

CPP 57: Organic Electronics and Photovoltaics IV - Excitonic Properties and Light-Emitting Devices

Time: Thursday 15:00–18:15

Location: H18

CPP 57.1 Thu 15:00 H18

Optical Probing of the Various Operation Regimes in Organic Light-Emitting Diodes Using Molecular Probes — ●THOMAS FERSCHKE¹, ALEXANDER HOFMANN², WOLFGANG BRÜTTING², and JENS PFLAUM^{1,3} — ¹Experimental Physics VI, Julius Maximilian University, 97074 Würzburg — ²Institute of Physics, University of Augsburg, 86135 Augsburg — ³ZAE Bayern, 97074 Würzburg

Photoluminescence (PL) studies on single guest molecules have been shown to enable determination of charge carrier distribution in organic opto-electronic devices on nanometer length scales.[1] In this work, this principle is adapted to the various operation regimes of Alq₃/α-NPD OLEDs. Tetraphenyl-dibenzoperiflanthene (DBP) dopants are incorporated at distinct vertical positions within the active layers of the OLED stack. Measuring the DBP optical properties under different operation conditions of the device, the significant reduction in PL upon charge carrier injection (forward bias regime) can be attributed to non-radiative decay channels promoted by the exciton-electron interaction. Studying this effect as function of current density and dopant position reveals information on the local charge carrier distribution. Under reverse bias, a strong PL quenching of DBP probes in close proximity to the Alq₃/α-NPD interface is observed as well. This can be related to the strong electric fields caused by Alq₃ charges localized at the interface.[2] We substantiate this hypothesis by complementary data obtained by impedance spectroscopy on the identical OLED devices.

[1] Nothaft *et al.*, *ChemPhysChem*, **2011**, 12, 2590–2595

[2] Noguchi *et al.*, *J. Appl. Phys.*, **2012**, 111(11):114508

CPP 57.2 Thu 15:15 H18

Temperature (De-)Activation in Donor-Acceptor based Organic Light Emitting Diodes — ●SEBASTIAN WEISSENSEEL, FELIX KLINGERT, JEANNINE GRÜNE, NIKOLAI BUNZMANN, ANDREAS SPERLICH, and VLADIMIR DYAKONOV — Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg

The world of organic light emitting diodes (OLEDs) regained a lot of attention with the publication of Goushi *et al.* in 2012 [1], where the thermal activation of non-radiative triplets via reverse intersystem crossing (RISC) was applied to enhance the fluorescence in OLEDs for the first time. Here, we investigate the donor-acceptor based system 4,4',4''-Tris(N-3-methylphenyl-N-phenylamino)triphenylamine (m-MTDATA): Tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB), which exhibits an intermolecular TADF mechanism. The devices are analyzed by means of temperature dependent current-electroluminescence-voltage (j-EL-V) characteristics and external quantum efficiency (EQE). These measurements were intended to estimate the activation energy of the triplet-to-singlet upconversion and thus the singlet-triplet gap. Surprisingly, we observe typical TADF-like efficiency enhancement with rising temperature only in a limited temperature range 180-250K, while at higher temperature (>250K), this trend inverts and we observe a decrease in EQE. This observation implies the competing process between thermally activated RISC and a non-radiative decay at ambient temperature in TADF OLEDs, which is essential for their further improvement.

[1] Goushi, *et al.*, *Nat. Photon.* **6**, 253 (2012)

CPP 57.3 Thu 15:30 H18

Time-resolved Spectroscopy of Organic Light Emitting Diodes based on Thermally Activated Delayed Fluorescence — ●JEANNINE GRÜNE, NIKOLAI BUNZMANN, SEBASTIAN WEISSENSEEL, VLADIMIR DYAKONOV, and ANDREAS SPERLICH — Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg

Organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) show increased efficiencies due to efficient upconversion from the non-emissive triplet states to the emissive singlet state via reverse intersystem crossing (RISC). Therefore a small energetic splitting between singlet and triplet states is required which can be achieved by formation of an exciplex state, a weakly bound electron-hole pair at a donor:acceptor interface. A proven material combination is among others 4,4',4''-Tris[(3-methylphenyl)phenylamino]triphenylamine (m-MTDATA), as donor and Tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB), as

acceptor. We investigated this system with time-resolved electroluminescence (trEL) in combination with time-resolved magnetic resonance techniques based on EL and photoluminescence detection (trELDMR, trPLDMR). In the latter case, microwave irradiation is used to induce transitions between the triplet states which are split in a present magnetic field. By applying microwave pulses over several microseconds, the spin-dependent EL modulation processes as well as the corresponding time frames can be identified, to get a better understanding of the triplet contribution to the TADF mechanism.

CPP 57.4 Thu 15:45 H18

A refined setup for an enhanced signal-to-noise ratio in angular resolved photoluminescence measurements — ●CHRISTIAN HÄNISCH, SIMONE LENK, and SEBASTIAN REINEKE — Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP), Technische Universität Dresden, 01187 Dresden, Germany

Controlling the orientation distribution of transition dipole moments in the emission layer of organic light-emitting diodes is one of the key approaches for further enhancements of the device efficiencies. In order to investigate this physical parameter typically angular resolved photoluminescence measurements are performed.

In this contribution, we present an advanced concept which adds two plano-convex lenses to the conventional measurement setup in order to collect and focus the initially emitted light to the detector fiber. In this manner, the signal-to-noise ratio of the recorded emission spectra can be drastically improved, which enables measurements of weakly emitting or fast degrading material systems.

A detailed ray transfer analysis is performed, which on the one hand reveals the required parameters of the optical components and on the other hand allows for a detailed evaluation and optimization of the setup alignment.

CPP 57.5 Thu 16:00 H18

Kinetic Modelling of Transient Photoluminescence from Thermally Activated Delayed Fluorescence — ●NILS HAASE^{1,2}, ANDREW DANOS³, CHRISTOF PFLUMM², ANTONIA MORHERR², PATRYCJA STACHELEK³, AMEL MEKIC^{2,4}, WOLFGANG BRÜTTING¹, and ANDREW P. MONKMAN³ — ¹University of Augsburg, Augsburg, Germany — ²Merck KGaA, Darmstadt, Germany — ³Durham University, Durham, UK — ⁴University of Regensburg, Regensburg, Germany

Thermally activated delayed fluorescence (TADF) is an established mechanism for harvesting triplet excitons in *metal-free* OLEDs [1] which gives a maximum attainable internal quantum efficiency of 100%. By minimizing the energy gap between the lowest lying singlet and triplet states, a conversion of slowly relaxing triplet states to faster relaxing singlet states via reverse intersystem crossing rate (rISC) is promoted. Although several highly efficient TADF emitters have been discovered, a reliable determination of the reverse intersystem crossing rate as a key parameter for the characterization of TADFs has not been provided yet. In this work, we present a kinetic model for the TADF process which allows to extract not only rate constants but also time dependent state populations from transient photoluminescence experiments. Using this model, we obtain temperature dependent rISC rates from which we calculate the activation energy for the TADF process. [1] Uoyama *et al.*, *Nature* **492** (2012), 234*238.

CPP 57.6 Thu 16:15 H18

Detecting magnetic resonance in Earth's magnetic field — ●SEBASTIAN MILSTER, TOBIAS GRÜNBAUM, SIMON KURRMANN, HERMANN KRAUS, SEBASTIAN BANGE, and JOHN M. LUPTON — Universität Regensburg, Institut für Experimentelle und Angewandte Physik, Universitätsstraße 31, 93053 Regensburg, Germany

Electron paramagnetic resonance in OLEDs [1] at magnetic field strengths comparable to Earth's field offers a way to model the migratory orientation ability of some birds [2] to a certain extent in a laboratory setting.

With the expected resonance position at a field of approximately 44 microtesla for a frequency of 1.315 MHz [3], even small stray fields as well as Earth's magnetic field have a rather large effect and create a shift on the magnetic field axis, depending on their orientation to the external applied field. As a consequence, the expected resonance

peaks partially overlap with other effects in the device, thus becoming almost unresolvable. By compensating all parasitic fields with a three-dimensional arrangement of Helmholtz coils, it is possible to nullify the shifting effects. Following this, the resonances become resolvable for frequencies even in the low MHz-regime. By optimizing the experimental parameters preliminary results are presented, showing EPR at a frequency of 1.315 MHz, in resonance with the Zeeman splitting induced by Earth's field.

- [1] H. Kraus et al., Phys. Rev. B 95, 241201(R)(2017)
 [2] W. Wiltschko et al., Science 176, 71-77 (1972)
 [3] W. Baker et al., Nat. Commun. 3, 898 (2012)

15 min. break

CPP 57.7 Thu 16:45 H18

Spectroscopic study of a novel iron based charge-transfer complex — ●NILS W. ROSEMANN¹, KASPER SKOV KJAER¹, NIDHI KAAUL², OM PRAKASH³, PAVEL CHÁBERA¹, ALIREZA HONARFAR¹, OLGA GORDIVSKA³, LISA A. FREDIN⁴, KARL-ERIK BERGQUIST³, LENNART HÄGGSTRÖM⁵, TORE ERICSSON⁵, LINNEA LINDH¹, ARKADY YARTSEV¹, STENBJÖRN STYRING², PING HUANG², JENS UHLIG¹, JESPER BENDIX⁶, DANIEL STRAND³, VILLY SUNDSTRÖM¹, PETER PERSSON⁴, REINER LOMOTH², and KENNETH WÄRNMARK³ — ¹Division of Chemical Physics, Department of Chemistry, Lund University, Sweden — ²Department of Chemistry - Ångström Laboratory, Uppsala University, Sweden — ³Center for Analysis and Synthesis, Department of Chemistry, Lund University, Sweden — ⁴Division of Theoretical Chemistry, Department of Chemistry, Lund University, Sweden — ⁵Department of Physics and Astronomy - Ångström Laboratory, Uppsala University, Sweden — ⁶Department of Chemistry, University of Copenhagen, Denmark

Complex molecules based on transition metals are used in solar light harvesting, e.g., dye-sensitized solar cells and photocatalysis. Standard complexes are based on scarce metals like ruthenium. This calls for replacements based on abundant metals like, e.g., Iron (Fe). Here, we present our latest results on a Fe-based complex. By coordination of two tris-carbene ligands to the Fe centre in an octahedral geometry the deactivation through metal centred states is drastically suppressed. Thus, unmatched 2 ns room temperature excited state lifetime and 2% photoluminescence quantum yield are achieved.

CPP 57.8 Thu 17:00 H18

Coherent dynamics of ultrafast singlet fission in Pentacene — ●AJAY JHA¹, HONG-GUANG DUAN^{1,2,3}, XIN LI⁴, VANDANA TIWARI¹, HANYANG YE⁵, PABITRA NAYAK⁵, XIAO-LEI ZHU⁴, ZHENG LI¹, TODD MARTINEZ⁴, MICHAEL THORWART^{2,3}, and R. J. DWAYNE MILLER^{1,3,6} — ¹MPSD, Hamburg, Germany — ²I. Institut für Theoretische Physik, UH, Germany — ³CUI, Hamburg, Germany — ⁴Stanford University, US — ⁵University of Oxford, UK — ⁶University of Toronto, Canada

Singlet fission is one of the possible ways to circumvent the Shockley-Queisser limit on efficiency. Pentacene and its derivatives have shown great promise towards their application in devices to harness photons for carrier multiplication via singlet fission process. Here we study the singlet fission process in a pentacene thin film using a combination of transient-grating and two-dimensional electronic spectroscopy complemented by quantum chemical and nonadiabatic dynamics calculations. Our study reveals that along with the high-frequency vibrations, intermolecular rocking motions drive the ultrafast dynamics at the multidimensional conical intersection in the singlet fission process.

CPP 57.9 Thu 17:15 H18

Molecular Structure and Geometry Packing Effects on Singlet Fission Mechanism — ●N. ALAGNA¹, J. HAN², N. WOLLSCHIED¹, J.L. PEREZ LUSTRES¹, J. HERZ¹, S. HAHN³, S. KOSER³, F. PAULUS³, U. BUNZ³, A. DREUW², T. BUCKUP¹, and M. MOTZKUS¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ²Institut für Wissenschaftliches Rechnen, Ruprecht-Karls Universität Heidelberg — ³Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg

Efficiency limit of organic photovoltaic can be overcome by singlet fission (SF), a photo induced processes where two triplet states are formed from an excited singlet state. Molecular structure and packing arrangement are critical for SF. In this work, quantum chemistry, organic synthesis and time resolved spectroscopy are applied to rationalize how SF is effected by systematic chemical modification intro-

duced in phenazinothiadiazoles (PTD). Substitution of an aromatic ring of TIPS-Tetracene by a thiadiazole group change in a considerable way the relative energy of S1 and T1 states. In contrast with TIPS-tetracene, SF became exothermic for PTD derivatives, which show an energy difference S1-2T1 higher of 0.44 eV. This enables SF in PTD derivatives, where the fs formation of the T-T state is identified by transient absorption spectroscopy and TD-DFT calculation. Moreover, we show via CDFT-CL calculations that dimer architecture control the strength and coaction between direct and superexchange couplings, that accelerate the SF rate constant beyond 100 fs.

CPP 57.10 Thu 17:30 H18

Investigating diffusion controlled singlet fission of a chlorinated phenazinothiadiazole. — ●NIKOLAUS WOLLSCHIED^{1,3}, NICOLA ALAGNA¹, JOSÉ LUIS PEREZ LUSTRES^{1,3}, VICTOR BROSIUS², FLORIAN GEYER², UWE BUNZ^{2,3}, TIAGO BUCKUP¹, and MARCUS MOTZKUS^{1,3} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ²Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ³Centre for Advanced Materials, Ruprecht-Karls-Universität Heidelberg

Singlet fission (SF) is a carrier multiplication process where one excited singlet state yields two triplet states upon close interaction of two chromophores. This ultrafast photoreaction was first observed in solid state and has strong implications in organic photovoltaics. In order to disentangle the mechanism by extending the dynamics to longer timescales, concentrated solutions of TIPS-Tetracene were investigated. Here, the reaction is controlled by the diffusion of the reaction partners, which allowed for the isolation of the spectrum of an intermediate excimer state [1]. In this work, we use ultrafast transient absorption spectroscopy to investigate concentrated solutions of a chlorinated phenazinothiadiazole in toluene. The observation of a correlation between singlet decay and triplet formation, combined with the linear dependence of the corresponding decay rate on concentration, indicates diffusion controlled SF. For high concentrations, spectral analysis suggests direct and efficient SF, whereas an additional process is observed for low concentrations.

- [1] H. L. Stern et al., PNAS, 112, 7656 (2015).

CPP 57.11 Thu 17:45 H18

Homocoupling defects limit exciton diffusion in a conjugated polymer — ●MARTIN STREITER¹, FABIAN MEIER¹, DANIEL BEER¹, CAROLINE LIENERT², FLORIAN LOMBECK², MICHAEL SOMMER², and CARSTEN DEIBEL¹ — ¹Institut für Physik, Technische Universität Chemnitz, 09126 Chemnitz, Germany — ²Institut für Makromolekulare Chemie, Universität Freiburg, 79104 Freiburg, Germany

Exciton diffusion has been studied in a range of conjugated polymers. It is both, of fundamental interest and an important step relevant for high performance organic solar cells. Copolymers such as PCDTBT are commonly employed as donor material in bulk heterojunction solar cells. Recently, chemical defects such as homocouplings have been shown to form at the material synthesis stage, severely limiting the short circuit current of organic photovoltaics. Here we show that indeed carbazole homocoupling limits exciton diffusion in PCDTBT. We propose a mechanism that explains the limitation of exciton diffusion caused by high homocoupling concentrations and short chain lengths. Diffusion is limited when either chain length or homocouplings impair the effective conjugation length of the polymer chain.

CPP 57.12 Thu 18:00 H18

Correlated Atomic Force Microscopy and Spatially-resolved Photoluminescence Spectroscopy Study of Merocyanine Aggregate Thin Films — ●LUKAS BÖHNER, THORSTEN LIMBÖCK, DIRK HERTEL, KLAS LINDFORS, and KLAUS MEERHOLZ — University of Cologne, Köln

Merocyanine molecules are interesting materials for organic solar cells (OSCs) due to their high absorption coefficients [1]. Large area OSCs can be produced at low cost. However, the in this way resulting disordered structure of the active material in OSCs is disadvantageous in terms of exciton- and charge mobility. One strategy to increase order in organic materials is the utilization of molecular aggregates wherein excitons are delocalized. Additionally aggregation of organic dye molecules leads to drastic changes of the optical properties compared to the monomeric form [2]. Here, we study thin films of merocyanine molecular aggregates fabricated by vacuum deposition. The morphology of the films is varied by using different substrates and controlling the deposition parameters. Combining atomic force microscopy and photoluminescence microspectroscopy we are able to correlate the

structural and optical properties of the aggregates. We find that by suitable choice of the fabrication parameters, thin films consisting of crystalline domains which scale in the range of tens of micrometers can be obtained. We will present the impact of molecular order on exciton

and charge transport properties. References: [1] H. Bürckstümmer, et al., *Angew. Chemie - Int. Ed.* 2011, 50, 11628-11632. [2] A. Liess, et al., *Adv. Funct. Mater.* 2018, 1805058, 1-9.