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Singlet Fission in Acene Blends

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Singlet fission in acene blends

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ABSTRACT

Singlet fission (SF), the photophysical process converting an excited singlet exciton into two triplet excitons, is a promising approach to boost solar cell efficiencies. It is controlled by various parameters such as intermolecular interactions, energetics, entropy and vibronic coupling and a controlled modification of these parameters is key to a fundamental understanding. Blends of organic semiconductors present an interesting alternative to established methods of chemical functionalization and their potential for the study of SF pathways will be discussed using acene blends as example. Mixed thin films of SF chromophores and weakly interacting, high-bandgap spacer molecules allow one to study the impact of a replacement of nearest neighbors on the SF rates. While the SF rate in pentacene, for which SF is a coherent process, is unaffected by the introduction of spacer molecules into the film, we observe a significant decrease in the SF rate in tetracene, indicating incoherent SF. Mixing the two SF chromophores pentacene and tetracene with low pentacene concentrations leads to heterofission of a singlet on pentacene into two triplets on pentacene and tetracene, respectively, when selectively exciting pentacene. This heterofission process is outcompeted by pentacene homofission if the pentacene concentration exceeds 5%. Photoexcitation above the tetracene band gap additionally allows for energy transfer from tetracene to pentacene and results in complex dynamics.

Keywords: Singlet fission; Pentacene; Time-resolved spectroscopy; Blends

1. INTRODUCTION

Organic semiconductors (OSCs) have great potential as active layers in novel optoelectronic devices due to the variety of available compounds and resulting structural, optical, and electronic properties. In several classes of these OSCs, such as acenes or isobenzofuranes, singlet fission (SF) has been observed, which describes the conversion of an excited singlet into two low-energy triplets on neighboring molecules via an electronically coupled triplet pair state $^1(TT)$ [1-3]. Research on SF has gained increasing interest in the last decade as it is a promising approach to overcome the Shockley-Queisser limit for single-junction solar cells [1,4], but for further optimization of SF chromophores for device applications an understanding of the underlying mechanisms of the SF process is needed. In the literature, various parameters for efficient SF have been identified, such as molecular arrangement [5-8], the coupling of electronic and nuclear motion [3,9-11] and, most importantly, intermolecular interactions [6,12-14]. The latter should be strong enough to enable the formation of the coupled triplet pair state, but still allow for efficient separation of the triplets [15,16]. There are very successful approaches to control the interaction strength via chemical modification [12], in nanoparticles [15, 17] or using dimers [18-20], in which the distances between the monomeric units can be controlled by the length and composition of the bridging unit. However, these methods are faced with several difficulties including limited flexibility in material choice or additional unpredictable effects of molecular arrangement and orientation.

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In this paper, we will discuss an alternative approach which is based on blends of SF chromophores with high-bandgap, weakly interacting OSCs [21,22]. Co-deposition of the SF chromophore with a suitably chosen OSC leads to the formation of a solid solution [21,23] i.e., a crystal structure in which lattice sites are randomly occupied by molecules of either compound. The OSC can now act as spacer molecule for the SF chromophore and reduces intermolecular interactions by reducing the number of like nearest neighbors or by introducing changes in the unit cell parameters compared to neat films of the SF chromophore [6,21,24]. The strength of interactions between neighboring SF molecules can be controlled via the mixing ratio and can be easily modified over a large range, bridging the gap between isolated chromophores and crystalline aggregates. Moreover, the structural order within the films is retained, which leads to a well-defined molecular arrangement, in contrast to amorphous systems, in which often complex dynamics are observed [26,27].

Here, we discuss the behavior of two prototypical SF chromophores, namely tetracene (TET) [2] and pentacene (PEN) [28] in blends with weakly interacting spacer molecules. First, we focus on the impact of changes in the unit cell parameters on the SF rate in PEN and compare our experimental results with theoretical predictions [21]. Comparing PEN- and TET-based blends we will show how such mixed films can help to shed light on the details of SF pathways [29]. Finally, by studying blends of TET and PEN we present a time-domain investigation of heterofission, i.e., the photophysical process in which fission of a singlet on one molecule leads to triplets on chemically distinct molecules [24].

2. MATERIAL AND METHODS

Mixed films of TET (Sigma Aldrich, 99.99%), PEN (Sigma Aldrich, 99.9% purity), [6]-phenacene (6PH, Lambson Japan Co. Ltd. 99%), [5]-phenacene (PIC, Tokyo Chemical Industry Co. Ltd. 99.9% and NARD Co. 99.9%) and diindenoperylene (DIP, Institut für PAH Forschung Greifenberg, 99.9% purity) were grown by organic molecular beam deposition at a base pressure of 1×10^{-9} mbar, see Refs. [21, 24, 29] for details. The structural characterization was performed on a GE-diffractometer (3303TT) ($\lambda = 1.5406 \text{ \AA}$) and a 1D detector (Meteor 1D, XRD Eigenmann) and on a Xeuss 2.0 SAXS/WAXS system (Xenocs) with a Dectris Pilatus3R 300K detector ($\lambda = 1.5406 \text{ \AA}$). UV-vis transmission spectra were measured using a Perkin Elmer Lambda 950 spectrophotometer. Steady-state photoluminescence (PL) measurements were performed on a Horiba Jobin Yvon LabRAM HR spectrometer under N₂ atmosphere using a wavelength of 532 nm for excitation. Time-resolved PL measurements were taken with a Hamamatsu C4334 Streakscope having a time resolution of 20 ps and a spectral resolution of 2.5 nm, see Ref. [29] for details. The pump-probe set-up for transient absorption (TA) spectroscopy consisted of an amplified laser system (Libra, Coherent), which delivers a 1 kHz pulse train of 4-mJ, 100-fs pulses at 800 nm. An optical parametric amplifier was used to adjust the wavelength of the pump pulse for excitation. The probe pulse was a white light continuum generated by focusing a small fraction of the 800 nm beam in a 2 mm Sapphire plate. The differential transmittance signal ($\Delta T/T$) was obtained by dispersing the probe pulse on an optical multichannel analyzer and by subtracting pump-on and pump-off spectra, see Ref. [21,24] for details.

3. RESULTS

The chemical structures of the SF chromophores and the three high-bandgap spacer molecules (DIP, PIC and 6PH) are shown in Fig. 1a. Co-deposition of two OSCs can lead to different scenarios of intermixing or phase separation depending on the strength of intermolecular interactions and the steric compatibility of the compounds [23]. The molecules which we study here, intermix, but without co-crystal formation. Instead, they form a solid solution, i.e., a common lattice where the lattice sites are randomly occupied by molecules of either compound. In such solid solutions, three different effects can contribute to a reduction of the interaction between SF chromophores, see Fig. 1b. First, the replacement of nearest neighbors of a given SF chromophore by spacer molecules, second, changes in the unit cell parameters and third, changes in the molecular arrangement within the unit cell. The latter has been found to be negligible in our mixed films [21,29] and, thus, will not be considered further. In the following we will discuss the impact of the first two parameters on SF rates based on selected examples, some of which have been published before [21,29].

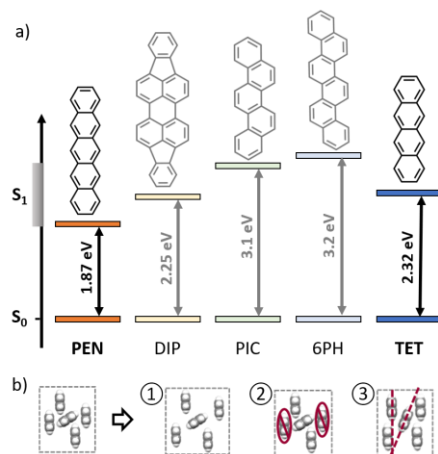


Figure 1. a) Investigated molecules and their optical band gaps. The spacer molecules (see text) are marked in grey. b) Schematic scenarios describing how the presence of spacer molecules can affect the molecular environment and arrangement of a given SF chromophore.

3.1 Impact of the unit cell expansion

In the first part of this paper, we will discuss how the SF rate is affected by changes in the unit cell parameters. The mixing-ratio dependent lattice spacing was determined by fitting the position of Bragg-peaks observed via X-ray reflectivity (XRR) and grazing incidence X-ray wide angle scattering (GIWAXS), see Fig. 2. For the out-of-plane lattice spacing d we observe a continuous change with increasing fraction of spacer molecules, which depends on the geometry of the spacer molecule and is either negative (PEN:PIC blends) or positive (PEN:DIP, TET:6PH and TET:PIC blends). In contrast, the trend observed for the in-plane unit cell parameters (a - and b -axis) is independent of the spacer molecule and shows an increase in these parameters with increasing fraction of the spacer molecules. Since the intermolecular interactions are strongest in the plane which is spanned by the unit cell vectors a and b and which is perpendicular to the long molecular axis, these parameters are crucial for our study. The observed changes of 1 Å are sufficient to impact the intermolecular interactions [6] and, thus, have consequences for the resulting optical properties, see Fig. 3.

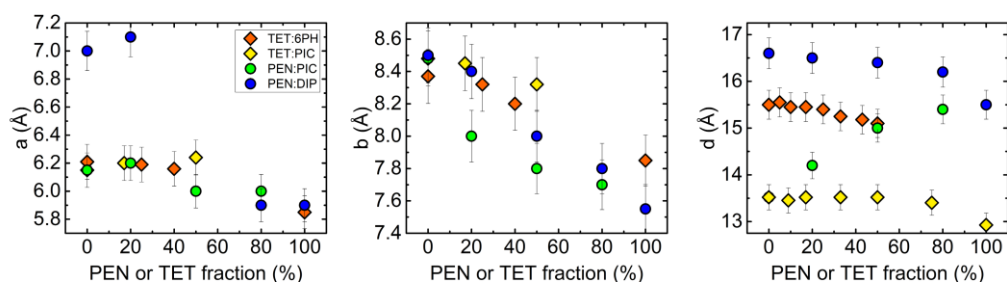


Figure 2. Unit cell parameters a and b and out-of-plane lattice spacing d of the four different blends discussed here. The legend applies to all. Adapted from Ref. [21,29].

In the following we will focus on PEN-based blends and compare the results for PEN- and TET-based blends in Sec. 3.2. The absorption spectra of PEN-based blends with DIP and PIC as spacer molecules are shown in Fig. 3a and b, respectively. Due to the wide band gap of the spacer molecules, the low energy part of the absorption spectrum is dominated by transitions between the electronic and vibronic states of PEN for all mixing ratios.

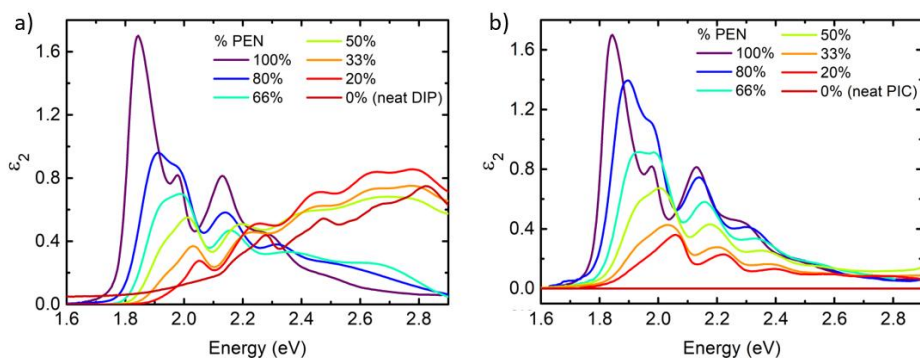


Figure 3. Absorption spectra of PEN:spacer blends. a) PEN:DIP, b) PEN:PIC. Adapted from Ref. [21].

The first two transitions at 1.84 eV and 1.96 eV, respectively, originate from the Davydov-splitting (DS) of the lowest excitation that is a result of the coupling of translationally inequivalent transition dipole moments. This is also the part of the spectrum that shows the most pronounced changes with changing fraction of spacer molecules. As this fraction increases, the intensity of the low-energy Davydov-component decreases compared to the high-energy component and the splitting between the two components is reduced. This is a result of changes in the intermolecular interactions induced by the increase of the *a*- and *b*-axis length and agrees with theories predicting that the DS in TET and PEN depends strongly on the coupling of Frenkel exciton (FE) and charge transfer (CT) states [6]. Since the distance of the molecules in the *ab* – plane increases with increasing spacer molecule fraction, see Fig. 2, this reduces the FE and CT state coupling and decreases the DS. Importantly, these changes are also expected to affect the SF rate either directly by the modification of the SF energy balance or indirectly via the CT-mediated superexchange coupling [6]. Thus, we used TA-spectroscopy to probe the mixing-ratio dependent SF rate in these PEN-based blends and compared our experimental results with theoretical predictions based on the expansion of the unit cell, see Fig. 3 and Ref. [21] for details on the calculations.

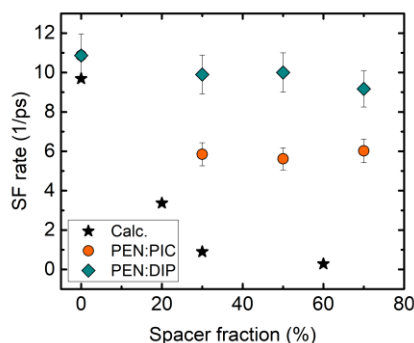


Figure 4. SF rates of PEN:spacer blends and comparison with calculations based on the expansion of the unit cell. Adapted from Ref. [21].

The results are surprising, as they show a large deviation between predictions (decrease by a factor of 10) and experiments (decrease by a factor of 2), the latter being furthermore independent of the spacer fraction. However, this can be explained based on the mixing behavior of these PEN:spacer blends. As mentioned before, they form a solid solution with a random occupation of lattice sites by molecules of either compound. The herringbone arrangement observed for neat PEN films is retained in the blends [21], resulting in four nearest neighbors for a given molecule. In the blends, a SF chromophore can now have zero to four SF chromophores as nearest neighbors, the others being spacer molecules. Since all sites are equivalent, the probability for a certain number of neighboring SF chromophores is given by a binomial distribution. This means that the relative abundance of a certain scenario changes with mixing ratio, but in principle, all scenarios can be present in the mixed film. For example, even in a 5% PEN blend, the probability for two PEN molecules to be nearest neighbors is still 18%, with the other 82% being fully isolated PEN molecules surrounded only by spacer molecules. For blends with higher PEN fractions, the probability for the existence of sites where a given

PEN molecule has other PEN molecules as nearest neighbors increases. In combination with singlet exciton hopping these sites can act as hotspots for fast SF [21,26] and can lead to the observation of robust SF in these blends despite a reduction of the intermolecular coupling.

3.2 Impact of the replacement of nearest neighbors

As a next step we take a closer look at the impact of the replacement of nearest neighbors on the SF rates. Already in the 1970's it has been proposed that this leads to a reduction of the SF rates due to a lack of reaction partners (replacement effect) [30] if SF proceeds via incoherent population transfer. However, for PEN evidence for a coherent SF mechanism has been found in which the triplet pair state is directly mixed into the photoexcited singlet state [3,6,9-11,14]. The impact of a replacement of nearest neighbors on this coherent mechanism can be elucidated by comparing the behavior of blends of PEN and TET with spacer molecules.

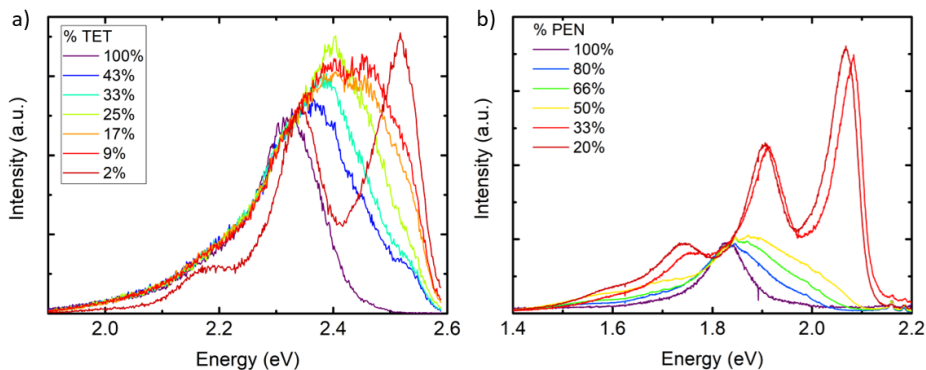


Figure 5. Photoluminescence spectra of a) TET:6PH and b) PEN:PIC. The spectra have been normalized to the maximum of the emission of the neat PEN and TET films, respectively. Adapted from Ref. [21,29].

Figure 5 shows the PL spectra of TET:6PH (Fig. 5a) and PEN:PIC (Fig. 5b) blends. For TET:6PH blends we restrict the discussion to fractions below 50% to avoid contributions of neat TET-phases that might form at high TET fractions [29]. Comparing the PL spectra, interesting differences can be observed. While the mixing ratio dependent PL spectra of PEN:PIC blends undergo an abrupt transition from a spectrum dominated by PEN bulk emission to a spectrum resembling the emission of PEN monomers, the trend is more continuous in TET:6PH blends. This indicates that in the TET-based blends excited TET molecules with different local environments decay slowly enough to contribute to the emission, in contrast to the PEN-based blends where the emission is dominated by PEN molecules with similar environments, namely the above-mentioned hotspots. Comparing the SF rates in PEN:PIC and TET:6PH blends, see Fig. 6, we find similarly clear differences. While the SF rate in PEN is robust against changes in the PEN fraction, we observe a dramatic decrease of this rate with decreasing TET fraction.

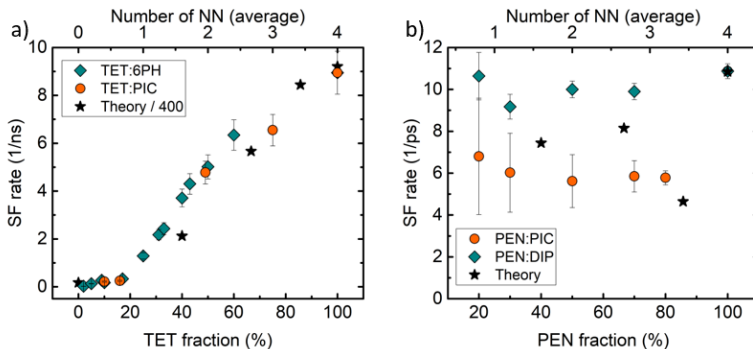


Figure 6. Singlet fission rates as a function of nearest neighbors (NN) for TET blends (left) and PEN blends (right) and comparison with calculations (stars). Adapted from Ref. [21,29].

To unravel the mechanisms behind these observations, we calculated the SF rate for a PEN and a TET lattice where we removed nearest neighbors as explained in Ref. [29], see black stars in Fig. 6. For TET blends we find that the SF rate scales with the number of nearest neighbors, while the SF rate in PEN blends is independent of this value. This points towards fundamental differences in the SF mechanism of PEN and TET. The decrease in the SF rate in TET blends is expected for incoherent population transfer from the excited singlet to the triplet pair state. In contrast, SF in PEN follows a coherent pathway and scales with the admixture of the triplet pair to the photoexcited state [29]. Thus, it is independent of the number of nearest neighbors as long as there is a high probability for at least one PEN neighbor.

3.3 Heterofission

Finally, in the third part of this paper, the photophysics of blends of the two previously discussed SF chromophores is investigated, see Ref. [24,25] for details. These blends are interesting from the viewpoint of heterofission, where the fission of the singlet results in triplets on PEN *and* TET and which has potential for solar cells applications, since it allows one to tune the energetic difference between singlets and triplets. Heterofission has been reported in heterodimers [31], in which two chemically distinct chromophores are covalently linked. The optical band gap of the heterodimer is defined by the chromophore with the lowest singlet energy, while the triplet energy levels of both chromophores remain largely unaffected [31]. However, the strong interaction between the two covalently bound chromophores makes the spatial separation of the triplets challenging. An alternative is the use of mixed thin films of non-covalently linked SF chromophores, prepared by coevaporation. This approach combines the potential of heterofission for band gap engineering with the facilitated triplet separation due to weak intermolecular interactions in van-der-Waals bound molecular aggregates.

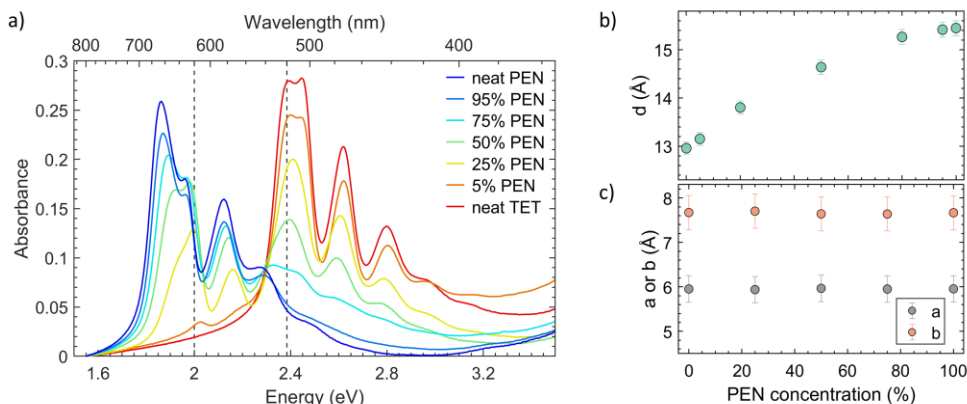


Figure 7. a) Absorption spectra and b) in-plane and out-of-plane lattice spacing of PEN:TET blends. Adapted from [24].

The absorption spectra of PEN:TET blends are shown in Fig. 7a and follow a very similar trend as observed before for the PEN:spacer blends (Fig. 3) in that the relative intensities of the two Davydov-components change with the mixing ratio and also the DS gets smaller. Interestingly, this cannot originate from an expansion of the unit cell since the *a*- and *b*-axis length is independent of the mixing ratio (Fig. 7c). The only parameter that varies is the out-of-plane lattice spacing (Fig. 7b) which could lead to a vertical displacement of the two translationally inequivalent molecules in the unit cell of a herringbone arrangement, and, thus, to slight changes in orbital overlap and intermolecular coupling [6,21,24].

Important information is the band gap since this allows us to disentangle the photophysical processes which can occur in PEN:TET blends: first, heterofission of a PEN singlet or a TET singlet, second, PEN and TET homofission, third, energy transfer from TET to PEN and, lastly, also radiative (or non-radiative) relaxation of PEN (TET) singlets. Using an excitation wavelength below the TET band gap allows us to selectively excite PEN and to exclude the possibility of energy transfer and TET homofission, otherwise leading to complex dynamics [24].

The photophysics of PEN:TET blends was investigated by TA spectroscopy, see Fig. 8 [24]. In the TA spectra we observe the expected PEN ground state bleach (GSB) as well as stimulated emission (SE), but two additional features deserve a more detailed discussion. These features are the PEN triplet excited state absorption (ESA) above 700 nm and the TET GSB between 500 nm and 550 nm. In a blend with 5% PEN, the probability of a PEN molecule to have another

PEN molecule as nearest neighbor is 18%, the rest (82%) are fully isolated PEN monomers surrounded by TET molecules. While these 18% PEN dimers could explain the observation of the PEN triplet ESA, they fail to rationalize the bi-exponential rise of this ESA and the bi-exponential decay of the SE, see Fig. 8b, let alone the observation of a TET GSB upon excitation below the TET band gap. However, both observations can be consistently explained by endothermic intermolecular heterofission, i.e., the spontaneous fission of a singlet exciton on PEN into two triplets, residing on PEN and TET, respectively [24].

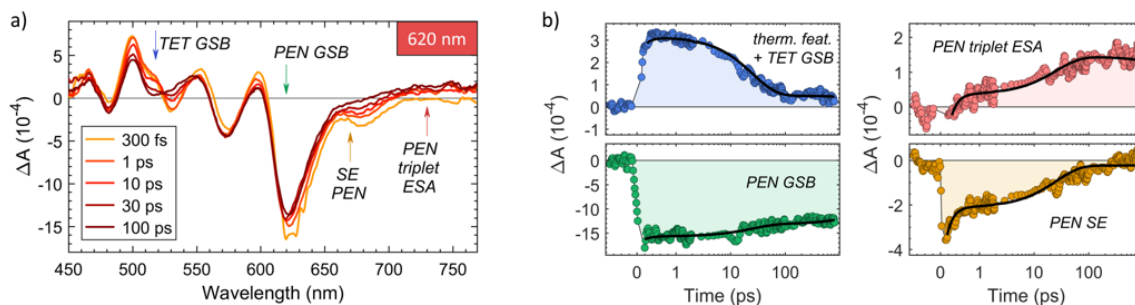


Figure 8. Photophysics of 5% PEN in 95% TET using an excitation wavelength of 620 nm, corresponding to a photon energy below the TET band gap. a) Transient absorption spectra at different delays between pump and probe. b) Time traces at selected wavelengths. Adapted from [24].

Thus, our data point towards the existence of two parallel relaxation channels for a PEN singlet in this blend. The first channel is PEN homofission in the PEN dimers and causes the fast increase (decay) of the triplet ESA (singlet SE). The subsequent, slow increase (decay) of triplet ESA (singlet SE) with a time constant of 26 ps originates from the second channel, i.e., heterofission of a PEN singlet into a PEN triplet and a TET triplet. The latter can lead to the bleaching of a TET molecule without direct photoexcitation of TET and, thus, explains the observation of a TET GSB [24].

4. CONCLUSION

In summary, we have investigated SF in blends of two prototypical SF chromophores with weakly interacting spacer molecules and compared the experimentally determined SF rates with calculations. Focusing on the expansion of the unit cell we find a robust SF rate in PEN at odds with theoretical predictions [21]. This is explained by the existence of hotspots, where an increased probability for neighboring PEN molecules facilitates SF. The impact of the number of nearest neighbors on SF rates was investigated in more detail by comparing PEN- and TET-based spacer blends. There, clear differences are observed with a decreasing SF rate in TET-based blends while the SF rate in PEN-based blends remains largely unchanged. This indicates fundamental differences in the two SF mechanisms. For TET, our results are consistent with incoherent population transfer that is expected to scale with the number of increase neighbors, while SF in PEN mainly depends on the coherent admixture of the TT state to the photoexcited state in PEN and is insensitive to the number of nearest neighbors. Finally, we used blends of PEN and TET as model systems to investigate heterofission and find for this process in 5% PEN blends a time constant of 26 ps. For higher PEN fractions it is outcompeted by PEN homofission [24]. Our study demonstrates the potential of mixed films of SF chromophores as a complementary approach to control SF and to unravel the details of SF mechanisms that otherwise require complex experimental setups.

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