

CPP 71: Organic Electronics and Photovoltaics - OLEDs and Molecular Excitations

Time: Thursday 15:00–18:00

Location: C 243

CPP 71.1 Thu 15:00 C 243

Intra- and Intermolecular TADF emission investigated by magnetic resonance methods — ●NIKOLAI BUNZMANN¹, BENJAMIN KRUGMANN¹, SEBASTIAN WEISSENSEEL¹, GINTARE GRYBAUSKAITE-KAMINSKIENE², DMYTRO VOLYNIUK², ANDREAS SPERLICH¹, JUOZAS V. GRAZULEVICIUS², and VLADIMIR DYAKONOV^{1,3} — ¹Experimental Physics VI, Julius Maximilian University of Würzburg — ²Kaunas University of Technology, Lithuania — ³Bavarian Center for Applied Energy Research (ZAE Bayern)

Organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) utilize molecules with a small energy splitting ΔE_{ST} between singlet and triplet states. This can either be realized in intramolecular charge transfer states of molecules with near-orthogonal donor and acceptor moieties or in exciplex states formed between a proper combination of individual donor and acceptor materials. Here, we investigate 4,4'-(9H,9'H-[3,3'-bicarbazole]-9,9'-diyl)bis(3-(trifluoromethyl) benzonitrile) (pCN-BCzmCF3), which shows intramolecular TADF but simultaneously can form intermolecular exciplex states in combination with 4,4',4''-Tris[phenyl(m-tolyl)amino]triphenylamine (m-MTDATA). In order to reveal which triplet states are involved in the RISC mechanism for both types of TADF emission, we apply electroluminescence and photoluminescence detected magnetic resonance (ELDMR, PLDMR). Thereby, we draw a comprehensive picture of which intermediate states are populated between optical or electrical excitation and light emission.

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The interplay of TADF and phosphorescence in warm-white hybrid OLEDs — ●LUDWIG POPP¹, PAUL KLEINE¹, RAMUNAS LYGAITIS², REINHARD SCHOLZ¹, SIMONE LENK¹, and SEBASTIAN REINEKE¹ — ¹Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP) and Institute for Applied Physics, TU Dresden, Germany — ²Kaunas University of Technology, Lithuania

White emission in OLEDs is usually a combination of two or more different emitters with individual colors. Therefore, it is necessary that all included systems are efficient. It has been shown that the concept of thermally activated delayed fluorescence (TADF) allows to synthesize very efficient light-emitting molecules with various emission colors.

In our work, we use the sky-blue TADF emitter 5CzCF₃Ph with an emission maximum at a wavelength of 495 nm, reaching a photoluminescence quantum yield of 70 % and up to 18% external quantum efficiency (EQE) in OLEDs. By combination with the common phosphorescent red emitter Ir(MDQ)₂(acac) within one emission layer it is possible to build warm white OLEDs with a high color rendering index of over 80 and correlated color temperatures about 2800 K.

Due to the variety of local and charge-transfer excited states in the emitter system, there are several probable scenarios for the energy transfer between 5CzCF₃Ph and Ir(MDQ)₂(acac) since excitons are formed mostly on the TADF emitter. Utilizing time-correlated single photon counting (TCSPC) with a wavelength-sensitive detection, we deliver a thorough investigation of the exciton transfer and exchange mechanisms in the emitter system of our warm-white hybrid OLEDs.

CPP 71.3 Thu 15:30 C 243

Blue emitting TADF Materials for Organic Light Emitting Diodes — ●SEBASTIAN WEISSENSEEL¹, FELIX KLINGERT¹, NIKOLAI BUNZMANN¹, LIUDMILA G. KUDRIASHOVA¹, NIKITA DRIGO², MOHAMMAD KHAJA NAZEERUDDIN², ANDREAS SPERLICH¹, and VLADIMIR DYAKONOV¹ — ¹Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — ²Group for Molecular Engineering of Functional Materials, EPFL, CH-1951 Sion, Switzerland

Since the mechanism of thermally activated delayed fluorescence (TADF) emission was proposed for organic light emitting diodes (OLEDs), the OLED community experienced renewed enthusiasm. The molecular design of TADF materials omits the expensive heavy metal atoms needed for phosphorescence emitters and thus promises a cost reduction and sustainability. Here, we investigate novel blue emitting molecules, which exhibit intramolecular TADF mechanism. OLED devices are analyzed by means of current-electroluminescence-voltage characteristics, emission spectra and external quantum efficiency. We also apply direct spin-sensitive measurements on OLED devices to extract information about the involved spin states and shed

some light on the TADF mechanism [1]. This may contribute to an overall better understanding of TADF, which is essential for further improvement of organic light emitting diodes.

[1] S. Vaeth, et al., *Adv. Optical Mater.* **5**, 1600926 (2017).

CPP 71.4 Thu 15:45 C 243

The Role of Molecular Environment in Thermally Activated Delayed Fluorescence — ●LIUDMILA G. KUDRIASHOVA¹, NIKITA DRIGO², SEBASTIAN WEISSENSEEL¹, ANDREAS SPERLICH¹, MOHAMMAD KHAJA NAZEERUDDIN², and VLADIMIR DYAKONOV^{1,3} — ¹Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg, Germany — ²Group for Molecular Engineering of Functional Materials, EPFL, CH-1951 Sion, Switzerland — ³Bavarian Center for Applied Energy Research (ZAE Bayern), 97074 Würzburg, Germany

Thermally activated delayed fluorescence (TADF) opened the way to overcome the efficiency-limiting spin statistics in a new generation of organic light-emitting diodes (OLEDs). Intensity of intramolecular TADF is mainly ruled by conformation of the donor/acceptor parts within the emitter molecule and temperature. At the same time, the role of host matrix is poorly discussed in literature. Here, we report luminescent properties of novel TADF molecules studied in a broad range of temperatures in various types of solid films. We show that emission consists of three components: prompt fluorescence, delayed fluorescence and phosphorescence. Temperature and environment of the TADF emitters have crucial effect on lifetimes and relative amplitudes of the components. Hindering of the emitting molecules in a polymeric matrix suppresses phosphorescence, while increasing both TADF lifetime and intensity a hundredfold. All in all, we demonstrate that the molecular environment can significantly improve TADF efficiency, which is decisive for the resulting OLED performance.

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Thermal spin polarization of OLEDs observed by correlated fluorescence and phosphorescence in dual emitters — ●TOBIAS SCHARFF, JONAS ZIPFEL, WOLFRAM RATZKE, SEBASTIAN BANGE, and JOHN M. LUPTON — Institut für Experimentelle und Angewandte Physik, Universität Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany

In organic light emitting diodes (OLEDs), injected charge carriers can undergo thermal relaxation processes. At low temperatures and high magnetic fields, where the Zeeman energy is comparable with the thermal energy, spin polarization can have a remarkable impact on the spin statistics of the electron-hole recombination process, which is monitored directly by electroluminescence. Here, we sensitize an organic semiconductor with a metal-free phenazine derivative which exhibits simultaneous fluorescence and phosphorescence. This approach allows us to study the impact of spin polarization on spin statistics directly through the ratio of fluorescence and phosphorescence, i.e. in an all-optical manner. Thermal spin polarization leads to an increase in phosphorescence with a concomitant decrease in fluorescence. Besides providing insight into carrier thermalization processes, the approach also offers a route to probing the effect of spin-orbit coupling on spin statistics.

CPP 71.6 Thu 16:15 C 243

Influencing and quantifying the intersystem crossing in biluminescent organic molecules by adding heavy atoms — ●FELIX FRIES¹, ANNA HAFT¹, RAMUNAS LYGAITIS², OLAF ZEIKA¹, and SEBASTIAN REINEKE¹ — ¹Dresden Integrated Center for Applied Physics and Photonic Materials, TU Dresden, Nöthnitzer Str. 61, 01187 Dresden — ²Kaunas University of Technology, K. Donelaičio g. 73, 44249 Kaunas

Organic molecules are able to show a broad variety of emission types. Fluorescence, phosphorescence or charge transfer (CT) state emissions have very different properties in energy and time regime. For one emitter, CT does not play a role and normally, those systems only show either fluorescence or phosphorescence. We name systems showing both fluorescence and phosphorescence at room temperature, biluminescent. An advantage of having experimentally access to both emission channels is that a very detailed description of the energetic behaviour of those molecules is possible. Here, we

focus on a series of molecules with different levels of bromination. Namely those molecules are, N,N,N',N'-tetraphenyl-[1,1'-biphenyl]-4,4'-diamine (TPB) and Br_xTPB, where $x = 1 \dots 4$. Extensive analysis of those molecules gives the luminescent lifetimes (\sim ns, \sim ms), their contribution to the quantum yield and allows to quantify the intersystem crossing rate as a function of the bromination. Furthermore, the experimental results can be compared to numerical simulations like a line shape analysis of the radiative transitions, allowing deeper understanding of the influences of the heavy atom effect on the molecules' energetic landscape.

15 min. break

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Photoswitchable Sn-Cyt c Solid-State Devices — SATOSHI NAKAMARU², WILLIAM FORD¹, YOSHIO GOTO², and •FLORIAN VON WROCHEM¹ — ¹Sony Europe Ltd., Materials Science Laboratory, Hedelfinger Strasse 61, D-70327 Stuttgart, Germany — ²Advanced Materials Laboratories, Sony Corporation, Atsugi Technology Center No.2, 4-16-1 Okata, Atsugi, Kanagawa, 243-0021, Japan

Electron transfer across proteins plays an important role in many biological processes, including those relevant for the conversion of solar photons to chemical energy. Previous studies demonstrated the generation of photocurrents upon light irradiation in a number of photoactive proteins, such as photosystem I or bacteriorhodopsin. Here, we show that Sn-cyt c layers act as reversible and highly efficient photoelectrochemical switches upon integration into large area solid state junctions. Photocurrents are observed both in the Soret-band ($\lambda = 405$ nm) and in the Q-band ($\lambda = 535$ nm), with current on/off ratios reaching values of up to 25. The underlying modulation in charge transfer rate is attributed to a hole-transport channel, created by the photoexcitation of the Sn-porphyrin.

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Conical intersection dynamics mediating coherent ultrafast singlet fission — •HONG-GUANG DUAN^{1,2,3}, AJAY JHA¹, VANDANA TIWARI¹, PABITRA NAYAK⁴, ZHENG LI¹, MICHAEL THORWART^{2,3}, and R. J. DWAYNE MILLER^{1,3,5} — ¹MPSD, Hamburg, Germany — ²IL Institut für Theoretische Physik, UH, Germany — ³CUI, Hamburg, Germany — ⁴University of Oxford, UK — ⁵University of Toronto, Canada

Carrier multiplication in organic semiconductors by singlet fission holds the key to break the Shockley-Queisser limit. Primary step of singlet fission process is a spin-allowed transition of a singlet exciton to a doubly excited pair of spin-correlated triplets. Consequently, two triplets are formed after the spin decoherence. Despite enormous studies, the mechanism of the primary step is still unclear. Here, we use transient grating spectroscopy to probe the vibrational dynamics of singlet fission process in pentacene thin films. Our observations guide us to propose the existence of the conical intersection mediating singlet state and spin-correlated triplet pair transition. The interplay of vibrational modes mediating this transition will be discussed.

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Excited States Dynamics in TIPS-Pentacene Studied with Femtosecond Time-Resolved Second Harmonic Generation — •VIPILAN SIVANESAN¹, SILKE KOSER², UWE BUNZ², and PETRA TEGEDER¹ — ¹Universität Heidelberg, Physikalisch-Chemisches Institut — ²Universität Heidelberg, Organisch-Chemisches Institut

Understanding the ultrafast excited state dynamics in organic semiconductors after optical excitation is a key requisite on the road towards the design of efficient organic solar cells (OPV). Recently, the singlet fission process has gained much attention since it may improve the energy conversion efficiency in OPVs. In this work we moni-

tored the ultrafast (sub-picosecond) excited states dynamics in TIPS-Pentacene (TIPS-Pn) using time-resolved second harmonic generation (TR-SHG). Sapphire was used as non-interacting substrate to analyse the dynamics of excitonic species in TIPS-Pn films. Thereby the dynamics of singlet fission process could be resolved. The process consists of the generation of singlet excitons localized on a single molecule followed by the fission into two triplet excitons on two TIPS-Pn molecules. While the overall singlet fission process occurred within 200fs, we could also resolve the transfer from the singlet exciton state to the mediating multiexciton state.

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Direct observation of double hydrogen transfer via quantum tunneling in a single porphycene molecule on Ag(110) — •MATTHIAS KOCH¹, MARK PAGAN², MATS PERSSON², SYLWESTER GAWINKOWSKI³, JACEK WALUK^{3,4}, and TAKASHI KUMAGAI¹ — ¹Fritz-Haber-Institut — ²University of Liverpool — ³Polish Academy of Sciences — ⁴Cardinal Stefan Wyszyński University

Quantum tunneling of hydrogen atoms plays a crucial role in many chemical and biological reactions. Although tunneling of a single particle has been studied extensively in one-dimensional potentials, many-particle tunneling in high-dimensional potential energy surface remains poorly understood. Recently tautomerization of a single molecules was observed in LT-STM experiments [1, 2]. Here we present a direct observation of double hydrogen atom transfer within a single porphycene molecule on Ag(110) using a low temperature STM [3]. We find that below ~ 10 K the tautomerization rate is temperature-independent and a large kinetic isotope effect (KIE) was observed upon substituting the hydrogen atoms by deuterium. Inelastic electron tunneling increases the tautomerization rate by a vibrational excitation. The observed KIE for three isotopologues and density functional theory calculations indicate that a stepwise transfer mechanism is dominant in the tautomerization. This is also in agreement with the observed third state in our time dependent tip height traces.

[1] L. J. Lauhon et al. Phys. Rev. Lett. 85, 4566 (2000)

[2] T. Kumagai et al. Phys. Rev. Lett. 100, 166101 (2008)

[3] M. Koch et al. J. Am. Chem. Soc. 139 (36), 12681 (2017)

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Nonlinear optical response of chromophores from real-time time-dependent DFT — •CATERINA COCCHI¹, STEFANO PITTALIS², and CARLO A. ROZZI² — ¹Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany — ²CNR Istituto Nanoscienze, Modena, Italy

The impulsive excitation scheme for time propagation in time-dependent density-functional theory [1] can be efficiently adopted to study the optical response also beyond the linear regime, mimicking a broadband laser beam illuminating the sample. We demonstrate the potential of this approach by investigating the nonlinear optical response of carbon-conjugated chromophores, e.g., phthalocyanines and thiophenes, that absorb visible light of specific frequencies while being transparent to others. At increasing intensity of the applied field, the sharp peak giving the absorption edge in the linear regime loses weight, while the oscillator strength concomitantly grows in the transparent windows. We clarify that this behavior, related to a third-order nonlinearity, is driven by reverse saturable absorption and is responsible for optical limiting in these compounds [2]. Upon strong incoming fields, incrementally populated dipole- and/or spin-forbidden excitations enhance the absorption in their frequency range while allowed transitions in the linear regime are partially quenched. Our results contribute to the understanding of the fundamental physical mechanisms behind nonlinear light absorption of chromophores.

[1] K. Yabana and G. F. Bertsch, PRB 54, 4484 (1996). [2] C. Cocchi et al., PRL 112, 198303 (2014).