













Excitonics For Photonic Applications



International Thematic School

Program

This school is made possible thanks to the support of :

National institutions :

CNRS (Centre National de la Recherche Scientifique)

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GDR (Research networks) :

HPERO (Hybrid Perovskites)

Electronique Organique (Organic electronics)



ELEC R@NIQUE RGANIQUE

Foreword

Over the last decades, the development of **organic semiconductors** has led to impressive developments; the most striking example being probably the dissemination of OLED (Organic Light-Emitting Diode) technology in many mass-produced smartphones. Organic photonic devices combine the advantages of low cost, solution-processability and a high versatility to adapt to almost all existing technological platforms. Recently, the irruption of **novel hybrid organic/inorganic materials** has shaken the community. Hybrid perovskites, colloidal quantum dots or low-dimensionality semiconducting nanoparticles are now full members of the "solution-processable materials for optoelectronics" family. These new materials not only share some advantages on a technological point of view. They also target the same applications, concentrated around the generation and detection of light. But that is not all. They also share many common physical properties with organic semiconductors, such as tunable absorption and emission spectra in the visible spectrum. More fundamentally, however, in all these novel materials, **the question of the nature and properties of excitons is central**.

Questioning the foundations of a new transdisciplinary field

To address these questions, the organizing committee has invited 16 renowned lecturers, internationally recognized in their respective fields of expertise, with outstanding research records and pedagogical skills.

We hope this thematic school will be a unique opportunity to question the basic foundations of this emerging discipline, and learn about the latest developments in material synthesis, advanced characterization techniques and device design strategies associated with "excitonic" materials.

Taking time to discuss, ask and share knowledge

A thematic school is not a conference. It is longer (11 days) and structured in long talks (at least 3 hours). Promoting interactivity and fruitful exchanges between all participants and lecturers will be a major objective of this School. That is why time spent out of the lectures is also very important. All participants are invited to bring a poster that will be on display during the whole duration of the School. Free time sessions (every day after lunch and after dinner) will enable informal debates as well as the organization of spontaneous group discussion sessions about topics that will need further treatment according to the participants needs.

The organizing committee,

Sébastien Chénais, Paris 13 University Emmanuelle Deleporte, ENS Cachan-Paris Saclay University Damien Garrot, Versailles Saint-Quentin University Riad Haïdar, ONERA Lionel Hirsch, IMS Bordeaux

And Catherine Hercé, administrative manager, French Optical Society (SFO)

All Lectures by theme :

Theme 1 : Theoretical foundations

Mark Fox (University of Sheffield, UK): Excitons in solids: fundamentals (4h30)

Jérôme Cornil (Mons University, Belgium): *Electronic Structure and Optical Properties of Organic Semiconductors: Basic Concepts (4h30)*

Jacky Even (INSA Rennes, France): Quantum and dielectric confinement (4h30)

Sergei Baranovski (Marburg University, Germany): Generation, transport and recombination of charge carriers in organic semiconductors (3h)

Theme 2: Excitonic materials and characterization techniques

Emmanuelle Deleporte (ENS Paris Saclay, France): *Introduction to hybrid perovskites (3h)*

Natalie Banerji (University of Fribourg, Switzerland): Ultrafast Techniques to Study Charge Carrier Dynamics in Organic and Hybrid Semiconductors (3h)

Emmanuel Lhuillier (UPMC Paris, France): Nanocrystals for optoelectronics (3h)

Peter Reiss (CEA, France): Materials for colloidal quantum dots (3h)

Xavier Marie (INSA Toulouse, France): MoS_2 and its Cousins: 2D Materials with Promising Optical Properties (3h)

Vladimir Dyakonov (Würzburg University, Germany): Spin states engineering in optoelectronic organic devices (3h)

Theme 3 : Excitonic devices and photonic applications

Chihaya Adachi (Kyushu University, Japan): Harvesting excitons in organic semiconductors: towards new generations of OLEDs and organic lasers (4h30)

Graham Turnbull (Univ. of St Andrews, UK): Organic luminescent devices: from basic concepts to emerging applications (4h(30))

Thuc-Quyen Nguyen (UC Santa Barbara, USA): Solution-Processed Organic Solar Cells: Current Progress and Challenges (3h)

Stéphane Kéna-Cohen (Polytechnique Montréal, Canada): Light-matter interaction with excitons from weak to strong coupling (3h)

Richard Williams (Wake Forrest University, USA): Excitonic scintillators (3h)

Noel Giebink (Pennsylvania State University, USA): Unusual concepts in organic photonics (3h)

International thermatic school on Excitonics for Photonic Applications Provisional schedule

FRI 27/04 MON 16/04 TUE 17/04 WED 18/04 THU 19/04 FRI 20/04 SAT 21/04 SUN 22/04 MON 23/04 TUE 24/04 WED 25/04 THU 26/04

Giebink 2		Closing								
Adachi 1	coffee break	Adachi 2	lunch break / poster session / discussions / nap		Williams 1	coffee break	Williams 2		Typical local dishes dinner	
Kena-Cohen 2	coffee break	Reiss 1	lunch break / poster session / discussions / nap	Bencheikh	(Adachi comp.) ^{coffee break}	Paice 7	Giebink 1		dinner	
Turnbull 3	coffee break	Marie 1	lunch break / poster session / discussions / nap		Marie 2	coffee break	Kena-Cohen 1		dinner	
Lhuillier 1	coffee break	Lhuillier 2	lunch break / poster session / discussions / nap		Turnbull 1	coffee break	Turnbull 2		dinner	
free time (trip to Chamonix valley)										
Dyakonov 1	coffee break	Dyakonov 2	lunch break / poster session / discussions / nap		free time				dinner	
Baranovski 1	coffee break	Banerji 1	lunch break / poster session / discussions / nap		Baranovski 2	coffee break	Banerji 2		dinner	
Even 2	coffee break	Nguyen 1	lunch break / poster session / discussions / nap		Nguyen 2	coffee break	Even 3		Typical Savoie dinner	
Deleporte 2	coffee break	Cornil 2	lunch break / poster session / discussions / nap		Cornil 3	coffee break	Even 1		dinner	
Fox 2	coffee break	Fox 3	lunch break / poster session / discussions / nap		Cornil 1 coffee break Deleporte 1			19 h welcome reception		
					Registration from 3.30 pm				dinner	Fox 1 evening session
8.45 - 9.15 9.45-10.15 10.15-10.45 10.15-10.45 11.15-11.45 11.45-12.15 11.45-12.15 11.45-12.15 16.30-16.30 16.30-16.30 16.30-17.30 17.00-17.30 17.30-18.30 17.30-19.00 19.30-20.00 19.30-20.30										

Theme 1 : Theoretical foundations Theme 2 : Excitonic materials and characterization techniques Theme 3 : Photonic applications

Provisional schedule

Introductory lecture

Theoretical foundations

Mark Fox University of Sheffield, United Kingdom

Excitons in solids: fundamentals (4h30)



Mark Fox is Professor of Optical Physics at the University of Sheffield. He studied physics at the University of Oxford, and completed his doctoral thesis in 1987. After a post-doctoral position with AT&T Bell Laboratories in the United States, he became a Royal Society University Research Fellow at Oxford in 1990. He moved to the University of Sheffield in 1998, becoming Professor there in 2006. He mainly works on III-V semiconductors and photonic structures, and his current research activity is focussed on the optical properties of III-V semiconductor quantum dots. This work is funded by the U.K.'s Engineering and Physical Science Research Council through a five-year programme grant on Semiconductor Quantum Photonics: Control of Spin, Exciton and Photon Interactions by Nano-Photonic Design. In the past, he has worked

on a wide variety of optical materials, including magnetic semiconductors, nitrides, organic materials, and III-V semiconductor quantum wells. He has more than 250 technical publications and is a Fellow of both the Optical Society of America and the U.K.'s Institute of Physics. In addition to his research work, he is committed to the teaching of physics at both undergraduate and postgraduate level. He is the author of two best-selling texts in the Oxford Masters Series in Physics: Optical Properties of Solids (Second edition, 2010) and Quantum Optics, an Introduction (2005). The former has been translated into German, while the latter has been translated into French, Greek and Japanese.

Lecture outline

I will cover the material in chapters 3-6 of my <u>textbook</u> on Optical Properties of Solids. The key topics I will cover are:

- 1. Interband absorption
- 2. Excitons
- 3. Luminescence
- 4. Quantum-confined structures

And a brief introduction to organic semiconductors.

Excitonic materials and characterization techniques Emmanuelle Deleporte

ENS Cachan, Paris Saclay University, France

Excitonic properties of Hybrid Organic Perovskites for photonic applications (3h)



Emmanuelle DELEPORTE (female), student of Ecole Normale Supérieure Paris (ENS Paris) from 1986 to 1990, received her PhD in Physics from Pierre et Marie Curie University in Paris in 1992. She was assistant professor at the Physics Department of ENS Paris (1992-2002), in Laboratoire Pierre Aigrain, where she gained strong experience in optical properties of II-VI and III-V inorganic semiconducting heterostructures. She is now full professor at ENS Cachan since 2002. In 2005, she founded her own research team: "Optical properties of hybrid nanostructures" in LPQM (Laboratoire de Photonique Quantique et Moléculaire) ENS Cachan. She moved her whole team in Laboratoire Aimé Cotton in 2013. In particular, her team is pioneer in France in the study of hybrid perovskites for opto-electronics. E. Deleporte studies experimentally the linear and non-linear, continuous and time-

resolved optical properties of semiconductors and hybrid (organic-inorganic) systems. The main topics she addresses are related to low-dimensional excitonic effects, carriers relaxation mechanisms, energy transfer between the inorganic and organic parts of the hybrid systems, light-matter interaction in cavities containing the hybrid systems in the framework of lasers and single photon sources. E. Deleporte is co-author of 85 publications in peer-reviewed international journals. In particular, since 2006, she is co-author of 36 papers, 12 invited presentations in international conferences, 10 invited lectures in french and foreign universities, about hybrid perovskites. She participated in several interviews and wrote papers about hybrid perovskites for the general public. Since 2006, she is the coordinator of 10 research projects on hybrid perovskites and she is member of several scientific committees of national and international conferences. She is the director, on the national level, of the GDR (Groupement de Recherche) HPERO "Pérovskites halogénées".

Lecture outline

Since 2012, Hybrid Organic Perovskites (HOPs) represent a "material breakthrough" for photovoltaics, HOP-solar cells reaching an efficiency record of 21%, competing with the efficiencies of the silicon-based cells. The explanation of such a success is related to a combination of good transport properties for both electrons and holes and appropriate excitonic properties. More broadly, HOPs have also high potentialities for light-emitting devices such as electroluminescent diodes and lasers. Thus, it seems that HOPs combine strengths of the inorganic semiconductors and organic semiconductors, likely to solve the contradiction that high charge carrier mobility and large stimulated emissions are required for lasing devices but can't be found, in general, in the same material.

A decisive advantage of the HOPs, allowing the access to this wide range of applications, come from the ability to tune the excitonic effects. In fact, the HOP family has the following chemical formula $(RNH_3)_2(CH_3NH_3)_{m-1}Pb_mX_{3m+1}$ (R: organic group, X: halogen). The variable *m* corresponds to the number of inorganic layers intercalated between the organic molecules (Figure 1). For m=1, the material adopts a two-dimensional structure (2D HOP), where carriers are confined in an atomically thin inorganic layer, made of PbX₆ octahedras, and form strongly bound excitons. At the limit case of $m = \infty$, we obtain the 3D hybrid perovskite structure AMX₃ (A: CH₃NH₃) for which the exciton binding energy is only of a few meV and the transport properties are dominated by free carriers at room temperature. As a consequence, from m = 1 (2D) to $m = \infty$ (3D), the dimensionality and thus the excitonic properties of HOP, can be "continuously" tailored and optimized to suit to different optoelectronic applications.

Another advantage of the HOPs is their chemical flexibility, especially the possibility of a molecular engineering of each part of the molecule in order to improve or add some functionalities and of a growth engineering (thin layers, nanocrystals, monocrystals). In particular, we will report on the growth of HOP monocrystals, presenting a very low density of defects, thus allowing a better understanding of the intrinsic photophysics of materials, necessary to improve of the performance of perovskite solar cells and optoelectronic devices. Additionnally, as the properties of films are very dependent of the grain structure, the optical properties of HOPs single crystals and those of thin polycrystalline films will be compared in order to investigate the relationship between the structure, the phase transition and the excitonic properties.





Theoretical foundations Jérôme Cornil Mons University, Belgium

Electronic Structure and Optical Properties of Organic Semiconductors: Basic Concepts (4h30)



Jérôme Cornil received his Ph.D. in Chemistry from the University of Mons-Hainaut in 1996 and then went for a postdoctoral stay at UCSB (with Alan Heeger) and MIT (with Bob Silbey). He is currently Research Director of the Belgian National Fund for Scientific Research (FNRS) in Mons and holds a Visiting Principal Research Scientist position at the Georgia Institute of Technology since 2005. His main research interests deal with the quantum-chemical characterization of the electronic and optical properties of organic conjugated materials in bulk or at interfaces, in relation to their use in opto-electronic devices. He is (co)-author of ~ 330 publications/book chapters.

Lecture outline

1) Isolated molecules

- Electronic structure of conjugated systems
- Chemical and physical defects
- Electronic gap versus optical gap
- Chain-size evolution
- Singlet excitons
- Exciton binding energy
- Impact of electroactive substituents
- Fluorescence
- Electron-phonon coupling
- Vibronic structure

- Solvent effects
- Circular dichroism
- Triplet excitons
- Phosphoresence
- Jablonski diagram
- Organometallic complexes
- Solitons, polarons, and bipolarons

2) Interacting molecules

- Intermolecular interactions
- Excitonic theories
- Dipole-dipole couplings
- Energy transfer processes
- Förster theory
- Dexter theory
- Photoinduced processes
- Marcus theory
- -

3) Devices

- Light emitting diodes
- Electroluminescence quantum yield
- Electrophosphorescent diodes
- Thermally activated delayed fluorescence (TADF)
- Organic solar cells
- Low bandgap materials
- Singlet Fission

Theoretical foundations Jacky Even INSA Rennes, France

Quantum and dielectric confinement (4h30)



Jacky Even is full Professor at INSA Rennes engineering school since 1999. He received a PhD in Physics from University Paris VI in 1992. He was assistant professor at the Physics Department of Rennes University (1992–1999), where he gained broad experience in phase transitions and solid-state chemical reactions in molecular materials, using theoretical and experimental approaches: neutron and X-ray scattering, Raman/FTIR spectroscopy, calorimetry, among others. In 1999,

he created FOTON laboratory's simulation team to study the optoelectronic properties of semiconductors using empirical methods (k.p, tight binding, group symmetry, envelope functions, ...) or the density functional theory, as well as to perform optoelectronic device simulations. Besides hybrid perovskite materials and colloidal nanoplatelets, his theoretical activity was also dedicated to semiconductor nanostructures, photovoltaic and light-emitting (LED, laser, ...) devices for silicon photonics, and optical telecommunications.

Lecture outline

- 1. DFT and empirical approaches to the computation of monoelectronic states
- 2. Quantum confinement
- 3. Dielectric confinement

based on various examples of 0D and 2D nanostructures, as well as III-V,II-VI, perovskite materials and Van der Waals heterostructures

Excitonic devices and Photonic applications Thuc-Quyen Nguyen University of California, Santa Barbara, USA

Solution-Processed Organic Solar Cells: Current Progress and Challenges (3h)



Thuc-Quyen Nguyen is Full Professor in the Center for Polymers and Organic Solids (CPOS) and the Department of Chemistry & Biochemistry at the University of California, Santa Barbara (UCSB). Professor Nguyen received her B.S., M.S., and Ph.D. degrees in Physical Chemistry from the University of California, Los Angeles, in 1997, 1998, and 2001, respectively. Her thesis research focused on processing and photophysics of conducting polymers using ultrafast spectroscopy under the supervision of Professor Benjamin Schwartz. She was a research associate in the Department of Chemistry and the Nanocenter at Columbia University working with Professors Louis Brus and Colin Nuckolls on molecular self-assembly, nanoscale

characterization and devices. She also spent time at IBM Research Center at T. J. Watson (Yorktown Heights, NY) working with Richard Martel and Phaedon Avouris on molecular electronics. She joined the faculty of the Chemistry and Biochemistry Department at UCSB in July 2004. She is co-authored 200+ publications that received over 15,500 citations and has the h-index of 63. She is a Scientific Editor of the Materials Horizons and a member of the Editorial Board of ACS Energy Letters, ChemPlusChem, and Journal of Advanced Materials and Devices. Recognition for her research includes the 2005 Office of Naval Research Young Investigator Award, the 2006 NSF CAREER Award, the 2007 Harold Plous Award, the 2008 Camille Dreyfus Teacher Scholar Award, the 2009 Alfred Sloan Research Fellows, the 2010 National Science Foundation American Competitiveness and Innovation Fellows, the 2015 Alexander von Humboldt Senior Research Award, the 2016 Fellow of the Royal Society of Chemistry, and the 2015, 2016, and 2017 World's Most Influential Scientific Minds; Top 1% Highly Cited Researchers in Materials Science by Thomson Reuters and Clarivate Analytics. Her current research interests are electronic properties of conjugated polyelectrolytes, interfaces in optoelectronic devices, charge transport in organic semiconductors and biofilms, characterization of organic solar cells, ratchets, and transistors, and device physics.

Lecture outline

Organic solar cells potentially can offer low cost, large area, flexible, light-weight, clean, and quiet alternative energy sources for indoor and outdoor applications. In this lecture, I will give an overview of the current progress and challenges in organic solar cells. Then, I will

discuss recent progress on the development of donor and nonfullerene acceptor materials for application in solution processed bulk heterojunction solar cells. Molecular donors offer potential advantages over conjugated polymer systems in terms of their ease of synthesis and purification; making them more affordable to produce on large scales. Additionally, small molecules do not suffer from molecular weight dependence and polydispersity, and thus large batch-to-batch variation as their polymer counterparts. The molecular design is based on donor/acceptor/donor or acceptor/donor/acceptor using common building blocks such as oligothiophenes, dithieno silole (DTS), pyridal thiadiazole (PT), diketopyrrolopyrrole (DPP), etc. Chemical structure and processing conditions be used to tune the energy level, bandgap, solubility, molecular packing, film morphology, exciton diffusion, charge generation, charge mobility, charge recombination, and therefore, the device performance. A series of compounds has been synthesized to establish structure-function-property relationships. A combination of techniques is employed to characterize material properties and the device physics including steady-state and time-resolved spectroscopy, atomic force microscopy (AFM), photoconductive AFM, Kevin probe, TEM, XRD, UPS, GIWAXS, RSoXS, and electroluminescence. The results from these studies provide design guidelines for new generation of materials for applications in organic solar cells.

Theoretical foundations Sergei Baranovski Philipps-University, Marburg, Germany

Generation, transport and recombination of charge carriers in organic semiconductors (3h)



Professor Sergei Baranovskii received his Ph.D. (1981) in Theoretical Physics from Ioffe Physical-Technical Institute of the Russian Academy of Sciences in St. Petersburg, where he worked as a senior researcher till 1990. Since 1990 he has been working at the Philipps University Marburg, Germany where he got Habilitation in Theoretical Physics (1995). His research interests are devoted to optical properties of semiconductor quantum structures, to charge transport and optical properties of amorphous organic and inorganic semiconductors. He edited 2 books, co-authored 7 book chapters and 240 peer-reviewed articles including 5 review papers.

Lecture outline

Organic semiconductors attract currently much attention in the scientific community as materials desired for applications in modern electronics. The term organic semiconductors covers a large class of materials with a broad variety of properties. Organic semiconductors can be fabricated in crystalline form, as for instance, pentacene and rubrene. The main focus in research on organic materials is put, however, on organic disordered semiconductors (ODSs), which include polymers and low-molecular weight systems. Manufacturability and low production costs of ODSs, along with their optoelectronic properties, make these materials favourable and in some cases unique for various applications, particularly for large-area devices. ODSs dominate already today the electrophotographic image recording on the industrial scale and they are becoming more and more important for applications in light-emitting diodes, in displays for smartphones, in field-effect transistors, and are also tried for photovoltaic applications. Generation, transport and recombination of charge carriers are decisive for all these applications. Therefore, understanding the mechanisms of charge generation, transport and recombination in ODSs is of vital importance for device applications of such materials.

Intensive study of ODSs is driven not only by their usefulness for valuable devices, but also by the interest of researchers in fundamental properties of such systems. Theoretical description of the electronic properties in solid state has been for many years confined to crystalline solids. University courses and textbooks offer mostly theories based essentially on the long-range atomic order. The lectures at the Les Houches Physics School will present theoretical concepts developed for description of the electronic processes in disordered solids without translational symmetry, such as ODSs. These materials possess neither structural regularity, nor spatially extended electronic states. Instead, electronic states in ODSs are spatially localized. This happens because the overlap integrals for the weak Van-der-Waals interactions between neighboring structural units (molecules or molecular complexes) in ODSs are much smaller than the energy scale of disorder, which prevents the formation of extended electronic states. Therefore charge transport in ODSs is due to incoherent tunneling (hopping) of charge carriers between localized states that are distributed in space without any regular structure. The lectures will be essentially focused on presenting the transparent analytical concepts for theoretical description of the hopping charge transport in ODSs. Also some essential peculiarities related to charge generation and recombination in ODSs will be highlighted addressing the basic mechanisms responsible for the effects.

Excitonic materials and characterization techniques

Vladimir Dyakonov Würzburg University, Germany

Spin states engineering in optoelectronic organic devices by electrically and optically detected electron spin resonance (3h)



Professor Vladimir Dyakonov holds the Chair of Experimental Physics on the Faculty of Physics and Astronomy of Julius-Maximilian University of Würzburg, Germany since 2004 and he is the Director of the Bavarian Centre of Applied Energy Research (ZAE Bayern) since 2005. He studied physics at the University of St. Petersburg and received his doctorate at the A. F. loffe Physico-Technical Institute in 1996. Since 1990, he has been a visiting researcher at the universities of Bayreuth (Germany), Antwerp (Belgium) and Linz (Austria). He finished his Habilitation in experimental physics at the University of Oldenburg (Germany) in 2001. In 2007-2009 he was the Vice-dean and in 2013-2015 the Dean of the Faculty of Physics and Astronomy at the University of Würzburg. Dyakonov's main research interests are in the fields of

organic photovoltaics and electronics, semiconductor spectroscopy and functional energy materials, in general. He published 170 peer-reviewed scientific papers and has h-index of 56. He is a member of several committees including the Board of Directors of German Renewable Energy Research Association (FVEE), the Advisory Board of Bavarian Energy Technology Cluster and the Board of Trustees at German Plastics Centre (SKZ).

Lecture outline (provisional)

In this lecture, we will discuss the application of non-conventional electron spin resonance techniques to investigate the photophysics and particularly the role of spin in charge transfer reactions in donor-acceptor systems widely used in organic solar cells (OSC) and light emitting diodes (OLED).

First, we will address organic photovoltaic materials and devices. A strategy for increasing the conversion efficiency of organic photovoltaics has been to increase the open circuit voltage V_{oc} by tuning the energy levels of donor and acceptor components. However, this may open up a new loss

pathway from an interfacial charge transfer (CT) state to a donor triplet exciton (TE) state called electron back transfer (EBT), which may be detrimental to device performance (Fig. 1). To test this hypothesis, we study triplet formation in high performing blends of the fullerene $PC_{70}BM$ with either the polymer PTB7 [1] or the soluble small molecule p-DTS(FBTTh₂)₂ [2] and determine the impact of the morphology-optimizing additives. Using photoluminescence and spin-sensitive optically and electrically detected magnetic resonance (ODMR, EDMR) measurements we find that TE formation does not only depend on the materials' energetics, but also on temperature and nano-morphology. Furthermore, we observe TEs in real devices under realistic working conditions even for the most efficient solar cells, which has implications not only for efficiency, but also for devices stability.





In a second part of the lecture, we will discuss an aspect of thermally activated delayed fluorescence (TADF) emission in organic light emitting diodes (OLEDs) related to the mechanism of triplet-singlet up-conversion leading to exciplex emission. In particular, whether the TADF mechanism is a spindependent process and, if yes, what is the exact mechanism. Again, we perform direct spin-sensitive measurements on TADF-OLED devices applying multi-frequency electroluminescence and electrically detected magnetic resonance (ELDMR, EDMR). The idea behind these experiments is that the static magnetic field applied to devices modifies only the energy levels of spin-carrying states due to Zeeman splitting, thus changing the emission rates. We observe that the resonant microwave radiation, applied to OLEDs leads to enhancement of the EL intensity. The effect was found to be very sensitive to experimental conditions, thus modifying the resonance frequency, temperature and microwave power we were able to shed light on the underlying mechanism of the reverse intersystem crossing and the spin states involved. With temperature-dependent ELDMR, the singlettriplet splitting ΔE_{sT} can be determined, as we reported in [3] for two model TADF systems. Comparing ELDMR, EDMR and photoluminescence detected magnetic resonance (PLDMR), we revealed differences in TADF processes under optical excitation and electrical injection. The information gained from magnetic resonance experiments can potentially help to design new costeffective OLED materials as well as to further improve their performance.

References

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- [2] S. Väth, K. Tvingstedt, A. Baumann, M. C. Heiber, A. Sperlich, J. A. Love, T.-Q. Nguyen, V. Dyakonov, Adv. Energy Mater. 7, 1602016 (2017).
- [3] S. Väth, K. Tvingstedt, M. Auth, A. Sperlich, A. Dabuliene, J. V. Grazulevicius, P. Stakhira, V. Cherpak, V. Dyakonov, Adv. Opt. Mater. 5, 1600926 (2017).

Excitonic materials and characterization techniques Natalie Banerji University of Fribourg, Switzerland

Ultrafast Techniques to Study Charge Carrier Dynamics in Organic and Hybrid Semiconductors (3h)



Natalie Banerji is currently a Full Professor of Physical Chemistry at the University of Bern. Her research interests include the study of organic and hybrid materials using ultrafast spectroscopic techniques, in view of solar cell and bioelectronic applications. She was born and raised in Geneva (Switzerland), although she is originally Austrian. She studied Chemistry at the University of Geneva and obtained her Ph.D. in Physical Chemistry in 2009, under the supervision of Prof. Eric Vauthey. She then moved to the University of California in Santa Barbara (USA), to work on organic solar cells during a post-doctoral stay with Nobel Laureate Prof. Alan J. Heeger

(2009-2011). In 2011, she was given the opportunity to start her independent research career in Switzerland at the Ecole Polytechnique Férérale de Lausanne (EPFL) with an Ambizione Fellowship by the Swiss National Science Foundation (SNSF). She obtained an SNSF-Professorship at the University of Fribourg (Switzerland) in 2014, and was subsequently nominated tenured Associate Professor in 2015. She was President of the Chemistry Department in Fribourg form 2016-2017 and moved to bern in 2017. In 2016, she was awarded an ERC Starting Grant.

Lecture outline

In this lecture, the concepts of ultrafast laser spectroscopy and non-linear processes will be introduced, with focus on visible transient absorption spectroscopy (TAS) and time-domain terahertz spectroscopy (TD-THz). We then describe ultrafast charge carrier generation and recombination processes occurring in polymer:fullerene blends for organic photovoltaics (OPV) and in perovskite materials used in solar cells and LEDs. Case studies from recent research will be presented to show how laser spectroscopy can be applied to study those processes in the organic and hybrid materials. Those will include micro-structural effects in the OPV systems, effects of mixing different cations in perovskites, and the use of additives in perovskite samples to increase the fluorescence quantum yield for LED applications.

Excitonic materials and characterization techniques Emmanuel Lhuillier Université Pierre et Marie Curie, Paris, France

Nanocrystals for optoelectronics (3h)



Emmanuel Lhuillier is an ESPCI engineer with a master in condensed matter physics. He did his PhD at Onera under the supervision of Emmanuel Rosencher where he studied the electronic transport in quantum well structure used as infrared detector. For post doc he joined the Guoyt-Sionnest group at the university of Chicago. He there worked on the mid infrared photoconductive properties of nanocrystal arrays. He then moved back to ESPCI and joined the LPEM lab and investigate the optoelectronic properties of colloidal quantum wells. Since 2015, he is CNRS researcher and his group work on the optoelectronic of confined nanomaterials. He is author of 45 papers and 6 patents.

Lecture outline

This class will be organized over three mains sections. The first part will be dedicated to the nanocrystal synthesis and their basic physical properties. I will review synthesis method focusing on II-VI semiconductors. I will discuss about the growth methods, how it is possible to control dimentionality and shape, the importance of surface chemistry. This first section will finished by a few words about the first mass market application of the colloidal nanocrystal which is their used as light source for displays.

In the second section, I will discuss about the electronic transport properties of nanocrystal arrays. I will address the transformation of colloidal solution into conductive films and the developed methods to tune the surface chemistry. I will in particular discuss the properties of nanocrystal arrays probed in a field effect transistor configuration and which physical parameters can be obtained from such device. I will briefly discuss about application to solar cell and light emitting diode

The last part of the class will be focused on narrow band gap materials and their optical properties in the mid-infrared. I will discuss the candidate material to reach this part of the electromagnetic spectrum. In particular, I will show that two types of device can be designed either based on inter or intraband transition.

Excitonic devices and Photonic applications Graham Turnbull University of Saint Andrews, United Kingdom

Organic luminescent devices: from basic concepts to emerging applications (3h)



Graham Turnbull is Professor of Physics at the University of St Andrews, and Head of the School of Physics and Astronomy. His research interests focus on photonic applications of soft materials, notably including organic semiconductors. This spans fundamental studies of light-matter interactions through to applications, including sensors for buried explosives, and technologies for lighting and optical wireless communications. A major theme of his research has been the development of low threshold polymer lasers, and has pioneered the use of LEDs as simple optical pump sources for visible organic lasers.

Lecture outline

The development of OLEDs for displays and lighting has been the major driving force of the plastic electronics sector. The technology has now reached maturity and is in commercial mass production for mobile phones and other consumer goods. The development of organic semiconductor lasers on the other hand is much less well developed, but is showing promise for several applications including spectroscopy and sensing. These lectures will introduce the physics and applications of photoluminescent polymer thin films, including their use in visible lasers. It will cover light emission from planar devices, optical gain in organic materials, organic laser physics, and emerging applications of organic photonics (including sensing, spectroscopy, lighting and data communications).

Excitonic materials and characterization techniques

Xavier Marie

Université de Toulouse, INSA, Toulouse, France

MoS₂ and its Cousins: 2D Materials with Promising Optical Properties (3h)



Xavier Marie is Professor at the National Institute of Applied Sciences (INSA- University of Toulouse). He has joined the Institut Universitaire de France (IUF) in 2005 as a Junior member and in 2015 as a Senior member.

He is currently in charge of the Laboratory of Excellence NEXT (Nano, EXtreme measurements and Theory) which brings together 200 permanent researchers from 6 laboratories in Toulouse.

He has worked for about 25 years on electronic and optical spectroscopy of

low dimensional semiconductor structures (quantum wells, quantum dots, 2D materials). His main present interest is

the optical, valley and spin coherence in semiconductor nanostructures and band structure engineering of semiconductors for optical telecommunication devices and solar cells.

Lecture outline

The spectacular progress in controlling the electronic properties of graphene has triggered research in alternative atomically thin two-dimensional crystals. Monolayers of transition-metal dichalcogenides such as MoS_2 have emerged as very promising nanostructures for optical and electronic applications.

In this lecture I will give an overview of the physical properties of 2D semiconductors based on transition metal dichalcogenides : band structure, exciton effects, optical and transport properties, and spin/valley dynamics. Prototype devices based on these 2D materials will also be presented (LED, Photo-detector, ...).



Figure : Schematic representation of MoS₂

Excitonic devices and Photonic applications Stéphane Kéna-Cohen Polytechnique Montréal, Canada

Light-matter interaction with excitons from weak to strong coupling (3h)



condensates.

Stéphane Kéna-Cohen is an Assistant Professor of Engineering Phyiscs at Polytechnique Montreal since 2014. He is the Canada Research Chair in Hybrid and Molecular Photonics and his group is active in the development of optoelectronic devices using a broad range of novel materials. Prof. Kéna-Cohen is recognized for his important contributions to the development of room-temperature polariton lasers and polariton superfluids using organic materials. He obtained his PhD in 2010 at Princeton University, where he worked on strong light-matter coupling. This was followed by a post-doctoral fellowship at Imperial College London on plasmonics and metamaterials. At Imperial College, he was a Junior Research Fellow between 2012 and 2014 where he performed independent research on quantum plasmonics and polariton

Lecture outline

Excitons are the low-lying excited states within most semiconducting materials. In this lecture, we will discuss the interaction of excitons with light within the dipole approximation. We will review the basic concepts underlying light-matter interaction and then discuss how radiation occurs and is affected by the environment. We will introduce concepts such as dyadic Green's functions, the local density of photonic states, Purcell effect, radiative and non-radiative loss. We will apply these ideas to technologically relevant systems such as OLEDs, organic lasers and waveguides. Then, we will discuss the extreme situation where light-matter interaction is faster than dissipation within the system: the so-called strong light-matter coupling regime. We will introduce polaritons, the resulting quasiparticles and describe some novel effects that result such as polariton lasers, parametric amplifiers and superfluidity.

Excitonic materials and characterization techniques

Peter Reiss CEA Grenoble, INAC/SPrAM, France

Materials for colloidal quantum dots (3h)



Dr. Peter Reiss is researcher at the Institute of Nanoscience & Cryogenics, CEA Grenoble (France), and Head of Laboratory Synthesis, Structure and Properties of Functional Materials (STEP). He graduated (1997) from University of Karlsruhe (Germany), and earned his PhD in inorganic chemistry under the supervision of Prof. Dieter Fenske (2000). His research activities focus on colloidal semiconductor nanocrystals, nanowires and metal halide perovskites (nanocrystals and thin films): development of synthesis methods, study of nucleation and growth mechanisms, surface functionalization and assembly, potential of the obtained materials to be used in energy conversion (photovoltaics, thermoelectrics) and storage, as emitters in LEDs, displays or in biological imaging and detection. Dr. Reiss acts as Associate Editor for Nanoscale Research Letters (Springer), is Editorial

Board Member of Scientific Reports (NPG) and Editorial Advisory Board Member of Journal of Materials Chemistry C (RSC). He co-organizes the biennial conference NaNaX – Nanoscience with Nanocrystals (cf. <u>http://nanax.org</u>), the most important European meeting in the field of colloidal nanocrystals. He has published > 120 scientific articles (> 7000 citations), 13 patents and 6 book chapters. Personal Website: <u>http://inac.cea.fr/Phocea/Pisp/index.php?nom=peter.reiss</u>

Nanocrystals group Website: <u>http://inac.cea.fr/spram/NanoX/index.htm //</u>

Solar cell research: http://www.spram-solar.fr

List of publications: <u>https://scholar.google.fr/citations?user=BeAIRJsAAAAJ&hl=fr</u>

Lecture outline

More than 30 years after the discovery of the quantum confinement effect, the field of colloidal semiconductor nanocrystals (quantum dots, QDs) has strongly involved in terms of materials diversity. Binary Cd- and Pb-chalcogenides have been (and still are) the most studied systems due to the relative simplicity for obtaining quasi monodisperse and highly luminescent samples by chemical synthesis. However, numerous emerging applications of QDs have fuelled research on alternative, less toxic compounds [1]. In the area of Cd-free binary semiconductors covering the visible range of emission, InP has evolved as the most

advanced type of QDs [2]. Going from binary to ternary or even multinary compounds opens a much wider space of semiconductor materials with band gap energies tuneable from the UV to the infrared range by changing the QD size and/or composition [3,4]. A prominent example of this class of materials are CuInS₂ nanocrystals. In contrast to their binary counterparts, optical transitions in ternary or multinary QDs generally involve intra gap states [5]. While the description of the precise emission mechanisms in these materials is still controversial, it has yet become clear that the reduction of the emission line width is a highly challenging task. Finally, the most recent class of emerging nanocrystals are metal halide perovskite QDs ABX3 (A = Cs / methylammonium / formamidinium; B = divalent metal, X = CI / Br / I [6]. In the prototypical compound CsPbBr₃, the band gap and hence emission colour can be tuned easily by changing the halide and for small sizes (< 5 nm) also quantum confinement effects have been observed. Intriguingly, very high fluorescence quantum yields can be obtained without further surface treatment, e.g. growth of a wide band gap semiconductor shell. The synthesis and properties of these three families of semiconductor nanocrystals, ranging from highly ionic (perovskite), over intermediate (chalcopyrites) to highly covalent (III-Vs) compounds and of their core/shell structures will be discussed.

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[2] Tamang, S.; Lincheneau, C.; Hermans, Y.; Jeong, S.; Reiss, P. Chemistry of InP Nanocrystal Syntheses. *Chem. Mater.* **2016**, *28*, 2491-2506.

[3] Aldakov, D.; Lefrancois, A.; Reiss, P. Ternary and Quaternary Metal Chalcogenide Nanocrystals: Synthesis, Properties and Applications. *J. Mater. Chem. C* **2013**, *1*, 3756-3776.

[4] Coughlan, C.; Ibanez, M.; Dobrozhan, O.; Singh, A.; Cabot, A.; Ryan, K. M. Compound Copper Chalcogenide Nanocrystals. *Chem Rev* **2017**, *117*, 5865-6109.

[5] Sandroni, M.; Wegner, K. D.; Aldakov, D.; Reiss, P. Prospects of Chalcopyrite-Type Nanocrystals for Energy Applications. *ACS Energy Letters* **2017**, *2*, 1076-1088.

[6] Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I. Properties and Potential Optoelectronic Applications of Lead Halide Perovskite Nanocrystals. *Science* **2017**, *358*, 745-750.

Excitonic devices and Photonic applications Chihaya Adachi Kyushu University, Japan

With the support of Fatima Bencheikh, Kyushu University

Harvesting excitons in organic semiconductors: towards new generations of OLEDs and organic lasers (3h + 1h30)

Prof. Adachi obtained his doctorate in Materials Science and Technology in 1991 from Kyushu University. Before returning to Kyushu University as a professor of the Center for Future Chemistry and the Department of Applied Chemistry, he held positions as a research chemist and physicist in the Chemical Products R&D Center at Ricoh Co., a research associate in the Department of Functional Polymer Science at Shinshu University, research staff in the Department of Electrical Engineering at Princeton University, and an associate professor and professor at Chitose Institute of Science and Technology. He became a distinguished professor at Kyushu University in 2010, and his current posts also include director of Kyushu University's Center for Organic Photonics and Electronics

Research (OPERA) since 2010 and program coordinator of Kyushu University's Education Center for Global Leaders in Molecular Systems for Devices and director of the Fukuoka i3 Center for Organic Photonics and Electronics Research since 2013.

Lecture outline

The class will be divided in two parts: a main tutorial on the harvesting of excitons in OLED devices (3h), and a supplementary course, given by Fatima Bencheikh, focused on organic lasers.

Harvesting excitons in organic semiconductors: applications in OLEDs (2X1h30)

- 1. History of OLED materials- importance of CT and exciplex-
- 2. TADF materials and mechanism for high performance OLEDs
- 3. TADF lasing materials and system
- 4. Long persistent luminescence

Supplementary course :

Harvesting excitons in organic semiconductors: toward electrically driven organic lasers (1h30)

This class will be given by Fatima Bencheikh, Kyushu University

Course Program:

- 1. Progress for the realization of electrically driven organic lasers
- 2. Loss processes in OLED under high electrical excitation
- 3. Design rules for OLED toward electrically driven lasers
- 4. Conclusion

Excitonic devices and Photonic applications Richard Williams Wake Forrest University, USA

Excitonic scintillators (3h)

Richard Williams is a research professor of physics at Wake Forest University, located in the mid-Atlantic region of the USA. He earned his Ph.D. in physics at Princeton University in 1973 and worked for 12 years at the US Naval Research Laboratory in Washington D. C. He used highenergy electron pulses in the early study of time-resolved exciton dynamics and defect formation in wide-gap solids, discovering the excited-state absorption of self-trapped excitons in metal halides. He then pioneered picosecond laser methods in the same field to jump 3

orders of magnitude in time resolution. In 1985 Williams moved to Wake Forest University as Reynolds Professor of Physics. He published Self-Trapped Excitons (Springer, 1993) with theorist K. S. Song and jumped another two decades of time resolution to study excitons, defects, and timeresolved photoelectron spectroscopy at the 100 fs scale. From about 1990, Richard started becoming more involved with scintillator research. Especially from about 2007, his group used femtosecond laser excitation across the band gap as a surrogate for some hard-to-measure aspects of gamma ray stopping events without the track structure, such as measuring nonlinear quenching rates and picosecond sequences in exciton formation, carrier trapping, dipole-dipole transfer, and recombination. Computational modeling was undertaken to build electron track structure back into the model based on laser-measured rate constants. His current research includes work on cesiumlead-halide nanocomposites as light emitters and possible scintillators, along with other scintillator research sponsored by the National Nuclear Security Agency through subcontract from Lawrence Berkeley National Lab, the Domestic Nuclear Detection Office, National Science Foundation, and Saint-Gobain Crystals. He has 173 scientific publications, 11 patents, and more than 6,680 citations.

Lecture outline

Energy-resolving detectors of ionizing radiation are used in fields as diverse as medical diagnostics, security inspection, particle physics, astrophysics, and oil exploration. There is a continual need for better performance in regard to energy resolution, time resolution, sensitivity, low background, and indeed low cost. While admitting some commonality of the physics of gamma detection with that of solar cells and lighting displays, extracting precise information on megavolt photons and other particles has its special constraints and challenges. This short course will start with a grounding in the extreme circumstances found in high-energy particle tracks and attendant nonlinearities and transport during conversion to countable carriers or photons, as well as the materials and tools of research on high-

energy radiation detection. Then we will explore current frontier challenges and some of what is being done and may be possible both with traditional materials and phenomena and with newer ones at the intersection with excitonics for photonic applications.

Excitonic Scintillators

Preliminary Outline

- I. Spectroscopic detectors of ionizing radiation
 - a) Applications
 - b) Principles
 - c) Semiconducting detectors
 - d) Scintillating detectors
- II. Energy Resolution, sensitivity, time resolution
 - a) Importance
 - b) Physical principles
 - c) Computational modeling
 - d) Femtosecond/picosecond studies of energy and charge transport
- III. Cost
 - a) Importance
 - b) Factors and approaches
- IV. Scintillation materials
 - a) Halides "old", "newer", and "newest"
 - b) Oxides
 - c) Semiconductors
- V. Excitonic scintillators
 - a) Intrinsic (undoped) scintillators
 - b) Exciton energy transport to dopants
 - c) Doping to influence exciton scintillation
 - d) Excitons & polarons in the insulators that comprise most conventional scintillators
- VI. Crystallinity and morphology in scintillators
 - a) Single crystal
 - b) Polycrystal
 - c) Segmented & granular
 - d) Polymer, glass, amorphous, liquid
 - e) Nanocrystals
 - 1) Suspensions in composites
 - 2) Hot electron range & track size vs nanocrystal size
 - 3) Exciton coherence volume, giant oscillator strength
 - 4) Quantum dots, wires, sheets
- VII. Perovskites and detectors of ionizing radiation
 - a) Semiconducting detectors using perovskites
 - b) Perovskites as scintillator candidates
 - c) Excitons, charge transport, traps, and dimensionality in perovskite scintillation candidates
- IX. Opportunities and challenges

Excitonic devices and Photonic applications Noel Giebink Pennsylvania State University, USA

Unusual concepts in organic photonics (3h)

Chris Giebink is the Charles K. Etner Assistant Professor of Electrical Engineering at Penn State University. He received his Ph.D. in electrical engineering from Princeton University and holds undergraduate degrees in both Physics and Engineering Science from Trinity University (TX). His research interests focus broadly on optics and organic optoelectronic materials and devices.

Lecture outline

The first portion of this lecture will discuss parity-time symmetry in optics and the use of organic materials as a platform to engineer unusual complex refractive index distributions that lead to unidirectional Bragg scattering and loss-induced transparency. The discussion will extend to engineering optical nonlinearity as well by creating an artificial second order susceptibility [$\chi(2)$] that stems from intermolecular charge transfer states at oriented donor-acceptor interfaces.

The second portion of the lecture will focus on recent progress toward the goal of realizing a hybrid organic-inorganic perovskite laser diode. This includes continuous-wave lasing from methylammonium lead iodide and some of the interesting mixed-phase physics that make it possible as well as the exploration of perovskite light emitting diode efficiency at high brightness.

The final portion of the lecture will focus on charged states in organic photonics, beginning with strong coupling between light and radical cation optical excitations in a doped organic semiconductor film. Recent experiments demonstrating these charged polaron polariton states and exploring some of the interesting possibilities they offer for interfacing with electric fields and current in optoelectronic devices will be discussed. The lecture will conclude with an exploration of bipolarons in organic devices, their unexpectedly common existence at organic semiconductor/electrode interfaces, and their role in unipolar organic magnetoresistance phenomena.