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Influence of Excited-State Delocalization on Singlet Fission: Tuning Triplet-Pair-State Emission in Thin Films

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ABSTRACT: The coherent distribution of an electronic excitation over multiple organic molecules in the solid state, namely excited-state delocalization, plays an important role in photophysical processes such as singlet fission. However, experimental studies of the influence of excited-state delocalization on singlet fission have been challenging mainly for two reasons. First, there is no easy way of measuring the excited-state delocalization, and second, tracking the resulting changes for singlet fission is demanding due to the triplet-pair state, which is a crucial intermediate in singlet fission, being an optically dark state and hence hard to access experimentally. Binary systems offer a way to adapt the growth conditions of a singlet fission material, which enables tuning of the excited-state delocalization, possibly due to the impact of structural disorder on exciton



localization. By varying the growth conditions, we demonstrate that emission from the triplet-pair state via Herzberg–Teller coupling is detectable in films with low growth rates of the singlet fission material, while the triplet-pair state shows no luminescence in the other cases due to triplet dissociation outcompeting the luminescent decay. With this we find that triplet-pair state luminescence correlates with higher excited-state delocalization.

INTRODUCTION

Singlet fission is an electronic exciton multiplication process, which has the potential to overcome the Shockley-Queisser limit of single junction solar cells^{1,2} by converting one excited singlet state into a coupled triplet pair, which subsequently evolves into two independent triplet states.³ To bring singlet fission toward application in solar cells, it is crucial to minimize the impact of loss channels. This can be achieved by the first step, triplet-pair formation, and the second step, which can be either triplet dissociation or charge collection⁴ from the tripletpair state, outcompeting alternative deactivation pathways for each respective state.^{5,6} One of the most common ways to manipulate the triplet-pair formation rate of solid-state singlet fission materials is a modification of the molecular arrangement, either by introducing structural changes via chemical modification of the molecules⁷⁻¹² or by a variation of the growth conditions.^{7,8,13-20} On the basis of these studies, it can be expected that in most cases the triplet-pair formation rate is higher in samples with better structural order7-9,11,15 and stronger intermolecular coupling.7,10,12-14

This is in line with current theoretical models, which link a stronger intermolecular coupling to higher exciton delocalization, which increases the admixture of the singlet fission mediating diabatic charge transfer (CT) state to the initially excited adiabatic singlet state S_1 , resulting in higher triplet-pair formation rates.^{21–24} Simultaneously, a better structural order and stronger intermolecular couplings increase the amount of

molecules over which an exciton is coherently distributed,^{24–26} and such an increase in excited-state delocalization enables ultrafast coherent triplet-pair formation.^{26,27} In addition, high structural order reduces the amount of undesired exciton deactivation via trap states because the density of deep trap states is reduced.⁹

In contrast, the second step, dissociation of the triplet pair into independent triplets, is enhanced by energy fluctuations, e.g., from static as well as dynamic structural disorder.^{28–34} For application in solar cells a fast conversion of the triplet-pair state into independent triplets is desirable because the tripletpair state has intrinsic loss channels like the ¹(TT) \rightarrow S₁ backtransition,^{35 1}(TT) fluorescence via Herzberg–Teller coupling,^{4,36 3}(TT) \rightarrow T_n + S₀ conversion,^{37,38} and nonradiative internal conversion to the ground state,^{28,39} which are not directly accessible for independent triplets.^{5,28,31}

One way to combine both aspects is by striking the balance between a low enough density of structural imperfections for efficient triplet-pair formation and preserving enough structural disorder to facilitate fast formation of independent triplets

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from the triplet-pair state.^{31,40} However, in order to observe this balance experimentally, a method is needed that is capable of unambiguously detecting the triplet-pair state while also having a time resolution in the picosecond range to track the triplet-pair state formation, which occurs with a rate of around 40 ns⁻¹ in the case of anthradithiophene⁴¹ (ADT, see Figure 1a



Figure 1. X-ray diffraction data of ADT:ZnPC films. (a) XRR data are vertically offset, and representative chemical structures of ZnPC and ADT are shown. (b) GIWAXS data of representative binary and neat films show the coexistence of ZnPC diffraction features and ring-like ADT diffraction features in the binary systems. The ADT concentration of each sample is given in mol %.

for chemical structure). Time-resolved photoluminescence spectroscopy (TRPL) fulfills these demands because it is capable to directly detect emission from the optically dark triplet-pair state via Herzberg–Teller coupling,³⁶ while it also has a sufficient time resolution to track the triplet-pair formation. Additionally, the free exciton emission and ¹(TT) emission are spectrally distinct from each other in ADT,³⁶ enabling a straightforward disentanglement of the first and second step of singlet fission, namely triplet-pair formation and triplet dissociation, by assigning the decay of the free exciton to the triplet-pair formation rate and the decay of the ¹(TT) state to the triplet dissociation rate.

In this work we prepare phase-separated films^{42,43} of the singlet fission material ADT with zinc phthalocyanine (ZnPC, see Figure 1a for chemical structure) to introduce minor mesostructural changes to the ADT crystallites and to eventually tune the excited-state delocalization of ADT, which is estimated from the spectral shape of the free exciton emission. The low steric compatibility of ADT and ZnPC ensures phase separation of the two components in binary

systems, and the lower bandgap of ZnPC enables energy transfer from ADT to ZnPC, which leads to a quenching of ADT excimers at grain boundaries, such that the ¹(TT) luminescence can be clearly observed. By simultaneously monitoring the triplet-pair formation dynamics and the temporal evolution of the ¹(TT) state with TRPL in the picosecond range, we find that structural changes can be introduced in the ADT crystallites by a variation of growth conditions, which not only influences the excited-state delocalization but also impacts the fate of the ¹(TT) state. Using this strategy, we show that loss channels of the ¹(TT) state in ADT, like luminescence from the ¹(TT) state, can be suppressed by subtle structural modifications of the crystallites, which are introduced by adaptions in the growth conditions.

METHODS

ADT (Sigma-Aldrich, 97% purity) and ZnPC (Sigma-Aldrich, 97% purity) were used as received. Hence, all studies were performed on isomeric ADT, but we expect no significant effect by this because both isomers show similar optical and structural⁴⁴ properties, as detailed in ref 41. The samples were prepared by codeposition (organic molecular beam deposition)⁴⁵ in a high-vacuum chamber with a base pressure of 10^{-8} mbar. The compounds were resistively heated in individual Knudsen cells, and the deposition rate for each compound was monitored by a separate quartz crystal microbalance (QCM), calibrated using X-ray reflectivity (XRR) measurements. The ratio between the two compounds was named by the molar percentage of ADT in the sample. All films have a nominal thickness of 80 nm, with the exception of the film with 4% ADT and the neat ZnPC film. The latter two have a nominal thickness of 50 and 40 nm, respectively, and the experimental results were treated accordingly. The molecules were deposited with a total growth rate of 6 Å/min on native silicon and quartz glass substrates which were kept at room temperature during growth. ADT single crystals were grown by means of horizontal physical vapor deposition.^{46,47} About 30 mg of the starting material was placed inside a two-zone horizontal furnace in a silica glass combustion boat. A steep temperature gradient was sustained over 48 h while the material was sublimed at 305 °C under a steady stream of molecular nitrogen (purity 6N, flow rate 30 sccm). Deep red, needle-like crystals with up to 7 mm in length were obtained. The crystals were slowly cooled to room temperature over a period of 12 h to minimize thermal stress. XRR measurements were performed on a Ge XRD 3003TT instrument using Cu K α_1 radiation ($\lambda = 1.541$ Å), and grazing incidence wide-angle Xray scattering (GIWAXS) measurements were performed on a Xeuss 2.0 (Xenocs) in-house instrument equipped with a Pilatus 300k detector using Cu K α radiation (λ = 1.542 Å). Absorption spectra were recorded with a PerkinElmer Lambda 950 UV-vis-NIR spectrometer. Steady-state photoluminescence (PL) measurements were performed with a LabRam HR 800 spectrometer (HORIBA Jobin Yvon, France) using a frequency-doubled Nd:YAG laser for 532 nm wavelength excitation. The emission light was collected normal to the sample surface, which reduces the effect of self-absorption, especially the one due to proximal grains. Scanning electron microscopy (SEM) images were taken with a JEOL JSM-6500F using an acceleration voltage of 5 kV. TRPL measurements were performed using a standard streak camera setup. A tunable pulsed titanium-sapphire laser with 100 fs pulse duration and 80 MHz repetition rate was used as excitation

source. The output wavelength of the laser was 960 nm, and the pulses were frequency-doubled to 480 nm. A microscope objective was used to focus the laser onto the samples with a spot size of $4 \,\mu$ m, leading to an excitation density of 2.0 × 10^{18} excitations/cm³ in the ADT crystallites. The power of the laser was attenuated to about 400 μ W at the sample. The samples were mounted in a cryostat, where they were kept under vacuum and cooled to 200 K using liquid helium during the measurement.

RESULTS AND DISCUSSION

Structural characterization of the neat and binary films of ADT and ZnPC has been performed by X-ray diffraction (Figure 1). In addition to GIWAXS, which provides insight into the inplane structure of thin films, XRR has been employed to determine the out-of-plane lattice spacing. The XRR data of neat ADT show first- and second-order Bragg peaks at q_z = 0.44 Å⁻¹ and $q_z = 0.88$ Å⁻¹, respectively, which agree well with the 14.0 Å reported for the *c*-axis of the ADT single crystal unit cell⁴⁴ (a spacing of 14.0 Å would result in a Bragg peak at 0.449 $Å^{-1}$). The Bragg peaks of neat ADT in the GIWAXS experiments can be found at $q_{xy} = 1.36$ Å⁻¹, $q_{xy} = 1.66$ Å⁻¹, and $q_{xy} = 1.96 \text{ Å}^{-1}$ and are vertically extended along the q_z direction. Under the assumption of an in-plane herringbone structure the Bragg peaks can be assigned to the (111), (021), and (12l) diffraction, respectively, resulting in a good agreement of the peak positions detected with those expected from the reported a- and b-axis of the ADT single crystal unit cell.⁴⁴ This suggests a preferred standing-up orientation of the molecules with respect to the substrate surface and a herringbone arrangement parallel to the substrate surface with a unit cell dimension comparable to that reported for ADT single crystals.⁴⁴ Neat ZnPC shows an out-of-plane Bragg peak at $q_z = 0.48$ Å⁻¹ in the XRR data. In GIWAXS two additional broad Bragg peaks can be found, one at $q_{xy} = 1.0 \text{ Å}^{-1}$ and $q_z = 0.55 \text{ Å}^{-1}$ and the other one at $q_{xy} = 1.85 \text{ Å}^{-1}$, which is smeared out along the q_z direction. These Bragg peak positions have been observed for neat ZnPC thin films before⁴⁸ and can be explained by the coexistence of the known thin film structures of ZnPC, namely α -phase ZnPC and β -phase ZnPC, with a clear domination of the metastable α -phase, which is preferentially observed in thin films.48-50

Diffraction peaks of both neat compounds can be observed in the data of the binary films, but a clear difference in their dependence on the other component is found. While the diffraction features that are assigned to neat ZnPC show a decrease in relative intensity with increasing ADT fractions without major changes in width or position (this effect is best visible for the Bragg peak at $q_z = 0.5 \text{ Å}^{-1}$ in XRR and for the Bragg peak at $q_{xy} = 1.9 \text{ Å}^{-1}$ in GIWAXS), more significant changes can be seen for the ADT features in the binary films compared to the neat film. The out-of-plane Bragg features of ADT are no longer visible in the binary films, indicating a loss of the preferred standing-up orientation of the ADT molecules with respect to the substrate surface. At the same time, diffraction rings appear in the GIWAXS data at $q_r = \sqrt{q_z^2 + q_{xy}^2} = 1.36 \text{\AA}^{-1}$, $q_r = 1.66 \text{\AA}^{-1}$, and $q_r = 1.96$ Å⁻¹; in some samples additional rings at $q_r = 0.95$ Å⁻¹ and $q_r =$ 2.15 \AA^{-1} are visible, which are assigned to the (110), (020), (120), (002), and (200) Bragg peaks, assuming a similar ADT unit cell structure in binary films as in neat films. Because the appearance of diffraction rings is typical for powder-like

samples and the absolute q values of the diffraction rings are similar to those found for the Bragg peaks of neat ADT, it can be concluded that the ADT crystallites are essentially isotropically oriented in binary films but keep a very similar crystal structure as in the neat ADT thin film. The random orientation of ADT crystallites is in line with the disappearance of the ADT Bragg peaks in XRR for the binary films. In analogy to the ZnPC features, the diffraction features assigned to ADT lose relative intensity with decreasing amounts of ADT in the films until they fall below the noise level. The fact that Bragg peaks of both individual components coexist in the binary films and that the absolute q values of the Bragg peaks of each neat compound do not change when moving from neat to binary films is suggestive of a phase separation between ADT and ZnPC,^{45,51} where both components keep their unit cell structure known from the respective neat film,^{44,48,49} but ADT loses its preferred standing-up orientation in the binary films.

This structural model is supported by the absorbance spectra (Figure 2a). The spectral positions of the absorbance features



Figure 2. (a) Absorbance spectra divided by the film thickness and (b) emission spectra of ADT:ZnPC thin films. Photoluminescence has been measured with photoexcitation at 2.33 eV. All spectra have been normalized with respect to the free exciton emission. In the case of neat ZnPC this normalization is not possible because it shows no luminescence in the shown spectral range.⁵⁷ The small sharp peaks visible at high photon energies for neat ZnPC are Raman peaks.⁶¹ ADT concentrations of the films are given in mol % in the legend.

in the neat films barely deviate from their respective positions in the binary films. This is a clear sign of phase separation because nanoscopically mixed films would exhibit spectral peak shifts due to changes in the polarizability of the environment and intermolecular interactions.^{19,52} The small changes in shape of the ZnPC absorption features between the samples are indicative of minimal changes in the molecular packing of ZnPC.⁵³ For films with low amounts of ADT, the ADT absorption characteristics, including the Davydov splitting indicative of translationally inequivalent molecules in the unit cell,^{19,54} are completely masked by the strong absorbance of ZnPC.⁵⁵ This finding confirms the powder-like orientation of substrate plane.⁴¹ The absorbance spectra of the binary films suggest that photoexcitation of predominantly ADT molecules should be possible at higher photon energies, but inter alia due to the lower bandgap of ZnPC, it should be expected that excitations of ZnPC might still play a role in the photoluminescence of the binary films. However, because neither the α nor the β polymorph of neat ZnPC shows luminescence in the spectral range, in which ADT luminescence is expected 36,41,57 (see Figure 2b), the luminescence of the binary films in the investigated spectral range is dominated by ADT with minor contributions from ZnPC (see note 04 in the Supporting Information for details). This allows us to distinguish between spectral contributions of ZnPC and ADT and hence to use PL and TRPL to obtain deeper insight into how the presence of phase-separating ZnPC affects the complex photophysics of ADT, which includes pronounced excimer emission and singlet fission at the same time already for neat ADT.^{36,41}

In the steady-state PL of neat ADT (Figure 2b) two distinct spectral features at 2.27 and 2.02 eV are found, which have been assigned to free exciton (highlighted as FE in Figure 2b) and excimer emission (EX in Figure 2b), respectively.⁴¹ While the free exciton emission of ADT at 2.27 eV also persists in all binary films, excimer emission is suppressed in the presence of ZnPC. Instead, a vibronic progression of the free exciton at 2.1 eV (FE* in Figure 2b) can be found, which is energetically 0.17 eV below the free exciton emission, hence reproducing the energetic spacing of the vibronic progression in the ADT absorption spectrum (compare to Figures 2a and S5a). Additionally, in films with 10% ADT and less, ¹(TT) luminescence via Herzberg–Teller coupling³⁶ at 1.98 eV (TT in Figure 2b) with a vibronic progression at 1.82 eV (TT* in Figure 2b) is visible, consistent with previous findings in an ADT derivative.³⁶ The assignment of the two latter peaks will be justified later on. Lastly, also luminescence from ZnPC molecules, which are incorporated into ADT crystallites, can be found at $1.78~{\rm eV}^{58-60}$ (best visible in the film with 50% ADT and in Figure S6a). The suppression of the ADT excimer peak due to changes in the photophysics at grain boundaries in binary films and the appearance and nature of the luminescence of ZnPC in the spectra of the binary films will be discussed in detail in notes 07 and 04 in the Supporting Information, respectively, while the proposed assignment of the other peaks appearing in the binary films will be justified and discussed further below in the context of time-resolved spectroscopic information based on TRPL. The use of TRPL allows us to disentangle the multitude of species involved in the photophysics of ADT not only spectrally but also with respect to their intrinsic photodynamics and examine differences in their characteristic decay rates. Importantly, also the influence of the amount of ZnPC in the films on the decay rates of each species can be tracked by TRPL.

In Figure 3, TRPL spectra time-integrated from 0 to 50 ps (Figure 3a) and decay rates of the free exciton emission (Figure 3b) can be found. The spectra are dominated by the



Figure 3. Photoluminescence spectra and dynamics in the picosecond range were extracted from TRPL measurements. (a) The timeintegrated, noise filtered, and normalized spectra at early times (integrated from 0 to 50 ps) are dominated by the free exciton band and its vibronic progression. ADT concentrations in the films are given in mol % in the legend. The spectral difference of neat ADT compared to the binary systems is due to ultrafast excimer formation. (b) Decay rates of the free exciton and its confidence intervals were evaluated by applying global analysis⁶² on the TRPL data of multiple measurements. Measurements were done at 200 K sample temper-

free exciton band emission at 2.24 eV and its vibronic progression at 2.07 eV. The assignment is based on the energy difference of 0.17 eV, which matches the energetic spacing of the vibronic progression in the absorption spectrum of ADT (Figure 2a), and on the fact that both features decay on the same time scale, which can be deducted from the results of the global analysis (Figure S4). Note that the $^{1}(TT)$ luminescence peak and the excimer luminescence peak are not visible in the time domain investigated here, indicating a longer lifetime of both of these species, leading to most of their respective luminescence occurring outside the investigated time window. The high singlet decay rate of more than 40 ns^{-1} (see Figure 3b) is strongly suggesting singlet fission, which has been shown before to be an important singlet decay channel in ADT and its derivatives.^{4,36,41} The decay rate of the ADT singlet might be slightly higher in binary ADT:ZnPC samples than for neat ADT. This, however, should not be interpreted as a sign that the singlet fission process itself is enhanced in binary films. Instead, it is more likely that the enhancement of decay rates occurs due to the presence of additional decay channels of the free exciton in binary films. Such decay channels are for example energy transfer and charge transfer state formation at grain boundaries between ADT and ZnPC. These additional decay channels for ADT excitons in binary systems that are not available to neat ADT can increase the overall ADT exciton decay rate in binary films. The sample with 5% ADT is an exception and has, surprisingly, a lower singlet decay rate than neat ADT, which we attribute either to imperfect thermal contact of the sample during the TRPL measurement or to differences in sample preparation conditions leading for example to a higher amount of electronically isolated ADT

molecules incorporated in ZnPC crystallites (see note 04 in the Supporting Information for details), which could decrease the exciton decay rate. However, also for this sample singlet fission is expected to be the dominant free exciton decay channel.

Due to the fast time scale of singlet fission, the free exciton band and its vibronic progression only contribute weakly to the spectrum at later times (Figure 4a). Interestingly, in some



Figure 4. Photoluminescence spectra and dynamics in the nanosecond range were extracted from TRPL measurements. (a) The time-integrated spectra are integrated from 0.5 to 2 ns, noise filtered, and normalized. ADT concentrations in the films are given in mol % in the legend. (b) Decay rates of the long-lived low-energy component and its confidence intervals were evaluated by applying global analysis⁶² on the data of multiple measurements. Note that rates below 1 ns⁻¹ are expected to be generally overestimated due to the fitting algorithm⁶² and the maximum delay time of 2 ns in the present experiment. Measurements were done at 200 K sample temperature.

cases the free exciton band exhibits a split peak with an additional higher energy component, which can be assigned to the high-energy Davydov component or to high-energy trap states. In the following we focus on the long-lived species present in the low-energy range, which play the major role in this time frame. While the low-energy region is dominated by the vibronic progression of the free exciton band during the first 50 ps (the peak at 2.07 eV is clearly visible in Figure 3a, but not in Figure 4a), a new, broad peak at 2.02 eV with a shoulder at the high-energy side, which possibly indicates a small contribution of the vibronic progression of the free exciton to this peak, is found for films with 25% ADT and more when integrating the spectra over the time window between 0.5 and 2 ns; this peak red-shifts further when moving to films with an ADT amount below 10%. Note that the high noise level and the applied noise filter lead to distorted spectral shapes, which makes the slight red-shift already present at 10% ADT hard to see. As outlined below, we suggest that this feature actually originates from two different species, namely the excimer state and the triplet pair state. By employing global analysis (see note 02 in the Supporting Information for details), the decay rates assigned to this long-lived peak in the low-energy region have been estimated for neat ADT and the

binary systems (Figure 4b). When moving from neat ADT to the films with at least 25% ADT, an increased decay rate can be found in the binary films, but, interestingly, when moving to films with 10% ADT and less, the decay rate decreases again compared to the binary films with high ADT fractions. This clear decrease in decay rate at low ADT fractions compared to the rate found in binary films with higher ADT fractions is concomitant with the observed spectral red-shift of the corresponding peak (Figure 4).

This correlation between the decline of decay rates and spectral red-shift of the signature for binary films with low amounts of ADT suggests that two species are involved in the corresponding luminescence. For the binary films with 25% ADT and more the peak at 2.02 eV is assigned to ADT excimer emission due to the spectral similarity to the excimer emission of neat ADT⁴¹ (Figure 4a). This assignment is further supported by the increase in excimer decay rate when moving from neat ADT to the binary samples with at least 25% ADT because quenching of ADT excimers at grain boundaries between ADT and ZnPC can be expected, which creates an additional excimer decay channel and hence increases the overall excimer decay rate in this binary system. However, because these arguments should apply to excimers in all binary films, the spectral red-shift and the decrease in decay rates, which are observed in films with low amounts of ADT, cannot be explained by assigning the luminescence found in these samples to excimer emission as well. Note that an assignment of the spectral red-shift of the excimer emission to excimers trapped at grain boundaries in analogy to ref 41 is not possible for the binary systems investigated here because in our case excimer quenching is expected at grain boundaries due to the presence of the low bandgap molecule ZnPC (see note 07 in the Supporting Information for details). Instead, to explain the red-shift and the decrease in decay rates, another excited-state species is needed, most likely the ¹(TT) state, which is visible in luminescence via Herzberg-Teller coupling.³⁶ The tripletpair state is expected to have a long lifetime for a variety of singlet fission materials^{5,29,35,63} and, in the case of ADT,³⁶ is expected to be visible by emission at an energy of

$$h\nu_{\rm TT} = 2E({\rm T_l}) - \hbar\omega_{\rm vib} \approx 2 \times 1.05 \text{ eV} - 0.17 \text{ eV} = 1.93 \text{ eV}$$
(1)

The energy value is calculated by taking twice the triplet energy⁴ minus the energy of the vibrational mode related to the vibronic progression of the ¹(TT) state luminescence (0.17 eV), which is needed for Herzberg–Teller coupling. Note that ¹(TT) luminescence has been found previously in an ADT derivative at 1.99 eV.³⁶ This resulting energy value for the triplet-pair state emission is red-shifted compared to the excimer emission (2.02 eV), and based on previous observations, the lifetime of the triplet-pair state^{5,29,35,63} is expected to be longer than those found for the excimer in ADT.⁴¹ Our experimental findings for the luminescence when moving to low ADT fractions also show a spectral red-shift and a reduction in decay rates, justifying the assignment to ¹(TT) luminescence.

With the knowledge gained from the TRPL data, we can revisit the steady-state PL spectra (Figure 2b) and refine the model of the ADT photophysics. The earlier assignments of the peaks at 2.27 and 2.10 eV to the free exciton band and its vibronic progression (visible in all binary systems), the peak at 2.03 eV to the excimer (visible in neat ADT), and the peak at 1.98 eV to the $^{1}(TT)$ state emission (visible in films with 10%

ADT and less) were verified in the analysis of the TRPL data. The small changes in energetic positions between TRPL spectra and steady-state spectra can be rationalized by the fact that two different setups were used for the respective measurements, including different photon energies of the laser used for excitation and different time windows under investigation. Although the peaks at 1.82 and at 1.78 eV in Figure 2b are beyond the detection range of TRPL, they can be assigned based on their energetic position. The peak at 1.82 eV is only visible in samples that also exhibit $^{1}(TT)$ luminescence at 1.98 eV, which is higher in photon energy by exactly the energy of a characteristic vibrational mode, and hence this peak is assigned to a vibronic progression of $^{1}(TT)$ luminescence. On the basis of the solution spectra of ZnPC^{59,60} and on luminescence spectra of ZnPC molecules diluted in an amorphous matrix of Alq₃,⁵⁸ the peak at 1.78 eV (best visible in the film with 50% ADT) is assigned to luminescence from ZnPC (see note 04 in the Supporting Information for details). However, when taking a closer look at the steady-state PL spectra, it needs to be investigated in detail (1) why excimer emission is strongly suppressed in binary films, (2) why $^{1}(TT)$ luminescence can only be seen in films with low amounts of ADT, and (3) why the vibronic progression of the free exciton emission is more pronounced in films with high amounts of ADT compared to the films with low amounts of ADT. While the first question is addressed in note 07 in the Supporting Information by analyzing the role of grain boundaries for excimers, the latter two questions will be answered in the following.

One possible reason the luminescence intensity of the first vibronic progression of the free exciton is less intense at low ADT fractions is excited-state delocalization. Excited-state delocalization leads to a change in the intensity ratio between the free exciton emission (0-0 emission at 2.27 eV) and its first vibronic progression (0-1 emission at 2.10 eV) compared to the ratio of an isolated molecule,^{64,65} as the case for molecules in solution (see Figure S5a for ADT PL in dilute CHCl₃ solution). The stronger the deviation from the ratio in solution, the more molecules are involved in the coherent excitation. $^{64-67}$ In the steady-state spectra (Figure 2b), the 0– 1 peak has a lower relative intensity for the binary films compared to the solution spectra (see Figure S5a), indicating that a coherent excitation distributed over more than one molecule suppresses the 0-1 emission relative to the 0-0emission in the films. It can be seen in Figure 2b that the suppression of the 0-1 emission due to excited-state delocalization is even more pronounced in films with low amounts of ADT (at 10% and less the 0-1 peak is barely visible anymore, also due to an overlap with weak $^{1}(TT)$ emission by coupling to a vibrational mode with an energy of around 33 meV^{68}) compared to the films with higher ADT fractions. Note that a quantitative analysis of the excited-state delocalization is not feasible because the 0-1 peak overlaps with contributions from excimer luminescence and $^{1}(TT)$ luminescence and the 0-0 peak intensity might be affected by self-absorption. However, because only the luminescence coming from ADT crystallites in a phase-separated system is investigated and because the film thickness is lower than the ADT crystallite size, self-absorption should affect all samples in a comparable fashion (the ADT crystallite size can be estimated in the SEM data, Figure S1b). Also, the contributions of excimer luminescence and ¹(TT) luminescence are small for binary blends in the energy range of the 01 peak, which means that one can still trust the qualitative finding of an increased ratio between the 0–0 peak and the 0–1 peak for binary films with low amounts of ADT. Effectively, this means that a higher amount of excited-state delocalization is maintained after excitation in the films with low amounts of ADT, hence in those which also exhibit $^{1}(TT)$ luminescence. This key result is sketched in Figure 5 with explanations in the



Figure 5. Sketch of the excited-state evolution of binary films. The size of the ovals represents the number of molecules over which an excitation is coherently distributed. During the first 50 ps after excitation no significant difference in excited-state delocalization is found between the samples, and triplet-pair formation is the dominant process in this time frame in all cases. In contrast, after 500 ps differences were found. While the binary films with low amounts of ADT maintain a higher excited-state delocalization and show ¹(TT) luminescence via Herzberg–Teller coupling (top part of the sketch), the films with higher amounts of ADT show a stronger reduction of excited-state delocalization) outcompete ¹(TT) luminescence (lower part of the sketch). Details about the estimation of the excited-state delocalization can be found in note 05 of the Supporting Information.

caption. Although there are more conclusive methods to get insight into the excited-state delocalization like PL yield measurements or pump—probe experiments, steady-state PL also allows to track this parameter as a less demanding method. We speculate that the higher excited-state delocalization found in films with low amounts of ADT might be assignable to a higher crystallite quality in these samples.

Interestingly, the steady-state emission of an ADT single crystal (see Figure S5b), which has a low defect site density, also exhibits detectable ¹(TT) luminescence with the same spectral fingerprint as the ¹(TT) emission of the binary films with low amounts of ADT. Note that the excited-state delocalization in the single crystal and neat film could not be estimated the same way as for the ADT:ZnPC binary films due to spectral overlap of the pronounced excimer emission and the 0-1 emission peak in the respective spectra. Also note that here only a correlation between excited-state delocalization and the triplet-pair state decay is found, but not for the tripletpair formation due to its short time scale, which is explained in detail in note 06 of the Supporting Information. The reason ¹(TT) luminescence can only be found in samples with high excited-state delocalization might be because in samples with a lower excited-state delocalization nonluminescent decay channels of the triplet-pair state like triplet separation are strongly enhanced, 30,31 possibly by dynamic and static disorder. Although disorder might also facilitate $^{1}(TT)$

luminescence by symmetry breaking, the enhancement of nonluminescent $^{1}(TT)$ decay channels at low excited-state delocalization is more significant, leading to a suppression of $^{1}(TT)$ luminescence in the corresponding samples.

CONCLUSIONS

In conclusion, phase-separating systems can be used to introduce changes to the excited-state delocalization of a SF material. By using binary films, mesostructural changes to the ADT crystallites can be introduced, leading to a tuning of the excited-state delocalization and resulting in changes of the SF dynamics. While for the first step of SF, triplet-pair formation, no influence on the triplet-pair formation dynamics was found due to its fast time scale, for the second step, dissociation of triplets from the triplet-pair state, emission from the triplet-pair state was only found when the excited-state delocalization is high, suggesting a correlation between the evolution of the triplet-pair state and the excited-state delocalization. These changes to the excited-state dynamics were achieved by subtle structural modifications of the ADT crystallites, introduced by utilizing mesostructural changes in the phase separating system of ADT and ZnPC. Generally, this approach can be used for further experimental studies of the influence of systematic changes of the excited-state delocalization on photophysical processes such as SF.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c08334.

Morphological analysis of the samples, PL spectra of ADT in solution and single crystals, details on the global analysis, time traces of the exciton, excimer and ¹(TT) luminescence extracted from the TRPL data, discussion on ADT excimer luminescence and ZnPC luminescence in binary films and the dependence of initial triplet-pair formation on excited-state delocalization (PDF)

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Notes

The authors declare no competing financial interest.

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