

# Morphology Effectively Controls Singlet-Triplet Exciton Relaxation and Charge Transport in Organic Semiconductors

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We present a comparative study of ultrafast photoconversion dynamics in tetracene (Tc) and pentacene (Pc) single crystals and Pc films using optical pump-probe spectroscopy. Photoinduced absorption in Tc and Pc crystals is activated and temperature-independent, respectively, demonstrating dominant singlet-triplet exciton fission. In Pc films (as well as C<sub>60</sub>-doped films) this decay channel is suppressed by electron trapping. These results demonstrate the central role of crystallinity and purity in photogeneration processes and will constrain the design of future photovoltaic devices.

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The strong potential for new technological applications provided by organic semiconductors has spurred extensive research efforts in these materials [1–3]. Applications include thin film transistors [4], light-emitting diodes (OLEDs) [5,6], photodiodes and photovoltaics (OPVs) [7,8]. To successfully utilize organic semiconductors in these technologies it is important to understand both the nature of the photogenerated states and their relaxation dynamics. In particular, for OPVs it is vital to understand and control exciton lifetimes at the materials level in order to fully optimize efficiency. Such studies involve understanding the role of crystallinity, defects, and molecular constituency in controlling relaxation dynamics in the time domain of relevance for photoconversion [9,10]. Here, we present a comparative study of ultrafast photogenerated state dynamics in pentacene (Pc) and tetracene (Tc) single crystals and in pure and C<sub>60</sub>-doped Pc films using optical pump-probe spectroscopy. We demonstrate for the first time how morphology may control relaxation behavior in an organic semiconductor by effectively turning singlet-triplet exciton fission decay channels on and off. Importantly, we show that triplet suppression, which is necessary for free carrier formation and thus photovoltaic and photodiode performance, is controllable via sample morphology.

Exposure of an organic semiconductor to light above the absorption edge gives rise to various photoexcited species. There is an ongoing debate in the literature as to the nature of these photoexcitations and their relaxation dynamics. This includes details of exciton formation versus the generation of charged polarons or free charge carriers [11–13]. These processes are important in determining the behavior of many organic semiconductor-based devices such as

solar cells and photodiodes. Organic polymers, such as poly(*p*-phenylene-vinylene), have been extensively studied providing observations of polarons, interchain excitons (indirect excitons or bound polaron pairs), self-trapped excitons, triplet excitons, and charge transfer dynamics [14–18]. In contrast to organic polymers with long chains, organic molecular crystals consist of shorter molecular units and form well-defined crystal structures. The intermolecular interactions are weak, and the excitons are largely confined to single molecules resulting in large exciton binding energies [19]. Polyacene organic crystals such as Tc and Pc are model systems for studying the intrinsic properties of exciton dynamics. Tc and Pc molecules consist of, respectively, 4 and 5 benzene rings fused along their sides and arranged in a herringbone stacking arrangement with two molecules in each unit cell [2]. Tc has an orange color and luminesces strongly when illuminated due to prompt and delayed fluorescence [20], while

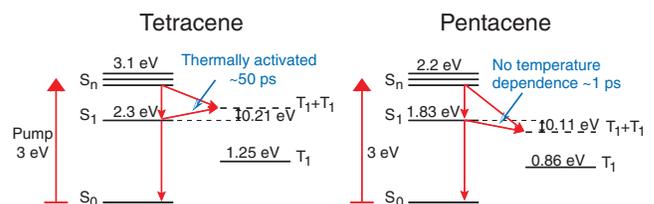


FIG. 1 (color online). Energy level diagram of Tc and Pc. Only the levels participating in the singlet-triplet fission processes following photoexcitation at 3.0 eV are shown. Here,  $S_N$  represents higher-lying states in the singlet manifold,  $S_1$  the lowest singlet exciton, and  $T_1$  the lowest triplet exciton.  $T_1 + T_1$  denotes two triplet excitons produced by fission. Important relaxation channels are denoted by arrows.

Pc is opaque and is nonluminescent [21]. In the polyacene series of organic crystals, the energy level of the lowest triplet exciton  $E(T_1)$  decreases faster than the lowest singlet-exciton energy  $E(S_1)$  with increasing molecular size. The energy difference  $E(S_1) - 2E(T_1)$  is  $-1.3$  eV in naphthalene (Nph),  $-0.55$  eV in anthracene (Ac),  $-0.21$  eV in Tc, and  $0.11$  eV in Pc [21]. In Pc, the excitonic fission process from the lowest singlet exciton to a pair of the lowest triplet excitons  $S_1 \rightarrow 2T_1$  is energetically allowed, while in Tc this same process is only possible by thermal activation. This process is strongly suppressed in Nph and Ac. An energy level diagram for Tc and Pc is presented in Fig. 1. Direct fission from higher-lying singlet states,  $S_N \rightarrow 2T_1$ , is another probable relaxation channel which competes with nonradiative relaxation to the lowest excited state,  $S_1$  [1]. Charge transfer processes, resulting in carrier generation, compete with both singlet and triplet exciton formation. In some device applications, such as solar cells and photodiodes it is beneficial to enhance carrier generation.

In addressing the importance of these processes we find singlet-triplet fission to be the dominant process in both Pc and Tc crystals with a prominent long-lived photoinduced absorption (PIA) peak originating from  $S_1 \rightarrow 2T_1$  and  $S_N \rightarrow 2T_1$  fission. In contrast to Pc, the triplet production in Tc is strongly temperature dependent in agreement with the thermally activated  $S_1 \rightarrow 2T_1$  fission process, where

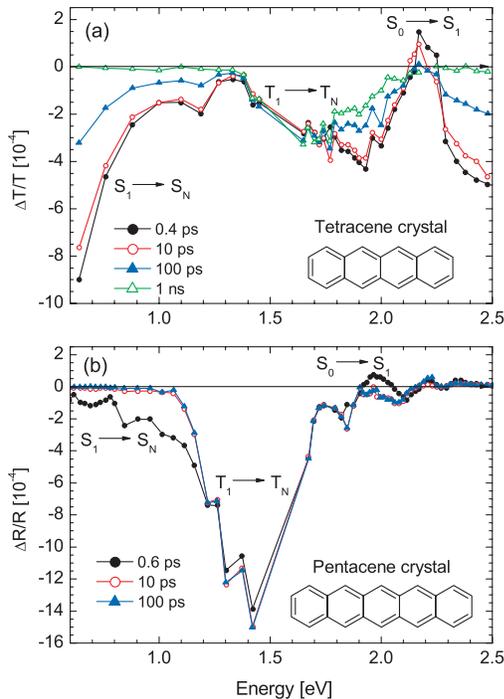


FIG. 2 (color). Transient spectra of Tc and Pc single crystals. The spectra are shown at different pump-probe delay times for photoexcitation at  $3.0$  eV at room temperature for (a) Tc crystal in transmission and (b) Pc crystal in reflection.  $S_0 \rightarrow S_1$  and  $S_N \rightarrow S_1$  ( $T_1 \rightarrow T_N$ ) refers to electronic transitions in the singlet (triplet) manifold. (See Fig. 1.)

fission competes with radiative fluorescence. In comparison to Pc crystals, we find that in Pc films the triplet production is quenched and the dynamics is largely dominated by charge transfer originating from defects (electron acceptors). This was further supported by measurements on  $C_{60}$ -doped Pc films, with  $C_{60}$  being a known electron acceptor [18].

High quality single crystals were grown in a flow of inert gas [22]. The Pc crystals used were typically  $3 \times 3$  mm<sup>2</sup> and approximately  $50$   $\mu\text{m}$  thick, while the Tc crystals were larger. The Pc films were evaporated onto  $10 \times 10$  mm<sup>2</sup> MgO substrates, with a film thickness of  $\sim 150$  nm, and  $\sim 0.03\%$  molecular  $C_{60}$  doping added to one film. In these optical experiments we utilized a commercial regeneratively amplified Ti : Al<sub>2</sub>O<sub>3</sub> laser system operating at  $250$  KHz producing nominally  $10$   $\mu\text{J}$ , sub- $50$  fs pulses at  $1.5$  eV. The samples were excited at  $3.0$  eV (high above the absorption band of  $\sim 1.9$  eV in Pc, and  $\sim 2.4$  eV in Tc), and changes in reflectivity  $\Delta R/R$  and transmissivity  $\Delta T/T$  were measured over the range of probe photon energies from  $0.6$ – $2.5$  eV using an optical parametric amplifier. We utilized an optical chopper operating at  $2$  kHz together with lock-in detection to measure relative changes with a sensitivity better than  $10^{-5}$ . In all samples the signal displayed linear dependence on excitation density in the range of fluences ( $F$ ) used (in Pc  $F = 10$ – $200$   $\mu\text{J}/\text{cm}^2$ , in Tc  $F = 5$ – $50$   $\mu\text{J}/\text{cm}^2$ ). The presented data was recorded at  $\sim 150$   $\mu\text{J}/\text{cm}^2$  (Pc) and  $\sim 30$   $\mu\text{J}/\text{cm}^2$  (Tc).

The transient PI spectra from Tc and Pc crystals are shown in Fig. 2 at different times after photoexcitation. The most prominent feature in both crystals is a long-lived ( $\gg 1$  ns) PIA peak centered at approximately  $\sim 1.7$  eV in Tc, and at  $\sim 1.4$  eV in Pc. The long relaxation time suggests that the state being probed is the triplet state  $T_1$  ( $T_1 \rightarrow T_N$ ), i.e., the PIA from the occupied  $T_1$  level to a higher-lying unoccupied excited state  $T_N$  [23]. Figure 3 shows the corresponding time-resolved dynamics for selected probe

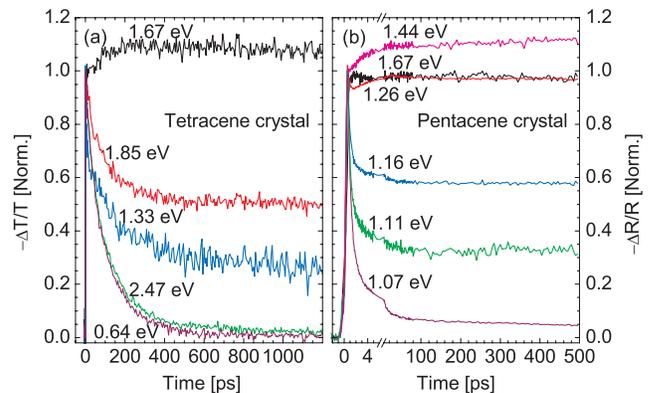


FIG. 3 (color). Time-resolved PI transmission (reflection) dynamics of Tc (Pc) single crystals at selected probe photon energies. The data are normalized to the value recorded after the initial sub-ps rise.

energies. In both crystals, the sub-ps rise is followed by an initial decay process after which a quasiequilibrium is reached with a decay much longer than 1 ns. This long-lived PIA is centered at  $\sim 1.7$  eV in Tc, and at  $\sim 1.4$  eV in Pc [24]. In Tc, the initial decay is exponential and occurs on a 50-ps time scale. The recovery of the PIA at low photon energies with a  $\sim 50$ -ps exponential decay [see the 0.64 eV data in Fig. 3(a)] can be associated with  $S_1 \rightarrow S_N$  transitions and indicates a large singlet-exciton population which recombines to the ground state. The data recorded at  $\sim 1.7$  eV reveal that some of the population is transferred to the triplet manifold on a sub-ps time scale (within the rise time). This is followed by a second process on a 50-ps time scale, attributed to activated singlet fission,  $S_1 \rightarrow 2T_1$ . The latter time scale reflects the decay of the  $S_1$  population. As Fig. 3(b) shows, in Pc the dynamics are quite similar except for the fact that the quasistationary state is established within a few ps. In Pc, the internal conversion from  $S_N$  to  $S_1$  is reflected by the 1.07 eV data with a  $\sim 0.50$ -ps exponential decay.

The correspondence of the long-lived PIA to triplet production in Tc (Pc) crystals is confirmed by probing the temperature dependence of the  $T_1 \rightarrow T_N$  transition with a probe energy of 1.67 eV (1.44 eV). Figure 4 shows the temperature dependence of the PIA signal at 200 ps after photoexcitation (when a quasistationary state has been reached) which is proportional to the population density of the  $T_1$  level. While there is no temperature dependence for Pc [which is expected, since  $E(S_1) > 2E(T_1)$  and  $E(S_N) > 2E(T_1)$ ], a pronounced temperature dependence is observed for Tc. There is a substantial PIA signal present at the lowest temperatures, indicative of a non-temperature-dependent triplet production process ( $S_N \rightarrow 2T_1$ ). At temperatures above 200 K, the second contribution to the PIA becomes important. It has a rise time of  $\sim 50$  ps (see inset to Fig. 4), attributed to the

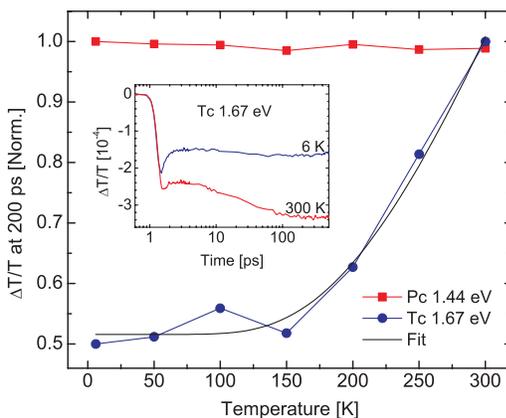


FIG. 4 (color online). Temperature dependence of the normalized PIA signal in Tc and Pc single crystals at 200 ps. The solid black line is a fit for Tc:  $\Delta T/T(T, 200 \text{ ps}) = 0.52 + 7.77 \times \exp[-\Delta E/k_B T]$ , where  $\Delta E \sim 70$  meV. The inset shows the time-resolved PIA changes in transmission for Tc probed at 1.67 eV at 6 and 300 K.

thermally activated fission process,  $S_1 \rightarrow 2T_1$ . The temperature dependence follows the thermal activation law,  $\Delta T/T(T, 200 \text{ ps}) = A + B \exp[-\Delta E/k_B T]$ . Here  $A$  and  $B$  are constants,  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $\Delta E$  is the activation energy. We find  $\Delta E \sim 70$  meV, in good agreement with previous experimental values of the activation energy in Tc, 22–237 meV [20].

The initial ultrafast dynamics observed on a sub-ps time scale involves both  $S_N \rightarrow 2T_1$  fission and  $S_N \rightarrow S_1$  internal conversion in the singlet manifold. In Tc, the time scale of the  $S_N \rightarrow 2T_1$  fission is  $\sim 0.3$  ps at 300 K (decreasing to  $\sim 0.25$  ps at 5 K), while in Pc, it is  $\sim 0.7$  ps and is temperature independent. Assuming an efficient triplet production in Pc crystals (neglecting charge generation [25]), an initial singlet-exciton concentration of  $2.2 \times 10^{17} \text{ cm}^{-3}$  (calculated from the excitation fluence) yields approximately  $4.4 \times 10^{17} \text{ cm}^{-3}$  triplets.

The transient PI spectra for Pc films, shown in Fig. 5, resemble a previously obtained spectrum published in Ref. [25], and the steady state absorption spectrum (not shown) is identical to the one given in Ref. [11]. In contrast to Pc crystals, the PI spectra for Pc films are dominated by sharp features at higher energies, while the long-lived PIA centered at  $\sim 1.4$  eV is substantially reduced. At room temperature we observe PI bleaching peaks at  $\sim 1.8$  eV and  $\sim 2.1$  eV, and a PIA peak at  $\sim 2.0$  eV. Their decay dynamics consists of two contributions; a fast exponential  $\sim 0.4$  ps decay followed by a sub-ns decay. The  $\sim 1.8$  eV and  $\sim 2.1$  eV peaks are assigned to  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_N$  transitions, respectively, while the PIA observed at  $\sim 2.0$  eV may be related to the formation of excimerlike excitons, as argued in Ref. [25]. At lower temperatures an additional PIA signal appears at  $\sim 1.9$  eV (see inset to Fig. 5), which overshadows the  $\sim 2.0$  eV peak observed at room temperature and persists well into the ns regime. This strongly temperature-dependent PIA observed at  $\sim 1.9$  eV is attributed to  $S_0^+ \rightarrow S_1^+$  transitions, and is re-

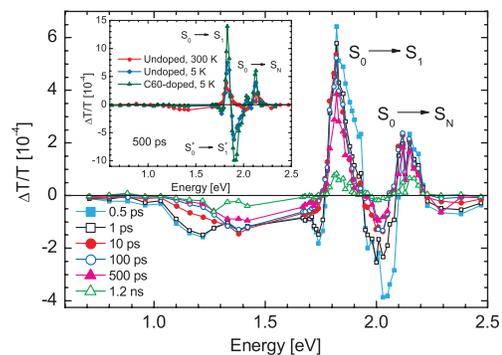


FIG. 5 (color). Transient spectra of Pc thin film.  $\Delta T/T$  is shown at different pump-probe delay times following photoexcitation of 3.0 eV at room temperature. The inset shows a comparison at 500 ps delay and 5 K of the undoped Pc film and a C<sub>60</sub>-doped Pc film.  $S_0^+ \rightarrow S_1^+$  refers to an ionized state at 1.9 eV due to electron transfer.

lated to charge transfer dynamics. ( $S_0^+ \rightarrow S_1^+$  refers to an ionized state, where an electron from the Pc molecule has been transferred to an electron trap.) Importantly, the same dynamics and spectral features are observed in the  $C_{60}$ -doped Pc film as shown in the inset to Fig. 5, except that the spectral features above  $\sim 1.7$  eV are enhanced by  $\sim 1.5$  times, while the PIA at  $\sim 1.4$  eV is further suppressed. Since  $C_{60}$  is a known electron acceptor this observation further lends support to the assignment of the  $\sim 1.9$  eV absorption peak to charge transfer due to electron traps intrinsic to Pc films.

The long-lived  $T_1 \rightarrow T_N$  transition at  $\sim 1.4$  eV, clearly prominent in the Pc crystal, is strongly suppressed in the Pc film, Fig. 5, where only a minor feature with sub-ns dynamics that vanishes at low temperatures is observed. Considering the identical dynamics, temperature dependence and enhancement of the spectral features in the  $C_{60}$ -doped Pc film as compared to the undoped Pc film, we attribute the quenching of the long-lived PIA at  $\sim 1.4$  eV (triplets) to ultrafast charge transfer dynamics related to electron traps, as seen in the Pc films.

In summary, we have shown that following optical excitation in Tc and Pc single crystals triplets are produced via fission, not only from the lowest singlet state,  $S_1 \rightarrow 2T_1$ , but also from higher-lying states,  $S_N \rightarrow 2T_1$ . In Pc, fission is a major relaxation channel, while in Tc there is strong radiative fluorescence from  $S_1$  which competes with  $S_1 \rightarrow 2T_1$  fission. At room temperature, half of the triplets in Tc are produced immediately from  $S_N$  within  $\sim 0.3$  ps while the other half are produced via thermally activated fission from  $S_1$  within  $\sim 50$  ps. This suggests that the internal conversion in Tc from  $S_N$  to  $S_1$  is comparable to  $\sim 0.3$  ps, which is the time scale for  $S_N \rightarrow 2T_1$  fission. Below  $\sim 200$  K the  $S_1 \rightarrow 2T_1$  fission is suppressed consistent with a thermally activated process. In Pc, the triplet production is temperature independent, and the majority of triplets are produced within  $\sim 0.7$  ps via  $S_N \rightarrow 2T_1$  fission, while  $S_1 \rightarrow 2T_1$  fission proceeds within a few ps following internal conversion.

Considering the rise time dynamics in Pc and Tc crystals we conclude that when the condition for fission, which conserves spin, is fulfilled,  $E(S_1) > 2E(T_1)$ , triplet production may occur on a sub-ps time scale. In thermally activated fission the time scale for triplet production increases considerably ( $> 100$  ps for Tc). In comparison, it is well known that for intersystem crossing (which does not conserve spin) the time scale may increase by orders of magnitude [1]. The ultrafast time scales demonstrated in Pc and Tc may enable fast organic optical switching devices based on triplet excitons.

Research and development of photoconversion-based devices such as OLEDs and OPVs has largely involved polymeric and polycrystalline materials in thin film morphologies and thus has not been concerned with the influence of defects. Here we have shown that defects can cause

triplet quenching and enhanced carrier generation. In particular, there is a large variation in triplet exciton dynamics between Pc crystals and films, suggesting that a route to enhanced triplet exciton lifetime is via the use of single crystals for hosting the photoconversion process. Thus, the present results provide motivation for further research aimed at incorporating crystalline material into the donor and acceptor regions of OPVs.

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