

CPP 32: Focus: Triplet States in Organic Optoelectronics I

Organizers: Wolfgang Brütting (Universität Augsburg), Anna Köhler (Universität Bayreuth), Sebastian Reineke (Technische Universität Dresden)

The spin of Coulombically bound electron-hole pairs or excitons is of paramount importance for the functioning of organic optoelectronic devices. In particular, triplet states play an important role as radiative and non-radiative intermediates in organic light-emitting diodes and solar cells. This focus session addresses topical questions and recent progress in understanding the role of triplets in this field.

Time: Wednesday 9:30–12:45

Location: H37

Invited Talk

CPP 32.1 Wed 9:30 H37
Towards 100% efficient OLEDs using thermally activated delayed fluorescence; how does the spin conversion work — ●ANDREW MONKMAN¹, MARC ETHERINGTON¹, PAUL KLEIN^{1,2}, DAVID GRAVES¹, PRZEMYSŁAW DATA¹, PALOMA DOS SANTOS LAYS¹, ROBERTO NOBUYASU¹, YOUHEI TACKED³, and FERNANDO DIAS¹ — ¹Durham University, Durham, England — ²Technical University, Dresden, Germany — ³Osaka University, Osaka, Japan

Detailed photophysical measurements of intramolecular charge transfer (ICT) states have been made both in solution and solid state. Temperature dependent time resolved emission, delayed emission and photoinduced absorption are used to map the energy levels involved in molecule decay, and through detailed kinetic modelling of the thermally activated processes observed, true electron exchange energies and other energy barriers of the systems determined with the real states involved in the reversed intersystem crossing mechanism elucidated.

For specific donor acceptor molecules, the CT singlet and local triplet states (of donor or acceptor) are found to be the lowest lying excited states of the molecule with very small energy barrier between them. In these cases the decay kinetics of the molecules become significantly different to normal molecules, and the effect of rapid recycling between CT singlet and local triplet states is observed which gives rise to the true triplet harvesting mechanism in TADF. Using a series of different TADF emitters we will show how the energy level ordering effects or does not effect TADF and how ultimate OLED performance is dictated by energy level ordering, from 5% to 22% EQE

CPP 32.2 Wed 10:00 H37
Thermally activated delayed fluorescence – A new route to more efficient OLEDs? — ●REINHARD SCHOLZ¹, RAMUNAS LYGAITIS^{1,2}, PAUL KLEINE¹, LUDWIG POPP¹, FLORIAN WÜST¹, SIMONE LENK¹, and SEBASTIAN REINEKE¹ — ¹Institut für Angewandte Photophysik, Technische Universität Dresden, Germany — ²Department of Organic Technology, Kaunas University of Technology, Lithuania

In molecules with small splitting between the lowest excited singlet and triplet states, reverse intersystem crossing (RISC) from the triplet to the singlet requires only a small activation energy, resulting in thermally activated delayed fluorescence (TADF). Donor-acceptor compounds with large dihedral angle between these subgroups allow for rather low singlet-triplet splitting $\Delta_{ST} = E(S_1 \rightarrow S_0) - E(T_1 \rightarrow S_0)$ between the observed fluorescence and phosphorescence transitions, at the price of a reduced transition dipole and slow radiative recombination rate. The present contribution investigates radiative recombination from thermal distributions in the excited potential surfaces S_n of TADF emitters with time-dependent density functional theory. On this basis, we suggest possible synthesis strategies for blue TADF emitters and report on selected compounds compromising between different desirable properties. The resulting OLEDs show external quantum efficiencies (EQE) between typical fluorescent and phosphorescent emitters, paving the way towards applications of white OLEDs to more efficient lighting.

CPP 32.3 Wed 10:15 H37
Biluminescence of purely organic semiconductors — ●CATERIN SALAS REDONDO, SIMONE LENK, and SEBASTIAN REINEKE — Institut für Angewandte Photophysik, TU Dresden, Dresden, Germany

Biluminescence is a property of certain organic molecules, where light is emitted from both their singlet (named fluorescence) and triplet (named phosphorescence) excited states. Although the latter is a quantum mechanically forbidden transition, phosphorescence can be achieved if non-radiative channels are suppressed effectively. For instance, creating a simple host:guest system in which a biluminophore

(i.e. materials with biluminescence property) is embedded in an optimum rigid matrix (e.g. polymers, small molecules), competitive thermal decay is suppressed, allowing emission from the triplet states in addition to the conventional fluorescence at room temperature. Not only the dual state emission is unique to this class of materials, but also the exciton dynamic range spanned by the two spin states is extreme, going from nanosecond-lifetime fluorescence up to second-lifetime phosphorescence.

In this presentation, we will report on our recent advances in different biluminescent systems. For example, we have identified a combination of PMMA[poly(methyl methacrylate)] as host and NPB[N,N-di(naphtha-1-yl)-N,N-diphenyl-benzidine] as biluminophore, giving rise to blue fluorescence and green phosphorescence. Additionally, we will report on the structure-property relationships between the host materials used and the resulting phosphorescence luminescence efficiency as well as the dependence of the persistent phosphorescence to oxygen.

CPP 32.4 Wed 10:30 H37
Understanding and predicting the orientation of heteroleptic phosphors in organic light-emitting diodes — ●TOBIAS D. SCHMIDT¹, MATTHEW J. JUROW², CHRISTIAN MAYR¹, THOMAS LAMPE¹, PETER I. DJUROVICH², MARK E. THOMPSON², and WOLFGANG BRÜTTING¹ — ¹Institute of Physics, University of Augsburg, 86135 Augsburg, Germany — ²Department of Chemistry, University of Southern California, 90089 Los Angeles, USA

Horizontal orientation of dye molecules, i.e. their transition dipole vectors (TDV), is a powerful feature improving the efficiency of organic light-emitting diodes. In order to understand the underlying mechanisms for emitter orientation of heteroleptic phosphors, we compared the anisotropy factor of emissive guest/host systems using different Ir-complexes incorporating coumarin and phenylpyridin based ligands. These molecules exhibit similar high permanent dipole moments and electrostatic surface potentials but differ in the molecular structure. Interestingly, only molecules with aromatic and aliphatic ligands show non-isotropic distributions of their TDVs when co-deposited with a matrix material by thermal evaporation. From these findings we conclude that molecular orientation of heteroleptic Ir-complexes occurs instantaneously at the surface of the growing film and is driven by chemical interactions with the surrounding media. Furthermore, it was possible to predict the anisotropy factor for arbitrary molecular orientation with a mathematical model taking into account the geometrical distribution of the TDV on the molecules.¹

[1] M. Jurow *et al.*, Nature Materials (2015), doi:10.1038/nmat4428

CPP 32.5 Wed 10:45 H37
Optical detection of spin states with dual singlet-triplet emitters in OLEDs — ●WOLFRAM RATZKE¹, LISA SCHMITT², PHILIPPE KLEMM¹, SEBASTIAN BANGE¹, SIGURD HÖGER², and JOHN LUPTON¹ — ¹University Regensburg — ²University Bonn

Doping OLEDs with dual emitters which exhibit simultaneous fluorescence and phosphorescence gives unique insight into spin statistics and dynamics. But bringing dipole forbidden triplets to light without perturbing the excited state of the organic semiconductor of interest and also conserving spin information requires a novel class of emitters. Typical phosphorescent molecules like heavy atom containing metalorganic complexes perturb their vicinity by the external heavy atom effect and destroy spin-coherence. Enhancing spin-orbit coupling by decreasing the singlet-triplet gap as exploited for TADF emitters is of limited utility for optical spin detection since singlet and triplet emission are hardly spectrally distinguishable and enhanced reversed intersystem crossing prevents spin-state preservation. Activating phosphorescence which is spectrally clearly shifted from singlet emission while preserving the spin state requires a more subtle principle. Here,

we present metal-free dual emitters with well separated singlet and triplet emission. This separation enables the simultaneous investigation of singlet and triplet decay channels. The emitters can be used as sensing molecules giving a direct reading of the spin states. Changes in spin statistics by external manipulations, i.e. magnetic fields, can be optically detected.

15 min. break

Invited Talk

CPP 32.6 Wed 11:15 H37

Effects of charge and exciton diffusion on triplet-polaron quenching and triplet-triplet annihilation in disordered organic semiconductors — ●REINDER COEHOORN¹, HARM VAN EERSEL², LE ZHANG¹, PETER BOBBERT¹, and RENE JANSSEN¹ — ¹Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513 — ²Simbeyond B.V., Den Dolech 2, 5612 AZ Eindhoven, The Netherlands

Triplet-polaron quenching (TPQ) and triplet-triplet annihilation (TTA) contribute to the efficiency roll-off in organic light-emitting diodes (OLEDs). In fluorescent OLEDs, TTA can also be beneficial, giving rise to partial triplet harvesting, which manifests itself as delayed fluorescence. Conventionally, TTA and TPQ are viewed as bimolecular processes with a rate coefficient which depends on the local density of all species involved, and on their diffusivity. Often, the rate coefficient is expressed in terms of an effective capture radius. We show from kinetic Monte Carlo simulations that in actual OLEDs strong deviations can occur from this picture. Firstly, the effective exciton or charge diffusion coefficient can be strongly time dependent. Secondly, the percolative nature of the charge or exciton diffusion gives rise to a highly non-trivial dye concentration dependence. For the case of TTA, results of an experimental study are presented which provide a test of a novel method [1] for quantifying the role of exciton diffusion. [1] H. van Eersel et al., *J. Appl. Phys.* 117, 115502 (2015).

CPP 32.7 Wed 11:45 H37

Electron-hole-pair magnetoresistance and magnetoelectroluminescence in OLEDs — ●HERMANN KRAUS¹, SEBASTIAN BANGE¹, ULLRICH SCHERF², and JOHN M. LUPTON¹ — ¹Universität Regensburg, 93053 Regensburg, Germany — ²Bergische Universität Wuppertal, 42119 Wuppertal, Germany

Large magnetoresistance effects which arise, for example, due to spin-dependent recombination rates are well-known for OLEDs, although models are still under debate given that they remain hard to verify from a measurement of integrated current and luminance. Spin resonance of paramagnetic species enables direct manipulation of charge carrier and excitonic precursor spins, providing a wealth of new insight into dynamic spin properties.

Previous work on electrical or optical detection of spin manipulation misses out on the opportunity to directly observe the presence of triplet exciton species that are at the heart of spin-dependent recombination models. Fortunately, a few organic materials are now known to exhibit reasonable triplet emission without modification of the polaron pair and exciton dynamics by strong spin-orbit interaction. They are ideal candidates to directly track spin singlet and triplet excitonic species in OLEDs under conditions of magnetic resonance, by comparing the fluorescence (singlet) to phosphorescence (triplet) intensity. Phosphorescence increases under resonance while fluorescence is quenched. Additionally, the magnetoelectroluminescence of the OLED can be measured at the same time by sweeping the magnetic field to directly correlate resonant and static magnetic field effects.

CPP 32.8 Wed 12:00 H37

Using deposition technique to control phosphorescent emitter orientation in doped organic films — ●THOMAS LAMPE, TOBIAS D. SCHMIDT, and WOLFGANG BRÜTTING — Institute of Physics, University of Augsburg, 86135 Augsburg, Germany

Introducing an overall horizontal orientation of transition dipole moments of heteroleptic Ir-complexes is a promising concept to improve efficiencies of organic light-emitting diodes. To investigate the impact of deposition technique on molecular orientation, we prepared doped films of four different phosphorescent iridium complexes in various organic host materials both by thermal evaporation and by solution processing and compared the observed emitter orientation. All heteroleptic Ir-complexes show comparable horizontal alignment if fabricated from the gas phase, while isotropic orientation or even a slightly vertical trend is observed in the solution processed samples. These findings can be explained by the creation of an interface between vacuum and the aromatic host material during evaporation and the lack of this feature when processed from solution. The underlying mechanism of molecular orientation can then be explained by the interaction of aliphatic and aromatic parts of the Ir-complexes with this interface during deposition from the gas phase. The absence of horizontal orientation of the phosphors in layers deposited from liquid preparation techniques has important implications for solution processed OLEDs.

CPP 32.9 Wed 12:15 H37

Active heterostructure of crystalline thin-film surface anchored metal-organic frameworks for optoelectronic applications — ●MICHAEL OLDENBURG¹, IAN ARTHUR HOWARD^{1,2}, ANDREY TURSHATOV¹, NICOLÒ BARONI¹, STEPHANIE WOLLGARTEN¹, ENGELBERT REDEL³, CHRISTOF WÖLL³, and BRYCE SYDNEY RICHARDS^{1,2} — ¹Institute of Microstructure Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany — ²Light Technology Institute, Engesserstrasse 13, 76131 Karlsruhe, Germany — ³Institute of Functional Interfaces, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Using surface anchored metal-organic framework (SURMOF) we could create a new kind of heterojunction. The process of triplet-triplet annihilation allowed us to track the triplets optically across the interface of the heterojunction. We are confident that this fundamental demonstration of selective transport over a SURMOF/SURMOF heterojunction will motivate further work in developing spray-on heterojunctions within the highly tunable SURMOF family that will have a wide variety of optoelectronic applications

CPP 32.10 Wed 12:30 H37

Recombination spectroscopy of organic solar cells by EDMR — MICHAEL ECKARDT^{1,2}, RENÉ WIECZOREK^{1,2}, FRÉDÉRIC LAQUAI³, and ●WOLFGANG HARNEIT^{1,2} — ¹Institut für Physikalische Chemie, JGU Mainz — ²Fachbereich Physik, Universität Osnabrück — ³KAUST, Saudi Arabia

Electrically Detected Magnetic Resonance (EDMR) is used to unravel different charge carrier recombination processes in P3HT:PCBM bulk heterojunction solar cells. Specifically, the dependence of the EDMR signal due to mobile P3HT polarons on electrical bias and illumination is correlated quantitatively to both, photo- and dark current of the cell. At moderate forward bias and all the way to reverse bias, solar cell operation and EDMR are dominated by recombination of photo-generated carriers. Near open circuit, injected charges accumulate near the electrodes, leading to additional recombination that depends strongly on details of fabrication and aging. EDMR allows quantifying this loss channel, which influences fill factor and maximum extractable power, with high precision.