Optically and electrically excited intermediate electronic states in donor:acceptor based OLEDs

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Abstract

Thermally activated delayed fluorescence (TADF) emitters consisting of donor and acceptor molecules are potentially highly interesting for electroluminescence (EL) applications. Their strong fluorescence emission is considered to be due to reverse intersystem crossing (RISC), in which energetically close triplet and singlet charge transfer (CT) states, also called exciplex states, are involved. In order to distinguish between different mechanisms and excited states involved, temperature-dependent spin-sensitive measurements on organic light-emitting diodes (OLEDs) and thin films are essential. In our work we apply continuous wave (cw) and time-resolved (tr) photoluminescence (PL) spectroscopy as well as spin-sensitive electroluminescence and PL detected magnetic resonance to films and OLED devices made of three different donor:acceptor combinations. Our results clearly show that triplet exciplex states are formed and contribute to delayed fluorescence (DF) via RISC in both electrically driven OLEDs and optically excited films. In the same sample set we also found molecular triplet excitons, which occurred only in PL experiments under optical excitation and for some material systems only at low temperatures. We conclude that in all investigated molecular systems exciplex states formed at the donor:acceptor interface are responsible for thermally activated DF in OLEDs with distinct activation energies. Molecular (local) triplet exciton states are also detectable, but only under optical excitation, while they are not found in OLEDs when excited states are generated electrically. We believe that the weakly bound emissive exciplex states and the strongly bound non-emissive molecular triplet excited states coexist in the TADF emitters, and it is imperative to distinguish between optical and electrical generation paths as they may involve different intermediate excited states.
I. Introduction

The major drawback of conventional fluorescent organic light emitting diodes (OLEDs) is the fact that only 25% of injected electrons and holes form emissive singlet excitons, whereas 75% form long-lived triplets, which mostly decay non-radiatively (Brown1992, Rothberg1996, Bruetting2012, Yang2017). However, reverse intersystem crossing (RISC) from triplets to singlets is strongly enhanced, if the used materials are designed to exhibit an energy splitting $\Delta E_{ST}$ between the singlet and triplet state in the order of thermal energy $k_B T$ (Endo2009, Uoyama2012, Goushi2012). One approach to fulfill this requirement is to find appropriate pairs of donor and acceptor materials, where electrons and holes are located on different molecules to form so called exciplex states (Goushi2012, Hung2013, Li2014). While high OLED efficiencies have been realized via this approach (Liu2016, Kim2016), the underlying spin-physics is still not very clear, as intrinsically spin-sensitive techniques are not commonly applied, particularly for studying efficient OLEDs under real-life operation conditions (Väth2017, Ogiwara2015). Thus, a detailed understanding of the spin-forbidden upconversion mechanism from triplets to singlets is still missing. Most controversial issues are related to the activation energy of delayed fluorescence (DF) and if it is related to the energy gap $\Delta E_{ST}$ between exciplex singlet ($^1$Exc) and exciplex triplet ($^3$Exc) levels, or to molecular triplet states, e.g. to a triplet located on the donor ($^3$LEd) or to a triplet located on the acceptor ($^3$LEa) (Dias2016, Santos2016). In this work we use techniques based on electron paramagnetic resonance (EPR), which are suitable tools to investigate spin states in OLEDs due to their sensitivity to triplets (Weil2007). The goal of this work is to reveal, which spin-bearing species are involved in the light generation mechanisms of TADF based OLEDs.
II. Materials and Devices

**FIG. 1.** Overview of device layout and electro-optical characterization. a) Schematic device structure of donor:acceptor based OLEDs and chemical structures of molecules used in this work b) EL and PL spectra of m-MTDATA:3TPYMB together with PL of the pristine materials. c) OLED current density and luminance *versus* voltage characteristics of m-MTDATA:3TPYMB at 248 and 295 K. Inset: OLED device under test. d) External quantum efficiency *versus* voltage characteristics of m-MTDATA:3TPYMB at *T*=248 and 295 K.

The molecular components for exciplex based OLEDs investigated in this work are the donor-materials 4,4′,4″-Tris[phenyl(m-tolyl)amino]triphenylamine (m-MTDATA) and Tri(9-hexylcarbazol-3-yl)amine (THCA) (Michaleviciute2012, Cherpak2015), combined with the acceptor-materials Tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB) and 4,7-Diphenyl-1,10-phenanthroline (BPhen). **Fig. 1a** shows the corresponding molecular structures and the OLED device structure. An ITO anode covered with a PEDOT:PSS layer is used for hole injection and an aluminum cathode for electron injection. The emission layer consists of a 1:1 mixture of donor and acceptor materials, sandwiched in between layers of the respective pristine molecules, acting either as electron, or hole transport layer. An electroluminescence (EL) spectrum of such a device based on the combination m-MTDATA:3TPYMB as well as a photoluminescence (PL) spectrum of a blend of those molecules and the respective pristine materials are depicted in **Fig. 1b**. One can recognize a clear red shift between the PL of the pure materials and the EL of a device, proving that the emission originates from energetically lower lying exciplex states formed at the interface between the two molecules. The material systems m-MTDATA:BPhen and THCA:BPhen show the same behavior (see **Fig. S2a, Fig. S3a**). Exemplary current density and luminance *versus*...
voltage characteristics for the combination m-MTDATA:3TPYMB at two different temperatures are shown in Fig. 1c and the resulting EQE versus current density curves in Fig. 1d. With the optimized structure which consists of ITO / PEDOT:PSS / m-MTDATA(30nm) / m-MTDATA:3TPYMB(70nm,1:1) / 3TPYMB(30nm) / LiF(5nm) / Al(120nm) we reached a maximum $\text{EQE}_{\text{max}}$ of 6.3% at room temperature (RT). We measured a photoluminescence quantum yield of 45% in oxygen free m-MTDATA:3TPYMB films, which allows for the estimation of a theoretical maximum EQE of 8.3% in OLEDs based on this donor:acceptor system (For details see SI). The maximum EQE we measured for a device comes close to this theoretical value, while the discrepancy between the theoretical and experimental numbers might be attributed to leakage currents. Surprisingly, temperature dependent EQE measurements show that the efficiency increases at temperatures below room temperature. At $T=248$ K an $\text{EQE}_{\text{max}}$ of 11.0 % was measured (Fig. 1d). While this observation is counterintuitive for TADF, we believe that the suppression of the non-radiative decay at lower temperatures actually outcompetes the decrease of RISC which is why efficiencies can increase below RT (Kim2016). We therefore attribute the limitation of the EQE at RT to non-radiative losses. Still an EQE of 6.3 % at RT exceeds the value of 5% which is the upper limit for purely fluorescent OLEDs. In any case, our spin-sensitive experiments presented in Section IV address the behavior of the reasonably efficient, state-of-the art devices.
III. Photoluminescence

FIG. 2. Time-resolved optical spectroscopy. a) Streak camera image of PL from an m-MTDATA:3TPYMB blend for excitation at $\lambda_{\text{exc}} = 400$ nm together with an integrated spectrum over the 1.5 ns detection window. b) Transient PL decay of an m-MTDATA:3TPYMB blend. A sum of two exponential decays was used to fit the curve and the corresponding lifetimes were extracted. c) Streak camera image of PL from pristine m-MTDATA with an integrated spectrum over the 1.5 ns detection window. Inset: PL decay curve of this emission. A lifetime of 0.6 ns is obtained from fitting the transient with a single exponential decay. d) Illustration of the charge transfer process within the instrument response time of 10 ps after optical excitation of m-MTDATA with UV light. Energies for HOMO and LUMO are taken from (Goushi2012).

In order to further investigate the optical properties of the materials used in this work, we performed time-resolved PL (TRPL) measurements on an m-MTDATA:3TPYMB blend. Fig. 2a shows a streak camera image which displays emission between 0 and 1.5 ns after excitation. Only emission from the exciplex singlet state ($^1\text{Exc}$) at around 550 nm can be observed within the measured time window. Fig. 2b shows the PL transient of the observed exciplex emission on a longer time scale proving that the lifetime of the decay is in the microsecond range because of thermally activated fluorescence. Fitting the curve with a double exponential decay yields lifetimes of $\tau_1 = 3$ $\mu$s and $\tau_2 = 12$ $\mu$s. Since separated features of prompt and delayed fluorescence cannot be identified in the transient, these lifetimes do not necessarily represent the decay times of prompt and delayed fluorescence, but they demonstrate a distinct prolongation of the overall fluorescence lifetime possibly due to thermally activated RISC.

For comparison, a streak camera image of pristine m-MTDATA was recorded (Fig. 2c). Here an emission between
400 nm and 450 nm occurs, reaching its peak at about 425 nm, which corresponds to the cw PL spectrum of m-MTDATA (see Fig. 1b). The decay of this emission is presented in the inset of Fig. 2c. A lifetime of 0.6 ns is obtained from fitting the transient with a single exponential decay. Considering the negligibly small absorption of the exciplex state itself (Santos2016, Attar2016, Huang2018) it is remarkable that only exciplex emission is observed in the blended film while emission from m-MTDATA is completely quenched. According to photoexcitation spectra (Fig. S1), with the 400 nm laser in the streak camera measurement only m-MTDATA can be excited in the blended film. We conclude that the initial singlet excitation (1LE0) of the donor molecule m-MTDATA is followed by an electron transfer to the acceptor molecule 3TPYMB and the formation of an exciplex state within the instrument response time of 10 ps. This ultra-fast electron transfer outcompetes PL from m-MTDATA, which is similar to what is usually observed in donor:acceptor blends for organic photovoltaics (Sariciftci1992, Hwang2008). Intersystem crossing (ISC) from singlet (1LE0) to triplet state (3LE0) can also contribute to the efficient quenching of the m-MTDATA emission and will be discussed on the basis of magnetic resonance data in more details below. An overview of the involved processes is schematically shown in Fig. 2d, illustrating how the exciplex state is formed after the charge transfer process, giving rise to ~µs long-living emission at 550 nm. For the sake of completeness, streak camera measurements were also performed on blends of m-MTDATA:BPhen and THCA:BPhen (see Fig. S2b, Fig. S3b). For m-MTDATA:BPhen, exciplex singlet emission at 560 nm can be observed within the measured time window of 500 ps. In contrast to the m-MTDATA:3TPYMB blend, there is additional emission between 410 and 430 nm at early times, which can be assigned to m-MTDATA. However, this emission decays within approximately 10 ps, which is much faster than the decay of pristine m-MTDATA, as shown in Fig. 2e. Again, the time scale, on which the CT from m-MTDATA to BPhen and the formation of the exciplex state take place, remains very short. The PL decay of an m-MTDATA:BPhen blend on a longer time scale is shown in Fig. S2c, where the ~µs long-lived emission of the exciplex becomes apparent. Here, a sum of two exponential decays was not sufficient to reasonably fit the curve and instead a sum of two stretched exponential decays was used. Stretched exponentials apply when a distribution of lifetimes is given, which is reasonable for donor:acceptor systems where the molecules are randomly oriented and the wave-functions overlap determining ΔE_ST can vary (Palmer1984, Rothschild1987). We extracted lifetimes of τ1 = 30 ns and τ2 = 0.2 µs (More details about this fitting procedure are given in Fig. S2c). The excitation of BPhen with the 400 nm wavelength in a streak camera experiment was not possible according to photoexcitation spectrum shown in Fig. S2a, which explains the absence of any emission from BPhen. The streak image for THCA:BPhen shows exciplex singlet emission at around 560 nm within the measured time window of 1.5 ns and a distinct signature of THCA emission at around 475 nm. Since the emission from THCA is also visible in the
steady-state PL from the THCA:BPhen blend, it is likely that the blend ratio for the measured sample deviates from 1:1. A comparison with the PL decay of pristine THCA (Fig. S3d) shows that the PL lifetime of THCA is considerably shortened in the blend with BPhen proving the occurrence of CT between THCA and BPhen. The PL decay of THCA:BPhen (Fig. S3c) demonstrates ~µs long-lived emission of the resulting exciplex state. Here fitting the curve with a sum of two stretched exponential decays yields lifetimes of $\tau_1 = 13$ ns and $\tau_2 = 3$ µs. In summary, all three donor:acceptor combinations exhibit similar photophysics, in which optical excitation of the donor molecule is followed by a fast charge transfer to the acceptor molecule upon formation of a long-lived emissive exciplex state.
IV. Magnetic Resonance

**FIG. 3.** Temperature dependent spin-resonance experiments on OLEDs. **a)** Illustration of exciplex states formed at the donor-acceptor interface and EL change due to spin-flip transitions between exciplex triplet states in an external magnetic field $B$. The exciplex wave function extent $r$ can be understood as spatial separation of hole and electron spins with magnetic dipolar interaction $D \sim r^{-3}$. Spin-flip transitions between Zeeman levels are induced by microwave photons ($h\nu_{MW}$) and can be detected via relative EL change $\Delta$EL/EL (or current $\Delta$I/I) as a Gaussian bell-shaped curve centred at $B=B_0$ with the width $\Delta B$ determined by $D$. **b)** Temperature-dependent EL contrast ($\Delta$EL/EL) under magnetic resonance conditions ($ELDMR$) for m-MTDATA:3TPYMB together with Gaussian fits (black lines). ELDMR spectra for other studied material systems are shown in Fig. S7. **c)** ELDMR and EDMR ($\Delta$I/I) spectra of m-MTDATA:3TPYMB are identical in shape implying the same spin-states are involved in recombination. As a reference, a PEDOT:PSS-only device (without emitter layer) shows no spin-resonance effect on the current, which excludes spin-dependent effects in the transport layers. **d)** Arrhenius plot of the integrated ELDMR spectra. The activation energy $E_A$ is derived from the slope of linear fits and tabulated in the inset for three studied material systems.

In the next step, we applied EPR to OLEDs. Here microwaves of a fixed frequency $\nu_{MW}$ (in the GHz range) drive transitions between Zeeman sublevels of a triplet spin state which is energetically split due to an external magnetic field $B$, as schematically shown in Fig. 3a. As soon as the following resonance condition is fulfilled, microwave-induced transitions take place:

$$h\nu_{MW} = g\mu_B B \Delta m_s \pm D (\cos^2 \theta - \frac{3}{4})$$  \hspace{1cm} (1)

Here $h$ is the Plank constant, $g$ is the g-factor of the spin system, $\mu_B$ is the Bohr magneton, $\Delta m_s = 1$ is the allowed change of the magnetic quantum number, $D$ is the magnetic dipole-dipole interaction of two spins and $\theta$ is the angle between the direction of the external magnetic field and the vector connecting the two spins. For a statistical
distribution of molecular orientations and electron-hole separations in heterogeneously mixed blends, a distribution of magnetic dipolar interaction energies $D$ can be expected. This results in a superposition of several possible EPR transitions. If $D$ is small, as in the case of distant electron-hole pairs, the EPR spectrum for an $S=1$ (triplet) state will consist of a single inhomogeneously broadened Gaussian bell-shaped curve. Alternatively, for strongly interacting close-by pairs of spins (large $D$), as for molecular (localized) triplet excitons, a broad spectrum ("powder pattern") with pronounced, separated side-peaks and shoulders is expected (Kraus2016, Väth2016).

In contrast to classical EPR, where microwave absorption in resonance is measured, we probe parameters which are directly related to optoelectronic properties of our samples, namely the EL or current $I$ in OLEDs, or PL in films. This creates a direct link between the spin species and the recombination or transport processes in devices or films. The respective techniques are called EL-detected magnetic resonance (ELDMR), electrically detected magnetic resonance (EDMR) and PL-detected magnetic resonance (PLDMR). In ELDMR and EDMR, the operating device is electrically driven, whereas in PLDMR, the donor:acceptor film is optically excited. Spin-flip transitions are particularly efficient, if the population difference between Zeeman sublevels is large enough (i.e. non-Boltzmann, 0.15% at RT). There are several mechanisms for this, either considering transformation between singlet and triplet excitons, or between singlet and triplet exciplex states. In neutral excitations, such as triplet states, the polarization can be achieved via spin-selective population of a particular Zeeman sublevel, e.g. of $m_s=0$ in an optical pumping cycle via ISC from initially photogenerated singlet excitons (Weil2007). Alternatively, selective depopulation of a particular Zeeman sublevel can also lead to polarization. In the case of weakly bound electron-hole pairs (CT or exciplex states, as in our case), optical excitation leads to formation of singlet excitons with 100% yield. If CT takes place, only singlet exciplex states can be formed due to spin conservation rule. Since the electron-hole dipolar coupling is weak (distant pairs), singlet and triplet exciplex states are energetically very close (almost degenerate). Therefore, a singlet-triplet mixing can occur, either via hyperfine interaction or via a so-called $\Delta g$-mechanism, depending on the material systems (Ogiwara2015, Wang2016), which in turn can lead to spin polarization of the triplet exciplex state, but only if the external magnetic field lifts the degeneracy of the Zeeman sublevels. In contrast to optical generation, electrical injection of charges leads to the statistical formation of electron-hole pairs with 75% share of triplets. If the rate constants for non-radiative decay and RISC are different between the three triplet Zeeman sublevels, a non-Boltzmann distribution occurs. In other words, under optical and electrical excitations, a steady-state population difference between the spin states can build up, and microwave-induced spin-flip transitions will change recombination rates. This results in a change of EL, I or PL depending on the applied method. We note that an additional relaxation pathway may open if the energy of a
molecular triplet exciton state is lower than the energy of the triplet exciplex state. Such a spin-conserving process can form triplet excitons from triplet CT or exciplex states.

To clarify the spin sensitive mechanisms in OLEDs, ELDMR is the most suitable method as it directly probes EL. Temperature-dependent ELDMR spectra measured on an m-MTDATA:3TPYMB OLED are shown in Fig. 3b. Each spectrum consists of a single, Gaussian shaped line centered at the magnetic field corresponding to \( g = 2.002 \) in Eq.(1). The g-factor is close to the free-electron value and typical for radicals, but also for triplet states in organic semiconductors due to the small spin-orbit coupling in carbon based materials, free of heavy atoms (Baker2011, Weil2007). Remarkable is the relative change \( \Delta EL/EL \) in resonance of almost 1%, which is large compared to the population difference between Zeeman sublevels expected from Boltzmann statistics (0.3-0.15% at 150-300K). According to Eq.(1) it is difficult to distinguish between \( S = 1/2 \) doublets and \( S = 1 \) triplets when \( D \) is small, e.g. in weakly interacting spin pairs, since two triplet transitions overlap and appear as one envelope curve (Fig. 3a). Further, although we probe electron-hole recombination from the excited singlet exciplex state (EL), we can only manipulate the population of the triplet Zeeman sublevels. To understand the origin of the observed magnetic resonance effect on EL, i.e. to explain why and how spin-flip transitions in a non-emissive triplet exciplex state (\( 3^\text{Exc} \)) lead to a change of EL from the singlet exciplex state (\( 1^\text{Exc} \)), we need to know the sign of the EL change. The lock-in based ELDMR technique does not allow to do this unambiguously. Therefore, we independently measured the EL intensity directly with a photodiode connected to a high-sensitivity digital oscilloscope, while applying the resonant on-off microwave pulses (Fig. S4). By doing so, we clearly observed a decrease in EL (negative sign) and correspondingly plotted the ELDMR spectra, as shown in Fig. 3b. Independently of this, we measured the magnetic field effect on EL (Wang2016, Basel2016) and found that EL increases with magnetic field (Fig. S5), which is due to the fact that the magnetic field lifts the degeneracy of triplet sub-levels (Zeeman effect). This behavior is in agreement to the negative sign of ELDMR since the resonant transitions connect the inner (strongly occupied) and outer Zeeman sublevels and accelerate the non-radiative recombination via triplet channel. Remarkably, the magnitude of the ELDMR contrast decreases with decreasing temperature. This is completely opposite to what is commonly observed in EPR experiments, where lower temperatures lead to an increase in spin polarization according to Boltzmann statistics and therefore enhanced signals (Weil2007). ELDMR spectra for OLEDs based on m-MTDATA:BPhe and THCA:BPhe show similar line shapes and temperature dependencies (Fig. S7a, b). In addition, the shape of the ELDMR spectra is independent of whether OLEDs are processed from the solution or evaporated in a vacuum (Fig. S7c). To ensure the same exciton generation rate for each temperature, all ELDMR spectra where measured at the same current density of 1 mA/cm². Consequently, the observed temperature dependence can be attributed to the thermal
activation of RISC in TADF-based OLEDs, unambiguously proving the TADF nature of the observed EL. From these experiments we can conclude that electrically generated triplet exciplex states are spin-polarized already at room temperature, since lifetimes of $m_s=+/-1$ states and $m_s=0$ states differ, which is therefore responsible for a non-Boltzmann distribution. The latter $m_s=0$ state is linked to the singlet exciplex state via RISC and therefore kinetically controls the EL intensity. The details of the RISC mechanism are also non-trivial. Recent reports attribute the driving force of this RISC process in donor:acceptor-based TADF emitters to the so-called $\Delta g$-mechanism (Wang2016, Basel2016). This mechanism facilitates intersystem crossing between the singlet state $S$ and the triplet state $T_0$ due to a difference in spin precession frequencies $\Delta \omega_p$ which arises from a difference in electron spin g-factors $\Delta g$ in the presence of an external magnetic field $B$ ($\Delta \omega_p = \mu_g \Delta g B / \hbar$) (Zhang2015). For donor:acceptor systems, a contribution of the $\Delta g$-mechanism can be expected because electron and hole, which form the exciplex state, reside on adjacent non-identical molecules. In order to obtain an estimate value for $\Delta g$ in our OLEDs we performed ELDMR measurements over an extensive range of magnetic fields (25 mT – 1.4 T) and microwave frequencies (0.7 GHz – 38 GHz) (Fig. S6). Here, an increase of the linewidth with increasing frequency is observed which indicates a non-negligible $\Delta g$. We used the software package EasySpin (Stoll2006) to perform a global fit of all spectra in the accessible frequency range and extracted an upper limit for $\Delta g$ of $9.2 \cdot 10^{-4}$. We emphasize that this value is derived directly from spectroscopic data and is not deduced by modelling magnetic field effects, such as magneto electroluminescence (MEL). In (Wang2016), the assumption of $\Delta g = 10^{-4}$ was sufficiently large to explain magnetic field effects in m-MTDATA:3TPYMB based OLEDs with a dominant $\Delta g$-mechanism. Investigations on other organic materials report values for $\Delta g$ in the range of $10^{-3}$ to $10^{-4}$ (Yu2012). Our measurement is consistent with these numbers and thus supports the scenario that $\Delta g$-mechanism is responsible for RISC.

To ensure that the observed ELDMR signals are directly related to the emitting layer, but not to the spin-dependent transport or injection in the adjacent transport layers or at the interfaces, comparative EDMR measurements on fully processed OLEDs without TADF emissive layers were performed. To remind, EDMR probes the microwave-induced change of current through the OLED while a constant voltage is applied to the device. ELDMR and EDMR on an OLED (m-MTDATA:3TPYMB) yield identical signals, as shown in Fig. 3c (see also Fig. S8 for THCA:BPhen). However, the relative change of the current in resonance is about one order of magnitude smaller than the EL contrast. The reference sample, consisting of ITO/PEDOT:PSS without donor and acceptor layers, yields no EDMR signal at temperatures between 20 K and 300 K at all. These observations clearly show that the ELDMR and EDMR signals originate from the same spin-dependent mechanisms in the emissive layer and we can exclude spin-dependent transport, or injection in the anode and cathode layers as source of the observed effects.
Moreover, we speculate that the EDMR signal can actually be induced by the ELDMR effect. A change of the recombination rate of exciplex states in magnetic resonance under constant voltage conditions can give rise to a change in the current. Consequently, the occurrence of an ELDMR signal can induce a smaller EDMR signal of identical shape. Similar correlations between a change in EL and current are observed in magnetic field effect studies on donor:acceptor based TADF OLEDs (Wang2016). We additionally measured ELDMR and EDMR spectra at different driving currents and found that both parameters are dependent on the current density through the device (Fig. S9a). Increasing ELDMR contrast with increasing current may be a signature of polaron-exciplex interaction, as also known for other types of OLEDs (Baker2011, Keevers2015).

From the temperature dependence of the ELDMR signal intensities we can calculate the activation energy $E_A$ from an Arrhenius plot. ELDMR is not yet a widely used method to determine $E_A$, although it probes the OLED response to a very fast spin-flip in the electron-hole pair, i.e. without possible artefacts due to charge injection, transport and exciplex formation. Fig. 3d shows Arrhenius plots of the integrated ELDMR spectral intensity for OLEDs made with three different material systems. From the slope of linear fits, values for $E_A$ were calculated for each material system. These values are in the range between 16 and 58 meV, which is in good agreement with the values for $\Delta E_{ST}$ of other donor:acceptor-based TADF systems (Goushi2012, Liu2015, Graves2014). Based on the assumption that the singlet exciplex is the emissive state and its rate-limited (de-)population occurs via RISC from the triplet exciplex state, we consider the deduced activation energies as good approximations for the singlet-triplet gap $\Delta E_{ST}$, since ELDMR probes thermally activated spin-conversion.
FIG. 4. a) Comparison of normalized ELDMR spectra for different donor:acceptor combinations. All systems exhibit a single Gaussian line assigned to the exciplex triplet (3Exc). The shown curves are each recorded at T=200 K. b) Temperature dependent PLDMR spectra of an m-MTDATA:3TPYMB film. Each spectrum consists of a broad and a narrow Gaussian line, which are superimposed. c) Comparison of normalized PLDMR spectra for different donor:acceptor systems, all recorded at T=200 K. The dashed line shows separate fits of the broad and narrow components for m-MTDATA:3TPYMB (green line). We assign the narrow component to the exciplex triplet (3Exc) and the broad component to a molecular triplet on m-MTDATA (3LE). d) Illustration of the triplet formation after the electrical injection of charge carriers. Electrons and holes are injected into the mixed layer of the OLED and form excited states, 75% of which are triplet exciplex states (3Exc). The spatial separation of the e-h pairs r can vary by the electric field. e) Illustration of the triplet formation under optical excitation. Initially, only singlet excitons are formed in the donor phase (1LE). They can diffuse and undergo ISC to form molecular triplet excitons (1LE) (i). Alternatively, the donor singlet (1LE) can undergo a charge transfer to form an exciplex singlet (1Exc) (ii). Subsequently, an exciplex triplet (3Exc) can be formed, e.g. via the Δg-mechanism (see text) or another spin-conversion process (iii). Note that the dipolar-coupling D and hence the ELDMR/PLDMR line width ΔB can vary due to the broad distribution of the electron-hole separations r. Charge separation to non-interacting electrons and holes is also possible (iv).

In order to understand the radiative recombination pathway in more detail, we now compare the spin-dependent recombination of exciplex states formed by electrical injection with photogenerated exciplex states. For this we first compare normalized ELDMR spectra for three different donor:acceptor combinations as shown in Fig. 4a. Although, we clearly see a difference in activation energies of the underlying RISC process in these blends, the ELDMR spectra are almost identical for all studied OLEDs, with the same resonance position (i.e., in the vicinity of g=2.002), similar signal shape and only slightly different linewidth of about 3 mT FWHM (full width at half maximum). This similarity can be explained by the fact that the donor molecule in each case is either THCA or m-MTDATA, which have very similar molecular structures, as shown in Fig. 1a. Although the electronic molecular environment determines the g-factor and hence the structure of the ELDMR signal, g-factor differences
are too small to be resolved in the used frequency range. On the other hand, an exciplex is a delocalized electron-hole pair over donor and acceptor molecules. As we will discuss in more detail later, the spatial separation between them is the parameter that might determine the ELDMR linewidth and since we expect a broad distance distribution of such pairs in the emissive blends, the influence of the structure of the involved individual molecules appears to be small and ELDMR signals appear rather similar for several donor:acceptor combinations.

Next, we measured PLDMR on m-MTDATA:3TPYMB films at temperatures between 50 and 290 K, as shown in Fig. 4b. The first thing one notices is another shape of the spectrum. All spectra consist of a superposition of a narrow and a broad component with Gaussian shape and the broad component becomes more and more visible as temperature decreases. As already mentioned, the sign determination with the lock-in amplifier is ambiguous, especially if there is a phase shift between individual spectral components which is temperature-dependent, as in our case (Lee2012, Boehme2017). Also here we used an oscilloscope for direct PL detection with pulsed resonant microwaves instead of a lock-in amplifier (Fig. S4). The broad component exhibits a positive sign and the narrow component a negative one. PLDMR spectra of the donor:acceptor combinations m-MTDATA:BPhen and THCA:BPhen are shown in Fig. S10 and exhibit a similar behavior. Remarkably, the broad components in these blends are only pronounced at low temperature, whereas at room temperature the narrow signal dominates strongly. Fig. 4c presents normalized PLDMR spectra of all studied donor:acceptor blends showing that each system exhibits the same behavior. In order to separate the two contributions, we exemplary fitted the PLDMR spectrum of m-MTDATA:3TPYMB with two Gaussians, shown as dashed lines in the upper part of Fig. 4c. The narrow PLDMR component is very similar to the ELDMR signals in sign and form, but has a slightly smaller linewidth of 2 mT compared to 3 mT in ELDMR. The reason for this can be slightly different spatial distributions of electron-hole pairs, as illustrated in Fig. 4d,e. But the broad PLDMR component with a linewidth of 6 mT is clearly a new feature not present in ELDMR. In order to exclude the influence of the film preparation method, we performed PLDMR on evaporated and solvent-processed films with the same outcome (Fig. S11).
V. Discussion

In order to assign the detected signals in ELDMR and PLDMR to particular excited states, we assume that electrical injection predominantly populates the energetically lowest triplet state according to the spin statistics. In the donor:acceptor blends studied in this work this is the triplet exciplex state (\(^3\)Exc) (Energies of all molecular singlet and triplet states as well as exciplex singlet states are shown in Fig. S12). The unusual temperature behavior strongly supports the scenario that the signals occurring in ELDMR and EDMR are due to thermally-activated RISC between triplet (\(^3\)Exc) and singlet exciplex (\(^1\)Exc) states. Although the narrow components in PLDMR and in ELDMR have slightly different widths, they are very similar in shape and, most importantly, in temperature-dependence. Directly measured microwave pulse - induced changes of PL (Fig. S4b) and EL (Fig. S4d) show that the narrow PLDMR and ELDMR signals (red curves) show up themselves as transients crossing the reference baseline (off-resonance measurement). These observations demonstrate that they are of the same origin and we assign the narrow PLDMR peak to exciplex triplets (\(^3\)Exc), too. Furthermore, the ratio \(\Delta P_L/PL\) (PLDMR contrast) does not depend on the intensity of optical pumping (Fig. S9b), which is indicative for monomolecular mechanism responsible for the singlet exciplex generation and singlet to triplet interconversion. Despite both PLDMR and ELDMR probe the exciplex triplet, their relative magnitudes (\(\Delta P_L/PL\) and \(\Delta E/EL\)) differ by at least a factor of 10. This can be due to different spin statistics. For optical excitation, triplet exciplex states are formed via ISC from optically generated singlets whereas for electrical injection triplet exciplex states are directly formed with a probability of 75% thus giving rise to a higher ELDMR contrast.

The second component in the PLDMR signal is a factor of two broader and therefore should have a different origin. We tentatively attribute it to molecular triplet excitons (\(^3\)LE), either on the donor or the acceptor molecule. The more localized character leads to a stronger dipolar-coupling \(D\) than in exciplex triplets, which are delocalized over at least two molecules. As schematically shown in Fig. 3a, \(D\) determines the linewidth of these magnetic resonance spectra \(\Delta B\), therefore, PLDMR from a localized triplet exciton on the donor or acceptor molecule is expected to be broader. Interestingly, PLDMR measurements on blends of m-MTDATA:3TPYMB and m-MTDATA:BPhen exhibit an additional information, a so-called half-field signal (Fig. S13). These signals arise from a spin-flip transition with a change of spin quantum number \(\Delta m_s = \pm 2\), i.e. between \(T_s\) and T. Zeeman states and are detected at half the magnetic field \(B_0/2\) of the full-field transition at \(B=B_0\). Their occurrence is unambiguous proof that the signal stems from a high spin state \(S>1/2\). Half-field transitions are much more likely to occur in triplets with a large dipolar interaction \(D\) (Weil2007), therefore we attribute the observed half-field signal to molecular triplets, rather than weakly bound triplet exciplexes.
An important consequence of the above assignment is that our experiments do not provide any evidence for the involvement of local triplets (1LE\textsubscript{D} or 3LE\textsubscript{A}) in the emergence of delayed fluorescence in electrically driven devices although our detection scheme is sensitive enough to probe them. Therefore, we cannot justify a scenario, in which the exciplex state couples to energetically higher lying local triplets via spin-orbit coupling (Dias2016, Santos2016), as in this case we would expect triplet signatures in ELDMR, too.

We now discuss the relationship between the width of the ELDMR/PLDMR lines and the spatial separation of electron and hole, which form a bound state. From EPR spectra, the distance between electron and hole \(r_{e-h}\), can be estimated by the following equation (Jeschke2002):

\[
r_{e-h}[\text{nm}] = \frac{3}{\sqrt{2\pi W_{\text{WHM}}}} \text{nm}
\]

Here \(r_{e-h}\) is obtained in units of nm, if \(D\) is used in units of mT. We use FWHM as an upper limit for \(2D\), as we cannot fully exclude other mechanisms of the EPR line broadening, e.g. unresolved hyperfine interactions with surrounding nuclei. Consequently, a lower boundary for \(r_{e-h}\) can be calculated by using Eq. (2). From the FWHM of our ELDMR spectra, one finds \(2D \leq 3\) mT resulting in \(r_{e-h} \geq 1.2\) nm (electrical generation), while for the narrow PLDMR component we estimate \(2D \leq 2\) mT resulting in \(r_{e-h} \geq 1.4\) nm (optical excitation). The broad 3LE PLDMR component yields \(2D \leq 6\) mT resulting in \(r_{e-h} \geq 1.0\) nm. These numbers can be explained by the different triplet formation mechanisms for electrical injection and optical excitation. Fig. 4d shows an illustration of the triplet exciton formation in the case of electrical generation. Here electrons and holes form exciplex triplets (1Exc) in the emission layer, which consists of a mixture of donor and acceptor molecules (see also Fig. 1a). Attar et al. reported that a voltage which is applied to a mixed m-MDATA:3TPYMB layer broadens the distribution of distances between electrons and holes forming exciplex states (Attar2016). Depending on the orientation of the exciplex dipoles with respect to the E-field, the electrostatic force causes either their compression (Fig. 4d (i)) or expansion (Fig. 4d (ii)), which leads to a broadening of the distribution of the electron hole radii. According to Equation (2), this leads to a distribution of the dipolar-coupling energies \(D\) and thus to a broadening of the ELDMR line. In contrast, PLDMR probes triplet states formed via ISC after optical excitation, i.e. without applied voltage. The respective processes are illustrated in Fig. 4e. Initially excited donor singlets (1LE\textsubscript{D}) can diffuse and undergo ISC to form a molecular triplet (3LE\textsubscript{D}) on the donor (Fig. 4e (i)). In this case, electron and hole are on the same molecule resulting in a broad PLDMR spectrum. Alternatively, excited singlets can undergo CT to form a singlet exciplex state (1Exc) (Fig. 4e (ii)). One of the two processes, or both together appear to be very efficient since we do not observe any emission from the donor phase in the blended m-MDATA:3TPYMB film (Fig. 2a). Magnetic field effect studies on m-MDATA:3TPYMB blends report that optically excited exciplex states can diffuse over
distances of up to 10 nm within the film, while the electron-hole distance increases during this diffusion process (Deotare2015, Hontz2015) (Fig. 4 e (iii)). The consequence for PLDMR would be that the dipolar interaction $D$ and the linewidth decrease, yielding the narrow component. Furthermore, the exciplex state can also be a precursor for the formation of free electrons and holes (Fig. 4 e (iv)). This process is expected to be similar to the generation of charge-separated states in organic solar cells, where a donor:acceptor interface significantly increases the yield of the free charge carriers (Sariciftci1992, Yu1995). To check this, we illuminated the m-MTDATA:3TPYMB OLED with the simulated AM1.5G sunlight and measured a photoinduced short-circuit current density $J_{SC}$ of 0.072 mA/cm$^2$ (see Fig. S14 for more details). The photovoltaic effect is not very strong, but it clearly shows the presence of free charges, which can have far-reaching consequences, as we will discuss below.

An increased generation of local triplets deserves some attention. As we previously mentioned, the CT and ISC compete, particularly in donor:acceptor blends. According to (Marcus1956), CT is mediated by molecular vibrations, therefore at low temperatures ISC should become a more efficient generation path for local donor triplets that yield the broad PLDMR signal (Fig. 4b). However, in pristine m-MTDATA, PLDMR is negligibly small compared to the signal observed in the m-MTDATA:3TPYMB blend (see Fig. S15), indicating that the ISC rate in m-MTDATA is very low, but charge transfer is not expected there. It can therefore be suggested that singlet exciton-polaron interaction is responsible for ISC in blends. In other organic materials singlet-exciton polaron interaction has been observed in the form of fluorescence quenching (Lim2003, Romanovskii2001). In our case the interaction facilitates ISC whereby the change in angular momentum associated with ISC is compensated by a flip of the polaron spin, similar to what has already been reported for RISC caused by triplet-exciton polaron interaction (Obolda2016, Song2010).
FIG. 5. Energy diagrams of excitation pathways a) Excitation of exciplex singlet (1Exc) and triplet (1Exc) via electrical generation in OLED devices. 1Exc can decay directly emitting prompt fluorescence (PF), while RISC between 1Exc and 1Exc enables delayed fluorescence (DF). In ELDMR a single Gaussian line is observed which is attributed to the exciplex triplet. b) Population of donor singlets (1LE0) via optical excitation. Depopulation via CT to exciplex singlet (1Exc) and charge carrier mediated ISC to donor triplet (1LE0). Subsequent ISC of 1Exc populates 3Exc. These triplets can be upconverted back to singlets, enabling DF. Donor triplets (1LE0) formed via ISC can populate 3Exc via CT. In PLDMR a broad signal of the donor triplet and a narrow signal of the exciplex triplet is observed.

Fig. 5 summarizes the excitation pathways of singlet and triplet states for electrical generation and optical excitation. Exact energies of singlet and triplet states for all studied donor:acceptor systems are shown in Fig. S12, however the relative positions of the energy levels in Fig. 5 are representative for all investigated systems. In an electrically driven OLED, free charges are injected to form excitons in the emissive layer. As presented in Fig. 5a, the exciplex singlet (1Exc) and triplet (1Exc) are the energetically lowest states within the system, which is why they are preferably populated in a 25:75 ratio. Singlets decay immediately as prompt fluorescence (PF) whereas triplets can undergo thermally activated RISC giving rise to delayed fluorescence (DF). In ELDMR, spin-flip transitions in the exciplex triplet significantly reduce EL intensity by intensifying the non-radiative triplet decay channel. Neither can the emission of molecular singlet excitons in the EL spectrum of an OLED be observed, nor can characteristic signatures of molecular triplets be found in ELDMR. Therefore, triplets of pristine materials (1LE0 or 3LE0) are hardly involved in the light generation mechanism of electrically driven devices.

Another scheme can be drawn for the optical excitation of the donor:acceptor blends studied in our work, as illustrated in Fig. 5b. Here the UV excitation at 365 nm first generates singlet excitons on donor molecules (1LE0), while the acceptor molecule with an even larger band gap cannot be excited at this wavelength. The singlet exciton of the donor undergoes either charge carrier mediated ISC to the donor triplet state (1LE0) or CT, which forms the exciplex singlet (1Exc) on a picosecond time scale. Donor triplets subsequently undergo CT to exciplex triplets (1Exc). Exciplex singlets (1Exc) decay radiatively as PF or form exciplex triplets (1Exc) via ISC. Finally, the exciplex triplets are upconverted back to singlet exciplexes via thermally-activated RISC, giving rise to DF. In PLDMR, the exciplex triplets appear as a narrow signal, which is almost identical to the ELDMR signal. A broad component in PLDMR is due to the molecular triplet exciton on the donor molecule, however it’s population is strongly temperature dependent. Note that the molecular triplets on the acceptor molecules were not considered in the scheme because they could not be generated with the available excitation energy.

VI. Conclusions

We applied three different spin-sensitive techniques in order to reveal the role of spin-bearing excited states in the light generation mechanism of TADF-based films and OLEDs. In the case of electrical injection of charge carriers
in the donor:acceptor emissive layer, which leads to EL, we found a characteristic signature of the triplet exciplex states ($^3$Exc), both in EL and in electrically detected magnetic resonance. By driving spin-flip transitions within triplet exciplex states the EL intensity changes by up to 1%. This is much higher than what is expected from the Boltzmann statistics at room temperature. From the temperature dependence, we deduced the activation energy of this process, which depends strongly on the donor:acceptor combination and is between 16 and 58 meV. We have assigned this characteristic energy to a singlet-triplet gap and the underlying mechanism of up-conversion to RISC. The underlying TADF mechanism includes a kinetic singlet-triplet exchange based on the g-factor difference, which ensures the conservation of angular momentum, while energy conservation is ensured by a thermal energy supply. As no molecular triplets are observed in the OLED experiments, we suppose they cannot be excited electrically. In the case of optical excitation of donor:acceptor films, the signature of triplet exciplex states ($^3$Exc) is observed in PL and it is similar to the one observed in EL from OLEDs. Additional spectral features from the triplet excitons localized on the donor molecules ($^3$LE) are also found, but their appearance strongly depends on the material system and on the temperature. Our experiments clearly show that the excited state which is majorly responsible for the occurrence of TADF in donor:acceptor systems is the triplet exciplex state ($^3$Exc). Molecular triplet excitons do not show up at all in efficient OLEDs, but only appear under optical excitation and in some systems mainly at low temperatures. We also emphasize the importance of comparative spin-sensitive, temperature-dependent PL and EL measurements, since the intermediate generation and recombination pathways may differ substantially.
Methods

The materials m-MTDATA and BPhen were purchased from Sigma-Aldrich. 3TPYMB was purchased from Lumtec (Luminescence Technology Corp.). THCA was supplied by A. Dabuliene and Prof. J. V. Grazulevicius from the Department of Polymer Chemistry and Technology at Kaunas University of Technology, Radvilenu pl. 19, LT-50254 Kaunas, Lithuania. All materials were used as received.

An overview of all studied samples, their preparation and measurements is given in the SI in Table S1.

PL samples were prepared by evaporating the emitting layer onto glass substrates. Evaporation rates for all organic materials were 1 Å/s for PL and all other samples. PL and photoexcitation spectra were measured with a calibrated fluorescence spectrometer FLS980-s (Edinburgh Instruments) equipped with continuous broad-spectrum xenon lamp Xe1. Time-resolved PL images were taken with a Streak Camera C5680 (Hamamatsu Photonics) using the second harmonic (400 nm) of MaiTai laser (Spectra-Physics) as an excitation source.

PLDMR was measured either on the same samples as for PL or samples were prepared from solutions of the materials in chlorobenzene. Both sample preparations yielded the same PLDMR results. For solution processing ~100 µl were poured into EPR quartz tubes and the solvent was then evaporated by vacuum pumping. The sample tubes were subsequently sealed under inert helium atmosphere.

PLDMR measurements were done in a modified X-Band spectrometer (Bruker E300, see Fig. S16). The sample tube was inserted into an EPR microwave cavity with optical access (Bruker ER4104OR) and an Oxford cryostat (ESR900). Optical excitation was provided by a 365 nm UV LED. The PL was detected by a silicon photodiode placed in front of the cavity behind a 409 nm longpass filter.

All OLED devices were fabricated on indium tin oxide (ITO) covered glass substrates (1 cm²). First, poly(3,4-ethylenedioxythiophene):polystyrylsulfonate (PEDOT:PSS, 4083Ai) from Heraeus was spin coated, resulting in a 40 nm thick film. All further device fabrication steps were done inside a nitrogen glovebox to avoid degradation, starting with annealing of the PEDOT:PSS layer for 10 minutes at 130 °C. For m-MTDATA:3TPYMB devices, 30 nm donor and 30 nm acceptor were thermally evaporated in an evaporation chamber with an additional 70 nm mixed layer (1:1) in between the pristine material layers. For THCA:BPhen devices, THCA was spin-coated from chlorobenzene solution yielding a layer thickness of 50 nm followed by evaporation of a 40 nm BPhen layer (bilayer device). For m-MTDATA:BPhen both methods were used yielding identical results for the spin-dependent EDMR and ELDMR measurements. The top electrode for all devices was evaporated (5 nm Ca / 120 nm Al), completing OLEDs with 3 mm² each. Evaporation rates for Ca were 0.3 Å/s and for Al 3 Å/s. For determination of layer thicknesses in spin coated and evaporated materials, a film of the material was scratched with a scalpel and the depth of this scratch was measured with a profilometer (Veeco Dektak 150).

EL spectra were recorded by biasing the OLED 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 a SPM002 spectrometer (Photon Control).

External quantum efficiencies were determined by placing an OLED at a distance of 20 mm from a 1 cm² area Hamamatsu S2281 Si photo detector. The OLED was forward biased via an Agilent 4155C parameter analyzer and the Si photodiode current was collected by the same. Knowledge about the spectral distribution of the OLED emission, the spectral response of the Si-photo detector, and the assumption of a lambertian emitter, allowed determination of the absolute EL photon flux from the OLED and the calculation of the external quantum efficiency of the OLED.

ELDMR measurements were either done in the microwave cavity (bilayer devices of THCA:BPhen and m-MTDATA:BPhen) or devices were placed in contact to a microwave transmission line (co-evaporated devices of m-MTDATA:BPhen and m-MTDATA:3TPYMB) (see Fig. S17). This changes slightly the ELDMR intensity due to different coupling of microwave field intensity to the OLED. Signal shape and analysis are however unaffected. The EL was detected by a silicon photodiode. For all OLEDs constant current (for ELDMR) or constant voltage (for EDMR) forward bias was provided by a source-measure unit (Keithley 237). For all ELDMR, PLDMR and EDMR measurements EL, PL and bias currents were fed to a current-voltage transimpedance amplifier (Femto). The signal change upon resonant microwave irradiation was then detected via a lock-in-amplifier (SR7230) with the on-off modulated microwave as reference.
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Author contributions
N.B., S.W., A.S. and V.D. designed the experiments. N.B., S.W., B.K. and J.G. prepared the devices. N.B., S.W., B.K. and J.G. carried out electro-optical device characterization. N.B., S.W., B.K. J.G and A.S. performed the magnetic resonance measurements. L.K. measured photoexcitation spectra and TRPL. A.S. and V.D. supervised the research project. N.B., S.W. and A.S. evaluated the data and wrote the manuscript together with VD, which all authors discussed and commented on.

Competing Financial Interests statement
The authors declare no competing financial interests
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