laboratories. Nowadays, photo-redox catalysis with organic photocatalysts^[1] (*organic photo-redox catalysis*, *photoorganocatalysis*) is of a growing interest because of low costs of organic dyes and different reactions that they are able to mediate thus expanding the boundaries of organic synthesis.

One of the most prominent natural chromophores is represented by flavin cofactors (FAD, FMN; see Figure 1) which are involved in several light-dependent processes, for example, in light generation by bacterial luciferase, in plant phototropism and in photolyases - in the cleavage of cyclobutane-pyrimidine dimers to repair DNA damage.^[2,3] Due to interesting photochemical properties, flavins (Figure 1) have also been tested in photocatalysis; nevertheless, their applications, except of photolyase models, have been limited for a long time. In the presentation, recent flavin-based photocatalytic procedures will be discussed, especially visible light [2+2] photocycloaddition^[4] and photocycloreversion,^[5] photooxygenation,^[6] and photocatalytic esterification.^[7] Examples from flavin-based photocatalysis will be used to explain basic principles of photocatalysis involving both electron- and energy transfer processes.

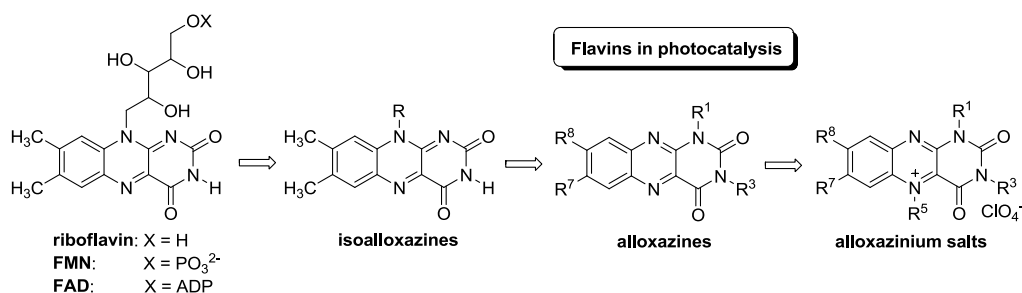


Figure 1. Structure of flavin cofactors and photocatalysts.

Author thanks the Czech Science Foundation (grant No 16-09436S) for financial support.

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[3] R. J. Kutta, N. Archipowa, L. O. Johannissen, A. R. Jones, N. S. Scrutton, *Scientific Reports* **7**, 44906 (2017).

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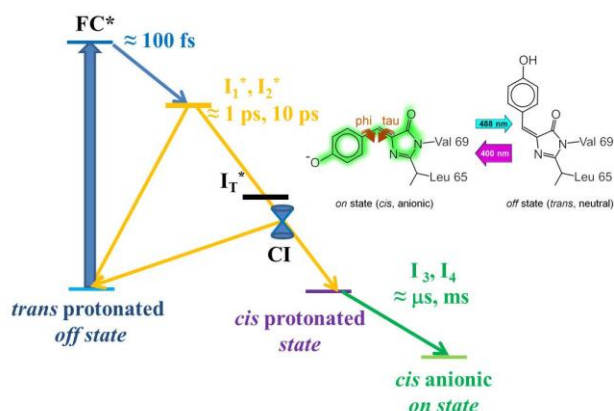
[7] M. März, J. Chudoba, M. Kohout, R. Cibulka, *Org. Biomol. Chem.* **15**, 1970 (2017).

Synergy between serial femtosecond crystallography & transient absorption spectroscopy to reveal the dynamics of photo-switchable fluorescent proteins.

Sliwa M.¹, Uriarte M. L.¹, Ruckebusch C.¹

¹ LASIR, Université de Lille, CNRS, UMR 8516, France, michel.sliwa@univ-lille1.fr

Reversibly photo-switchable fluorescent proteins find growing applications in cell biology, yet mechanistic details, in particular on the ultra-fast photochemical time scale, remain unclear. We



choose to study rsEGFP2 (Fig. 1) which is the most common protein used in RESOLFT super-resolution microscopy. We first employed time-resolved pump-probe absorption spectroscopy (TA) in solution to study photo-switching from the non-fluorescent (off) to the fluorescent (on) state. As reported for other photo-switchable fluorescent proteins evidence is also provided here for the existence of several intermediate states on the pico- and microsecond time scales that are attributed to chromophore isomerization and proton

Fig.1 Photo-Dynamics of rsEGFP2

transfer, respectively. Indeed isotopic experiments show clearly that Off-to-on photoswitching in rsEGFP2 involves excited-state isomerization and ground state proton transfer. Using an X-ray free-electron laser, time-resolved crystallography (SFX) on the picosecond time-scale showed that for one of the excited states the hydroxybenzylidene imidazolinone chromophore assumes a near-canonical twisted configuration with the two cyclic moieties perpendicular. Formation of the twisted chromophore, halfway between the trans and cis isomers, is accommodated by a shift in the central α -helix and restricted by the close proximity to the V151 side chain. Mutation of the latter into alanine modify the Off-to-on photoswitching quantum yield and clarify the photo-dynamic for wild type one. The data provide insight into the mechanism of cis-trans isomerization in photoswitchable fluorescent proteins and suggest a strategy based on excited-state structures to rationally tailor their photophysical characteristics [1]. We will discuss here the difference between TA and SFX.

This research is carried out in collaboration with the Institut de Biologie Structurale in Grenoble (Adam, Bourgeois, Byrdin, Colletier, Coquelle, Feliks, Field, Fieschi, Guillon, Schirò, Thepaut, Weik, Woodhouse), Max-Planck-Institut für medizinische Forschung in Heidelberg (Barends, Doak, Foucar, Hilpert, Kovacsova, Nass, Roome, Schlichting, Shoeman), Department of Physics in Rennes (Cammarata), and the SLAC National Accelerator Laboratory in Menlo Park (Aquila, Boutet, Hunter, Koglin, Liang, Robinson).

[1] N. Coquelle, M. Sliwa, J. Woodhouse, G. Schirò, V. Adam, A. Aquila, T. R. M. Barends, S. Boutet, M. Byrdin, S. Carbajo, E. De la Mora, R. B. Doak, M. Feliks, F. Fieschi, L. Foucar, V. Guillon, M. Hilpert, M. Hunter, S. Jakobs, J. E. Koglin, G. Kovacsova, T. J. Lane, B. Lévy, M. Liang, K. Nass, J. Ridard, J. S. Robinson, Christopher M. Roome, Cyril Ruckebusch, Matthew Seaberg, Michel Thepaut, M. Cammarata, I. Demachy, M. Field, R. L. Shoeman, D. Bourgeois, J-P. Colletier, I. Schlichting, M. Weik, *Nature Chemistry*, DOI: 10.1038/NCHEM.2853 (2017)

Exploring Photocatalysis by Time Resolved Spectroscopy

Lochbrunner S.

Institute of Physics, University of Rostock, Albert-Einstein-Str. 23, 18059 Rostock, Germany,
stefan.lochbrunner@uni-rostock.de

Photocatalysis attracts currently intense scientific interest since it allows to use sunlight for the sustainable synthesis of energy rich compounds. An example is photocatalytic water splitting. It is a promising approach to generate hydrogen which can then be used as environmentally friendly fuel. In collaboration with M. Beller and coworkers from the Leibniz Institute of Catalysis we investigate the water reduction side of the process by means of a homogenous system based on iridium or copper complexes as photosensitizer. We apply time resolved spectroscopy on photocatalytic model systems to obtain insights into the electronic dynamics and to understand the reaction mechanisms and efficiency limiting factors. Several different spectroscopic techniques are used in order to cover a wide range of timescales. By femtosecond pump-probe experiments the ultrafast intramolecular electronic relaxation processes of the metal complexes are studied including intersystem crossing and interligand charge transfer [1]. The population and lifetime of the electronically excited states are in addition characterized by a streak camera with a time resolution of 35 ps. The analysis of photoluminescence quenching provides thereby insights into the interaction between molecular components resulting e. g. in bimolecular reactions and intermolecular charge transfer. For the iridium sensitizer we find that the electron transfer from a donor substrate to the metal complex, which is the first charge transfer step in the photocatalytic reaction path, is surprisingly improbable [2]. However, the long triplet lifetime of the Ir-complex in combination with a high substrate concentration leads nevertheless to an efficient system. In the case of copper complexes the situation is different. The photoluminescence studies indicate that the oxidative electron transfer from the sensitizer to the catalyst is the first step. To observe the ionic products of this reaction we resort to absorption measurements applying a YAG-laser system for excitation. This allows to perform pump-probe experiments on timescales from nano- to milliseconds by means of an electronic delay generator. The measurements not only show that the electron transfer takes indeed place but provide also information about its efficiency and the contribution of non-reactive loss channels.

The emergence of new semiconductor materials like carbon nitride fuels the hope for efficient heterogenous water splitting systems. Here the semiconductor absorbs the light and the charge carriers have to get to the surface where the catalytically active sites are. We applied our spectroscopic techniques to powder samples of photocatalytically active carbon nitrides to characterize the light induced processes [3]. The results indicate that the charge carriers are almost instantaneously formed and exhibit then a quasi-one dimensional mobility due to hopping processes perpendicular to the molecular layers of the material.

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[2] A. Neubauer, G. Grell, A. Friedrich, S. Bokarev, P. Schwarzbach, F. Gärtner, A.-E. Surkus, H. Junge, M. Beller, O. Kühn, and S. Lochbrunner, *J. Phys. Chem. Lett.* **5**, 1355 (2014).

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Invited Lectures

Supersonic jet spectroscopy of aza-aromatic molecules with intra- and intermolecular hydrogen bonds

Gil M.¹, Kijak M.¹, Peukert S.², Mengesha E.³, Sepioł J.¹, Waluk J.¹

¹ Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, mgil@ichf.edu.pl

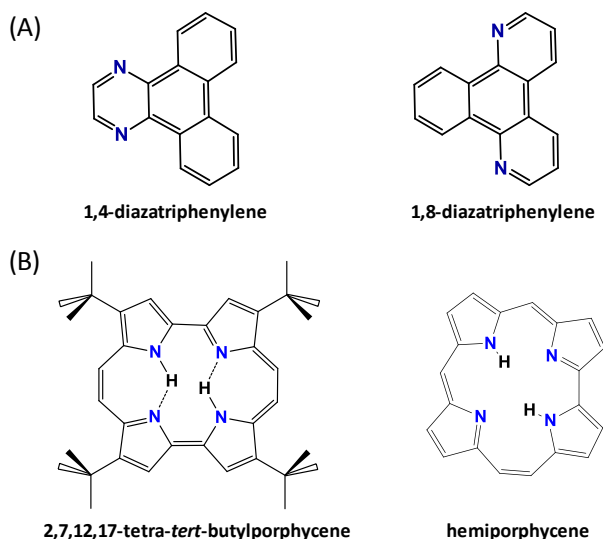
² Institute for Combustion and Gas Dynamics - Reactive Fluids; University of Duisburg-Essen

³ CEA, CNRS, IRAMIS/LIDyL/Laboratoire Francis Perrin, Gif-sur-Yvette, France

Structure, hydrogen bond interactions and tautomerism of heterocyclic molecules isolated in supersonic jets have been studied using high resolution spectroscopy.

The departure from planarity of the excited-state structure of 1,4-diazatriphenylene (Fig. 1A) is discussed and compared with situation in 1,8-isomeric form [1]. Distinct activity of out-of-plane vibronic modes is analyzed with the help of (TD)DFT calculations. A large increase of fluorescence intensity upon selective complexation with protic partners is reported and explained in terms of different energetics of (π,π^*) and (n,π^*) excited states in hydrogen-bonded species.

Spectroscopy and tautomerization reaction in two isomers of porphyrin having different molecular symmetry (Fig. 1B) is discussed [2-4]. Influence of bulky *tert*-butyl substituents on proton transfer rates in porphycene and stability of tautomeric forms in hemiporphycene is presented.



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Decomposition of biologically relevant molecules by electron impact

Kopyra J.¹

¹ Faculty of Science, Siedlce University, Siedlce, kopyra@uph.edu.pl

Radiation exposure of human beings to both natural as well as human-made radiation sources may cause fatal effects such as structural and chemical modifications of the cellular deoxyribose nucleic acid (DNA) containing genomic information. The interaction of high-energy radiation (particles and/or photons in the MeV range) with condensed matter like a living cell results in the formation of highly reactive charged and neutral radical species and secondary electrons (SEs). Among them, the SEs are the most abundant of post-radiational species. They are produced in a large number of 5×10^4 per 1 MeV of primary energy deposited and mainly comprise low energy electrons (LEEs) with kinetic energies < 30 eV [1].

For a long time it was thought that radiation damage is due to a direct ionization via impact of primary quanta of radiation, radical chemistry and secondary electrons with energy above the ionization threshold. Only two decades ago, it has been demonstrated the ability of low energy secondary electrons to irreversibly damage DNA by causing, e.g., single- and double-strand breaks at energies below the ionization threshold of the DNA macromolecule [2]. Hence, the detailed knowledge of the reactions induced by the pre-solvated electrons is considered as crucial to understand and properly describe radiation damage to biological entities [3].

In our studies we used different model compounds of the DNA/RNA building-blocks to observe electron induced reactions in DNA and/or RNA. The dissociative electron attachment (DEA) results indicate that both the backbone components as well as nucleobases are able to efficiently capture electrons leading to various fragmentation reactions. It remains to be evaluated to which degree properties obtained for these isolated building blocks are still preserved when the particular unit is coupled within DNA/RNA. To shed the light on the role of different fragmentation pathways recent results of DEA to gas phase nucleobases, nucleosides, nucleotides [4], and their halo-substituted derivatives [5] will be presented and discussed.

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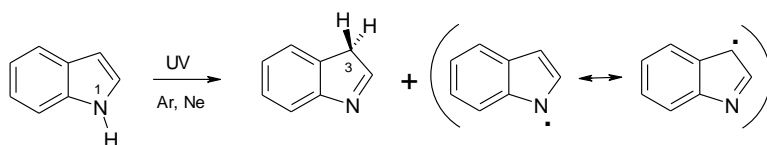
Solid H₂ versus solid noble-gases: Matrix-environment effect on photoinduced hydrogen-atom transfer in heterocyclic compounds

Łapinski L.¹, Nowak M.J.¹, Rostkowska H.¹, Reva I.²

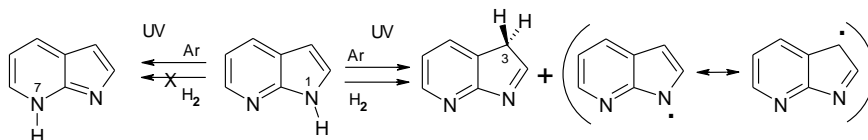
¹ Institute of Physics, Polish Academy of Sciences, Warsaw, lapin@ifpan.edu.pl

² CQC, Department of Chemistry, University of Coimbra, Coimbra, Portugal

Photochemical transformations were studied for indole monomers isolated in low-temperature Ar and Ne matrices. Upon UV irradiation of the matrix-isolated compound, 3*H*-tautomer and indolyl radical were photoproducted.[1]



For 7-azaindole isolated in Ar matrices, N7*H*-tautomer was photogenerated (alongside 3*H*-tautomer and 7-azaindolyl radical) as one of the major products. However, for 7-azaindole isolated in solid molecular hydrogen, the initial 1*H*-form of the compound was transformed only into 3*H*-tautomer and 7-azaindolyl radical; the N7*H*-tautomer was not photoproducted.[2]



Analogous dependence on matrix environment (solid noble gas or solid hydrogen) was observed also for the oxo→hydroxy phototautomerism in 4(3*H*)-pyrimidinone and for the thione→thiol phototautomeric conversion in 3-thio-1,2,4-triazole. The hydroxy and thiol forms, generated as the major products of the phototransformations of these compounds isolated in solid noble gases, were not generated in solid H₂ environment.[3,4]



The drastic, qualitative dependence of the photoinduced N1*H*→N7*H*, NH→OH and NH→SH hydrogen-atom-transfer conversions on the matrix environment looks as a characteristic feature of this class of photoreactions. Can this class be identified as that governed by hydrogen-atom detachment on surfaces of repulsive σ^* states? This hypothesis needs further evidence to be proven.

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Panel Discussion

Problems, dilemmas and predictions - the future of science on Molecules and Light

Organic photovoltaics with *p-f-n* junctions: a computational suggestion

Andrzej L. Sobolewski

Institute of Physics, Polish Academy of Sciences, Warsaw, sobola@ifpan.edu.pl

In the field of photovoltaics (PV), in which manufacturing cost is essential, organics that can be solution-processed at low temperatures offer great advantages as compared to their inorganic counterparts [1]. Although a tremendous progress in the organic PV (OPV) technology has been achieved over the years, OPV devices still suffer from several losses or bottlenecks – a major one of them being recombination of photogenerated electron-hole pairs. Generally, an external bias voltage is required to efficiently separate the electrons and holes in organic material and thus prevent their recombination.

In this contribution results of *ab initio* theoretical explorations of photophysical properties of ferroelectric molecular stacks and ‘wires’ will be presented. It will be shown that in such systems the photogenerated, due to absorbed light, electrons and holes are driven by the polarization-induced internal electric field in opposite directions toward the cathode and anode, respectively, and thus directly contribute to the photovoltaic output without a need for construction of the *p-n* junction [2]. This provides an intriguing possibility to replace of the ‘intrinsic’ (*i*) layer in a *p-i-n*-type architecture for organic solar cells [3] by the ferroelectric layer (*f*). As the term *p-i-n* means the PV device where the photo-active layer is sandwiched between two doped wide-gap layers; a *p*-doped layer and *n*-doped layer, the term *p-f-n* is proposed for this new junction.

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Molecular Nanostructures for Photonics: Some Challenges

Lochbrunner S.

Institute of Physics, University of Rostock, Albert-Einstein-Str. 23, 18059 Rostock, Germany,
stefan.lochbrunner@uni-rostock.de

Nanostructures based on molecular constituents are highly interesting candidates for photonic applications. For instance, aggregates can couple more strongly to the electromagnetic field than monomeric dye molecules and they can guide excitons and might be used as photonic wires. Donor-acceptor complexes facilitate charge separation on a molecular scale and polymer strands are discussed as electric nanowires. While devices based on organic bulk materials are already very successful, several challenges have to be overcome for the development of functional assemblies and devices in which single molecules or molecular nanostructures act as functional elements. In this talk we will introduce some of these critical points. In particular it will be discussed that strategies are missing to combine several elements to complex and specific structures and finally to circuits. Another problem are temporary losses due to the population of long living states as well as permanent losses caused by photo degradation.

Panel Discussion

Bandgap determination: shall we rely on DRS measurements?

Wojciech Macyk, Patrycja Makuła, Michał Pacia

Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, 30-387 Kraków,
macyk@chemia.uj.edu.pl

Band gap energy determination is usually based on analysis of UV-vis absorption spectra. Application of this technique (absorbance or reflectance measurements) and Tauc transformation is very simple and leads to reliable results, if the methodology is used correctly. Unfortunately, despite of its simplicity this approach is very often misused, in particular in the case of materials showing a considerable absorption of sub-band gap energy photons.

How to use UV-vis spectroscopy properly in solid state studies? What are the most common mistakes and how to avoid them? Is still any room for a further development of this technique? These questions will be addressed during the discussion.

Acknowledgements

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Between success and failure: The history of Singlet Oxygen

Sikorski M.

Adam Mickiewicz University in Poznan, Poznań, sikorski@amu.edu.pl

The interest in singlet oxygen, the lowest-energy excited electronic state of molecular oxygen, is driven by its unique properties and the role of singlet oxygen and oxygen in general in chemistry, oxidation and/or oxygenation of many organic and biologically relevant molecules. Because of its role, singlet oxygen, one of the reactive oxygen species (ROS), is an important intermediate in processes that range from cell death (apoptosis and necrosis) to cell proliferation (stimulated mitosis). Despite of the great interest of the scientific community in the role of singlet oxygen, there is still much to be done, some of the issues associated with such studies involve difficulty in controlling and quantifying the amount and location of singlet oxygen production in, on or out of a cell. Understanding of oxygen concentration and possible location of singlet oxygen would help to act on a cell precisely according to our goal.^[1-5]

The history of singlet oxygen is lasting for long time. The research in that area brought many breakthroughs, many paths have been successfully discovered, but also many other have been lost or forgotten.

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Novel aspects of the key process in the Fischer-Tropsch synthesis: transition-metal-free catalysis of carbon monoxide hydrogenation reaction

Skurski, P.

Faculty of Chemistry, Department of Theoretical Chemistry, University of Gdańsk, Gdańsk, piotr.skurski@ug.edu.pl

Strong electron acceptors commonly called "superhalogens" are effective oxidizing agents and might initiate (as trigger-compounds) the radical substitution reactions. Upon an excess

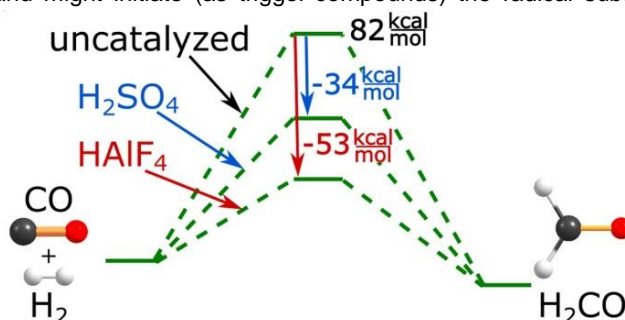


Fig.1 Hydrogenation of carbon monoxide yielding formaldehyde might be effectively catalyzed by the superacids

electron attachment they evolve to superhalogen anions whose further protonation results in the formation of superacids. As indicated by the recent studies, the superacids might be utilized as effective catalysts in the Fischer-Tropsch (F-T) synthesis. The key process in the F-T synthesis is the carbon monoxide hydrogenation. In contrast to the transition-metal-catalyzed homogeneous or heterogeneous hydrogenations, it is proposed that

superacid-catalyzed hydrogenations undergo according to the reverse-activation mechanism. Namely, in most hydrogenation reactions that involve nonsuperacid catalysts (e.g., transition metal catalysts) the hydrogen molecule is usually activated, whereas in superacid-catalyzed hydrogenations an acid catalyst activates either the carbon monoxide or the hydrocarbon reactant forming carbocationic sites, which are then quenched by hydrogen to reduced products. Due to its difference, the latter mechanism might be called the ionic hydrogenation.

The usefulness of acidic catalysts in reducing the reaction barriers of the carbon monoxide hydrogenation that leads to formaldehyde formation will be discussed on the basis of the ab initio CCSD(T)/MP2/aug-cc-pVDZ calculations (with the effects of the surrounding solvent molecules approximated by employing the polarized continuum solvation model). Three representative acids were chosen to verify the usefulness of such catalysts in this process: sulfuric acid (as a strong mineral acid) and HAIF₄ and HSbF₆ (as superacids). Detailed mechanisms in both gas and liquid phases proceeding either along a concerted path or according to a stepwise route will be presented and discussed. The most important findings include the observation that all acids considered seem to catalyze the carbon monoxide hydrogenation in a qualitatively similar way but only the superacids are predicted to effectively reduce the activation barriers to render the whole process plausible.

Charge transfer triplet states - still elusive or yet promising?

Karpiuk, J.

Institute of Physics, Polish Academy of Sciences, Warsaw, jkarpiuk@ifpan.edu.pl

In early research on photophysics and luminescence of organic molecules, triplet states were often considered undesired long-lived products of singlet state deactivation. With time, it was discovered that, especially in combination with excited-state charge separation, they play fundamental role in a number of chemical or biologically relevant processes, including, for instance, long-lived charge separation, photosynthesis, or magnetoreception, thus in phenomena where spin dynamics provides a basis for transformation of physical signals into chemically or biologically relevant information. The spin dynamics has recently been also exploited in organic light emitting devices (OLED) where charge transfer triplet states (^3CT) can be used as reservoir of energy from electron-hole recombination for upconversion of a triplet exciton into singlet excited state via reverse intersystem crossing (RISC). The mechanism of the RISC-based thermally activated delayed fluorescence (TADF) is under debate, with experimental and theoretical work emphasizing that vibronic coupling between the lowest locally excited (LE) triplet and the lowest ^3CT state is important for TADF to be operative. One of the reasons hindering progress in this area is the incomplete understanding of structure- and environment-related mechanisms behind spin correlation and dephasing in $^1\text{CT} \leftrightarrow ^3\text{CT}$ conversions. The talk will address some of these aspects and their effect on spin dynamics in multichromophoric organic systems.

Panel Discussion

Oral Communications

Photocatalytic water oxidation – the new approach to water splitting

Morawski O., Sobolewski A. L.

Institute of Physics, Polish Academy of Sciences, Warsaw, morawo@ifpan.edu.pl

Research of water splitting with solar light is dominated by the photoelectrochemical approach, in which a semiconductor photoanode is used to generate holes able to oxidize water molecules [1-3]. Much less explored is an alternative, mimicking Nature, approach in which a supramolecular structure consisting of electron donor, acceptor and chromophore absorbs photons and triggers charge separation. The separated charges may then neutralize hydroxide anions and protons [4,5].

Searching for an effective water splitting mechanism Sobolewski and Domcke have proposed the direct photoinduced homolytic cleavage of H₂O molecules into H• and OH• radicals with oxotitanium porphyrin (TiOP) as photocatalytically active chromophore [6]. In their theoretical model the excited state of water – oxotitanium porphyrin hydrogen bonded complex decays into TiOPH• - OH• biradical which then splits into separated TiOPH• and hydroxyl radicals. Photoexcitation of TiOPH• radical leads to recovery of TiOP and a release of H• what closes the partial water splitting cycle [6]. The first step of the proposed mechanism (generation of hydroxyl radicals) was experimentally confirmed for oxotitanium tetraphenyl porphyrin (TiOTPP) and oxotitanium phthalocyanine (TiOPc) [7,8]. In a theoretical work on pyridine the photoinduced homolytic dissociation of water in the pyridine–water complex was predicted [9]. The phenomenon was experimentally verified under supersonic jet conditions proving the water splitting mechanism and the regeneration of photocatalyst with second photon absorption [10]. Recently, photochemistry of heptazine-water complex have been theoretically explored, with the conclusion that photocatalytic water splitting is possible also with this molecule [11]. Such statement however contrasts with numerous reports on hydrogen evolution in graphitic carbon nitrides (2D structures like melon), comprising of heptazine units, which are expressed in the photoelectrochemical framework [12-14]. This work will provide experimental evidences for the photoinduced homolytic dissociation of H₂O in the water suspension of melon. We hope our results will help to better understand mechanism of the photocatalytic cycle.

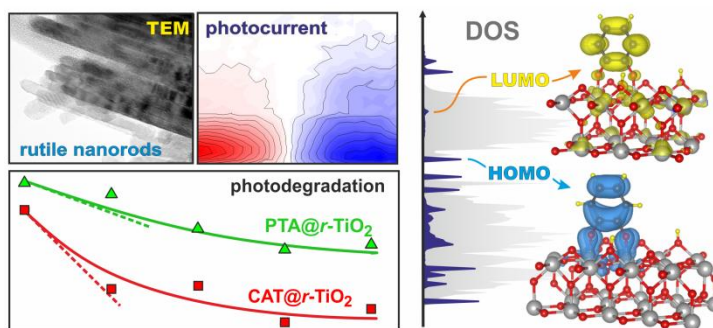
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Self-Sensitized Photocatalytic Degradation of Colorless Organic Pollutants Forming Surface Ti(IV) Complexes

Wojciech Macyk, Kezhen Qi, Filip Zasada, Witold Piskorz, Paulina Indyka, Joanna Gryboś, Mateusz Trochowski, Marta Buchalska, Marcin Kobielski, Zbigniew Sojka

Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, 30-387 Kraków, macyk@chemia.uj.edu.pl

The surface attachment of colorless organic pollutants (COP) to TiO₂ is an effective way to stimulate their photocatalytic degradation. By means of the spectroscopic, photoelectrochemical, spectroelectrochemical and photocatalytic studies combined with the DFT+D molecular modelling, we demonstrated how disubstituted benzene derivatives, including catechol, salicylic acid, phthalic acid and terephthalic acid can tune the photocatalytic properties of rutile with the dominant (110) termination. The COP ligand binding configurations, energy levels alignment and charge-transfer pathways from the organic admolecules to titania, were evaluated. The appearance of additional states within the band gap and in the conduction band allows for one step HOMO→CB ligand to metal charge transfer and two step HOMO→LUMO→CB sensitization. The photocatalytic performance of the COP@r-TiO₂ samples revealed that the self-degradation efficiency gauged by the initial rate constant varies in the order: catechol > salicylate > phthalates, showing a beneficial role of hydroxyl groups at early steps of degradation. It was found that the higher activity of the OH-bearing catechol and salicylate adspecies was associated with the direct HOMO→CB electron transfer pathway operating in the visible light. The two step HOMO→LUMO→CB mechanism (requiring UV light) characteristic of carboxyl-bearing functionalities, despite favourable energy level alignment and coupling, is less efficient. The in situ diffuse reflectance spectroscopic (DRS) measurements revealed that at early stages of the photocatalytic degradation the aromatic rings of the COP moieties are readily photohydroxylated, fostering the visible light utilization via the HOMO→CB electron transfer route. Such autocatalytic hydroxylation processes are relevant for photocatalytic degradation of those pollutants that originally do not exhibit hydroxyl functionalities.



Acknowledgements

The work was supported by the National Science Center (NCN) and the Foundation for Polish Science (FNP).

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Spectroelectrochemical method of surface states characterization and DOS determination for titanium dioxide

Marcin Kobięlus,¹ Mateusz Trochowski,¹ Kacper Pilarczyk,^{2,3} Elżbieta Świętek,¹ Konrad Szaciłowski,² Wojciech Macyk¹

¹ Jagiellonian University in Kraków, ul. Gronostajowa 2, 30-387 Kraków, Poland,

² Academic Centre for Materials and Nanotechnology,

³ Faculty of Physics and Applied Computer Science,

AGH – University of Science and Technology, al. A. Mickiewicza 30,
30-059 Kraków, Poland

kobięlus@chemia.uj.edu.pl, macyk@chemia.uj.edu.pl

In recent years a number of publications on heterogeneous photocatalysis is increasing along with the growing number of semiconductors applications as photocatalysts. More and more sophisticated materials designed to facilitate various photocatalytic processes are engineered. Photocatalytic processes which may occur at the surface of wide bandgap semiconductors depend not only on the potentials of the valence and conduction band edges, but also on the electronic states within the bandgap. The electronic states (ES), which are localized close to the conduction band edge, may act as an electron-trapping sites or electron donors, depending on their origin and the electrostatic potential distribution in their vicinity. Thus, they can mediate various electron transfer mechanisms either within the semiconductor or between molecules adsorbed at the surface, which are crucial for the photocatalytic processes.[1-2] Moreover, ES can significantly affect photoinduced processes which are related to the charge carriers diffusion in nanostructured material.[3] They can become an efficient recombination centers[4] or participate in electron transfer between the semiconducting support and redox-active species.[2]

One of the most often used photocatalyst is titanium dioxide. Electronics states, as well as other parameters (crystallinity, specific surface area, phase composition etc.), may influence the photocatalytic activity of titanium dioxide. Although this material has been intensively studied for many years, its electronic structure is usually oversimplified using concepts of the band edges or the flatband.

Recently, we proposed a modified spectroelectrochemical method as a new technique to characterize the electronic states.[5-6] Distribution of additional electronic states localized within the bandgap can be qualitatively and quantitatively characterized using this approach. The proposed method has been applied to determine the influence of the surface states localized within the bandgap on the photocatalytic processes such as carbon dioxide, oxygen and water reduction. Correlations between efficiencies of those reactions and electronic structures will be presented and discussed.

Acknowledgement: The work was supported by National Science Centre within the project number 2015/19/B/ST5/00950 (OPUS 10).

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Photoinduced reactive oxygen species generation by particulate matter standard material SRM1648a

Mikrut Magdalena, Regiel-Futyra Anna, Macyk Wojciech, Stochel Grażyna,
van Eldik Rudi

Faculty of Chemistry, Jagiellonian University,
mikrut@chemia.uj.edu.pl, macyk@chemia.uj.edu.pl

Air pollution is one of the most important global threat to the environment. Introduction of such substances as particulate matter (PM) to the atmosphere can lead to diseases, allergies or even deaths. It has been proven that exposure on PM promotes the development of asthma attacks, chronic bronchitis, diabetes and cardiovascular diseases [1]. PM containing transition metals affects autoimmune diseases what is significant for human health [2]. Reactive species generation by particulate matter depends on the properties of PM [3]. Chemical composition, particle size and trace element content should be considered as the most important.

In this study the SRM 1648a (standard reference material, NIST) and the dust after plasma treatment have been analysed. The main goal of this work was to investigate photoinduced ROS generation by these materials. Organic compounds present in the reference powder have been removed by oxygen plasma treatment. Content of carbon and nitrogen has been controlled by a total carbon analyser. Particle morphology and chemical composition were evaluated by scanning electron microscopy, SEM/EDX. Inductively coupled plasma - optical emission spectrometer was used to analyse water-soluble elements. Nanoparticles Tracking Analysis method has been used to examine size of particles. Oxidation of terephthalic acid has been used as a method of HO[•] radicals detection. For ¹O₂ determination the phosphorescence of singlet oxygen was measured. In this presentation the influence of organic and inorganic content of PM on ROS generation, both in photoinduced and thermal reactions, will be presented and discussed.

Acknowledgement: The authors would like to thank SYMPHONY project (grant No. 2015/16/W/ST5/00005) for the financial support.

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Spectroelectrochemical approach to estimation of bands position and density of introduced electronic states in rhodium-doped titania

Kuncewicz J.¹, Ohtani B.²

¹ Faculty of Chemistry, Jagiellonian University, kuncewic@chemia.uj.edu.pl

² Institute for Catalysis, Hokkaido University

Introduction of rhodium ions into the titania crystalline structure causes significant improvement of its photoactivity within visible range of light. Recently, it was found, that in the case of rutile-based Rh-doped materials containing low Rh-concentration (below 0.5mol.%) the photosensitization mechanism is based on two-step bandgap excitation of titania.^{1,2} Such a mechanism involves Rh³⁺ and Rh⁴⁺ species acting as built-in redox mediators and allows for generation of both: electrons in the conduction band and positive holes in the valence band of titania under irradiation with visible light.

In the present work electrochemical, photoelectrochemical, spectroscopic and spectroelectrochemical measurements have been used for the estimation of bands position of titania and density of the electronic states introduced by doping and taking part in the photosensitization process (Fig. 1 a and b). The obtained results, supported by photocatalytic tests, allowed to confirm the photosensitization mechanism and determine dependency of the observed properties on concentration of Rh ions and crystalline structure of titania. In the present work the obtained results with particular emphasis on spectroelectrochemical approach to determination of the position of introduced electronic states within the bandgap of host semiconductor will be presented and discussed.

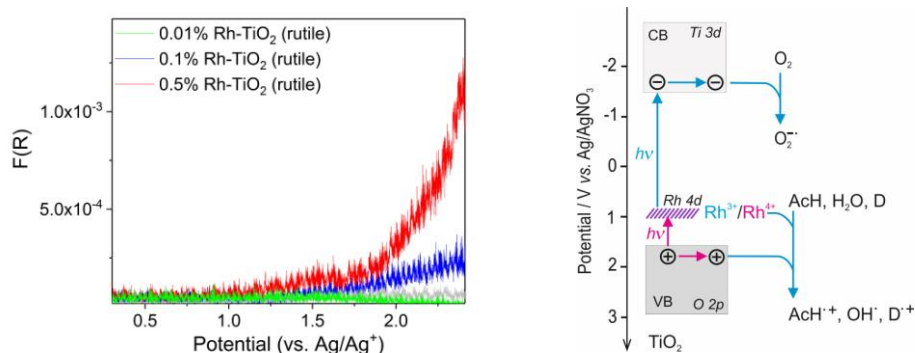


Fig.1 Changes of KM function at 625 nm with the applied potential recorded for Rh-doped titania with various Rh-concentration (a). Scheme of the electronic bands structure on the scale of potential and possible light-induced electron transfer processes presented for Rh-TiO₂ (b).

Acknowledgements

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Photoelectrochemical sensors, neuromimetic devices and reservoir computers

Andrzej Blachecki¹, Michał Kawa¹, Maria Lis¹, Krzysztof Mech¹, Kacper Pilarczyk¹, Maciej Suhecki¹, Ewelina Właźlak¹, Željko Črljen², Zoran Konkoli³ and Konrad Szaciłowski¹

¹ AGH University of Science and Technology, Kraków, Poland, szacilow@agh.edu.pl

² Ruđer Bošković Institute, Zagreb, Croatia

³ Chalmers University of Technology, Göteborg, Sweden

Digital electronics is so widely used in everyday life that it is almost impossible to find an electric device that does not make use of digital electronic components. On average, 85% of the circuitry in all the electronic devices is digital and only 15% is analog. Digital systems are much less sensitive to any interference due to wide margins of allowed signal values resulting from highly nonlinear characteristics. On the other hand the whole Nature acts in nonlinear, but highly analog manner and all possible variables of any natural system may have much more possible values than just two. Therefore we want to develop sensing and information processing devices devoid of limitations of binary digital systems, but having similar robustness.

Sensing and information processing can be considered as two sides of a coin. They are strictly bound together at the formal and functional level. Sensing usually translates one form of information into another one (with possible amplification) and also extracts the useful signals from the background. It corresponds to translation of information from syntactic to semantic and pragmatic levels. Apart from classical (monolithic semiconductor-based) approaches to information processing, various nanoscale and molecular approaches have been suggested. One on the successful (at least at laboratory scale) approaches uses semiconducting nanoparticles

decorated with various molecular species, especially coordination compounds. They are perfectly suited for these applications due to their structural diversity, optical properties and photophysical activity.

This contribution presents an overview of photoelectrochemical systems with diverse functionalities from binary logic gates and photoelectrochemical ion sensors, through ternary and fuzzy logic systems, to neuromimetic information processing, reservoir computing and analysis of musical harmony and tonality.

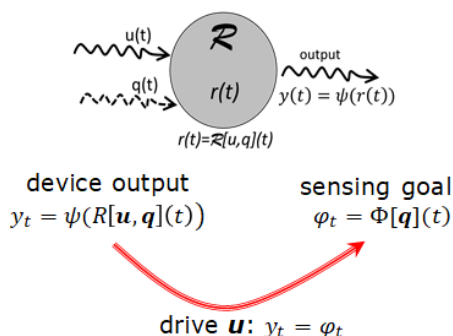


Fig. 1. The principle of operation of reservoir computer in sensing applications.

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Acknowledgements

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Acridinium chemiluminescent salts – physicochemistry and examples of application

Karol Krzywiński¹, Beata Zadykowicz¹, Justyna Czechowska¹, Lucyna Holec-Gąsior²

¹ Faculty of Chemistry, University of Gdańsk, karol.krzywinski@ug.edu.pl

² Gdańsk University of Technology, Faculty of Chemistry

Due to their ability for efficient chemiluminescence in aqueous environments (CL, Fig. 1), acridinium salts are widely applied in modern medical and environmental analysis. Such a molecular systems bear a labile group at position 9 in the acridine nucleus and represent mainly aromatic esters or sulphonamides of 10-substituted acridine-9-carboxylic acid. Acridinium salts can serve for the identification and trace analysis of entities expressing oxidative properties, because they can react with hydrogen peroxide or peroxidases, producing visible light (blue or green range).

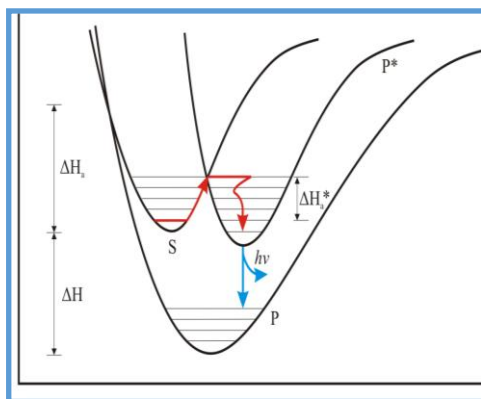


Fig.1 Generation of CL - idea

Acridinium salts are mainly employed as CL labels, which can be covalently attached to biomolecules (such as antibodies or specific antigens), thus enabling to assess their quantity in given matrix. They consist of a chemiluminogenic fragment (C) connected to a reactive group via a

spacer. When C is oxidised – usually in reaction with alkaline solution of H_2O_2 – it is quantitatively converted to an electronically excited molecule, the emission of which reflects its quantity in the system. They need no catalyst to trigger the emission of light and thus are extremely sensitive enabling to attain detection limits on the level of 10^{-16} – 10^{-19} mole of analyte in modern immunoassays.

The examples of newly developed acridinium/acridane esters employed as CL indicators, which are added to the system and used in non-bonded form, will also be presented. Basing on them, an original method to assess the anti-oxidative activity of extracts derived from medicinal formulates was developed.

During the presentation some aspects of our novel research on the physicochemistry of acridinium esters, including their structure, thermodynamics, kinetics of transformation, influence of environment on CL as well some theoretical aspects of the mechanism of light generation, will be presented. An examples of application of a new acridinium labels in luminescent immunodiagnosics and pharmaceutical analysis will be presented. The advantages of acridinium technology over the classical CL systems based luminol will also be addressed.

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Fluorescence Excitation-Emission Spectroscopy: Principles and Applications

Sikorski M.

Adam Mickiewicz University in Poznan, Poznań, Poland, sikorski@amu.edu.pl

One of the most important advantages of the fluorescence method is its sensitivity and selectivity; however in its application to complex natural systems, the selectivity of conventional fluorescence techniques appears to be insufficient. Instead, multidimensional fluorescence techniques are used in such applications, providing additional information about the samples. One of such techniques is fluorescence excitation-emission spectroscopy (EES, sometimes also called total luminescence spectroscopy, TLS), which involves simultaneous acquisition of multiple excitation and emission wavelengths in order to increase the method selectivity. Resulting emission-excitation data matrix (EEM) provides a total intensity profile of the sample over the range of excitation and emission wavelengths scanned.^[1-3]

This presentation attempts to cover the principles and to show wide range of applications of excitation-emission spectrofluorimetry (EES). For example the EES has been used, among others, for: identification and quantification of polyaromatic hydrocarbons (PAHs) in environmental samples, identification of oil spills by analysis of fluorescent PAHs, identification of oil and fuel samples in forensic studies, characterisation, differentiation and classification of natural organic matter such as humic matter in water, analysis and characterisation of pharmaceutical compounds, observation of luminescent properties of rocks and minerals, bacterial identification, and studies of marine phytoplankton.^[3-5] EES techniques have been successfully used in the analysis of all kind of food products as regards to their quality and authentication.^[6,7]

During presentation Author will provide some of comments on advantages, disadvantages and drawbacks of EES. Some comparison of EES versus other techniques, factors influencing EES signals, representation of EES spectra, relationships and changes in intensity of fluorescence, multivariate calibration combined with EES, quenching of fluorescence, will also be given.

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Vibronic Structure of Single Terrylene Molecules in Crystalline Matrices

Bolesław Kozankiewicz

Institute of Physics, Polish Academy of Sciences, kozank@ifpan.edu.pl

Terrylene (Tr) molecules are between the most frequently used dyes in the single-molecule spectroscopic studies at cryogenic temperatures.[1] Isolated Tr molecule is planar (D_{2h} symmetry) and the symmetry selection rules limit the number of observed a_g vibronic components in its fluorescence excitation spectrum. Additional vibronic lines, if observed, are fingerprint of the out-of-plane deformation, which results from a site-specific molecule-matrix interaction.

In the work I'll present and discuss the fluorescence excitation spectra of single Tr molecules embedded in several crystalline matrices [2-4], see the spectra shown in figure 1. It will be argued that the extra vibronic lines indicate lowering of the Tr symmetry to C_{2h} , D_2 and C_i .

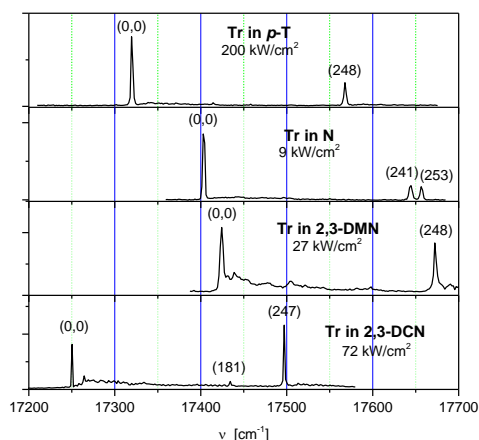


Fig.1 Fluorescence excitation spectra (purely electronic (0,0) and lowest energy vibronic components) of single Tr molecules in *p*-terphenyl (*p*-T), naphthalene (N), 2,3-dimethylnaphthalene (2,3-DMN) and 2,3-dichloronaphthalene (2,3-DCN) crystals at 5 K.

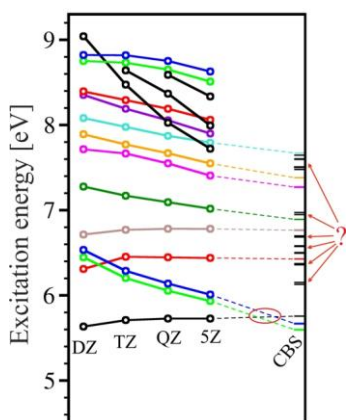
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Missing states and irregularities in excited states manifold of 2,2'-bithiophene – what basis set is large enough?

Andrzejak M.¹, Kukułka M.¹, Witek H. A.²

¹ Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

² Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu, Taiwan



The excitation energy spectra of organic chromophores, computed using long sequences of cc-pVnZ and aug-cc-pVnZ basis sets reveal surprisingly strong dependence of the excited states manifold on the quality of the basis set. The observed computational artefacts include: numerous missing states, wrong order of states, and considerable shifts in the energy spectrum [1]. The presented results demonstrate that not only the cc-pVnZ basis sets are completely unsuitable for modelling optical spectra of organic molecules (which is not very surprising), but also the predictive power of the aug-cc-pVnZ basis sets is limited to only the lowest portion of the energy spectrum. A simple and inexpensive remedy for the observed problems is suggested: an additional set of molecule-centered, diffuse orbitals should be rudimentarily used in quantum chemical calculations aiming at modeling optical spectra of molecules. The main conclusions

seem to be general and independent of the chemical identity of the studied system (as demonstrated also for other organic chromophores) and of details of the employed computational methodology.

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Photochromic reactions of 3*H*-naphthopyrans

Burdziński G.

Faculty of Physics, Adam Mickiewicz University in Poznań, gotar db@amu.edu.pl

Light-induced processes in 3*H*-naphthopyrans, which are one of the thermally reversible photochromic compounds, have been extensively studied in fundamental science and have been employed in commercially available photochromic lenses [1]. The photoreaction is initiated when the molecule absorbs the UV photon bringing the molecule to the singlet excited state. Then C(sp³)-O bond cleavage leads to the opened-ring form or the internal conversion IC repopulates back the ring in the electronic ground state. The opened-ring form structurally relaxes to the colored transoid-*cis* TC form or transoid-*trans* TT form. The thermal back reaction for 3*H*-naphthopyran is, in general, biexponential with a slower time constant (minutes/hours) assigned to TT decay. The residual color is one of the serious issue for the photochromic lenses. Recently, the suppression of the TT form generation (Fig. 1) was achieved simply by substituting a bulky substituent to the 2-position of the naphthopyrans [2].

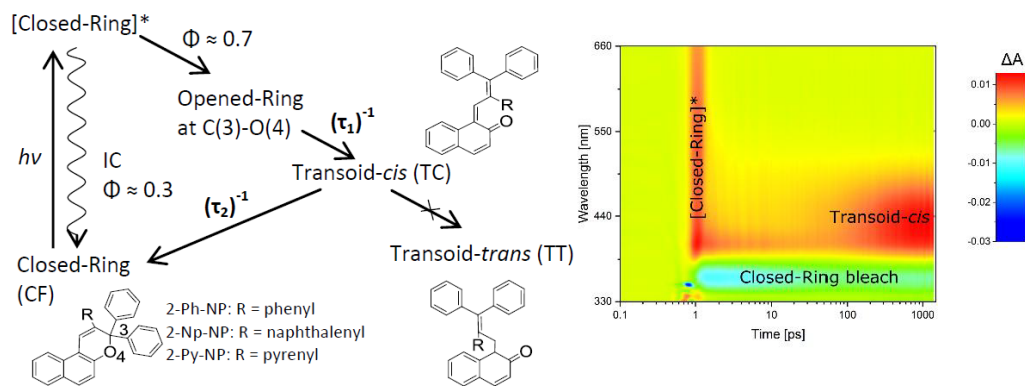


Fig. 1. Photochromic reaction mechanism for derivatives of 3*H*-naphthopyrans and transient UV-vis absorption data obtained in acetonitrile after photoexcitation of 2-Ph-NP at 320 nm (time zero was shifted to 1 ps in order to present the time axis in logarithmic scale).

We characterized mechanism of the photoreaction using electronic and vibrational time-resolved spectroscopies [3]. The substituent R (Fig. 1) exerts a great impact on the rates of TC formation and the subsequent decay of TC leading to the closed-ring form. Important role is played by steric and electrostatic repulsions between the aryl substituent group and C=O group. Moreover, solvent viscosity and polarity affect the kinetics: a viscous solvent decelerates TC formation, while the opposite effect is caused by high solvent polarity. A polar solvent stabilizes the polar TC species and decelerates the subsequent back closing-ring reaction.

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Excited state relaxation pathways in substituted phthalides

Rode M. F.¹, Karpiuk J.²

¹ Institute of Physics, Polish Academy of Sciences, Warsaw, mrode@ifpan.edu.pl

Very low fluorescence quantum yields of simple benzene derivatives composed of an aromatic ring with annealed saturated heterocycle, e.g., coumarin, phthalimide, or phthalide result

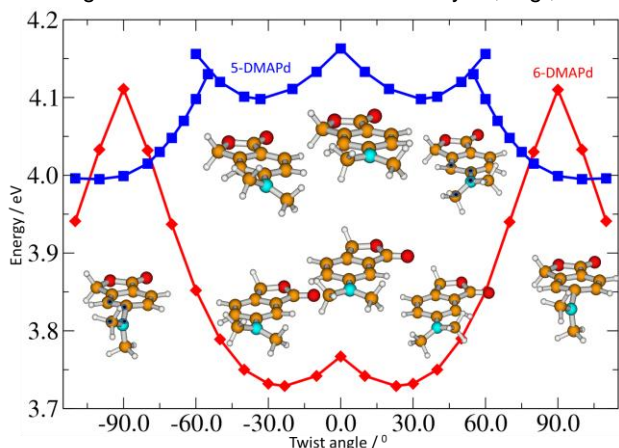


Fig.1 Potential energy surfaces along the DMA-twist angle.

from efficient ultrafast non-radiative processes in these molecules. The phenomenon was originally explained as being due to intersystem crossing between the $\pi\pi^*$ or $n\pi^*$ singlet and triplet states, but recent work on coumarin has shown an important role of the heterocyclic ring opening due to excited state α -cleavage within the pyrone moiety as a pathway for internal relaxation [1]. Phthalide and its derivatives form electron-accepting subunits in rhodamine and triarylmethane lactones, including recently discovered white fluorophores [2], where the ground-state β -cleavage of the elongated C–O lactonic bond gives rise to an industrially important color reaction [3], and the excited-state β -cleavage in the lactonic ring is a unique example of adiabatic photodissociation [4].

Using a CC2 computational approach and potential energy surface mapping we show that substitution of phthalide with single dimethylamine (DMA) group results in profound change of its photoluminescence properties (Fig. 1). Large stabilization of the (π,π^*) state makes the α - and β -cleavage processes uncompetitive to the low-energy rotation of the DMA group. The shape of the excited-state potential energy surface along the twist angle coordinate of the DMA group is very sensitive to the position of the DMA, in line with experimentally measured single and dual fluorescence of phthalide derivatives. In this report we explore the ground and excited state potential energy surfaces and their possible conical intersections (CI) as a function of the C–O bond extension and the DMA-group torsion angle. Keeping selected reaction coordinate fixed, the remaining internal degrees of freedom were optimized without symmetry constraints using the CC2/cc-pVDZ method.

This work was supported by the BIFLUORG grant (PBS3/A1/17/2015) from the National Centre for Research and Development.

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Photodynamics of ruthenium dyes interacting with titania nanoparticles for solar cells and water splitting systems

Grądzka I.¹, Gierszewski M.¹, Glinka A.¹, Karolczak J.¹, Ziótek, M.¹

¹ Adam Mickiewicz University, Faculty of Physics, Umultowska 85, 61-614 Poznań, Poland, iwona.gradzka@amu.edu.pl

The interaction of ruthenium dyes coded N719 and RuP (Fig. 1) with TiO₂ mesoporous layer was studied by means of ultrafast transient absorption, time-resolved emission and electrochemical impedance spectroscopy. N719 is a standard dye for dye-sensitized solar cells (DSSC) [1], while RuP is commonly tested for water splitting systems due to more positive redox potential and stronger anchoring unit [2]. The results obtained give new insights into the limitations of electron transfer efficiency in both systems.

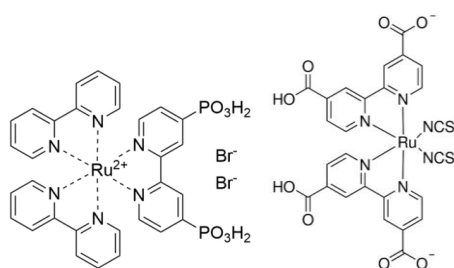


Fig.1 Chemical structures of the studied ruthenium dyes: RuP (left) and N719 (right).

Employing cobalt-based electrolyte instead of iodine one led recently to champion efficiencies (>13%) of DSSCs with porphyrin [3] and all-organic dyes [4]. However, this strategy does not work with classical ruthenium dyes [1]. Therefore, we compared the performance of solar cells sensitized with N719 using these two different electrolytes [5]. Transient absorption studies revealed that there exists additional, pronounced recombination between injected electrons and the oxidized dyes on sub-ns time scale, responsible for smaller photocurrent in cobalt-based cells. Moreover, electrochemical impedance studies showed the increased recombination of injected electrons with cobalt redox pair than with the iodine/iodide redox shuttle, resulting in lower photovoltage and fill factor for the cells with cobalt electrolyte.

Next, we compared the electron transfer dynamics in N719 and RuP. Both transient absorption and time-resolved emission studies showed that electron injection from the photoexcited ruthenium dye to titania nanoparticles is significantly slower for RuP than N719. Furthermore, unwanted back electron transfer occurring on the time scale of tens and hundreds of picoseconds was much more pronounced for RuP dye. The observed behaviour can be probably explained by different LUMO energy positions and different electronic coupling to titania for both dyes. The observed overall lower electron transfer efficiency from RuP to TiO₂ than from N719 to TiO₂ is in good agreement with the lower photocurrent measured in complete devices with these dyes.

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Revealing the Dynamics of Excited State Proton Transfer of a π -Conjugated Salicylidene Compound

M.G. Vivas^{1,2}, J.C. Germino², C.A. Barboza³, D.A. Simoni², P.A.M. Vazquez²,
L. De Boni³, T. D. Z. Atvars², C.R. Mendonça³

¹ Physics Institute, University of São Paulo, São Carlos, Brazil

² Chemistry Institute, University of Campinas - UNICAMP, Brazil

³ Institute of Physics, Polish Academy of Sciences, Warsaw, Poland, crissetubal@ifpan.edu.pl

Excited state intramolecular proton transfer (ESIPT) in a novel salicylidene sal-3,4-benzophen chromophore was evaluated through white light femtosecond pump-probe and time-resolved fluorescence techniques, as well by theoretical calculations within the density functional theory framework. Our results suggest that when the sal-3,4-benzophen chromophore is excited at 390 nm to the *cis*-enol^{*} form, which is quickly converted to the hot *cis*-keto^{*} form due to the fast ESIPT process ($\tau_{\text{ESIPT}} = 150$ fs), which is stabilized by the intramolecular hydrogen bond, observed in the optimized structure of the first excited state at PBE0/cc-pVTZ level. Subsequently, cooling from the hot *cis*-keto^{*} to cold *cis*-keto^{*} occurs with a characteristic time constant of ~ 600 fs, with following relaxation decay time of 37 ps related to the photodynamic from the ligand due to the occurrence of the *cis* \rightarrow *trans* photoisomerization and intersystem crossing mechanisms. Finally, emission fluorescence was observed from the *cis*-keto^{*} at 575 nm. The dynamics of the optical process was modelled using rate equations and supported by theoretical calculations. The occurrence of the ESIPT leads to an *enol* \rightleftharpoons *keto* balance in the excited state, hence a broader emission range spectrum is obtained, allowing its applications in photonics and organic electronics devices such as white OLEDs.

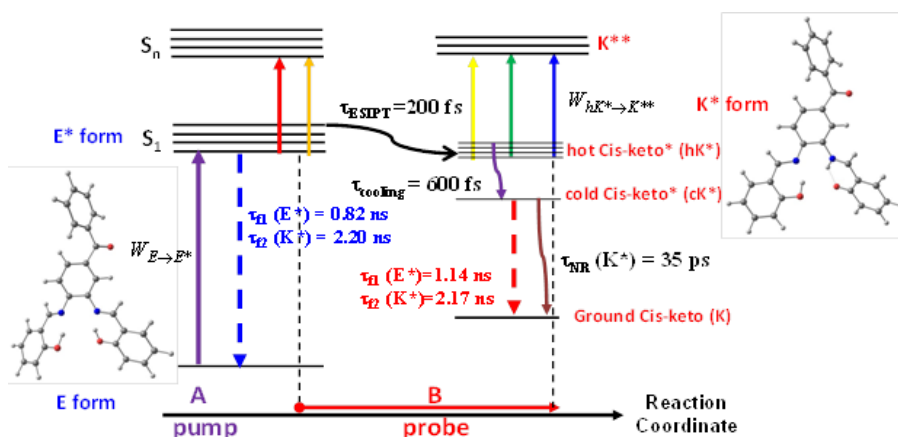


Fig.1 Proposed mechanism for the dynamics of the excited proton transfer of the sal-3,4-benzophen.

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Intramolecular electron transfer in solid hosts

Jerzy Karpiuk

¹ Institute of Physics, Polish Academy of Sciences, Warsaw, jkarpiuk@ifpan.edu.pl

In solid environment, such as crystalline solvent or organic solvent glass, photoinduced intramolecular electron transfer is usually inhibited because the solvent molecules cannot reorganize to stabilize the photogenerated charge separated state. Electron transfer can, however, be enabled with sufficiently large driving force for charge separation and suitable molecular structure of the donor–acceptor ([D–A]) system. We have recently shown [1] that in frozen solvents at 77 K, ultrafast (≤ 250 fs) photoinduced intramolecular electron transfer (ET) in bichromophoric [D–A] diarylmethane lactones (MGLA, Figure 1) produces quantitatively a covalently linked radical ion pair, $^1[D^{+\bullet}-A^{\bullet-}]$. The steady-state luminescence spectrum of MGLA at 77 K shows high variability and large red shift with increasing medium polarity. Time-resolved luminescence measurements allow for decomposition of the complex luminescence spectrum in

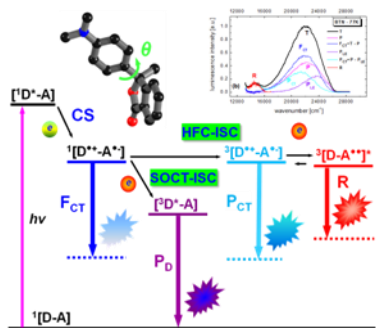


Fig.1 Scheme of photophysical processes in MGLA in butyronitrile glass at 77 K.

fluorescence and phosphorescence components and reveal that $^1[D^{+\bullet}-A^{\bullet-}]$ decays to charge-separated ($^3[D^{+\bullet}-A^{\bullet-}]$) and donor-centered ($[^3D^*-A]$) triplet states, which display dual phosphorescence. $^3[D^{+\bullet}-A^{\bullet-}]$ and $[^3D^*-A]$ are formed in parallel via two different intersystem crossing mechanisms: spin orbit charge transfer (SOCT) and hyperfine coupling (HFC), with solvent dependent branching ratio.

The observed glassochromism comes mainly from the fact that the solvent drives the D–A alignment (with torsion angle θ as critical parameter) during the freezing process to adapt to increasing solvent polarity, producing inhomogeneous ground-state population distribution with solvent-dependent D–A exchange interaction, J . J plays a key role in determining the energy gap, ΔE_{ST} , between the $^1[D^{+\bullet}-A^{\bullet-}]$ and $^3[D^{+\bullet}-A^{\bullet-}]$ states, and in partitioning intersystem crossing into SOCT and HFC mechanisms. In polar glasses, a third phosphorescence band appears due to dissociative back ET in $^3[D^{+\bullet}-A^{\bullet-}]$ resulting in excited open ring biradical.

The ability to identify triplet state intermediates in MGLA and related systems by phosphorescence raises interesting possibilities for using MGLA and its analogues for optical studies of singlet-triplet dynamics and magnetic field effects on chemical reactions.

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Posters

Formation of H_3O^+ Cations Due to Aluminum Fluoride Interactions with Water

Anusiewicz I., Wileńska, D., Skurski, P.

Faculty of Chemistry, Department of Theoretical Chemistry, University of Gdańsk,
iwona.anusiewicz@ug.edu.pl

The isomeric structures formed by the aluminum fluoride (AlF_3) system and surrounding water molecules were theoretically examined by employing MP2 and CCSD(T) methods and the aug-cc-pVDZ basis set together with the polarized continuum solvation model within a self-consistent reaction field treatment. The calculations performed for the $\text{AlF}_3 \cdot n(\text{H}_2\text{O})$ systems ($n = 1-6$) revealed that facial and meridional octahedral structures correspond to the lowest energy isomers for the $\text{AlF}_3 \cdot 4\text{H}_2\text{O}$, $\text{AlF}_3 \cdot 5\text{H}_2\text{O}$, and $\text{AlF}_3 \cdot 6\text{H}_2\text{O}$ systems, whereas the isomers containing the H_3O^+ and AlF_3OH^- fragments were predicted to be less stable by only 5–7 kcal/mol,

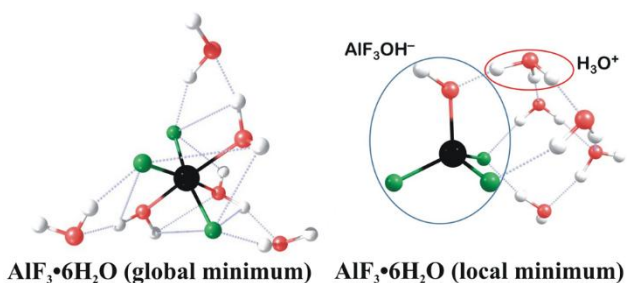


Fig.1 Aluminum fluoride induces the formation of H_3O^+ cations upon interactions with water

which indicates the possible formation of the hydronium cations in such systems even at room temperature.

Synthesis and photophysics of phthalide-based white fluorophores

Paweł Gawryś, Elena Karpiuk, Jerzy Karpiuk

¹ Institute of Physics, Polish Academy of Sciences, Warsaw, pgawrys@ifpan.edu.pl

White fluorophores are compounds emitting spectrally broad fluorescence over the entire visible range (e.g., 430-700 nm, spectral width $\geq 9000 \text{ cm}^{-1}$). Such emission cannot come from a single chromophore, but must involve radiative deactivation of at least two subunits in a molecule.

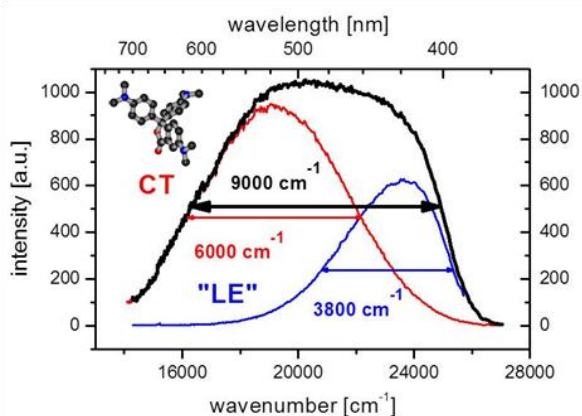


Fig.1 Fluorescence spectrum of CVL in dichloromethane decomposed in bands emitted by locally excited and CT states.

One approach to obtain white light from a molecule is to make use of dual fluorescence displayed as a balanced combination of the emission from a locally excited (LE) and a charge (CT) or proton transfer (PT) states. A molecule displaying in polar solvents such fluorescence is Crystal Violet Lactone (CVL) with a donor-acceptor-donor (D-A-D) structure (Figure 1). CVL emits a blue band from an LE state and an orange band from a highly polar CT state identified as intramolecular exciplex. [1] The

observed photoluminescence spectrum and photostability are greatly affected by the substitution pattern of the electron donating (D) and accepting (A) parts.

We have recently found that the CVL-like structure with D and A subunits linked by an sp^3 carbon is a versatile platform for development of white fluorophores displaying fluorescence with CIE coordinates in solution approaching closely pure white (0.33, 0.33). The purpose of the present study was to explore the best synthetic routes leading to different CVL analogues and to examine the photophysics of these molecules in solution as a function of solvent polarity. The simplest CVL analogues are easily synthesized in a condensation reaction between 3-dialkylaminobenzoic acid and 4-dialkylaminobenzaldehyde, but in spite of the emission pattern resembling that of CVL they are not photochemically stable enough due to benzylic hydrogen at the spiro carbon. Therefore novel systems were prepared whose observed photostability in solution is greatly improved.

Acknowledgement: This work was supported by the BIFLUORG grant (PBS3/A1/17/2015) from the National Centre for Research and Development.

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The effect of temperature and light on tetracycline degradation by Na[Fe(EDTA)] and Fe(III)citrate

Margas M.¹, Rydzyński D.¹, Piotrowicz-Cieślak A.¹, Smyk B.², Grajek H.²

¹ Faculty of Biology and Biotechnology, University of Warmia and Mazury in Olsztyn, dariuszrydz@wp.pl

² Department of Physics and Biophysics, University of Warmia and Mazury in Olsztyn, grajak@uwm.edu.pl

Tetracyclines (TC) are among the most commonly used antibiotics worldwide [1]. The content of antibiotics in arable land may in some cases reach 1420 mg/kg of soil [2]. Methods for the removal of TC from the aquatic environment were described which included ozonation and treatment with iron(III) chelates [3]. There have been many articles on the formation of TC degradation products due to the binding of Mg, Ca, Te, Cu by TC.

The purpose of our work was to investigate the effect of light and temperature on the rate of degradation of TC by its interaction with the compounds containing Fe(III) in its structure. The following solutions were prepared: (1) TC ($5 \times 10^{-5} \text{M}$) with Fe(III)CIT ($5 \times 10^{-5} \text{M}$) and (2) TC ($5 \times 10^{-5} \text{M}$) with Na[Fe(EDTA)]·3H₂O (10^{-4}M). The samples were stored for 10 days in incubators at 20°C and 30°C in the dark or under fluorescent lamps illumination (PHILIPS ESSENTIAL 14W / 840 COOL WHITE). The light intensity was 5.5 klx. Absorption spectra were measured with a Cary 5000 spectrophotometer (Varian, Australia) at $t = 20^\circ\text{C}$ and 30°C .

The greatest decrease in TC absorption spectra after 10 days was observed with Fe(III)CIT samples, especially those that were illuminated. Changes in the TC absorption spectra in solutions treated with Na[Fe(EDTA)] were small, particularly in samples stored in the darkness at 20°C and they were slightly higher for samples stored in darkness at 30°C. The decrease of TC concentration was 2% and 6%, for 20°C and 30°C treatments, respectively. On the other hand, the illuminated samples, particularly those stored at 30°C, completely changed the shape of their spectra after 10 days and their TC content dropped by 60%. When Fe(III)CIT was used, TC degradation was very rapid and it occurred even in the darkness. After 6 days in darkness, or after 3 days of exposure to light the absorption spectrum completely changed its shape.

The TC degradation process was described by the II order kinetics. The TC degradation rate constants k were determined: in the presence of Na[Fe(EDTA)] in the darkness the constant was $55 \text{ M}^{-1} \text{ day}^{-1}$ and $226 \text{ M}^{-1} \text{ day}^{-1}$ at 20°C and 30°C, respectively. These values were quite small compared to the values determined for the illuminated samples: $1012 \text{ M}^{-1} \text{ day}^{-1}$ and $2050 \text{ M}^{-1} \text{ day}^{-1}$ at 20°C and 30°C, respectively. In the light the reaction was, therefore, 18 times faster (at 20°C). With Fe(III)CIT, the TC degradation rate constants were very high and were: $4240 \text{ M}^{-1} \text{ day}^{-1}$ and $11330 \text{ M}^{-1} \text{ day}^{-1}$ in the dark at 20°C and 30°C, respectively and $14470 \text{ M}^{-1} \text{ day}^{-1}$ and $48970 \text{ M}^{-1} \text{ day}^{-1}$ in the light at 20°C and 30°C, respectively.

The observed decrease in TC absorption spectra under the influence of the compounds containing Fe(III), can be attributed to the reaction of capture of iron ions from the Na [Fe(EDTA)] and Fe(III)CIT by TC. The concentration of free Fe(III) ions in the solution of Fe(III)CIT is greater than in solution of Na[Fe(EDTA)], thus facilitating the capture of Fe(III) by the TC molecules. Therefore, we have obtained high values of k constants for TC with Fe(III)CIT: 77 to 50 times higher than for Na[Fe(EDTA)] at 20°C and 30°C, respectively. Light strongly activates detachment of Fe(III) from Na [Fe(EDTA)] and it transfer to TC.

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TWO SYNTHETIC APPROACHES FOR THE PREPARATION OF CORE-SHELL UPCONVERTING NANOPARTICLES

Jarosz A.,¹ Majewska P.,¹ Kuncewicz J.,¹ Łabuz P.,¹
Dzierżęga K.,² Macyk W.,¹

¹ Faculty of Chemistry, Jagiellonian University, jarosza@chemia.uj.edu.pl

² Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University

Upconverting nanoparticles (UCNPs), capable of visible and ultraviolet (UV) light luminescence under near infrared (NIR) irradiation, have a great potential for application in biology and medicine. The main advantage of such particles is their strong absorption within NIR range of light. NIR radiation, in contrast to the UV and visible light, is capable of deep penetration of tissues and causes minimal photodamage. The materials composed of upconverting nanoparticles combined with other photoactive compounds sensitive within the range of upconversion luminescence may have a great potential for use in imaging, bio-sensing or light-activated therapy. However, it is still challenging to obtain small nanoparticles with preserved high efficiency of upconversion, since luminescence is strongly quenched by the surface defects, ligands and solvent molecules. Therefore, research on new synthetic approach that allows a strict control of size, shape and crystal structure of the nanoparticles constitutes a crucial step in obtaining high-quality and uniform materials.

In the present work, NaGdF₄:Yb,Tm nanoparticles were synthesised using high-temperature coprecipitation and solvothermal methods. The core particles were coated with the protective shells (NaYF₄, NaYbF₄, NaGdF₄) in order to minimise photoluminescence quenching. Beneficial role of the protective layers was confirmed by a large enhancement of upconversion luminescence intensity of the core-shell-structured particles. The synthesised nanoparticles exhibit strong upconversion photoluminescence in the UV and visible range of light at 980 nm excitation wavelength, making them good candidates for future investigations of their potential medical applications.

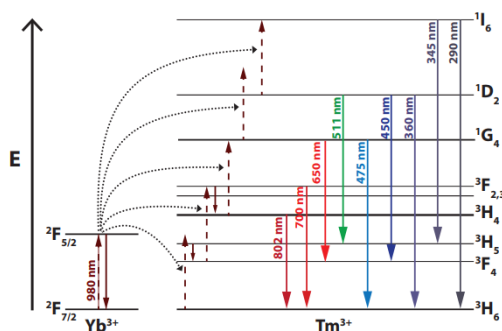


Fig. 1. Energy diagram of Yb³⁺-sensitised energy transfer upconversion from Tm³⁺ ions with all the possible emission pathways

CORE-SHELL UPCONVERTING NANOPARTICLES COATED WITH SURFACE-MODIFIED TITANIA FOR PHOTOCATALYTIC APPLICATIONS

Majewska P.,¹ Jarosz A.,¹ Kuncewicz J.,¹ Łabuz P.,¹
Dzierżęga K.,² Macyk W.,¹

¹ Faculty of Chemistry, Jagiellonian University majewska@chemia.uj.edu.pl
² Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University

Photocatalysis seems to be a feasible solution for the emerging environmental and economic issues of humankind. It can be used for water treatment, air purification, hydrogen production and photoelectrochemical conversion powered only by the sunlight. However, conventional photocatalysts, such as TiO₂ or ZnO, absorb only ultraviolet (UV) light, which constitutes less than 10% of the energy received from the Sun. In contrary, near infrared (NIR) radiation accounts for approximately 50% of the solar spectrum. Lanthanide-doped nanoparticles are the materials able to harvest NIR photons and convert them into UV and visible light as they exhibit unique spectroscopic property, known as upconversion. Therefore, combining upconverting nanoparticles with photocatalysts should increase the efficiency of photocatalytic reactions..

In the present work, NaYbF₄:Tm and core-shell NaGdF₄:Yb,Tm@NaYF₄ nanoparticles were synthesised using solvothermal method. The nanoparticles were then coated with a titania layer and further modified with rutin and Tiron. The XRD and EDX analysis confirmed the formation of crystalline titanium dioxide on the surface of upconverting nanoparticles. Moreover, UV-Vis spectra showed that the rutin-modified materials absorb light in the visible range. It may suggest that surface complexation results in photosensitisation of TiO₂ for visible light. The obtained results indicate that the synthesised materials may open promising research opportunities in the field of utilizing the full solar energy spectrum for photocatalytic and photovoltaic purposes.

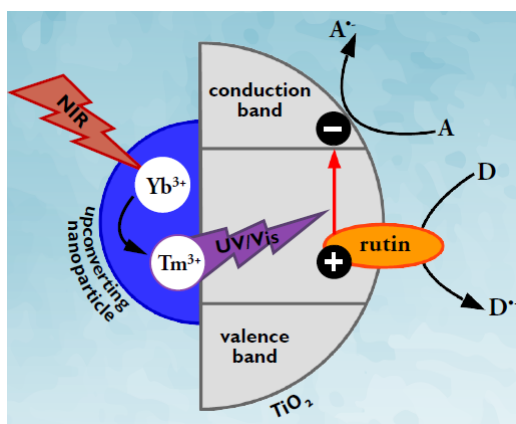


Fig. 1. Proposed mechanism of the UCNP-assisted photocatalysis on the rutin-modified TiO₂

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Photocatalysis at shaped TiO₂ crystals.

Mikrut P., Pacia M., Macyk W.

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków,
pavel.mikrut@gmail.com, macyk@chemia.uj.edu.pl

Titanium dioxide is one of the most important oxides that finds extensive application in the field of photocatalysis in processes such as water treatment, hydrogen evolution, carbon dioxide conversion. The performance in the aforementioned applications predominantly depends on the surface physicochemical properties of TiO₂ crystals. The relationship between structure and reactivity is a crucial issue in heterogeneous catalysis, therefore it is worth to precisely control the morphology of TiO₂ crystals and understand their growth mechanism.

Under equilibrium conditions, anatase TiO₂ crystals grow along [001] axis which exposes the low-energy {101} facets, thereby minimizing the surface energy and increasing the crystal stability by forming truncated bipyramidal shapes. Theoretical calculation reveals, that the surface energy of major exposed facets of anatase TiO₂ crystal follows the order {110} > {001} > {100} > {101}. The difference in the energy levels drives the electrons and holes to different crystal faces, leading to separation of charge carriers. This separation is probably the key to the high efficiency of some photocatalytic reactions, such as reactive oxygen species (ROS) generation, including hydroxyl radicals (HO•).

The aim of this study was to investigate the efficiency of generation hydroxyl radicals depending on the shape of anatase crystals in the present or absence hydrogen peroxide.

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Photophysical properties of *E*-hydroxystilbazols in dependence of *pH*

Prukala D.

Photochemistry Lab, Faculty of Chemistry, Adam Mickiewicz University, Poznan
dprukala@amu.edu.pl

Fluorescent molecules that interact with various proteins has been widely use as probes in many different areas of biological research, including the localization of specific proteins in cell organelles and the characterization of cellular binding sites. Of

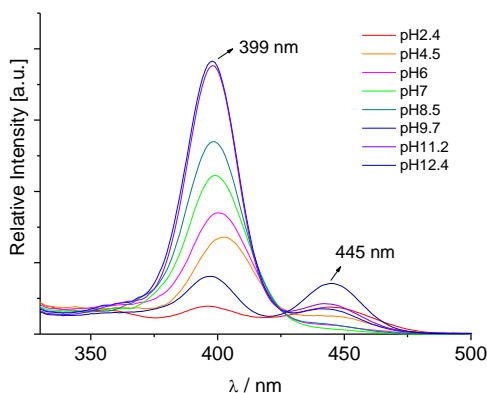


Fig.1 Synchronous fluorescence spectra of the selected compound at different pH values

ortho-, *meta*- or *para*- position at the benzene ring, and the nitrogen atom located in positions 2 and 4 of the pyridine ring.

Absorption and emission spectra of *E*-hydroxystilbazols show interesting dependence on *pH*. It was postulated that these compounds show dual fluorescence in water under neutral conditions, suggesting the emission from both non-ionized and ionized species in the excited state. Our conclusions resulted from our studies are slightly different. We analyzed spectral and photophysical properties of six azastilbene derivatives in entire range of *pH*, using UV/Vis steady-state and time-resolved techniques; including synchronous spectra (Fig.1).

The absorption spectra of compounds in entire *pH* range show at least three absorbing species. Compounds possessing *meta*-hydroxyl group at the benzene ring have two absorbing species.

Emission intensity of protonated and deprotonated forms of *ortho*-, and *para*-hydroxystilbazols decrease in compare to their neutral forms. Contrary to that *meta*-hydroxystilbazols reveal high emission only at very low and very high values of *pH*.

The characteristic pK_a values for protonation / deprotonation steps of studied compounds in the ground state are shown. The pK_a values in the excited state were calculated according to two methods (using the Förster cycle and spectrofluorimetric titration) and compared.

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Hydroxy derivatives of anthraquinone as a TiO₂ sensitizers

Mateusz Trochowski, Wojciech Macyk

Jagiellonian University in Kraków, ul. Gronostajowa 2, 30-387 Kraków, Poland
 mateusz.trochowski@doctoral.uj.edu.pl, macyk@chemia.uj.edu.pl

Titanium(IV) oxide is one of the most popular semiconductors used in photocatalytic reactions due to its high photoactivity upon ultraviolet light irradiation, stability and lack of toxicity. Unfortunately, remarkably good photocatalytic properties of this transition metal oxide under UV irradiation need to be expanded to the visible light range. Surface engineering based on deployment of organic compounds with donor bonding groups is one of the ways to achieve it [1]. Previous studies confirm that aromatic compounds with hydroxyl and carboxyl groups can bind to TiO₂ surface efficiently, forming surface complexes that absorb visible light [2,3]. Anthraquinone derivatives deposited at TiO₂ form an interesting type of photoactive materials. The bond between the chromophore and the titanium atom at the semiconductor surface shows a strong covalent character which makes the material stable [4].

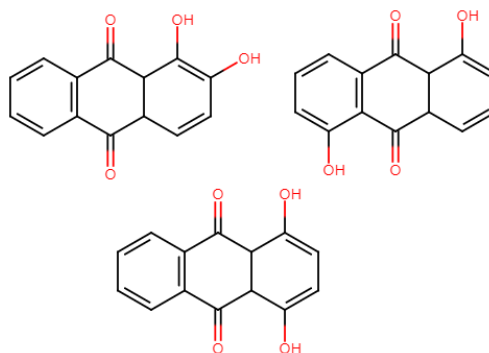


Fig.1. Structures of used organic modifiers.

Our research shows that anthraquinone derivatives deposited at TiO₂ surface exhibits higher photoactivity and photostability than frequently used organic compounds such as catechol, salicylic acid or 2,3-naphthalenediol. All obtained materials were examined towards the photocatalytic and photoelectrochemical activity. Detailed results of these studies will be presented and discussed.

Acknowledgement: The work was supported by National Science Centre within the project number 2015/19/B/ST5/00950 (OPUS 10).

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Isoindolo[5,8]diones - Structurally Unique Fluorescent Dyes

Vakuliuk O.¹, Oii Sh.¹, Deperasińska I.², Staszewska-Krajewska O.¹, Banasiewicz M.², Kozankiewicz B.², Gryko D.T.¹

¹ Institute of Organic Chemistry, Polish Academy of Sciences, ovakuliuk@icho.edu.pl
² Institute of Physics, Polish Academy of Sciences

Organic electronics and fluorescence imaging place demands for the heterocycles with π-extended conjugation.¹ Rational design, aided by combinatorial and diversity-orientated approaches, provides invaluable routes toward novel functional materials.² Notwithstanding, certain set of chromophores evades even the best designed retrosynthetic analysis. Frequently that is the case for the complex molecular structures.

Herein we would like to report the first set of asymmetrical dyes possessing isoindolo[5,8]dione core, linearly fused with thiophene, furan or benzene ring (INDs). Serendipitously discovered rearrangement of the diketopyrrolopyrroles (DPPs) leads to these structurally unique molecules in up to 75% yield (Fig.1). The significance of the discovered transformation also bases on the first known to date rearrangement of the DPP core.³

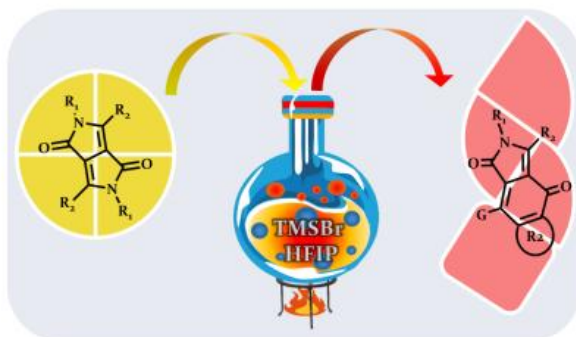


Fig.1 Lewis acid catalysed rearrangement of the diketopyrrolopyrroles

Reported INDs possess favorable photophysical properties with the emission maxima within the range of 581–635 nm and high fluorescence response. The combination of these parameters with straightforward synthesis, relatively small molecular mass and reasonable stability may open doors for presented dyes to potential applications in fluorescence microscopy (bioimaging).

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Excited-state proton transfer in purine analogues: kinetic analysis

Wierzchowski J., Smyk B.

Department of Biophysics, University of Varmia & Masuria in Olsztyn, Poland,
jacek.wie@uwm.edu.pl

Neutral 8-azaxanthine (8-azaX) and protonated 2,6-diamino-8-azapurine (8-aza-2,6-DaPu·H⁺) are known to undergo excited-state proton dissociation in protic solvents, resulting in phototautomerism [1]. Here we present a kinetic analysis of the dual emission observed in both compounds in methanol.

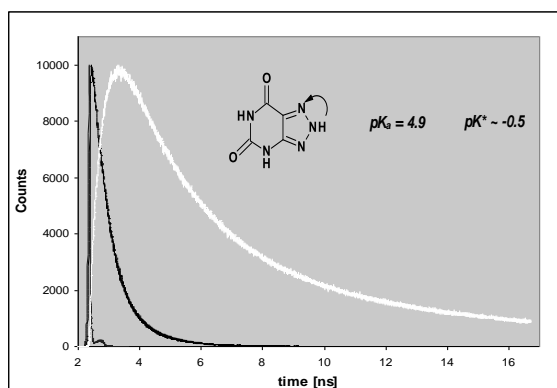


Fig.1 Kinetics of emission of the neutral 8-azaxanthine in acidified methanol, observed at 340 nm (dark) and 480 nm (light).

Emission decays were measured using a PicoQuant FluoTime 200 spectrometer with a MCP PMT detector. Sources of excitation were SuperK EXTREME EXW-20 (High Power Systems) with a supercontinuum extension unit (265 - 345 nm, 3 – 30 μ W) from NKT Photonics. The half-peak excitation pulse time was ca. 75 ps.

The results are summarized in Fig. 1 and Table 1. No measurable risetime(s) are observed in the short-wavelength bands in both compounds, and the decays are bi-exponential. In the long-wavelength emission bands the observed risetime is close (8-azaX) or identical (8-aza-2,6-DaPu·H⁺) to the faster decay time of the short-wavelength band (Table 1), while the decay is bi-exponential for 8-azaX and tri-exponential for 8-aza-2,6-DaPu·H⁺. This complex behaviour may result from the ground-state prototropic tautomerism characteristic for purine analogues and/or from a reversible character of the proton transfer [2].

The results are summarized in Fig. 1 and Table 1. No measurable risetime(s) are observed in the short-wavelength bands in both compounds, and the decays are bi-exponential.

Table 1. Decay and risetimes of two-band emission observed for 8-azaX and 8-aza-2,6-DaPu·H⁺ in methanol, containing 2 mM HCl. Fractional intensities are given in parentheses.

| Compound | λ_{obs} [nm] | rise time [ns] | decay: τ_1 [ns] | decay: τ_2 [ns] |
|-------------------------------|-----------------------------|----------------|----------------------|----------------------|
| 8-azaX | 340 | none | 0.50 (67%) | 1.17 (33%) |
| 8-azaX | 480 | 0.39 | 2.41 (44%) | 10.1 (56%) |
| 8-aza-2,6-DaPu·H ⁺ | 325 | none | 0.36 (93%) | 3.24 (7%) |
| 8-aza-2,6-DaPu·H ⁺ | 450 | 0.36 | 1.06 (27%) | 10.0 (62%) |

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