PANIC 2016

PhoBiA Annual Nanophotonics
International Conference

18-20 April 2016
Wrocław, Poland

Publication co-financed by Wrocław University of Technology and KNOW programme.

Printed by
Oficyna Wydawnicza Politechniki Wrocławskiej
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław
Tel./fax: (0-71) 328 29 40
www.oficyna.pwr.edu.pl

ISBN 978-83-7493-934-8

Table of contents

I. Committees

The conference will be held under the patronage of:

Prof. dr hab. inż. Andrzej Trochimczuk
– Dean of the Faculty of Chemistry

Honorary and Scientific committee:

Prof. Marek Samoć - Wrocław University of Technology, POLAND
Prof. Jan Misiewicz - Wrocław University of Technology, POLAND
Dr Katarzyna Matczyszyn - Wrocław University of Technology, POLAND
Dr Marcin Nyk - Wrocław University of Technology, POLAND
Dr Joanna Olesiak-Bańska - Wrocław University of Technology, POLAND
Dr Mateusz Bański - Wrocław University of Technology, POLAND
Prof. Isabelle Ledoux-Rak - ENS de Cachan, France
Prof. Luana Persano - Nanoscience Institute of the National Research Council in Lecce, ITALY
Prof. Robert Luxenhofer - Julius Maximilian University of Würzburg, GERMANY
Dr Artur Bednarkiewicz - European Institute of Innovation and Technology (EIT) Wrocław, Poland
Prof. Keitaro Nakatani - ENS de Cachan, FRANCE
Prof. Nicolas Joly - Max-Planck Institute, Erlangen, GERMANY
Prof. Malcolm Buckle - ENS de Cachan, FRANCE
Prof. Sven Hoefling - Universität Würzburg, GERMANY
Prof. Paweł Machnikowski - Wrocław University of Technology, POLAND
Dr Piotr Młynarz - Wrocław University of Technology, POLAND
Dr Artur Podhorodecki - Wrocław University of Technology, POLAND
Dr Neil Robertson - The University of Edinburgh, UK
Dr Grzegorz Sęk - Wrocław University of Technology, POLAND
Prof. Kishan Dholakia - University of St Andrews, UK
Prof. José Garcia Solé - Universidad Autonóma de Madrid, SPAIN
Dr Claude Nogues - ENS de Cachan, FRANCE
Dr Grzegorz Cywiński - UNIPRESS, POLAND

Dr Maciej Dems - Łódź University of Technology, POLAND
Dr Grzegorz Dariusz Sulka - Jagiellonian University, Kraków, POLAND
Dr Marek Grzelczak - Centre for Cooperative Research in Biomaterials-CIC biomaGUNE, San Sebastian, SPAIN
Dr Peter Zijlstra - Molecular Biosensors for Medical Diagnostics, Technische Universiteit Eindhoven, NEDERLAND
Dr Marcin Motyka - Laboratory for Optical Spectroscopy of Nanostructure, Wrocław, POLAND
Prof. Lucyna Firlej - Universite Montpellier II, Montpellier, FRANCE
Prof. Stephane Parola - Functional Materials and Photonics, Ecole Normale Superieure of Lyon, Lyon, FRANCE
Prof. Chantal Andraud - The Chemistry Laboratory, Ecole Normale Superieure of Lyon, Lyon, FRANCE
Dr Krzysztof Janus - Wrocław University of Technology, Wrocław, POLAND
Prof. Bogdan Kuchta - Universite Aix-Marseille, Marseille, FRANCE
Prof. Mark Humphrey - Australian National University, Canberra, AUSTRALIA

PhoBiA
Photonics & Bionanotechnology Association

Organizers committee – the members of PhoBiA association:

Dr. Katarzyna Matczyszyn - association tutor
Dr. Mateusz Bański - association tutor

Magdalena Waszkielewicz - president
Adam Szukalski - vice-president
Marta Chołuj- treasurer
Radosaw Deska - webmaster
Katarzyna Brach
Marianna Chmiel
Maciej Chrzanowski
Joanna Jaworska
Magdalena Klekotko
Radosław Kołkowski
Leszek Mazur
Joanna Noga
Joanna Olesiak-Bańska
Dominika Wawrzyńczyk
Jan Zaręba
Marta Ziemianek

II. Sponsors and coorganizers

Sponsors

scienion

ENABLING LIFE SCIENCE

KNO

ROYAL SOCIETY OF CHEMISTRY

Coorganizers

Wrocław University of Technology

Politechnika
Wrocławska

Faculty of Chemistry

L. Hirszfeld Institute of Immunology and Experimental Therapy

Krajowa
Reprezentacja
Doktorantów

KRD

III. Programme

Monday 18 April 2016

Session I Chairman: Adam Szukalski

10:00 – 10:30	*Official opening ceremony*
10:30 – 11:30	**Dario Pisignano -** Invited lecture: Nanopatterning and electrospinning technologies for organic materials and polymer nanofibers
11:30 – 12:00	*Coffee break*
12:00 – 13:00	**Frederic Paul -** Invited lecture: Isocyanurate-cored organic and organometallic octupoles: linear and nonlinear optical properties
13:00 – 13:15	**SCENION**
13:15 – 14:45	*Lunch time*

Session II Chairman: Mateusz Bański

14:45 – 15:00	**Izabela Kondratowicz** - Pyrene-functionalized chemically reduced graphene oxide films for the covalent immobilization of bilirubin oxidase
15:00 – 15:15	**Jolanta Konieczkowska** - Physicochemical investigations of azopolyimides
15:15 – 15:30	**Kacper Parafiniuk** - Broadening of DFB laser wavelength tuning range achieved *via* FRET process
15:30 – 16:00	*Coffee break*
16:00 – 16:15	**Konrad Cyprych** - Random lasing in dye doped organic and biologically derivated polymers
16:15 – 16:30	**Katarzyna Lenczewska** - Energy transfer mechanisms in Yb^{3+} and Bi^{3+} co-doped $GdVO_4$ phosphor
16:30 – 16:45	**Witold Nawrot** - The Influence of Silver Nanoparticles on Sulphur Compounds Sensing by ZnO Gas Sensors
19:00 – 24:00	*Conference dinner*

Tuesday 19 April 2016

Session III Chairman: Dominika Wawrzyńczyk

9:00 – 10:00	**Jacek Waluk** - Invited Lecture: What can we learn from studying single molecules?
10:00 – 10:15	**Łukasz Janasz -** Ultrathin poly(3-hexylthiophene) films with controllable, nanofibrill morphology for application in organic, field-effecttransistors
10:15 – 10:30	**Fatima Aparicio -** Spontaneous second harmonic generation through organogelation
10:30 – 10:45	**Marta Chołuj -** Electric properties of spatially confined OCS molecule - the directional character of orbital compression
10:45 – 11:15	*Coffee break*

Session IV Chairman: Radosław Kołkowski

11:15 – 12:15	**Alain Wagner** - Invited Lecture: The living as reaction media: towards the development of bio-specific and chemo-switchable therapeutic agents
12:15 – 12:30	**Sylvain Ursuegui -** Development of a droplet-based microfluidic process for biomolecule capture, purification and detection at the single-cell level
12:30 – 12:45	**Dorota Buczyńska -** Investigation of fluorescence properties of single quaternary alloyed Ag-In-Zn-S nanocrystals
12:45 – 13:00	**Jan Zaręba -** How to measure the two-photon cross section of a coordination polymer?
13:00 – 14:30	*Lunch time*
14:30 – 16:30	*Poster session + Coffee break*
18:00 – 21:00	*Odra river cruise*

Wednesday 20 April 2016

Session V Chairman: Leszek Mazur

9:00 – 10:00	**Wojciech Pisula** - Invited Lecture: Conjugated polymers in ultrathin film field-effect transistors
10:00 – 10:15	**Lech Sznitko -** The influence of amyloid fibrils presence on the common laser dyes luminescence and lasing performance
10:15 – 10:30	**Joanna Bednarska -** Modeling the optical properties of fluorescent zinc probe using quantum-chemical methods
10:30 – 10:45	**Radosław Kołkowski -** Plasmonic band gap and plasmonic band edge resonances probed by second harmonic generation
10:45 – 11:15	*Coffee break*

Session VI Chairman: Joanna Olesiak-Bańska

11:15 – 12:15	**Halina Podbielska** - Invited Lecture
12:15 – 12:30	**Bartosz Kalota -** Lanthanide porphyrins in luminescence-based oxygen sensing
12:30 – 12:45	**Marco Deiana -** Two-photon fluorescent anthracenyl probe for sensitive recognition and discrimination of Human Serum Albumin (HSA) from BSA and other biological interferents
12:45 – 13:00	**Hanna Woźnica -** Synthesis and optical properties of PbS nanocrystals with controlled size
13:00 – 14:30	*Lunch time*

Session VII Chairman: Katarzyna Brach

14:30 – 14:45	**Magdalena Waszkielewicz** - Two-photon phenomena of gold nanoclusters
15:00 – 15:15	**Adam Szukalski** - All-optical switching in pyrazoline based systems
15:15 – 15:30	*Closing*

IV. Abstracts

Monday

18.04.2016

Nanopatterning and electrospinning technologies for organic materials and polymer nanofibers

D. Pisignano[1,2]

[1]ECMT, Istituto Nanoscienze-CNR, via Arnesano, I-73100 Lecce (Italy)
[2]Dipartimento di Matematica e Fisica "Ennio De Giorgi", Universitŕ del Salento, via Arnesano 73100 Lecce (Italy)

Abstract

Active nanopatterns involving organic materials or nanoparticles [1,2] as well as electrospun polymer nanofibers [3,4] are appealing building blocks for a variety of scientific fields, such as optoelectronics, photonics, nanoelectronics, and microelectromechanical systems. In particular, electrospinning technologies can be easily up-scaled to industrial level. Demonstrated devices and applications include various sub-wavelength optical components and nanofiber lasers [6-7], pressure-sensors, accelerometers and wearables made of piezoelectric polymer nanofibers [8, 9]. Next-generation electrospun nanosystems are being developed, which couple opto-mechanical properties through proper molecular components [10]. Here nanopatterning and electrospinning methods developed in our group will be presented as well as recent results on active organic nanofibers. Investigated properties include light-confinement, optical losses, stimulated emission, and anisotropy [11,12]. The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement n. 306357 (ERC Starting Grant "NANO-JETS", www.nanojets.eu).

References

[1] A. Camposeo et al., J. Myśliwiec, D. Pisignano, ACS Nano 8, 10893 (2014).
[2] A. Camposeo et al., D. Pisignano, Y. Xia, ACS Nano 9, 10047 (2015).
[3] L. Persano, A. Camposeo, D. Pisignano, Prog. Polym. Sci. 43, 48 (2015).
[4] D. Pisignano, Polymer Nanofibers, Royal Society of Chemistry (2013).
[5] G. Morello, et al., D. Pisignano, ACS Appl. Mater. Interf. 7, 5213 (2015).
[6] V. Fasano et al., D. Pisignano, Macromolecules 46, 5935 (2013).
[7] D. Di Camillo et al., D. Pisignano, Nanoscale 5, 11637 (2013).
[8] L. Persano et al., D. Pisignano, Y. Huang, J. A. Rogers, Nature Commun. 4, 1633 (2013).
[9] L. Persano et al., D. Pisignano, Adv. Mater. 26, 7574 (2014).
[10] V. Fasano et al., A. Credi, D. Pisignano, J. Am. Chem. Soc. 136, 14245 (2014).
[11] A. Camposeo et al., E. Zussman, D. Pisignano, Macromolecules 47, 4704 (2014).
[12] A. Camposeo et al., E. Zussman, D. Pisignano, Nano Letters 13, 5056 (2013).

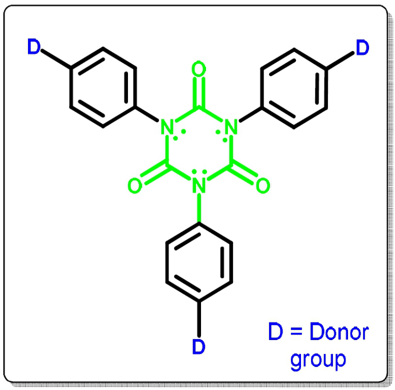
Isocyanurate-cored organic and organometallic octupoles: linear and nonlinear optical properties

F. Paul

Institut des Sciences Chimiques de Renne (UMR CNRS 6226), Université de Rennes I, France

Abstract

Octupolar molecules are of increasing interest in the field of nonlinear optics due to their potentially large two or three-dimensional quadratic nonlinearities.[1] These molecules arenon-dipolar species whose NLO response is related to multidirectional charge-transfer excitations, rather than to dipolar unidirectional excitations. A number of molecules with three-fold rotational symmetry, as well as molecular ions of D_{3h}, C_{3v} or D_3 symmetry, have been shown to display promising properties. In order to investigate new molecules that possess this type of structure, we have synthesized a new family of organic 1,3,5-triazine-2,4,6-trione derivatives.[2]



Albeit being known since the late 1890's, these simple octupolar structures have never been investigated for their optical properties. Straigthforward syntheses of these derivatives, along with their full spectroscopic characterization (IR, UV–Vis) will be presented. Their linear optical (LO) and nonlinear optical (NLO) properties will then be discussed. In addition to good hyperpolarizabilities and good transparencies, some of these derivatives present also remarkable two photon absorption (TPA) properties. Structural modifications allowing improving this particular property in purely organic derivatives will be presented and their NLO activity will be rationalized with the help of DFT computations.

Organometallic derivatives have also been obtained from precursors possessing pendant alkyne groups (Scheme 1). [3] The syntheses of these organometallic derivatives, along with their spectroscopic characterization (UV– Vis), and including the molecular structure of one example, will be presented. The positive impact of the peripheral organometallic substituents on the NLO performances will finally be analyzed based on additional DFT calculations. Finally, in the last part, part, the development of organic chromophores with large brightnesses and improved two-photons absorptions will be briefly related.

References

[1]. J. Zyss, I. Ledoux, *Chem. Rev.* **94** (1994), 77.

[2]. G. Argouarch, R. Veillard, T. Roisnel, A. Amar, H. Meghezzi, A. Boucekkine, V. Hugues, O. Mongin, M. Blanchard-Desce and F. Paul, *Chem. Eur. J.* **18** (2012), 11811.

[3]. A. Trujillo, R. Veillard, G. Argouarch, T. Roisnel, A. Singh, I. Ledoux and F. Paul *Dalton Trans.* **41** (2012) 7454.

Pyrene-functionalized chemically reduced graphene oxide films for the covalent immobilization of bilirubin oxidase

I. Kondratowicz[1], S. Sahin[2], K. Żelechowska[1], E. Yu[2]

[1]Faculty of Applied Physics and Mathematics, Gdańsk Univeristy of Technology, Narutowicza 11/12 80-233 Gdańsk, Poland

[2]School of Chemical Engineering and Advanced Materials, Merz Court, Newcastle upon Tyne, NE1 7RU, UK

Abstract

We report a simple and general method of the noncovalent modification of chemically reduced graphene oxide using 1-pyrenebutyric acid with the subsequent covalent attachment of bilirubin oxidase. The composite material with multiwalled carbon nanotubes was also prepared. This approach enhanced the electron transfer between BOD and the rGO electrode surface. Reduced graphene oxide was reduced with two different reducing agents namely hydrazine and ascorbic acid. By using different reducing agents, different level of graphene oxide reduction is obtained. This may influence the electrical transport between the electrode and the enzyme as well as the enzyme attachment due to the residual oxygen functionalities. The materials were then modified with pyrene derivative with the use of EDS- sulfo-NHS crosslinking reaction for the successful anchoring of the enzyme. We expect that pyrenyl groups should irreversibly stack to the rGO surface through π-π interactions of aromatic rings existing both on pyrene and rGO. All materials were characterized by IR, UV-Vis and SEM measurements. The activity of the electrodes was investigated by cyclic voltammetry.

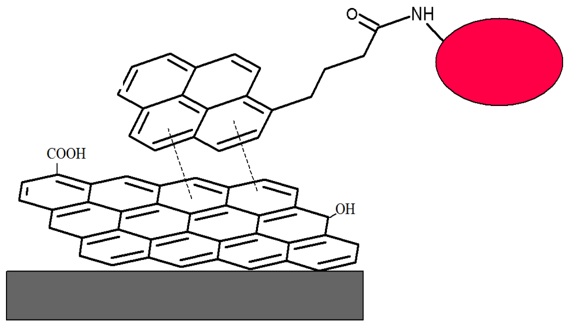


Fig.1. Pyrene-functionalized reduced graphene oxide with bilirubin oxidase

References

[1] A. Star, Y. Liu, K. Grant, L. Ridvan, Macromolecules, vol. 36, no. 3. pp. 553–560, 2003.
[2] Lalaoui N, Le Goff A, Holzinger M., Chemistry. Feb 16;21(8):3198-201, 2015.
[3] S. Krishnan and F. a. Armstrong, Chemical Science, vol. 3, no. 4. p. 1015, 2012.

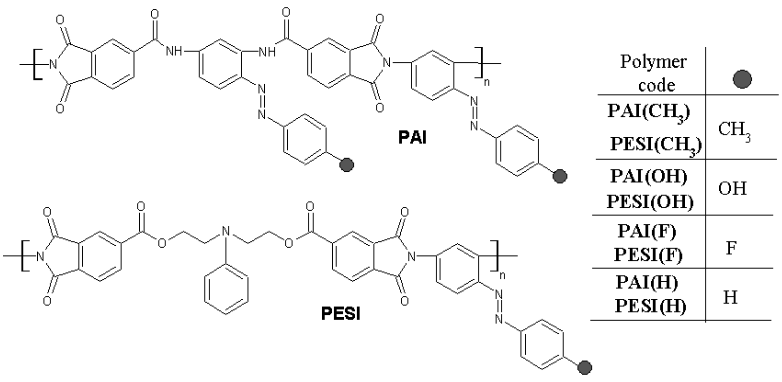
Physicochemical investigations of azopolyimides

J. Konieczkowska[1], A. Kozanecka-Szmigiel[2], R. Węgłowski[3], W. Piecek[3], E. Schab-Balcerzak[1]

[1]Centre of Polymer and Carbon Materials PAS, 34 Marii Skłodowskiej-Curie Str., 41-819 Zabrze, Poland
[2]Faculty of Physics, Warsaw University of Technology, 75 Koszykowa Str.,
66-662 Warsaw, Poland
[3]Institute of Applied Physics, Military University of Technology,
2 S. Kalińskiego Str., 00-908 Warsaw, Poland

Abstract

Azobenzene polymers *i.e.* the polymers containing the azobenzene moieties are known from their exceptional potential for technological applications as materials for applications in optical devices [1]. Here, we report the synthesis and characterization of a series of poly(amide imide)s (PAI) and poly(ester imide)s (PESI) bearing azobenzene units with different substituent in *para*-position (Fig. 1). We investigate the influence of the polymer structure on the selected polymers properties, such as the solubility, thermal stability, supramolecular structure and linear optical properties. We also investigate the POA by the photoinduced birefringence (*Δn*). For these polymers a large birefringence (~ 0.06). Moreover, the birefringence generated in poly(amide imide)s showed an extraordinary stable behavior in the dark, remaining its value on the ca. 98% level [2]. To compare, poly(ester imide)s are characterized by a maximum birefringence of order of ~ 0.02 and birefringence decrease in the dark by ca. 5-10% [3]. Recent studies have shown the ability of one of the developed poly(ester imide)s to align nematic liquid crystals.



Polymer code	●
PAI(CH_3) PESI(CH_3)	CH_3
PAI(OH) PESI(OH)	OH
PAI(F) PESI(F)	F
PAI(H) PESI(H)	H

Fig. 1. The chemical structure of the investigated polymers.

References

[1] A. Natansohn, P. Rochon. *Chem. Rev.* **102**, 4139 (2002).

[2] J. Konieczkowska, E. Schab-Balcerzak, M. Siwy, K. Switkowski, A. Kozanecka-Szmigiel, *Opt. Mater.* **39**, 199 (2015).

[3] A. Kozanecka-Szmigiel, J. Konieczkowska, D. Szmigiel, K. Switkowski, M. Siwy, P. Kuszewski, E. Schab-Balcerzak, *Dyes & Pigm.* **114**, 151 (2015).

Broadening of DFB laser wavelength tuning range achieved via FRET process

K. Parafiniuk, L. Sznitko, M. Żelechowska, J. Myśliwiec

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27,
50-370 Wrocław, Poland

Abstract

Here we report on the broad band distributed feedback (DFB) laser wavelength tuning in organic dye-doped polymeric layer. In order to expand the range of tunability we have utilized the mixture of organic dyes capable to act in process of Förster resonance energy transfer (FRET). As a donor compound we have used 3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (DCNP) luminescent dye, having relatively broad stimulated emission (STE) band itself. [1] As an acceptor we have chosen Rhodamine 700 (Rh700) laser dye because of its well-matched absorption band to the emission band of the donor. The dyes embedded in the poly(methyl methacrylate) (PMMA) host matrix, with different relative donor/acceptor ratio, were deposited onto glass substrates as thin films.

Temporary distributed feedback resonator in the planar waveguide was created using optical system based on degenerated two wave mixing of pumping Nd:YAG (second harmonic 532 nm) pulsed laser beams. Such approach results in formation of the interference pattern in the sample volume and generation of one-dimensional population diffraction grating which fulfils the Bragg condition for light amplification. Period of the interference pattern, and thus the period of DFB resonator, can be easily changed by changing the angle of intersection between pumping beams, what allows for laser emission tuning in a real time.

The components concentration optimization of the gain medium led to nearly twice broadening of STE spectral range, due to the utilization of both, donor as well as acceptor emission bands, what directly reflects in the ability of DFB laser wavelength tuning range. Moreover, additional random feedback, supported by DCNP crystals formed in the material, results in random lasing action along whole gain profile, while no well-defined DFB resonator inscribed.

Acknowledgements

We would like to thank the Polish National Science Centre for grant no. DEC-2013/09/D/ST4/03780 for financial support.

References

[1] K. Parafiniuk, L. Sznitko, J. Myśliwiec; Optics Letters 40(7) (2015) 1552

Random lasing in dye doped organic and biologically derivated polymers

K. Cyprych, L. Sznitko, J. Myśliwiec

Advanced Materials Engineering and Modelling Group, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract

Nowadays issue of lasing acquired on disordered media is becoming more and more popular. Such phenomenon known as random lasing, assumes formation and continuous rearrangement of random resonators [1], where multiple scattering simultaneously occurs with light amplification [2], result in generation of coherent or incoherent laser action [3]. Studies are being conducted in order to define optimal parameters to obtain random lasing of desired properties according to wavelength, resolution and photostability. Highly developing are also topics of tunable random lasing [4] and studies based on materials modification with the purpose of acquiring effective new materials having low lasing generation threshold [5].

Within this work we would like to present possible modifications of materials in order to manipulate the coherence of lasing generated in polymeric materials doped with fluorescence dyes, tunability of lasing action and application of new materials in RL. Our system are based on organic polymeric matrices (PVK, PMMA) and biopolymers (starch, liposomes, DNA, DNA-CTMA) doped with well-characterized laser dyes like DCM, DCNP or Rhodamine 6G. Dye-doped polymeric matrices prepared with drop casting method were optically pumped with Nd:YAG laser beam of nanosecond duration. Sample roughness manipulation was followed by mechanical modifications resulting in lasing coherence modification.

This work was supported in part by National Science Centre DEC-2013/09/D/ST4/03780, DEC-2013/11/N/ST4/01488.

References

[1] Wiersma, D.S., *Nat. Photonics*, 2013. **7**(3): p. 188-196.
[2] Polson, R.C. and Z.V. Vardeny, *Appl. Phys. Lett.*, 2004. **85**(7): p. 1289-1291.
[3] Redding, B., S.F. Liew, R. Sarma, and H. Cao, *Nat. Photonics*, 2013. **7**(9): p. 746-751.
[4] Cyprych, K., L. Sznitko, and J. Myśliwiec, *Org. Electron.*, 2014. **15**(10): p. 2218-2222.
[5] Sznitko, L., A. Szukalski, K. Cyprych, P. Karpinski, A. Miniewicz, and J. Myśliwiec, *Chem. Phys. Lett.*, 2013. **576**: p. 31-34.

Energy transfer mechanisms in Yb^{3+} and Bi^{3+} co-doped $GdVO_4$ phosphor

K. Lenczewska, D. Hreniak

Department of Spectroscopy of Excited Stated, Institute of Low Temperature and Structure Research
Polish Academy of Sciences, Okólna 2, 50-422, Wrocław, Poland

Abstract

The orthovanadate $GdVO_4$ is an attractive host lattice for several lanthanide ions to produce efficient phosphors emitting a variety of colours because of the efficient resonant energy transfer from the host to the lanthanide ions. This is also an interesting case for studying of energy transfer in co-doped systems, where energy transfer occurs between the transition metal and lanthanide ions. The nanocrystals of $GdVO_4$ co-doped with Bi^{3+} and Yb^{3+} ions in various concentration ratios were synthesized by a modified Pechini method. Effects of the presence of Bi^{3+} dopant on photoluminescence properties of $GdVO_4:Yb^{3+}$ nanocrystals, especially the analysis of cooperative processes was performed. In the studied system the Bi^{3+} ion has a role of sensitizer for lanthanide dopant (Yb^{3+}), enhancing the broadness of the excitation band and improving the emission intensity [1]. On the other hand, it can be observed an intense NIR luminescence, resulting from the energy transfer between the host or Bi^{3+} ions to Yb^{3+} ions. Therefore it is possible also to achieve a near-infrared quantum cutting via cooperative energy transfer (CET) process [2,3] and the $GdVO_4:Bi^{3+}$, Yb^{3+} system can be a candidate e.g. for efficient downconverting luminescent concentrators of incident broad band UV into Vis / NIR emission [4].

In this work, in particular the mechanisms of energy transfer occurring in the $GdVO_4:Bi^{3+}$, Yb^{3+} system depending on the concentration of both dopants were investigated.

References

[1] X. Y. Huang, J. X. Wang, D. C. Yu, S. Ye, Q. Y. Zhang, X. W. Sun, *J. Appl. Phys.* **109**, 113526 (2011).

[2] U. Rambabu, Sang-Do Han, *Ceramics International* **39**, 1603 (2013).

[3] X. Y. Huang, Q. Y. Zhang, *J. Appl. Phys.* **107**, 063505 (2010).

[4] G. Jiang, X. Wei, Y. Chen, M. Yin, *J. Nanosci. Nanotechnol.* **11**, 9484 (2011).

The Influence of Silver Nanoparticles on Sulphur Compounds Sensing by ZnO Gas Sensors

P. Suchorska-Woźniak, W. Nawrot, H. Teterycz

Laboratory of Chemical Sensor Diagnostics and Nanostructure Technology, Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology, ul. Janiszewskiego 11-17, 50-370, Wrocław

Abstract

Bulk doping is the most common method for improving both sensitivity and response times of chemical resistive gas sensors [1]. Generally used dopants are noble metals, such as gold, platinum or palladium. They form multiple Schottky junctions with semiconductor [2], which results in a band gap modification. Moreover such dopant can act as a catalyst. In this work results of doping ZnO thick film resistive gas sensor with silver nanoparticles are presented. The additive had been characterised in respect of particle size and purity. Developed structures were analysed against sulphur compounds, such as hydrogen sulphide and dimethyl sulphide. Sensitivity, response and recovery times were measured.

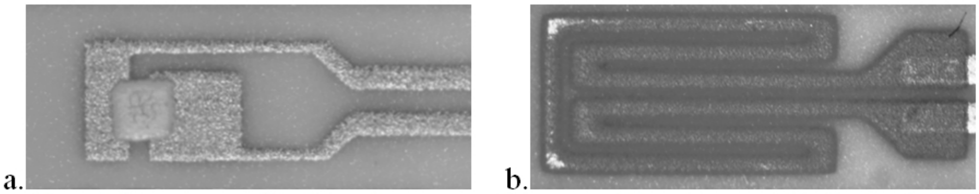


Fig. 1. Structure of analysed sensors: a) gas sensitive layer with electrodes, b) platinum heater on the reverse side.

Acknowledgments

Scientific work was financed by Polish Ministry of Science and Higher Education from funds for young researchers and PhD students as well as by National Science Centre as a project no. DEC-2012/07/N/ST7/02304.

References

[1] H. Teterycz "*Thick-film gas sensors based on tin dioxide*", Wrocław, Oficyna Wydawnicza Politechniki Wrocławskiej (2005)

[2] J. Guo, J. Zhang, H. Gong, D. Ju, B. Cao, *Sensors and Actuators B: Chemical* **226**, 266-272 (2016)

Tuesday

19.04.2016

Invited Lecture

What can we learn from studying single molecules ?

J. Waluk[1,2]

[1]*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland*
[2]*Faculty of Mathematics and Natural Sciences, College of Science, Cardinal Stefan Wyszyński University, Dewajtis 5, 01-815 Warsaw, Poland*

Abstract

The ability to monitor structure and dynamics of single molecules opens up new perspectives in fundamental research and nanotechnology. I will present basic experimental techniques and discuss the results of investigations of single molecules using three different methodologies: fluorescence [1-4], Raman [5], and scanning tunneling microscopy [6-8]. Our work focuses on tautomerization in porphycene (Fig. 1), a porphyrin isomer with exceptionally strong intramolecular hydrogen bonds. Studies of single porphycene molecules show interconversion between two different tautomeric forms, *trans* and *cis*, a process that could not be observed by experiments performed for bulk samples. It is also possible to exploit tautomerization for extracting information on 3D orientation of a single chromophore [2]. Finally, differences in photostability of single molecules embedded in different polymer matrices [4] will be discussed.

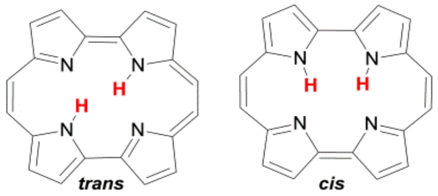


Fig. 1. Tautomeric forms of porphycene.

References

[1] H. Piwoński, C. Stupperich, A. Hartschuh, J. Sepioł, A. Meixner, J. Waluk, *J. Am. Chem. Soc.* **127**, 5302 (2005).
[2] H. Piwoński, A. Hartschuh, N. Urbańska, M. Pietraszkiewicz, J. Sepioł, A. Meixner, J. Waluk, *J. Phys. Chem. C* **113**, 11514 (2009).
[3] H. Piwoński, A. Sokołowski, , M. Kijak, S. Nonell, J. Waluk, *J. Phys. Chem. Lett.* **4**, 3967 (2013).
[4] H. Piwoński, A. Sokołowski, J. Waluk, *J. Phys. Chem. Lett.* **6**, 2477 (2015).
[5] S. Gawinkowski, M. Pszona, A.Gorski, J. Niedziółka-Jönsson, I. Kamińska, W. Nogala, J. Waluk, *Nanoscale* **8**, 3337 (2016).
[6] T. Kumagai, F. Hanke, S. Gawinkowski, J. Sharp, K. Kotsis, J. Waluk, M. Persson, L. Grill, *Nature Chem.* **6**, 41 (2014).
[7] T. Kumagai, F. Hanke, S. Gawinkowski, J. Sharp, K. Kotsis, J. Waluk, M. Persson, L. Grill, *Phys. Rev. Lett.* **111**, 246101 (2013)
[8] J. N. Ladenthin, L. Grill, S. Gawinkowski, S. Liu, J. Waluk, T. Kumagai, *ACS Nano* **9**, 7287 (2015).

Ultrathin Poly(3-hexylthiophene) Films with Controllable, Nanofibrill Morphology for Application in Organic, Field-effect Transistors

Ł. Janasz[1], M. Gradzka[2], D. Chelbosz[2], A. Kiersnowski[2], W. Pisula[3], K. Müllen[3], J. Ulański[3]

[1]Department of Molecular Physics, Łódź University of Technology, Zeromskiego 116, 90-924, Łódź, Poland

[2]Polymer Engineering & Technology Division, Wrocław University of Technology, Norwida 4/6, 50-373 Wrocław, Poland

[3]Max Planck Institute for Polymer Research, Ackermannweg 10, 55-128, Mainz, Germany

Abstract

Poly(3-hexylotiophen) due to its stable and efficient semiconducting properties is widely used as hole-transporting (p-type) active material for application in organic, photo-voltaic cells (OPVs) or organic, filed-effect transistors (OFETs) [1]. Morphology of the semiconducting, polymeric film plays a crucial role in obtaining efficient charge transport properties and thus higher performance of fabricated devises [2]. Pre-aggregation of P3HT in solution leads to a network of elongated nanofibrill structures in deposited active films [2]. Such morphology tends to significantly increase charge carrier mobility in OFETs [3]. We present a systematic approach of controlling the nanofibrill morphology of ultrathin (thickness below 10nm) P3HT films in terms of density and length of fibrillic aggregates. Impact of obtained morphology is correlated with working parameters of produced OFETs. By providing a dense network of nanofibills charge carrier mobility of 0.1 cm^2/Vs can be achieved for OFETs with 8 nm thick P3HT film.

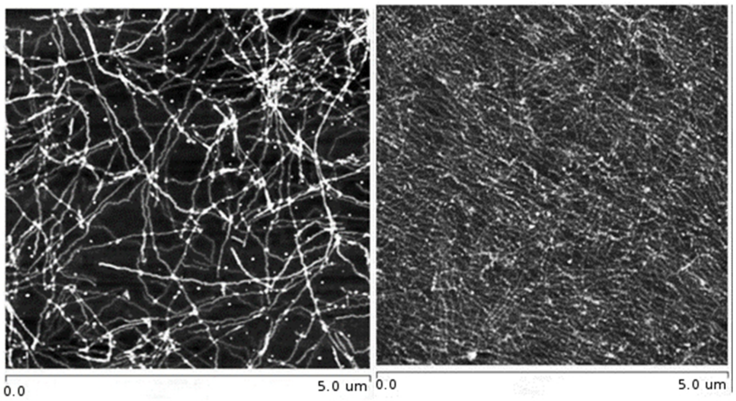


Fig.1. Examples of nonofibtill morphology in ultrathin P3HT layers

References

[1] S. Holliday *et al., Chem. Mater.* 26, 647−663 (2014).
[2] H. Tsao *et al., Chem. Soc. Rev.* 39, 2372–2386 (2010).
[3] H. Hu *et al,. J. Mater. Chem. C*, 3, 7394 (2015).

The authors gratefully acknowledge the financial support of this research by the National Science Centre of Poland, grant NCN Harmonia 2013/08/M/ST5/00914 and by the Polish Science Foundation, grant FNP Mistrz 9/2013.

Spontaneous Second Harmonic Generation through Organogelation

F. Aparicio,[1] B. Marco,[2] L. Faour,[1] K. Iliopoulos,[1] B. Sahraoui,[1] D. Gindre,[1] S. Franco,[2] R. Andreu,[2] D. Canevet,[1] M. Sallé.[1]

[1]*Laboratoire MOLTECH-Anjou, Université d´Angers 2, Bd Lavoisier, 49045 Angers Cedex 01, France*
[2]*Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain*

Abstract

Important efforts are continuously dedicated to the development of higher efficiency organic and Second Harmonic Generation (SHG) active materials for applications in photonics, optoelectronics or anti-counterfeiting. [1,2]

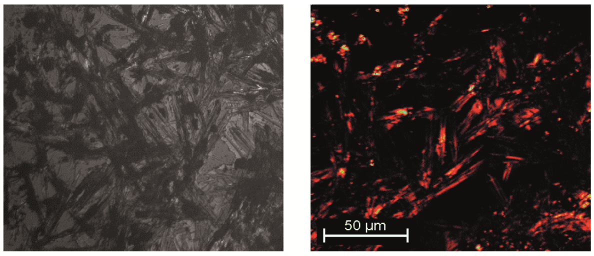


Fig.1. Optical micrograph (left) and corresponding SHG image (right) obtained from one NLO-active gel under study.

Our strategy [3] lies on the supramolecular gelation of nonlinear optically (NLO)-active compounds. The corresponding materials display a SHG response without any need for pre-processing and this activity proves to be stable over several months (Fig. 1). These findings, based on an *intrinsic* structural approach, are supported by favorable supramolecular interactions, which locally promote a non-centrosymmetric NLO-active organization. This is in sharp contrast with most SHG active materials, which generally require the use of expensive or heavy-to-handle *external* techniques for managing the dipoles alignment.

References

[1] G. Zerbi, *Organic Materials for Photonics : Science and Technology*; Elsevier (1993).
[2] K. Iliopoulos, O. Krupka, D. Gindre, M. Sallé, *J. Am. Chem. Soc.* **132**, 14343 (2010).
[3] B. Marco, F. Aparicio, L. Faour, K. Iliopoulos, B. Sahraoui, D. Gindre, S. Franco, R. Andreu, D. Canevet, M. Sallé, *Submitted.*

Electric properties of spatially confined OCS molecule - the directional character of orbital compression

M. Chołuj, W. Bartkowiak

Department of Physical and Quantum Chemistry, Faculty of Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, Wrocław 50-370, Poland

Abstract

The studies of molecular systems in spatial confinemnet has become a topic of great significance during the past few decades and increasingly attract attention of researchers from various fields of science. Among many physical and chemical properties, strongly affected by the confining environment, the linear and nonlinear optical properties are of particular importance.

The exposure of a molecular system to the spatial confinement usually leads to a decrease of the linear and nonlinear optical response of this system. Nevertheless, some important examples, which do not follow this rule, have been demonstrated in the literature [1,2]. One of these examples is carbonyl sulfide (OCS) molecule. It was shown that in the presence of cyllindrical harmonic oscillator potential, employed in order to render the confining environment, the electric properties of OCS indicate very unusual behaviour [3]. Therefore, the purpose of this study is to analyze the influence of spatial confinement on the dipole moment, polarizability and first hyperpolarizability of OCS molecule using supermolecular approximation, which is, next to the external analytical potentials, the most commonly used technique in quantum chemical studies of spatial confinemnet. To represent the chemical confining environment, various number of helium atom probes, at different orientations and distances from the OCS molecule, are used. Such approach allows to distinguish the orbital compression effect among other factors, which affect the electric properties of spatially restricted molecule. Our results demonstrate that the investigated electric properties strongly depend on the topology of confining environment, which proves the directional character of orbital compression.

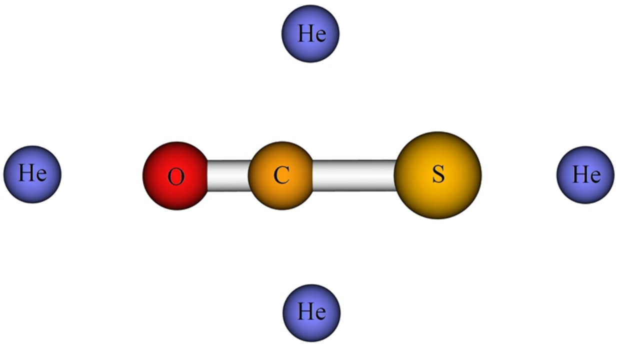


Figure 1. OCS molecule embedded in helium confining environment

References

[1] R. Zaleśny, R. W. Góra, J. Kozłowska, J. M. Luis, H. Ågren, W. Bartkowiak, *J. Chem. Theory Comput.* **9** 3463 (2013).
[2] M. Chołuj, J. Kozłowska, A. Roztoczyńska, W. Bartkowiak, *Chem. Phys.* **459** 24 (2015).
[3] J. Kozłowska, A. Roztoczyńska, W. Bartkowiak, *Chem. Phys.* **456** 98 (2015).

The living as reaction media: towards the development of bio-specific and chemo-switchable therapeutic agents

A. Wagner

Research Director CNRS
Laboratory of Functional ChemoSystem, UMR 7199 – LabEx MEDALIS

Abstract

The development of chemical reactions that are compatible with biological media has attracted increasing attention over the past decade. These reactions, qualified as bio-orthogonal when they can take place in a complex biological medium without distorting it, or as bio-specific when they touch only a precise part of it, opened the door to new methods of exploring complex phenomenon. Progress in controlling these bio-functional reactions quickly helped to increase the significance of the studies from *in vitro* model to cellular environments and finally to living organisms. Further integration of such chemistry driven endeavor to therapeutic approaches contributed to the birth of chemical-biology.

Taking advantage of imaging and bio-analytic methods we have developed original chemometric methodologies to figure the bio-response profile of bond-forming and bond-breaking chemical reactions.

By applying this methodology, we were able to characterize novel functional groups that exhibit a clean activation profile but also to uncover unexpected bio-specificity. We will focus on recent results obtained on functional groups that undergo cleavage in response to biothiols or bioacidity miss regulation.

As part of the study to be presented we will also show that it is possible, through a bio-orthogonal reaction, to alter the molecular structure of a drug after its administration in live animal. This strategy allowed to switch a compound from a bioactive state to a bio-inert state and concomitantly to switch from a long circulating to a fast excretion compound. This case-study illustrates the need of integrating into the periphery of chemistry a variety of knowledge and technologies from different research area i.e. analytical chemistry, medicinal chemistry, pharmacology, metabolomics, cell biology, development of animal models.

Development of a droplet-based microfluidic process for biomolecule capture, purification and detection at the single-cell level

S. Ursuegui[1], K. Pernod[3], H. Cockenpot[2], G. Lamanna[1], M. Ryckelynck[3], A. Griffiths[2], A. Wagner[1]

[1]Systèmes Chimiques Fonctionnels, UMR 7199 CAMB, Faculté de Pharmacie Illkirch, France
[2]Laboratoire de Biochimie, ESPCI Paris Tech, France
[3]Architecture et Réactivité de l'ARN, CNRS-UPR 9002, IBMC Strasbourg, France

Abstract

Droplet-based microfluidic has emerged as a powerful miniaturized platform allowing the reliable production of compartmentalized micro-meter sized incubators in which complex systems can be isolated and manipulated at high throughput rates [1]. This technology has largely contributed to the recent developments in single-cell analysis notably for genomic studies at the single-cell level [2]. In droplet-based microfluidic, fluorosurfactants are essential to ensure the stability of the microemulsion. Beyond this primary role, fluorosurfactants can be engineered to provide droplet inner surface specific interaction characteristics with analytes present in droplet content. Despite the high potency of such capture system in term of micro-compartmentalization and surface/analyte ratio, only few studies have reported the use of the water/fluorinated oil interphase to immobilize target molecules [3]. In this project, we developed specific functionalized fluorosurfactants able to generate custom-made interphase and provide efficient capture system at the microdroplet inner surface via affinity interaction or bioorthogonal ligation.

First, fluorinated surfactants bearing a biotin moiety were specifically designed and synthesized for protein capture and purification after single-cell compartmentalization and lysis in microdroplets containing affinity capture system at the interphase. This affinity capture system has been coupled to an innovative purification process by phase inversion which allows separation of captured proteins from the other cellular components under smooth and efficient conditions preserving their integrity.

In a second approach, we are investigating a ready-to-use click chemistry-based approach that enables intra-droplet chemical modification. This strategy opens access to a wide variety of functional heads via Copper-free click chemistry using a pre-functionalized fluorosurfactant. For this purpose, we have synthesized an azide fluorosurfactant capable of stabilizing microdroplets and performed intra-droplet surface functionalizations by introducing fluorescent-labeled cycloalkyne derivatives in the aqueous phase. Furthermore we also showed that the density of azide function at the inner surface could be adjusted by diluting the functionalized surfactant in a non-functionalized one. Fluorescence polarization analysis revealed that these dilutions result in the production of microdroplets with controlled azide surface density. The control of fluorosurfactants synthesis and intra-droplet functionalization opens interesting prospects for the droplet microfluidic development approaches relying on specific capture at the W/O interface.

References

[1] a) A. B. Theberge, F. Courtois, Y. Schaerli, M. Fischlechner, C. Abell, F. Hollfelder, W. T. S. Huck, Angew. *Chem. Int. Ed.*, 2010, **49**, 5846–5868. b) A. D. Griffiths, D.S., Tawfik, *Trends Biotechnol.*, 2006, **24**, 395-402. c) H. Song, D. L. Chen, R. F. Ismagilov. Angew. *Chem., Int. Ed.*, 2006, **45**, 7336-7356.

[2] a) H. N. Joensson, H. Svahn, *Angew. Chem. Int. Ed.*, 2012, **51**, 12176–12192. b) A. Rakszewska, J. Tel, V. Chokkalingam, W. T. S. Huck, *NPG Asia Materials*, 2014, **6**, e133.

[3] a) J. E. Kreutz, L. Li, S. Roach, T. Hatakeyama, R. F. Ismagilov, *J. Am. Chem. Soc.*, 2009, **131**, 6042–6043. b) Platzman, J. W. Janiesch, J. P. Spatz, *J. Am. Chem. Soc.*, 2013, **135**, 3339–3342. c) A. B. Theberge, G. Whyte, M. Frenzel, L. M. Fidalgo, R. C. R. Wootton, W. T. S. Huck, *Chem. Commun.*, 2009, 6225–6227. d) D. J.Holt, R. J. Payne, C. Abell, *J. Fluorine Chem.*, 2010, **131**, 398–407.

Investigation of fluorescence properties of single quaternary alloyed Ag-In-Zn-S nanocrystals

D. Buczyńska[1], P. Bujak[2], A. Proń[2], S. Maćkowski[1]

[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland
[2] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Abstract

We studied nanocrystals in the form of an alloy of $AgInS_2$ and ZnS. Alloying $AgInS_2$ and ZnS yields nanocrystals with bandgap energies between 1.87 eV and 3.7 eV, which are energy bandgaps of the respective bulk materials. Bandgap energies can be tuned by changing the ratio of $AgInS_2$ and ZnS in the structure by varying the ratios of precursors, temperature of synthesis reaction etc. [1].

A set of three AgInZnS quaternary alloyed nanocrystals, with ZnS or CdS shell and without a shell, were studied. The nanocrystals in chloroform feature wide fluorescence spectra spanning from ~450 nm to ~750 nm.

Emission spectra show that compared to nanocrystals without the shell, there is more pronounced emission of lower energy photons for the AgInZnS/CdS nanocrystals, while for the AgInZnS/ZnS nanocrystals emission intensity is higher for higher photon energies. Single nanocrystals were studied using a wide-field fluorescence microscope [2].

A series of movies were collected for each sample. We find blinking behavior for majority of the high intensity spots visible in the images. In addition series of fluorescence intensity maps were collected for the wavelengths of 550, 610 and 675 nm within the emission band of the AgInZnS NCs' fluorescence.

Analysis of collected time traces measured for the core/shell structures, indicate that the on-times are not significantly affected by the presence of a particular shell, in spite of the differences in emission spectra. The analysis of fluorescence intensity maps for different observation wavelengths shows limited overlap between positions of single fluorescent spots observed at 550 nm and 675 nm indicating that samples contain fractions of nanocrystals that emit light at different wavelengths.

This work was supported by the National Research and Development Center (NCBiR) under Grant ORGANOMET No: PBS2/A5/40/2014.

References

[1] G. Gabka et al., *Inorganic Chemistry* 53, 5002-5012 (2014).
[2] D. Kowalska et al., *The Scientific World Journal* 2013 (2013).

How to measure the two-photon cross section of a coordination polymer?

J. K. Zaręba[1], R. Medishetty[2], M. Nyk[1], R. A. Fischer[2], M. Samoć[1]

[1] *Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

[2] *Inorganic Chemistry II-Organometallics and Materials Chemistry, Ruhr University Bochum, Bochum, Germany*

Abstract

Z-scan is an effective method for determination of both nonlinear absorption and nonlinear refraction coefficients for a variety of materials such as organic dyes, metal complexes, soluble polymers, semiconductor quantum dots and many more [1]. A proper evaluation of nonlinear parameters relies on the quality of two main factors: the laser beam parameters (intensity, spatial profile, and repetition rate) and the sample characteristics (uniformity, photostability, low scattering).

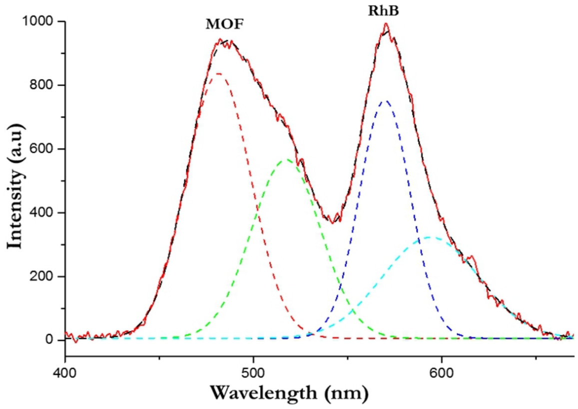


Fig. 1. Two-photon excited emission from MOF (left) and rhodamine B (right)

A crucial condition which should be met while performing a Z-scan is that the transmitted beam detected by open- and closed-aperture detectors should preserve its coherent character. When the laser radiation is lost in a process other than absorption events, such as an excessive scattering of the beam, then results become unreliable. Thus, for solid samples of certain crystallinity and/or of big grain size (> 100 nm), such as coordination polymers, a method other than Z-scan should be applied.

To address this issue we have introduced a new approach for σ_2 measurements of strongly scattering dispersions, which is a modification of TPEF (two-photon excited fluorescence) technique [2]. In our setup we measure simultaneously the two-photon induced emission from a solution containing both the sample and a reference so the scattering losses are the same for both species. (Fig. 1) In this presentation an explanation of the experimental conditions and results obtained using this method for highly emissive pyrene-based CPs will be briefly presented.

Acknowledgements

We acknowledge financial support from the National Science Centre under the Maestro grant no. DEC-2013/10/A/ST4/00114.

References

[1] M. Samoć *et al.*, *MRS Proceedings* **1698** (2014)
[2] N. S. Makarov, M. Drobizhev, A. Rebane, Opt. Express **16** , 4029 (2008)

Wednesday

20.04.2016

Conjugated Polymers in Ultrathin Film Field-Effect Transistors

W. Pisula,[1,2] Ł. Janasz,[1] M. Li,[2] K. Müllen,[2] J. Ulański[1]

[1]*Department of Molecular Physics, Łódź University of Technology, Zeromskiego 116, 90-924 Łódź, Poland*
[2]*Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

Abstract

Organic field-effect transistors (OFETs) have attracted extensive attention due to their potential applications in flexible, large-area and low-cost electronic devices. The microstructure and molecular orientation relative to the substrate surface have vital influence on device performance.

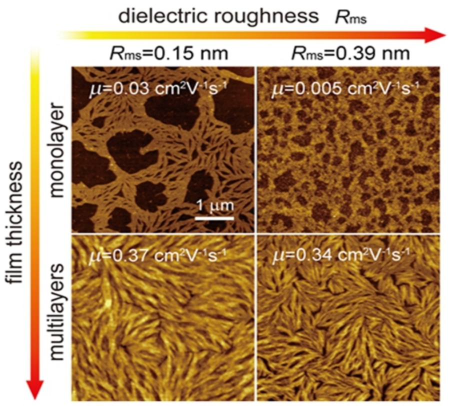


Figure 1. Relation between surface roughness, microstructure and charge carrier transport.

In this work, we present the effect of the first layers on the structure growth in the bulk film and the thickness dependence on the charge carrier mobility [1,2]. Furthermore, it is shown how the surface roughness of the dielectric is precisely tuned allowing a fine control over solely the interfacial microstructure in the semicrystalline semiconductor polymer film without affecting the morphology in the upper layers [3,4].

This work was supported by grant 2013/08/M/ST5/00914 of the Polish National Science Centre and by grant Master 9./2014 of the Foundation for Polish Science. We acknowledge the BL09 beamline at DELTA synchrotron in Dortmund for support for GIWAXS measurements.

References

[1] S. Wang, A. Kiersnowski, W. Pisula, K. Müllen, *J. Am. Chem. Soc.* **134**, 4015, (2012).
[2] M. Li, C. An, W. Pisula, K. Müllen, *Small* **10**, 1926 (2014).
[3] M. Li, C. An, T. Marszałek, M. Baumgarten, K. Müllen, W. Pisula, *Adv. Mater.* DOI: 10.1002/adma.201503552 (2016).
[4] M. Li, T. Marszalek, Y. Zheng, I. Lieberwirth, K. Müllen, W. Pisula, submitted, 2016.

The influence of amyloid fibrils presence on the common laser dyes luminescence and lasing performance

L. Sznitko[1], P. Hańczyc[2], A. Heeger[2], A. Justyniarski[1], M. Samoć[1], J. Myśliwiec[1]

[1]Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370, Wrocław, Poland
[2]Center for Oligomers & Organic Solids, University of California, Santa Barbara, 2520A Physical Sciences Building North, Santa Barbara, United States

Abstract

The main goal of presented research was to check if the presence of amyloids can affect the laser emission of two common laser dyes: the Rhodamine 6G and Stilbene 420. We have tested the influence of lyzosyme and insulin types of amyloids on the emission in water solutions and in solid layers. Both of the used proteins are containing negatively and positively charged amino acids, so they can electrostatically interact with dye molecules introduced to the sample as a chloride salt in case of Rhodamine 6G and sulfonic acid sodium salt in case of Stilbene 420. The Linear Dichroism (LD) measurements confirmed that Stilbene 420 molecules can bind to the amyloid fibrils contrary to Rhodamine 6G for which LD signals were almost two orders of magnitude weaker, what can be linked to low pH = 2.0 of amyloid solutions. For the second case the matrix is forcing the aggregation process leading to so called molecular crowding. The complex morphology of solid layers of amyloids in both cases is responsible for possibility of random feedback constitution and therefore it has an influence on lasing performance [1-2].

Due to the presence of different negatively and positively charged groups amyloids are promising from the point of view of potential functionalization, like for example controlled by aggregation lasing tuneability [2].

Acknowledgements

We would like to thank the Polish National Science Centre for financial support (grant number: DEC-2013/09/D/ST4/03780).

References

[1] L. Sznitko, P. Hańczyc, J. Myśliwiec, M. Samoć, Appl. Phys. Lett. **106** (2015) 023702
[2] P. Hańczyc, L.Sznitko, Ch. Zhong, Alan J. Heeger, ACS Photonics **12** (2015) 1755-1762

Modeling the optical properties of fluorescent zinc probe using quantum-chemical methods

J. Bednarska[1], R. Zaleśny[1], W. Bartkowiak[1], N. Arul Murugan[2], H. Ågren[2], M. Odelius[3]

[1]Department of Physical and Quantum Chemistry, Faculty of Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, PL–50370 Wrocław, Poland; [2]Division of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, SE–10691 Stockholm, Sweden; [3]Division of Chemical Physics, Department of Physics, Stockholm University, SE-106 91 Stockholm, Sweden

Abstract

In this work we examine, by means of computational methods, the mechanism of Zn^{2+} sensing by bipyridine centered, D-π-A-π-D type ratiometric molecular probe. According to recently published experimental data, the probe after coordination to zinc ions exhibits large enhancement of the two-photon absorption cross section[1]. The goal of our investigations was to elucidate this phenomenon. For this purpose, linear and nonlinear optical properties of the unbound (cation-free) and bound probe were calculated using polarizable continuum model as well as employing QM/MM approach. Results of our simulations demonstrate that one-photon absorption bands for the both forms correspond to bright $\pi\rightarrow\pi^*$ transition to the first excited state which, on the other hand, exhibits much smaller two-photon activity than the second excited state. Moreover, there is an experimental evidence that a red shift of absorption band upon zinc ion coordination takes place. Due to the fact that experimental two-photon absorption spectrum was measured in the narrow range (760–840 nm), we put forward a notion that observed 13-fold enhancement in TPA cross section upon ion binding corresponds to the transition to the second excited state. Since the results of calculations indicate that many probe conformers are present in the solution at room temperature, structure-property relationships were also taken into account.

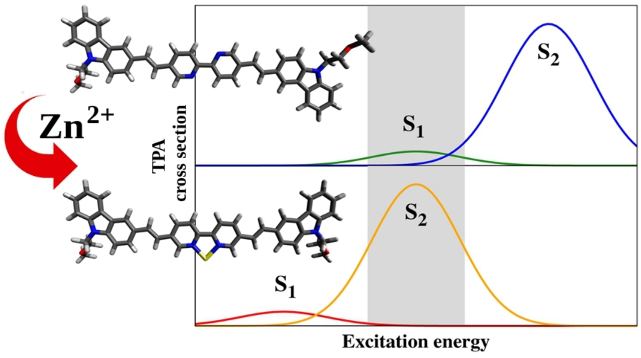


Fig. Schematic representation of suggested mechanism of Zn^{2+} sensing by bipyridine probe

Acknowledgements

The work was supported by a subsidy from the Polish Ministry of Science and Higher Education (Grant No. 0237/DIA/2014/43).

References

[1] K. P. Divya, S. Sreejith, P. Ashokkumar, K. Y., Qiwen Peng, S. K. Maji, Y. Tong, H. Yu, Y. Zhao, P. Ramamurthy and A. Ajayaghosh, Chem. Sci. , 2014, 5, 3469

Plasmonic band gap and plasmonic band edge resonances probed by second harmonic generation

R. Kołkowski[1,2], J. Szeszko[3], B. Dwir[3], E. Kapon[3], J. Zyss[2]

[1] *Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, ul. Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

[2] *Laboratoire de Photonique Quantique et Moléculaire, École Normale Supérieure de Cachan, 61 Avenue du Président Wilson, 94230 Cachan, France*

[3] *Laboratory of Physics of Nanostructures, École Polytechnique Fédérale de Lausanne, 1015, Lausanne, Switzerland*

Abstract

Surface plasmon polaritons (SPPs) are excitations of electron plasma oscillations which can propagate across the metal-dielectric interface. By analogy with photonic crystals, a periodic metallic nanostructure with lattice constants in the range of SPP wavelength can be called “plasmonic crystal”. Such kind of meta-surface should possess a band structure featuring forbidden energy gaps where SPPs cannot exist.

We investigate backscattered second harmonic generation (SHG) excited by a normally incident femtosecond laser beam (λ = 900 nm) in rectangular arrays of tetrahedral cavities (“pyramids”, Fig. 1a) of various lattice parameters. It is found that the nonlinear emission is almost completely extinguished inside the plasmonic band gap, while being strongly enhanced by plasmonic standing waves formed at the band edge near the Γ point (Fig. 1b). Both effects enable very efficient control over the magnitude and symmetry of the effective second order susceptibility tensor [1].

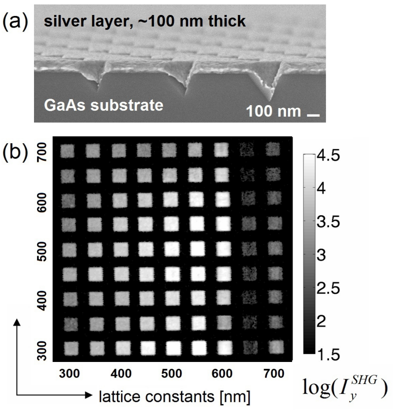


Fig. 1. (a) SEM image of a plasmonic crystal in cross section. (b) SHG image of an array of plasmonic crystals of various lattice constants, showing the effect of plasmonic band gap at periodicity 650 nm. The intensity scale is logarithmic.

References

[1] R. Kołkowski, J. Szeszko, B. Dwir, E. Kapon, J. Zyss, *Laser & Photonics Reviews* **10**, 287 (2016).

Lanthanide porphyrins in luminescence-based oxygen sensing

B. Kalota, M. Tsvirko

Institute of Chemistry, Environmental Protection and Biotechnology, Jan Długosz University, Armii Krajowej 13/15, 42-200 Częstochowa, Poland

Abstract

Luminescence-based oxygen sensing relies on quenching of luminescence by oxygen. It enables a determination of oxygen concentration with luminescence intensity or lifetime. Porphyrin ligands exhibit tunable photophysical properties by flexible structural modification abilities. Hence, in the last decades, a large number of oxygen sensitive metalloporphyrins were reported [1]. A great majority of the metalloporphyrins are based on platinum(II)- and palladium(II)-porphyrins which are less economically attractive than lanthanide porphyrins [2].

Lanthanide porphyrins are well-known as light-emitting materials [3], probes for luminescent diagnostics, photodynamic therapy [4], and as magnetic resonance imaging contrast agents [5], to mention only some. However, these moieties have recently attracted more attention as oxygen sensitive materials.

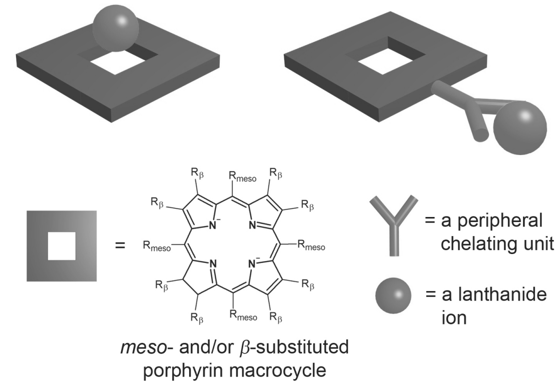


Fig. 1. Schematic presentation of the molecules discussed in the review.

We present the current state review of lanthanide porphyrins used in luminescence-based oxygen sensing. Porphyrin complexes including a lanthanide ion bound to the cavity of the porphyrin macrocycle as well as selected examples of lanthanide porphyrins with a lanthanide ion bound to a multidentate peripheral chelating unit are discussed (Fig. 1). We describe the design, photophysical properties, and luminescence-based oxygen sensing properties of the aforementioned molecules.

References

[1] X. D. Wang *et al.*, *Chem. Soc. Rev.* **43**, 3666 (2014).
[2] E. G. Ermolina *et al.*, *Dyes Pigm.* **97**, 209 (2013).
[3] H. He, *Coord. Chem. Rev.* **273-274**, 87 (2014).
[4] Yu. Korovin *et al.*, *Rev. Inorg. Chem.* **21**, 299 (2001).
[5] C. Chen *et al.*, *FEBS Lett.* **168**, 70 (1984).

Two-photon fluorescent anthracenyl probe for sensitive recognition and discrimination of Human Serum Albumin (HSA) from BSA and other biological interferents

M. Deiana[1], B. Mettra[2], L. Mazur[1], D. Pitrat[2], J. Olesiak-Bańska[1], C. Monnereau[2], C. Andraud[2], M. Samoć[1], K. Matczyszyn[1]

[1]Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław (Poland)

[2]Laboratoire de Chimie, CNRS UMR 5182, Ecole Normale Supérieure de Lyon, Université Lyon 1, Lyon, (France)

Abstract

The binding interaction of a biocompatible water-soluble polycationic two-photon fluorophore (**Ant-PIm**) towards serum albumin protein (HSA), was thoroughly investigated under simulated physiological conditions by using a combination of steady-state, time-resolved and two-photon excited fluorescence techniques. Emission properties of both **Ant-PIm** and the fluorescent amino acid residues in HSA underwent remarkable changes upon complexation allowing to accurately establish the thermodynamic profile associated to the **Ant-PIm**-HSA complexation. The marked increase of the **Ant-PIm** fluorescence intensity and quantum yield in the proteinous environment seemed to be the outcome of the attenuation of radiationless decay paths via the motional restriction imposed on the fluorophore. Fluorescence resonance energy transfer and site marker competitive experiments bring conclusive evidence regarding the binding site in which the association process takes place. The pronounced hypsochromic effect and increased fluorescence enhancement upon association with HSA, compared to BSA and other biological interferents, makes such probe a valuable sensing agent in rather complex biological environment, even allowing for naked eye discrimination between the closely related HSA and BSA. Furthermore, the high 2PA maximum located at 820 nm along with a $\sigma_2 > 800$ GM , and the marked changes in position and intensity of the band upon complexation, definitely makes **Ant-PIm** a promising probe for future sensing applications in biological environments.

Synthesis and Optical Properties of PbS Nanocrystals with Controlled Size

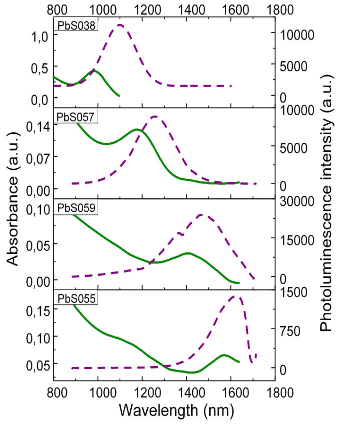
H. Woźnica, M. Bański, J. Misiewicz, A. Podhorodecki

Department of Experimental Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27,
50-370 Wrocław, Poland

Abstract

Colloidal Quantum dots (QDs) are of great interest in recent years, since they can be used in various fields, such as photovoltaics, light emitting devices, photodetectors or bio-imaging. However, practical application requires QDs with clearly defined size and shape. Literature studies reveal that using higher concentrations of free acid in the synthesis solution can increase the size of nanocrystals, due to its influence on the solute solubility and the nucleation process [1].

We synthesized colloidal PbS quantum dots using various concentration of oleic acid and their size dependence was studied. Absorbance and photoluminescence spectra indicate that the more acid is added to the reaction mixture, the bigger nanocrystals grow, with diameters ranging from 3.0 to 5.5 nm. These results were confirmed by the TEM and XRD analysis. Precise controlling of the nanocrystal dimensions is especially important, since it is known, that PbS quantum dots show some size-dependent properties [2,3]. Stokes shift and photoluminescence decay time for different QDs diameters were examined and their size-sensibility was investigated.



References

[1] S. Abe, R. K. Capek, B De Geyter, Z. Hens, *ACS Nano*, **7**, 943 (2013)

[2] J. H. Warner, E. Thomsen, A. R. Watt, N. R. Heckenberg and H. Rubinsztein-Dunlop, *Nanotechnology* **16**, 175 (2005)

[3] E. V. Ushakova, A. P. Litvin, P. S. Parfenov, A. V. Federov, M. Artmeyev, *ACS Nano,* **6**, 8913 (2012)

Two photon phenomena of gold nanoclusters

M. Waszkielewicz, J. Olesiak-Bańska, M. Samoć

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Technology, Wrocław 50-370, Poland

Abstract

Nanoclusters are very small metallic nanomaterials with size corresponding to the de Broglie wavelength of the conduction electrons, which place them between single metal atoms and nanocrystals [1]. Consisting of a few to a few hundred metal atoms stabilized with organic ligands, nanoclusters give distinct quantum-size effect which leads to a discrete electronic structure in the core. Although the linear optical properties have been systematically studied both experimentally and theoretically, optical properties in nonlinear regime were highly neglected. Only few results of measurements at a single wavelength are available and still large differences in the values of two-photon absorption (TPA) cross-sections have been reported (several hundred GM to several hundred thousand GM).

In this contribution we present a study of third-order nonlinear optical properties of captopril-protected gold clusters in a wide range of wavelengths. The nanoclusters were synthesized with size-focusing method by reduction with $NaBH_4$ [2]. The products characterization was performed by transmission electron microscopy (TEM) and spectroscopic methods (absorption, fluorescence, CD). To obtain a full TPA spectrum, the clusters were investigated with the z-scan technique and a wavelength-dependent interplay between two-photon absorption and saturable absorption phenomena was observed. In this presentation the main differences between nanoclusters and plasmonic gold nanoparticles will be discussed [3].

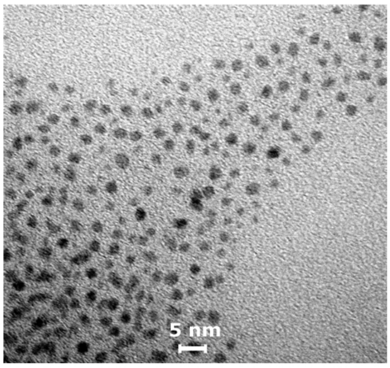


Fig. 1. TEM image of gold-captopril nanoclusters.

Acknowledgements

We acknowledge financial support from the National Science Centre under the Maestro grant no. DEC-2013/10/A/ST4/00114.

References

[1] J. Zheng, C. W. Zhang, R. M. Dickson, *Physical Review Letters* **93**, 077402 (2004).
[2] S. Kumar and R. Jin, *Nanoscale* **4**, 4222 (2012).
[3] J. Olesiak-Bańska, M. Gordel, R. Kolkowski, K. Matczyszyn and M. Samoć *J. Phys. Chem. C* **116**, 13731 (2012).

All-optical switching in pyrazoline based systems

A. Szukalski[1], A. Miniewicz[1], K. Haupa[2], D. Pisignano[3,4], J. Myśliwiec[2]

[1]*Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-320, Wrocław, Poland*
[2]*Deptartment of Applied Chemistry & Institute of Molecular Science National Chiao Tung University, Hsinchu, Taiwan*
[3]*National Nanotechnology Laboratory, CNR-Nano, Via Arnesano, I-73100, Lecce, Italy*
[4]*Department of Mathematics and Physics, University of Salento, Via Arnesano, I-73100, Lecce, Italy*

Abstract

In the beginning of XXI century, many research groups work on the organic and smart materials which could be used instead of the exploited inorganic ones. Organic materials are easy and cheap fabricated. They can be controlled during the process very easily in the meaning of size, shape and functionality. Moreover, organic materials can be biofriendly and much more associated with nature than inorganic systems such as metals, metal complexes, acids, salts, etc. Such biodegradable materials like DNA (also functionalized by different types of surfactants), starch, collagen etc. are commonly used for various photonic applications [1-3].

Here we present the results showing great potential in all-optical switching of organic hybrid systems based on DNA-CTMA and PMMA polymers, doped with pyrazoline derivatives - examples of typical *push-pull* type of low molecular compound. Using Optical Kerr Effect experiment as an example of 3rd order nonlinear optical phenomenon we have showed great potential of abovementioned system for ultrafast all-optical switching application in the form of thin films or fibers. Control only by light of full molecular alignment and physicochemical properties associated to two well-defined conformational states can be used for construction of fast organic optical switchers.

References

[1] A. Camposeo, P. Del Carro, L. Persano, K. Cyprych, A. Szukalski, L. Sznitko, J. Myśliwiec, D. Pisignano, *ACS Nano*, **8**, 10893 (2014).
[2] K. Cyprych, L. Sznitko, O. Morawski, A. Miniewicz, I. Rau, J. Myśliwiec, *J. Phys. D: Applied Physics*, **19**, 195101 (2015).
[3] K. Cyprych, L. Sznitko, J. Myśliwiec, *Organics Electronics*, **10**, 2218 (2014).

V. Posters

Tuesday

14.30-16.30

List of posters

P1	**Kacper Klarzyński**	Highly orientation-sensitive plasmonic nanoparticles
P2	**Karolina Smolarek**	Enhanced luminescence of organic light-emitting diodes with metallic nanoparticles
P3	**Katarzyna Jackiewicz**	Multiple emulsions obtained by membrane emulsification and their application in food and pharmaceutical industry
P4	**Mariusz Cyris**	Stabilization of liquid crystal phases with gold nanoclusters
P5	**Mariusz Grębowiec**	Towards efficient photoluminescence of gold-silver nanoclusters
P6	**Małgorzata Skibińska**	The structure of halloysite
P7	**Maciej Chrzanowski**	CdSe-CdS core-shell nanocrystals synthesis and spectroscopic investigations
P8	**Nina Tarnowicz**	Spectroscopic studies of three new azobenzene derivatives
P9	**Agnieszka Fiszka-Borzyszkowska**	The effect of sol-gel synthesis procedure on photocatalytic activity TiO2 modified by 2,5% CNTs
P10	**Alina Adamów**	Random lasing obtained on nematic liquid crystals doped with luminescent dye
P11	**Beata Jędrzejewska**	Photostability of 2-[4-(*N*,*N*-dimethylamino)styryl]-1*H*-phenanthro[9,10-d]imidazole upon one- and two-photon excitation
P12	**Anna Krukowska**	Environmental application of Er-doped $K_2Ta_2O_6$ photocatalysts
P13	**Justyna Grzelak**	Energy harvesting in up-converting nanocrystal/polymer blends
P14	**Dorota Chlebosz**	Crystal morphology and phase transitions of alkyl-substituted naphthalene and perylene diimide derivatives
P15	**Katarzyna Brach**	DNA liquid crystals doped with negatively charged gold nanorods
P16	**Magdalena Klekotko**	Synthesis of gold nanoparticles using green chemistry approach
P17	**Joanna Noga**	Willow structure formation in supramolecular azo-polymer complex by irradiation of single polarized laser beam

P18	**Kama Piskorek**	The environmental photonic sensor for protein toxin detection
P19	**Magdalena Ciesielska**	Antibacterial functionalization of fabrics by zinc oxide
P20	**Marta Lipka**	Amplified spontaneous emission in a perylene doped liquid crystalline system
P21	**Anna Pniakowska**	Gold plasmonic nanoparticles - synthesis and multiphoton imaging
P22	**Manuela Grelich**	Synthesis and thermal stability of model azobenzene switches used in biology
P23	**Magdalena Gołąb**	Synthesis of gold nanostars and characterization of the obtained structures
P24	**Anna Lesiak**	Nanocrystals functionalization by D-penicillamine
P25	**Wioletta Trzpil**	Synthesis and spectroscopic investigations of colloidal, anisotropic CdS nanostructures
P26	**Adam Łuczak**	Influence of moisture on performance of Organic Thin Film Transistors
P27	**Sebastian Mucha**	Influence of substituents on optical properties of geometric isomers of azobenzene derivatives - determination of the quantum yield and lifetime of fluorescence
P28	**Karolina Kinastowska**	Application of a new semiconductor polymer in non enzymatic NADH fotoregeneration

P1

Highly orientation-sensitive plasmonic nanoparticles

K. Klarzyński, R. Kołkowski, J. Olesiak-Bańska, M. Samoć

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, ul. Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract

We use COMSOL software to perform numerical simulations investigating theoretically the optical properties of triangular gold nanoparticles deposited on a glass substrate. A realistic geometry of the studied nanostructures, in a form of a triangular frustum (parallel truncation of a pyramid) with rounded corners and edges − as shown in Figure 1a − is created based on the TEM images of such nanoparticles obtained by wet-chemistry synthesis.

There are two possible orientations of these objects in respect to the substrate: one with larger base adjacent to the substrate, second - adjacent with smaller base. It is observed that the spectral position of the dipolar plasmon peak shifts by ~40 nm, from 680 to 640 nm (Figure 1b), which is due to the strong sensitivity of plasmon resonances to the refractive index of surrounding environment. This allows to determine the orientation of individual nanoparticles based on their spectroscopic response, for instance by means of spectrally-resolved dark field microscopy.

Moreover, thanks to their non-centrosymmetric shape and plasmonic field enhancement (reaching up to 260, see Figure 1b - insets), these nanoparticles may be used as efficient emitters of the second-harmonic generation (SHG), hence they can be imaged by nonlinear microscopy, where the effect of orientation should produce a dramatic difference in the SHG intensity. This aspect is being currently addressed in the ongoing research.

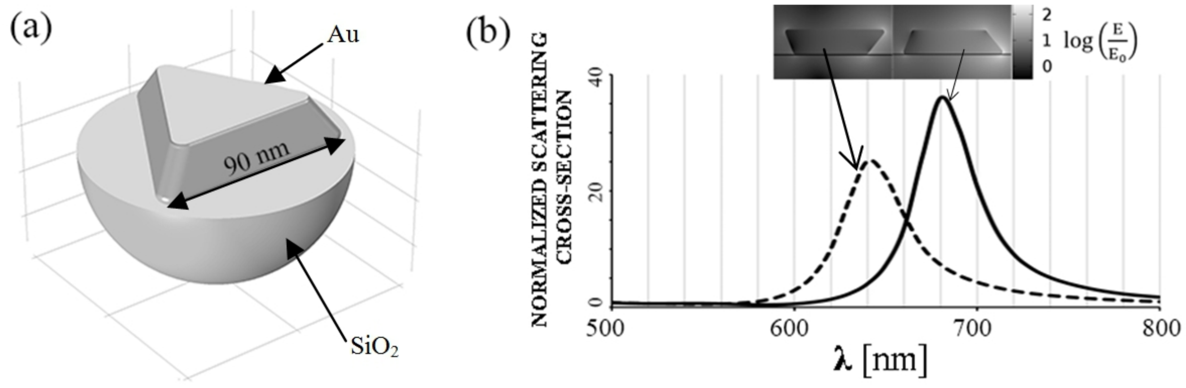


Fig. 1. (a) Geometry of the nanoparticles. Side length of larger base: ~90 nm, smaller base: ~70 nm, nanoparticle thickness: ~20 nm. (b) Scattering spectra of nanoparticles with different orientation in respect to the glass substrate. Insets: electric field distribution, showing plasmonic hot spots at the nanoparticle corners.

Enhanced luminescence of organic light-emitting diodes with metallic nanoparticles.

K. Smolarek, S. Maćkowski

Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziądzka 5, 87-100 Torun, Poland

Abstract

Thin film devices based on polymers and macromolecule materials like for example organic light emitting diodes (OLED) have a great attention as an alternative to traditional silicon inorganic technologies. They are expected to become key electronic components in the near future. To compete with currently used inorganic LEDs, OLEDs must have higher luminescence efficiency. Fabrication such devices is still a challenge.

It is well known that the fluorescence of the emitters can be enhanced when molecule is close to the metallic nanoparticle. The localized surface plasmon resonance enhances the optical fields and can improve the light absorption and emission process of fluorophores placed in a vicinity of metallic nanoparticles. Overlapping between nanoparticle absorption spectrum and the emission spectrum of the emitters generate resonance between the surface plasmons at the nanoparticles and the radiated light from the emitter thus enhancing the luminescence.

In this study we fabricated OLEDs based on polymers and macromolecules. Next to this OLED devices we added different metallic nanoparticles in order to test plasmonic enhancement effect. Using silver nanowires, gold island films, or silver island film we prepared devices with different geometry. Finally, to determine enhancement level we measured fluorescence intensity maps and electroluminescence spectra from these devices.

Further work will concentrate on optimizing the structure of the devices for better performance as well as elucidating the contributions of fluorescence and absorption rate increases towards the measured enhancement.

This work was supported by the National Research and Development Center (NCBiR) under Grant ORGANOMET No: PBS2/A5/40/2014.

P3

Multiple emulsions obtained by membrane emulsification and their application in food and pharmaceutical industry

K. Jackiewicz, J. Wolska

Department of Polymeric and Carbonaceus Materials, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370, Wrocław, Poland

Abstract

Multiple emulsions provide higher yield of active compounds encapsulation and better protection from external factors than simple emulsions. Obtaining a stable multiple system as well as operating with fragile active compounds and unsaturated oils used in food and pharmaceutical industry require mild process conditions. One of mild techniques for obtaining emulsions is membrane emulsification process [1]. In this work examples of succesful usage of this method are presented such as more efficient encapsulation of resveratrol and vitamine B_{12} in water/oil/water (W_1/O/W_2) systems in comparition to mechanical agitation technique [2] or production of antigen-loaded microcapsules small enough to be biocompatible [3].

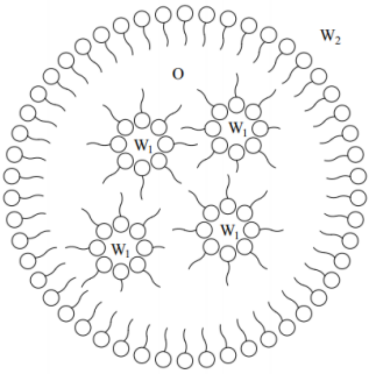


Figure 1. Structure of water-in-oil-in-water emulsion.

References

[1] R. Berendsen, C. Güell, M. Ferrando, *Food Hydrocolloids* **43**, 636-648 (2015).

[2] M. Matos, G. Gutiérrez, O. Iglesias, J. Coca, C. Pazos, *Journal of Food Engineering* **166**, 212-220 (2015).

[3] Q. Wei, W. Wei, R. Tian, L. Wang, Z. Su, G. Ma, *Journal of Colloids and Interface Science* **323**, 267-273 (2008).

Stabilization of liquid crystal phases with gold nanoclusters

M. Cyris, M. Waszkielewicz, J. Olesiak-Bańska, M. Samoć

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract

Gold nanoclusters are gaining an increasing interest in the scientific world, mainly because of their interesting quantum structure and optical and catalytic properties [1, 2]. Thiol-stabilized gold nanoclusters have found applications in many fields: biomedicine, catalysis, optics, nanoelectronics and chemical as well as biological research [3].

We present here the gold nanoclusters obtained from chloroauric acid ($HAuCl_4 \cdot 3H_2O$) and 2-phenylethanetiol ($PhCH_2CH_2SH$) by reduction with sodium borohydrate ($NaBH_4$). The reaction was carried out overnight in tetrahydrofuran (THF) and then the aging process was run at 40°C for several hours [2]. The liquid crystal (N-(4-Methoxybenzylidene)-4-butylaniline, MBBA) was mixed with Au(PET) nanoclusters. To determine the effects of gold nanoclusters on the liquid crystal, the sample was examined with a polarized light microscope. MBBA with THF was used as a control. The liquid crystal mixed with THF had a lower final temperature of the phase transition than the one mixed with Au(PET), which means that nanoclusters have caused the MBBA liquid crystal to become more stable. It was also noticed that a number of smaller defects and Schlieren structures have emerged (Fig.1). In the presentation the influence of the nanoclusters chirality on the properties of liquid crystals and the possibility of their use will be reviewed.

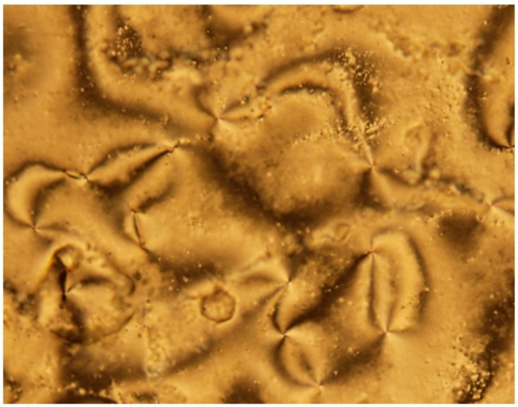


Fig.1: Schlieren structures - characteristic to the liquid crystal MBBA.

References

[1] R. Philip, P. Chantharasupawong, H. Qian, R. Jin, J. Thomas, Nano Lett., **12**, 4661 (2012)
[2] H. Qian, M. Zhu, Z. Wu, R. Jin, *Acc Chem Res.*, **45**, 1470-9 (2012)
[3] Z. Wu, J. Suhan, R. Jin *J. Mater. Chem.* **19**, 622 (2009)

P5

Towards efficient photoluminescence of gold-silver nanoclusters

M. Grębowiec[1], M. Waszkielewicz[1], J. Olesiak-Bańska[1], J. Siednienko[2], K. Matczyszyn[1], K. Pawlik[2], M. Samoć[1]

[1]Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

[2]Ludwik Hirszfeld Institute of Immunology and Experimental Therapy, Polish Academy of Sciences, Rudolfa Weigla 12, 53-114 Wrocław, Poland

Abstract

Metal nanoclusters (Au, Ag) are recognized by a very small size (average diameter of about 2 nm), good photostability and low toxicity [1]. They are promising for applications in cell labeling, photo-therapy and photonics [2]. However, most of the nanoclusters have a low photoluminescence quantum yield. In our work, we aim at increasing the photoluminescence quantum yield of gold nanoclusters. The substitution of silver atoms for gold ones in the 25-atom matrix can drastically change photoluminescence efficiency and increase the quantum yield [3]. Thus, we prepared silver-gold nanoclusters (Au-Ag NCs) by adding $HAuCl_4*3H_2O$ to glutathione. After 2 days at high temperature we could observe that the color of the solution changed to pale yellow and gold nanoclusters were precipitated from the solution [4]. Then we added silver nitrate in various gold to silver ratios and obtained Au-Ag NCs. Nanoclusters with an average diameter of 2 nm were visible under transmission electron microscope (Fig.1.). We discuss how the amount of silver influences the morphology, stability and optical properties of Au-Ag NCs. Then, we show also a study of the gold nanoclusters toxicity with MMT assays to establish a cytotoxic effect and the potential of application of the nanoclusters as fluorescent bioprobes.

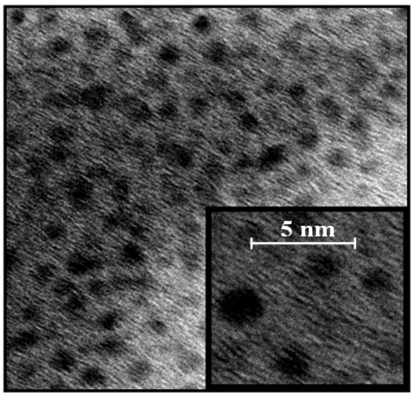


Fig. 1. TEM images of AuAgGSH nanoparticles.

References

[1] T. G. Schaaff, R. L. Whetten, J. Phys. Chem. B, **104**, 2630 (2000).
[2] J. Liu, M. Yu, C. Zhou, S. Yang, X. Ning, J. Zheng, J. Am. Chem. Soc., **135**, 4978 (2013).
[3] L. Polavarapu, M. Manna, Q. H. Xu, Nanoscale, **3**, 429. (2011).
[4] X. Le Guével, V. Trouillet, C. Spies, K. Li, T. Laaksonen, D. Auerbach, G. Jung, M. Schneider, Nanoscale, **4**, 7624 (2012).

The structure of halloysite

M. Skibińska

Department of Crystallography, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland

Abstract

Halloysite is a two-layer mineral from the group of aluminosilicates with the empirical formula $Al_2Si_2O_5(OH)_4$*nH_2O [1]. It is mined from natural deposits in China, New Zealand, America, Brazil and France. The Polish deposits of this mineral, Dunino are one of the largest in the world. Halloysite has a structure similar to the kaolinite. It often contains dopants of chromium, iron, magnesium, copper, nickel. It is composed of a tetrahedral layers of silica and octahedral layers of hydrated aluminum oxide. Distinguished two types of minerals: dehydrated halloysite (7Å) and hydrated (10Å). The transition from one form to another may already be at room temperature[2]. It is characterized by high porosity, surface area, ion-exchanging, absorptive capacity and chemical resistance [1].

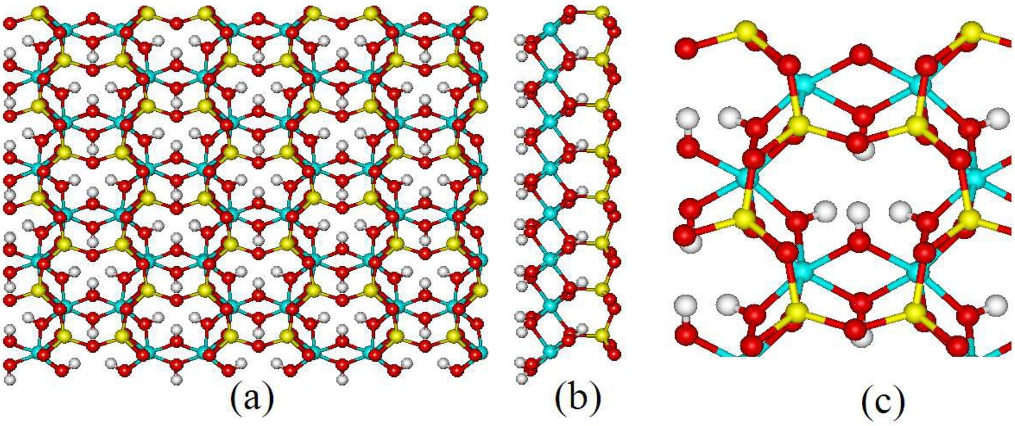


Fig. 1. Structure of monolayer halloysite [3].

References

[1] E. Abdullayer, Y. Lvov, *J. Nanosci Nanotechnol.* **11**, 10007 (2011).
[2] E. Joussein, S. Petit, C. Fialips, P. Vieillard, D. Right, *Clays and Clay Minerals,* **54**, 473 (2006).
[3] L. Guimaraes, A. N. Euyashin, G. Seifert, H. A. Durate, *J. Phys. Chem.* **114**, 11358 (2010).

P7

CdSe-CdS core-shell nanocrystals synthesis and spectroscopic investigations

M. Chrzanowski, M. Bański, A. Podhorodecki, J. Misiewicz

Department of Experimental Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław

Abstract

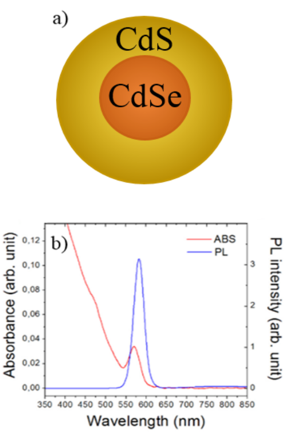


Fig.1. Scheme of CdSe/CdS NCs (a) and absorption and photoluminescence spectra (b).

Colloidal quantum dots of the II-VI group are in high interest due to their expansion in optical applications including LEDs and solid state lightning, displays and photovoltaics. Bare core semiconductor nanocrystals (NCs) such as CdSe emitting from blue to red can be easily obtained, but their luminescent properties are strongly dependent on surface ligand cover and defects quenching photoluminescence. These limitations are easily overcome by a shell growth resulting in heterostructures exhibiting different properties depending on relative conduction and valence band alignment of the core and shell material.

In our approach, the CdSe-CdS core-shell semiconductor NCs have been synthesized by wet chemistry method. CdSe cores were prepared by hot injection technique resulting in narrow size distribution followed by slow infusion of sulfur precursor desired for CdS shell growth. Three different surfactant agents were used: oleic acid (OA), oleylamine (OAm) and octanethiol. NCs will be characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD) as well as optical spectroscopy such as absorption (ABS), photoluminescence (PL), and time stability of PL.

References

[1] P. Reiss, M. Protière, L. Li, *Small* **5**, 154 (2009)
[2] D. Chen, F. Zhao, H. Qi, M. Rutherford, X. Peng, *Chemistry of Materials* **22**, 1437 (2010).
[3] O. Chen, J. Zhao, V. P. Chauhan, J. Cui, C. Wong, D. K. Harris, H. Wei, H.-S. Han, D. Fukumura, R. K. Jain, and M. G. Bawendi, *Nat. Mater.* **12**, no. 5, 445–451 (2013)

P8

Spectroscopic studies of three new azobenzene derivatives

N. Tarnowicz[1], M. Ziemianek[1,2], Z. Pokładek[2],
K. Matczyszyn[1], M. Samoć[1]

[1]Advanced Materials Engineering and Modelling Group [2]Department of Bioorganic Chemistry, Wrocław University of Technology,
Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Interactions between light and matter have been investigated for ages and became a basis for contemporary spectroscopic techniques. Among them ultraviolet-visible spectroscopy can be distinguished as a very specific research tool applied to various examinations of chromophores. UV-Vis spectroscopy was used within the scope of the presented studies to investigate kinetics of photoisomerization of three azobenzene derivatives: Azo1, Azo2, Azo3 [Fig.1].

Azobenzenes due to a presence of double bond in their structure exist in *cis* or *trans* conformations [1]. *Trans* to *cis* isomerization of molecule can be caused by irradiation of UV light. Significantly higher thermodynamic stability of *trans* isomers causes spontaneous *cis* to *trans* isomerization, appearing while irradiating with appropriate wavelength or thermally in the dark [2,3].

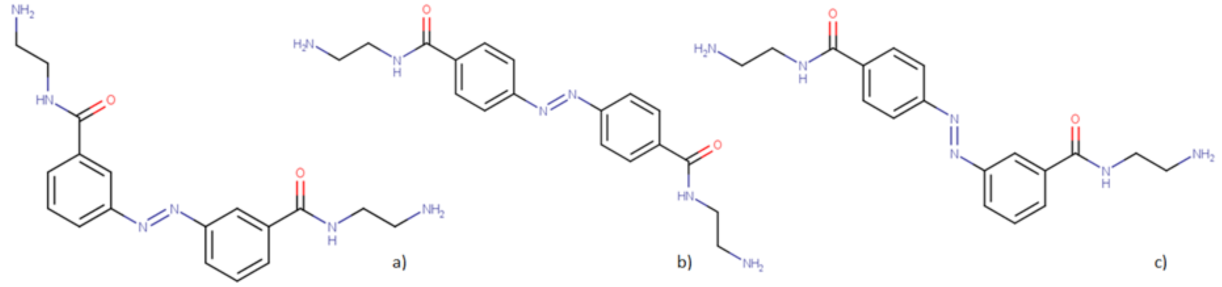


Figure 1. Structural formulas of the investigated azobenzene derivatives: a) Azo1, b) Azo2, c) Azo3.

Spectroscopic studies enabled to determine kinetic parameters such as rate constants k for *trans-cis* and *cis-trans* photoisomerizations of Azo1, Azo2 and Azo3. Differences between this parameters will be used to determine general view about influence of substituents positions on the aromatic ring on the kinetics of isomerization [1]. Thanks to their photoresponsive properties azobenzene derivatives found broad applications in many fields such as optoelectronics, material engineering and biology [2]. Further development requires detailed studies and kinetic parameters are important factors supporting further investigations of azobenzene compounds and their possible use.

References

[1] H. M. Dhammika Bandara, S. C. Burdette, *Chem. Soc. Rev.,* 2012, **41,** 1809-1825.

[2] A. Airinei, N. Fifere, M. Homocianu, C. Gaina, V. Gaina, B. C. Simionescu, *Int. J. Mol. Sci.* **2011**, *12*(9), 6176-6193.

[3] Garcia-Amorós J, Sánchez-Ferrer A, Massad WA, Nonell S, Velasco D., *Phys Chem Chem Phys.,* 2010 Oct 28;12(40): 13238-42.

The effect of sol-gel synthesis procedure on photocatalytic activity TiO_2 modified by 2,5% CNTs

A. Fiszka Borzyszkowska, A. Ofiarska, A. Pieczyńska, E. M. Siedlecka

Department of Environmental Technology, Faculty of Chemistry, University of Gdansk, Wita Stwosza str. 63, 80-308 Gdańsk, Poland

Abstract

Current studies indicate that the composite based on titanium dioxide (TiO_2) and carbon nanotubes (CNTs) can enhance photocatalytic response under both ultraviolet and visible light irradiation for the degradation of many different organic pollutants [1,2]. CNTs can reduce e^-/h^+ recombination, promote e^- diffusion, and act as photosensitizers and dispersing agents for TiO_2 particles by reason of CNTs electric conductivity [3].

These composite materials have been prepared by a range of different methods, including sol–gel synthesis of TiO_2 in the presence of CNTs, mechanical mixing of TiO_2 and CNTs, evaporation-drying process, hydrothermal method and chemical vapor deposition [4]. The sol–gel method exhibited higher photocatalytic activity due to more homogeneous distribution of CNTs in the composite [1].

In this work, we have performed a systematic study of sol-gel synthesis procedure. We investigated the effect of different TiO_2 precursors (Titanium (IV) butoxide and Titanium(IV) isopropoxide) and reaction conditions (influence of HNO_3 and HCl addition) on photocatalytic activity CNTs/TiO_2 composite. CNTs has been washing in HNO_3 solution before every synthesis. The composites CNTs/TiO_2 contained 2,5% of CNTs (2,5_CNTs/TiO_2). The photocatalytic activity of obtained samples was estimated by measuring the decomposition of phenol and cyclophosphamide in aqueous solution. Our research examines the photoactivity under light irradiation above 350 nm. Results of these experiments indicate that 2,5_CNTs/TiO_2 synthesized with using Titanium (IV) butoxide as precursor of TiO_2 and with addition of HNO_3 showed better efficiency of photodegradation than another samples.

References

[1] Q. Cao, Q. Yu, D.W. Connell, G. Yu, *Clean. Techn. Environ. Policy* **15**, 871–880 (2013).
[2] G. Ma, Y. Zhu, Z. Zhang, L. Li, *Appl. Surf. Sc.* **313,** 817–822 (2014).
[3] K. R. Reddy, M. Hassan, V. G. Gomes, *Appl. Catal. A: General* **489,** 1–16 (2015).
[4] Y. Dong, D. Tang, C. Li, *Appl. Surf. Sc.* **296**, 1–7, (2014).

P10

Random lasing obtained on nematic liquid crystals doped with luminescent dye

A. Adamów, L. Sznitko, K. Kaliciak, J. Myśliwiec

The Advanced Materials Engineering and Modelling Group (W3/K1), Wrocław University of Science and Technology, Wybrzeże Stanisława Wyspiańskiego 27, 50-370 Wrocła, Poland

Abstract

Here we report on random laser emission obtained in 5CB and E7 nematic liquid crystal (LC) mixtures doped with 1% weight to weight ratio of DCM laser dye. The liquid crystalline panel was constructed in geometry of a planar waveguide formed "transverse emitter"[2]. There was tested the influence of applied DC voltage as well as the presence of metalized diffraction grating which was introduced into liquid crystal cell. There was used two types of LC cells: the first one was commercially available with rubber polyimide coatings on indium tin oxide (ITO) and 11.6 micrometer thickness and the second one as handmade of two ITO glass plates cell. In this case one of the glasses contained photochromic polymer coating on which the Surface Relief Grating (SRG) was inscribed.

Prepared LC cells were investigated in experimental set-up which is called Variable Stripe Length (VSL) method. The aim of this experiment was to estimate gain and losses coefficients for stimulated emission. The second part of measurements has concerned the influence of metalized surface relief grating on DFB lasing.

References

[1] J. Li, C.H. Wen, S. Gauza, R.B. Lu, S.T. Wu, Refractive Indices of Liquid Crystals for Display Applications, J. Disp. Technol., 1 (2005) 51-61

[2] S.P. Palto, L.M. Blinov, M.I. Barnik, V.V. Lazarev, B.A. Umanskii, N.M. Shtykov, Photonics of liquid-crystal structures: A review, Crystallogr. Rep., 56 (2011) 622-649

[3] G. Somasundaram, A. Ramalingam, Cain studies of Rhodamine 6G dye doped polymer laser, J. Photochem. Photobiol. A-Chem., 125 (1999) 93-98.

P11

Photostability of 2-[4-(*N*,*N*-dimethylamino)styryl]-1*H*-phenanthro[9,10-*d*]imidazole upon one- and two-photon excitation

B. Jędrzejewska[1], M. Gordel[2], J. Szeremeta[2], M. Samoć[2], A.Wrzyszczyński[1]

[1]*University of Technology and Life Sciences, Faculty of Chemical Technology and Engineering*
Seminaryjna 3, 85-326 Bydgoszcz, Poland, beata@utp.edu.pl
[2]*Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

Abstract

High-tech materials used in chemical sensors, non-linear optics, solar cells, photo-voltaic optics, molecular electronics, semiconductors, liquid crystals, optical storage devices, laser dyes, catalyst and photo dynamic therapeutic agents (PDT) require chemical compounds having special properties such as strong delocalized p-electronic structures, good stability and suitable visible range optical properties. Thus, the synthesis and characterization of new optimized compounds is one of the most important research topics for materials chemists.

Many of the high-tech optical materials are designed based on the aromatic heterocyclic segments, e.g. pyridine [1], quinoline [2], and oxidazole [3]. A new building block for constructing such compounds is phenanthro[9,10-d]imidazole (PI) which exhibits excellent thermal stability, highly efficient fluorescence and balanced carrier injection [4]. The simplest examples are 2-(4-substituted-phenyl)phenanthroimidazoles which have an absorption band at around 350 nm and a strong fluorescence band, red-shifted by about 50-60 nm [5].

In the present work, we designed, synthesized and studied a linear PI derivative, 2-[4-(*N*,*N*-dimethylamino)styryl]-1*H*-phenanthro[9,10-*d*]imidazole. The separation of the electron acceptor and the electron donor moieties by introduction of the vinylene unit shift bathochromically the wavelengths of its excitation and emission maxima. However, along with the red shift of the wavelength, the photostability of the dye decreases notably.

Acknowledgment

The authors acknowledge financial support from the Ministry of Science and Higher Education (MNiSW) (BS-9/2014).

References

[1] N. Li, P. Wang, S.-L. Lai, W. Liu, C.-S. Lee, S.-T. Lee, Z. Liu, *Adv. Mater.* **22**(4) 527-530 (2010).

[2] S. Tao, L. Li, J. Yu, Y. Jiang, Y. Zhou, C. S. Lee, S. T. Lee, X. Zhang, O. Kwon, *Chem. Mater.* **21**(7) 1284-1287 (2009).

[3] J. Huang, Q. Liu, J.-H. Zou, X.-H. Zhu, A.-Y. Li, J.-W. Li, S. Wu, J. Peng, Y. Cao, R. Xia, D. D. C. Bradley, J. Roncali, *Adv. Funct. Mater.* **19**(18) 2978-2986 (2009).

[4] Z. Wang, P. Lu, S. Chen, Z. Gao, F. Shen, W. Zhang, Y. Xu, H. S. Kwok, Y. Ma, *J. Mater. Chem.* **21** 5451-5456 (2011).

[5] Y. Ooyama, K. Uwada, H. Kumaoka, K. Yoshida, *Eur. J. Org. Chem.* **34** 5979-5990 (2009).

P12

Environmental application of Er-doped $K_2Ta_2O_6$ photocatalysts

A. Krukowska[1], T. Klimczuk[2], W. Lisowski[3], A. Zaleska-Medynska[1]

[1]Department of Environmental Technology, Faculty of Chemistry,
University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland
[2]Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland
[3]Institute of Physical Chemistry, Polish Academy of Sciences,
ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

Abstract

Heterogeneous photocatalysis under sunlight has been considered as the most promising novel process to solve the environmental pollution problems in highly selective and eco-friendly route. Hence photocatalysts are hopeful photoactive materials for such applications as self-cleaning surfaces [1], wastewater and air purification [2], bacteria inactivation [3] and hydrogen generation [4].

The present work is aimed to study correlation between photocatalytic activity and physicochemical properties of Er-$K_2Ta_2O_6$ composites prepared by hydrothermal method. The influence of Er^{3+} dopant on the morphology, surface area, structure, photoabsorbance and photoluminescence features of Er-$K_2Ta_2O_6$ photocatalysts were investigated. The photocatalytic properties under UV-Vis and Vis light irradiation have been studied in the reaction of phenol degradation in the aqueous phase.

SEM images show Er-$K_2Ta_2O_6$ microcubes with their particle size from 4 to 1.1 µm. The specific surface area of RE-$K_2Ta_2O_6$ powders fluctuated from 6.9 to 10.1 m^2g^{-1}. XRD analysis reveals a significant dominating pyrochlore over perovskite structure in obtained Er-$K_2Ta_2O_6$ samples. The Er-$K_2Ta_2O_6$ composites present significantly much lower PL emission intensities as compared with bare $K_2Ta_2O_6$ powder. The highest UV-Vis and Vis light activity in phenol decomposition was observed for $K_2Ta_2O_6$ doped with 2 mol% Er. The obtained results confirmed incorporation Er^{3+} ions in $K_2Ta_2O_6$ lattice, which could demonstrate effective suppressing of photogenerated charge carries recombination and provoking the formation of high specific surface area.

References

[1] T. Kamegawa, Y. Shimizu, H. Yamashita, *Commun.* **24**, 3697 (2012)
[2] C. Sarantopoulos, E. Puzenat, C. Guillard, J. M. Herrmann, A. N. Gleizes, F. Maury, *Appl. Catal. B* **91**, 225 (2009)
[3] O. Modesto Jr., P. Hammer, R. F. Pupo Nogueira, *J. Photochem Photobiol A Chem*. **253** 38 (2013)
[4] F. Meng, S. K. Cushing, J. Li, S. Hao, N. Wu, *ACS Catal.* **5** 1949 (2015)

P13

Energy harvesting in up-converting nanocrystal/polymer blends

J. Grzelak[1], K. Ciszak[1], M. Nyk[2], D. Piatkowski[1], S. Maćkowski[1]

[1] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
[2] Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract

We study interaction between up-conversion nanocrystals with F8BT polymer which is one of the most commonly used bulding block in bulk heterojunction solar cell [1]. Up-converting materials are promising candidates for sensitizing organic solar cells to infrared radiation [2,3].
We report on single nanocrystals fluorescence microscopy of up-converting $NaYF_4$ nanocrystals doped with rare-earth ions [4] mix with the F8BT polymer. As a reference, we prepared a sample containing only the $NaYF_4$:Er^{3+}/Yb^{3+} nanocrystals with identical concentration. One of the emission bands of the nanocrystals overlaps with the absorption of the F8BT polymer.
The nanostructure, in which nanocrystals were mixed directly into the F8BT layer, was studied by means of high-resolution luminescence microscopy. By probing luminescence properties of individual nanocrystals we demonstrate that energy is efficiently transferred from the nanocrystals to polymer. We found that emission of F8BT increases in a presence of nanocrystals. The life-time of nanocrystals emission gets shorter for nanocrystals embedded in F8BT polymer compared to a reference sample.
The intensity of polymers can be further enhanced by an order of magnitude using metallic nanoparticles. These results are important for improving the spectral response of organic bulk heterojunction solar cells towards infrared region.

Acknowledgments

This work was supported by project DEC-2013/09/D/ST3/03746 from the National Science Center and by the National Research and Development Center (NCBiR) under Grant ORGANOMET No: PBS2/A5/40/2014.

References

[1] John Chappel, *Nature Materials* **2**, 616 – 621 (2003)
[2] D. Piatkowski, *ACS Nano*, **7(11),** pp 10257-10262 (2013)
[3] D. Piatkowski, *Nanoscale*, **7**, 1479-1484 (2015)
[4] J. Grzelak, *Appl. Phys. Lett.,* **105**, 163114 (2014)
[5] K. Smolarek, *Appl. Phys. Lett.,* **103**, 203302 (2013)

P14

Crystal morphology and phase transitions of alkyl-substituted naphthalene and perylene diimide derivatives

D. Chlebosz, W. Goldeman, M. Gazińska, A. Kiersnowski

Faculty of Chemistry, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław

Abstract

Among aromatic diimides for applications in organic electronics those based on naphthalenediimide (NDI) or perylenediimide (PDI) derivatives (Fig. 1) were found particularly useful [1]. Both naphthalenediimide and perylenediimide derivatives are relatively compact molecules having a strong tendency to self-organization in solution [2]. In solid state the crystalline NDI and PDI are n-type semiconductors. The electronic properties of NDI and PDI are related to crystal structure and morphology including crystal perfection, crystalline domain shapes, and sizes. Here we demonstrate that crystallinity and phase behavior of either type of diimide can be tailored by substitution at the imide nitrogen atom [3].

This study is focused on synthesis, crystal structure and phase transitions of alkylated NDI and PDI derivatives (Fig. 1). All compounds for the study were synthesized according to the protocols described in the literature [4]. In order to analyze the crystal structure and phase transitions we used optical microscopy and differential scanning calorimetry respectively. Our results indicate a complex phase behavior of the compounds including thermally induced formation of smectic or nematic mesophases, depending on the alkyl substituents on the nitrogen atoms. The substituents also exert an influence on the crystal morphology. For instance: the crystals of PDI substituted with octyl groups were found needle-like while those while those with larger substituents reveal spherulitic morphology.

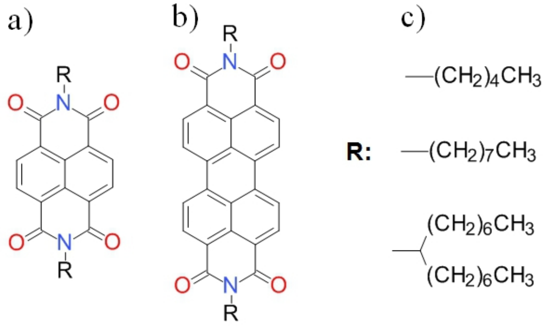


Figure 1. Chemical structures of alkylated naphtalene (a) and perylene (b) diimide derivatives used in the study. Structures of alkyl substituents are shown in c)

References

[1] H. E. Katz, A. J. Lovinger, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, A. Dodabalapur, *Nature*, 2000, **404**, 478–481

[2] W. W. Stewart, *Nature*, 1981, **292**, 17–19

[3] F. Wurthner, S. Ahmed, C. Thalacker, T. Debaerdemaeker, *Chem.–Eur. J.,* 2002, **8**, 4742–4750

[4] Y. Zhang, L. Zhang, H. Liu, X. Li, *CrystEngComm*, 2015,**17**, 1453-1463

P15

DNA liquid crystals doped with negatively charged gold nanorods

K. Brach, J. Olesiak-Bańska, K. Matczyszyn, M. Samoć

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract

Recently, the topic of liquid crystals (LCs) doped with nanoparticles has been extensively studied. Dispersion of nanoparticles in a liquid crystalline matrix may serve as a simple method for improving the physical properties of LCs. On the other hand, it may be also useful for ordering nanoparticles, which might result in preparation of new advanced functional materials. The aim of our work was to investigate the influence of doping with negatively charged gold nanorods (GNRs) on the formation and stability of DNA LCs. GNRs were synthesized using a seed-mediated growth approach [1] and additionally functionalized with negatively charged polystyrene sulfonate. Different textures of cholesteric and columnar mesophases, as well as phase transitions, were observed using a polarized light microscope. It was noticed that phases formed in the samples were qualitatively the same, but they differed in their stability. The introduction of GNRs into DNA LCs decreased the thermal stability of cholesteric phases and induced higher stability in the case of columnar phases. In addition, we compared these results with those obtained previously concerning DNA LCs doped with positively charged GNRs [2]. Detailed results of this study will be presented and discussed.

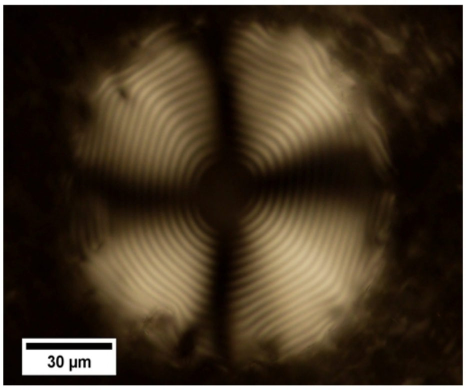


Fig. 1 DNA liquid crystalline cholesteric phase.

Acknowledgments

Funding from the NCN Opus grant UMO-2013/09/B/ST5/03417 is highly acknowledged.

References

[1] T. K. Sau, C. J. Murphy, *Langmuir* **20**, 6414 (2004).
[2] K. Brach, K. Matczyszyn, J. Olesiak-Bańska, M. Gordel, M. Samoć, *Phys. Chem. Chem. Phys.* **18***,* 7278 (2016).

P16

Synthesis of gold nanoparticles using green chemistry approach

M. Klekotko, J. Olesiak-Bańska, K. Matczyszyn, M. Samoć

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract

Noble metal nanoparticles (NPs) have received considerable attention due to their size and shape dependent physico-chemical properties. There are various methods of the production of nanomaterials. However, use of chemical and physical techniques in the synthesis of nanoparticles is often very expensive and cumbersome. Moreover, those methods usually lead to formation of nanostructures capped with some toxic chemicals, which may have adverse effects in applications, so there is a growing need to develop environmentally benign nanoparticles [1,2].

In our work, we used plant extracts to achieve bioreduction of gold ions and stabilization of the formed nanostructures. We synthesized gold nanoparticles applying water extracts of ginger (*Zingiber officinale*), mint (*Mentha piperita*), aloe (*Aloe vera*) and cistus (*Cistus incanus*). The obtained NPs were characterized by UV–Vis absorption spectroscopy and transmission electron microscopy (TEM).

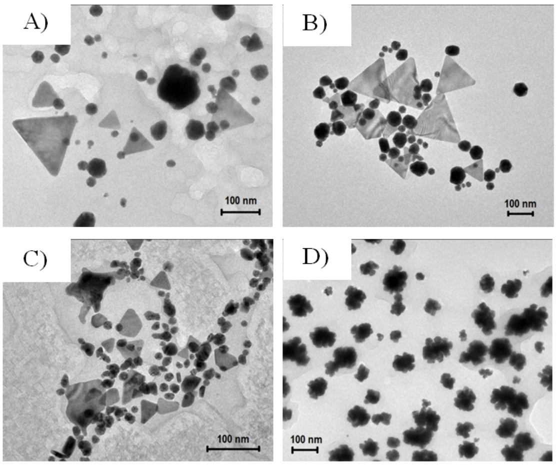


Fig 1. TEM images of gold nanoparticles synthesized using extract of A) ginger; B) mint; C) aloe; D) cistus.

References

[1] M. C. Daniel, D. Astruc, *Chem Rev*, **104**, 293-346 (2004).

[2] J. Huang, L. Lin, D. Sun, H. Chen, D. Yang, and Q. Li, *Chem. Soc. Rev.*, **44**, 6330–6374 (2015).

P17

Willow structure formation in supramolecular azo-polymer complex by irradiation of single polarized laser beam

J. Noga[1], A. Sobolewska[1], S. Bartkiewicz[1], A. Priimagi[2]

[1] *Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

[2] *Supramolecular Photochemistry, Department of Chemistry and Bioengineering, Tampere University of Technology, Korkeakoulunkatu 8, FI-33720 Tampere, Finland*

Abstract

Azobenzenze-containing polymers are one of the most interesting class of organic materials for photonic applications due to their features as high efficiency, all-optical character, one-step inscription process and reversibility [1].

It is well known for a long time that periodic structures can be easily formed in azo-polymer compounds. One of the most common example of periodic structure induced on the surface of azobenzene-polymer film during illumination the material of interference pattern is surface relief grating (SRG).

Here, we would like to present that for some group of azo-polymers, it is possible to formation of photoinduced spontaneous periodic structure during irradiation of material by single polarized laser beam with normal incidence to the polymer surface [2]. Obtained in this way structure is in the shape of regularly oriented stripes of micrometer width and substantial groove depth observed clearly under an atomic force microscope (AFM). The structure is formed perpendicular to the polarization direction. Due to similarity to willow basket, we called this structure a willow structure. Amplitude and period of the willow structures are dependent on the recording conditions (beam power, recording time, wavelength), which allows to obtain reliefs on the given parameters.

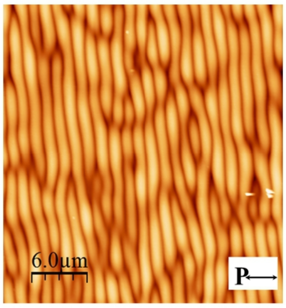


Fig.1 AFM images of willow structures inscribed in supramolecular azo-polymer complex surface by single light beam of linear polarization.

References

[1] (a)Y. Gritsai, L. M. Goldenberg, O. Kulikovska , J. Stumpe, *J. Opt. A: Pure Appl. Opt.* **10**, 125304 (2008). (b)A. Kravchenko, A. Shevchenko, V. Ovchinnikov, A. Priimagi, M. Kaivola, *Adv. Mater.* **23**, 4174 (2011).

[2] A. Sobolewska, S. Bartkiewicz, *J. Mater. Chem. C* **3**, 5616 (2015).

P18

The environmental photonic sensor for protein toxin detection

K. Piskorek[1], B. Bednarz[2], M. Klekotko[1], D. Wawrzyńczyk[1], J. Olesiak-Bańska[1], K. Matczyszyn[1], K. Pawlik[2], M. Samoć[1]

[1]*Advanced Materials Engineering and Modelling Group, Wrocław University of Technology,*
Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
[2]*Institute of Immunology and Experimental Therapy, Polish Academy of Science,*
Rudolfa Weigla 12, 53-114 Wrocław, Poland

Abstract

Chemical and physical properties of plasmonic gold nanoparticles (AuNP) and upconverting lanthanide nanocrystals (UPNC) give wide opportunities to create useful applications. In the field of environmental biosensors, such nanoparticles are an excellent material due to its easy detection, possibility of biofunctionalization and relatively good biocompatibility.

In the presented project we use the mechanism of signal quenching for detection of toxic protein Stx in the environment. Shiga toxin (Stx) is a virulence factor produced by *E. coli* (STEC), in 2011 strain *E. coli* O104:H4 caused a serious outbreak of foodborne illness focused in northern Germany. As a result of the spread of pathogens 3,950 people were affected and 53 died.If particles sizes are well-adjusted, plasmonic absorption band of AuNP overlaps the green emission band of UPNC so the close proximity of both results in signal quenching. Nanoparticles functionalized with polyclonal antibodies against the protein STX will be linked in the presence of STX protein and the quenching effect on UPNC emission can be observed. The use of polyclonal antibodies allows interaction with multiple protein epitopes which enhances the signals from aggregated nanoparticles. This approach allows for direct, fast and cheap, 'one pot' detection of some particularly dangerous bacterial toxins.

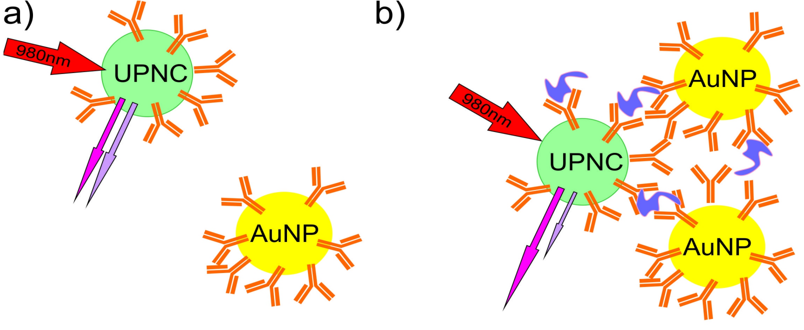


Fig. 1. Functional diagram of the biosensor. a) state in the absence of protein, b) state in the presence of protein. Emission of UPNC is modified by the plasmonic effect of AuNP.

This research is supported by the National Science Centre (NCN) under project Harmonia nr 2012/04/M/ST5/00340.

P19

Antibacterial functionalization of fabrics by zinc oxide

M. Fiedot[1], M. Ciesielska[1], H. Teterycz[2]

[1] *Wrocław University of Technology, Department of Chemistry,*
C.K. Norwida Street 4/6, 50-373 Wrocław, Poland
[2] *Wrocław University of Technology, Department of Microsystems and Photonic,. Janiszewskiego Street 11/17, 50-372 Wrocław, Poland*

Abstract

Main assumption of fabrics' modification is to improve already existing features of a given material or to provide new, particularly functional characteristics to the material of interest [1]. Antibacterial materials stand out as an innovative solution in the fight against pathogenic microorganisms. Among the most popularly used modifying agents, zinc oxide has particular meaning. Zinc oxide, apart from its antibacterial properties, possesses also a broad spectrum of additional advantageous characteristics, such as: biocompatibility, ability to absorb UV-radiation and non-toxicity [2].

Presented results concern an antibacterial functionalization of polyester, polyamide and polypropylene fabrics. In order to provide antimicrobial activity to polymer materials, two-stage surface deposition of zinc oxide was carried out. First, fabrics were immersed in the colloidal ZnO in order to create nucleation centres. Then, the chemical bath deposition of zinc oxide rods, with the use of hexamethylenetetramine and zinc nitrate, was performed.

The main goals of conducted studies were: the determination of time dependence on the quantity, shape and size of obtained ZnO structures, establishment of the optimal time of the process and the evaluation of actual antibacterial activity, exhibited by modified fabrics, against both Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria. Obtained modified materials were subjected to SEM and XRD analysis, which indicated the presence of hexagonal zinc oxide rods. Performed microbiological assays confirmed the antibacterial properties of ZnO against *E.coli* and *S. aureus*.

Acknowledgement

Scientific work financed from funds for science in the years 2013 – 2017 as a research project within the program under the name „Diamond Grant" No DI2012 008542.

References

[1] A. Moezzi, A. M. McDonagh, M. B. Cortie, *Chemical Engineering Journal*, **185-186**, 2012, p. 1-22.

[2] N. Vigneshwaran, "*Surface modification of textiles",* Cambridge, Woodhead Publishing Limited, 2009, p.164-184

P20

Amplified spontaneous emission in a perylene doped liquid crystalline system

M. Lipka[1], A. Adamów[1], E. Chrzumnicka[2], T. Martynski[2], J. Myśliwiec[1]

[1]Advanced Materials Engineering and Modelling Group(W3/K1), Wrocław University of Science and Technology, Wybrzeże Stanisława Wyspiańskiego27, 50-370 Wrocław, Poland

[2]Department of Physics, Poznań University of Technology, Plac Marii Skłodowskiej-Curie 5, 60-965 Poznań, Poland

Abstract

Here we report on the results of amplified spontaneous emission measurements obtained for nematic 6 CHBT liquid crystalline cell doped with derivative of perylene luminescent dye. For our studies we have used three different samples which were characterized by: a) horizontal alignment of molecules, b) vertical aligment of molecules, c) vertical aligment of molecules and variable thickness of the cell (from 20 to 60 micrometers). We have measured amplified spontaneous emission in function of DC voltage applied to the sample, excitation energy density and polarization state of excitation wavelength coming from Nd:YAG nanosecond pulsed laser. Finally we have checked photostability of our systems on longtime excitation light exposure.

P21

Gold plasmonic nanoparticles - synthesis and multiphoton imaging

A. Pniakowska, J. Olesiak-Bańska, K. Brach, M. Samoć

Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract

Gold nanorods received great attention in recent years because of their unique optical properties, which can be helpful in biomedical imagining, sensing, gene delivery, drug delivery and therapy. [1] In particular, gold nanorods (NRs) with well-defined shapes and sizes prove to have excellent surface plasmon resonance (SPR) properties. Thus, it is worth to examine the relation of SPR and possibility of multiphoton excitation and evaluate the potential of such nanostructures as markers in the multiphoton microscopy.

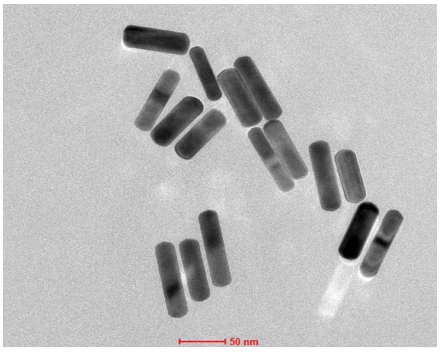


Fig.1. TEM image of gold NRs.

Our measurements were based on two types of gold nanostructures: nanorods and triangular nanoplates. The synthesis of nanoplates was a rapid one-pot seedless process [2] and the synthesis of NRs was a slow seeded process [3]. The NRs were synthesized using binary surfactant (CTAB and NaOL). This effective method gives high dimensional tunability, which results in a broadly tunable SPR. Gold NRs with the overall dimensions 69 nm x 22nm (Fig.1) are perfect for studies on plasmonic coupling, therefore the prepared nanostructures were analyzed under a multiphoton microscope. We considered the relation between the position of plasmon bands and two-photon excited emission. The research shows the dependence between type and size of plasmonic nanoparticles and their nonlinear optical properties.

References

[1] S. Wang et al., *Theranostics* **5**, 3 (2015), p. 251-266
[2] L. Chen et al., *Nano Lett.* **14**, 12 (2014), p. 7201–7206
[3] X. Ye et al., *Nano Lett.*, **13**, 2 (2013) p. 765–771

P22

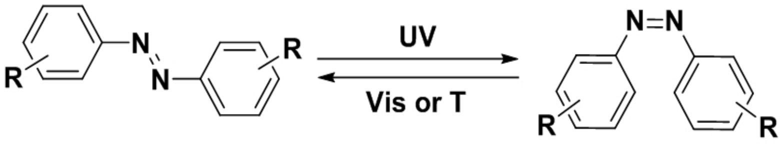
Synthesis and thermal stability of model azobenzene switches used in biology

M. Grelich[1], M. Ziemianek[1,2], Z. Pokładek[2], K. Matczyszyn[1], M. Samoć[1]

[1] *Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Technology*
Wybrzeże Wyspiańskiego 27, 50-370, Wrocław (Poland)
[2] *Department of Bioorganic Chemistry, Faculty of Chemistry, Wrocław University of Technology,*
Wybrzeże Wyspiańskiego 27, 50-370, Wrocław (Poland)

Abstract

Azobenzenes (AB) are compounds consisting of two phenyl rings which are linked by an azo (-N=N-) moiety. Their common characteristic is ability to reversible photo-isomerization. Azobenzenes found use in many areas, among others in photocontrol of ion channels or enzymes [1,2]. Position (ortho, meta, para) and substituent type connected to the phenyl rings have a dramaticall influence on the thermal relaxation of AB. It has therefore been decided to synthesize and study the thermal stability of two model azobenzene derivatives (Fig. 1). To synthesise 1 and 2 corresponding azobenzene-dicarboxylic acid derivates was reacted with *N*-Boc-ethylenediamine. After deprotection of Boc group target molecules were obtained as a TFA salt with global yield 56% for 1 and 53% for 2. Next thermal stability of the corresponding compounds was investigated to determine kinetic parameters of thermal cis => trans relaxation.



1 R= 4,4' $CONHCH_2CH_2NH_2$
2 R= 3,4' $CONHCH_2CH_2NH_2$

Fig.1. Structures of studied azobenzenes

References

[1] B. L. Feringa, R. Wesley, *Molecular Switches 2nd Ed.*, Wiley-VCH, (2011)
[2] W. Szymański, B. L. Feringa, *Chem. Rev.* **8**, 113(2013)

P23

Synthesis of gold nanostars and characterization of the obtained structures

M. Gołąb, M. Klekotko, K. Matczyszyn, M. Samoć

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract

Noble metal nanoparticles offer new chemical and physical properties, which are not observed in the bulk materials. By changing the shape and size of the formed structures, it is possible to produce nanoparticles with desirable features, useful in various fields of science and technology [1,2].

There are numerous methods of the synthesis of metal nanoparticles. This work describes two-step synthesis of star-shaped gold nanoparticles (GNPs). At first, we synthesized gold nanospheres with the diameter of around 15 nm. The obtained nanoparticles were stabilized with citrate. In the next step, we used the gold nanospheres as seeds for the further growth of gold nanostars. For this purpose we applied various stabilizing agents with thiol groups. After the synthesis, we characterized the obtained structures using UV–Vis absorption spectroscopy and transmission electron microscopy (TEM).

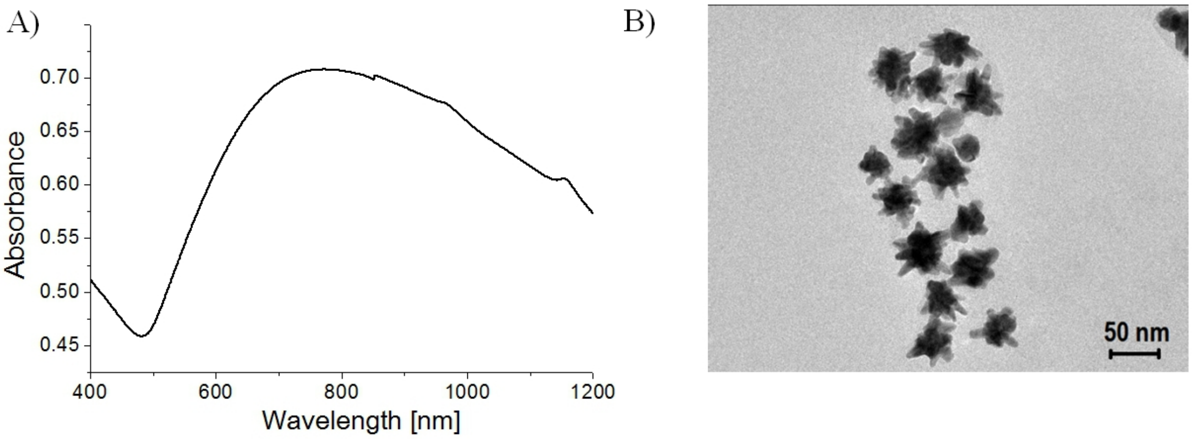


Fig.1. A) UV-Vis spectrum and; B) TEM image of gold nanostars stabilized with β-mercaptoethanol.

References

[1] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, *J. Phys. Chem. B*, **107**, 668-677 (2003).
[2] H. Yuan, C.G. Khoury, H. Hwang, C.M. Wilson, G.A. Grant, T. Vo-Dinh, *Nanotechnology*, **23**, 075102 (2012).

P24

Nanocrystals functionalization by D-penicillamine

A. Lesiak[1], M. Bański[1], A. Podhorodecki[1], J. Misiewicz[1], S. Krawiec[2], J. Cabaj[2]

[1]Department of Experimental Physics, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław
[2] Department of Medicinal Chemistry and Microbiology,
Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław

Abstract

Quantum dots (QDs) are interesting fluorescent tools for many applications in the life science [1]. Fluorescent QDs can be linked with bioactive moieties (e.g. antibodies, receptor ligands) [2]. However, to be useful, they need to meet several conditions: water solubility, small size, chemical stability and high fluorescence quantum yield [1]. Specific functionalization of QDs by biocompatible compounds lets obtain wide range of applications [1]. Long temporal stability of nanoparticles in desired solvent is a fundamental challenge. For that purpose, the ligand molecule on the surface can be exchanged by others that can possibly provide additional properties or functionality to the particles [3].

D-penicillamine (DPA) is commercially available ligand, useful because of its functions: non-toxic, small size, zwitterionic and biocompatibility (e.g. can works like cysteine) [4].DPA contains two methyl groups at the carbon atom in α-position to the thiol group. This structure has a strong influence on the reactivity of molecule [4]. Due to this, DPA is optical active ligand. When it is attached to the QDs, may cause them chiral, and this induced fluorescent properties [4].

In the present study, we have described first attempts of functionalization CdSe/CdS nanocrystals. At basic pH ~11, we attached DPA to the previously prepared QDs.

References

[1] Breus, V. V., et al.,*Zwitterionic biocompatible quantum dots for wide pH stability and weak nonspecific binding to cells*, ACS nano, 3(9), 2573-2580, 2009.
[2] Hardman, R.,*A toxicologic review of quantum dots: toxicity depends on physicochemical and environmental factors*. Environ health persp, 165-172, 2006.
[3] Sperling, R. A.et al.., *Surface modification, functionalization and bioconjugation of colloidal inorganic nanoparticles*. Philos T R Soc A,368(1915), 1333-1383, 2010.
[4] Tamang S., *Synthese et fonctionnalisation des nanocristaux emettant dans le proche infrarouge pour l'imagerie biologique*, Autre, Universite de Grenoble, Francais, 2011.

P25

Synthesis and spectroscopic investigations of colloidal, anisotropic CdS nanostructures

W. Trzpil, M. Bański

Department of Experimental Physics, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław

Abstract

Inorganic particle synthesis is rapidly developing field of research, not only because new materials are consistently synthesized, but because fine tuning of reaction schemes enables the creation of nanocrystals with precise control of their size, shape, composition and crystal structure. In semiconductors, the shape is an important parameter because it affect strongly the electronic spectrum of charge carriers as well as the optical properties of the nanocrystals [1].

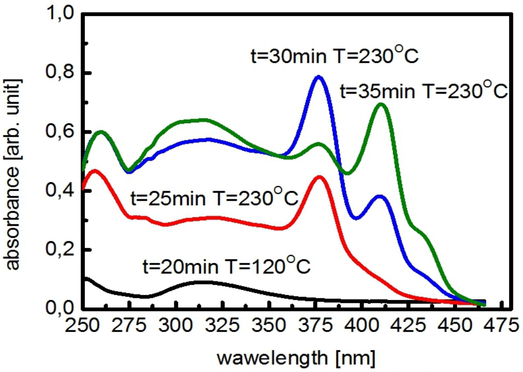


Fig. 1. Absorption spectra of CdS measured during the synthesis.

Colloidal nanocrystals are prominent candidates to displace current electronic active layers in solid-state device technologies and offer a body of physics which diverges from those of bulk materials and discrete molecules. Development of methods of growth methods for anisotropic nanocrystals with one dimension much smaller than two others, such as nanoplatelets, promise new opportunities to study shape-dependent electronic and optical devices. Moreover synthesis of such structures is still greatly undeveloped.

The work demonstrate the formation of atomically flat quasi two-dimensional colloidal CdS with atomic precision, as well as effect of the reaction temperature on growth and study how optical properties vary according to quantity of monolayers.

References

[1] Ithurria, S., et al. "Colloidal nanoplatelets with two-dimensional electronic structure." Nature materials 10.12 (2011): 936-941.

P26

Influence of moisture on performance of Organic Thin Film Transistors

A. Łuczak, J. Jung, J. Ulański

Department of Molecular Physics, Faculty of Chemistry, Łódź University of Technology, Żeromskiego 116, 90-924, Łódź, Poland.

Abstract

Organic Thin Film Transistors (OTFTs) are the main components of any organic electronic devices; therefore stability of their performance is crucial for development of emerging new technology – Flexible Large Area Organic Electronics. For this reason the aim of this study was determination of influence of moisture on the long term stability of the OTFT.

The transistors were made in two configurations: top gate, bottom contacts (TGBC), using glass as the substrate and poly(2-chloro-p-xylylene) (Parylene C) layer as the gate insulator (Fig.1 B); or bottom gate, top contacts (BGTC), using silicon wafer as the substrate covered by thin SiO_2 insulating layer (Fig.1 C).

In both types of transistors poly(triaryloamine) (PTAA, see Fig. 1A), deposited by spin coating, was used as the *p*-type semiconductor.

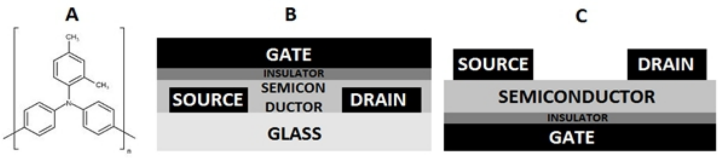


Fig.1 A) Chemical structure of PTAA; B) transistor with TGBC configuration; C) transistor with BGTC configuration.

Stability of the produced OTFTs was examined by means of the bias stress effect experiments performed under ambient atmosphere (with variable humidity). The bias stress experiments consists application of voltage (-20 V in our case) between the gate and short-circuited source and drain electrodes. During such long term polarization, the transfer characteristics were measured in 15 min. intervals.

In the BGTC transistors an increase of relative humidity was causing an increase of the threshold voltage and decrease of the charge carrier mobility; however, these effects were reversible. For the TGBC transistors with Parylene C layer, no influence of moisture on these parameters was observed.

Acknowledgements

This work was partially supported by Grant 2012/07/B/ST8/03789 of the Polish National Science Centre (NCN) and MASTER/MISTRZ 9/2013 of the Foundation for Polish Science.

P27

Influence of substituents on optical properties of geometric isomers of azobenzene derivatives - determination of the quantum yield and lifetime of fluorescence

S. Mucha[1], L. Mazur[1], K. Matczyszyn[1], Z. Pokładek[2], M. Ziemianek[2], M. Samoć[1]

[1]Advanced Materials Engineering and Modelling Group, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

[2]Department of Bioorganic Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract

Azobenzene derivatives are well-known group of chromophores. The common structure for this group is a double bond (-N=N-), wherein additionally nitrogen atoms have a bond to the phenyl ring.(1) This determines the presence of two geometric isomers: *cis* and *trans*. The transition from *trans* (thermodynamically stable form) to the *cis* can be induced by UV light of exact wavelength. However, to return to the trans form of the samples is irradiated with a different wavelength. (2)

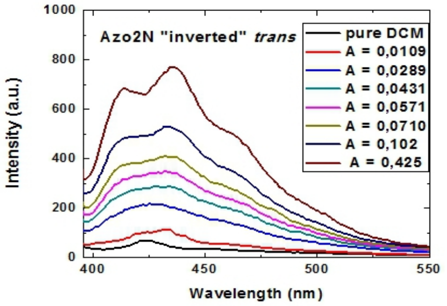


Fig. 1. Fluorescence spectra obtained for seven different concentrations of Azo2N "inverted" trans and DCM.

Photoisomerization of azobenzene derivatives affects the physical properties due to differences in the structure. The presence of a double bond (-N=N-) results in the possibility n → π* and π → π* excitation by use monochromatic light beam (λexc.). The end result, which is to return to the ground state, is caused by the emission of photons, which previously absorbed. Special magnitudes defining photochromism of azobenzene are the fluorescence quantum yield (ΦF) and lifetime (LT). Their values are characteristic of the individual isomers.

Φ_F is defined as the ratio of photons emitted through fluorescence to photons absorbed by the fluorophore at specific conditions.(3) The fluorescence LT is a measure of the rate of fluorescence quenching using the exponential decay, as the time at which intensity reduced to 1/e or 36,8 % its initial value. We measured LT and delimited Φ_F for *trans*/*cis* forms three compounds: Azo2N, Azo2N "inverted" and Azo18 by using dichloromethane (DCM) as the solvent and excitation wavelength λ = 375 nm. To determine Φ_F we used a method based on the linear relationship of integrated fluorescence intensity of absorbance, using Coumarin540A in methanol as reference.

References

[1] P. Cattaneo and M. Persico, An *ab initio* study of the photochemistry of azobenzene, *Phys. Chem. Chem. Phys.*, 1, 4739 - 4743 (1999)
[2] M. Han, D. Ishikawa, E. Muto, M. Hara, Isomerization and fluorescence characteristics of sterically hindered azobenzene derivatives. *Journal of Luminescence* 129, 1163-1168 (2009)
[3] Jobin Yvon Horiba, A Guide to Recording Fluorescence Quantum Yields

P28

Application of a new semiconductor polymer in non-enzymatic NADH fotoregeneration

K. Kinastowska[1], M. Grzelczak[2], F. Vilela[3], W. Bartkowiak[1]

[1]*Department of Quantum and Physical Chemistry, Wrocław University of Technology, Wrocław, Poland*
[2]*Bionanoplasmonics Group, CIC biomaGUNE, San Sebastián, Spain*
[3]*School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, Great Britain*

Abstract

The specificity and efficiency of enzymes in many reactions, contribute to their applicability in organic reactions of industrial relevance [1]. However, the possibility of using enzymes on a larger scale is significantly limited by the high cost of cofactors that are involved in reactions. Actual approaches for cofactor regeneration are usually quite sophisticated as they require a simultaneous presence of substrates and products. Thus, searching for new, efficient, economical and eco-friendly methods for cofactors regeneration is one of the most actual challenges of modern biotechnology.

Mimicking photosynthetic processes through applying visible-light absorbing, synthetic materials constitutes an exceptional attempt. Semiconductor materials turn out to be particularly relevant for this purpose, serving as specific red-ox centers where photo-generated electrons and holes may take active part in reduction and oxidation processes respectively [2].

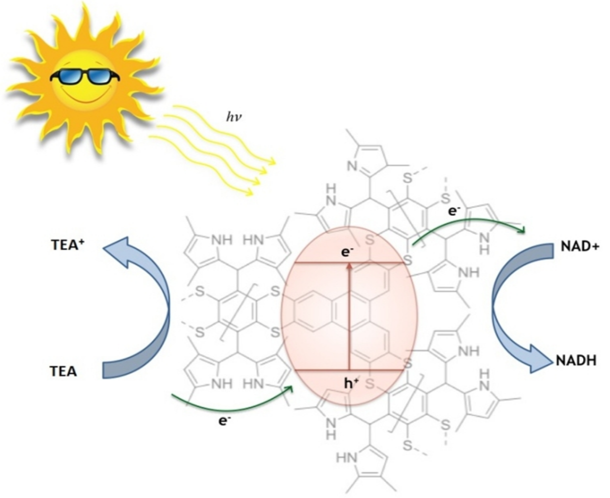


Fig. 1 Schematic illustration of the proposed photocatalytic reaction.

In this study we developed an interesting method for non-enzymatic NADH fotoregeneration that involves a new semiconductor polymer as a photocatalyst, allowing for the effective NADH regeneration according to the scheme presented in Fig. 1. We performed an optical and microscopic characteristics of the material and examined the NADH regeneration efficiency as a function of various parameters. What is more, we evaluated the enzymatic activity of such obtained cofactor using a biochemical approach.

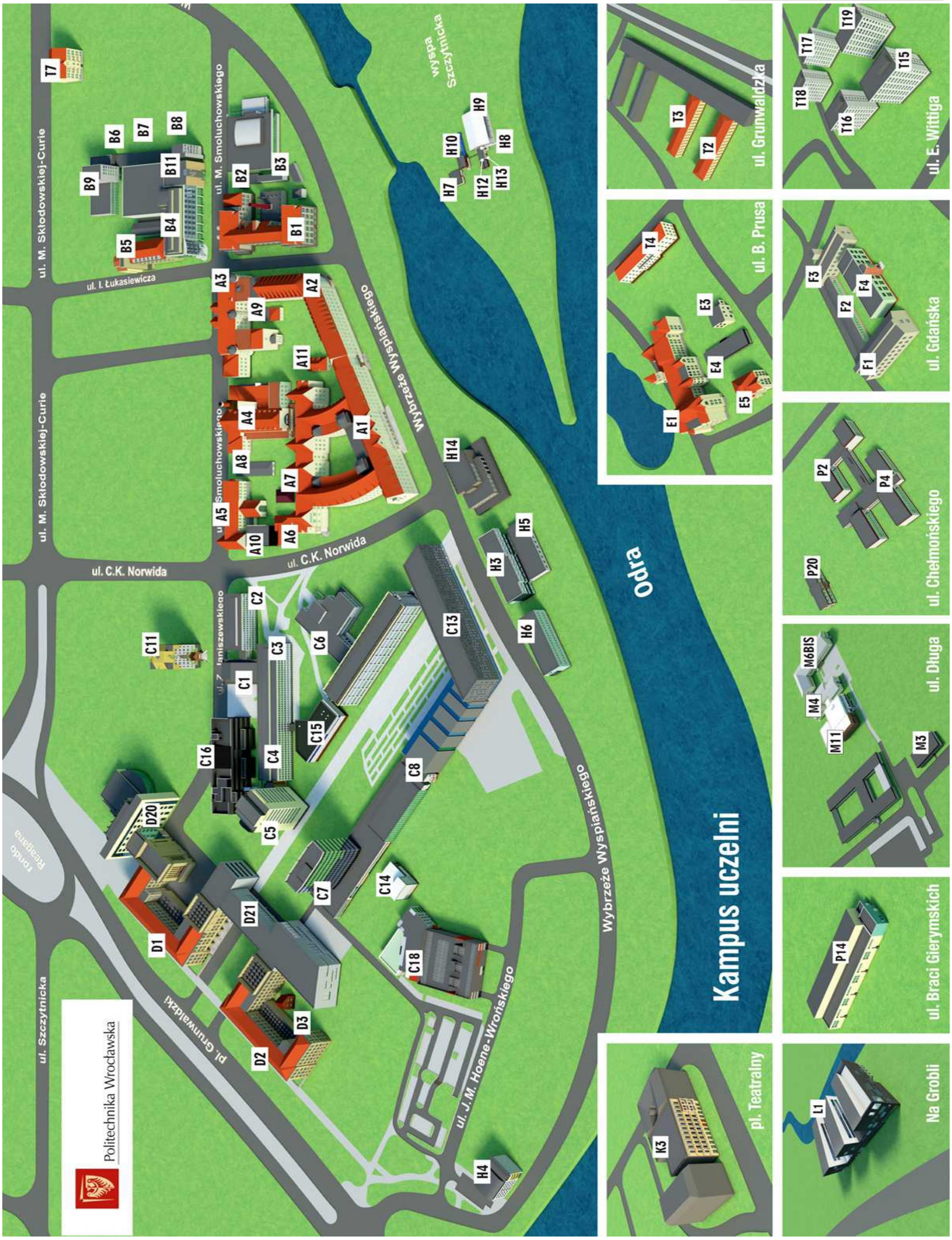
References

[1] J. Liu, M. Antonietti, Bio-inspired NADH regeneration by carbon nitride photocatalysis using diatom templates, *Energy Environ. Sci.*, **6** (2013), p.1486-1493.

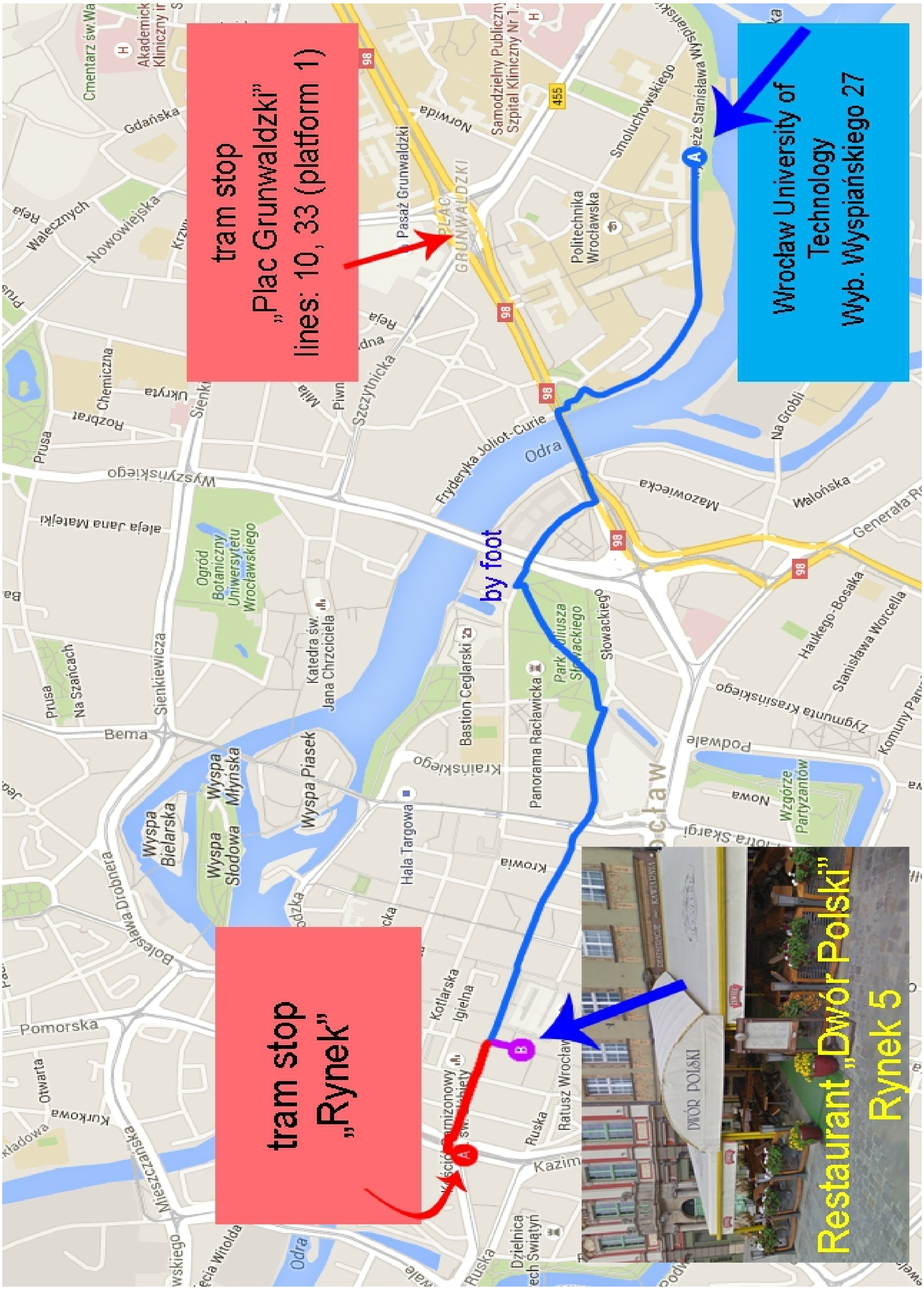
[2] Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. Stuart-Williams, H. Yang, J. Cao, W. Luo, Z. Li, Y. Liu, R. L. Withers, An Orthophosphate Semiconductor with Photooxidation Properties under Visible-Light Irradiation., *Nat. Mater.,* **9** (2010), p. 559–564.

VI. Maps

Map of campus



Dwór Polski restaurant location (place of conference dinner)



tram stop „Plac Grunwaldzki"
lines: 10, 33 (platform 1)

Wrocław University of Technology
Wyb. Wyspiańskiego 27

by foot

tram stop „Rynek"

Restaurant „Dwór Polski"
Rynek 5

VII. Index of presenting authors