ISLS 2018 Brest

XVIII **INTERNATIONAL SYMPOSIUM**

19 > 22 June

On Luminescence Spectrometry : Fundamentals and Applications

UBO Université de Bretagne Occidentale

FACULTÉ DES SCIENCES & TECHNIQUES

OPTIMAG Optics and Magnetism Laboratory

UNIVERSITE BRETAGNE LOIRE

International Symposium on Luminescence Spectrometry history

The XVIII[th] International Symposium on Luminescence Spectrometry, is oganised in **Brest, France, from 19 to 22 June 2018,** by the OPTIMAG Laboratory.

For the past 34 years ISLS has provided an excellent framework for the presentation of new concepts, recent developments, instruments, methods, systems, and applications covering all aspects of **modern luminescence spectroscopy**.

World scientists from universities, research institutes, state organizations, and the industry come together during these meetings to present and experience the current state of the art in luminescence spectrometry.

At the same time, the conference provides the opportunity for graduate and post graduate **students to present a communication** (oral or poster), discuss scientific collaborations and explore employment opportunities.

Professor Philippe GIAMARCHI
ISLS 2018 chairman

OPTIMAG
Optics and Magnetism Laboratory

	Date	Location	Chairman
	Sept 1984	Ghent, Belgium	Prof. W.R.G. Baeyens
	May 1987	Ghent, Belgium	Prof. W.R.G. Baeyens
	May 1989	Ghent, Belgium	Prof. W.R.G. Baeyens
	May 1991	Ghent, Belgium	Prof. W.R.G. Baeyens
	May 1993	Ghent, Belgium	Prof. W.R.G. Baeyens
	June 1994	Ghent, Belgium	Prof. W.R.G. Baeyens
	April 1996	Nice, France	Prof. W.R.G. Baeyens
	May 1998	Las Palmas de G.C., Spain	Prof. J.J. Santana Rodríguez
	May 2000	Montpellier, France	Prof. D.A. Lerner
	June 2002	Granada, Spain	Prof. A.M. García Campaña
	Sept 2004	Beijing, China	Prof. X. Zhang
	July 2006	Lugi, Spain	Prof. A. Cepeda
	Sept 2008	Bologna, Italy	Prof. A. Roda
	July 2010	Prague, Czech Republic	Prof. P. Solich
	June 2012	Barcelona, Spain	Prof. M. Asuncion Alsina
	Sept 2014	Rhodes, Greece	Prof. Th. Christopoulos
	Sept 2016	Taipei, Taiwan	Prof. J.A. Lee
	June 2018	Brest, France	Prof. P. Giamarchi

Scientific topics of the conference deal with all aspects of luminescence spectrometry:

- Fluorescence
- Phosphorescence
- Chemiluminescence
- Bioluminescence
- Electroluminescence
- Thermoluminescence
- Plasmaluminescence (LIBS)
- Cathodoluminescence
- Radioluminescence

The works presented deal with:

- Fundamental research
- New concepts
- Industrial methods and applications
- Instrumentation development

In the domain of:

- Environmental and agrochemical analysis and monitoring
- Pharmaceutical and toxicological analysis
- Automated analytical systems
- Lab-on-chip
- Food control
- Luminescent nanostructures
- Luminescent complexes and metal-organic frameworks
- Luminescence imaging
- Multiphoton luminescence microscopy
- Archaeometry, luminescence dating
- Artwork diagnostics
- Biotechnological applications
- Sensors, biosensors and molecular Switches
- Labelling and detection of biomolecules
- Genomics, proteomics and metabolomics
- Luminescence and the dynamics of biological systems

Contributions from commercial organizations are encouraged, including detailed descriptions of new instrumentations, specific applications, and future commercial trends and opportunities.

OPTIMAG
Optics and Magnetism Laboratory

International scientific committee

Honorary President:

Prof. Willy R.G. Baeyens, Ghent University, Belgium.
Founder of the ILSL events in 1984

Honorary members of the scientific committee:

(important contributors to past ISLS events)

Prof. Kazuhiro Imai, Emeritus Professor of Tokyo University.
Prof. Kenichiro Nakashima, President of Nagasaki International University.

Other permanent members of the International scientific committee.

With members from **9 different countries** ensuring the scientific quality of the symposium.

NAME	INSTITUTION	COUNTRY
Aaron, J. J.	Paris 7 University	France
Alsina, M. A.	Barcelona University	Spain
Blum, L. J.	Lyon 1 University (Claude-Bernard)	France
Christopoulos, Th.	Patras University	Greece
Del Castillo, B.	Complutense University, Madrid	Spain
Della Ciana, L.	Cyanagen s.r.l., Bologna	Italy
García-Campaña, A. M.	Granada University	Spain
Giamarchi, P.	Brest University	France
Girotti, S.	Bologna University	Italy
Hamase, K.	Kyushu University	Japan
Imai, K.	Musashino University, Tokyo	Japan
Lee, J.-A.	Taipei Medical University	Taiwan
Lerner, D.	Montpellier University	France
Lin, J. M.	Tsinghua University, Beijing	China
Nakashima, K.	Nagasaki International University	Japan
Niessner, R.	Technical University of Munich	Germany
Ouyang, J.	Beijing Normal University	China
Roda, A.	Bologna University	Italy
Santana Rodriguez, J. J.	Las Palmas de Gran Canaria University	Spain
Sanz-Medel, A.	Oviedo University	Spain
Solich, P.	Charles University, Hradec Kralove	Czech Rep.
Zhang, X.	Tsinghua University, Beijing	China

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Local scientific committee

Brest University - OPTIMAG Laboratory - Spectroscopy team

- Prof. Giamarchi Philippe (Chairman)

- Prof. Yann Le Grand
- Prof. Bernard Le Leune
- Dr. Matthieu Dubreuil
- Dr. Sylvain Rivet
- Ms. Jacqueline Le Bars, administrative support

SYMPOSIUM LOCATION and BREST UNIVERSITY

Université de Bretagne Occidentale

The University of West Brittany located in Brest is a multidisciplinary university with approximately 15 000 students in its campuses.

BREST
UFR SCIENCES & TECHNIQUES

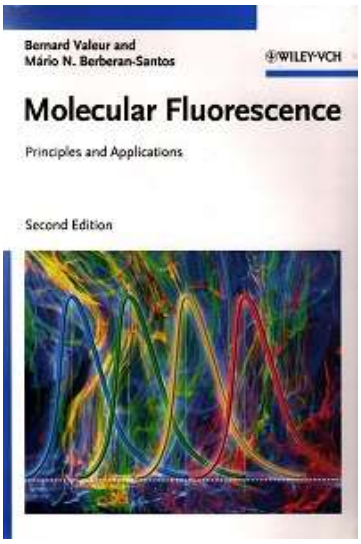
The faculty of Science and Techniques is located in city center and directly accessible by bus (line 1, stop "Universités"), welcomes the congress **ISLS 2018**.

OPTIMAG
Optics and Magnetism Laboratory

The spectroscopy team of the laboratory is specialized in laser spectroscopy and in confocal fluorescent microscopy.
OPTIMAG laboratory supports the congress **ISLS 2018** which is organized by the spectroscopy team.

Awards

The following awards has been attributed

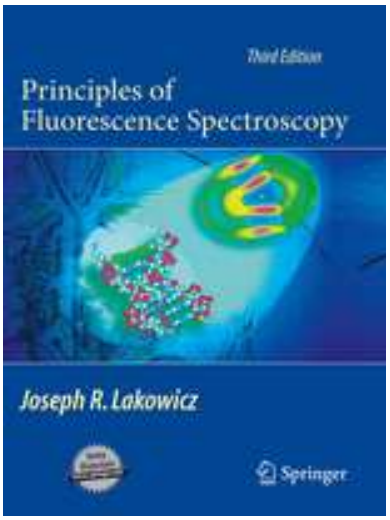


Prize of the best poster:
Chosen by all participants.

Guillaume DEMOL
ONERA / CNES

Offered by

WILEY



Prize of the best oral communication "Student or Post-doc"
Chosen by the ISLS scientific committee.

Laura GUIDORZI
University of Torino

Offered by

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Luminescence Special Issue 2019

The ISLS conference in partnership with the international journal, **Luminescence**, will edit a special issue for the Brest symposium.

All attendees are warmly invited to submit their manuscripts **before October 31st, 2018**.
Please submit your manuscript to https://mc.manuscriptcentral.com/bio
and assign it to the ISLS 2019 Special Issue.

Please note that all the manuscripts will follow the standard peer review system of this Wiley journal, and attending to the symposium does not guaranty a publication.
Editors of the Special Issue:

Prof. Philippe Giamarchi
Brest University, France

Prof. Ana M. García Campana
Granada University, Spain

Prof. Aldo Roda
Bologna University, Italy

SYMPOSIUM LOCATION : COMING TO BREST

Brest airport

Many direct flights each day from / to
- Paris Orly - Paris Roissy - Lyon - Marseille

From the airport to the city center:
- **Taxi:** about 20 min (around 25 €)
- **Bus shuttle** to the The tramway terminal, plus **tramway** to the city center: about 1 hour (around 1.5 €, one way ticket can be bought in the shuttle).

Train in the city center

High speed train connections (SNCF) from / to
- Paris Montparnasse (direct, 3h30)
- Lille (change in Rennes)
- Lyon (change in Rennes)

Direct bus between:

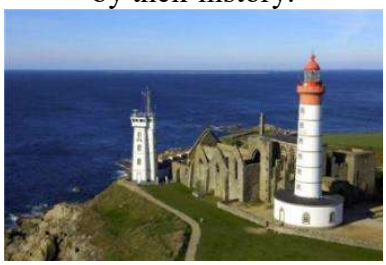
- The Science Faculty (line1, stop"Universités")
- City center (line1, stop"Liberté Place")
- SNCF train station (line1, stop"Gare SNCF")

Guided tour : THE LIGHTHOUSE ROAD.

(optional with additive registration fees)

- Departure from the science faculty in tourism bus.
- Guided tour in English to discover the lighthouses road.
- From Brest to Plouguerneau, extraordinary coastal and marine landscapes of the northern Finistère area are dotted with many lighthouses.

- We will discover the famous "**Pointe St Mathieu**". On Saint Mathieu promontory, there are not only the remains of an abbey but also a lighthouse and a modern semaphore. Even if it seems anachronistic, this site as a whole keeps its coherence as these various elements are bound together by their history.



- We will discover also **Trézien lighthouse** : Keeper of "Le Four". Located inland, 500 meters from the shore, not far from the "Cross Corsen", Trézien lighthouse is part of an impressive observation system in the Iroise Sea.

- We will stop for a walk in the typical village of **Le Conquet**.

- Then we will enjoy an **evening "castle life"** in the castle of Kergroadez.
- The tour will end with a **candlelit dinner**.

- Return to Brest in the late evening.

With "L'été évasion" Travel Agency.

A free afternoon in Brest

A seaside walk at the "Moulin Blanc" beach

- Bus number 3 direction "Océanopolis", Stop "Port de plaisance"

A visit of "Océanopolis" to explore the world's seas: http://www.oceanopolis.co.uk

- Bus number 3 direction "Océanopolis", terminus of the line.

A visit of the marine museum and the old castle of Brest to enjoy a beautiful view on Brest Harbour: http://en.musee-marine.fr/brest

- Bus number 1 direction "Fort Montbarey", Stop "Musée de la Marine".

ABSTRACTS OF ISLS 2018 SYMPOSIUM

The abstracts are sorted:

- **By topics:**
  - **Analytical development of luminescence methods** (environment analysis and monitoring, drug analysis, food analysis, ….).
  - **- Biology and medicine luminescence techniques** (biophysics, membranes study, FRET, proteomics, metabolomics,…).
  - **- New fluorescence probe and chemosensor** (synthesis, fluorescence properties, applications,…).
  - **- Imaging and microscopy luminescence developments**.
  - **- Nanomaterials and quantum dots luminescence and applications**.

- **Then by type of documents:**
  - **Oral communication**
  - **Posters**

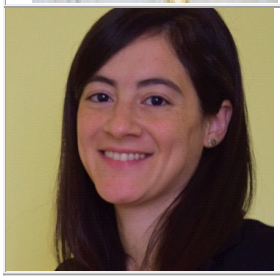
- **Then by the alphabetic order of the title of the communication.**

Poster mounting

- The number of each poster (indicated in the upper part of each billboard) corresponds to its page number.

PLENARY LECTURES

Analytical development of luminescence methods.

	**Michael SEIDEL**	**Bioanalytic & Microarray Group, Institute of Hydrochemistry, Technical University of Munich, Germany**	**Flow-based Chemiluminescence microarrays as tool for rapid detection of pathogens**
	**Bruno BOUSQUET**	**Centre Lasers Intenses et Applications (CELIA), UMR5107, University of Bordeaux, France**	**Laser-induced breakdown spectroscopy (LIBS): a review.**
	**Stefano GIROTTI**	**Dept. of Pharmacy and Biotechnology. University of Bologna, Italy**	**Chemometric analysis and bioluminescent assay combined to identify honey geographical origin and adulterations**
	**Kenji HAMASSE**	**Graduate School of Pharmaceutical Sciences, Kyushu University, Fukuoka, Japan**	**Multi-dimensional HPLC with fluorescence detection as a promising method for trace analysis of chiral amino acids and hydroxy acids in clinical, food and extraterrestrial samples**
	**Martina ZANGHERI**	**Department of Chemistry, University of Bologna, Italy**	**Chemiluminescence-based biosensors for life science applications in space**

Nanomaterials and quantum dots luminescence and applications.

	Jose COSTA-FERNANDEZ	Department of Physical and Analytical Chemistry, University of Oviedo, Spain	Metal-doped luminescent Quantum Dots for multimodal bioimaging.
	Patricia FORBES	Department of Chemistry, University of Pretoria, South Africa	Quantum dot based photonic sensor materials for emerging chemical pollutants in water

Imaging and microscopy luminescence developments.

	Matthieu DUBREUIL	Optics and Magnetism Laboratory (OPTIMAG), University of Brest, France	Second harmonic generation polarimetry of biological tissues

New fluorescence probe and chemosensor

	Jin OUYANG	College of Chemistry, Beijing Normal University, Beijing, China	Synthesis and application of highly sensitive fluorescent probes
	Jean Jacques AARON	Laboratoire Géomatériaux et Environnement, EA4508, University Paris-Est, France	Polymer-based fluorescent sensors for toxic heavy metals: a new, electrosynthesized benzene sulfonic acid-polypyrrole for Cu(II) and Pb(II).

Biology and medicine luminescence techniques

	Etienne HENRY	Lab. Microbiology of Extreme Environments, UMR6197 Institut Français de Recherche pour l'Exploitation de la Mer (IFREMER), Brest University	Fluorescence-based methods to study hyperthermophilic archaeal family B DNA polymerase: Measurements of DNA binding and real-time enzymatic activities

PLANNING

Tuesday, June 19, 2018

TIME	EVENT
12:30 - 14:00	**Opening Cocktail and Registration (First floor hall)**
14:00 - 14:30	**Opening ceremony (Amphitheatre B) - University President and Vice-President; Chairman of the Science Faculty**
14:30 - 15:40	**Analytical development of luminescence methods (environment analysis and monitoring, drug analysis, food analysis, ….) (Amphitheatre B) - CHAIRMAN: Petr SOLICH, and Kenji HAMASE**
14:30 - 15:00	› Chemometric analysis and bioluminescent assay combined to identify honey geographical origin and adulterations - *PLENARY LECTURE: Stefano Girotti, University of Bologna*
15:00 - 15:20	› Establishment of an EC50 database of pesticides using Vibrio Fischeri bioluminescence method - *Snezna Efremova Aaron, Department of Medical and Experimental Biochemistry*
15:20 - 15:40	› Multicolor bioluminescent 3D cell biosensors for effect-directed smartphone-based analysis - *Maria Maddalena Calabretta, Department of Chemistry "Giacomo Ciamician", Alma Mater Studiorum University of Bologna*
15:40 - 16:10	**Coffee break and Poster Session (First floor hall)**
16:10 - 17:30	**Biology and medicine luminescence techniques (biophysics, membranes study, FRET, proteomics, metabolomics,…) (Amphitheatre B) - CHAIRMAN: Loïc BLUM, and Snezna Efremova AARON**
16:10 - 16:40	› Fluorescence-based methods to study hyperthermophilic archaeal family B DNA polymerase: Measurements of DNA binding and real-time enzymatic activities - *PLENEARY LECTURE: Etienne HENRY, Lab. Microbiology of Extreme Environments*
16:40 - 17:00	› Bacteriochlorin–Naphthalimide Conjugates for Simultaneous Photodynamic Therapy and Fluorescence Imaging - *Pavel Panchenko, A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences*
17:00 - 17:20	› Bacterial bioluminescence: Biology and applications - *Chatragadda Ramesh, Department of Ocean Studies and Marine Biology, Pondicherry University, Andaman Nicobar Center for Ocean Science and Technology (ANCOST)*
17:30 - 19:00	**Poster mounting and Session (First floor hall)**

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Wednesday, June 20, 2018

TIME	EVENT
08:30 - 09:00	**Poster Session (First floor hall)**
09:00 - 10:10	**Imaging and microscopy luminescence developments (Amphitheatre B) - CHAIRMAN: Xinrong ZHANG, and Valery BARACHEVSKY**
09:00 - 09:30	› Second harmonic generation polarimetry of biological tissues - *PLENARY LECTURE: Matthieu DUBREUIL, Laboratoire d'Optique et de Magnétisme*
09:30 - 09:50	› From Picoseconds to Milliseconds: Time-Resolved Fluorescence Spectroscopy on Different Time Scales Combined with Spatial Resolution - *Volker Buschmann, PicoQuant GmbH*
09:50 - 10:10	› Pyclen-based Ln(III) complexes as fluorescent bioprobes for two-photon microscopy - *Nadège HAMON, Chimie, Electrochimie Moléculaires et Chimie Analytique*
10:10 - 10:50	**Coffee break and UNEVEN number poster session : Presenters of a poster with a uneven number, are invited to stay in front of it. (First floor hall)**
10:50 - 11:30	**Imaging and microscopy luminescence developments (Amphitheatre B) - CHAIRMAN: Matthieu DUBREUIL, and Volker BUSCHMANN**
10:50 - 11:10	› Photofluorescent recording media for 3D optical memory devices - *Valery Barachevsky, Photochemistry Centre of Federal Scientific Research Centre "Crystallography and Photonics" of the Russian Academy of Sciences*
11:10 - 11:30	› Photoluminescence Imaging of Newly Synthesized Proteins in Living Cells - *Xinrong Zhang, Tsinghua University [Beijing]*
11:30 - 12:10	**Biology and medicine luminescence techniques (biophysics, membranes study, FRET, proteomics, metabolomics,…) (Amphitheatre B) - CHAIRMAN: Etienne HENRY, and Pavel PANCHENKO**
11:30 - 11:50	› The use of in vivo bioluminescence for designing synthetic gene delivery systems - *Tony LE GALL, Equipe « Transfert de gènes et thérapie génique », INSERM U1078, UFR Médecine, UBO, Brest, France*
11:50 - 12:10	› Differential proteomic analysis in the progression of aristolochic acid nephropathy in mice using the FD-LC–MS/MS method - *Jen-Ai LEE, Taipei Medical University*
12:10 - 12:45	**Exhibitors presentations : - COHERENT - Spectra-Physics - IDIL Fibres Optiques - Freiberg Instruments - EVOSENS - PICOQUANT**
12:45 - 14:30	**Lunch (Ar Men Restaurant)**
14:30 - 16:00	**Analytical development of luminescence methods (environment analysis and monitoring, drug analysis, food analysis, ….) (Amphitheatre B) - CHAIRMAN: Jen Ai LEE, and Martina ZANGHERI**
14:30 - 15:00	› Multi-dimensional HPLC with fluorescence detection as a promising method for trace analysis of chiral amino acids and hydroxy acids in clinical, food and extraterrestrial samples - *PLENARY LECTURE: Kenji HAMASE, Kyushu University [Fukuoka]*
15:00 - 15:20	› On-line derivatization strategies for the sensitive fluorescent detection of aflatoxins in food and feed by liquid chromatography - *Ana M. García-Campaña, University of Granada*
15:20 - 15:40	› Ultra-high performance liquid chromatography with fluorescence detection as a powerful analytical tool for the analysis of oestrogens in environmental waters - *Rayco Guedes-Alonso, Universidad de Las Palmas de Gran Canaria*
15:40 - 16:00	› Determination of three triterpenic acids in dried rosemary by HPLC-fluorescence detection with DIB-Cl - *Wada Mitsuhiro, Kyushu University of Health and Welfare*
14:30 - 16:00	**Nanomaterials and quantum dots luminescence and applications (Amphitheatre C) - CHAIRMAN: Eulogio J. LLORENT-MARTINEZ, and Rocio ROJAS HERNANDEZ**
14:30 - 15:00	› Quantum dot based photonic sensor materials for emerging chemical pollutants in water - *PLENARY LECTURE: Patricia Forbes, University of Pretoria*
15:00 - 15:20	› Ultrabright Polymeric Nanoparticles for FRET Mediated Ratiometric Detection of Molecular Oxygen - *Nagappan Pillai Adarsh, Laboratoire de Bioimagerie et Pathologies - UMR 7021*
15:20 - 15:40	› Photoluminescence properties of MoS2 quantum dots synthesized by one-step hydrothermal method - *Shailendra Sharma, Indian Institute of Technology (Indian School of Mines) Dhanbad*
15:40 - 16:00	› Development of a quantum dot molecularly imprinted polymer sensor for fluorescence detection of atrazine - *Sifiso Nsibande, University of Pretoria [South Africa]*
16:00 - 16:40	**Coffee break and EVEN number Poster Session: Presenters of a poster with an even number, are invited to stay in front of it. (First floor hall)**

Wednesday, June 20, 2018

16:40 - 18:10	**Analytical development of luminescence methods (environment analysis and monitoring, drug analysis, food analysis, ….) (Amphitheatre B) - CHAIRMAN: Ana Maria GARCIA-CAMPANA, and Kenichiro NAKASHIMA**
16:40 - 17:10	› Chemiluminescence-based biosensors for life science applications in space - *PLENARY LECTURE: Martina Zangheri, Department of Chemistry "Giacomo Ciamician", University of Bologna*
17:10 - 17:30	› Coupling Size exclusion chromatography and 3D Fluorescence for studying DOM in estuarine waters - *Johann Breitenstein, Laboratoire des Sciences de l'Environnement Marin*
17:30 - 17:50	› A new automatic online detector for determination of benzoyl- and phenylurea pesticides in natural waters- *Pape Abdoulaye DIAW, Equipe des Matériaux, Electrochimie et Photochimie Analytique, Laboratoire de Photochimie et d'Analyse, OPTIMAG Laboratory*
17:50 - 18:10	› FLOW ANALYSIS WITH LUMINESCENCE DETECTION – AN OVERVIEW - *Petr Solich, Charles University, Faculty of Pharmacy*
16:40 - 18:10	**New fluorescence probe and chemosensor (synthesis, fluorescence properties, applications,…)(Amphitheatre C) - CHAIRMAN: Jin OUYANG, and Sylvain ACHELLE**
16:40 - 17:10	› Polymer-based fluorescent sensors for toxic heavy metals: a new electrosynthesized benzene sulfonic acid-polypyrrole sensor for Cu(II) and Pb(II) detection - *PLENARY LECTURE: Jean-Jacques Aaron, University Paris-Est Marne la Vallée*
17:10 - 17:30	› Spectroscopic studies of the interactions of 3,8-bis(alkylamido)-5-ethyl-6-phenyl-5-phenanthridinium bromide derivatives with G-quadruplex DNA - *Ergin YALCIN, Graduate School Of Natural And Applied Sciences of Gazi Uni.*
17:30 - 17:50	› Molecular luminescent probes to explore the pores and the surface of metal organic frameworks (MOF) drug carriers. - *Dan Lerner, Ecole Nationale Supérieure de Chimie de Montpellier*
17:50 - 18:10	› Approaches for variation of luminescence characteristics of lanthanide coordination compounds - *Elena Mikhalyova, L. V. Pisarzhevskii Institute of Physical Chemistry of the NAS of the Ukraine*
18:10 - 19:00	**Poster Session (First floor hall)**

Thursday, June 21, 2018

TIME	EVENT
08:30 - 09:00	**Poster Session (First floor hall)**
09:00 - 10:10	**New fluorescence probe and chemosensor (synthesis, fluorescence properties, applications,…)(Amphitheatre B) - CHAIRMAN: Dan LERNER, and Elena MIKHALYOVA**
09:00 - 09:30	› Synthesis and application of highly sensitive fluorescent probes - *PLENARY LECTURE: Jin Ouyang, Beijing Normal University*
09:30 - 09:50	› Luminescence modulation of rhenium complexes induced by the structural isomerism of their organic ligand - *Fery-Forgues Suzanne, Suzanne Fery-Forgues*
09:50 - 10:10	› Protonable nitrogen-based heterocyclic chromophores for white light emission. - *Sylvain ACHELLE, Laboratoire Institut des sciences chimiques de Rennes - Equipe OMC - UMR CNRS 6226*
10:10 - 10:40	**Coffee break and UNEVEN number Poster Session: Presenters of a poster with a uneven number, are invited to stay in front of it. (First floor hall)**
10:40 - 12:10	**Nanomaterials and quantum dots luminescence and applications (Amphitheatre B) - CHAIRMAN: Patricia FORBES, and Shailendra SHARMA**
10:40 - 11:10	› Metal-doped luminescent Quantum Dots for multimodal bioimaging - *PLENARY LECTURE: Jose Costa-Fernandez, University of Oviedo*
11:10 - 11:30	› Near Infrared Long Persistent Nanophosphors for Bio Imaging Applications - *Jairam Manam, Indian Institute of Technology (Indian School of Mines) Dhanbad*
11:30 - 11:50	› Graphene quantum dots-terbium ions as novel time-resolved luminescent probes - *Eulogio J. Llorent-Martínez, Department of Physical and Analytical Chemistry, Faculty of Experimental Sciences, University of Jaén*
11:50 - 12:10	› Tb3+ / Yb3+ doped aluminosilicate phosphors for visible emission and efficient up-conversion - *ROCIO ROJAS HERNANDEZ, Centro de Química Estrutural, Instituto Superior Técnico,*
12:10 - 14:00	**Lunch (Ar Men Restaurant)**
14:00 - 23:00	**Tour and Gala Dinner - THE LIGHTHOUSES ROAD**

Friday, June 22, 2018

TIME	EVENT
08:30 - 09:00	**Poster Session (First floor hall)**
09:00 - 10:10	**Analytical development of luminescence methods (environment analysis and monitoring, drug analysis, food analysis, ….) (Amphitheatre B) - CHAIRMAN: Stefano GIROTTI, and Bruno BOUSQUET**
09:00 - 09:30	› Flow-based chemiluminescence microarrays as tool for rapid detection of pathogens and toxins - *PLENARY LECTURE: Michael Seidel, Technical University of Munich*
09:30 - 09:50	› Combined IonoLuminescence and PIXE micro-analyses of natural diopside for activators and quenchers identification - *Laura Guidorzi, Dipartimento di Fisica - Università degli Studi di Torino, Istituto Nazionale di Fisica Nucleare, Sezione di Torino*
09:50 - 10:10	› Phototransferred thermoluminescence and thermally-assisted optically stimulated luminescence dosimetry using α-Al2O3:C,Mg - *J. M. Kalita, Rhodes University*
10:10 - 10:50	**Coffee break and EVEN number Poster Session: Presenters of a poster with an even number, are invited to stay in front of it. (First floor hall)**
10:50 - 12:20	**Analytical development of luminescence methods (environment analysis and monitoring, drug analysis, food analysis, ….) (Amphitheatre B) - CHAIRMAN: Michael SEIDEL, and Philippe GIAMARCHI**
10:50 - 11:20	› Laser-induced breakdown spectroscopy (LIBS): a review - *PLENARY LECTURE: Bruno Bousquet, Centre Lasers Intenses et Applications*
11:20 - 11:40	› LIBS analysis of agricultural soils: from laboratory to on-site measurements - *Julian Guézénoc, Centre d'Études Lasers Intenses et Applications*
11:40 - 12:00	› Ultra-high performance liquid chromatography with fluorescence detection to determine benzimidazole compounds in farmed fish samples - *Carmen Tejada-Casado, University of Granada*
12:00 - 12:20	› Fluorescence analysis of polyaromatic hydrocarbons photodegradation - *Olga Tchaikovskaya- Tomsk State University*
12:20 - 12:40	**Awards and Closing Ceremony (Amphitheatre B) - Philippe GIAMARCHI**
12:40 - 14:00	**Farewell cocktail (First floor hall)**

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Table of contents

Analytical development of luminescence methods (environment analysis and monitoring, drug analysis, food analysis, ...)

A new automatic online detector for determination of benzoyl- and phenylurea pesticides in natural waters

P. A. Diaw[1,2,3], J. P. Bakhoum[2,3], M. Mbaye[2,3], O. M. A. Mbaye[2,3], D. D. Thiaré[2], L. Cissé[2], D. Sarr[1], M. D. Gaye-Seye[2,4], A. Coly[2], A. Tine[2], J. J. Aaron[4], B. Le Jeune[3], P. Giamarchi[3]

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Introduction

We worked previously on an online automatic detector for the determination hydrocarbons in aqueous medium by fluorescence detection to monitor pollution in natural water [1]. We worked also on photo-induced fluorescence (PIF) methods based on UV irradiation (classical PIF) and laser irradiation (DL-PIF) for the quantitative determination of pesticides in natural waters [2-3]. In this present work, we have associated these two technics to propose a new automatic on-line detector by PIF method (namely "AUTOPIF") for the monitoring of pesticides in natural waters. Two evolutions of the system are studied and compared, and then applied to the detection of benzoyl- and phenylurea pesticides (diflubenzuron, fluometuron and monolinuron) in natural waters.

Materials and Methods

A peristaltic pump (Gilson Minipuls 3), is used to carry and regulate the liquid flow. Photoproducts were formed in a 25 mL flow quartz tubes under irradiation of a 300 W UV lamp. Fluorescence was detected after excitation at 280 nm by the UV diode throw a quartz flow cell. The fluorescence is then collected by two optic fibers.

"AUTOPIF" is derived from a commercial AQUAPOD system (HOCER, France) where the detection is done by diode array spectrometer (Oceans Optics).

"AUTOPIF+" is equipped with a SpectraPro-550i spectrometer (Acton, MA, USA), and a CCD intensified Camera (Princeton instruments, NJ, USA).

Results and discussion

For DFB, only one fluorescence photoproduct was detected at 410 nm by AUTOPIF+ and is not detected by AUTOPIF because its scanning range is limited between 200 and 400 nm. Same photoproduct was detected by Diaw et al. [1] during determination DFB in mixture water/methanol (30/70, v/v) at pH 4 under UV irradiation. For MLN, one fluorescence photoproduct was detected by AUTOPIF and AUTOPIF+ with peaks emission ranged of 342 nm to 350 nm. This emission wavelength is characteristic of aromatic amines as aniline and its derivatives [4]. FLM PIF was detected at 370 nm and 420 nm, respectively for AUTOPIF and AUTOPIF+ methods. Analytical performances of AUTOPIF and AUTOPIF+ methods were satisfactory with relative low limits of detection.

Conclusion

The fluorescent photoproducts of MLN, FLM and DFB are successfully determinate in aqueous medium. AUTOPIF and AUTOPIF+ methods are then suitable to determine phenylurea pesticides in river, and tap water samples. AUTOPIF + method give best result with great sensibility due to by the CCD intensified camera. LOD were relatively lowest and the recovery rates found for are satisfactory and range between 98 and 108% and belong to the area of validity of the analytical method.

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Chemiluminescence-based biosensors for life science applications in space

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Introduction

Portable diagnostic devices are ideal tools for performing analyses outside of a laboratory environment. There is a strong demand for simple portable analytical devices suitable for space applications, that astronauts can use to perform clinical monitoring (e.g. detection of biomarker in blood, urine, saliva samples) during space missions, or that can be used for astrobiology investigations (e.g. detection of specific molecules outside of the Earth). Our research group is taking part in some projects involving the use of portable chemiluminescence (CL) biosensors for space applications.

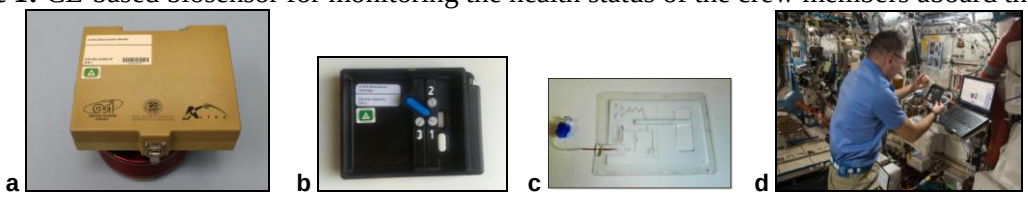
Materials and Methods

The developed biosensors are based on different approaches. As part of the IN SITU Bioanalysis project, we developed a portable analytical device which relies on the Lateral Flow Immunoassay (LFIA) technique, in which the immunological reaction is performed on a nitrocellulose membrane, employing immunoreagents immobilized in specific areas. The payload comprised a 3D-printed plastic cartridge (Fig.1b) containing a sealed fluidic element (Fig.1c) with the LFIA strip, a port for sample loading, pressure-activated reagent reservoirs and valves. The analysis required a simple manual procedure, and the flow of sample and reagents was obtained by pressing buttons on the cartridge or (across the LFIA strip) by exploiting capillary forces. Detection was performed by CL imaging, using a CL reader based on an ultrasensitive, thermoelectrically cooled charge-coupled device (CCD) camera (Fig.1a). The results were collected on an ISS laptop, then sent to ground personnel for processing and evaluation by medical experts. Another CL-based approach was selected in the frame of PLEIADES project involving in a microfluidic cartridge integrated with an array of thin-film hydrogenated amorphous silicon (a-Si:H) photosensors for acquiring the CL signal for the detection of bio-organic molecules in extra-terrestrial environments, exploiting immunoassays of DNA-based switch biosensors.

Results and Discussion

The CL-LFIA biosensor was successfully used on board the ISS by the Italian astronaut Paolo Nespoli during the VITA mission (July-December 2017) (Fig.1d). As a technological proof-of-concept, the device demonstrated the feasibility of performing sensitive (nanomolar level) immunological clinical chemistry analyses directly on board the ISS. As concern the PLEIADES microfluidic platform for life biomarker detection, a preliminary study was conducted for selecting the most suitable bioanalytical approach (e.g. immunoassay, gene probe assay).

Figure 1: CL-based biosensor for monitoring the health status of the crew members aboard the ISS.



Conclusion

The developed biosensors can find a variety of applications in space, for early detection of physiological changes that astronauts often experience during spaceflight, such as inflammation, infection, bone loss, muscle atrophy and cardiovascular disorders. In addition, they may applied on Earth for health monitoring, food safety, environment control, bio-terrorism.

Chemometric analysis and bioluminescent assay combined to identify honey geographical origin and adulterations.

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Introduction

Honey quality is currently object of great attention in EU, since the self-production covers about the 60% of the inner market's demand. This could induce the producers to increase the honey amount by adding syrup or other compounds to natural honey, obtaining a honey-like product able to pass the testing analysis according to the law now in force [1]. Another possible fraud concerns deception of traceability of the product.

Multivariate analysis, by simultaneous exploration of all the variables, may highlight frauds even when each single chemical and physical criterium prescribed by legislation (LAW variables) is fulfilled. On the other hand, the fingerprint character of spectroscopic signals like luminescence allows for rapid and inexpensive analysis.

Materials and Methods

In this work, principal components analysis and linear discriminant analysis have successfully been applied to identify sugar-added honeys and to explore geographical traceability using bioluminescent signals (LUM) produced by *Vibrio fischeri* as chemometric variables. This analytical method employs bacteria changing their bioluminescent activity as a function of the surrounding environment. The inhibition of light emitted by strains of marine bioluminescent bacteria is currently used to evaluate the toxicity of many chemicals.

Results and Discussion

This work is at our knowledge the first application of bioluminescence to the discrimination of adulterated honeys, and the discrimination is successful even when the determination of the check parameters prescribed by the law fails this discrimination. No correlation between botanical origin and LAW or LUM variables was found. On the contrary, the correlation between geographical origin and both LAW and LUM variables was significant.

The developed method can be applied as very rapid and inexpensive routine screening for checking honeys' authenticity. Only samples which would not be recognized as authentic by the chemometric models should be brought to suitable analyses like $^{13}C/^{12}C$ stable isotope ratio [2].

The complete validation of the method is in progress

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Combined IonoLuminescence and PIXE micro-analyses of natural diopside for activators and quenchers identification

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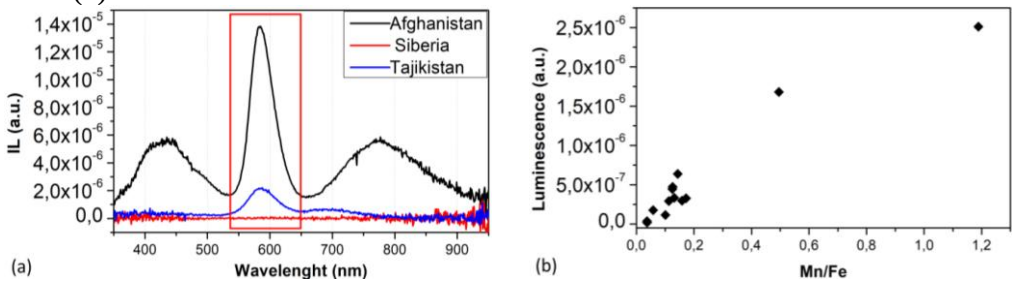
Diopside is a mineral belonging to the pyroxene group, a single chain inosilicate with chemical formula $CaMgSi_2O_6$, occurring mostly in basic and ultrabasic igneous rocks or in metamorphic rocks. Natural diopside displays a large variety of luminescence centers: main features at room temperature are an intense band around 585 nm that can be ascribed to Mn^{2+} ions in M2 (Ca^{2+}) sites[1] and a 430 nm band, attributable to the silicate-based network[2,3]. Also, Ti^{3+} and Fe-related impurities have a role as activators of luminescence[4].
The presented study is part of a huge characterisation project of lapis lazuli of historical and archaeological interest, hence a hundred of diopside crystals selected in lapis lazuli samples of different provenances (Afghanistan, Tajikistan and Siberia) have been investigated. Micro-beam PIXE (Particle Induced X-ray Emission) and IL (IonoLuminescence) have been simultaneously performed at the INFN-LNL (Legnaro National Laboratories of the Italian National Institute of Nuclear Physics) with a 2 MeV proton microbeam provided by a Van de Graaff accelerator.
The great amount of data collected during these irradiation sessions has already been used to extrapolate relevant information for lapis lazuli provenance determination[5]. In addition, we have also been able to investigate the correlations between some features of the ionoluminescence behaviour and elements detected in traces as possible activators. For example, while the 585 nm band resulted in a strong signal for Afghanistan and Tajikistan samples, it was almost undetectable in samples from Siberia (fig.1a). These latter samples have also a much higher iron content: we found out that the intensities of the IL peak are in a good linear correlation with concentrations of Mn in the crystal, once the competition with the action of quenchers, such as Fe^{2+}, is suitably taken into account[6] (fig.1b). Other newly attribution in diopside are a band at 785 nm, probably due to the presence of V, and two peaks at 603 and 641 nm, correlated to Y.

Figure 1: (a) IL spectra of diopside crystals from different provenances. The 585 nm peak is highlighted. (b) Correlation of the 585 nm band intensities with Mn/Fe concentrations.



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Coupling Size exclusion chromatography and 3D Fluorescence for studying DOM in estuarine waters

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Introduction

In estuarine systems, dissolved organic matter (DOM) has been extensively studied by quantifying total dissolved organic carbon concentration (DOC) or using fluorescence technics. Although these approaches can give clues to the bulk DOM complexity and reactivity, uncertainties remain on the acquisition of quantitative data and relationship with the size distribution is poorly resolved. Size exclusion chromatography combined with UV, carbon and nitrogen detection (LC-OCD-OND-UVD called LC-OCD) could partially make the gap between these different technics by providing information on size distribution, polarity, aromaticity and C/N ratio of DOM without any sample processing[1]. In this work we examined how 3D fluorescence can give further insights to the information provided by LC-OCD on DOM changes in estuarine systems.

Materials and Methods

Estuarine waters were collected in January 2018 along the Aulne estuary (Bay of Brest, France) on board of R.V. Hesione (INSU-CNRS-UBO). Stations were selected according to their salinity from 0 to 35 with a step of 2 (17 sampling stations). Chromatography analyses were performed by a LC-OCD designed and assembled by DOC-Labor® (Karlsruhe, Germany). The chromatographic sector consisted in two weak cation exchange columns on polymethacrylate gel (250 mm x 20 mm, TSK HW 50S, Toso Japan) wherein the on-line filtered (0.45 µm PES-filter) mixture is separated into 6 distinct fractions : i) the bypass used to calculate the total DOC and the global absorbance of the sample ; ii) the fraction called biopolymer (BP) typically representative of high molecular weight compounds including polysaccharides and proteins ; iii) the humic fraction (HS); iv) the building blocks fraction (BB), composed by breakdown products of HS ; v) the low molecular weight acids fraction (LMW-acids) and vi) the low molecular weight neutrals fraction (LMW-neutrals) mostly composed of alcohols, aldehydes and ketones. In this work, we isolated as extracts some of these fractions and 3D fluorescence was applied to further study the footprint of DOM. The fluorescence emission spectra were obtained on a Cary Eclipse spectrophotometer with an arc-xenon lamp pulsed at 80 Hz as source excitation.

Results and Discussion

Concentrations of the LC-OCD fractions within the estuarine system varied between 700 and 4000 ppb-C for DOC, 50 and 120 ppb-C for BP, 400 and 2000 ppb-C for HS, 150 and 400 ppb-C for BB and between 200 and 800 for LMWN. The HS fraction was the main contributor to DOC representing 68 % at low salinities and 52 % in the marine part of the estuary. All the fractions displayed a relative conservative behavior in the estuary with a decrease in concentrations from upstream to downstream. The BP and SH+BB fractions were extracted and analyzed by 3D fluorescence. The fluorescence of BP extracts was characteristic of tryptophan and proteins compounds and the signal intensity of this fraction significantly increased in the marine part of the estuary (salinity > 28). By contrast, the fluorescence of SH+BB extract corresponded to pedogenic fulvic acids and the intensity of the related signal decreased conservatively with salinity.

Conclusion

The application of 3D fluorescence on fractions separated by LC-OCD allowed a better characterization of the nature and the sources of the biopolymers and the humic compounds in the Aulne estuary. Our study is a first step demonstrating that the coupling of LC-OCD and 3D fluorescence can be used for a finer characterization of DOM in natural waters.

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Determination of three triterpenic acids in dried rosemary by HPLC-fluorescence detection with DIB-Cl

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Introduction

Rosemary has been widely used as a functional food owing to its antioxidative and anti-inflammatory activities. Recently, ursolic acid (UA) and betulinic acid (BA) which are triterpenic acids in rosemary take notice of their skin whitening activities. Therefore the determination of the acids in rosemary is important for the quality evaluation rosemary products. In this study, an HPLC-fluorescence (FL) detection method with 4-(4,5-diphenyl-1*H*-imidazole-2-yl)benzoyl chloride (DIB-Cl) as a derivatization reagent was developed for UA, BA and oreanolic acid (OA). Moreover, the method was applied to determine these acids in commercialy avairable dried rosemary.

Materials and Methods

Extraction: 50 mg of dried rosemary grinded with a finger masher were added to 3 mL of EtOH. The mixture was sonicated for 40 min and then filtered with a membrane filter. Derivatization: 100 μL of sample were added to the mixture of 100 μL of 1% trimethylamine in CH_3CN and 100 μL of 1mM DIB-Cl in CH_3CN suspension. The resultant was stood for 5 min at room temperature and applied to HPLC analysis. HPLC: The triterpenic acids were separated on a Wakopak Handy ODS (250×4.6 mm) with 25 mM acetate buffer (pH 4.5)/MeOH/CH_3CN (=8:10:82 v/v/v%). The fluorescence intensity (FI) of the eluent at 365 (λ_{ex}) and 490 nm (λ_{em}) was monitored.

Results and Discussion

After optimization of separation and derivatization conditions, the triterpenic acids were well separated without interfering peaks from rosemary extract with 26 min (BA), 29 min (UA) and 30 min (OA) of retention time (Fig. 1). The calibration curves using rosemary extract with standards indicated good linearities ($r \geqq 0.997$) in the range of 2.5-100 ng/mL. The detection limits at a 3σ of internal peak in rosemary extract for BA, UA and OA were 0.2, 0.4 and 0.5 ng/mL, respectively. Accuracy (ranging from 80.5 to 106.8%), precisions of intra-day (less than 5.6%) and inter-day assays (less than 6.8%) were acceptable (n=5).

The concentration ranges of BA, UA and OA in commercially available dried rosemary (n=7) were 8.0-13.7 mg/g, 10.0-13.3 mg/g and 20.9-31.9 mg/g, respectively.

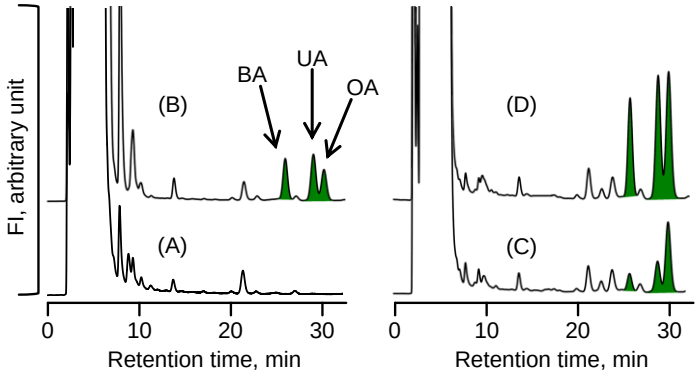

Figure 1: Chromatograms of the proposed method. Sample: blank (A), standards with 10 ng/mL (B), rosemary extract (C) and that spiked with 20 ng/mL of standards (D).

Conclusion

The proposed method was enough sensitive to determine the triterpenic acids in dried rosemary and could be successfully applied to analyse the acid compounds in practical samples. Therefore the method might be a powerful tool for the quality evaluation of rosemary products on the basis of three triterpenic acids amounts.

Establishment of an EC50 database of pesticides using *Vibrio Fischeri* bioluminescence method

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Introduction

Due to the influence of instrumental conditions, the laboratories involved in research on pesticide toxicity should possess their database of EC 50 and curve of dependence of toxicity versus concentration. The toxicity will be determined by using *Vibrio Fischeri* bioluminescence method (1), (2).

Material and methods

Toxicity measurements were performed, according to the international procedure (DIN/EN/ISO 11348-2) - *Vibrio Fischeri* luminescent bacteria test LCK 487 LUMISTOX (Dr Lange, Germany), with a luminometer LKB 1250, thermostated at 15 °C. Pesticides of analytical grade and commercial formulations were used to establish the database. All measurements were done on pesticide and blank organic solutions (1 mL of ethanol-acetone-water 1/3/97 v :v : v containing 2% NaCl). The pH value of the samples was 7,0 ± 0,1. Bioluminescence measurements were performed after 5 and 15 min exposure of the *Vibrio Fischeri* marine bacteria to the pesticide solutions. The EC 50 was calculated from the standard curve created from serial dilutions of each pesticide (Fig.1).

Results and discussion

The EC50 database includes standard pesticides (chlorothalonil, cyprodinil, dichlobenil, α-endosulfane, trifluraline, dimethoate, glyphosate, 2,4-dichlorophenoxyacetic acid (2,4-D), tebuconazole and clomazone), and commercial formulations (thiomethoxam-Actara, clomazone–Gamit, difenoconazol–Difcor, carbamat fam.–Methomil, tebuconazole–Acord). The EC 50 values are between 0.0009– 0.37 mg/L for standard pesticides, and between 0.23– 740 mg/L for commercial formulations.

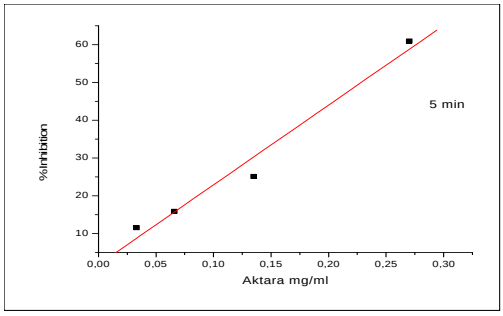

Figure 1. Inhibition of V. fischeri activity (%) vs Actara concentration (mg/L) , after 5-min exposition on Actara..

Conclusion

These EC50 values constitute very important and irreplaceable data to estimate the global and individual toxicity of pesticides present in environment.

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FLOW ANALYSIS WITH LUMINESCENCE DETECTION – AN OVERVIEW

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Introduction

Flow techniques (FIA, SIA, SIC, MSFIA, LOV, etc.) connected with luminescence detection (fluorescence, chemiluminescence) are already well established analytical methods, which are characterized by several factors essential for research or routine analysis, e.g. simplicity of fundamental principles, inexpensive instrumentation, automated sampling and analytical procedures, low sample consumption and short analysis time. Connection of flow methods with luminescence detection can further increase the sensitivity and selectivity of these methods.

Materials and Methods

Several examples of the use of luminescence detection in various applications connected to flow methods will be shown and discussed.

Results and Discussion

For example, in vitro permeation studies are one of the methods widely used in pharmaceutical research in evaluation of drug interaction with membrane transporter proteins or drug-drug interactions. These tests are performed using cellular monolayers seeded on a semi-permeable membrane of commercially produced inserts. Solution of the tested drug is applied to apical chamber and the interactions are evaluated by the permeation to the basolateral chamber. The universal set-up is based on a sequential injection (SIA) manifold connected to the liberation unit, a Franz diffusion cell (FDC), with on-line fluorimetric detection, thus allowing to monitor automated drug transport to get more detailed kinetic profile. Automated flow analytical methods are recently also more and more used for long-term monitoring. Another application will show the advantage of microSIA method for fluorescence determination of zinc in seawater as a portable manifold for shipboard use.

Conclusion

An overview of several other applications of the use of luminescence detection in flow techniques will be further discussed.

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Flow-based chemiluminescence microarrays as tool for rapid detection of pathogens and toxins

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Introduction

Small quantities of hazardous contaminants like pathogens and toxins have to be identified as fast as possible to prevent outbreaks associated with water, food and air. Therefore, rapid concentration and detection technologies are emergently needed to replace cultivation methods in future. Microarray-based detection methods are needed to detect the entity of possible pathogens and toxins in parallel.

Methods and Results

A hygiene online monitoring (HOLM) system was established for the analysis of pathogenic viruses and bacteria in raw water and drinking water. Ultrafiltration, monolithic adsorption filtration, centrifugal ultrafiltration was combined to reduce sample volumes from 1 m^3 to 1 mL in 2 h. After nucleic acid extraction, DNA of bacteria and viruses was amplified on DNA microarrays by means of heterogeneous asymmetric recombinase polymerase amplification (haRPA) reaction. The detection was processed automatically on the flow-based chemiluminescence microarray analysis platform MCR 3.[1] We have shown that bacteriophages spiked in a drinking water pipeline (flow rate 14 m^3/h) could be found after 40 m by our developed HOLM system.

Another example is the detection of *Legionella pneumophila*. Legionellosis outbreaks have occurred consistently during the last years worldwide. Aerosolized *L. pneumophila* from evaporative cooling towers were found frequently as source. *Legionella pneumophila* are concentrated in acidified process water with high efficiency by combining monolithic adsorption filtration and centrifugal ultrafiltration.[2] Concentrated samples are quantified by flow-based chemiluminescence sandwich microarray immunoassays (CL-SMIA). Viable *Legionella* spp. can be quantified by combination of promidium monoazide treatment and haRPA analysis.[3] The measurement of *Legionella* spp. by PMA-haRPA is important for rapid risk assessment qualifying the hygiene status of evaporative cooling towers which are treated with biocides.

The detection of Staphylococcus enterotoxins B (SEB) in milk is important for food safety. Superparamagnetic iron oxide-shell silica-core nanocomposites were synthesized as a new material for immunomagnetic separation (IMS).[4] IMS is combined with CL-SMIA to quantify SEB in 100-mL milk samples. The detection limit could be reduced from 0.13 µg/L (CL-SMIA) to 0.39 ng/L (IMS-CL-SMIA).

Conclusion

Flow-based chemiluminescence microarrays are a powerful analytical tool for rapid and multiplexed quantification of pathogens and toxins in water and food samples. Combination of concentration methods and microarray-based analysis is important to quantify bioorganic traces in large volume sample volumes like water or milk.

Bibiography

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Fluorescence analysis of polyaromatic hydrocarbons photodegradation

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Introduction

Annual discharges of pollutants from industrial sources exceed the permissible standards established by the governments. Researchers are working to create a membrane bioreactor that would effectively purify waste water and then turn into a source of fuel. There are still no reports on the creation of a biocomposite plant to remove a wide class of stable toxic substances. A disadvantage of such a reactor is that such installations can not operate at low temperatures. This serves as an argument in favor of physico-chemical reactors. Studies of the dependencies of the structure of pollutants and the parameters of existing reactors are needed.

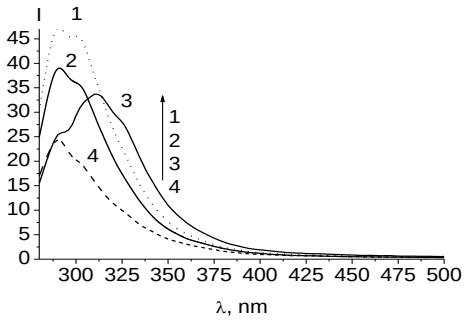
Methods

The choice of the most suitable source of radiation for a given photochemical reaction begins with a study of the absorption spectra of the reagents. Then, a radiation source is selected which gives the maximum energy at the wavelength of the detected absorption band. The wavelengths of the emission bands of the source and the absorption of the reagents must coincide. As sources of radiation, excilamps are used, under the influence of which both direct photolysis of the pollutant molecule and indirect, due to the interaction of the contaminant with the photosensitizers, takes place. The test solution was analyzed by a chromato-mass spectrometer. Express analysis was performed using fluorescence spectra.

Results and Discussion

When studying the phototransformation of phenol and naphthalene in water under UV irradiation, the samples were left for 5 days. An increase in the intensity from the absorption spectra of water in the visible spectral range was recorded, which indicates the appearance of inhomogeneities in the solution. The best fixation showed a polypropylene microfibre material (PMM) with TiO_2. After irradiation, the PMM samples were squeezed out and placed in hexane. Then systems were placed in an ultrasonic mixer. The obtained absorption and fluorescence spectra of hexane was observed formation of phenol phototransformation products which are adsorbed on the surface of PMM (Fig.1). Presumably these are quinones, pyrocatechol, 4-hydroxybenzoic acid, 1,4-benzoquinone, 4-hydroxybenzaldehyde. In the presence of PMM only after the XeBr excilamp irradiation, an increase in the efficiency of photoconversion of phenol was observed in comparison with the aqueous solution. The best fixation was shown by a PMM sample with a pH of 2.38.

Figure 1: Fluorescence spectra of phenol photoproducts in hexane obtained after irradiating 60 minutes of an aqueous phenol solution in the presence of PMM: KrCl (1), XeCl (2), Solar (3), and XeBr (4)



Conclusion

An array of data on the photochemical properties of polyaromatic hydrocarbons (anthracene and naphthalene) when exposed to UV radiation in photoreactors was obtained. The phototransformation products as a function of the irradiation wavelength were established. There is relationship between the structure of pollutants, their initial concentration, oxidizer concentration, etc., with the efficiency of utilization. Schemes for photochemical processes were constructed. The conditions for the degradation of molecules in photoreactors were optimized. Kinetic models for predicting photodegradation of molecules was constructed. The radiation source for the minireactor was selected.

LIBS analysis of agricultural soils: from laboratory to on-site measurements

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Introduction

Agronomic research has a growing interest in collecting faster, cheaper and still efficient information about agricultural matrices in order to achieve a better monitoring of soil quality and fertility[1]. Laser-induced breakdown spectroscopy (LIBS) has been identified to be a high potential technique for on-site elemental analysis of geological materials such as soils[2].

Materials and Methods

The study of agricultural soils, more precisely the multi-elemental quantification of several chemical elements of interest (P, Mg, Fe, Al, Ca, K…), was realized using a portable LIBS system.

Results and Discussion

The good practices related to sample preparation and LIBS experimental setup to achieve relevant LIBS measurements of soil samples will be discussed. Since quantitative LIBS measurements are generally limited by strong matrix effects, the advantages of applying multivariate approaches for data processing will be presented. Finally, we will discuss the influence of environmental parameters on the LIBS signal in order to assess the feasibility of on-site analysis.

Conclusion

LIBS analyses of agricultural soil samples have been successfully performed in laboratory through the use of multivariate processing, and studies about the influence on the LIBS signal of both sample preparation and experimental conditions are in progress.

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Laser-induced breakdown spectroscopy (LIBS): a review

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Laser-induced breakdown spectroscopy (LIBS) is a technique based on the detection of the optical atomic emission spectrum resulting from the de-excitation of a plasma created at the sample surface after laser ablation. LIBS requires the use of pulsed laser and gated detector since the transient plasma emission is temporally short. It allows fast and stand-off measurements with little or no sample preparation.

From laser ablation to plasma expansion and cooling, the principal physical processes involved in LIBS will be commented in the first part as well as the typical values of relevant parameters.
Then, a selection of both scientific and commercial LIBS setups and the international LIBS community in 2018 will be presented.
In the last part, a review of selected LIBS applications will be commented, with particular emphasis for geology, environment and agriculture, cultural heritage and forensics.

As a conclusion, a vision of the future of LIBS will be drawn, with a particular interest on LIBS imaging.

Multi-dimensional HPLC with fluorescence detection as a promising method for trace analysis of chiral amino acids and hydroxy acids in clinical, food and extraterrestrial samples

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Introduction

Amino acids and hydroxy acids are one of the main components of living organisms on the Earth. Most of the amino acids and hydroxy acids have the "asymmetric carbon" and enantiomers are present chemically. However, due to the homochirality of the terrestrial molecules, one of the enantiomers are usually predominant and are playing essential roles in the life systems (e.g. L-forms for amino acids). On the other hand, the minor forms of the enantiomers like D-amino acids are considered to be "not present/not significant" especially in higher animals. However, along with the progress of sensitive and enantioselective analytical technologies, various minor enantiomers have been found in animals, plants and even in human beings. These minor enantiomers are increasingly recognized as new biomarkers in clinical samples and functional molecules in foods/beverages. In the extraterrestrial samples, these organic molecules are considered as origin compounds of life on the Earth. Therefore, enantioselective and quantitative analysis of amino acids, hydroxy acids and related compounds is useful for wade range of research areas. However, the determination of minor enantiomers is frequently interfered with various known/unknown intrinsic substances, and the highly selective analytical method is essential. In the present study, multi-dimensional (2D and 3D) chiral HPLC systems with fluorescence detectors have been designed/developed for the quantitative analysis of these chiral molecules.

Materials and Methods

The biological samples (tissues and physiological fluids) were homogenized with MeOH and centrifuged. The obtained supernatant was dried and amino acids, hydroxy acids were derivatized with 4-fluoro-7-nitro-2,1,3-benzoxadiazole (NBD-F) or 4-nitro-7-piperazino-2,1,3-benzoxadiazole (NBD-PZ). Food samples were also homogenized with MeOH, while the beverage samples were normally diluted with H_2O before derivatization. Extraterrestrial samples were hydrolysed with HCl and were subjected to the derivatization procedure. These reaction mixtures were injected into the 2D- and 3D-HPLC systems combining reversed-phase, anion-exchange/mixed-mode and enantioselective columns. Fluorescence detection of the NBD-derivatives was carried out at 530 nm with excitation at 470 nm.

Results and Discussion

In the first dimension of the multi-dimensional HPLC, a reversed-phase column was used and the target analytes were separated by their hydrophobicity. Because this step is "achiral", target chiral compounds were separated and fractionated as their scalemic D plus L mixtures. These fractions were on-line collected into the "multi-loop" device independently, and injected into the second dimension successively. As the second dimension, an "achiral" anion-exchange mode or a mixed-mode column was used and the target compounds were again separated and fractionated as their D plus L mixtures. The target fractions were on-line collected again to the loop and injected to the third dimension, where the final chiral separations were carried out. For the third dimension, a variety of enantioselective columns including Pirkle-type, cinchona alkaloid type and polysaccharide type columns could be used. The second dimension can be skipped when the sample matrices are not extremely complicated. The present 2D and 3D HPLC systems enable the highly selective analysis of target compounds without losing the sensitivity, because the whole fraction transfer concept is adopted both from 1D to 2D and from 2D to 3D separations. The present systems also enable the highly reproducible and quantitative analysis because the determination is carried out by the fluorescence detectors. By using these multi-dimensional HPLC systems, various D-amino acids, especially, D-Ala, D-Asn, D-Asp, D-Leu, D-Pro and D-Ser were observed in human tissues and physiological fluids, and the amounts were associated with diseases such as chronic kidney diseases. Chiral hydroxy acids (lactate and 3-hydroxybutyrate), and chiral dipeptides (especially containing D-Ser, Ser-Gly and Gly-Ser) were also found in various clinical, food/beverage and extraterrestrial samples, and further studies focusing on their origins and functions are in progress.

Multicolor bioluminescent 3D cell biosensors for effect-directed smartphone-based analysis

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Introduction

Bioluminescent (BL) cell-based assays represent bioanalytical tools for drug discovery process providing simple, fast and cost-effective assays avoiding the use of animals. Thanks to their easy adaptability to high-throughput and high-content screenings, cell models can identify bioactive molecules interacting with molecular targets well in advance of preclinical studies. In the last years, three-dimensional (3D) cell-culture models have gained great attention due to their capability to faithfully replicate intrinsic physiological conditions and in vivo cellular responses to external stimuli. Firstly, a transcriptional biosensor system relying on BL 3D spheroids has been developed for high-throughput tumor necrosis factor α (TNFα) detection in a 96-well micro-patterned microplate.[1] For implementing these 3D cell-based assays into portable formats we developed a smartphone-based platform for effect-based analysis relying on multicolor bioluminescent 3D cell biosensors.

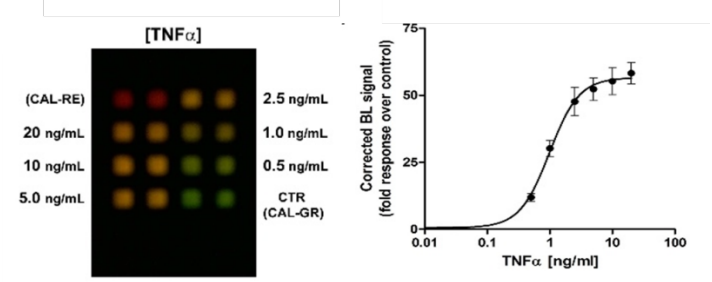
Materials and Methods

Two powerful *P. Pyralis* variants, PpyGR-TS and PpyRE-TS luciferases emitting at different wavelengths have been selected respectively as viability control and inflammation reporter. Spheroids were incubated with different concentrations of TNFα (concentration range 0.5-20 ng/mL) for 5 h. We fabricated a cell cartridge and smartphone adaptor using a desktop 3D printer to provide a mini-darkbox and an aligned optical interface between the smartphone camera and the cell cartridge for BL signals acquisition.

Results and Discussion

We report the development of a dual-color BL spheroid-biosensor in which a red-emitting luciferase is induced by the presence of pro-inflammatory molecules and a green-emitting reporter is constitutively expressed and used as viability control allows to obtain a color-coding visual information in which the green emission is associated to "safe" while the red correspond to "harmful" samples. Smartphone-based bioassay provides a limit of detection (LOD) of 0.15 ± 0.05 ng/mL and an EC50 of 1.0 ± 0.1 ng/mL TNFα.

Figure 1: Image acquired with the smartphone obtained by incubating the spheroid-biosensor with increasing concentration of TNFα (left), corrected dose-response curve for TNFα (right).



Conclusion

To the best of our knowledge this is the first implementation of a multicolor bioluminescent spheroid biosensor in a smartphone-based platform. The proposed biosensing platform could become a useful tool for an initial on-site screening of potentially toxic substances, prioritizing samples for a more accurate chemical analysis.

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On-line derivatization strategies for the sensitive fluorescent detection of aflatoxins in food and feed by liquid chromatography

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Introduction

Aflatoxins (AFB1, AFB2, AFG1 and AFG2) are highly carcinogenic fluorescent mycotoxins produced by *Apergillus* genera. The emission from AFB1 and AFG1 is strongly quenched in the aqueous mixtures used as mobile phase in liquid chromatography, which is usually overcome by a derivatization step. Several strategies can be applied, being the most common the off-line pre-column derivatization with trifluoroacetic acid (TFA). As alternative, two on-line methods based on high performance liquid chromatography (HPLC) with photoinduced (PI) derivatization and ultra-high performance liquid chromatography (UHPLC) with post-column chemical reaction by adding pyridinium bromide perbromide (PBPB), are proposed in this work.

Materials and Methods

UHPLC-FLD method: a mobile phase consisting on water, acetonitrile and methanol in gradient mode was used and a "T" connector to mix the PBPB solution with the eluate from the chromatographic column. A reaction coil was placed in an oven at a 25 ºC joining the outlet of the "T" connector with the inlet of the FLD cell.

HPLC-PI-FLD method: a UV- derivatization module previous to the fluorescence detector was used. The excitation and emission wavelengths were 365 and 460 nm, respectively.

Results and Discussion

The UHPLC-FLD method was characterized in rice, while the HPLC-PI-FLD method was validated in different feedstuffs. Solid-liquid extraction was used as sample treatment in all the cases. The HPLC-PI-FLD method was also applied for the determination of AFs in vegetables milks and yogurt, using dispersive liquid-liquid extraction as sample treatment.

Conclusion

Different derivatization strategies were evaluated for the fluorescent detection of aflatoxins by UHPLC and HPLC, obtaining low LOQs that allowed their determination at levels established by current legislation.

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Phototransferred thermoluminescence and thermally-assisted optically stimulated luminescence dosimetry using α-Al_2O_3:C,Mg

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Introduction

Aluminum oxide doped with carbon and co-doped with magnesium (α-Al_2O_3:C,Mg) is a high-sensitivity luminescence material used as a fluorescent nuclear track detector in the dosimetry of neutrons as well as energetic protons[1]. Recent studies using thermoluminescence (TL) and optically stimulated luminescence (OSL) showed that the material could also be used as a TL and OSL dosimeter. However, a major drawback of using α-Al_2O_3:C,Mg in TL/OSL dosimetry is that its luminescence signal fades faster than the rate desired for a dosimeter. It happens due to release of the radiation-induced trapped electrons from shallow and main traps.

Phototransferred TL (PTTL) and thermally-assisted OSL (TA-OSL) are two useful methods to study luminescence from deep traps where the electrons are stable at ambient condition. PTTL is technically the TL measured from a phosphor after illumination of light of specific wavelength. On the other hand, TA-OSL is the luminescence measured from a sample under simultaneous thermal and optical stimulation. Using these methods, luminescence can be obtained from deep electron traps. The previous studies of PTTL and TA-OSL in an un-annealed α-Al_2O_3:C,Mg showed that the concentration of deep traps in the sample is not very high[2,3]. Therefore, the PTTL and TA-OSL signals are weak to use in dosimetry. However, a recent study showed that the trap-distribution of the sample drastically affected by annealing at 1200 ^oC. Therefore, we studied the PTTL and TA-OSL features of the sample after annealed at 1200 ^oC to explore its application in luminescence dosimetry.

Materials and Methods

α-Al_2O_3:C,Mg chips of size 5×2.5×1 mm (Landauer, Inc; Oklahoma, USA) were used. The samples were annealed at 1200 ^oC for 15 min before use. Luminescence was measured using a RISØ TL/OSL DA-20 Luminescence Reader from a sample irradiated at ambient temperature using a $^{90}Sr/^{90}Y$ beta source at a nominal dose rate of 0.1028 Gy/s. For PTTL and TA-OSL measurements, the samples were illuminated by 470 nm blue LED with 72 mW/cm^2 power density.

Results and Discussion

A common TL glow curve measured at 1 $^oC/s$ from a sample annealed at 1200 ^oC shows glow peaks at 54, 80, 102, 174, 239, 290, 330 and 389 ^oC. The peaks at 54, 80, 102 and 174 ^oC can be reproduced as PTTL peaks when the irradiated sample is illuminated by 470 nm light after preheated to 230 ^oC. Pulse annealing experiments, intended to study the dependence of PTTL peak intensity on preheating temperature, show that the electron traps corresponding to peaks at 239, 290, 330 and 389 ^oC act as donor traps whereas the traps corresponding to peaks at 54, 80, 102 and 174 ^oC act as acceptor traps in the phototransfer process. The intensity of PTTL peaks increases with illumination time to a maximum within 200 s for measurements corresponding to doses between 1 and 10 Gy. The dose response of the PTTL peaks at 80, 102 and 174 ^oC is linear within 1 to 15 Gy. The peak at 80 ^oC, fades to background level within 18000 s whereas in the same time, the peaks at 102 and 174 ^oC fades only 25 and 5 % of its initial intensity. The peaks are also well reproducible.

Regarding the TA-OSL analyses, the sample show the maximum TA-OSL intensity at 200 ^oC under simultaneous optical stimulation. The dose response is sublinear between 10 and 300 Gy and saturates above 300 Gy.

Conclusion

The analyses show that the material can be used for radiation dose reassessment in extreme conditions such as accidental exposure to light as well as temperatures.

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Ultra-high performance liquid chromatography with fluorescence detection as a powerful analytical tool for the analysis of oestrogens in environmental waters

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Introduction

Oestrogens are naturally excreted by mammals and are also widely used as pharmaceuticals in many therapeutic treatments[1] which means that they could reach aquatic compartments through wastewaters producing changes in aquatic biota, even at trace concentrations[2]. In this work we present different studies which use Ultra-high performance liquid chromatography with fluorescence detection **(**UHPLC-FD) for the optimization of extraction and preconcentration processes as well as to determine the levels of some hormones in water samples.

Materials and Methods

In a first study, the optimization of a solid phase extraction (SPE) procedure is shown. In this study, several parameters of SPE as cartridge type, sample volume, ionic strength and pH of the sample or elution volume were optimized following a factorial experimental design. Chromatographic and detection parameters such as chromatographic gradient or excitation and emission wavelengths were also optimized. In this work, the separation and detection of the four oestrogens (estriol, 17β-estradiol, 17β-estradiol glucuronide and 17α-ethynylestradiol) were performed in less than 7 minutes.

In the second work, it was studied the use of molecularly imprinted polymers (MIPs) as sorbent in solid phase extraction. This type of sorbents is designed using a molecule as a template and for that reason, only analytes with a similar structure of the template molecule could be adsorbed, which means that the selectivity is greater in comparison with conventional polymeric sorbents. All the variables involved in the extraction process were optimized and the results were compared with those obtained for traditional sorbents.

Results and Discussion

In the optimization of the conventional SPE method, it was observed that the highest recoveries were using C_{18} cartridges and also it was checked that ionic strength of the sample had a negative influence in the extraction process. The optimized SPE-UHPLC-FD method showed very satisfactory analytical parameters and a high preconcentration factor of 125.

Regarding the optimization of molecular imprinted solid phase extraction (MISPE), it was observed that the selectivity of the cartridges was really good. The optimized MISPE-UHPLC-FD method was applied to real wastewater samples from a wastewater treatment plant and from a veterinary hospital. The analytical parameters obtained were really good, with recoveries which were over 60% and detection limits which ranged from 0.18 to 0.45 $ng \cdot mL^{-1}$.

Conclusion

The development of UHPLC-FD methods could be used to evaluate the presence of steroid hormones in environmental samples, achieving appropriate analytical parameters and quantification limits. Moreover, UHPLC-FD technique could be also very useful in the optimization and development of extraction and preconcentration procedures which are absolutely essential to quantify trace levels of this type of pollutants in environmental systems.

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Ultra-high performance liquid chromatography with fluorescence detection to determine benzimidazole compounds in farmed fish samples

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Introduction

Benzimidazoles (BZs) are veterinary drugs widely used as anti-parasitic agents in domestic animals. More recently, some BZs have also found applications in aquaculture to treat tape-worm infections. However, their widespread use could lead to BZ residues in animal-producing food, which may cause some negative effects on the consumer health, such as congenic malformations and teratogenicity among others. In this sense, the development of analytical methods to determine the presence of these residues is mandatory in order to fulfill European legislation, although for fish, maximum residue levels are not regulated yet.

Materials and Methods

UHPLC (Jasco-X-LC) separation was performed in a Zorbax Eclipse Plus RRHD C_{18} column (50×2.1 mm, 1.8 µm), involving a total analysis time lower than 12 min. The mobile phase consisted of water (solvent A) and acetonitrile (solvent B) at a flow rate of 0.4 mL/min. The column temperature was 40 °C and the injection volume 20 µL. Fluorescence detection was performed at maximum exc/em wavelengths: 316/400 nm for 5-OH-Thiabendazole (5-OH-TBZ); 290/325 nm for Albendazole 2-aminosulfone (ABZ-NH_2-SO_2); 280/320 nm for (Carbedazim)CBZ and (Benomyl) BEN; 290/325 nm for Albendazole sulfoxide (ABZ-SO), Thiabendazole (TBZ), Fuberidazole (FUB) and Albendazol sulfone (ABZ-SO_2); 290/340 nm for Oxibendazole (OXI) and 290/340 nm for Albendazole (ABZ), Triclabendazole sulfone (TCB-SO_2), Triclabendazole sulfoxide (TCB-SO) and Triclabendazole (TCB). Detector gain was set at 100.

Results and Discussion

The best separation in terms of resolution was achieved when MeCN was employed as organic solvent (B) in the mobile phase. Afterwards, water was selected as eluent (A) over 50 mM ammonium acetate. Although better resolution of TCB metabolites was achieved with ammonium acetate, it was discarded due to backpressure problems. On the other hand, mobile phase flow rate was studied from 0.4 to 0.6 mL min^{-1}, selecting 0.4 mL min^{-1} as optimum because higher flow rates involved a decrease of resolution between ABZ-SO and TBZ. The temperature of the column was evaluated from 30 to 50 ^{0} C, selecting 40 ^{0} C since all peaks were baseline resolved. Then, salting-out assisted liquid-liquid extraction (SALLE) was applied as sample treatment to different types of farmed fish (trout, sea bream and sea bass). To obtain satisfactory extraction efficiencies for the studied analytes, several parameters affecting the SALLE procedure were optimized including the amount of sample, type and volume of the extraction solvent, and the nature and amount of the salt used. Characterization of the method in terms of performance characteristics was carried out, obtaining satisfactory results in terms of linearity ($R^2 \geq 0.997$), repeatability (RSD≤6.1%), reproducibility (RSD≤10.8%) and recoveries (R≥79%; RSD≤7.8%). Detection limits ranged between 0.04 and 29.9 µg kg^{-1}.

Conclusion

This method has demonstrated to be suitable to determinate 13 BZs with high selectivity and sensitivity. Above all, it involves an easy, fast and inexpensive method for BZs monitoring in fish samples such as trout, sea bream and sea bass, allowing high extraction efficiency with low consumption of reagents, solvent and samples, and hence, it complies with Green Chemistry principles.

Acknowledgments

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Posters

A NEW DIRECT PHOTO-INDUCED FLUORESCENCE METHOD COUPLING UV LAMP IRRADIATION AND LASER DETECTION

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Introduction

Pesticides are widely used in agriculture to improve productivity. Thus, their residues can be found in crops, soils and surface water. However, their persistence in the environment is a major matter of concern due to their toxicity and possible carcinogenicity. Therefore, it is important to develop sensitive and selective analytical methods for determining pesticides in surface water, groundwater, soils. In this works, we have developed a new direct analysis method for the simultaneous determination of fipronil, oxadiazon and isoproturon, tree pesticides naturally non-fuorescent. The method is done in only a single step and is a new evolution of the Direct Laser PIF Methods previously published [1-2].

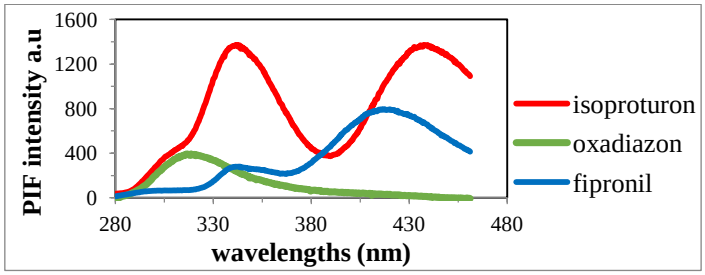
Materials and Methods

Non fluorescent compounds are irradiated by a power UV lamp, (300 w). The so formed photoproducts are excited by a tunable laser (Nd – YAG-OPO) and detected by a spectrophotometer and high-sensitive ICCD camera.

Results and Discussion

Fipronil, oxadiazon and isoproturon exhibited no native fluorescence, while UV irradiation yielded the formation of strongly fluorescent(s) photoproduct(s). These photoproducts were obtained after 1 min of UV irradiation and the emission spectra were recorded after laser excitation (figure 1). The analytical performances of our method are satisfactory compared to the classical PIF method. The calibration curves are linear and over two order of magnitude. Low limit of detection and quantification (in the ng mL^{-1} range) were obtained in 80:20 (v/v) methanol-water mixture.

Figure 1 : fluorescence emission spectra of fipronil, oxadiazon and isoproturon in the 80:20 (v/v) methanol-water mixture.



Conclusion

We have demonstrated in this work that UV irradiation coupled with laser excitation is a sensitive, rapid and reproducible method for the analysis of fipronil, oxadiazion and isoproturon pesticides in water samples.

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Analysis of agmatine in shrimps by fluorescence method

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Introduction

Biogenic amines are compounds containing nitrogen and naturally present in animals and certain plants. They are derived from enzymatic degradation of amino acids or from microbial degradation of protein foods[1]. At low concentrations, biogenic amines have important physiological functions. However, in high doses these amines become toxic[2]. In the face of food poisoning caused by their presence in foods, it is necessary to develop a reliable, accurate and lower cost analysis method for their determination in food products. In this work we developed a new spectrofluorometric method for agmatine determination in shrimp after derivatization with orthophthalaldehyde (OPA).

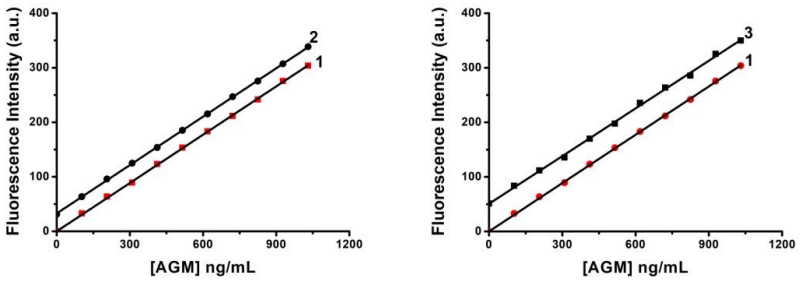
Materials and Methods

Fluorimetric analyzes were made using a Varian Cary Eclipse fluorescence spectrophotometer. This method required solid phase extraction (SPE) with 6% trichloroacetic acid (TCA). Analyticals applications were evalued using the standard addition method (figure 1).

Results and Discussion

The analysis of agmatine was performed in aqueous medium at pH 13 after 20 minutes of agitation. We obtained satisfactory analytical performances with very low limits of detection and quantification (2.2 ng/mL and 5.4 ng/mL respectively). The correlation coefficients are close to unity and the very low relative standard deviation (RSD) values indicate good precision and reproducibility of the method. This method was applied to the analysis of agmatine in gambas and bouquets to evaluate its effectiveness. Very satisfactory recovery rate ranging from 96.3% and 103.4% were found.

Figure 1 : Straight calibration curve of agmatine (1); Standard addition curve of these samples in shrimp: bouquet (2), and gambas (3).



Conclusion

In this study, we have shown that the fluorescence method is simple, fast and easy to analyze agmatine. Satisfactory results were found by applying this method to the determination of agmatine in shrimp.

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Cathodoluminescence analysis of space used polymers

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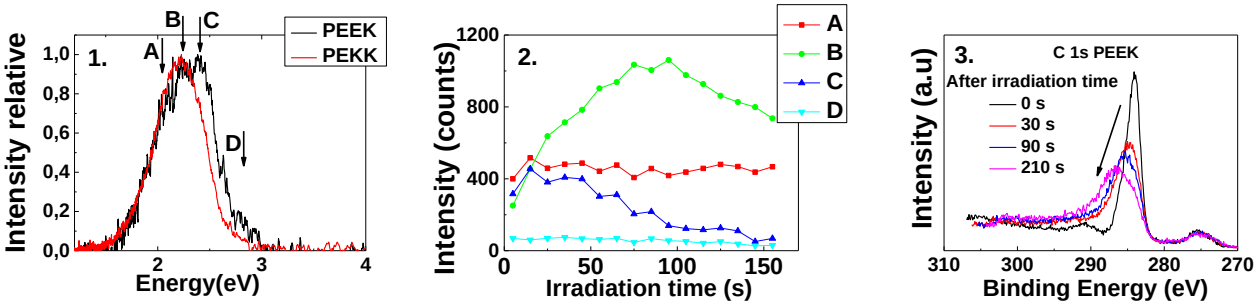
Dielectric materials used on spacecraft have to cope with strong levels of charging under electron irradiation in space environment. This charging process could lead to potential hazardous discharges and electric arcs on different parts of the satellite generating anomalies, such as electromagnetic disturbances, power losses, and, in worst case, the destruction of some on-board systems. It is therefore essential to test and qualify space materials under representative conditions and to assess their electrical and optical properties.

It has been shown previously [1], that charging effect is usually smoothed by ionization processes due to high energy electron irradiation that enhances significantly the bulk electrical conductivity in space materials (Radiation-Induced Conductivity "RIC"). Models based on solid-state physics have been developed at ONERA to describe and predict charge and ionization effects of space materials. These models take into account the effects of: charge carrier generation, trapping-detrapping and recombination. Some physical mechanisms are however not taken into account such as: radical formation, energy transfer processes, ageing effect. To improve our understanding of charge transport mechanisms in space used materials, we have developed several experimental techniques including cathodoluminescence spectroscopy (CL). This technique is interesting for extracting transition energies and bringing into evidence ageing processes. CL is the photon emission from electron bombardment that induces energy transfer to and from the material. This technique is relevant to characterize several mechanisms (radical formation, recombination, trapping, defect and impurities) occurring in irradiated materials. In this paper, we present the results of two polymers having a close chemical structure, PEEK (poly-ether-ether-ketone) and PEKK (poly-ether-ketone-ketone). These materials are used as wiring, insulating parts and mechanical support on spacecraft. Charge transport in these polymers is very complex and CL would bring new information on radiation processes occurring during irradiation. A parametric study on PEEK and PEKK was carried out (chemical structure, irradiation time/dose and temperature) in order to improve our knowledge on the nature and occupation of trapping sites, and creation and influence of radical formation and recombination processes.

PEEK and PEKK showed the same spectral contributions (A → D) but at different intensities (Fig.1). This observation means that the trapping or recombination centers at the origin of the radiative transitions are identical (in relation to the chemical structure) but at different yields. These discrepancies on their spectra could be assigned to ether and ketone groups. Fig. 2 shows the evolution of each contribution as a function of the irradiation time with electron beam. This behavior was attributed to the degradation of the material (chemical bond scission, crosslinking …)[2]. To support our analysis, we performed XPS (X-ray Photoelectron Spectroscopy) tests to assess the chemical degradation of materials. Fig. 3 shows one of the spectra (C1s) obtained on the PEEK. This evolution reveals a modification of the chemical structure. The increase of the shoulder towards high binding energies could be attributed to the creation of new chemical groups (carboxylic acid - ester - aldehyde ...) following the scission of the main chain[3]. CL tests were also performed at 150 K to 300 K (not shown here). For PEEK, the lowering of luminescence intensity with decreasing temperature could be related to oxygen due to polymer fragmentation possibly quenching the luminescence[4].

Figure 1: CL spectra of PEEK and PEKK. – **Figure 2:** Evolution of contributions (A to D) as a function of irradiation time. – **Figure 3:** XPS C 1s spectra for PEEK for the following times (0 s, 30 s, 90 s, and 210 s).



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Chemiluminescence of luminol in presence of humic acids

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Introduction

Quantitative analysis of persistent toxic substances (PTS) in natural waters is essential to understanding global biogeochemical cycling. The study of humic acids in aqueous solution has been of particular interest over the past 50 years due to their role in various chemical, physical and biological processes in natural waters[1]. The study of the role of humic acids in photodegradation of PTS is the aim of this work. One solution is the use of chemiluminescence (CL) detection coupled with humic acids, which has been rapid and highly sensitive.

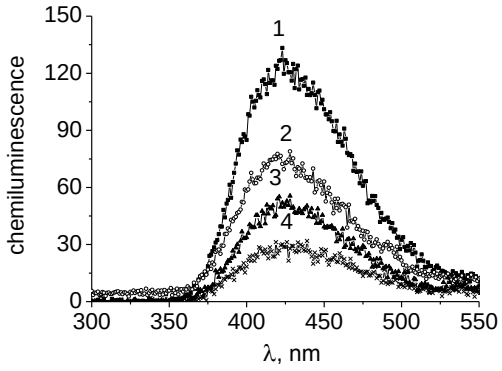
Materials and Methods

Many compounds have been shown to emit light upon oxidation; the most studied is probably 5-amino-2,3-dihydro-1,4-phthalazinedione, commonly known as luminol[2]. The antiradical activity of humic acids before and after irradiation was analyzed in the CL reaction of luminol using the Cary Eclipse spectrophotometer ("Varian", Australia) by "Chemiluminescence" and "Kinetics" regimes.

Results and Discussion

Humic acids are biopolymers and contain natural antioxidants, which are free radical scavengers. The intensity of CL is markedly reduced in the presence of unirradiated humic acids (Fig.1). After irradiation with KrCl excilamp, humic acids effectively quench luminescence of luminol. This may be due to the formation under the action of ultraviolet free radicals of humic acids, which contribute to quenching the CL reaction. It is fixed that the CL time is the maximum with the addition of humic acids irradiated for 8 minutes. The graphic form of the luminol CL kinetics corresponds to the exponential law. The damping of CL luminol in the presence of irradiated humic acids can be divided into two components-a fast one (up to 1 s) and a slow one (up to several minutes).

Figure 1: Chemiluminescence spectra of 3 mM luminol (1) in the presence of unirradiated (2) humic acids and irradiated for 2 min (3) and 32 min (4) by KrCl excilamp.



Conclusion

The results of experiments indicate that, the intermediate products of photo-oxidation of humic acids of molecular nature are the source of quenchers of luminol chemiluminescence. The obtained quantitative characteristics can be used to develop methods for monitoring the peroxide oxidation of pollutants in water and detailing the mechanisms of their phototransformation in the presence of humic acids, which will be the subject of further research.

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Combination of photo-induced fluorescence and GC-MS for elucidating the photodegradation mechanisms of diflubenzuron and fenuron pesticides

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Introduction

Diflubenzuron (DFB) and fenuron (FEN) are non-fluorescent benzoyl- and phenylurea pesticides. Recently, we have applied classical photo-induced fluorescence (PIF) and direct laser PIF (DL-PIF) methods, based respectively on UV and laser irradiation, to transform DFB and FEN into strongly fluorescent photoproducts [1,2]. Combining these methods with gas chromatography-mass spectrometry (GC-MS), we have elucidated the photodegradation mechanisms of both pesticides.

Material and methods

In the case of PIF, a Kontron SFM-25 spectrofluorimeter and an Osram 200-W high-pressure mercury lamp were used, and in the case of DL-PIF, a Varian Cary Eclipse spectrofluorimeter with a Powerlite Precision 9010 pulsed ND:YAG pump laser beam was utilized. FEN aqueous solutions and DFB methanol-water mixtures at pH 4 were prepared. A Thermo Fisher Scientific model ISQ-Trace-1300 GC-MS was used for the separation and identification of DFB and FEN photoproducts.

Results and discussion

Applying the PIF and DL-PIF methods, one fluorescent DFB photoproduct was obtained at $\lambda_{ex}/\lambda_{em}$ = 230/342 nm, and two fluorescent FEN photoproducts were found at $\lambda_{ex}/\lambda_{em}$ = 225/308 nm and 280/342 nm. GC-MS confirmed that phenol and hydroxylamine were the main DFB and FEN fluorescent photoproducts. Indeed, fluorescence spectral characteristics similar with standards indicated that hydroxyl-aniline was the common, main photoproduct of both pesticides, and that phenol was the second main photoproduct of FEN. GC-MS indicated also the presence of a number of photoproducts formed during the photodegradation of both pesticides. Finally, we showed that the photodegradation mechanisms of DFB and FEN were complex and involved several reaction steps, such as dehalogenation, decarboxylation, demethylation, deamination and hydroxylation, in agreement with literature data [3,4].

Conclusion

Using GC-MS, we were able to separate and to identify several DFB and FEN photoproducts formed during the photodegradation of both pesticides. Combination of the PIF methods and GC-MS allowed us to propose schemes of reaction mechanisms for the DFB and FEN photodegradation.

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Construction of a laser diode fluorescence detection system for creatinine determination

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Introduction

Serum creatinine is an important and the most commonly used indicator of renal function because creatinine is removed from the blood primarily by the kidney glomerular filtration. Any changes of creatinine levels in the blood are related to excretion and therefore reflect kidney function. There are two common determination methods of creatinine, one is enzymatic assay and the other one is spectrophotometric method based on the Jaffe reaction. The enzymatic assay exhibits good accuracy, but it is relatively expensive and highly complicated, and time consuming. The chemical picric acid used in the spectrophotometric method is inflammable. Creatinine will be reacting with 3,5-Dinitrobenzoic acid under the highly alkaline condition. The complexes have fluorescent characteristic that absorb excitation light at 400 nm and release fluorescence at 491 nm. In this study, we established a novel laser diode fluorescence detection system for the fast and low-cost determination of creatinine.

Materials and Methods

The creatinine fluorescent sensing system developed in this study used a 400-nm wavelength laser diode (LD) as the excitation light source with a wave width of ± 5 nm and an LD drive current of only 24 mA. With low energy consumption, small size and high coherence characteristics, then micro-spectrometer as a fluorescent receiver, the grating opening is 50 μm, and the spectrometer is connected with a two-dimensional translation stage, and it is adjusted to the optimal light receiving position, and select the capacity of 500 μL black double-sided light quartz cuvette containing the sample to be measured.

Creatinine solution with 0.3 mM of concentration was added with 0.625 M LiOH and 37.5 mM 3,5-dinitrobenzoate solution. After one minute, the excitation and emission spectra were measured by Fluorescence Spectrophotometer F-4500 (Hitachi, Ltd., Tokyo, Japan). Separately prepared 2.5 mM LiOH solution and 150 mM 3.5-dinitrobenzoate solution were mixed and 0.25 mL of the mixture was used as the test reagent. Each of the creatinine standard solution with the concentrations of 0, 5, 12.5, 25, 50, 75, 150, 300 μM was evenly shaked and placed in an optical fluorescence detection system set up in this laboratory for 20 minutes of fluorescence detection.

Results and Discussion

The results showed that the fluorescent bio-system had good linearity from 5 μM to 300 μM (R^2 = 0.9934) and the limit of detection (LOD) was 5 μM. The intra-day accuracy and precision ranged from 81.82 to 99.75% and 7.33 to 10.11%, respectively. The inter-day accuracy and precision ranged from 86.75 to 87.85% and 3.08 to 9.39%, respectively. Compared the results with those from National Laboratory Animal Center, the results showed good correlations with 0.80 of (R).

Conclusion

A new creatinine fluorescence sensing system was successfully developed using a micro-spectrometer combined with a laser diode and a three-dimensional translation stage. Compared with the existing measurement methods, it has high measurement sensitivity and is suitable for the determination of creatinine in the blood.

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Determination of homocysteine and its related compounds in hair by HPLC-fluorescence method (1) -Estimation of extraction conditions-

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Introduction

Homocysteine (Hcy), one of the sulfur-containing amino acids, is an intermediate metabolite of methionine (Met) to metabolite cysteine (Cys). The elevated level of Hcy and its related compounds in organisms play an important role in a variety of diseases. Therefore, the simultaneous determination of Hcy and its related compounds such as Met and Cys is required to appropriate clinical management. The purpose of the study is to develop the HPLC-fluorescence (-FL) method combined with 4-(*N*,*N*-dimethylaminosulfonyl)-7-fluoro-2,1,3-benzoxadiazole (DBD-F) for determination of Hcy and its related compounds in hair as a non-invasive sample. In this presentation, the extraction condition of Hcy from hair matrix was examined.

Materials and Methods

Extraction: One milligram of grinded hair was treated as follows: 1) 6M NaOH (80℃, 1 h), 2) 6 M HCl (110 ℃, 24 h), 3) 5% HCl in MeOH (1 h sonication) and 4) 5% trifluoroacetic acid in MeOH (1 h sonication). After reduction with 4 mM dithioerythritol in 400 mM borate buffer (pH 8.5) at 80 ℃ for 15 min, the solution was applied to the derivatization reaction. Derivatization: The extract was added to 60 μL of 400 mM borate buffer (pH 8.5) and 60 μL of DBD-F in CH_3CN. After heating at 80℃ for 15 min the mixture was centrifuged at 2670 *g* for 10 min. Then, 150 μL of the mixture were cleaned up by liquid-liquid extraction with 300 μL of ethyl acetate. The organic layer was dried up and reconstituted with 150 μL of mobile phase. HPLC: The DBD derivatives were separated on a Daisopak SP-120-5-ODS-BP (250 × 2.0 mm, i.d.) with 25 mM phosphate buffer (pH 2.0)/CH_3CN/MeOH (=57:37:6, v/v/v%) as a mobile phase. The detection wavelength at 400 (λ_{ex}) and 570 nm (λ_{em}) was used.

Results and Discussion

The DBD-Hcy could be observed in the hair samples extracted with acid-MeOH, however, no peak from the samples with acid or alkaline treatment. On the other hand, Met and Cys in sample treated with 6 M NaOH were detected effectively.

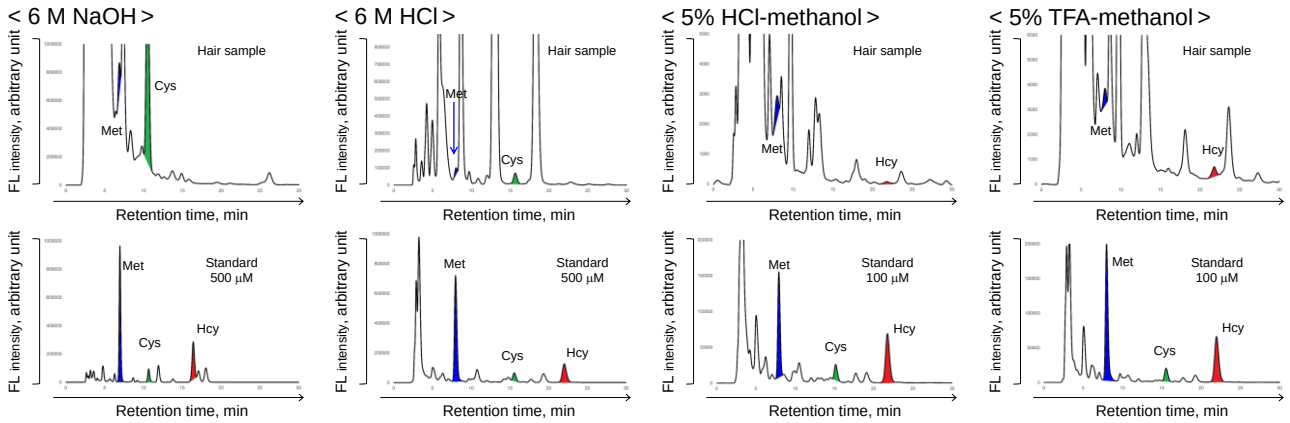

Figure 1. Chromatograms of hair sample and standards.

To improve the extraction yield of Hcy and related compounds the conditions in detail should be examined.

Determination of pharmaceutical compounds in wastewaters from constructed wetlands using ultra-high performance liquid chromatography with fluorescence detection

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Introduction

Pharmaceutical compounds constitute an important group of active compounds which can produce deleterious effects over aquatic ecosystems when they reach them through wastewaters[1]. For this reason, it is necessary to develop treatment methods which permit the elimination of these compounds. Nevertheless, in small communities, the construction of traditional treatment facilities could not be the most suitable option and constructed wetlands (CW) have revealed as a sustainable and economic solution[2]. In this work, we present a methodology based in solid phase extraction (SPE) combined with ultra-high performance liquid chromatography with fluorescence detection **(**UHPLC-FD) for the determination of five different drugs (acetylsalicylic acid, naproxen, ibuprofen, gemfibrozil and ciprofloxacin) and its application to samples from a pond-CW system.

Materials and Methods

The pond-CW system under study is located in a university area and it consists of a facultative lagoon and a horizontal flow CW. It has been operating since 1999 treating raw wastewater from the campus. The efficiencies for BOD_5 (biological oxygen demand), COD (chemical oxygen demand), total suspended solids and turbidity have been moderately high, over 75%.

OASIS HLB SPE cartridges were used to extract the pharmaceuticals from 250 mL of wastewater at pH=7. After the elution of the target compounds using 5 mL of HPLC methanol, the extracts were dried under a stream of nitrogen and after that, the extracts were reconstituted in 1 mL of methanol, achieving a preconcentration factor of 250.

Regarding the chromatographic procedure, it was performed using an ACQUITY UPLC system with a fluorescence detector and an ACQUITY BEH C_{18} column (50 x 2.1 mm, 1.7 µm). The separation of the target compounds was done in gradient mode in 7.5 minutes. Excitation and emission wavelengths were also optimized for each compound.

Results and Discussion

The SPE-UHPLC-FD method was applied to real wastewater samples obtained in a natural wastewater treatment plant. Samples from influent, the facultative lagoon effluent and the CW effluent were analysed every week from February to May 2018. The concentrations of the pollutants in the influent were significantly different from those of the effluent. Moreover, the method allowed the evaluation of the removal efficiencies of this natural treatment system.

Naproxen and ibuprofen showed the highest concentrations of detected compounds while acetylsalicylic acid cannot be quantified in any sample.

Conclusion

The development of a SPE-UHPLC-FD method for the determination of pharmaceutical compounds in wastewaters have been successful. Despite of many interferences from the matrix, the developed method has shown a great selectivity and sensitivity, resulting to be appropriate for the determination of the target pharmaceuticals, even at trace concentrations.

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Determination of the Oxadiazon Herbicide in Natural waters by a Micellar-Enhanced Photochemically-Induced Fluorescence Method.

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Introduction

Pesticides are widely used in agriculture to improve productivity. Oxadiazon is a oxadiazolone herbicide water soluble which can remain in soil for several months following application, residues can migrate to crops and enter he food chain, which can lead in general to diseases such as cancer. In this works, the objective is to develop an analysis method based on micellar-enhanced photochemically induced fluorescence (PIF) for the determination of oxadiazon. Generally, the use of micellar media was found to significantly enhance the PIF signal of pesticide relative to an aqueous solution [1-2]. In this work the quantification methods were evaluated and compared in aqueous solution and with two surfactants *i.e.:* cetyl trimethyl ammonium chloride (CTAC) or tweed 20 (tw20).

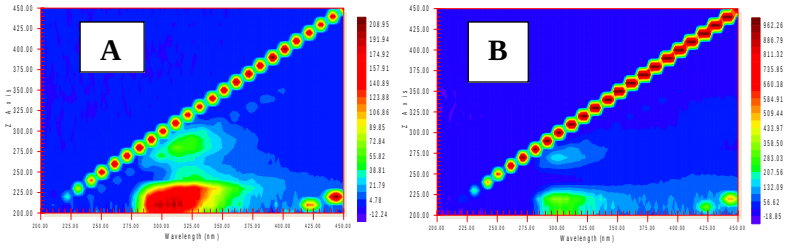
Materials and Methods

Not fluorescent compounds are irradiated by a power UV lamp, (300 w). All spectral of the so formed photoproducts were measured by a Cary Eclipse fluorescence spectrophotometer (Varian).

Results and Discussion

Oxadiazon exhibited no native fluorescence, while photoconversion under UV irradiation of the herbicide gives strongly fluorescent photoproducts in aqueous solution and in the presence of CTAC or tw20 at micellar concentrations (figure 1). Fluorescent photoproducts and emission spectra were obtained in optimal irradiation time. The calibration curves are linear over two order of magnitude and very low detection and quantification limits (in the ng mL^{-1} range) were obtained in the presence of surfactants.

Figure 1 : 3D excitation and emission spectra of oxadiazon (10 µg/ml) after 5min and 7min of irradiation in respectively: A) CTAC (5.10^{-3} M) and B) TW20 (6.10^{-5} M)



Conclusion

We have demonstrated in this work that method is simple, sensitive, rapid and reproducible for the analysis of oxadiazion herbicide in water samples.

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Determination of thiacloprid in teas by its quenching on terbium luminescence

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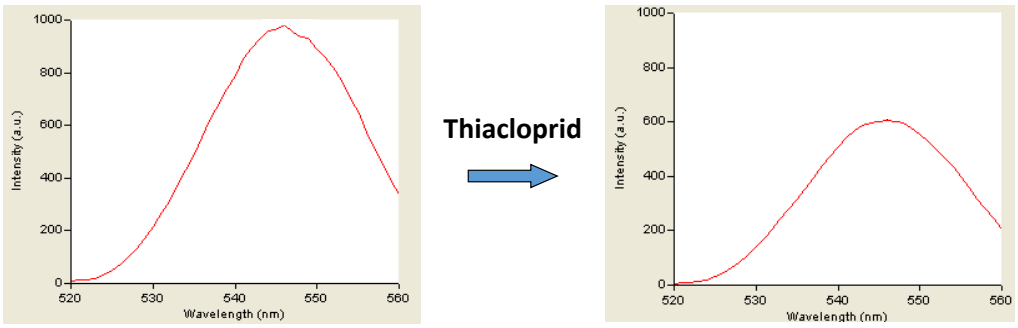
Thiacloprid is a broad-spectrum neonicotinoid insecticide, used against sucking insects and chewing insects. It is widely used in many crops, such as rice, fruits, and vegetables. There are many analytical methods for its determination, mostly liquid chromatography. However, the development of simple methods of analysis can provide an interesting alternative for routine analysis. In this work, we report the use of time-resolved luminescence for the quantitation of thiacloprid in tea samples. Terbium ions are commonly used in analytical chemistry in terbium-sensitized luminescence, which presents some exciting characteristics: large Stokes shift, narrow-band emission, and a long luminescence lifetime. The most common approach consists in the improvement of the analytical signal when terbium ions form chelates with appropriate fluorescence organic analytes. In this work, the approach is different, consisting in the measurement of the quenching produced by thiacloprid on the terbium luminescence.

After the optimization of instrumental (wavelengths, detector voltage, slits, delay time, and gate time) and chemical (terbium concentration, pH, dodecyl sulfate sodium concentration) variables, the analytical method presents a detection limit of 0.06 µg mL^{-1} and a linear response between 0.2 and 7 µg mL^{-1}. For the analysis of tea samples, a solid phase extraction methodology was optimized and validated. This analytical method complies with the maximum residue limit for thiacloprid in tea samples in the European Union, 10 mg kg^{-1}. Recovery experiments were carried out in spiked tea samples, obtaining excellent recovery yields. These results were compared with an HPLC reference method, obtaining no significant differences. Hence, this novel approach can be used for routine control of thiacloprid in teas, although positive results would need additional confirmation by mass spectrometry.



Tb^{3+} Tb^{3+} - thiacloprid

Development of a three-dimensional HPLC system with fluorescence detection for the simultaneous determination of lactate and 3-hydroxybutyrate enantiomers in human clinical samples

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Introduction

Lactate (LA) and 3-hydroxybutyrate (3HB), typical chiral hydroxy acids in living beings, are considered to have relationships with diseases such as metabolic disorders. Because both of them are chiral compounds, their enantioselective analysis in our bodies is the matter of interest since they might become the new drug candidates or clinical biomarkers. In order to determine the trace amounts of LA and 3HB enantiomers in various biological matrices containing uncountable intrinsic interfering compounds, we have developed a two-dimensional HPLC system following the fluorescence labeling of the carboxylic acid with 4-nitro-7-piperazino-2,1,3-benzoxadiazole (NBD-PZ). Although the 2D-HPLC is one of the most suitable methods for the trace analysis of chiral compounds in complicated matrices[1], the selectivity is still insufficient in some cases. Therefore, in the present study, an online 3D-HPLC system with fluorescence detection has been designed combining reversed-phase, mixed-mode and enantioselective separations and applied to human physiological fluids.

Materials and Methods

To the plasma or urine (10 μL), 5 μL of water and 85 μL of acetonitrile (MeCN) were added. The mixture was centrifuged at 3,300 rpm at 4˚C for 10 min, and the supernatant was collected. To 10 μL of the supernatant, 20 μL of an MeCN solution containing 5 mM NBD-PZ, 50 mM 2,2'-dipyridyl disulfide, and 50 mM triphenylphosphine was added. The mixture was stored at 25˚C for 60 min, and 220 μL of 0.1% trifluoroacetic acid (TFA) aqueous solution was added. An aliquot (100 μL) of the reaction mixture was subjected into the 3D-HPLC system and the elution of NBD-LA and 3HB in all 3 dimensions was monitored by fluorescence detectors (emission at 530 nm with excitation at 470 nm).

Results and Discussion

In the first dimension, a reversed-phase column (KSAARP, 1.0 mm i.d. x 250 mm) was used to separate the NBD-derivatives of LA and 3HB. For the mobile phase, various concentrations of MeCN (10 to 20% in water) at different temperatures were investigated. As a result, NBD-LA and NBD-3HB were separated well using an aqueous solution containing 15% MeCN and 0.05% TFA at 40˚C. The peaks of NBD-LA and NBD-3HB enantiomers were fractionated respectively as their scalemic D plus L mixtures and introduced into the next (second) dimension. In the second dimension, NBD-LA or NBD-3HB were isolated again from other interfering compounds by a mixed-mode column (KSAAMX-001, an originally designed column by the collaboration with Shiseido having 3,5-dinitrophenylaminocarbonyl-Gly as a selector, 1.5 mm i.d. x 250 mm). The mobile phase conditions in this dimension were tested with the organic solvents including MeCN, methanol and ethanol. As a result, 100% ethanol was selected as a mobile phase for both NBD-LA and NBD-3HB. The peaks of their D+L mixtures were collected again and transferred to the final (third) dimension. In the third dimension, the enantiomers of NBD-LA and NBD-3HB were separated into the D-form and L-form by a polysaccharide type chiral column (Chiralpak AD-H, 2.0 mm i.d. x 250 mm). As the mobile phase, the mixture of MeCN, methanol and ethanol were investigated in detail and both NBD-LA and NBD-3HB enantiomers were completely separated by 100% ethanol with resolution values higher than 2.01. The present 3D-HPLC system was applied to human plasma and urine and trace levels of LA and 3HB enantiomers were successfully determined.

Conclusion

The 3D-HPLC system is suitable to evaluate the amounts/alternations of LA and 3HB enantiomers in real world matrices, and various clinical applications including metabolic disorders, cardiovascular diseases are ongoing.

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Effect of Dy doping on the thermoluminescence properties of ZnO phosphors

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Introduction

The optoelectronic properties of ZnO have been the subject of a number of investigations. It is a non-toxic wide band gap (3.2 eV) semiconductor with a 60 meV exciton binding energy that can be obtained through low cost and easy synthesis routes[1]. In this work we report on the effect of Dy doping on the thermoluminescence (TL) characteristics of ZnO with the aim of proposing it as a TL dosimeter.

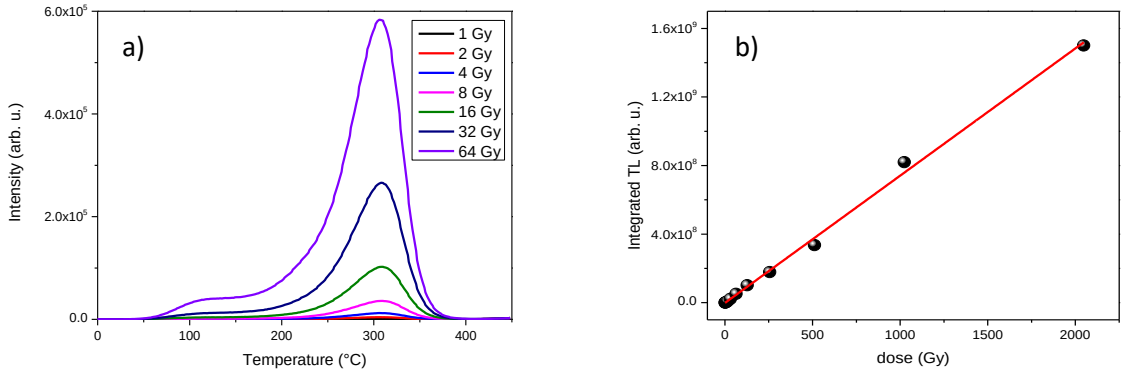
Materials and Methods

Dy doped ZnO was synthesized using a controlled precipitation reaction with weight percent Dy/Zn 5 % and sintered at 1000 °C for 48 h.

Results and Discussion

X-ray diffraction patterns revealed ZnO hexagonal wurtzite phase. The TL glow curves were recorded using a 5 °C/s heating rate (figure 1a). The integrated TL increases by increasing the beta particle irradiation dose and a linear behavior from 1.0 Gy to 2,048 Gy (figure 1b). A 10 % TL fading was observed 96 h after 20 Gy irradiation, and the reusability in 10 irradiation – normalized TL readout cycles presents a $\sigma = 0.0143$ standard deviation. The computed lower detectable dose was 3.6 mGy.

Figure 1: (a) TL glow curves and (b) integrated TL of synthesized ZnO:Dy as obtained after exposure to different doses of beta particle irradiation.



Conclusion

Based in the properties here reported, we conclude that Dy doped ZnO is a promising phosphor material for application in different branches of radiation dosimetry.

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Investigation of 4-amino-TEMPO spin label interactions with some dihydroxycoumarins

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We report herein dihydroxycoumarins as fluorescent probes suitable for the detection and determination of 4-amino-TEMPO in aqueous solution. Among different coumarins studied, only dihydroxy-substituted derivatives show high sensitivity, specificity and selectivity for the nitroxide radical.

In this assay, dihydroxy-substituted coumarins under the action of 4-amino-TEMPO undergo very fast and significant increase in the fluorescence intensity. In the presence of 100 μM nitroxide, 6,7-dihydroxycoumarin (esculetin) exhibits the strongest fluorescence enhancement (up to 40 times) with estimated limits of the detection and quantitation equal to 0.43 μM and 1.04 μM, respectively. A linear relationship has been observed between the fluorescence enhancement of the chosen dihydroxycoumarins and 4-amino-TEMPO concentration up to 50 μM. The mechanism of the interaction between 6,7-dihydroxycoumarin and 4-amino-TEMPO has been examined with the use of a series of complementary techniques, such as steady-state and time-resolved fluorescence spectroscopy, UV-Vis spectroscopy, electron paramagnetic resonance spectroscopy (EPR) and the potentiometric titration. It has been proven that the only route of the reaction in the system studied is a proton transfer from the molecule of esculetin to the amino group of the nitroxide radical.

Furthermore, in the current project, it has been shown that 6,7-dihydroxycoumarin incorporates easily into the cancer cells (probably contrary to normal cells). It has been confirmed that esculetin exhibits anticancer properties[1]. Additionally, the cytotoxicity of that derivative was evaluated on the prostate (PC3) and breast (T47D) cancer cell lines as well as non-cancerous cells (normal fibroblasts) by the MTT assay.

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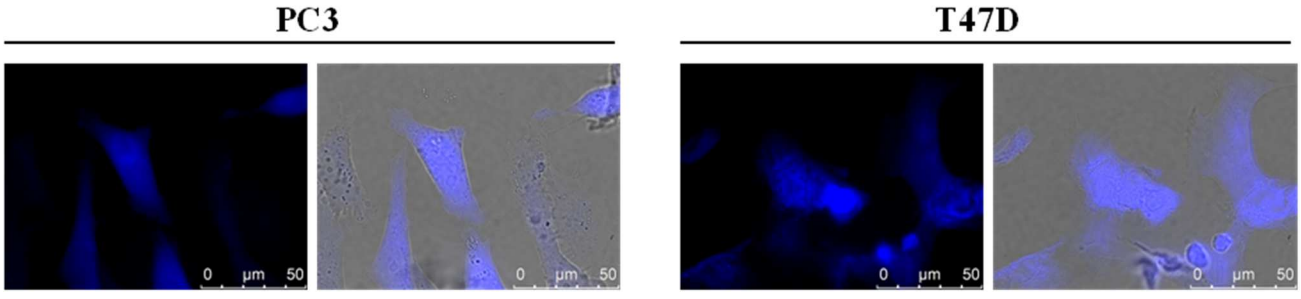
Figure: Representative images of 6,7-dihydroxycoumarin fluorescence in prostate (PC3) and breast (T47D) cancer cells. Phase contrast and fluorescence images were aquired with fluorescence microscope with a 100x oil objective.



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New ultra-rapid detection of pesticides in honeybee

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Introduction

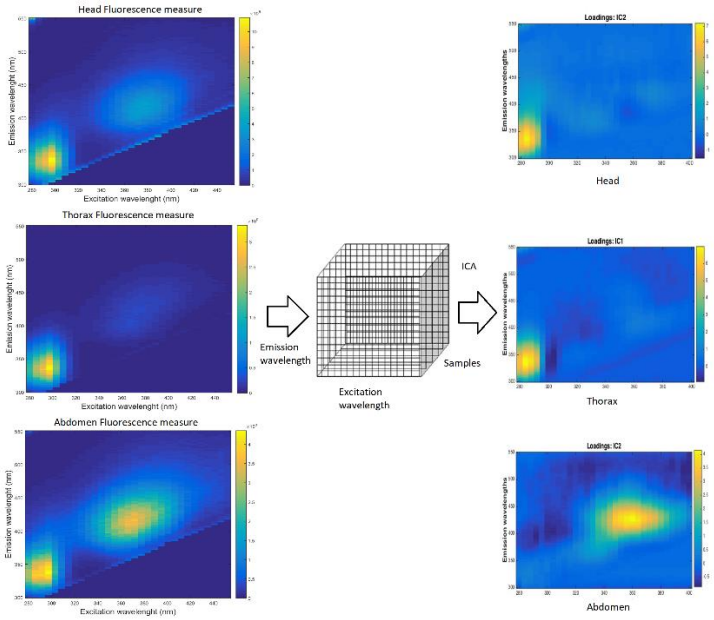
The development of 3D-Fluorescence Spectroscopy to follow biological fluorophores into honeybees allows for detecting variations in honeybees' metabolism linked to pesticide exposure, in combination with the Independent Component Analysis, which used as a means of source signals extraction from raw spectra.

Materials and Methods

6 boxes of 40 honeybees/box with pesticide and 6 others without pesticide. Fluoromax-4 Spectrofluorimeter (Spex-Jobin Yvon, Longjumeau, France) for fluorescence analysis and Matlab environment to perform the ICA and ANOVA analyses onto the ICA scores.

Results and Discussion

Figure and Table 1: Description of the Independent Component Analysis and ANOVA results of some of the fluorophores detected, with their identification.



Body Part	IC	Ex/Em **Pair (nm)**	df	F	Probability	Fluorophore
Head	IC2	280/340	17	9,62	0,0069*	Trp-Protein[1]
Thorax	IC2	280/340	17	5,66	0,0302*	Trp-Protein[1]
Abdomen	IC3	330/440	17	16,53	0,0009*	NADH[3]

The variation in ICA signals' proportions of these fluorophores shows the presence of pesticide, the response to stress and detoxification process in the honeybee[2].

Conclusion

The variation between main fluorophores of the honeybee metabolism shows that the presence of pesticide can be detected with the Front-Face Fluorescence Spectroscopy. The stress response modelling makes it possible to have a more general idea of the detoxication response to stress in a very fast way.

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Quantitative study of the substituent effects on the electronic absorption and fluorescence spectra of coumarins

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Introduction

The fluorescence properties of coumarins are highly dependent on their molecular structure. Recent studies have demonstrated that substituted coumarin quantum fluorescence yields were related to the substituent type[1,2]. In this work, we have used the Hammett equation[3] to evaluate the substituent effects on coumarin absorption and fluorescence spectra.

Materials and Methods

UV absorption and fluorescence spectra were recorded using a Perkin-Elmer Lambda2 absorption and a LS-50 spectrofluorimeter at room temperature. We applied the Hammett equations: $\bar{\nu} = \rho\sigma + \bar{\nu}_0$. The carbonyl oxygen negative electronic charges Q and HOMO and LUMO energies were calculated by the AM1 method.

Results and discussion

The correlation ρ positive values of $\bar{\nu}$ vs. σ (Fig. 1) correspond to coumarin red-shifts absorption and fluorescence bands by electron-donor substituents and to blue-shifts of these bands by electron-acceptor substituents. Thus, the inductive and mesomeric electron-donor effects of C-7 NEt_2, NMe_2, NH_2, OH substituents reduce the energy gap between the S_0 and S_1 electronic states, while the inductive electron-acceptor effects of C-7 Cl and Br substituents increase the gap between both states. These results are in agreement with the AM1theoretical data based on the HOMO and LUMO energy calculations. Moreover, the Stokes shift decreases and increases, respectively observed for the electron-donor and for the electron-acceptor substituents, can be also explained by the Hammett correlations. The negative charge of the carbonyl oxygen underwent the influence of the C-7 substituents, which would explain the observed absorption and fluorescence bands shifts.

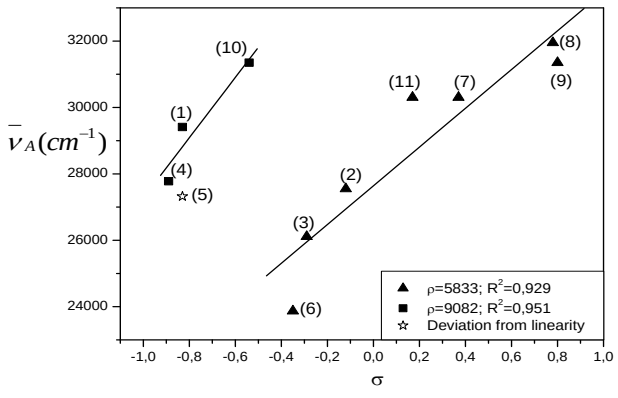

Fig. 1. Hammett plots of $\bar{\nu}_A$ vs. σ in 1,4-dioxan solvent. **(1)**7-amino-4-methylcoumarin; **(2)**7-amino-4-trifluoromethyl coumarin; **(3)**7-dimethylamino-4-trifluoromethylcoumarin; **(4)** 7-diethylamino-4-methylcoumarin; **(5)**7-diethylaminocoumarin-3-carboxylic acid; **(6)** 7-diethylaminocoumarin; **(7)**coumarin-3-carboxylic acid; **(8)**7-Cl-4 trifluoromethylcoumarin; **(9)**7-Br-4-trifluoromethylcoumarin; **(10)**7-OH-4-methyl coumarin; **(11)**7-OH-4-trifluoromethyl coumarin.

Conclusion

It exists linear correlations between the coumarin electronic spectral properties and Hammett substituent constants σ. The ρ positive values indicate that inductive and mesomeric electron-donor effects of the C-7 substituents decrease the $\bar{\nu}_A$, $\bar{\nu}_F$, $\bar{\nu}_A - \bar{\nu}_F$ and electronic charge Q values.

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Biology and medicine luminescence techniques (biophysics, membranes study, FRET, proteomics, metabolomics,...)

Bacterial bioluminescence: Biology and applications

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Luminous bacteria are light emitting prokaryotes that carry *lux* genes responsible for luminescence emission. Luminous bacterial diversity is well known with symbiotic association with luminescent organisms such as squid and fishes. Nevertheless, recent study revealed that their diversity is found across the all invertebrate and vertebrate taxa, indicating their essential role of association with those organisms. Luminous bacterial species distribution in different environments and their role in association with different organisms are very interesting to present. Various physico-chemical parameters and genetical factors which affecting bacterial bioluminescence are overviewed herein. The importance of *luxA* gene in luminescence regulation and its ecological distribution via horizontal gene transfer are detailed. Luminescence intensities and types of luminescence color are compared between different species. Luminous bacteria have been used in different applications to monitor several toxicants from different environments. Recent studies have also revealed that phenolic compounds produced by luminous bacterial species exhibited potential antimicrobial applications against human pathogens. Bacterial luciferases and *lux* genes have numerous applications in environmental, industrial and medical applications. This review shows the last decade and recent discoveries on ecological distribution and diversity of several novel luminous bacterial species in various samples and their function. Major outlines about history of bacterial bioluminescence and other luminous organisms will also be delivered. A proper guidelines and suggestions to work on bacterial bioluminescence aspect will be shared for the benefit of new researchers.

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Bacteriochlorin–Styrylnaphthalimide Conjugates for Simultaneous Photodynamic Therapy and Fluorescence Imaging

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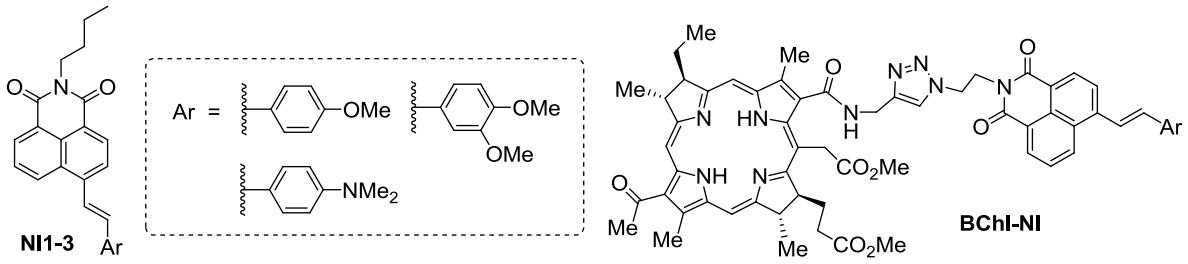
1,8-Naphthalimide derivatives are famous organic fluorophores which generally exhibit high thermo and photostability and are known to act as fluorescent brighteners and dyes for polymer fibers, laser active media, electroluminescent materials and optical memory devices. Because of its intense fluorescence, large Stokes shifts along with the relative ease of synthetic operations for targeted modification of the molecular structure, this type of compounds has found application in the construction of fluorescent chemosensors for biologically relevant cations and anions, labels or probes for proteins, cells, lysosomes and other acidic organelles. However, the emission bands of most naphthalimides are in blue and green-yellow regions. This limits their application as fluorescent probes and imaging agents in life sciences. Although it is well-known that electron-donating groups at the C-4,5-positions of naphthalene ring usually increase the fluorescence quantum yield of the compounds and cause the red shift in the spectra, the reports on 1,8-naphthalimide derivatives with emission wavelengths longer than 600 nm are very few.



In the present work, we focused on the spectroscopical investigation of styryl-1,8-naphthalimides **NI1–3** as promising long wavelength imaging units in bifunctional conjugates for simultaneous fluorescence diagnostics and photodynamic therapy of cancer. Firstly, steady-state and time resolved photophysical properties of these compounds were studied in protic and aprotic solvents of different polarity. We have found very interesting behavior related to the interplay between fluorescence, formation of TICT states and *E,Z*-isomerization[1]. The observed spectral effects have been rationalized using quantum-chemical calculations, X-ray data and NMR spectroscopy. At the second step, conjugates (**BChl-NI**) of styryl naphthalimides with propargyl-15[2],17[3]-dimethoxy-13[1]-amide of bacteriochlorin *e* known as a highly effective natural photosensitizer (PS) in PDT have been prepared[2]. The idea was to combine the modalities of PS and fluorescent probe in one molecule where the excitation of the naphthalimide fragment is expected to produce the strong emission signal, which could be used to monitor tumor responses to treatment. Further excitation by an other light wavelength corresponding to the absorption maxima of PS would lead to formation of singlet oxygen responsible for cancer cell damage. In this work, the details of our study of optical characteristics as well as evaluation of photosensitizing activity of **BChl-NI** in solution and in living cells are presented.

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Differential proteomic analysis in the progression of aristolochic acid nephropathy in mice using the FD- LC–MS/MS method

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Introduction

The fluorogenic derivatization-liquid chromatography-tandem mass spectrometry (FD-LC-MS/MS) method has been extensively applied to proteomics analysis from cells to tissue homogenates due to efficient, sensitive, reproductive properties[1,2,3]. Aristolochic acid nephropathy (AAN) is a well-known nephritis which might progress into end-stage renal disease. This study aimed to investigate the biomarkers in the progression of AAN without any specific indicators for diagnosis using a proteomics method with FD-LC–MS/MS.

Materials and Methods

The C3H/He female mice were given *ad libitum* aristolochic acid (AA)-distilled water (0.5 mg/kg/day) and distilled water for 56 days in the AA and normal groups, respectively. The mice were sacrificed on 0, 14, and 28 days after 56-day administration of AA/distilled water. The kidneys were made into sections for histological examination and homogenate for proteomics study, including fluorogenic derivatization with 7-chloro-*N*-[2-(dimethylamino) ethyl]-2,1,3-benzoxadiazole-4-sulfonamide (DAABD-Cl), followed by high-performance liquid chromatography analysis with flurescence detection and then identified by LC-MS/MS with a MASCOT database searching system.

Results and Discussion

The renal damage, including cell infiltration, fibrosis, tubular atrophy, was certainly induced in the AA- group mice under histological examination. The number of altered peaks between normal and AA groups on 0, 14 and 28 days after administration of AA/distilled water were 16, 54, and 24, respectively. In terms of functions, these identified proteins could categorized into anti-oxidant effect, extracellular matrix regulation, inflammations, apoptosis, oncogenesis, and ATP synthesis.

Conclusion

AA-induced proteins were found in the current proteomics study with FD-LC–MS/MS. According to the results, we could further understand the pathological mechanisms in the progression of AAN.

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Fluorescence-based methods to study hyperthermophilic archaeal family B DNA polymerase: Measurements of DNA binding and real-time enzymatic activities

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We report fluorescence-based methods to study polymerase and exonuclease activities of thermostable DNA polymerases in real-time on primer/template DNA duplex (P/T).

The methods are based on the use of (*i*) a fluorescent reporter which becomes fluorescent upon binding to newly synthesized double-stranded DNA, (*ii*) a quencher reporter from a tripartite Primers/Template (P/T) DNA duplex in strand-displacement polymerase assays, (*iii*) fluorescence fading of a nucleic acid stain concomitantly to DNA degradation in exonuclease assays, (*iv*) steady-state anisotropy to evaluate polymerase-P/T DNA duplex binding affinities. These methods are compatible with standard spectrofluorimeters, plate-readers or real-time PCR instruments.

Here, the efficiency of primer extension and degradation on P/T DNA duplex by *Pyrococcus abyssi* thermostable family B DNA polymerases (PabPolB) has been monitored at 55°C in real-time. In addition, the size of extension products was systematically examined by gel electrophoresis followed by fluorescence visualization[1]. Besides, The equilibrium apparent dissociation constant (K_D) characterizing the PabPolB-P/T DNA complex was calculated by fitting the plot of steady-state anisotropy versus PabPolB concentrations with a Hill model[2].

These real-time methods are very sensitive, quantitative, and well suited for the screening of DNA synthesis and degradation activities by different DNA polymerases. As such, novel intrinsic properties might be discovered with possible evolutionary scenario for the origin of families DNA polymerases. More generally, these fluorescent assays might be applied to other nucleic acid enzymes like helicases or nucleases.

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The use of *in vivo* bioluminescence for designing synthetic gene delivery systems

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Introduction

Bioluminescence imaging (BLI) is a powerful versatile tool for monitoring transgene expression in living animals. BLI can be combined with biofluorescence imaging (BFI) to provide further spatial and temporal information. Here, we show some applications of BLI and BFI that have been used to evaluate synthetic gene delivery systems (SGDS) for *in vivo* gene transfer to the lungs or the skeletal muscles.

Materials and Methods

Animal experimentations are carried out following protocols approved by the Institutional Animal Care and Research Advisory Committee. Original cationic lipids (UMR CNRS 6521, Brest) and Firefly Luciferase-encoding plasmid DNA (pDNA) are assembled to form supramolecular aggregates called lipoplexes. These are administrated in mice (Janvier Labs) following a specific delivery route. BLI is done thereafter *via* non-invasive imaging of luciferase expression (with emission at 560 nm) thanks to a CCD camera (NightOWL NC320, Berthold). Following an intraperitoneal injection of D-Luciferin, animals are anesthetized and laid inside an acquisition chamber. Luminescence images are captured with a binning and for an exposure time depending on the intensity of the signals. Luminescence is quantified within the regions of interest in the unit of photons/sec. For BFI, the same device is used following an adequate acquisition procedure with appropriate filters.

Results and Discussion

BLI allows to evaluate – in a semi-quantitative way – *in vivo* luciferase expression. This allows to distinguish between effective and non-effective SGDS[1], notably depending on the administration route (Fig.1). BLI can be challenged by measuring luciferase expression in organ/tissue homogenates, thus highlighting some technical limitations (e.g. tissue absorption and sensitivity threshold). BFI allows to track fluorescent lipoplexes once administered in animals and to correlate biodistribution with transgene expression[1,2]. BLI also emphasizes the critical role of the pDNA to deliver[3]; when its sequence is optimized, transgene expression can be monitored after single or multiple administration(s) throughout the lifespan of animals.

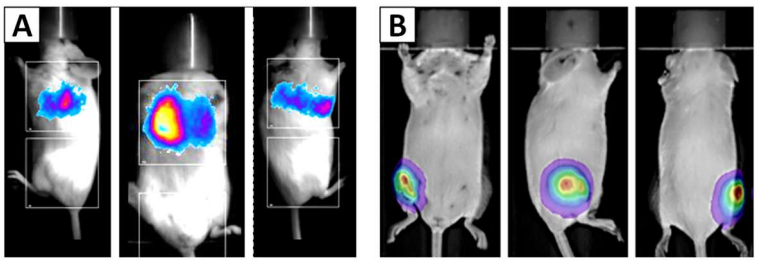

Figure 1: Examples of *in vivo* bioluminescence in living mice following efficient gene delivery to the lungs (A) or to the muscles in the hind limb (B). Each mouse was imaged according to three positions. Luminescence intensity is color-coded.

Conclusion

Besides some limitations/drawbacks, BLI has many practical advantages for *in vivo* screening of gene delivery systems. It allows the identification of efficient SGDS following general (systemic) or local (aerosol, hydrodynamic limb vein) administrations in living animals. Future developments in this field could consist in multiplexing luminescent and fluorescent reporters for gaining deeper insights into the potential/fate of SGDS.

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Posters

Interaction between Human Serum Albumin and Toxic Free, PEG-InP/ZnS QDs using Multi-Spectroscopic Study: Excellent Alternate to Heavy Metal Based QDs

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Introduction

To date most explored and applied core shell semiconductor nanocrystals (CdSe/ZnS, CdSe/ZnSe, CdSe/CdS, CdS/PbS, CdS/HgS, ZnSe/ZnS, ZnS/CdS, HgS/CdS, PbS/ZnS) exhibits toxicity[1]. Greener, heavy metal and toxic free semiconductor nanocrystals are the most interested segment of the current bio-nanotechnology. In the present paper, structural changes of human serum albumin (HSA) due to its interaction with toxic free poly ethylene glycol ligand coated InP/ZnS QDs (PEG-InP/ZnS QDs) was probed by employing multi-spectroscopic tools.

Materials and Methods

Various concentrations of PEG-InP/ZnS QDs (2 nM-10 nM) were prepared in double distilled water and HSA samples of 1µM concentration were prepared in Phosphate buffer saline at pH-7.0. Later such samples were used in steady state, temperature dependent fluorescence, synchronous fluorescence spectral and time resolved measurements. Then SFS scans for HSA-InP/ZnS Qs were performed at $\Delta\lambda$=15 and 60 nm corresponds to tyrosine and tryptophan residues, respectively.

Results and Discussion

Experimentally calculated $K_{SV} = 0.48\times10^{8} M^{-1}$ and $k_q = 8.14\times10^{15} M^{-1}s^{-1}$ fluorescence quenching constants from Fig. 1 for HSA-QDs conjugates are much greater compared to the values obtained for biological macromolecules due to the collision mechanism[2]. A close examination of Fig.2 reveals that reduction in HSA synchronous fluorescence intensity after conjugation with PEG-InP/ZnS QDs is more and uniform for $\Delta\lambda$= 60 nm which showed PEG-InP/ZnS QDs binds predominantly to Trp-214 residue.

Figure 1: Stern-Volmer Plot.

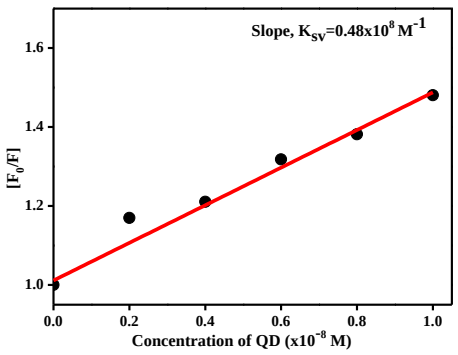
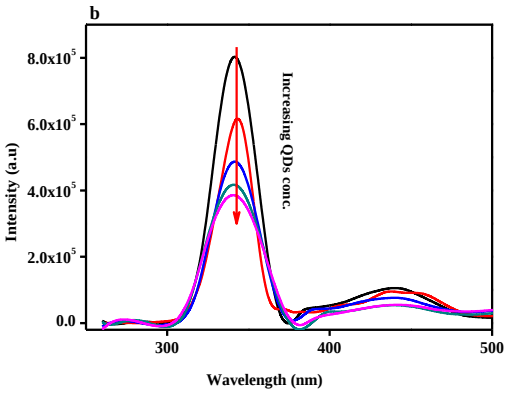


Figure 2: SFS spectra of HSA-QDs at Δλ=60 nm.



Conclusion

At higher temperatures these bioconjugates are unstable and static quenching mechanism shifts towards collisional quenching phenomenon. Binding and synchronous fluorescence analysis showed PEG-InP/ZnS QDs binds predominantly to Trp-214 residue through hydrophobic forces. Observed blue shift from 343 to 338 nm in PL spectra of indicates conformational deformation around Trp-214. The E_T, K_T and R_0 were all calculated for HSA and PEG-InP/ZnS QDs system from FRET studies. The -ΔG, +ΔH, +ΔS implied, HSA-InP/ZnS QDs bioconjugation is spontaneous, endothermic, entropy driven. Hill coefficient (n≅1) and binding affinities (k_b) confirmed strong binding of HSA to QDs surface through 'non-cooperative interactions'.

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Selective chemosensors in bioimaging applications

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Introduction

Molecules which spectral characteristic is dependent on properties of their environment are called molecular probes. Under biological conditions and the influence of enormous quantities of chemical compounds, many chemosensors may undergo both non-specific reactions and changes in their structure, triggered by local environment. Such complex conditions cause problems with selectivity and stability of different groups of fluorescent probes[1]. Fluorescent probes for bioimaging can be divided into two main groups. Sensor which fluorescence depend on microenvironment properties (such as pH, micropolarity, microviscosity) and sensors which spectral properties depend on highly selective biological reactions (especially enzymatic reactions)[2]. Based on the choosen method of the developent of fluorescent probes, different moieties are needed to be built-in to the structure of a sensor. Probes which fluorescence characteristics depend on pH of the solution, must contain a specific moieties such as amines or hydroxyls[1]. This groups can reversibly change their structure, depending on acid-base equilibrium in a solution. This transformation provides changes in electronic structure of the whole molecule, also in fluorescence and absorption spectra. Spectral properties of fluorophores can depend also on spatial arrangement of moieties. Conformational changes can be obtained for example by placing a tertiary amine group with free electron pair conjuncted with aromatic structure in plenary, but disengaged after convolution. Fluorescent probes which spectra abilities depend on more specific structural changes, or peculiar chemical reactions, were much more complicated to design and obtain. Development of such structures requires knowledge of specific entities existing in biological environment. New structures exhibiting selective bondability to biological structures were most desirable not only as fluorescent probes, but also in different uses in medical sciences[1,3].

Results and Discussion

Purpose of research was assessment of the possibility of penetrating biological membranes and visualization of structures using compound derivatives of 2-amino-3-cyano-4,6-diphenyl-pyridine and their inclusion complexes with (2-Hydroxypropyl)-β-cyclodextrin. During research line of non-small-cell lung carcinoma (A549) have been used. The test compounds showed the ability to penetrate the cells and emit fluorescence. The test compounds are safe for cells and do not affect their physiological properties after 3 hours of incubation, and also after 24 hours.

Conclusion

In the view of the fact that biological systems are the most complicated of known environments, new fluorescent probes should be designed, investigated and developed on different levels – from common spectral measurements, through cell penetration, to cytotoxicity and pharmacokinethics. Despite great properties in synthetic conditions, most fluorophores were unsuitable for biological uses due to being prone to undergo side reaction or decomposing. Part of probes also shows influence on metabolism of investigated biostructures and due to this in those cases results of measurements are disrupted. Variety of parameters must be taken into consideration on every step of developing of new fluorescent sensors[2,3].

Acknowledgment

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The use of fluorescent probe ANS to determination of influence of tocopherol derivatives on the structure of the phospholipid membrane

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Introduction

Alpha-tocopherol (Toc) and its derivatives fulfils a number of biochemical and biological functions in the cell[1]. The wide spectrum of biological effects observed for them is related to their interactions with the components of the biological membrane. These interactions may in turn lead to modification of membrane properties (stiffness, fluidity, permeability). Research carried out concerned the assessment of the influence of selected Toc ester derivatives on the physical parameters of the lipid membrane in model systems - liposomes.

Materials and Methods

The tests were carried out for: alpha-tocopherol succinate (TS), alpha-tocopherol malonate (TM) and alpha-tocopherol oxalate (TO) incorporated into liposomes composed of dipalmitoylphosphatidyl choline (DPPC). The studies consisted in measurements of fluorescence emission of fluorescent probe 8-Anilino-1-naphthalenesulfonic acid (ANS) in temperature-dependent manner (in the range 25–60°C).

Results and Discussion

For pure DPPC membrane, ANS fluorescence intensity enhancement was observed around the temperature of 42°C with simultaneous shift of the fluorescence maximum towards shorter wavelength (Fig.1). It is known that ANS emission intensity increases and the wavelength of maximum emission undergoes a blue shift as ANS passes from a polar environment to a non-polar medium[2]. Observed sharp growth of ANS's fluorescence emission intensity expressed the increased hydrophobicity of the probe's environment. On the other hand, it is known, that membrane permeability increases at the temperature of the main membrane crystalline transition and is relatively low above and below this temperature. For pure DPPC membrane the main phase transition occurs at around 41-42°C. In this case, the observed perturbation of ANS fluorescence could be related to more effective penetration of the DPPC membrane by ANS molecules, caused by the increase in the membrane permeability as a results of DPPC membrane transition from gel to the crystalline phase.

For liposomes with incorporated Toc and its esters, ANS fluorescence intensity increase was observed around 39-41°C as consequence of the membrane permeability change. However only for Toc and TO a blue shift of ANS maximum emission was noted around temperature of transition. In the case of TS and TM, we observe the maximum shift towards longer wavelengths, what suggests another perturbation of the membrane structure caused by these esters.

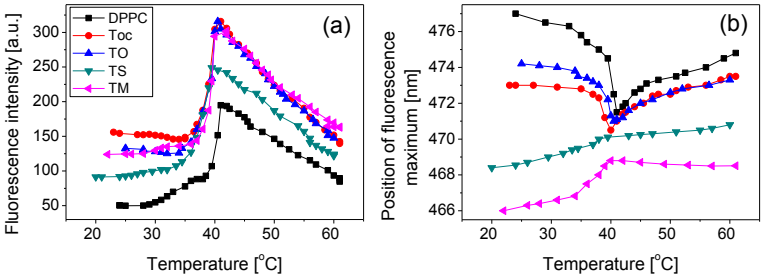

Figure 1: Changes of ANS fluorescence intensity (a) and position (b) of emission maximum in pure liposomal membranes and liposomes containing 2mol% of Toc, TO, TS and TM at different temperatures.

Conclusion

Presented results revealed that Toc ester derivatives embedded into DPPC membrane modify its structure much more compared to Toc. Also some differences is observed among studied esters which may be due to the different mechanism of interaction of esters molecules with phospholipid at bilayer interface, resulting from their location or number of hydroxyl groups.

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New fluorescence probe and chemosensor (synthesis, fluorescence properties, applications,...)

Approaches for variation of luminescence characteristics of lanthanide coordination compounds

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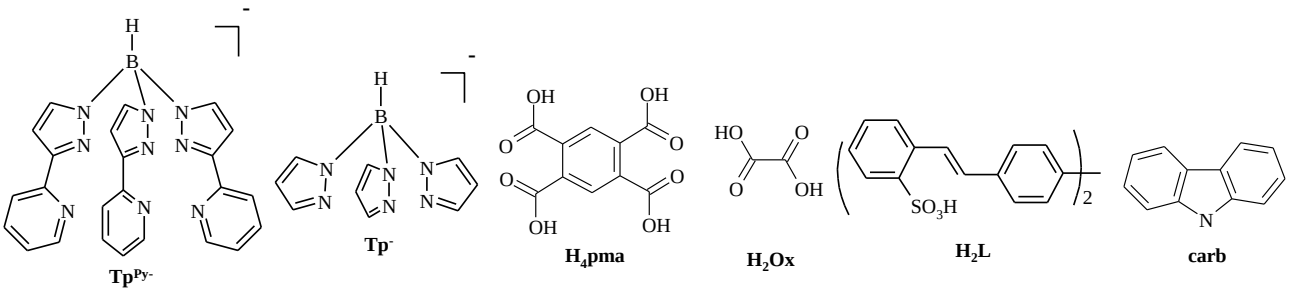
The electronic structure of the lanthanide ions provides for high purity and reproducibility of the emitted color, so these compounds are prospective candidates as components of materials for lasers, displays, biomarkers, *etc*. At the same time, variation of luminescence color and prediction of emission characteristics is still a challenging task. The aim of this study was to search for ways to tune the luminescence properties of lanthanide coordination compounds. Two approaches were studied: (i) the variation of different lanthanide ions' ratio in their complexes and (ii) generation of molecular structures with a highly luminescent anion and inclusion of carbazole in the crystal lattices of these complexes.

For (i) two types of mixtures (**A** and **B**) with composition $x[(Tp_2Eu)_2Ox]\cdot(1\text{-}x)[(Tp_2Ln)_2Ox]$ and $x[(Tp^{Py}Eu)_2pma]\cdot(1\text{-}x)[(Tp^{Py}Eu_xLn_{1-x})_2pma]$ (Ln = Tb, Gd, x = 0.0, 0.1, 0.5, 0.9, 1.0) were obtained and the metals' ratios were confirmed by X-ray fluorescence spectroscopy. Mixtures **A** were obtained by cocrystallization of the different lanthanide ions' complexes from solution in the appropriate ratio, while mixtures **B** were obtained by mechanical grinding of appropriate quantities of the respective homodinuclear compounds. In the luminescence spectra of mixtures of Eu^{3+} and Tb^{3+} compounds, the emission from both these ions appeared with quantum yields up to 30% and 80%, respectively. This allowed us to achieve variation of the emission color in the range red-yellow-green by changing the metals' ratio. In type **A** mixtures, sensitization of Eu^{3+} emission was observed, whereas in the **B** ones, Tb^{3+} to Eu^{3+} energy transfer didn't occur. For mixtures of Eu^{3+} and Gd^{3+} complexes, Eu^{3+}-centred emission was observed in the luminescence spectra; in the type **A** mixtures, sensitization was more efficient than in the type **B** mixtures and this effect was more significant in the case of compounds with pma^{4-}.

To study the approach (ii), complexes with composition $(Tp_2Ln)_2L$, $(Tp^{Py}Ln)_2L$, $(Tp^{Py}Ln)_2L\cdot0.7carb$, Ln_2L_3 and $Ln_2L_3\cdot0.7carb$ (Ln = Eu, Tb, Gd, Dy) were synthesized and characterized by single crystal X-ray diffraction and luminescence spectroscopy. It was shown that in Tb^{3+}, Gd^{3+} and Dy^{3+} complexes, the emission of L^{2-} appeared, its color was dependent on the structure of the compound and varied from violet to cyan. Carbazole inclusion showed no significant influence on the emission colors of the compounds studied.

Figure 1: Ligands used in this study.



This work was partially supported by a joint project of Trilateral Partnerships between researchers of Ukraine, Russia, and Germany of VolkswagenStiftung (Ref. No. 90343) and the National Academy of Sciences of Ukraine Program of Fundamental Research "New Functional Substances and Materials for Chemical Engineering" (contracts No. 9-17 and 9-18).

Luminescence modulation of rhenium complexes induced by the structural isomerism of their organic ligand

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Introduction

Transition metal complexes which are weakly emissive when molecularly dissolved, but highly emissive when aggregated, have recently attracted intense research interest for applications in optics, optoelectronics and bio-imaging.[1] However, among them, the rhenium complexes have been scarcely studied. It is shown here that the simple structural isomerism of a chelating organic ligand in these complexes may significantly govern their electronic properties, and modify their aggregation-induced phosphorescence emission (AIPE) ability.

Results and Discussion

This study focuses first on two very similar tricarbonyl Re(I) complexes **ReL1** and **ReL2**, each incorporating a different structural isomer of the pyridyl-triazole (pyta) ligand [2] connected to a 2-phenylbenzoxazole (PBO) moiety (Fig. 1). The X-ray structures indicate that in **ReL1** the PBO moiety and the pyta ligand almost form a right angle hindering the electron delocalization, while in **ReL2** their nearly planar arrangement favors the electron delocalization in the whole organic ligand. The geometry of these complexes deeply influences their electrochemical and optical properties. Indeed, in solution and in the solid state, the color and intensity of their phosphorescence emission is quite different, and only **ReL1** clearly exhibits an AIPE behavior. TD-DFT calculations are in good agreement with all the experimental data. In a second step, to improve the emission properties of our rhenium compounds, two new complexes have been prepared. **ReL3** presents a PBO moiety substituted by a bulky group. **ReL4** is an isomer of **ReL1** in which the PBO moiety is now linked via its phenyl group to the pyta fragment. A comparison with the first two complexes thereby allows the impact of the new structural modifications on the spectroscopic properties to be evaluated.

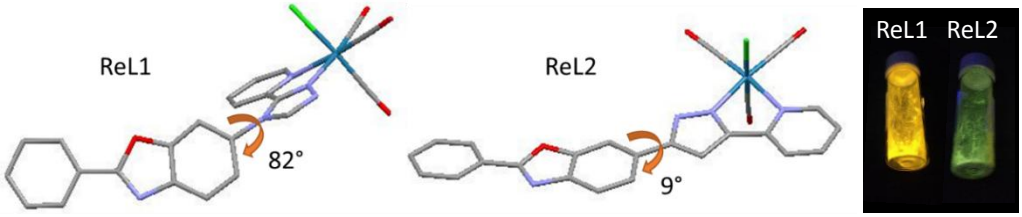

Figure 1. From left to right: Molecular views of **ReL$_1$** and **ReL$_2$**; Pictures of the complexes in the solid state under UV light (365nm).

Conclusion

This comprehensive study aims to rationalize the links existing between the intimate nature of the pyta-PBO ligands and the electronic properties of their corresponding rhenium complexes.[3] It paves the way for a new generation of AIPE-active compounds that associate good emission efficiency to the intrinsic advantages of tricarbonyl rhenium complexes, i.e. stability, versatility and biocompatibility, in view of bio-imaging applications.

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Molecular luminescent probes to explore the pores and the surface of metal organic frameworks (MOF) drug carriers

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Introduction

In short, a metal–organic framework (MOF) is an extended coordination network obtained by the linking of identical units formed by a metal atom complexed by polydentate ligands. These microporous crystalline compounds possess cavities and windows. Small molecules may diffuse through the windows to fill the nanopores and interact with the ligands or escape from the pores. Most applications are in catalysis, gas separations or drug storage and release.[1] Much remains to understand the interaction of molecules with the inner and outer surface of MOFs. The preliminary work presented is centered on the use of selected fluorescent molecules to probe these surfaces and reveal the potential presence of different sites of adsorption on a well-known MOF named ZIF8.

Materials and Methods

The probes used were anthracene and methyl orange. The results obtained are based on excitation and emission spectra analysis. ZIF8 was provided by BASF and used as received without any purification. As the windows of MOFs are generally too small to let in these rather large molecules to probe the inner surface, a classical synthesis of ZIF8 was performed in the presence of the probes in controlled molar ratios.[2] The effective inclusion of the probe within the micropores of ZIF8 was ascertained by TGA, XRD and luminescence.

Results and Discussion

Modifications of the luminescence parameters of the probes were observed for the two probes. The modification of the spectra (maximum location, vibronic structure and anisotropy) clearly indicates the existence of confinement effects undergone by the adsorbed probes. The properties of adsorbed anthracene are different to that of pure crystalline anthracene, as evidenced by XRD and will be discussed in terms of luminescence.

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Polymer-based fluorescent sensors for toxic heavy metals: a new, electrosynthesized benzene sulfonic acid-polypyrrole sensor for Cu(II) and Pb(II)

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Introduction

A number of polymers have been recently used as fluorescent sensors for the detection of heavy metal ions, yielding high sensitivity and selectivity[1-3]. In this lecture, after reviewing the literature, we have described the building and performances of a quenching-fluorimetric sensor, based on a new electrosynthesized, fluorescent benzene sulfonic acid-doped polypyrrole (BSA- PPy), for monitoring Cu(II) and Pb(II) traces in water.

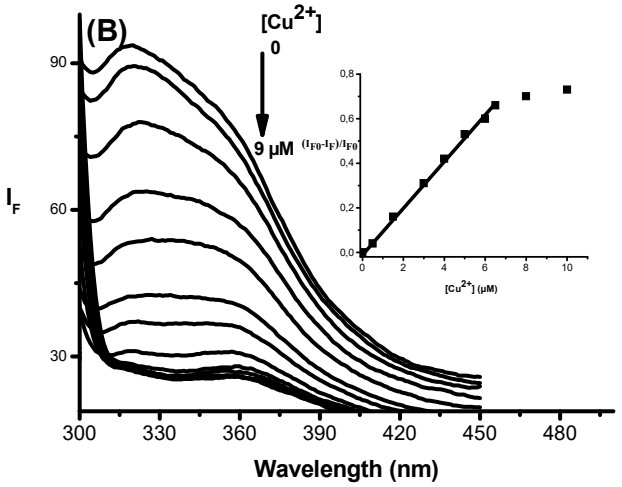
Materials and Methods

BSA-PPy films were electrosynthesized on flexible ITO in aqueous solution, and characterized by FT-IR spectrometry and XPS. BSA-PPy electronic absorption (Lambda Perkin-Elmer spectrometer) and fluorescence spectra (Kontron SFM-25 spectrofluorimeter) were recorded in DMSO at room temperature.

Results and Discussion

BSA-PPy fluorescence spectra were quenched upon increasing [Cu^{2+}] (Fig. 1). A linear Stern-Volmer relationship was obtained between the BSA-PPy fluorescence intensity and [Cu^{2+}] (0-7 µM - Insert), suggesting a dynamic fluorescence quenching process. The limit of detection values were very low (3.1 and 18.0 nM for Cu^{2+} and Pb^{2+}, respectively), indicating a high sensitivity for this quenching-fluorimetric sensor.

Figure 1: Effect of [Cu^{2+}] varying on the fluorescence emission spectra of BSA-PPy in aqueous solution.



Conclusion

The PPy-BSA quenching-fluorimetric sensor is very sensitive for Cu^{2+} and Pb^{2+}, and may be of great interest for the determination of heavy metal ions in environmental and biologic samples.

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Protonable nitrogen-based heterocyclic chromophores for white light emission.

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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 Internationale de l'Eclairage* (CIE) 1931 diagram).[2]

A new strategy for WOLED fabrication has recently emerged that involves the use of only one emitting material with two forms of complementary colours, such as neutral/protonated species.[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.[7] Recently we have extended this strategy to pyridine derivatives.[8]

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).

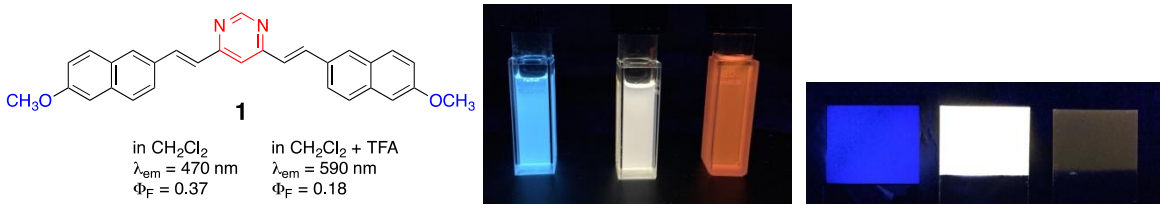

Figure 1. Chemical structure of **1** (left). Colours of CH_2Cl_2 solutions of **1** (middle) and polystyrene thin films doped with 1 wt% of **1** (right) in absence and the presence of 50 and 1000 equivalents of trifluoroacetic acid.

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Spectroscopic studies of the interactions of 3,8-bis(3-aminoalkylamido)-5-ethyl-6-phenyl-5-phenanthridinium bromide derivatives with G-quadruplex DNA

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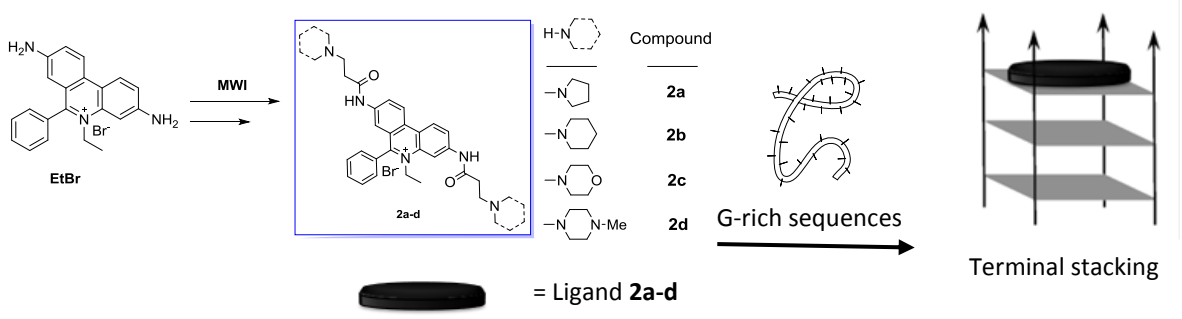
Abstract: An improved microwave-induced synthesis of four 5-ethyl-6-phenyl-3,8-bis{[1-oxo-3-(alkylamino)propyl]amino}-5-phenanthridinium derivatives (Ethidium derivatives, 2a-d) is presented. As the derivatives **2a–d** have been proposed previously to be telomerase inhibitors, the binding interactions of these ethidium derivatives with G-quadruplex DNA were evaluated by means of photometric and fluorimetric titration, thermal DNA denaturation, CD and ^{1}H-NMR spectroscopy. In particular, the bis-pyrrolidin-1-ylpropanamido-substituted derivative **2a** exhibits high selectivity for quadruplex DNA relative to duplex DNA. Overall, the results show that ethidium derivatives such as **2a–d** are promising lead structures for the development of telomer-targeting drugs.

Introduction: The selective stabilization of G-quadruplex DNA (G4-DNA) by artificial ligands is a challenging task to identify biological important processes and also a useful strategy for the development of anti-cancer drugs because the formation of quadruplex structures may cause transcriptional repression of oncogenes and/or anti-telomerase activity in cancer cell. The ligands, derivatives of ethidium bromide, i.e. a classical DNA intercalator have been demonstrated to bind to quadruplex DNA with high affinity and to inhibit telomerase activity. The serious knowledge gap with regard to the telomerase inhibition by derivatives **2a**–**d** prompted us to perform the necessary complementary studies to get further insight into interactions of the bioactive ligands **2a**–**d** with quadruplex DNA[1]. In this study, an improved synthesis of the compounds **2a**–**d** along with spectroscopic studies of their binding interactions with quadruplex DNA.



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Synthesis and application of highly sensitive fluorescent probes

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Introduction

Fluorescence probe plays a significant role in bioanalysis and biosensing. Traditional organic fluorescent dyes are widely applied duo to the stability and sensitivity. Recently, novel fluorescent nanomaterials also attract great attentions for merits of photostability, biocompatibility and selectivity. Based on the advantages and deficiencies of the fluorescent probes, we devote ourselves to synthesize plasmon-enhanced fluorescence (PEF) nanomaterials and aggregation-induced emission (AIE) molecules, thus improving the sensitivity and broadening the applications. .

Materials and Methods

The PEF nanomaterials with different cores of nanorods, nanobipyramids, nanoprisms, and nanocubes were synthesized. Then we achieved the largest fluorescence enhancement through the adjustment of the thickness of silica coating on the nanomaterials. Besides, a kind of the fluorescent molecules-based nucleotides were constructed to improve the methods of next generation sequencing.

Results and Discussion

To improve the sensitivity of fluorescent molecules, we studied the PEF effects of nanorods, nanobipyramids, nanoprisms, and nanocubes with different "hot spots" in aqueous solution, and achieved the largest enhancement of 10 fold. Then we applied them to the detection of pyrophosphate, microRNA, single nucleotide polymorphisms, and real-time monitoring of polymerase chain reaction products.[1,2] Besides, based on the PEF effect, we developed a single-molecule probe, which showed the single molecular message directly in biosensing and then we applied it to the imagining of intracellular telomerase in situ.[3] Moreover, given the requirement of environmentally friendly fluorescent probes, we developed a kind of DNA-templated fluorescent copper nanoparticles and designed a three-way junction DNA to differentiate single nucleotide polymorphism (SNP). Through the smart design, we realized the fast, simple and universal detection of SNP.[4] To improve the sensitivity and accuracy of next generation sequencing, we are studying the novel fluorescent-molecule-based sequencing methods. We synthesized the dye-based nucleotides, which possessed two emission wavelengths, thus we can improve the accuracy of sequencing through the simultaneous detection of two fluorescent signals.

Conclusion

The smart synthesis of different kinds of fluorescent probes successfully improved the sensitivity and broadened the applications. Now we are studying more novel fluorescent materials and making efforts to apply them to DNA sequencing and detection of the change of protein conformation.

Acknowledgements

The authors gratefully acknowledge the support from the National Natural Science Foundation of China (21475011, 21675014).

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Posters

Biocompatible quantum dots micelles for cancer cell imaging

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Introduction

Quantum dots are highly fluorescent, but it cannot be soluble in water. Therefore, it cannot be used directly for diagnosis and treatment of human disease. To circumvent this limitation, the surface of quantum dots must be modified to increase their water solubility and biocompatibility.

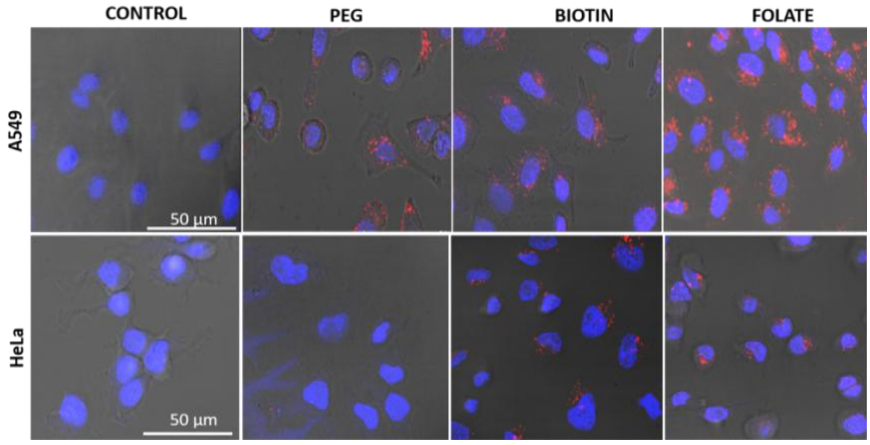
Materials and Methods

CdSe/ZnS core-shell-type QDs stabilized with octadecylamine ligands were purchased from Sigma-Aldrich.Fe3O4 NPs in chloroform with oleic acid coating was from Nanotech Ocean. DSPE–PEG (2000)–biotin DSPE–PEG (2000)–Folate, DSPE–PEG (2000) was from Avanti Polar Lipids. All chemicals were used without further purification. HeLa (RCB0007) and A549 (RCB0098) cell lines were obtained from Riken Bio- Resource Center (Tsukuba, Japan).We used fluorescence confocal microscopy for Cellular uptake of the different surface modified micelles.

Results and Discussion

We prepared three kinds of surface modified quantum dot micelles for cancer cell imaging.the size of the micelle were around 120 nm. In the case of A549 cancer cell lines, the uptake order is PEG < Biotin < Folate, for HeLa cell lines PEG < Folate < Biotin. We checked Th-1 cell lines ther is no uptake. (Fig.1)

Figure 1: Cellular uptake of fluorescence phospholipid micelles[2].



Conclusion

Folate-conjugated phospholipid lipid micelles were a more efficient biomarker for cancer cell detection.

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Enhancement of near infrared upconversion in $LuNbO_4:Yb^{3+},Tm^{3+}$ with Ga^{3+} and Ta^{5+} substitutions

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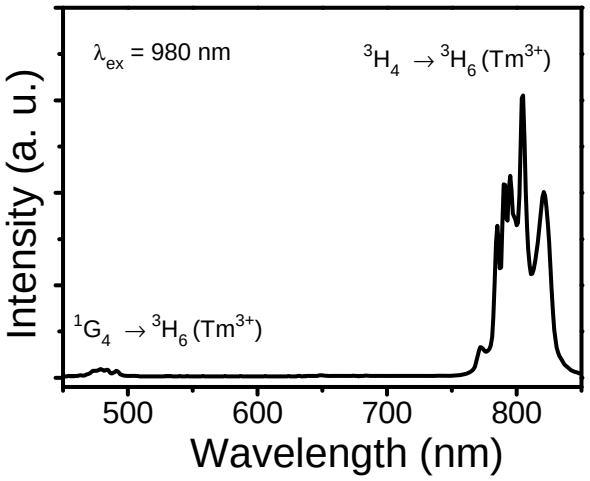
Yb^{3+} and Tm^{3+} co-doped upconversion (UC) phosphors typically exhibit near infrared (NIR) emissions and have attracted great attention because of the advantages for bio-applications[1,2]. In this study, we investigated the UC luminescence of $LuNbO_4:Yb^{3+},Tm^{3+}$ with Ga^{3+} and Ta^{5+} substitutions. Under 980 nm excitation, the UC spectra of $LuNbO_4:Yb^{3+},Tm^{3+}$ predominantly exhibited NIR emission bands at approximately 805 nm, whereas other UC emissions including a greenish-blue emission were insignificant. The UC emissions originated from Tm^{3+} via an energy transfer from Yb^{3+} to Tm^{3+}. A two-photon process was responsible for the NIR UC emission. Ga^{3+} and Ta^{5+} ions were substituted for Lu^{3+} and Nb^{5+} ions, respectively, resulting in the enhancement of the NIR UC emissions. These findings were explained using the modification of the local crystal structure and the crystal field asymmetry surrounding the Tm^{3+} ions. The results demonstrated that $(Lu,Ga)(Nb,Ta)O_4:Yb^{3+},Tm^{3+}$ has a high potential for NIR UC phosphors.

Figure 1: UC spectra of $LuNbO_4:Yb^{3+},Tm^{3+}$.



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Solid state fluorescence of push-pull distyrylbenzenes

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Introduction

It is known that majority of materials based on organic conjugated molecules that exhibit efficient solid-state fluorescence (SSF) emit in blue/green region. The goal of this work was to study an influence of different substituents on optical properties with focus on SSF in the red region. A series of potential fluorophores based on bulky diphenyl-distyrylbenzene (DP-DSB) core substituted with diphenylamine (DPA) as electron donor and various electron acceptor moieties with variable electron-withdrawing strength was synthesized and their fluorescence was characterized.

Materials and Methods

A series of prepared fluorophores is shown in (Figure 1). Their absorption and fluorescence was studied in solvents with various dielectric constants and in solid state. Fluorescence life-times were measured using TCSPC method.

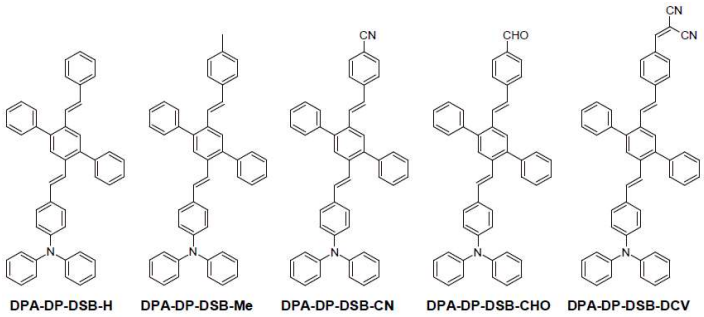

Figure 1 The studied DPA-DP-DSB derivatives.

Results and Discussion

All five compounds show a remarkable solid-state fluorescence covering the range from blue over green to red. Strong electron-acceptor moieties can shift the emission toward longer wavelegnths as can be seen in (Figure 2). The bulky diphenyl-distyrylbnzene core prevented the fluorescence quenching in solid state.

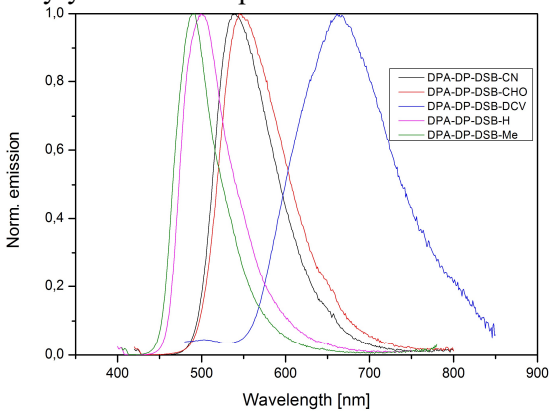

Figure 2 Solid state fluorescence spectra of the studied derivatives.

Acknowledgement

This work was supported by Czech Science Foundation via project No. GA 17-21105S, research infrastructure was supported by project MŠMT No. LO1211. from the National Programme for Sustainability I (MEYS CR)

Temperature-dependent luminescence emission of $YNbO_4$ and $YNbO_4$:Bi phosphor powders

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Introduction

Self-activated phosphors that contain metal-oxides groups with the closed-shell transition metal ions, such as NbO_4^{3-}, WO_4^{3-}, MoO_4^{3-}, VO_4^{3-}, have attracted great attention for display and lighting applications. Luminescence phenomenon in these tetrahedral groups originates from one electron charge transfer from oxygen to the empty d orbital of the central metal ion. Yttrium niobate ($YNbO_4$) belongs to this group of phosphors, and is generally used in X-ray intensifying screens. It exhibits intense blue light emission at around 410 nm under X-ray and UV excitation[1,2]. Introducing Bi^{3+} into $YNbO_4$ is causing red-shift of luminescence emission because 6s electron of Bi^{3+} is transferred to d orbital of Nb^{5+}, enabling metal-to-metal charge transfer and forming a new low-lying emitting state[3]. This emission appears as a wide band in the 400-600 nm range and the maximum at ~450 nm. $YNbO_4$:Bi was firstly proposed as a good candidate for use in field emission displays[3]. Recently, Bi^{3+} is being added to $YNbO_4$ matrix as a co-dopant and a sensitizer, in order to transfer energy to other rare earth ions and tune the absorption/emission in white light emitting diodes (w-LEDs)[4] and solar cells[5,6].

Yttrium niobate is usually synthesized by a solid state reaction method, where precursors are ball milled for tens of hours[7,8]. Here we prepared the single-phase pure and Bi^{3+}-doped $YNbO_4$ phosphor powders, using fast and energetically efficient mechanochemical method followed by annealing. The precursors were firstly mixed in a ball-mill at 100 rpm for 3h, then pre-calcinated at 800°C for 2h, ball-milled again, and finally annealed at 1200°C for 2h.

The crystalline structure of the samples is confirmed by XRD measurements. The crystallite size of ~300 nm for both samples was estimated from Rietveld refinement. Optical characterization was performed using diffuse reflectance and photoluminescence spectroscopy. We measured excitation spectra at room temperature and emission spectra in the different temperature ranges (293-403 K for pure and 293-533 K for Bi^{3+}-doped sample). Both samples exhibit intense emission and both mechanisms are discussed. Luminescence emission quenching temperatures were also determined.

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The French National Firefly Observatory, Flaugergues' bioluminescent earthworm & "Absence" of natural fluorescence in Arctic waters

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In 2015 we founded the **French National Firefly and Glowworm Observatory**, a citizen science project that asks the general public to help the scientific community to know in which regions of France these animals are thriving. The creation of this observatory through a novel approach and first results of the many thousands of observations (18000 in 2017) will be presented. We are also trying to use a similar approach in Italy, Spain and Romania.

Amongst the about 7000 known **earthworm** species, thus far only 40 are reported to produce light. A short review will be presented about the **bioluminescence** of these interesting animals and hypotheses concerning the function of producing underground light will be discussed and illustrated with some preliminary data obtained on Flaugergues' worm that we recently re-discovered in the French Loire valley after 250 years of absence from the scientific literature. Isolation of the luciferase and luciferin of this animal will provide new **imaging tools** for cell biology, medicine and industry.

Recently the UTPIII expedition (https://www.underthepole.com/) deep-dived down to -100m the waters of the North-Ouest Passage between Greenland via Canada to the south of Alaska. Organisms were collected and verified for **natural fluorescence** and **bioluminescence**. The hypothesis that these dark and cold waters are not favorable for fluorescent signal communication seems true. Preliminary results will be shown. Extraction and characterization of the fluors could again provide new **imaging tools**.

Imaging and microscopy luminescence developments

From Picoseconds to Milliseconds: Time-Resolved Fluorescence Spectroscopy on Different Time Scales Combined with Spatial Resolution

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Introduction

Time-resolved luminescence spectroscopy combined with microscopic techniques is a valuable and powerful tool to investigate the photophysical properties not only of different classes of molecules and molecular systems, but also of semiconductors[1], solid-state and biological systems. In recent years, the study of luminescence properties has gained in popularity in many scientific fields, e.g. in Life, Materials or Food[2] Sciences.

The investigations to be carried out in each of these fields impose different requirements. On one side, monitoring dynamic processes in the excited state necessitates high time resolution that can be achieved by fast pulsed lasers and detectors along with appropriate time-correlated single photon counting (TCSPC) units and suitable monochromators. On the other hand, high spectral resolution is desirable for fluorophore characterization, which requires detectors with high quantum efficiencies not only over the complete visible range, but also – especially for many semiconductor materials - deep into the IR. Up to now, fluorescence spectrometers have been usually developed towards either one of these two specifications.

Spectrometers, such as the FluoTime300, equipped with pulsed lasers capable of working in a burst mode, fast hybrid detectors and high end TCSPC cards with optional long time range modes offer a combined solution, for most of needs like high time and high spectral resolution. Coupling to a microscopic system (MicroTime 100) allows for applying these features into microscopic domains.

Results and Discussion

We will demonstrate the performance of a spectrometer/microscope assembly in terms of its time resolution, the ability to measure emission spectra, decays (incl. long decays such as phosphorescence, or luminescence of lanthanides using bunched excitation) and record time-gated lifetime images using laser drivers with burst capabilities.

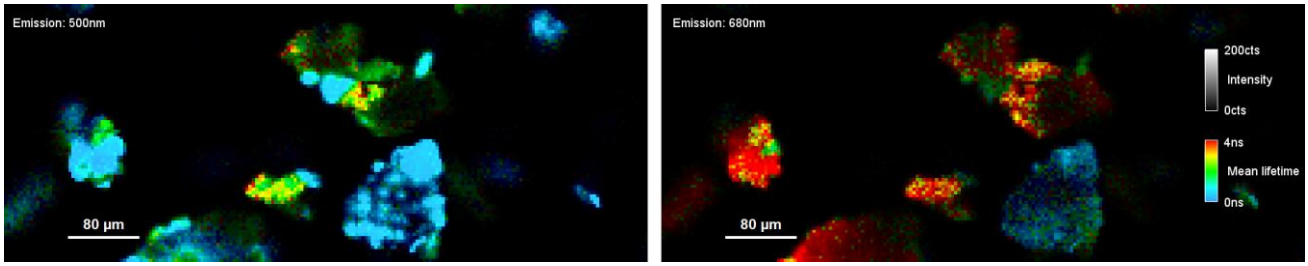

Figure 1: Lifetime images of mixed red paprika and curcuma powder recorded at two different emission wavelengths

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Photofluorescent recording media for 3D optical memory devices

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Now it is important to develop a new generation of optical recording media with super high information capacity and fast processing. The process of recording information in such carriers is based on a two-photon photochemical transformation of photosensitive systems in a multilayer recording medium. This paper discusses own results on the development of photochromic and photochromogenic polymer materials for two-photon three-dimensional (3D) bitwise working and archival optical memory with fluorescent readout.

In the course of the research, multilayered polymeric recording media with alternating transparent waveguide, information and locking layers have been developed. These media provide layer-by-layer two-photon photoconversion of photochromic and photochromogenic organic substances and layered fluorescence readout of optical information due to the choice of refractive indices for each layer.

The possibility of creating 3D multilayered bitwise working optical disks using the phenomenon of Forster resonance energy transfer (FRET) from the organic fluorophore (phenalenone) to the cyclic form of photochromic diarylethene is shown. Samples of 3D multilayer optical disks of archival type based on the irreversible photochemical transformation of non-fluorescing chromon into a fluorescent photoproduct are created. The main characteristics of recording by laser radiation and fluorescence readout of optical information are determined.

The results of studding the functional properties of a sample of a three-layer optical disk with the use of the home-made optical device for recording and readout optical information indicate the possibility of creating multilayer optical disks of standard size with an information capacity of up to 2.6 TB and fluorescent readout.

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Photoluminescence Imaging of Newly Synthesized Proteins in Living Cells

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Introduction

It is of great significance to study the newly synthesized proteins in living cells. Currently, two types of fluorescence probes (turn-on and always-on) could be applied to the purpose. Turn-on type probe can effectively distinguish the reaction probe and unreacted probe, but the imaging based on fluorescence intensity is a little difficult to completely exclude the fluorescence background from free probe interference. Recently, we introduced a lifetime probe for imaging of new synthesized proteins in living cells.

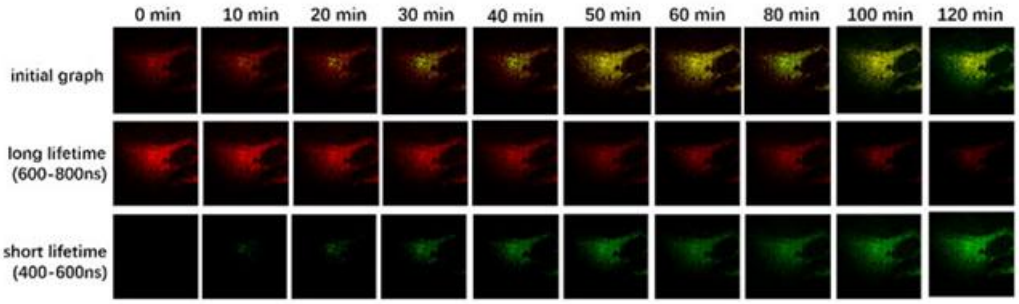
Materials and Methods

The probe was synthesized by a three-step synthetic route. The structure of the probe was characterized by 1H NMR. The probe exhibited large Stokes shift that could effectively avoid the interference of excitation and autofluorescence of cells.

Results and Discussion

An excellent group of the lifetime probes for the imaging of new synthesized proteins have been synthesized. The remarkable lifetime shifts over 400 ns before and after click reaction makes them easy to eliminate the background interferences and well distinguishes the reacted probes from the unreacted probes, thus enabling the wash-free imaging of the newly synthesized proteins in single living cells (Fig.1). In this symposium we would like to introduce the development of new synthesized proteins studies in living cells by our group very recently. [1-3]

Figure 1: A example of the photoluminescence lifetime images of HeLa cells



Conclusion

We are exploring applications of this strategy so as to take full advantage of this lifetime probe for living-cell analysis.

Acknowledgements

We acknowledges financial support from the National Natural Science Foundation of China (No. 21390413).

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Pyclen-based Ln(III) complexes as fluorescent bioprobes for two-photon microscopy

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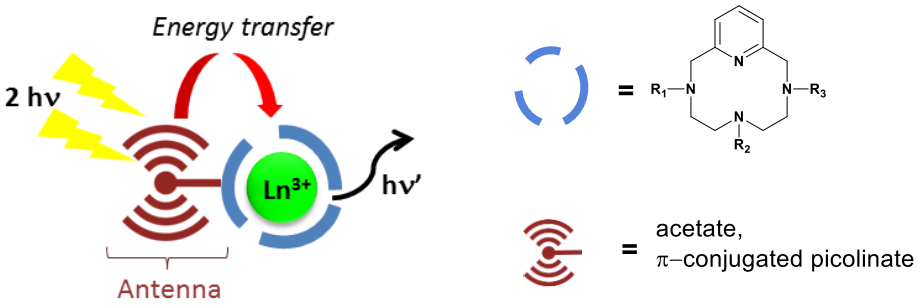
Two-photon (2P) microscopy using lanthanide(III) complexes is of wide interest in optical imaging because it combines the advantages of 2P excitation (NIR excitation in the biological transparency window, 3D resolution) with the sharp emission properties and long excited-state lifetimes of lanthanides.[1] However the conception of 2P-lanthanide luminescent bioprobes (2P-LLBs) combining good photophysical properties, long-term stability in biological media and the ability to be internalized by living cells is still challenging. Polyazamacrocycles such as tacn, cyclen and cyclam are widely studied platforms for metal complexation and their lanthanide(III) complexes have been successfully investigated as LLBs. In particular it is well established that the functionalization with π-conjugated antennae optimizes the 2P absorption cross section of such lanthanide complexes.[2] For example one of our cyclen-based Eu(III) complexes featuring appropriate antennae led to the rapid internalization in living cells and allowed 2P microscopy imaging.[3] Pyclen derivatives (3,6,9,15-tetraazabicyclo[9.3.1]pentadeca-1(15),11,13-triene) are also interesting ligands because they form stable and inert complexes thanks to the rigidity of the macrocycle brought by the pyridine unit.[4] We recently developed a new family of pyclen-based Ln(III) complexes bearing π-conjugated chromophores (Scheme 1). Our optimized strategies of synthesis allowed the regiospecific introduction of different antennae adapted to given lanthanides. The use of the pyclen platform considerably improved the photophysical properties of the complexes, in particular the quantum yields and the brightness. In addition 2P bio-imaging studies of fixed T24-cells stained with our complexes proved to be very promising.



Scheme 1: Pyclen-based Ln(III) complex bearing conjugated antenna optimized for two-photon microscopy.

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Second harmonic generation polarimetry of biological tissues

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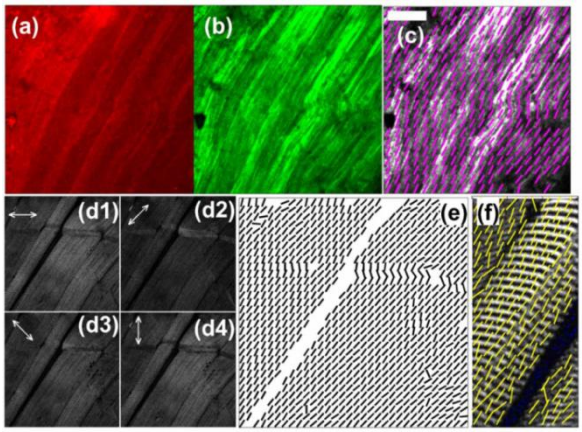
Introduction

Second harmonic generation (SHG) is a nonlinear coherent optical process induced by intense laser radiation in non-centrosymmetric structures. SHG microscopy has been usefully implemented for biomedical imaging so as to reveal complex macromolecular arrays, including collagen and myosin fibrillar proteins. Owing to its close relationship with the anisotropy of the nonlinear medium, SHG is strongly dependent on the polarization of the excitation laser beam. Thus, polarimetric features of SHG provide meaningful information for advanced characterization of biological tissues.

Results and Discussion

In this presentation, technological aspects, main applications and future outlook[2] of SHG polarimetric methods implemented in the context of biological imaging will be discussed.

Figure 1: Orientation fields of myosin fibers in fresh veal muscle[1]



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Posters

Algae observation by two-photon microscopy.

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Introduction

Two-photon microscopy allows to image biological specimen from both two-photon excitation fluorescence (TPEF) of their endogenous fluorophores and second harmonic generation (SHG) of some of their non-centrosymmetric molecules assembled in macromolecular organized structures; i.e. cellulose and amylopectin in the case of vegetals. TPEF and SHG microscopy images of some microalgae revealing complementary structures are presented here for the first time to our knowledge.

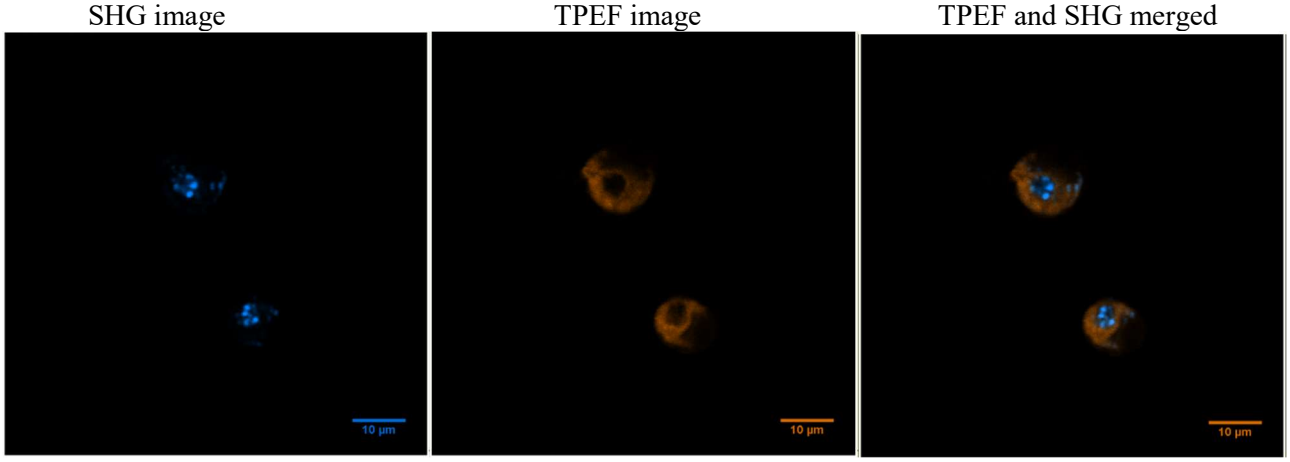
Materials and Methods

TPEF and SHG microscopy was performed on a modified confocal microscope (FV300/BX51WI, Olympus) and a femtosecond Ti:Sapphire laser (Verdi-V5/Mira, Coherent) tuned at 830 nm. Endogenous TPEF signal was epi-collected, then descanned and detected by the internal photomultiplier tube (PMT) of the microscope. SHG signal was forwardly collected through the sample, then detected by an external PMT. 2048x2048 pixels TPEF and SHG images were acquired in parallel.

Results and Discussion

Our study focused on the Chlorophyte *Dunaliella salina,* a unicellular micro-algae (Fig.1). TPEF image (overall fluorescence at all the emission wavelengths) unequivocally reveals the chloroplast location. SHG image (specific of cellulose and/or amylopectine) brightly point out the amylopectin content in the starch storages, which are included in the chloroplast. Furthermore, concerning cellulose, the absence of SHG signal around the cell is consistent with the fact that *Dunaliella salina* has no cell wall. Overlapping the two images reveals the complementary of TPEF and SHG contrasts: areas rich in amylopectine do not exhibit fluorescence.

Figure 1: Observation of *Dunaliella salina*.



Conclusion

SHG give additional information on the structure of the algae by highlighting the cellulose skeleton, and / or the localisation of the amylopectine provision. These results show that SHG brings important complementary information to TPEF observations and prove the interest to develop its application to observation of vegetal.

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Self-assembly and Optical Characteristics of *meso*-Bodipy-Encapsulated Micellar Clusters

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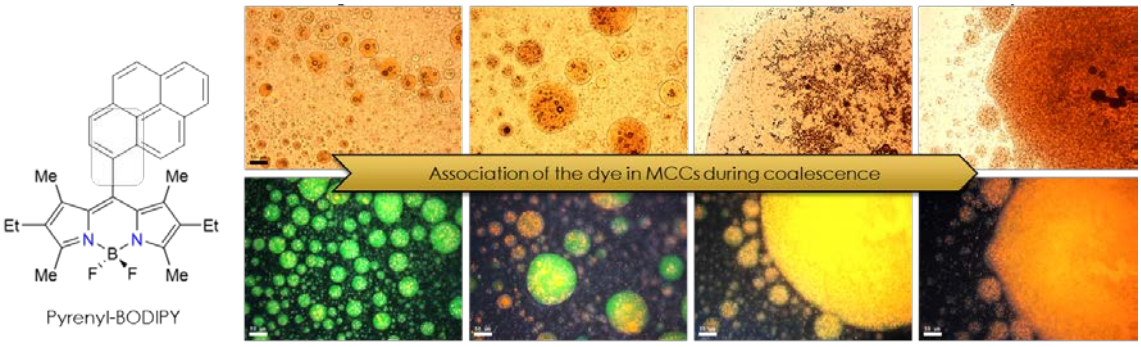
Functional materials built on a "bottom-up" principle represent a class of the most diverse substances with practically useful characteristics. Based on this concept, a new approach to the surfactants (Triton X-100 and X-114) modification has been developed, allowed them to form non-covalent dynamic conjugates at room temperature. The method is based on 1) the formation of strong complexes between a hydrophobic chelating ligand (eg, batofenantroline, BPhen) and micelles, forming chelated micelles. At this stage, the hydrophilic parts of BPhen (nitrogen atoms) remain on the surface of the micelle, while its hydrophobic fragment is embedded in the hydrophobic core. This system is stable due to the strong hydrophobic forces between the surfactant and the chelator; and 2) upon the addition of a complexing agent having affinity to BPhen and capable of binding to two or more BPhen molecules, such as a transition metal ion chelated micelles form a three-dimensional supramolecular aggregate system of micellar coordination clusters (MCCs). These systems exhibit an extremely high ability to solubilize hydrophobic compounds, such as anti-cancer drugs, toxic substances (bilirubin), etc. In addition, these clusters are capable of encapsulating hydrophobic phosphors and changing their optical characteristics. Here we demonstrate the features of MCCs to encapsulate a number of fluorophoes of meso-substituted bodipy family. It was shown that these compounds retain their fluorescence being encapsulated inside of MCCs but depending on the substituent nature it is possible to control the optical characteristics of encapsulated bodipys.

Figure 1: Evolution of micellar clusters, containing meso-pyrenyl substituted bodipy.



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Single-scan swept source Mueller microscopy

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Introduction

Polarized light microscope[1] is widely used to observe biological structures[2] that present by themselves optical anisotropic properties such as refraction (birefringence) and absorption (diattenuation). Among polarization sensitive specimens, collagen fibrils, stress fibers made of filamentous actin and myosin, and microtubules display birefringence, while dye molecules associated to anisotropic transition moments exhibit diattenuation. Light polarization can also be modified randomly (depolarization) by scattering through specimens. In most configurations polarized light microscopes, made of two crossed linear polarizers, provide qualitative images by simplifying the specimen as a unique linear birefringence.

Materials and Methods

A full Mueller polarimetric microscope based on a wavelength-swept-laser source is implemented in a commercial laser-scanning microscope[2]. The device uses no moving parts for the polarized state generator (PSG) and the polarized state analyser (PSA), but linear polarisers and fixed thick retarders to encode light polarization in spectral domain[3-5]. From the channelled spectrum measured by a single detector, the full Mueller matrix is determined at each point of the specimen according to the speed of the swept-source, i.e. 10 µs in our case. This new microscope is a promising tool due to (1) the simplicity of using passive PSG and PSA blocks, (2) the fast acquisition to image Mueller elements (0.65 s for a 256x256 pixel image), (3) the good signal-to-noise ratio by means of coherent illumination, (4) the possibility of combining nonlinear optic imaging modalities such as Second Harmonic Generation (SHG) microscopy.

Results and Discussion

We present a completed Mueller microscope provided with a real-time image module to display the change of polarization by the specimen and make the adjustment of the microscope easier. Another functionality has been added to switch from the Mueller microscope to a SHG microscopy configuration in order to image the same region of interest with the same objective and take advantage of the specific SHG signal sensitive to intrinsic nonlinear signatures of biological molecules such as collagen type II fibers. The performances of our Mueller microscope are illustrated by imaging several structural organisations of free labelled biological samples that can not be reduced to a simple linear birefringence. In particular all polarimetric parameters are imaged at a unique frame rate of 1.5 Hz, and unstained liver collagen fibers embedded in paraffin is revealed through a degree of alignment based on the structural organisation of fibers.

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Nanomaterials and quantum dots luminescence and applications

Development of a quantum dot molecularly imprinted polymer sensor for fluorescence detection of atrazine

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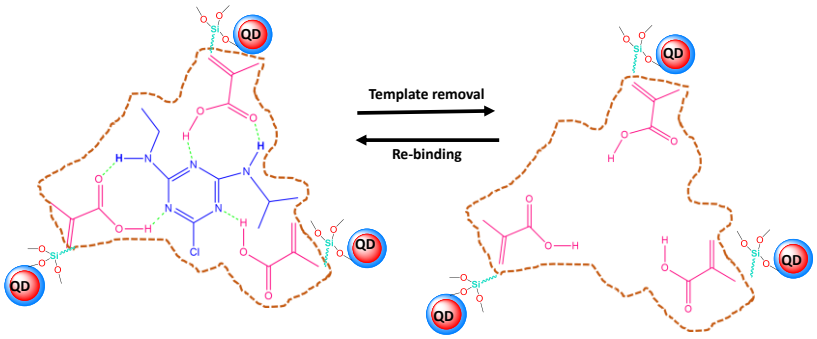
Introduction

Quantum dots (QDs) have attractive optical properties which have allowed them to find application in pesticide sensing[1]. Atrazine is a common pesticide used in agriculture for controlling various weeds, but has been reported to widely occur in surface drinking water, making it an environmental pollutant of concern[2]. Coupling of QDs to molecularly imprinted polymers (MIPs) has been shown to offer excellent selectivity and sensitivity in sensor development for target analytes[3]. In this work we show the development of a QD-MIP fluorescence sensor and its application towards atrazine detection in water.

Materials and Methods

Highly fluorescent CdSeTe/ZnS QDs were fabricated using the conventional organometallic synthesis approach. The QDs were further encapsulated with MIP in order to offer selectivity. Atrazine was used as a template while methacrylic acid (MAA) and ethylene glycol dimethacrylate (EDMA) were used as monomer and cross-linker, respectively. Further, a non-imprinted CdSeTe/ZnS@NIP, was fabricated in the same way but without atrazine as template. The CdSeTe/ZnS@MIP sensor was characterized using TEM, FT-IR, XRD, Raman, UV-vis and fluorescence spectroscopy. The materials were then applied towards atrazine sensing with 5 min interaction time for analyte binding.



Sheme 1: Interaction of atrazine with the QD@MIP

Results and Discussion

The synthesized CdSeTe/ZnS QDs showed excellent fluorescence properties, with a strong emission peak at 619 nm, and stability that was retained after encapsulating with MIP following removal of the atrazine template. The interaction between the QD@MIP and atrazine was likely through hydrogen bonding on the MAA units (Scheme 1), which led to linear quenching of the QD@MIP fluorescence with increasing atrazine concentration. Atrazine analogues are used demonstrate selectivity of the sensor and finally, the sensor was used the detect atrazine in real water samples.

Conclusion

The developed QD@MIP fluorescence sensor has potential application in atrazine monitoring in water and may be used as a simple and cheaper alternative to conventional analytical methods.

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Graphene quantum dots-terbium ions as novel time-resolved luminescent probes

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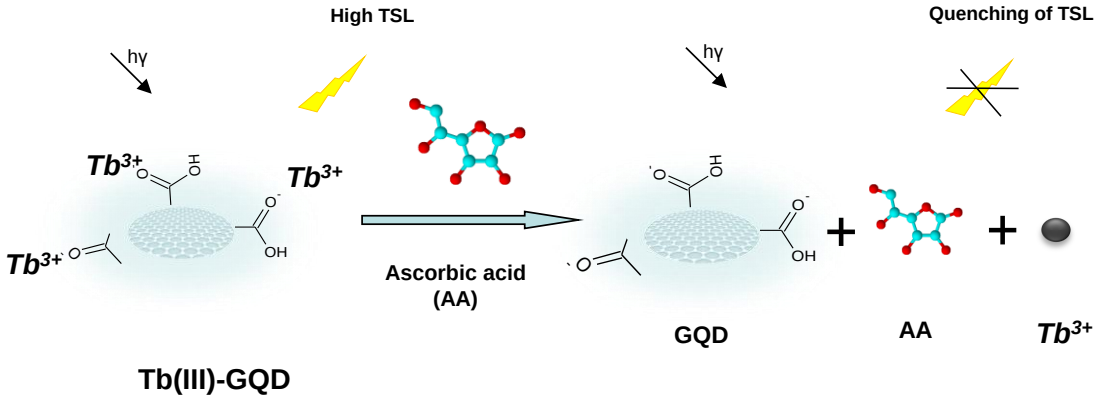
Although luminescent analytical methods are widely used in most research fields, different approaches are usually required to improve the analytical characteristics, depending on the analyte(s) and sample to be analyzed. Lanthanide-sensitized luminescence (LSL) presents interesting features that make it a highly sensitive and selective detection technique. Lanthanide cations (mainly europium and terbium) can form chelates with ligands that present specific functional groups (such as carboxylic groups). However, the use of surfactants and synergistic agents is common to improve the luminescence signal. We discuss here a novel approach for LSL, implementing the use of nanomaterials. In particular, we have used terbium-sensitized luminescence (TSL) and graphene quantum dots (GQD), due to the inherent advantages of these nanomaterials for the development of analytical methodologies.
We have selected L-ascorbic acid (AA) as a model analyte to show the advantages of the implementation of GQD in TSL. AA quenches the luminescence of terbium. However, the selectivity and sensitivity of the analytical method are highly improved if the quenching is produced on GQD-Tb(III). The advantages of the use of these nanoparticles will be critically discussed, examining the results obtained in our laboratory. This novel approach can lead to simpler and easy-to-use analytical methods, avoiding the use of surfactants and additional reagents. In addition, GQD can be modified with different (bio)chemicals compounds, which may expand their potential applications in different research fields.



Metal-doped luminescent Quantum Dots for multimodal bioimaging

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Nanotechnology is a scientific discipline with great potential to contribute to the development of new advantageous imaging nanoprobes. The use of nanoparticles (NPs) as imaging probes offers several advantages over conventional molecular-scale contrast agents, such as: (1) high loading capacity, where the concentration of the imaging agents can be controlled within each nanoparticle during the synthesis process; (2) tunable surface that can potentially extend the circulation time of the contrast agents in the blood, or target them to specific locations in the body; or (3) provide multimodal imaging capacities because NPs can combine two or more contrast properties, which can be used in multiple imaging techniques simultaneously[1].

The development of NPs combining different functionalities (e.g. photoluminescent and magnetic resonance) is nowadays an attractive area of research due to their great potential for the advance of biomedical imaging technologies. Colloidal metal semiconductor nanocrystals (quantum dots, QDs) constitute an attractive new class of optical contrast agents, which exhibit excellent properties: broad absorption bands, tunable emission colors, high resistance against photobleaching and large surface area for further functionalization[2]. However, tissue auto-fluorescence also imposes a limitation to the application of fluorescent QDs like these for in vivo imaging, as it leads to low signal-to-noise ratios that complicate their detection in biological environments, reducing contrast and the clarity of the resulting image.

There are different ways to overcome this limitation. One possibility is the development of metal nanoparticles with excitation/emission in the NIR spectral area. Such type of novel fluorescent labels are very promising in bioanalysis as combine their binary advantages of both QDs and NIR light. Another approach consists in the introduction of transition metals (e.g. Mn, which is also an essential chemical element in living organisms) in nanocrystals, as this confers them characteristics typical of phosphorescent emitters, which exhibit longer Stokes shift between excitation and emission wavelengths, and longer luminescent lifetime. The advantage of this is that the resulting phosphorescent emission allows simple discrimination between the luminescent emission from Mn doped QDs from the background fluorescence of the sample using time-resolved photoluminescence (PL) measurements[3]. Additionally, some of the possible doping ions (e.g. Mn) can be paramagnetic, and therefore act as excellent MRI contrast agents. Therefore, doping with such elements the photoluminescent nanocrystals confers additional MRI contrast capabilities to the QDs. The development of NPs combining both optical and magnetic resonance functionalities is an attractive area of research due to their great potential for the advance of biomedical imaging technologies[4].

In this presentation, an overview will be offered showing some of the novel developments on such new type of QDs for biomedical applications.

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Near Infrared Long Persistent Nanophosphors for Bio Imaging Applications

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Long persistent phosphorescence is a phenomenon in which luminescence can last for few minutes to several hours after the removal of the excitation source[1]. The materials which exhibit this phenomenon are known as long persistent phosphors. When these materials are excited by UV or Visible light, free electrons and holes are produced which can be captured by the various traps present in the materials. When the room temperature energy is close to the energy difference between the trapping level and host bands, these charges are detrapped and recombine with the ions and prolong the emission in visible or NIR region. Because of this unique property these materials find potential applications in versatile fields such as security application, safety signage, night vision materials, ratiometric thermometry, storage media, in vivo bio imaging[2]. NIR region (650-1100 nm) is considered as biological optical window as in this range biological tissues become most transparent. Therefore the materials exhibiting emission in this region can be used as a probe for in vivo small animal optical imaging. The autofluorescence from the living tissues is prevented as the materials are excited externally before injecting into the animal body which improves the signal to noise ratio. For bioimaging application the materials must also be nanocrystalline and biocompatible.

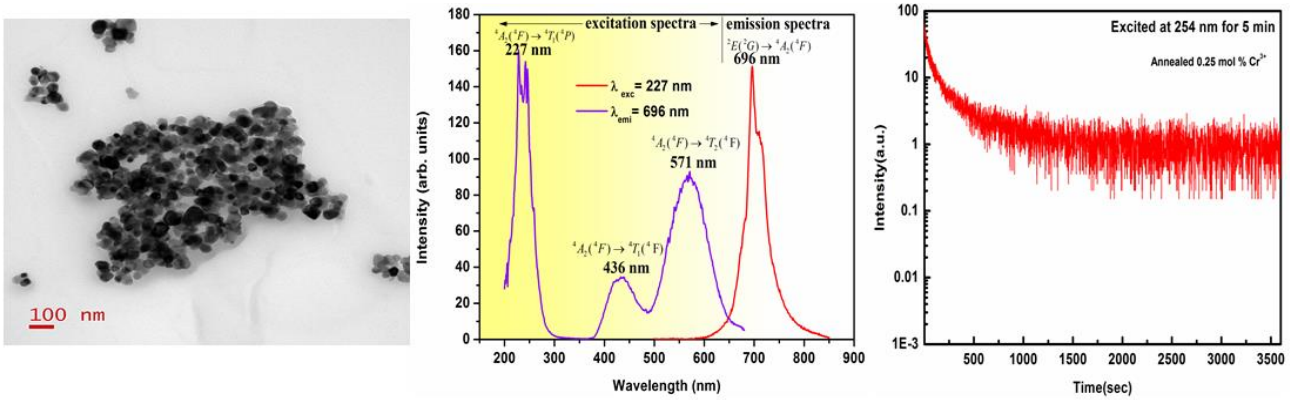

Figure 1: TEM image, PL spectra and afterglow decay curve of $ZnGa_2O_4$:Cr^{3+} phosphor

In this context, we have shown the Cr^{3+} doped MGa_2O_4 (M=Mg, Zn) nanophosphors with the NIR long persistent phosphorescence properties. The materials were prepared by hydrothermal and CTAB assisted hydrothermal reaction method respectively. As the ionic radius of Cr and Ga are nearly equal therefore Cr^{3+} ion substitutes the Ga^{3+} ions. The successful doping of Cr^{3+} ion and single cubic phase formation were confirmed from XRD pattern. The HRTEM micrographs confirmed the formation of nanoparticles (10-70 nm). The PL excitation spectra showed $^4A_2(^4F)\rightarrow{}^4T_1(^4P)$, $^4A_2(^4F)\rightarrow{}^4T_1(^4F)$, $^4A_2(^4F)\rightarrow{}^4T_2(^4F)$ d-d transitions of Cr^{3+} at 225 nm, 442 nm and 558 nm for $MgGa_2O_4$ host and at 227 nm, 436 nm and 571 nm for $ZnGa_2O_4$ host. A broad PL emission spectra ranging from 600-800 nm due to $^4T_2(^4F)\rightarrow{}^4A_2(^4F)$ spin allowed transition of Cr^{3+} with a sharp peak corresponding to $^2E(^2G)\rightarrow{}^4A_2(^4F)$ spin forbidden transition of Cr^{3+} ion were observed at 707 nm and 696 nm for $MgGa_2O_4$ and $ZnGa_2O_4$ host respectively. The afterglow decay of the LLP phosphors were measured after exciting them at 254 nm UV light for 15 minutes externally. Significant LLP signal was being observed for 1 hour. Small particle size and long persistent phosphorescence in NIR region confirms the suitability of the materials to be used as probes in bio imaging.

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Photoluminescence properties of MoS_2 quantum dots synthesized by one-step hydrothermal method

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Quantum Dots (QDs) are nanocrystal semiconductors that is so small to consider as dimensionless. These have unique optical and electrical properties which makes them a potential candidate in the field of optoelectronic and bio-imaging applications. QDs are optically active from ultraviolet to near infrared portion of the electromagnetic spectrum and show size dependent photoluminescence phenomena. Due to this, it is possible to produce white light by mixing QDs of same material having different particle sizes. The QDLEDs are getting much attention due to the improved colour saturation, high colour rendering index and stability. Recently two dimensional (2D) transitional metal dichalcogenides (TMDC) are attracted much attention due to their non toxicity, tunable optical band gap and stability which make them suitable candidate in the field of photovoltaic, photonics, bio-sensing and bio-imaging application. Among the TMDC family, MoS_2 got enormous attention due to its layered structure and direct band gap properties.

The MoS_2 quantum dots were synthesized by low cost one step hydrothermal method. In this work, ammonium tetrathiomolybdate $(NH_4)_2MoS_4$ was used as a source of Mo and S. Hydrazine hydrate was used as reducing reagent. The optical and structural properties of MoS_2 quantum dots were investigated by PL, UV-Vis, FTIR and TEM measurements. MoS_2 quantum dots show blue emission. It also exhibits excitation dependent emission properties due to polydispersion of QDs as evident from colour co-ordinate diagram. The UV-Vis spectrum exhibits strong blue shift due to quantum confinement effect. The band gap value of the quantum dot is much larger than the bulk MoS_2. The functional group present in MoS_2 quantum dot was confirmed by FTIR spectroscopy. The particle size of quantum dots was calculated by TEM measurement.

Keywords: Quantum dot, Photoluminescence, Optical properties

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Quantum dot based photonic sensor materials for emerging chemical pollutants in water

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Introduction

Emerging chemical pollutants (ECPs) are defined as chemicals which do not have a regulatory status, but which may have an adverse effect on human health and the environment [1]. The ECPs of current concern encompass many compound classes such as pesticides, polycyclic aromatic hydrocarbons (PAHs), pharmaceutical and personal care products (PPCPs), flame retardants, perfluorinated compounds and industrial additives. Analytical sensors used for screening applications are of great use in environmental monitoring since they offer cost savings, cater for on-site real time monitoring, and are easier to handle compared to laboratory measurements using conventional instruments. Here we describe the development of optical measurement methods based on quantum dot (QD) nanomaterials for fluorescence sensing of ECPs (particularly PAHs) in water.

Materials and Methods

Semiconductor QDs, including CdSeTe/ZnSe/ZnS QDs, were prepared using the hot organometallic synthesis route, whilst graphene QDs and graphene oxide nanosheets were prepared from graphite powder based on a modified Hummer's method. The QDs were converted to water soluble forms by ligand exchange reactions, using L-cysteine as a hydrophilic capping agent. After thorough characterisation of the synthesised materials, they were applied in a range of sensing experiments to allow for the optimisation thereof.

Results and Discussion

The synthesized QDs were of high quality, as evident from their high quantum yields, and expected broad absorption peaks, whilst their fluorescence emission spectra had narrow, symmetric, size dependent peaks which were independent of excitation wavelength. The QDs were also found to be photostable.

As an example, L-Cysteine- CdSeTe/ZnSe/ZnS QDs coupled to graphene oxide was applied to the sensing of PAHs in water where a limit of detection of 0.19 µg L^{-1} was obtained for phenanthrene under optimum conditions[2]. Interaction between the electron-rich π-system of the PAH molecules and the π-electron system of the graphene oxide nanomaterial leads to an adsorption-photoluminescence enhancement effect, making this type of photonic sensor material suitable for the detection of PAHs[3].

Conclusion

The environmentally relevant detection limits obtained for these optical sensors demonstrates their potential for environmental screening applications. Means to enhance the selectivity of QD-based fluorescence sensors is an area of ongoing research, which will allow for the widespread, commercial application of these methods.

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Tb^{3+} / Yb^{3+} doped aluminosilicate phosphors for visible emission and efficient up-conversion

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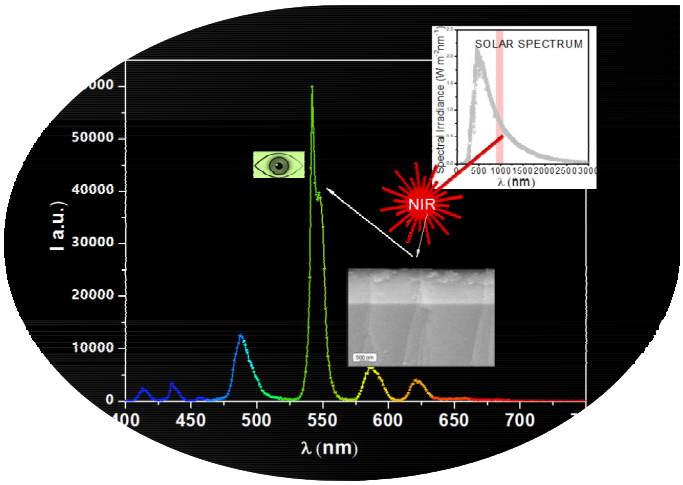
ABSTRACT

Conventional energy sources have severe drawbacks in terms of environmental pollution and limited availability. Therefore, the solar energy market-has been growing quickly in the last decades, but one of the challenges is to increase the efficiency of solar photovoltaic technologies. Different paths have been followed, including the matching of the solar spectrum with the solar cell spectral efficiency through down-conversion and up-conversion (UC) processes. In particular, UC is a promising route to solve the transparency losses of sub-bandgap photons [1]. With the incorporation of UC material, transmitted sub-bandgap photons can be converted into above-bandgap light which is absorbed by the cell material. To date, Ho^{3+}/Yb^{3+}, Er^{3+}/Yb^{3+} and Tm^{3+}/Yb^{3+} emitter/absorber pairs have been widely employed together with 980 nm laser excitation. Tb^{3+} is another candidate for emitter ion, since it exhibits ultraviolet, violet, blue, green, yellow and red emissions and has much longer luminescence lifetime than Ho^{3+}, Er^{3+} and Tm^{3+} [2]. Therefore, the Tb^{3+}/Yb^{3+} pair is also a potential choice for UC applications. While Ln-doped luminescent layers may be deposited by methods like CVD or PVD, sol-gel (SG) processing is a low-cost technology which can be a versatile and scalable alternative. This technique has the added advantage that it can easily be coupled with the deposition of multilayered 1-D photonic crystal (PC) structures like Bragg Mirrors (BMs) and microcavities (MCs) in order to integrate the spectral conversion function into a more efficient photonic structure. In the present work, we report the synthesis of Tb^{3+}/Yb^{3+} co-doped aluminosilicate glass films and MC structures by SG. Efficient blue (~ 488 nm), green (542 nm) orange (585 nm) and red (~ 621 nm) UC emissions have been demonstrated with excitation in the NIR at 975 nm. The phosphor layers studied in this work represent a valuable and promising approach for the preparation of efficient UC coatings to be integrated in solar cell and optoelectronic technologies.



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Ultrabright Polymeric Nanoparticles for FRET Mediated Ratiometric Detection of Molecular Oxygen

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Optical sensing of molecular oxygen has attracted a great deal of scientific attention since the determination of oxygen concentration is essential in diverse areas ranges from life sciences to environmental sciences. It is particularly important for biomedical applications because tissue hypoxia has been found to be closely related to the clinical course of a variety of diseases, such as tumor growth, rheumatoid arthritis etc.[1] Fluorescent polymer nanoparticles (NPs), composed of conjugated polymers and organic dyes, have received great attention due to a number of unique properties, such as exceptional brightness, color tuning from visible to NIR region, potential biodegradability and low toxicity.[2] We previously reported the formulation of ultrabright dye-loaded fluorescent NPs based on biocompatible polymers such as PLGA, PMMA, etc loaded with cationic dyes and bulky hydrophobic counterions.[3]

With an objective to develop a FRET based ratiometric oxygen sensor, we made fluorescent polymeric nanoparticles containing a cyanine-based donor dye with a fluorinated counter ion and a porphyrin acceptor as the oxygen sensitive moiety. The preparation of the NPs was achieved by charge-controlled nanoprecipitation,[3c] by varying the ratio between donor and acceptor concentrations in order to optimize their ratiometric emission response. The as formed nanoparticles were characterized through UV-Vis spectroscopy and DLS measurements. Steady state experiments suggest the efficient energy transfer from cyanine donor to porphyrin acceptor in the PMMA matrix. However, the phosphorescence emission of the porphyrin at 650 nm was suppressed by the dissolved oxygen in the solution, which recovered by the addition of increasing concentrations of sodium sulfite, a well-known oxygen scavenger. By varying the oxygen concentration in the mixture from 0 to 95%, we could able to observe the enhancement of acceptor emission whereas the donor emission remained same, which facilitated the ratiometric detection. Time-resolved measurements also suggest the decrease in phosphorescent life time of the acceptor with increase in oxygen concentration. Further, we investigated the potential of the probe in single particle fluorescence imaging, after immobilizing NPs on a glass coverslip. Interestingly, we could observe bright emission from donor channel and no emission from acceptor channel in the presence of oxygen, and the enhancement in acceptor emission upon oxygen scavenging. The cellular uptake of NPs and ratiometric imaging of oxygen in cells are currently in progress. The small sizes, high brightness, and the ratiometric emission response make these NPs a good candidate for the quantitative detection and imaging of molecular oxygen in biological samples.

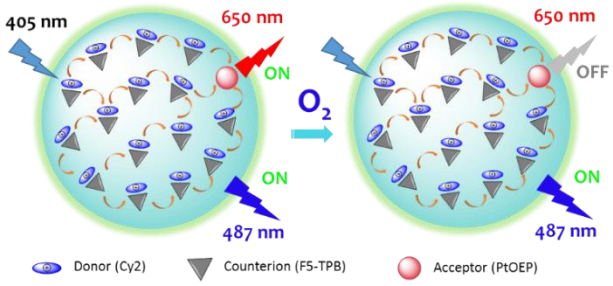

Figure 1. Schematic representation of dye-loaded NPs for ratiometric detection of molecular oxygen.

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Posters

Determination of glyphosate based on its quenching effect on CdTe-quantum dots fluorescence

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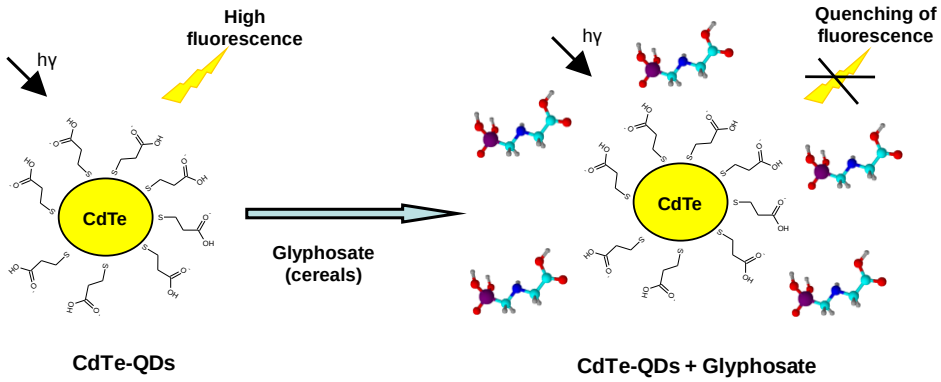
Glyphosate is the most widely used herbicide at the moment. It presents a broad spectrum of action, hence its use for many different crops. Regulatory agencies have constantly mentioned the low hazard potential to mammals. However, the International Agency for Research on Cancer concluded in 2015 that glyphosate is "probably carcinogenic to humans." In this work, we propose a multicommutated flow analysis method for the determination of glyphosate, based on the quenching effect produced by this herbicide on the fluorescence of CdTe quantum dots ($\lambda_{exc}/\lambda_{em}$: 400/548 nm/nm). The proposed analytical method presents detection and quantitation limits of 0.5 and 1.7 µg mL^{-1}, respectively. A sample throughput of 30 samples per hour was obtained by the proposed flow system. Interference studies were carried out to assessing the selectivity of the method, observing no interference from other common pesticides. We carried out recovery experiments in water and cereal samples (amaranth, barley, oat, and quinoa), obtaining recovery yields between 92 and 108% in all the analyzed samples.
The high sample throughput of the proposed method makes it suitable for screening purposes in order to dismiss non-contaminated samples, although positive results would have to be confirmed by mass spectrometry. Hence, we consider that the simplicity, selectivity, and rapidity of this method make it an interesting alternative to other existing methodologies for the analysis of glyphosate in agri-food samples.



Effect of heat treatment in vacuum on photoluminescence of anodic alumina

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Introduction

It is known that as porous anodic alumina (PAA) is exposed to UV radiation, the photoluminescence (PL) is observed in the range of 350-650 nm with a maximum at 450-500 nm. At present, it is assumed that the PL of PAA is caused either by a simultaneous action of F^+-centers and impurities in the form of electrolyte anions e embedded in the oxide during the anodizing process[1] or is determined by oxygen vacancies with one (F^+-center) and two electrons (F -center)[2]. In addition, it was shown[3] that the PAA PL is due to F- and F_2-centers in different charge states. In this paper, we consider the possibility of controlling optical characteristics of PAA by modifying the specimens through annealing in vacuum or in air and alloying them with manganese ions.

Materials and Methods

Formation of the PAA was carried out by electrochemical oxidation of aluminum foil (99.99%) in an electrolyte based on oxalic acid (0.3 M). Alloying of the PAA was carried out by adding $KMnO_4$ (0.4 g / l) to the electrolyte. Optical absorption (OA) and photoluminescence (PL) were studied on the original unalloyed specimens and Mn-alloyed PAA specimens annealed at temperatures T_a = 200, 400 and 600 °C in air and in vacuum and held at constant temperature for 30 min. The luminescence spectra were measured by using an SDL-2 automated spectrofluorometer. The excitation wavelengths were λ_{ex} =275 and 325 nm. The optical absorption spectra in the wavelength range from 200 to 800 nm were obtained using a Cary 500 Scan (Varian) spectrophotometer.

Results and Discussion

A strong dependence of the PL intensity of PAA on the annealing temperature in vacuum was found: at T_a = 600°C, the PL intensity is 15 and 5 times higher than that of the original specimens when excited at λ = 275 and 325 nm, respectively. As follows from the results obtained, the PL spectra represent broad bands and are qualitatively similar for the original specimens and specimens annealed to 600 °C. As the annealing temperature is increased, an increase in the PL intensity is observed, and for the specimens annealed in vacuum the intensity increase is substantially higher than for those annealed in air. Thus, for the PAA annealed at T_a = 400°C, the intensity rises twofold, and at T_a = 600°C it increases by 4.5 and 1.4 times when PL is excited at wavelengths λ = 275 and 325 nm, respectively. A different shape of the PL intensity curves is observed for the alloyed specimens. The PL intensity of the Mn ions-alloyed specimens is practically not different from that of the unalloyed PAA specimens at annealing temperatures of 200 °C and 400 °C both in vacuum and in air. A significant difference is observed for the specimens annealed in vacuum at T_a = 600°C. In this case, the PL intensity of the alloyed specimens is much less than that of the unalloyed PAAs and practically coincides with the values found for the samples annealed in air. The increase in the PL intensities is interpreted within the framework of the vacancy mechanism. When annealing in vacuum takes place, a low partial pressure of oxygen is ensured resulting in that the lattice oxygen atoms diffuse into the vacuum (the environment), creating anion vacancies. In case of annealing in air, atmospheric oxygen diffuses into the PAA structure and partially reduces the concentration of oxygen vacancies. This is manifested in smaller values of the PL intensity as compared with the specimens annealed in vacuum. In addition, the conditions for removing hydroxyl groups from the volume of PAA in vacuum and in air may also be different, which determines the difference in the vacancy concentrations. In the alloyed specimens annealed at T_a = 600°C, formation of aggregate centers with the participation of Mn ions is possible, the process of formation of single vacancies being limited. This explains the smaller value of the PL.

Conclusion

It has been found that under annealing of the PAA in vacuum a significant increase in the PL intensity is observed in comparison with the annealing in air. The peculiarity of the PL from the alloyed specimens is that its intensity is lower during heat treatment in vacuum and in air. Based on the assumption that the optical characteristics of the PAA are determined by the F- and F_2- centers in different charge states, the possibility is demonstrated of changing the PL intensity by modifying the specimens using thermal annealing in vacuum and at high temperatures and by alloying them with Mn ions.

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Efficient adsorption of Rhodamine B onto a synthetic nano-talc: Towards the understanding of an unexpected process

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Introduction

Synthetic clay minerals of nanometric dimension are layered solids that offer unique control over the chemical structure and physical aspect. Their combination with organic dye molecules leads to organo-mineral hybrids that can be tailored to promote specific optical properties.[1] Since 2006, our team has elaborated a new synthetic talc (ST) under hydrothermal conditions.[2] This mineral shares some similarities with natural talc, in particular the lamellar tetrahedral-octahedral-tetrahedral (TOT) structure. It also has several distinctive features such as its submicronic size (Fig.1a), hydrophilic behaviour and chemical purity. Moreover ST shows strong and unprecedented adsorption potential towards charged organic dye molecules.[3,4] This behaviour is particularly intriguing because non-swelling clays like talcs do not contain exchangeable cations, and are therefore known to interact very weakly with organic molecules.

Materials and Methods

In this work, the interaction between ST and Rhodamine B (RhB) was thoroughly analyzed using complementary analytical techniques (XRD, NMR, IR, electron microscopy, UV-visible absorption and fluorescence spectroscopies). In particular, equilibrium data acquired at various temperatures were fitted to access the thermodynamic parameters.

Results and Discussion

Very stable organo-mineral hybrids were prepared (Fig.1b and c). The presence of ST induced an increase of the fluorescence intensity together with a bathochromic effect with respect to pure water (Fig. 1d). It was shown that the dye molecules adsorb both at the nano-talc surface and on the edges. The edge/surface ratio and the number of crystal defects played a key role. The nature of the interactions was clarified.

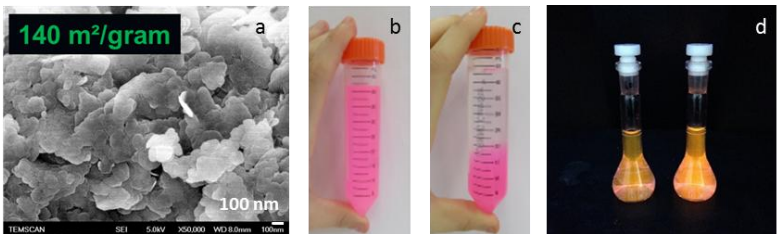

Figure 1: a) Scanning electron microscopy image of ST. b) Suspension of ST in the presence of RhB. c) Formation of a stable gel after centrifugation. d) Emission of RhB in pure water (left) and in the presence of ST (right), under illumination at 365 nm. [RhB] = 5.5×10^{-6} M; ST: 19.2 mg/L.

Conclusion

The elaboration of such nanocomposites is easy, cost-effective and versatile. This study opens a new route towards optical brighteners, cosmetics and fluorescent polymers.[4] Applications could also be found in the fields of paper milling, inks and depollution.

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Super-quenching effect of optoelectronically important bipolar fluorescent probe by metal nanoparticles

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Abstract

In the present investigation, we have designed and synthesized a novel molecule 2-(4-((E)-2-(5-((E)-4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)styryl)thiophen-2-yl)vinyl) phenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (TVP)based on Donor-π-Acceptor strategy by employing Wittig reaction. The structural integrity of the new compound was characterized by ^{1}H NMR, ^{13}C NMR, HR-MS and FT-IR analysis. In addition, super-quenching effect and surface energy transfer (SET) have been studied using this optoelectronically important TVP molecule as efficient donor and gold metalnanoparticles (Au MNPs) as excellent acceptors employing steady-state and time resolved spectroscopic techniques. The size and distance dependant SET between TVP and Au MNPs was explored. It is demonstrated that quenching efficiency increases as the size of Au MNPs increases from 40 to 53 nm. The super-quenching effect and nonradiative energy transfer were analyzed using Stern–Volmer plots. The impact of the present investigation about super-quenching effect of the Au MNPs can be exploited for biosensing applications that demand high degree of sensitivity, if conjugated to the biomolecules.

Keywords: gold nanoparticles, SET, solvatochromism, fluorescence quenching, bipolar molecule, oxadiazole.

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