

## Charge-transfer excitons in strongly coupled organic semiconductors

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Time-resolved and temperature-dependent photoluminescence measurements on one-dimensional sexithiophene lattices reveal intrinsic branching of photoexcitations to two distinct species: self-trapped excitons and dark charge-transfer excitons (CTXs;  $\geq 5\%$  yield), with radii spanning 2–3 sites. The significant charge-transfer exciton (CTX) yield results from the strong charge-transfer character of the Frenkel exciton band due to the large free-exciton bandwidth ( $\sim 400$  meV) in these supramolecular nanostructures.

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The physics of organic semiconductor materials attracts enormous multidisciplinary interest due to emerging applications in optoelectronics. Their electronic properties depend sensitively upon supramolecular structure. A promising strategy to enhance carrier mobilities, for example, is to induce supramolecular order in configurationally disordered systems such as solution-processable conjugated polymers.<sup>1</sup> Prototypical examples of this approach are regioregular polythiophenes, which display field-effect mobilities up to  $0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in film microstructures showing lamellar interchain packing,<sup>2–4</sup> resulting in two-dimensional delocalization of charge carriers.<sup>5,6</sup> Cofacial interactions between polymer chains lead to H-aggregates with spatially correlated energetic disorder.<sup>7</sup> In the film microstructures that result in the best field-effect mobilities the supramolecular electronic (resonant Coulomb) coupling energies  $J$  are  $\sim 30$  meV,<sup>8,9</sup> which are weak compared to molecular reorganization energies ( $\sim 180$  meV). This is a result of long conjugation lengths in the lamellar architecture, such that local site interactions are weak.<sup>10</sup> As the chain length decreases below the conjugation length,  $J$  increases and may enter an “intermediate” regime.<sup>11–15</sup> Here, we address the nature of primary photoexcitations in this regime. We demonstrate, by means of time and temperature-dependent photoluminescence (PL) measurements on chiral, helical sexithiophene stacks<sup>16</sup> (labeled T6 for brevity), that excitation of the H-aggregate band with femtosecond laser pulses produces a high intrinsic yield ( $\geq 5\%$ ) of charge-transfer excitons (CTXs) in which the center of mass of electron and hole are localized at different sites of the stack. These are dark states, which recombine to populate luminescent states with a distribution of rate constants, and we determine that their radius is confined to 2–3 sites. The direct CTX yield is a consequence of the large exciton bandwidth, providing access to charge-transfer states.

T6 (99.9% purity<sup>16</sup>) solutions of  $10^{-4}$  M in anhydrous *n*-butanol were studied in a temperature-controlled UV-grade fused silica cuvette (1 mm pathlength). Films were produced by drop casting the solution on Spectrosil substrates. Absorption spectra were measured with a Varian Cary-500 spectrometer. Time-resolved PL measurements were performed with a femtosecond laser system (KMLabs Dragon, 780 nm, 40 fs FWHM, 1 kHz repetition rate, 1.4 mJ/pulse), which

was frequency doubled in a  $\beta$ -BBO crystal to generate 390-nm (3.19-eV) pulses, and a spectrograph with a gated, intensified CCD camera (Princeton Instruments SP-2156 and PIMAX 1024HB). Femtosecond absorption transients were measured with this ultrafast source, and probing with a white-light continuum generated in a  $\text{CaF}_2$  window.

Spontaneous supramolecular organization of T6 (Fig. 1) into chiral, columnar stacks is observed with thermotropic irreversibility<sup>17</sup> below a transition temperature of  $(313 \pm 12)$  K at the solution concentration used in this study. The supramolecular packing and the size distribution of these nanostructures, which grow by a nucleation self-assembly mechanism, depend sensitively on the material purity and on the solution cooling protocol.<sup>16</sup> In all of the studies reported here, the sample was cooled at a rate of  $\sim 1 \text{ K min}^{-1}$ , but the PL spectral band shape and the time-resolved PL dynamics do not depend sensitively on the cooling protocol. Figure 1(a) displays the solution absorption spectrum in the supramolecular phase (283 K). We have previously extracted a free-exciton bandwidth  $W=4J$

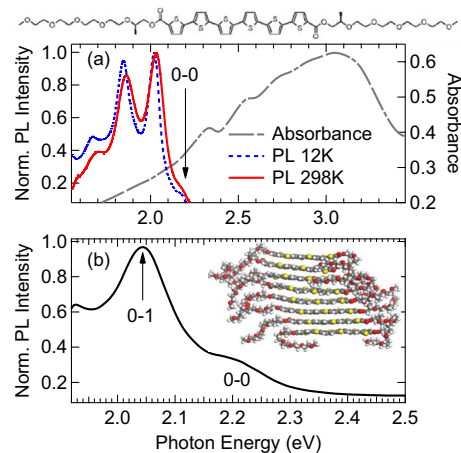


FIG. 1. (Color online) Molecular structure of T6. (a) Absorption spectrum of T6 nanostructures in *n*-butanol solution at 283 K, and steady-state PL spectra of a drop-cast film at 12 and 298 K. (b) Delayed PL spectrum from  $6.5 \mu\text{s}$  after excitation and a gate width of  $500 \mu\text{s}$  in *n*-butanol solution. The inset depicts the chiral, cofacial T6 stacks.

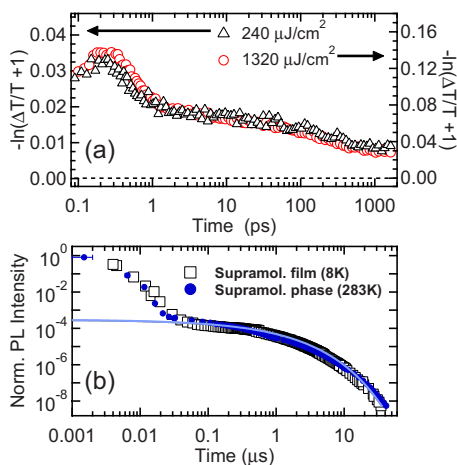


FIG. 2. (Color online) (a) Femtosecond absorption transients probing at 1.42 eV with two pump fluences indicated in the caption. (b) Time-resolved PL intensity for T6 in the supramolecular phase (blue filled circles) in solution, and in a drop-cast film of the stacks at 8 K (black open squares). The curves through the delayed PL decay are stretched-exponential fits with  $\beta=0.5$  and  $\tau=300 \pm 50$  ns for the solution at 283 K and for the film.

$\approx 400$  meV by analyzing this spectrum,<sup>13</sup> which places these nanostructures firmly in the ‘intermediate’ electronic coupling regime.<sup>10</sup> Also shown are the corresponding steady-state PL spectra of a drop-cast film at room and low temperatures. These display a similar spectral band shape as in cold solution,<sup>13</sup> indicating that we preserve the supramolecular structure upon casting the film. The origin (0–0) vibronic band is weak due to the H-aggregate nature of the architecture,<sup>18</sup> and is only visible due to energetic disorder.<sup>19</sup> Its weak temperature dependence is consistent with the large  $W$  deduced from the absorption spectrum; even at room temperature, thermal excitation is not sufficient to partially allow this vibronic feature. This is unlike the case in polythiophene films, which feature much smaller  $W$ , and are in a weak excitonic coupling regime.<sup>8,9</sup> Quantum chemical calculations of related supramolecular nanostructures indicate that the PL spectrum is due to vibrationally dressed Frenkel excitons with a highly localized center of mass due to a disorder width of several hundred meV and low spatial correlation.<sup>18–20</sup> Figure 1(b) shows the delayed PL spectrum over  $\mu$ s time scales, which is identical to the steady-state spectra in part (a), and displays linear integrated intensity below excitation fluences of  $\sim 800 \mu\text{J cm}^{-2}$ .<sup>21</sup>

We now consider photoexcitation dynamics in T6 lattices by comparing the  $1B_u$  femtosecond transient absorption [Fig. 2(a)] and time-dependent PL measurements over microsecond time windows [Fig. 2(b)]. All decay behavior is independent of fluence [as demonstrated in part (a)]. Following a rapid initial relaxation ( $< 1$  ps) the exciton decay is biphasic over a microsecond time window. We observe an exponential decay with  $\sim 1$  ns time constant, characteristic of exciton lifetimes in conjugated oligomer nanostructures.<sup>13,22</sup> We observe a concomitant delayed PL signal (filled circles) which is spectrally identical to the steady-state PL (Fig. 1); the delayed PL is therefore excitonic. The spectrally integrated, delayed PL intensity is linear over the pump fluence range

investigated,<sup>21</sup> and the decay kinetics are independent of temperature (see below), ruling out bimolecular recombination events such as triplet-triplet annihilation as the origin of this delayed PL. We therefore attribute it to recombination of CTXs, analogous to geminate polaron pairs in conjugated polymer films.<sup>24</sup>

The functional form of the delayed PL decay is stretched exponential,  $(I_0 \exp[-(t/\tau)^\beta])$ , with  $\beta=0.5$  and  $\tau=300 \pm 50$  ns. Figure 2(b) displays this function.

In order to explore the origin of the nonexponential decay of the delayed PL, we present related measurements in a drop-cast film of supramolecular stacks at 8 K [open squares in Fig. 2(b)]; in which the PL spectra are consistent with those in Fig. 1. The delayed PL decay follows a stretched exponential with similar parameters as the supramolecular phase in solution, ruling out a time-dependent rate constant due to endothermic activation. We therefore ascribe the nonexponential PL decay simply to a distribution of rate constants  $\gamma$ .

The relative contribution of the delayed PL to the time-integrated PL intensity provides a lower limit to the CTX photogeneration yield,  $\eta$ . We extract  $\eta=4.8 \pm 1.0\%$  in the supramolecular phase in solution. In contrast, we measure  $\eta=0.25 \pm 0.15\%$  at 350 K, well above the transition temperature for disassembly. In the stack,  $\eta$  does not depend strongly upon temperature down to 8 K, where we find  $3.9 \pm 1.0\%$ , indicating that CTXs are produced directly by photoexcitation. We propose the following photophysical picture. Initial photoexcitation of the Frenkel free-exciton band branches into highly localized (self-trapped) excitons,<sup>18</sup> displaying prompt exponential dynamics, in which the electron and hole centers of mass are delocalized over essentially one oligomer lattice site. Concomitantly, CTXs are produced directly with  $\geq 5\%$  efficiency. The branching occurs due to resonance between Frenkel excitons and CT states, which normally lie 0.2–0.3 eV above localized Frenkel exciton states,<sup>23</sup> because the exciton bandwidth in these strongly coupled stacks is large enough to encompass the CT states.<sup>25</sup> CTXs then recombine with a distribution of rate constants resulting in the nonexponential delayed PL decay.

We have performed quantum-chemical calculations on a stack of 8 T6 molecules. These extend previous force-field molecular-dynamics (MD) simulations.<sup>17</sup> Fig. 3(a) displays the ensemble absorption spectrum obtained by averaging 20 snapshots extracted along the MD trajectory (solid line), and that in a single snapshot (dotted line), simulated at the INDO/SCI level.<sup>26</sup> We calculate the CT radius (for which the spatial extent of the wave function spans more than one oligomer; see Ref. 25) as a function of the vertical excitation energy [Fig. 3(b) for one stack snapshot]. We also plot the fractional CT character versus excitation energy in Fig. 3(c). We note that the CT character and the corresponding radius increase with energy, and that it dominates above  $\sim 3$  eV.

A PL decay function characterized by a distribution of decay constants  $P(\gamma)$  is its Laplace transform,

$$I(t) = I_0 \int_0^\infty P(\gamma) \exp(-\gamma t) d\gamma, \quad (1)$$

where  $\int_0^\infty P(\gamma) d\gamma = 1$ . For a stretched-exponential decay with  $\beta=0.5$ , the probability distribution is

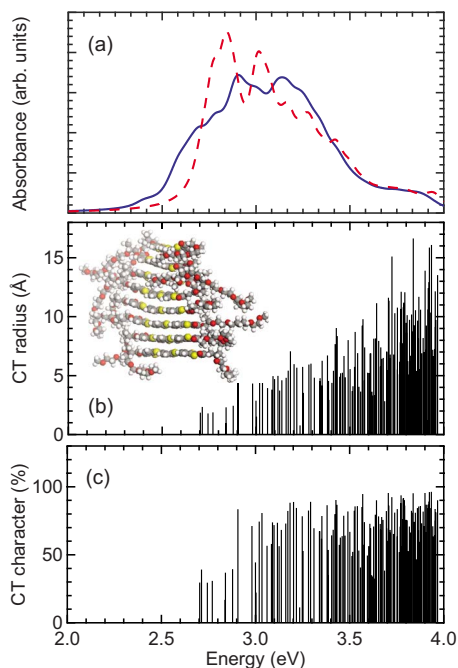


FIG. 3. (Color online) (a) Ensemble (solid line) and single-stack (dashed line) absorption spectra of a stack of 8 T6 simulated at the INDO/SCI level (Ref. 17). Lorentzian functions with linewidth 0.05 eV have been used to convolute the spectra. The ensemble spectra are obtained by averaging over 20 snapshots extracted along the MD trajectory. (b) Charge-transfer radius versus vertical excitation energy for one snapshot (see inset), and (c) its fractional charge-transfer character.

$$P(\gamma) = \frac{\exp[-(4\gamma\tau)^{-1}]}{\sqrt{4\pi\gamma^3\tau}} \quad (2)$$

and is shown in Fig. 4(a) with  $\tau=300$  ns. This distribution is centered at  $\gamma_{\text{peak}}=(0.55 \pm 0.1) \mu\text{s}^{-1}$ .

We postulate that  $P(\gamma)$  arises from a distribution of CTX radii  $P(r)$ . Figure 4(b) displays a histogram of  $P(r)$  based on the quantum-chemical calculations described above, and Fig. 4(c) plots the exciton participation ratio. This quantity displays the distribution of the population in which the electron and hole center of mass are separated by a specific number of lattice sites, determined from the calculations presented in Fig. 3, and expresses the extent of exciton delocalization.  $P(\gamma)$  is temperature independent; therefore, recombination must occur via a tunneling mechanism. The electron-hole electronic coupling matrix element decreases exponentially with distance due to the exponential radial character of the electronic wave functions. If  $\gamma$  follows a golden rule, then  $\gamma(r) = \nu \exp(-ar)$ . We hence plot  $P(r)$  in Fig. 4(b) for various values of  $\gamma_0$  and  $\alpha$ , and find the best agreement with the quantum-chemical calculations for  $\gamma_0=40.5 \mu\text{s}^{-1}$  and  $\alpha=0.9 \text{ \AA}^{-1}$ . We note that  $\gamma_{\text{peak}}$  is comparable to rates measured in donor-bridge-acceptor triads<sup>27</sup> but is surprisingly low for a cofacial  $\pi$  stack. We speculate that the polar environment surrounding the  $\pi$  stack defined by the oligoethyl-eneoxide end groups plays a role by stabilizing the CTX. Such environment may also play a role in establishing  $\eta$ .

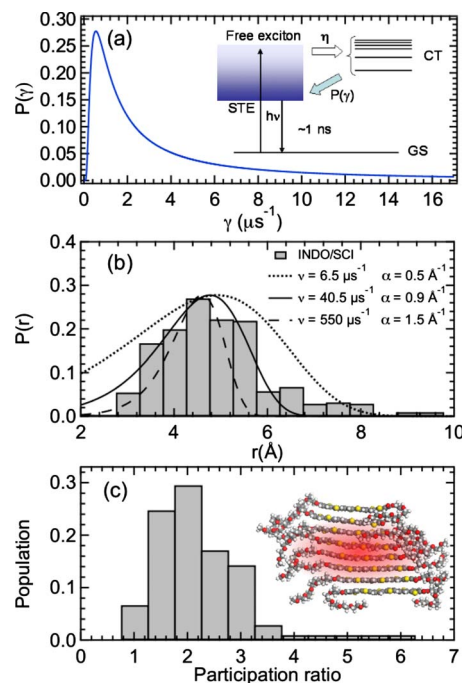


FIG. 4. (Color online) (a) Distribution of recombination rate constants given by Eq. (2). The inset depicts the photophysical model put forth here. Vertical excitation of the free-exciton band is followed by branching to self-trapped (Frenkel) excitons (STE, 95%) and charge transfer (CTX, 5%). The latter recombine to the former state with  $P(\gamma)$ . (b) INDO/SCI histogram of charge-transfer radii built on the basis of an ensemble of 20 structures extracted from MD simulations. All excited states with dominant ( $>50\%$ ) CT character that are located below 3.3 eV have been included. The curves show fits to the exponential distance dependence of the rate constant. (c) Participation ratio (measure of excited-state delocalization) for the ensemble of 20 snapshots (b). The inset depicts the spatial extent of exciton.

The high value of  $\eta$  is in contrast to that in configurationally disordered conjugated polymer films, where  $\eta \ll 1\%$ .<sup>28</sup> The magnitude of  $J$  is important in this respect. In such cofacial aggregates with strong excitonic coupling, intermolecular interactions enable quasiparticle energy dispersion supporting CT states. In T6 stacks a large free-exciton bandwidth  $W$  renders an intermolecular CT state accessible. As  $W$  decreases with increasing  $\pi$ -conjugation length,<sup>13</sup> the influence of CT states decreases along with  $\eta$ . Nevertheless, weakly allowed CTX states are important in a complete theoretical description of photoinduced absorption spectra of conjugated polymers in the solid state.<sup>23,29</sup>

We have demonstrated that in organic semiconductors, the supramolecular coupling energy dominates the nature of the primary photoexcitations. The large free-exciton bandwidth is significantly larger than attainable in the most highly organized semiconductor polymer microstructures,<sup>8</sup> but the primary photoexcitations are highly localized. The Frenkel exciton band mixes with charge-transfer states, which play an important role in the primary photophysics. This work is consistent with independent experimental evidence for discrete, localized CTX states at the surface of pentacene crystalline films, probed by means of time-resolved two-photon

photoemission spectroscopy by exciting well in the lowest unoccupied molecular orbital band.<sup>30</sup> We consider that these conclusions are of general importance for a detailed description of the electronic structure of organic semiconductors.

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