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Direct Observation of Spin States involved in Organic Electroluminescence Based on Thermally Activated Delayed Fluorescence

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Organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) have high potential for economical and sustainable lighting applications. The efficiency of the TADF pathway is only partially governed by the spin statistics of injected electrons and holes, in which the intermediate exciplex state at the interface of two molecules is formed in the emissive singlet spin configuration with a probability of 25% ^{1,2,3}. Rather, if the energetic separation between the singlet- and triplet exciplex spin configurations ΔE_{ST} is in the range of thermal energy, an efficient reverse intersystem crossing (RISC) from triplet- to singlet state may take place ^{3,4,5,6}. In this study, we report the first application of electroluminescence detected electron spin resonance (ELDMR) technique and indubitably proof the involvement of spins in the emergence of TADF electroluminescence. Temperature dependent studies of bilayer devices revealed that such spin-dependent process of light emission is truly thermally activated in two different material systems with an energetic separation of the singlet and triplet exciplex state to be $\Delta E_{ST} = (20.5 \pm 1.2)$ meV for THCA:Bphen and $\Delta E_{ST} = (58.2 \pm 4.5)$ meV for MTDATA:BPhen, respectively.

In OLEDs, the spins of injected charge carriers are generally uncorrelated. Prior to recombination, electrons and holes form an intermediate state with a ratio between singlet- and triplet spin configuration of 1:3. Assuming this simple statistics is correct ^{7,8,9}, the internal quantum efficiency of OLEDs based on fluorescence is limited to 25% ^{1,2,3}, as only the singlet state recombines radiatively to the ground state. Hence, the radiative efficiency can be increased if the triplet energy is used as well, i.e. by converting the triplet- to an emissive singlet state ^{1,2,10}. The most commonly used approach to access the triplet states are phosphorescent materials containing a heavy metal atom like iridium or platinum. The strongly increased inter system crossing (ISC) rate yields internal efficiencies of emission as high as 100 % ². Recently, another mechanism which enables the up-conversion of non-radiative triplet- to radiative singlet states in fluorescent materials was introduced ^{3,4,5,6}. This mechanism is based on materials where the energy difference between the triplet- and the singlet state ΔE_{ST} is in the range of thermal energy at room temperature. The thermal up-conversion process results in delayed fluorescence, since the triplet state possesses a longer lifetime. Consequently, light emitting devices exploiting this mechanism are

referred to as thermally activated delayed fluorescence (TADF) OLEDs. An energetic scheme depicting the important involved processes is shown in Fig. 1a.

TADF occurs in inter-[6, 11](#) and intra-molecular material systems [3, 4, 12, 13, 14](#). In both cases, the wavefunction overlap of the two particles forming the emissive state defines the energetic difference between the singlet and triplet states ΔE_{ST} , to which the most dominant parameter is the distance between the participating charge carriers. If this is large enough, both spin configuration will be energetically nearly degenerate and can be interconverted by thermal energy and/or by spin-orbit or hyperfine interaction.

The reference donor-material for TADF is 4,4',4''-Tris[phenyl(*m*-tolyl)amino]triphenylamine (m-MTDATA), which can be combined with different acceptor molecules in order to obtain the pursued exciplex emission [3, 14](#). The donor material tri(9-hexylcarbazol-3-yl)amine (THCA) combined with different acceptors have recently also showed very promising properties in the development of white OLEDs^{[15, 16](#)}. Both material systems possess large external quantum efficiency values, rendering them highly attractive for lighting applications^{[3, 14, 15, 16](#)}.

Generally, the dependence of recombination processes on the spin states follows from the magnetic field effect (MFE) ^{[17](#)}. In TADF materials and devices, MFE on electroluminescence (MEL), photoluminescence (MPL) and photocurrent (MPC) were also reported^{[18, 19, 20, 21](#)}. Strong temperature dependence of MEL, MPL and MPC indicate a crucial role of the thermal activation in the generation of EL ^{[18, 21](#)}. As pointed out in ^{[18](#)}, however, it is difficult to distinguish between recombination pathways involving exciplex states formed at donor-acceptor interfaces and weakly bound polaron pairs formed otherwise, as both are magnetic field dependent. Moreover, the formation of (weakly) bound excited pair (or exciplex) states from injected charge carriers may depend on charge transport properties of device active layers, which are intrinsically temperature dependent, e.g. due to imbalanced mobilities. Hence, measuring the influence of a magnetic field on the EL at various temperatures is important, but alone does not allow to decipher the underlying spin-dependent recombination channel^{[22](#)}.

Here, we apply an electron paramagnetic resonance (EPR) based technique, where spin populations in the triplet spin-sublevels are altered directly by microwaves with a fixed frequency. When these are applied to the sample in addition to a static magnetic field the condition

$$h\nu_{mw} = g \mu_B B \Delta m_s$$

is fulfilled, only when the spin system is in resonance with the oscillating field. Accordingly, spin-flips will take place, equalizing the populations of triplet spin-sublevels. Here, h is the Planck constant, ν_{mw} the microwave frequency, g the g -factor of the system, μ_B the Bohr magneton, B the applied external static magnetic field, and m_s the magnetic quantum number. Since we are interested in studying the EL, the principal observable should be

the EL intensity itself under spin-resonance conditions. The measurement principle, referred to as ELDMR²³, is schematically shown in Fig. 1a. Important to note, EPR induced spin-flips in a triplet state can only influence the quantum yield of the emission from singlet states, if there is a magnetic interaction mixing triplet and singlet manifolds obeying the spin angular momentum conservation rules, e.g. via spin-orbit (ISC or reverse ISC, RISC), as schematically shown in Fig. 1a, or via much weaker hyperfine interaction (HFI).

Here, we demonstrate a strong effect of spin-flip transitions within triplet states on the intensity of electroluminescence originating from the singlet exciplex state. This unambiguously proves the direct involvement of triplet states in the radiative pathway of TADF OLEDs at ambient conditions. Moreover, temperature activated behavior clearly revealed the underlying TADF mechanism and allowed us to determine the singlet-triplet energy gap ΔE_{ST} for two different material systems.

First, we certified the formation of exciplexes in our devices by evaluating the emission originating from injected charge carriers. We fabricated OLEDs using THCA combined with 4,7-diphenyl-1,10-phenanthroline (Bphen) and compared them with m-MTDATA:BPhen ones. The respective molecular structures are shown in Fig. 1b. All devices discussed in this Letter were prepared in bilayer configuration, i.e. the two single components are processed subsequently, forming two stacked single layers, as schematically depicted in Fig. 1c. The electroluminescence in THCA-based devices shows a broad spectrum that peaks around 600 nm, as shown in Fig. 2a. In the same graph, the photoluminescence (PL) spectra of neat THCA and BPhen are shown, with peak maxima at 480 nm and 380 nm, respectively. Upon electrical injection, the emission of singlet excitons, clearly visible in the neat material PL, is strongly quenched in bilayer devices. Hence, the electroluminescence originates only from the emissive singlet exciplex state, formed at the donor-acceptor interface.

ELDMR measurements at room temperature revealed a remarkably strong spin resonant signal. For the material system THCA:BPhen, the electroluminescence is enhanced by ca. 1.3% (Fig. 2b), when the population of triplet sublevels corresponding to $\Delta m_s \pm 1$ is converted to the singlet exciplex state. In order to prove the TADF nature of the up-conversion mechanism, we monitored the ELDMR magnitude over a large range of temperatures. The respective spin resonance signals are shown as colored dots in Fig. 2b, which are fitted by Gaussians (black lines). The integrated values of the fits are presented in the Arrhenius plot, shown in Fig. 2c. The plot reveals activation energy of (20.7 ± 1.2) meV, which corresponds to a thermal energy of 240 K and is assigned to the energetic difference ΔE_{ST} between the singlet- and triplet exciplex states. We highlight that the first two points above 240 K were excluded from the fit which we justify by the fact that above this temperature, the RISC process should show less pronounced temperature dependency.

We further performed very similar magnetic resonance experiments, in which PL, rather than EL intensity was monitored. An additional, broader signal appeared which we assigned to bound triplet excitons either localized on THCA- or on BPhen-molecules, as shown in Fig. 2d. They may originate from primarily excited singlet excitons formed via ISC. This signal is superimposed to a “narrow” contribution from exciplex states, but fortunately can be separated from the latter due to their different temperature dependences. Finally, the excitonic triplet signal was completely missing when performing ELDMMR measurements. As a consequence, we exclude an involvement of excitonic triplet states in the thermally activated mixing of triplet- and singlet exciplex states. Subsequently, we performed the same set of measurements on the reference donor-material m-MTDATA, again in combination with BPhen. In Fig. 3a, the photoluminescence spectra of the neat materials are shown together with the electroluminescence of a bilayer device. Again, the appearance of exciplex emission occurs along with suppressed singlet exciton emission of individual components. Temperature dependent ELDMMR measurements, which are shown in Fig. 3b, reveal a reduced effect of spin resonance on the EL intensity. The maximal ELDMMR signal is only 0.85% at room temperature, which is approx. 35% lower than for THCA:BPhen. That implies either a reduced magnetic interaction, or a larger ΔE_{ST} -gap. Evaluating the temperature dependence of the ELDMMR reveals, however, a much larger energetic splitting $\Delta E_{ST} = (58.2 \pm 4.5)$ meV, as shown in Fig. 3c. Therefore, the reduced ELDMMR signal intensity can be assigned to the enhanced value of ΔE_{ST} , which makes the spin mixing less efficient.

ΔE_{ST} is proportional to the overlap of the molecular orbitals of the recombining charge carriers, which, in turn, is affected by their spatial orientation and their separation. Consequently, the decreased energy gap for THCA:BPhen with respect to m-MTDATA:BPhen can be explained either by a larger separation of the charge carriers forming the exciplex or a more suitable orbital wavefunction alignment. For future improvement of TADF OLEDs, material systems with the lowest possible energy gap ΔE_{ST} need to be found, while maintaining high interfacial recombination efficiency. Consequently, the electron-hole distance, together with the wavefunction overlap define crucial parameters for future material synthesis and combinations.

In summary, resonant spin sensitive measurements based on electron paramagnetic resonance provide important insights on the role of spin states in two TADF donor-acceptor systems. We found a direct contribution of triplet states to electroluminescence in TADF OLEDs being of intersystem crossing type (RISC). This process is strongly temperature dependent; clearly evidencing that triplet to singlet up-conversion is indeed thermally activated. Moreover, we exclude the contribution of triplet excitons to TADF. The energetic separation of the singlet- and triplet exciplex state ΔE_{ST} were determined for the material systems THCA:BPhen and m-

MTDATA:BPhen to be $\Delta E_{ST} = (20.7 \pm 1.2)$ meV and $\Delta E_{ST} = (58.2 \pm 4.5)$ meV, respectively. An optimized separation distance is needed in order to reduce ΔE_{ST} while maintaining sufficient interfacial recombination efficiency. Finally, as triplet to singlet up-conversion implies that both energy and momentum spin conservation rules are fulfilled, we believe that thermal activation of triplet-singlet up-conversion and magnetic interactions coexist in our TADF devices.

Experimental

THCA was synthesized at the Kaunas University of Technology (Lithuania). m-MTDATA and BPhen were purchased from Sigma-Aldrich. For the initial solutions, THCA and m-MTDATA were dissolved in chlorobenzene with a concentration of 20 mg/ml.

Bilayer devices were fabricated on indium tin oxide (ITO) covered glass substrate. First, poly(3,4-ethylenedioxythiophene):polystyrolsulfonate (PEDOT:PSS, 4083Ai) from Hereaus was spin coated with 3000 rpm for 1 minute, resulting in a 40~nm thick film, which was subsequently annealed for 10 minutes at 130 °C in a nitrogen glovebox. Afterwards, the hole transport layer (HTL) was spin coated at 1000 rpm for 1 minute yielding a film thickness around 50 nm. In the next step, the samples were transferred into an evaporation chamber, where 20 nm BPhen was thermally evaporated on top of the HTL. Finally, the top electrode (3 nm Ca / 120 nm Al) was evaporated, completing the device.

For the ELDMR measurements, we used ITO covered glass substrates with 2.7 x 50 mm size and prepared the OLEDs according to the aforementioned procedure. The devices were electrically connected and placed inside the vacuum-sealed glass tube in the EPR microwave cavity. All device fabrication steps were done inside the glovebox to avoid degradation.

The ELDMR measurements were done in a modified X-Band spectrometer (Bruker E300) equipped with a continuous flow helium cryostat (Oxford ESR 900). Forward bias was provided by a source-measure unit (Keithley 237). The EL was detected by a silicon photodiode placed in front of the EPR microwave cavity with optical access (ER4104OR). The change of EL was detected via a Lock-In-Amplifier (SR7230) with the TTL modulated microwave as reference.

The spectrally resolved photoluminescence (PL) was measured at room temperature by an Edinburgh Instruments FLS980 spectrometer. The steady-state EL spectra were recorded by biasing the completed device with an Agilent 4155C parameter analyzer in constant current mode and coupling the emitted light via light guides to an Acton Spectra SP-2356 spectrometer (Princeton Instruments) or to a small SPM 002 spectrometer (Photon Control).

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Author contributions

S.V., A.S., V.C. and V.D. designed the experiments. S.V. and M.A. prepared the devices and carried out the ELDMR measurements. K.T. performed the electroluminescence measurements. A.D. and J.V.G. measured photoluminescence. A.D. and J.V.G. synthesized the THCA molecules. S.V. evaluated the data and wrote the manuscript, which all authors discussed and commented on.

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Figure legends

Figure 1: **TADF principles** a) Jablonski diagram showing relevant processes of the occurrence of exciplex emission. The triplet to singlet exciplex formation ratio is 3:1, whereas their conversion is due to a thermally activated inter system crossing process (shown in green). The energetic splitting of the triplet exciplex state caused by external magnetic field and measurement principles of ELDMR are also shown. b) Molecular structures of the investigated materials. c) Layout of the investigated OLED devices.

Figure 2: **THCA:BPhen exciplex system** a) normalized photoluminescence spectra of neat THCA (blue) and BPhen (purple), together with the normalized electroluminescence of THCA:BPhen exciplex emission (orange). b) Temperature dependent ELDMR spectra of THCA:BPhen (colored dots). The Gaussian fits (black lines) were weighted with the standard deviations of the respective measurements. c) Arrhenius plot of the integrated fits (red dots) together with a linear fit (black line) and the corresponding error margins (grey shaded area). d) PL detected magnetic resonance (PLDMR) spectra at different temperatures (colored lines). The exciplex spin signature is superimposed to an additional broad contribution, which we assigned to triplet excitons localized on one of the individual material components. Both PLDMR signals show different temperature dependences and activation energies.

Figure 3: **m-MTDATA:BPhen exciplex system** a) normalized photoluminescence and electroluminescence spectra of pristine m-MTDATA (blue), pristine BPhen (purple), and m-MTDATA:BPhen exciplex emission (yellow), respectively. b) Temperature dependent ELDMR spectra of m-MTDATA:BPhen. The data (colored dots) was fitted with Gaussians (black lines). c) Arrhenius plot of the integrated fits (red dots) along with a linear fit (black line) and the corresponding error margins (grey shaded area).

Figures

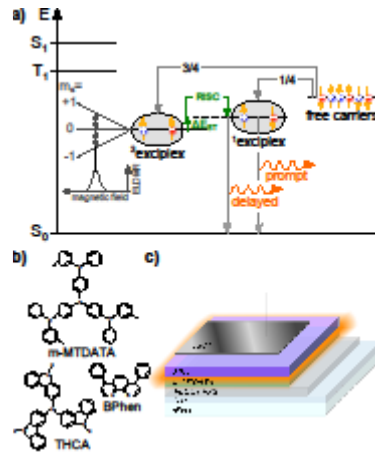


Figure 1.

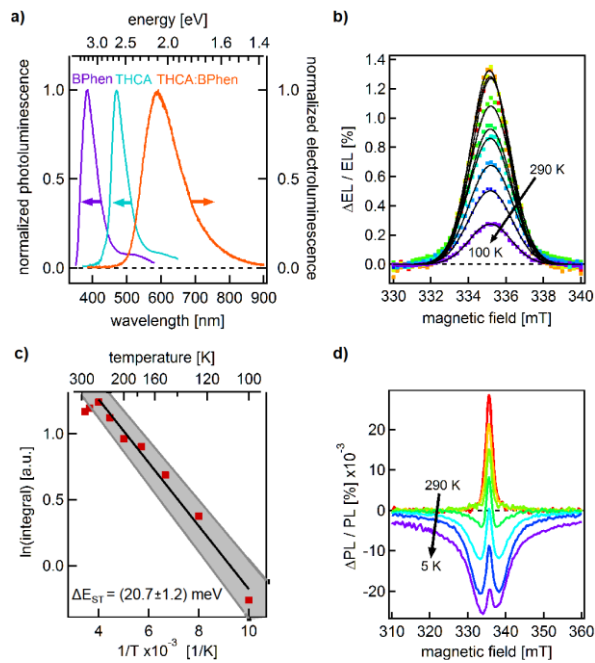


Figure 2.

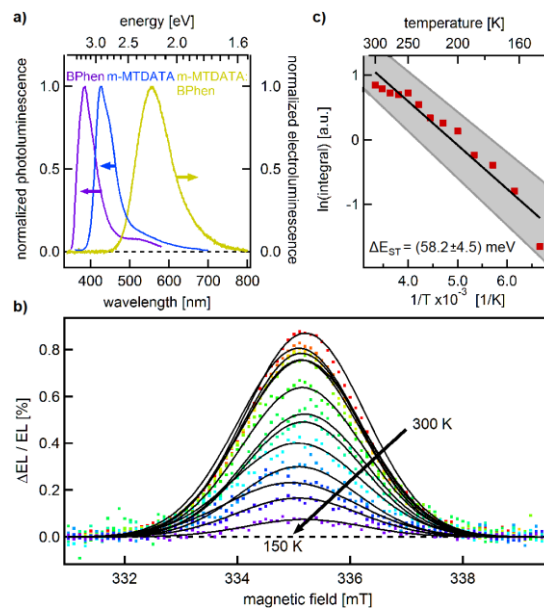


Figure 3.