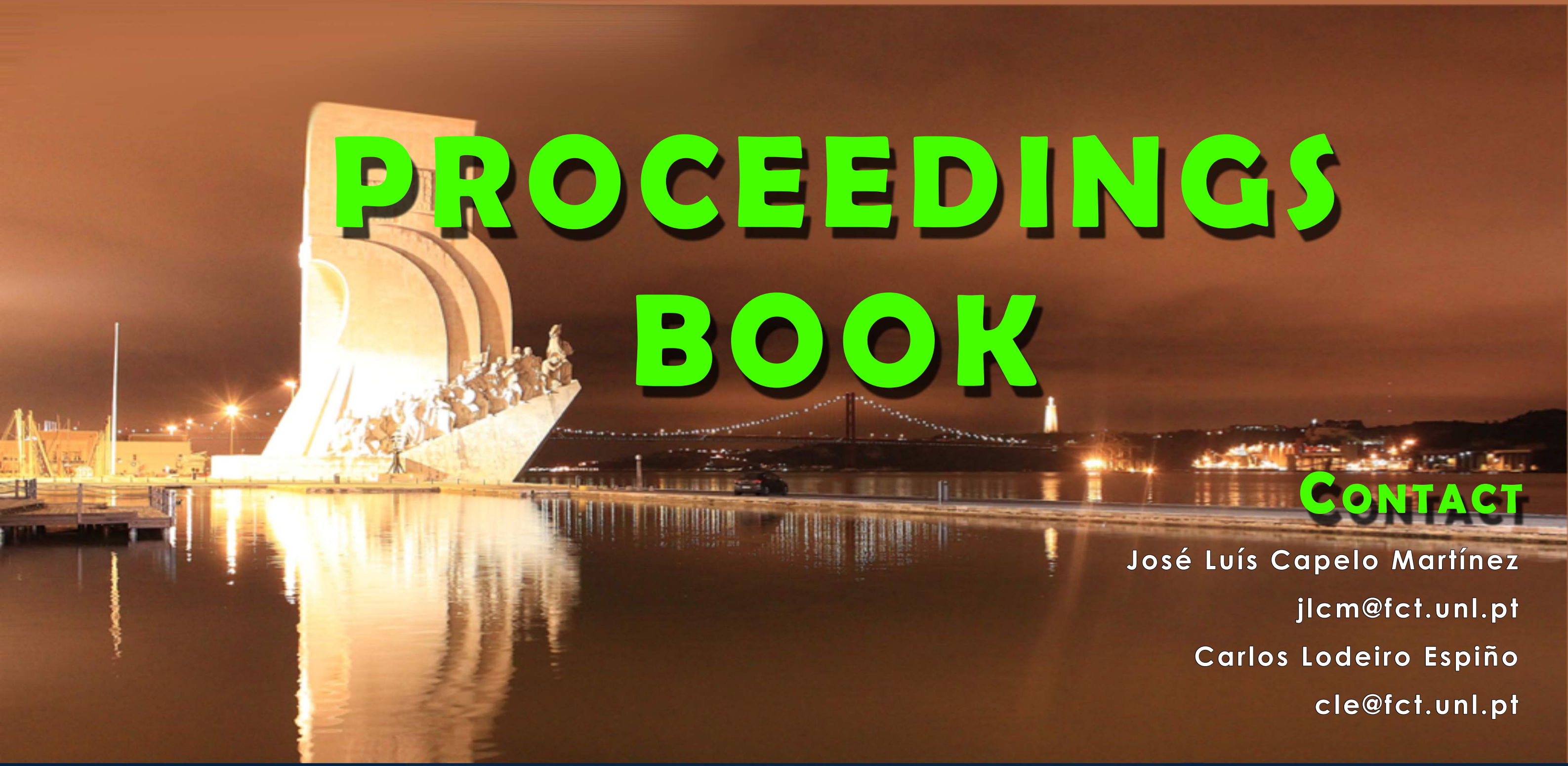
IC^{3}EM 2016

September 2016 Lisbon, Portugal

2nd International Caparica Conference on Chromogenic and Emissive Materials

SYMPOSIUM SUBJECTS

- Fluorescence and Absorption Spectroscopy
- Microscopy Applications: From Optical to Electronical
- Chromogenic Compounds for analysis
- Colour as analytical tool
- Emissive Probes, Chemosensors
- Cell and Tissue Imaging
- Fluorescence in Biology/Medicine/Biochemistry
- Luminescent Peptides and Proteins
- Single Molecule Spectroscopy
- Fluorescence in High Throughput



PROCEEDINGS BOOK

CONTACT

José Luís Capelo Martínez
jlcm@fct.unl.pt
Carlos Lodeiro Espiño
cle@fct.unl.pt

PROTEOMASS
scientific society | www.proteomass.org

WWW.IC3EM2016.COM

www.bioscopegroup.org
BIOSCOPE
in the forefront of science

IC^{3}EM 2016 Book of Abstracts

2nd International Caparica Conference on Chromogenic and Emissive Materials

Caparica – Portugal

5th – 8th September 2016

2nd International Caparica Conference on Chromogenic and Emissive Materials – IC^{3}EM 2016

Cover design: Tomás Miranda
Authors: Carlos Lodeiro, Elisabete Oliveira, Hugo Santos, José Luis Capelo.
ISBN: 978-989-99639-0-0
Printed by Proteomass Scientific Society (Portugal)
Printage: 50 copies (paper)
Caparica, Portugal, 2016

Committees

Conference Chairs

Carlos Lodeiro Espiño, PhD. FRSC

UCIBIO-REQUIMTE, Chemistry Department, Universidade NOVA de Lisboa, Portugal.

José Luis Capelo Martínez, PhD. FRSC

UCIBIO-REQUIMTE, Chemistry Department, Universidade NOVA de Lisboa, Portugal.

Scientific Committee

Carlos Lodeiro Espiño, PhD. FRSC

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

José Luis Capelo Martínez, PhD. FRSC

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Elisabete Oliveira, PhD, PhD

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Hugo Miguel Santos, PhD, PhD

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Emilia Bertolo, PhD

Biomolecular Research Group, School of Human and Life Sciences, Canterbury Christ Church University, UK

Andrea Bencini, PhD

Universita degli Studi di Firenze, Department of Chemistry Ugo Schiff, Florence, Italy.

Luca Prodi, PhD

Chemistry Department, University of Bologna, Italy.

Javier Fernandez, PhD

UCIBIO-REQUIMTE, Chemistry Department, FCT- Universidade NOVA de Lisboa, Portugal.

Fernando Pina, PhD

REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Alcindo Aparecido dos Santos, PhD

Instituto de Quimica, Universidade de Sao Paulo Brazil.

Graça Neves Morgado, PhD

Organic Chemistry Department, Aveiro University, Portugal.

Andrea Pucci, PhD

University of Pisa, Chemistry and Industrial Department, Pisa, Italy.

Julia Lorenzo Rivera, PhD

Biochemistry Department, University Autonoma of Barcelona, Spain.

Local Organizing Committee

Carlos Lodeiro Espiño, PhD. FRSC

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

José Luis Capelo Martínez, PhD. FRSC

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Elisabete Oliveira, PhD, PhD

UCIBIO-REQUIMTE, FCT- Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Gilberto Igrejas, PhD

Universidad de Trás-os-Montes e Alto Douro. Portugal, UCIBIO-REQUIMTE

Hugo Santos, PhD, PhD

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Javier Fernández-Lodeiro, PhD

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Adrián Fernández-Lodeiro

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Eduardo Araújo

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Susana Jorge

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Jamila Djafari

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

António Soares

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Jemmyson Jesus

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Joana Coelho

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Gonçalo Pinto

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Marta Silva

BIOSCOPE Group, ProteoMass Scientific Society, FCT-Universidade NOVA de Lisboa, Portugal.

Ana Laço

BIOSCOPE Group, ProteoMass Scientific Society, FCT-Universidade NOVA de Lisboa, Portugal.

Tomás Miranda

BIOSCOPE Group, ProteoMass Scientific Society, FCT-Universidade NOVA de Lisboa, Portugal.

Paulo Ferreira

BIOSCOPE Group, ProteoMass Scientific Society, FCT-Universidade NOVA de Lisboa, Portugal.

Nuno Morais

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

Yegor Borovkov

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

Henrique Mourão

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

Erica Rosa

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

Verónica Weng

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

Diogo Costa

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

Catarina Salgueiro

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

André Seco

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

Carolina Abelho

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

João Sarrato

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

Jéssica Machado

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal

Conference Secretariat

Elisabete Oliveira, PhD, PhD

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Adrián Fernández-Lodeiro , MSc

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Hugo M. Santos, PhD, PhD

UCIBIO-REQUIMTE, Chemistry Department, FCT-Universidade NOVA de Lisboa, Portugal.

Faculdade de Ciências e Tecnologia - Universidade NOVA de Lisboa

Faculty of Science and Technology, University NOVA of Lisbon

UCIBIO-REQUIMTE, Department of Chemistry
Campus de Caparica, 2829-516 Caparica, Portugal

E-mail: jlcm@bioscopegroup.org / clodeiro@bioscopegroup.org

Phone: +351 919404933 / +351 916949133

Web: www.ic3em2016.com

Web page designer: Tomás Miranda

Sponsors

Bruker

(www.bruker.com)

LaborSpirit

(www.laborspirit.com)

Royal Society of Chemistry

(www.rsc.org)

Biogen Cientifica

(www.biogen.es)

Computational and Structural Biotechnology Journal

(www.journals.elsevier.com/computational-and-structuralbiotechnology-journal/)

Paralab

http://www.paralab.pt/

Sociedade Portuguesa de Química

(www.spq.pt/)

STAB Vida

(stabvida.com/en/)

Partners

Faculdade de Ciências e Tecnologia
Universidade Nova de Lisboa

(www.fct.unl.pt)

UCIBIO@REQUIMTE
(www.requimte.pt/ucibio/homepage)

Câmara Municipal de Almada

(www.m-almada.pt)

Journal of Integrated OMICS

(www.jiomics.com/index.php/jio)

Bioscope

(www.biocopegroup.org/)

Proteomass Scientific Society

(http://www.bioscopegroup.org)

Caparica Científica

(http://www.bioscopegroup.org)

Welcome

Dear Colleagues and Friends,

It is with great pleasure that the BIOSCOPE group welcome you to the seafaring village of Costa de Caparica in Portugal.

The series of International Caparica Congress on Chromogenic and Emissive Materials, IC3EM, was created with two main aims, to promote the sharing of knowledge, both theory, and practice, in dyes and light areas; and to foster the creation of international teams to boost advances in the chromogenic and emissive materials and applications. Luckily, such goals have been achieved.

In 2014 during the first edition, close to 250 participants from 30 countries share their last results and contributions in emissive and colored materials fields. The quality of the researchers attending the conference was excellent.

To continuous with this outstanding event, during the 2nd IC3EM Congress, outstanding worldwide distinguished plenary speakers, the best in the arena; excellent keynotes, remarkable orals, impressive shot-gun presentations and brilliant posters are going to make of 2nd IC3EM an extraordinary event. Sharing of knowledge is thus ensured.

The commitment to the internationalization of the 2nd IC3EM has been accomplished as 29 countries (152 participants) are represented (see the list given bellow). Therefore, it is expected the creation of new collaborations between teams of different countries and continents. The venue is located in a little and pictorial village, which will aim people to stay together, thus promoting the interchange of ideas. And yet, the capital, Lisbon, can be reached within the blink of an eye, giving thus the chance for a quick visit to relax.

The 3rd IC3EM conference will be held in 2018 in a place decided during the 2nd event.

On behalf of the organizing committee, the scientific committee, the people of Caparica, The Mayor of Almada, and the Dean of the Faculty of Science and Technology of the University NOVA of Lisbon, We wish you a pleasant stay at Caparica.

List of countries with researchers attending IC^{3}EM:

Spain
Italy
United Kingdon
Portugal
Belgium
USA
China
Japan
Poland
Singapore
Germany
Denmark
South Korea
India
Switzerland
Thailand
Norway
Sweden
Ireland
Lithuania
Israel
Oman
Brazil
France
Russia
Croatia
Taiwan
Hungary
Romenia

Prefaces

Blake R. Peterson

Dept. of Medicinal Chemistry, The University of Kansas, 2034 Becker Dr., Lawrence, KS 66047, USA

Over the past few decades, fluorophores have become critical tools for studies of biological systems. These luminescent molecules are widely used to label antibodies for immunofluorescence detection of antigens on western blots, labeling of cell surfaces, and imaging of proteins in fixed cells. Related fluorescent sensors also allow detection of ions, small molecules, and numerous enzymatic activities. The most valuable commercially available fluorophores are generally highly optimized for a few specific physicochemical properties. These properties include brightness, defined as the product of the extinction coefficient and quantum yield, photostability, and selective chemical reactivity, to allow control over labeling of biomolecules of interest. Popular fluorophores such as the AlexaFluor dyes further include polar functional groups that both enhance aqueous solubility and limit quenching of the fluorophore when bound to proteins or other biomolecules. These efforts to optimize the photophysical properties of fluorophores have provided outstanding tools for labeling of antibodies, among other applications. However, common chemical modifications made to confer high aqueous solubility, or that involve inclusion of cationic functional groups, which can increase non-specific binding to proteins, membranes, and specific cellular organelles, can limit chemical biology investigations involving living cells or more complex biological systems such as live model organisms.

To use fluorescent molecular probes to study biomolecules that reside in living cells and model organisms, other physicochemical properties become increasingly important. These properties can include bioavailability, high cellular permeability, and avoidance of non-specific interactions with proteins, membranes, and cellular organelles. Optimization of these properties involves many of the same challenges that are faced by medicinal and pharmaceutical chemists during the discovery and development of therapeutics. To create fluorescent probes that penetrate the plasma membrane of living cells, engage specific intracellular targets, and not otherwise perturb the biological system, properties such as affinity for the target (K_d), avoidance of off-target interactions (specificity), acidity (pKa), partitioning between aqueous and organic phases (cLogP, cLogD), metabolic stability, toxicity, and molecular weight are parameters that must be considered, optimized, and/or controlled. By applying a medicinal chemistry mindset to the design and synthesis of more drug-like fluorescent molecular probes, new opportunities will emerge for discoveries at the interface between chemistry and biology.

Nicola Armaroli

Istituto per la Sintesi Organica e la Fotoreattvità (ISOF), Consiglio Nazionale delle Ricerche (CNR)
Via Gobetti 101, 40129 Bologna, Italy, nicola.armaroli@isof.cnr.it

Since times immemorial, chromogenic and emissive materials have been part of people's daily life. Artists belonging to past civilizations all across the world have mastered the preparation of marvelous pigments of any colors using minerals or naturally occurring dyes. Some of them have survived harsh ambient conditions for centuries, leaving us amazed by their beauty and historical record. As chemists, we find it astonishing that quantum dots had been unintentionally prepared centuries before their discovery and will continue to adorn the glasses of magnificent cathedrals across Europe for millennia to come, even under unforgiving sunlight.

As far as luminescence is concerned, natural "mysterious" phenomena such as lightning, aurora borealis, or some luminous animals have long fascinated (and even scared) humans. Also in the luminescence domain, human curiosity made serendipitous discoveries that afforded luminescent materials well before chemistry became an established scientific discipline. In this regard, a landmark event was the discovery of the so-called Bolognian stone, occurred in 1603. Vincenzo Casciarolo, a cobbler and amateur alchemist working in Bologna (Italy), while trying to convert poor materials into gold, calcined a stone containing barium sulphate with coal and obtained luminescent barium sulfide. It was the first reported example of a *phosphor*, because the "magic" stone released light in the dark after exposure to sunshine. Probably, Mr. Casciarolo did not suspect that, after some centuries, this class of materials would become more important then gold itself in the daily life of people.

It was an inspired idea to start the series *International Caparica Conference on Chromogenic and Emissive Materials* in Portugal. Of course, not only due to the historical tradition of Europe in this area, but also for the increasing importance exhibited by these materials in fundamental science and applied technologies. I look forward to attending an exciting conference where hot topics in the area will be discussed, from pigments in ancient artwork to new white emissive materials, and from the most advanced near-infrared luminophores for bioimaging to new hybrid emitting materials for lighting or laser technologies.

In the future, I trust that this *IC3EM Book of Abstracts* will not only be the permanent record of the state-of-the-art in chromophores and luminophores in mid-2016, but a memory of the start of new collaborations that will widen the frontiers of knowledge in the field and enrich the next editions of the Conference.

B. Mark Heron

Department of Chemical Sciences, School of Applied Sciences, The University of Huddersfield, Huddersfield, HD1 3DH, UK.

The investigation of chromogenic and emissive materials represents an exciting and challenging modern day research activity which has the potential to offer significant reward. Chromogenic and emissive materials are involved in diverse applications ranging from traditional coloration for aesthetic purposes through to complex switching systems for data storage. Today we can use dyes, pigments and complexes to harness sunlight to generate electricity and conversely we can electrically stimulate molecules to generate light; indeed the 2014 Nobel Prize (Physics) was awarded for "the invention of efficient blue light-emitting diodes (LEDs)", which offer the potential to limit the impact of our activities on global climate change. Research continues apace in this area with the development of a full colour gamut of organic light emitting diodes (OLEDs) and their phosphorescent relations, PhOLEDs, for low energy lighting and displays. Also in 2014 the Nobel Prize for chemistry was awarded "for the development of super-resolved fluorescence microscopy", which is immensely useful in imaging science, bioscience and medicine since the technique is capable of revealing the presence of a single molecule. Each of the foregoing prize-winning themes relies upon the performance of emissive (fluorescent, phosphorescent) materials.

There has been a tremendous upsurge over the last few years in the area of sensors for biologically important metal ions and organic compounds; such sensors invariably employ fluorescence though often in conjunction with traditional absorption spectroscopy. The sensitivity and selectivity of modern day sensors is remarkable and is a credit to the chemists and biochemists that design, build and employ such compounds. However, emissive materials are not just involved in biomedical detection (sensors, microscopy) but are also employed to cure disease. One of the earliest azo dyes, Prontosil (1932, Bayer), was employed as a useful antibacterial against Gram-positive cocci and today we make use of the sensitizing ability of complex polycyclic compounds, e.g. porphyrins, phthalocyanines and phenothiazines, for the destruction of tumors and blood and wound disinfection.

Chromogenic and emissive materials also feature in many stimuli responsive systems (thermo-, piezo-, photo- and electro- chromic). These dynamic systems are not just academic curiosities, but offer potential in the design of new machines which can operate at the molecular level and also have been harnessed to extend our visual perception into the UV region. Commercial applications of stimuli responsive molecules include their use in time / temperature sensors, ophthalmic sunlenses and privacy / anti-glare glazing.

For the graduate chemist seeking new complex challenges there is an exciting colorful world awaiting you which embraces all branches of chemistry from synthesis, polymers and spectroscopy to molecular modeling and which will test your knowledge and skill to the full. The impact of chromogenic and emissive materials on society has yet to be fully realized and research on this fascinating theme will continue well into the 21st century.

Todd B. Marder

Institute of Inorganic Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Luminescent chromophores have a major role to play in many modern and potentially future applications. These include molecular systems based on organic compounds as well as organo-main group systems and organometallic complexes. Indeed, our own work covers a broad range of such types of compounds, including conjugated rigid-rod organics, pyrene chemistry, organoboron compounds, and organo-transition metal systems, and both fluorescent and phosphorescent compounds. In addition to selective sensors and numerous applications in biological imaging, including both live cells and tissues, there is a wide range of applications in optoelectronic materials including both liquid crystals and organic light emitting diodes (OLEDs). It is also interesting to consider the relationship between light emitting materials such as OLEDs which are triggered by electrical charge injection, and light absorbing ones such as organic photovoltaics (OPVs) which produce an electrical current. In both cases, similar photophysical principles are involved, and there remain many interesting, fundamental aspects of photophysics which require further exploration. It can be envisaged that systems capable of photoinduced charge separation will play a key role in new materials and, in this regard, fundamental issues such as twisted intramolecular charge transfer (TICT) and related excited state dynamic phenomena will be important issues to understand in detail. Thermally activated delayed fluorescence is another interested and related phenomenon which has recently come to the forefront of the field. Thus, there are many new areas to explore, and much to be learned about excited state phenomena in even rather simple molecules. One can envisage, in this regard, the growth of pump-probe or transient absorption spectroscopy of various kinds and on various timescales including both optical and IR probes, as a means by which to study the basic processes which occur following absorption of light. In summary, while there is a long history to the field, there is much still to be done, and many opportunities for a new generation of researchers to make major breakthroughs both in fundamental and applied areas.

J.C Lima

REQUIMTE, Departamento de Química, CQFB, Universidade Nova de Lisboa, Monte de Caparica, Portugal. e-mail: lima@fct.unl.pt.

The inherent double crosscheck of fluorescent signals (specific excitation wavelength input – specific wavelength emission output) makes fluorescence unbeatable in the discrimination of the presence of a specific target over spectrally complex backgrounds inherent to real-world samples. The mature state of the field of photophysics and photochemistry, the existence of a large collection of fluorescent sensors and labels, together with the existence of a library of chemical tools that allow efficient labeling of very different systems, has spread the use of fluorescence across many fields ranging from biological markers, luminescent displays, energy harvesting and a plethora of sensing applications. As such, fluorescent and colorimetric markers, are routinely used in many different fields where the researchers typically attend to specialized forums where the exchange of information is limited to common interests and goals not concerning the fluorescent tools that are used. For that reason, there is the complementary need to put together the diversified research fields that use fluorescent and colorimetric markers in dedicated forum of fluorescent and colorimetric applications across all fields, which allow the exchange of information on relevant targets and smart strategies to produce mature products for the daily needs, based on the established knowledge on these chromogenic materials.

Pier Luigi Gentili

Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di sotto 8, 06123 Perugia, Italy.

Chromogenic and emissive materials are informative and amusing compounds. They are informative because chromogenic and emissive molecules bridge the gap between the microscopic and the macroscopic worlds. They have the power of receiving stimuli and sending back optical signals bearing information about what is happening down there, at the bottom, i.e. at the molecular level. At the same time, they are amusing. In fact, they send optical signals that are, quite often, coloured. As the English poet Leigh Hunt said, “the colours are the smile of nature”.

In our group, chromogenic and emissive materials are used as surrogates of the elements of human sensory system for the development of Chemical Artificial Intelligence. In fact, they are responsive to physical and chemical inputs and they are switchable, i.e. they are reversible in their functioning. They behave as if they were electronic transistors. Therefore, chromogenic and emissive compounds are suitable to implement the basic elementary YES/NOT logic functions. Moreover, two “molecular transistors” in series or in parallel implement the AND or OR logic functions, respectively. Connecting the input and output of several, AND, OR and NOT gates, it is possible to set up complicated logic functions. To implement complicated logic functions there are two main strategies. One consists in designing multi-switchable responsive molecules, i.e. chromogenic and emissive compounds with many accessible states. The other consists in implementing multi-components chemical systems that are far-from thermodynamic equilibrium and strongly interconnected; they can exhibit emergent properties. In my view, if we want to approach the computational performances of our human sensory system, we need to focus, in particular, on the second strategy. As soon as we deeply comprehend the emergent properties, we will unveil secrets of Complexity. And everyone knows that understanding Complexity is a great challenge for science.

Mogens Brøndsted Nielsen

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Development of chromophores for harvesting of solar energy in photovoltaics devices has for several years been an important research field, while there has been much less focus on how to store solar energy using molecules. Indeed, for efficient exploitation of solar energy, a major challenge is to store the energy as periods of solar energy supply do not always match periods of demand. Photochromic molecules that upon irradiation undergo conversion to meta-stable, high-energy isomers may offer one possible solution to this problem. One additional advantage of using photoisomerizations of photochromic molecules is that the cycle of light-harvesting, energy storage, and on-demand energy release corresponds to a closed energy cycle with no emission of CO_2 or other chemical oxidation products.

Andrea Pucci

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, 56124 Pisa, Italy.

INSTM, UdR Pisa, Via Moruzzi 13, 56124 Pisa, Italy.

Fluorescence was used for the first time as an analytical tool for the determination of various and diverse organic and/or inorganic species. It was found that sensing based on fluorescence is one of the most effective methods for the detection of analytes with high sensitivity and selectivity thanks to the specially designed emitting probes. Materials which respond to external solicitations (physical or chemical) through variations in their fluorescence are called fluorogenic. Nature illustrates several ways on how color response towards external stimuli may be obtained. For example, chameleons, cephalopods and lizards are well known for their awesome abilities to change the skin color in response to mood, temperature and light intensity. These and other inspiring examples, together with the growing knowledge on the photophysics of chromophores, will stimulate the design of new effective tools for the development of sensors, probes and information displays.

Recent advances have been focused on luminogenic materials with aggregation-induced emission (AIE) attributes. Materials showing the AIE phenomenon are more efficient emitters while in the aggregated state than in the dissolved form. In comparison to the conventional chromogenic systems, the sensors based on the turn-on nature of the AIE luminogens appear to be more sensitive also at moderate perturbations. Moreover, they represent a powerful tool for investigating the structure and dynamics of matter or living systems being sensitive to polarity, fluidity and molecular mobility.

Fluorescence is not only an essential research tool and an everyday technique. It also plays a pivotal role in solar energy harvesting in luminescent solar concentrators (LCSs). In LSCs, sunlight penetrates the top surface of an inexpensive plastic or glass waveguide. This light is absorbed by luminescent molecules which are either embedded in the waveguide or applied in a separate layer on top or bottom of the waveguide. A fraction of the re-emitted light is trapped in the waveguide by total internal reflection and then collected at the edges of the device to produce electric power by means of photovoltaic (PV) cells even with a cloudy sky.

In summary, the enormous number of available organic/inorganic fluorophores opens unlimited possibilities for the development of advanced materials with strongly emissive and chromogenic properties. We expect that these concepts assisted by sustainable routes may steer innovative, smart and intelligent materials to be used in the everyday life.

Table of Contents

Plenary Lectures

PL 1 - Discovery of new therapeutic strategies using fluorescent molecular probes

Blake R. Peterson

Dept. of Medicinal Chemistry, The University of Kansas, 2034 Becker Dr., Lawrence, KS 66047, USA

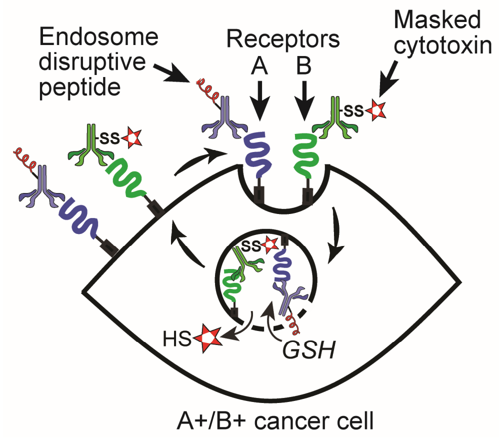
Abstract

My laboratory creates fluorescent molecular probes that are designed to target specific organelles of living cells. We use these probes both for fundamental studies of chemical biology and as tools for validation of new methods to treat cancer. One project that I will describe involves the synthesis of disulfide-linked fluorophores that accumulate in endosomes of cancer cells. These agents were used to discover peptides that form pores in endosomal membranes and disrupt these membrane-sealed compartments. This disruption can be used to trigger the release of fluorophores and cytotoxins into the cytoplasm and nucleus of cancer cells, providing a new mechanism to activate the toxicity of anticancer agents. As a potential therapeutic application of this discovery, we are exploring the hypothesis that derivatives of these peptides targeted to cancer cells might help address one of the greatest challenges in cancer therapy: the need to kill all cancer cells in a patient without harming any normal cells. In our approach, termed synthetic lethal targeting, we are creating pairs of antibody conjugates that bind two distinct growth factor receptors frequently overexpressed on the surface of cancer cells. In this system, one antibody conjugate is designed to function as a cytotoxic warhead, whereas the other is designed to function as a trigger that disrupts endosomes and releases the cytotoxin only in targeted cancer cells. This novel approach may provide a less toxic platform to eradicate cancer across cell types. I will additionally describe a second subcellular targeting project that focuses on the synthesis of fluorophores that accumulate in the endoplasmic reticulum (ER). These fluorophores can be linked to cytotoxins to allow selective inactivation of pathways in the ER that are critical for the proliferation of specific types of cancer. These projects share a common focus on optimizing the biological properties of fluorescent probes to identify strategies and compounds with therapeutic potential.

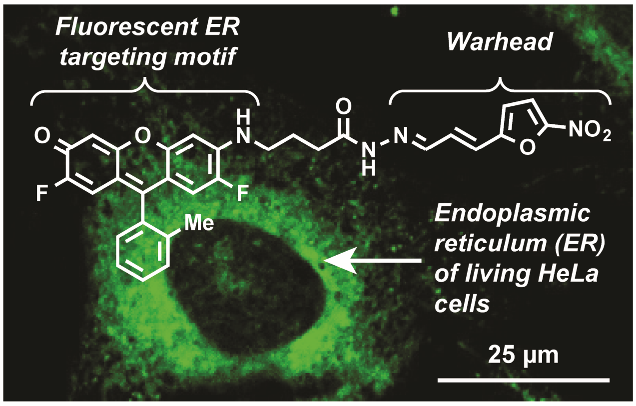
Key Words: fluorescent probes, anticancer agents, subcellular targeting, endosomes, endoplasmic reticulum

Acknowledgements: We thank the NIH and the University of Kansas Cancer Center for financial support. **Correspondence:** brpeters@ku.edu

Synthetic lethal targeting:



Fluorophores that target small molecules to the ER:



PL2 - Designing metal complexes as bifunctional liquid crystal and photoluminescent materials for molecular electronics.

Mercedes Cano

Department of Inorganic Chemistry I, Faculty of Chemical Sciences, Complutense University of Madrid, Spain.

Abstract

Purpose: Technologies based on light emission are receiving significant attention owing their multiple applications such as solar cells, data treatment storage, displays or OLED devices, among others. On the other hand, ordered molecular materials are being increasingly used in active photonic and electronic devices, and then, luminescent liquid crystals can be considered of high interest for optoelectronic devices. In the current work, we pursue to ascertain whether the self-assembly of the supramolecular liquid crystal structure can be tailored to improve such devices.

Experimental description: To this purpose, a series of luminescent compounds based on: i) the coordination of mesogenic or promesogenic pyrazole type ligands towards metal ions as Ag(I), Zn(II) or Pt(II), among others (Fig. 1); ii) long chained difluoride β-diketonate boron complexes as excellent fluorophores ($\Phi > 90\%$); iii) ionic liquid crystals (ILCs) established from mesogenic cations of the type pirazolium or diketonyl pyridinium and classical anions, have been synthesized and their bifunctional behaviour analysed on the light of different effects included on the compounds.

Results: The ability as fluorescent sensors towards external stimuli (chemo, thermo and mechanochromic stimuli) is also determined for some of the investigated compounds. Several bispyridylpyrazolate Pt(II) complexes have been proved as useful dopant in the fabrication of organic light emitting diodes (OLEDs) with the tunable emission colour depending on the concentration of dopant. The strategical inclusion of keto defects gave rise to white emission representing a singular class of small molecules Pt(II)-based white OLEDs (Fig. 1).

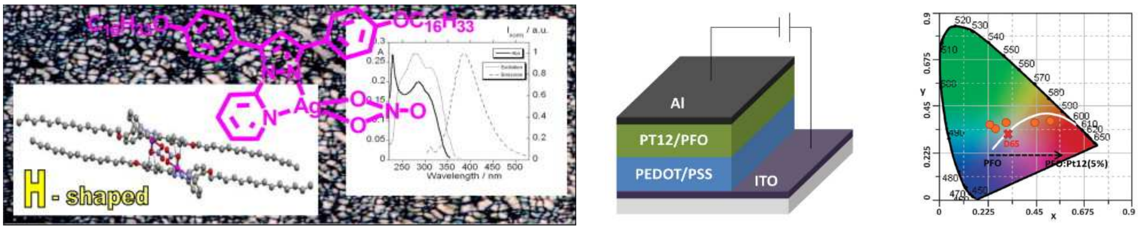


Fig. 1. X-ray, molecular structure, luminescence spectra and POM texture of a selected pyridylpyrazole silver complex (left); OLEDs fabrication with phosphorescent bispyridylpyrazolate Pt(II) metallomesogens (right).

Conclusions: This work includes the design and preparation of liquid crystal materials and the analysis of their photo and electro optical effects as basis for liquid crystal devices.

Key Words: metallomesogens, OLEDs, fluorescence, ionic liquid crystals.

Acknowledgements: M. Cano thanks the Spanish Ministerio de Economía y Competitividad (projects CTQ2011-25172 and CTQ2015-63858) and Complutense University (GR3/14-910300), for funding.

Correspondence: Department of Inorganic Chemistry I, Faculty of Chemical Sciences, Complutense University of Madrid. Ciudad Universitaria, Avda. Complutense s/n, E-28040 Madrid (Spain). E-mail: mmcano@ucm.es.

PL3 - Hunting for luminophores: Ir(III) and Cu(I) complexes, Eu(III)-MWCNT hybrids, metal free systems

Nicola Armaroli
Istituto per la Sintesi Organica e la Fotoreattvità (ISOF), Consiglio Nazionale delle Ricerche (CNR)
Via Gobetti 101, 40129 Bologna, Italy, nicola.armaroli@isof.cnr.it

Over the years, our group has investigated several classes of luminescent molecules, metal complexes and materials. The lecture is an overview of the work carried out in this area. First, cationic cyclometallated Ir(III) complexes will be introduced,[1] highlighting the ligand design criteria to be followed for obtaining bright and stable blue emitters, which is of key importance for the implementation in light-emitting electrochemical cells (LECs).[2-4] Pros and cons of the use of iridium for this purpose will be highlighted. Then Cu(I) metal complexes – particularly those based on phenanthroline and phosphine ligands[5-7]– will be presented, showing that the emission performance and stability can be improved by molecular design, but these compounds are still less mature than Ir(III) complexes as active materials for electroluminescent devices. Eventually, hybrid materials made of Eu(III) complexes which are adsorbed, electrostatically bound or even encapsulated inside multi-walled carbon nanotubes will be illustrated.[8] Finally, the possibility of creating fully organic triplet emitters, getting rid of metal elements all together will be discussed.[9] In a nutshell, the lecture will present recent advances in two of the most important classes of luminescent metal complexes – Ir(III) and Cu(I) – highlighting alternative approaches to emitting materials in the hybrid and fully organic domain.

[1] R. D. Costa, E. Orti, H. J. Bolink, F. Monti, G. Accorsi, N. Armaroli, *Angew. Chem. Int. Ed.* **2012**, *51*, 8178-8211.

[2] F. Monti, A. Baschieri, I. Gualandi, J. J. Serrano-Perez, J. M. Junquera-Hernandez, D. Tonelli, A. Mazzanti, S. Muzzioli, S. Stagni, C. Roldan-Carmona, A. Pertegas, H. J. Bolink, E. Orti, L. Sambri, N. Armaroli, *Inorg. Chem.* **2014**, *53*, 7709-7721.

[3] F. Monti, A. Baschieri, E. Matteucci, A. Mazzanti, L. Sambri, A. Barbieri, N. Armaroli, *Faraday Discuss.* **2015**, *185*, 233-248.

[4] F. Monti, M. G. I. La Placa, N. Armaroli, R. Scopelliti, M. Gratzel, M. K. Nazeeruddin, F. Kessler, *Inorg. Chem.* **2015**, *54*, 3031-3042.

[5] M. Mohankumar, F. Monti, M. Holler, F. Niess, B. Delavaux-Nicot, N. Armaroli, J. P. Sauvage, J. F. Nierengarten, *Chem.-Eur. J.* **2014**, *20*, 12083-12090.

[6] A. Kaeser, M. Mohankumar, J. Mohanraj, F. Monti, M. Holler, J. J. Cid, O. Moudam, I. Nierengarten, L. Karmazin-Brelot, C. Duhayon, B. Delavaux-Nicot, N. Armaroli, J. F. Nierengarten, *Inorg. Chem.* **2013**, *52*, 12140-12151.

[7] J. J. Cid, J. Mohanraj, M. Mohankumar, M. Holler, G. Accorsi, L. Brelot, I. Nierengarten, O. Moudam, A. Kaeser, B. Delavaux-Nicot, N. Armaroli, J. F. Nierengarten, *Chem. Commun.* **2013**, *49*, 859-861.

[8] J. Mohanraj, N. Armaroli, *J. Phys. Chem. Lett.* **2013**, *4*, 767-778.

[9] A. Kremer, C. Aurisicchio, F. De Leo, B. Ventura, J. Wouters, N. Armaroli, A. Barbieri, D. Bonifazi, *Chem.-Eur. J.* **2015**, *21*, 15377-15387.

PL4 - Directing the Performance of Photochromic Naphthopyrans

B. Mark Heron, Christopher D. Gabbutt, Stuart Aiken, Kieran Chauhan
Department of Chemical Sciences, School of Applied Sciences, The University of Huddersfield, Huddersfield, HD1 3DH, UK

Abstract

Purpose: This lecture summarizes our advances and observations concerning the design, synthesis, and properties of the isomeric photochromic 3*H*-naphtho[2,1-*b*]pyran **1** and 2*H*-naphtho[1,2-*b*]pyran **2** systems (Figure 1).

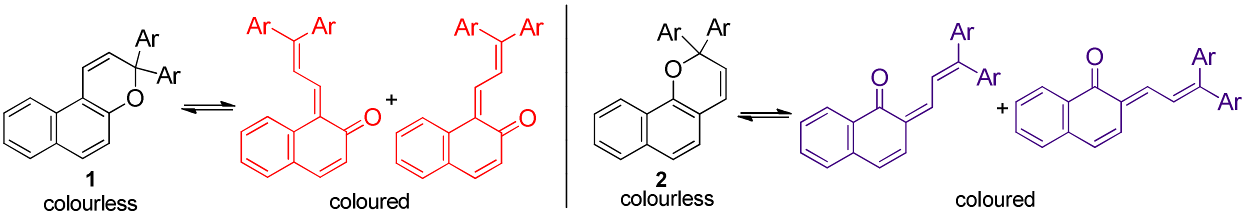


Figure 1

The impact of structural diversity of the starting diarylpropynols on the outcome of the acid-catalyzed pyran ring forming reaction (Figure 2) and the subsequent photochromic performance of the substituted naphthopyrans will be discussed. The usefulness and vagaries of Pd-mediated reactions employed for post functionalizing naphthopyrans will be examined (Figure 2). The competitive formation of naphthofurans from each of the foregoing types of reaction will rationalized.

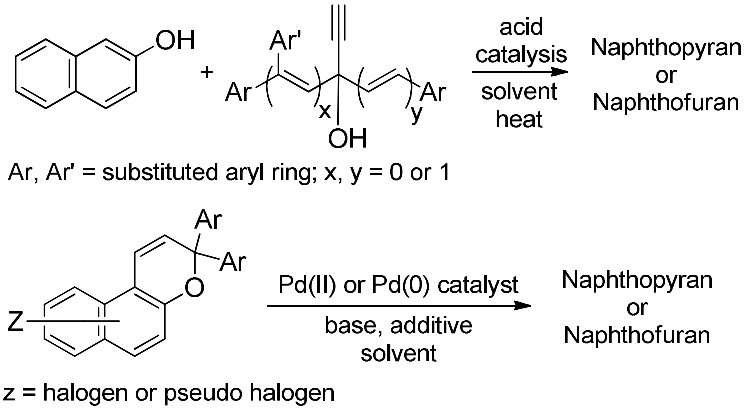


Figure 2

Key Words: Photochromism, naphthopyran, synthesis, color, half-life, naphthol, diarylpropynol, Pd-catalysis

Acknowledgements: We thank the following organizations who have funded our research on photochromic naphthopyrans over the years: Essilor SA (France), James Robinson Ltd (UK), Yorkshire Forward (UK), The EPSRSC, The Worshipful Company of Clothworkers of the City of London (UK), The University of Huddersfield.

Correspondence: Department of Chemical Sciences, School of Applied Sciences, The University of Huddersfield, Huddersfield, HD1 3DH, UK. Email: m.heron@hud.ac.uk

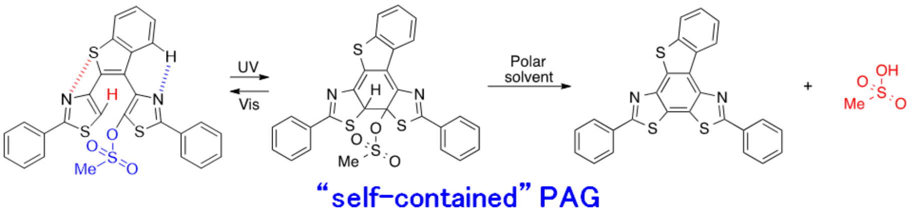
PL5 - Efficient Photo- and Electro-Chromic Reactions of Photochromic Terarylenes

Tsuyoshi KAWAI[1,2],
Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara, Japan
NAIST-CEMES International Collaborative Laboratory, CEMES-CNRS, 29 rue Jeanne Marvig, BP94347, 31055 Toulouse, France

Abstract

We have recently explored on efficient photochromic reaction system based on triangle terarylene structure, which is a scaffold related to photochromic diarylethenes. Although photochemical quantum yield of diarylethenes is possible to be almost unity in some cyctals, those in solution phase are mosty about 50 % or less. Some exceptional compounds showed relatively high cyclization quantum yield, in which ground state conformation of is stabilized in the photoreactive “anti-parallel” conformation. We sucessfuly achieved photochromic quantum yield almost 100% in solution phase after systematic investigation on their ground state geometory of terarylenes. The compounds with “photonquantitative” reactivity were achieved by selectively stabilizing the reactive *C2* symmetric structure. [T.Kawai etal, *Chem. Asian J.*, **2015**, *Angew Chem.I.E.*, **2011**]. We also reported new Photoacid Generators, PAGs, which is derived from terarylene scaffold by introducing H- and RSO_3- units at the reaction center carbon atoms. After the photochemical cyclization reaction, the configuration on the carbon atoms converts to the tetrahedral sp^3. The H- and CH_3SO_3- are then released forming CH_3SO_3H and a fused aromatic compound. The new PAG showed photo-initiation of polymerization of epoxy monomers and photosolbilization of photopolymer materials [*J.Amer.Chem.Soc.*, **2015**]. Quantum yield of this reaction was 52 % which is sufficiently higher than those of usual PAGs. It will be also discussed that our recent compound shows complate oxidation-induced fading isomerization reaction with 0.001 eq. of oxidizing reagent. That is, one electron oxidation of ring-closed form molecule induced cycloreversion reaction of 1000 molecules after chemical amplification through a highly efficient Domino-like reaction mechanism.

Scheme 1. Reaction of New PAG based on Triangle Terarylen



1. O. Galangau, T. Nakashima, F. Maurel, T. Kawai, *Chem. Eur. J.*, 21, 23, 8471-8482 (2015)
2. R. Li, T. Nakashima, O. Galangau, S. Iijima, R. Kanazawa, T. Kawai, *Chem. Asian J.*, 10, 1725-1730 (2015) (highlighted as *AngewChem Spotlight*)
3. R. Kanazawa, T. Nakashima, T. Kawai, *New J. Chem.*, 39, 7397-7402 (2015)
4. T. Nakashima, K. Tsuchie, R. Kanazawa, R. Li, S. Iijima, O. Galangau, H. Nakagawa, K. Mutoh, Y. Kobayashi, J. Abe, T. Kawai, *J. Am. Chem. Soc.*, 137, 7023-7026 (2015) (highlited as *JACS Spotlight,* Featured in *Synfact*, 2015)
5. J. P. Calupitan, T. Nakashima, Y. Hashimoto, T. Kawai, *Chem. Eur. J., in press* (cover and Hot Paper)

KEYWORDS: photochromism. terarylene, diarylethene, quantum yield, electro-isomerization

Correspondence: tkawai@ms.naist.jp

Keynote Lectures

KN1 – Silica-based nanomaterials in sensing applications

Ramón Martínez-Máñez[1,2,3]

1. *Centro de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Unidad Mixta Universidad Politécnica de Valencia-Universidad de Valencia, Spain.*
2. *Departamento de Química, Universidad Politécnica de Valencia, Spain.*
3. *CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN).*

Abstract

Progress in bio-molecular chemistry and nanotechnology has recently resulted in the design of biologically inspired systems with innovative bio-related functions. A key issue in this field is the design of new “smart” systems based on nanoscopic structures and a variety of biomolecules which perform unprecedented functions, boosting areas such as bio-engineering, bio-sensing, bio-nanotechnology and drug delivery into new directions.[1] In delivery applications, the development of stimuli-responsive nanoscopic hybrid gated materials involving biomolecules as caps and showing the ability to release entrapped guests upon application of an external stimulus has attracted tremendous attention.[2] These devices contain a support that constitutes a reservoir in which certain compounds can be stored and molecules or molecularly appended objects attached on these containers that act as “gates”, allowing the controlled release of entrapped molecules at will. Both components have been carefully selected and arranged to achieve a wide range of control functions. Capped materials have been mainly used in drug delivery applications. In contrast, examples of their use in sensing are much less common.[3] For sensing, the carrier system is commonly loaded with an indicator and the capping mechanism is designed in a way that only a target analyte is able to trigger uncapping and the delivery of the cargo.

Bases in this latter concept (i.e. capped materials for sensing applications) selected examples of sensory materials that use a combination of nanotechnology and supramolecular recognition principles will be shown.[4] In this later case the design strategies in most cases involve synergisms of bio- concepts and nanoscale inorganic supports which create functional sensing systems showing enhanced functions and properties.

Key Words: Mesoporous materials. Gates materials. Sensing

Acknowledgements: We thank the Spanish Government (project MAT2012-38429-C04) and the Generalitat Valenciana (project PROMETEOII/2014/047) for support.

Correspondence: *Centro de Reconocimiento Molecular y Desarrollo Tecnológico (IDM). Departamento de Química. Universidad Politécnica de Valencia. Camino de Vera s/n, 46022, Valencia (Spain). E-mail: rmaez@qim.upv.es*

References:

[1] (a) A. B. Descalzo, R. Martínez-Máñez, F. Sancenón, K. Hoffmann, K. Rurack, *Angew. Chem., Int. Ed*, 2006, *45*, 5924; (b) K. Rurack, R. Martínez-Máñez (Eds), The supramolecular chemistry of organic-inorganic hybrid materials. John Wiley & Sons, 2010.

[2] C. Coll, A. Bernardos, R. Martínez-Máñez, F. Sancenón., *Acc. Chem. Res.*, 2013, *46*, 339

[3] F. Sancenón, L. Pascual, M. Oroval, E. Aznar, R. Martínez-Máñez, *ChemistryOpen*, 2015, *4*, 418

[4] See for instnace: (a) E. Climent, L. Mondragón, R. Martínez-Máñez, F. Sancenón, M.D. Marcos, J.R. Murguía, P.Amorós, K. Rurack, E. Pérez-Payá, *Angew. Chem. Int. Ed.*, 2013, *52*, 8938; (b) L. Pascual, I. Baroja, E. Aznar, F. Sancenón, M.D. Marcos, J.R. Murguía, P. Amorós, K. Rurack, R. Martínez-Máñez, *Chem. Commun.*, 2015, *51*, 1414.

KN2 – Endogenous fluorophores in studies of chlorophyll biosynthesis and photosynthetic activity- new findings

Beata Mysliwa-Kurdziel, Gracjana Leonowicz , Piotr Leśniak, Agata Zubrycka, Andrzej Waloszek, Kamil F. Trzebuniak
Department of Plant Physiology and Biochemistry, Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian Uniwersity in Krakow, Krakow, Poland

Abstract

Purpose: Important physiological processes in plants may be investigated using fluorescence methods due to the presence of numerous endogenous fluorophores. Chlorophyll (Chl), the primary photosynthetic pigment, is a useful probe to study light photosynthetic reactions. Fluorescence of chlorophyllide (Chlide) and protochlorophyllide (Pchlide), *i.e.* intermediates of Chl biosynthesis, is a good observable for monitoring the Chl biosynthesis and the assembly of the photosynthetic apparatus. Our research is aimed at the understanding of the regulatory mechanisms of the assembly of the photosynthetic apparatus in angiosperms, in particular those related to light-triggered Pchlide photoreduction. This study is focused around two themes: (1) the effect of bleaching herbicide (norflurazone, NF) on deetiolation process under different light regimes and (2) the photosynthetic activity in seedlings of *A. thaliana* mutants affected in carotenoid biosynthesis (*lut*) or in light photosynthetic reactions (*npq, lhc*).

Experimental description: Experiments on deetiolation were performed on etiolated seedlings of *A. thaliana*, *H. vulgare* and *T. aestivum*, control and treated with NF. Fluorescence emission spectra were measured at 77 K using a Perkin Elmer LS-50B spectrofluorimeter (UK). In experiments on photosynthetic activity, plants were grown in soil (10 h photoperiod) for 1-3 weeks. Chl *in vivo* fluorescence was imaged using an Open FluorCam FC 800-O/1010 fluorometer equipped with CCD camera (PSI, CZ). Measurements were performed every third day for juvenile plants, which were dark-adapted for 30 min. Fluorescence analysis were supplied with measurements of the photosynthetic pigment content and composition, and the activity of antioxidant enzymes.

Results: On the basis of 77 K fluorescence emission spectra, we found that for etiolated plants treated with NF, the balance between non-photoactive and photoactive Pchlide is affected. Relatively more Pchlide remain unbound to complexes with LPOR enzyme. In consequence, the yield of Pchlide to Chlide photoreduction was lowered and the emission maximum of Chlide was blue-shifted to 675-678 nm in NF-treated plants, as compared to control ones. Deetiolation in NF-treated monocot plants is strongly retarded in top and medium part of leaves and inhibited in basal fragments. We found some differences in Chl *in vivo* fluorescence between *A. thaliana* mutants and wild plants in the juvenile stage. The non-photochemical quenching (NPQ) was significantly reduced (about 35 %) in *lut 1* mutant and it decreased during the plant growth. The maximal PSII quantum yield, represented by Q_{Ymax} fluorescence parameter, was similar in mutants and wild plants and stayed at the level of 0.87±0.01 during the whole experiments.

Conclusions: Analysis of endogenous porphyrin and chlorin fluorescence is useful for study of the assembly of the photosynthetic apparatus and photosynthetic activity.

Key Words: angiosperms, chlorophyllide; chlorophyll, deetiolation; fluorescence, protochlorophyllide.

Acknowledgements: This work was financially supported by grant UMO-2013/10/E/NZ3/00748 from the Polish National Science Centre (NCN).

Correspondence: Beata Mysliwa Kurdziel; Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian Uniwersity in Krakow, ul Gronostajowa 7; 30-387 Krakow, Poland; e-mail: b.mysliwa-kurdziel@uj.edu.pl

KN3 - DNA-based molecular tools for monitoring cellular activity

Ola Söderberg

Uppsala University, Department of Immunology, Genetics & Pathology, Science for Life Laboratory, Biomedical center, 751 08 Uppsala, SWEDEN.

Abstract

High-resolution analysis of proteins or protein complexes requires either advanced microscopy, or molecular methods that combine distance dependence with signal amplification. By using DNA molecules as a tool in such molecular methods one can predict hybridization between DNA molecules and use the vast variety of enzymes to modify and amplify the DNA molecules used in the method. One such method is Proximity Ligation Assay (PLA) where pairs of antibodies equipped with DNA oligonucleotides (so-called proximity probes) are used to target proteins. Proximal binding of such probes template the creation of a circular DNA molecule, which can be amplified using rolling circle amplification (RCA). The single-stranded RCA product from a single recognition event will contain several hundreds of repetitive motifs that can be visualized by hybridization of fluorophore-conjugated oligonucleotides. The distance requirement for the formation of the DNA circles will be dependent on the size of the affinity reagents and the length and polarity of the oligonucleotides used, ranging from a few nm up to several tens of nm. However, the RCA product will be much larger than the distance between the targeted epitopes, up to a micron in diameter. To provide an increased dynamic range, alternative designs may be used to compact the RCA products, or to generate different species of products that can be detected with unique fluorophores. An alternative to PLA would be the proximity-dependent initiation of hybridization chain reactions (proxHCR) where the proximity probes consists of DNA hairpins. The addition of an activator oligonucleotide that can hybridize to one of the hairpins will liberate a sequence motif that will invade the second species, if they are in close proximity. The now bridged proximity probes will reveal the initiator motif that will prime a hybridization chain reaction of fluorophore-labeled hairpins, creating a long fluorophore-labeled double-stranded DNA molecule.

I will describe different approaches to use DNA-based molecular tools for analysis of cell signaling and what advantages the different variants provide.

Key Words: protein interactions, proximity ligation assay, cell signaling

Correspondence: ola.soderberg@igp.uu.se

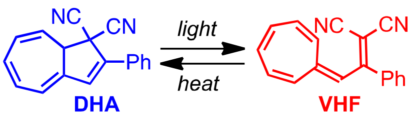
KN4 - Photochromic molecules for solar energy storage.

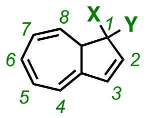
Mogens Brøndsted Nielsen[1]
Department of Chemistry, University of Copenhagen. Copenhagen. Denmark.

Abstract

Purpose: We aim at developing photochromic molecules for storage of solar energy. Upon irradiation, molecules are converted into high-energy photoisomers. These isomers should store the energy until needed so that the energy is released on demand. This corresponds to a closed-energy cycle of light-harvesting, energy storage, and release. We need to develop molecules with sufficiently high energy storage capacities and with long-lived meta-stable photoisomers.

Experimental description: Our work focuses in particular on tuning the properties of the dihydroazulene/vinylheptafulvene (DHA/VHF) photo/thermoswitch. This couple is particularly attractive as only the DHA to VHF conversion is induced by light and the quantum yield of photoisomerization is reasonably high (ca. 55%). Guided by quantum chemical calculations, we aim at preparing new derivatives with an increased DHA – VHF energy difference. In parallel, we seek to increase the lifetime of the metastable VHF isomers. Ideally the back-reaction should be completely on hold until triggered by either high temperature or a catalyst.





Many sites available for functionalzation and cyano groups can be changed to other groups (X, Y)

Results: By changing the substituents at position C1 of the parent DHA shown above from two cyano groups to one cyano group and one hydrogen atom, we have achieved a doubling in the energy storage capacity from 0.11 MJ kg^{-1} to 0.25 MJ kg^{-1} (*J. Phys. Chem.* 2015, *119*, 896-904; *Chem. Eur. J.* 2015, *21*, 7454-7461). This value can be increased further by other structural modifications, which will be presented. The rate of the VHF to DHA back-reaction is controlled by donor-acceptor substitution at positions C2 and C7, and the kinetics follows linear free energy relationships / Hammett correlations (*Chem. Eur. J.* 2013, *19*, 9542-9548). The absorption maxima of the DHA and VHF chromophores are also influenced by donor-acceptor substitution. We are also investigating the possibility for controlling the VHF to DHA back-reaction using various metal ion catalysts.

Conclusions: A variety of structural modifications of the DHA/VHF couple will be presented and the consequences for energy storage capacities and rate of the energy-releasing back-reaction will be discussed.

Key Words: dihydroazulenes, electrocyclic reactions, photochromic molecules, vinylheptafulvenes, solar energy storage

Acknowledgements: University of Copenhagen is acknowledged for support.

Correspondence: Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark. E-mail: mbn@chem.ku.dk

KN5 - Synthesis, Linear and Nonlinear Optical Properties and Applications of New 3-Coordinate Organoboron Compounds.

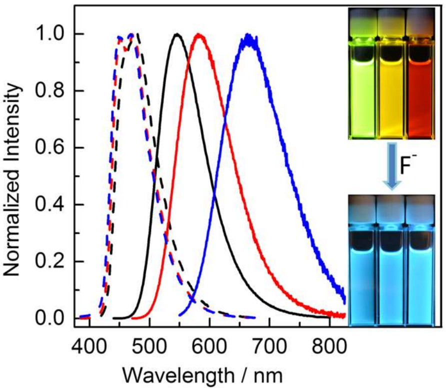
Todd B. Marder
Institute of Inorganic Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Abstract

Three-coordinate boron, with a vacant pz-orbital and isoelectronic with a carbonium ion, can conjugate with organic π-systems as a strong p-acceptor in the excited state. Most 3-coordinate boron compounds are Lewis acidic, bind Lewis bases which disrupt this conjugation, and are sensitive to hydrolysis. Bulky substituents on B, such as mesityl (mes) groups, provide steric protection of the vacant p-orbital without disrupting the electronic communication with a π-system, resulting in compounds which are usually air and water stable. We focus on the synthesis of dipolar, quadrupolar and octupolar compounds containing B(Ar)2 groups, including those containing new π-acceptors considerably stronger than B(mes)2, and their linear and nonlinear (2nd and 3rd order NLO, TPA and TPEF) optical properties.

[1] L. Ji, T.B. Marder, et al. "Electron Delocalization in Reduced Forms of 2-(BMes$_2$)pyrene and 2,7-Bis(BMes$_2$)pyrene," *J. Am. Chem. Soc.,* **2015**, *137*, 6750.
[2] Z. Zhang, T. B. Marder, et al. "Taming the Beast: Fluoromesityl Groups Induce a Dramatic Stability Enhancement in Boroles," *Chem. Sci.*, **2015**, *6*, 5922.
[3] Z. Zhang, T. B. Marder, et al. "D-π-A Triarylboron Compounds with Tunable Push-Pull Character Achieved by Modification of Both the Donor and Acceptor Moieties," *Chem. Eur. J.,* **2015**, 21, 177.
[4] Z. Zhang, T.B. Marder, et al. "Optical and Electronic Properties of Air-stable Organoboron Compounds with Strongly Electron-accepting Bis(fluoromesityl)boryl Groups," *Chem. Sci.*, **2015**, 6, 308.
[5] L. Ji, T.B. Marder, et al. "Experimental and Theoretical Studies of Quadrupolar Oligothiophene-cored Chromophores Containing Dimesitylboryl Moieties as π-Accepting End-groups: Syntheses, Structures, Fluorescence, One- and Two-photon Absorption," *Chem. Eur. J.*, **2014**, 20, 13618.
[6] X. Yin, T.B. Marder, F. Jäkle, et al. "Highly Electron-Deficient, Air-Stable Conjugated Thienylboranes," *Angew. Chem. Int. Ed.*, **2014**, 53, 9761.
[7] Reviews: C.D. Entwistle and T.B. Marder, "Applications of Three-Coordinate Organoboron Compounds and Polymers in Optoelectronics," *Chem. Mater.*, **2004**, 16, 4574; C.D. Entwistle and T.B. Marder, "Boron Chemistry Lights the Way: Optical Properties of Molecular and Polymeric Systems," *Angew. Chem. Int. Ed. Engl.*, **2002**, 41, 2927.

Solvatochromic emission of a donor-π-B(mes)2 compound



Effect of F$^-$ complexation on emission

KN6 - Photodynamics of optogenetic BLUF coupled photoactivated adenylyl cyclases.

Alfons Penzkofer[1], Suneel Kateriya,[2] Peter Hegemann[3]
Fakultät für Physik, Universität Regensburg, Universitätsstraße 31, D-93053 Regensburg, Germany
School of Biotechnology, Jawaharlal Nehru University, New Delhi, India-110067
Institut für Biologie/Experimentelle Biophysik, Humboldt Universität zu Berlin, Invalidenstraße 42, D-10115 Berlin, Germany

Abstract

Optogenetics is a biological technology which combines optical and genetic methods with the aim to trigger certain functional actions in specific cells or tissues with light. For this purpose optogenetic tools are developed and inserted in cells. Optogenetics allows fast temporal and spatial localized control of exactly defined events in complex biological systems.

An optogenetic tool consists of a light sensor protein domain that absorbs light and an effector protein domain that exerts biological activity (e.g. ion transport, catalysis, protein interaction). Natural photoreceptors or artificial photoreceptor may be applied. The different photoreceptor classes are microbial rhodopsins, photosensitive flavoproteins (LOV domains, BLUF domains, cryptochromes), xanthopsins, phytochromes, plant UV-B receptors, and photo-transformable fluorescent proteins.

BLUF domains are Blue Light sensors Using Flavin having a novel FAD-binding fold exemplified by the N-terminus of the AppA protein from *Rhodobacter sphaeroides*. The flavin is non-covalently bound in a binding pocket with adjacent tyrosine. Photo-excitation causes an electron transfer from Tyr to excited flavin with subsequent protein conformational changes and hydrogen bond restructuring. BLUF domains are found in many micro-organisms either as single sensor domain proteins or as multi-domain sensor actuator proteins. In single light sensing BLUF domain proteins the activation of downstream protein modules is thought to occur via intermolecular interaction. In BLUF domain containing multi-domain proteins the activation occurs via intra-molecular interaction. BLUF-PACs are BLUF domain coupled Photoactivated Adenylyl Cyclases (double domain proteins) which have elevated adenylyl cyclase activity (conversion of ATP to cAMP cellular second messenger) upon blue light irradiation.

Blue-light exposure of dark-adapted BLUF proteins (BLUF domain in receptor state) leads to light-adapted BLUF proteins (BLUF domain in signaling state) with a red-shift of the first electronic absorption band due to tyrosine/glutamine/flavin hydrogen-bond restructuring and protein re-conformation. After light switch-off the domain recovers back to its initial absorption behavior in the dark. The fluorescence efficiency of dark-adapted BLUF domains is small - and it is even smaller in the light adapted state - due to photo-induced electron transfer from an adjacent tyrosine residue to the flavin cofactor.

The cyclase activity of PACs may be assessed in assay buffer containing the PAC protein. The reaction is started by addition of ATP. Enzymatic assays of the protein are executed in the dark and under irradiation with blue light. After a certain time of incubation the reaction is stopped and the sample is analyzed for cAMP content. Two BLUF-PACs, bPAC from *Beggiatoa* sp. and TpPAC from *Turneriella parva*, have excellent cyclase activity characteristics for optogenetic toolkit applications. bPAC found already various optogenetics applications (e.g. bPAC expression in the nervous system of *Drosophila melanogaster* led to light-induced behavioral changes of the freely moving flies).

Key Words: optogenetic toolkits; blue light sensors unsing flavin (BLUFs); photoactivated adenylyl cyclases (PACs)

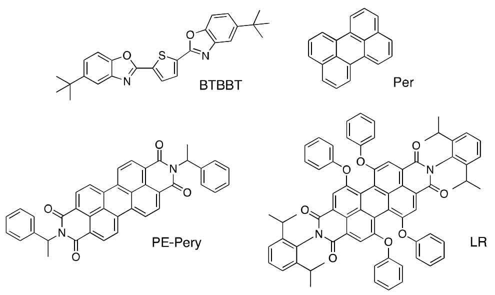
Acknowledgements: A. P. thanks Prof. F. J. Gießibl, University of Regensburg, for his kind hospitality.

Correspondence: Alfons Penzkofer, Fakultät für Physik, Universität Regensburg, D-93040 Regensburg, Germany. Email: alfons.penzkofer@physik.uni-regensburg.de

KN7 - Enhancing Optical Efficiency of Thin-Film Luminescent Solar Concentrators by Combining Energy Transfer and Stacked Design.

Marco Carlotti,[1] Giacomo Ruggeri,[2,3] Fabio Bellina,[2,3] Andrea Pucci[2,3]
Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Goningen, The Netherlands
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, 56124 Pisa, Italy.
INSTM, UdR Pisa, Via Moruzzi 13, 56124 Pisa, Italy.

Sunlight concentration is a promising path to cost-effective photovoltaic (PV) technologies. Compared to standard concentrators based on geometrical optics, luminescent solar concentrators (LSCs) appear as a viable and convenient alternative being sunlight concentration to PV occurs with diffuse light and no needs of sun tracking or cooling apparatuses. LSCs are thin, flat or bulk plates of highly fluorescent materials that absorb sunlight and concentrate most of the resulting fluorescence to their edges by internal reflection. The photoactive elements are organic dyes, luminescent nanoparticles or Eu^{3+} complexes dispersed in a transparent polymer matrix such as poly(methyl methacrylate) (PMMA). The solar radiation is thus conveniently transmitted to PV cells at their edges, even with a cloudy sky. Nevertheless, current LSC-PV devices achieve too low power conversion efficiencies, being strongly plagued by a multitude of unfavourable processes that hinder their ability to deliver light to PV cells. In striving to contribute towards improved LSC outcomes, we report on the preparation of LSCs based on fluorophore-doped poly(methyl methacrylate) (PMMA) thin-films coated onto high optical quality glass slab. In detail, a series of high-energy absorbing fluorophores (HEF, such as 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BTBBT) and perylene (Per)) and perylene bisimides (PBI, such as N,N'-bis-(1'-phenylethyl)-perylene-3,4,9,10-tetracarboxydiimide (PE-Pery) and Lumogen F 350 (LR)) red-emitting dyes were utilized. The LSCs were prepared taking inspiration from the previously mentioned geometries for bulk-dyed LSCs, namely a stacked geometry that was also flanked with a cascading of emission via FRET. In this last design, two distinct polymer layers containing different dyes were coated on the opposite faces of the glass slab. The top layer was coated by the polymer film containing the PBI molecules that are responsible of the highest LSC optical efficiency. Conversely, the bottom layer was coated with the polymer film containing an appropriate mixture of HEF and red emitting PBI. In this configuration, the light transmitted through the slab is absorbed by HEF and efficiently re-emitted by the PBI molecule via FRET, thus amplifying the electric current production. In light of these peculiar features, the sandwich LSC design showed optical efficiencies 10–14% greater than the maximum values gathered from LSC based on single PBI fluorophores.



Scheme 1. Chemical structures of the investigated fluorophores

Key Words: fluorophores, poly(methyl methacrylate), dye dispersion, optical efficiency, luminescent solar concentrators
Acknowledgements: the research leading to these results has received funding from MIUR-FIRB (RBFR122HFZ) and in part from the Università di Pisa under PRA 2015 (project No. 2015_0038).

Correspondence: Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, 56124 Pisa, Italy. Email: andrea.pucci@unipi.it.

KN8 - Water-Soluble PEGylated β-Dicyanodistyrylbenzene : Smart Fluorescent Micelle Showing Thermo-responsive Fluorescent Switching

Soo Young Park, Junjie Cui, Hyeong-Ju Kim, and Dong Ryeol Whang

Center for Supramolecular Optoelectronic Materials, Department of Materials Science and Engineering, Seoul National

University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Korea

Abstract

Supramolecular self-assembly of amphiphiles have received much attention because it offers a new strategy for developing the biological and environmentally friendly materials [1]. These amphiphiles often consist of rigid rod segments with hydrophobic aromatic rings and flexible coil segments with hydrophilic poly ethylene glycol (PEG) chains (called rod-coil molecules)[2]. Among the versatile amphiphiles, temperature-responsive fluorescent switching rod-coil molecules with LCST behaviors have great potential in the design of fluorescence probes, sensors, thermometer and bio-imaging.

Herein we report on a novel water-soluble PEGylated small molecule, namely EO7-Ph-DCS. It forms a fluorescent micelle which uniquely shows temperature-dependent multi-color fluorescence switching and lower critical solution temperature (LCST) behavior. At low temperature (T < LCST), EO7-Ph-DCS in aqueous solution emits yellow fluorescence (λPL = 561 nm) attributed to an excimeric emission of DCS. Interestingly, at elevated temperature (T >LCST), the emission distinctly changes from yellow to green (λPL = 531 nm) with increasing proportion of monomeric emission associated with LCST behavior. The fluorescence switching is attributed to the disassembly of selfassembled rod segments of chromogenic EO7-Ph-DCS in aqueous solution, which is triggered by the coil-to-globule transition of PEG chains upon heating.

References

[1] T. Shimizu, M. Masuda, H. Minamikawa, Chemical Reviews. 2005, 105, 1401-1444; Y.-b. Lim, K.-S. Moon, M. Lee,

Chemical Society Reviews 2009, 38, 925-934; S. I. Stupp, L. C. Palmer, *Chemistry of Materials* 2014, 26, 507.

[2] Y. Kim, W. Li, S. Shin, M. Lee, *Accounts of Chemical Research* 2013, 46, 2888.

KN9 - Luminescence Centres in Silicon Carbide Nanocrystals: TRANES and DAS Analysis of Luminescence Spectroscopy Data.

David Beke[1,2], Tibor Z. Janosi[3,4], Balint Somogyi[5], Daniel A. Major[2], Zsolt Szekrenyes[1], Janos Erostyak[3,4], Katalin Kamaras[1], Adam Gali[1,5]

1. Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary. 2. Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Budapest, Hungary. 3. University of Pécs, Institute of Physics, Pécs, Hungary. 4. University of Pécs, Szentágothai Research Centre, Spectroscopy Research Group, Pécs, Hungary. 5. Department of Atomic Physics, Budapest University of Technology and Economics, Budapest, Hungary.

Abstract

Purpose: Understanding the luminescence of small nanocrystals with various surface terminations in solution is still a scientific challenge. We show that advanced time-resolved spectroscopy is a powerful tool for identifying luminescence centres of these systems.

Experimental description: Wavelength-dependent time-resolved luminescence measurements were carried out at 321 nm excitation in all samples using a Horiba Jobin-Yvon Nanolog spectrofluorometer. Emission was measured in the 340–570 nm wavelength range with 10 nm steps. Decay curves free from excitation pulses' distortion were reconstructed using deconvolution and then were used for TRANES (Time Resolved Area Normalized Emission Spectra) and DAS (Decay Associated Spectra) analysis.

Results and Conclusions: Aqueous solutions of molecular-sized SiC nanocrystals are very promising candidates to become bioinert, non-perturbative fluorescent nanoparticles for in vivo bioimaging, thus the identification of their luminescent centres is of immediate interest. Our analysis of steady-state and time-resolved spectra and decay curves is based on the successful combination of DAS and TRANES methods. Here we present identification of two emission centres of these nanocrystals: surface groups involving carbon – oxygen bonds and a defect consisting of silicon – oxygen bonds which becomes the dominant pathway for radiative decay after total reduction of the surface. The identification of these luminescent centres is confirmed by ab initio simulations. These results and the developed evaluation method help to design optimized fluorophores and nanosensors for in vivo bioimaging.

Key Words: Quantum dot, luminescence spectroscopy, Decay Associated Spectra, Time Resolved Area Normalized Emission Spectra

Acknowledgements: Z.S. and K.K. acknowledge the joint project of the Scientific Research Fund (OTKA) and the Austrian Science Fund (FWF) under Grant No. ANN107580. D.B. acknowledges the support from the European Union and the State of Hungary, cofinanced by the European Social Fund in the framework of TÁMOP-4.2.4.A/2-111/1-2012-00001 National Excellence Program. A.G. acknowledges the support from the Hungarian Scientific Fund (OTKA) project nos. K101819 and K106114 and the Lendület program of Hungarian Academy of Sciences. T.Z.J. and J.E. acknowledge the grant SROP-4.2.2.D-15/1/Konv-2015-0015: Environmental industry related innovative transand interdisciplinary research team development in the University of Pécs knowledge base.

Correspondence: Janos Erostyak, erostyak@fizika.ttk.pte.hu

KN10 - The sensing ability of new porphyrin-rhodamine conjugates

Maria A. F. Faustino,[1] Sónia M. G. Pires,[1] Cristina Nuñez,[4] Vanda V. Serra,[5] Carlos Lodeiro, [2,3] Maria G. P. M. S. Neves[1]

[1]*Department of Chemistry & QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal*

[2]*Bioscope group. Chemistry Department. Faculty of Sciences and Technology. New University of Lisbon. Campus de Caparica. 2829-516. Caparica. Portugal.*

[3]*ProteoMass Scientific Society. Madan Parque. Building VI. Office 23. Faculty of Sciences and Technology. Campus de Caparica. 2829-516. Caparica. Portugal.*

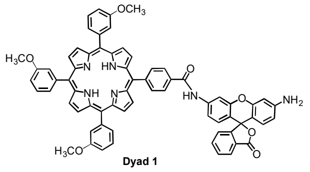
[4]*Pharmacology Department, Faculty of Veterinary, University of Santiago de Compostela, 27002 Lugo, Spain*

[5]*Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa Portugal*

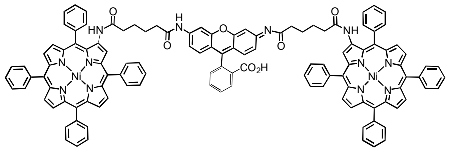
Abstract

Purpose: Based on the ability of porphyrins and rhodamines to be used as fluorescent and colorimetric chemosensors of different metal ions (*e.g.* Ag^+, Hg^+, Hg^{2+}, Cu^{2+}, $Zn^{2+}$and Cd^{2+}), it was envisaged that the conjugation of both units could potentiate their ability to recognize different metal ions.

Experimental description: It was compared the sensing ability of dyad **1** and of its porphyrinic precursor by spectrophotometric and spectrofluorimetric titrations towards the metal ions Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} and Hg^+. The studies were extended to triad **2** and to its porphyrinic precursor in order to evaluate the role of the rhodamine unit when the porphyrinic core is impeded to coordinate with metal ions.



Dyad 1



Triad 2

Results: Titrations of dyad **1** and of its porphyrinic precursor, with Hg^+, Hg^{2+} and Pb^{2+} led to significant alterations in the UV-Vis and emission spectra, displaying with Hg^{2+} a naked-eye colour change from pale pink to green or orange, respectively. Triad **2** was able to coordinate via the rhodamine unit with Hg^+, Hg^{2+} and Pb^{2+} and a colourless/pink colour transition took place. In the competitive cation titration experiments, the dyad **1** displayed a higher affinity and selectivity for the Hg^{2+} metal ion and only Ni^{2+} interfered in the coordination of this metal.

Conclusions: The binding of dyad **1** and of its precursor with Hg^+, Hg^{2+} and Pb^{2+} induced significant changes in the ground state and in the ratio of the fluorescence peaks typical from a fluoroionophoric probe. However, the same metals only induced changes in the ground state of triad **2**. The different absorption spectra found reflects different coordination modes. In some cases, the rhodamine system participated in the cation sensing.

Key Words: Porphyrin, Rhodamine, fluorescent probes, cation dyads, triads

Acknowledgements: University of Aveiro, FCT/MEC for the financial support to the project PPCDT/QUI/64658/2006 and to the QOPNA Research Unit (FCT UID/QUI/00062/2013) through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and also to the Portuguese NMR Network. S.M.G.P. and V.V.S. thanks FCT/MEC for their grants respectively, SFRH/BD/64354/2009 and SFRH/BPD/74270/2010. C.N. acknowledges to Xunta de Galicia (Spain) for her post-doctoral contract (I2C programme). This work was supported by the Unidade de Ciências Biomoleculares Aplicadas-UCIBIO financed by national funds from FCT/MEC (UID/Multi/04378/2013) and co-financed by the FEDER under the PT2020 Partnership Agreement. CL are grateful to the Scientific Society PROTEOMASS (Portugal) for funding and facilities

Correspondence: MAF Faustino, Chemistry Department & QOPNA, University of Aveiro, Portugal, faustino@ua.pt

KN11 - Aurophilic gels.

Artur Moro [1], Elisabet Aguiló [2], Raquel Gavara [2], Laura Rodríguez [2], João Carlos Lima [1]
[1] *REQUIMTE, Departamento de Química, CQFB, Universidade Nova de Lisboa, Monte de Caparica, Portugal. e-mail: lima@fct.unl.pt*
[2] *Departament de Química Inorgànica, Universitat de Barcelona, Barcelona, Spain*

Abstract

Metallogels are a subject of study in the last few years.[1] The reason for the growth of interest stems from the availability and the diversity of metal-ligand coordination that could readily induce or control the self-assembly process of the gel formation and thereby influence the gel properties, as a difference with what occurs in organic gels. Organometallic Au(I) complexes present the additional advantage to use both classical supramolecular interactions (*e.g.* □-□ stacking or hydrogen bonding) together with the establishment of Au(I)···Au(I) bonds (aurophilic interactions), which are particularly strong. Furthermore, these complexes exhibit interesting emissive properties that usually are modulated by the presence of the aurophilic interactions.

We have reported on the formation of luminescent Au(I) hydrogels based on water soluble organometallic alkynyl complexes where aurophilic intermolecular interactions are involved on the gelation process.[2-5] Slight modifications on the chemical structure can induce significant changes on the supramolecular assemblies leading to hydrogels, rods or vesicles.

A detailed analysis of the thermodynamic and photophysical parameters that modulate and are modulated, respectively, by the gel formation has been performed and the results are supported by theoretical data.

The mononuclear[2,3] and polynucleal gold(I) supramolecular assemblies that are formed in water can be reorganized by the presence of particular molecules. In particular the assemblies containing charged residues or coordinating moyeties are sensitive to the presence of anions and cations and the changes in morphology impact the spectroscopic features opening an unexplored potential of these assemblies for sensing.

References

[1] Tam, Y.-Y., Yam, V. W.-W., *Chem. Soc. Rev.,* 2013, *42*, 1540.
[2] Gavara, R.; Llorca, J.; Lima, J.C.; Rodríguez, L. *Chem. Commun.* 2013, *49*, 72.
[3] Aguiló, E.; Gavara, R.; Lima, J.C.; Llorca, J.; Rodríguez, L *J. Mat. Chem. C.* 2013, *1,* 5538.
[4] Arcau, J.; Andermark, V.; Aguiló, E.; Gandioso, A.; Moro, A.; Cetina, M.; Lima, J.C.; Rissanen, K.; Ott, I.; Rodríguez, L. *Dalton Trans.* 2014*, 43*, 4425.
[5] Rome, B.; Moro, A.; Aguiló, E.; Gavara, R.; Arcau, J.; Gandioso, A.; Rodríguez, L.; Lima, J.C. *Organic & Biomolecular Chemistry,* 2015, *13*, 2026 - 2033.

Key Words: aurophilicity; hydrogels; luminescence

Acknowledgements: The support and sponsorship provided by COST Action CM1005, Ministerio de Ciencia e Innovación of Spain (Project ENE2012-36368) and Associated Laboratory for Sustainable Chemistry- Clean Processes and Technologies- LAQV (financed by national funds UID/QUI/50006/2013 and co-financed by POCI-01-0145-FEDER-007265).
Correspondence: *REQUIMTE, Departamento de Química, CQFB, Universidade Nova de Lisboa, Monte de Caparica, Portugal. e-mail: lima@fct.unl.*

KN12 - pH-Tunable fluorescence and photochromism in flavylium-based materials

A. Jorge Parola[1]
LAQV@REQUIMTE, Department of Chemistry, Faculty of Science and Technology,
Universidade NOVA de Lisboa. Campus de Caparica, 2829-516 Caparica, Portugal,
ajp@fct.unl.pt

Abstract

Flavylium salts are 2-phenyl-1-benzopyrylium derivatives exhibiting large colour tunability and fluorescence quantum yields depending on the substituents. They are the core of natural anthocyanin dyes responsible for the reds and blues of most flowers and berries. In aqueous solution, flavylium cations establish a pH dependent chemical reaction network that includes photoreactive species, in particular *trans*-2-hydroxychalcones that undergo photoisomerization, leading these compounds as pH-coupled photochromic systems.[1] Transfer of this solution photochromism to the solid state through immobilization of the systems in organized matrices is an undergoing project with the aim of developing photochromic and luminescent materials.

A series of flavylium salts or the corresponding *trans*-2-hydroxychalcones were incorporated or covalently attached to several heterogeneous media (micelles,[1] gels,[1] polymers,[2] zeolites,[3] mesoporous silica [4]) and their photochromic behaviour characterized in the different microenvironments. Since the chalcone/flavylium photochromism is known to be enhanced in CTAB micelles, flavylium species were recently incorporated in CTAB micelles and a sol-gel process followed for the formation of MCM-41 silica particles, avoiding the calcination step in order to keep the micellar phase inside the pores. The pigments thus prepared show pH dependent photochromism with strong colour contrasts and fluorescence quantum yields between 10 – 40 % for flavylium-based materials and in the range 20 – 45% for the chalcones.

Key Words: photochromism, fluorescence, mesoporous silica, hybrid systems, chalcones, flavylium

Acknowledgements: This work was supported by the Unidade de Ciências Biomoleculares Aplicadas-UCIBIO which is financed by national funds from FCT/MEC (UID/Multi/04378/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007728).

References:

[1] F. Pina, M. J. Melo, C. A. T. Laia, A. J. Parola, J. C. Lima, *Chem. Soc. Rev.*, 2012, *41*, 869.
[2] N. Jordão, R. Gavara, A. J. Parola, *Macromolecules*, 2013, *46*, 9055
[3] R. Gomes, R. Q. Albuquerque, F. Pina, A. J. Parola, L. De Cola, *Photochem. Photobiol. Sci.*, 2010, *9*, 991
[4] S. Gago, I. M. Fonseca, A. J. Parola, *Micropor. Mesopor. Mat.*, 2013, *180*, 40

Correspondence: Photochemistry and Supramolecular Chemistry Group, Department of Chemistry, Faculty of Science and Technology, Universidade NOVA de Lisboa. Campus de Caparica, 2829-516 Caparica, Portugal; email: ajp@fct.unl.pt

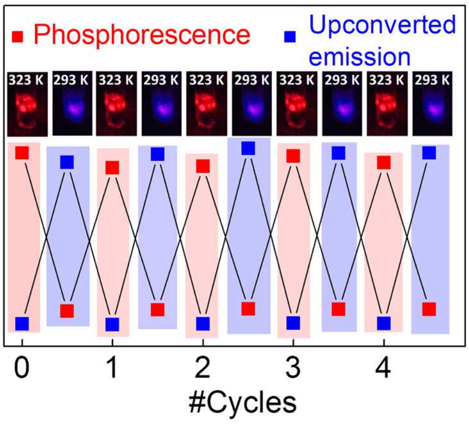
KN13 - Thermally switchable optical systems based on phase change materials.

Claudio Roscini,[1] Alex Julià Lolrol,[1] Daniel Ruiz-Molina,[1] Giuseppina Massaro,[2] Jordi Hernando,[3] Loredana Latterini.[2]

***1.** Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra. 08193. Barcelona. Spain.* ***2.** Department of Chemistry, Biology and Biotechnology, Perugia University, Via Elce di sotto, 8, 06123. Perugia. Italy.* ***3.** Departament de Química, Universitat Autònoma de Barcelona, Edifici C/n, Campus UAB, 08193. Bellaterra. Spain.*

Abstract

Phase change materials (PCMs) are mainly known for their capacity to store and release a large amount of heat during their melting and recrystallization processes.[1] This property, combined with the fact that the phase transition can be reversibly performed several times without inducing chemical degradation, make PCMs promising materials for energy saving insulating coatings in smart buildings. However, the solid-liquid transition of PCMs could be further exploited to modify the absorption or luminescence properties of a dispersed dye, thus providing thermally switchable optical systems. So far, the only well-established example of PCM-based optical switch is given by commercial dye-based thermochromic pigments, in which the solid-liquid transition of an encapsulated acidic PCM induces the reversible development of the color of the pH-sensitive dye dissolved in.[2]



In this presentation I will overview novel, straightforward and versatile strategies we developed in our group to achieve thermally tunable optical properties based on PCMs. In particular, it will be showed how the solid-liquid transition of these materials was successfully exploited to obtain switchable photochromic or upconverting emission properties of organic molecular dyes.[3]

Key Words: upconversion, emission, thermochromism, phase change materials.

Acknowledgements: Our work is supported by Ministero Istruzione dell'Università e della Ricerca (MIUR), the Spanish Government and by FEDER funds. ICN2 acknowledges support from the Severo Ochoa Program.

Correspondence: claudio.roscini@icn2.cat

[1] A. Sharma, V. Tyagi, C.R. Chen, D. Buddhi, *En. Rev.* 2009, *13*, 318–345.
[2] S. M. Burkinshaw, J. Griffiths, A. D. Towns, *J. Mater. Chem.* 1998, *8*, 2677–2683.
[3] G. Massaro, J. Hernando, D. Ruiz-Molina, C. Roscini, L. Latterini, *Chem. Mater.* 2016, *28*, 738−745.

KN14 - Implementation of Biologically Inspired Photochromic Fuzzy Logic (BIPFUL) Systems that extend human vision to UV.

Pier Luigi Gentili,[1] Amanda L. Rightler,[1,2] B. Mark Heron,[3] Christopher D. Gabbutt[3]

Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di sotto 8, 06123 Perugia, Italy

Department of Chemistry and Biochemistry, University of Tulsa, Tulsa, Oklahoma, USA

Department of Chemical and Biological Sciences, School of Applied Science, University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, UK

Abstract

Purpose: We present the analysis of the deterministic part of human colour perception at the computational, algorithmic and implementation levels. At the computational and algorithmic level, we invoke the theory of Fuzzy sets. At the implementation level, we present Biologically Inspired Photochromic Fuzzy Logic (BIPFUL) systems that are useful to discriminate between the three regions of the UV spectrum: UV-A, UV-B and UV-C.

Experimental description: To implement the BIPFUL systems, we have used five photochromic compounds. One belongs to spirooxazine family and the other four are naphthopyrans. The performances of the BIPFUL systems have been investigated in acetonitrile solutions. The activity of one of the best performing BIPFUL systems has also been studied on white paper [1].

Results: This work demonstrates that the theory of Fuzzy logic is effective in interpreting the main features of the deterministic part of human colour perception. In fact, by implementing the formulated algorithms, we achieved BIPFUL systems that allow us to visually discriminate between the three regions of the UV spectrum.

Conclusions: The analysis of the human nervous system at the computational, algorithmic and implementation levels is a fruitful strategy to develop Chemical Artificial Intelligence [2]. The implementation of the basic functions of human intelligence requires the emergent properties of Systems Chemistry.

Key Words: Chemical Artificial Intelligence; Fuzzy logic; Photochromism; Systems Chemistry.

Acknowledgements: P. L. Gentili acknowledges the financial support by the University of Perugia (Fondo Ricerca di Base 2014, D. D. n. 170, 23/12/2014). A. L. Rightler thanks the American Chemical Society IREU Program and the National Science Foundation for support under award number DMR-1262908.

References:

[1] Pier Luigi Gentili, Amanda L. Rightler, B. Mark Heron, Christopher D. Gabbutt, "*Extending human perception of electromagnetic radiation to the UV region through biologically inspired photochromic fuzzy logic (BIPFUL) systems.*" ChemComm. DOI: 10.1039/c5cc09290f.

[2] Pier Luigi Gentili, "*Small steps towards the development of chemical artificial intelligent systems.*" RSC Advances, 2013, 3, 25523-25549.

Correspondence: Pier Luigi Gentili: Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di sotto 8, 06123 Perugia, Italy. E-mail: pierluigi.gentili@unipg.it

Oral Presentations

O 1A – Fluorescent metal ions probes based on β-functionalized porphyrinic derivatives

Nuno M. M. Moura[1,2], Cristina Nuñez[2], M. Amparo F. Faustino[1], Carlos Lodeiro[2], M. Graça P. M. S. Neves[1]

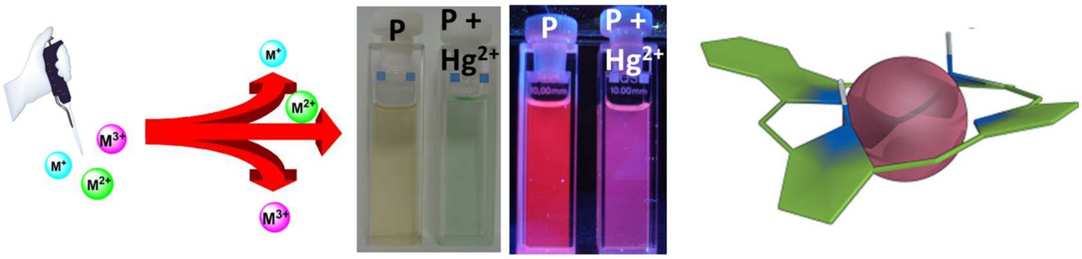
Department of Chemistry and QOPNA, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal.

Bioscope group. Chemistry Department. Faculty of Sciences and Technology. New University of Lisbon. Campus de Caparica. 2829-516. Caparica. Portugal.

Abstract

Purpose: The chemical and physical properties displayed by tetrapyrrolic macrocycles render them particularly attractive to be used in a wide range of fields like supramolecular chemistry, catalysis, electronic materials, sensors and medicine. The development of new fluorescent sensors for metal ion recognition is an area in high expansion due the advantages in terms of sensitivity, selectivity, response time in contrast with others analytical techniques usually used for metal ion detection. The selective detection and monitorization of metal ions using simple techniques based on optical detection are of particular interest due to their high toxicity for living organisms or their significant roles in biological, environmental and industrial fields. In particular, porphyrins and analogues are considered attractive candidates to be used as fluorescent and colorimetric chemosensors due to their remarkable photophysical properties.

Results: The sensing ability of different series of porphyrinic derivatives were explored in solution, by absorption and fluorescence spectroscopy, gas phase, and on solid-supported polymers towards different metal ions. Significant changes in the ground and excited state were observed for metals such as Cu(II), Zn(II), Cd(II) and Hg(II). Some of them presented a significant and unexpected increase in the emission intensity in the presence of Hg(II).The studied compounds are also able to detect metal ions in gas phase and when immobilized in solid-supports. These new emissive hybrid inorganic–organic materials have the potential to be also explored as metal-ion chemosensors.



Conclusions: We are able to prepare from readily available *meso*-tetraarylporphyrins *beta* substituted porphyrins with different moieties through simple and efficient synthetic approaches that demonstrated sensing ability towards metal ions in solution, gas-phase and when supported in solid polymers.

Keywords: Porphyrins, Metal ions, Binding Studies

Acknowledgements: Thanks are due to FCT/MEC for the financial support to the QOPNA research Unit (FCT UID/QUI/00062/2013), through national founds and where applicable co-financed by the FEDER, within the PT2020 Partnership Agreement, and also to the Portuguese NMR Network. Scientific PROTEOMASS Association (Portugal) and REQUIMTE-UCIBIO (PESt-C/EQB/La0006/2013) for general funding. Nuno MM Moura thanks FCT for their Post-Doc scholarship SFRH/BPD/84216/2012.

Correspondence: Department of Chemistry and QOPNA, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal. Email: nmoura@ua.pt

References: Moura, N, et al., Chem. Eur. J., 2014, 20, 6684-6692; Moura, N. et al., ChemPlusChem., 2016, 81, 262-273.

O 2A – A new FRET-based approach to assess polarity in multicompartment nanostructures with solvatofluorochromic probes

Nelsi Zaccheroni,[1] Damiano Genovese,[1] Francesco Palomba,[1] Enrico Rampazzo, [1] Luca Prodi, [1] Cecilia Velino[1]

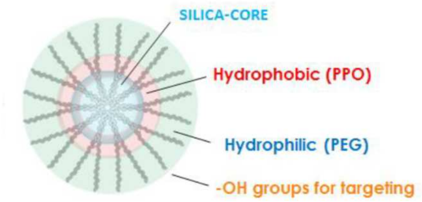
Department of Chemistry "G. Ciamician". School of Sciences. University of Bologna. Via Selmi 2, 40126 Bologna. Italy.

Abstract

Purpose: multicompartment nanostructures are characterized by different chemical and physical properties of their various constituent sections and, due to their dimensions, it is usually difficult to measure them locally. We propose here a general method to probe polarity in such complex structures with subnanometric resolution, unambiguously localizing the information yielded by two different solvatofluorochromic probes, Prodan and Nile Red.

Experimental description: Electronic absorption, emission, excitation spectra and fluorescence lifetimes were measured in aqueous solutions of Prodan and Nile Red in the presence of silica core-shell nanoparticles.

Results: As a multicompartment model system, we have investigated water soluble silica/core-PEG/shell nanoparticles (NP) (circa 25 nm if total diameter) characterized by a hard core (circa 10 nm if diameter) and a softer shell that is responsible for their long term stability. We have recently demonstrated the possibility of hosting water-insoluble dyes in the outer shell, thanks to the unique structure of these nanoparticles, that present hydrophobic and hydrophilic nano-environments intimately interconnected and interfaced with external water. However, due to this intimacy, the polarity of each single domain is not yet fully understood and consequently the exact positioning and stabilization of the molecular guests. We used two lipophilic solvatofluorochromic probes, Prodan and Nile Red, in combination to investigate the local polarity of the soft PEG/shell. In a water solution of NP these species are both loaded in the shell and the information coming from them was spatially resolved by monitoring fluorescence resonance energy transfer (FRET) between them. The results show an increasing polarity gradient from the core surface toward the external NP surface and the positioning of the lipophilic gests as a function of the loaded amount.



Conclusions: FRET between two solvatofluorochromic probes was used as a molecular ruler to co-localize them and hence the environments with different polarities with subnanometric resolution in multicompartment nanostructures.

Key Words: solvatofluorochromic probes - multicompartment nanostructures – nanoparticles – fluorescence – FRET - polarity

Acknowledgements: This work was supported by: MIUR (PON 01_01078 granted to L.P.); University of Bologna (FARB project A.10.N2.RICER.FARB2RODAA, FARB project linea1. NANOX)

Correspondence: Nelsi Zaccheroni, nelsi.zaccheroni@unibo.it, Department of Chemistry "G. Ciamician". School of Sciences. University of Bologna. Via Selmi 2, 40126 Bologna. Italy.

O 3A - Amino-alkyl-rhodamine derivatives as chemo-sensors for mercury ions

Bamaprasad Bag[1]

Colloids and Materials Chemistry Department, CSIR-Institute of Minerals and Materials Technology Bhubaneswar, P.O.:R.R.L., Bhubaneswar-751013, Odisha. India.

Abstract

Induced toxicity due to exposure and bioaccumulation of mercury ions into physiological functionalities leads to many health hazards; therefore, desirably presets its on-site, real time, selective detection and analysis for impact assessment. Rhodamine based signaling probes for selective detection of metal ion have been of enormous interest because of their ability to evaluate the environmental pollutant and physiological hazardous ion's critical concentration through their advantages as signaling module following a straight forward structure-function correlation protocol and ability to modulate signal in aqueous media. In an effort aligned in this direction, photophysical behavior of few substituted 'amino-alkyl-rhodamine' based probes (1-23) were investigated in presence of various metal ions with dual channel chromogenic and fluorogenic signaling as monitoring window. The non-fluorescent probes exhibited chelation enhanced fluorescence and absorption spectral enhancements as well as colourless to pink colour transition in presence of various metal ions, mercury ion in particular. The focus of the investigation was centered on tuning the stereo-electronic contributions of receptor units responsible for metal ion coordination and solvent medium in inducing selectivity, which was carried out with modulation of various parameters such as methodological designs, operational conditions, electronic decoupling etc. to address selectivity, sensitivity, response time, reproducibility/reversibility of signaling operation and probe's reusability issues in mercury ion detection at requisite sub-micromolar level.

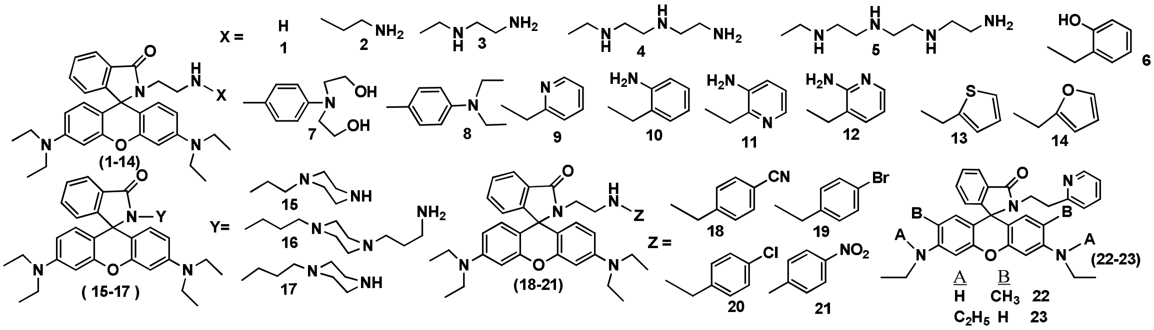


Fig. 1: Pictorial representation of amino-alkyl rhodamine derivatives (1-23)

Structural modification to these xanthene based probes and their functional modulation lead to selective detection of mercury ions with desired sensitivity. These chemosensors were further demonstrated their ability in intracellular mercury ion detection in plant tissues, microorganisms, algae species through bio-imaging and in solid phase through surface immobilization for subsequent removal of the toxic metal ion in an alignment with industrial wastewater treatment.

Key Words: Rhodamine, Dual mode signaling, structural/functional selectivity, mercury ions, bio-imaging

Acknowledgements: Financial support from Council of Scientific and Industrial Research (CSC-0101) and Department of Science and Technology, New Delhi (SB/EMEQ-226/2013) for this work is gratefully acknowledged.

Correspondence: bpbag@immt.res.in (Bamaprasad Bag)

O4A - Thermodynamics of ligand binding to an amidohydrolase from Bordetella/Alcaligenes

Christian Meyners[1], Matthias G.J. Baud[2] , Matthew J. Fuchter[3], Franz-Josef Meyer-Almes[1]

Chemical Engineering and Biotechnology, University of Applied Sciences, Darmstadt, Germany.

MRC Laboratory of Molecular Biology, Francis Crick Avenue, Cambridge Biomedical Campus, Cambridge CB2 0QH, UK.

Department of Chemistr, Imperial College London, London SW7 2AZ, UK.

Abstract

Purpose:

Understanding the driving forces of ligand binding to histone deacetylases.

Experimental description:

A novel sensitive competitive fluorescence resonance energy transfer-based binding assay was developed and the thermodynamics of interaction of both fluorescent ligands and inhibitors to histone deacetylase like amidohydrolase were investigated. The assay consumes only small amounts of valuable target proteins and is suitable for fast kinetic and mechanistic studies as well as high throughput screening applications.

Results:

Binding affinity increased with increasing length of aliphatic spacers (n=4–7) between the hydroxamate moiety and the dansyl head group of ligand probes. Van’t Hoff plots revealed an optimum in enthalpy contribution to the free energy of binding for the dansyl-ligand with hexyl spacer. The selectivity in the series of dansyl-ligands against human class I HDAC1 but not class II HDACs 4 and 6 increased with the ratio of ΔH0/ΔG0.

Conclusions:

The data clearly emphasize the importance of thermodynamic signatures as useful general guidance for the optimization of ligands or rational drug design.

Key Words:

Histone deacetylase; HDAC; thermodynamic signatures; ligand binding; inhibitors

Acknowledgements:

Correspondence:

Prof. Dr. Franz-Josef Meyer-Almes

University of Applied Sciences Darmstadt

Schnittspahnstr. 12, 64287 Darmstadt, Germany

O 5A - Coordination polymer nanoparticles: interaction with biological media, cytotoxicity and cellular uptake.

J. Lorenzo[1], J. García-Pardo[1], D. Montpeyó[1,2], S. Suarez[2], F. Nador[2], F. Novio[2] and D. Ruiz-Molina[2]

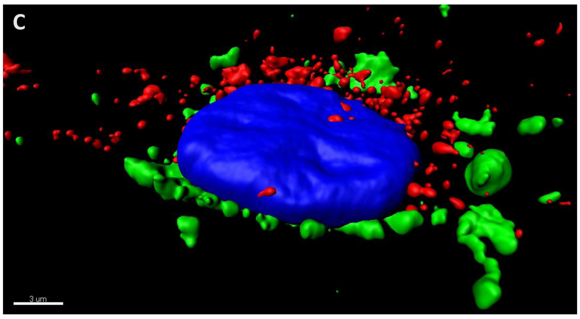
Institut de Biotecnologia i Biomedicina, Dept. Bioquímica i Biologia Molecular, Universitat Autònoma de Barcelona, 08913, Cerdanyola del Vallès (Barcelona), Spain.

ICN2-Institut Català de Nanociència i Nanotecnologia, Campus Universitat Autònoma de Barcelona, 08913, Cerdanyola del Vallès (Barcelona), Spain.

Abstract

Nanoparticles (NPs) are attracting increasing interest in biomedicine as they offer novel solutions for drug delivery, bioimaging and cell targeting. Understanding the interactions of NPs with cells and how these interactions might influence their cytotoxicity or cellular uptake is essential to exploring their biomedical applications [1]. Considering bioimaging and drug delivery, coordination polymer particles (CPPs) are receiving increasing attention because their rational design allow to optimize their functional properties and thereby the release kinetic profile [2,3].

In this study we focused on the assessment of the characteristics of CPPs in the cell culture environment and on understanding the influence of these characteristics on the observed biological effects, in particular on cytotoxicity and cell uptake of CPPs. Characterization of CPPs including size distribution, zeta potential and fluorescence parameters was carried out in different solvents including PBS, PBS-albumin and in cell culture media taking into account the timeframe of the cell experiments and the specific conditions such as temperature or humidity. Preliminary results indicate that CPPs offer promising nanoplatforms with low toxicity and high cellular uptake to be used as multifunctional systems for biological and biomedical applications.



Uptake of CPPs by living cells Three-dimensional reconstruction of endocyted CPPs by neuronal cells. Blue: Nuclei; Red: Lysosomes; Green: CPPs.

1. T. L. Moore, L. Rodriguez-Lorenzo, V. Hirsch, S.Balog, D.Urban, C. Jud, B. Rothen-Rutishauser, M. Lattuada, A. Petri-Fink., Chem. Soc. Rev., 2015, 44, 6287-6305.

2. F. Novio, J. Lorenzo, F. Nador, K. Wnuk, D. Ruiz-Molina. Chem. Eur. J. 2014, 20, 1-9.

3. M. Borges, S. Yu, A. Laromaine, A. Roig, S. Suárez-García, J. Lorenzo, D. Ruiz-Molina, F. Novio. RSC Adv, 2015, 5, 86779-83.

Key Words: Coordination polymer nanoparticles, cell uptake, cytotoxicity.

Correspondence: Unitat d´Enginyeria de Proteïnes i Proteòmica. Institut de Biotecnologia i Biomedicina, Universitat Autònoma de Barcelona, 08913, Cerdanyola del Vallès (Barcelona), Spain. Julia.lorenzo@uab.es.

O 6A - Fluorescent Probes for Redox-active Biomolecules

Dong-Nam Lee,[1] Jong-In Hong[1]
Department of Chemistry, Seoul National University, Seoul 151-747, Korea.

Abstract

We report a new approach for the detection of mitochondrial flavins through photo-oxidation of a probe molecule. Probe 1 showed high brightness ($\varepsilon \times \Phi_f = 6.50 \times 10^3\ M^{-1}cm^{-1}$) at long wavelengths (maximum emission wavelength, $\lambda_{max} = 600$ nm) upon photo-oxidation, assisted by the strong electron accepting ability of the isoalloxazine moiety in flavins. Probe 1 also exhibited high selectivity for flavins over various biological oxidants, remarkable photo-stability, and, most importantly, mitochondrial localization. Furthermore, confocal images revealed that the probe allowed fluorescence monitoring of mitochondrial oxidation status of flavins in cells and tissues, with minimal photobleaching and deep tissue penetration. The method described herein would be a prototype for the development of bioprobes for understanding flavin-linked biological reactions in mitochondria. We also present our recent efforts towards the development of selective fluorescent chemosensors and imaging probes especially for redox-related biomolecules (FMN, FAD, NAD^+, $NADP^+$, etc.).

Key Words: fluorescent probe; redox-active; flavin; mitochondria

Acknowledgements: This work was supported by the NRF grant funded by the MSIP of Korea.

Correspondence: Jong-In Hong, Department of Chemistry, Seoul National University, Seoul 151-747, Korea.

E-mail: jihong@snu.ac.kr

O 7A - Electrochromic Display Devices with Metallo-Supramolecular Polymers

Masayoshi Higuchi

Electronic Functional Macromolecules Group, National Institute for Materials Science, Tsukuba 305-0044, Japan

Abstract

Purpose: Electrochromism is color change triggered by electrochemical oxidation and reduction (= redox) in material. Compared with liquid crystalline (LC) displays and electro-luminescence (EL) ones, displays using electrochromic (EC) materials have an advantage from the viewpoint of energy consumption, because no energy is necessary to keep a display in the EC devices. However, examples of the commercialized applications are very limited due to the insufficient performance of conventional EC materials. Here I report our recent progress on electrochromic display devices using metallo-supramolecular polymers.

Experimental description: Metallo-supramolecular polymers were synthesized by the complexation of metal ions (Fe(II), Ru(II), Co(II), Cu(I) etc.) with multi-topic organic ligands (bisterpyridines, tristerpyridine, bisphenanthroline etc.). The polymer film was prepared on an ITO glass by spin-coating or spray-coating. The performance of the obtained EC materials were evaluated concerning transmittance in the colored and bleached states, contrast, times for the color changes, coulomb number for the color changes, and coloration efficiency. Electrochromic devices were fabricated using gel electrolyte and another ITO glass.

Results: Fe(II)-, Ru(II)-, and Co(II)-based metallo-supramolecular polymers were synthesized by the 1:1 complexation of the metal ions with bisterpyridines. The obtained polymers displayed blue, red, and yellow color, respectively, based on the metal-to-ligand charge transfer (MLCT) absorption. The polymer films on an ITO glass showed color change between the colored state and colorless by electrochemical redox of the metal ions. Cu(I)-based polymer exhibited green color and the color disappeared by the oxidation of Cu(I) to Cu(II). Use of triterpyridine in metallo-supramolecular polymer synthesis changed the polymer structure from linear to hyperbranched. The 3D hyperbranched polymer exhibited higher coloration efficiency in the EC change than the linear polymer, probably because of the porous polymer film formation in the hyperbranched polymer and the efficient ion transfer properties. Introduction of two metal ion species in the polymer enabled multi-color EC behavior due to the different redox potentials of the two metal ion species. Black EC change was achieved using the redox between Co(II) and Co(I) in the Co(II)-based polymer [1]. In addition we successfully fabricated various types of EC devices with metallo-supramolecular polymers [2].

Conclusions: Blue, red, yellow, and black electrochromism was observed in metallo-supramolecular polymers. Multi-color electrochromism and improvement of EC properties were also realized by modifying the polymer structure. Now we are investigating the EC devices with the polymers toward wide applications including smart window and digital signage.

Key Words: Electrochromism; Metallo-supramolecular polymer; Coloration efficiency; Color variation

Acknowledgements: This research is financially supported by CREST project, JST.

Correspondence: Dr. Masayoshi Higuchi, Electronic Functional Macromolecules Group, 1-1 Namiki, Tsukuba 305-0044, Japan; e-mail: HIGUCHI.Masayoshi@nims.go.jp

References: [1] *ACS Appl. Mater. Interfaces*, 2015, *7*, 18266; [2] *ACS Appl. Mater. Interfaces*, 2015, *7*, 25069.

O 8A – Iridium(III) Complex-based Photodynamic Therapy Reagents

Tae-Hyuk Kwon
Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST),
Ulsan 44919, Republic of Korea

Abstract

Purpose: Recently metal complexes have a great attention for various human diseases, such as cancer, Alzheimers and neurodegenerative disorder. Among various metal complexes, Ir(III) complexes are very promising candidates in these applications on account of their intense emission, wide range of emission energies, and high luminescence quantum yield. Here, using Ir(III) complexes, in this presentation, I will introduce photodynamic therapy (PDT) reagent for cancer cells and photoactivatable modulators for amyloid-□ aggregation for Alzheimer treatment.

Experimental description: We prepared four different types of Ir(III) complexes and then analyzed their energy level by photophysical and electrochemical studies. For their PDT ability, we observed cytotoxicity of light-activated Ir(III) complexes for three cancer cell lines (*e.g.*, SK-OV-3, MCF7 and Caco-2) by MTT assay. To clarify the reason of great PDT ability, ROS analyses, photo-crosslinking and protein oxidation analysis *via* Western blot and mass spectrometry with Ir(III) complexes were progressed. In second, for modulating amyloid-□ aggregation, we prepared new Ir(III) complex, Ir-1 and then investigated oxidative modification and morphological change of amyloidogneic peptides by photoactivation .

Results: We developed PDT agents composed of Ir(III) complexes for cancer cells via a molecular design strategy for efficient ROS generation that accounted for appropriate energy levels and high emission quantum yields. TIr3 and TIr4 effectively triggered the death of cancer cells through spatiotemporal cytotoxic activity via superior ROS generation ability (□$_s$ = 0.95 and 0.78, respectively) localized at the endoplasmic reticulum (ER), even under low concentration (≤ 2 □M) and weak light energy (≤ 1 J cm^{-2}). Additionally, TIr3 efficiently induced cancer cell death by two-photon irradiation. Using MS, we characterized the modes of action for Ir(III) complexes for both protein crosslinking and protein oxidation. In living cells, the damage was predominantly found in proteins near the ER and mitochondria with significant association to cell death pathways. Therefore, these Ir(III) complexes efficiently functioned as PDT agents in cancer cells. Furthermore, we found that rationally designed Ir-1 could alter Aβ aggregation pathways specifically with light exposure. Such an activity of Ir-1 is observed to be associated with multiple mechanisms (i.e., peptide oxidation, complex formation, or both), confirmed by our biochemical and biophysical investigations.

Conclusions: We developed Ir(III) complexes that efficiently functioned as PDT reagents in cancer cells and revealed their mechanism. Further optimization of these iridium(III) photosensitizers could lead to rapid cell death following effective protein disablement. In addition, we also demonstrated the feasibility of innovatively constructing Ir(III) complex as photoactivatable chemical tools for modulating Aβ aggregation, which clearly indicates an expansion of metal complexes' biological applications.

Key Words: Ir(III) complexes, Photodynamic therapy, Amyloid-□ aggregation, Two-photon activation, Protein modification, Photo-crosslinking, Protein oxidation, Reactive oxygen species (ROS), Photoactivation

Acknowledgements: This research was supported by Ulsan National Institute of Science and Technology research fund (1.150117.01, 1.140101.01, and 1.160001.01).

Correspondence: kwon90@unist.ac.kr

O 9A (P38) – Synthesis of Discotic Molecules derived from Heterocyclic Tris [1,2,4] Triazolo [1,3,5] Triazine

Alexandre Gonçalves Dal-Bó,[1] Eduardo Zapp,[2] Georgina Gisel López Cisneros,[1] Rodrigo Cercena,[1] Jackson Mendes, [1] Letícia Matos da Silveira, [1] Rodrigo da Costa Duarte,[3] Fabiano Severo Rodembusch,[3] Tiago Elias Allievi Frizon,[1]*

1- Universidade do Extremo Sul Catarinense, Av. Universitária, 1105 - CP 3167, 88.806-000, Criciúma -SC, Brazil. 2- Universidade Federal de Santa Catarina – R. Gov. Jorge Lacerda, 3201, 88905-355, Araranguá - SC, Brazil. 3- Universidade Federal do Rio Grande do Sul - CEP 91501-970 Porto Alegre-RS, Brazil.

Abstract

Compounds having [1,3,5]- triazines as a center have been designed to display light-emitting and semiconductor properties, therefore good candidates for use in discotics functional materials with luminescent characteristics. This work presents the synthesis and characterization of compounds based on the heterocycle tris-[1,2,4]-triazolo-[1,3,5]-triazine (TTT), obtained by a new building block which can be used to get various discotic materials in one step. The chemical structure of the heterocycle was characterized by FTIR, ^{1}H and ^{13}C NMR and MS. Thermal properties were measured by TGA, DSC and MOLP. Membranes were prepared by spin coating technique, and the optical properties were obtained by absorption spectroscopy analysis (UV). The synthesized compounds have shown strong blue fluorescence in solution. The ionic conductivity was determined by electrochemistry and the results show great potential for application as optical sensors.

Experimental description: Compounds containing the heterocycle tris-[1,2,4]-triazolo-[1,3,5]-triazine (TTT) were synthesized and characterized by FTIR, ^{1}H and ^{13}C NMR and MS. These compounds present rigid central units having a high organization, excellent transport loads and thermal stability. The UV–Vis absorption spectrum of the different compounds were obtained by analysis of diluted solutions in dichloromethane solvent, showing wavelength of maximum absorbance at approximately 298 nm and resulting in elevated molar absorption coefficient (ε) in the range values of 38700 to 81906 $\text{Lmol}^{-1}\text{cm}^{-1}$, which are assigned to π-π* electronic transitions of aromatic molecules. For the compound containing hydroxyl groups at the extremities, an intense absorption band at 247 nm ($\varepsilon = 13740\ \text{Lmol}^{-1}\text{cm}^{-1}$) was exhibited, showing that the length and number of flexible side chains had influence on absorption behavior. The cyclic voltammetry measure showed distinct anodic and cathodic behavior. The electrochemical band-gaps of TTT molecules were calculated by onset peak values. Spectroelectrochemical showed changes in the absorption spectra due to changes in electronic structure under oxidation and reduction conditions. The results of thermogravimetric analysis for all compounds showed high thermal stability, which is of great interest for use in the electronics industry.

Conclusions: A series of compounds based in heterocycle tris-[1,2,4]-triazolo-[1,3,5]-triazine (TTT), as central unity in discotic molecules, was synthesized by reactions with different alkyl bromides and a versatile building block containing three hidroxyl groups in their structure. This versatile building block can be used to obtain different materials in only one step. The compounds obtained were characterized by FTIR, ^{1}H e ^{13}C NMR and mass spectrometry (MS). Thermal properties were available by DSC, TGA, and MOLP, presenting good thermal stability at 400°C. The optical properties of compounds were analyzed by UV-Vis and showed maxima absorption at approximately 285 – 298 nm to compounds containing long alkyl chains at the extremities. These molecules also presented blue fluorescence both in solution and films and additionally exhibited the properties of remain in the supercooled state after melting. When the derived of TTT heterocycle were studied in relation to charge transport, the compounds presented conductive properties of electrons, but with low conductivity.

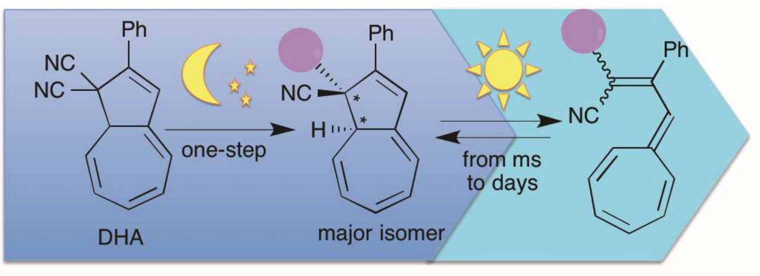
Key Words: tris-[1,2,4]-triazolo-[1,3,5]-triazine, Discotics liquid crystals. Fluorescence. Heterocycles.

Acknowledgements: The authors would like to thank the National Council for Scientific and Technological Development CNPq.

Corresponding author: Tiago Elias Allievi Frizon; *E-mail address:* (tiagofrizon@gmail.com). Av. Universitária, 1105 - CP 3167, 88.806-000, Criciúma (SC), Brazil Tel.: +55 (48) 3431 2775.

O10A – Monocyano-monosubstituted dihydroazulenes: from energy storage to fast-responsive materials

Martina Cacciarini[1,2], Martyn Jevric,[2] Mogens Brønsted Nielsen[2]
Chemistry Department "U Schiff". University of Firenze. Via della Lastruccia 3-13, 50019. Sesto Fiorentino (FI). Italy.
Chemistry Department. University of Copenhagen. Universitetsparken 5, 2100. Copenhagen Ø. Denmark.
martina.cacciarini@unifi.it



The aim of this research is to study the influence of substituents on C-1 of the dihydroazulene scaffold (DHA) on the lifetime of the corresponding vinylheptafulvenes (VHF) and on the energy storage capacities of the DHA/VHF pair.

The DHA/VHF system is a T-type photoswitch based on the light- or thermal-induced interconversion between the DHA and the VHF components, and is characterized by the presence of two cyano groups in position 1 of DHA. So far, alternative functionalizations at C-1 have attracted little attention, considering the two nitriles essential for the photochromic properties of the system.[1] We experienced a peculiar reactivity of one of the two nitriles towards 2-aminothiols and explored the removal of this functional group for energy storage purposes.[2]

In this communication, we will describe the one-step syntheses from the parent DHA of a selection of monocyano-monosubstituted DHAs, together with the stereochemical outcome of the reactions, and the influence of the nature of the new substituents on the lifetimes of the corresponding VHFs.[3]

Key Words: photo/thermo-switch, fast-responsive materials, energy storage, nitrile

Acknowledgements: University of Firenze and Carlsbergfondet are acknowledged for financial support.

[1] (a) J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas and U. Seitz, *Chem. Ber.*, 1986, **119**, 2631. (b) J. Daub, S. Gierisch, T. Knöchel, E. Salbeck and G. Maas, *Z. Naturforsch.*, 1986, **41b**, 1151.

[2] (a) M. Cacciarini, E. A. Della Pia, M. B. Nielsen. *Eur. J. Org. Chem.*, **2012**, 6064-6069. (b) M. Cacciarini, A. B. Skov, M. Jevric, A. S. Hansen, J. Elm, H. G. Kjaergaard, K. V. Mikkelsen, and M. B. Nielsen. *Chem. Eur. J.*, **2015,** *21,* 7454–7461.

[3] M. Cacciarini, M. Jevric, J. Elm, A. U. Petersen, K. V. Mikkelsen, and M. B. Nielsen. *RSC Adv.,* **2016**, *6,* 49003-49010.

O11A - Peptide Conjugated Metal Complex Luminophores for Imaging and Sensing in Live Cells.

Tia E. Keyes.
School of Chemical Sciences, Dublin City University, Dublin 9, Ireland.

There is growing demand for novel luminophores customised for sensing and imaging in live cells and tissues. This demand has been driven by the evolution in diversity and sophistication of luminescence-based imaging technologies over the past twenty years. Conventionally, fluorophores used in cell imaging are organic, usually polyaromatic molecules and whilst such species have high fluorescence quantum yields they often exhibit a range properties, including poor photostability, small Stokes shift and short emission lifetimes (typically 1 – 10 ns), that can constrain their application in diverse imaging and sensing applications. Luminescent transition metal probes, including in particular, the polypyridyl coordination compounds of ruthenium and osmium, are valuable alternative emission probes that can potentially address many of the limitations of organic fluorophores. However, until relatively recently, a significant barrier to the application of transition metal probes has been their poor membrane permeability and perceptions that they are cytotoxic. Herein, some of our recent work in developing ruthenium polypyridyl peptide conjugates as cell imaging and sensing probes is described. We outline the application of cell penetrating and signal peptides to promote metal complex permeation of the cell membrane and organelle targeting in living cells. And, strategies for designing ruthenium metal polypyridyl complexes for application in multimodal, (fluorescence lifetime, intensity and Raman microscopy), cell imaging to provide insights into cell structure, and dynamic concentration of analytes such as oxygen and H^+ are discussed.

References

[1] An Osmium (II) Polypyridyl Polyarginine Conjugate as a Probe for Live Cell Imaging; A Comparison of Uptake, Localization and Cytotoxicity with its Ru(II) Analogue., A.Byrne, R Moriarty, C. Dolan, Y. Aaron Martin U Neugebauer, R J. Forster A. Davies Y. Volkov T. E. Keyes, Dalton Transactions, 2015 2015, 44(32):14323

[2] RGD peptide Labelled Metal complex Probes reveal activation Status of Integrin from fluorescence Anisotropy. K Adamson, M Devocelle, N Moran, R.J. Forster, T.E. Keyes, Bioconj. Chem, 2014, 25, 928.

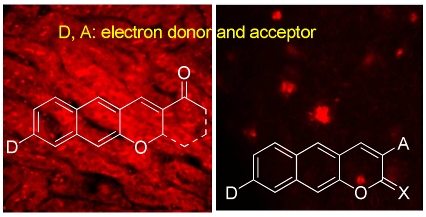
[3] Peptide-Bridged Dinuclear Ru(II) Complex for Mitochondrial Targeted Monitoring of Dynamic Changes to Oxygen Concentration and ROS Generation in Live Mammalian Cells. A Martin, A Byrne, C.S. Burke, R J. Forster and Tia E. Keyes, J. Am Chem Soc., 2014, 136, 15300.

O12A - Small-molecule two-photon absorbing dyes for tissue imaging

Kyo Han Ahn
Department of Chemistry, POSTECH, 77 Cheongam-Ro, Nam-Gu, Pohang, Gyungbuk, Korea 37673.
ahn@postech.ac.kr

Fluorescence imaging of organ tissues is an essential means to investigate various biological processes beyond the cellular level. In tissue imaging using a fluorescent dye, suppressing the autofluorescence from intrinsic biomolecules and looking into deeper tissue become two key issues along with other considerations such as the dye's photo-stability, biocompatibility, toxicity, etc. The conventional one-photon confocal microscopy (OPM) is a powerful technique to image subcellular parts with submicron high resolution; however, OPM allows imaging of tissue only to a shallow depth (50-80 μm), limiting its use for tissue imaging. Two-photon microscopy (TPM) using a two-photon absorbing dye offers an alternative means for deeper tissue imaging (500-1000 μm) with a similar level of resolution).[1] TPM under excitation in the NIR wavelength region (650–950 nm) also causes much less photo-damage and photo-bleaching to both the tissues and probe than the case of OPM, allowing live tissue imaging for a long period. These promising features of TPM have motivated a quest for fluorescent molecules (fluorophores) with favourable two-photon absorbing properties and with necessary biocompatibility.[2]

Small-molecule fluorophores such as acedan, coumarin, and napthalimide dyes are dipolar dyes composed of a donor and an acceptor groups, which have been extensively used as one-photon as well as two-photon absorbing dyes in the development of fluorescence probes. These dyes, however, show limitations in tissue imaging by TPM, owing to significant autofluorescence and poor emission behaviour in aqueous media. To address these issues, we have developed π-extended analogues of acedan and coumarin analogues, respectively, which enable deeper tissue imaging with suppressed autofluorescence. In this conference, I like to present our recent progress in the development of small-molecule two-photon absorbing dye flatforms for tisse imaging.[3]



Keywords: Two-photon absorbing dyes, fluorescence probes, bioimaging

References:
[1] F. Helmchen and W. Denk. Nat. Methods **2005**, 2, 932.
[2] For recent reviews on two-photon probes for bioimaging, see: (a) D. Kim, H. G. Ryu, and K. H. Ahn, Org. Biomol. Chem. **2014**, 12, 4550. (b) H. M. Kim and B. R. Cho, Chem. Rev. **2015**, 115, 5014.
[3] (a) D. Kim, S. Sambasivan, H. Nam, K. H. Kim, J. Y. Kim, T. Joo, K.-H. Lee, K.-T. Kim, and K. H. Ahn, Chem. Commun. **2012**, 48, 6833. (b) S. Singha, D. Kim, B. Roy, S. Sambasivan, H. Moon, A. S. Rao, J. Y. Kim, T. Joo, J. W. Park, Y. M. Rhee, T. Wang, K. H. Kim, Y. H. Shin, J. Jung, and K. H. Ahn, Chem. Sci. **2015**, 6, 4335. (c) D. Kim, Q. P. Xuan, H. Moon, Y. W. Jun, and K. H. Ahn, Asian J. Org. Chem. **2014**,3, 1089. (d) M. Tasior, D. Kim, S. Singha, M. Krzeszewski, K. H. Ahn and D. T. Gryko, J. Mater. Chem. C, **2015**, 3, 1421. (e) D. Kim, H. Moon, S. H. Baik, S. Singha, T. Wang, K. H. Kim, B. S. Park, J. Jung, I. Mook-Jung, and K. H. Ahn, J. Am. Chem. Soc. **2015**, 137, 6781. (f) K. H. Ahn and co-workers, unpublished results.

O 13A – Luminescent Nanoparticles for Protein Screening and Imaging

Elisabete Oliveira[1,2]
[1]BIOSCOPE Research Group, UCIBIO-REQUIMTE, Department of Chemistry, Faculty of Science and Technology, Universidade NOVA de Lisboa, 2829-516, Caparica, Portugal.
[2]ProteoMass Scientific Society, Madan Parque, Rua dos Inventores, 2825-182 Caparica, Portugal

Abstract

Purpose: Luminescent nanoparticles emerged as new platform for imaging and identification of low abundance proteins in biological samples. Quantum Dots (QDs) covered with mesoporous silica nanoparticles are a new generation of multifunctional nanocarriers acting as all-in-one diagnostic and therapeutic tools, and can be used to simultaneously visualize and treat various diseases. Herein, Luminescent CdTe QDs covered with mesoporous silica ($mSiO_2$) nanoparticles, their ability to screening low abundance proteins in complex biological samples as blood and urine, and internalization in cancer cells as drug delivery systems will be addressed.

Experimental description: CdTe QDs will be synthetized accordingly with ref. (Wu, S. *J. Mater. Chem.* 2012, *22*, 14573), and further mixed to cetylmethyl ammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS). Drugs as doxorubicin as cisplatin were encapsulated in these systems. The final nanoparticles were fully characterized and studied in biological environments.

Results: The QDs@$mSiO_2$ were mixed with urine and blood samples and the proteins adsorbed to its surface separated by common proteomic techniques and identified by Mass spectrometry. The QDs@$mSiO_2$ revealed to be smart systems for controlled drug delivery, releasing the doxorubicin at acid pH.

Conclusions: Proteins were successfully extracted from urine samples by the luminescent doped mesoporous silica nanoparticles and identified by mass spectrometry. These nanomaterials internalizated in cancer cells by endocytosis, relasing then the doxorubicin leading to cellular apoptosis.

Key Words: Luminescence, Inorganic Nanoparticles, proteins screening, cancer cells.

Acknowledgements: We are grateful to the financial support to Scientific PROTEOMASS Association (Portugal), LAQV/REQUIMTE (UID/QUI/50006/2013) and UCIBIO/REQUIMTE (UID/Multi/04378/2013). E.O.acknowledge the post-doctoral grant SFRH/BPD/72557/2010 and to Foundation L'Oreal (UNESCO and FCT) for the Prize *For Women in Science* 2015, "Medalhas de Honra L'Oréal Portugal para as Mulheres na Ciência", healthy Sciences area.

Correspondence: BIOSCOPE Group, REQUIMTE/UCIBIO, Chemistry Department, FCT, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal. E-mail: elisabete.oliveira@bioscopegroup.org

O14A - Thermally activated delayed fluorescence – can we achieve deep blue?

Simone Lenk[1], Paul Kleine[1], Ramunas Lygaitis[1,2], Ludwig Popp[1], Olaf Zeika[1], Reinhard Scholz[1], Sebastian Reineke[1]

Institut für Angewandte Photophysik. George-Bähr-Straße 1. 01062 Dresden. Germany

Department of Polymer Chemistry and Technology. Kaunas University of Technology. Radvilenu plentas 19. LT50254 Kaunas. Lithuania

Abstract

Thermally activated delayed fluorescence (TADF) has gained increasingly high interest in the field of organic light-emitting diodes (OLEDs) in the last years. In OLEDs, the singlet to triplet ratio is 1:3 due to quantum mechanical control of spin statistics of electron-hole recombination. Hence, about 75% of the injected charge carriers are lost when using a fluorescent emitter on which only the singlet excitons recombine radiatively (Fig. 1). This problem can be overcome by using phosphorescent emitters, which efficiently emit from the triplet state. Here, the intersystem crossing (ISC) rate is increased and leads to a transfer of singlets to the triplet state. Another approach to increase the efficiency is the use of TADF by strong reduction of the energy splitting between singlet and triplet level. Now, the reverse intersystem crossing rate (RISC) becomes large and triplets can be up-converted into singlet excitons.

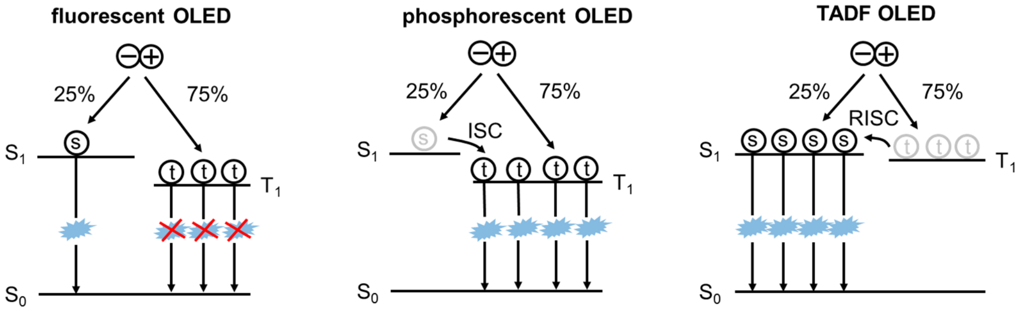


Figure 1. Schematic working principle of fluorescent, phosphorescent, and TADF OLEDs

Fluorescent and phosphorescent emitters are used in OLEDs for many years. However, both concepts have significant drawbacks. While fluorescent OLEDs have low efficiency due to non-radiative triplet state, phosphorescent emitters require the use of expensive rare metal complexes. The fundamental understanding of TADF is still in its infancy and especially the development of deep blue emitters, highly needed by industry, is a mayor challenge. In this contribution, we present our recent efforts in understanding basic concepts of TADF mechanisms and molecular design. A donor-acceptor type TADF emitter family is investigated by time-dependent density functional theory. Furthermore, time-dependent spectroscopy allows us to characterize our emitters by all photo-physical means and the external quantum efficiency reached by TADF OLEDs is well above that of fluorescent emitters.

Key Words: OLED, TADF, charge transfer

Acknowledgements: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 641725 (PHEBE).

Correspondence: simone.lenk@iapp.de

O15A –Candlelight emitting organic electroluminescence

Jwohuei Jou
Materials Science and Engineering Department, National Tsing Hua University, Taiwan

Abstract

Purpose: The electric light of modern world, especially that with intensive white or blue emission, has caused increasing concern for being potentially hazardous to human health as well as ecosystems. Blue hazard free lighting sources are now in high demand and will become the mainstream of future lighting. The purpose of this study is to devise an energy efficient organic light emitting diode (OLED) with either electro-fluorescent or -phosphorescent emitters to mimic the emission of a candle that is blue hazard free but energy-wasting.

Experimental description: First, we measured the color and color temperature of a candle. Then, we employed four candlelight emission complementary emitters and deposited them into two emission layers of an OLED device. The desirable candlelight color and color temperature, which is around 1,910K at the brightest spot, were obtained by tuning the ratios of the different emitters and emission layer thicknesses.

Results: It was found that the color temperature of candlelight varied with different flame position. To represent, the brightest spot was taken and showed a color temperature of 1,910K. The resultant candlelight-style OLED showed a color temperature of 1,900 to 2,000K, depending on the above ratios. With the employment of electroluminescence active phosphorescent dyes, coupling with an efficiency-effective device architecture, a highly efficient device was made with a power efficiency of 90 lm/W. It was about 300 to 900 times that of a candle, which ranges between 0.1 and 0.3lm/W according to different reports. To quantify how human-friendly this candlelight OLED could be, an action spectrum of melatonin suppression sensitivity (MSS) was used, and the MSS as calculated was less than 1/5 of those of the white light counterparts of compact fluorescent lamp, LED and OLED. From retina protection perspective, it was at least 10 times safer.

Conclusions: We find candlelight emission to be easily obtainable via the latest OLED lighting technology with the employment of multiple low-color-temperature blackbody-radiation complementary dyes, whereby only sky-blue instead of deep-blue emitter is required to form a high quality light that is much free of blue hazard. The resultant candlelight OLED also exhibits a power efficiency approaching that the energy-saving fluorescent tubes. Hopefully, such a physiologically-friendly lighting measure can be used to trigger a “Lighting Renaissance” to safeguard human health and ecosystems.

Key Words: Candlelight, human-friendly, blue hazard free, OLED,

Acknowledgements: This work was financially supported in part via grants MEA 104-EC-17-A-07-S3-012, and MOST104-2119-M-007-012 and 103-2923-E-007-003-MY3.

Correspondence: J. Jou, Materials Science and Engineering Department. National Tsing Hua University, Taiwan; email: jjou@mx.nthu.edu.tw

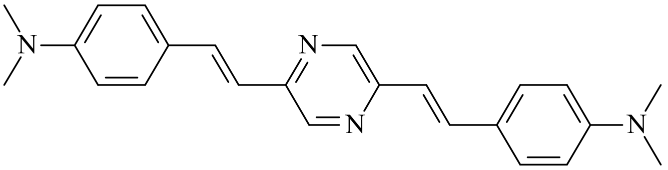
O16A – Acidochromism and Solvatochromism of the Fluorescence of Oligo(phenylenevinylene)s with Multiple Basic Sites.

Heiner Detert[1], Sebastian Moschel,[1] Volker Schmitt,[1]

Institute for Organic Chemistry, Johannes Gutenberg-University Mainz, 55099 Mainz Germany.

Abstract

Purpose: Pyridine and related hetarenes are used as functional subunits in conjugated oligomers and polymers with applications from electronic materials to building blocks in supramolecular chemistry. Key features of these rings are their high electron affinity and their ability to interact with protons and alkylating agents. As part of our interest[1-3] in donor/acceptor-substituted π-conjugated oligomers, we use pyridine-type hetarenes as electron-deficient rings in oligo(phenylenevinylene)s. These acceptor groups are combined with electron pair donating groups like alkoxy and especially amino groups.



Experimental description: Absoption and fluorescene were measured in different solvents and in the presence of acid. Furthermore, some results from two-photon absorption measurements and electrooptical absorption spectroscopy are reported.

Results: A quadrupolar arrangement of electron donating and withdrawing groups results in chromophores with a solvent-depending fluorescence. Bathochromic shift and reduced efficiency correlate with increasing solvent polarity. Additionally the basic sites make these chromophores to protonation, altering both, absorption and emission spectra. These interactions of the π-systems with electric dipoles (solvatochromism) and protons (acidochromism) can differ greatly, in the ground state as well as in the excited state. Moreover, the positions of the basic centres relative to the conjugated system are controlling the impact of solvent dipoles and, even more pronounced, of protons on the electronic spectra. Depending on the relative basicities of the different sites, multiple changes in the electronic spectra result from increasing concentration or pK_A of the acid. Especially the fluorescence can be switched between spectra of lower or higher energy, sometimes separated by concentration regimes, with a totally quenched emission. These dyes are interesting for sensor technology[4], as different ways of interaction with the environment can result in two different molecular answers (absorption/fluorescence). Furthermore, as these aza-OPVs are characterized by a quadrupolar electronic structure, they are also attractive as two-photon absorbing chromophores[5].

Conclusions: Distyrylbenzenes with a quadrupolar donor-acceptor-donor including basic sites are sensitive indicators for solvent polarity and protons, these compounds are efficient TPA fluorophores and show high dipole moments in their excited states

Key Words: fluorescence, solvent effect, halochromism, two-photon absorption, EOAM

Correspondence: Prof. Dr. Heiner Detert

References: [1] V. Schmitt, J. Fischer, H. Detert, *ISRN Org. Chem.* **2011**, Article ID 589012, doi:10.5402/2011/589012
[2] N. A. Nemkovich, H. Detert, V. Schmitt, *Chem. Phys.* **2010**; (378) 37.
[3] V. Schmitt, S. Moschel, H. Detert, Eur. J. Org. Chem., **2013**, 5655
[4] V. Schmitt, S. Glang, J. Preis, H. Detert, Sens. Lett. **2008**; *6*, 1.
[5] B. Strehmel, A. M. Sarker, H. Detert, *ChemPhysChem*. **2003**; *4*, 249.

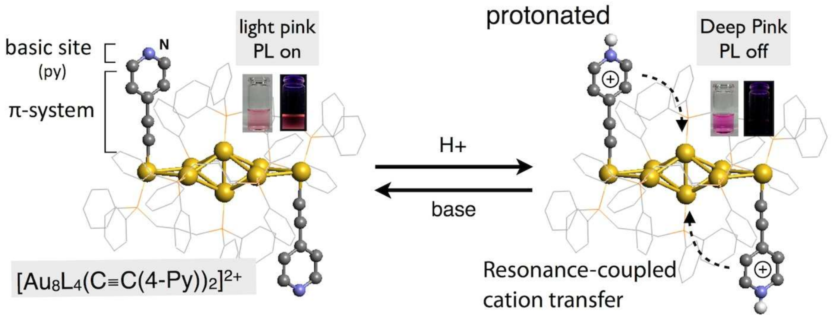
O17A - Unique Optical features and Chromism Behaviors of Molecular Gold Clusters

Katsuaki Konishi[1,2], Yukatsu Shichibu,[1,2] Mizuho Sugiuchi,[1] Mitsuhiro Iwasaki
1 Graduate School of Environmental Science, Hokkaido University, Sapporo, 060-0810, Japan
2 Faculty of Environmental Earth Science, Hokkaido University, Sapporo, 060-0810, Japan

Abstract

The chemistry of small metal cluster compounds has attracted considerable interest because of their unique molecule-like optical/electronic features. Especially, the electronic interaction of the metallic framework with the protecting organic moieties is interesting since it potentially offers unique optical properties/responses. During the recent study on the exploration of diphosphine-coordinated gold clusters, we have found some examples of exceptional non-spherical geometries in the crystal structures of Au_6, Au_7, Au_8, and Au_{11} clusters [1]. Unlike conventional spherical Au nanoparticles, these non-spherical clusters all exhibited isolated visible absorptions arising from the intracluster metal-to-metal transitions. Furthermore some clusters exhibit photoluminescence. Therefore, they are expected to serve as building units of chromogenic sensing modules. Herein we studied the electronic interaction of π-units and gold frameworks in the optical responses of a series of pyridine-functionalized Au8 clusters.

A series of $[Au_8(dppp)_4(L)_2]^{2+}$ (L = C≡CR or SR) with a core+exo type octagold unit were synthesized and their optical properties and responses were investigated. Although the C≡C moieties of the alkynyl-modified clusters did not affect the absorption properties, the pyridylethynyl-bearing clusters exhibited reversible visible absorption and photoluminescence responses to protonation/deprotonation events of the terminal pyridyl moieties. The chromism behaviors were highly dependent on the relative position of the pyridine nitrogen atom, suggesting that the resonance-coupled movement of the positive charge upon protonation is involved in the optical responses [2]. The pyridinethiolate-modified clusters also showed definite optical responses. These observations provide examples of electronic communication between the gold unit and the distal organic functionality through π-conjugated linker, and also demonstrate the utility of the combination with organic chemistry in the design of cluster-based responsive systems.



Refs.) [1] *Angew. Chem. Int. Ed.*, 2011, 50, 7442; *Chem. Commun.*, 2012, 48, 7559; *Inorg. Chem.*, 2013, 52, 6570; *J. Am. Chem. Soc.*, 2014, 135, 12892; *J. Phys. Chem. C*, 2015, 119, 10995. [2] *J. Am. Chem. Soc.*, 2013, *135*, 16078 (JACS spotlights)

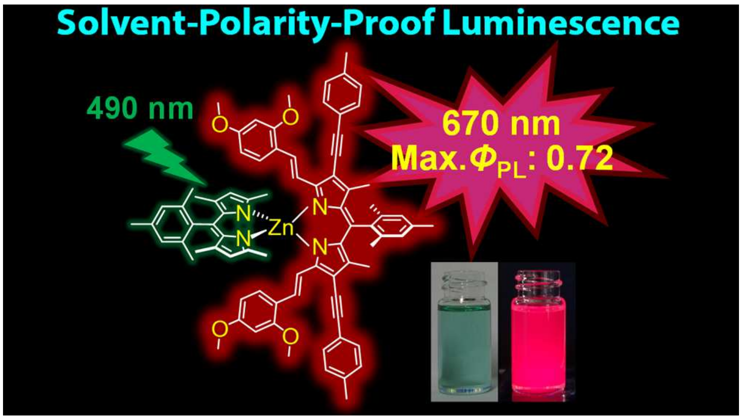
Key Words: Gold cluster, optical response, absorption and photoluminescence, chromism behaviors. **Correspondence:** konishi@ees.hokudai.ac.jp

O18A - Dissymmetric Bis(dipyrrinato)zinc(II) Complexes: Rich Variety and Bright Red to Near-Infrared Luminescence with a Large Pseudo-Stokes Shift.

Ryota Sakamoto[1,2]
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
JST-PRESTO, 4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan

Abstract

Bis(dipyrrinato)metal(II) and tris(dipyrrinato)metal(III) complexes have been regarded as much less useful luminophores than their boron difluoride counterparts (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes, BODIPYs), especially in polar solvent. We proposed previously that dissymmetry in such metal complexes (i.e., two different dipyrrinato ligands in one molecule) improves their fluorescence quantum efficiencies. In this work, we demonstrate the universality and utility of our methodology by synthesizing eight new dissymmetric bis(dipyrrinato)zinc(II) complexes and comparing them with corresponding symmetric complexes. Single-crystal X-ray diffraction analysis, ^{1}H and ^{13}C NMR spectroscopy, and high-resolution mass spectrometry confirm the retention of dissymmetry in both solution and solid states. The dissymmetric complexes all show greater photoluminescence (PL) quantum yields (ϕ_{PL}) than the corresponding symmetric complexes, allowing red to near-infrared emissions with large pseudo-Stokes shifts. The best performance achieves a maximum PL wavelength of 671 nm, a pseudo-Stokes shift of 5400 cm^{-1}, and ϕ_{PL} of 0.62–0.72 in toluene (dielectric constant ε_s = 2.4), dichloromethane (ε_s = 9.1), acetone (ε_s = 21.4), and ethanol (ε_s = 24.3). The large pseudo-Stokes shift is distinctive considering BODIPYs with small Stokes shifts (~500 cm^{-1}), and the ϕ_{PL} values are higher than or comparable to those of BODIPYs fluorescing at similar wavelengths. Electrochemistry and density functional theory calculations illustrate that frontier orbital ordering in the dissymmetric complexes meets the condition for efficient PL proposed in our theory.



Key Words: dipyrrin, luminescence, zinc, metal complex

Correspondence: sakamoto@chem.s.u-tokyo.ac.jp

O19A - Protonable diazine chromophores for white light emission.

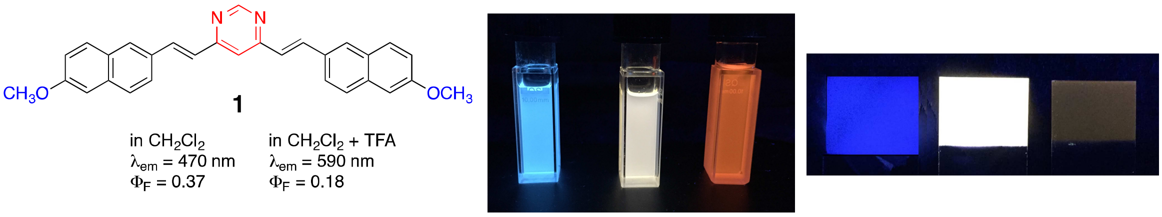
Sylvain Achelle,[1,2] Julián Rodríguez-López,[2] Françoise Robin-le Guen,[1]
Institut des Sciences Chimiques de Rennes UMR CNRS 6226, IUT de Lannion Rue E. Branly BP 30219 F22302 Lannion Cedex, France
Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain.

Abstract

In the context of the reduction of energy consumption, and taking into account that lighting accounts for ~20% of energy consumption worldwide, there is a great interest in research into new light emitting devices, particularly Light Emitting Diodes (LED), that consume less energy. White Organic LEDs (WOLEDs), first reported by Kido,[1] can now outperform incandescent light bulbs and even fluorescent tubes in terms of luminous efficiency. A good white-light emitter should be a 'warm' white, as defined by colour coordinates close to the Planckian locus around the equi-energy white point (x = 0.33, y = 0.33 in the Commission International de l'Eclairage (CIE) 1931 diagram).[2] A new strategy for WOLED fabrication has recently been proposed and this involves the use of only one emitting material that can take two forms of complementary emitting colours: it can consists of a neutral compound and its protonated form.[3]

During the past decade, we have described a large library of push-pull diazine chromophores.[4] When substituted by electron-donating fragments via π-conjugated linkers, these compounds are highly fluorescent and their emission properties are highly sensitive to external stimuli such as solvent polarity, pH, and metal cation complexation. Protonation of push-pull pyrimidine derivatives leads to a bathochromic shift in the absorption. Whereas the emission is often quenched upon protonation, methoxy-substituted pyrimidines generally exhibit a red-shifted emission.[5] However, it should be noted that methoxy-substituted compounds with high emission quantum yields require an extended π-conjugated bridge.[6] Some compounds of our library possess these requested specifications.

In this communication, we will describe the emission properties of a mixture of neutral and protonated forms of these compounds both in solution and in thin films. The controlled protonation of these blue emitting dyes led to white photoluminescence (Figure 1).[7]



1

in CH_2Cl_2
λ_{em} = 470 nm
Φ_F = 0.37

in CH_2Cl_2 + TFA
λ_{em} = 590 nm
Φ_F = 0.18

Figure 1: Change in the colour of a CH_2Cl_2 solution of 1(center) /polystyrene thin film doped with 1% of 1 (right) in the presence of various amount of trifluoroacetic acid.

Key Words: pyrimidine, diazines, π-conjugation, intramolecular charge transfer, protonation, luminescence.

Acknowledgements: SA acklowledges a short-term scholarship for invited professor from the Universidad de Castilla la Mancha / Correspondence: sylvain.achelle@univ-rennes1.fr

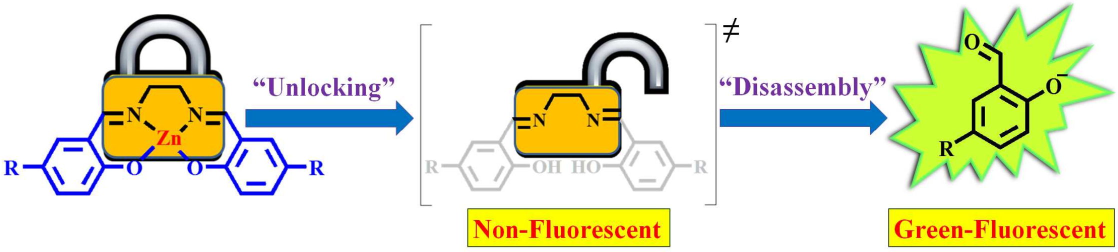
[1] J. Kido *et al Appl. Phys. Lett.* **1994**, *64*, 815. 2 S. Mukherjee *et al. Dyes Pigm.* **2014**, *110*, 2. [3] D. Liu *et al. Chem Commun.* **2013**, *49*, 10001. [4] a) S. Achelle *et al. J. Org. Chem.* **2009**, *74*, 3711. b) C. Hadad *et al. J. Org. Chem.* **2011**, *76*, 3837. c) S. Achelle *et al. J. Org. Chem.* **2014**, *79*, 7564. d) S. Achelle *et al. RSC Adv.* **2015**, *5*, 39218. [5] S. Achelle *et al. Tetrahedron Lett.* **2013**, *54*, 4491 [6] C. Denneval *et al. Dyes Pigm.* **2014**, *110*, 49 [7] S. Achelle *et al. RSC Adv.* **2015**, *5*, 107396.

O20A - Metal-Salen Complexes for Analyte Detection Following A Disassembly Strategy

Felix Zelder[1], Gilles Gasser[1], Hui Chao,[2] Huaiyi Huang[2], Namita Kumari[1]
Department of Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zürich, Switzerland. Fax: +41 44 635 6803; E-mail: felix.zelder@chem.uzh.ch, www.felix-zelder.com.
School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China.

This talk presents a stimulus-induced disassembly approach in water.[1] In particular, the selective fluorometric detection of polyphosphates in water and biological media is described.

In this method, an analyte selectively sequesters a metal ion from a metal-chelate complex. The "unlocked" ligand subsequently hydrolyses into its molecular subunits. Since the optical properties of the disassembled ligand and its ancestor are distinguishable, this reaction leads to a detectable signal.



The concept is described for the selective detection of pyrophosphate with metal-salen complexes.[1-3] Initially the intrinsic fluorescence of the salicylaldehyde signaling units is suppressed, but is unfolded during the disassembly of the molecule. Applications of this strategy for analyte detection in cells are presented.

References

[1] N. Kumari, F. Zelder, Chem. Commun., 2015, 51, 17170-17173.

[2] S. Lee, K. K. Y. Yuen, K. A. Jolliffe and J. Yoon, Chem. Soc. Rev., 2015, 44, 1749-1762.

[3] S. Bhowmik, B. N. Ghosh, V. Marjomäki, K.Rissanen, J. Am. Chem. Soc., 2014, 136, 5543–5546.

[4] N. Kumari, H. Huang, H. Chao, G. Gasser, F. Zelder, submitted.

O21A - $YFMo_2O_7$ and Related Compounds: Tuning the Excitation Range by Adjusting the Size of the Oxidomolybdate Units

Ingo Hartenbach

University of Stuttgart, Institute for Inorganic Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Abstract

Other than the direct excitation of trivalent lanthanoid cations, which has to take place at distinct wavelengths, the charge-transfer absorption of oxidomolybdate(VI) units and the subsequent energy transfer to luminescence-active cations offers a much broader excitation range. Host materials containing isolated $[MoO_4]^{2-}$ tetrahedra exhibit their excitation maximum at around 290 nm, thus within the UV range. If these units are enlarged, either by condensation via common vertices (e. g. $[Mo_2O_7]^{2-}$) or by increasing the coordination number of Mo^{6+} to five or six, the aforementioned excitation range displays a shift towards the visible area of the electromagnetic spectrum. Rare-earth metal (*RE*) oxidomolybdates(VI) are synthesized via a classical solid-state route by utilizing RE_2O_3 and MoO_3 in the desired molar ratios in fused silica ampoules, which are heated at 850 °C for six to nine days. In case of the halogenide (*X*) derivatives the addition of REX_3, in suitable molar amounts to the oxide mixture results in the respective rare-earth metal halogenide oxidomolybdates. Focusing on the yttrium compounds, rather interesting results with respect to the luminescence properties were obtained either with or without the addition of fluoride anions. Comparing $Y_2[MoO_4]_3{:}Eu^{3+}$ [1], comprising exclusively isolated $[MoO_4]^{2-}$ tetrahedra, to $Y_2[MoO_4]_2[Mo_2O_7]{:}Eu^{3+}$ [1], where one of the $[MoO_4]^{2-}$ units is substituted by a pyroanionic $[Mo_2O_7]^{2-}$ entity the maximum of the charge-transfer excitation within the oxidomolybdate(VI) units displays a shift from 290 to 315 nm. The same effect is visible by comparison of the fluoride derivatives $YF[MoO_4]{:}Eu^{3+}$ [2], again with isolated $[MoO_4]^{2-}$ units, with $YFMo_2O_7{:}Eu^{3+}$ [3]. The structure of the latter compound does not consist of isolated $[Mo_2O_7]^{2-}$ pyroanions, but of chains of distorted $[MoO_5]^{4-}$ pyramids, which are connected via common edges (*e*) and vertices (*v*) according to $^{1}_{\infty}\{[MoO^{e}_{2/2}O^{v}_{1/2}O^{t}_{2/1}]^{-}\}$ (*t* = terminal). The increase of the coordination number combined with the enhanced degree of condensation leads to an even bigger shift of the maximum within the excitation spectrum from 281 nm in $YF[MoO_4]{:}Eu^{3+}$ to 331 nm in $YFMo_2O_7{:}Eu^{3+}$.

These findings can be considered as a proof of principle that larger oxidomolybdate(VI) units cause a shift of the maximum ligand-to-metal charge transfer within these respective units towards lower energies. However, the presented results merely represent the first step in efforts to extend this theory towards other systems, e. g. the analogous oxidotungstates(VI).

References: [1] S. Laufer, S. Strobel, Th. Schleid, J. Cybinska, A.-V. Mudring, I. Hartenbach, *New. J. Chem.* 2013, *37*, 1919.

[2] Th. Schleid, S. Strobel, P. K. Dorhout, P. Nockemann, K. Binnemans, I. Hartenbach, *Inorg. Chem.* 2008, *47*, 3728.

[3] I. Hartenbach, H. A. Höppe, K. Kazmierczak, Th. Schleid, *Dalton Trans.* 2014, *43*, 14016.

Key Words: Molybdates, Rare-Earth Metals , Crystal Structure, Luminescence, Excitation

Acknowledgements: I thank Prof. Dr. Thomas Schleid for allowing me to pursue this branch of research on my own within his laboratories at the Institute for Inorganic Chemistry (University of Stuttgart, Germany). Furthermore, the luminescence spectra were measured in the groups of Prof. Dr. Henning A. Höppe (University of Augsburg, Germany), Prof. Dr. Anja-Verena Mudring (Ruhr-University Bochum, Germany; Iowa State University, Ames, IA, USA), and Prof. Dr. Koen Binnemans (Katholieke Universiteit Leuven, Belgium). **Correspondence:** see above, e-mail: hartenbach@iac.uni-stuttgart.de

O22A - Synthesis and fluorescence properties of bisboron complexes having β-iminoenolate ligands.

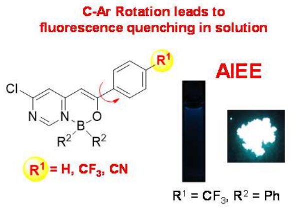
Yasuhiro Kubota, Kazumasa Funabiki, Masaki Matsui
Department of Chemistry and Biomolecular Science Faculty of Engineering, Gifu University 1-1 Yanagido, Gifu 501-1193 (Japan)

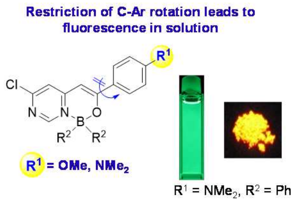
Abstract

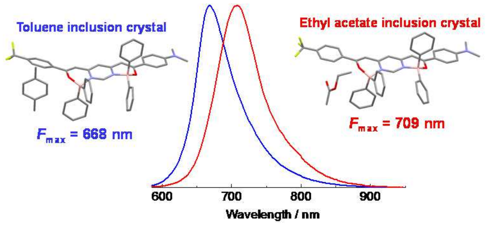
Purpose: Near infrared (NIR)–emitting organic compounds have become the focus of attention because of their potential applications in NIR light-emitting diodes, telecommunications, and bio-imaging. However, because of aggregation-caused quenching (ACQ), little has been reported on dyes showing fluorescence beyond 700 nm in the solid state. The purpose of this study is to obtain the organic dyes that show solid-state fluorescence in the NIR region.

Experimental description: Pyrimidine-based mono and bisboron complexes bearing β-iminoenolate ligands were synthesized, and their fluorescence properties were investigated both in solution and in the solid state.

Results: The non-, trifluoromethyl-, and cyano-substituted monoboron complexes showed a pronounced aggregation-induced emission enhancement (AIEE) effect. In the monoboron complexes, substitution with BPh_2 effectively enhanced the fluorescence quantum yield compared to the corresponding BF_2 complexes in the solid-state. The dimethylamino bisboron complexes exhibited positive fluorescence solvatochromism; the most dramatic red-shift of the F_{max} values (from 551 nm in *n*-hexane to 710 nm in acetonitrile) was observed for the cyano derivative. The bisboron complexes showed fluorescence in the solid state (F_{max}: 578–706 nm and Φ_f: 0.06–0.27). The trifluoromethyl derivative formed clathrate compounds upon recrystallization. The toluene-inclusion crystal (F_{max}: 668 nm and Φ_f: 0.16) exhibited a blue-shifted F_{max} and higher Φ_f compared to those of the original trifluoromethyl derivative (F_{max}: 694 nm and Φ_f: 0.08) in the solid state. On the other hand, the F_{max} (709 nm) and Φ_f (0.04) values of the ethyl acetate–inclusion crystal were red-shifted and lower, respectively.







Conclusions: The trifluoromethyl-substituted bisboron complex formed toluene-inclusion and ethyl acetate–inclusion crystals that showed fluorescence at 668 and 709 nm, respectively, in the crystalline state.

Key Words: Fluorescence · boron complex · solvatochromism · Near infrared dye · Aggregation induced emission enhancement

References: (1) Y. Kubota, K. Kasatani, T. Niwa, H. Sato, K. Funabiki, M. Matsui, *Chem. Eur. J.* 22, 1816–1824 (2016); (2) Y. Kubota, K. Kasatani, H. Takai, K. Funabiki, M. Matsui, *Dalton Trans.* 44, 3326−3341 (2015). **Correspondence:** E-mail: kubota@gifu-u.ac.jp

O23A - Novel light-emitting materials based on complexes of *d*- and *f*-elements with pyrazole substituted 1.3-diketones.

Ilya Taydakov[1,2], Rasim Saifutjarov[1], Andrew Khomyakov[1], Roman Avetisov[1], Igor Avetissov[1]

D. Mendeleyev University of Chemical Technology of Russia. Miusskaya sq. 9, 125047, Moscow, Russian Federation.

P.N. Lebedev Institute of Physics of Russian Academy of Sciences, Department of Luminescence, Leninskiy pr-t, 53,119991, Moscow, Russian Federation.

Abstract

Purpose: Recently we have developed a new class of β-diketonate ligands bearing pyrazole moiety. Some of these compounds are promising candidates for efficient phosphors like neutral ternary or anionic quaternary lanthanide complexes and cyclometallated Pt(II) and Ir(III) complexes with ancillary ligands based on the above compounds.

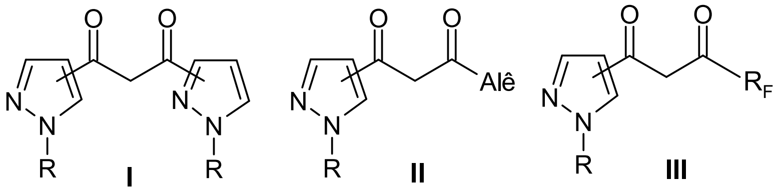


Figure 1. Structural types of ligands.

Results: New synthetic approaches, luminescent properties and structural peculiarities of novel complexes will be discussed. The study of OLEDs made using novel complexes as an emissive layer materials demonstrated that some of the produced complexes have been very efficient comparing to the known phosphors base on these metals.

Conclusions: New complexes, obtained by methodology, described below, can be promising candidates for various type of luminescent applications, namely optoelectronics, functional inks for ink-jet printing, luminescent markers and other.

Key Words: Luminescence, complexes, lanthanides, platinum group metals, pyrazole, 1.3-diketones

Acknowledgements: The research was partially financially supported by Russian Science Foundation grant N 14-13-01074.

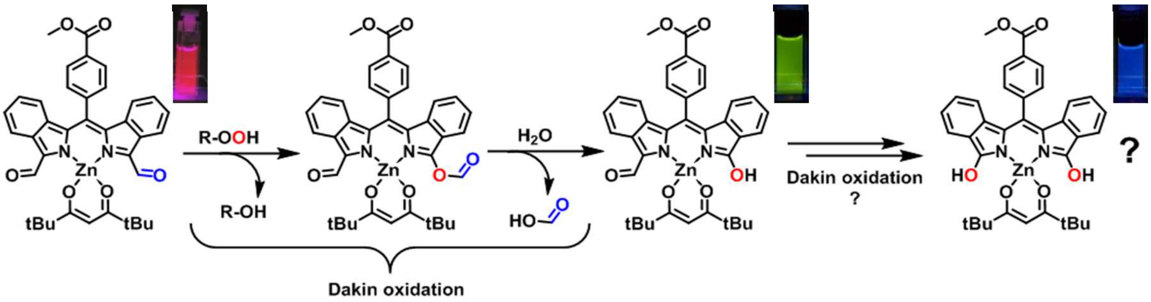
Correspondence: P.N. Lebedev Institute of Physics of Russian Academy of Sciences, Department of Luminescence, Leninskiy pr-t, 53,119991, Moscow, Russian Federation. E-mail: taidakov@gmail.com

O24A - Shining light on benzodipyrrins: from NIR-emissive complexes to hydroperoxide sensing and "dial-a-color" fluorescence

Luca Ravotto[1], Dr. Tatiana Esipova[2], Dr. Massimo Baroncini[1], Dr. Giacomo Bergamini[1],
Prof. Paola Ceroni[1], Prof. Sergei Vinogradov[2].
Department of Chemistry "G.Ciamician", University of Bologna, 40126, Bologna (Italy).
Department of Biochemistry and Biophysics, University of Pennsylvania, Philadelphia, Pennsylvania, 19104 (USA).

Abstract

Benzodipyrrins, the benzofused analogues of dipyrrins, are a strongly colored class of molecules, recently made much more accessible through an easy and versatile synthetic strategy[1]. As ligands, they readily form stable complexes with a variety of metal ions. Some of these complexes, like the Zn^{2+} ones, have already been identified as strongly fluorescent in preliminary studies[2]. However, benzodipyrrins and their metal complexes remain a still largely unexplored class of compounds. To address this issue, we synthesized and spectroscopically investigated a family of benzodipyrrins with different carbonyl substituents, focusing on the tuning of the photophysical properties.



During the investigation we discovered that one of the complexes, containing formyl groups, undergoes an unexpected reaction in THF, associated with a change of the emission color of the solution from red to green to blue. A combined spectroscopic and synthetic study allowed to elucidate the mechanism, which involves hydroperoxide species formed upon reaction of the solvent with oxygen and leads to the formation of at least one new class of fluorescent complexes. Interestingly, the reaction can be induced and controlled by UV light irradiation of the solvent, constituting an unusual way to perform it and allowing the precise control of the emission color within an RGB scheme (with the possibility to generate white light emission). Moreover, the ratiometric fluorescent response of the system may lead, upon optimization of the reaction conditions, to sensing applications in the field of food quality analysis and explosives detection.

Key Words: Benzodipyrrins, Light Induced Reactions, Multicolor Fluorescence, Hydroperoxide Sensing.

Acknowledgements: ERC Starting Grant project "PhotoSi" for funding this project.

Correspondence: Gruppo di Fotochimica, Dipartimento di Chimica "G.Ciamician", Università di Bologna, Via Selmi 2, 40126, Bologna (Italy). E-mail: luca.ravotto2@unibo.it

---

[1] M. A. Filatov, A. V. Cheprakov, I. P. Beletskaya, *Eur. J. Org. Chem*. **2007**, *21*, 3468; M. A. Filatov, A. Y. Lebedev, S. A. Vinogradov, A. V. Cheprakov, *J. Org. Chem.* **2008**, *73*, 4175.

[2] M. A. Filatov, A. Y. Lebedev, S. N. Mukhin, S. A. Vinogradov, A. V. Cheprakov, *J. Am. Chem. Soc.* **2010**, *132*, 9552.

O25A - Phosphorus/nitrogen dual-doped carbon dot sensor for recognition of chromium(VI) and ascorbic acid.

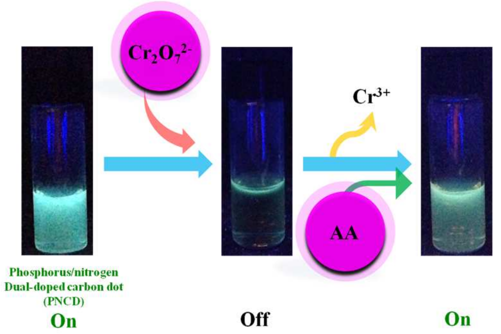
Xiaojuan Gong, Yan Zhang, Chuan Dong, Shaomin Shuang*
Institution of Environmental Science, Department of Chemistry, Shanxi University,
Taiyuan 030006, P. R. China.

Abstract

Purpose: Chromium(VI) [Cr(VI)] is considered as a severe environmental pollutant, due to its highly toxic and carcinogenic properties. Ascrobic acid (AA), a water-soluble vitamin C, is an antiooxidant in human diet, pharmaceutical formulation, and cosmetic application. Therefore, low cost, highly sensitive sensors for the determination of Cr(VI) and AA are highly demand. Carbon dots (CDs) possess a series of merits and can serve as a high-efficiency fluorescent sensor for determination of Cr(VI) and AA.

Experimental description: Phosphorus/nitrogen dual-doped carbon dots (PNCDs) were conveniently synthesized by mixing glucose, 1,2-ethylenediamine, and concentrated phosphoric acid and systematacially characterized by FTIR, XPS, TEM, UV-vis absorption, photoluminescence, fluorescence lifetime, et al. The as-prepared PNCDs were used as sensor for the recognition of Cr(VI) and AA by a significant fluorescence quenching and recovery, respectively. PNCDs were used to monitor Cr(VI) and AA in SiHa cells.

Results: We have demonstrated the rationale of a simple, time-saving, and economical "on-off-on" fluorescent method for detection of Cr(VI) and AA using PNCDs as a fluorescent sensor based on the fluorescence resonance energy transfer (FRET). The linear range is 0.1-30 μmol·L^{-1} Cr(VI) and 5-200 μmol·L^{-1} AA with the detection limit 20 nmol·L^{-1} Cr(VI) and 0.45 μmol·L^{-1} AA, respectively. To the best of our knowledge, this is the first demonstration of a fluorescent sensor for Cr(VI) and AA based on the FRET. Furthermore, PNCDs could be utilized as a reagent capable of detecting Cr(VI) and AA in biosystem.



Conclusions: In summary, we have demonstrated the rationale of a simple, time-saving, and economical on-off-on fluorescent method for detection of Cr(VI) and AA using PNCDs as a fluorescent sensor based on the FRET. Combining its simple and fast synthetic method, it is anticipated that PNCDs could have potential applications in biological labeling, disease diagnosis, biosensing, biomedical, and biological fields.

Key Words: phosphorus/nitrogen dual-doped, carbon dot sensor, chromium(VI), ascorbic acid, FRET

Acknowledgements: Financial supports from National Natural Science Foundation of China (21575084 and 21475080) and Graduate student education innovation project (2016BY005).

Correspondence: Address: Institution of Environmental Science, and Department of Chemistry, Shanxi University, Taiyuan 030006, P. R. China. Email: S. Shuang (smshuang@sxu.edu.cn)

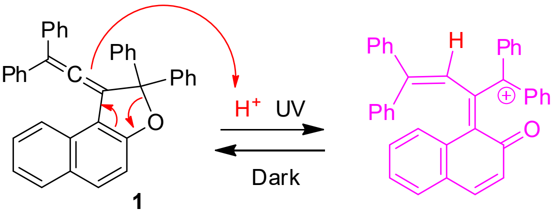
O26A - Photochromism of vinylidene-naphthofurans

Paulo Coelho[1], Céu Sousa[1], Jerome Berthet[2], Stephanie Delbaere[2]
Centro de química – vila Real. Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal
Université Lille Nord de France, CNRS UMR 8516, UDSL, Faculté des Sciences Pharmaceutiques et Biologiques, F-59006, Lille, France.

Abstract

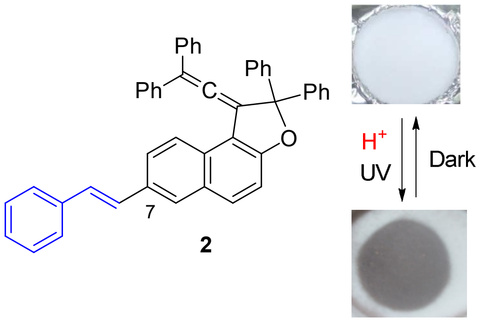
Purpose: Vinylidene-naphthofurans 1 are a new class of photochromic compounds with some special proprieties: they are uncoloured, are activated by sunlight when dispersed in an acidified media or methanolic solution, in few seconds, to afford coloured species with a broad visible absorption which return to the uncoloured state after a few minutes in the dark. In this work we describe new NMR results that clarify the mechanism behind this phenomena and we depict the synthesis of a new uncoloured vinylidene-naphthofuran derivative, with an extended conjugation, that affords a grey colouration under sunlight.

Experimental description:



1
Uncoloured

Violet



2

Results: NMR analysis of UV irradiated solutions of vinylidene-naphthofurans in THF-D8 + MeOD + TFA shows that the mechanism of the photochromic reaction involves the addition of one proton of the media to the allene function, promoted by the UV light, with overture of the dihydrofuran ring, affording a coloured conjugated tertiary carbocation that is unstable and returns thermally, in the dark, to the closed uncoloured state. The solvent, methanol, plays an important role in the reaction.

The extension of the conjugation of vinylidene-naphthofurans by introduction of a styryl group in the 7-position allows to obtain the uncoloured compound 2 that affords a grey photoproduct under sunlight with a lifetime of 2 min at room temperature.

Conclusions: The mechanism behind the photochromism of vinylidene-naphthofurans involves an acid addition to the allene function, promoted by the UV light, with formation of a conjugated tertiary carbocation that returns thermally, in the dark, to the uncoloured state. The introduction of a styryl group in the naphthalene core provides a photochromic compound that switches between the uncolored and grey states being appropriate for use in photochromic ophthalmic lenses.

Key Words: UV light, Naphthofuran, colour change, photochromism, ring-opening, thermal stability, photoswitches

Acknowledgements: FCT, POCI, COMPETE and FEDER through project PTDC/QEQ-QOR/0615/2014 **Correspondence:** pcoelho@utad.pt

O27A - Control over the blue-to-red color transition of polydiacetylene assemblies upon UV light irradiation: Effects of monomer structures, polymeric and cationic additives

Nipaphat Charoenthai[1*], Chanita Khanantong[1], Chittima Kamrak[1], Rungarune Saymung[1], Rakchart Traiphol[1,2*]

Department of Chemistry and Research Center for Academic Excellence in Applied Physics, Faculty of Science, Naresuan University, Phisanulok 65000, Thailand

Materials Science and Engineering Program, Faculty of Science, Mahidol University, Bangkok 10400,Thailand

Abstract

This research seeks versatile approaches for controlling the color-transition behaviors of polydiacetylene (PDA) assemblies upon exposure to UV light irradiation. It is known that this class of materials exhibits blue-to-red color transition during prolonged UV light irradiation allowing the utilization in sensing technology. In this study, we focuses on the effects of monomer structures, polymeric and cationic additives on the photopolymerization process of PDA assemblies in aqueous suspension. The structure of 8 diacetylene (DA) monomers, constituting a carboxylic head group, are varied by systematically decreasing the alkyl chain length. The initial polymerization process of these PDA assemblies initiated by UV light irradiation results in a blue phase. The increase of photoirradiation time causes the blue-to-red color transition. We have found that the shortening of DA alkyl tail causes the blue-to-red color transition to take place at different photopolymerization time. In some systems, PDAs with extended conjugation length also form prior to the blue-to-red color transition. When the polymeric additives, polyacrylic acid(PAA), poly(styrene sulfonic acid)(PSS) and poly(vinyl alcohol)(PVA) are present in the systems, the polymerization rate of PDA assemblies systematically increases. This result suggests that the polymeric additives promote the molecular arrangement of PDA monomers. The comparison of PAA, PSS and PVA systems detects the difference of photopolymerization rate. This discrepancy is attributed to the difference of the head group of polymeric additives. The change of PAA molecular weight (MW) affects the photopolymerization process. The system of PDA/PAA with lowest MW exhibits the lowest polymerization rate. We also observe that the blue-to-red color transition of these systems takes place at different photopolymerization time. The use of cationic ions, Zn^{2+}, Cd^{2+}, Cu^{2+}, as additives induces the blue-to-red color transition at different photopolymerizatime as well. Our results could be utilized for the development of UV light sensing materials.

Key Words: polymeric additives, photopolymerization process, polydiacetylene assemblies, UV light sensor, cationic additives

Acknowledgements: Faculty of Science, Naresuan University

Correspondence: nipaphatc@nu.ac.th, rakchart.tra@mahidol.ac.th

O28A - Photoluminescence Chalcogen Clusters Confined in Sodalite Composites

Andreia Ruivo[1,2], Eduardo Coutino-Gonzalez[3], Miguel Santos,[1] Fernando Pina,[1] Johan Hofkens,[3] César A.T. Laia[1]

LAQV-REQUIMTE, Chemistry Department, Faculty of Science and Technology,
Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal.
Research Unit VICARTE, Vidro e Cerâmica para as Artes, Faculty of Science and
Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal.
Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven,
Celestijnenlaan 200F, 3001 Leuven, Belgium.

Abstract

Active lightning and/or chromic systems have an important role in our daily life. These devices either require organic compounds that are frequently prone to degradation or inorganic combinations that usually involve toxic and/or expensive raw materials (e.g. rare earths, indium or ruthenium). The production of stable, cost effective inorganic photoluminescent materials based on the confinement of clusters in porous materials could represent an affordable alternative. Sodalite minerals ($Na_8[SiAlO_4]_6[Cl,S]_2$), for example, can give rise to photoluminescent materials due to the existence of entrapped S_2^- clusters. These sodalite minerals, with photoluminescent properties, are known for a long time, but there are few studies dealing with the systematic synthesis of such materials. [1]

In this work the initial studies were focused on the development of photoluminescent sodalites $Na_8[SiAlO_4]_6S_xCl_{2-2x}$ with variable S and Cl molar fractions, by mixing inexpensive inorganic raw materials such as Na_2SO_4, NaCl and different zeolites, followed by a sinterization process of 1h at 900 °C, under a reducing atmosphere (5%H_2/95% Ar). An emission band at 650 nm for samples with low x values (with a lower sulphur content) is observed, fully consistent with S_2^- clusters as light emitting centres. When the sulphur concentration increases a conversion to other emissive centers at 780 nm is detected, attributed to polysulfide clusters. High photoluminescence external quantum efficiencies (EQE) are obtained for $x = 0.2$ (53%), however a quenching phenomenon is observed with increasing x, probably due to the suppression of the S_2^- excited state by the polysulfide clusters. These sodalites also exhibit extremely high Stokes-shifts (*ca.* 250 nm across the visible region) making them promising candidates for solid state lightning devices. Besides sulphur, other chalcogens such as selenium and tellurium were employed on the synthesis of sodalite analogues with distinct photoluminescent properties using the same synthetic strategy.

[1] A. Sidike, A. Sawuit, X. Wang, H. Zhu, S. Kobayashi and I. Kusachi, *Phys. Chem. Miner.* 2007, 34, 477.

Key Words: Photoluminescent materials, zeolites, sodalite, sulphur, chalcogen clusters

Acknowledgements: EC (project NMP4-SL2012 SACS GA-310651 under FP7-NMP-2012-SMALL-6) and Portuguese FCT-MCTES (UID/EAT/00729/2013 and UID/QUI/50006/2013) co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER – 007265) are acknowledged for financial support.

Correspondence: Andreia Ruivo, Faculty of Science and Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal. *a.ruivo@campus.fct.unl.pt*

O29A - Lighting-up breast cancer mRNA markers towards personalized medicine

Bilha Fischer,*a Marina Kovaliov,a Lital Zilberstein,a Meirav Segal,a
Eylon Yavin,b and Yaron Shav-Talc
a *Group of B. Fischer, Department of Chemistry, Bar-Ilan University,* b *School of Pharmacy, Hebrew University, Jerusalem,* c Life science faculty, *Bar-Ilan University*
e-mail: bilha.fischer@biu.ac.il

Abstract

Breast cancer at the molecular level is a heterogeneous disease with distinct entities which have distinct clinical features, drug responsiveness and prognoses. Expression levels for breast cancer biomarkers are currently assessed by immunohistochemical staining, and sometimes with fluorescent in-situ hybridization methodology. Limitations of these methods including analysis of fixed cells and possible loss of information, and limited precision, reproducibility and reliability prompted us to develop novel fluorescent probes to allow the sensitive detection of mRNA breast cancer markers and the diagnosis of the sub-type of breast cancer of patients. Specifically, we devised two types of probes: NIF (Nucleoside with Intrinsic Fluorescence) and NIC (Nucleoside interCalator) analogues incorporated in oligonucleotide probes targeting cyclin D1 mRNA breast cancer marker. The NIF analogues included a minimal extension of the natural chromophore of the nucleobase by a substituted cinnamyl group at a position not involved in base-pairing. This approach resulted in several highly fluorescent analogues which were >3000-fold more emissive than the natural nucleosides (Φ up to 0.81) and emitted at up to 170 nm red-shifted wavelength. These NIF-analogues were incorporated in DNA duplexes, where one of the strands was complementary to part of target cyclin D1 mRNA. These probes were relatively dark, and upon recognition of target mRNA, they underwent de-hybridization followed by hybridization with the target and release of the fluorescent ss-probe. The fluorescent signal indicated the presence of target mRNA. The second approach we applied, the NIC-approach, was based on a single strand hosting a dU bearing thiazole orange intercalator on the end of a flexible spacer (dU_{TO}). The NIC-oligonucleotide was complementary to a part of target mRNA and upon recognition of the target, the formed duplex lights up due to intercalation of TO. We next used NIF and NIC probes to identify cyclin D1 mRNA in total RNA extracts from cancerous human cells vs. WT. Indeed, these probes identified specifically and sensitively the target. Furthermore NIC-probe allowed the detection of a small concentration of cyclin D1 mRNA, in total RNA extract (250 ng/μL vs. 1842 ng/μL, for NIF-probe), and emitted at 540 vs. 480 nm for NIF-probe. Therefore NIC probes seem to be more promising than NIC probes, and are potentially useful for breast cancer diagnosis.

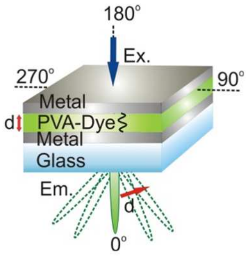
O30A - Fluorescence with plasmonic and photonic substrates.

Sharmistha Dutta Choudhury[1], Joseph R. Lakowicz[2]
Radiation & Photochemistry Division. Bhabha Atomic Research Centre. Mumbai. 400085. India.
Center for Fluorescence Spectroscopy. University of Maryland Baltimore. Baltimore. 21201. USA.

Abstract

Purpose: Fluorescence technology pervades all areas of chemical and biological sciences. Although present day fluorescence technology is highly evolved, there are some natural limitations of traditional fluorescence methods. In recent years, it is being realized that fluorescence can be enriched in many ways by harnessing the power of plasmonic/photonic structures that have remarkable ability to mold the flow of optical energy. This work describes our efforts in tailoring fluorescence with different kinds of planar metallic, dielectric and hybrid structures. Our studies reveal that these substrates modify the optical environment surrounding the fluorophores to provide selective control over the direction, polarization and wavelength-dispersion of the emitted light. Such features are extremely desirable for many applications like imaging, single molecule spectroscopy and optical communication.

Experimental description: Thin metal films (Au, Ag, Al) were deposited on glass slides by thermal vapor deposition, and the dielectric layer containing the fluorescent dyes was obtained by spin coating. Samples were illuminated in reverse Kretschmann configuration and the fluorescence was collected using an optical fiber. Both the detector and the sample were placed on a rotation stage to enable excitation and detection at different angles.



Tunable emission with metal-dielectric substrates

Results: Our studies show that the composition of the metal layers, the location of the fluorophore in the plasmonic/photonic substrates and the dielectric thickness are important parameters that can be chosen to tune the color of the emission wavelength, the angle of observation and the angular divergence of the emitted light. For example, the emission from fluorophores present in a thin dielectric layer above a metal film (metal-dielectric substrate) can couple with surface-plasmon oscillations, to provide directional p-polarized emission. Interestingly, when the thickness of the dielectric layer is increased, the emission can couple to optical modes other than surface-plasmons to provide additional spatial emission patterns. This remarkable phenomenon has been exploited by us for inducing selective polarization properties to the otherwise unpolarized luminescence of lanthanide ions. Further, the interaction of fluorescence with Fabry-Pérot-like modes in metal-dielectric-metal substrates leads to beaming emission normal to the substrate surface. Fluorophores also interact with Bloch surface waves in 1-dimensional photonic crystals, giving rise to sharply directional Bloch surface wave-coupled emission.

Conclusions: The near-field coupling of fluorescence with spectrally overlapping optical modes in plasmonic and photonic structures provides a rational approach to collect, manipulate and direct emission from fluorophores without bulky optical components. The cost-effective and simple fabrication of the planar substrates makes them suitable for applications in several areas of technological significance. We anticipate that the ability to control the flow of emitted light in the nanoscale will lead to the development of a new generation of fluorescence-based assays, instrumentation, portable diagnostics and emissive devices.

Key Words: surface-plasmon, optical mode, near-field, metal-dielectric, coupled fluorescence
Acknowledgements: S.D.C acknowledges support from SERB Women Excellence Award Grant, SB/WEA-010/2013. Correspondence: **Email:** sharmidc@barc.gov.in

O 1B – Fluorescent chemosensors based on sulfur functional groups.

Nathaniel S. Finney,[1,2] Rahul a. Kathayat,[1] Mireille Vonlanthen,[1] Lijun Yang,[2] Kim K. Baldridge[1,2]
Department of Chemistry, University of Zurich, Winterthurerstrasse 190, Zurich, Switzerland, CH-8057
School of Pharmaceutical Science and Technology, Tianjin University, 92 Weijin Road, Nankai District, Tianjin, 300072, China.

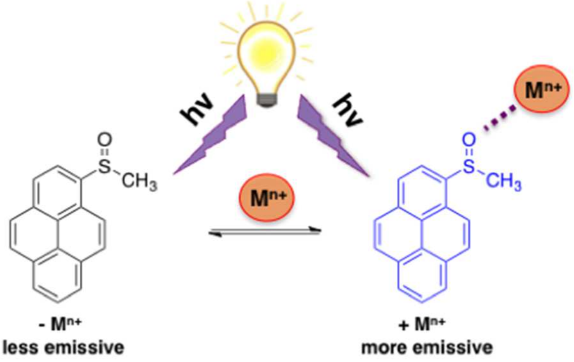
Abstract

Purpose: The primary objective of our research has been to develop new fluorescent chemosensor motifs that do not rely on nitrogen atom coordination to report metal ion coordination or oxidation events. This will allow fluorescence-based detection of new metal binding events and the detection of, e.g., oxidizing explosives or reactive oxygen species (ROS).

Experimental description: We have found that sulfoxides and thioureas are excellent reporting functional groups for chemosensor development. Thioureas can quench fluorescence via photoinduced electron transfer. Sulfoxides quench fluorescence by more complex mechanisms, which we have studied in detail.

Results: Both thioureas and sulfoxides respond to metal ion coordination and oxidation. Thioureas can be used used to image Hg^{2+} in live human cells, and also hold promise for detecting H_2O_2 and HO•. Sulfoxides can be used to detect peroxide-based explosive, as well as report the presence of metal ions in queous solution. They can also report the presence of $^1O_2$.

Conclusions: Sulfur based functional groups have proven to be useful in the development of fluorescent probes for multiple purposes. They have behavior that is distinct from the classical nitrogen-based fluorescent probe designs. We have shown some of the initial advantages of this approach, and anticipate further beneficial developments.



Key Words: fluorescent probes; sulfur functional groups; mechanism; metal ion detection; ocidation response

Acknowledgements: We are grateful to numerous funding agencies, including the University of Zurich and the University of Tianjin.

Correspondence: nfinney@tju.edu.cn

O 2B – Development of an emissive layer for temperature measurement of materials under shock-loading.

Camille Chauvin[1]., Jacques Petit,[1]Frédéric Sinatti,[1]
CEA, DAM, GRAMAT, F-46500 Gramat, France.

Abstract

Purpose: Reliable low temperature measurement of a material under dynamic loadings is of fundamental importance to understand its behavior, to investigate its phase-diagram and to differentiate its equation of state. In this work, diamond-like carbon coatings obtained by different deposition processes have been developed and applied on different metallic and ceramic materials such as copper, tin and lithium fluoride in order to improve the temperature measurement by high-speed multi-wavelength infrared optical pyrometer of material under shock-loading. This coating is made of different layers of diamond-like carbon films from 100 to 1500 nm obtained by two physical vapor deposition processes: sputtering and electron beam physical vapor deposition from carbon targets. In order to obtain a satisfying adhesion of the emissive layer, a multiple layer coating has been necessary.

Thanks to this DLC coating, the emissivity of the surface has been artificially increased up to an apparent value of approximately 0.8 reducing uncertainties of the true temperature due to the lack of knowledge of the dynamic emissivity of the material under shock loading.

Experimental description: In order to investigate the influence of this DLC coating, different configurations of plate impact experiments were performed: the temperature measurements with pyrometer of tin and copper under shock wave compression (from 8 to 15 GPa) with or without DLC coating are compared. We have verified that the detected radiance is then amplified with the DLC coating, the range of dynamic emissivity is restricted and so the temperature becomes accurate. Thanks to the Fourier's law, DLC coating surface temperature and material temperature can be linked depending on the thermal properties of each material: the thermal conductivity of DLC coating must be enough important and its thickness enough thin to enable an efficient heat exchange and to obtain the temperature of the emissive layer as close as possible to that of the material.

Results: The use of this DLC emissive layer gives promising results: the thermal-mechanical properties of this layer are determined, the emissivity and opacity are verified. Thanks to a 1-D lagrangian code Unidim including thermal conduction modelling under shock-wave compression, experiments can be simulated to obtain material temperature

Conclusions: Promising results at material and lithium fluoride interface below 15 GPa are obtained with an emissive layer: the mechanical, thermal and optical properties of this layer are satisfying to reduce uncertainties of the interface temperature and so to deduce the temperature of the material to be compared with the calculations

Key Words: temperature measurement, pyrometry, shock loading, tin, copper

Correspondence: Camille Chauvin, *CEA, DAM, GRAMAT, F-46500 Gramat, France,* *camille.chauvn@cea.fr*

O 3B - Solid-state fluorescence of dyes.

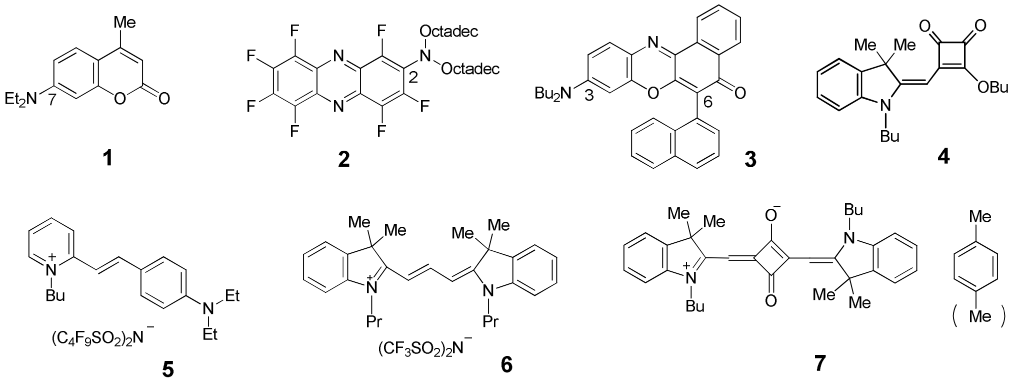
Masaki Matsui and Yasuhiro Kubota
Department of Chemistry and Biomolecular Science. Faculty of Engineering. Gifu University. Yanagido. Gifu. 501-1193. Japan.

Abstract

Inhibition of intermolecular hydrogen bond and consequent π–π stacking was very effective to obtain solid-state fluorescent coumarins, 2-(dialkylamino)perfluorophenazines, naphthooxazines, semi-squaryliums, styryls, and cyanines. Toluene-included squarylium dye could show fluorescence in the crystalline form.

Results: Coumarin 1 showed its fluorescence maximum (F_{max}) at 432 nm with the fluorescence quantum yield (Φ_f) of 0.29 in the crystalline form due to isolated monomer packing. 2-(Dioctadecylamino)perfluorophenazine 2 exhibited F_{max} at 581 nm with the Φ_f of 0.29 in the solid state due to strong alkyl-alkyl interactions in the crystalline form. 3-Dibutylamino-6-(1-naphthyl)naphthooxazine dye 3 could show F_{max} at 711 nm with the Φ_f of 0.04 in the crystalline form due to isolated dimer packing. Semi-squarylium dye 4 could show its F_{max} at 536 and 563 nm with the Φ_f of 0.21 in the crystalline form due to isolated dimer packing. In this compound, the fluorescence comes from the vibration level and AIEE were observed.

Styryl dye 5 was fluorescent in the solid state showing its F_{max} at 652 nm with the Φ_f of 0.15 due to isolated dimer packing. Cyanine dye 6 exhibited its F_{max} at 657 nm with the Φ_f of 0.31 in the crystalline form due to isolated monomer packing. Only *N,N'*-dibutyl squarylium dye 7 could include toluene and *p*-xylene in the crystalline to exhibit fluorescence. The included toluene and xylene could inhibit the π–π-stacking of squarylium dye.



1 2 3 4 5 6 7

Figure Solid-state fluorescent dyes

Conclusions: Dyes 1–7 could exhibit fluorescence in the solid state mainly due to inhibition of consequent π-π stacking.

Keywords: dye, fluorescence, solid state, single X-ray crystallography, intermolecular interactions

Correspondence: matsuim@gifu-u.ac.jp

O 4B - Water Soluble Unsymmetrical Sulfoxanthene Dyes, and Access to a Novel Class of Broad Spectrum Dark Quenchers.

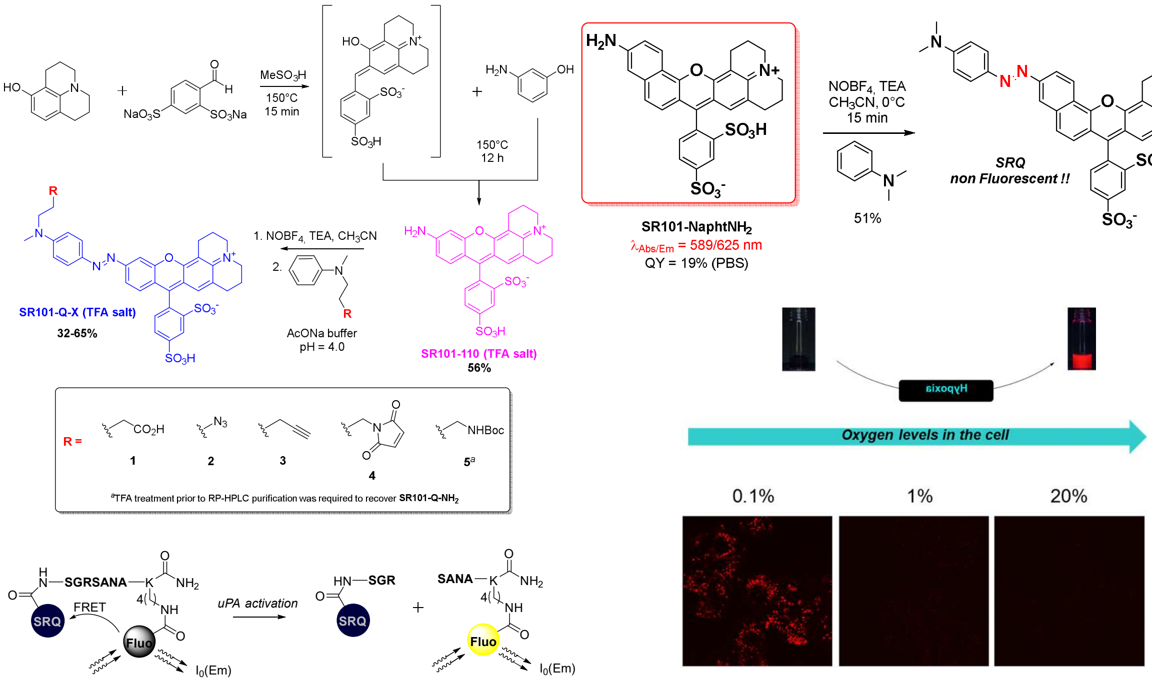
Arnaud Chevalier[1,], Anthony Romieu,[2] Pierre-Yves Renard [2]

1. *Normandie Université, COBRA UMR 6014 & FR 3038, UNIV Rouen, INSA Rouen, CNRS, IRCOF, 1, Rue Tesnières, 76821 Mont-Saint-Aignan Cedex, France.*

2. *ICMUB, UMR CNRS 6302, Université de Bourgogne 9, Avenue Alain Savary, 21078 Dijon cedex (France)*

Abstract

We developed an efficient synthesis of water soluble unsymmetrical sulforhodamine/sulforhodol fluorophores containing a single julolidine fragment. Due to their valuable spectral properties in aqueous buffers, these dyes, especially those bearing a free aniline or phenol moiety, are valuable components of fluorogenic probes for a variety of biosensing applications. As an application, a rapid access to a novel class of water-soluble dark quencher dyes was developed, using an azo-coupling reaction between a fluorescent primary arylamine derived from a sulforhodamine 101 scaffold and a tertiary aniline equipped with different bioconjugatable groups. The thus obtained nonfluorescent azo-sulforhodamine hybrids display a broad quenching range spanning the visible to NIR regions. This was demonstrated through the preparation and enzymatic activation of FRET-based fluorogenic substrates of urokinase, and as hypoxia off/ON profluorescent probes.



Key Words: Sulfoxanthene probes, FRET based proteases probes, Fluorescence quenchers, hypoxia detection

Acknowledgements: Financial support from FEDER (TRIPODE, n°33883) for the Ph. D. grant of Arnaud Chevalier, Institut Universitaire de France (IUF) and the CRUNCh program (CPER 2007-2013) are greatly acknowledged.

Correspondence: Pr Pierre-Yves Renard, Normandie Université, COBRA UMR 6014 & FR 3038, UNIV Rouen, INSA Rouen, CNRS, IRCOF, 1, Rue Tesnières, 76821 Mont-Saint-Aignan Cedex, France. Pierre-yves.renard@univ-rouen.fr.

O 5B - Photophysical properties of cycloalkyl-2,2’-bithiophenes and heterocyclic chiral ligands based on 1,2-diaminocyclohexane

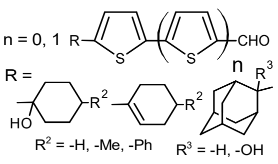
Violetta V. Meshkovaya, Alexander V. Yudashkin

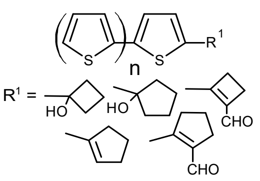
Laboratory of organic chemistry. Chemical-technological Department. Samara State Technical University. 443100. Samara. Molodogvardeyskaya street. 244. Samara. Russia.

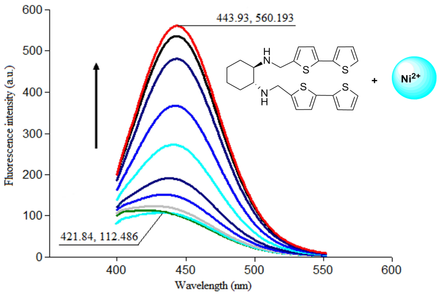
Abstract

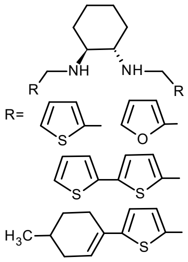
Purpose: the aim of work is to study photophysical properties of new heterocyclic compounds based on cycloalkyl-2,2’-bithiophene and novel chiral heterocyclic ligands with 1,2-diaminocyclohexane unit and their complexes with metal ions.

Experimental description: a series of novel cycloalkylbithiophenes and their derivatives were synthesized via Grignard and Vilsmeier-Haack reactions, novel chiral 1,2-diaminocyclohexane ligands were synthesized under ultrasonic irradiation. The photophysical properties such as absorption and fluorescence spectra were measured in different solvents, and relative quantum yields were measured using as internal standard quinine sulfate.









Results: Vilsmeier-Haack formylation of 2,2’-bithiophenes with alicyclic fragment C4-C5 results formation of α,β-unsaturated aldehydes whereas cycloalkenes C6 form 5’-formylbithiophenes as the main isomers. Cycloalkyl (C4-C6) 2,2'-bithiophes with electronwithdrawing groups have solvatochromic properties with abnormal Stokes’ shifts (~150 nm) and good quantum yields (~0.45) in polar protic solvents. Adamantane bulk fragment in combination with 2,2'-bithiophene significantly increase quantum yield (~0.60). An increase in the emission intensity was found for several complexes. The p-electron structure of thiophene and bithiophene containing sensors is the most active toward several metal ions and is highly selective for Ni(2+) and Cd(2+).

Conclusions: the value of bathochromic shift in absorption and emission spectra linearly increases with rise Kamlet π*-values for organic solvents according to Lippert equation. Significant bathochromic shifts for aldehydes due to the possible hydrogen-bond formation in the ethanol and diethylene glycol. Strong decrease of the fluorescence intensity is suggested to a chelation enhanced quenching effect during complex formation with Cu(2+). Possibly, a short spacer such as methylene group between the bithiophene and diaminocyclohexane may be suitable for effective energy transfer.

Key Words: organic fluorophores, bithiophene, Vilsmeier-Haack reaction, photophysical properties, chiral ligand.

Acknowledgements: this work was financially supported by the Russian Foundation for Basic Research, project 15-43-02565.

Correspondence: 443100, Russia, Samara, Molodogvardeyskaya st., 244, ayudashkin@mail.ru

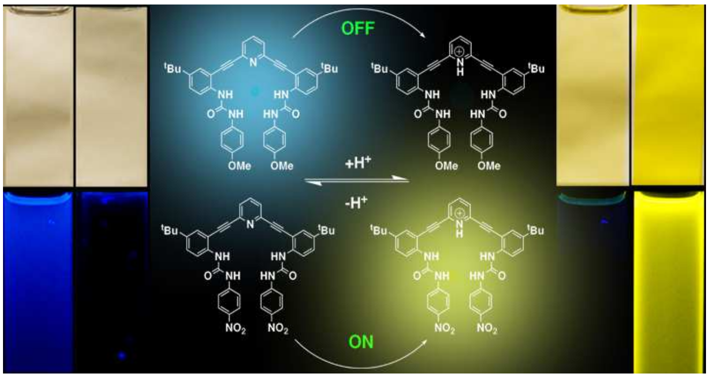
O 6B - Modular supramolecular fluorescent receptors: functional materials and applications as probes for anions.

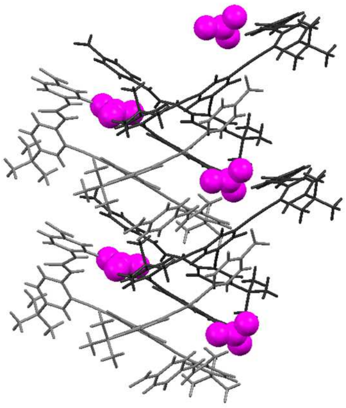
Michael M. Haley,*[1,2] Darren W. Johnson,*[1,2] Calden N. Carroll,[1,2] Jesse V. Gavette,[1,2]
Ryan J. Hansen,[1,2] Blakely W. Tresca,[1,2] Michelle M. Watt[1,2]
Department of Chemistry & Biochemistry. 1253 University of Oregon. Eugene, Oregon 97403-1253. United States.
Materials Science Institute. 1252 University of Oregon. Eugene, Oregon 97403-1252. United States.

Abstract

Purpose: Functionalized phenylacetylene scaffolds show broad applicability as rigid, linear subunits in the modular synthesis of shape-persistent supramolecular complexes. Their pi-electron conjugation and molecular planarity allow observation of the electronic perturbation upon formation of host-guest complexes through simple spectroscopic methods (e.g., absorption, emission). Facile substitution of the arene building blocks lends tunability to the host system via bite angle, cavity size or available hydrogen bonding sites, while donor-acceptor modification enables tunability in the electronic response within each receptor class.

Results: This presentation will describe the synthesis and binding studies of sulfonamide and urea receptor complexes with a series of anionic guests, and the effect of donor-acceptor modification on their emission spectra. Emphasis will be placed on utilizing these molecules as sensors for detection of environmentally relevant anions (e.g., nitrate, phosphate).





Key Words: anion-binding, hydrogen bonds, phenylacetylenes, fluorescence

Acknowledgements: This work was supported by NIH grant R01-GM087398, which also funded early stage intellectual property that was licensed by SupraSensor Technologies, a company co-founded by the principal investigators.

Correspondence: haley@uoregon.edu; dwj@uoregon.edu

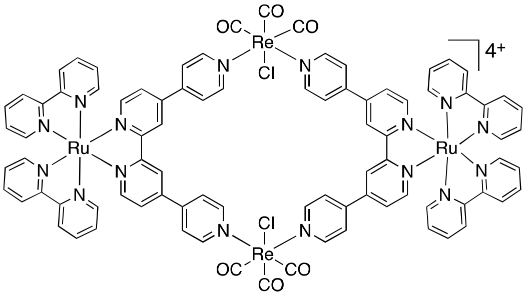
O 7B - Self-assembled metallomacrocycle as biomolecular sensors and therapeutics.

Jim A Thomas
Department of Chemistry, University of Sheffield. Brook Hill. Sheffield S3 7HF, UK.

Abstract

There is much interest in metal directed self-assembly and this has led to a huge variety of often very complex molecular architectures. Using this approach hosts, sensors for ions and molecules, and catalysts have been produced.[1] Although the interaction of such architectures with biomolecules has been investigated; much of this work focused on helicate structures. The Thomas group has previously reported on the synthesis and structure of self-assembled, kinetically inert, water-soluble metallomacrocycles, such as **1**.[2] As these water stable systems are based on inert *d*^{6}-metal ions and possess highly structured binding pockets composed of hydrophobic aromatic residues their ability to bind biomolecules such as nucleotide-based anions (eg ATP and GTP) and DNA in biologically relevant conditions have been investigated.[3]

Furthermore, since **1** incorporate polypyridyl Ru^{II} and Re^{I} moieties related to systems used in photodynamic therapy, we have also investigated its cellular internalisation and photocytotoxicity towards human cancer cells. Employing clinically relevant light doses, we find that **1** is successfully taken up by cells where it functions as a potent photosensitizer though ROS generation.[4]



1

1. ***See for example***: (a) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369–378. (b) J. A. Thomas, *Chem Soc Rev*, **2007**, *36*, 856–868. (c) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810–6918. (e) J. A. Thomas, *Dalton Trans* **2011**, *40*, 12005–12016

2. (a) P. de Wolf, S. L. Heath, J. A. Thomas, *Chem. Commun.* **2002**, 2540–2541. (b) P. de Wolf, *et al*, *Chem. Eur. J.* **2006**, *12*, 2188–2195.

3. (a) D. Ghosh, H. Ahmad, J. A Thomas, *Chem. Commun.* **2009**, 2947–2949. (b) H. Ahmad, *et al*, *Chem. Eur. J.* **2013**, *19*, 5081–5087. (c) H. Ahmad, D. Ghosh, J. A. Thomas, *Chem. Commun.* **2014**, *50*, 3859–3861.

4. M. G. Walker, *et al.*, *Chem. Eur. J.* **2016**, *22*, DOI: 10.1002/chem.201600852

Key Words: Self-assembly • singlet oxygen • ruthenium • PDT • luminescence

Acknowledgements: We are grateful for funding from EPSRC, The Royal Society, The Wellcome Trust, the EU (MC-IIF scheme), and the Malaysian Government.

Correspondence: Jim A THOMAS, University of Sheffield S3 7HF, UK (email: james.thomas@shef.ac.uk)

O 8B - Photo-responsive and photo-switchable fluorescent nanoparticles.

Marco Montalti, Giulia Battistelli, Andrea Cantelli, Matteo di Giosia, Gloria Guidetti,
Jeannette Manzi
Department of Chemistry "G. Ciamician", Via Selmi 2, 40126, Bologna (Italy)

Abstract

A very versatile approach to the design of nanosized contrast agents for bio-application exploits the incorporation of fluorescent molecules into nanoparticles (NPs). (10.1002/wnan.1351) A proper design yields fluorescent NPs with unique features such as, for example, ultra-brightness, enhanced photostability and biocompatibility (10.1039/c4cs00486h).

Local activation of specific properties of the NPs in response to an environmental, or externally applied, stimulus represents one of the most intriguing aspect of the future generations NPs for bio-application. In this context light activation (10.1039/C3CC48464E), also in combination with other stimuli, become important for selective labelling, sensing and controlled release. In fact, light offers several advantages compared to other forms of stimulation: Light beams are poorly invasive, remotely addressable and focusable with high spatio-temporal resolution. Moreover, wavelength selection permits, implicitly, multiplexed detection.

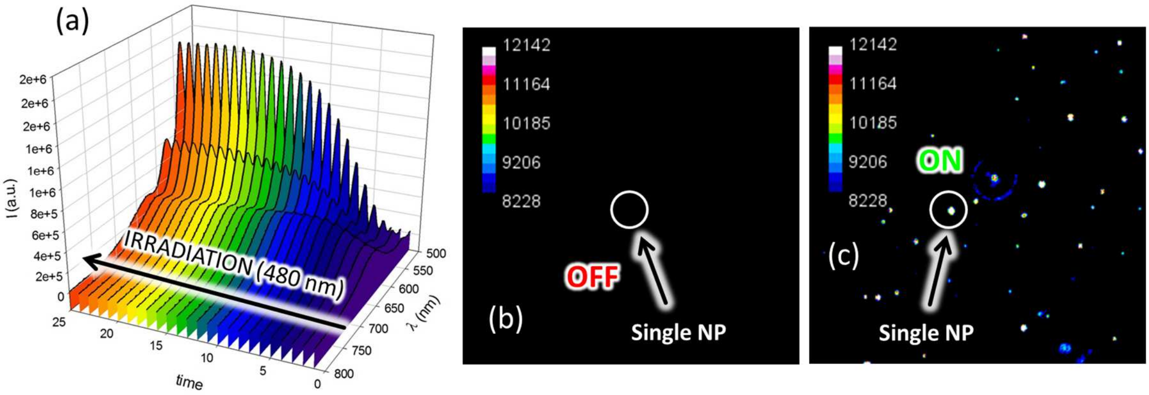


Figure 1 *(a) Changes in the fluorescence spectrum of photo-responsive NPs upon irradiation with blue light. (b) Individual NPs are not fluorescent when observed at the microscope (lateral size 440 μm). (c) Their fluorescence is individually switched-on upon blue irradiation. (c)*

Here we will present a new family of photo-responsive NPs prepared by cross-linking a fluorescent precursor hosted in micelles in water dispersion. As shown in figure 1a irradiation of the NPs with blue light causes a dramatic fluorescence enhancement which can be observed at the single NP level by fluorescence microscopy (figure 1b and 1c). The same process was observed in NIH/3T3 cells allowing us to activate selectively the fluorescence of individual cells upon controlled illumination.

Key Words: Nanoparticles, Stimuli-responsive, Photo-active, Fluorescence, Bio-imaging.

Acknowledgements: Financial support from US-ARO Grant W911NF-16-1-0324; H2020-GRAPHENE CORE1 – G.A.Nr 696656

Correspondence: marco.montalti2@unibo.it

O 9B - Photophysics, Mechanism and Applications of TADF Molecules.

Roberto Nobuyasu, Rongjuan Huang, Fernando B. Dias
Physics Department. Durham University. Durham, South Road DH1 3LE. UK.

f.m.b.dias@durham.ac.uk

Abstract

Thermally Activated Delayed Fluorescence (TADF) has emerged recently as one of the most suitable methods to harvest triplet states in metal-free organic materials for application in organic light emitting diodes (OLEDs). Numerous TADF molecules have been designed with the purpose of enhancing device efficiency, by converting non-emissive triplet states into emissive singlet states that give origin to delayed fluorescence. TADF emitters are thus able to harvest both singlets and triplet states, and allow pure fluorescent OLEDs to overpass their intrinsic limitation of 25% internal quantum efficiency (IQE), which is imposed by the 1:3 singlet triplet ratio, appearing from charge recombination. Fluorescent OLEDS with IQEs close to 100% are now routinely fabricated in the green spectral region. However, blue and red emitters still show relatively lower efficiencies, and still major challenges persist concerning the full understanding of the TADF mechanism and the stability of these materials, which need to be solved in order to fully implement TADF in OLEDs, and expand their application to other areas. TADF has been so far exploited mainly in the field of organic light emitting diodes (OLEDs), but applications in areas as sensing, and fluorescence microscopies are envisaged. In this talk, we first discuss the main concepts involved on the photophysics of TADF molecules, and then address the influence of molecular geometry and energy alignment between the singlet charge transfer state, and localized triplet states on the TADF mechanism.

Key Words: TADF; Charge Transfer, OLEDs

References:

[1]- Dias FB, Bourdakos KN, Jankus V, Moss KC, Kamtekar KT, Bhalla V, et al. Triplet harvesting with 100% efficiency by way of thermally activated delayed fluorescence in charge transfer OLED emitters. *Adv Mater.* 2013;25(27):3707–14.

[2]-Roberto S. Nobuyasu, Zhongjie Ren, Gareth C. Griffiths, Andrei S. Batsanov, Przemyslaw Data, Shouke Yan, Andrew P. Monkman, Martin R. Bryce FBD. Rational Design of TADF Polymers Using a Donor–Acceptor Monomer with Enhanced TADF Efficiency Induced by the Energy Alignment of Charge Transfer and Local Triplet Excited States. *Adv Opt Mater.* 2016;4:597.

O 10B - Dye functionalized nanofibers for fast, reversible and easy read-out colorimetric sensor materials.

K. De Clerck1, E. Schoolaert1, J. Geltmeyer1, I. Steyaert1, G. Vancoillie2, R. Hoogenboom2
Department of Textiles, Ghent University, Technologiepark 907, 9052 Ghent, Belgium
Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281 S4, 9000 Ghent, Belgium

Abstract

The development of smart colorimetric materials that sense the concentration of a specific analyte by a change in absorbance is particularly interesting, since a color change directly visible for the naked eye is obtained [1]. Color changing textiles play a prominent role among these colorimetric sensors due to their high flexibility, reusability, mechanical stability and breathability. Halochromic, i.e. pH-sensitive, textiles may be highly valuable for various applications in the biomedical field, agriculture, safety and technical textiles. Electrospun sensor materials show a great potential due to their unique properties, resulting in improved sensor sensitivity and response time.

Functionalization of these polymer nanofibres can be done by doping the electrospinning solution prior to fibre formation with pH-sensitive dyes. This technique results in easy-to-produce halochromic nanofibres [3-4]. Dye leaching, however, is a major problem. An alternative approach to reduce dye leaching is a covalent linkage of the dye to the polymer prior to electrospinning resulting in the most efficient immobilization method. Incorporation of the dye-containing polymer into a nanofibrous membrane can subsequently be achieved by blend electrospinning. Using this method robust halochromic nanofibers can be produced without the dye leaching drawbacks. [5-6].

References: P.T Mather, “Responsive materials: Soft answers for hard problems”, Nature Materials, 6 (2007), 93-94

Van der Schueren, L., Mollet, T., Ceylan, O., De Clerck, K. “The development of polyamide 6.6 nanofibres with a pH-sensitive function by electrospinning” European Polymer Journal 46 (2010) 2229-2239

Van der Schueren, L., De Meyer, T., Steyaert, I., Ceylan, O., Hemelsoet, K., Van Speybroeck, V., De Clerck, K. “Polycaprolactone and polycaprolactone/chitosan nanofibres functionalised with the pH-sensitive dye Nitrazine Yellow” Carbohydrate Polymers 91 (2013) 284-293

I. Steyaert, G. Vancoillie, R. Hoogenboom, K. De Clerck, “Dye immobilization in halochromic nanofibers through blend electrospinning of a dye-containing copolymer and polyamide-6”, Polymer Chemistry, 6 (2015) 2685-2694

E. Schoolaert, I. Steyaert, G. Vancoillie, J. Geltmeyer, K. Lava, R. Hoogenboom, K. De Clerck, “Blend electrospinning of dye-functionalized chitosan and polycaprolactone: towards biocompatible pH-sensors”, J. Mater. Chem. B, (2016), DOI:10.1039/c6tb00639f.

Correspondence: Karen.DeClerck@Ugent.be, Department of Textiles, Ghent University, Technologiepark 907, 9052 Ghent, Belgium

O11B - Selective imaging and cancer cell death via pH switchable near-infrared fluorescence and photothermal effects

Jingye Zhang, Zining Liu, Jun Qian, Xinwei Li and Cong Li*
Key Laboratory of Smart Drug Delivery, Ministry of Education, School of Pharmacy,
Fudan University, Shanghai, China.

Abstract

Purpose: Accurately locating and eradicating sporadically distributed cancer cells whilst minimizing damage to adjacent normal tissues is vital in image-guided tumor ablation.

Experimental description: Four heptamethine cyanine based theranostic probes (IR1–4) were synthesized to specifically visualize and photoablast cancer cancer at the same time.

Results: While the fluorescence quantum yields of these theranostic probes increased up to 1020-fold upon acidification from pH 7.4 to 2.4, their photothermal efficiencies decreased up to 7.1-fold concomitantly. Theoretical calculations showed that protonation of the probes increased the orbital energy gaps, which resulted in the conversion of absorbed light energy to NIR fluorescence instead of hyperthermia. IR2 with pKa_{fluo} of 4.6 not only specifically illuminated cancer cells by sensing their increased lysosomal acidity, but also selectively ablated cancer cells via its maximized photothermal effects in the alkaline mitochondrial matrix.

Conclusions: As far as we are aware, IR2 not only offers the highest physiological acidity triggered NIR fluorescence enhancement as small molecules, but is also the first to specifically visualize and eradicate cancer cells by sensing the altered pHs in cellular organelles. IR2 hold the promise in the image-guided tumor ablation.

Key Words: Near-infrared fluorescence, theranostic probe, pH switchable probe, photothermal effect.

Acknowledgements: This work was financially supported by the National Basic Re-search Program of China (973 Program, 2013CB932500) and the National Natural Science Foundation of China (Nos 81171384, 81371624)

Correspondence: Dr. Cong Li. Email: congli@fudan.edu.cn

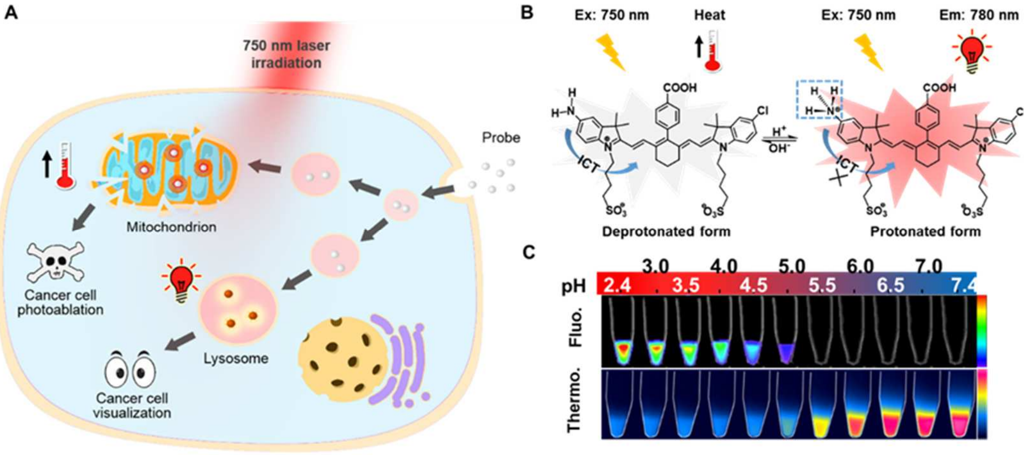


Figure (A) pH responsive theranostic probe specifically imaging and photoablating cancer cells. (B) Structures of IR2 and its proposed mechanism; (C) IR2 showing pH switchable NIR fluorescence and photothermal effects.

O12B – A boronate dipyrrin-based chemosensor for visual detection of hydrogen peroxide

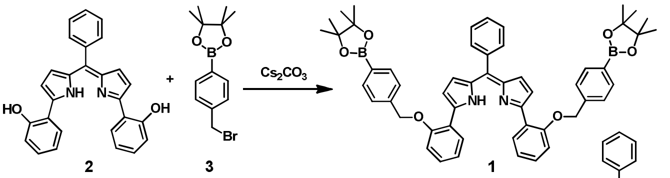
Yuji Kubo

Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji Tokyo, 192-0397, Japan. E-mail; yujik@tmu.ac.jp

Abstract

Among targeted analytes, reactive oxygen species have received much attention due to not only the significance of biological processes but also security purpose. In the latter case, trace detection of peroxide-based explosives is of urgent importance. Our motivation to develop visual H_2O_2-detection systems with outstanding optical properties led to synthesis of boronate dipyrrin-based chemosensors. Those versatile structural modifications involving coordination capability with metal ions as well as main elements enable us to propose colorimetric detection systems for H_2O_2.

The target **1** was straightforwardly prepared through condensation of Bis(2-hydroxyphenyl)-substituted dipyrrin **2** with 4-pinacolborylbenzylbromide **3** in the presence of Cs_2CO_3 in 14% yield after purification (Scheme 1), being assigned by several spectroscopic data. Compound **1** is pale pink in color which absorbs a visible light at 518 nm as λ_{max} value with molar extinction coefficient (ε) of 3.13 × 10^4 M^{-1} cm^{-1}. As expected, a stoichiometric 1:1 complex was formed with $Zn(OAc)_2$ in EtOH. Figure 1 shows time-dependent spectral change in the absorption band of **1** with Zn^{2+} and an excess amount of H_2O_2; it has been found that the H_2O_2-triggered reaction apparently involves two kinetic profiles where a new peak with λ_{max} of 581 nm appeared within 13 nm, the pseudo first kinetic constant (K_1) being 0.370 min^{-1}. Subsequently, a slower kinetic change in the absorption spectra (K_2 = 0.00371 min^{-1}) showed a bathochromic shift of 16 nm with an isosbestic point at 588 nm. The resultant blue solution was investigated by ESI-MS measurement to suggest the formation of Zn^{2+}-coordinated dipyrrin analogue **4**, being isolated as tetrabutyl ammonium salt. The H_2O_2-induced colorimetric change was monitored by ^1H NMR measurement, indicating that the reaction involved oxidation of the C−B bond by H_2O_2 and consequent hydrolysis reaction. Although the reaction was kinetically slow, setting up basic conditions by adding tetrabutylammonium hydroxide (TBAOH) led to an acceleration of the reaction. As a result, dipyrrin-based chemosensor for visually detection of H_2O_2 has been proposed in the presence of Zn^{2+}. H_2O_2 vapor detection test is also presented at the conference.



Scheme 1. Synthesis of **1**.

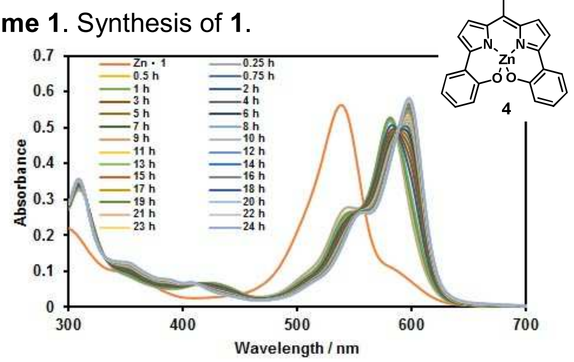


Figure 1. Change in absorption spectra of **1** (10 μM) with $Zn(OAc)_2$ (30 μM) and H_2O_2 (1 mM) in EtOH as a function of time (0.25 – 24 h) at 25 °C.

1. M. Giorgio, M. Trinei, E. Migliaccio, and P. G. Pelicci, *Nat. Rev. Mol. Cell. Biol.*, 2007, **8**, 722−728.
2. R. Schulte-Ladbeck, M. Vogel, and U. Karst, *Anal Bioanal Chem.*, 2006, **386**, 559–565.

Key Words: Chemosensor, hydrogen peroxide, dipyrrin, boronate ester

Acknowledgements: This research was partially supported by JSPS KAKENHI Grant Number 26620033.

O13B – Chromogenic anion chemosensors

Augusto C. Tomé
Department of Chemistry and QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal
Email: *actome@ua.pt*

Abstract

Chemosensors capable of recognizing selectively anionic substrates are of particular interest due to the relevance of such species in areas as diverse as biology, environmental chemistry, and nuclear waste treatment. In this context, chromogenic anion chemosensors are particularly useful. In recent years, we have developed several calixpyrrole-,[1] porphyrin-,[2] phthalocyanine-,[3] and hexaphyrin-based[4] anion chemosensors. Some of them display sharp changes in color when in the presence of fluoride, cyanide, acetate and dihydrogen phosphate anions. The synthesis and the optical features of such chemosensors will be discussed.

Key Words: calix[4]pyrroles, porphyrins, phthalocyanine, hexaphyrins

Acknowledgements: Thanks are due to Fundação para a Ciência e a Tecnologia for the financial support to the project PTDC/QEQ-QOR/6160/2014 and the QOPNA research project (FCT UID/QUI/00062/2013) through national funds and where applicable co-financed by FEDER under the PT2020 Partnership Agreement, and also to the Portuguese NMR Network.

References:

1. a) A. S. F. Farinha, A. C. Tomé, J. A. S. Cavaleiro.(*E*)-3-(*meso*-Octamethylcalix[4]pyrrol-2-yl)propenal: a versatile precursor for calix[4]pyrrole-based chromogenic anion sensors. *Tetrahedron Lett*. 2010, *51*, 2184-2187. b) A. S. F. Farinha, A. C. Tomé, J. A. S. Cavaleiro. Synthesis of new calix[4]pyrrole derivatives via 1,3-dipolar cycloadditions. *Tetrahedron* 2010, *66*, 7595–7599. c) N. I. P. Valente, P. V. Muteto, A. S. F. Farinha, A. C. Tomé, J. A. B. P. Oliveira, M. T. S. R. Gomes. An acoustic wave sensor for the hydrophilic fluoride. *Sensors and Actuators B: Chem.*, 2011, *157*, 594–599. d) A. S. F. Farinha, M. R. C. Fernandes, A. C. Tomé. Chromogenic anion molecular probes based on β,β'-disubstituted calix[4]pyrroles. *Sensors & Actuators: B. Chem.*, 2014, *200*, 332–338.

2. J. M. M. Rodrigues, A. S. F. Farinha, P. V. Muteto, S. M. Woranovicz-Barreira, F. A. A. Paz, M. G. P. M. S. Neves, J. A. S. Cavaleiro, A. C. Tomé, M. T. S. R. Gomes, J. L. Sessler, J. P. C. Tomé. New porphyrin derivatives for phosphate anion sensing in both organic and aqueous media. *Chem. Commun.*, 2014, *50*, 1359–1361.

3. a) A. S. F. Farinha, M. J. F. Calvete, F. A. A. Paz, A. C. Tomé, J. A. S. Cavaleiro J. L. Sessler, J. P. C. Tomé. Octatosylaminophthalocyanine: a reusable chromogenic anion chemosensor. *Sensors & Actuators: B. Chem.*, 2014, *201*, 387–394. b) J. M. M. Rodrigues, A. A. S. Farinha, A. C. Tomé, J. A. S. Cavaleiro, J. P. C. Tomé, Highly selective optical chemosensor for cyanide in aqueous médium. *Sensors & Actuators: B. Chem.*, 2016, *224*, 81–87.

4. F. Figueira, A. S. F. Farinha, P. V. Muteto, M. D. Polêto, H. Verli, M. T. S. R. Gomes, A. C. Tomé, J. A. S. Cavaleiro, J. P. C. Tomé. [28]Hexaphyrin derivatives for anion recognition in organic and aqueous media. *Chem. Commun.*, **2016**, *52*, 2181–2184.

O14B - Flow cytometry used to study cell activity and membrane integrity in *Tetraselmis suecica*.

Ingunn Alne Hoell[1], Ole-Kristian Hess-Erga,[2] Aud Larsen,[3] Friederike Hoffmann,[3,4] Gunnar Thuestad,[1] Ranveig Ottøy Olsen[1]

Faculty of Technology/Business/Maritime Education , Stord/Haugesund University College, Haugesund, Norway

Norwegian Institute for Water Research, Thormoehlensgt. 53 D, 5006 Bergen, Norway

Uni Research Environment and Hjort Centre for Marine Ecosystem Dynamics, 5006 Bergen, Norway

University of Bergen, PO Box 7800, 5020 Bergen, Norway

Abstract

Purpose: Disinfection of microorganisms is important to prevent the spread of pathogens and non-indigenous species in the environment. With IMO's ballast water convention soon entering into force, many new ballast water treatment systems (BWTS) have been developed. Ship owners must install BWTS in new ships and in their existing fleet, which will cause great economic consequences. According to the IMO regulations, ballast water compliance tests must include reliable results regarding organism concentration, size and viability. Today traditional analysis methods are mainly used, including cultivation-based methods and visual counts. These methods are time-consuming, require highly skilled persons, and may introduce errors as a majority of the microorganisms are uncultivable. There is therefore a great need for new, reliable and fast analysis methods. The aim of the study was to develop a flow cytometry (FCM) protocol to evaluate the performance of UV based water treatment techniques.

Experimental description: In our research we have studied the indicator organism *Tetraselmis suecica*, a phytoplankton often used for approval of ballast water treatment systems. To inactivate the algae, a collimated medium pressure UV lamp was used, followed by dark incubation to simulate a ballast water transport. Subsequent analysis of cell activity and membrane integrity was performed with FCM combined with various staining techniques, whereas reproducibility was measured by the number of colony forming units (CFU).

Results: FCM analysis separated the cells into distinct FCM populations based on their fluorescent intensity. UV irradiated samples followed a different staining pattern compared to non-irradiated samples. FCM results were also compared to corresponding plate count results, separating culturable and highly metabolic active cells from non-culturable cells with low metabolic activity.

Conclusions: We argue that FCM facilitates and improves ballast water analysis when evaluating the performance of UV based water treatment systems.

Key Words: Phytoplankton, *Tetraselmis suecica*, Ultraviolet irradiation, Staining, Flow cytometry

Acknowledgements: This research was founded by the Norwegian Research Council (project no. 208653) and Knutsen OAS Shipping AS, and supported by Solstad Shipping, Stord/Haugesund University College, VRI Rogaland, UH-nett Vest and TeknoVest.

Correspondence: I. A. Hoell. Tel: (+47) 52 70 26 39, E-mail address: ingunn.hoell@hsh.no

O15B - Fluorescent probes for DNA detection based on mono- and bisstyryl dyes.

Olga A. Fedorova,[1] Daria V. Berdnikova,[1,2] Yuri V. Fedorov,[1] Teimur M. Aliev,[1] and Heiko Ihmels[1]

1. A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova 28, 119991 Moscow, Russia

2. Universität Siegen, Department Chemie-Biologie, Organische Chemie II, Adolf-Reichwein-Str. 2, 57068 Siegen, Germany

Abstract

Purpose: Cyanine dyes, in particular styryl dyes, exhibit remarkably high affinity towards nucleic acids along with a significant change of their photophysical properties upon DNA binding. These properties are used for DNA detection and quantification in a variety of methods and techniques such as the polymerase chain reaction, DNA fragment sizing, DNA staining, DNA damage detection, flow cytometry, and evaluation of biological activity. Although interactions of several styryl dyes with DNA have already been described, only relatively few investigations include sufficient data to deduce the binding modes.

Experimental description: To access the factors that influence the DNA association in the series of 15-crown-5- derived mono- and bis-styryl dyes, the structure of the molecules was varied by either changing size of the heterocyclic moiety or altering the position of the styryl substituents.

Results: The major binding mode for the monostyryl dyes is intercalation, for bisstyryl dyes the interaction with DNA through the minor groove binding was found. Notably, binding of the dyes to the nucleic acids leads to a fluorescence enhancement by a factor of up to 54.

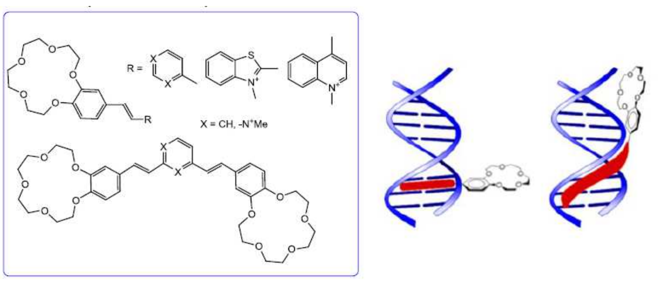


Fig. 1. Structures of the studied dyes and modeles of their interactions with DNA

Recently, we described novel oxidative photocyclization of styryl substituted azines to polycyclic heteroaromatic cations involving formation of a new C-N bond [1]. This photochemical transformation was successfully used for *in situ* generation of a DNA-intercalating photoproduct directly in the presence of nucleic acid representing a rare example of photocontrolled binding with DNA.

Conclusions: DNA-binding properties of 15-crown-5-derived mono- and bis-styryl dyes were investigated in the presence of calf thymus DNA.

References: [1] Daria V. Berdnikova, Olga A. Fedorova, Elena V. Tulyakova, Haixing Li, Sarah Kölsch, and Heiko, *Photochemistry and Photobiology*, 2015, 91(3),723.

Key Words: DNA, styryl dye, intercalation, fluorescence, ‘light-up’ probe

Acknowledgements: This work was supported by RNF project № 16-13-10226 Correspondence: Prof. Olga A. Fedorova, A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova 28, 119991 Moscow, Russia. *E-mail:* fedorova@ineos.ac.ru

O16B - Photoactive complexes on the basis of crown-containing 2-styrylbenzothiazole and host molecules: 2-hydroxypropyl-β-cyclodextrin and cucurbit[7]uril

Yury V. Fedorov[1], Sergey V. Tkachenko[2], EkaterinaYu. Chernikova[1], Alexander S. Peregudov,[1] Ivan A. Godovikov[1], Olga A. Fedorova[1,2]
A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova str., 28, Moscow, Russia
D. Mendeleyev University of Chemical Technology of Russia, 9 Miusskaya square, Moscow, Russia

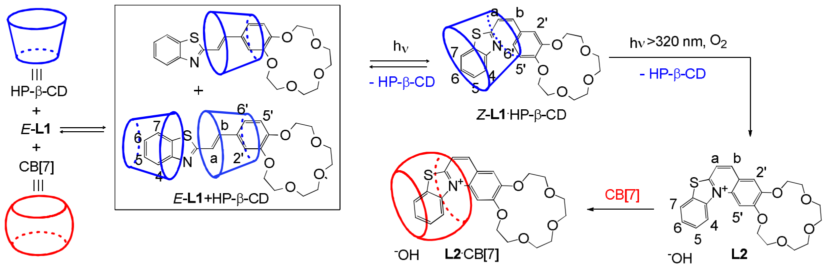
Abstract

Purpose: At the present time different molecular devices, created on the basis of organic supramolecular host-guest complexes, are becoming increasingly popular. In this work we focused on the three-component supramolecular system consisting of crown-containing 2-styrylbenzothiazole (**L1**) as guest molecule and 2-hydroxypropyl-β-cyclodextrin (**HP-β-CD**) and cucurbit[7]uril (**CB[7]**) as host molecules that undergo photoinduced transformation and translocation of the styryl guest from the cavity of **HP-β-CD** to **CB[7]**.

Experimental description: The complex formation process and photochemical transformation of guest molecule in the presence of two host molecules were studied using a combination of electronic absorption and 1D and 2D NMR-spectroscopy.

Results: The photochemical transformations of *trans*-**L1** includes two steps: (1) a photochemical *trans–cis* isomerization to yield cis-**L1**, and (2) 6π-electron electrocyclic ring closure and oxidative aromatization to yield heteroaromatic cation **L2**. The critical structural feature that enables the translocation process is the irreversible transformation of neutral styryl dye *trans*-**L1** into cationic dye **L2**. The contrasting preferences of **HP-β-CD** for neutral guests and **CB[7]** for cationic guests drives the translocation process.

We have also found that the present system can be manipulated by chemical stimuli in the form of changes in pH or Ba^{2+} ion concentration which cause dissociation of the complexes by guest protonation and formation of **CB[7]**–Ba^{2+}.



Conclusions: This work further establishes the CB[n] family of containers as particularly well suited for the creation of multi-stimuli responsive systems.

Acknowledgments: The work was supported by the Russian Foundation for Basic Research (№ 16-03-00423 and № 16-33-00748) and the RNF project 16-13-10226.

Key Words: cyclodextrin, cucurbit[7]uril, host-guest complexes, photochemical transformation

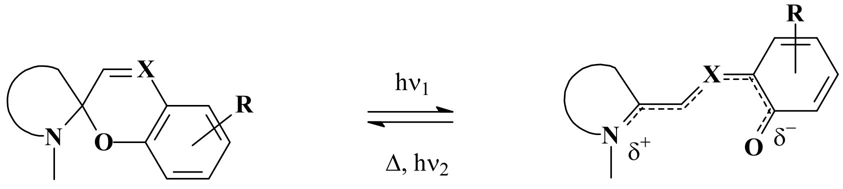
Correspondence: Dr. Y.V. Fedorov, A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova str., 28, Moscow, Russia, e-mail: fedorov@ineos.ac.ru.

O17B - New opportunities for the use of spirocyclic compounds as sensors for toxic pollutant

Anatoly Metelitsa[1,2], Christophe Coudret[2], Jean-Claude Micheau[2] and Nikolay Voloshin[1]
Institute of Physical Organic Chemistry, Southern Federal University, Stachki Av.194/2,
344090 Rostov on Don, Russia.
IMRCP, UMR 5623, Universit´e P. Sabatier, Toulouse 3, F-31062 Toulouse Cedex, France.

Abstract

The design and synthesis of functional dye molecules that could serve as molecular devices for sensors, photo-switching, and signal transduction is an area of intense activity. Among the compounds that could be used for such purpose are the photochromic spirocyclic compounds: spiropyrans and spirooxazines [1]. Spirocyclic compounds belong to a group of photo-switchable organic molecules which photochromism involves UV light induced cleavage of the C-O bond of the neutral spirocyclic form SP producing a strongly coloured merocyanine open form **MC**. The latter slowly decaying through a thermal process back to the **SP** form, this allows reversible switching between a colourless closed form **SP** and conjugated zwitterionic form **MC**. Well known application of spirocyclic compounds as chemosensors associated with the presence of a negatively charged oxygen atom in the merocyanine isomeric structure that makes it a potential ligand that can bind to a metal ion to form a coordination complex.



SP **MC**

X = CH: Spiropyran; X = N: Spirooxazine

New opportunities of spirocyclic compounds for the sensing may be associated with the ability to aggregate merocyanine isomers [2]. For the first time, we have been obtained the solvent and surfactant induced aggregation of hydrophobic spirooxazines. Aggregation occurs when a large amount of water is added in an acetonitrile solution of the dye. It exist an optimum value of the water–acetonitrile molar ratio giving rise to the sharper H-aggregate visible absorption spectrum. A balance between H- and J-aggregates has been observed in presence of SDS anionic surfactant. Excess of surfactant induces the collapse of all the aggregates and the re-dissolution of the dye under the form of a merocyanine–SDS ion-pair. The observed high sensitivity of aggregation processes to the presence of SDS could be the basis of a technique for aqueous anionic surfactants assessment.

References 1. V.I. Minkin., Chem. Rev., 2004, 104, 2751–2776.

2. A.V. Metelitsa, C. Coudret, J.C. Micheau, N.A. Voloshin, RSC Adv., 2014, 4, 20974-20983.

Key Words: chemosensors, spirooxazines, merocyanine, H-aggregate, J-aggregate, surfactants.

Acknowledgements: This work was supported by the Russian Foundation for Basic Research (Project No. 16-03-01086).

Correspondence: Institute of Physical Organic Chemistry, Southern Federal University, Stachki Av., 194/2, 344090 Rostov on Don, Russian Federation; E-mail: met@ipoc.sfedu.ru (Anatoly Metelitsa).

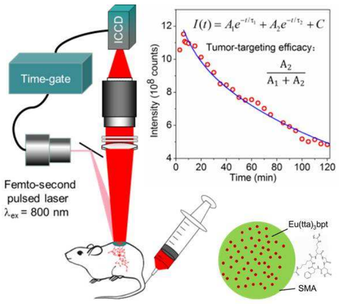
O18B - Analysis of in vivo tumor-targeting dynamics of nanocarriers by noninvasive two-photon excitation time-resolved imaging.

Yuan Wang,[1] Jan-Ping Zhang,[2] Li-Min Fu,[2] Xue Wen,[1] Zhi-Yue Gao,[1] Yan-Jie Huang[1]
College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China
Department of Chemistry, Renmin University of China, Beijing, 100872, China.

Abstract

Purpose: This work aims at exploring and understanding the transportation and tumor-targeting dynamics of nanocarriers in living animals which is of significance for the development of anti-cancer nanomedicine.

Experimental description: Luminescent nanoparticles $Eu(tta)_3bpt@SMA$, which exhibited good water dispersion stability and high yields of red Eu^{3+}-luminescence under near-infrared two-photon excitation, were prepared by a modified microfluidic mixing method in the absence of surfactants, with $Eu(tta)_3bpt$ and Poly(styrene-co-maleic acid) (SMA) as the starting materials. Tumor-targeting agents, Arg-Gly-Asp-D-Phe-Lys (cRGD) polypeptide or transferrin (Tf), were then anchored on the nanoparticle surfaces to form the desired nanocarriers Eu@SMA-RGD or Eu@SMA-Tf. The tumor-targeting processes of the prepared nanocarriers in intact living mice were analyzed on a two-photon excitation time-resolved (TPE-TR) imaging apparatus having a wide view filed.



Scheme 1. TPE-TR imaging analysis of tumor-targeting dynamics of nanocarriers in living mice

Results: The TPE-TR strategy could effectively suppress the interference from biological autofluorescence, allowing the nanocarrier-containing domains to be visualized with a high signal-to-noise ratio. Three parameters were acquired from the TPE-TR imaging analysis for evaluating the circulation performance and tumor-tissue trapping efficacy of the nanocarriers. The tumor-tissue trapping efficacy of Eu@SMA-RGD was higher than that of Eu@SMA-Tf, and the desorption process from the tumor tissues of Eu@SMA-RGD was slower than that of Eu@SMA-Tf.

Conclusions: The reliable noninvasive observation and quantitative analysis of the tumor-targeting dynamic behaviors in living mice of the designed and prepared nanocarriers were successfully carried out. The present work provides new insights into the dynamic characteristics of nanocarriers in the tumor tissues of living animals, and the new methods established in this work will find wide applications in the fields of life science researches such as biomedicine and pharmacokinetics of nanocarriers (*Biomaterials*, 2016, 100, 152).

Key Words: Tumor-targeting dynamics, Two-photon excitation time-resolved imaging, nanocarriers, luminescence

Acknowledgements: This work was supported by NSFC (grants 21227803, 21133001, 21373268). **Correspondence:** Prof. Yuan Wang at Peking University, Wangy@pku.edu.cn

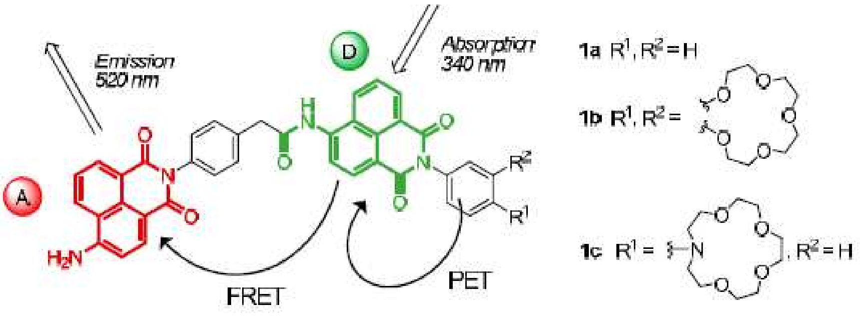
O19B – FRET versus PET: ratiometric chemosensors assembled from naphthalimide dyes and crown ethers.

Pavel A. Panchenko[1], Olga A. Fedorova,[1] Yuri V. Fedorov,[1] Gediminas Jonusauskas[2]
1. A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, 119991, Vavilova str., 28,
Moscow, Russian Federation.
2. Laboratoire Ondes et Matière d'Aquitaine (LOMA), UMR CNRS 5798, Bordeaux University, 33405, Cours de la Libération
351, Talence, France.

Abstract

Purpose: 1,8-Naphthalimide derivatives with EDG at the 4-th position of naphthalene ring are well known organic chromophores and fluorophores showing good photostability and strong emission and absorption bands in the visible region. Due to versatile photophysical characteristics, compounds of this type have been successfully used as signaling units for the design of ion-active optical molecular systems [1].

In our previous work we have demonstrated that the presence of benzo-15-crown-5 and *N*-phenylaza-15-crown-5 groups as an *N*-aryl substituent in 4-amino- and 4-amido-*N*-arylnaphthalimides results in fluorescent PET (Photoinduced Electron Transfer) sensors in CH3CN solutions [2–3]. The present paper reports synthesis and inverstigation of cation-dependent spectral properties of bis(chromophore) naphthalimide derivatives 1a-c.



Results: The compounds under study exhibited Förster resonance energy transfer (FRET) between donor (D) 4-amidonaphthalimide and acceptor (A) 4-aminonaphthalimide fragment [4]. The efficiency of FRET was calculated using both time-resolved and steady-state experiments. It was shown that the introduction of crown ether substituents decreases FRET efficiency in ligands 1b,c and thereby emission output at 520 nm, w hich is a result of competition between FRET and PET processes occurring in the initially excited 4-amidonaphthalimide fragment. The addition of Ca^{2+}, Mg^{2+} and H^+ to acetonitrile solutions of 1b,c resulted in pronounced enhancement of emission intensity of acceptor 4-aminonaphthalimide chromophore due to inhibition of PET quenching process.

Conclusions: The study performed has shown compounds 1b,c to be advantageous to development of probes for monitoring cations with ratiometric fluorescent methods.

Key Words: naphthalimide, crown ether, FRET, PET, chemosensor, metal ion.
Acknowledgements: The work was supported by RSF (project No. 16-13-10226).
Correspondence: pavel@ineos.ac.ru, Dr. Pavel A. Panchenko.
References: 1. P. A. Panchenko et al. *Russ. Chem. Rev.* 2014, 83(2), 155–182.
2. P. A. Panchenko et al. *J. Phys. Chem. A* 2010, 114, 4118–4122.
3. P. A. Panchenko et al. *Dyes Pigm.* 2013, 98, 347–357.
4. P. A. Panchenko et al. *Phys. Chem. Chem. Phys.* 2015, 17, 22749-22757.

O20B - Fluorescent probes for sensing DNA and intracellular H_2O_2 close to DNA

Tao Yi *
Department of Chemistry, Fudan University, Shanghai, 200433, China, E-mail: yitao@fudan.edu.cn

Abstract

Purpose: To develop fluorescent probes for sensing and imaging DNA and intracellular H_2O_2 close to DNA

Results: A serials of fluorescent probes were developed for the detection of DNA. A thiazole orange -modified diarylethene derivative (1) performs DNA-gated photochromic properties, which can act as an effective DNA marker, whereas DNA can light-up the chromophore and unlock the photochromic activity of the diarylethene even within cells. A DNA responding molecule (2) including two sequential responsive groups (naphthalimide and thiazole orange) presents programmed photophysical output with different concentration of StDNA. Two linear changes in the fluorescent intensity with different wavelengths were observed with the increase of the basepair concentration. Thus 2 can be used to semi-quantitativly estimate the concentration of StDNA from the fitted standard fluorescent curve. Moreover, those molecules have low cellular toxicity, and can be effectively used for intracellular detection of nuclear DNA. DNA is sensitive to reactive oxygen species (ROS). Oxidative modifications of DNA bases may induce mutations and even cancer, if not repaired in a timely manner. Thus, it is important to detect intracellular H_2O_2 near DNA. For this purpose, we further designed a fluorescent probe by linking a H_2O_2 sensitive group to a nuclear localization signal (NLS) peptide. The probe can be used for ratiometric detection of nuclear H_2O_2 in living cells. In terms of DNA oxidative damage, mitochondrial DNA (mtDNA) is a more sensitive target than nuclear DNA (nDNA), due to lack of protection from histones, close to the site of oxidant production and has a relatively low DNA repair capacity. H_2O_2 near mtDNA, therefore, deserves more extensive attention. Based on a DNA-binding peptide tagged with a positively charged red-emitting styryl fluorophore, we developed a new probe which could accumulate in mitochondria and target DNA, making it be capability of detecting H_2O_2 in the mtDNA microenvironment.

Conclusions: Fluorescent probes which can selectively binding to DNA with obviously fluorescent signal changes both on intensity and wavelength are developed. Some of the probes can further follow the concentration change of intracellular H_2O_2 close to DNA in nuclear or mitochondria.

Key Words: Fluorescence, Photochromism, Diarylethene, DNA, H_2O_2, Bioimaging

Acknowledgements: The authors thanks for the financially support by 973 (2013CB733700), NNSFC (51373039).

Correspondence: Tao Yi, Department of Chemistry, Fudan University, Shanghai 200433, China, E-mail: yitao@fudan.edu.cn

O21B – Bioimaging Based on Phosphorescent Metal Complexes

Youngmin You[1*]

Division of Chemical Engineering and Materials Science, Ewha Womans University, Seoul 03760, Republic of Korea.

Abstract

Phosphorescence bioimaging is an attractive complement to the fluorescent techniques, because the long-lived phosphorescence emissions are free of unwanted autofluorescence backgrounds inherent to biological specimens. The recent advances of phosphorescent transition metal complexes provide a strong impetus to the development of the molecular tools for phosphorescence bioimaging. Our group have developed a series of phosphorescent probes based on cyclometalated Ir(III) complexes for detection of labile zinc. Bioimaging utility of the probes have been evaluated by applying the probes into mammalian cells. In particular, time-gated visualization of intracellular zinc has been successfully demonstrated to reveal the effectiveness of removing autofluorescence. Mechanistic studies employing laser flash photolysis and electrochemical and quantum chemical techniques were performed, which established the molecular parameters that governed the phosphorescence responses. The mechanistic understanding enabled creation of the zinc probe that exhibited phosphorescence turn-on responses in red-emission regions. We observed that the phosphorescent Ir(III) complexes are highly efficient photosensitizers for singlet dioxygen. Taking advantage of this sensitizing property, we created molecular dyads capable of the photosensitization and visualization of singlet oxygen. The dual functionality enabled real-time monitoring of the progress of single oxygen-mediated cell death. Given the broad bioimaging utility, it is anticipated that the phosphorescent probes and labels will find a range of useful applications.

Key Words: phosphorescence, zinc sensor, singlet oxygen, iridium complex

Acknowledgements: This work is supported by the MSIP of Korea through the GFP (CISS-2012M3A6A6054204).

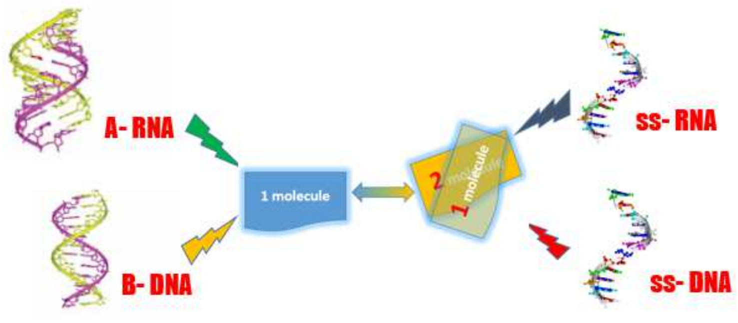
Correspondence: odds2@ewha.ac.kr

O22B - Exploiting dye monomer-dimer equilibrium for sensing of various ds-DNA/RNA secondary structures.

Ivo Piantanida
Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, 10000 Zagreb, Croatia, E-mail:pianta@irb.hr

Abstract

Small molecules targeting DNA and RNA have attracted significant scientific interest not only because of their biomedicinal applications, but also due to widespread use of spectrophotometric markers in the related scientific research – for instance, fluorescent techniques significantly developed during the last two decades and now represent about 60% of the detection enabling technologies used in molecular biology and medicine. Small molecules targeting double stranded (ds)-DNA/RNA often rely on the one dominant non-covalent binding mode for their interaction. However, design of small molecule (Mw<600) for recognition of any ds-DNA/RNA sequence is very challenging due severely limited number of modifications in such restricted size.



Scheme 1. Aggregation-prone dye interacting with various DNA/RNA structures and reporting the structural specificity of each polynucleotide by sensitive and biologically applicable spectrometric method.

Our research is focused on one of very under-investigated approaches: exploitation of intrinsic property of some dyes for aggregation, whereby monomeric and aggregated dye differ strongly in spectroscopic properties. Under favourable dye structure-DNA/RNA binding site relations, one dye molecule would give several different spectroscopic responses depending on a binding mode to DNA/RNA: to some DNA/RNA dye would bind as monomer, for other DNA/RNA as dimer, and moreover dimer response could depend strongly on the steric properties of DNA/RNA binding site (Scheme 1). We target several ds-DNA/RNA and ss-RNA (e.g. Scheme 1; A-DNA/RNA, B-DNA, subtypes of DNA characterized by narrower minor groove, etc.) by sensitive and biologically applicable methods (UV/Vis, CD, fluorescence, SERS, ITC, DSC). Studies on implementation of dye monomer-dimer equilibrium in recognition of DNA/RNA (Scheme 1) would be demonstrated for several dye types, including perylene bisimide[1] and cyanine[2] chromophores.

References: [1] J. Gershberg et al, Chem. Eur. J. 21 (2015) 7886, Rehm et al, Chem. Sci., 3, (2012), 3393; [2] L.-M. Tumir et al, Chem., Eur. J., 18 (2012), 3859.

Key Words: dye aggregation, DNA and RNA recognition, fluorescence, circular dichroism,

Correspondence: Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, 10000 Zagreb, Croatia, E-mail:pianta@irb.hr

O23B - Copper(I) bisphosphine complexes from synthesis to electroluminescent properties.

Béatrice Delavaux-Nicot,[*1,2] Adrien Kaeser,[1,2] Omar Moudam,[1,2,3] Meera Mohankumar,[3]
Nicola Armaroli,[*4] Jean-François Nierengarten,[*3]
CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, F-31077, Toulouse Cedex 4, France. E-mail: beatrice.delavaux-nicot@lcc-toulouse.fr
Université de Toulouse, UPS, INPT, F-31077 Toulouse Cedex 4, France.
Laboratoire de Chimie des Matériaux Moléculaires, Université de Strasbourg et CNRS (UMR 7509), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France.
Institute for Organic Synthesis and Photoreactivity (ISOF), Consiglio Nazionale delle Ricerche (CNR), Via Gobetti 101, 40129 Bologna, Italy.

Abstract

Electroluminescent properties of group 11 elements have attracted attention only in recent years. The discovery of strongly luminescent copper(I) complexes incorporating bisphosphine ligands in their coordination sphere has been the starting point of this research. In particular, McMillin et al. have reported heteroleptic Cu(I) complexes prepared from 1,10-phenanthroline derivatives and bis[2(diphenylphosphino)phenyl]ether (POP),[1] characterized by remarkably high emission quantum yields from their long lived metal-to-ligand charge-transfer (MLCT) excited states. Following this key finding, numerous examples of related heteroleptic Cu(I) complexes have been prepared from bisphosphine and aromatic diimine ligands.[2] Eventually, copper(I) compounds prepared exclusively from bisphosphine ligands were also reported.[3] Some of these compounds exhibit excellent emission properties exploited to fabricate efficient electroluminescent devices; therefore, inexpensive and earth-abundant copper(I) is an attractive alternative to noble metal ions for such applications.[3b,4] In recent years, investigations have been also extended to analogous silver (I) and gold(I) derivatives.[3b,5] We will highlight how our results in this research field led us to use a recent concept combining topological and steric ligand constraints for obtaining unprecedented Cu(I) complexes with remarkable photophysical properties.[6]

Acknowledgements: CNRS, International Center for Frontier Research in Chemistry, MIUR and CNR (Italy), and EC.

[1] (a) D. G. Cuttell, S.-M. Kuang, P. E. Fanwick, D. R. McMillin, R. A. Walton, *J. Am. Chem. Soc.* **2002**, *124*, 6; b) S.-M. Kuang, D. G. Cuttell, D. R. McMillin, P. E. Fanwick, R. A. Walton, *Inorg. Chem.* **2002**, *41*, 3313.

[2] (a) P. Coppens, I. I. Vorontsov, T. Graber, A. Y. Kovalevsky, Y.-S. Chen, G. Wu, M. Gembicky, I. V. Novozhilova, *J. Am. Chem. Soc.* **2004**, *126*, 5980; (b) N. Armaroli, G. Accorsi, G. Bergamini, P. Ceroni, M. Holler, O. Moudam, C. Duhayon, B. Delavaux-Nicot, J.-F. Nierengarten, *Inorg. Chim. Acta* **2007**, *360*, 1032; (c) A. Kaeser, M. Mohankumar, J. Mohanraj, F. Monti, M. Holler, J.-J. Cid, O. Moudam, I. Nierengarten, L. Karmazin-Brelot, C. Duhayon, B. Delavaux-Nicot, N. Armaroli, J.-F. Nierengarten, *Inorg. Chem.* **2013**, *52*, 12140.

[3] (a) A. Tsuboyama, K. Kuje, M. Furugori, S. Okada, M. Hoshino, K. Ueno, *Inorg. Chem.* **2007**, *46*, 1992; (b) O. Moudam, A. Kaeser, B. Delavaux-Nicot, C. Duhayon, M. Holler, G. Accorsi, N. Armaroli, I. Séguy, J. Navarro, P. Destruel, J.-F. Nierengarten, *Chem. Commun.* **2007**, 3077; (c) A. Kaeser, O. Moudam, G. Accorsi, I. Seguy, J. Navarro, A. Belbakra, C. Duhayon, N. Armaroli, B. Delavaux-Nicot, J.-F. Nierengarten, *Eur. J. Inorg. Chem.* **2014**, 1345.

[4] (a) Q. Zhang, Q. Zhou, Y. Cheng, L. Wang, D. Ma, X. Jing, F. Wang, *Adv. Mater.* **2004**, *16*, 432; (b) Q. Zhang, T. Komino , S. Huang, S. Matsunami , K. Goushi, C. Adachi, A*dv. Funct. Mater.* **2012**, *22*, 2327.

[5] (a) L. H. Gade, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 1171; (b) A. Kaeser, B. Delavaux-Nicot, C. Duhayon, Y. Coppel, J.-F. Nierengarten, *Inorg. Chem.* **2013**, *52*, 14343.

[6] M. Mohankumar, F. Monti, M. Holler, F. Niess, B. Delavaux-Nicot, N. Armaroli, J.-P. Sauvage, J.-F. Nierengarten, *Chem. Eur. J.* **2014**, *20*, 12083.

Shotgun Presentations

SG 1 (P23) - The Light at the End of the Cycle: Reductive Coupling of Diynes at Rhodium Gives Fluorescent Rhodacyclopentadienes or Phosphorescent Dibenzorhodacyclo-pentadienes

Carolin Sieck[1*], Meng Guan Tay[4], Marie-Hélène Thibault[2], Robert M. Edkins[1], Karine Costuas[3], Jean-François Halet[3], Andrei S. Batsanov[2], Martin Haehnel[1], Andreas Lorbach[1], Andreas Steffen[1] and Todd B. Marder[1,2]
[1]Institute of Inorganic Chemistry, Würzburg University, Germany
[2]Department of Chemistry, Durham University, Durham, U.K.
[3]Institut des Sciences Chimiques de Rennes, CNRS-Université de Rennes, France
[4]Faculty of Resource Science and Technology, Sarawak University, Kota Samarahan, Malaysia
* carolin.sieck@uni-wuerzburg.de

Abstract

Rigid rod conjugated systems, such as 1,4-bis(phenylethynyl)benzenes are the subject of intense interest due to their structural, electronic, linear, and nonlinear optical properties. The same could be expected from structurally similar 2,5-bis(phenylethynyl)-metallacyclopentadienyl derivatives which can be prepared *via* reductive coupling of two diarylbuta-1,3-diyne molecules on a transition metal centre. We have recently found a simple rhodium system which forms exclusively the 2,5-isomers in high yields.[1-6] The products exhibit unexpected fluorescence rather than phosphorescence and can be synthesised using a wide range of diarylbutadiynes and linked bis(diynes) *e.g.* (A). Interestingly, using [Rh(acac)(PMe$_3$)$_2$] we obtain, instead, two isomers rhodacyclopentadiene A and dibenzorhodacyclopentadiene B. Isomer A is highly fluorescent whereas B is highly phosphorescent.

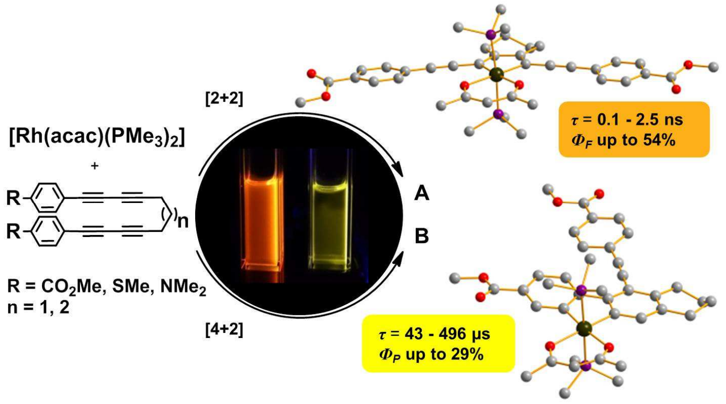


Figure 1. Synthesis of fluorescent rhodacyclopentadienes (A) and phosphorescent dibenzorhodacyclopentadienes (B).

References

[1.] Rourke, J.P.; Batsanov, A.S.; Howard, J.A.K.; Marder, T.B. *Chem. Commun.* 2001, 2626.
[2.] See also: Hill, A.F.; Rae, A.D., Schultz, M.; Willis, A.C. *Organometallics* 2007, *26*, 1325.
[3.] Steffen, A.; Ward, R.M.; Jones, W.; Marder, T.B. *Coord. Chem. Rev.* 2010, *254*, 1950.
[4.] Steffen, A., Marder, T.B.; *et al.*, *Angew. Chem. Int. Ed.* 2010, *49*, 2349.
[5.] Steffen, A.; Ward, R.M.; Tay, M.G.; Edkins, R.M.; Seeler, F.; van Leeuwen, M.; Palsson, L.-O.; Beeby, A.; Batsanov, A.S.; Howard, J.A.K., Marder, T.B. *Chem. Eur. J.* **2014**, *20*, 3652.
[6.] Steffen, A.; Marder, T.B.; *et al.*, *Inorg. Chem.* **2014**, *53*, 7055.

SG 2 (P24) - Water-Soluble 3-Coordinate Boron Chromophores for One- and Two-Photon Excited Fluorescence Imaging of Mitochondria in Live Cells

Stefanie Griesbeck1*, Zuolun Zhang1, Marcus Gutmann2, Tessa Lühmann2, Guillaume Clermont3, Adina Lazar3, Mireille Blanchard-Desce3, Lorenz Meinel2, Todd B. Marder1
1Institut für Anorganische Chemie, Julius-Maximilians Universität Würzburg, 97074 Würzburg, Germany
2Institut für Pharmazie und LMC, Julius-Maximilians Universität Würzburg, 97074 Würzburg, Germany
3Institut des Sciences Moléculaires, Université de Bordeaux, 33405 Talence cedex, France
* stefanie.griesbeck@uni-wuerzburg.de

Abstract

Triarylboranes have attracted a huge amount of interest due to their application in many different fields such as anion sensing, OLEDs and non-linear optical materials.[1] Over the last few years, we have studied the use of dimesitylboron-based □-acceptors (A) in two-photon absorption (TPA) chromophores. We designed dipolar, quadrupolar and octupolar compounds with exceptional TPA cross sections and high fluorescence quantum yields.[2] Furthermore, we reported structure-TPA cross section relationships for our quadrupolar A-π-A compounds.[3] Recently, we synthesized oligothiophene-$BMes_2$ chromophores, with significantly enhanced TPA cross sections of up to 1930 GM in the near-infrared region, the "biological transparent window".[4] We present herein the further functionalization of such chromophores with ammonium groups, an approach pioneered by Gabbaï,[5] in order to achieve hydrophilicity and biocompatibility, and our initial results of both one- and two-photon excited fluorescence (TPEF) microscopy allowing the imaging of mitochondria in live cells with our chromophore.

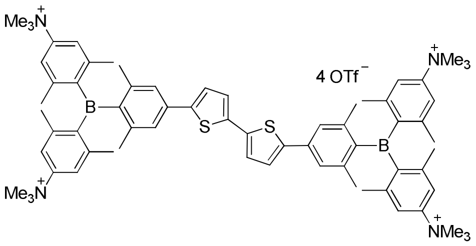


Figure 1. Water-soluble and water-stable triarylborane chromophore for mitochondrial imaging.

References

[1] (a) C. D. Entwistle, T. B. Marder, Angew. Chem. Int. Ed. Engl. 41 (2002) 2927-2931. (b) C. D. Entwistle, T. B. Marder, Chem. Mater. 16 (2004) 4574-4585.

[2] J. C. Collings, C. Katan, A. Beeby, D. Kaufmann, W.-Y. Wong, M. Blanchard-Desce, T. B. Marder *et al.*, Chem. Eur. J. 15 (2009) 198-208.

[3] (a) M. Charlot, L. Porrès, C. D. Entwistle, A. Beeby, T. B. Marder, M. Blanchard-Desce, Phys. Chem. Chem. Phys. 7 (2005) 600-606. (b) C. D. Entwistle, J. C. Collings, A. Steffen, A. Beeby, A. S. Batsanov, J. A. K. Howard, W.-Y. Wong, A. Boucekkine, J.-F. Halet, T. B. Marder *et al.* J. Mater. Chem. 19 (2009) 7532-7544.

[4] L. Ji, R. M. Edkins, A. Beeby, A. S. Batsanov, J. A. K. Howard, A. Boucekkine, Z. Liu, J.-F. Halet, C. Katan, T. B. Marder *et al.* Chem. Eur. J. 20 (2014) 13618-13635.

[5] C.-W. Chiu, Y. Kim, F. P. Gabbaï, J. Am. Chem. Soc. 131 (2009) 60-61.

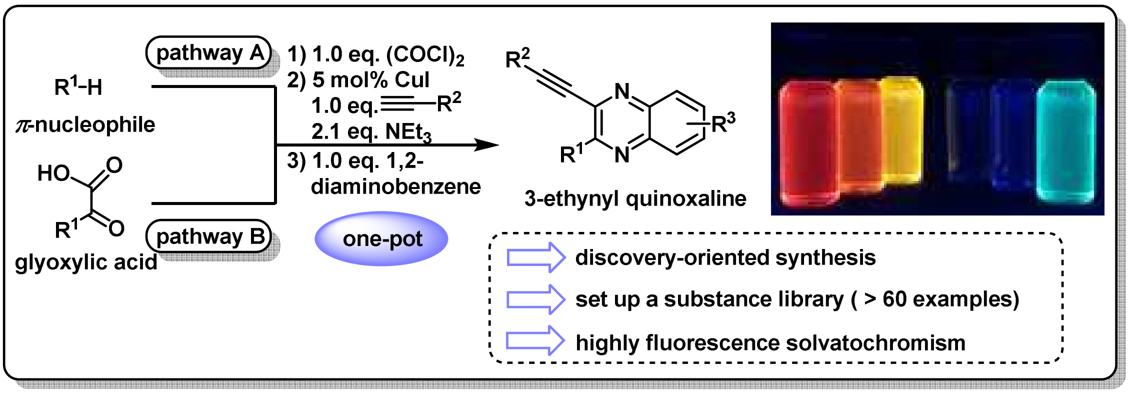
SG 3 (P25) - Highly Emission-Solvatochromic 3-Ethynyl Quinoxalines: Synthesis, Photophysical Properties and Electronic Structures

Franziska K. Merkt, Simon P. Höwedes, Thomas J.J. Müller
Heinrich-Heine-Universität Düsseldorf, Institut für Organische Chemie und
Makromolekulare Chemie, Universitätsstraße 1, 40225 Düsseldorf, Germany.
E-Mail: franziska.merkt@hhu.de, thomasjj.mueller@hhu.de

Abstract

Recent biological research needs the continuous development of highly sensitive fluorophors for sensoring a wide range of molecular processes. Regarding this research subject, the development of highly fluorescent dyes that also possesse the characteristics of a remarkable emission-solvatochromism has received increasing interest in the past decades. Furthermore, fluorescence spectroscopy is much more sensitive than absorption spectroscopy, even a lower concentration of analyte suffices in order to detect fluorescence directly. These intrinsic features make it to a valuable tool for monitoring interactions and dynamics. [1]

The increasing requirement of those specific chromophors result in their consistent construction. During this process, special attention is given to innovative synthetic approaches. The conception of environmental, economical and rapidly performed synthesis adopts a great contribution. For this purpose, our group has recently developed a set of complementary one-pot syntheses of fluorescent and solvatochromic 3-ethynyl quinoxalines (Scheme 1) [2] based on intermediary ynediones. [3]



Scheme 1: Four-component (pathway A) and three-component (pathway B) one-pot syntheses of remarkable emission-solvatochromic 3-ethynyl quinoxalines.

In addition, the triple bond exhibits a high reactivity for further derivatization. For instance, this reactive centre undergoes *Michael*-addition-type reactions with halide and nitrogen nucleophiles. Latter synthetic method leads to the corresponding 2-aminovinylquinoxalines. [4] Further varied structural changes of the triple bond are conceivable. Consequently, we set out to investigate the reaction scope as well as the photophysical and chemical properties of the synthesized compounds.

Keywords: 3-ethynyl quinoxaline, highly fluorescence solvatochromism, one-pot sequence

[1] G. S. Loving, M, Sainlos, B. Imperiali, Trends Biotechnol. 2010, 28, 73-83.
[2] C. F. Gers, J. Nordmann, C. Kumru, W. Frank, T. J. J. Müller, J. Org. Chem. 2014, 79, 3296-3310.
[3] E. Merkul, J. Dohe, C. Gers, F. Rominger, T. J. J. Müller, Angew. Chem. Int. Ed. 2011, 50, 2966-2969.
[4] C. F. Gers, H. Fischer, J. Nordmann, W. Frank, U. Resch-Genger, T. J. J. Müller, manuscript in preparation.

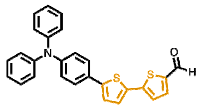
SG 4 (P26) - Engineering ofHyperbright and Stable Fluorescent Organic Nanoparticles

Paolo Pagano[1], Marine Delgado[1], Mireille Blanchard-Desce[1].

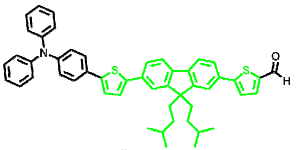
Université de Bordeaux, Institut des Sciences Moléculaires (CNRS UMR 5255), Groupe IPM, 351 Cours de la Libération, 33405 Talence, France.

Abstract

Purpose: In the course of our approach towards molecular-based fluorescent organic particles as biocompatible ultra-bright luminescent alternatives to QDs for bioimaging purposes, we have recently shown that molecular engineering of multipolar dyes could indeed lead to FONsdisplaying giant brightness, tunable luminescence and exceptional stability and photostability.[1-4] These FONs can be easily prepared in water using a robust, expeditious and simple nanoprecipitation process. Of major importance is the realization that modification of the dye subunits structure can be used to tune both the photophysical and the colloidal and structural stability of the FONs, thus opening an intriguing bottom-up engineering route.[1-2,5] With the aim of extending the scope of this route, we here investigate the effect of the modification of the π-conjugated system of a "push-pull" dipolar generic dye (Ia) by inserting a fluorene unit in the middle of the conjugated system (IIa). This was aimed both at enhancing the two-photon absorption (2PA) response,[2,4,6] and tuning interchromophoric interactions so as to control the FONs optical and luminescence properties.

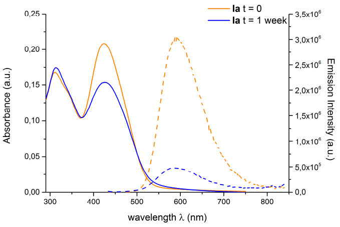


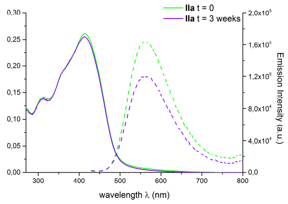
Ia



IIa

Results: The new synthesized dye was found to produce hyper-bright yellow-emitting FONs (λ_{abs}^{max}= 414 nm, λ_{em}^{max}= 559 nm, $\varepsilon^{max}\Phi_f$ = 4.2 10 ^{7} M^{-1}cm $^{-1}$) of about 34 nm diameter *via* nanoprecipitation in water. Interestingly, a broadening of the absorption band of FONs made from **IIa** is observed as compared to that ofthe monomeric dye dissolved in CHCl$_3$, revealing that molecular confinement of **IIa** promotes excitonic coupling (not observed with dye **Ia**). FONS made from dye **IIa** are found to be slightly blue-shifted compared to those made from **Ia** and show larger 2PA response in the biological spectral window (σ_2^{max} = 7.5 10^6 GM at 730 nm). Even more importantly, FONs made from dye **IIa** show largely improved structural and colloidal stability overtime, in relation with a highly negative surface potential up (-73 mV).





Conclusion: The present study shows that subtle engineering of the dyesubunits of this new class of nanoparticles (i.e. FONs made from dedicated dipolar chromophore) is indeed operative in improving key criteria for use as contrast agents for (bio)imaging purposes. Furthermore, control of interchromophoric interactions allows tuning photophysical properties and enhancing 2PA responses. As a result, hyper-bright molecular-based nanoparticles showing much larger one-photon and two-photon brightness as compared to QDs (2.6 10^5 GM FONs **IIa**; 4.7 10^4 GM QDs[7]) while exhibiting suitable colloidal and structural stability in water have been designed.

Key Words: Fluorescent organic nanoparticles, Two-photon absorption,Multistep synthesis, Dipolar interactions. **Correspondence:** mireille.blanchard-desce@u-bordeaux.fr; paolo.pagano@u-bordeaux.fr

Acknowledgements: The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n°607721. TEM microscopy was done in the Bordeaux Imaging Center (UMS 3420 CNRS-University of Bordeaux/INSERM US4).

References: [1] Genin E. *et al., Advanced Materials,* **26**, 2014, 2258-226119, [2] Amro K.*et al.*, *Tetrahedron*, **70**, 2014, 1903-1909; [3] Daniel J. *et al.*, *J. Phys. D: Appl. Phys.*, **49**, 2016; [4] Verlhac J.-B. *et al*, *C. R. Chimie*, **19**, 2016, 28-38 ; [5] Daniel J. *et al.*, *ACS Photonics*, **2**, 2015, 1209-1216; [6] Terenziani F. *et al.*, *Advanced Materials*, **20**, 2008, 4641-4678; [7] Larson D. *et al.*, *Science*, **300**,2003, 1434-1436

SG 5 (P27) - Directed Self-Assembly of Block Copolymers for Well-Ordered Nanostructures

Dong-Eun Lee, Byung Doo Chin, Seok-Ho Hwang, Oh Young Kim, and Dong Hyun Lee*
Department of Polymer Science and Engineering, Dankook University, 152 Jukjeon-ro, Suji-gu, Yongin-si, Gyeonggi-do, 448-701, Republic of Korea.

Abstract

Purpose: The aim of our research is to produce well-ordered nanostructures in large area by means of directed self-assembly of block copolymers (BCPs) in thin films for a variety of optical and electrical applications.

Experimental description: For long-range ordering of BCP nanostructures, polymeric nano-stripes were fabricated by rubbing a Teflon bar on Si substrates. Then thin films of polystyrene-*block*-poly(2-vinylpyrdine) copolymer ($M_{n,PS}$ = 175 kg/mol, $M_{n,P2VP}$ = 70 kg/mol, and PDI = 1.08) were directly spin-coated on the nano-stripes. To induce well-ordered nanostructures of the block copolymers, the thin films were solvent-annealed in vapor of organic solvents like chloroform, THF, and toluene. The orientation of BCP nanostructures could be also determined by choosing solvents and soaking times. As those BCP thin films were used as templates, both nano-dots and nano-lines of Si, Pt, and Au were converted from their precursors by oxygen plasma treatment. In addition, the BCP thin films and arrays of nanostructures were characterized by using AFM and SEM.

Results: Nano-stripes of poly(tetrafluoro ethylene) (PTFE) having ~ 20 nm of amplitude and ~ 200 nm of pitch were simply generated by rubbing a PTFE bar on various substrates like Si wafer, glass, and polyimide film due to its low friction coefficient and high wear rate. It was fount that the resulting nano-stripes were extremely oriented along the rubbing direction. Then thin films of asymmetric polystyrene-*block*-poly(2-vinylpyrdine) copolymer were spin-coated and exposed to vapor of various organic solvents to induce phase separation. By adjusting annealing time and type of solvent, both ordering and orientation of BCP nanostructures could be controlled on the underlying nano-stripes. Hexagonally packed cylinders of P2VP oriented normal to the surface were generated in large area as the BCP thin films were solvent-annealed in THF vapor. In contrast, parallel orientation of P2VP cylinders were observed by solvent-annealing in chloroform vapor. As the thin films were immersed into ethanol solutions of precursors of inorganic substances, the precursors selectively positioned in P2VP cylinders. By oxygen plasma treatment, the inorganic precursors were converted to nano-dots or nano-stripes of gold, platinum, and silica that were originated from the orientation of BCP nanostructures while organic components were completely removed.

Conclusions: In summary, large scale assembly of BCP nanostructures were achieved by utilizing the underlying nano-stirpes of PTFE fabricated by simple rubbing technique. Because the nano-stripes were oriented along the rubbing direction, they could guide well-ordered BCP nanostructures in large area as they enlarged grain size extremely during solvent-annealing process. In addition, the well-ordered nanostructures were used as templates to synthesize nano-dots and nano-lines of Au, Pt, and Si.

Key Words: Block Copolymers, Self-Assembly, Nanoparticles, Long-Range Ordering, Solvent-Annealing

Acknowledgements: This work was supported by The Brain Korea 21 Plus Project "Organic Optoelectronics Materials Team" in 2015 (22A2013 0000050) and Gyeonggi Regional Research Center (GRRC) Program (GRRC DANKOOK 2014-B01). Correspondence: Dong Hyun Lee (dlee@dankook.ac.kr)

SG 6 (P28) - Blend electrospinning of dye-functionalized chitosan and polycaprolactone: towards biocompatible pH-sensors.

Ella Schoolaert[1], Richard Hoogenboom,[2] Karen De Clerck.[1]
Department of Textiles, University of Ghent, Technologiepark 907, Ghent, Belgium.
Department of Organic and Macromolecular Chemistry, University of Ghent, Krijgslaan 281 S4, Ghent, Belgium.

Abstract

Purpose: The development of so-called smart materials, *i.e.* materials that are able to sense and respond to changes in their environment, is a hot topic in today's research. Halochromic dyes show high potential within this field as pH-changes are visualized by a fast and simple change of color. A smart halochromic sensor can be fabricated by incorporating such halochromic dye into a suitable matrix material, resulting in a custom, user-friendly product, providing clear information in a non-destructive way. Polymer nanofibers are a very well suited matrix material since nanofibrous nonwovens are characterized by a high specific surface area, small pore size, high pore volume and high absorbance capacity, making them ideal candidates for advanced, fast-responding sensor applications. Dye-immobilization is, currently, a major challenge in nanofibrous sensor design as dye-doped solvent electrospinning, *i.e.* the most commonly applied processing technique, suffers from leaching of the dye out of the nanofibrous network. Our research focuses on dye-immobilization through covalent dye-modification, where the polymer backbone is modified with a halochromic dye before the electrospinning process, providing a covalent linkage between the dye and the polymer. This technique is of particular interest for the application of natural (bio)polymers, such as chitosan.

Experimental description: The nanofibrous structure is ideally produced via blend electrospinning, which allows for the selection of a suitable carrier polymer that is widely available and well electrospinnable along with an appropriate amount of dye-modified polymer for the specific application. In this work, halochromic nanofibers were produced by blend electrospinning of chitosan. Before electrospinning, chitosan was either doped or modified with a halochromic dye. Thorough analysis and comparison of dye-doped and dye-modified nanofibers was carried out in terms of the nanofiber morphology as well as the halochromic and migration behavior.

Results: Of course, the question arises, if the modification of the polymer has a significant influence on the electrospinning process and, moreover, if the halochromic properties of the dye are maintained within the nanofibrous network. Within our research, chitosan was successfully modified and blend electrospun for the production of halochromic nanofibers. We found that the covalent modification could, indeed, influence the electrospinnability of the polymer, yet suitable nanofibers were obtained. More important, dye-migration was significantly reduced compared to the dye-doped nanofibers, within the entire pH-range, without majorly affecting the halochromic properties of the dyes.

Conclusions: This research paved the road for the production of halochromic nanofibrous sensors by covalent dye-modification combined with blend electrospinning, which has major potential, particularly, in the area of natural (bio)polymers, as it provides a universal method for versatile dye-functionalization of large area nanofibrous membranes, accompanied with proper dye-immobilization.

Key Words: Halochromism, optical sensor, nanofibers, blend electrospinning, dye-leaching

Correspondence: Technologiepark 907, Ghent, Belgium – Karen.DeClerck@UGent.be

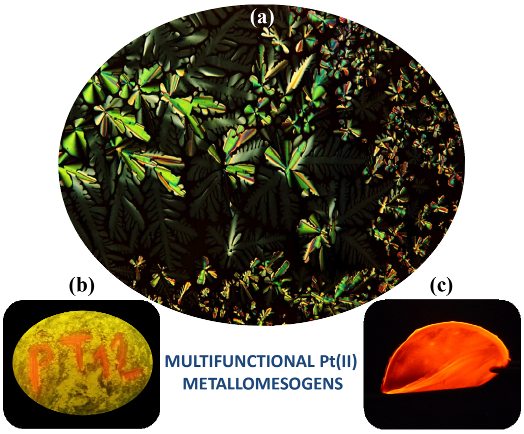
SG 7 (P29) - Tuning the luminescence properties of novel Pt(II) metallomesogens: from the molecule to the smart materials.

Cristián Cuerva[1], José A. Campo[1], Mercedes Cano[1], Carlos Lodeiro[2,3]
Department of Inorganic Chemistry I, Faculty of Chemical Sciences, Complutense University of Madrid, Ciudad Universitaria, E-28040 Madrid. Spain.
Bioscope Group, Chemistry Department, Faculty of Sciences and Technology, New University of Lisbon, Campus de Caparica, 2829-516 Caparica. Portugal.
ProteoMass Scientific Society, Madan Parque. Building VI, Office 23, Faculty of Sciences and Technology, Campus de Caparica, 2829-516 Caparica. Portugal.

Abstract

Purpose: Square-planar Pt(II) complexes containing bidentate ligands with extended conjugation may be good candidates to achieve highly-stable columnar mesophases and, additionally, to exhibit photoluminescence properties which can be easily tuned by application of external stimuli.

Experimental description: Pt(II) complexes were synthesized by reaction of the previously designed pyrazole-type ligands and K_2PtCl_4 in a 2:1 molar ratio, respectively. PMMA and PVP thin films were obtained from a mixture of these polymers and the Pt(II) complexes in CH_2Cl_2, followed by a slow evaporation of the solvent.



Results: Novel pyridine and isoquinoline-functionalized pyrazolate Pt(II) complexes with mesomorphic and luminescent properties have been recently designed and synthesized. The best liquid crystal properties were found by functionalizing the pyrazolate core with the isoquinoline group, which stabilizes the Col_h mesophase (Fig. a) in a wide range of temperature (> 300 °C). In addition, all compounds show thermo-, mechano-, vapo-, and solvatochromic behaviors (Fig. b). Photoluminescence studies, in combination with XRD experiments, evidence that the nature of these properties is related to the formation/rupture of intermolecular Pt···Pt interactions. Low-cost stimuli-responsive polymer thin films have been proved to be useful as sensors for real technological applications (Fig. c).

Conclusions: The columnar stacking of these metallomesogens as well as their attractive luminescence properties could be useful for the development of security inks, data-recording devices or encryption systems.

Key Words: Stimuli-responsive materials, Metallomesogens, Platinum liquid crystals, Polymers, Sensors.

Acknowledgements: Authors thanks to the Ministerio de Economía y Competitividad (projects CTQ2011-25172 and CTQ2015-63858-P (MINECO/FEDER)), Complutense University (GR3/14-910300), Scientific PROTEOMASS Association and Unidade de Ciências Biomoleculares Aplicadas-UCIBIO. C. Cuerva acknowledges the Universidad Complutense de Madrid for his predoctoral contract and the financial help for international research stays.

Correspondence: Department of Inorganic Chemistry I, Faculty of Chemical Sciences, Complutense University of Madrid. Ciudad Universitaria, Avda. Complutense s/n, E-28040 Madrid (Spain). E-mail: c.cuerva@ucm.es.

SG 8 (P30) - Highly Fluorescent Carbon Free-Radical Excimers in Organic Nanoparticles

Davide Blasi[1,], Domna Maria Nikolaidou[2], Francesca Terenziani[2], Imma Ratera[1], Jaume Veciana[1]

Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC) and Ciber-BBN, Campus UAB, 08193, Bellaterra (Barcelona), Spain

Università degli Studi di Parma, Department of Chemistry, Parco Area delle Scianze 17A, 43124, Parma, Italy

Abstract

Polychlorotriphenyl methyl radicals are considered as an inert carbon free-radicals for their elevate chemical and thermal stability both in solution and in solid state, where their half-lives are on the order of decades. The “open-shell” configuration, due to the presence of unpaired electron mainly localized on the α-carbon, leads to specific optical characteristics like an emission at long wavelength without the need of elongated π-systems, a huge Stokes shift, an emission lifetime on the order of tens ns and a doublet electronic configuration both for ground and excited states. Despite such interesting properties, there are two limiting factors for the use of these molecules as photoactive materials in devices or as probes in bio imaging applications: the low value of fluorescent quantum yield (φ_F) and the low photostability, in particular in solution. Recently, several molecular approaches have been proposed in order to enhance these two fundamental parameters, but so far it is not known what happens when radical molecules are confined in rigid organic matrix and processed as organic nanoparticles (ONPs). This kind of system could be promising for the fabrication of optoelectronic devices or fluorescent probes for bioimaging. In this work, we report the optical behavior of ONPs made by the optically neutral tris(2,3,4,5,6-chlorophenyl)methane (TTM-αH), doped with different amount of optically active tris(2,4,6-trichlorophenyl)methyl radical (TTM), focusing our attention on how, the change of the concentration of radicals inside ONPs, affects their emission properties. We compared the emission characteristics of these ONPs with the emission of the radical in THF and 2-methyl THF frozen solution at 77K. It’s been found that TTM radical, confined in ONPs shows an improvement of luminescence and photostability and moreover, it forms excimers presenting a broadband emission from 530 nm up to 850 nm. These excimers, observed for the first time in the case of a carbon free-radical, are promising for the fabrication of OLEDs, in particular for two color (blue/yellow-orange) white organic light emitting diodes (WOLEDs), as alternative to the more expensive heavy-metal complexes.

Key Words: Polychlorotriphenyl methyl radicals, Fluorescent Nanoparticles, Excimer

Correspondence: dblasi@icmab.es

SG 9 (P31) - Photophysical and theoretical characterization of newly synthesized naphthyl substituted pyrazolines dyes

Amal H. Al Sabahi, Saleh N. Al-Busafi, Salma M. Z. Al-Kindy, FakhrEldin O. Suliman
Department of Chemistry, College of Science, Sultan Qaboos university, P.O. Box 36, Al-Khod 123, Sultanate of Oman, Email address: amal3510@hotmail.com

Abstract

Fluorogenic dyes containing pyrazoline are among the profusely studied compounds due to their applications and electron rich properties. The addition of naphthyl group extends the π-conjugation and enhances the intramolecular charge transfer (ICT). Therefore, introducing different electron directing groups in 5-phenyl ring of pyrazoline influences the photophysical and electronic properties of these dyes.

Purpose: To investigate the effect of electron donating and withdrawing groups on the photophysical characteristics of naphthyl substituted pyrazoline.

Experimental: In this work Naphthyl substituted 2-pyrazoline with different electron donating and withdrawing groups were synthesized and characterized by IR, NMR, ESI-MS and elemental analysis. The photophysical properties were studied in three solvents of different polarities using absorption, steady state and time-resolved fluorescence fluorometers. Theoretical calculation were performed using Gaussian 09 program using DFT and TD-DFT at B3LYP 6-31G*(d, p) level of theory.

Results: The spectral effect of substitution in 5-phenyl ring of 2-pyrazoline with six different electron donating and withdrawing groups (CH_3O, CH_3, Cl. Br, CF_3, and CN) indicated a bathochromic shift occur more distinctly in fluorescence than absorption and depends on the solvent polarity. Moreover, pyrazolines with electron donating groups displayed an increased red shift compared to the one with no substitution and to those with electron withdrawing groups. The decay profiles of studied compounds in toluene were observed to fit a two exponential decay model and found to possess two lifetimes with the mean lifetime that decreases as the electron donation property decreases.

The molecular electronic properties, geometry and dipole moment of the compounds in ground and excited state were determined. It was found that different substituents in 5-phenyl group have inconsiderable influence on the molecular geometry of the compound in the ground state. The HOMO-LUMO energy gap were also obtained from cyclic voltammetry measurements in acetonitrile and were found to be in good agreement with the those obtained from theoretical calculations.

Conclusion: A series of pyrazoline derivatives were synthesized and found to be sensitive for the nature of substituents on the 5-phenyl ring which is manifested clearly in their fluorescence. The theoretical results corroborated those obtained experimentally.

Key words: Naphthyl substituted Pyrazoline, fluorescence, time-resolved, Td-DFT calculation.

Acknowledgments*:* The author is grateful to Sultan Qaboos University for financial support.

References

1. Easwaramoorthi, S., et al., *Synthesis of green light emitting fused pyrazolinopiperidines - photophysical and electrochemical studies.* RSC Adv., 2013. 3(4): p. 1243-1254.

2. Zhao, P., Zhao, S., Guo, Z., Zhu, Y., Crystal structure spectra properties and comparative studies on 2-pyrazoline derivative. Spectrochimica Acta., 2012. A94: p65-71

SG10 - The interplay of thermally assisted delayed fluorescence (TADF) and room temperature organic phosphorescence in sterically-constrained donor–acceptor charge-transfer molecules.

Roberto S. Nobuyasu1, J. Ward2, M. Eringthon1, A. S. Batsanov2, P. Data1, A. Monkman1, M. Brice2, Fernando B. Dias1
1. Department of Physics, Durham University, Durham, UK
2. Department of Chemistry, Durham University, Durham, UK

Abstract

Spin statistics drives the efficiency of pure fluorescent emitters, which utilise only singlet excited states for electroluminescence, limited to 25%. Thermally assisted delayed fluorescence (TADF) mechanism allows the harvest of non-emissive triplet states into emissive singlet states via intersystem crossing process. Achieved when decreasing the ΔE_{ST} that requires a spatial separation of HOMO and LUMO in the molecule. Charge transfer state, in Donor-Acceptor molecules, is way to promote this spatial separation when donor and acceptor moieties are orthogonal. Here, we present the optical spectroscopic investigation of a set of pure organic small molecules, which have substituents bulky side groups. These side groups restrict the rotation around the D-A axis. The dynamics of thermally delayed assisted fluorescence (TADF) is significantly affected when such rotation is not possible. We report the study of a family of D-A and D-A-D molecules based on a phenothiazine (donor) and a dibenzothiophene-S,S-dioxide (acceptor), with addition of bulky substituents in donor, acceptor or in both units. Luminescence may vary from an efficient TADF to RT phosphorescence, as consequence to this side groups.The experimental works comprises the time resolved measurements, performed in solution, as well as in solid state, inert matrix, in function of temperature, e.g. time resolved spectra and photo induced absorption. The basics photophysics were also performed, in order to fully explore its potential.

Key Words: TADF, small molecules, RT Phosphorescence

Correspondence: South Road, Department of Physics, Durham University, Durham, DH1 3LE, UK

r.s.nobuyasu@durham.ac.uk

SG11 (P32) - Development of chemiluminescent probes for enzymatic detection

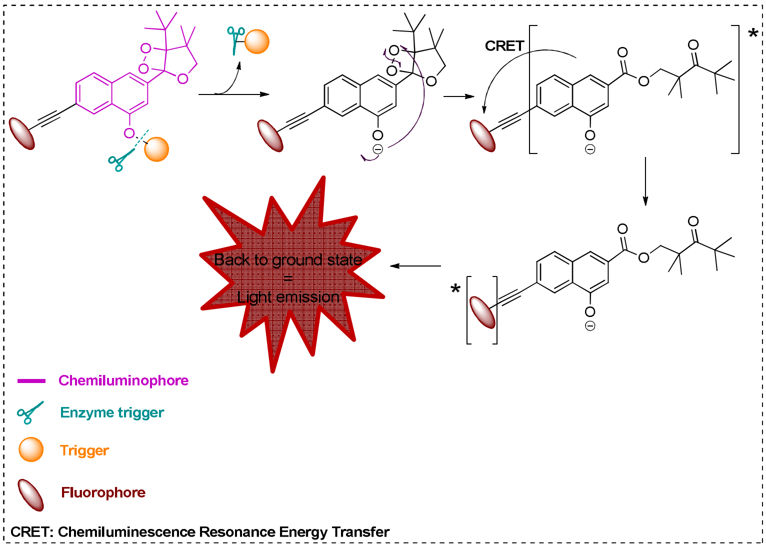
Solmont K[1], Grandclaude V., Haefelé A[1], Renard P.Y. [1]
Laboratoire COBRA UMR 6014, 1 rue Lucien Tesnieres 76130 Mont Saint Aignan
kathleen.solmont@etu.univ-rouen.fr

Abstract

Since several years, it is easier to exploit cellular phenomena through technologies dealing with bioimaging.[1]This method gathers fluorescence, bioluminescence and chemiluminescence (CL).

CL is a phenomenon that can be employed to avoid biological autofluorescence *in cellulo* and *in vivo* imaging, thus improving the sensibility of fluorescent probes. 1,2-dioxetane[2] is one of the moieties that, upon decomposition, can generate an excited state on a connected fluorophore, giving rise to its intrinsic luminescence.

The aim of our project is to develop new chemiluminescent probes for *in cellulo* and *in vivo* bioimaging. We first obtained chemiluminescent coumarins by direct grafting of 1,2-dioxetane moieties.[3] To further shift the luminescence to longer wavelengths, we elaborated a chemiluminescent platform with which we observed NIR chemiluminescence by connecting Nile Red fluorophore. A water-soluble version of this platform is already under development for *in vivo* bioimaging application. Furthermore, this chemiluminescent platform allows us to graft any fluorophore (different emission wavelengths) and different trigger moieties. Thus chemiluminescent multiplexing could be envisaged.



Keywords: 1,2-dioxetane, chemiluminescence, CRET, enzymatic probe

(1) Yao, J.; Yang, Y.; Duan, Y. *Chem. Rev* 2014., *114*, 6130-6178

(2) Matsumoto, M.; Watanabe, N.; Hoshiya, N.; Ijuin, H. K. *Chem. Rec.* 2008, *8*, 213-228.

(3) Koči, J.;Grandclaude, V.; Massonneau, M.; Richard, J.-A.; Romieu, A.; Renard, P.-Y. *Chem. Commun.* 2011, *47*, 6713-6715.

SG12 (P33) - Development of caspase-3 activatable probe for dual optical-nuclear imaging.

Morgane DETRAZ[1], Alexandre HAEFELÉ[1], Pierre-Yves RENARD[1], Pierre BOHN[2]
[1]*Normandie Univ, COBRA, UMR 6014 & FR 3038; Univ Rouen - Normandie ; INSA Rouen;*
CNRS, 1 rue Tesnière 76821 Mont-Saint-Aignan, Cedex
[2]*Centre Henri Becquerel, Rue d'Amiens, CS11516, 76038 Rouen Cedex1, France*

Abstract

The development of *in vivo* imaging agents of cellular events has grown significantly.

Imaging apoptosis, or programmed cell death, is particularly interesting because apoptosis deregulation is involved in many diseases. For instance, inhibition of apoptotic program is a hallmark of cancer which leads to an anarchic development of cells.

The aim of this project is the synthesis and development of a dual optical/nuclear probe to monitor the apoptotic activity targeting a key mediator of this process. This multi-modal strategy has been chosen to combine high sensitivity and resolution of different non-invasive imaging techniques.

An important family of intracellular proteases called CASPASE (Cysteine-dependent ASPartate-directed proteASE) plays a critical role in the apoptotic event, especially caspase-3.

The designed probe is based on a cell permeant peptidic backbone whose sequence is specifically recognized and cleaved by caspase-3, our target enzyme.

The first modality is a FRET-based probe, including a fluorescent dye (cyanine) and an efficient quencher dye. Moreover, the second modality will consist of chelation of a radionuclide (^{99m}Tm)[2] for SPECT (Single Photon Emission Computed Tomography) imaging. Once cleaved by the enzyme, this radiolabelled moiety of the probe is designed so as to accumulate inside cells.

The synthesis of the probe will be presented and *in vitro* characterizations will be discussed.

Key Words: OFF/ON fluorescent probe, dual optical/nuclear imaging, apoptosis, caspase-3

Correspondence: [1]morgane.detraz@etu.univ-rouen.fr

SG13 (P34) - An Investigation on the Effect of Deuteration on the Photophysics of TADF Molecules

Rongjuan Huang,[1] Jonathan Ward,[2] Paloma L. dos Santos,[1] Martin Bryce,[2] Fernando B. Dias[1]

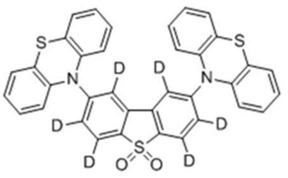
[1]*Physics Department. Durham University. Durham, South Road DH1 3LE. UK*

[2]*Chemistry Department. Durham University. Durham, South Road DH1 3LE. UK.*

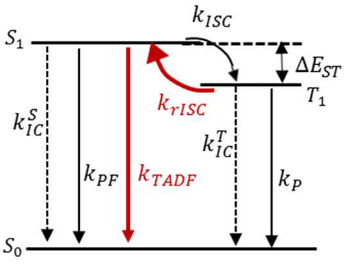
rongjuan.huang@durham.ac.uk

Abstract

Thermally activated delayed fluorescence (TADF), also known as E-type delayed fluorescence, was first reported by Perrin in 1929, and by G. Lewis in 1941, and later in 1961, by Parker and Hatchard in the study of eosin and benzyl solutions. This relatively well known mechanism was recovered recently by C. Adachi for application in organic light emitting diodes (OLEDs), as a way to harvest non-emissive triplet excited states. The singlet production yield from direct charge recombination in OLEDs is limited to 25%, the remaining 75% of charge recombination events give origin to triplet states that are not emissive at room temperature. This represents a major loss mechanism in the efficiency of OLEDs, and different mechanism have been attempted to solve this problem. TADF based OLEDs are now routinely fabricated with efficiencies close to 100% in the green region. However, devices with similar efficiency are difficult to fabricate for emission in the blue and red regions. Blue and red TADF emitters have specific requirements that make their design more difficult. In particular, red emitters are strongly affected by internal conversion (IC) due to their low energy singlet and triplet excited states. Here, we report the photophysics of TADF in $(\text{DPTZ-DBTO2})_d$, a TADF emitter formed by two phenothiazine moieties, as the electron donor units, and a deuterated dibenzothiophene-S,S-dioxide acceptor, see scheme 1. Strong TADF is obtained in solution and solid media with the deuterated compound, showing a significant increase on the TADF efficiency, when compared to its non-deuterated counterpart, which indicates that suppression of IC by deuteration of the acceptor unit is an efficient strategy to facilitate rISC.



$(\text{DPTZ-DBTO2})_d$



Key Words: TADF; reverse intersystem crossing; internal conversion; OLEDs

References :

[1]- Fernando B. Dias et al., Triplet harvesting with 100% efficiency by way of thermally activated delayed fluorescence in charge transfer OLED emitters. *Adv. Mater.* 2013, 25,3707.

[2]-Fernando B. Dias et al., The Role of Local Triplet Excited States and D-A Relative Orientation in Thermally Activated Delayed Fluorescence: Photophysics and Devices, *Adv. Sci.* 2016, 1600080.

SG14 (P35) - Role of triplet exciton diffusion in light-upconverting polymer glasses

Steponas Raišys,[1] Karolis Kazlauskas,[1] Saulius Juršėnas, [1] Yoan C. Simon[2,3]

1. Institute of Applied Research, Vilnius University, Saulėtekio 3, LT-10222 Vilnius, Lithuania.

2. Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland.

3. School of Polymers and High Performance Materials, the University of Southern Mississippi, 118 College Dr., Hattiesburg, MS 39406, USA.

Abstract

Purpose: Light upconversion (UC) implemented *via* triplet-triplet annihilation (TTA) in organic materials attracted much attention due to its low power densities of incoherent excitation required for upconversion processes to perform, as well as manufacturing advantages of organic materials enabling fast and large area production. The efficiencies of UC (ΦUC) in solutions or liquid medium exceed 30%, but for the practical applications solid state materials are preferred, which, in fact, exhibits one order of magnitude lower ΦUC. Often, the efficiency decrease of the solid films as compared to solutions is explained by insufficient triplet exciton diffusion in solid state. However, to fully address the problems of low UC efficiency in solid upconverting films systematic study of triplet exciton diffusion in these films are needed.

Experimental description: Triplet exciton diffusion (*L*D) in the poly(methyl methacrylate) (PMMA) films containing 9,10-diphenylanthracene (DPA) as an emitter and platinum octaethylporphyrin (PtOEP) as a triplet exciton sensitizer was investigated. The films were prepared by melt-processing technique for suppressing emitter aggregation at high concentrations. The determination of exciton diffusion was based on the evaluation of emission quenching efficiency in the DPA:PtOEP:PMMA films with randomly distributed quenchers. Stern-Volmer formalism was applied to quantitatively model excited state relaxation dynamics in DPA:PtOEP:PMMA / quencher blends with increasing quencher concentration (0 – 2 wt%) for the evaluation of *L*D.

Results: Quantum efficiency measurements for the upconversion performed as a function of emitter concentration revealed optimal DPA concentration (25%), which is necessary to achieve maximal upconversion efficiency (~1%) in the solid DPA:PtOEP:PMMA films. An increase of *L*D from 22 nm up to 60 nm with increasing DPA concentration was observed.

Conclusions: The increase of DPA concentration in PMMA:DPA:PtOEP films causes enhancement of triplet *L*D, but not ΦUC, which rapidly degrades above 25 wt% of DPA. This finding clearly implies the triplet exciton diffusion to be the non-governing loss mechanism of UC efficiency and points to alternate loss channel, which is associated with nonradiative decay of triplet excitons in DPA.

Key Words: Triplet-Triplet annihilation, sensitized light upconversion, triplet exciton diffusion, exciton diffusion length, platinum octaethylporphyrin, diphenylanthracene.

Acknowledgements: Lithuanian Science Council is thanked for mobility scholarship.

Correspondence: steponas.raisys@tmi.vu.lt

SG15 (P36) - Harnessing Excited State Proton Transfer in liquid and solid protic media

Illia E. Serdiuk[1], Alexander D. Roshal,[2] Jerzy Błażejowski,[1] Milena Reszka,[1] Beata Liberek,[1] Anna Synak,[3] Piotr Bojarski[3]

Faculty of Chemistry, University of Gdańsk, 63 Wita Stwosza st., 80-308 Gdańsk, Poland.

Institute of Chemistry, V. N. Karazin Kharkiv National University, 4 Svoboda sq., 61022 Kharkiv, Ukraine.

Faculty of Mathematics, Physics and Informatics, University of Gdańsk, 57 Wita Stwosza st., 80-308 Gdańsk, Poland.

Abstract

Purpose: Fluorophores which suffer tautomerization via intramolecular proton transfer in the excited state (ESIPT) are characterized by abnormally high Stokes shift values (difference between the absorption and fluorescence bands maxima) and thus their emission is unaffected by the self-reabsorption effect and generally much less susceptible to light dispersion in the samples of high turbidity. Such compounds serve as useful tools for biophysical and medico-chemical investigations, and have been widely explored in the role of main components for various solid-state optoelectronic and photovoltaic devices. Due to susceptibility of proton-transfer reactions to the internal H-bonding, fluorescence intensity of the ESIPT fluorophores is much lower in the presence of protic solvents or in protic media. This phenomenon limits substantially the range of applicability of the ESIPT fluorophores and causes low reproducibility under humid conditions. Taking into account high applicative interest in the ESIPT fluorophores, we focused our attention on ways of enhancement of their fluorescence intensity in aqueous solutions and protic polymers. Various novel and already known hydroxyflavones (hydroxy-2-phenyl-4*H*-chromen-4-ones) participating in proton-transfer transformations were selected as objects for investigations.

Experimental description: The hydroxyflavones were obtained according to the known synthetic routines including oxidative intramolecular condensation of chalcone derivatives. Investigations of physico-chemical properties of compounds involved steady-state absorption and fluorescence, time-resolved fluorescence measurements in solutions and polymer films, titrations and quantum-chemical calculations on the DFT/TD DFT levels of theory.

Results: Flavone derivatives containing hydroxyl groups at various positions and substituents enabling ESIPT and/or energies of the electronic transitions were synthesized. The conclusions on origin of fluorescent features and excited-state transformations of the compounds were drawn on the basis of the experimentally obtained data on their spectral and acid-base features, and computationally predicted thermodynamic parameters. To achieve the enhancement of dual-fluorescence intensity the compounds were investigated (*i*) in solutions in the presence of albumins, which formed non-covalent complexes with the hydroxyflavones and (*ii*) in thin polyvinyl alcohol (PVA) films on the plasmonic platforms containing silver nanoparticles. In all the cases, more than a tenfold increase of emission intensity was observed together with rise of the ESIPT efficiency.

Conclusions: The utilized methods of emission enhancement represent promising solution for the problem of low fluorescence quantum yields of the ESIPT fluorophores in protic media. The results can be interesting from the point of view of possible applications of the ESIPT phenomenon, improvements of fluorescence measurements, synthesis, spectral features and photochemical processes occurring in fluorophores.

Key Words: excited state proton transfer, flavones, albumin, surface-plasmon enhanced emission.

Acknowledgements: The research was financed by the Polish National Science Centre (NCN) under Grants No. 2014/13/N/ST4/04105 and 2015/17/B/ST5/03143.

Correspondence: Faculty of Chemistry, University of Gdańsk, 63 Wita Stwosza st., 80-308 Gdańsk, Poland. Email: illia.serdiuk@gmail.com

SG16 (P37) - Thermochromic behaviors and morphologies of polydiacetylene assemblies prepared from diamidodiacetylene monomer: Effect of solvent and monomer

Chanita Khanantong[1], Nipaphat Charoenthai[1]*, Sumrit Wacharasindhu[2], Mongkol Sukwattanasinitt[2], Rakchart Traiphol[3*]

Laboratory of Advanced Polymers and Nanomaterials, Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand.

Organic Synthesis Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University,Bangkok 10330, Thailand

Materials Science and Engineering Program, Faculty of Science, Mahidol University, Bangkok 10400,Thailand

Abstract

In this study, we investigate thermochromic behaviors and morphologies of polydiacetylene(PDA) assemblies, prepared from two types of diamidodiacetylene monomers, by utilizing various techniques including UV/vis absorption spectroscopy, X-ray diffraction, differential scanning calorimetry(DSC) and scanning electron microscopy. Structures of PDA assemblies are modified by varying length of alkyl linkers, which are ethyl and hexyl, between the diamide groups.1 Different solvents including water, butanol and decane are used as media. We have found that the change of solvent media significantly affects the morphologies of PDA assemblies. The use of water provides the PDA assemblies with irregular shape while the sheet–like structure is obtained from the systems of butanol and decane. The interlamellar d-spacing of PDA assemblies also varies with type of solvent media, indicating the difference of molecular arrangement. DSC study detects the variation of phase transition temperature. When the PDA assemblies are prepared in butanol or decane, the color-transition temperature is higher compared to the aqueous system. The increase of alkyl linker length also causes the increase of color-transition temperature.

Key Words: polydiacetylene, thermochromic, color transition, nano-sensor

Acknowledgements: Faculty of Science, Naresuan University

Correspondence: nipaphatc@nu.ac.th, rakchart.tra@mahidol.ac.th

Poster Presentations

P 1 - Kinetic study of organic dye photodegradation over ZnO-Ag nanoparticles – polymer films using fluorescence spectroscopy.

Emil C. Buruiana, Viorica Podasca, Tinca Buruiana

Petru Poni Institute of Macromolecular Chemistry, 41 A Gr.Ghica Voda Alley, 700487 Iasi, Romania.

Abstract

Purpose: evaluation of the photodegradation of methylene blue (MB) by the thin hybrid films based on novel polymer/ ZnO-Ag nanocomposites under UV and visible light irradiation using fluorescence measurements

Experimental description: hybrid polymer composites incorporating preformed ZnO (5-15 nm) and Ag (~3 nm) nanoparticles created during UV irradiation of some urethane acrylic monomers including trietoxysilylpropyl carbamoyloxyethyl methacrylate were obtained in presence of Irgacure 819 using a Hg-Xe lamp of 365 nm and light intensity of 40 mW/cm^2; the changes in fluorescence and UV/vis spectra of MB dye by hybrid films under UV/visible light exposure for different times were monitored.

Results: it was found that the composite films containing ZnO-Ag nanoparticles placed in ethanol induced the photodecomposition of MB (over 90%) under 2 min of UV (2.7x10^{-2} s^{-1}) and 25 min of visible irradiation (k = 2.9 x 10^{-2} min^{-1}), the degradation rate of MB with UV irradiation being higher than that with visible light illumination; if the films are in water, the photodegradation of MB was about 87% after 100 min of visible irradiation; the decrease of the emission and absorption band intensities of the dye in ethanol solution (1.5 x 10^{-5} M) sustains a fast degradation in presence of hybrid composite tested as photocatalyst, the fluorescence measurements showing that the fluorescence intensity of MB at 685 nm decreased at 95 %, confirming the photodegradation of MB.

Conclusions: the good efficiency of the NPs from the hybrid polymer films make them attractive for applications in photocatalysis of organic dye molecules.

Key Words: nanocomposites, photopolymerization, silver/ZnO nanoparticles, methylene blue decomposition, UV/visible irradiation

Acknowledgements: the authors acknowledge the financial support of the CNCSIS-UEFISCDI through the project PN-II-ID-PCE-2011-3-0164 (Nr. 40/5.10.2011).

Correspondence: Petru Poni Institute of Macromolecular Chemistry, 41 A Gr.Ghica Voda Alley, 700487 Iasi, Romania;

e-mail: emilbur@icmpp.ro

P 2 - Effect of fluorescence probe on the photobehaviour of some photopolymerizable compositions containing graphene.

Anton Airinei[1], Tinca Buruiana[1], Andreea Chibac[1], George Epurescu[2], Ioana Ion[3], Emil Buruiana[1]

1. Petru Poni Institute of Macromolecular Chemistry, 41 A Grigore Ghica Voda Alley 700487 Iasi, Romania.
2. National Institute for Lasers, Plasma and Radiation Physics, Atomistilor 409, 077125 Bucharest-Magurele, Romania.
3. National Institute for Research and Development in Electrical EngineeringICPE-CA, Splaiul Unirii no.313, sector 3, Bucharest, Romania.

Abstract

Purpose: to monitor the photopolymerization of urethane dimethacrylates in combination with graphene by means of the fluorescence of pyrene methacrylate present in formulation upon exposute to UV/ laser irradiation.

Experimental description: hybrid formulations incorporating oligodimethacrylates, graphene and a fluorescent monomer were irradiated with UV light or femtosecond laser beam to achieve fluorescent hybrid composites.

Results: the photopolymerization of monomer compositions with and without graphene investigated by photo-DSC, FT-IR and fluorescence methods revealed a good photoreactivity of the monomers besides 0.5% filler (65-77% conversion) after 1 minute of irradiation; the response of the pyrene's emission to changes in its environment during photopolymerization of the viscous monomer mixture up to a hard polymeric network, is affected by the mobility of the molecules/molecular chains from the medium; two-photon photopolymerization of some formulations in presence/absence of graphene nanosheets (0.1 wt.%) generated 2D microstructures by direct laser writing procedure.

Conclusions: the fluorescent monomer is suitable for monitoring photopolymerization of some urethane dimethacrylates in presence of graphene.

Key Words: graphene-polymer composites, photocuring/two photon polymerization, fluorescent probe

Acknowledgements: this work was supported by CNCSIS-UEFISCDI, project number PN-I-PT-PCCA-2011-3.1-1422.

Correspondence: Petru Poni Institute of Macromolecular Chemistry, 41 A Gr.Ghica Voda Alley, 700487 Iasi, Romania; e-mail: airineia@icmpp.ro.

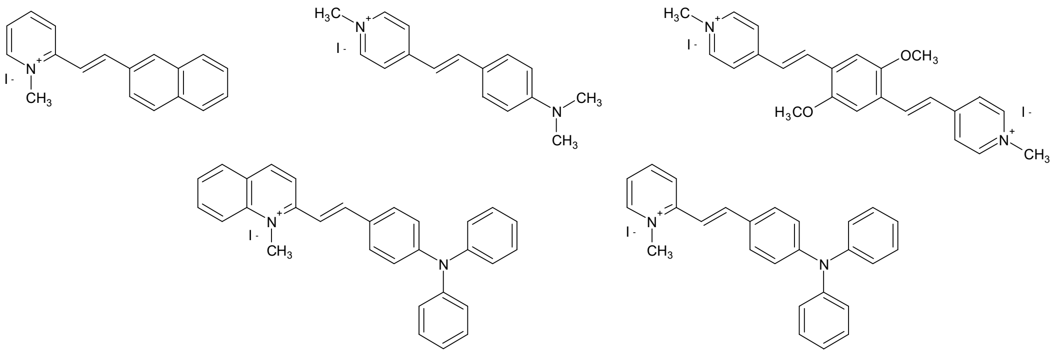
P 3 - Photophysics of methyl-pyridinium and methyl-quinolinium salts in the presence of biological targets.

Valentina Botti[1], Alessandra Mazzoli[1], Lorena Urbanelli[2], Cosimo G. Fortuna[3], Fausto Elisei[1]
Department of Chemistry, Biology and Biotechnology and Centro di Eccellenza sui Materiali Innovativi Nanostrutturati (CEMIN), University of Perugia, via Elce di Sotto 8, 06123 Perugia, Italy.
Department of Chemistry, Biology and Biotechnology, University of Perugia, via del Giochetto, 06126 Perugia, Italy.
Department of Chemical Sciences, University of Catania, viale Andrea Doria 6, 95125 Catania, Italy.

Abstract

Purpose: Photophysical description of methyl-pyridinium and methyl-quinolinium derivatives in aqueous solution before and after complexation with nucleic acids and their uptake by tumor cell lines MCF7.

Experimental description: The spectral and kinetic properties of some styryl-azinium iodides (structures in figure) have been investigated in the absence and in the presence of DNA, RNA and in breast cancer cells MCF7. The efficiency of their interaction with nucleic acids has been quantified in terms of the association constant by spectrophotometric and fluorimetric titrations. Steady-state techniques have been used to determine the quantum yields for the relaxation processes, and ultrafast time-resolved methods (transient absorption and emission) allowed the dynamics of the substrate and the substrate-nucleic acid complexes to be investigated. In vitro measurements of confocal fluorescence microscopy have been carried out in order to locate the cellular compartments where these substrates accumulate once uptaken.



Results: An overall steady and time-resolved spectroscopic characterization of the lowest electronic excited states of the examined compounds has been achieved and their association constants have been found to belong in the 10^3-10^6 M^{-1} range. As a result of the up-taking process, it was possible to ascertain that these substrates have a particular affinity for RNA-rich sub-cellular compartments.

Conclusions: The subject compounds have shown interesting features required to potential anticancer drugs and helped to improve our understanding of the structure-properties relations.

Key Words: photophysics of styryl-azinium iodides, nucleic acid-ligand interaction, confocal fluorescence microscopy, MCF7, RNA binding

Acknowledgements: The authors thank the University of Perugia (Basic Research Project 2015 and 2016) and the Fondazione Cassa di Risparmio di Perugia Grant (no.2016-0050.021) for financial support.Correspondence: valentina.botti@studenti.unipg.it.

P 4 - Facile Access to Reduced Carbon Dots with Superior Luminescence Properties

[1] Zhengyu Yan, [1] Jiao Chen, [1] Juan Shu, [1] An Xiao, Jianqiu Chen[1*]
1. School of science, China Pharmaceutical University, Nanjing 210009, China.

Abstract

Purpose: To establish a facile, expedient and environmental approach for preparing reduced carbon dots (rCDs).

Experimental description: Briefly, starch as carbon source was heated under refluxing in acetic acid and hydrogen peroxide to generate original carbon dots. Then rCDs were obtained through the reduction reaction between sodium borohydride and original CDs. Additionally, chemiluminescence behavior based on the interaction between metal ions and [NBS-rCDs(OH-)-H2O] system was briefly investigated.

Results: The high-quality rCDs exhibited excellent water solubility, good photostability, small size with fluorescence (QY: 12.4%). Moreover, Preliminary investigation showed that the CL intensity of [NBS-rCDs (OH-)- H2O] system can be significantly increased by cobalt ions.

Conclusions: It may provide reference value to extend applications of carbon dots to detect metal ions.

Key Words: reduced carbon dots (rCDs), preparation, optical properties

Correspondence: Jianqiu Chen: Department of Analytical Chemistry, China Pharmaceutical University, Nanjing 210009, China, Tel.: + 86 25 86185190, Fax: + 86 25 86185190. E-mail address: cjqercarbon@yeah.net

Participant：Jiao Chen, email: Chenj_cpu@163.com

P 5 - The Application of BODIPY Fluorophores to Cell Imaging and Metal Ion Sensing

Ciarán Dolan,[1] Aaron Martin,[1] Aisling Byrne,[1] Roisin Moriarty[1] and Tia E. Keyes.[1]

[1] *School of Chemical Sciences and National Centre for Sensor Research, Dublin City University, Glasnevin, Dublin 9, Ireland.*

Corresponding authors: tia.keyes@dcu.ie and ciaran.dolan@dcu.ie

Abstract: 4,4'-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) based fluorescent dyes have been the focus of intensive research over the past number of years due to their excellent photophysical properties. Most notably these favourable properties include high fluorescent quantum yields, narrow visible absorbance and emission spectra, good solubility, high chemical stability, and good biocompatability. In this contribution we describe a range of novel BODIPY fluorophores that have been synthesised in our lab. In particular, we focus on the applications of mega-Stokes shifted,[1,2] self-referenced O_2 sensitive[3] and metal ion detecting BODIPY dyes.

Results have shown that near-infrared emitting BODIPY fluorophores (with a Stokes shift of approximately 165 nm) are effective as contrast reagents for live mammalian cells, enabled by a reduced tendency to self-quench when accumulated at high concentrations within the cells.[1] In addition, a ruthenium-BODIPY dyad is also presented which displayed a solvent switchable dual emission. Intense oxygen sensitive emission from the ruthenium(II) centre and O_2 independent emission from the BODIPY centre, are both observed in organic media (Figure 1). In aqueous media however, the BODIPY emission is reversibly switched off.[3] Finally, a series of 1,10-phenanthroline and 2,2'-bipyridine BODIPY-based sensors are described which exhibit good recognition of biologically important ions, particularly Cu^{2+} and Fe^{2+}, at relatively low (3 equiv.) metal ion concentrations. Metal binding was transduced by fluorescence intensity reduction of the probe of up to 90%.

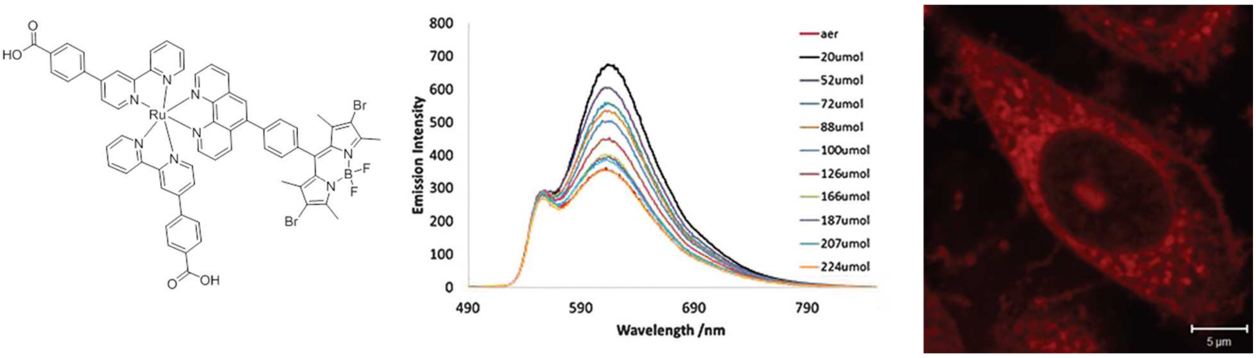


Figure 1: (Left) Schematic structure of Ru-BODIPY dyad. (Middle) Corresponding emission spectra (50 μmol concentration) in methanol as a function of O_2 concentration. (Right) Confocal image of dyad in CHO cells. Cells were incubated with 15 μM complex for 24 h.[3]

Key Words: BODIPY, cell imaging, metal ion sensor.

Acknowledgements: The authors gratefully acknowledge support of Science Foundation Ireland under Grant No. Grant No.s 10/CE/B1821, and 14/IA/2488 and The Irish Research Council for Postgraduate Scholarships.

References:

[1] R. Moriarty et al., *Journal of Microscopy (2014) 253, 204–218.*

[2] A. Martin et al., *Chem. Commun.* (2012) 48, 5617-5619.

[3] A. Martin et al., *Chem. Commun. (*2015) 51, 15839--15841.

P 6 - Spectroscopic and thermo-optical characterization of anthocyanin extracted from *Tradescantia pallida purpurea.*

Vanessa Mendes[1], Sthanley R. de Lima[1], Jaqueline O. B. Torres[1], Andrea Antunes[1], Djalmir N. Messias[1], Acácio A. Andrade[1], Noelio O. Dantas[1], Sérgio C. Zilio[1], Viviane Pilla[1]
Physics Institute. Federal University of Uberlândia-UFU. Campus Santa Mônica. 38400-902.
Uberlândia. Minas Gerais. Brazil.

Abstract

Purpose: In this work, we presented the spectroscopic and thermo-optical characterization of anthocyanin extracted from the leaves of *Tradescantia pallida purpurea.* Natural dyes derived from ornamental plants were extracted in different solvents and concentrations. Thermo-optical parameters, such as the refractive index temperature coefficients (dn/dT), thermal diffusivity values (D), fractional thermal load (φ) and quantum yield (η), were determined for anthocyanin solutions.

Experimental description: Thermo-optical characterizations were performed using mode-mismatched dual-beam thermal lens (TL) technique and conical diffraction (CD) techniques [1,2]. A He-Ne laser (λ_p= 632.8 nm) was used as the probe beam, and an Ar$^+$ laser (λ_e= 514.5 nm) was used as the excitation beam for both techniques, TL and CD. The dn/dT parameter was obtained using a commercial refractometer. Five independent samples were prepared for each solvent, and the spectroscopic results presented are average values.

Results: Fluorescence and absorption techniques were accomplished for different solvents and/or concentrations of the anthocyanin dye extracted. For anthocyanin extracted in ethanol, the potential of hydrogen pH and dn/dT values were measured in function of the concentrations. The thermo-optical techniques were applied for determination of the D, φ and η. The thermal diffusivity parameters obtained were characteristic of the solvents in which the natural dye was extracted. The η results were compared with those obtained for other dyes such as annatto, biotinylated cyanine and boron-dipyrromethene.

Conclusions: The dye fluorescence and absorbance spectra are dependent on the concentration and solvent used for the extraction of anthocyanin. The fractional thermal load and the fluorescence quantum yield were determined for anthocyanin extracted in aqueous solutions. η results were compared with those obtained for other dyes applied in biotechnology.

[1] V. Pilla, E. Munin, M. R. R. Gesualdi, J. Opt. A: Pure Appl. Opt. 11 (2009) 105201; [2] L. F. Santos, V. M. Dias, V. Pilla, A. A. Andrade, L. P. Alves, E. Munin, V. S. Monteiro, S. C. Zilio. Dyes Pigm. 110 (2014) 72-79.

Key Words: Anthocyanin; Spectroscopy; Fluorescence; Thermal Effects; Quantum Yield

Acknowledgements: The authors are thankful to the Brazilian funding agencies CNPq (Proc. 479084/2013-0; 305425/2012-9; 202553/2014-0), UFU and FAPEMIG (CEX - APQ-00360-14) for their financial support of this work.

Correspondence: Instituto de Física, Universidade Federal de Uberlândia UFU, Av. João Naves de Ávila 2121, 1X-31, Uberlândia, MG, Brazil, 38400-902. vivianepilla@infis.ufu.br

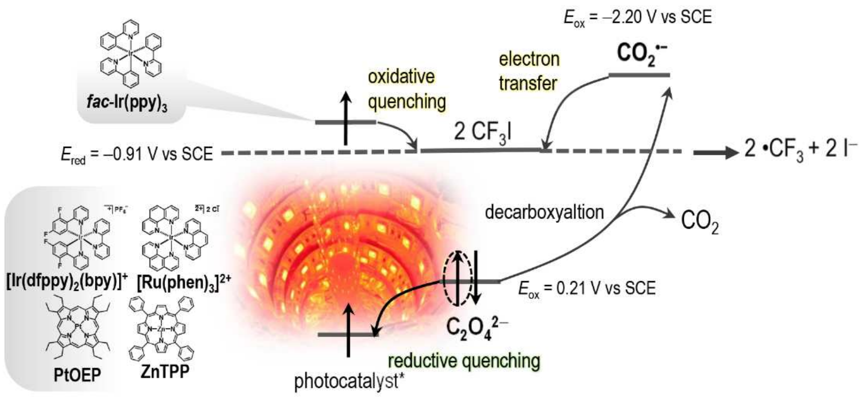
P 7 - Use of Oxalate Coreactant Enables Photoredox Catalytic Trifluoromethylation under Low-Energy Photoirradiation

Sinheui Kim,[1] Gyurim Park,[2] and Youngmin You[1*]

1. Division of Chemical Engineering and Materials Science, Ewha Womans University, Seoul 03760, Republic of Korea.

2. Department of Food Science, Ewha Womans University, Seoul 03760, Republic of Korea.

Photoredox catalysis emerges a powerful principle in radical-mediated organic transformations. Among various photoredox catalytic transformations, visible light-driven trifluoromethylation is the most representative example. The catalysis involves reductive cleavage of electrophilic precursors of trifluoromethyl radicals ($\bullet CF_3$) as the key step. Transition metal complexes involving Ru(II), Ir(III), and Pt(II) serve as the photoredox catalysts for the process. However, it is noted that high-energy photon sources, such as UV and blue LEDs, have mainly been employed in the photocatalysis. Such an energy demand is due to the thermodynamic conditions that require positive driving force (i.e., –(Gibbs free energy changes)) for electron transfer. That is, exergonic electron transfer is allowed for photoredox catalysts having the ground-state reduction potential or the excited-state oxidation potential as negative as possible. This requirement can be met using wide-bandgap catalysts, but they cannot perform photoredox catalysis under low-energy photoirradiation. Therefore, radical generation with low-energy photons has remained as a significant challenge. To address this challenge, we propose to employ an oxalate ($C_2O_4^{2-}$) coreactant as a strong, low-energy-photon-activatable electron source. Catalytic sequence is initiated by one-electron oxidation of $C_2O_4^{2-}$ upon photoirradiation of catalysts. Subsequent cleavage of the C–C bond in the one-electron-oxidized species of oxalate ($C_2O_4^{\bullet -}$) generates CO_2 and radical anion of CO_2 ($CO_2^{\bullet -}$), where the latter has the oxidation potential as negative as –2.20 V vs SCE (CH_3CN). Thus, the driving force for the reductive cleavage by electron transfer from $CO_2^{\bullet -}$ to CF_3I is predicted to be as large as 1.29 eV. Photoredox catalytic trifluoromethylation using the oxalate coreactant has been demonstrated at various conditions. In particular, we employed the low-bandgap metalloporphyrins, ZnTPP and PtOEP, as well as well-established complexes, *fac*-Ir(ppy)$_3$, [Ru(phen)$_3$]Cl$_2$, and [Ir(dfppy)$_2$(bpy)]PF$_6$, as the photoredox catalysts. Photoirradiation using green or red LEDs of the reaction mixtures furnished the desired trifluoromethylation products of terminal alkenes. Electrochemical and steady-state and transient photophysical investigations were also performed to reveal that there are two photoinduced electron-transfer pathways for the oxalate-mediated $\bullet CF_3$ generation.



Key Words: Photoredox catalysis, trifluoromethylation, radical chemistry

Correspondence: odds2@ewha.ac.kr (Y.Y.)

P 8 - Fluorescence Zinc Sensor That Exhibits pH-Independent Turn-On Responses

Jinju Kim1, Yukyung Moon1, and Youngmin You1*
1. Division of Chemical Engineering and Materials Science, Ewha Womans University, Seoul 03760, Republic of Korea.

Labile zinc is intimately associated with many pathological and physiological conditions in the human body. To investigate the zinc biology, a variety of fluorescence zinc sensors have been created to date. However, many of the previous sensors carry disadvantages due to pH-induced false signaling. We have developed a new fluorescence zinc sensor (HBO-ACR) based on a derivative of the well-established fluorophore, 2-(2'-hydroxyphenyl)benzoxazole (HBO). HBO is known to display dual fluorescence emissions due to excited-state intramolecular proton transfer (ESIPT), while intramolecular charge transfer (ICT) fluorescence, instead of ESIPT emission, is mainly observed in the biological milieu due to deprotonation. An azacrown ether receptor (ACR) was tethered to HBO through a methylene linker to provoke zinc-induced fluorescence signaling. HBO-ACR exhibits one order of magnitude enhancement in fluorescence emission upon zinc binding in pH 7.4 buffers containing 25 mM PIPES and 100 mM KCl (fluorescence quantum yield = 0.023 (zinc-free), 0.23 (zinc-bound)). The zinc dissociation constant was determined to be 57 μM, which indicates loose binding. HBO-ACR possesses exceptional zinc selectivity over other competing biological metal ions, including Na, Mg, Ca, Cr, Mn, Fe, Co, and Ni, as well as Cd and Hg. Of particular interest is unaltered fluorescence intensities over a wide range of pH values (pH = 3.0–10.8). It is noted that HBO-ACR retains its ability for producing fluorescence turn-on responses to zinc ions at pH as low as 5.0. This pH tolerance is ascribed to abrogation of twisted intramolecular charge transfer (TICT) upon zinc binding. It is anticipated that such pH-independent zinc sensing properties will enable monitoring of the release, trafficking, and down-regulation of labile zinc in acidic subcellular organelles, such as lysosomes. Bioimaging utility of our probe is currently being evaluated with a variety of biospecimens.

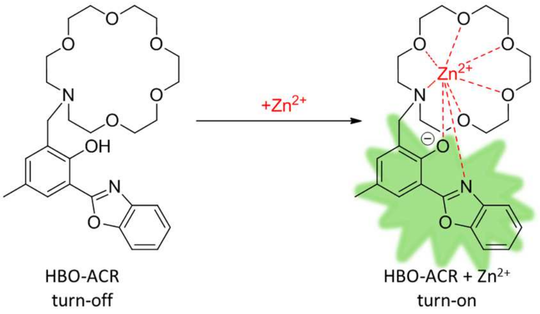


Figure 1. Fluorescence turn-on zinc response of HBO-ACR

Key Words: zinc sensor, azacrown ether, fluorescence

Acknowledgements: This work is supported by the MSIP of Korea through the GFP (CISS-2012M3A6A6054204).Correspondence: odds2@ewha.ac.kr (Y.Y.)

P 9 - A fluorescent probe for selective detection of hypochlorite in aqueous media

Peng Wei[1], Tao Yi*[1]

Department of Chemistry & Innovation Center for Energy Materials, Fudan University,
220 Handan Road, Shanghai 200433, P. R. China

Abstract

Purpose: Hypochlorite (ClO^-) which has been widely applied for disinfection also has vital importance in biology. Unregulated production of ClO^- may associated with many diseases. So we try to develop sensitive and selective fluorescent probes for accurate and precise detection of ClO^-.

Results: Herein, we designed and synthesized a new fluorescent probe FDClO-1, whose fluorescence intensity increased more than 2800-fold when treated with only 2.5 equiv of ClO^- at 690 nm in PBS (10 mM, pH 7.2, 0.1% CH_3CH_2OH) solution. Meanwhile, other ROS/RNS (H_2O_2, $NO^\bullet$, O_2^-, $^\bullet OH$, $ROO^\bullet$, t-BuOOH, t-$BuOO^\bullet$, $ONOO^-$) of different concentrations could not induce measurable increase of fluorescence intensity. Further investigation is still ongoing.

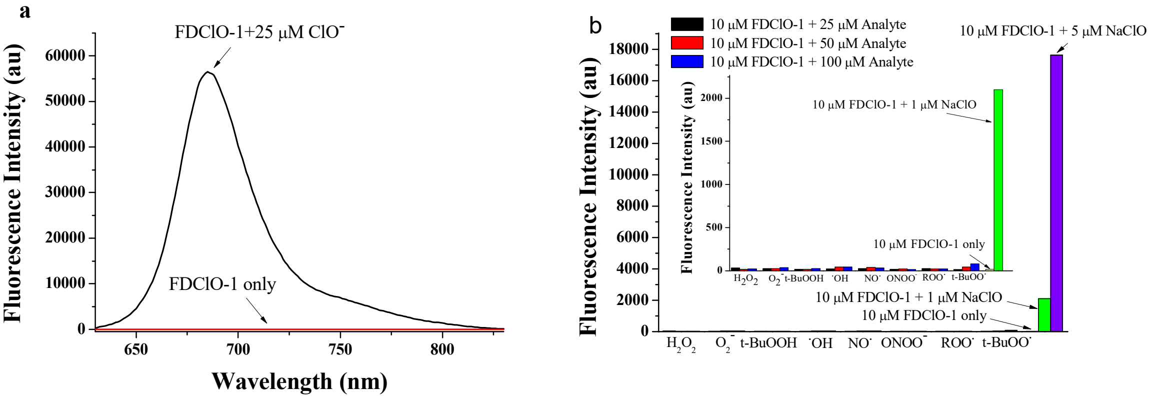


Fig.1 Fluorescence spectra of FDClO-1 responding to NaClO in PBS (10 mM, pH 7.2, 0.1% CH_3CH_2OH) solution. (a) The emission spectra of FDClO-1 (10 μM) before/after adding 25 μM NaClO with an excitation at 620 nm. (b) Fluorescence intensity of FDClO-1 at 686 nm after treated with various ROS/RNS with an excitation at 620 nm.

Conclusions: We have successfully developed a new near-infrared fluorescent probe FDClO-1, whose fluorescence intensity has a tremendous increase when treated with NaClO. While other ROS/RNS of different concentrations could not induce measurable increase of fluorescence intensity. Due to the advantages of this probe we believe that this probe provides a promising tool for ClO^- imaging.

Key Words: Fluorescent probe; Hypochlorite; Detection; Near-Infrared

Acknowledgements: The authors are thankful for the financial support of 973 (2013CB733700), NNSFC (51373039**).****Correspondence:** Fudan University, 220 Handan Road, Shanghai 200433, P. R. China. E-mail: yitao@fudan.edu.cn

P10 - Aggregation-Induced Emission (AIE) Active Poly(Acrylate) Polymers for Explosive Detection

Ming Hui Chua[1,2], Hui Zhou,[1] Jishan Wu,[1,2] Jian Wei Xu, [1,2]
*Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR). 3 Research Link, Singapore, 117602*
Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543

Abstract

Purpose: Novel poly(acrylate) polymers with aggregation-induced emission (AIE) properties were developed for the purpose of nitro-aromatics explosives detection.

Experimental description: The structural design of these polymers involve different AIE-active moieties attached to polymer backbone via long pendant alkyl chains. Preliminary investigation of its explosive-detecting properties were first performed with the polymers solutions in nano-aggregates form, where quenching of fluorescence was observed by exposure to explosives. Polymer-coated paper probes were then prepared and used to for the detection of nitro-aromatics explosives in both solution and solid powder form.

Results: It was found that the polymers, both as nano-aggregate solutions and subsequently paper probes, exhibit excellent performance in detection of nitro-aromatic compounds (picric acid, TNT and p-nitrotoluene) via visibly-observable fluorescence quenching. The sensitivity and selectivity towards detection of different nitro-aromatics compounds depends on the AIE-active moieties attached.

Conclusions: The positive results obtained has demonstrated the potential and effectiveness of AIE-active poly(acrylate) polymers as excellent nitro-aromatics explosive detectors. This is especially so for the development of paper-probes that may serve its real purpose for convenient on-site detection of explosives in face of terrorism threats.

Key Words: Aggregation-Induced Emission; Explosive Detection; Fluorescence; Sensors; Poly(acrylate)

Acknowledgements: The authors would like to thank the financial support from Institute of Materials Research and Engineering, A*STAR, as well as A*STAR Graduate Academy for sponsoring the presenter's participation in this conference.

Correspondence: M.H. Chua (stu-chuamh@imre.a-star.edu.sg); J.W. Xu (jw-xu@imre.a-star.edu.sg)

P11 - One-pot synthesis of gold nanoclusters with orange luminescence for cell imaging and Hg(II) sensor

Yan Zhang*, Chuan Dong, Shaomin Shuang*
Department of Chemistry, Institution of Environmental Science, Shanxi University,
Taiyuan 030006, P. R. China.

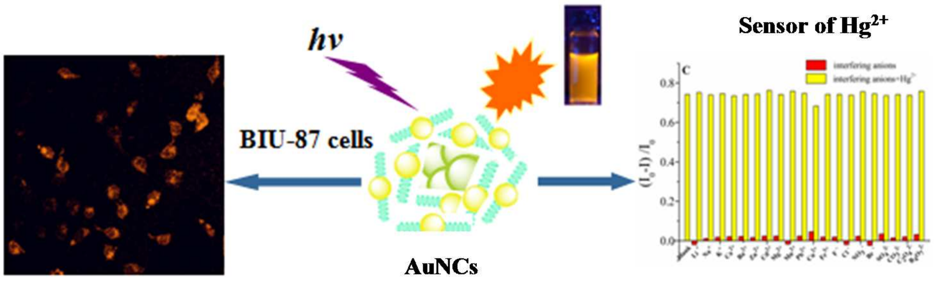
Abstract

Purpose: The drawbacks of the existing synthetic methods of gold nanoclusters (AuNCs) are that they require ether multiple/complex steps or long reaction times, or some strategy used extra assistant chemical reagent such as NaOH. We devoted to study a facile strategy to synthesize novel fluorescent gold nanoclusters in one-pot approach.

Experimental description: The AuNCs were formed by mixing the solutions of NAC and $HAuCl_4$ at 25 °C for 30 min, followed by heating to 70 °C with reflux for 24 h. An aqueous solution of strongly orange emitting AuNCs was formed. The AuNCs aqueous solution was added to BIU-87 cells cultured in DMEM, and incubation for 2 h for optical imaging. The fluorescence spectra of AuNCs containing various concentrations of Hg^{2+}were recorded for sensing Hg^{2+}.

Results: The as-prepared AuNCs exhibited a fluorescence emission at 590 nm and a quantum yield of 13.6%. The AuNCs offered ultra-small size, excellent stability, large Stokes shift and microsecond-scale lifetime. The as-synthesized AuNCs have been successfully applied as a photoluminescent probe for human bladder cancer cellular imaging. The fluorescent AuNCs offer a limit of detection of 0.2 nM and a linear response range of 2.0–3200 nM for determination of Hg^{2+} ions.

Conclusions: We have successfully developed a “green” method for the preparation of AuNCs using NAC as both a reducing and protecting agent in a facile one-pot strategy. The developed facile synthesis method is scalable and may provide a meaningful reference for the further design and application of metal nanoclusters in the fields of bioimaging, biosensing, sensing, and other applications.



Key Words: Gold nanoclusters, one-pot synthesis, Hg(II), cell imaging

Acknowledgements: Financial supports from the National Natural Science Foundation of China (21305082 and 21403135), Program for the Outstanding Innovative Teams of Higher Learning Institutions of Shanxi, Research Project Supported by Shanxi Scholarship Council of China (2014-017), Fund Program for the Scientific Activities of Selected Returned Overseas Professionals in Shanxi Province.

Correspondence: Address: Department of Chemistry and Institution of Environmental Science, Shanxi University, Taiyuan 030006, P. R. China. Email: Y. Zhang (yanzhang@sxu.edu.cn), S. Shuang (smshuang@sxu.edu.cn)

P12 - Luminescent activity of Cd (II) and Ag(I) complexes with 2,2':6',2"-terpyridine-type ligand

Aleksandra Bocian[1], Adam Gorczyński[1], Marta A. Fik[1], Damian Marcinkowski[1,2], Zbigniew Hnatejko,[1] Violetta Patroniak[1,]

Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland

Institute of Technology and Life Science, Biskupińska 67, 60-463 Poznań, Poland

Abstract

Purpose: Preparation of Cd(II) and Ag(I) complexes followed by investigation of their luminescent properties in accordance with observed structure

Experimental description: Four complexes of different Cd(II) salts with 6,6"-dimethyl-2,2':6',2"-terpyridine ligand (L) have been synthesized. 6,6"-Dimethyl-2,2':6',2"-terpyridine ligand (L) reacts in equimolar ratio with Ag(I) ions.

Results: Properties of complexes of Cd(II) have been established through spectroscopic and analytical methods. Quite high quantum yield values were obtained for the solution luminescence, despite the fact that presented compounds are 'open species' i.e. are susceptible to the effect of external environment. Filled d^{10} shell of studied cadmium(II) complexes precludes any redox activity or electron transfer processes; therefore, observed fluorescence is a result of ILCT transitions from excited states to the ground state. 6,6"-Dimethyl-2,2':6',2"-terpyridine (L) self-assembles with Ag(I) ions in the presence of different counterions to form two kinds of helical systems in the solid state. Symmetric and dissymmetric character of ligands binding was negligible in solution, nonetheless helical supramolecular architectures were found to persist in solvents used in biological studies.

Conclusions: Spectroscopic analyses prove existence of both 2:1 and 1:1 (L:Cd(II)) species in solution, with only the latter form observed in the solid state. A rare example of mixed halide species $[CdL(Cl/Br)_2]$ should also be emphasized, which exhibits ca. a magnitude lower luminescence quantum yield than its isostructural analogue $[CdLCl_2]$. Terpyridine ligand and Ag(I) ions form dinuclear double helicates which differ in terms of framework and complexity in accordance to counterions and solvent applied. Electronic absorption and emission spectra of ligand (L) and its silver(I) complexes were recorded in methanol and acetonitrile at room temperature. Investigated ligand and its complexes absorb solely in the UV region what is represented by one or two bands with λ_{max} at ca. 288 nm for (L), and 285 nm and 312 nm for the latter ones. We took advantage of their emissive character and probed their anticancer properties via confocal microscopy.

Key Words: terpyridine; cadmium complexes; self-assembly silver(I) helical complex; luminescent materials;

Acknowledgements: This research was carried out as a part of the National Science Centre – Poland project (Grant No. 2011/03/B/ST5/01036), the National Center for Research and Development –Poland (LIDER/024/391/L-5/13/NCBR/2014) and as a part of the Polish Ministry of Science and Higher Education project POWER.03.03.00-00-P001/15 "Best of the best!"

Correspondence: violapat@amu.edu.pl, abocian17@gmail.com

References: Gorczyński, A., Marcinkowski, D., Pakulski, D., Kubicki, Harrowfield, J.M., Stefankiewicz, A.R., Hnatejko, Z., Patroniak, V., 2016 Arabian J. Chem.ASAP; Fik, M.A., Gorczyński, A., Kubicki, M., Hnatejko, Z., Fedoruk-Wyszomirska, A., Wyszko, E., Giel-Pietraszuk, M., Patroniak, V., 2014. Eur. J. Med. Chem. 86, 456–468.; Hayami, S., Komatsu, Y., Shimuzu, T., Kamihata, H., Lee, Y.H., 2011. Coord. Chem. Rev. 255, 1981–1990.

P13 - Molecular switching of copper complexes with quterpyridine

Martyna Szymańska,[1] Ariel Adamski,[1] Małgorzata Osińska,[2] Zbigniew Hnatejko,[1] Teresa Łuczak,[1] Maciej Kubicki,[1] Violetta Patroniak[1]
Faculty of Chemistry, Department of Bioinorganic Chemistry, Adam Mickiewicz University, Umultowska 89B, 61-614, Poznan, Poland,
Faculty of Chemical Technology, Institute of Chemistry and Technical Electrochemistry, Poznań University of Technology, Berdychowo 3, 60-965, Poznan, Poland

Abstract

Purpose: Herein, we present luminescent and electrochemical properties of quaterpyridine complexes of copper(I) and copper(II), which can be used as molecular switches.[1]

Experimental description: The solution of a suitable copper salt in an 1:1 (v:v) mixture of methanol and acetonitrile was added to the solution of ligand L - 6,6'''-dimethyl-2,2':6',2'':6'',2'''-quaterpyridine in dichloromethane. The reactions were carried out for 24 hours with stirring at room temperature under argon atmosphere. The helicates were obtained by the reduction of the corresponding complexes of copper (II) by using the metallic copper.

Results: On the basis of luminescence we observed no absorption in the range of ~450 nm for the complexes of copper (II). After addition of metallic copper to this solutions we see emergence of bands at this area, what indicates a change in the valence of copper from II to I.

Conclusions: We received five new complexes of copper (II) and their helicates. We examined the effects of counterions such as: Cl^-, ClO^{4-}, $[Fe(NO_3)_4]^-$, BF_4^-, $CF_3SO_3^-$ on their electrochemical and luminescent properties. The CV profiles of our complexes are close to those previously recorded.[2] Counteranion $[CuCl_4]^{2-}$ the most stabilizes helicate.

Key Words: Quaterpyridine, Copper Complex, Helicates, Molecular Switch

Acknowledgements: Realized in the frame of project POWER.03.03.00-00-P001/15 "Best of the best!"

Correspondence: Adam Mickiewicz University, Faculty of Chemistry, Department of Bioinorganic Chemistry, Umultowska 89B, 61-614, Poznan, Poland, e-mail: szymanska.m93@gmail.com

[1] A. Adamski, M. Osińska, Z. Hnatejko, T. Łuczak, M. Kubicki, V. Patroniak – submitted

[2]E. C. Riesgo, Y.-Z. Hu, R. P. Thummel, *Inorg. Chem.* 2003, *42*, 6648-6654.

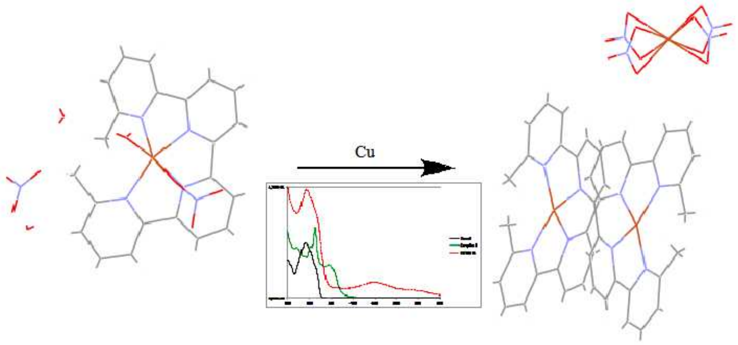


Fig.1 Crystal structures $Cu^{II}L(NO_3)_2$ (left) and $Cu^I_2L_2(NO_3)_2$ (right)

P14 - Colorimetric sensors for selective sensing and separating of cysteine

Sulkyung Kim, Hyung-il Lee*
Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea
E-mail: sims0904@ulsan.ac.kr

Abstract

Cysteine is classified as a semi-essential amino acid but often participates in enzymatic reactions and serves an important role in human body. And cysteine may be essential for infants, the elderly and someone who have certain metabolic diseases. Therefore it is very important to detect cysteine levels in the human body. Herein, polymeric probe for selective sensing and separating of cysteine by facile chemical reaction with aldehyde moieties was designed and synthesized. In this work, we prepared polymeric film by spin-coating solutions of polymer on quartz slide and exposed to UV light. This sensor detected cysteine in aqueous media and exhibited a 30 nm blue-shift in absorption maximum accompanied by color change from orange to yellow by naked eye. The selectivity toward other amino acids was achieved by amino acid analysis. After dipping polymeric film in the aqueous solution that containing other 10 amino acids, only cysteine decreased significantly. These results demonstrated that this sensor can detect and separate cysteine efficiently and selectively.

Key Words : colorimetric sensing, cysteine, polymeric film

P15 - Novel thermoresponsive polymers for the selective sensing of Cu(II) ions in aqueous media and their tunable thermosensitivities driven by copper coordinate interactione

Jae Min Bak, Hyung-il Lee*

Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea

E-mail: sims0904@ulsan.ac.kr

Abstract

We report the synthesis of novel thermoresponsive random copolymers, poly{[*N,N*-dimethylacrylamide]-*co*-[*N*-phenyl-2-(3-vinylbenzylidene)hydrazinecarbothioamide]} [p(DMA-*co*-PVHC)]. The lower critical solution temperature (LCST) of these copolymers can be tunable by the extent of copper coordinate interaction. *N,N*-dimethylacrylamide (DMA) and 3-vinylbenzaldehyde (VBA) were copolymerized to produce a series of p(DMA-*co*-VBA) copolymers by reversible addition-fragmentation chain transfer (RAFT) polymerization, using 2-dodecylsulfanylthiocarbo-nylsulfanyl-2-methylpropionic acid (DMP) as the chain transfer agent (CTA) and 2,2'-azobisisobutyronitrile (AIBN) as the initiator. After the polymerization, the resulting p(DMA-*co*-VBA) copolymers were reacted with N-phenylthiosemicarbazide to yield the target thermoresponsive polymers, [p(DMA-*co*-PVHC)). Molercular weight, molercular weight distribution, and the ratio of the final incorporation of DMA and VBA were determined by size exclusion chromatography (SEC) and ^{1}H NMR spectroscopy. The number-average molecular weight (M_n) of the resulting polymer ranged from 1.0×10^4 to 1.1×10^4 depending on the monomers ratio. The molecular weight distribution was narrow (M_w/M_n = 1.12 − 1.22). The addition of Cu(II) ions to the aqueous solution of these polymers led to the formation of Cu(II)/N-phenylthiosemicarbazone complexes. Turbidimetry by UV-Visble spectroscopy and dynamic light scattering (DLS) measurements were carried out to determine LCST values of the aqueous solutions of the copolymers with different extent of copper coordinate interaction. Results showed that the LCST could be dramatically affected by the extent of copper coordinate interaction. LCST values increased with the gradual addition of Cu(II) ions, indicating that the formation of copper coordinate interaction rendered the resulting copolymers to be more hydrophilic.

Key Words : RAFT, LCST, thermoresponsive polymer, copper ion sensor

P16 - Photophysics and OLEDs in TADF Polymers.

Roberto S. Nobuyasu[1], Z. Ren[3], P. Data[1], G. Griffiths[1], A. Monkman[1], S. Yan[3], M. Brice[2], Fernando B. Dias[1]
1. Department of Physics, Durham University, Durham, UK
2. Department of Chemistry, Durham University, Durham, UK
3. State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical
Technology, Beijing, China

Abstract

Thermally Activated Delayed Fluorescence (TADF) emerged recently as a method to harvest triplet states in pure organic materials. TADF has been used mainly in the field of organic light emitting diodes (OLEDs), as a way to enhance device efficiencies by converting non-emissive triplet states into singlet-fluorescent species. TADF has attracted great attention due to the fact that pure fluorescent OLEDs, were allowed to largely overpass their intrinsic IQE of 5%, imposed by the 25% limit on the singlet yield appearing from charge recombination. TADF devices with IQE close to 100% are now routinely fabricated to emit in the green spectral region. Notwithstanding, TADF mechanism in polymers or in solution process molecules have rarely been reported in literature, due the knotty task in confining the excited states in molecules containing many atoms. Triplet-triplet annihilation and internal conversion strongly competes with reverse intersystem crossing, and often leads to a strong quenching of TADF. Here, we present a series of copolymers with efficient TADF pendantsbased in a asymmetrical D-A molecule, using phenothiazine as the electron donor unit, and dibenzothiophene-S,S-dioxide as the acceptor, confined between styrene spacers.This study elucidates the complex photophysics of TADF in these copolymers, and adresses the role of molecular conjugation, and the energy alignment between charge transfer and localized triplet states. A complete photophysical investigation was carried out in solution and in prestine thin film, and it was complemented by teh fabrication and charactrization of devices,based on these polymers.

Key Words: TADF, copolymer, solution process, OLED

Correspondence: Department of Physics, Durham University, South Road, Durham, DH1 3LE, UK

r.s.nobuyasu@durham.ac.uk.

P17 - Novel fluorescent probe Cresyl Violet-based bearing a Histidine amino acid: Metal ion sensorial ability

Joana Coelho,[1] Elisabete Oliveira,[1,2] Hugo M. Santos,[1,2] Javier Fernandez Lodeiro, [1,2] Adrián Fernandez Lodeiro, [1,2] Susana Jorge, [1,2] Eduardo Araujo, [1,2] Jamila Djafari, [1,2] José L. Capelo,[1,2] Carlos Lodeiro.[1,2]

[1]*Bioscope group. UCIBIO-REQUIMTE, Chemistry Department. Faculty of Sciences and Technology. University NOVA of Lisbon. Campus de Caparica. 2829-516. Caparica. Portugal.*

[2]*ProteoMass Scientific Society. Madan Parque. Building VI. Office 23. Faculty of Sciences and Technology. Campus de Caparica. 2829-516. Caparica. Portugal.*

Abstract

Purpose: A new compound histidine-based containing as signalling unit the visible excitable chromophore cresyl violet was synthetized and fully characterized. Its sensorial ability in organic and aqueous media towards several metal ions was evaluated by absorption and emission spectroscopy. Histidine amino acid is well known by its affinity to Cu (II) metal ions, making this probe a very promising colorimetric and fluorimetric sensor towards this metal ion in environmental and biological media.

Experimental description: Compound L was obtained by the reaction between the cresyl violet and histidine reagents by common synthetic techniques. The photophysical studies were performed in absolute ethanol, methanol, acetonitrile, water, dichloromethane, chloroform and dimethylsulfoxide.

Compound L was titrated with Ni (II), Hg (II), Cr (III), Pb (II), Cu (II), Ca (II), K (I), Na (I), Cd (II), Co(II) in acetonitrile and absolute ethanol.

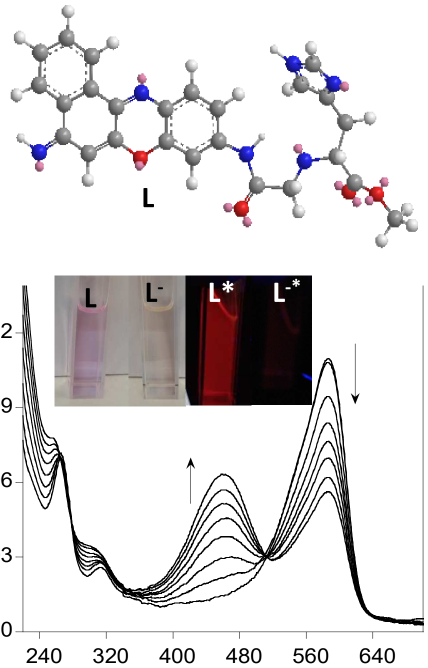


Figure 1. Above: Probe L.
Bellow: Spectrophotometric titration of L with OH-, in ACN.

Results: Probe L is pH dependant being more reactive at basic values, whereas at basic pH a naked eye change of colour (red to yellow) followed by a quenching in the emission intensity are observed. In its protonated form probe L did not show any photophysical changes towards the metal ions studied, being necessary a previous deprotonation of the system. Taking these conditions as the initial ones, upon addition of metals, is observed in all cases (except for sodium and potassium) a recovering of the initial colour and fluorescence. Moreover, in the case of copper (II) beyond the colour and emission signal recovery, a complex is formed from the third metal equivalents added. A solvatochromic behaviour was also visualized.

Conclusions: Probe L is an interesting colorimetric and fluorimetric sensor for Cu (II), being also a very promising solvatochromic system.

Key Words: Cresyl Violet, histidine, copper (II), solvatochromic studies.

Acknowledgements: We are grateful to the financial support to Scientific PROTEOMASS Association (Portugal), LAQV/REQUIMTE (UID/QUI/50006/2013) and UCIBIO/REQUIMTE (UID/Multi/04378/2013). E.O.acknowledge the post-doctoral grant SFRH/BPD/72557/2010 and to Foundation L'Oreal (UNESCO and FCT) for the Prize *For Women in Science* 2015, "Medalhas de Honra L'Oréal Portugal para as Mulheres na Ciência", healthy Sciences area.

Correspondence: BIOSCOPE Group, REQUIMTE/UCIBIO, Chemistry Department, FCT, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal. E-mail: elisabete.oliveira@bioscopegroup.org

P18 - Using the fluorescent tetracycline molecule in a one-pot synthesis of gold nanoparticles: Environmental applications in water

Jamila Djafari,[1,2] Javier Fernández-Lodeiro,[1,2] Adrián Fernández-Lodeiro,[1,2] Elisabete Oliveira,[1,2] Hugo M. Santos,[1,2] Eduardo Araujo, [1,2] Susana Jorge, [1,2] Carlos Lodeiro,[1,2] José L. Capelo[1,2]
Bioscope group. Chemistry Department. Faculty of Sciences and Technology. New University of Lisbon. Campus de Caparica. 2829-516. Caparica. Portugal.
ProteoMass Scientific Society. Madan Parque. Building VI. Office 23. Faculty of Sciences and Technology. Campus de Caparica. 2829-516. Caparica. Portugal.

Abstract

Purpose: Metallic nanoparticles exhibit many physical and chemical properties which differ with the nature of the metal, size, shape of nanoparticles and molecules used for the stabilization of the system. Furthermore, tetracycline molecule is a low fluorescence quantum yields antibiotic (protonated form) responsible for the inhibition of bacteria protein synthesis by binding to a sub ribosomal unit. By deprotonating the acidic sites of the molecule, it is possible to create a nano-system stabilized by the tetracycline charges. Continuing with our scientific interest in synthesis and application of noble metal nanomaterial as chemical sensor, we have designed a new aqueous one-pot synthesis of gold nanoparticles functionalized with the antibiotic tetracycline (AuNPs@TC). This nano-sensor can detect specifically Aluminum(III) in nanomolar range in aqueous solution.

Experimental description: AuNPs@TC were obtained by using tetracycline as reducing and stabilizing agent. For this, tetracycline deprotonation by sodium hydroxide was studied by UV and Fluorescence spectroscopies in order to determine the equivalent number of sodium hydroxide necessary to fully deprotonate tetracycline molecule and create a colloidal system stabilized by charges. AuNPs@TC were synthetized by adding a pre-heated solution of deprotonated tetracycline into aqueous $HAuCl_4.3H_2O$ solution under temperature stimulation. AuNPs@TC were analyzed by UV-vis spectroscopy, FT-IR, DLS and Transmission Electron Microscopy.

Results: Deprotonation tetracycline studies reveal that 4 equivalents of sodium hydroxide are necessary to completely deprotonate tetracycline molecule. The pink colloidal system obtained is composed by spherical nanoparticles and shows a SPR band at *ca.* 530 nm having an average size of 25 +/- 10 nm. AuNPs@TC can detect colorimetrically 200 nM of Al(III) inducing a color change from pink to blue as a result of interaction with Al(III) which produce aggregation of the colloidal system. The reversibility of this colorimetric reaction was explored adding EDTA to the solution of AuNPs@TC-Al(III) where complexation between EDTA and Al(III) cation permit the release of AuNPs@TC restoring the original pink color of the colloidal system.

Conclusions: Spectrometry studies and use of tetracycline as reducing and stabilizing agent allows the synthesis of spherical gold nanoparticles which can be used as a colorimetric selective chemical sensor of Al (III) in water. The reversibility observed permits to use the system as Al(III) extractor in environmental sample waters.

Key Words: gold nanoparticles, tetracycline, aluminum, chemosensor

Acknowledgements: E.O.,H.M.S, J.F.L. acknowledge the post-doctoral grants SFRH/BPD/72557/2010, SFRH/BPD/73997/2010, SFRH/BPD/93982/2013, respectively, and A.F.L. and J.E.A for the doctoral grants SFRH/BD/52528/2014 and SFRH/BD/109201/2015 from Fundação para a Ciência e a Tecnologia (FCT-MEC) (Portugal). J.D and S.J. thanks to Proteomass Scientific Society and UCIBIO for support. Financial supported from funds from the Scientific PROTEOMASS Association (Portugal) and LAQV/REQUIMTE (UID/QUI/50006/2013) and UCIBIO/REQUIMTE (UID/Multi/04378/2013) are acknowledged.

Correspondence: BIOSCOPE Group, REQUIMTE/UCIBIO, Chemistry Department, Faculty of Science and Technology, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal. E-mail: j.djafari@fct.unl.pt

P19 – Multifunctional Colorimetric Probe Porphyrin-based for toxic metal ions in water.

Nuno Morais[1], Sónia Pires[2], Carlos Lodeiro[1,3], M. Graça P. M. S. Neves[2], Mário M. Q. Simões[2] and Elisabete Oliveira[1,3]

1BIOSCOPE Research Group, UCIBIO-REQUIMTE, Chemistry Department, Faculty of Science and Technology, Caparica Campus, NOVA University of Lisbon, 2829-516, Caparica, Portugal.

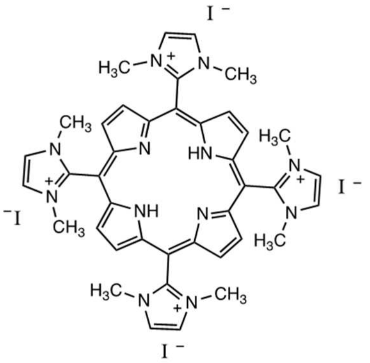
2Chemistry Department and QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal

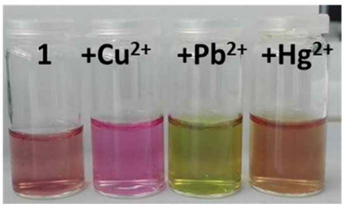
3ProteoMass Scientific Society. Madan Parque. Rua dos Inventores. 2825-182. Caparica. Portugal

Abstract

Purpose: Based on the amazing ability of porphyrin to bind metal ions, a multifunctional colorimetric sensor porphyrin-based to detect Cu^{2+}, Pb^{2+} and Hg^{2+} in aqueous solution is presented. Such binding ability comes from the size of the host cavity of the porphyrin macrocycle and the presence of NH groups in free-base porphyrins. Due to the high stability of these macrocycles, their optical and electrochemical properties, and the possibility to coordinate with different types of metal ions, these macrocycles are often integrated into functional materials or devices as fluorescent and colorimetric metal-responsive chemosensors.

Experimental description: Into an aqueous solution (1×10^{-5}M) containing compound **1**, small amounts of each metal ion (0-10 equivalents), such as Cu^{2+}, Pb^{2+} and Hg^{2+} were consequently added and measured by absorption and emission spectroscopy. To the final metal complex formed, small amount of amino acids, such as, cysteine, alanine, methionine, and phenylalanine.





Results: Addition of Cu^{2+}, Pb^{2+} and Hg^{2+} metal ions produces a quenching on the emission intensity, as well as, a colour change (see figure). Moreover, trough addition of cysteine amino acid a recovery of the emission intensity is observed in the case of Pb^{2+} and Hg^{2+} metal complex.

Conclusions: Probe **1** reveals to be a very promising colorimetric system to toxic metal ions, as Cu^{2+}, Pb^{2+} and Hg^{2+}.

Key Words: Copper (II), Mercury (II), Lead (II), Colorimetric, Fluorimetric, Cysteine, Porphyrin.

Acknowledgements: We are grateful to the financial support to Scientific PROTEOMASS Association (Portugal), LAQV/REQUIMTE (UID/QUI/50006/2013) and UCIBIO/REQUIMTE (UID/Multi/04378/2013). E.O.acknowledge the post-doctoral grant SFRH/BPD/72557/2010 and to Foundation L'Oreal (UNESCO and FCT) for the Prize *For Women in Science* 2015, "Medalhas de Honra L'Oréal Portugal para as Mulheres na Ciência", healthy Sciences area.

Correspondence: BIOSCOPE Group, REQUIMTE/UCIBIO, Chemistry Department, FCT, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal. E-mail: elisabete.oliveira@bioscopegroup.org

P20 - New Selenide and Telluride Rhodamine Spirolactam dyes as Off-On effective Fluorescent mercury(II) scavengers

Antonio A. Soares-Paulino[1], Augusto Cesar Gonçalves[1], Elisabete Oliveira[2,3], Filipe A. Almeida Paz[4], José Luis Capelo[2,3], Alcindo A. Dos Santos[1], Carlos Lodeiro[2,3]
Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, CxP. 26077, São Paulo, 05508-00, Brazil.
Bioscope group. Chemistry Department. Faculty of Sciences and Technology. New University of Lisbon. Campus de Caparica. 2829-516. Caparica. Portugal.
ProteoMass Scientific Society. Madan Parque. Building VI. Office 23. Faculty of Sciences and Technology. Campus de Caparica. 2829-516. Caparica. Portugal.
Chemistry Department and CICECO, University of Aveito, 3810-193, Aveiro (Portugal)

Abstract

Purpose: Detecting Cr(III), Al (III), Fe(III) and Hg(II) using non-destructive techniques is a challenged for many applications. Fluorescent chemosensors are non-destructive analytical tools used with this purposes. In this context, rhodamine molecules containing a chalcogen unit can be explored.

Experimental description: The synthesis of the Selenium/Tellurium containing-rhodamine ligands 1 and 2 was based on the formation of an amide, which stabilizes the molecule. Starting with commercial reactants, molecules Chalcogen Rhodamine were synthesized in few steps. AE, IR, UV-vis, NMR 1H, 13C, 77Se, 127Te, X-ray diffraction and HRMS, characterized all Compounds.

Results: The Chalcogen Rhodamine was obtained with 62-68% yield, showing good stability. In Figure 1 $MeCN/H_2O$ (75/25 v/v) compound 1 exhibited low selectivity for mercury (II) complexing with various metals - Cr (III), Fe (III), Al (III), Ag (I), Hg (I) and Hg (II). However, compound 2 showed high selectivity for Hg (II) for fast analyzes. Compounds 1 and 2 shows different stoichiometry for Hg (II) being 1:1 and 1:2 (ligand:metal) respectively. Compound 2 presented a kinetic up to 6x faster for stabilizing the emission intensity.

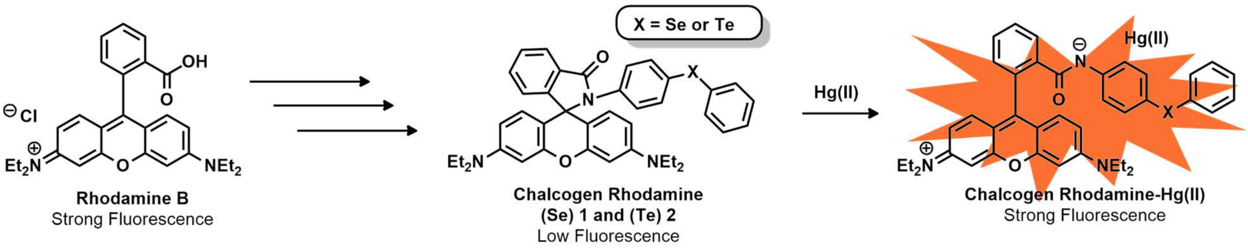


Figure 1: Synthesis of Chalcogen Rhodamine and the complexation with Hg(II).

Conclusions: Was successfully synthesized an off/on-type fluorescence chemosensor containing a rhodamine B unit. Compound 2 can be used to detect selectively Hg(II) for fast analysis in aqueous environment.

Key Words: Rhodamine, Tellurium, chemosensors, fluorescent probes and mercury (II).

Acknowledgements: We are grateful to the financial and structural support offered by the University of Sao Paulo through the NAP-CatSinQ (Research Core in Catalysis and Chemical Synthesis), FAPESP CAPES (2011/11613-8) and CNPq (401797/2013-9) for financial support. Funds from the Scientific PROTEOMASS Association (Portugal) and LAQV/REQUIMTE (UID/QUI/50006/2013) and UCIBIO/REQUIMTE (UID/Multi/04378/2013) are acknowledged.

Correspondence: BIOSCOPE Group, REQUIMTE/UCIBIO, Chemistry Department, FCT, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal. *E-mail:* antonioasp_@hotmail.com

P21 - A selective green emissive chromogenic and fluorogenic seleno-coumarin probe for Cu^{2+} detection

Augusto C. Gonçalves[1,2], José L. Capelo[2,3], Carlos Lodeiro[2,3], A. A. Dos Santos[1]

1. Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, CxP. 26077, São Paulo, 05508-000, Brazil.

2. BIOSCOPE Group, UCIBIO-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Portugal.

3. Proteomass Scientific Society, Rua dos Inventores, Madan Park, 2829-516 Caparica, Portugal.

Abstract

Purpose: The main objective of this work was to synthetize a new seleno containing fluorescent probe for Cu^{2+} detection based on the affinity between the ion and the coumarin-selenide as a ligand.

Experimental description: Absorption, stationary and time-resolved fluorescence spectroscopies were employed.

Results: The molecular probe was properly characterized, and the photophysical properties in acetonitrile, ethanol and chloroform solutions were studied. The probe spectroscopic behavior was evaluated in the presence of different metal cations (Na^+, K^+, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Hg^+, Ag^+, Al^{3+}, Fe^{3+}, Ga^{3+} and Cr^{3+}) in acetonitrile solution. Among the tested cations, the probe exhibited selective interaction with Cu^{2+}, which was evidenced by the absorption hypsocromic shift and intense chelation-enhanced fluorescent quenching (CHEQ). We performed spectrophotometric and spectrofluorimetric titrations of the probe upon the addition of Cu^{2+}. From this data, the minimal detectable and quantifiable amounts were calculated (0.2 and 0.4 μM, respectively). The ligand-Cu^{2+} complex stoichiometry was found to be 1:1, and the stability constant value observed of $\log\beta = 5.80$ (absorption data) and $\log\beta = 6.30$ (emission data). The probe is a very promising fluorescent dye to be applied in studies concerning the Cu^{2+} involvement in aprotic environments, such as cell membrane and organelle, micelle systems and to the elucidation of reactional mechanisms.

Conclusions: A new seleno derivative of coumarin-519 was synthetized and applied as a fluorescent probe for Cu^{2+} detection. The probe showed high selectivity and sensibility, with detection limits under the micromolar range. The probe displayed interesting attribute to applications in aprotic systems.

Key Words: Coumarin-519, organic selenide, copper (II).

Acknowledgements: This work was supported by the Unidade de Ciências Biomoleculares Aplicadas-UCIBIO, which is financed by national funds from FCT/MEC (UID/Multi/04378/2013), Scientific PROTEOMASS Association (Portugal), LAQV/REQUIMTE (UID/QUI/50006/2013 co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007728)). A. Gonçalves thanks to CNPq/Brazil for his PhD grant. C. Lodeiro thanks to the CNPq program, Science without borders 2014-2016 for the “Special Guest Researcher” grant (Brazil). All authors are also grateful to the financial and structural support offered by the University of São Paulo through the NAP-CatSinQ (Research Core in Catalysis and Chemical Synthesis), FAPESP and CAPES for financial support (Brazil).

Correspondence: *Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, CxP. 26077, São Paulo, 05508-000, Brazil. Email:* aucegon@gmail.com

P22 – 2,1,3-benzothiadiazole based fluorophores. Synthesis, electrochemical, thermal and photophysical characterization

Tiago Elias Allievi Frizon,[1] Julio César Valdivia Martínez,[1] Rodrigo da Costa Duarte,[2]
Eduardo Zapp,[3] Kelvin Guessi Domiciano[3], Fabiano Severo Rodembusch[2] and
Alexandre Gonçalves Dal-Bó,[1]*

1- Universidade do Extremo Sul Catarinense, Av. Universitária, 1105 - CP 3167, 88.806-000, Criciúma (SC), Brazil.

2- Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, CEP 91501-970 Porto Alegre-RS, Brazil.

3 Universidade Federal de Santa Catarina, Rodovia Jorge Lacerda, 3201 - Km 35,4 CEP 88906072. Araranguá-SC – Brazil.

Abstract

This work describes the synthesis of three photoactive compounds with π-extended conjugation based on the 2,1,3-benzothiadiazole unit through Sonogashira's coupling reactions. The electrochemical, photophysical and thermal properties of these compounds were evaluated. The compounds band-gaps of were calculated by onset peak values to be 2.370, 2.370 and 2.312 eV, respectively. Spectroelectrochemical show changes in the absorption spectra due to changes in electronic structure of the conjugated molecules. The thermal properties were analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis indicating high thermal stability with decomposition temperatures and compounds, not exhibit thermotropic mesomorphism. The compounds show absorption in the violet-blue region (~442 nm) with molar absorptivity coefficient and radiative rate constant values ascribed to spin and symmetry allowed π–π^* electronic transitions. An emission located in the green region (532-562 nm), with a large Stokes's shift (90-117 nm) was observed, probably due to charge transfer mechanism (ICT) in the excited state. A small solvathochromic effect (~6 nm) was observed in the ground state. However, a significative solvatochromism was observed in the excited state (~30 nm) probably indicating that the excited state is more polar than the ground state. The electrochemical, photophysical and thermal properties of these compounds showed properties required for materials for building electronic devices.

Key Words: 2,1,3-benzothiadiazole, photosensitive material, quadrupolar compounds, opto-electronic application.

Acknowledgements: The authors would like to thank the National Council for Scientific and Technological Development CNPq.

***Corresponding author**: Alexandre G. Dal-Bó E-mail address: (adalbo@unesc.net). Av. Universitária, 1105 - CP 3167, 88.806-000, Criciúma (SC), Brazil Tel.: +55 (48) 3431 2775.

Author Index

List of e-mails

Adrian Fernandez Lodeiro	a.lodeiro@fct.unl.pt
Alba Barrios	julialorenzorivera@gmail.com
Aleksandra Bocian	abocian17@gmail.com
Alexandre Gonçalves Dal Bo	adalbo@unesc.net
Alfons Penzkofer	alfons.penzkofer@physik.uni-regensburg.de
Amal Al Sabahi	amal3510@hotmail.com
Amparo Faustino	faustino@ua.pt
Anatoly Metelitsa	met@ipoc.sfedu.ru
André Seco	am.seco@campus.fct.unl.pt
Andrea Pucci	andrea.pucci@unipi.it
Andreia Ruivo	aruivo@gmail.com
Anne Brunelle	todd.marder@uni-wuerzburg.de
Anton Airinei	airineia@icmpp.ro
Augusto Gonçalves	aucegon@gmail.com
António Soares	antonioasp_@hotmail.com
Bamaprasad Bag	bamapbag@gmail.com
Beate Joanna Mysliwa Kurdziel	b.mysliwa-kurdziel@uj.edu.pl
Béatrice Delavaux-Nicot.	beatrice.delavaux-nicot@lcc-toulouse.fr
Bilha Fischer	bilha.fischer@biu.ac.il
Blake Peterson	brpeters@ku.edu
Camille Chauvin	Camille.CHAUVIN@CEA.FR
Carlos Lodeiro	cle@fct.unl.pt
Carolin Sieck	carolin.sieck@uni-wuerzburg.de
Carolina Abelho	c.abelho@campus.fct.unl.pt
Catarina Salgueiro	c.salgueiro@campus.fct.unl.pt
Chanita Khanantong	nipaphatc@nu.ac.th
Ciaran Dolan	ciaran.dolan@dcu.ie
Claudio Roscini	croscini@cin2.es

Cong Li	congli@fudan.edu.cn
Cristian Cuerva	c.cuerva@ucm.es
Davide Blasi	dblasi@icmab.es
Diogo Costa	dma.costa@campus.fct.unl.pt
Dong Eun-Lee	72140244@dankook.ac.kr
Elisabete Oliveira	elisabeteoliveira@bioscopegroup.org
Ella Schoolaert	Ella.Schoolaert@UGent.be
Emil Constastin Buruiana	emilbur@icmpp.ro
Erica Rosa	es.rosa@campus.fct.unl.pt
Felipe Barrios	julialorenzorivera@gmail.com
Franz-Josef Meyer-Almes	franz-josef.meyer-almes@h-da.de
Felix Zelder	felix.zelder@chem.uzh.ch
Fernando Dias	f.m.b.dias@durham.ac.uk
Franziska Merkt	Franziska.Merkt@uni-duesseldorf.de
Gabrielkla Janos	erostyak@fizika.ttk.pte.hu
Heiner Detert	detert@uni-mainz.de
Henrique Mourão	h.mourao@campus.fct.unl.pt
Hugo Santos	hmsantos@fct.unl.pt
Hyung-il Lee	sims0904@ulsam.ac.kr
Illia E. Serdiuk	illia.serdiuk@gmail.com
Ilya Taydakov	taidakov@mail.ru
Ingo Hartenbach	hartenbach@iac.uni-stuttgart.de
Ingunn Alne Hoell	ingunn.hoell@hsh.no
Ivo Piantanida	Ivo.Piantanida@irb.hr
Jae Min Bak	suning1004@naver.com
Jamila Djafari	j.djafari@fct.unl.pt
Janos Erostyak	erostyak@fizika.ttk.pte.hu
Javier Fernández-Lodeiro	javierfernandez@bioscopegroup.org
Jéssica Machado	ja.machado@campus.fct.unl.pt
Jiao Chen	chenj_cpu@163.com
Jim A Thomas	james.thomas@sheffield.ac.uk
Jinju Kim	rlawlswn27@ewhain.net
Joana Coelho	j.coelho@campus.fct.unl.pt
Joao Carlos Lima	lima@fct.unl.pt
João Sarrato	j.sarrato@campus.fct.unl.pt
Jong-In Hong	jihong@snu.ac.kr

Jorge Parola	ajp@fct.unl.pt
José Eduardo Araújo	jeduardoaraujo88@gmail.com
José Luis Capelo	jlcm@fct.unl.pt
Jou, J.-H	jjou@mx.nthu.edu.tw
Julia Lorenzo Ribera	julialorenzorivera@gmail.com
Karen De Clerck	karen.declerck@ugent.be
Katherine Hero	M.Heron@hud.ac.uk
Kathleen Solmont	kathleen.solmont@etu.univ-rouen.fr
Katsuaki Konishi	konishi@ees.hokudai.ac.jp
Kawai Tsuyoshi	tkawai@ms.naist.jp
Kyo Han Ahn	ahn@postech.ac.kr
Luca Ravotto	luca.ravotto2@unibo.it>
Lyndsay Heron	M.Heron@hud.ac.uk
Mark Heron	M.Heron@hud.ac.uk
Marta Silva	mch.silva@campus.fct.unl.pt
Martina Cacciarini	martina.cacciarini@unifi.it
Martyna Szymanska	szymanska.m93@gmail.com
Masaki Matsui	matsuim@gifu-u.ac.jp
Masayoshi HIGUCHI	HIGUCHI.Masayoshi@nims.go.jp
Mercedes Cano	mmcano@quim.ucm.es
Michael Haley	dwj@uoregon.edu; haley@uoregon.edu
Ming Hui Chua	stu-chuamh@imre.a-star.edu.sg
Mogens Brøndsted Nielsen	mbn@kiku.dk
Morgane Detraz	detraz.morgane.etudesup@live.fr
Nathaniel Finney	nfinney@tju.edu.cn
Nelsi Zaccheroni	nelsi.zaccheroni@unibo.it
Nicola Armaroli	nicola.armaroli@isof.cnr.it
Nipaphat Charoenthai	nipaphatc@nu.ac.th
Nuno Morais	n.morais@campus.fct.unl.pt
Nuno Moura	nmoura@ua.pt
Ola Soderberg	ola.soderberg@igp.uu.se
Olga Fedorova	fedorova@ineos.ac.ru
Paolo Pagano	paolo.pagano@u-bordeaux.fr
Paulo Jorge Dos Santos Coelho	pcoelho@utad.pt
Pavel Panchenko	pavel@ineos.ac.ru
Peng Wei	15110220023@fudan.edu.cn

Pier Luigi Gentili	pierluigi.gentili@unipg.it
Pierre Yves Renard	pierre-yves.renard@univ-rouen.fr
Rafaela Neves	rp.neves@campus.fct.unl.pt
Ramon Martinez Mañez	rmaez@qim.upv.es
Rebecca Moore	brpeters@ku.edu
Robert Häner	rohaener@swissonline.ch
Roberto S. Nobuyasu	r.s.nobuyasu@durham.ac.uk
Rongjuan Huang	rongjuan.huang@durham.ac.uk
Ryota Sakamoto	sakamoto@chem.s.u-tokyo.ac.jp
Sabine Strobel	hartenbach@iac.uni-stuttgart.de
Shaomin Shuang	smshuang@sxu.edu.cn
Sharmistha Dutta Choudhury	sharmisthadc@gmail.com
Simone Lenk	simone.lenk@iapp.de
Sinheui Kim	sinheui_kim@ewhain.net
Soo Young Park	parksy@snu.ac.kr
Stefanie Griesbeck	stefanie.griesbeck@uni-wuerzburg.de
Steponas Raisys	steponas.raisys@tmi.vu.it
Sulkyung Kim	ksk900623@naver.com
Susana Jorge	su.jorge@bioscopegroup.org
Sylvain Achelle	sylvain.achelle@univ-rennes1.fr
Tae-Hyuk Kwon	kwon90@unist.ac.kr
Tao Yi	yitao@fudan.edu.cn
Tia Keyes	tia.keyes@dcu.ie
Tiago Frizon	tiagofrizon@gmail.com
Tinka Buruina	emilbur@icmpp.ro
Todd B. Marder	todd.marder@uni-wuerzburg.de
Valentina Botti	valentina.botti@studenti.unipg.it
Verónica Lee Weng	leew.veronica@gmail.com
Violetta Meshkovaya	violetta.meshkovaya@yandex.ru
Viviane Pilla	vivianepilla@gmail.com
Yan Zhang	yanzhang@sxu.edu.cn
Yasuhiro Kubota	kubota@gifu-u.ac.jp
Yegor Borovkov	y.borovkov@campus.fct.unl.pt
Youngmin YOU	odds2@ewha.ac.kr
Yuan Wang	wangy@pku.edu.cn
Yuji Kubo	yujik@tmu.ac.jp

Yury Fedorov	fedorov@ineos.ac.ru