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Interplay of coulomb and exciton–phonon coupling controls singlet fission dynamics in two pentacene polymorphs

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ABSTRACT

Pentacene is an important model organic semiconductor in both the singlet exciton fission (SF) and organic electronics communities. We have investigated the effect of changing crystal structure on the SF process, generating multiple triplet excitons from an initial singlet exciton, and subsequent triplet recombination. Unlike for similar organic semiconductors that have strong SF sensitive to polymorphism, we find almost no quantitative difference between the kinetics of triplet pair (TT) formation in the two dominant polymorphs of pentacene. Both pairwise dimer coupling and momentum-space crystal models predict much faster TT formation from the bright singlet excited state of the Bulk vs ThinFilm polymorph, contrasting with the experiment. GW and Bethe–Salpeter equation calculations, including exciton–phonon coupling, reveal that ultrafast phonon-driven transitions in the ThinFilm polymorph compensate the intrinsically slower purely Coulomb-mediated TT formation channel, rationalizing the similarity in observed rates. Taking into account the influence of subtle structural distinctions on both the direct and phonon-mediated SF pathways reveals a predictive capability to these methods, expected to be applicable to a wide variety of molecular crystals.

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I. INTRODUCTION

Organic semiconductors show promise in myriad applications, from next-generation electronics to photovoltaics. Key to their eventual success lies in the tunability afforded by organic synthesis and solution processability. Organic semiconductors may act as conductors directly in, e.g., field effect transistors,¹ and they may also be utilized as the active absorber layer in organic solar cells.^{2,3} In addition, a special class of organic chromophores can undergo singlet exciton fission (SF), a process that could potentially increase solar cell efficiency above the Shockley–Queisser limit of 33%–45% via exciton multiplication when a singlet exciton splits into two triplet excitons.^{4,5} Effective control of, e.g., electronic energy levels and intermolecular coupling through molecular engineering offers a

potential command of both excited-state photophysics and electron and hole transport.⁶ Processing conditions also greatly impact transport by changing defect density, grain boundaries, and crystallinity. These factors play a role in determining function in either light harvesting or quantum information science (QIS) applications.⁷

Many of these characteristics have been borne out in studies of tetracene.⁸ In thin films, grain size and polymorph type have both been shown to influence singlet fission rates. Proximity to a symmetry-breaking interface has been considered as a potential mechanism for these variations,^{9,10} as have the relative dispositions of molecules in these architectures.¹¹ However, an initial analysis of pairwise coupling between tetracenes in two polymorphs did not find a correlation between singlet fission matrix elements and the rate of triplet formation. The inherently delocalized nature of singlet

excitons in polyacenes was considered a potential culprit for this discrepancy, but a definitive understanding is lacking.

Pentacene is an archetypal organic semiconductor, with a wide variety of studies on the impacts of processing and molecular engineering on thin film conductivity and photophysics.⁶ Pentacene is particularly important because it has been studied in the context of both organic electronics^{12,13} and SF.^{14,15} Theoretical studies have suggested that the “Bulk” polymorph should possess a triplet pair (TT) formation rate that is roughly two orders of magnitude higher than that of the “ThinFilm” polymorph if relative couplings are considered in Fermi’s Golden Rule formalism.^{16,17} The underlying physics of the situation was further articulated using a heuristic model that considered “hidden” symmetries in the unit cells of the respective structures.¹⁶ However, the impact of pentacene crystal structure has never been studied experimentally in the context of SF. Here, we report a comprehensive study on the triplet formation kinetics (SF process) and triplet recombination dynamics (triplet annihilation) in two crystal structures of pentacene. We compare the experimental results to two types of theoretical models: one including electronic couplings between pairs of molecules and the other using a reciprocal-space Green’s function approach. From the comparison of experimental and computational results, we find disagreement that can be ameliorated by including electron–phonon coupling in the theoretical framework. The conclusions provide insight into the nature of the photophysical phenomena relating to SF and triplet recombination.

II. EXPERIMENTAL

A. Film preparation and characterization

Pentacene was purchased from Sigma-Aldrich and used as received. An Angstrom Engineering Nexdep thermal evaporator was used to deposit 50 nm thick films on 1 in² glass coverslips at 0.5 Å/s in a vacuum of $<10^{-6}$ Torr. To convert the as-deposited ThinFilm films to Bulk, we put 1 ml of chlorobenzene on the film and spun at 3000 rpm for 30 s, followed by heating on a hotplate in ambient air at 120 °C for 10 min. Films were sealed under nitrogen with a picture frame cutout of Surlyn melted between the film and another coverslip. X-ray diffraction was measured with a Rigaku DMax 2500 x-ray diffractometer operating in $\theta/2\theta$ mode using Cu-K α radiation. Linear absorption was measured using a Cary 5000 equipped with an integrating sphere and calculated as $A = -\log 10(R + T)$.

B. Transient absorption spectroscopy

150 fs time resolution transient absorption datasets were acquired using a Coherent Libra Ti:sapphire laser with an output of 800 nm at 1 kHz. A TOPAS-C OPA was used to generate the pump pulse at 670 nm. A small amount of 800 nm light was used to pump a 1 cm thick sapphire crystal to generate 750–1650 nm probe light for NIR TA. The data were collected using an Ultrafast Systems Helios spectrometer with time delays up to 5.5 ns. For sub-50 fs time resolution experiments, a Quantronix Integra-HE output 3.5 mJ 800 nm pulses at 1 kHz to pump a home-built noncollinear optical parametric amplifier tuned to output 25 fs 670 nm pulses (autocorrelation in Fig. S4). A small portion of the 800 nm pumped a 1 cm sapphire crystal to generate the NIR probe light. The data were collected with Ultrafast Systems NIR cameras run by LabVIEW. Chirp was

corrected using the nonresonant response in a 1 mm path length cuvette of hexane. The autocorrelation was measured using a 0.1 mm BBO crystal. TA data were analyzed using a combination of Ultrafast Systems Surface Xplorer for extracting kinetic traces and MATLAB for analysis and fitting to differential equations.

C. Calculations

Methods for calculating dimer matrix elements from the pentacene unit cell are directly analogous to those in Arias *et al.*¹¹ The pentacene molecular and crystal structures were substituted for those of tetracene in the calculations (see [supplementary material](#)). The CT state energy was assumed to be 0.4 eV above the lowest singlet. First-principles exciton–phonon coupling rates were computed using density functional perturbation theory (DFPT)¹⁸ for the electron–phonon and hole–phonon coupling combined with many-body perturbation theory within the GW and Bethe–Salpeter equation approximation (GW-BSE)¹⁹ for the exciton coupling, from a recently derived Green’s function approach²⁰ with numerical grids and convergence parameters similarly to Cohen *et al.*²¹

III. RESULTS AND DISCUSSION

We thermally evaporated pentacene onto cleaned glass substrates to produce 50 nm thick polycrystalline films with the ThinFilm crystal structure. Solvent annealing¹² was then used to convert from ThinFilm to Bulk crystal structure, verified by XRD [Fig. 1(a)]. Integrating sphere UV–Vis absorption experiments were performed, and a slight redistribution of oscillator strength was found, with the bulk polymorph having more relative oscillator strength at higher energies [Fig. 1(b)]. This could be due to several factors, such as increased mixing between higher-energy states and lower-energy states, e.g., increased Frenkel exciton and charge transfer coupling. It could also be due to the change in orientation of the transition dipoles, as the molecular orientation with respect to the substrate normal is different in the two polymorphs. In the bulk polymorph, the molecular long axis is tilted with respect to the substrate normal, potentially altering alignment between the $S_0 \rightarrow S_1$ transition and light polarized in the plane of the film.

Femtosecond transient absorption (TA) data were collected for both polymorphs, exciting near the band edge (650–670 nm). We performed one broadband probe experiment (350–1650 nm) with ≈ 150 fs time resolution and another with ≈ 20 –30 fs time resolution (Fig. 2) but with a more limited probe bandwidth. We also performed a fluence-dependent TA study probing the NIR (800–1650 nm) with ≈ 150 fs time resolution to track the triplet recombination dynamics. In all TA experiments, both polymorphs exhibited similar spectra and kinetics. In the VIS region, singlet and triplet features are heavily overlapped with each other and with thermal artifacts,¹⁵ complicating the deconvolution of the kinetics. In the NIR at 800–1000 nm [Fig. 2(a)], there is a strong excited-state absorption (ESA) that is assigned as primarily due to the triplet ($T_1 \rightarrow T_n$ absorption).¹⁴ The 1100–1400 nm signal is due to singlet and triplet ESA at early and late times, respectively.²²

Kinetic slices from the triplet ESA [930 nm, Figs. 2(b) and 2(c)] directly reflect triplet dynamics. There is a fast ≈ 130 fs rise followed by a ≈ 1 ps rise in both polymorphs. The fast component can be attributed to TT formation, and with sufficient time resolution

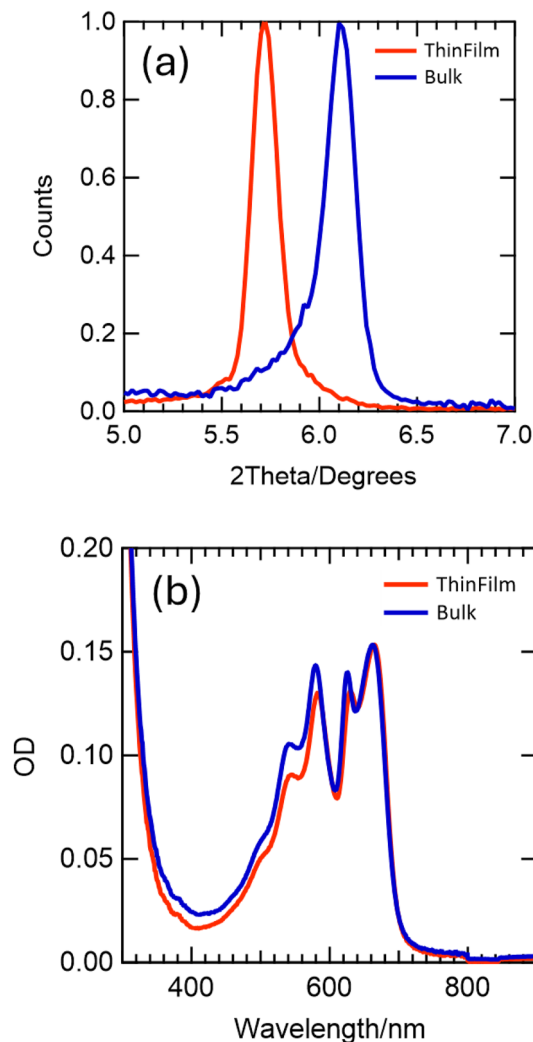


FIG. 1. (a) XRD (001) diffraction peaks for ThinFilm and Bulk structures at 5.73° and 6.18°, respectively. (b) UV-vis absorption spectra for both film structures.

[Fig. 2(b), 25 fs pulse], a slight enhancement of TT formation rates was measured in the Bulk vs ThinFilm polymorph (123 vs 152 fs). The singlet band near 1230 nm was also probed (gray curve), but the signal was weak in this region and overlapping with triplet signals. It nonetheless shows the instrument-limited rise of the singlet and its decay concomitant with triplet rise. The kinetics at 1230 nm (mainly singlets) was also probed with a time resolution of 150 fs [Fig. 2(d)]. The singlets fully decay on the 1 ps timescale for both polymorphs. Pensack *et al.* have suggested this slower time constant represents an initial correlated triplet pair state converting to a second triplet pair state that is spectrally indistinct from independent triplets but exists before spin dephasing.²² In addition, it has been suggested that the slower component in TIPS Pc thin films is related to the triplet hopping timescale, and it is possible that such dynamics are also in effect here.^{23,24}

The fluence-dependent TA kinetics probing triplet dynamics at 930 nm are shown in Fig. 3. At the two highest fluences, the TA signal shows signs of saturation and was not included in the analysis of triplet recombination [Fig. 3(a)]. The remaining data were analyzed after the triplet ESA rise (time >3 ps) by including the first-, second-, and third-order terms in the differential equation for recombination,

$$dN/dt = -N/\tau + k_b N^2 + cN^3. \quad (1)$$

The ThinFilm polymorph data and fit are shown in Fig. 3(b) (see supplementary material, Fig. S2 for Bulk), and the fit parameters τ , k_b , and c for both polymorphs are tabulated in Table I. Using the Smoluchowski equation for isotropic particles, $k_b = 8\pi RD$, the larger k_b for the ThinFilm polymorph implies a larger diffusion constant D , as the radius R is expected to remain unchanged.

However, we can also fit the data by assuming that the bimolecular term in Eq. (1) dominates the triplet recombination.²³ Then, for each fluence, a plot of $1/\Delta A$ vs time should yield a straight line, with the slope proportional to the bimolecular recombination constant, k_b ,

$$1/\Delta A = k_b t + 1/\Delta A_0. \quad (2)$$

This analysis is displayed in Fig. 3(c). Here it can be seen that the lowest fluence and two highest fluence traces are nonlinear when plotted in this fashion, implying the need for more complex modeling to capture the dynamics across all the regimes of fluence. However, in the intermediate fluence regime, this model works well. The extracted k_b for each fluence (for 4500 ps > t > 3 ps) and the k_b from Table I for both polymorphs are shown in Fig. 3(d). Focusing on the region of fluence independent k_b in the central fluence range, the ThinFilm polymorph has a slightly larger diffusion constant. In addition, the k_b gives a systematically higher estimate of the value compared to modeling all the fluence-dependent traces at once. This may be because none of the traces are purely second-order but instead always contain a contribution from third-order or higher processes.

We performed calculations of electronic couplings between states relevant for SF and of orbitals relevant for triplet transfer (via a Dexter process) for each polymorph. We matched the position of the (001) diffraction peak of ThinFilm and Bulk polymorphs to calculate patterns from cif files PENCEN10²⁵ and PENCEN08,²⁶ respectively, from the Cambridge Crystal Database. The mediated pathway for SF was assumed, and we calculated one-electron orbital coupling matrix elements for the three unique nearest-neighbor dimers in the ab-plane.^{11,27} The matrix elements were then used to calculate the diabatic coupling, V , between singlet excitons (S_1S_0 or S_0S_1) and the SF product state TT , assuming a CT energy 0.4 eV above the singlet.²⁸ The LUMO and HOMO orbitals were used to calculate electron and hole transfer matrix elements, respectively.²³ The dimer geometries and calculated couplings are shown in Fig. S3 and Table II, respectively. The Bulk [$\frac{1}{2} \frac{1}{2}$] dimer has the largest SF coupling due to the large slip along the long axis of the molecule, leading to reduced destructive interference of electron and hole transfer pathways that must be summed in determining V . This is similar to what we previously found in tetracene.¹¹

In contrast to the computational results, experimental data points to very similar SF rates and triplet recombination rates in

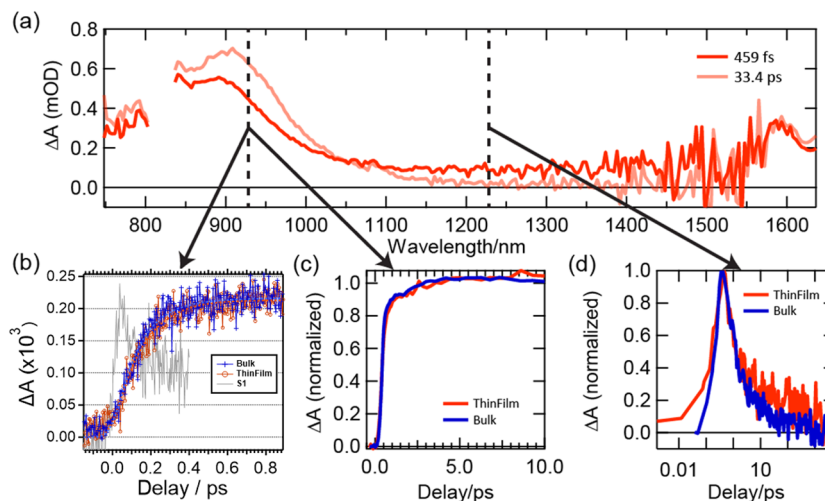


FIG. 2. (a) ThinFilm NIR TA spectra at early (459 fs) and intermediate (33.4 ps) timescales. Dashed lines mark wavelengths for kinetic traces in (b)–(d). (b) Early time (<1 ps) kinetics for ThinFilm and Bulk, showing rise of triplet signal in 120–150 fs. The signal at 1230 nm, primarily reflecting S_1 decay, is shown for the bulk film in gray. (c) Kinetic traces at same wavelength as (b) showing secondary 1–1.3 ps rise. (d) Kinetic trace at 1230 nm showing loss of singlet ESA in 1–1.3 ps.

the two pentacene crystal structures. Specifically, in a Marcus-like picture, the rate constant for SF depends on the square of the SF coupling, and using the largest coupling elements $(24.32/3.95)^2$ gives a factor of 38 times increase for the Bulk compared to ThinFilm polymorph. However, the dimer calculations do not incorporate several potentially important pieces of relevant physics. Exciton

TABLE I. Fit parameters to Eq. (1) for both pentacene polymorphs.

	τ (ns)	k_b (cm^3s^{-1})	c (cm^6s^{-1})
ThinFilm	10.71	3.46×10^{11}	6.30×10^{27}
Bulk	7.55	2.16×10^{11}	8.15×10^{27}

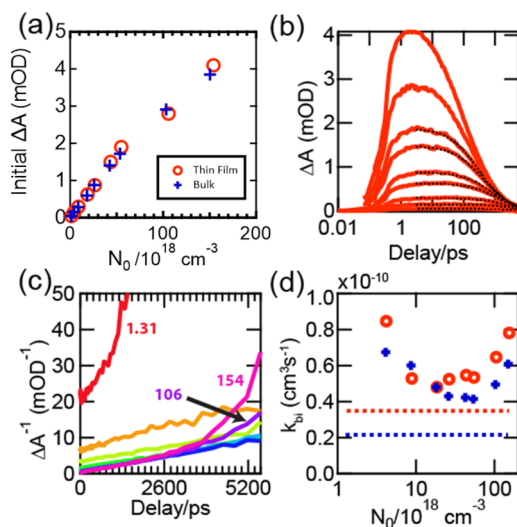


FIG. 3. (a) Initial TA signal as a function of initial excitation density, showing linearity for fluences $<10^{20}\text{cm}^{-3}$. (b) ThinFilm fluence-dependent triplet kinetics, taken at 930 nm. Included as black dotted lines are fit to the model in Eq. (1) (excluding the two highest fluences). (c) Plot of $1/\Delta A$, showing non-linearity of lowest and two highest fluences. These traces are labeled by the initial excitation density $\times 10^{18}\text{cm}^{-3}$. (d) Extracted k_b for all traces (symbols) for ThinFilm (red) and Bulk (blue) structures. The dotted lines are the values of k_b fit using Eq. (1).

delocalization, which can be extensive due to electronic coupling among singlets,²⁹ is ignored in these calculations. Strong mixing between Frenkel excitons and charge transfer excitons³⁰ is not included in this approach either, as the charge transfer diabatic states only serve to mediate coupling between the singlet and correlated triplet. We do not think exciton transport is a compounding factor in the dynamics like it may have been for tetracene^{9,11} because the very high SF rates mean that singlets undergo SF before significant transport to interfaces can occur. However, as suggested by Yost *et al.*, SF in pentacene may occur in an adiabatic regime wherein the SF rate does not depend strongly on the electronic coupling but rather is limited by the timescale of nuclear motions necessary to proceed from the singlet-like to double-triplet-like portion of the excited-state potential energy surface.³¹

Unlike the dimer-based calculations for SF couplings, the calculated transfer integrals, t_{elec} and t_{holes} , are more in line with the experiment that measures triplet transport. The ThinFilm polymorph has a slightly larger overall coupling averaged over the three dimers, which can be translated to faster triplet hopping through the product of electron and hole transfer in the weak coupling limit. This aligns with the ThinFilm polymorph having a slightly larger k_b and, therefore, diffusion constant, compared to the bulk polymorph. We note the similarity between these calculated couplings and those from prior calculations of the Bulk polymorph.^{32,33} The dimer picture may more accurately capture the physics of triplet transfer than SF because triplets are generally localized to a single

TABLE II. Calculated diabatic state electronic couplings for SF (V) and orbital couplings relevant for triplet transfer (t). All values in meV.

	Bulk $[-\frac{1}{2} \frac{1}{2}]$	TF $[-\frac{1}{2} \frac{1}{2}]$	Bulk $[\frac{1}{2} \frac{1}{2}]$	TF $[\frac{1}{2} \frac{1}{2}]$	Bulk [1 0]	TF [1 0]
$ V\rangle (S_1S_0 \rightarrow {}^1TT)$	3.95	3.84	0.85	3.8	1.95	1.33
$ V\rangle (S_0S_1 \rightarrow {}^1TT)$	3.11	2.75	24.32	2.72	1.95	1.33
t_{elec}	-94.17	88.43	95.79	-80.15	55.19	58.08
t_{hole}	-92.94	86.67	53.28	-82.02	43.55	63.26

molecule, and transfer involves interactions between pairs of molecules as opposed to delocalized excitons requiring simultaneous interactions among several molecules.

To address crystal effects beyond the dimer model for singlet fission relevant exciton-phonon couplings, we turn to the reciprocal space approach to modeling electronic structure, exciton states, phonon modes, and the coupling between them in pentacene. GW-BSE computations show two nearly degenerate, low-lying singlet states, one optically bright and the second dark.¹⁷ Similar to the dimer model, the transition rate of coherent, Coulomb-mediated decay from the lowest bright exciton to a bitriplet was shown to be much smaller for the ThinFilm polymorph than the Bulk one due to intermolecular orientation and slip stacking.¹⁶ In addition, from symmetry considerations, the Coulomb decay rate from the bright singlet state to a bitriplet is significantly lower than from the dark one. These are competing channels, where the bright state—initially populated upon photoexcitation—either decays directly or goes through a phonon-mediated fast transition to the SF-active dark state. This dark state occupation channel was recently explored by Cohen *et al.*,²¹ where GW-BSE-based exciton-phonon coupling calculations showed similar decay rates for bright intra-band thermalization and bright-to-dark inter-band transitions.

Here we extend these calculations to compare between the two polymorphs.

Figure 4(a) shows the exciton band structures of the two low-lying singlet states, the bright (blue) and the dark (gray) ones, with exciton momentum Q along the $\Gamma - X$ and the $\Gamma - Y$ direction, for the two polymorphs. The excitation energy of the dark state is continuous along Q in this momentum path, while the bright state, which typically includes some exchange electron-hole interactions, is split at $Q = 0$, in the so-called exciton longitudinal-transverse (LT) split.^{21,34} This LT split is considerably smaller in the case of the ThinFilm structure compared to the Bulk due to differences in their excitonic nature, as further manifested in the relative alignment between the dark and bright states. We compute the phonon modes using density functional perturbation theory (DFPT)¹⁸ and couple the GW-BSE exciton states with the phonons within a first principles Green's function approach, following recent developments.^{20,21}

Figure 4(b) shows the magnitude of this coupling averaged over the phonon and exciton momentum, $|\overline{G}|^2$, as a function of phonon energy $\hbar\omega_\nu$ for each phonon mode ν . The upper panel presents the coupling associated with inter-band scattering from the bright exciton to the dark one, and the lower panel presents intra-band scattering within the bright state. The coupling in the case of the

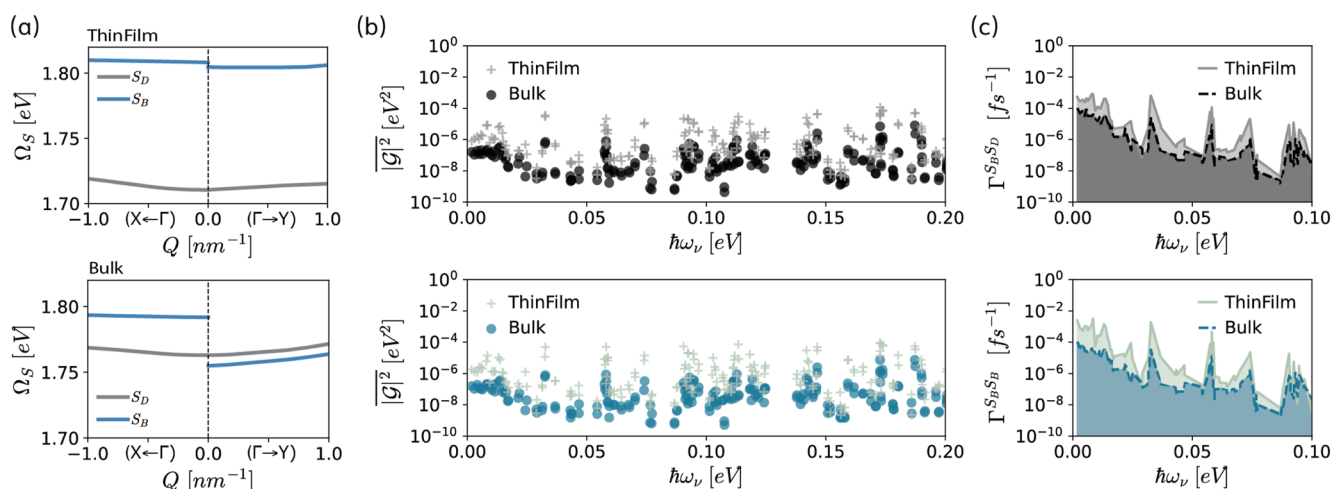


FIG. 4. (a) Exciton band structure for the ThinFilm (top) and Bulk (bottom) pentacene polymorphs. In each structure we present the energy, Ω_S , of the two lowest singlet states, one optically bright (blue) and one dark (gray), as a function of exciton momentum for small momenta around the optical transition at $Q = 0$ and along the crystal directions ($X \rightarrow \Gamma$) ($\Gamma \rightarrow Y$). (b) The absolute value squared of the exciton-phonon coupling for the inter-band (top) and intra-band (bottom) transitions, averaged over the exciton and phonon momentum, plotted as a function of the phonon energy. (c) Exciton-phonon coupling rate for the two channels as a function of phonon energy.

ThinFilm structure is about two orders of magnitude larger than in the Bulk for both inter- and intra-band channels. As a result, the transition rates associated with these relaxation channels, $\Gamma^{S_b S_b}$ and $\Gamma^{S_b S_b}$, presented in Fig. 4(c) as a function of phonon energy and calculated following Cohen *et al.*²¹ are larger in the ThinFilm polymorph.

Our computations result in an average transition scattering time of ~ 500 fs for both inter- and intra-band transitions in the bulk polymorph, compared to ~ 20 and ~ 50 fs for the inter- and intra-band transitions in the ThinFilm polymorph. This points to a phonon-induced decay channel that has an opposite trend than the previously computed coherent Coulomb SF channel, which showed a larger SF rate in the Bulk polymorph due to the intermolecular stacking.¹⁶ Our results suggest that the same structural consideration also increases the exciton–phonon coupling. From a simplified rate equation perspective, non-radiative transition channels—substantially faster in ThinFilm—can complement the Coulomb channels, which are faster in the bulk phase. This finding supports the experimental observations of minor differences between the SF rates of the two polymorphs.

We now turn to the issue of placing our results in the context of a significant body of prior work on the formation of TT and T + T in pentacene, many of which invoke electronic or vibronic coherence.³⁵ Our experiment does not specifically detect the involvement of vibrations, and we observe no oscillations in our signals that might be used to characterize such a coherence. Instead, we find agreement with angle-resolved photoemission spectroscopy (trARPES) results on a bulk pentacene crystal³⁶ that show a loss of S_1 character concomitant with the TT rise on a roughly 100 fs timescale but without an evident coherent S_1 -TT mixing channel. The secondary singlet decay feature may reflect the separation of TT, which others have suggested may be promoted by nuclear motions.^{22,37} We find with transient absorption that both polymorphs exhibit this behavior, with only a small change in the TT formation constant as a distinction.

The question arises about whether calculations are consistent with this result or might instead predict a distinct mechanism for Coulomb vs. phonon-induced pathways. Prior work has suggested that low-frequency intermolecular motions in acene crystals can instigate TT formation.^{38,39} The modes responsible, whether on the ground-state or excited state potential energy surface (PES), are thought to modulate the strength of electronic coupling, leaving the molecules momentarily “poised” to undergo the transformation from S_1 to TT. In other models, motions are stimulated through initial excitation into the electronically excited S_1 in the Franck–Condon regime, where the generated wavepacket then evolves. Subsequent motion on the PES toward a crossing with TT may then proceed to populate the bitriplet with a vibronic coherence (and possibly with the assistance of a conical intersection).^{40,41} Calculations here reflect a different regime, where scattering with phonons is considered alongside the excitonic picture derived from the crystal structure and cannot be easily merged with the “vibronic” models. Despite the fundamental differences in interpretation, the conclusion drawn from these works supports our results, emphasizing the crucial role of phonons in facilitating the SF process. Our computations further highlight the role played by the occupation of a dark state in mitigating phonon-assisted SF.

IV. CONCLUSION

We have characterized singlet fission and triplet recombination dynamics in two crystal structures in polycrystalline films of pentacene. TA measurements reveal that SF and triplet recombination dynamics in both polymorphs are similar. The former contrasts with calculations of SF-relevant electronic couplings between pairs of molecules in the dimers of the two polymorphs and with GW-BSE calculations of the Coulomb-induced transitions to TT, both of which predict a large disparity in SF rates favoring the Bulk polymorph. This agreement between two very different approaches to describing the $S_1 \rightarrow TT$ transition is remarkable but likely originates from the same symmetry changes that accompany the polymorph type. However, only when including exciton–phonon coupling in the calculations is it revealed that a phonon-mediated route to fast SF preferentially in the ThinFilm polymorph likely exists, bringing predicted TT formation also within the 200 fs regime and in line with experimental findings. These results demonstrate the utility of crystal structure engineering combined with examination using multiple theoretical formulations to form a full understanding of exciton dynamics in systems that have potential in optoelectronic and light harvesting architectures.

SUPPLEMENTAL MATERIAL

Computational details, additional transient absorption data, and femtosecond pulse characterization.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Dylan H. Arias: Formal analysis (lead); Investigation (lead); Writing – original draft (lead). **Galit Cohen:** Formal analysis (equal); Investigation (equal); Writing – review & editing (supporting). **Niels H. Damrauer:** Formal analysis (equal); Methodology (equal); Supervision (supporting). **Sivan Refaely-Abramson:** Conceptualization (equal); Formal analysis (equal); Supervision (equal); Writing – review & editing (equal). **Justin C. Johnson:** Conceptualization (lead); Investigation (supporting); Supervision (lead); Writing – review & editing (equal).

DATA AVAILABILITY

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

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