

Ultrafast Dynamics of Exciton Fission in Polycrystalline Pentacene

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S Supporting Information

ABSTRACT: We use ultrafast transient absorption spectroscopy with sub-20 fs time resolution and broad spectral coverage to directly probe the process of exciton fission in polycrystalline thin films of pentacene. We observe that the overwhelming majority of initially photogenerated singlet excitons evolve into triplet excitons on an ~ 80 fs time scale independent of the excitation wavelength. This implies that exciton fission occurs at a rate comparable to phonon-mediated exciton localization processes and may proceed directly from the initial, delocalized, state. The singlet population is identified due to the brief presence of stimulated emission, which is emitted at wavelengths which vary with the photon energy of the excitation pulse, a violation of Kasha's Rule that confirms that the lowest-lying singlet state is extremely short-lived. This direct demonstration that triplet generation is both rapid and efficient establishes multiple exciton generation by exciton fission as an attractive route to increased efficiency in organic solar cells.

The field of organic photovoltaics has arisen to explore possibilities for low-cost, flexible, and large-area devices to generate electricity from sunlight.¹ The Shockley–Queisser limit to the power conversion efficiency of any single-bandgap photovoltaic device under solar irradiation exists because sub-bandgap photons cannot be absorbed and the excess energy of supra-bandgap photons is wasted.² However, as has been investigated in the context of multiple exciton generation in inorganic nanocrystals,^{3,4} this limit could be overcome if the excess energy of supra-bandgap photons was efficiently harnessed to generate additional electron–hole pairs. In molecular organic semiconductors, an analogous opportunity is provided by the well-established phenomenon of exciton fission.^{5,6}

In conjugated organic molecules, exciton fission refers to the spin-allowed conversion of one photogenerated singlet exciton into two triplet excitons residing on different chromophores.⁶ Following bandgap excitation, fission proceeds rapidly and without thermal activation if the lowest-lying triplet state (T_1) has less than half of the energy of the lowest-lying singlet state (S_1).⁷ This is the case for pentacene, which has made it the subject of several ultrafast spectroscopic studies.^{7–10} As shown in Figure 1, the energy of S_1 in pentacene is 110 meV greater than twice the energy of T_1 .⁷ We note therefore that regeneration of the singlet via triplet–triplet recombination is unlikely at room temperature.

Following work by Kippelen et al. that showed that pentacene/C60 bilayer photovoltaic devices exhibit very high photon-to-electron conversion efficiencies,^{11,12} as well as a report from Baldo et al. of a pentacene/C60 photodiode with greater than 100% quantum

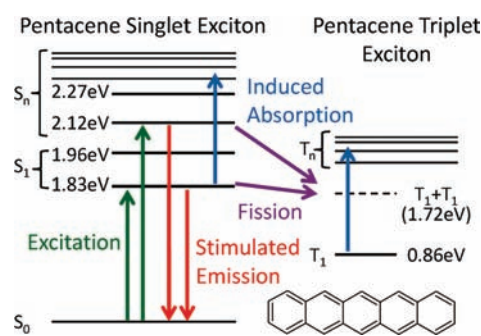


Figure 1. Energy level diagram for excitonic states in pentacene. Labeled arrows indicating transitions relevant to the work are added. The Davydov levels of the singlet exciton lie at 1.83 and 1.96 eV, with higher-lying levels at 2.12 and 2.27 eV. All four of these transitions are readily apparent in the ground-state absorption spectra presented in the Supporting Information (SI). The molecular structure of pentacene is inset.

efficiency under reverse bias,¹³ we recently used transient absorption spectroscopy (TA) with improved spectral coverage and resolution to demonstrate that charge generation in these polycrystalline devices is achieved via the long-range diffusion of long-lived triplet excitons to the heterointerface, where they are ionized. These triplet excitons were formed within the 200 fs time resolution of the measurement.¹⁴ This upper limit on the time scale of triplet generation is too short to be explained by intersystem crossing, which suggests that the triplet population results from exciton fission. A similar mechanism has been recently proposed to explain steady-state spectroscopic measurements on monocrystalline rubrene.^{15,16}

Although a previous study on pentacene films reported TA data that contained rapidly evolving features which were assigned to exciton fission,⁷ inconsistencies, for example with solution-phase measurements¹⁷ and modeling,¹⁸ have caused this interpretation to be disputed, with the features in question being alternatively assigned to the formation of excimers,⁸ cations,⁹ singlet-coupled biradicals,⁶ and doubly excited states.^{19,20} Here, we perform TA with sub-20 fs time resolution and broad spectral coverage (500–1000 nm). As we will show, both capabilities are required to directly observe the fission process in neat pentacene films.

Transient absorption spectroscopy is a technique which probes the temporal evolution of the differential transmission ($\Delta T/T$) of the sample in response to a pump pulse, allowing the observation of the population dynamics of photoexcited species. Negative regions

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in a $\Delta T/T$ vs wavelength plot indicate the photoinduced absorption (PIA) of an excited species; positive regions can correspond to stimulated emission (SE) from an excited state, or ground state bleaching (GSB), which is the induced transmission caused by the depopulation of the ground state. However, these features commonly overlap. Further details regarding spectroscopic technique can be found in the literature^{14,21,22} as well as in the SI.

We make TA measurements on 110 nm pentacene films produced by evaporation onto 1.1 mm-thick fused-quartz substrates. The TA data must be processed to remove significant coherent artifacts. These artifacts are observed when the pump–probe delay is comparable to both the dephasing time of the material polarization and the temporal width of the cross-correlation of the pump and probe pulses and arise due to nonlinear coupling between the pulses via the refractive index.^{23,24} In brief, our filtering technique uses single-variable decomposition (SVD) to break down the two-dimensional TA data set into weighted pairs of one-dimensional spectral curves and kinetic traces. As the signals of interest in this system have largely time-invariant spectral shapes before 1 ps, they are effectively captured in a few heavily weighted spectral/kinetic pairs. By contrast, the spectral features associated with the artifacts vary simultaneously with wavelength and time and so are instead captured by a series of lightly weighted components, which can then be truncated. The validity of this technique is verified as the sum of the truncated components qualitatively reproduces the TA signal observed from a bare glass substrate. More detailed descriptions of the filtering procedure along with the raw data are presented in the SI.

Figure 2a presents the evolution of the TA spectra in the first picosecond after excitation with a broad-band (600–700 nm) pump tuned to the lowest-energy pair of peaks in the absorption spectrum (See SI). We note that the excitation intensities used in this experiment are relatively high (~ 1 mW/cm²/pulse) and correspond to a high peak signal. These conditions were required to bring out the weaker features in the spectrum with high temporal resolution. However, we verified that the measured signal scales linearly when the pump is attenuated by a factor of 4, thus demonstrating that bimolecular processes do not play a significant role on the subpicosecond time scale.

The signal evolves considerably in the first 150 fs, but is largely stationary thereafter. At 1 ps, the TA signal is in agreement with previous measurements,^{8,9,14} and we similarly attribute the positive features at 585, 635, and 680 nm to GSB. However, our high temporal resolution and broad-band detection allow us to track the considerable spectral evolution that occurs in the first 150 fs. The most dramatic effect is the rapid decrease of the positive feature at 680 nm, which falls 40% from its peak with a 35 fs monoexponential time constant (See Figure 3). Comparing the signals at 20 and 500 fs, we note also the paired rise of the TA signal from 550 to 650 nm and all of the signal in the region of 700–1000 nm. The signals in these two regions rise and fall with monoexponential time constants of 78 and 85 fs, respectively, which are equivalent to within uncertainty. These observations are consistent with the coupled decay of an initial state, associated with a negative PIA feature of 550–650 nm, and buildup of a final state, characterized by a PIA band 700–1000 nm. (See also the dynamics in Figure 3.)

Figure 2b shows a comparable set of time-dependent TA spectra taken using the same sample, but exciting higher-lying transitions in the absorption spectrum (475–575 nm). The striking difference compared to Figure 2a is the marked reduction of the magnitude of the spectrally narrow, short-lived component of the positive signal at 680 nm, and its replacement by a broad

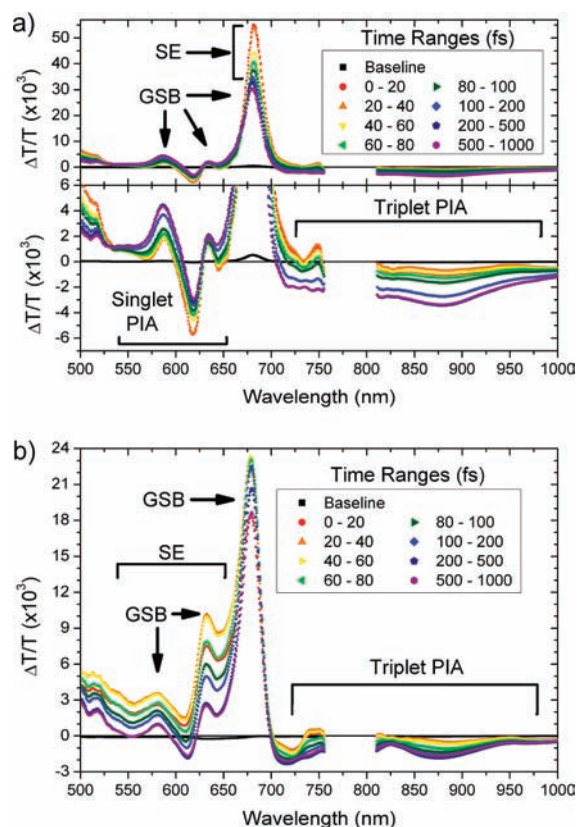


Figure 2. SVD-cleaned transient absorption spectra for a pentacene thin film excited using a broad-band pulse tuned to (a) low-lying absorptions (600–700 nm) or (b) higher-lying absorptions (475–575 nm). Data from 550 to 750 nm and from 750 to 1000 nm are derived from sequential experiments on the same sample performed using pulses with an irradiance of approximately (a) 0.5 and 1.3 mJ/cm² and (b) 1.1 and 5.3 mJ/cm², respectively. In both cases, the magnitude of the signal measured from 810 to 1000 nm is scaled by the ratio of the excitation intensities. Important spectral features are labeled and the data in (a) are presented twice, the second time with an expanded y-axis. Spectra are averaged over the time ranges indicated.

(490–680 nm) but less intense positive component with similar dynamics. This difference is incompatible with dynamics caused by bimolecular recombination but is readily explained if the short-lived positive component is assigned to SE from the initially photogenerated singlet exciton. Specifically, the narrow SE at 680 nm that we observe if the S_1 transition is directly excited is in agreement with reported photoluminescence spectra of free (non-self-trapped) excitons in ultrathin pentacene films and clusters.^{25,26} By contrast, the SE observed at a wide range of blue-shifted wavelengths when a higher-lying transition is excited is understood as light emitted by the ‘hot’ exciton before it is able to relax to S_1 (as suggested by the red arrows in Figure 1). We emphasize that this violation of Kasha’s rule (i.e., that the higher-energy SE is not overwhelmed in intensity by the SE from the lowest excited state) implies that the S_1 state is short-lived, even on the time scale of excitonic cooling. This is consistent with the very low luminescence efficiency that has been observed in pentacene.^{7,8}

With this information about the singlet population dynamics in hand, we return to the spectra shown in Figure 2a and the time traces in Figure 3 and note the similar, rapidly decaying dynamics of the PIA feature from 550 to 650 nm, which is then readily assigned as the PIA from singlet excitons. Due to spectral overlap with the positive GSB,

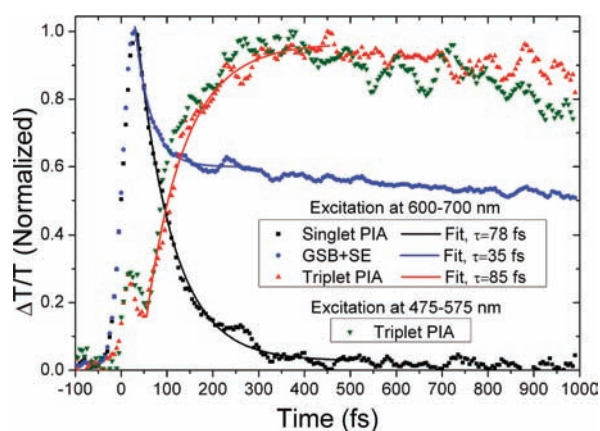


Figure 3. Normalized transient absorption dynamics for a pentacene thin film. SVD-cleaned data (identical to Figure 2) are presented as points, with monoexponential fits shown as solid lines. The synchronous decay of the PIA signal of the singlet (595–601 nm) and rise of that of the triplet (850–870 nm) capture the fission process. (Both signals have been inverted, and the singlet PIA trace is taken at a node in the spectrum at 1 ps to eliminate the contribution of the GSB.) The loss of the singlet is also reflected in the rapid decay of the SE component of the signal at 668–673 nm. The zigzag feature in the triplet PIA curve near zero delay remains from the coherent artifact, and uncertainty in the fits is on the order of 5 fs. The dynamics of triplet formation are shown for both experimental excitation wavelengths as indicated.

the PIA feature should be seen to extend over the entire region where the spectrum at 20 fs is significantly more negative than at 500 fs, rather than being limited to the small range where $\Delta T/T$ is negative.

Following our previous work,¹⁴ spectroscopy done on single crystals,⁹ as well as theoretical predictions,¹⁸ we assign the negative $\Delta T/T$ signal at wavelengths greater than 700 nm to the PIA of triplet excitons. With this assignment, as shown in Figure 3, the correlated rise of the triplet and decay of the singlet population at these very short time scales strongly suggests exciton fission as the generation mechanism. In addition, we note the similar dynamics at wavelengths shorter than 530 nm. The signal in this region is consistent with a growing PIA superimposed on the largely static GSB. A triplet PIA ($T_1 \rightarrow T_n$) at these wavelengths with the expected polarization has been observed⁸ and also predicted by modeling.¹⁸ However, we find that this transition is weaker, relative to the PIA beyond 700 nm, than has been calculated.¹⁸

We have accounted for our short time measurements using singlet fission to triplet pairs. Alternatively, it has been put forward that these transient phenomena can be explained by the very rapid formation of an excited dimerlike state via the rotation and displacement of a pair of pentacene molecules from their initial herringbone configuration to a parallel (face-to-face) geometry.⁸ We note that these rapid time scales seemingly preclude explanations that would involve exciton migration to a defect site; thus, excimer formation would need to be an intrinsic process, which Kuhlman and co-workers have suggested is energetically unfavorable.¹⁹ It has also been proposed that the PIA signal beyond 700 nm could correspond to the absorption of a radical cation–anion pair.⁶ Although we cannot rule out this possibility and have noted that the pentacene cation does have some absorption in this region,¹⁴ we note that the peak at 870 nm of the PIA signal observed here is not apparent in charge-modulation studies²⁷ and that such an explanation would require a long-lived, mobile, charge-transfer-like state to be generated very rapidly. Further study is warranted to clarify the nature of the spectrum in this region.

The most significant consequence of our results is that they firmly place the dynamics of fission on a time scale comparable to

the period of the highest-energy vibrations expected to be present in the system. This suggests that fission proceeds from a nonequilibrium state and, given the strong intermolecular coupling evidenced by the considerable solution-to-solid redshift of the absorption spectrum, that fission proceeds directly from a state which is delocalized across several molecules. Such a delocalized state has been found to be of critical importance for the efficiency of fission by Bardeen et al. in experiments performed on conjugated tetracene dimers.²⁸ However, we emphasize the difference between the relatively slow (9.2 ps) fission process in tetracene that proceeds from the fully relaxed (lowest-lying) singlet exciton, and the extremely fast (~ 80 fs) nonequilibrium fission process observed here. Rapid nonradiative evolution of this type can be associated with conical intersections, and we note that recent calculations by Musgrave and co-workers suggest that such a conical intersection explains the rapid and efficient fission process in pentacene.²⁰ In such a picture, the initial delocalization of the S_1 wavepacket would allow the system to rapidly evolve into two triplets on different chromophores.

Further insight could be obtained into the nature of the initially photoexcited state by considering the structure of the SE spectrum, particularly the peaks at 680 and 750 nm that have been observed in steady-state spectroscopy. The nature of the peak at 750 nm is debated. Photoluminescence measurements of isolated pentacene molecules in a host crystal²⁹ or solution³⁰ suggest that a vibrational sideband should exist approximately 0.17 eV (1400 cm^{-1}) away from the primary luminescent transition. Alternatively, low-temperature measurements of the luminescence from pentacene thin films,^{31–33} ultrathin films, and clusters^{25,26,34,35} have assigned the prominent luminescence feature at 750 nm to emission from self-trapped excitons or defects.

Although the SVD-filtered data in Figure 2 do show a small, short-lived positive feature consistent with SE at 750 nm, more careful analysis shows that this feature is primarily due to the coherent artifact, implying that emission at this wavelength is largely suppressed at these early times. Further experiments incorporating improved control of the coherent artifact are clearly necessary to gauge the strength and dynamics of this transition, as its very small apparent strength relative to the primary SE peak at 680 nm could either indicate that the emissive species is significantly delocalized, as has been observed and modeled in anthracene and tetracene at low temperature,^{36–39} or that the emissive self-trapped exciton is not efficiently formed directly from the singlet, perhaps instead generated at later times via triplet–triplet recombination.³² In summary, although the magnitude of the signal from the coherent artifact presently complicates detailed analysis of the SE spectrum in polycrystalline pentacene, it is already clear that the luminescence spectrum from the S_1 state shows a markedly reduced peak at 750 nm relative to steady-state spectroscopy measurements on either isolated molecules or thin films.

We return to the dynamics of pentacene excited to S_1 shown in Figure 3 to examine the difference in the time constants for the decay of the SE (35 fs) and the decay of the singlet PIA (78 fs). The feature at 680 nm is made up of overlapping SE and GSB signals and could conceivably also contain a portion of the triplet PIA signal. Consequently, the experimental kinetic trace would be affected not only by the decrease of the SE but perhaps also by a reduction in the magnitude of the GSB due to localization of the triplet population. However, the data could also be consistent with a fission process that proceeds momentarily through an intermediary nonemissive state. Such a possibility has been explored theoretically by Musgrave and collaborators who proposed an intermediate dark state with multiexcitonic character²⁰ and also

by Ratner and co-workers for the case of an initially localized excitation and charge-transfer intermediate state.⁴⁰ Further TA measurements with higher temporal resolution and improved signal-to-noise could shed light on this fundamental process.

Of relevance to the nature of any intermediate states are the data shown in Figure 3 comparing the dynamics of triplet generation at the two experimental excitation wavelengths. The graph shows that the nature of the initially photoexcited state makes no detectable difference in the onset of the triplet signal, implying that the fission process does not require the system to first relax to S_1 and can proceed directly from higher-lying singlet states on a similarly rapid (~ 80 fs) time scale. Although fission from higher-lying states has been previously demonstrated in tetracene,⁹ it is significant from the perspective of efficiency that the fission process in pentacene exhibits faster dynamics than excitonic cooling.

Finally, inspection of the dynamic traces in Figure 3 reveals that the composite GSB+SE peak at 680 nm is not completely time-invariant after the first 150 fs but decays by 15% over the remainder of the first picosecond. If this decrease were the result of triplet decay, perhaps due to bimolecular processes, there would be a corresponding change in the triplet PIA signal. Instead, the triplet feature is static. Accordingly, the decay of the feature at 680 nm is most readily explained as resulting from the decay of a small residual population of singlet excitons which do not undergo fission, perhaps because of localizing interactions with defect sites or kinetic competition with the well-established process of self-trapping.²⁶

In conclusion, we have probed the dynamics of exciton fission in polycrystalline pentacene thin films. Triplets are generated very rapidly (~ 80 fs time constant) regardless of the excitation wavelength, which is consistent with fission occurring from a nonequilibrium delocalized state. Fission in polycrystalline pentacene appears to be very efficient, as there is little ($\sim 15\%$) further evolution of the spectra after 150 fs. Stimulated emission is observed briefly from the photogenerated singlet exciton, confirming the very rapid nature of the fission process as well as providing insight into the nature of the initial photoexcited state. These results bear significantly on the task of realizing a solar cell that takes advantage of exciton fission, as it may prove important to ensure the formation of ordered molecular aggregates that can support delocalized excitations, as opposed to simply including pentacene moieties in a disordered system.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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