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Singlet Exciton Fission in Polycrystalline Pentacene: From Photophysics toward Devices

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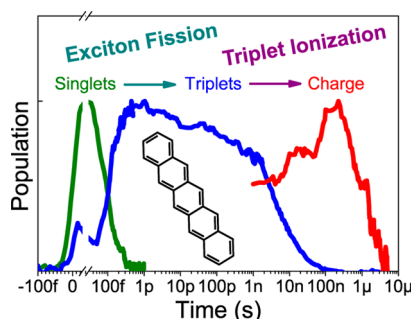
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RECEIVED ON DECEMBER 26, 2012

CONSPECTUS

Singlet exciton fission is the process in conjugated organic molecules by which a photogenerated singlet exciton couples to a nearby chromophore in the ground state, creating a pair of triplet excitons. Researchers first reported this phenomenon in the 1960s, an event that sparked further studies in the following decade. These investigations used fluorescence spectroscopy to establish that exciton fission occurred in single crystals of several acenes. However, research interest has been recently rekindled by the possibility that singlet fission could be used as a carrier multiplication technique to enhance the efficiency of photovoltaic cells. The most successful architecture to-date involves sensitizing a red-absorbing photoactive layer with a blue-absorbing material that undergoes fission, thereby generating additional photocurrent from higher-energy photons. The quest for improved solar cells has spurred a drive to better understand the fission process, which has received timely aid from modern techniques for time-resolved spectroscopy, quantum chemistry, and small-molecule device fabrication. However, the consensus interpretation of the initial studies using ultrafast transient absorption spectroscopy was that exciton fission was suppressed in polycrystalline thin films of pentacene, a material that would be otherwise expected to be an ideal model system, as well as a viable candidate for fission-sensitized photovoltaic devices.

In this Account, we review the results of our recent transient absorption and device-based studies of polycrystalline pentacene. We address the controversy surrounding the assignment of spectroscopic features in transient absorption data, and illustrate how a consistent interpretation is possible. This work underpins our conclusion that singlet fission in pentacene is extraordinarily rapid (~ 80 fs) and is thus the dominant decay channel for the photoexcited singlet exciton. Further, we discuss our demonstration that triplet excitons generated via singlet fission in pentacene can be dissociated at an interface with a suitable electron acceptor, such as fullerenes and infrared-absorbing inorganic semiconducting quantum dots. We highlight our recent reports of a pentacene/PbSe hybrid solar cell with a power conversion efficiency of 4.7% and of a pentacene/PbSe/amorphous silicon photovoltaic device. Although substantive challenges remain, both to better our understanding of the mechanism of singlet exciton fission and to optimize device performance, this realization of a solar cell where photocurrent is simultaneously contributed from a blue-absorbing fission-capable material and an infrared-absorbing conventional cell is an important step towards a dual-bandgap, single-junction, fission-enhanced photovoltaic device, which could one day surpass the Shockley–Queisser limit.



Introduction

Excitons are electrically neutral quasi-particles consisting of an electron and a hole that experience mutual Coulombic attraction.¹ In contrast to crystalline inorganic semiconductors, where charge carriers interact only weakly, excitons in low-dielectric organic semiconductors are strongly bound relative to a separated electron–hole pair.¹ Additionally, because optical transitions conserve spin, photoexcitation

from the ground state creates excitons with zero total angular momentum that are, accordingly, referred to as singlets. By contrast, spin-triplet excitons are usually generated indirectly, for example, from singlets via spin–orbit-mediated intersystem crossing.¹

Exciton fission, where one singlet exciton spontaneously decays into two triplet excitons residing on different chromophores, was first proposed by Singh et al. to explain the

unusual temperature dependence of the “delayed” fluorescence from crystalline anthracene.² The creation of *multiple* triplets was critical, because conservation of angular momentum could be satisfied if the triplets were created as a coupled state with pure singlet character. Hence, singlet fission was spin-allowed, clearly distinguishing it from slow, spin-forbidden intersystem crossing.^{3–5} These results spurred considerable research effort in the 1960s and 1970s, which has been recently reviewed by Smith and Michl.⁴

Much of the early research into singlet exciton fission focused on tetracene, because its near-degenerate singlet and triplet-pair energy levels permitted fission to occur, while also allowing the regeneration of some emissive singlets via subsequent triplet–triplet fusion.⁴ Thus, the “delayed” fluorescence from regenerated singlets was an experimentally convenient, if indirect, probe of the triplet population.^{6–8} However, in pentacene, where the relaxed triplet has significantly less than half the energy of the singlet, fission is expected to be exothermic and unidirectional.⁹ As a consequence, pentacene should exhibit substantially simplified population dynamics, making it an ideal model system to study the fission process uncomplicated by the effects of singlet regeneration and triplet diffusion. Nevertheless, due to the experimental difficulties caused by the dearth of emission from bulk pentacene, early photophysical insight came only from extrapolation of the behavior of the smaller, more luminescent members of the acene family,^{5,9} as well as fluorescence studies of the “heterofission” between isolated pentacene molecules and a tetracene matrix.^{10,11} Further understanding followed the development of new techniques, particularly transient absorption spectroscopy (TA), which is able to directly probe the evolution of both emissive and nonemissive excited-state populations with ultrafast time resolution. However, the fact that TA simultaneously observes all optically active transitions carries the drawback that spectral features tend to overlap, so that experimental data require careful interpretation.

Thus, a fundamental question to be addressed is whether a complete, consistent model of the photophysical dynamics in pentacene can be deduced from TA measurements, and thereby whether singlet fission indeed occurs in easily fabricated evaporated films of pentacene. Further, given the potential for application in solar cells, we also consider the practicalities involved in harnessing singlet exciton fission in a photovoltaic device: whether fission is efficient, whether fission-generated triplets can be dissociated into charges, and whether these processes can occur in a device architecture that generates complementary

photovoltaic performance from absorbed infrared light.⁴ Hence, in this Account, we describe our recent experimental efforts to address these questions. In particular, we gather together the suite of evidence from our studies using transient absorption spectroscopy that demonstrates that singlet exciton fission is rapid and efficient in polycrystalline pentacene films and additionally shows that the triplet exciton in pentacene is readily dissociated at suitable heterojunctions. Additionally, we highlight our recent efforts to pair pentacene with inorganic semiconductors, which have yielded photovoltaic devices where pentacene and a complementary infrared absorber operate together.

Transient Absorption Spectroscopy

Transient absorption (TA) measures the change in the transmission (T) of a sample in response to the generation of photoexcited states. The differential transmission ($\Delta T/T$) spectrum is measured simultaneously using broad-band light^{12–14} or built up from sequential narrow-band experiments.^{9,14,15} Time resolution is achieved by varying the relative delay between the pulsed pump and probe beams. A number of effects can contribute to the TA spectrum. The depletion of available ground-state chromophores results in a positive contribution to the $\Delta T/T$ signal in the shape of the linear (i.e., ground-state) absorption spectrum. We refer to this as the ground-state bleach (GSB). Photoinduced absorptions (PIA) occur when excited states themselves absorb probe light and have a negative contribution to the TA signal.^{15,16} Notably, each type of excited-state species (singlets, triplets, polarons, etc.) has a unique PIA spectrum, allowing population dynamics to be deduced if the features can be distinguished and identified. Excited species that optically couple to the ground state can cause stimulated emission (SE), which adds a positive contribution to the $\Delta T/T$ in the shape of the photoluminescence spectrum.^{14,17} Phenomena that alter the linear absorption of the sample, such as thermal modulation^{16,18} or the Stark effect,¹³ can also contribute to the TA signal. In particular, awareness of the thermal modulation effect is vitally important to studies of exciton fission, because its rapid onset and long lifetime mimics the expected characteristics of fission-generated triplet excitons.¹⁶ Taken together, these last two often-overlooked phenomena add considerable complexity to the interpretation of TA data in the spectral vicinity of the ground-state absorption. As with all spectroscopic studies, care must be taken to control for sample degradation, unwanted bimolecular recombination dynamics, and steady-state heating.

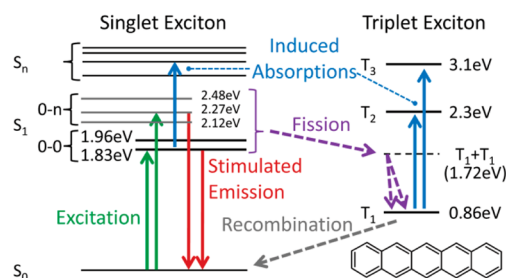


FIGURE 1. Partial Jablonski diagram illustrating the states and transitions in crystalline pentacene that are relevant to this work. Energies are expressed relative to the ground state and derive from the work described here as well as refs 4, 11, and 23–26. All arrows indicate population transfer, and solid arrows indicate optical transitions probed in transient absorption spectroscopy. The dominant decay channel following photoexcitation of the singlet exciton is the formation of a spin-coherent triplet pair via singlet exciton fission. The molecular structure of pentacene is shown at the bottom right.

Singlet Exciton Fission in Polycrystalline Pentacene

Pentacene is a polycyclic aromatic hydrocarbon and the five-ringed member of the family of unsubstituted linear acenes. Its molecular structure and a partial Jablonski diagram illustrating the energy levels and transitions relevant to this work are presented in Figure 1. Although singlet fission was expected to occur efficiently in crystalline pentacene by extrapolation of the properties of the historically well-studied smaller polyacenes,^{4,9} the first modern studies of easily fabricated evaporated polycrystalline films implied that the process was not efficient.^{12,15} However, reports of pentacene-based photovoltaic devices with exceptionally high internal quantum efficiencies^{19–22} and extreme exciton diffusion lengths¹⁹ were consistent with efficient singlet fission. Accordingly, this controversy has been addressed by several groups, and a consensus interpretation is emerging.

Although the comparatively large size and rigid structure of the pentacene molecule renders it relatively difficult to dissolve,²⁷ the photophysical properties of the isolated molecule have been measured in gas jets,⁴ cryogenic matrices,⁴ carefully chosen solvent preparations,^{27,28} and host crystals.^{10,11} These efforts were reviewed by Smith and Michl,⁴ so we highlight two key results. First, all authors agree that the Stokes shift between the absorption and emission of the isolated molecule is small.⁴ This implies that the lowest-energy absorption feature is associated with an optically active singlet and that there is little conformational relaxation upon photoexcitation. Second, there is a consensus that the lowest-energy observable excited-state absorption from triplets in the isolated molecule is at ~ 500 nm (2.5 eV),^{4,28} even though a lower-lying transition²⁹ with reduced oscillator strength³⁰ has been predicted theoretically.

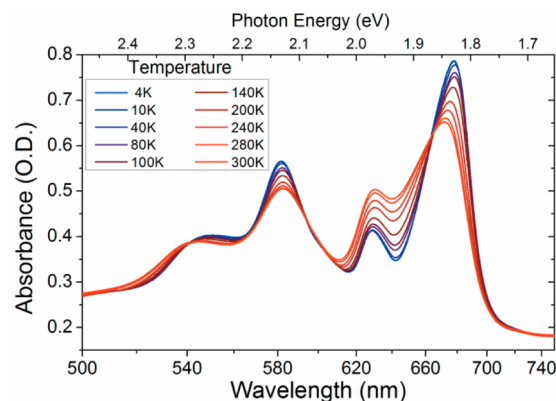


FIGURE 2. Temperature-dependent absorption spectrum of a 150 nm thick polycrystalline film of pentacene formed by thermal evaporation onto a fused-silica substrate.

In the solid state, pentacene forms crystals with “herringbone” edge-to-face packing.^{31,32} Although there is some distortion of the lattice parameters in thin evaporated films,²⁶ the general structure of the bulk crystal persists even to monolayers.^{26,32} Notably, the molecules robustly self-organize at room temperature such that the long molecular axis is normal to silica substrates.^{31–33}

Figure 2 presents the ground-state absorption spectrum of pentacene measured at a range of temperatures. Experimental details are presented elsewhere.¹⁶ We consider that the two lowest-energy features of the absorption spectrum of pentacene at 675 and 630 nm correspond to the Davydov-split lowest-lying singlet state,^{4,24,25,34} giving an optical bandgap of 1.83 eV.⁹ We note that the absorption spectrum of crystalline pentacene is significantly (~ 400 meV) red-shifted from that of the isolated molecule, even when allowing for the increased local dielectric constant.⁴ This is indicative of strong intermolecular coupling, which is consistent with the large Davydov splitting and a somewhat-delocalized optically active singlet exciton.^{4,34,35} Although the three peaks observed at 584, 542, and 500 nm were identified as intermolecular charge-transfer transitions on the basis of electroabsorption measurements,²⁴ this interpretation was questioned due to a possible experimental artifact.³⁶ Instead, we consider that these features are vibrational sidebands of the main electronic transitions, following the theoretical work of Spano et al.^{34,37,38}

While the photoluminescence quantum efficiency of pentacene in solution is $\sim 8\%$, it is reduced to virtually zero in the solid state.⁹ This was consistent with a new, rapid, nonradiative decay channel for the singlet (i.e., singlet fission) being enabled in the presence of multiple molecules. Although the energy of the singlet (~ 1.83 eV) can be readily

inferred from the optical gap,^{4,13,28} the energy of the non-luminescent triplet is more challenging to ascertain. Triplet energies of ~ 0.81 – 0.90 eV in the solid state have been estimated from measurement of the activation energy of heterofission,¹¹ inelastic tunneling spectroscopy,³⁹ and electron energy-loss spectroscopy.²³ We have very recently corroborated that the triplet energy is greater than 0.85 eV by analyzing the dependence of the photocurrent onset on the band alignment between pentacene and a size series of PbSe quantum dots.⁴⁰ Simultaneous work from the Baldo group was broadly consistent with a triplet energy of 0.86 eV.⁴¹ The significance of this energetic landscape is that singlet exciton fission in pentacene is exothermic (~ 4 kT at ambient), and is thereby expected to be rapid and unidirectional.⁹

However, though the first reported study using pump–probe spectroscopy on polycrystalline pentacene ascribed the very rapid photophysical dynamics to singlet exciton fission,⁹ a consensus emerged from subsequent reports from Marciniak et al. and Thørmolle et al. that fission was suppressed in polycrystalline thin films.^{12,15} Although all authors agreed that the lack of observable photoluminescence at short times (~ 200 fs) implied that the singlet was rapidly quenched, they differed in their proposed models and rationales. The critique of Marciniak et al. highlighted the absence of the strong PIA feature near 500 nm that characterizes the pentacene triplet exciton in solution.¹² Instead, they proposed that the photoexcited singlet exciton rapidly decays to a nonemissive excited dimer associated with a PIA feature at 630 nm.¹² However, we note that QM/MM simulations performed by Kuhlman et al. suggested that such an excited-state dimer was energetically unfavorable.⁴² Importantly, Marciniak et al. also identified the significance of the macroscopic orientation of the sample on the observed TA spectrum, due to the substrate-directed self-organization during film deposition^{31,33} and the predicted polarization of the triplet PIA along the long molecular axis.^{28,30} By contrast, Thørmolle et al. identified the theoretically predicted^{29,30} but hitherto unobserved $T_1 \rightarrow T_2$ excited-state absorption of triplets in monocrystalline pentacene and consequently concluded that fission was efficient.¹⁵ However, they observed that the long-wavelength triplet feature was markedly weaker in evaporated polycrystalline films and so suggested that exciton fission was suppressed.¹⁵ Instead, the authors proposed that singlets were quenched by ultrafast electron transfer to trapping sites and hence associated the apparent PIA feature near 630 nm with the pentacene hole polaron.¹⁵

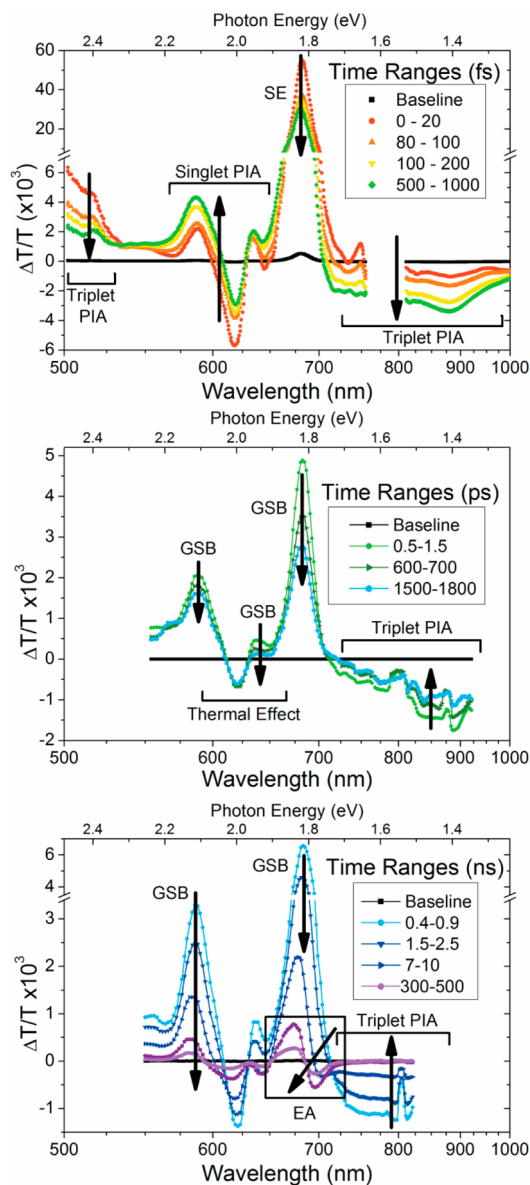


FIGURE 3. Temporal evolution of the transient absorption spectrum of (a) a 110 nm pentacene film and (c) pentacene/ C_{60} ($150/10$ nm) bilayer. The panels show the data obtained from separate measurements covering the (a) sub-picosecond,¹⁷ (b) sub-nanosecond,^{13,16} and (c) sub-microsecond^{13,16} time ranges. Singlet fission proceeds rapidly during the first 200 fs, while there is little further spectral evolution until the generation of charge from triplet excitons dissociated at the heterointerface on a 1 – 10 ns time scale. All species eventually recombine.

To clarify the observed TA signals and deduce the underlying photophysical processes, we made a suite of measurements with sufficient spectral coverage (500 – 1000 nm), resolution, and temporal range (10 fs to 5 μ s) to map the entire lifecycle of photoexcitations in pentacene. The experimental details have been reported elsewhere,^{13,16,17,43} but we present here a summary of the evolution of the TA spectrum (Figure 3) and population dynamics of major

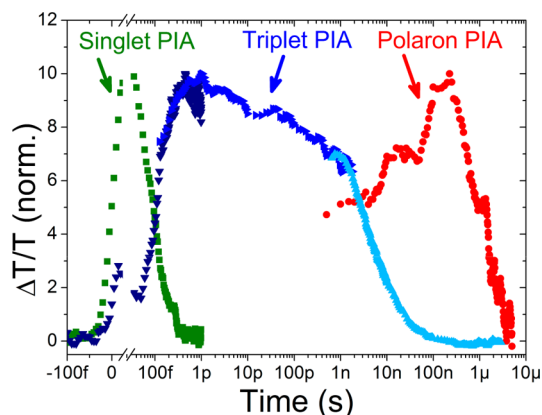


FIGURE 4. Dynamics of singlet exciton fission and charge generation from triplet excitons in pentacene film (<1 ns) and a pentacene/ C_{60} bilayer (>1 ns). Sub-picosecond curves are kinetic cuts through the transient absorption spectra presented in Figure 3a, taken at 595–601 nm (singlets, green) and 850–870 nm (triplets, navy). The picosecond-scale and nanosecond-scale triplet kinetics are a cut at 730–800 nm through the data presented in Figure 3, panels b (triplets, blue) and c (triplets, cyan), respectively. The nanosecond-scale polaron data is measured at 1650 nm (polarons, red). Methods are described in detail elsewhere,^{13,16,17,43} and each composite trace is normalized to the peak value.

excited-state species (Figure 4) over the three experimental time ranges (sub-picosecond, sub-nanosecond, and sub-microsecond).

As shown in Figure 3a, the TA spectrum evolves considerably in the first 200 fs, but is largely stationary for the remainder of the first nanosecond following excitation (Figure 3b). The TA spectrum agrees with previous measurements made at comparable delay times (e.g., 1 ps).^{12,15} We note that positive $\Delta T/T$ features at ~ 535 , ~ 630 , and ~ 675 nm are observed on all time scales (Figures 3a–c) and correspond to the peaks in the ground-state absorption spectrum (Figure 2). Hence we consider there to be a positive contribution from the GSB across this entire spectral range. However, the spectral shape of the TA signal is evidently altered from the linear absorption, which implies the presence of additional, overlapping spectral features. First, we observe the prominent, rapid decrease of the signal at 680 nm, which falls 40% from its peak within the first 100 fs. This feature matches the highest-energy peak in the luminescence spectrum of pentacene,^{25,26} so we assign it to SE from the rapidly decaying singlet exciton. This assignment was corroborated by additional measurements made with higher-energy pump photons,¹⁷ which cause blue-shifted emission from nonequilibrium, vibrationally excited states, instead of the “band-edge” emission observed here. Because this extraordinarily rapid decay implies that virtually all singlet excitons have decayed by 200 fs, we consider the residual

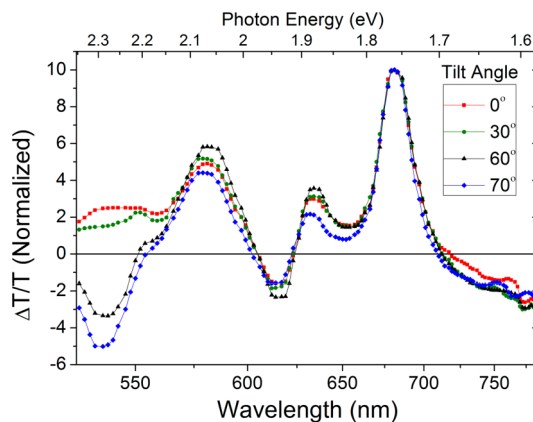


FIGURE 5. Normalized transient absorption spectra from a 150 nm thick polycrystalline pentacene film at 5 ps following excitation.¹⁶ The different curves are labeled by the “tilt” angle between the normal to the substrate and the pump beam. Due to the molecular self-organization of the pentacene relative to the substrate,^{31,33} features that become enhanced as the substrate is tilted arise from transitions that are polarized along the long molecular axis.^{12,27,28}

signal at 680 nm at later times to be a linear combination of GSB and the thermal effect (as discussed later).

Returning to Figure 3a and examining the evolution of the TA signal from 20 to 500 fs, we note the paired rise of the TA signal from 540–660 nm and fall of the signal in both the regions from 700 to 1000 nm and 500 to 520 nm. Kinetic traces corresponding to these features (Figure 4) rise and fall with time constants of 78 and 85 fs, respectively, which are experimentally equivalent.¹⁷ These observations are consistent with the coupled decay of instantaneously formed singlets, associated with the PIA feature from 540–650 nm, and the growth of triplets, associated with two PIA bands (500–520 nm and 700–1000 nm). We emphasize that there is considerable spectral overlap between these negative PIA features and the positive GSB. Thus, the PIA feature at 540–650 nm (500–520 nm) should be seen to extend over the entire region where the spectrum at 20 fs is significantly more negative (positive) than at 500 fs, rather than being limited to the small range where $\Delta T/T$ is less than zero. Our association of the triplet with the pair of PIA features is supported by the observation that, once formed (~ 200 fs), neither feature shows any further evolution over the remainder of the first picosecond and both only decay by $\sim 40\%$ over the first 1.8 ns following excitation (Figure 4). Such a long time constant rules out short-lived singlets but could be consistent with either triplets,^{13,16,17,43} polarons,¹⁵ or excimers.¹² Additional experiments show that these two features also exhibit matched decay kinetics in the 1–10 ns time range.¹⁶ Further, as shown in Figure 5, by means of

“tilting” the substrate with respect to the probe beam, we demonstrated that the PIA feature at 500 nm is strongly polarized along the long molecular axis, as is expected for this triplet transition.^{12,27,28} Hence, we consider the totality of rapid formation from the singlet, slow decay dynamics, long-axis polarization, and the good agreement of the both transition energies with calculations^{29,30} to form a strong case that the two PIA features (500–520 and 700–1000 nm) correspond to the first two excited-state absorptions of the triplet.

We note that a preliminary statement of this conclusion¹³ was challenged⁴ on the grounds that the T1 → T2 transition at 700–1000 nm has not been observed in solution^{4,28} and is calculated to have a vanishing oscillator strength in the isolated molecule.³⁰ Instead, it was proposed that this long-wavelength feature arises from polaronic species,⁴ which might relate to the directly photogenerated “free” charges invoked to explain sub-picosecond transient (terahertz) conductivity results.⁴⁴ Charge modulation spectroscopy has shown that pentacene cation does have some absorption from 700 to 1000 nm in the solid state,⁴⁵ and thus, we cannot rule out that any polarons that are present may partially contribute to the TA signal in this region. However, the cation does not absorb at 500 nm⁴⁵ and so would not straightforwardly explain the near-identical dynamics (10 fs to 10 ns) exhibited by the paired PIA features at 500 nm and from 700 to 1000 nm. Lastly, although the PIA from 700 to 1000 nm is formed rapidly, it is evidently associated with the terminal excited state in pure pentacene films.^{13,16} Thus, as described below, the measurements on bilayer pentacene-acceptor devices, which demonstrate that photocurrent arises predominately from fission-generated triplets,^{40,41,46} do not indicate the presence of a substantive population of directly generated free charges under mild experimental conditions. Accordingly, we consider that the ensemble of experimental results now assembled provide robust evidence that the PIA from 700 to 1000 nm in pentacene is associated with the triplet and add that an analogous PIA has now been reported by Roberts et al. in the TIPS derivative.⁴⁷ We note, however, that our interpretation requires that this transition is enhanced in the solid state relative to the pentacene molecule in solution. Although we speculate that the transition may gain oscillator strength from in-plane intermolecular coupling,⁴⁸ particularly of the higher-lying (T2) triplet state, we welcome further theoretical efforts to elucidate this effect.

To complete our accounting for the shape of the TA spectrum at 1 ps after excitation (Figure 3b), it is necessary

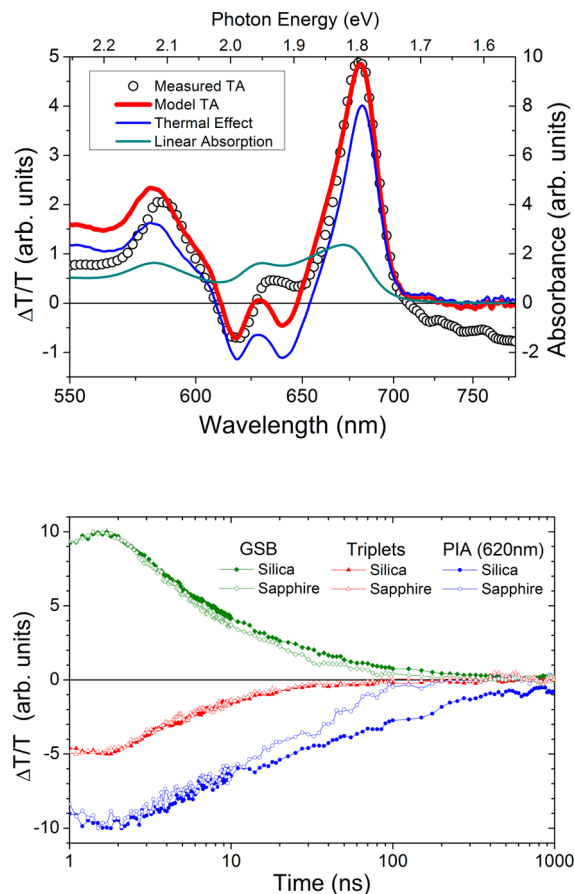


FIGURE 6. (a) Measured transient absorption spectrum of polycrystalline pentacene at 1 ps, along with the measured linear absorption spectrum and the predicted shape of the “thermal effect”. A linear combination of the latter two spectra yields the curve labeled “Model TA”. (b) Transient absorption kinetics for polycrystalline pentacene measured on silica (closed symbols) or sapphire (open symbols) substrates. Spectral features associated with excited-state species (triplets, GSB) show unchanged dynamics, while the PIA feature at 620 nm (“thermal effect”) decays more rapidly on the thermally conductive sapphire substrate.

to determine why the TA signal from 550 to 650 nm continues to be “pulled down” relative to the ground-state absorption spectrum (Figure 2), even after the singlet PIA has died away. As suggested by Figure 6a and described in detail elsewhere,¹⁶ this spectral signature is consistent with thermal modulation of the sample by the pump pulse. Specifically, we estimate that each pump pulse locally heats the sample by a few kelvins. Hence, irrespective of any features from excited-state species, a signature will arise in the TA spectrum that is proportional to the difference between the ground-state absorptions of “hot” and “cold” pentacene. The shape of the “thermal effect” in pentacene at room temperature can be estimated by taking the difference of the linear absorption spectra as a function of temperature and is

presented in Figure 6a.¹⁶ As is evident, we can achieve good agreement with the experimental TA spectrum (550–700 nm) using a linear combination of the GSB (i.e., the linear absorption spectrum) and the thermal effect. The obvious discrepancies <550 and >700 nm reflect the overlapping two-lobed PIA from triplets described above. To test this hypothesis, we measured the kinetics of the TA signal at 630 nm on a nanosecond time scale for pentacene films grown simultaneously on two different substrates, fused silica and sapphire (Figure 6b). Although the TA signals from both films are comparable at short times, we find that the signal at 630 nm decays an order of magnitude more rapidly on the sapphire than on glass. This is consistent with the much greater thermal conductivity of sapphire, which allows the pump-induced heating of the film to dissipate more rapidly.¹⁸ By contrast, the $\Delta T/T$ signals from “real” excited state features (GSB and triplets) are unaffected. As shown elsewhere,¹⁶ this “thermal effect” is more pronounced at cryogenic temperatures due to the lessened heat capacity and thermal diffusivity.

Hence, taken together, we consider these assignments to form a complete description of the transient spectra that result from the photoexcitation of polycrystalline pentacene, as well as a demonstration that singlet excitons undergo rapid, efficient fission to form triplet pairs, and that no other intrinsic decay channels are appreciable under moderate excitation densities.

Charge Generation from Fission-Generated Triplets

Although these spectroscopic studies demonstrated that singlet excitons are rapidly converted to triplets via fission in easily fabricated evaporated pentacene films, this was only the first step in realizing a fission-enhanced photovoltaic device. This is because in efficient organic solar cells photo-generated excitons are dissociated at an interface between electron-donating and electron-accepting materials.⁴³ As a result, it was of considerable practical importance to establish that triplet excitons could be ionized.

In hindsight, the first evidence that this was readily achievable came from the earlier demonstrations of pentacene/acceptor evaporated bilayer solar cells with high internal quantum efficiency.^{19–21} In these cells, singlets decay so rapidly via fission that they would not have been able to reach the interface and interact with the acceptor molecules in their 80 fs lifetime. Also, the long (tens of nanometers) hypothesized exciton diffusion lengths in pentacene–fullerene devices is also consistent with triplets in retrospect.¹⁹ Contemporary, targeted studies provided more unequivocal evidence. Lee et al. observed

that the photocurrent in pentacene–fullerene photodetectors under reverse bias was modulated by a magnetic field in a manner expected for the dissociation of triplets following fission,⁴⁶ while Hong et al. reported that the slow transient photocurrent response in zinc phthalocyanine/pentacene/fullerene devices was consistent with triplet dissociation.²²

As shown in Figure 3c (“EA”), and discussed in detail elsewhere,¹³ we observed a spectral signature consistent with the dynamic Stark shift of the primary pentacene absorption feature on a nanosecond time scale when performing TA on pentacene/fullerene bilayers. This was consistent with the creation of local electric fields due to the charges generated at the interface; the fact that it did not occur until a few nanoseconds following excitation ruled out the dissociation of short-lived singlets as the main source of photocurrent and instead pointed to the ionization of slow-diffusing triplets.¹³ To confirm this, we then directly measured the dynamics of a PIA feature at 1650 nm associated with the pentacene hole polaron⁴⁵ and found that charge generation does primarily take place several nanoseconds following excitation in pentacene/fullerene bilayers.⁴³ These demonstrations that fission-generated triplets are dissociated at the pentacene/fullerene interface were in agreement with recent two-photon photoemission and time-resolved second-harmonic generation results from Chan et al.⁴⁹ These authors observed that triplets were created via subpicosecond fission in ultrathin pentacene/fullerene films and then decayed via charge transfer to nearby fullerene molecules.⁴⁹

However, for the predicted gain in solar energy conversion efficiency to be realized,^{4,50} the more technologically relevant interface for triplet ionization is one between pentacene and a material that strongly absorbs in the infrared. Here, lead chalcogenide nanocrystalline quantum dots are a natural choice, because they show good photovoltaic performance, can form thin films via solution processing, and possess an optical gap that is tunable through the infrared. As detailed previously, we fabricated pentacene/PbS⁵¹ and pentacene/PbSe⁴⁰ solar cells (Figure 7) that exhibit the telltale absorption features from pentacene in a spectrally resolved plot of their photon-to-electron (external) quantum efficiency. Noting that the majority of light is absorbed in the bulk of the 50 nm pentacene layer in these devices, and recalling the aforementioned spectroscopic results, which showed that photoexcitations are overwhelmingly converted to triplets within a picosecond,^{17,49} the observation of any substantive photocurrent contribution from pentacene immediately implied that triplets could be ionized at the pentacene/nanocrystal interface.

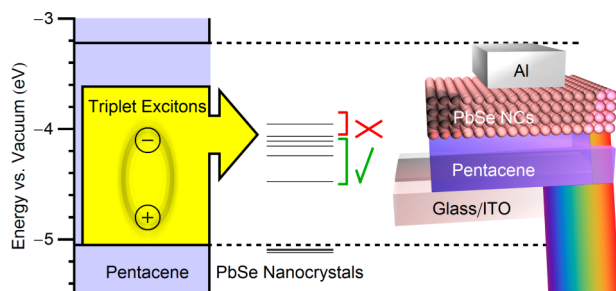


FIGURE 7. Illustration of the use of a size series of quantum dots with varying bandgaps to establish a lower limit on the energy of the ionizing exciton, and a schematic diagram of a pentacene/nanocrystal hybrid solar cell. HOMO energies are taken from ultraviolet photoelectron spectroscopy, and LUMO energies are estimated using the optical bandgap.

However, this conclusion was corroborated by further independent measurements by Jadhav et al. and ourselves.^{40,41} Taking advantage of the size-tunable conduction-band energy in quantum dots, both groups examined the onset of the photocurrent contribution from pentacene as a function of the effective “diagonal bandgap” (i.e., the energetic difference between the pentacene HOMO and the conduction band on the quantum dot). In the work of Jadhav et al., this data set was supplemented by an additional series of organic acceptors.⁴¹ Thus, without any assumptions regarding its nature, these experiments determined that the energy of the state in pentacene that immediately precedes charge generation closely matches the previously measured energy of the triplet (0.86 eV).^{11,23} Further, the particular pairing of pentacene with lead selenide quantum dots yielded devices with power conversion efficiencies up to 4.7%⁴⁰ and, very recently, permitted the fabrication of a hybrid pentacene/PbSe/a-silicon solar cell.⁵²

Outlook

These advances in our understanding of the photophysics of pentacene will serve to underpin further investigations of singlet exciton fission. Fundamentally, a consistent set of spectral assignments will allow further targeted experimental studies, for example, a systematic investigation of the relationship between molecular geometry and fission efficiency through a series of chemical derivatives. Work of this nature will naturally inform theoretical efforts. However, the time is now ripe to explore the physics of higher-gap materials, particularly those, such as tetracene, where more complex “equilibrium-like” photophysics of fission and recombination must be better understood. This is because such systems often possess triplet excitons that have enough energy to be conceivably paired with existing industry-standard

crystalline silicon solar cell technology, which is a key technological advantage. Lastly, we note that robust, direct measurements of the singlet fission yield have been lacking. As we have described, it is difficult to obtain a truly background-free signal in TA, and quantitative efforts often require the discomfiting assumption that the absorption cross sections of excited-state species are unchanged from those of the isolated molecule. By contrast, while the observation of a raw photon-to-electron conversion efficiency greater than 100% in a fission-based photovoltaic device would provide incontrovertible evidence that the carrier multiplication is indeed taking place, these measurements are complicated by the usual loss channels present in organic photovoltaic devices, such as light absorption, exciton dissociation, and transport. Still, such challenges must also be overcome if practical fission-enhanced solar cells are to be a reality: we eagerly await further advances!

The authors acknowledge all their collaborators, especially Brian Walker, Jenny Clark, Kerr Johnson, Sebastian Albert-Seifried, Marcus Böhm, R. Sai Santosh Kumar, and Giulio Cerullo, as well as helpful discussions with Marc Baldo, Chris Bardeen, Heinz Bässler, Anna Köhler, and Xiaoyang Zhu. This work was supported by the EPSRC.

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FOOTNOTES

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