

Efficient Energy Transfer and Singlet Fission in Co-Deposited Thin Films of Pentacene and Anthradithiophene

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Co-deposited molecular heterostructures with statistical intermixing of the constituents are attractive candidates to tune the optical and the transport properties, as well as the ability to promote photophysical processes like singlet fission. In order to comprehend and control the singlet fission mechanism in these systems, it is of utmost interest to study the underlying excited state dynamics. In this work, thin films of anthradithiophene blended with the efficient singlet fission material pentacene are investigated by means of time-resolved and temperature-dependent photoluminescence spectroscopy with a time resolution of a few picoseconds. The analysis of the photoluminescence dynamics points toward efficient funneling of excitons from anthradithiophene via isolated pentacene molecules to agglomerates of pentacene, where eventually singlet fission occurs. The efficient and largely temperature-independent quenching of the luminescence in anthradithiophene is attributed to a favorable cascade-like alignment of the energy levels, and it is hypothesized that Förster resonance energy transfer is the main driving mechanism for exciton transport to pentacene agglomerates. The system investigated here can serve as a blueprint for the design of other molecular heterostructures with spatially separated light harvesting and singlet fission regions.

absorption coefficients, and the abundance of their main constituent carbon.^[1–4] A special property of some of these compounds is the ability to promote singlet fission (SF), a photophysical process where one photon generates two triplet excitons, when the energy of the initially created singlet state is at least on the order of twice the triplet state energy.^[5,6] For organic photovoltaics, SF is considered as a technologically relevant process, because in principle four charge carriers can be harvested from a single photon.^[7]

In addition to choosing from a multitude of commercially available conjugated molecules, the material properties can also be tuned over a broad range via co-deposition of two or more individual compounds. This approach is of particular interest for SF materials, since there is only a limited number of materials for which the process is efficient.^[8] Depending on the intermolecular interactions and steric compatibility of the constituents, co-deposition may

either result in phase-separated domains or in heterostructures with intimately mixed compounds.^[9] An important prerequisite for the latter scenario are sufficiently similar geometries of the co-deposited molecules. Depending on the intermolecular interactions, the intimate mixing can be either statistical or in an ordered fashion leading to co-crystalline phases with defined stoichiometry.^[9] When continuous tuning of the optical and dielectric properties via the stoichiometry is desired, statistical intermixing is preferred. Recently, several molecular heterostructures with statistical intermixing also referred to as solid solutions, have been investigated.^[10–15]

One such model system with statistical intermixing is pentacene (PEN) blended with structurally similar anthradithiophene (ADT). In several aspects, these materials behave in a complementary fashion, allowing for tuning of the optical, dielectric, and transport properties in heterostructures.^[14,15] Excitons in both neat compounds undergo SF, which is very efficient for PEN with a time constant of ≈ 80 fs.^[16] On the other hand, for ADT, recent studies suggest that SF is less efficient and depends strongly on the molecular arrangement with time constants on the order of nanoseconds for various derivatives,^[17–19] whereas for films of neat ADT, a time constant of ≈ 20 ps has

1. Introduction

Molecular semiconductors are attractive materials for optoelectronic devices owing to their synthetic flexibility, their strong

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been reported.^[12] In particular for materials where SF is slow, it is presently recognized that excimer formation is a parallel and often dominant process, which can strongly reduce the efficiency of SF.^[12,20,21] Blends of PEN with ADT were also investigated in terms of their transport properties.^[14] The carrier mobility in PEN thin film transistors can reach values above $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[22,23] On the other hand, presumably due to the poor crystallinity, a much lower mobility on the order of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported for ADT.^[13,14] However, when blended with PEN, ADT was found to stabilize the devices and impede oxidation, which is a well-known degradation mechanism for PEN,^[14] illustrating how the properties of the individual constituents can complement each other in a beneficial way in the blend.

Since weakly screened excitons are the primary photoexcitations in molecular materials, it is of great interest to explore their photophysical properties and the fate of photoexcitations in mixed molecular semiconductors. Recently, two statistically mixing systems based on ADT blended with weakly interacting molecules, namely tetracene (TET) and 6-phenacene, were investigated in terms of their exciton physics, demonstrating a pronounced, red-shifted emission presumably arising from excimers in ADT, the formation of which competes with SF as a parallel decay channel.^[12] On the other hand, PEN was investigated in blends with weakly interacting spacer molecules. Surprisingly, even in the mixtures, SF was found to occur on ultrafast time scales, which was attributed to the presence of statistically emerging regions with a high PEN concentration, acting as SF “hot spots”.^[10] In contrast to TET and ADT, it was suggested that SF in PEN is a coherent process that does not significantly depend on the number of neighboring molecules, as long as there is one PEN molecule in direct vicinity, which would explain the ultrafast generation of triplets in molecular blends containing PEN.^[24]

While earlier work of PEN-based mixtures has mainly focused on the ultrafast formation of triplet states on time scales below 1 ps,^[10,11,15] the time-delayed formation of these species via exciton hopping toward PEN agglomerates has not been explored in greater detail yet. In this work, we investigate the exciton dynamics in ADT/PEN mixtures, for which we expect structural properties similar to the above-mentioned compounds. However, a significant difference is the spectral overlap of the ADT emissive features with the absorption of the efficient SF material PEN (see Figure 1), opening up the possibility of efficient exciton transfer from ADT to PEN, in particular for the excimer state. We employ time-resolved photoluminescence spectroscopy (TRPL) to explore the exciton dynamics focusing on small PEN concentrations. We find that even small amounts of PEN ($\leq 5\%$) lead to very efficient quenching of the luminescence of ADT, which is accompanied by a high photoluminescence (PL) yield originating from isolated PEN molecules. With increasing PEN concentration, also the PL originating from PEN molecules is quenched. This is in accordance with the previously suggested efficient transport to PEN agglomerates, which give rise to SF and therefore act as PL quenchers. Moreover, we demonstrate that the underlying mechanisms of exciton transfer are only weakly thermally activated, and we discuss their origin. Overall, we find the energetic arrangement of the excitonic states in PEN/ADT very beneficial to drive SF and avoid losses caused by excimer formation. Thus, our study demonstrates that with a suitable energy level arrange-

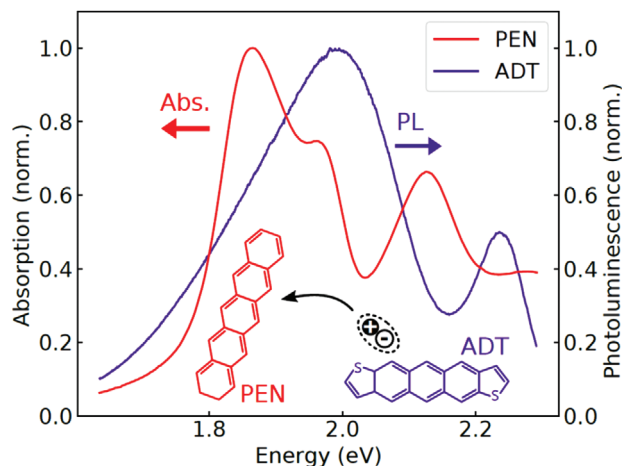


Figure 1. ADT emission and PEN absorption spectrum in the solid state, together with a scheme of the molecules and the presumed exciton transfer mechanism.

ment of the heterostructure compounds, even small amounts of an efficient SF material can make SF the dominant process.

2. Experimental Section

ADT (Sigma Aldrich, 97% purity, synthesis pathway reported in ref. [13]) and PEN (Sigma–Aldrich, 99.9% purity) were used as received. The samples were prepared by co-deposition (organic molecular beam deposition)^[9] in a vacuum chamber with a base pressure of 10^{-8} mbar. The compounds were resistively heated in crucibles 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. All films have a nominal thickness of 80 nm and were deposited with a total growth rate of 6 \AA min^{-1} on native silicon and quartz glass substrates, which were kept at room temperature during growth. The mixing ratio of each film was calculated in molar % of PEN. XRR measurements were performed on a Ge XRD 3003TT instrument using $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$), and grazing incidence wide-angle X-ray scattering (GIWAXS) measurements on a Xeuss 2.0 (Xenocs) in-house instrument with a Pilatus 300k detector using CuK_{α} radiation ($\lambda = 1.542 \text{ \AA}$). Absorption spectra were recorded with a PerkinElmer Lambda 950 UV–vis–NIR spectrometer. Steady-state PL measurements were performed with a LabRam HR 800 spectrometer (HORIBA Jobin Yvon, France) using a frequency-doubled Nd:YAG laser for 532 nm excitation wavelength. The PL spectra were converted to the energy scale via a Jacobian transformation.^[25]

Time-resolved measurements were carried out using an 80 MHz titanium-sapphire oscillator (Spectra Physics, Tsunami) with a tunable output wavelength of 700–1000 nm and a pulse duration of ≈ 100 fs. The wavelength range of the system was extended to the blue and ultraviolet range by a unit for second harmonic generation (CSK Optronics, SuperTripler). For the measurements in this work the wavelength of the Ti:Sa oscillator was tuned to 910 nm and frequency doubled to 455 nm (2.73 eV) to efficiently excite ADT with negligible direct excitation of PEN (see Figure 3). For neat ADT, the excitation density created per laser

pulse was estimated to $\approx 3 \times 10^{18} \text{ cm}^{-3}$, see Note S1 (Supporting Information) for details. For time and spectrally resolved detection of the PL signal, a streak camera (Hamamatsu, C6860) was operated in synchroscan mode. The instrument response time of the setup depends on the selected temporal window for the measurements and varied between 2 and 4 ps for short time ranges with high time resolution and 35 ps for long time ranges with lower temporal resolution. The wavelength scale of the setup was calibrated with a mercury lamp and a tungsten lamp with a continuous spectrum was used for calibration of the spectral sensitivity. Like for the static data, the obtained emission datasets were transformed from the wavelength to the energy scale via a Jacobian transformation. For the temperature-dependent measurements, the samples were placed in an evacuated microscopy cryostat (CryoVac) and cooled with liquid helium. The measured PL intensities and dynamics were found to be similar for different spots on the sample (see Figure S1, Supporting Information for exemplary data).

3. Results

3.1. Structural Characterization

Structural characterization was performed by X-ray diffraction methods. XRR and GIWAXS were employed to obtain insight into the out-of-plane and in-plane structures, respectively. Based on the positions of the second order Bragg peaks in the XRR scans of the neat films and blends, the lattice spacings normal to the substrate surface, d_z , have been calculated (Figure 2a; Figure S2, Supporting Information). All films exhibit a split Bragg peak in XRR with a weak and strong component. The results for the weak components are represented as datapoints with fainter color. The d_z values found for neat ADT and neat PEN agree well with those found for the bulk (fainter color) and thin film phase (stronger color) of each respective compound.^[12,14,26,27] The mixtures show the coexistence of thin film phase and bulk phase as well and, importantly, a continuous change in d_z can be found for both phases upon changes in the mixing ratio.

Next, to obtain insight into the in-plane structure of the films, the GIWAXS maps (see Figure S3, Supporting Information) were integrated along q_z from $q_z = 0.1 \text{ \AA}^{-1}$ to $q_z = 0.3 \text{ \AA}^{-1}$, resulting in a scan along q_{xy} exhibiting three Bragg peaks for each film (see Figure S4, Supporting Information), which can be assigned to the (11n), (02n), and (12n) reflections under the assumption of an in-plane herringbone arrangement typical for these systems. Retaining this presumption of the underlying structural motive, we further note the presence of a weak (20n) reflection at $\approx 2.1 \text{ \AA}^{-1}$ in the GIWAXS maps, in combination with the absence of the corresponding (10n) peak, which is expected for a herringbone structure. By also assuming a rectangular unit cell, the positions of the Bragg peaks were used to estimate the in-plane unit cell vectors a and b , which are plotted in Figure 2b. Even though our results provide some general insight into the lattice parameters of the system, it is important to note at this point that the ADT molecules employed for this work are actually a mixture of two isomers, that is, *syn*-ADT and *anti*-ADT. While the crystal structure of the individual isomers is known,^[26] we cannot make a statement about the precise orientation of the molecules within the lattice of the mixtures. Moreover, in some of the mixtures the

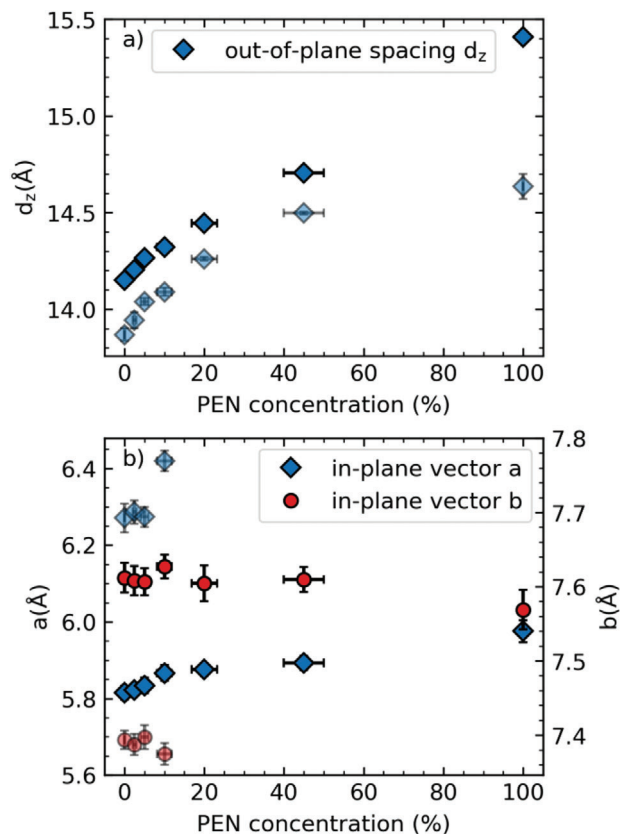


Figure 2. Structural investigations of ADT:PEN blends. a) lattice spacings normal to the substrate surface (d_z) were obtained from XRR scans (Figure S2, Supporting Information), b) in-plane lattice vectors (a and b) were obtained from GIWAXS scans (Figures S3 and S4, Supporting Information) under the assumption of an in-plane herringbone arrangement and a rectangular unit cell. The fainter data points in (a) and (b) are calculated by taking the component of weaker intensity in the case of a split Bragg peak being present and can be assigned to a bulk phase present in the respective sample additionally to the dominant thin film phase.^[14,27] Error bars of the concentration are based on assuming 10% uncertainty of the QCM.

(11n) peak is split, yielding slightly different values for the unit cell parameters, depending on whether the strong or weak component of the split peak is taken. The results obtained when taking the components of weaker intensity are plotted as data points with fainter color. Due to the assumption of a rectangular unit cell (i.e., ignoring deviations from an in-plane angle of 90°), the values for the in-plane unit cell vectors of the neat films appear to deviate slightly from the literature,^[26–28] but still support a preferred standing up orientation of the molecules against the surface and an in-plane herringbone arrangement for both neat compounds and the blends. While for neat PEN the in-plane structure of the thin film phase and the bulk phase is hard to disentangle, in neat ADT signatures of both phases can be found. Tracking the mixing-ratio dependent evolution of both in-plane lattice vectors assigned to the bulk phase, it can be seen that a exhibits a continuous increase with increasing amounts of PEN, while all changes in the value of b are within the confidence interval. The continuous change in in-plane and out-of-plane lattice parameters of the co-deposited films with changing mixing ratio strongly

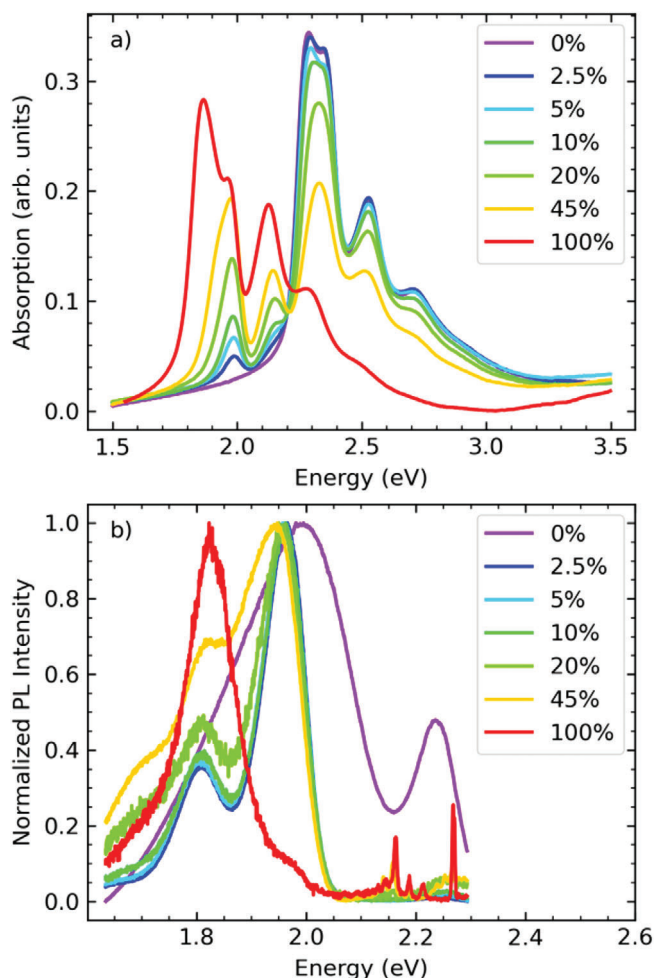


Figure 3. a) Absorbance and b) photoluminescence spectra of the neat films and blends. Photoluminescence measurements were carried out under excitation at 2.33 eV (532 nm). Molar fractions of PEN molecules for each sample are given in % in the legend. Absorption data is displayed as the logarithmic quantity absorbance, but to correct for scattering losses, the minimum of the curves was set to zero. Normalization factors of the PL data are summarized in Table S1 (Supporting Information). For a clearer comparison between the ADT excimer and the PEN monomer emission, we refer the reader to Figure S6 (Supporting Information).

indicates statistical intermixing of the two compounds, in which both compounds form a common lattice structure, which is comparable to those of the respective neat films with lattice sites being statistically occupied by molecules of each compound.^[10,29]

3.2. Static Optical Spectroscopy

Our conclusions about the underlying nanostructure are further supported by static optical spectroscopy. Absorption spectra of neat ADT and PEN films and the blends with different PEN concentrations are presented in Figure 3a. The spectra of both neat compounds are similar in shape, but, compared to ADT, the electronic transitions of PEN are situated at lower energies, making the contributions of PEN and ADT to the spectra of the mixed films easily distinguishable. Both neat films exhibit a Davydov

splitting of the exciton transition with a vibronic progression toward higher photon energies. The Davydov splitting is a clear indication for the presence of two strongly interacting molecules in the unit cell, possessing herringbone arrangement.^[30] Moreover, the strong absorption features obtained from the white light impinging normal to the sample surface indicate an in-plane arrangement of the transition dipole moment. This agrees with a standing-up orientation of the molecules on the substrate and consequently, due to the stronger in-plane interactions, an in-plane arrangement of the herringbone structure,^[31–35] in accordance with the GIWAXS and XRR results.

In the mixtures, the Davydov splitting is strongly reduced, in accordance with earlier studies on comparable blend systems.^[10,11] The observation can be attributed to the fact that with an increasing fraction of PEN (ADT), it becomes less likely to encounter two adjacent ADT (PEN) molecules, that is, less pairs of like molecules. Consequently, the absorption spectra of the blends resemble rather the spectra of the monomers in solution.^[10,33] Quantum chemical calculations suggest that the lowest Davydov state of PEN is energetically stabilized due to a strong charge transfer (CT) state admixture.^[30] This CT character is reduced in blends with other molecules^[10] and, consequently, leads to the strong blue shift of the PEN absorption edge. Another contribution to the overall blue shift of the PEN signatures with increasing ADT fraction originates from a decrease in polarizability due to the substitution of PEN molecules with a higher band gap material.^[36,37] The blue shift of the ADT absorption edge is less pronounced, potentially due to the smaller Davydov splitting that could be connected to a smaller CT state admixture to the lowest singlet transition.^[38] Moreover, the change in the polarizability induced by PEN is of opposite sign, leading to partial compensation of the above-described effect. In accordance with our structural investigations, the continuous energetic shifts of the spectral features as well as the reduced Davydov splitting in the blends indicate statistical mixing of the molecules on a microscopic level, since the absorption peaks are the concerted result of different microscopic environments comprised of different combinations of molecules.

Steady state PL spectra of neat PEN, ADT, and the blends are presented in Figure 3b. The PL spectrum of ADT shows two signatures, that is, a comparably narrow peak ≈ 2.23 eV related to free exciton emission and a broader and more intense feature at 1.98 eV, which was attributed to excimers.^[12] In this context, it should be mentioned that optical signatures attributed to self-trapped excimers are observed in a variety of molecular systems and there is an ongoing discussion, whether they mediate SF or whether they represent a competing decay channel for singlet excitons (see also discussion in the next section).^[20,21,39] For some systems, it was also proposed that the red-shifted emission originates from correlated triplet pair states that are precursors of free triplet excitons, and which could be partly emissive through Herzberg–Teller coupling.^[18] The actual origin of the red-shifted emission may depend on the investigated system. For ADT, however, it is reasonable to assume excimeric character due to the strong influence of the dielectric environment on the emission energy.^[12] The emission of neat PEN peaks ≈ 1.83 eV, as expected for the exciton transition of thin films.^[38] The PL spectra of the mixtures on the other hand show very distinct behavior. The signatures related to ADT are almost entirely quenched even for

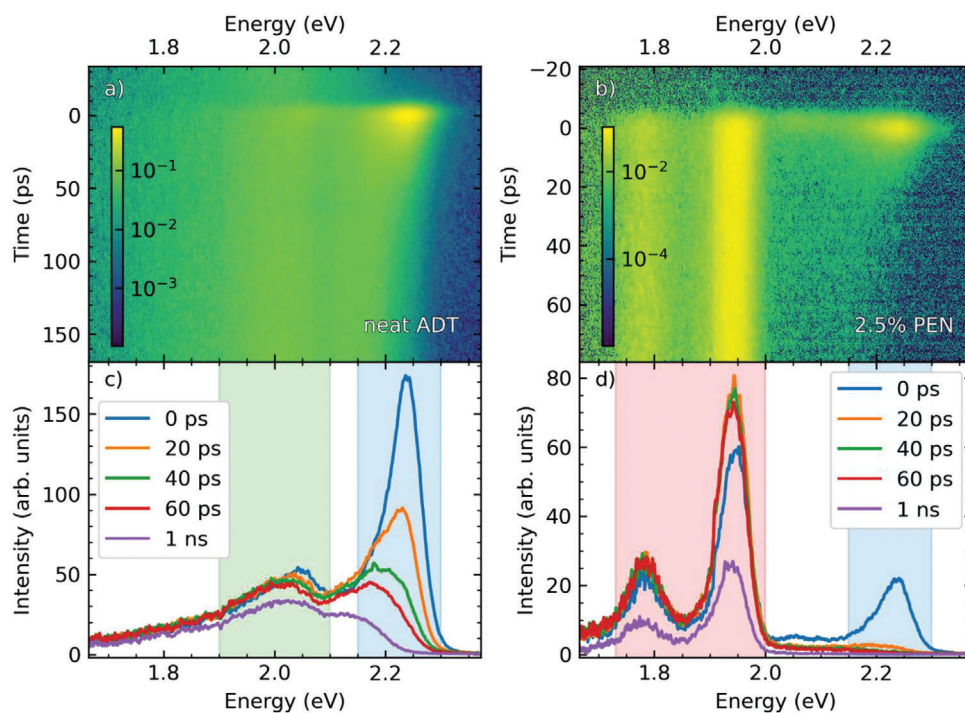


Figure 4. a) Heatmaps of the TRPL data recorded at 70 K of neat ADT and b) the mixture with 2.5% PEN. c) Spectra extracted from the TRPL data at different times after excitation for ADT and d) the mixture. The colored boxes indicate the emission of the ADT excimer (green), the ADT exciton (blue), and the emission of PEN (red).

PEN fractions as small as 2.5%, suggesting efficient exciton transfer to PEN. This is supported by the fact that the PL spectra of the blends are dominated by the emission of isolated PEN molecules at 1.95 eV, as observed in solution or in molecular blends (see Figure S6, Supporting Information and refs. [10,40-42]). At first glance, this assignment appears counterintuitive, because the PEN emission in the blend with the lowest PEN concentration is the brightest. However, as we will further elaborate in the time-resolved analysis below, the efficiency of PEN SF is strongly increased already by a small increase in PEN concentration and, in accordance with the model proposed in earlier work on PEN-based mixtures,^[10] we suggest that the presence of small PEN agglomerates gives rise to efficient quenching of the monomer-like PEN emission via SF. Contrary to the absorption spectra, the PL does not show clear evidence for a spectral shift related to different local environments. The main transition of the PEN emission ≈ 1.95 eV shows a red-shift with increasing PEN concentration; however, such a red-shift is not observed for the first vibronic sideband at lower energies. Therefore, we hypothesize that here re-absorption of the emission arising from the main PL signature due to spectral overlap with the PEN absorption alters the peak position and also the intensity ratio of the main peak and the first vibronic sideband, which becomes more pronounced with increasing PEN concentrations. This view is supported by the assumption that the PL of the blends must originate almost exclusively from isolated PEN molecules with adjacent ADT, since adjacent PEN would quench the emission via SF, so the dielectric environment of the emissive states should remain similar. On the other hand, even though ultrafast quenching of the PL arising from SF of PEN excitons in the bulk phase was also demon-

strated in TRPL experiments,^[43] we cannot fully exclude contributions from the PEN bulk phase to the emission at higher PEN concentrations.

The most striking observation in the static spectra of the blends is the absence of any signature related to the ADT excimer emission, even for small PEN concentrations, which contrasts with studies on similar ADT-based mixtures.^[10,12] Also the signature of free ADT excitons is barely visible in the blends. The reason for this could be an extremely efficient exciton transfer from ADT to PEN. To further validate the exciton dynamics and the underlying funneling mechanisms, we performed temperature-dependent TRPL studies on the picosecond time scale.

3.3. Time Resolved Photoluminescence

Exemplary TRPL data of neat ADT and the blend with a fraction of 2.5% PEN obtained from the streak camera setup at a sample temperature of 70 K are presented in Figure 4. Time and spectrally resolved datasets comparable to those presented in the heatmaps in Figure 4a,b were recorded for neat ADT and all mixtures with PEN in a temperature range between room temperature and 10 K. In addition, we present PL spectra that were integrated over different time windows after the excitation pulse (cf. Figure 4c,d). Here, we chose to present some of the data recorded at 70 K, because in the temperature range between 70 and 100 K, the contribution of the excimer emission in ADT (absolute and relative) was most pronounced (cf. Figure S7, Supporting Information), allowing us to explore the fate of the excimers in the blends in the best possible way.

For neat ADT, the free exciton peak at 2.23 eV decays more rapidly than the excimer emission (Figure 4c). Since the excimer band is already present at the earliest time frame, we conclude that a delayed excimer formation from free exciton states on a time scale of a few picoseconds plays only a minor role. Since it is difficult to disentangle the excimer signature from the vibronic side bands of the free exciton emission, we have also validated this statement by exploring the dynamics of the individual contributions by means of global analysis (Figure S8, Supporting Information). Our findings are consistent with the work of Hausch et al., who suggested a kinetic model, in which excimers and free excitons are populated through a common precursor state, whereas at later times, there is no significant exchange between both populations. Instead, it was proposed that the fast decay of free excitons in the solid originates from SF.^[12]

In accordance with the steady state PL spectra, the time-dependent spectra of the 2.5% mixture (Figure 4d) are dominated by the exciton signatures of PEN, whereas the free exciton emission of ADT decays already within the first time frame presented here (20 ps), which is significantly faster than in neat ADT. Because of this fast decay, the signature of ADT is almost not visible in the steady state PL spectra of the mixtures. Notably, the excimer emission of ADT seems to be entirely quenched on time scales faster than the instrument response even for the blend with the lowest PEN concentration, which is further confirmed by global analysis, where no decay component related to the excimer was found (Figure S8, Supporting Information). Combined with the high intensity of the PEN emission, which is already present at the earliest time frame after excitation, this gives further support for the presence of an extremely efficient transfer mechanism for free excitons and in particular for excimers from ADT to PEN.

For a more detailed investigation of the PL dynamics, we analyzed the transient decay in the spectral ranges of the free exciton emission of ADT (2.23 ± 0.02 eV) and the emission from isolated PEN molecules (1.78 ± 0.02 eV). In order to analyze the PEN decay, we chose to investigate the energy range corresponding to the first vibronic sideband of the PEN emission, in order to exclude any influence of lower-energetic emission arising from the ADT exciton. Results obtained for neat ADT and the blends at 70 K are presented in Figure 5a,b. In order to quantify the PL dynamics, we fit the data with a biexponential model function convoluted with the instrument response time (for details, see Note S8, Supporting Information). We note that the underlying decay behavior is rather multiexponential, because due to the statistical intermixing of both compounds, we expect that excitons in ADT face a plethora of distances to the next PEN quenching molecule. However, biexponential fits were found to represent the decays adequately.

Comparing the free exciton decay of neat ADT to the blends reveals that a remarkable fraction (>90%) of the ADT emission is already quenched on a time scale shorter than the instrument response time, which is 2–4 ps for the short time window. This becomes apparent from the initial amplitudes of the transients, which are remarkably reduced in the blends compared to neat ADT. This efficient quenching occurs even for the lowest PEN concentration of 2.5%. Overall, we estimate the intensity drop of the ADT excitons in the blends caused by static and dynamic quenching to be on the order of 99%.

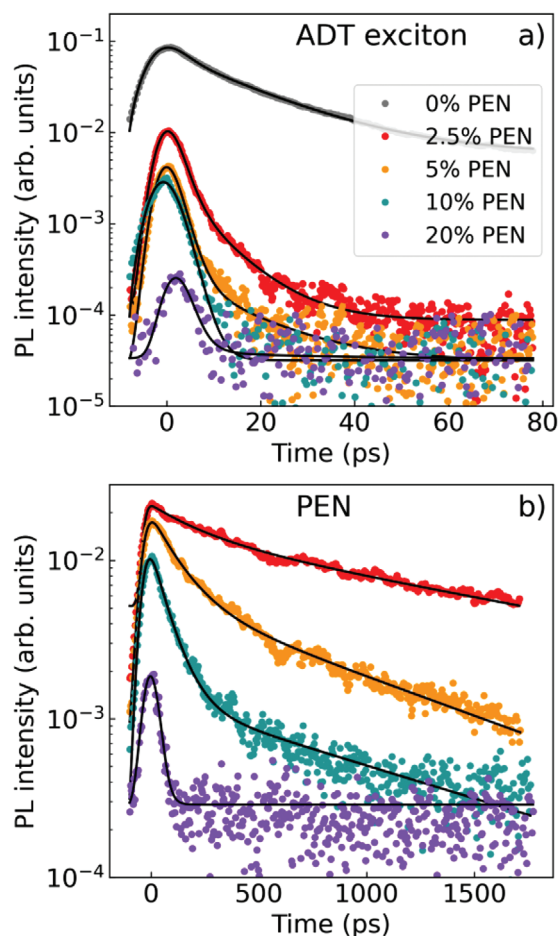


Figure 5. a) PL dynamics of the free excitons in ADT at an energy of 2.23 ± 0.02 eV for different PEN concentrations and b) transients in the energetic range of the PEN emission at 1.78 ± 0.02 eV, shown together with the results obtained from a biexponential fit (black curves).

For the PEN emission in blends, the overall decay is slower compared to ADT, but we observe a drastic decrease of the decay times with increasing PEN concentration. This decrease of decay times can be attributed to the funneling of excitons from isolated emissive PEN molecules into PEN agglomerates, where the emission is negligible because of ultrafast SF.^[10]

In order to justify that the proposed exciton funneling mechanisms from ADT to PEN and from PEN to PEN agglomerates do in fact dominate the exciton dynamics of the system, we briefly discuss potential contributions of other kinetic processes. Non-radiative decay originating from impurities or structural imperfections certainly cannot be disregarded in the investigated system. However, we assume that it does not affect the key findings made here for several reasons. First, the X-ray analysis of all samples shows pronounced Bragg peaks clearly indicating that all samples are well-ordered in a lattice, also in the blends. Since we do not expect PEN to have a strong influence on the structural quality, but on the other hand observe significant quenching of the luminescence signatures of ADT even for the smallest PEN concentration, we infer that energy transfer from ADT

to PEN should dominate the kinetics in the blends. This process clearly outcompetes other nonradiative processes in ADT, which are not expected to be faster than the observed PL dynamics in neat ADT. Second, the energetics of both molecular constituents favors exciton rather than charge transfer, from which we conclude that charge transfer states, which are often considered as interfacial traps, do not play a major role in the investigated blends. Efficient exciton transfer to PEN without significant losses at the PEN/ADT interface is also suggested by a comparison of the relative luminescence yields of the neat ADT sample and the blend with the smallest PEN fraction (cf. Figure S6, Supporting Information). It turns out that the emission intensity originating from the small fraction of PEN molecules in the blend film is actually comparable to the intensity of the neat ADT film. From this finding and from the fact that PEN absorbs only weakly at the excitation energy of 2.73 eV, we conclude that most of the emission of the PEN molecules in blends should actually originate from exciton transfer and not from direct excitation of PEN. A last option that should be considered is the contribution of nonradiative centers to the exciton dynamics in PEN. However, here it is important to stress that SF in PEN is exothermic and hence very efficient, also in mixed systems.^[10] Hence, we expect SF with time constants of ≈ 80 fs in PEN agglomerates to outperform any other decay process that may be present in PEN agglomerates.

Regarding the generated triplet population, it should be mentioned that, due to the high repetition rate of the laser, we cannot expect the triplet population to fully recombine within one cycle of 12.5 ns. As a consequence, a background triplet population could lead to enhanced non-radiative recombination originating from triplet–singlet-annihilation or triplet–triplet-annihilation. In the latter, two triplet excitons undergo either an Auger-like process where one triplet exciton is annihilated or two triplets re-generate one emissive singlet exciton. Notably, delayed luminescence from such a time-delayed formation of singlet excitons is not observed in the blends before $t = 0$. On the other hand, regarding the estimated excitation density of $3 \times 10^{18} \text{ cm}^{-3}$, non-radiative annihilation effects could play a role and accelerate the observed kinetics. To the best of our knowledge, no critical densities, at which exciton annihilation effects become pronounced, were reported for ADT. However, for TET, annihilation effects were found to become pronounced beyond exciton densities of $\approx 2 \times 10^{17} \text{ cm}^{-3}$.^[44] Assuming similar conditions for exciton annihilation in ADT and a pile-up effect from long-lived triplet excitons, we need to take non-radiative processes into account, especially those induced by a background triplet population. While such processes could certainly accelerate the overall PL dynamics, we do not expect them to substantially affect the exciton funneling mechanisms observed in this study.

Before further discussing the origin of the efficient exciton transfer, it is instructive to investigate the temperature dependence of the decay dynamics. Representative temperature-dependent decay curves of the ADT and the PEN excitons of the 2.5% mixture are presented in Figure 6a,b and the same fitting routine as for the data in Figure 5 was applied to the data recorded for PEN concentrations up to 10% in the temperature range between 10 and 295 K (cf. Figures S9 and S10, Supporting Information).

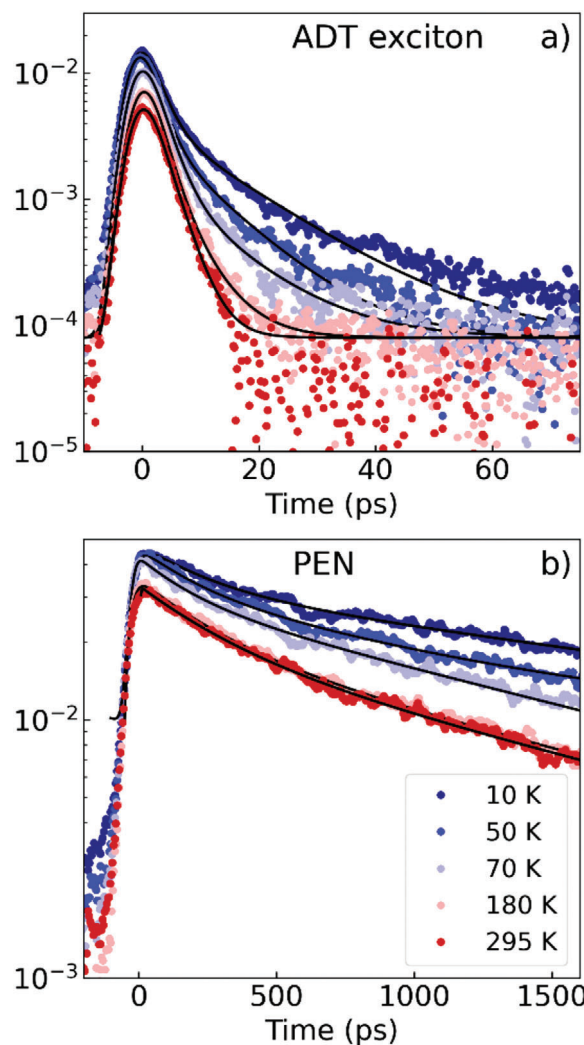


Figure 6. Temperature-dependent transients extracted from the mixture with 2.5% PEN content. Transients in (a) were extracted from an energy range of 2.23 ± 0.02 eV, corresponding to the free excitons in ADT, and the data in (b) represent the decay of the emission of isolated PEN molecules at 1.78 ± 0.02 eV.

From the time constants τ_1 and τ_2 and the fit amplitudes A_1 and A_2 of the biexponential fits we calculated the amplitude-weighted average lifetimes:^[45]

$$\langle \tau \rangle = \frac{A_1 \tau_1 + A_2 \tau_2}{A_1 + A_2} \quad (1)$$

The lifetimes $\langle \tau \rangle$ of the ADT and PEN excitons for different blend compositions and temperatures are summarized in Figure 7 and in Tables S2 and S3 (Supporting Information). Overall, the dynamics of the free excitons in neat ADT is not substantially altered with temperature. For the blends, we note a slight trend toward a faster decay with increasing temperature, which is not considerably captured by $\langle \tau \rangle$, but is observed for the longer-lived tail of the transients (Figure 6; Figure S9, Supporting Information). At elevated temperatures and for PEN fractions $> 5\%$, the decay of the ADT excitons in the blends is

spectrum of neat ADT, is completely absent even for the lowest PEN concentration. Our structural investigations do not indicate any severe changes in the ADT lattice upon intermixing with small amounts of PEN that could explain the absence of excimer emission. We also note that in statistically mixing systems with a comparable structure the excimer emission of ADT is not quenched, which supports our view that the underlying structure should in principle support excimer formation.^[12]

Instead, we consider two potential explanations for the absence of excimer signatures in the blends: Either 1) the excimer state is bypassed via a precursor state from where excitons undergo ultrafast transfer to PEN and that may be the same as for the free excitons or 2) the transfer of the excited state energy from the ADT excimer state to PEN molecules is extremely efficient, such that it outcompetes recombination via excimers. In principle, both effects could contribute to the observations. On the one hand, it could be possible that transfer over short distances occurs via a “hot” mechanism, involving a precursor state, which could be a vibronically excited singlet exciton in our experiment, such that the excimer state is bypassed. Ultrafast quenching of excitons and charge generation close to internal interfaces is a well-known phenomenon in organic solar cells and the presence of more delocalized vibronically excited states or higher electronic states acting as precursors for charge separation was proposed.^[47–51] However, the presence of excimer signatures in related systems such as diindenoperylene (DIP)/PEN^[10] and ADT/TET or ADT/6-phenacene^[12] contradicts this idea. Moreover, for PEN/ADT we can exclude that exciton transfer is mediated via a vibronically excited precursor state from the fact that efficient quenching of ADT luminescence was also observed in the steady state experiments presented in Figure 3a, where the excitation energy (2.33 eV) was below the first vibronic resonance of ADT. On the other hand, in contrast to the systems mentioned above, the large spectral overlap of the excimer emission and the PEN absorption should give rise to very efficient Förster transfer, whereas the spectral overlap between the emission spectrum of the ADT free exciton and the PEN absorption spectrum is considerably smaller (cf. Figure 1). Thus, from comparison to earlier studies, we infer that the particular energy level arrangement in PEN/ADT with the emission energy of the ADT excimer being isoenergetic to the energy levels of PEN^[10] plays an important role for the quenching of excimers, that is, hypothesis (2) from above. It is noteworthy that excimer states are typically associated with substantial structural relaxation, leading to strong self-trapping and potentially also more nonradiative decay pathways. Despite this localized character and the comparably low oscillator strength, the excimer state in ADT/PEN can apparently mediate efficient energy transfer to moieties where the desired photo-physical process occurs, in this case SF.

With increasing distance to a quenching molecule, electronic coupling diminishes rapidly and we expect exciton transfer via a hot process or the Dexter mechanism to become insignificant on length scales exceeding 1 nm. As our estimation of distances to the next quenching sites suggests, this regime of distances is relevant for exciton transfer from isolated PEN molecules to PEN agglomerates (Figures S11b and S12b, Supporting Information). While isolated PEN molecules are emissive, PEN agglomerates were proposed to give rise to ultrafast SF and thus do not significantly contribute to the PL.^[10] Since the quench-

ing of the PEN emission observed here increases drastically with increasing PEN fraction, our work confirms PEN agglomerates as the origin of SF, while other possible mechanisms such as singlet heterofission at PEN/ADT interfaces should be insignificant. PEN agglomerates can therefore be considered as quenching sites. Based on the statistical intermixing, we expect typical distances between isolated PEN molecules and PEN agglomerates to be on the order of 2–5 nm. Excitons can overcome such distances either directly via FRET or via incoherent hopping involving several sites. We expect FRET to play a significant role here, because due to the small Stokes shift there is considerable overlap between the emission spectrum of the PEN monomer and the absorption of isolated PEN molecules or PEN molecules in the bulk phase (cf. Figure 3a). The slower dynamics related to these mechanisms compared to the transfer of the ADT free exciton becomes apparent in the longer decay times of the PEN emission and the significantly reduced amount of static quenching.

Our temperature dependent experiments indicate that the investigated exciton funneling mechanisms are not significantly affected by thermal barriers. This finding is in accordance with our discussion (see previous paragraphs) about the underlying mechanisms of exciton transfer. For the transfer of excitons from ADT to PEN, no additional energy is needed since the singlet exciton energies of exciton accepting PEN molecules are energetically below the exciton energies of ADT, or approximately isoenergetic in case of the excimer emission. A similar situation arises for the transfer of excitons from isolated PEN molecules to PEN agglomerates: The latter are found at lower energies due to a shift of the dielectric constant as well as electronic interaction between PEN molecules,^[40] giving rise to an energy gradient that drives exciton funneling from isolated PEN molecules to PEN agglomerates, where SF occurs. This overall presumed alignment of energy levels in ADT/PEN is sketched in Figure 8. We also note that there is no explicit temperature dependence of the FRET and the Dexter process. However, both transfer mechanisms depend on the so-called overlap integral J , which describes the spectral overlap of the emission spectrum of the exciton donor and the absorption spectrum of the acceptor.^[37] This overlap may diminish when the temperature is reduced, because the homogeneous broadening of the respective signatures reduces with a decreasing amount of vibrational excitations.^[46] Thermal activation of exciton hopping from one site to another can thus become important when there is only a limited number of acceptor sites in the vicinity of the exciton. Kinetic frustration of the exciton transport at low temperatures is mainly known from triplet states, which can only migrate via the short-ranged Dexter mechanism,^[52] however, the situation may also apply to singlet excitons that have energetically relaxed into local minima of the Gaussian density of states, where no adjacent sites with lower energy are available.^[46] In the temperature-dependent transients of the PEN emission, we have observed that the longer-lived subset of the population does reveal some temperature-dependent dynamics, which could originate from thermally activated hopping transport into which several low-energetic sites are involved.

As indicated above, the observed efficient quenching of excimers, potentially via FRET, is a remarkable observation for PEN/ADT, which contrasts with previous results on seemingly

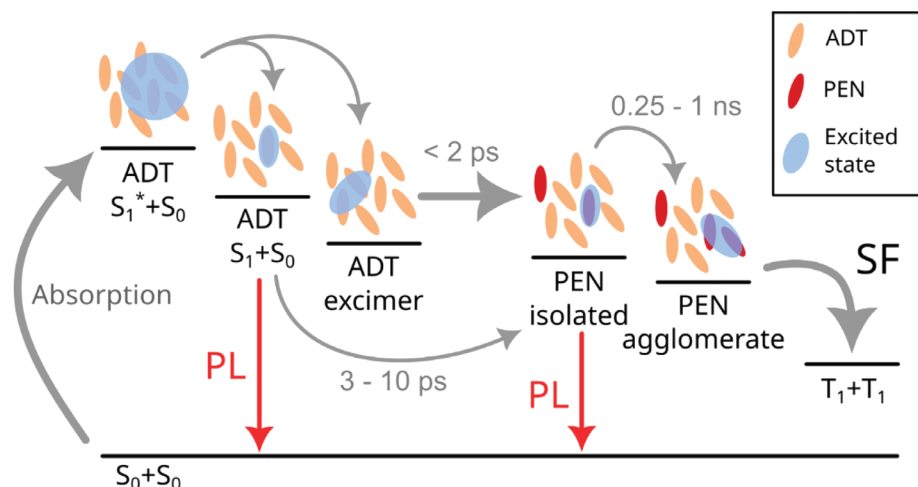


Figure 8. Suggested photophysical model of ADT/PEN. Singlet excitons are created with some excess energy. From these “hot” states they relax energetically into emissive free exciton or excimer states.^[12] We assume that excimers formed in ADT are efficiently quenched by energy transfer to PEN and thus no PL from the excimer is observed for the blends. Emissive transitions to the ground state from ADT free excitons and isolated PEN molecules are highlighted by red arrows. Alternatively, excitons from isolated PEN can funnel to PEN agglomerates where they undergo SF.

similar systems.^[10,12] In general, the role of excimers in the SF process is a matter of ongoing research. On the one hand, some studies indicate that excimers are precursor or intermediate states in the SF process in some systems such as, for example, crystalline PEN and perfluoropentacene.^[53–55] On the other hand, in particular in systems with a co-facial arrangement of the molecules, which results in high stabilization of the excimer state, excimer formation seems to be a channel competing with SF.^[8,20,53,56–59] In this context, our study points toward a new pathway of overcoming the obstacle of excimer formation by the energetic tailoring of the molecular constituents in co-deposited heterostructures, which leads to energetic funneling to the desired sites where SF is efficient. Thus, here we demonstrate how a rather inefficient SF material can be transformed into an efficient SF material by adding just a small amount of PEN, which forms SF “hotspots”^[10] due to statistical mixing. Notably, already a PEN fraction of 2.5% leads to quenching of >99% of the PL of the host material ADT and PEN fractions as small as 5% give rise to efficient SF due to the statistical formation of agglomerates. The possibility to spatially separate the light-harvesting from the exciton fission moieties can also be beneficial to improve the material stability and for an independent choice of the absorption properties of the light-harvesting material.^[59] However, as important next steps, future work on these molecular heterostructures needs to explore if the generated triplet excitons can also be efficiently harvested for device applications. Moreover, triplet charge annihilation is a considerable loss channel in devices that needs to be controlled.^[60] Additionally, from a fundamental point of view, it would be interesting to obtain more insight into the excimer quenching mechanism and the achievable quenching distances, which could be implemented with specially designed samples. From a methodological point of view, the present study cannot provide insight into the kinetics beyond the generation of free triplets in PEN, however, we believe that the experimental results acquired in this work can serve as a basis for further theoretical and device-based studies of PEN/ADT.

5. Conclusion

Our study has expanded the knowledge of statistically mixing molecular heterostructures by exploring the photophysics of ADT with small fractions of the SF material PEN. Even for PEN concentrations of only a few percent, we find efficient quenching of the free exciton and the excimer state of ADT. This can be rationalized by the close spacing of ADT and PEN molecules on the order of 1–2 nm, which is already fulfilled for comparably small concentrations of PEN due to the statistical mixing of both compounds. Moreover, the energy level alignment between the ADT emission and the PEN absorption is favorable for FRET, especially for the ADT excimer, which is entirely quenched already for a PEN concentration of 2.5%. By further studying the PL dynamics originating from isolated PEN molecules on time scales of several 100 ps, we find evidence that excitons situated at these molecules migrate to energetically more favorable PEN agglomerates, where they undergo efficient SF. Since SF is a multimolecular process, the overall PL intensity decreases and decays more rapidly with an increasing amount of PEN. We argue that also the slower transport from PEN to PEN agglomerates on estimated length scales of 2–5 nm is governed by FRET. The PL dynamics does not reveal any remarkable temperature dependence, suggesting that the underlying transport mechanism is robust against thermal relaxation in a disordered density of states. Overall, our study provides a new pathway for the design of efficient SF materials through rational tailoring of the energetics in molecular heterostructures.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

exciton transfer, molecular heterostructures, singlet fission, statistical mixing, time-resolved photoluminescence

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