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Time-resolved measurements of photoinduced electron transfer from polyfluorene to C_{60}

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The excited state dynamics of polyfluorene and the dynamics of the photoinduced electron transfer from polyfluorene to a C_{60} derivative have been studied with time-resolved pump-probe measurements at low excitation density. Using the stimulated emission and photoinduced absorption spectra, the decay of the neutral excited state and the growth of the ionic excited state have been time resolved; the photoinduced charge transfer reaction occurs with a characteristic time constant of approximately 3 ps.

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I. INTRODUCTION

Advances in ultrafast spectroscopic techniques[1,2] have enabled the study of photoinduced processes in semiconducting (π-conjugated) polymers in real time.[3] Ultrafast studies, using laser pulses with wavelengths in the spectral range from the ultraviolet-visible to the midinfrared, have contributed to the understanding of the underlying photophysics of this class of electronic polymers.[3–7]

Ultrafast photoinduced electron transfer from poly(phenylene vinylene) (PPV) and its soluble derivatives to C_{60} and its derivatives has been reported.[8,9] The ultrafast charge transfer and the associated high quantum efficiency for charge separation provide a pathway for the development of high efficiency photodetectors and photovoltaic cells fabricated from π-conjugated polymers.[10] Moreover, since C_{60} and its derivatives stabilize the charge separation by photoinduced electron transfer, the study of such polymer/C_{60} mixtures creates an opportunity to probe the nature of the photoexcitations in semiconducting polymers.

In this work, the excited state dynamics of polyfluorene (PFO) and the dynamics of the photoinduced electron transfer from PFO to a C_{60} derivative have been studied with time-resolved pump-probe experiments carried out under low excitation intensity. As high efficiency blue-emitting materials, the polyfluorenes are promising for use in full-color displays.[11] Moreover, copolymers of PFO are the only family of conjugated polymers that emit colors spanning the entire visible spectrum.[11]

We report here ultrafast measurements of the photoinduced transient absorption spectra of a blend of polyfluorene with a C_{60} derivative. Both the decay of the neutral excited state and the growth of the ionic, charge-separated state have been time resolved. The photoinduced charge transfer reaction occurs with a time constant of approximately 3 ps.

II. DETAILS OF THE EXPERIMENT

The ultrafast pump-probe experiments were performed using a Spectral-Physics amplified Ti:sapphire system to produce 150 fs (full-width at half-maximum) pulses with a center wavelength of 800 nm at a repetition rate of 1 kHz. The 800-nm beam was split into two parts. The stronger beam was frequency-doubled through a nonlinear (BBO) crystal to generate the 400-nm pump beam. The weaker beam was focused onto a 1-mm sapphire plate to generate the white light continuum which was also split, with one beam serving as the probe beam and the other serving as the reference beam. The probe was delayed with respect to the pump by a computer-controlled translation stage. The 400-nm pump was focused onto the sample with a beam size of $\sim 500\ \mu m$. The probe beam was focused onto the same spot but with a smaller size to make certain that only the photoexcited region was probed. The signal was detected using a silicon photodiode and a lock-in amplifier after passing through an Oriel tunable bandpass filter (for 400–700 nm) or an interference filter (for 750 and 850 nm) to select the detection wavelength. Except for measurements of the pump fluence dependence, the pump beam was attenuated to $\sim 10\ \mu J/cm^2$, well below the onset of bimolecular (fluence dependent) processes which are observed at fluence levels levels greater than $25\ \mu J/cm^2$. For all experiments, consecutive measurements at the same spot were carried out, and reproducible results were obtained; there was no observable optical damage during the measurements.

The poly(9,9-dioctylfluorene) (PFO) sample was purchased from American Dye Source, Inc. (ADS129BE). Several sources of PFO were examined. Care was taken to choose material with no indication of undesired green fluorenone emission between 2.2 and 2.4 eV.[12] The steady state spectra of the PFO films used in this study (cast from chloroform) are characteristic of the best available PFO.

The C_{60} derivative, 1-(3-methoxycarbonyl)-propyl-1-phenyl[6,6]C_{61} (PCBM) was obtained from Professor Fred Wudl (UCLA). All films (both pristine PFO and the PFO/C_{60} blend) were prepared by spin-casting on quartz substrates from chloroform solution (10 mg/ml), with an optical density of ~1.2 at the absorption maximum. To prevent aggregation, the solution was heated to 65 °C for 10 min and then cooled to approximately room temperature before spin casting. The spin-cast films were subsequently baked for 1 h at 60 °C to remove any residual solvent. Using a dry/glove box filled with nitrogen, the sample was loaded into a vacuum chamber which was subsequently kept under a dynamic vacuum ($<10^{-5}$ mbar) during the experiment.

In these initial experiments, a PFO/C60 blend containing 17% weight/weight C_{60} was chosen to study the electron transfer dynamics. At this concentration, the absorption at 400 nm is dominated by the PFO. Thus we can be confident that we are pumping into the π-π^* transition of the PFO

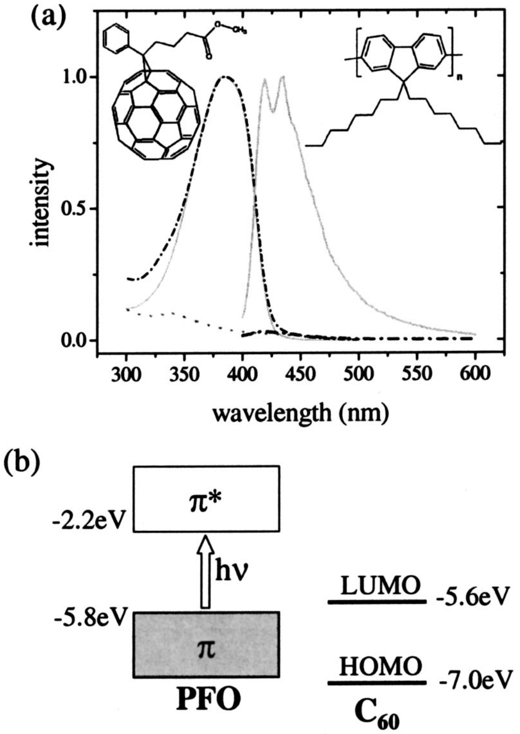

FIG. 1. (a) Absorption and fluorescence spectra of PFO (gray solid lines) and 17% wt ratio PFO/C_{60} blend (black dot-dashed lines). The dotted line is the absorption spectrum of the C_{60} derivative. The absorption and emission spectra of the pristine PFO films were normalized. The emission spectrum of the blend was rescaled to account for the small difference of the absorption maximum for direct visualization of the quenching effect. The molecular structure of the PFO and PCBM are shown in the inset. (b) Schematic energy diagram of the π and π^* bands of PFO and the LUMO and HOMO levels of C_{60}. The energy level values are with respect to the vacuum level.

with subsequent electron transfer to the C_{60} derivative. Based on the earlier work on MEH-PPV/C_{60},[13] the underlying photo-physics can be properly characterized at this intermediate concentration. A more thorough investigation of the concentration dependence will be carried out in future studies.

III. RESULTS AND DISCUSSION

A. Steady state measurements

After addition of the PCBM, the absorption spectrum of the PFO/PCBM blend is a superposition of the absorption spectra of the two components; no new absorption feature is observed (Fig. 1). However, the strong fluorescence of the pristine PFO film is quenched by a factor of ~28 in the blend with 17% weight ratio of PCBM. The quenching suggests efficient photoinduced electron transfer between excited PFO macromolecules and the C_{60} derivative. Based on the energy levels of the two species, efficient photoinduced electron transfer is expected. The energies of the top of the π-band and the bottom of the π^* band of PFO are sketched in Fig. 1 along with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of C_{60}.[14,15] Based upon these energies, it is energetically favorable for electron transfer from the excited state of PFO to the LUMO of C_{60}. On the other hand, since the HOMO of C_{60} is lower in energy than the top of the π band of PFO, the hole will remain on the semiconducting polymer. During the electron transfer process, energy can be conserved by promoting the hole left behind to a higher energy state within the π band.[16]

B. Wavelength dependent measurements of the pristine PFO film

The excited state dynamics of conjugated polymers typically exhibit a strong dependence on the pump fluence.[17,18] When the pump fluence increases, nonlinear processes (bimolecular exciton-exciton annihilation, etc.) cause the excited state to decay faster. In our earlier experiments on polyfluorene, a strong dependence on the pump fluence was observed.[19] Moreover, since previous studies on polyfluorene by other research groups were also carried out at relatively high excitation densities,[4,5,20] nonlinear processes were typically dominant. We found that nonlinear fluence dependent decay occurs at pump fluence greater than 25 μJ/cm^2. Thus to to avoid the complication of such bimolecular processes, we used a pump fluence of 10 μJ/cm^2 to study the photoinduced electron transfer process.

Three major features in the visible to near infrared region are typically observed in transient absorption studies of polyfluorene:[4,5,20] a stimulated emission (SE) band on the red side of the absorption spectrum (SE region, 420–500 nm), a photoinduced absorption (PA) band on the red side of the SE region, peaking at ~600 nm (PA_2) and a second photoinduced absorption band in the near-infrared (IR) with a peak at ~800 nm (PA_1). In earlier publications,[4,5,20] PA_1 and SE were characterized as having similar dynamics. As a result the authors attributed both to neutral excitons. However, since PA_2 exhibited somewhat faster decay dynamics than those of the SE and PA_1, the former was assumed to be of different origin; PA_2 was attributed to charge separated pairs.[5,20] Note, however, that Kraabel *et al.*[4] reported opposite results; the decay of PA_2 was slower than that of the SE and PA_1.

We carried out a series of single wavelength measurements within the visible spectral region. The photoinduced transient spectra at time delays of 0.5 and 50 ps, respectively, are reconstructed in Fig. 2(a). The data are similar to those reported in earlier publications (similar spectral features were observed) (Refs. 4, 5, and 20): stimulated emission on the red side of the absorption spectrum (SE) and photoinduced absorption from the visible into the near-IR (PA_2 and PA_1). The photoinduced transient spectra at 0.5 and 50 ps after excitation are quite similar [Fig. 2(a)], except the amplitude is reduced.

Figure 2(b) displays several single wavelength measurements with the wavelengths selected to represent the dynamics of the three different regions. The PA_1 band has a peak at 800 nm. Since our measurements at 750 and 850 nm showed identical decay behavior, the data at 750 nm is chosen to represent the dynamics of the PA_1 band. The decay profiles

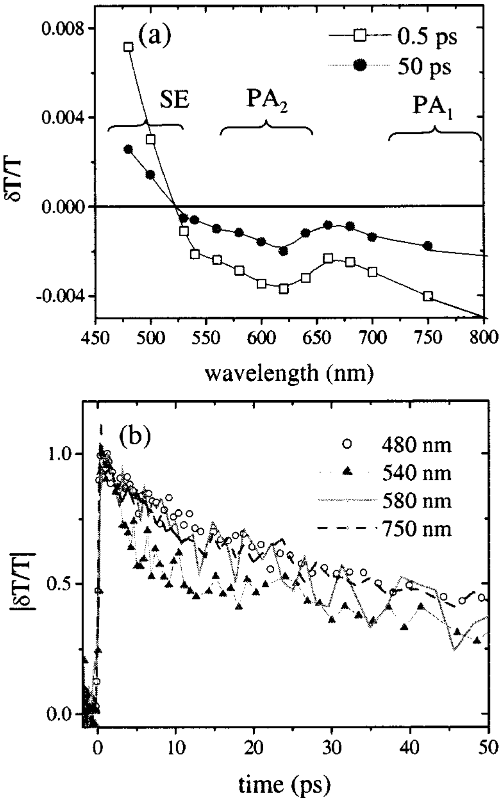

FIG. 2. Photoinduced dynamics in pristine PFO (a) photoinduced transient spectra at 0.5 and 50 ps delay times. (b) Decay dynamics at four different detection wavelengths: 480, 540, 580, and 750 nm.

for wavelength at 560, 580, and 600 nm showed no observable difference. Thus, the 580-nm data were selected to represent the dynamics of the PA_2 band. After normalization, the dynamics in the three different regions show no significant difference (within the experimental error) at low excitation density. In the earlier studies of polyfuorene, the decay of PA_2 was usually observed to be faster than those of PA_1 and SE region.[20] As noted, however, the opposite result has also been reported.[4] Different experimental conditions, such as excitation density or sample quality, must be responsible for such inconsistencies.

At 540 or 530 nm, the decay becomes slightly faster [Fig. 2(b)]. If these wavelengths were chosen to represent the dynamics of PA_2, the data would be consistent with those reported previously.[5,20] Note, however, that because 540 or 530 nm are close to the isosbestic point (~515 nm) of the positive stimulated emission and negative photoinduced absorption, the differences might arise from a subtle crossover effect associated with the evolutions of the two different spectral regions. Following pulsed photoexcitation, the fluorescence or stimulated emission spectra usually shift to the red in the picosecond time scale due to excitation migration from short conjugation segments to long conjugation segments and geometric relaxation processes.[21–23] For wavelengths on the red edge of the fluorescence spectrum, this time-dependent shift will result in a gradual increase of the stimulated emission signal before it decays. This well-known phenomenon[21–23] was also observed in our experiments. This evolution of the positive stimulated emission contribution has the effect of making the overall negative signal appear to decay more rapidly.

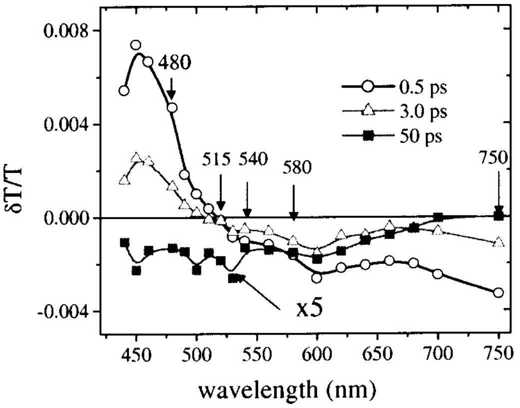

FIG. 3. Photoinduced transient spectra of PFO/PCBM blend at 0.5-ps (open circles), 3.0-ps (open triangles) and 50-ps (solid squares) time delays. Note that the 50-ps data are multiplied by a factor of 5 for the convenience of comparison. Several single wavelengths are indicated with arrows.

C. Wavelength dependent measurements in PFO/PCBM blends

The pump-probe experiments were carried out on the PFO/PCBM blends under the same experimental conditions. The transient spectra at different time delays were reconstructed (Fig. 3). Although the transient spectrum shape at 0.5 ps is quite similar to that of the corresponding pristine PFO film, the transient spectrum in the blend decays much faster than that in the pristine PFO film. The amplitude at 3.0 ps is only ~1/3 of that at 0.5-ps-time delay, with no significant change in the spectral shape. However at longer delay times, e.g., 50 ps, the entire transient spectrum is dominated by photoinduced absorption.

Figure 4 shows the single wavelength measurements for the same four detection wavelengths used to obtain the data in Fig. 2(b). The corresponding data obtained from the pristine film are also included in Fig. 4 for comparison. At all four wavelengths, the decay in the blend is much faster than in the pristine film, consistent with ultrafast electron transfer from the PFO excited state to C_{60} (the photoinduced electron transfer eliminates the initially created species). The signals in the blend start to decay immediately and quickly relax to a negative, wavelength dependent level, which is the spectral signature of the photoinduced absorption of the charge separated state (see Fig. 4). After subtraction of the photoinduced absorption characteristic of the charge separated state at each wavelength and normalization of the curves, the decay profiles from the blend with C_{60} at the four wavelengths, 480, 540, 580, and 750 nm, show essentially identical decay (Fig. 5).

The electron transfer (ET) rate can be extracted by fitting the decay of the stimulated emission (or photoinduced absorption). At 480 nm, the decay toward the negative offset is

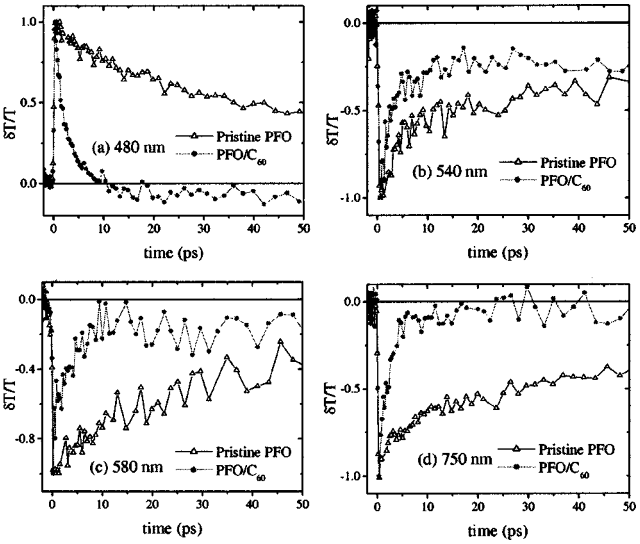

FIG. 4. Wavelength dependent decay dynamics in a PFO/PCBM blend (solid circles): 480 nm (a), 540 nm (b), 580 nm (c), and 750 nm (d). The corresponding dynamics in the pristine film (open triangles) is also plotted in the same curve for comparison.

not a simple exponential; it can be approximated as a biexponential function with time constants of 1.2 ps (63.7%) and 5.9 ps (36.3%). The apparent distribution of time constants may correspond to a range of ET rates associated with different distances between the excited PFO donors and the C_{60} acceptors. The overall decay time is approximately 3 ps, compared with the overall decay rate of 78 ps in the pristine film. This significantly faster decay is consistent with the observation of fluorescence quenching by a factor of approximately 28.

The negative photoinuced absorption at longer times corresponds to the transient absorption of the charge-separated state. Its decay, i.e., the back electron transfer process, cannot be resolved within the time scale of our experiments. The lifetime of the charge-separated state in MEH-PPV/C_{60} blend has been determined to be on the time scale of μs.[14,24]

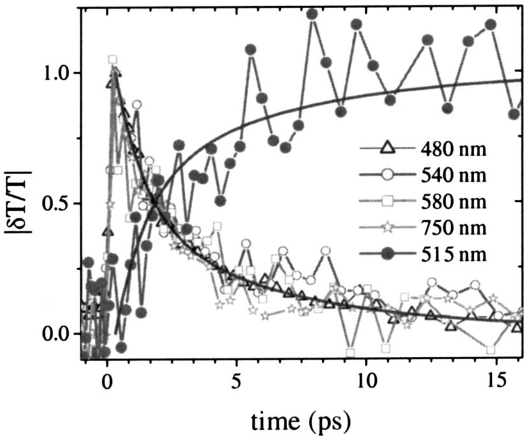

FIG. 5. Demonstration of ultrafast electron transfer and charge generation in the PFO/PCBM blend: pump-probe measurements at different detection wavelengths: 480 nm (open triangles), 515 nm (solid circles), 540 nm (open circles), 580 nm (open squares), and 750 nm (open stars). After subtraction of the long time offset characteristic of the charge separated state, the 480-, 540-, 580-, and 750-nm data were normalized.

A comparison of the decay dynamics in the PFO/C_{60} blend and pristine PFO film at identical wavelengths (Fig. 4) shows that the electron transfer rate is faster than any competing process. As a result, the charge separation efficiency should be close to unity in the PFO/C_{60} blend. At long delay times, e.g., 50 ps after the electron transfer process has finished, all the initially created excitations will be transformed into the charge separated state; i.e., electrons in the LUMO of PCBM (C_{60}^-) and positive polarons (P^+) in the PFO. However, the absorption of C_{60}^- has been reported to be at 1.1 eV (1100 nm),[25] and will not, therefore, contribute to the spectrum in Fig. 4. Thus, the absorption resulting from the positive polarons in PFO spans the spectral region from 430 to 680 nm.

It can also be seen from Fig. 3 that after charge separation, the absorption of the charge-separated state is at least five times weaker than the initial photoinduced absorption in the PA_2 region (e.g., 0.5 ps), suggesting that photogenerated carriers make a relatively minor contribution to the photoinduced absorption in the pristine PFO film.

The electron transfer process can also be visualized via the growth of the PA from the charge transferred state by probing at the isosbestic point, 515 nm, where the SE and photoinduced absorption of the pristine PFO cancel one another (at 515 nm there is a significant contribution to the PA from the charge separated state). Thus, an increase in PA is expected at this wavelength with the evolution of the charge transferred state.

As shown in Fig. 5, this is exactly what was observed in the experiments. The solid curve in Fig. 5 is the increase predicted from the decays at the other wavelengths, assuming a photoinduced charge transfer reaction with species *A* (the excited neutral PFO) evolving into species *B* (the charge transferred state). The decays at 480, 540, 580, and 750 nm exactly match the rise of the charge-separated state absorption at 515 nm. As in MEH-PPV/C_{60} blends,[17] the PA characteristic of the charge separated state is metastable; the back charge transfer cannot be resolved within the time scale of our experiments; charge separation is stabilized by the electron transfer to C_{60}.

The electron transfer rate from PFO to C_{60} is significantly slower than in the MEH-PPV/C_{60} system,[9,14] although it is energetically more favorable (more exothermic) in PFO/C_{60} [Fig 1(b)]. Such a behavior is predicted from Marcus theory for electron transfer and referred to as the ‘‘inverted region.’’ [26] A similar ‘‘slowing’’ of the ET rate has been previously reported by Janssen *et al.* in their study of photoinduced electron transfer from MEH-PPV to different electron acceptors.[27]

The similar decay dynamics of the three spectral features observed for pristine PFO suggests that a single initial excitation, the neutral exciton, is responsible for the stimulated emission and photoinduced absorption at low excitation densities. This tentative conclusion is consistent with recent photoinduced absorption studies of PFO by Cadby *et al.*;[28] they did not observe the infrared active vibrational modes which are the unambiguous signature of free carriers.[6,7,29] Note, however, that the ratio of the excitonic and charge-separated contributions might vary with the excitation density since it has been reported that the contribution of the charge-separated state can be greatly enhanced at higher excitation density.[5] Under the low excitation density used in the measurements reported here, the initial excitation appears to be a neutral exciton.

IV. SUMMARY

We have reported the results of time-resolved measurements on the excited state dynamics of polyfluorene and the photoinduced electron transfer reaction of polyfluorene with a C_{60} derivative (PCBM). With 17% PCBM by weight in the PFO/PCBM blend, the electron transfer process is found to be biphasic, with a fast component of 1.2 ps and a slow component of 5.9 ps. The electron transfer stabilizes the charge generation and allows the absorption spectrum of the charge-separated (ionic) state to be determined. In the charge-separated state, photoinduced absorption is observed over the broad spectral range from 430 to 680 nm.

The data are fully consistent with a photoinduced charge transfer reaction with species A (the excited neutral PFO) evolving into species B (the charge transferred state) within approximately 3 ps following photo-excitation. Thus, although slower than in the PPV system (where the ET time if of order 50 fs[9]), the electron transfer rate from PFO to the C_{60} derivative is still faster than any competing process.

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[1] G. R. Fleming, *Chemical Applications of Ultrafast Spectroscopy* (Oxford University, New York, 1986).

[2] C. Rulliáere, *Femtosecond Laser Pulses: Principles and Experiments* (Springer, Berlin, 1998).

[3] N. S. Sariciftci, *Primary Photoexcitations in Conjugated Polymers: Molecular Excitation versus Semiconductor Band Model* (World Scientific, Singapore, 1997).

[4] B. Kraabel, V. I. Klimov, R. Kohlman, S. Xu, H. L. Wang, and D. W. McBranch, Phys. Rev. B **61**, 8501 (2000).

[5] M. A. Stevens, C. Silva, D. M. Russell, and R. H. Friend, Phys. Rev. B **6316**, 5213 (2001).

[6] D. Moses, A. Dogariu, and A. J. Heeger, Thin Solid Films **363**, 68 (2000).

[7] P. B. Miranda, D. Moses, and A. J. Heeger, Phys. Rev. B **6408**, 1201 (2001).

[8] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Science **258**, 1474 (1992).

[9] C. J. Brabec, G. Zerza, G. Cerullo, S. De Silvestri, S. Luzzati, J. C. Hummelen, and S. Sariciftci, Chem. Phys. Lett. **340**, 232 (2001).

[10] F. Wudl, J. Mater. Chem. **12**, 1959 (2002).

[11] M. Leclerc, J. Polym. Sci., Part A: Polym. Chem. **39**, 2867 (2001).

[12] X. Gong, P. K. Iyer, D. Moses, G. C. Bazan, A. J. Heeger, and S. S. Xiao, Adv. Funct. Mater. **13**, 325 (2003).

[13] B. Kraabel, D. Mcbranch, N. S. Sariciftci, D. Moses, and A. J. Heeger, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **256**, 733 (1994).

[14] N. S. Sariciftci and A. J. Heeger, Int. J. Mod. Phys. B **8**, 237 (1994).

[15] X. Gong, S. Liu, A. K. Y. Jen, D. Moses, and A. J. Heeger, Appl. Phys. Lett. (to be published).

[16] M. J. Rice and Y. N. Gartstein, Phys. Rev. B **53**, 10 764 (1996).

[17] D. Vacar, E. S. Maniloff, D. W. McBranch, and A. J. Heeger, Phys. Rev. B **56**, 4573 (1997).

[18] V. I. Klimov, D. W. McBranch, N. Barashkov, and J. Ferraris, Phys. Rev. B **58**, 7654 (1998).

[19] Q.-H. Xu, D. Moses, and A. J. Heeger (unpublished).

[20] O. J. Korovyanko and Z. V. Vardeny, Chem. Phys. Lett. **356**, 361 (2002).

[21] G. R. Hayes, I. D. W. Samuel, and R. T. Phillips, Phys. Rev. B **54**, R8301 (1996).

[22] L. M. Herz and R. T. Phillips, Phys. Rev. B **61**, 13 691 (2000).

[23] J. L. Bredas, J. Cornil, and A. J. Heeger, Adv. Mater. (Weinheim, Ger.) **8**, 447 (1996).

[24] L. Smilowitz, N. S. Sariciftci, R. Wu, C. Gettinger, A. J. Heeger, and F. Wudl, Phys. Rev. B **47**, 13 835 (1993).

[25] K. H. Lee, R. A. J. Janssen, N. S. Sariciftci, and A. J. Heeger, Phys. Rev. B **49**, 5781 (1994).

[26] R. A. Marcus, Rev. Mod. Phys. **65**, 599 (1993).

[27] R. A. J. Janssen, M. P. T. Christiaans, C. Hare, N. Martin, N. S. Sariciftci, A. J. Heeger, and F. Wudl, J. Chem. Phys. **103**, 8840 (1995).

[28] A. J. Cadby, P. A. Lane, M. Wohlgenannt, C. An, Z. V. Vardeny, and D. D. C. Bradley, Synth. Met. **111**, 515 (2000).

[29] M. D. McGehee, E. K. Miller, D. Moses, and A. J. Heeger, in *Advances in Synthetic Metals: Twenty Years of Progress in Science and Technology*, edited by S. Lefrant, P. Bernier, and G. Bidan (Amsterdam, Elsevier, 1999), p. 98.