

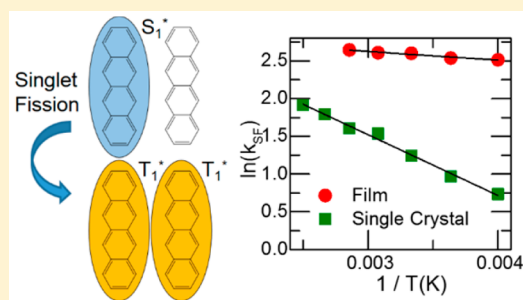
How Morphology Affects Singlet Fission in Crystalline Tetracene

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S Supporting Information

ABSTRACT: The dependence of exciton dynamics on the crystalline morphology of tetracene is investigated using time-resolved photoluminescence. Single crystals exhibit relatively slow singlet decays with times that range from 130 to 300 ps depending on the sample. This decay has an activation energy of $\sim 450\text{ cm}^{-1}$ over the temperature range of 200–400 K. Single-crystal samples also exhibit more pronounced quantum beats due to the triplet pair spin coherences. Polycrystalline thin films grown by thermal evaporation have singlet decay times on the order of 70–90 ps with a much weaker temperature dependence. Many thin-film samples also exhibit a red-shifted excimer-like emission. When a polycrystalline thin film is thermally annealed to produce larger crystal domains, single-crystal behavior is recovered. We hypothesize that the different dynamics arise from the ability of singlet excitons in the thin films to sample regions with defects or packing motifs that accelerate singlet fission.



Singlet fission (SF), in which an excited singlet state (S_1) splits into a pair of triplet (T_1) states,^{1,2} represents a possible mechanism for increasing solar energy conversion efficiencies.^{3,4} Tetracene is a prototypical SF system thanks to the fact that its singlet and triplet pair energies are nearly degenerate, allowing singlets and triplet pairs to interconvert.^{5,6} This permits both singlet and triplet dynamics to be monitored via the prompt and delayed fluorescence signals, respectively.

Despite extensive study, there remain discrepancies in the literature as to the kinetics of SF in crystalline tetracene. The first unresolved issue concerns the initial decay rate of the S_1 state. Time-resolved fluorescence measurements on tetracene single crystals consistently yielded singlet lifetimes on the order of 200–300 ps.^{7–12} Fluorescence lifetime and transient absorption measurements on polycrystalline films (PCFs) revealed singlet lifetimes ranging from 30 to 90 ps.^{13–17} Two-photon photoemission experiments on tetracene monolayers yielded an even shorter SF time on the order of 8 ps.¹⁸ A second question concerns the existence of an activation energy ΔE_{act} for SF. Early investigators making temperature-dependent fluorescence quantum yield measurements on single crystals deduced that SF was an activated process with $\Delta E_{\text{act}} = 1200\text{--}1800\text{ cm}^{-1}$.^{12,19,20} These values correlated well with the $\Delta E_{\text{act}} = 2E(T_1) - E(S_1)$ obtained from measurements of the $S_0\text{--}T_1$ and $S_0\text{--}S_1$ optical transition energies.²¹ However, recent measurements on PCFs show that the initial singlet decay has little or no dependence on temperature over the range of 300–5 K.^{15,17,18,22,23} This apparent lack of activation barrier has been attributed to entropic contributions due to exciton diffusion in the solid,^{18,24} as well as to the presence of “dull” or dark intermediate states.^{17,22,23}

The discrepancies between the single crystal and PCF results are hard to understand if the SF rate depends only on the local ($\sim 1\text{ nm}$) crystal environment because both samples are

crystalline on this length scale. One possible explanation is experimental error, but the variations are large enough and widespread enough to make this unlikely. A second explanation is that the picosecond dynamics are sensitive to differences in crystal morphology, like crystallite size, defect concentration, or modified molecular packing near interfaces. It is this second mechanism that is the subject of this Letter. We investigate the differences in dynamics between PCFs and single crystals grown from solution. We find that single crystals and PCFs have different singlet decay rates and different temperature dependences. Other notable divergences in behavior include the absence of spin state quantum beats and the appearance of a red-shifted excimer-like emission in many PCF samples. We confirm that morphology is the dominant factor by showing that when a PCF is thermally annealed to produce larger crystal domains, single-crystal behavior is recovered. The results in this Letter should help resolve discrepancies as to the intrinsic time scale for SF in crystalline tetracene, which we think is in the range of 250–300 ps. We hypothesize that the faster rates observed in PCFs are likely mediated by singlet exciton diffusion to defects or interfaces. These results suggest that crystal morphology as well as molecular packing should be taken into account when analyzing SF rates in molecular solids.

Details of the preparation of the crystalline tetracene samples can be found in the Supporting Information and in ref 25. Briefly, single crystals were grown from toluene solution on a glass slide, while PCFs were prepared using a Pelco vacuum evaporator with a background pressure of 1.5×10^{-5} Torr. Time-resolved fluorescence data were obtained using front face detection with a Hamamatsu C4334 Streakscope picosecond

Received: March 17, 2015

Accepted: April 27, 2015

Published: April 27, 2015

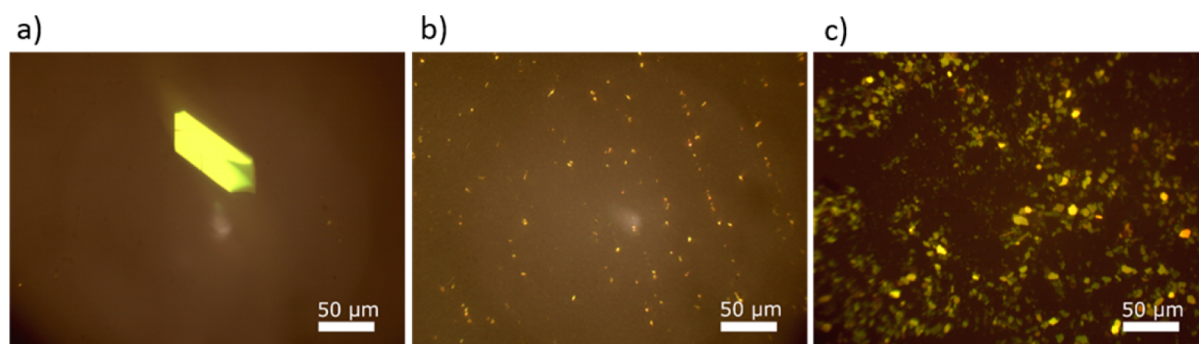


Figure 1. Polarized light microscopy images of (a) a solution-grown single crystal of tetracene, (b) an evaporated PCF of tetracene, and (c) an evaporated film of tetracene that has been annealed at 400 K for 30 min. These images illustrate the differences in the sizes of the crystalline domains for the different samples.

streak camera with 2.5 nm wavelength resolution and 15 ps time resolution. Unless otherwise specified, the fluorescence decays were integrated over 460–665 nm. The 800 nm output of a 80 MHz Spectra-Physics Mai Tai oscillator was passed through a pulse picker to achieve a 125 kHz repetition rate and then focused into a BBO crystal to generate the 400 nm excitation pulse. The laser fluences at the sample were measured to be less than $2 \mu\text{J}/\text{cm}^2$, well below the threshold for singlet–singlet annihilation.²² All measurements were done inside of an evacuated Janis ST-300 cryostat at pressures below 1×10^{-3} Torr. As a precaution against sublimation of the crystals or films, a second microscope slide was placed on top of the sample. When this was not done, the samples sublimed quickly at higher temperatures. The temperature-dependent experiments were conducted from lowest temperature to highest temperature in order to avoid thermal annealing effects on the measurements at lower temperatures.

Figure 1 shows polarized light microscopy images of three types of tetracene samples. In Figure 1a, a single solution-grown tetracene crystal, on the order of $100 \mu\text{m}$ wide and 20 nm thick, shows uniform birefringence, indicative of a single-crystal domain. The evaporated PCF in Figure 1b shows only a few birefringent specks, suggesting that most of the crystal domains are smaller than the microscope resolution and randomly oriented. This is consistent with previous X-ray diffraction and electron microscopy studies of tetracene thin films grown by sublimation.^{26,27} After the PCF film is heated to 400 K in vacuum, one observes the formation of larger crystalline domains, as shown in Figure 1c. This thermal annealing process provides a way to increase the crystallinity of the sample without introducing other chemical species. This approach allows us to prepare three different samples, grown from the same batch of tetracene, with distinct morphologies. We did not examine vacuum-sublimed single crystals due to the difficulty of isolating optically thin specimens.

The initial fluorescence decay in solid tetracene samples is roughly 20× faster than that for tetracene by itself in solution.²⁸ The extensive experimental work cited above has established that this accelerated decay is due to SF, although the enhanced radiative decay channel makes a small contribution (0.08 ns^{-1}).¹⁴ In Figure 2, we show that the three different solid-state morphologies give rise to different initial fluorescence decay rates on the subnanosecond time scale, as measured by the slope of the natural log of the signal over the first two natural logs (86%) of the decay (Supporting Information). We take this region to reflect the intrinsic decay of the initially excited singlet state, before triplet fusion gives rise to a slower delayed

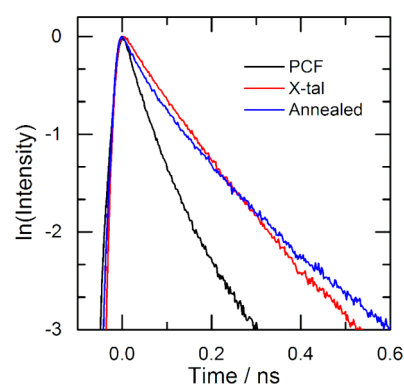


Figure 2. Comparison of the fluorescence decays (log scale) for a solution-grown tetracene single crystal (red) and a tetracene PCF before (black) and after annealing (blue). The $1/e$ time for the tetracene single crystal is 170 ps, while that of the PCF is 70 ps before annealing and 140 ps after annealing.

fluorescence component. The solution-grown single crystal yields a decay time of 170 ps. This value is at the low end of the range reported by earlier workers.^{7–12} Other single crystals yielded slower decay times of up to 300 ps, and the initial decay rates could vary by a factor of 2 depending on sample. The evaporated films, on the other hand, always have more rapid decays. The example shown in Figure 2 has an initial decay time of 70 ps. This decay time is close to the average reported by most workers who have studied tetracene PCFs deposited by evaporation.^{13–15} In general, we saw more uniform decay times for the PCF samples, with initial lifetimes varying between 70 and 90 ps. When the PCF is thermally annealed, the initial fluorescence decay slows dramatically to 140 ps, close to that of the single crystal. The conclusion is that the singlet decay is at least 2× faster in a PCF than that in a single crystal, on average.

We note that recent transient absorption experiments on tetracene single crystals have reported more rapid singlet decay times of 50–80 ps, leading to the opposite conclusion that SF is more rapid in single crystals.^{29,30} In those experiments, high pump pulse fluences mean that exciton–exciton annihilation always plays a role in the observed dynamics, complicating analysis of the singlet decay. Higher defect densities resulting from different crystal growth methods could also contribute to a faster apparent SF rate (see below).

In Figure 3, we compare the temperature-dependent initial decays for the PCF and single crystal over the range of 200–400 K. In a PCF, we and others have found that the initial singlet decay has almost no temperature dependence in the

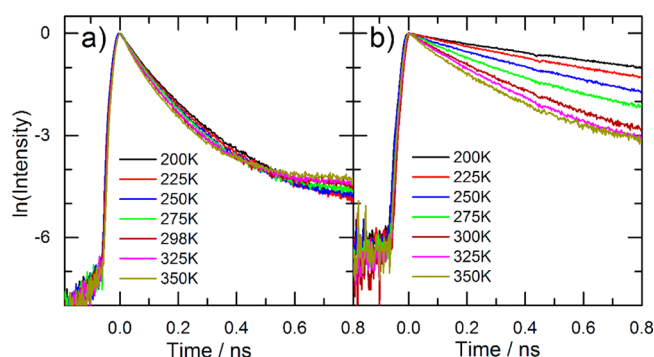


Figure 3. Temperature-dependent fluorescence decays (log scale) for (a) a tetracene evaporated PCF and (b) a tetracene single crystal. The singlet lifetime of the single crystal exhibits a much greater response to temperature than that of the thin film.

range of 300–4 K.^{17,18,22,23} However, this conclusion must be qualified by the knowledge that tetracene can undergo at least one phase transition at around the temperature of 150 K.^{31–33} In the present work, we measure the SF rate over the range of 200–400 K, where there are no known phase transitions. In Figure 3a, the fluorescence decays for the PCF sample over this temperature range exhibit almost no change, while the single crystal decays in Figure 3b show a dramatic increase in the initial singlet decay rate. As described above, there was a significant variation in the initial decay rate in the single crystals, but all showed a larger temperature dependence than the PCF. In Figure 4, we show Arrhenius plots for a PCF

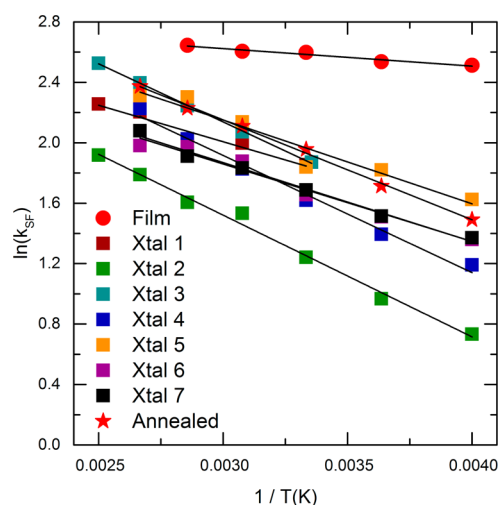


Figure 4. Arrhenius plot showing the relationship between the initial decay rate versus temperature for a tetracene PCF (purple squares) and seven different tetracene single crystals in order to demonstrate the spread in initial singlet decay times. The data for the annealed PCF is also shown (red stars).

sample and for seven different single crystals. The PCF has a small slope, from which we extract an activation energy $\Delta E_{act} = 55 \pm 30 \text{ cm}^{-1}$. For the single-crystal samples, there is a larger variation in rate constants, but we can extract an average value for $\Delta E_{act} = 440 \pm 100 \text{ cm}^{-1}$. If the PCF is thermally annealed and its temperature-dependent singlet decay rate measured, the $\Delta E_{act} = 460 \pm 100 \text{ cm}^{-1}$ is similar to that of the single crystals.

There are two other reproducible differences between the PCFs and the more crystalline samples. First, as shown in our

previous work,²⁵ the PCF exhibits little or no oscillation in the delayed fluorescence signal due to quantum beating of the triplet pair spin states, as shown in Figure 5. The oscillation

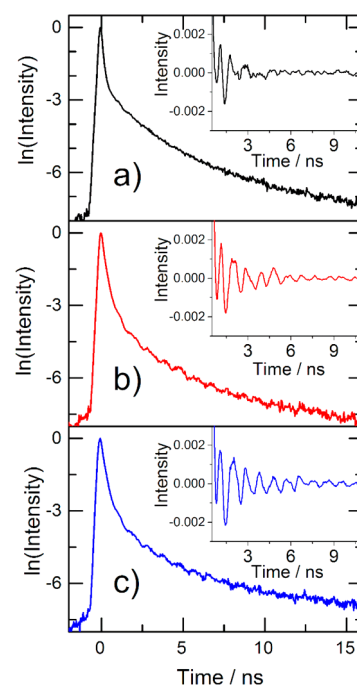


Figure 5. Normalized time-resolved fluorescence decays for (a) a tetracene PCF, (b) a tetracene single crystal, and (c) an annealed tetracene PCF. All three decays have similar levels of delayed fluorescence that display quantum beats (insets), but the annealed film and the single crystal exhibit more intense beating over a longer time.

visibilities are consistently higher in the single crystal and thermally annealed samples, as shown in Figure 5b and c. A second difference between the PCF and single crystal is that many PCF samples exhibit a red-shifted, broadened emission centered close to 600 nm. The amplitude of this feature in the spectrum shown in Figure 6 varies between PCF samples, and in our previous work, we concentrated on samples where this feature was minimized or absent altogether. Its decay time of 2.5 ns (Supporting Information) is much slower than that of the exciton fluorescence peaked at 535 nm, but it can dominate

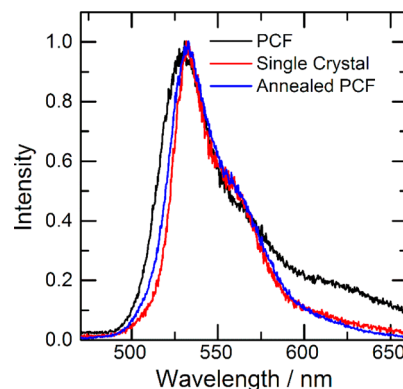


Figure 6. Fluorescence spectra of a tetracene PCF (black), single crystal (blue), and annealed PCF (red). The data are integrated over 0–15 ns. The unannealed PCF sample exhibits an additional feature at 625 nm that has a lifetime of approximately 2.5 ns.

the delayed fluorescence spectrum in samples where it is present. This feature is largely absent in single crystals and can be removed by thermally annealing the PCFs (Figure 6). The fact that it can be minimized by improving sample crystallinity suggests that this emission is associated with a defect in crystal packing. Its lower energy and lack of vibronic features suggests that it could be an excimer species associated with sites where the tetracenes experience face-to-face packing rather than the edge-to-face packing in a perfect crystal lattice. This type of defect-induced excimer emission has been well-studied in crystalline anthracene^{34–36} and has been characterized to a limited degree in tetracene single crystals.³⁷

We now examine the origin of the faster singlet decay in the PCFs. We consider three types of nonradiative relaxation processes: internal conversion to the ground state, relaxation to a lower energy dark state, and accelerated SF. We rule out internal conversion because transient absorption experiments on PCFs show no evidence for recovery of the ground-state bleach on the 1 ns time scale.^{16,17,28} Formation of a lower-energy dark state would be expected to have a recognizable signature in the PCF transient absorption signal, but experiments on thin films and single crystals yield similar results, all of which are consistent with SF being the dominant nonradiative decay pathway.^{16,17,22,29,30} Additional evidence that SF is the main decay channel in the PCFs is that the ratio of prompt to delayed fluorescence signals is similar for both PCFs and single-crystal samples, as can be seen from the decay curves in Figure 5. If the accelerated singlet decay in the thin film did not produce triplets, we would expect the magnitude of the delayed fluorescence to decrease because there would be fewer triplets to recombine.

Our observations are consistent with the idea that structural differences between the PCF and single crystal play a central role in determining the SF rate. The fluorescence spectra in Figure 6 provide evidence that the PCF has defect sites associated with tetracene molecules that have adopted a more cofacial arrangement. However, there is also evidence that when tetracene is evaporated onto a surface, subtle differences in the molecular packing can arise.^{38,39} These differences, which presumably would be most pronounced for molecules closer to the substrate surface, could also lead to an accelerated SF rate. The diffusion length for the singlet exciton in crystalline tetracene has been estimated to be 10–15 nm at room temperature,^{40,41} allowing a large fraction of the excited singlet population to access regions of the sample with modified packing and/or defect sites. The physical picture of the dynamics in the PCFs starts to resemble that postulated for amorphous films of diphenyltetracene⁴² and rubrene,⁴³ in which the singlet excitons diffuse until they reach a site where the molecules are suitably oriented to undergo rapid SF. In this scenario, the singlet decay in the PCFs reflects a weighted average of different SF rates, including the intrinsic SF rate of the single crystal. Different preparation methods could affect the density of defect sites and/or the presence of substrate-induced packing changes, resulting in the wide variance in reported SF rates for PCFs. Of course, our single-crystal samples also exhibit substantial variations in both the SF rates and ΔE_{act} values. The physical origin of these variations, which seem to be uncorrelated with each other (Supporting Information, Figure S3), is not understood at this time. We suspect they can be attributed to variations in defect type or density between crystals. We have observed similar variations in the fluorescence decays of distyrylbenzene microcrystals grown

from by solvent evaporation.⁴⁴ It may be that more controlled crystal growth methods would yield more consistent behavior.

The evidence that SF in tetracene can be mediated by defects raises the question of what type of defect states could accelerate SF. Cofacial “slip-stack” packing can enhance the charge-transfer (CT) interactions that enable rapid SF,^{45,46} and this type of packing can also give rise to excimer emission, as seen in some of the PCF samples. Excimer formation has been invoked as both an intermediate state in SF^{47–49} and as a competing channel.^{50–53} It is possible that in a disordered film, there exist multiple cofacial packing motifs. For efficient SF, at least some of these motifs should have CT interactions that are stronger than those of the edge-to-face-packed molecules in the pristine crystal but too weak to form stable excimer states that cannot dissociate into triplets. In this scenario, excimer emission signals the presence of the type of structural defects that can enhance SF, but the emissive excimer states themselves are not necessarily intermediates in the SF process.

Last, we address the question of whether SF is thermally activated in tetracene. SF mediated by singlet exciton diffusion to “hotspots” would be expected to depend only weakly on temperature because Forster energy transfer relies on spectral overlaps that change only slightly over this temperature range. The absence of such hotspots in a solution-grown crystal allows us to measure an activation energy, $\Delta E_{\text{act}} = 450 \text{ cm}^{-1}$, that probably represents a lower bound for that of a perfect tetracene crystal. We should also note that this activated process is only operative in the range of 200–400 K. The results of this Letter cannot explain the lower temperature data in both the PCF and the single crystal, where the singlet decays remain rapid while the signature delayed fluorescence is replaced by red-shifted, longer-lived emission features.^{22,23} Early workers simply integrated over the entire emission spectrum, assuming that it all originated from the singlet state, and derived roughly Arrhenius behavior. We now know that the situation is more complicated and that multiple emitting states are involved, but the nature of the state formed by the rapid decay of the initial singlet state at lower temperatures remains unclear.

In this Letter, we explored how SF dynamics in tetracene depend on sample preparation. We found consistent differences between the behaviors of polycrystalline thin films grown by thermal evaporation and thin crystals grown from solution. In the more crystalline samples, we saw a slower SF rate that has a substantial activation energy over the range of 200–400 K. More crystalline samples also exhibited more pronounced quantum beats due to the triplet pair spin coherences and less red-shifted excimer-like emission. We hypothesize that these differences arise from the ability of rapidly diffusing singlet excitons to sample defect sites or areas with different molecular packing in the PCFs. Our results provide a dramatic demonstration of how sample preparation can affect exciton dynamics in molecular crystal semiconductors.

■ ASSOCIATED CONTENT

● Supporting Information

Sample preparation, prompt decay fitting details, activation energy versus fission rate, and excimer lifetime. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00569.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the National Science Foundation Grant CHE-1152677.

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