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Singlet Fission in 9,10-Bis(phenylethynyl)anthracene Thin Films

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* Supporting Information

ABSTRACT: Singlet fission (SF) in two or more electronically coupled organic chromophores converts a high-energy singlet excitation into two low-energy triplet excitons, which can be used to increase solar cell efficiency. Many known SF chromophores are unsuitable for device applications due to chemical instability and low triplet state energies. The results described here show that efficient SF occurs in polycrystalline thin films of 9,10-bis(phenylethynyl)anthracene (BPEA), a commercial dye that has singlet and triplet energies of 2.40 and 1.11 eV, respectively, in the solid state. BPEA crystallizes into two polymorphs with space groups C2/c and Pbcn, which undergo SF with \( k_{\text{SF}} = (109 \pm 4 \text{ ps})^{-1} \) and \( k_{\text{SF}} = (490 \pm 10 \text{ ps})^{-1} \), respectively. The high triplet energy and efficient SF evidenced from the 180 ± 20% triplet yield make BPEA a promising candidate for enhancing solar cell performance.

Singlet fission (SF), the process by which a singlet excitation created in an assembly of two or more interacting chromophores energetically down-converts into two triplet excitons, was first discovered in 1965 in crystalline anthracene. Over the past decade, SF chromophores have attracted renewed attention because of their ability to overcome the Shockley–Quirier limit on the theoretical efficiency of single-junction solar cells. Specifically, SF chromophores can mitigate thermalization losses, where the absorbed photon energy in excess of the band gap is lost to heat. The triplet excitons can be harvested by either energy transfer or charge transfer to ultimately create charge carriers. For example, Dexter-type energy transfer from triplet excitons of pentacene and tetracene to lead-based quantum dots has been demonstrated. Charge transfer from the triplet exciton is also possible if the SF chromophores are paired with a suitable electron acceptor or donor, following the architecture of conventional organic solar cells. According to detailed balance, the maximum theoretical efficiency for a single-junction photovoltaic cell is achieved with a band gap of 1.1–1.3 eV. Thus, the triplet energy of a SF chromophore incorporated into a photovoltaic device should be >1.1 eV. In addition, because Frenkel excitons in organic chromophores have large binding energies, higher triplet energies facilitate charge transfer to a nearby donor or acceptor.

9,10-Bis(phenylethynyl)anthracene (BPEA) is a robust, industrial dye that has been widely used for chemiluminescent lighting, photoswitches, optical waveguides and solar cells. Its good chemical and thermal stabilities along with its facile synthesis and functionalization allow a wide range of different photochemical and photophysical applications. BPEA is a strong blue light absorber with a near unity quantum yield (\( \Phi_l = 1 \)) of green fluorescence. Various structural modifications of BPEA have been reported and highlight its tunable electronic properties. Although BPEA has been suggested as a potential SF candidate, only one study of SF in BPEA nanoaggregates has appeared following submission of this manuscript. Moreover, a recent report on 9,10-bis(TIPS)anthracene aggregates in solution showed only modest SF yields. Crystalline BPEA powder obtained from Sigma-Aldrich contains 59.90 ± 0.02% C2/c and 40.10 ± 0.02% Pbcn polymorphs (Figure 1a) based on a quantitative powder X-ray diffraction (PXRD) analysis (Figure S1). BPEA films were prepared by thermal vapor deposition under high vacuum onto a sapphire substrate followed by two annealing methods: solvent vapor annealing with dichloromethane for 12 h or thermal annealing at 120 °C for 3 h. Samples for PXRD analysis were scraped off the annealed films to remove preferred orientations. Analysis of the PXRD data (Figure 1b) using full-profile Rietveld fitting against the two reported crystal structures of BPEA reveals that the solvent-annealed film contains 61.2 ± 0.5% of the C2/c and 38.8 ± 0.5% of the Pbcn polymorphs, while the thermally annealed film contains >97% of the Pbcn polymorph.

BPEA in solution has a 2.64 eV \( S_1 \) state energy, \( \Phi_l = 1 \), and a 3.17 ± 0.02 ns \( S_1 \) lifetime (Figure S2). In both the solvent- and thermally annealed films, the \( S_1 \) energy decreases to 2.40 eV (Figure 2), which is expected from transition dipole–dipole coupling and orbital overlap-driven electronic coupling among chromophores. The fluorescence of both the solvent and thermally annealed films is significantly quenched to \( \Phi_l = 0.04 \pm 0.01 \) and 0.27 ± 0.04, respectively. BPEA phosphorescence in glassy 2-methyltetrahydrofuran at 77 K is essentially undetectable because of its extremely low spin–orbit-induced intersystem crossing quantum yield (10–5). Even in thin films where a significant triplet population is formed (vide infra), phosphorescence is undetectable at 77 K. Thus, we used palladium octabutoxyphthalocyanine, PdFe(OBu)₈, which has
Figure 1. (a) BPEA dimer from the crystal structure of the C2/c (left) and Pbcn (right) polymorphs. (b) Comparison of the simulated PXRD patterns of the C2/c (red) and Pbcn (blue) polymorphs with the PXRD pattern of the solvent-annealed (black) and the thermally annealed (green) BPEA thin films.

Figure 2. Steady-state absorbance (black) and emission (red) spectra of (a) solvent-annealed (b) thermally annealed polycrystalline BPEA thin films.

Figure 3. (a) FsTA spectra of a solvent-annealed 170 nm BPEA film using (a) 414 nm, 100 fs, 1 kHz laser pulses, (b) species-associated spectra and rate constants and (c) comparison of the transient difference spectrum of the triplet state to the thermal difference spectrum. Wavelengths for panels b and c are shown in reciprocal space to highlight the blue region of the spectrum. Reported values are the average and std. deviation from multiple experiments.

Following selective photoexcitation of PdPc(OBu)$_8$ at 720 nm (Figure S3), rapid intersystem crossing populates $^3$PdPc(OBu)$_8^*$, which then energy transfers to BPEA to produce $^3$BPEA (Figure S4). This observation places an upper bound on the $^3$BPEA energy as $E(T_1) \leq 1.24$ eV in the solid film. In addition, the observation of delayed fluorescence (Figure S6) from the photoexcited solvent-annealed film indicates that the $^3$BPEA energy must be close to 1.20 eV, which is half the $S_1$ energy, 2.40 eV. Observation of singlet oxygen emission at 0.98 eV (Figure S7) gives the lower limit and based on these data, $E(T_1) = 1.11 \pm 0.13$ eV, so that SF in the BPEA film should be nearly isoergic, and somewhat slower than for exoergic polyacenes.31,32 However, efficient SF is observed even in films of endoergic chromophores.33–35 Figure 3 shows the femtosecond transient absorption (fTsTA) spectra of the solvent-annealed 170 nm BPEA film following excitation with a 414 nm, 100 fs laser pulse at a 1 kHz repetition rate and an excitation density of $7.8 \times 10^{19}$ cm$^{-3}$. The transient spectrum (Figure 3a) at early times exhibits ground-state bleaching (GSB) overlapped with stimulated emission (SE) near 420 and 550 nm, which is consistent with the steady-state absorption and emission spectra (Figure 2), and $S_0 \rightarrow S_1$ excited-state absorption (ESA) features from 550 to 1400 nm, which are broadened compared to those in solution (Figure S2b). At later times, the ESA at 445–495 nm is assigned to $T_0 \rightarrow T_1$ absorption based on the triplet-sensitized spectrum (Figures S4 and S5) with an overlapping GSB feature at 495–550 nm. The kinetic fits and species
The largest structural differences occur in the lateral distance, and since the SF rate is mainly due to the significant electronic coupling between the two polymorphs. The large slip distance is an important factor in determining SF rates, and since the SF rate is proportional to \( |J_{SE}\text{eff}|^2 \), the SF rate for C2/c is estimated to be 4.4 times faster than that of Pbcn. The large \( J_{SE}\text{eff} \) value for the C2/c polymorph is mainly due to the significant LUMO–LUMO coupling, \( V_{LL} \), which is 120 meV for C2/c and 11.7 meV for Pbcn (Table S4). This large LUMO–LUMO coupling is also visualized in the molecular orbital diagrams shown in Figure S22, where the electron density of the LUMO is mainly localized on the anthracene. The spatial overlap of the LUMOs of the C2/c dimer is larger than that of the Pbcn dimer, resulting in energy splitting of the degenerate LUMOs.

It is widely known that the slip distance is an important factor in determining SF rates. In order to understand the effect of lateral slip distance (X), the effective electronic coupling and the one-electron couplings were calculated with the fixed |\( \pi – \pi \) and longitudinal slip distances of the C2/c.
polymorph, where X is varied (Figure 5). The value of $|J_{SE, eff}|^2$ for the C2/c polymorph decreases as X increases from 3.0 Å to 3.5 Å, then increases and peaks at 4.3 Å (Figure 5a). Thus, we know that the lateral slip distance is a major factor influencing the difference in the electronic couplings between the two polymorphs. Among the four one-electron couplings, VLL changes most drastically in respect to X (Figure 5b) indicating that LUMO–LUMO coupling primarily determines the overall SF rate in BPEA. The SF rate ratio between the C2/c and Pbcn polymorphs obtained from experiment is 4.5 ± 0.2, while that from the computations is 4.4, and are therefore in very close agreement, indicating that simple electronic coupling calculations of the dimer unit can provide useful information regarding SF dynamics; however, caution should be taken since the dimer model does not entirely represent the thin film system and has shown to fail in predicting polymorph dependent SF in tetracene system.\(^\text{47}\) Our results show that the lateral slip distance in BPEA is a significant factor determining SF dynamics; thus, in future work we will improve the effective coupling between the BPEA molecule in the C2/c polymorph by increasing the lateral slip distance. The results presented here show that BPEA has a strong potential as an SF chromophore for enhancing solar cell performance.

**REFERENCES**
