

## MATERIALS SCIENCE

# Long-lived spin-polarized intermolecular exciplex states in thermally activated delayed fluorescence-based organic light-emitting diodes

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Spin-spin interactions in organic light-emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) are pivotal because radiative recombination is largely determined by triplet-to-singlet conversion, also called reverse intersystem crossing (RISC). To explore the underlying process, we apply a spin-resonance spectral hole-burning technique to probe electroluminescence. We find that the triplet exciplex states in OLEDs are highly spin-polarized and show that these states can be decoupled from the heterogeneous nuclear environment as a source of spin dephasing and can even be coherently manipulated on a spin-spin relaxation time scale  $T_2^*$  of 30 ns. Crucially, we obtain the characteristic triplet exciplex spin-lattice relaxation time  $T_1$  in the range of 50  $\mu$ s, which far exceeds the RISC time. We conclude that slow spin relaxation rather than RISC is an efficiency-limiting step for intermolecular donor:acceptor systems. Finding TADF emitters with faster spin relaxation will benefit this type of TADF OLEDs.

## INTRODUCTION

The technological development of organic light-emitting diodes (OLEDs) has undergone remarkable progress, and the market share of OLED displays in television and smart device applications is growing steadily. Initially started with fluorescence-based emitters with a maximum internal quantum efficiency (IQE) of 25%, phosphorescent molecular emitters with enhanced spin-orbit coupling (SOC) enabled much higher device efficiencies through singlet-to-triplet intersystem crossing (ISC) (1–4). To achieve 100% IQE with molecular systems that do not contain heavy elements, the concept of thermally activated delayed fluorescence (TADF), originally known as E-type delayed fluorescence (5–8), has been successfully used in devices and substantially affected OLED development over the past decade (9–11). In the TADF or E-type delayed fluorescence process, the first excited singlet state is populated by a thermally activated transition from the first excited triplet state. The mechanism for harvesting nonradiative triplet states is described as reverse ISC (RISC) (12–16). Upon injection of electrons and holes from the contacts into the active layer, which consists of donor and acceptor molecules, intermolecular exciplex states are formed. In general, such Coulomb-bound quasiparticles can be in either the singlet ( $S = 0$ ) or triplet ( $S = 1$ ) state, where the latter should, in principle, be accurately described by the spin Hamiltonian and can also be selectively controlled, e.g., by an external magnetic field or electron paramagnetic resonance (EPR), to track the population transfer to the singlet manifold. Of the two possible spin orientations of the exciplex state, EPR can selectively influence (flip) only triplet states, while the effect of the spin-flip is observed in a change of a radiative singlet exciplex state recombination. The missing puzzle piece is the connection between these two spin states, as RISC is a first-order spin-forbidden process (17–20). However, it can be thermally activated, i.e., as a result of electron-phonon interactions or through

the admixture of other spin states, which, for example, enhance SOC, through a  $\Delta g$ -mechanism (21–23), or due to hyperfine interaction (HFI) with paramagnetic nuclei (protons, nitrogen, etc.). In a spin-resonance experiment, microwaves with a properly chosen energy (frequency) flip the spin orientation and connect the  $m_s = \pm 1$  and  $m_s = 0$  substates of a triplet exciplex, which, in turn, facilitates population transfer to an emissive singlet exciplex final state. However, the underlying spin physics is quite complex as the spin-spin interactions in such electron-hole pairs depend strongly on the molecular environment, as well as on the details of how these excited states are created, e.g., optically excited or by injection from electrodes (24, 25). Furthermore, the strength of the spin-spin interaction determines the energy gap between the states  $m_s = 0$  and  $m_s = \pm 1$ , the so-called zero-field splitting (ZFS), and in practice is given by the spatial distance. As expected, the radii of the e-h pairs in the disordered organic systems have a very broad distribution. Thus, the sought-after spectroscopic precision of EPR methods for manipulating spin states is compromised by the fact that the excited spin pairs [charge transfer (CT) states, exciplexes] are broadly distributed in a heterogeneous mixture of molecules, leading to inhomogeneously broadened envelopes instead of discrete resonance transitions (spin flips) and complicating access to the parameters of the spin Hamiltonian.

Here, we analyze the role of spin-spin interactions in the electroluminescence (EL) emission of an OLED using the method of EL detected magnetic resonance (ELDMMR). We were able to disentangle the complexity associated with a broad distribution of spin pairs and propose an original technique to select sub-ensembles of e-h pairs and reconstruct the details of the inhomogeneously broadened ELDMMR envelope in this way. For this purpose, a two-frequency hole-burning experiment is used, which pumps and saturates the spin system at a fixed frequency during the second probe frequency sweep (26–29). This pump-probe method allows not only the separation and addressing of individual spin packets in the inhomogeneously broadened ELDMMR spectrum but also the observation of coherent population oscillations (CPOs), which are observed as

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spikes with a very narrow linewidth (26–35). The hole-burning effect is caused by decoupling of the triplet exciplex spin state from the heterogeneous molecular environment, while the CPO can be described as a two-level quantum system oscillating with the beat frequency between pump and probe. The observation of CPO implies highly spin-polarized exciplex triplet states, which are not at all expected in an electrically driven OLED, where injected charge carriers are generally not spin-correlated.

## RESULTS

### Spin-spin interactions in OLEDs

The results presented in this work were obtained on OLEDs based on the donor:acceptor system m-MTDATA:BPhen {4,4',4''-tris[phenyl(*m*-tolyl)amino]triphenylamine:4,7 diphenyl-1,10-phenanthroline} in a device configuration of PEDOT:PSS (40 nm)/m-MTDATA (30 nm)/m-MTDATA:BPhen (70 nm, 1:1 ratio)/BPhen (30 nm)/Ca (5 nm)/Al (120 nm), as shown in Fig. 1A. With the pure m-MTDATA and BPhen layers as hole and electron transport layers, PEDOT:PSS [poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)] was used as a hole injection layer and a mixed layer of m-MTDATA and BPhen was used as an emission layer. Typical *j*-*V*-EL and external quantum efficiency (EQE) curves are shown in fig. S1. The photoluminescence (PL) spectra of the pure materials are shown in Fig. 1B. The EL spectrum of the device made from the mixed layer is red-shifted and much broader compared to the emission spectra of the pristine molecules. The former is due to the formation of a bound exciplex state at the interface of the two molecules, with the electron localized at the lowest unoccupied molecular orbital (LUMO) of the acceptor BPhen and the hole localized at the highest occupied

molecular orbital (HOMO) of the donor m-MTDATA, as schematically shown in the inset of Fig. 1B (36–39). The much larger width is probably due to the broad energetic distribution of the emitting states, which we address below.

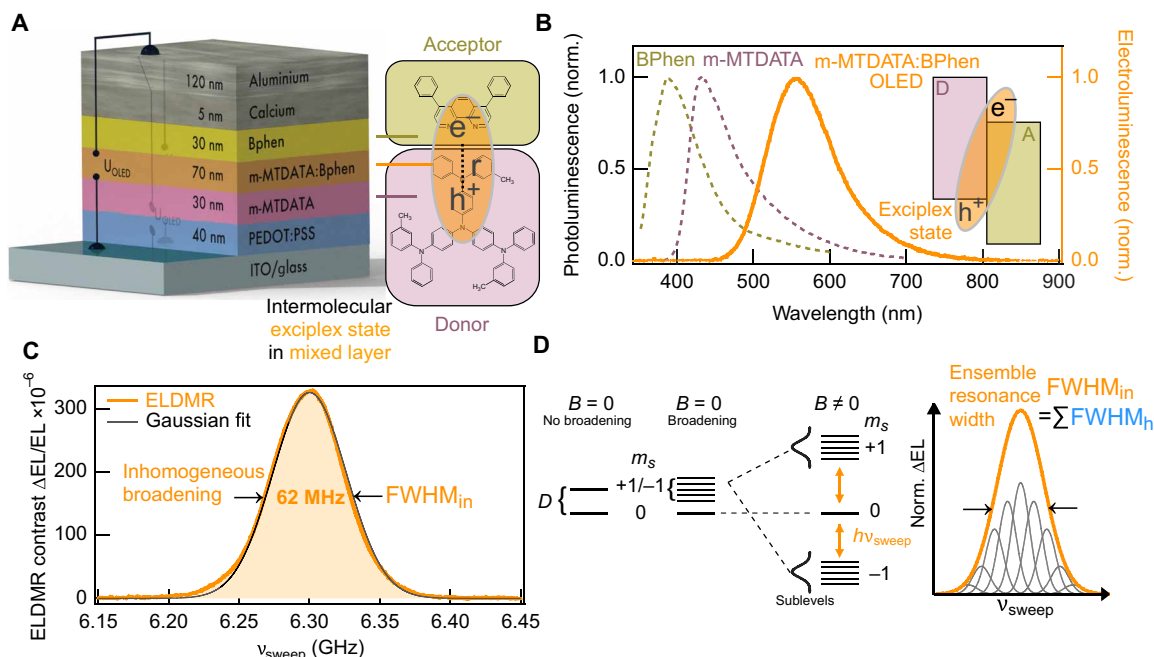
The electron and the hole both have a spin of  $S = 1/2$ . If these particles form a bound exciton or an exciplex (which we consider equivalent to a CT state), the total spin will be either  $S = 0$  or  $S = 1$ . The Hamilton operator describing the triplet state is according to (40)

$$\mathcal{H} = \underbrace{-S_a^T J S_b}_{\text{exchange}} + \underbrace{g \mu_B S \vec{B}}_{\text{e-Zeeman}} + \underbrace{S^T \mathbf{D} S}_{\text{ZFS}} + \underbrace{S^T \mathbf{A} I}_{\text{HFI}} \quad (1)$$

The first interaction term describes the exchange interaction of the two spins  $S_a, S_b$  through the orbital overlap of their wave functions, where the exchange integral  $J$  determines the energy gap  $\Delta E_{ST}$  between singlet and triplet energy levels. The second term is the electron-Zeeman interaction with the static external magnetic field  $B$ , the Landé factor  $g$ , the Bohr magneton  $\mu_B$ , and the spin operator  $S$ . The third and fourth terms describe spin-spin interactions: the electron-spin ZFS and the electron-nuclear HFI, with their respective tensors  $\mathbf{D}$  and  $\mathbf{A}$ . Quadrupole interaction and nuclear Zeeman splitting are neglected in this work because their contribution is negligible. A schematic representation of ZFS and broadening due to HFI is shown in Fig. 1D. The  $m_s = 0$  and  $m_s = \pm 1$  triplet states are split by the ZFS parameter  $D$  (in frequency units) (41)

$$D/h = -\frac{\mu_0 \mu_B^2 g_a g_b}{4\pi \hbar r_{ab}^3} (3 \cos^2 \theta - 1) \quad (2)$$

Here,  $\mu_0$  is the vacuum permeability,  $g_a$  and  $g_b$  are the Landé factors for spins  $a$  and  $b$ , and  $\theta$  is the angle between the direction of the



**Fig. 1. Magnetic resonance on OLEDs.** (A) Schematic of the m-MTDATA:BPhen OLED architecture. (B) Photoluminescence spectra of pure materials (left axis, dashed lines) and electroluminescence (EL) spectrum of an OLED device (right axis, solid orange line). The inset shows a bound exciplex state formed at the donor:acceptor interface. (C) EL detected magnetic resonance (ELDMR) spectrum (orange line) of the m-MTDATA:BPhen OLED in a magnetic field of  $B = 225$  mT and a Gaussian fit (black line) with FWHM of 62 MHz. (D) Triplet sublevels with zero-field splitting  $D$  may exhibit broadening due to HFI. The sublevels split in an external magnetic field, and under resonant microwave irradiation with frequency  $\nu_{\text{sweep}}$ ,  $\Delta E_L$  is detected, which, as we will show later, is the envelope of the sum of homogeneous subspectra.

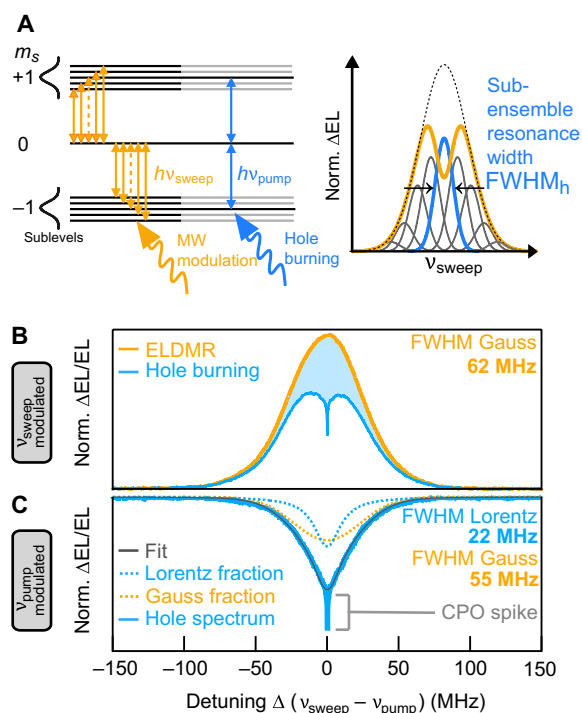
magnetic field and the radius vector  $r_{ab}$  connecting the two spins. The HFI term is given by the interaction of the exciplex triplet with surrounding paramagnetic nuclei represented by the nuclear spin operator  $I$ . This leads to a further splitting of the  $m_s = \pm 1$  sublevels, where each nucleus contributes with  $A_{0,i}$  and the HFI term in Eq. 1 is extended by the summation over all nuclei. The total number  $N_{\text{tot}}$  of HFI sublevels for  $i$  nonequivalent nuclei is then given by  $N_{\text{tot}} = (2I + 1)^i$ . For  $i$  equivalent nuclei, several HFI levels degenerate and the total number is given by  $N_{\text{eq}} = (2iI + 1)$  (42).

In conventional EPR, the external magnetic field is swept at a fixed microwave frequency, resulting in microwave absorption and spin-flip in the sample if the resonance criteria are met. For the ELDMR method used in this work, we couple an OLED to a stripline circuit that serves as an antenna for the frequency-swept microwaves at a fixed magnetic field. The strength of the effect is evaluated by the ELDMR contrast  $\Delta\text{EL}/\text{EL}$ . A detailed description of ELDMR can be found in previous publications (24, 25), where also the singlet-triplet energy gap  $\Delta E_{\text{ST}} = 58$  meV was estimated for the MTDATA:BPhen blends, which is, by far, the largest energy contribution among the spin-spin interaction terms in Eq. 1. An example ELDMR spectrum of an m-MTDATA:BPhen OLED device at  $T = 220$  K is shown in Fig. 1C, with the microwave frequency  $\nu_{\text{sweep}}$  swept from 6.15 to 6.45 GHz at fixed magnetic field  $B = 225$  mT. The spectrum exhibits a featureless shape, which can be fitted with a Gaussian with a full width at half maximum (FWHM) of 62 MHz. This indicates that the ELDMR spectrum is inhomogeneously broadened. The working hypothesis that we verify in the following is that we are dealing with an ensemble of triplet states with different spin-spin interaction parameters and thus transition frequencies, showing up themselves as a featureless envelope, as schematically shown in Fig. 1D. With knowledge of the details of the broadening of the ELDMR spectrum, e.g., due to the distribution of the spin-spin interaction, the broadening of the EL spectrum can also be better understood and potentially eliminated once it is assigned to a controllable structural or morphological parameter.

### Hole-burning spectroscopy

To explore the origin of spectral broadening, we apply a two-frequency ELDMR technique realized by introducing a second frequency ( $\nu_{\text{pump}}$ ) fixed within the ELDMR spectrum while simultaneously sweeping the frequency  $\nu_{\text{sweep}}$  during the measurement, as schematically shown in Fig. 2A. As illustrated, a dip occurs when a sufficiently high-power pump microwave field saturates a transition between triplet spin sublevels (see figs. S2 and S3). The width of the dip is associated to the energetic span of the sublevels in the energy diagram (Fig. 2A) (26, 27, 30–35). In Fig. 2B, a continuous wave ELDMR spectrum is shown (orange curve). Applying the second microwave frequency results in a dip at the position of the applied pump frequency of  $\nu_{\text{pump}} = 6.3$  GHz (Fig. 2B, blue curve). This so-called hole-burning technique is widely used in optical absorption and fluorescence spectroscopy, as well as in spin resonance, but it has never been reported for ELDMR (28, 29, 43–45).

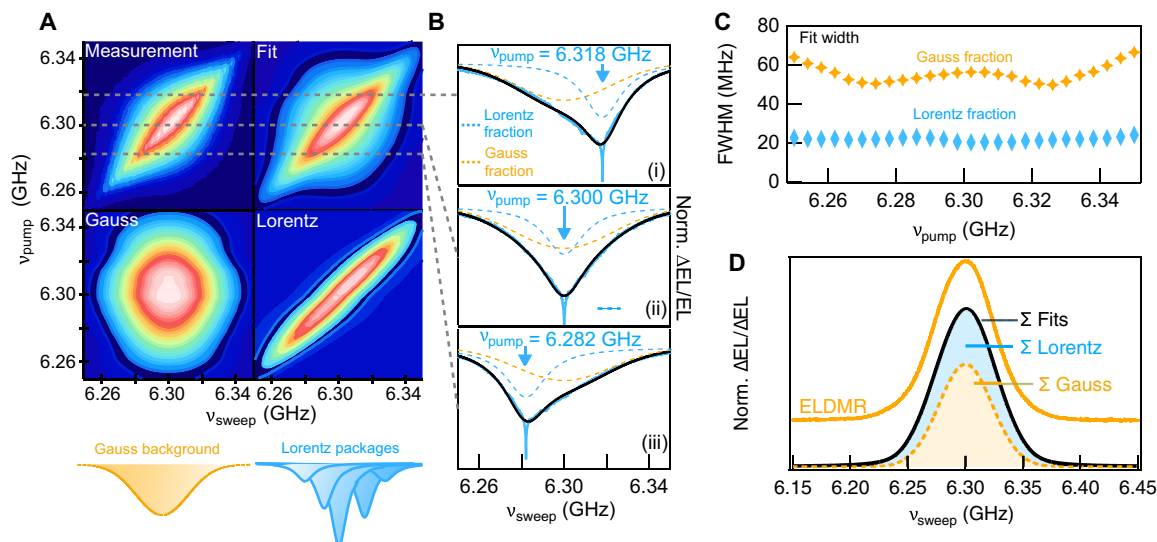
To directly unveil the shape of the "spectral hole" shown in Fig. 2B, we now modulate the pump frequency. The resulting spectrum in Fig. 2C has a distinct broad shape with a narrow spike on top. The latter is assigned to CPO, whose origin will be discussed in detail later. The broad spectrum can be perfectly fitted by the sum of Gauss and Lorentz functions with FWHM linewidths of 55 and 22 MHz, respectively, represented by the dotted lines in Fig. 2C. Note



**Fig. 2. ELDMR hole burning.** (A) Schematic of the energetically broadened triplet sublevels with resonance transitions induced by a variable (orange arrows) and fixed microwave (MW) frequency (blue arrows) and hole burning in an inhomogeneously broadened ensemble. (B) ELDMR spectrum (orange) and hole-burning spectrum (blue) of m-MTDATA:BPhen for a frequency sweep of  $\pm 150$  MHz around  $\nu_{\text{pump}} = 6.3$  GHz. The sweep frequency  $\nu_{\text{sweep}}$  is modulated "on-off" for lock-in detection, and the pump frequency  $\nu_{\text{pump}}$  is kept in continuous wave mode. (C) Directly measured hole spectrum by modulating the fixed frequency ( $\nu_{\text{pump}}$ ) instead of the sweep frequency ( $\nu_{\text{probe}}$ ). The signal consists of a broad Gaussian background (FWHM of 55 MHz), a narrower Lorentzian peak (FWHM of 22 MHz), and a very narrow spike in the center (FWHM of 12 kHz). The fitting curve (black) is a superposition of a Gaussian (dotted orange) and a Lorentzian (dotted blue) contribution.

that the "hole" spectral shape is independent of which of the two frequencies is on/off modulated,  $\nu_{\text{sweep}}$  or  $\nu_{\text{pump}}$ , but because the pump frequency directly saturates a particular transition in the triplet sub-ensemble, we have used it in Fig. 2C and in the following.

To investigate the structure of the hole in more detail, we varied the pump frequency, as shown in Fig. 3. It shows a two-dimensional map in which the hole spectra are recorded as a function of  $\nu_{\text{pump}}$  and  $\nu_{\text{sweep}}$  in a frequency range from 6.25 to 6.35 GHz. The analysis shows that the hole spectrum can be decomposed into two contributions, Gaussian and Lorentzian. Furthermore, the Lorentzian contribution can be moved through the entire ELDMR spectrum, while the Gaussian contribution remains constant. The individual fits to the hole spectra are shown in fig. S4. Figure 3B exemplarily shows the corresponding cuts for three pump frequencies. When the pump frequency is shifted from the central  $\nu_{\text{pump}} = 6.3$  GHz to the side flanks, the holes become asymmetric, also indicating that the Gaussian background does not depend on  $\nu_{\text{pump}}$  (Fig. 3A, bottom left), but the Lorentzian line does (Fig. 3A, bottom right). However, the width of the Gaussian background (55 MHz) is slightly less than the total measured ELDMR linewidth, which is 62 MHz, which



**Fig. 3. Spectral analysis of the hole by varying the pump frequency  $\nu_{\text{pump}}$ .** (A) Color map of the hole spectrum as a function of  $\nu_{\text{sweep}}$  and  $\nu_{\text{pump}}$ . The fit map is the sum of the Gauss and Lorentz maps. The Gaussian contribution is centered at  $\nu_{\text{sweep}} = 6.30$  GHz, while the Lorentzian varies with  $\nu_{\text{pump}}$ , as shown schematically at the bottom. (B) Hole contributions as a function of  $\nu_{\text{pump}}$ . While the Lorentz line shifts with pump frequency, the Gaussian contribution remains fixed. (C) FWHM for Gauss and Lorentz contributions as a function of  $\nu_{\text{pump}}$ . (D) Reconstruction of the ELDMR signal from the Lorentzian and Gaussian contributions. The sum of all fits has the same linewidth and shape as the ELDMR spectrum.

could indicate a different origin. To verify this, we evaluated the two contributions separately and used them to reconstruct the experimental ELDMR spectrum. The individual linewidths for Gaussian and Lorentzian contributions are shown in Fig. 3C. While the Lorentz linewidth remains constant at 22 MHz and does not change with  $\nu_{\text{pump}}$ , the Gauss linewidth varies between 50 and 62 MHz in the applied range of pump frequencies. As shown in Fig. 3D, we can perfectly reconstruct the ELDMR spectrum by summing all contributions in the pump frequency range studied. This illustrates that the inhomogeneously broadened spectrum is the envelope of superimposed subspectra that can be revealed by hole-burning spectroscopy.

The fitted intensities of the Lorentz fraction can be further used to determine the dipolar interaction  $D$  of electron and hole within the exciplex as shown in fig. S5B. The fitted intensities reveal the underlying triplet spectrum without the Gaussian background, and this spectrum can be simulated with  $D = 50 \pm 5$  MHz. From  $D$ , we can also estimate the e-h separation within the exciplex (41) to be  $r_{e-h}$  [nm] =  $\sqrt[3]{78.05/D}$  [MHz] nm = 1.1 to 1.2 nm, i.e., matching the expected delocalization over neighboring molecules. The coupling distance of emissive exciplex states is therefore quite uniform.

This analysis shows that the inhomogeneous broadening of the ELDMR spectrum is not due to a broad distribution of triplet exciplex states with different e-h separations and thus dipolar interactions. Instead, we propose spectral diffusion of overlapping spin packets as a reason for unresolved HFI, which has also been reported for other spin systems, e.g., for color centers in diamonds (27), and which we discuss in the following. The same process is responsible for the inhomogeneous broadening and thus for the Gaussian background.

### Inhomogeneous spectral broadening by unresolved HFI

With the hole-burning method, we revealed an underlying homogeneous linewidth and identified an additional inhomogeneous Gaussian broadening. For this broadening, we can exclude effects

due to high microwave power and the  $\Delta g$ -mechanism as shown in detail in the Supplementary Materials. In the following, we will show that it can be assigned to unresolved HFI with paramagnetic nuclei in the molecules. For m-MTDATA:BPhen, this includes  $i_H = 64$   $^1\text{H}$  protons with a nuclear spin of  $I = 1/2$  and  $i_N = 6$   $^{14}\text{N}$  nitrogen nuclei with  $I = 1$ , while other paramagnetic isotopes have negligible abundance. The isotropic hyperfine coupling constant  $A$  depends on the electron-nuclei wave function overlap—the Fermi contact interaction (46). In organic molecular systems, e-h wave functions delocalize, involving more interacting nuclei but decreasing the average HFI (motional narrowing) (47–49). Electron-proton HFI  $A_H$  is usually weak and unresolved, leading to inhomogeneous broadening (50–54). For exciplexes in a similar TADF system,  $A_{H,\text{max}} < 5.5$  MHz was determined as an upper limit (55), whereas for charge-separated states in polymer:fullerene blends,  $A_{H,\text{max}}$  of 2 to 3 MHz (50) or 4 to 5 MHz (51) was estimated. Considering the large molecular extent of m-MTDATA:BPhen and that protons at the edges of molecules are not part of the conjugated electron system, we can expect  $A_H < 2$  MHz. HFI with a discrete number ( $i_N = 4$ ) of  $^{14}\text{N}$  nuclei directly incorporated in the conjugated system of triphenylamine derivatives has been determined to be  $A_N = 2.5$  to 3.8 MHz (56). We performed exemplary HFI simulations (57) of the exciplex triplet with  $i_N = 6$   $^{14}\text{N}$  as presented in the Supplementary Materials and estimate  $A_N < 2$  MHz.

The unresolved and weak HFI in m-MTDATA:BPhen can explain the inhomogeneous linewidth broadening. More intriguing, however, is the fact that  $A_{H,N} < 2$  MHz is considerably smaller than the ZFS  $D < 50$  MHz. This suggests that HFI is too weak to mediate RISC rates as the exciplex triplet is decoupled from the nuclear spin bath by the stronger ZFS  $D$ .

### CPOs of spin-polarized exciplex states

In a hole-burning experiment, we apply two microwave fields to the spin system. From a classical viewpoint, when two electromagnetic

waves with nearby frequencies interfere, a beat oscillation of intensity occurs with the beat frequency  $\Delta\nu = \nu_{\text{sweep}} - \nu_{\text{pump}}$ , where  $\Delta\nu$  is the detuning between pump and probe frequencies (see fig. S9). While the application of a single microwave resonance frequency tends to equilibrate the population of spin sublevels, the simultaneous application of two frequencies to a highly spin-polarized system can cause the triplet population to oscillate, especially when the beat frequency is in the range of or lower than the inverse spin relaxation time of the spin system. This CPO effect has been reported for various inorganic spin systems in the past (27, 44, 58, 59) and is also known from laser spectroscopy of two-level systems (60). In a lock-in detected ELDNR experiment, as in ours, these oscillations are time-averaged. This leads to a beat frequency  $\Delta\nu$ -dependent depth of the burned spectral hole. Spin relaxation is mediated by a longitudinal spin-lattice relaxation time  $T_1$  and a transverse dephasing time  $T_2^*$ , and they will determine the eigenfrequencies of the spin state. In the case of a forced oscillation with the variable beat frequency, the hole depth will be affected. In a continuous detuning scan, the beat frequency is varied from a few hertz to megahertz, and we observe such a very narrow spike on the top of the hole, as shown in Fig. 4. The homogeneous linewidth  $\text{FWHM}_h = 22$  MHz allows to estimate a lower limit for the dephasing time  $T_2^* > 2/(\pi \cdot \text{FWHM}_h) = 30$  ns, while the width of the spike corresponds to the spin-lattice relaxation time. The dephasing time agrees well with that estimated from pulsed Rabi experiments on similar OLED systems (55, 61).

When changing from frequency to time domain, one can assume a simple decay model. The net magnetization of a sub-ensemble of

$S = 1$  states formed at  $t = 0$  decays exponentially with the time constants  $T_2^*$  and  $T_1$ . In an external magnetic field, it is also undergoing precession with the Larmor frequency  $\nu_L = \omega_L/2\pi$ . Thus, we can write for the intensity of net magnetization of a sub-ensemble

$$I(t) = \left[ A \cdot \exp\left(-\frac{t}{T_2^*}\right) + B \cdot \exp\left(-\frac{t}{T_1}\right) \right] \cdot \sin(\omega_L \cdot t) \quad (3)$$

with amplitudes  $A$  and  $B$ , respectively. The fast Fourier transform (FFT) of this equation is shown in Fig. 4B. The fast decay due to  $T_2^*$  gives a broad signal, while the FFT of the long decay with  $T_1$  reproduces the spike. By zooming in on the spike in Fig. 4A, it turns out that the shape is more complex and cannot be perfectly fitted with a single Lorentzian function. The shape can, however, be fully reproduced by applying a modified three-level model of (27). This is possibly due to inhomogeneous broadening of the triplet sublevels involved, but the issue cannot be fully elucidated. For further details, we refer to the Supplementary Materials. We can nevertheless estimate  $\text{FWHM}_{\text{relax}} = 12$  kHz for the narrowest contribution as shown in Fig. 4C with which we can estimate an upper limit of the spin-lattice relaxation time  $T_1 < 2/(\pi \cdot \text{FWHM}_{\text{relax}}) = 50$   $\mu\text{s}$ . These measurements were performed at an experimental temperature of  $T = 220$  K. In between 290 and 160 K (fig. S12), we observed that  $T_1$  is not very temperature sensitive as it increases from 50 to 70  $\mu\text{s}$  when cooling. Modulation sidebands appear due to on-off modulation of the pump frequency with  $\nu_{\text{mod}} = 911$  Hz, which rules out the possibility that on-off modulation effects are responsible for contributions to CPO in the kilohertz to megahertz range. We also exclude  $\nu_{\text{mod}}$  to influence the determined  $T_1$  time by measuring with different modulation frequencies (see fig. S13).

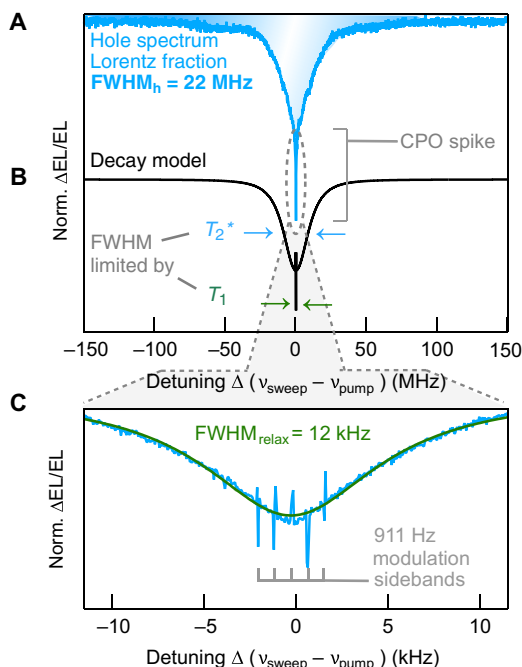
## DISCUSSION

### Interplay between RISC and spin relaxation of triplet exciplex states

In the following, we discuss the role of the determined spin-spin interactions and spin relaxation times in comparison with RISC time constants. Interaction strengths ( $A$ ,  $D$ , and  $g_{\mu_B B}$ ) and FWHM linewidths are given in frequency units, while time constants are always given in time units and not as rates.

The observation of CPO in the EL of working OLEDs is notable as it proves that the emitting exciplex states are highly spin-polarized. This is a remarkable finding as injected charge carriers are generally not spin-correlated and, upon recombination at the donor:acceptor interface, will populate the exciplex singlet and triplet  $m_s = 0, \pm 1$  sublevels evenly. Singlet states recombine on a nanosecond time scale, leaving the triplets to undergo RISC to facilitate delayed fluorescence. The fact that we observe spin-polarized exciplexes in electrically driven devices unambiguously teaches us that recombination of triplet exciplexes is highly spin-dependent with unequal RISC rates for the  $m_s = 0, \pm 1$  sublevels. The selection rules ( $\Delta S = \pm 1$ ,  $\Delta m_s = 0$ ) for transitions between singlet ( $S = 0$ ,  $m_s = 0$ ) and triplet ( $S = 1$ ,  $m_s = 0, \pm 1$ ) exciplex states would favor faster depletion of  $m_s = 0$  triplet exciplexes and can thus be responsible (compare fig. S6).

Spin polarization decays with the spin-lattice relaxation time  $T_1 < 50$   $\mu\text{s}$ , which by far exceeds RISC on the time scale of 30 to 220 ns for this material system (25). Similar  $T_1$  times around 30  $\mu\text{s}$  were reported for other OLED systems and even organic solar cells probed by electrically and optically detected magnetic resonance (62–65).



**Fig. 4. Coherent population oscillations.** (A) Lorentz fraction of the hole spectrum with CPO spike. We subtracted the Gaussian background (see Fig. 3A) for clarity. (B) FFT of the decay model in Eq. 3. The FWHM is limited by dephasing time  $T_2^*$  and spin-lattice relaxation time  $T_1$ . (C) Zoomed-in measurement of the hole spectrum. The spike can be described by one Lorentzian, which results from CPO between triplet levels due to microwave beating between  $\nu_{\text{sweep}}$  and  $\nu_{\text{pump}}$ .

A long spin relaxation time is hereby typical for organic materials with weak HFI and strong ZFS as this decouples the electron spin system from relaxation caused by the nuclear spin bath. Note that while the presented experiments are carried out in an external magnetic field that results in a triplet state Zeeman splitting of  $g\mu_B B = 6.3$  GHz, i.e., much larger than ZFS and HFI, the spin polarization mechanism will be identical even without applied magnetic field. The ZFS of  $D = 50$  MHz is sufficiently large to decouple the electron spin system from the nuclear spin bath in zero magnetic field, preserving a long  $T_1$  time. RISC time constants for other donor:acceptor exciplex (9, 66–69) and molecular TADF materials (70–73) were reported around 0.5 to 2  $\mu\text{s}$  (68–72) or up to 30  $\mu\text{s}$  (66, 67, 73), always being shorter or even significantly shorter than  $T_1$ . This imbalance between RISC and  $T_1$  time constants by up to more than an order of magnitude leads to spin polarization between  $m_s = 0, \pm 1$  levels, and we can thus assume it to be in the order of or greater than 90% ( $= 1 - \frac{T_{\text{RISC}}}{T_1}$ ). Therefore, in most TADF OLEDs, a strong spin polarization is expected, which unnecessarily prolongs the lifetime of the excited states. This may ultimately limit quantum efficiencies, especially at high OLED current densities, and lead to efficiency roll-off that is usually ascribed to triplet-triplet and triplet-charge annihilation (10, 12, 67). This finding strongly implies that spin polarization of triplets must be suppressed by a mechanism to accelerate spin relaxation.  $T_1$  can be substantially shortened by molecular curvature-enhanced SOC, as has been shown theoretically (74) and experimentally (75, 76). In addition,  $T_1$  scales with the  $\Delta g$ -mechanism as  $T_1 \sim (\Delta g)^{-2}$  (77). Both mechanisms can be used for the design of next-generation TADF systems.

In contrast to the long  $T_1$  time, the spin dephasing time  $T_2^* > 30$  ns is exceptionally short and actually limits the homogeneous linewidth  $\text{FWHM}_h = 22$  MHz. Such fast dephasing is often mediated by interaction with multiple, almost equally coupled nuclei (78), as in our case with nitrogen nuclei and protons. RISC is on the same time scale or even considerably longer than  $T_2^*$ , which means that spins will dephase quickly and RISC is not affected by a short  $T_2^*$ . Consequently, the ensemble of exciplexes in an OLED is highly incoherent, i.e.,  $T_2^*$  is short enough to not affect the operation of the OLED at all.

### Comparison with other donor:acceptor systems

Last, it is intriguing to compare the exciplex states in intermolecular TADF emitters studied here with excited states in other material systems, such as CT states in intramolecular TADF emitters and polymer:fullerene blends used in organic photovoltaics (OPV) (while exciplex and CT states are essentially the same kind of species). Both exciplex- and CT-based TADF emitter systems exhibit high IQEs and have singlet-triplet gaps  $\Delta E_{\text{ST}}$  in the range of thermal energy. However, dipolar interactions differ by at least an order of magnitude, with  $D > 500$  MHz determined for intramolecular TADF emitters (18, 20), indicating their stronger localization compared to the system studied here. In contrast, OPV CT states have an order of magnitude smaller dipolar interaction of  $D < 5$  MHz and  $\Delta E_{\text{ST}} < 5$  MHz, which corresponds to 20 neV, i.e., more than six orders of magnitude smaller than for TADF (79). This corresponds to a much wider excited state delocalization and a weaker oscillator strength. Hence, it is not unexpected that OPV CT states exhibit very low EL quantum efficiency in the order of  $10^{-6}$  (80). We conclude that the m-MTDATA:BPhen exciplex emitter with  $D = 50 \pm 5$  MHz and a singlet-triplet gap of  $\Delta E_{\text{ST}} = 58$  meV (24, 25) is an intermediate case, between highly emissive intramolecular TADF and poorly emissive

OPV CT states, revealing large or nearly zero dipolar interactions, respectively.

### Conclusion

In conclusion, we have experimentally shown that electrical injection of charge carriers into OLEDs based on the TADF system m-MTDATA:BPhen results in the buildup of a spin-polarized triplet exciplex population with long spin-lattice relaxation time. This phenomenon is initially due to spin-statistically injected charges in the devices but can be considered detrimental to OLED efficiency because these exciplex species are not undergoing RISC. The observation was made possible by implementing a novel two-frequency spin-resonance spectroscopy based on the so-called hole burning by direct monitoring of the EL intensity. We used it to observe CPOs that exhibit an EL spike of extremely narrow width, from which we not only prove >90% spin polarization itself but also estimate the spin-lattice relaxation time of 50  $\mu\text{s}$ , which is thus longer than the RISC time constants in this and similar TADF systems. Furthermore, our spin-resonance protocol provided insights into the inhomogeneously broadened triplet exciplex spectra consisting of individual sub-ensembles or “spectral holes” with a characteristic ZFS parameter  $D = 50 \pm 5$  MHz, indicating exciplex states of 1.1 to 1.2 nm extent, i.e., over adjacent donor:acceptor molecular pairs. The broadening is the result of the disordered nature of the molecular blends, but it can also be quantitatively understood as the result of unresolved HFIs with the surrounding protons and the nitrogen nuclei, and we provide an estimate of the strength of an averaged nuclear field that is in the range of 2 MHz. The fact that the spin relaxation time is much longer than the RISC time implies that the type of TADF OLEDs studied here is efficiency-limited due to the spin polarization, which needs to be suppressed by a mechanism to accelerate the relaxation, such as SOC. Our findings further put the commonly targeted small singlet-triplet gap and thus high RISC rate into perspective.

### MATERIALS AND METHODS

#### Device fabrication

For OLED devices, indium tin oxide (ITO)-covered glass substrates (Vision-Tek Systems) were used. The hole injection layer PEDOT:PSS (4083Ai, Heraeus) was spin-coated at 3000 rpm, resulting in a 40-nm-thick film. It is thermally annealed for 10 min at 130°C. Remaining layers are evaporated under vacuum. The hole transport layer (m-MTDATA) and electron transport layer (BPhen) have a thickness of 30 nm. In between, a 70-nm mixed layer of both materials is deposited as emission layer. A top electrode consisting of calcium (5 nm) and aluminum (120 nm) was used, resulting in an active area of 3 mm<sup>2</sup>.

#### Device characterization

*J-V-EL* and EQE characteristics were measured with a parameter analyzer (Agilent, 4155C), and a silicon photodetector was placed on top of the OLED.

#### Magnetic resonance

For ELDMR measurements, we used a modified EPR spectrometer (Bruker, ESP300) with a nitrogen flow cryostat (Oxford, 935). The temperature for all measurements was  $T = 220$  K, except for fig. S12. The microwaves are generated with a signal generator (Anritsu,

MG3694C). The output power for all measurements was set to 0 dBm, amplified by a 3-W amplifier (Mini-Circuits, ZVW-3W-183+). The OLED device was placed on top of a microwave stripline to enable spin control in the emission layer. A source measure unit (Keithley 237) drives the OLED in constant current mode ( $j = 1.6 \text{ mA/cm}^2$ ), and the EL is detected with a photodiode (Hamamatsu, S2387-66R) and amplified with a current-voltage amplifier (Femto, DLPCA-200). The change of EL upon resonant microwaves,  $\Delta\text{EL}$ , was detected with a lock-in amplifier (SR7265).

### Hole-burning spectroscopy

In a hole-burning experiment, the pump microwave generator (Synth HD, Windfreak) was amplified with a secondary 3-W amplifier. The outputs of both amplifiers are merged with a high-power combiner (Mini-Circuits, ZN2PD-183W-S+). Hole-burning spectra are detected by modulation of the sweep microwave generator. Direct detection of hole spectra is realized by modulation of the pump generator.

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <https://science.org/doi/10.1126/sciadv.abj9961>

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## Long-lived spin-polarized intermolecular exciplex states in thermally activated delayed fluorescence-based organic light-emitting diodes

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