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University of Łódź
Faculty of Chemistry
Department of Organic & Applied Chemistry



Polish Chemical Society

VIth International Mini-Symposium
**Current Problems in Materials
Chemistry**

The Year of Jan Czochralski



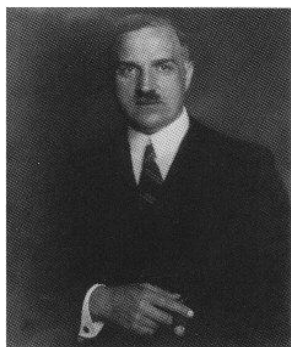
May 23th 2013

Acknowledgement
The City of Łódź Office for financial support



Organizing Committee thanks to WITKO
company for support during Mini-Symposium





Jan Czochralski
(23.10.1885 - 22.04.1953)

Jan Czochralski was born in a small Polish town Kcynia lying between Poznań and Bydgoszcz. He spent his scientific life in Berlin, Frankfurt on Main (Germany), and in Warsaw (Poland) creating in the two latter towns the well equipped research and technical laboratories. After the World War II he returned to native Kcynia. There he died and was buried in the Old Cemetery and forgotten by almost all the people.

During his life Jan Czochralski was well-known metallurgist, chemist, materials science man, and he invented several new research methods, patents etc. Now, in the time of electronic revolution, Prof. Czochralski is known mainly from his excellent and worldwide used method of single crystal growing, named as "Czochralski method", which was published 97 years ago. Fortunately, the use of his method of measuring the rate of crystallization as a method suitable for growing of semi-conducting single crystals gave to Czochralski the significant position in the science and technology. His name will be associated forever with this method. But only several years ago Czochralski was recognized as a person and rediscovered for people within the world.

On December 7th 2012, the Polish Parliament established the year 2013 as The Year of Jan Czochralski, Julian Tuwim and Witold Lutosławski. On February 6th 2013, in the Parliament's House the exhibition in memory of Prof. Jan Czochralski was officially open.

Program & Abstracts

Conference venue:

University of Łódź, Faculty of Chemistry, Tamka-Str. 12,
The Faculty Council Room, #1-020

Organizing committee:

Chairman: Prof. dr. hab. Grzegorz Młostoń
Secretary: Prof. UŁ, dr. hab. Jarosław Romański
Members: Dr. Katarzyna Urbaniak
Małgorzata Celeda
Zenona Frydrych

Program

12:55 **Invitation and opening**

Session 1: **Chairman: Prof. Piotr Kiełbasiński (PAS Łódź)**

13:00 – 13:30 **Klaus Banert** (Chemnitz University of Technology, Germany)
L-1 *Nitrogen-Rich Binary CN Compounds as Highly Energetic Materials*

13:30 – 14:00 **Kazimiera Wilk** (Wroclaw University of Technology, Poland)
L-2 *From Molecular Self-Organization to Multifunctional Nanocarriers*

14:00 – 14:30 **Stefan Lis** (Adam Mickiewicz University in Poznań, Poland)
L-3 *Importance of Luminescent Properties of Lanthanides in the Study of their Complexes and Inorganic Nanomaterials*

14:30 – 14:50 **Piotr Bałczewski** (Centre of Molecular and Macromolecular Studies, PAS Łódź, Poland)
L-4 *Aromatic o-Bromo Substituted Aldehydes and Dialdehydes in Synthesis of Functional Materials*

14:50 – 15:10 **Konrad Kowalski** (University of Łódź, Poland)
L-5 *Highly Efficient Thermally Activated Fluorescence of a New Rigid Cu(I) Complex [Cu(dmp)(phanephos)]⁺*

15:10 – 15:40 *Coffee break*

Session 2 **Chairman: Prof. Janusz Zakrzewski (UŁ)**

15:40 – 16:10 **Heinz Langhals** (University of Munich, Germany)
L-6 *Molecular Functional Components for Materials Chemistry. Multichromophoric Structures as Building Blocks for Picotechnology*

16:10 – 16:40 **Bohdan Korybut-Daszkiewicz** (Institute of Organic Chemistry, PAS Warsaw, Poland)
L-7 *Macrocyclic Metal Complexes as Building Blocks for Construction of Molecular Receptors and Devices*

16:40 – 17:10 **Adam Proń** (Warsaw University of Technology, Poland)
L-8 *Materials for Organic and Hybrid (Organic/Inorganic) Electronics: Preparation Strategies, Characterization and Application to Field Effect Transistors and Photovoltaic Cells*

17:10 – 17:30 **Marcin Jasiński** (University of Łódź, Poland)
L-9 *Synthesis of Functionalisable 6-Oxoverdazyls*

17:30 – 17:50 **Denis Svechkarev** (Kharkov V. N. Karazin National University, Ukraine)
L-10 *Excited-States Proton Transfer Dynamics and Sensing Abilities of Heterocyclic Derivatives of 3-Hydroxychromone*

17:45 – 19:30 *Garden Grill Party*



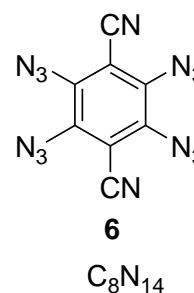
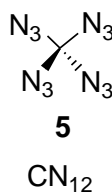
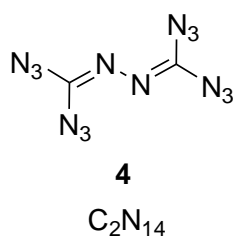
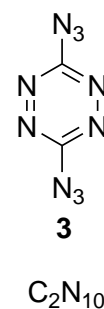
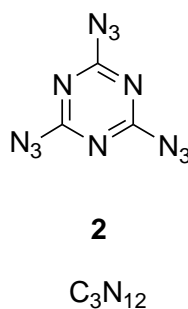
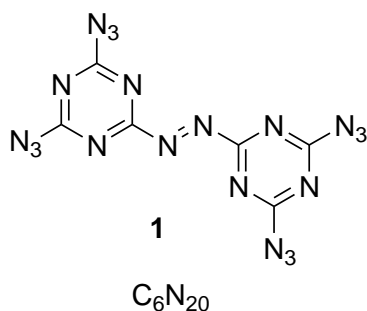
L-1

Nitrogen-Rich Binary CN Compounds as Highly Energetic Materials

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Nitrogen-rich organic compounds have gained attention recently because of their high heats of formation and possible applications as highly energetic materials.¹ Especially, binary CN compounds such as known polyazides **1**, **2**, and **3** have been discussed although they are notorious for their extreme sensitivity towards friction and impact.² We report here on the synthesis and structure assignment of the very explosive title compounds **4**, **5**, and **6**.^{3,4} Furthermore, some interesting reactions of these polyazides and other nitrogen-rich CN compounds are presented.



1. a) H. Gao, J. M. Shreeve, *Chem. Rev.* **2011**, *111*, 7377–7436. b) A. Hu, F. Zhang Shock, *AIP Conf. Proc.* **2009**, *1195*, 809–812.
2. a) M.-H. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya, R. Gilardi, *Angew. Chem.* **2004**, *116*, 5032–5036; *Angew. Chem. Int. Ed.* **2004**, *43*, 4924–4928. b) W. Zheng, N.-B. Wong, X. Liang, X. Long, A. Tian, *J. Phys. Chem. A* **2004**, *108*, 840–847. c) M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, R. Gilardi, *Angew. Chem.* **2004**, *116*, 5776–5779; *Angew. Chem. Int. Ed.* **2004**, *43*, 5658–5661. d) M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud, R. D. Gilardi, *J. Am. Chem. Soc.* **2005**, *127*, 12537–12543. e) Y. Zhou, X. Long, Y. Shu, *Chin. J. Chem.* **2010**, *28*, 2123–2129. f) E. Keßenich, T. M. Klapötke, J. Knizek, H. Nöth, A. Schulz, *Eur. J. Inorg. Chem.* **1998**, 2013–2016.
3. K. Banert, S. Richter, D. Schaarschmidt, H. Lang, *Angew. Chem.* **2013**, *125*, 3583–3586; *Angew. Chem. Int. Ed.* **2013**, *52*, 3499–3502.
4. K. Banert, Y.-H. Joo, T. Ruffer, B. Walfort, H. Lang, *Angew. Chem.* **2007**, *119*, 1187–1190; *Angew. Chem. Int. Ed.* **2007**, *46*, 1168–1171.

L-2

From Molecular Self-Organization to Multifunctional Nanocarriers

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Molecular self-organization has attracted attention as, in principle, it represents a unique opportunity to construct nanoparticles, nanosurfaces and nanobiostructures. Amphiphilic molecules (e.g. surfactants, phospholipids, amphiphilic block copolymers) can self-aggregate in selective solvents (e.g., water), spontaneously and reversibly, without external intervention but as a result of non-covalent interactions, into a variety of phase segregated (and ordered) structures such as micelles, spherical or cylindrical structures, mono- and multilayered vesicles, and also microemulsions, emulsions or LLC's. Furthermore, surfactant aggregates can be used in nanotechnology as templates in two fundamentally different ways. One approach according to the concept of morphosynthesis focuses on the use of the interface environment as a compartmentalized reaction space for the interface polymerization of amphiphilic monomers or surfmers. The other approach, in line with the concept of transcriptive synthesis, exploits the aggregate interface as a receptive surface in the controlled growth of polyelectrolytes, DNA, polymers and silica from precursor solutions. The key issues in surfactant-based nanoproducts are the structure-performance relationships along with surfactant-polyelectrolyte interactions [1,2].

A beautiful example of the use of spontaneously self-organized ordering to produce new biodegradable, biocompatible nanomaterials with incidental adverse effects is the application of the surfactant aggregate as a template to make multifunctional nanocarriers for both combination therapy, and theranostic applications. One of the key functions of the nanocarriers are (i) to successfully encapsulate hydrophobic drugs in order to target cells; (ii) to improve drug/dye efficacy; (iii) to serve as shields to protect multi-component cargoes (e.g., photosensitizers and other NIR dyes, cytostatics, quantum dots) from degradation and various toxic interactions with the biological environment. The lecture will cover first of all the most unique strategies - the layer-by-layer (LbL) subsequent adsorption of polyelectrolytes from their solutions on nanoemulsion liquid cores [3-5] and microemulsion-mediated interfacial polymerization [6,7] - applied for fabrication and *in vitro* release of the above mentioned active cargoes from polymeric nanocapsules along with their imaging (AFM, SEM, DLS), cellular uptake and internalization (CLSM, TIRF, FACS), photostability and ROS evaluation (UV, fluorescence and colorimetric methods).

1. R. Skrzela, G. Para, P. Warszyński, K. A. Wilk, *J. Phys. Chem. B*, **2010**, *114*, 10471.
2. A. Lewińska, M. Witwicki, R. Frąckowiak, A. Jezierski, K. A. Wilk, *J. Phys. Chem. B*, **2012**, *116*, 14324.
3. U. Bazylińska, R. Skrzela, K. Szczepanowicz, P. Warszyński, K. A. Wilk, *Soft Matter*, **2011**, *7*, 6113.
4. U. Bazylińska, R. Skrzela, M. Piotrowski, K. Szczepanowicz, P. Warszyński, K.A. Wilk, *Bioelectrochemistry* **2012**, *87*, 147.
5. U. Bazylińska, J. Pietkiewicz, J. Saczko, M. Nattich-Rak, J. Rossowska, A. Garbiec, K.A Wilk, *Eur. J. Pharm. Sci.*, **2012**, *47*, 406.
6. J. Pietkiewicz, K. Zielińska, J. Saczko, J. Kulbacka, M. Majkowski, K. A. Wilk, *Eur. J. Pharm. Sci.*, **2010**, *39*, 322.
7. K. A. Wilk, K. Zielińska, J. Pietkiewicz, N. Skońska, A. Choromańska, J. Rossowska, A. Garbiec, J. Saczko, *Int. J. Oncol.* **2012**, *41*, 10.

L-3

Importance of Luminescent Properties of Lanthanides in the Study of their Complexes and Inorganic Nanomaterials

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Luminescence properties of lanthanide(III) ions, Ln(III), characterised by very narrow emission bands and a long decay time, are important tools in the study of photophysical and coordination aspects of lanthanide compounds. Factors affecting the Ln(III) luminescence in solution and in solid state, that can both quench and/or increase the luminescence effectiveness are presented. The factors which markedly increase luminescence intensity, lifetime and quantum yield, efficiently reducing nonradiative energy degradation of Ln(III) ions are presented. Highly luminescent Ln(III) systems based on complex formation with several groups of both inorganic (polyoxometalates) and organic ligands (e.g. β -diketones, macrocyclic ligands, cryptands, heterobiaryl ligands, etc.) as well as energy transfer processes are discussed. The uses of europium luminescence lifetime measurements and the excitation spectroscopy of the $^5D_0 \rightarrow ^7F_0$ transition as a unique and sensitive way to characterize the species, binding sites of various ligands and complex stoichiometries, are briefly shown.

Nanocrystalline inorganic matrices, based on fluorides, oxyfluorides, oxides, borates, vanadates and phosphates doped with luminescent Ln(III) ions, synthesized with the use of various methods, are discussed concerning their structure, morphology and photophysical properties. Crystal structures of the prepared materials are confirmed using IR, XRD, TEM, Raman spectroscopy and EDX analysis. Morphology of nanocrystals, obtained by various synthesis methods, is examined with the use of TEM images and calculations based on Scherrer equation. Luminescence properties of the obtained luminophors, with different concentrations of Ln(III) ions, were characterized and compared based on registered excitation and emission spectra, measured emission lifetimes, quantum efficiency, calculated values of Judd-Ofelt intensity parameters and chromaticity coordinates were calculated. Investigated inorganic matrices are effective host materials for the Ln(III) ions, resulting in the intensive luminescence even with a very low concentration of the emitter. Obtained products characterized by exceptional luminescence properties and chromaticity coordinates have nanosized dimensions, chemical and physical stability and therefore can be considered as promising inorganic phosphors.

L-4

**Aromatic *o*-Bromo Substituted Aldehydes and Dialdehydes in
Synthesis of Functional Materials**

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and

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³on scientific leave in Organic Materials Research Group, Department of Chemistry, Vanderbilt University, USA

The subject of this presentation is to show the use of *ortho*-bromo aromatic aldehydes **1** and dialdehydes **5** in synthesis of fused polycyclic (hetero)aromatic hydrocarbons **4** and **7**. Diarylmethanols **3** and **6** with protected aldehyde and hydroxyl groups to avoid formation of isobenzofurans, underwent a new Friedel-Crafts modification which has recently been elaborated in our laboratory.¹⁻⁴ This approach involves the intramolecular cyclization of the latter in the one-pot procedure under acidic conditions (Scheme).

The new, planar compounds of type **4** and **7** may be utilized in various areas, as organic ligands for catalysts, drugs including DNA intercalators, nanoobjects or useful synthetic reagents. This time, besides synthetic aspects, there will be described their application in organic optoelectronics which currently is our main research interest. Moreover, *o*-bromo aldehydes **7** with expanded systems of fused (hetero)aromatic rings are unknown and constitute excellent synthons for further structural modifications.

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References

- [1] P. Bałczewski, M. Koprowski, A. Bodzioch, B. Marciniak, E. Różycka-Sokołowska, *J. Org. Chem.*, **2006**, 71, 2899;
[2] P. Bałczewski, A. Bodzioch, E. Różycka-Sokołowska, B. Marciniak, P. Uznański, *Chem. Eur. J.*, **2010**, 16, 2392;
[3] P. Bałczewski, A. Bodzioch, J. Skalik, M. Koprowski, P-385794, application 31.07.2008, P-389778, application 05.12.2009; P-396700, application 19.10.2011; European Patent Office, Submission No 1833848, Application No EP 121877088, 12.09.2012;
[4] A. Bodzioch, B. Marciniak, E. Różycka-Sokołowska, J. K. Jeszka, P. Uznański, S. Kania, J. Kuliński, P. Bałczewski, *Chem. Eur. J.*, **2012**, 18, 4866.

L-5

Highly Efficient Thermally Activated Fluorescence of a New Rigid Cu(I) Complex [Cu(dmp)(phanephos)]⁺

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In the past decade, substantial investigations were carried out to develop novel materials for organic light emitting diodes (OLEDs), in particular, to increase the device efficiency and stability. In this respect, luminescent materials and excitation mechanisms play a crucial role. A breakthrough was reached by applying organometallic and inorganic complexes. This contribution presents a new, adequately designed Cu(I) complex (Fig. 1) that may be used for OLED applications.

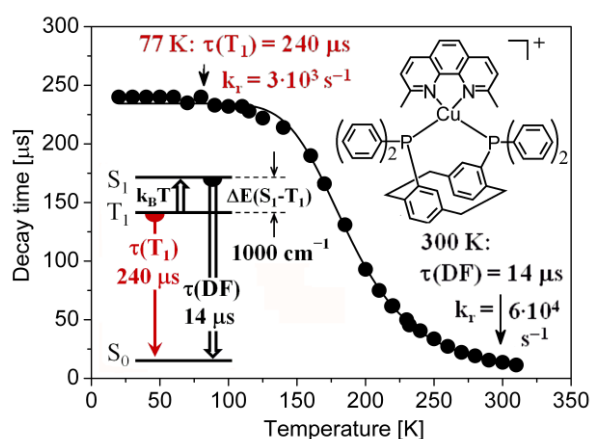


Fig. 1

The rigid [Cu(dmp)(phanephos)]⁺ complex displays high luminescence quantum yield of 80 % at ambient temperature. In contrast to the long-lived phosphorescence of 240 μs below $T < 120 \text{ K}$, the ambient-temperature emission represents a thermally activated delayed fluorescence (TADF) with a decay time of only 14 μs. This material has a high potential to be applied in efficient OLEDs taking advantage of the singlet harvesting mechanism.

R.C. and K.K. thank the German Academic Exchange Service (DAAD) for financial support.

L-6

**Molecular Functional Components for Materials Chemistry.
Multichromophoric Structures as Building Blocks for Picotechnology**

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Functional components are becoming more and more important for Materials Science. A high level of integration of functionalities is targeted and seems to progress until molecular dimensions. As a consequence, the next generation of functional building blocks may reach picometer dimensions where molecular technology¹ will be required for Materials Science. Electric interactions dominate highly integrated technology requiring suitable components. Molecular electronics can be developed in analogy to conventional electronics where conductors may be replaced by conjugated electronic systems with delocalizable electrons and resonating circuits by the eigenvalues of molecular structures. Both requirements are fulfilled by chromophores because of their special electronic structures and distinct light-absorption. Highly stable chromophores would be ideal components for such applications. The *peri*-arylenes including the perylene dyes² as the most prominent class are very promising candidates for molecular electronics because of their extraordinary chemical and photochemical stability. Many synthetic methods are available and will be reported for the adaptation of this class of compounds to the special requirements of Materials Chemistry. Complex molecular architectures were established for multichromophoric systems with special properties such as photo induced electron transfer (PET) and energy transfer (FRET) for light collection and concentration. The investigation of model compounds indicate that the established theory of FRET has to be altered;³ novel concepts will be as well presented as materials with unusual optical properties.



1. Review: H. Langhals, *Chromophores for picoscale optical computers* in K. Sattler (ed.), *Fundamentals of picoscience*, p. 1-50, Taylor & Francis Publisher, London 2013.

2. Reviews: (a) H. Langhals, *Molecular devices. Chiral, bichromophoric silicones: Ordering principles in complex molecules* in F. Ganachaud, S. Boileau, B. Boury (eds.), *Silicon Based Polymers*, p. 51-63, Springer, 2008, ISBN 978-1-4020-8527-7, e-ISBN 978-1-4020-8528-4. (b) H. Langhals, *Helv. Chim. Acta.* **2005**, *88*, 1309-1343. (c) H. Langhals, *Heterocycles* **1995**, *40*, 477-500.

3. H. Langhals, A. J. Esterbauer, A. Walter, E. Riedle, I. Pugliesi, *J. Am. Chem. Soc.* **2010**, *132*, 16777-16782.

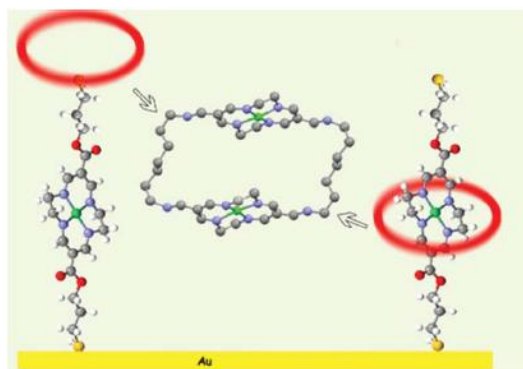
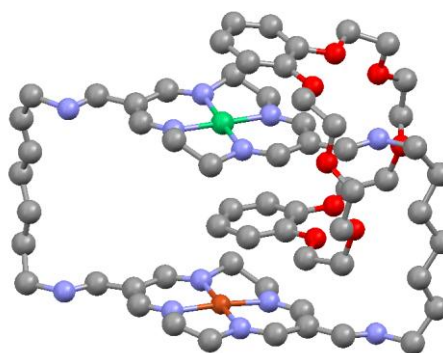
L-7

Macrocyclic Metal Complexes as Building Blocks for Construction of Molecular Receptors and Devices

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Face-to-face bis-cyclidene cations linked by polymethylene chains form host-guest complexes with π -donor, aromatic molecules. Subtle changes in the molecular structure, for example, varying the metal-to-metal distance, changing the metal oxidation state or its kind, allow to modify the electron donor-acceptor properties of the system. In several interactions, not the metal centres, but ligand electrons are involved in the electronic interactions. This recognition phenomenon has been applied to synthesise of mechanically interlocked supramolecules exhibiting intramolecular motion triggered by an appropriate potential.^[1] Self-assembled monolayers of dithiolated neutral tetraazamacrocyclic complexes of copper(II) or nickel(II)^[2,3] can provide molecularly defined platforms for the formation of a pseudorotaxane-like nanostructures on the gold electrode surface. Oxidation of neutral complexes leads to formation of cations and switching off interaction with charged π -acceptor. This electrochemically controlled association opens a new route for constructing molecular structures, such as rotaxanes and catenanes bound to a conducting support. Such supported mechanomolecular arrays are promising for the preparation of molecular materials and devices.^[4]



1. B. Korybut-Daszkiewicz, A. Więckowska, R. Bilewicz, S. Domagała, K. Woźniak, *Angew. Chem. Int. Ed.* **2004**, 1668-1672; *Angew. Chem.* **2004**, 1700-1704.
2. U. Wawrzyniak, M. Woźny, J. Kowalski, S. Domagała, E. Maicka, R. Bilewicz, K. Woźniak, B. Korybut-Daszkiewicz, *Chem. Eur. J.* **2009**, 15, 149-157.
3. U. E. Wawrzyniak, M. Woźny, I. Mames, B. Pałys, B. Korybut-Daszkiewicz, R. Bilewicz, *Dalton Trans.* **2010**, 39, 730-735.
4. B. Korybut-Daszkiewicz, R. Bilewicz, K. Wozniak, *Coord. Chem. Rev.* **2010**, 254, 1637-1660.

L-8

**Materials for Organic and Hybrid (Organic/Inorganic) Electronics:
 Preparation Strategies, Characterization and Application to Field
 Effect Transistors and Photovoltaic Cells***

**Grzegorz Gąbka, Kamil Kotwica, Renata Rybakiewicz, Piotr Bujak, Małgorzata
 Zagórska and Adam Proń**

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Organic semiconductors constitute an important class of materials suitable for applications in such electronic devices as light emitting diodes (LEDs), photodiodes (PD), photovoltaic cells (PCs) and field effect transistors (FETs). In the first part of the lecture synthetic strategies leading to low and high molecular weight organic semiconductors with tunable ionization potential (IP) and electron affinity (EA) will be outlined. Their spectroscopic, electrochemical and spectroelectrochemical will be discussed. Processing techniques leading to ordered 2D (for monolayer) and 3D (for thin films) supramolecular organization will be described. Finally, fabrication of an organic FET will be given as an example.

Molecular composites of inorganic semiconductor nanocrystals and organic semiconductors are also promising materials for fabrication of hybrid (organic/inorganic) electronic devices. Preparative techniques used for the fabrication of such materials will be reviewed in the second part of the lecture. This will include three principal methods: i) initial ligands exchange for semiconducting ones; ii) initial ligands exchange followed by covalent grafting of the organic semiconductors *via* specially designed linker ligands and iii) hydrogen bond-assisted molecular recognition of specially designed functional groups in the semiconducting molecule and the capping ligand (bio-inspired approach) (see Fig. 1). Instructive examples of each method will be given. Spectroscopic, electrochemical and electrical transport properties of the prepared nanocomposites will also be discussed. Fabrication of a hybrid PCs will be presented as an example.

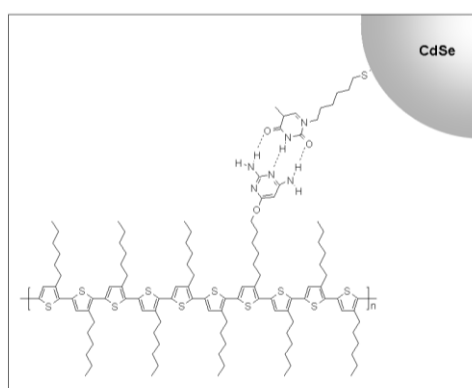


Fig.1 Molecular recognition between mercaptothymine capped CdSe nanocrystals
 and diaminopyrimidine functionalized poly(3-hexylthiophene)

* a part of research financed by the TEAM program entitled „New solution processable organic and hybrid (organic/inorganic) functional materials for electronics, optoelectronics and spintronics.” TEAM/2011-8/6 (2012-2015)

L-9

Synthesis of Functionalisable 6-Oxoverdazyls

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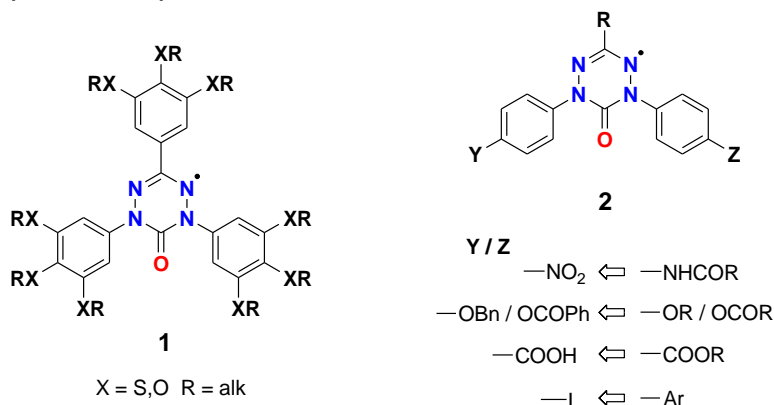
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Stable π -delocalised radicals, including verdazyl derivatives, become important structural elements of advanced materials for various technological and biological applications.¹ For example, they are investigated in the context of harvesting and storage of energy, non-invasive *in vivo* measurements, and spintronics. More recently we have reported² a series of photoconductive liquid-crystalline 6-oxoverdazyl discotics (**1**) as the first step towards photovoltaic materials.



Further progress in the development of liquid crystalline radicals requires the presence of various functional groups on the heterocycle, suitable for preparation of compounds with specific mesogenic, photophysical, and electrochemical properties. For this purpose we have developed functional group interconversion in verdazyl system **2**, and applied this chemistry to the preparation of bent-core mesogens. Synthesis and properties of compounds **1** and **2** will be presented.

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¹ a) R. G. Hicks, T. Suga, H. Nishide, V. V. Khramtsov, J. L. Zweier, in *Stable radicals: Fundamentals and applied aspects of odd-electron compounds*, Hicks, R. G. Ed.; Wiley&Sons, 2010; b) S. Sanvito, *Chem. Soc. Rev.* **2011**, *40*, 3336-3355.

² a) A. Jankowiak, D. Pociecha, J. Szczytko, H. Monobe, P. Kaszyński, *J. Am. Chem. Soc.* **2012**, *134*, 2465-2468; b) A. Jankowiak, D. Pociecha, H. Monobe, J. Szczytko, P. Kaszyński, *Chem. Commun.* **2012**, 7064-7066.

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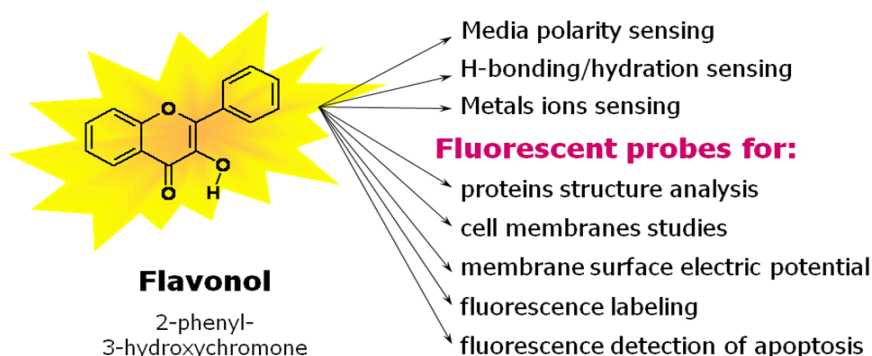
Excited-State Proton Transfer Dynamics and Sensing Abilities of Heterocyclic Derivatives of 3-Hydroxychromone

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Among a large variety of natural and synthetic fluorescent dyes, derivatives of the 3-hydroxychromone (3HC) family attract particular attention. Exhibiting dual-band fluorescence owing to the proton transfer reaction in their excited state (ESIPT), these molecules are highly sensitive to different parameters of their environment – polarity, H-bonding ability, viscosity etc. This particularity has become the basis for development of a new approach in the applied fluorescent spectroscopy – ratiometric detection in physico-chemical, environmental and biological analysis. The main advantage of this method is that the analytical signal becomes independent on the parameters which are hard to control while analyzing complex natural objects, such as excitation light intensity, fluorescent probe concentration in the sample, etc. However, an important question of the photophysical reason of the existence of the ratiometric response to the changes of the molecule's microenvironment is still not completely solved.



It is a well-known fact that, due to a non-radiative process that causes energy losses in the excited state, the ESIPT compounds are usually characterized by low-to-moderate fluorescence quantum yields. However, it is important for a compound to possess an effective emission in order to be used for sensing applications. Combining well-known highly fluorescent moieties, such as 2,5-diphenyloxazole or 1,3,5-triphenyl-4,5-dihydro-1H-pyrazole, with the 3-hydroxychromone core was shown to be an efficient way to obtain effective multi-band fluorescent dyes.

Complexity of the emission spectrum of the ESIPT compounds gives them advantage over the single-band fluorophores in sensing applications. Thus, an interesting challenge emerges to develop and create compounds with either tunable or multiple ESIPT pathways through introduction of alternative proton accepting centers, or additional intramolecular hydrogen bonds into the dye's molecule.

Derivatives of 3HC are also promising with regard of developing new composite materials on their base. Thus, a highly-sensitive and selective fluorescent probe for mercury(II) ions in water was designed upon incorporation of a 3HC dye in a polybutylmetacrylate film. The same dye was recently used to probe the surface properties of dodecanethiol-coated gold nanoparticles. All these applications, together with the most interesting and pronouncing examples from other research groups, are discussed in the present talk.

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Notes

