# Exciton Fission and Charge Generation via Triplet Excitons in Pentacene/C$_{60}$ Bilayers

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***Abstract:*** Organic photovoltaic devices are currently studied due to their potential suitability for flexible and large-area applications, though efficiencies are presently low. Here we study pentacene/C$_{60}$ bilayers using transient optical absorption spectroscopy; such structures exhibit anomalously high quantum efficiencies. We show that charge generation primarily occurs 2−10 ns after photoexcitation. This supports a model where charge is generated following the slow diffusion of triplet excitons to the heterojunction. These triplets are shown to be present from early times (<200 fs) and result from the fission of a spin-singlet exciton to form two spin-triplet excitons. These results elucidate exciton and charge generation dynamics in the pentacene/C$_{60}$ system and demonstrate that the tuning of the energetic levels of organic molecules to take advantages of singlet fission could lead to greatly enhanced photocurrent in future OPVs.

## Introduction

As detailed by Shockley and Queisser, a limit on the efficiency of any single-bandgap photovoltaic (PV) device operating under solar conditions is the inability to harvest the full energy of supra-bandgap photons.[1] One attractive method to circumvent this limit is to generate multiple electron−hole pairs from absorbed high-energy photons. Multiple exciton generation has been demonstrated in inorganic semiconductor nanocrystals[2−4] but not in organic semiconductors (OSCs). However, an available route to OSCs is spin-singlet exciton fission to form two spin-triplet excitons. This process begins when a photon is absorbed by a conjugated organic material to create a singlet exciton (S$_n$), with energy $E(S_n)$. If the lowest-lying triplet state (T$_1$) has energy $E(T_1)$, and $E(S_n) > 2E(T_1)$, then it is energetically favorable and spin-allowed for the singlet to undergo fission to form two triplets (S$_n{\rightarrow}$2T$_1$). First observed and studied in the late 1960s, exciton fission has been shown to occur in a range of molecular crystals.[5−7] Recently there have been several theoretical studies of the mechanism of singlet fission,[8,9] yet to date there have been few experimental studies of this process in the context of organic photovoltaic devices (OPVs).

Pentacene/C$_{60}$ bilayer OPVs have attracted considerable interest due to recent demonstrations of large exciton diffusion lengths and quantum efficiencies approaching unity.[10,11] The regular arrangement of molecules and the well-defined hetero-interface also make this an attractive model system for theoretical studies of exciton dissociation in OPVs. Charge generation and exciton dynamics have been probed via several experimental and theoretical techniques,[12−16] but uncertainty remains as to the origin of the high quantum efficiencies. Figure 1 shows the molecular structures of pentacene and C$_{60}$ and a schematic diagram showing the relevant excitonic energy levels. It should be noted that the triplet energy of pentacene ($E(T_1) = 0.86$ eV) is less than half the energy of the lowest-lying singlet ($E(S_1) = 1.83$ eV);[17] hence, the singlet exciton fission process is expected to occur without thermal activation. The low photoluminescence yield in pentacene films indicates the rapid evolution of the

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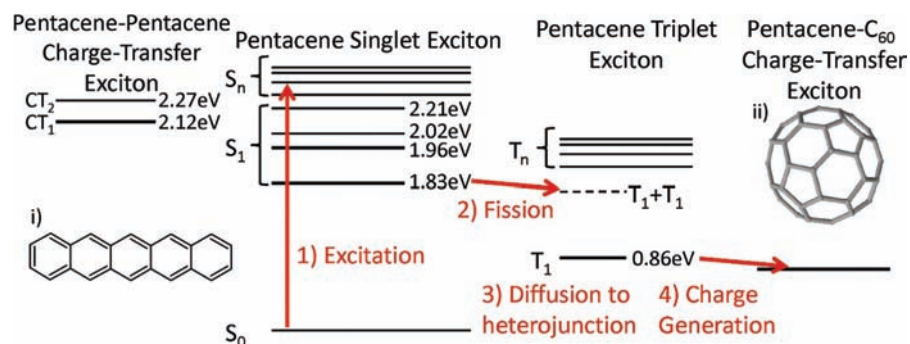(4) Nozik, A. J. *Nano Lett.* **2010**; DOI: 10.1021/nl102122x.
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**Figure 1.** Molecular structures of (i) pentacene and (ii) C$_{60}$ and an energy level diagram for excitonic states in pentacene. The Davydov levels of the singlet exciton lie at 1.83 and 1.96 eV, and the sidebands within our spectral range lie at 2.02 and 2.21 eV.

initial excited state to a nonemissive species. However, previous pump−probe measurements and theoretical studies have been inconclusive, and several models have been proposed, including fission to form triplets, the formation of bound triplet pairs with overall singlet character, and the formation of excimers.[8,17−21]

Here we use transient absorption (TA) spectroscopy with a broad spectral (550−925 nm) and temporal (200 fs−1 ms) range to study the pentacene/C$_{60}$ system. As we will show, both capabilities are required to fully characterize the exciton and charge generation dynamics in this system. We show that the photocurrent in pentacene/C$_{60}$ OPVs results from the dissociation of triplet excitons (formed via fission) as they reach the heterojunction. Our results not only help explain the photophysics of this widely studied system but also demonstrate that the exciton fission process could be harnessed to augment efficiencies in future OPVs.

## Results and Discussions

Figure 2 shows the absorption spectra of pentacene, C$_{60}$, and a pentacene/C$_{60}$ bilayer. In pentacene the primary singlet transition (S$_0$→S$_1$) undergoes Davydov splitting, with the lower level at 680 nm and the upper level at 632 nm, as has been discussed previously in the literature.[22,23] The sidebands of the S$_0$→S$_1$ transition lie at 613, 565, and 523 nm[24] but are obscured at room temperature due to thermal broadening. Absorptions peaks at 585 and 546 nm correspond to pentacene−pentacene charge-transfer (CT) transitions (S$_0$→CT$_n$) as identified using electric field modulated absorption spectroscopy by Bässler et al.[24] These CT states involve a partial transfer of an elementary charge from one pentacene molecule to a neighboring molecule. This results in an excitation with significant dipole moment but that does not directly generate free charge carriers.

In order to study the photoexcitation dynamics we use TA spectroscopy, as described elsewhere.[25] Briefly, a monochro-
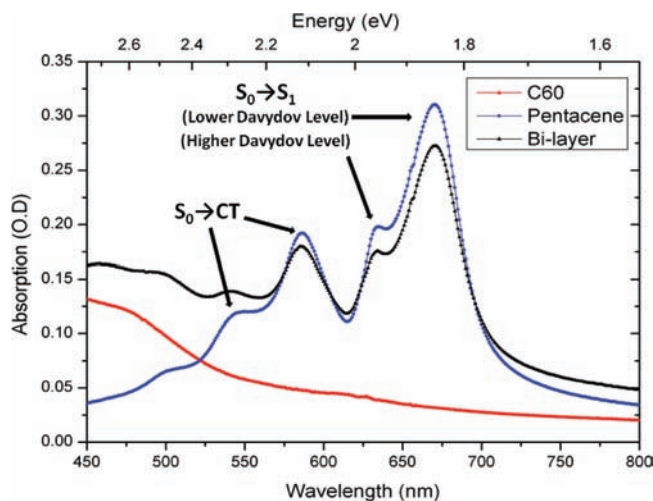
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**Figure 2.** Absorption spectra of pentacene (40 nm, blue), C$_{60}$ (50 nm, red), and a pentacene/C$_{60}$ bilayer (40 nm/50 nm, black). Note that the films used in transient absorption experiments consisted of 150 nm/10 nm of pentacene/C$_{60}$.

matic pump beam is used to create a population of excited states at time $t = 0$. A broadband probe beam is then used to interrogate the system at some later time $t = t'$, and the differential transmission $\Delta T/T$ is then calculated. Since the pump beam promotes species from the ground state to a higher-lying excited state, the magnitude of the absorption of the ground state is reduced (i.e., transmission is increased), giving a positive $\Delta T/T$ signal known as the ground-state bleach (GSB). Conversely, excited-state species can absorb at a new spectral position, causing a negative TA feature know as a photoinduced absorption (PIA). Singlet excitons can also radiatively relax to the ground state, leading to a positive feature termed stimulated emission (SE). For the layer thicknesses used here, almost all optical absorption at the pump excitation energy (490 and 532 nm) takes place in the 150 nm thick pentacene film, with very little excitation of the 10 nm thick and weakly absorbing C$_{60}$ layer. We studied the TA signal of C$_{60}$-only films, and in the region probed we found only a broad, flat absorption (not shown here); this signal is very weak for thin layers of C$_{60}$. Additionally, the absorption peak of C$_{60}$ anions lies between 1050 and 1100 nm,[26] outside our spectral window. Thus, the spectrum of the bilayers can be accounted for primarily by excitations in pentacene. We also note that $\Delta T/T$ values are no greater than 1%, which implies that only a small fraction of chromophores were excited.

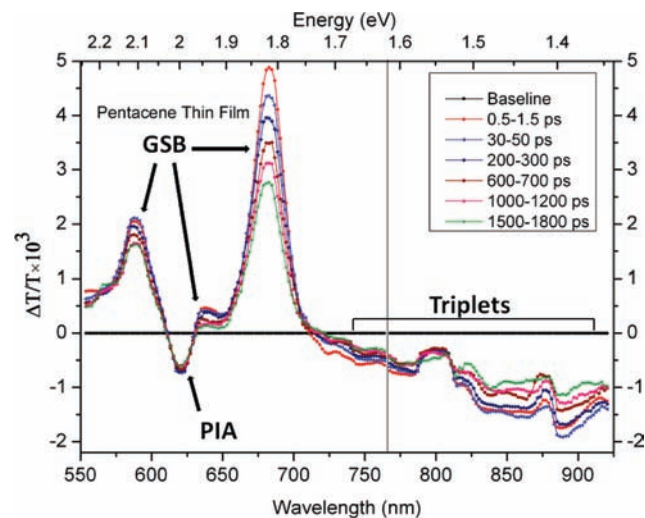(26) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695−703.

**Figure 3.** Transient optical absorption spectra at early times for a pentacene thin film excited at 490 nm and a pulse irradiance of 80 $\mu$J/cm$^2$. The various spectral features are indicated, where GSB indicates ground-state bleach and PIA indicates photoinduced absorption. Data from 550 to 765 nm and from 768 to 925 nm are derived from sequential experiments on the same sample under the same experimental conditions. The feature at ~800 nm is an artifact in the white light continuum used as a probe. Spectra are integrated over the time ranges indicated.

Figure 3 shows the temporal evolution of the TA spectrum of a pentacene thin film from 500 fs to 2 ns. Each spectral slice in the figure is integrated over the time range indicated, and these data (up to 2 ns) are consistent with previous work.[18,20] The main features we observe are the bleaching of the ground-state absorption bands at 585 and 680 nm and the presence of an induced absorption in a broad band extending from 720 nm to the limit of our measurement range at 925 nm. The GSB and PIA decay very slowly, and significant portions of both remain after 2 ns. The long-lived GSB indicates the presence of a species which decays to the ground state very slowly; this species is most probably associated with the similarly long-lived PIA centered at 860 nm. We note that we see no evidence for any stimulated emission within our time resolution (200 fs), indicating that singlet excitons have relaxed to a nonemissive species by this time.

As shown in Figure 4 for a pentacene thin film and a pentacene/C$_{60}$ bilayer, we extend the time range of our TA measurements using an electrical delay between a $q$-switched pump pulse (532 nm, 600 ps duration) and the white light probe. It can be seen for both samples that the decay back to the ground state extends over hundreds of nanoseconds. For the pentacene-only film, this decay happens without significant further spectral evolution. However, in the presence of C$_{60}$, the long-wavelength PIA has evolved to a broader and flatter structure, extending from 720 to 925 nm.

For the pentacene/C$_{60}$ bilayer (Figure 4b) we draw particular attention to the negative TA signal at 700 nm which grows in beyond 2 ns along with the simultaneous blue-shift of the primary GSB peak from 683 to 674 nm. This effect is due to electroabsorption (EA), the mechanism of which is discussed below, and indicates the formation of electric fields within the thin films. The first critical observation is that these fields are not externally applied and instead form due to charge generation at the heterojunction. The second is that the time scale for this process (2−10 ns, as judged by the onset and rise of the EA signal) is too long to be accounted for by charge generation directly from singlet excitons. We propose that this effect results
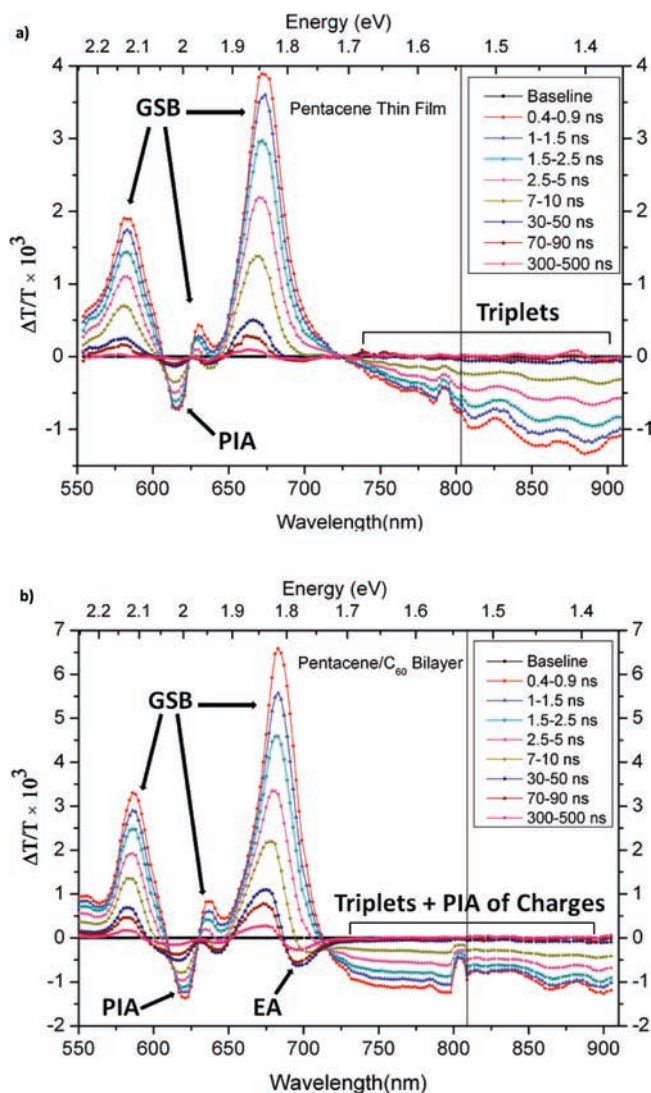


**Figure 4.** Transient optical absorption spectra at longer time delays for (a) a pentacene thin film and (b) a pentacene/C$_{60}$ bilayer excited at 532 nm and a pulse irradiance of 120 $\mu$J/cm$^2$. Data from 550 to 810 nm and from 810 to 915 nm are derived from sequential experiments on the same sample under the same experimental conditions. The feature at ~800 nm is an artifact in the white light continuum used as a probe. Spectra are integrated over the time ranges indicated.

from the field set up by the dissociation of triplet excitons after their slow diffusion to the heterointerface with C$_{60}$.

In order for dissociation of the pentacene triplet exciton at the heterojunction with C$_{60}$, the pentacene/C$_{60}$ CT state must be lower in energy than the triplet exciton. The energy of the CT state can be estimated as $E_{CT} = IP_{pentacene} + EA_{C_{60}} + E(P^+/C_{60}^-)$ as discussed by Brédas et al.,[15] where $IP_{pentacene}$ and $EA_{C_{60}}$ are the ionization potential and electron affinity of pentacene and C$_{60}$, respectively, and $E(P^+/C_{60}^-)$ represents the electrostatic stabilization energy between the cation of pentacene and the anion of C$_{60}$. Koch et al.[14] performed a detailed ultraviolet photoelectron spectroscopy (UPS) study of the energy level alignment at the pentacene/C$_{60}$ heterojunction and found no interface dipole formation. Using established values for $IP_{pentacene}$ (5.0 eV)[27] obtained by UPS, and the $EA_{C_{60}}$ (4.5 eV) obtained

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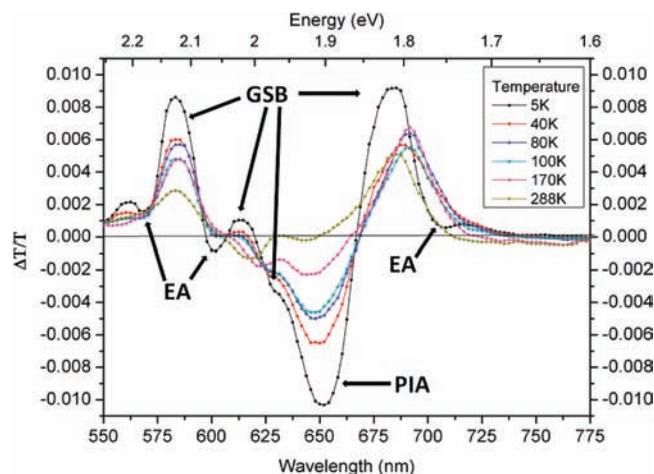
**Figure 5.** Transient optical absorption spectra of pentacene thin films at a range of temperatures. Spectra are measured 1.5 ns after excitation with a 532 nm laser at 290 $\mu$J cm$^{-2}$ pulse$^{-1}$.

by inverse photoelectron spectroscopy,[28] we estimate that $E_{CT}$ is around 0.5 eV, with the exact value depending on the electrostatic stabilization energy. This places $E_{CT}$ lower than the triplet energy and allows for the efficient dissociation of triplets at the pentacene/C$_{60}$ heterojunction. The low value of $E_{CT}$ also helps to explain the low $V_{oc}$ observed in pentacene/C$_{60}$ solar cells (0.4 V), since the $V_{oc}$ is normally slightly lower than the CT state energy. It is interesting to note that dissociation of singlet excitons would also proceed through the lowest CT state, and since the CT state effectively controls the $V_{oc}$, the dissociation of singlets instead of triplets would not allow for any increase in $V_{oc}$. Thus, in the present case, the dissociation of two triplets instead of one singlet amounts to a two-fold gain in efficiency.

We now turn to a detailed assignment of the TA spectral features of pentacene, which is enabled by measurements performed at 5 K (Figure 5) as the reduced thermal broadening minimizes the spectral overlap that complicates the interpretation of room-temperature observations. The majority of the spectrum 1.5 ns after excitation can be explained by the GSB of the previously described features in this spectral range (two Davydov levels of the S$_0$→S$_1$ transition, the first and second sidebands, and the lowest-energy S$_0$→CT transition, as identified in Figure 1a). A large, temperature-dependent PIA feature which grows in over 700 ps is observed at 650 nm (early time data not shown). This feature has been previously assigned to a cation transition (S$_0^+$→S$_1^+$) by Thorsmølle et al.[20] However, previous charge modulation spectroscopy (CMS) work using field-effect diode structures has shown that the hole on pentacene has no absorption in this region but shows a weak, flat absorption between 750 and 1000 nm and a strong absorption between 1400 and 2000 nm.[29] Instead we consider that this absorption is associated with a low-lying excitonic state associated with defect sites or a bound triplet pair state that has recently been proposed as the lowest-energy excited state.[21] Within such models, excitons occupy these states at low temperatures but can overcome the activation energy barrier to form free triplet excitons at room temperature.
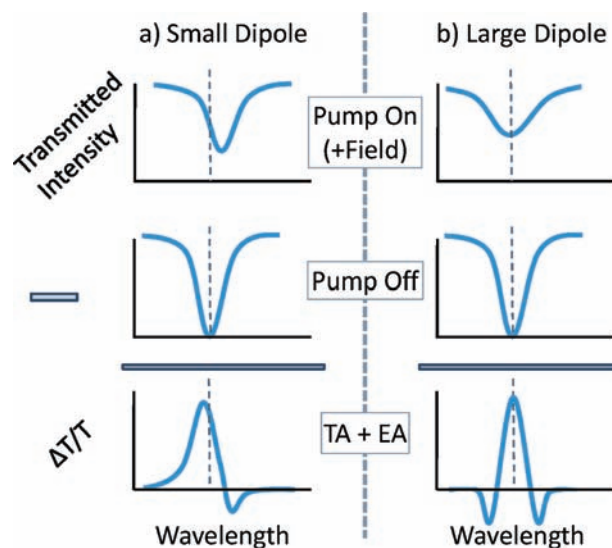


**Figure 6.** Schematic cartoon illustrating the effect of electroabsorption (EA) on a feature in the ground-state bleach for two hypothetical transitions. (a) The transition has a small intrinsic dipole, and so produces a transient absorption (TA) spectrum that incorporates the first derivative of the feature. (b) The transition has a large intrinsic dipole, and so produces a TA spectrum involving the second derivative.

We now return to the assignment of the features at 565, 600, and 700 nm that are visible at 5 K (Figure 5). Drawing on the work of Bässler et al.,[24] we attribute each to the effect of EA on an adjacent GSB peak. The negative TA signal at 700 nm results because the primary excitonic absorption at 670 nm is red-shifted by the quadratic Stark effect, which adds a signal proportional to the first derivative of the associated GSB peak to the TA spectrum (Figure 6a). The negative features at 570 and 600 nm are both associated with the peak assigned to the CT exciton at 585 nm and arise because EA adds a signal proportional to the second derivative of a GSB peak if the underlying transition has a large intrinsic dipole[21] (Figure 6b). We again emphasize that the electric field that causes EA is not externally applied in this case and hence must arise intrinsically due to the evolution of locally asymmetric charge distribution. Such a distribution would naturally occur due to exciton dissociation at the heterojunction in pentacene/C$_{60}$ bilayers, as is observed in Figure 4b, but could also arise in pentacene-only thin films via charge trapping at defect sites or on pentacenequinones that may be present at crystallite surfaces.

We note that there is some evidence for a weak EA response in the TA spectrum of the pentacene-only film (Figure 4a) but that in the presence of the heterojunction with C$_{60}$ this response is greatly amplified (Figure 4b). It was necessary to keep the pump irradiance low (below 140 $\mu$J/cm$^2$), as the EA in the pentacene-only film increased slightly at higher excitation intensities, indicating that other channels for charge generation are present. These may include exciton−exciton annihilation and sequential excitation within the duration of the pump pulse,[30] both of which may lead to the formation of polaron pairs.

We assign the large, broad PIA seen in pentacene films centered at 860 nm (Figures 3 and 4a) to the triplet transition

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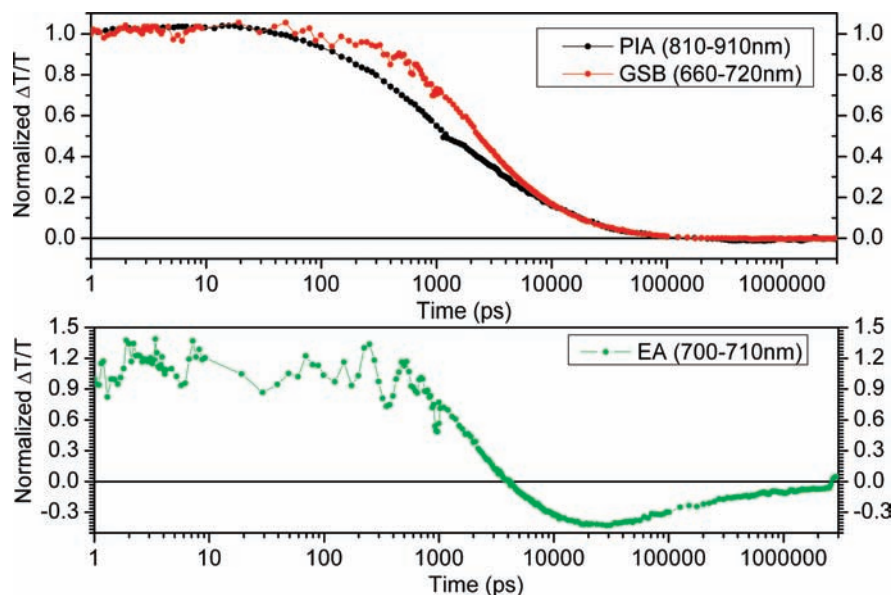
**Figure 7.** Normalized transient absorption dynamics of various spectral regions of pentacene/$C_{60}$ bilayers on time scales from 1 ps to 3 $\mu$s. The data from 1 ns onward are the same as those used in Figure 4b, while shorter-time data derive from a separate experiment and are scaled by the excitation density. The PIA decays faster than the GSB at earlier times, while the EA grows in. At later times the PIA and GSB decay at the same rate. This suggests that at early times the decay of the PIA is controlled by diffusion and dissociation of triplets to form charge pairs; however, the GSB does not decay substantially because excitations are still present on pentacene. At later times the decay of the PIA is controlled mainly by geminate recombination of charge pairs, which also results in the decay of the GSB and EA.

($T_1 \rightarrow T_N$). This assignment is supported by previous work on single-crystal pentacene which demonstrated that triplets have a PIA (750−990 nm) centered at 860 nm.[20] The $T_1 \rightarrow T_N$ transition in single-crystal pentacene is assigned by analogy with tetracene, where the singlet fission process is thermally activated and hence readily identified.[20] From Figure 3 we can see that the triplet population is long-lived and appears within the time resolution of the measurement (200 fs), too fast to be accounted for by intersystem crossing, and hence must be formed via singlet fission. This is consistent with the fact that we observe no stimulated emission from pentacene, as well as previous demonstrations that the photoluminescence decays with a time constant of 70 fs in polycrystalline pentacene films.[18,20] We also note the difference in the shape of the PIA (750−925 nm) in the bilayer (Figure 4b) and the pentacene-only film (Figure 4a). We attribute this to the combination of the triplet absorption (peaked at 860 nm) with a broad, flat charge absorption (at wavelengths >725 nm). This result is consistent with previous CMS work[29] and the fact that charge is created efficiently in the bilayer (see below).

An alternative relaxation channel for singlets, namely to excimer states with a PIA at 620 nm, has been proposed by Marciniak et al.[18,19] However, as is evident in Figure 3, the PIA at 620 nm has a small integrated spectral weight compared to the large feature centered at 860 nm and hence cannot represent a significant fraction of room-temperature excitations. As discussed previously, the PIA feature at 860 nm is strongly associated with triplets.[20] As this feature accounts for the vast majority of the spectral weight, it implies that triplets are the preferred decay channel. Figure 5 also shows that the feature that appears at 620 nm at room temperature is not due to a single species but is instead the result of the overlap of GSBs at 613 and 632 nm with the large temperature-dependent PIA centered at 650 nm. We also note that the role of excimers was questioned by recent quantum chemical and molecular modeling results reported by Kuhlman et al.[21] that suggest that an excited-state rearrangement of molecules to form excimers is energeti-

cally unfavorable. It must also be noted that OPVs fabricated using pentacene/$C_{60}$ display quantum efficiencies approaching unity.[10,31] This suggests that the excited-state species present in thin films have long diffusion lengths and can be efficiently dissociated at the heterojunction with $C_{60}$, which is more consistent with a model of triplet exciton formation.

Figure 7 presents the kinetic traces of the three main features of the TA spectra in bilayer films as they evolve from 1 ps to 3 $\mu$s. As is apparent, the growth of the EA, and hence the formation of charge, is coincident with the decay of the PIA signal centered at 860 nm. We thus conclude that the charge responsible for the EA is formed by the dissociation of triplet excitons which diffuse to the heterojunction with $C_{60}$. Previous investigations on PV devices have established that the diffusion range of excitons in pentacene thin films is approximately 40 nm.[10,31] Combining this value with our exciton lifetime of 5 ns, we estimate a diffusion coefficient ($D_T$) of $3 \times 10^{-3}$ cm² s⁻¹, which is similar to reported values for triplet diffusion along the *b*-axis of tetracene ($D_T = 4 \times 10^{-3}$ cm² s⁻¹).[32] The EA signal, and hence the underlying population of charge pairs, then decays over hundreds of nanoseconds. This long lifetime for geminate recombination is similar to that of P3HT-PCBM[33] and correlates well with the high quantum efficiencies of this system since it allows adequate time for the charges to be extracted in the presence of the external electric field created by the electrodes in OPVs.

Taken together, the TA data show that photogenerated singlet excitons rapidly relax to form two triplet excitons which can then diffuse to a heterojunction with $C_{60}$ and undergo charge separation. This allows for the possibility that two electrons can be extracted for every absorbed photon. Indeed, Kippelen et al. have demonstrated pentacene/$C_{60}$ OPVs with internal quantum efficiencies approaching unity,[10,31] and recently Baldo et al.

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demonstrated a photodetector based on 30 multilayers of pentacene/$C_{60}$ with an external quantum efficiency (EQE) greater than 100% at −5 V reverse bias.[34] We have also fabricated pentacene/$C_{60}$ devices and studied their current−voltage characteristics under monochromatic and broadband illumination. Our results are similar to recent reports, with high EQEs and high dark currents at reverse bias.[34] These high dark currents make quantitative analysis of this data difficult. Still, given the evidence of triplet fission and charge generation from triplets presented here, it is reasonable to conclude that the exciton fission process is indeed contributing to the photocurrent in these systems.

## Summary

In conclusion, we use TA spectroscopy to demonstrate that spin-singlet excitons in pentacene thin films undergo fission to two spin-triplet excitons on a sub-200 fs time scale. The triplets can then diffuse to a heterojunction where they can be dissociated, resulting in charge formation on a 2−10 ns time scale, leading to high quantum efficiencies.

As noted previously, multiple exciton generation (MEG) has been demonstrated in numerous quantum dot systems; however, to date no solar cells that make use of this effect have been demonstrated. It has proved hard to extract charges from the excitons formed via MEG due to issues of limited exciton lifetimes and exciton−exciton annihilation.[2−4] Exciton fission overcomes this problem by forming long-lived triplet excitons which may diffuse to a heterojunction where they are dissociated by a suitable donor. We also find no evidence of rapid triplet−triplet annihilation within our time resolution (200 fs). Since two triplets do not have enough energy to regenerate the singlet (Figure 1), they are the lowest-energy configuration for this system. This removes a major decay channel for triplets.

Recent theoretical work on the mechanism of singlet fission has focused on either single molecules[9] or the case of localized initial excitation.[8] However, there is both theoretical and experimental evidence that the singlet excitation in polyacene thin films is delocalized over several molecules.[35] This makes a strong case for further theoretical work and ultrafast measurements with better time resolution in order to fully understand the mechanism of exciton fission. Future organic materials could then be designed to take advantage of this process and boost OPV efficiency. This mechanism could also allow for a new class of OPVs in which a small bandgap material is paired with a larger bandgap material which undergoes exciton fission. Both species of excitons could then be dissociated using an appropriate electron acceptor, leading to greatly enhanced photocurrent while harnessing the energy of high-energy photons.

## Methods

**Materials.** Pentacene (triple sublimed grade) was obtained from Sigma-Aldrich. $C_{60}$ was obtained from NanoC. All materials were used as received without further purification.

**Vacuum Sublimation.** Pentacene films 150 nm thick were deposited at a rate of 0.4 Å/s in a vacuum of $5 \times 10^{-5}$ mbar or better. To fabricate bilayers, a layer of 10 nm of $C_{60}$ was added on top without breaking vacuum.

**TA Spectroscopy.** A 1 kHz train of 90 fs pulses was generated in a Ti:sapphire amplifier system (Spectra-Physics Solstice). Portions of this light were used to pump a TOPAS optical parametric amplifier (Light Conversion) as well as a home-built broadband non-collinear optical parametric amplifier (NOPA) that allowed for single-shot measurement in a range from 550 to 800 nm or from 750 to 925 nm, depending on its alignment. For short-time measurements (500 fs to 2 ns), the TOPAS was used as the pump beam, and the probe beam from the NOPA was delayed using a mechanical stage (Newport). For long-time measurements (1 ns to 1 ms), sub-nanosecond excitation pulses were provided by a frequency-doubled $q$-switched Nd:YVO$_4$ laser (AOT-YVO-25QSPX, Advanced Optical Technologies). The non-collinear pump and probe beams were focused to the same spot on the sample. Generally, the pump irradiance was 120 $\mu$J cm$^{-2}$ pulse$^{-1}$, which is similar to that used in previous studies by Thorsmølle et al.[20] Every second pump pulse was omitted electronically when using the $q$-switched source, or with a mechanical chopper for short-time measurements. Each shot was detected and the differential transmission ($\Delta T/T$) calculated after accumulating and averaging 500 "pump on" and "pump off" shots for each data point. A reference beam that also passed through the sample was used to correct for shot-to-shot variation in the probe beam. Both the probe and reference beams enter an imaging spectrograph (PI Acton Spectrapro 2150i) in the same vertical plane and are spectrally dispersed onto two 256-pixel photodiode arrays (Hamamatsu S3901256Q). Samples were contained in a vacuum chamber ($\sim$10$^{-5}$ mbar) during TA measurements at room temperature and in a cryostat under helium for low-temperature measurements.

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