

Virtual Symposium
of
Research Group 2482 / ModISC
“Modulation of Intersystem Crossing”

Program

September 29th 2021



Research Training Group 2482 / ModISC Modulation of Intersystem Crossing

Electronic excitation of molecules affects diverse areas ranging from photobiology to molecular electronics, from basic science to applications, such as organic light emitting diodes (OLED). Intersystem crossing (ISC), the non-radiative interconversion of electronic states with different spin multiplicities, is a key process in photochemistry and photophysics. The efficiency and kinetics of ISC can render electronically excited molecules photo-labile or -stable, emissive or dark. This Research Training Group proposes to study and modulate ISC in molecules by chemical substitution and by varying the molecular environment. It promotes and fosters interdisciplinary research seeking for a deeper understanding of emission enhancement by controlling ISC from singlet to triplet and its reverse. Closely related to this highly topical research, a cross-curricular PhD training program was established, taking into special consideration diverse scientific backgrounds of the candidates. The doctoral researchers are strategically mentored by co-supervision teams of PIs holding complementary expertise. In addition, workshops with international speakers, RTG symposia, and the RTG training will enhance the educational and subject-specific didactical skills of the young researchers as an optimal preparation for future work in academia or industry.

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Program

September 29th, 2021

Time	Speaker	Topic
10:00	Thomas J. J. Müller	Welcome and Introduction
10:15 – 11:00	Michael Reggelin	Synthesis of crosslinkable low molecular weight and high molecular weight semiconductor materials
11:00 – 11:30	Barbara Nogueira de Faria	TADF Emitter Studied by Time Resolved Near-Infrared Spectroscopy
11:30 – 12:00	Christian Wulkesch	Photocatalyzed Perfluoroalkenylation - A synthetic application of ISC processes in organic chemistry
12:00 – 13:00	Lunch Break	
13:00 – 13:45	Denis Jacquemin	Ab initio Studies of ESIPT Dyes
13:45 – 14:30	Cristian Strassert	Light-driven coordination compounds and hybrid assemblies as multimodal (bio)imaging agents, ROS-sensitizers, oxygen sensors and (electro)luminophores – From synthesis to implementation
14:30 – 14:45	Coffee Break	
14:45 – 15:30	Daniel D'Souza	From research to manufacturing of OLED Materials
15:30 – 16:15	Birgit Esser	Spiro-donor-acceptor compounds and conjugated nano hoops as optoelectronic materials
16:30	Closing Remarks	

Abstracts of Talks

Synthesis of crosslinkable low molecular weight and high molecular weight semiconductor materials

Michael Reggelin

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The talk describes our efforts to provide materials for the production of components for organic electronics by wet processing. If successful, this would result in enormous cost reductions compared to established processes, while at the same time expanding the possibilities for manufacturing large-area displays. The problem to be solved is that in the manufacture of multilayer components, intermixing of the successive layers must be avoided. To reach this goal, various approaches have been pursued including the Synthesis of (cross-linkable) functional materials, innovative approaches to fluid formulation through the use of organogelators and positioning of functional units and crosslinkable groups in the repeat units of stereoregular polymers with the final goal to produce CPL-emitting OLEDs.

Photocatalyzed Perfluoroalkenylation - A synthetic application of ISC processes in organic chemistry

Christian Wulkesch

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The perfluoroalkylation of organic compounds has been under intense investigation during the last decade.

In particular photocatalytic approaches using visible light stand out because of their mild reaction conditions.

We report herein a mild and experimentally simple synthesis of (per)fluorinated enals in one step straight from the corresponding aldehydes.

Based on the formation and irradiation of electron donor-acceptor-complexes between phosphines and perfluoroiodoalkanes with blue light, an inter-system-crossing process appears to generate electrophilic perfluoroalkyl-radicals.

TADF Emitter Studied by Time Resolved Near-Infrared Spectroscopy

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Fluorophores featuring thermally activated delayed fluorescence (TADF) show great potential as emitters in organic light-emitting diodes (OLEDs). These emitters convert triplet into emissive singlet excitons via reverse intersystem crossing reaching internal quantum efficiency close to 100%. Efficient TADF molecules need to exhibit singlet-triplet energy gaps of the order of the thermal energy $k_B T$ (~ 25 meV), and high rate constants for intersystem crossing (ISC) and reverse intersystem crossing (rISC) between these states. As small gaps are encountered in charge transfer (CT) excitations, TADF emitters are commonly composed of donor and acceptor moieties. Yet, for “pure” CT states spin-orbit coupling is negligible and no ISC or rISC transitions ought to occur. As shown theoretically, spin-vibronic coupling can mediate these transitions¹. The respective expressions contain $S_1 \rightarrow S_n$ ($n=2,3,4,\dots$) and $T_1 \rightarrow T_n$ ($n=2,3,4,\dots$) transition energies as energy denominators. The respective transition energies ought to be found in near-infrared (NIR) spectral region.

Here, we report on ongoing developments regarding NIR spectroscopy as well as first measurements of $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ transition energies. Experiments were carried out on a TADF emitter containing a triarylamine donor and 1,4-dicyanobenzene acceptor moiety². Upon pulsed excitation the emitter exhibit NIR transitions on the nanosecond ($S_1 \rightarrow S_n$) and microsecond ($T_1 \rightarrow T_n$) timescale. Theoretical calculations predicting the transition energies and strengths are provided and compared to our experimental results.

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Ab initio Studies of ESIPT Dyes

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Keywords: ESIPT dyes, theoretical chemistry, modelling, TD-DFT, CC2

During this talk, I will illustrate recent applications of Time-Dependent Density Functional Theory (TD-DFT) and wavefunction approaches (e.g., ADC(2) and CC2) for dyes undergoing Excited-State Intramolecular Proton Transfer (ESIPT). Several families of ESIPT dyes, such as hydroxyphenylbenzoxazoles, hydroxyphenylbenzimidazoles and benzothiadiazoles derivatives, will be considered. These dyes are particularly useful as they might lead to single-molecule dual-fluorescence when ESIPT is not quantitative. The interest of theoretical calculations will be illustrated not only for reproducing experimental spectroscopic data [1,2] but also for determining transition states on the excited-state surface [1,2] as well as estimating the relative emission quantum yields of the various forms in a very simplified approach [3]. Theory was used to design from first principles a series of dual-emitters from single ESIPT dyes [4]. In several cases, it could also induce a re-interpretation of experimental outcomes [5,6]. Finally, the possibilities to design systems encompassing several ESIPT centres [7], ratiometric probes [8], or zwitterionic systems [9] will be discussed.

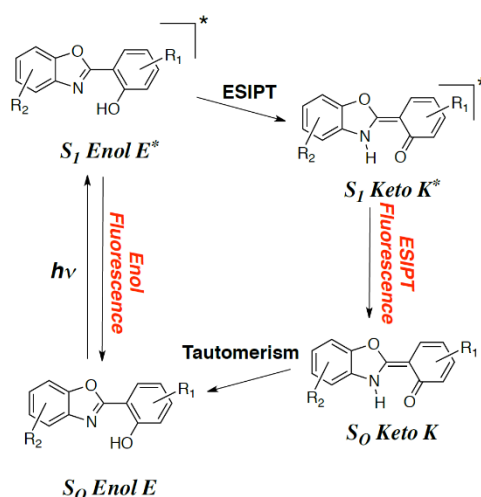


Fig. 1: Representation of a typical ESIPT process

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Light-driven coordination compounds and hybrid assemblies as multimodal (bio)imaging agents, ROS-sensitizers, oxygen sensors and (electro)luminophores – From synthesis to implementation

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Diverse approaches have allowed us to fully control the aggregation of planar coordination compounds and to tune their photophysical properties for phototherapy, functional microscopy and multimodal bioimaging.

We have designed a series of photosensitizers able to target, to label and to photoinactivate pathogenic and antibiotic resistant bacteria upon irradiation with red light. For this purpose, it was necessary to avoid stacking by diverse (supra)molecular strategies [1-4]. Currently, we are extending these concepts to targeted, fully water-soluble and biodegradable platforms, a prerequisite for biomedical applications. These approaches include the use of dextrin conjugates [5] and cyclodextrin vesicles [6] that selectively photoinactivate Gram-positive strains. On the other hand, axially decorated dicationic Si(IV) phthalocyanines can kill both Gram-positive and Gram-negative bacteria, despite showing antibiotic resistance [7]. We have also implemented light-driven arrays for spatiotemporally resolved functional microscopy to monitor *in situ* the response towards ROS of eukaryotic [8] as well as prokaryotic [9] cells and biofilms. Insertion of open-shell transition metal cations and tuning of the macrocycles' substitution pattern yielded NIR-absorbing sonophores for *in vivo* photoacoustic imaging [10]. An outlook will be presented regarding the use of Pt(II)-based triplet emitters as multimodal agents for electron microscopy and phosphorescence lifetime imaging without unwanted quenching by triplet molecular dioxygen and related cytotoxicity due to photoproduction of reactive oxygen species [11,12,13]. Finally, our recent progress in the design and realization of Pt(II) complexes as triplet molecular dioxygen sensors and for electroluminescent devices will be discussed, going from bidentate [14] to tridentate [15,16,17,18] and tetradentate [19,20,21] luminophores.

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From research to manufacturing of OLED Materials

Daniel D'Souza

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OLED materials are low volume but high quality, premium priced performance chemicals used for the production of OLED panes. OLED materials are exclusively sold within the OLED industry and according to specifications rather than performance criteria. Typically, due to the low volumes these performance chemicals are manufactured in campaign fashion in multipurpose plants starting from commodity chemicals and involving several distinct synthetic steps, recrystallizations and sublimations, relying on contract manufacturing services.

Cynora, established in Germany in 2003, develops next generation OLED materials based on exclusively-licensed technology.

Spiro-donor-acceptor compounds and conjugated nano hoops as optoelectronic materials

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In this talk I will present our research on spiro compounds with donor-acceptor structure as well as on chiral conjugated nano hoops as emitters with chiroptical properties. The spiro compounds are based on heterospirenes with either internal donor-acceptor structure or with donor character, connected to acceptor moieties, and have low predicted singlet-triplet energy gaps. I will discuss their structural design and synthesis as well as optoelectronic properties. The conjugated nano hoops are chiral due to the incorporation of diketone units with discrete stereocenters or bent dibenzopentalene units. I will present synthetic strategies to such strained, chiral hoops as well as their chiroptical and electronic properties.