Reduced Charge Transfer Exciton Recombination in Organic Semiconductor Heterojunctions by Molecular Doping

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We investigate the effect of molecular doping on the recombination of electrons and holes localized at conjugated-polymer–fullerene interfaces. We demonstrate that a low concentration of p-type dopant molecules ($<4\%$ weight) reduces the interfacial recombination via charge transfer excitons and results in a favored formation of separated carriers. This is observed by the ultrafast quenching of photoluminescence from charge transfer excitons and the increase in photoinduced polaron density by $\sim 70\%$. The results are consistent with a reduced formation of emissive charge transfer excitons, induced by state filling of tail states.

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The doping of conjugated polymers has been extensively explored in order to modify the electrical characteristics of these solution processable semiconductors [1–4]. Different amounts of chemical doping have resulted in increased charge carrier densities, reaching levels sufficient for metallic conductivity [5]. Similarly interesting, but less investigated, is the influence of doping on optical excitations [6], as these play a crucial role in the functioning of devices such as solar cells and light-emitting diodes [7]. In pristine polymers several investigations have clarified that strongly bound Frenkel excitons, with binding energies of ~ 0.5 eV [8], are the primary photoexcitations in this class of materials [9,10]. As a consequence, effective charge separation preferentially occurs at type II heterojunctions with a favorable energy offset for exciton dissociation [11]. In general, the process leading to fully separated electrons and holes is thought to be influenced by an intermediate state, where carriers are localized on two adjacent molecules [12–14]. There, localized electron-hole pairs are still bound by a weakened Coulomb interaction of ~ 0.2 eV [15]. Such states have been termed charge transfer (CT) excitons [13,16] or exciplexes [17–19] and have recently aroused considerable experimental and theoretical interest [20–23]. It remains a fundamental question whether emissive CT excitons are necessarily populated for each charge separation event, or if their appearance is entangled with the electronic characteristics of the materials constituting the heterojunction and the density of states (DOS) experienced by the photoexcitations. In other words, can recombination via CT excitons be reduced in favor of charge separation by influencing the electronic properties of the materials? Doping is known to influence the electrical characteristics, because of the increased ground-state carrier density and filling of localized states [24].

In this Letter, we show how exciton dissociation and carrier separation in a blend between a conjugated polymer and a fullerene derivative can be influenced by adding small amounts of dopant molecules to the polymer. The p-type dopant increases the density of holes in the ground state of the system and is expected to fill the DOS of the polymer in the low energy tail. We used time-resolved photoluminescence (PL) spectroscopy to reveal a lower initial population of emissive CT excitons as a function of increasing dopant concentration. In addition, a comparison of PL experiments with infrared (IR) photoinduced absorption (PA) transients probing the generation of separated carriers (polarons) demonstrates that the dopant-induced increase in the density of holes promotes the ultrafast generation of polarons. The experiments, based on the unique combination of PL and PA spectroscopy, are modeled by a system of rate equations, which shows how doping reduces the probability for populating CT excitons and promotes dissociation into polarons.

We have focused our experiments on blends between [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) and the polymer PCPDTBT (see Ref. [25] for the chemical name). The sketches of the fullerene derivative and the polymer unit are displayed in the insets in Figs. 1(a) and 1(b), respectively. To achieve effective doping of PCPDTBT, we used the molecule 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) [inset in Fig. 1(d)], which was added to the polymer solution before mixing with PCBM. F4-TCNQ is known to be one of the most effective dopants for conjugated polymers, resulting in p-type doping [26]. The solutions of the polymer mixed with the dopant were added to PCBM to obtain 1:1 (polymer:fullerene) weight ratio blends and spin-coated

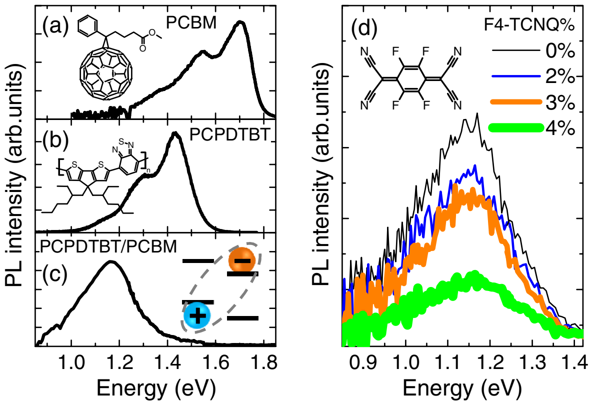

FIG. 1 (color online). (a)–(c) Photoluminescence spectra of PCBM, PCPDTBT, and PCPDTBT/PCBM (1:1 weight ratio) blend, respectively. The insets show the chemical structure of PCBM and PCPDTBT. (d) CT PL spectra as a function of F4-TCNQ concentration in PCPDTBT/PCBM blends. The inset shows the chemical structure of F4-TCNQ. Excitation was performed at 3.1 eV. Note that the spectra and all other experiments were corrected by considering the differences in the number of absorbed photons.

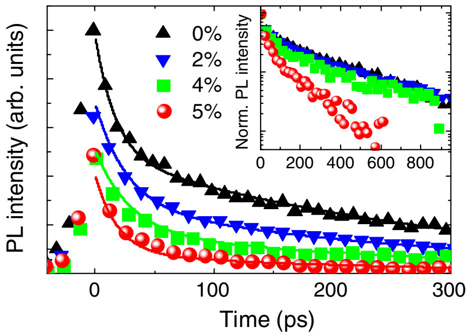

FIG. 2 (color online). Transient decays of photoluminescence recorded at 1.17 eV for PCPDTBT/PCBM blends with different concentrations of F4-TCNQ (excitation: 3.1 eV). The inset shows the normalized decays plotted on a longer time scale. Solid lines are fits according to the model presented in the text.

on quartz in an N_2 atmosphere. The PCPDTBT/PCBM ratio was kept constant for all samples, whereas different weight percentages of F4-TCNQ with respect to the polymer were explored. The samples showed similar morphologies independently of dopant concentration [27]. Time-resolved PL was performed with a streak camera. Transient PA experiments were conducted with 100 fs pump and probe pulses generated with a Ti:sapphire laser after optical parametric amplification [28,29]. For PA, overlap of optical beams and beam-walking effects were carefully adjusted by using markers and a beam-profiler camera. Excitation intensities were kept below 5 $\mu J/cm^2$, thus minimizing exciton annihilation effects [9]. Samples were measured in vacuum (10^{-6} mbar) at $T = 295$ K.

Figure 1 shows the PL spectra of PCBM (a), PCPDTBT (b), and a blend of these two materials in a 1:1 weight ratio (c). While the thin films of the pure materials show the typical PL features ascribed to the excitonic transitions [25], the blend film is characterized by a broad unstructured emission peaking at 1.17 eV. Residual PL from the Frenkel excitons in PCBM and PCPDTBT, expected to appear above 1.4 eV, is not discernible in the blend. In agreement with prior studies on the PL of such a blend, the emission centered at 1.17 eV is due to a CT exciton, a bound electron-hole pair at the interface [25]. Such excitation considers the hole localized on the highest occupied molecular orbital of the polymer and the electron on the lowest unoccupied molecular orbital of the fullerene [inset in Fig. 1(c)]. Figure 1(d) shows how the PL intensity of the CT transition is quenched in the presence of an increasing amount of F4-TCNQ dopant. The data demonstrate a monotonic quenching of the CT PL as a function of dopant concentration. While the observation of CT emission quenching is interesting, it is not clear from the steady-state experiments alone which doping-related mechanism is influencing the recombination characteristics of CT excitons.

To gain insights on the quenching process as a function of doping, we show in Fig. 2 the dynamics of the CT emission at 1.17 eV. For the 0% sample (black triangles) an initial fast decay is followed by a longer-living component, giving rise to a biexponential decay with $\tau_1 = 20$ ps and $\tau_2 \approx 300$ ps. As shown in the inset, the normalized decays, plotted on a log-linear scale, do not differ in the PL lifetimes up to the 4% sample (green squares). The dynamics start to exhibit a clearly faster decay only at larger dopant concentrations (5%: $\tau_2 = 150$ ps). Significant differences among all samples can be instead noticed in the initial amplitude of the signal at time zero $I_{PL}(t = 0)$, as can be observed in the figure main frame. The steady state [Fig. 1(d)] and time-resolved PL data of Fig. 2 can be discussed considering two hypotheses: (i) The increased carrier density induced by the dopant in the polymer domains influences the rate of recombination, changing the nonradiative rate of the CT exciton luminescence, or (ii) the carrier density has an influence on the charge separation channel, by lowering the probability for population of the bound-emitting CT exciton and resulting in separated electrons and holes (polarons), already on a time scale comparable to the resolution of the PL transients, ~20 ps.

Since (i) would require a change in the lifetime of PL, observed only above 4%, we have explored (ii) by monitoring the fast formation of polarons by femtosecond PA spectroscopy [30]. In such an experiment, electron-hole pairs are photogenerated by a short laser pulse (pump) and the formation of polarons can be monitored by a second pulse (probe) delayed in time and with a suitable photon energy, resonant with polaron absorption. The polaronic nature of carriers in organic semiconductors gives rise to optical transitions in the IR region of the spectrum [31]. For PCPDTBT/PCBM blends, two prominent polaron transitions are located at 0.4 and 0.9 eV as detailed in Ref. [32]. Here, we have opted to probe the polaron absorption at 0.4 eV, thus avoiding the overlap with excitonic features in the near-IR, which may not provide the genuine signal of polarons [32]. Figures 3(b)–3(e) show the PA transients probing photoinduced polarons for the doped and undoped films. The signal amplitude, expressed as differential transmission in the probe $\Delta T/T$, is proportional to the photogenerated polaron density [27]. The data clearly exhibit a difference in the time zero amplitudes: $\Delta T/T(t = 0)$. Remarkably, the 2% and 4% doped blends shown in Figs. 3(c) and 3(d) have larger signal amplitudes with respect to the 0% by a factor of 1.4 and 1.7, respectively. This observation indicates that, within our time resolution ($\sim$ 150 fs), there is a larger density of polarons upon photoexcitation of blends which were doped with 2% and 4% F4-TCNQ. For higher concentrations (5%), the amplitude is below the one for the undoped sample [Fig. 3(e)]. On a long time scale (not shown) the dynamics reveal that the 2% and undoped films are similar with a quasimonoexponential time decay of >1 ns. We conclude that up to 2% doping a larger population of charge carriers is photogenerated, with only small differences on the recombination dynamics. Fast (<1 ns) recombination processes are instead appearing at 4% and dominate at 5%.

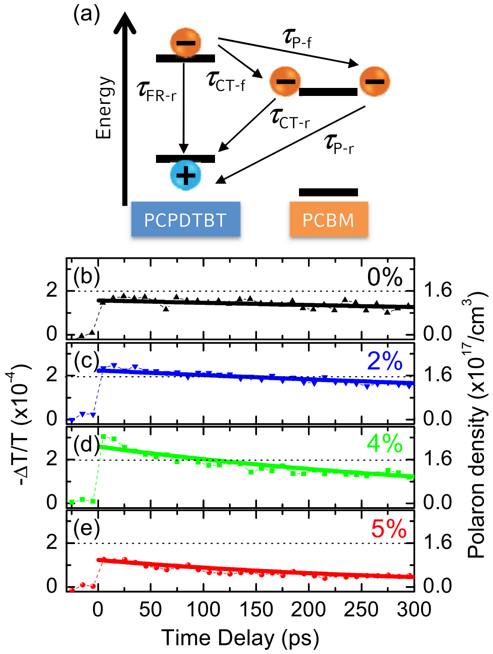

FIG. 3 (color online). (a) Energy scheme for the highest occupied molecular orbital and lowest unoccupied molecular orbital levels of PCPDTBT and PCBM together with the most significant transitions. (b)–(e) PA transients of PCPDTBT/PCBM blends with different concentrations of F4-TCNQ (0%–5%, respectively). Pump (3.1 eV) and probe (0.4 eV) beams had a cross correlation of ~150 fs. Solid lines are fits according to the model presented in the text.

Comparing the PL and PA of samples with the same doping concentration, we note that the two experiments reveal distinct decay dynamics. This is a strong indication that recombination of charges populating the CT exciton and separated polaronic states follows two distinct mechanisms apparently not interrelated. The experiments described in Fig. 2 and 3 suggest that the introduction of a higher hole density by doping is influencing the fate of photoexcitations at early times during the formation of emissive CT excitons. Consistent with this picture is the decrease in the PL ($t = 0$) and the larger PA $\Delta T/T$ ($t = 0$). These observations exclude that the CT emission intensity is quenched because of a nonradiative recombination channel, at least up to 4% doping, and point to the fact that doping can determine whether the initial photoexcitations will form an emissive CT exciton or will result quasi-instantaneously in separated polarons.

To discuss our observations in a more quantitative manner, we modeled the PL and PA transients with a system of coupled rate equations [27]. The model, based on the scheme of Fig. 3(a), considers that Frenkel excitons can form CT excitons or polarons with two different probabilities given by the time constants $\tau_{\text{CT-}f}$ and $\tau_{P\text{-}f}$. Frenkel and CT excitons can recombine giving rise to the first and second components in the PL decays, while PCPDTBT polarons are detected in the PA experiment. A model considering the generation of polarons only from dissociation of CT excitons was not capable of fitting our experimental results. Since for PCPDTBT/PCBM the photoinduced electron transfer is expected to occur on a time scale of 200 fs [33], we have considered this as a value for $\tau_{P\text{-}f}$ and $\tau_{\text{CT-}f}$ in the undoped sample. The recombination time of CT excitons ($\tau_{\text{CT-}r}$) was fixed at 300 ps for all the samples up to 4% doping as well as the recombination time of Frenkel excitons in PCPDTBT (125 ps). Only for the 5% sample were the recombination times varied to obtain the best fitting to the curves [27]. The simulated transients, reported as solid lines in Figs. 2 and 3, are in good agreement with the experiments. Differences in the signal amplitudes of PL and PA, which are the most important observations of our study, can be quantitatively described simply by variations in the initial probability of CT exciton formation, which at 2% is $1/500\ \text{fs}^{-1}$ and decreasing to $1/950\ \text{fs}^{-1}$ at 4%–5%. Variations in $\tau_{P\text{-}f}$ were not considered, since for doped PCPDTBT films we did not observe a larger photoinduced polaron density. The PA decays for the 4% and 5% samples were modeled by shortening the recombination lifetimes of Frenkel excitons and polarons, which confirms that additional processes such as exciton-polaron quenching or Auger recombination are opening up. Based on the mechanism proposed in this model, we can make the hypothesis that photoexcitations in the presence

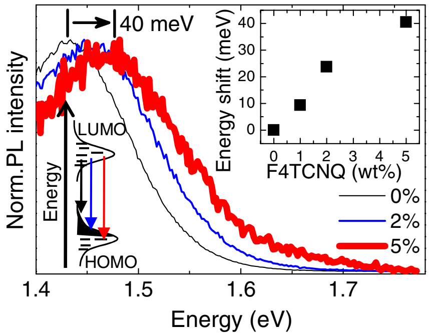

FIG. 4 (color online). Photoluminescence spectra of PCPDTBT with different concentrations of F4-TCNQ. The top inset shows the relative shift in the PL peak position as a function of F4-TCNQ concentration expressed in weight% with respect to the polymer.

of doped polymer chains are less prone to form CT excitons. This leads to a more favorable formation of polarons up to 4% doping.

Considering the DOS of conjugated polymers, which is broadened by disorder, doping is known to fill the states at low energy in the tail [24]. When considering heterojunctions, these states are likely responsible for being sites where CT excitons are formed, localize, and recombine. This assumption is supported by the fact that CT excitons are known to be rather immobile excitations [17]. A possible interpretation is that doped polymer domains do not support the formation of CT excitons having their low energy chromophores occupied (blocked). This results in a more favorable formation of polarons. To confirm that the charge carriers fill the states of PCPDTBT, we looked at the high energy side of the PL spectrum, since holes constituting Frenkel excitons should have the lowest energy part of the DOS blocked (inset in Fig. 4). Because of the undetectable PL from PCPDTBT in blends, we show in Fig. 4 the spectra of PCPDTBT films doped by different amounts of F4-TCNQ without PCBM. The PL peak position representing the recombination of Frenkel excitons is clearly shifted toward higher energies with doping by 24 and 40 meV for the 2% and 5% doped samples, respectively (inset in Fig. 4). Because of the disordered nature of conjugated polymers, doping may act in an inhomogeneous way and leave some domains unaffected. Those are likely to exhibit a residual CT exciton emission.

In conclusion, using a dopant we have influenced the carrier separation in blends of PCPDTBT and PCBM. Doped blends can show larger densities of photogenerated polarons and a lower population of CT excitons. This work shows that doping-induced state filling offers a new interesting avenue to improve charge separation in organic photovoltaics.

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[1] B. A. Bolto, R. McNeill, and D. E. Weiss, Aust. J. Chem. **16**, 1090 (1963).
[2] H. Shirakawa *et al.*, J. Chem. Soc. **1977**, 578 (1977).
[3] P. Piromreun *et al.*, Appl. Phys. Lett. **77**, 2403 (2000).
[4] M. Gross *et al.*, Nature (London) **405**, 661 (2000).
[5] K. Lee *et al.*, Nature (London) **441**, 65 (2006).
[6] A. O. Patil, A. J. Heeger, and F. Wudl, Chem. Rev. **88**, 183 (1988).
[7] G. G. Malliaras and R. H. Friend, Phys. Today **58**, No. 5, 53 (2005).
[8] S. Barth and H. Bässler, Phys. Rev. Lett. **79**, 4445 (1997).
[9] V. Gulbinas *et al.*, Phys. Rev. Lett. **89**, 107401 (2002).
[10] E. Hendry *et al.*, Phys. Rev. Lett. **92**, 196601 (2004).
[11] S. Morita, A. A. Zakhidov, and K. Yoshino, Solid State Commun. **82**, 249 (1992).
[12] T. Drori *et al.*, Phys. Rev. Lett. **101**, 037401 (2008).
[13] T. Drori, J. Holt, and Z. V. Vardeny, Phys. Rev. B **82**, 075207 (2010).
[14] R. Kersting *et al.*, Phys. Rev. Lett. **73**, 1440 (1994).
[15] M. Hallermann, S. Haneder, and E. Da Como, Appl. Phys. Lett. **93**, 053307 (2008).
[16] M. Muntwiler *et al.*, Phys. Rev. Lett. **101**, 196403 (2008).
[17] Y. S. Huang *et al.*, Nature Mater. **7**, 483 (2008).
[18] A. C. Morteani *et al.*, Phys. Rev. Lett. **92**, 247402 (2004).
[19] K. Aryanpour, D. Psiachos, and S. Mazumdar, Phys. Rev. B **81**, 085407 (2010).
[20] C. Deibel, T. Strobel, and V. Dyakonov, Phys. Rev. Lett. **103**, 036402 (2009).
[21] R. A. Street and M. Schoendorf, Phys. Rev. B **81**, 205307 (2010).
[22] M. Hallermann *et al.*, Appl. Phys. Lett. **97**, 023301 (2010).
[23] T. Kirchartz *et al.*, Phys. Rev. B **80**, 035334 (2009).
[24] Y. Zhang, B. de Boer, and P. W. M. Blom, Phys. Rev. B **81**, 085201 (2010).
[25] M. Morana *et al.*, Adv. Funct. Mater. **20**, 1180 (2010).
[26] Y. Zhang, B. de Boer, and P. W. M. Blom, Adv. Funct. Mater. **19**, 1901 (2009).
[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.107.127402 for data on the morphology, absorption spectra, and rate equations model.
[28] G. Cerullo and S. De Silvestri, Rev. Sci. Instrum. **74**, 1 (2003).
[29] D. Herrmann *et al.*, Opt. Express **18**, 18 752 (2010).
[30] C. X. Sheng *et al.*, Phys. Rev. B **75**, 085206 (2007).
[31] R. Österbacka *et al.*, Science **287**, 839 (2000).
[32] D. Di Nuzzo *et al.*, Adv. Mater. **22**, 4321 (2010).
[33] I. W. Hwang *et al.*, Adv. Mater. **19**, 2307 (2007).