Absence of photoinduced electron transfer from the excitonic electron-hole bound state in polydiacetylene conjugated polymers

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We present the results of comparative studies of photoinduced electron transfer from semiconducting polymers onto C_{60}, focusing on the effect of strong Coulomb correlations, which lead to excitons (bound electron-hole pairs) as the primary photoexcitations. For this purpose, we investigated two different soluble polydiacetylene (PDA) derivatives in which the lowest-energy photoexcitations are excitons with a binding energy of approximately 0.5 eV. The experimental studies (absorption and emission spectroscopy, subpicosecond and millisecond photoinduced absorption spectroscopy, and picosecond transient and near-steady-state photoconductivity) were carried out in pristine materials and in composites of PDA with C_{60}. The PDA data are compared with the results of similar studies on semiconducting conjugated polymers such as poly(*para*-phenylene-vinylene) and its derivatives, the PPV's, and polythiophene and its derivatives, the P3AT's. The results show clearly that in contrast to the high quantum efficiency photoinduced electron transfer discovered earlier in the PPV's and the P3AT's, the excitonic bound state of the electron and hole inhibits photoinduced electron transfer from PDA onto C_{60}. We conclude that in the PPV's and the P3AT's, the Coulomb interaction is sufficiently well screened that upon photoexcitation free carriers are created, thereby making possible facile electron transfer to a nearby acceptor.

I. INTRODUCTION

Recently, we reported the observation of ultrafast, reversible, metastable, photoinduced electron transfer from semiconducting conjugated polymers onto C_{60}.[1-8] Upon photoexcitation of the electronic structure of semiconducting conjugated polymers mixed with C_{60} (as a weak acceptor) with photon energies grater than the π-π^* energy gap of the semiconducting polymer, the photoexcited electron transfers onto C_{60} within 700 fs creating charged species on both components, i.e., holes (positive polarons) on the polyconjugated semiconductor and electrons on the C_{60}^- anions.[1-4] The observation of two well-resolved light-induced electron-spin resonance signals originating from positive polarons on the conjugated polymer backbone (g value around 2.00) and C_{60}^- anions (g value around 1.99) provides definitive evidence of the photoinduced charge transfer.[1,3]

As a result of the ultrafast photoinduced electron transfer and charge separation, the photoconductivity of the host conjugated polymer can be sensitized and significantly increased (by one to two orders of magnitude) upon mixing in just a few weight percent of C_{60} as shown through picosecond transient and near steady-state photoconductivity studies.[4,6,7,9,10] The results demonstrate that the strong enhancement of the photocarrier generation efficiency arises from ultrafast charge separation prior to the early time recombination which dominates in the pristine polymer.[6] Moreover, the lifetime of the photogenerated carriers is strongly enhanced since the C_{60} molecules act as well-defined deep traps for the electron, thereby making the free holes on the conjugated polymer backbone metastable.[6,7]

This photoinduced electron transfer phenomenon was utilized to achieve photoinduced charge separation at the interface in semiconducting polymer/C_{60} thin film bilayers.[2,7] The donor-acceptor (DA) heterojunctions have diode current-voltage characteristics with rectification ratios as high as 10^5. Upon photoexcitation, the DA heterojunctions exhibit strong photoresponse due to the photoinduced electron transfer at the interface, resulting in (photodoped) conducting layers on both sides. These heterojunction devices are promising for use as photodiodes and solar cells.[2,7]

A schematic diagram of the photoinduced electron transfer process is displayed in Fig. 1. Upon excitation of the semiconducting polymer, the backbone structure relaxes to self-trapped polarons with electronic energy eigenstates within the gap. The upper polaron level is occupied by the electron, which, under favored energetic and kinetic conditions, rapidly transfers over to a nearby C_{60} molecule, resulting in the metastable charge-separated configuration. The hole (positive polaron) left on the conjugated polymer backbone is free to move away if there is effective screening of the Coulomb attraction to the electron, resulting in metastable *photodoping*.

The conditions under which this photoinduced electron transfer is favored are not yet clear. The energetics of the donor-acceptor couple are certainly important, as described in Marcus's theory.[11] The dielectric constant of the medium also plays an important role. As shown earlier, electronic stabilization through the formation of solitons with energies deep in the energy gap of degen-
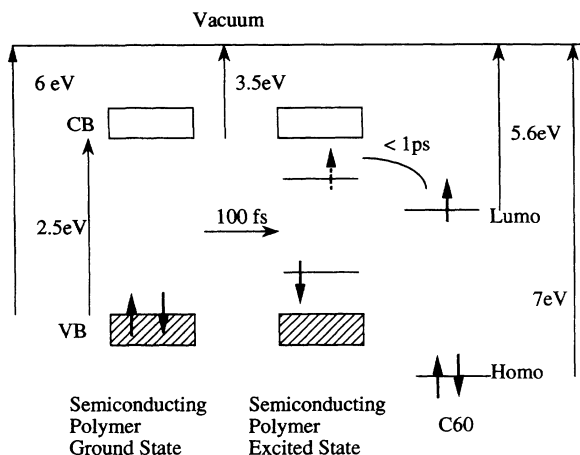
FIG. 1. Schematic band diagram of the photoinduced electron transfer reaction between conjugated polymer semiconductors and C_{60}.

erate ground-state conjugated polymers (e.g., polyacetylene) inhibit the electron transfer.[3]

Coulomb correlations on the conjugated polymer donor might be expected to play a crucial role. In a system where the excited electron and hole are strongly bound, leading to the exciton as the lowest-energy photoexcited state, the electron will have to overcome a Coulomb barrier to achieve full charge separation. Since this Coulomb barrier is comparable to the exciton binding energy, one might expect that photoinduced charge separation would be inhibited in systems with a large exciton binding energy. The polydiacetylenes (PDA's) offer an excellent example for testing these ideas, for it has been well established that the lowest-energy photoexcitations in the PDA's are excitons with a binding energy of approximately 0.5 eV.[12−15]

We report here the results of subpicosecond time-resolved photoinduced absorption, millisecond photoinduced absorption, transient and near-steady-state photoconductivity experiments which clearly demonstrate that the formation of bound electron-hole pairs (excitons) upon photexcitation of the conjugated polymer effectively inhibits the photoinduced electron transfer. In contrast to the results obtained from the PPV's and the P3AT's, photoinduced electron transfer is not observed in the photophysics of PDA:C_{60}. We conclude, therefore, that whereas strongly bound excitons are formed on the PDA's, the Coulomb interaction is sufficiently well screened compared to the π-electron bandwidth in the PPV's and the P3AT's that upon photoexcitation free carriers are created, thereby making possible facile electron transfer to a nearby acceptor.

II. EXPERIMENT

The synthesis and preparation of polydiacetylenes [PDA-ClCin22 = poly(bis-p-chlorocinnamate,10,12-docosadiyn-1,22-diol) and PDA-4BCMU = PDA-$(CH_2)_3$-OCO-NH-CH_2-OCO-C_4H_9] is described in earlier reports.[12−15] Powders of C_{60} were purchased from Polygon Enterprises, Texas and used without further

purification. Poly(2-methoxy,5-(2'-ethyl-hexoxy)-*para*-phenylene) vinylene (MEH-PPV) and bisdicholestanoxy-*para*-phenylene vinylene (BCHA-PPV) were purchased from UNIAX Corp., Santa Barbara and used without further purification. Thin film samples of PDA's and their composites with C_{60} were prepared by dissolving the compounds in 1,2-dichlorobenzene and drop casting onto substrates (sapphire and quartz disks for optical studies and Al_2O_3 substrates for the transient photoconductivity experiments).

The femtosecond photoinduced absorption (PIA) studies were carried out using a colliding pulse mode-locked laser with 80-fs pulses at 2.01 eV. After amplification of the pulses, a white light continuum is generated by passing the beam through an ethylene glycol cell. Further details of the femtosecond photoinduced absorption instrumentation are described elsewhere.[4]

For the millisecond photoinduced absorption studies, we used standard lock-in amplifier techniques with a chopped Ar^+ ion laser as source and an optical monochromator for spectral resolution[3] to obtain the normalized changes in transmission ($-\Delta T/T = \Delta \alpha d$).

Transient photoconductivity data were taken using the Auston microstripline switch technique.[16] The 600-μm-wide microstripline gold electrodes were deposited on top of the sample (with a gap of 200 μm) on an alumina substrate with a gold evaporated back plane to form a 50-Ω transmission line with frequency response over 100 GHz. One side of the microstripline was biased with 200-V dc and the other side was connected to a boxcar (PAR 4400) system fitted with a Tektronix S-4 sampling head. The boxcar was triggered with the light pulse via a photodiode. Excitation was obtained from a PRA LN105A dye laser pumped with a PRA LN1000 nitrogen laser operated at 3–5 Hz. The pulse width was 20–30 ps and typical intensities were about 2 μJ/pulse at 2.9 eV. The temporal resolution is limited by the electronic detection system to 50 ps without the preamplifier. Adding the prepamplifier further limits the temporal resolution, to approximately 400 ps. Data were obtained by illuminating the polymer in the 200-μm gap (bias field of 10^4 V/cm) with pulses from the laser.

For steady-state photoconductivity experiments, the standard photomodulation techniques (using a lock-in amplifier) with dispersed monochromatic light from a xenon lamp were utilized. To obtain the background from the spectral response of the system, the photoconductive cell is replaced by a calibrated photodiode.[6]

III. RESULTS AND DISCUSSION

The optical absorption spectra of PDA's have been studied extensively and reported in the literature.[12−15] The onset of absorption is at ~ 1.9 eV with a relatively sharp maximum at 2.3 eV (see Fig. 2). This lowest-energy absorption is commonly accepted as due to absorption into the exciton excited state. Upon mixing C_{60} into PDA, the linear absorption does not exhibit any new absorption features within the gap, ruling out the possibility of a ground-state charge transfer (see Fig. 2). The spectra in Fig. 2 are normalized to unity at the peak of
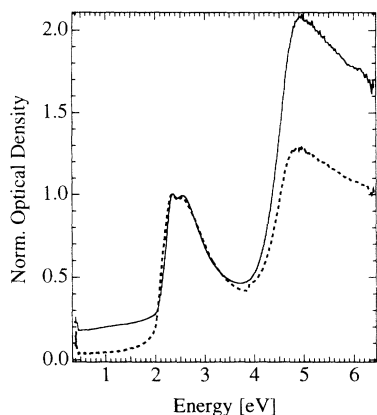
FIG. 2. Normalized optical absorption spectra: pristine PDA-4BCMU (dashed line); PDA-4BCMU:C_{60} (50 wt. %) (solid line).

the exciton absorption band. Note that the absorption spectrum of the composite film in Fig. 2 has a scattering background which increases with frequency due to the nonuniformity of the sample. This scattering contributes to the enhanced optical density of the 5 eV band. The fact that the C_{60} absorption bands at 3.7 and 4.6 eV are not evident in the optical absorption of the mixture is due to the much stronger optical absorption coefficient of PDA's ($\sim 8 \times 10^5$ cm^{-1} at the exciton absorption[17]) compared to C_{60} [$\sim 10^4$ cm^{-1} at 2.5 eV (Ref. 18)].

A. Near-steady-state photoconductivity

In Fig. 3, we display the near-steady-state photoconductivity results from two different soluble PDA derivatives with and without C_{60}. For both materials, the onset of photoconductivity is observed at approximately 2.7 eV, above which the photocurrent increases with photon energy. This is indicative for long-lived charge carriers (possibly trapped, thermally released, and retrapped etc.) generated by photoexcitation across the π-π^* band gap.[19]
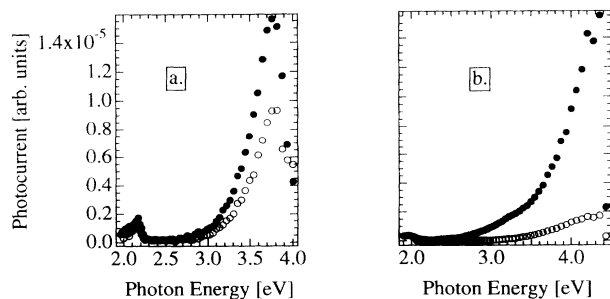
For PDA-ClCin22 [Fig. 3(a)] a weak photocurrent

peak at around 2.2 eV is clearly observable. In the pure PDA-4BCMU samples [Fig. 3(b)] the photoconductivity of the cast film is so small that it is not detectable at photon energies below 2.7 eV, although the optical absorption shows a strong absorption at lower energies (onset ~ 1.9 eV). This confirms the assignment of the lowest-energy optical absorption as an exciton band in PDA-4BCMU; the neutral excitons do not contribute to the photoconductivity and relax back to the ground state within nanoseconds.[20,19]

Since the data shown in Fig. 3 are from the near-steady-state photoconductivity experiments (and thus particularly sensitive to long-lived charge carriers with lifetimes up to milliseconds), the probability of creating long-lived charge carriers via secondary process such as exciton-exciton annihilation is remarkably low in PDA-4BCMU (below our limit of detection). Thus the exciton-exciton annihilation process with subsequent generation of trapped, long-lived charge carriers upon pumping into the exciton absorption band seems to be more efficient in the PDA-ClCin22 derivative. This might originate from a higher concentration of traps.

We emphasize that the data of Figs. 2 and 3 were obtained from disordered films cast from solution (rather than from single crystal samples). Nevertheless, the exciton binding energy (the energy separation between the onset of absorption and the onset of photoconductivity) of ~ 0.5 eV is clearly and unambiguously evident.

Upon addition of C_{60}, the photocurrent action spectrum slightly changes. The overall photocurrent response increases by a relatively small factor: for 2% C_{60} in PDA-ClCin22, the increase is a factor of 1.5 at 3.6 eV, while adding 50% C_{60} in PDA-4BCMU increases the photocurrent by less than a factor of 5 at 3.6 eV. This enhancement is attributed to longer lifetimes from trapped carriers as a result of the increased disorder upon adding C_{60} and, in part, to the photoconductivity of C_{60} itself.

The observed effect of adding C_{60} into the PDA's is

FIG. 3. (a) Spectral response of the steady-state photoconductivity of PDA-ClCin22 (open circles) and PDA-ClCin22:C_{60} (2%) (full circles). (b) Spectral response of the steady-state photoconductivity of PDA-4BCMU (open circles) and PDA-4BCMU:C_{60} (50%) (full circles).
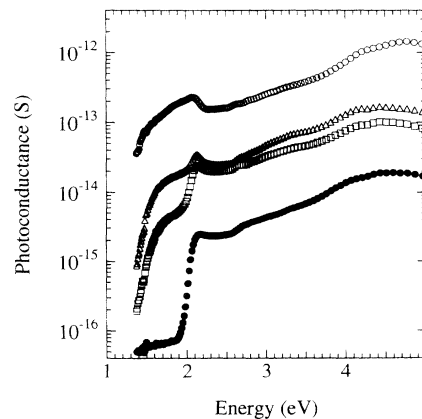

FIG. 4. Spectral response of the steady-state photoconductivity of MEH-PPV (full circles) and MEH-PPV:C_{60} (1%) (squares), MEH-PPV:C_{60} (5%) (triangles), and MEH-PPV:C_{60} (50%) (open circles).

particularly small when compared to the efficient sensiti-
zation of the PPV's and the P3AT's by C_{60}. As reported
earlier[6] and discussed in the Introduction, adding 50%
C_{60} into soluble derivatives of PPV enhances the overall
near-steady-state photocurrent by approximately two or-
ders of magnitude (even up to three orders of magnitude
below 2 eV).[4,6,7] For direct comparison with the data in
Fig. 3 , we display the effect of various concentrations of
C_{60} in MEH-PPV on the photoconductivity in Fig. 4.

B. Picosecond transient photoconductivity

The generation of charge carriers, their lifetimes, and
relaxation behavior upon photoexcitation of PDA's are
studied and compared with the results of similar studies
of the PPV's. In both derivatives of polydiacetylenes,
there was no detectable transient photocurrent upon
pumping into the excitonic absorption band at 1.98 eV.
By pumping at 2.9 eV, we could observe a small transient
photocurrent as displayed in Fig. 5. These semilog plots
are fitted to a double exponential relaxation with relaxa-
tion times $\tau_1 = 235$ ps and $\tau_2 = 2.7$ ns.

Addition of C_{60}, up to 50 wt. %, into the PDA matrix
does not affect the transient photocurrent response (Fig.
5). This is indeed in strong contrast to the observation of
the effect of C_{60} on the transient decay in the PPV's; in
the PPV's the carrier generation efficiency and the photo-
carrier lifetimes are strongly enhanced due to the ul-
trafast photoinduced electron transfer.[4,6,7] This efficient
sensitization of MEH-PPV by C_{60} is demonstrated in Fig.
6 for comparison. Even at C_{60} concentrations as low as 1
wt. %, the peak photocurrent is enhanced by an order of
magnitude with an associated increase in the lifetime of
the charge carriers.[4,6,7] These data directly indicate the
inhibition of ultrafast photoelectron transfer from the
PDA onto C_{60}. We attribute this inhibition of photoin-
duced charge transfer to the relatively strong Coulomb
binding of the electron and hole in PDA (exciton), which
creates a barrier for the charge separation. On the con-
trary, in PPV/C_{60} composites the photoinduced electron
transfer is ultrafast, efficient, and long lived, implying *no*

FIG. 6. Transient photoconductivity of MEH-PPV (circles)
and MEH-PPV:C_{60} (1%) (squares), MEH-PPV:C_{60} (5%) (dia-
monds); and MEH-PPV:C_{60} (50%) (triangles).

barrier for the electron to transfer onto C_{60}.[1-7]

The photoconductivity tail in Fig. 5 (with C_{60}) are not
cut off by charge transfer even though these carriers are
obviously not bound in a neutral exciton. We infer that
this implies that the transport results from carrier hop-
ping through defect states sufficiently deep in the gap
that they also do not transfer onto C_{60}. The pho-
toresponse of a spin cast, oxygen exposed, pure C_{60} film is
small compared to the peak photocurrents in Figs. 5 and
6 and therefore neglected.

C. Near-steady-state photoinduced absorption

The excited state of the pure PDA's and in PDA:C_{60}
has been studied using photoinduced absorption (excita-
tion spectroscopy) with chopped photoexcitation in the
millisecond regime. The results are shown in Fig. 7. The
photoinduced absorption spectrum of the pristine materi-
als exhibit one strong PIA band centered at 1.55 eV for
PDA-ClCin22 [Fig. 7(a)] and at 1.45 eV for PDA-
4BCMU [Fig. 7(b)] and along with the photoinduced
bleaching of the linear absorption at photon energies
above about 2.3 eV. The frequency dependence of this
PIA feature in both PDA's studied follows a monomolec-
ular decay characteristic with relaxation times $\tau = 660$ μs
for pristine PDA-4BCMU and $\tau = 750$ μs for the 50
wt. % PDA-4BCMU:C_{60} composite [Fig. 7(b)]. The in-
tensity dependence is sublinear following $I^{0.69}$ for the
pristine PDA-4BCMU and $I^{0.72}$ for PDA-4BCMU:C_{60}
(50%). We support the assignment of this PIA feature to
triplet-triplet absorption as described in the literature
(see, for example, Ref. 21).

The effect of adding C_{60} is negligible in both PDA-
4BCMU and PDA-ClCin22. The weak luminescence of
PDA/ClCin22 is not affected by the addition of C_{60}. All
these facts demonstrate clearly and without ambiguity
that charge separation does not exist at millisecond times.
The excitation spectroscopy of the PPV's, on the other

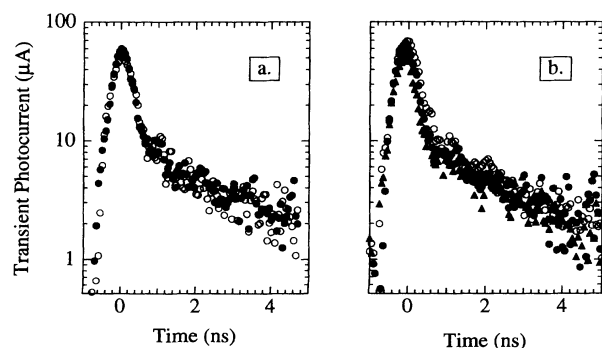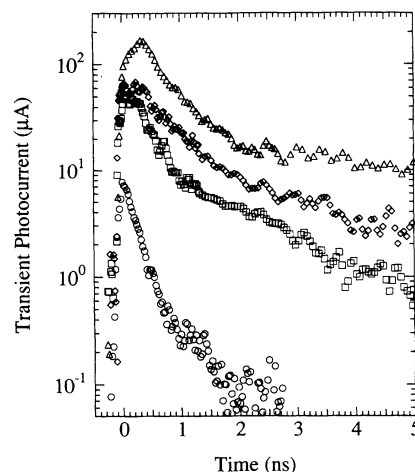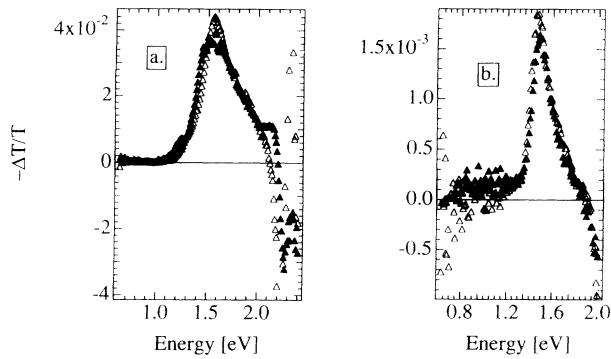

FIG. 5. (a) The transient photoconductivity of PDA-ClCin22
(open circles) and PDA-ClCin22:C_{60} (50%) (full circles). (b) The
transient photoconductivity of PDA-4BCMU (open circles),
PDA-4BCMU:C_{60} (5%) (triangles), and PDA-4BCMU:C_{60}
(50%) (full circles).

FIG. 7. (a) Near-steady-state photoinduced absorption spectrum of PDA/ClCin22 (open triangles) and PDA-ClCin22:C_{60} (50%) (full triangles). (b) Near-steady-state photoinduced absorption spectrum PDA-4BCMU (open triangles) and PDA-4BCMU:C_{60} (50%) (full triangles).

FIG. 9. (a) Subpicosecond photoinduced absorption spectrum of PDA-ClCin22:C_{60} (1%) at various delay times after the excitation by an 80-fs pump pulse with $\hbar\omega = 2.01$ eV. (b) Subpicosecond photoinduced absorption spectrum of PDA-4BCMU:C_{60} (1%) at various delay times after the excitation by an 80-fs pump pulse with $\hbar\omega = 2.01$ eV.

hand, exhibits clear indications of photoinduced charge transfer upon addition of C_{60}.[1,3,7]

D. Subpicosecond photoinduced absorption

We display in Figs. 8 and 9 the results of femtosecond photoinduced absorption spectra ($\Delta T/T$) of PDA-4BCMU and PDA-ClCin22. Since high-concentration samples of C_{60} in PDA were unstable upon exposure to the extreme peak power of the pump beam (as required for these experiments) we limited the C_{60} concentration to 1%.

The subpicosecond photoinduced absorption spectrum of pristine PDA/ClCin22 material [Fig. 8(a)] is slightly different from the PDA-4BCMU [Fig. 8(b)]. The bleaching at 1.9 eV and the two PIA features at 1.4 and 1.8 eV
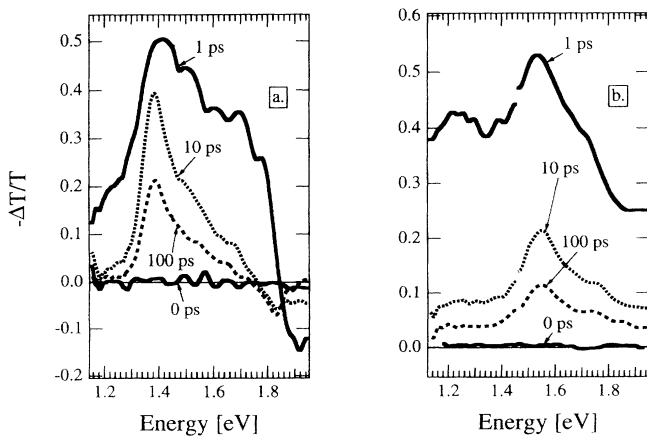

FIG. 8. (a) Subpicosecond photoinduced absorption spectrum of PDA-ClCin22 at various delay times after the excitation by an 80-fs pump pulse with $\hbar\omega = 2.01$ eV. (b) Subpicosecond photoinduced absorption spectrum of PD-4BCMU at various delay times after the excitation by an 80-fs pump pulse with $\hbar\omega = 2.01$ eV.
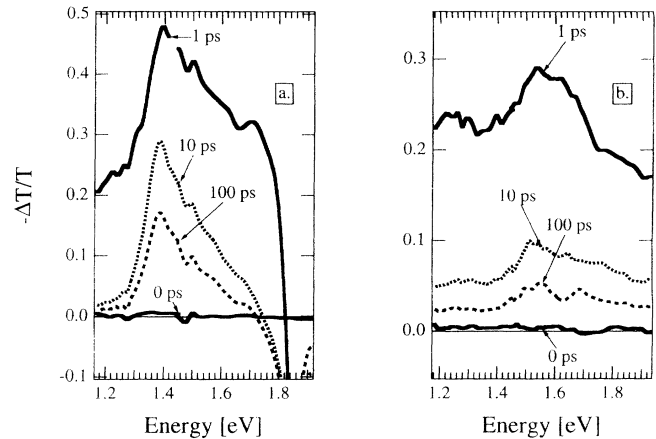
are directly observable in PDA-ClCin22 [Fig. 8(a)]. Rapid decay of the 1.8-eV PIA band to a single PIA peak at 1.4 eV after 10 ps is in full agreement with published data on PDA/3BCMU.[22]

The spectral response of the pristine PDA/4BCMU is displayed in Fig. 8(b) with subpicosecond resolution. At very early times after the pump [1 ps on Fig. 8(b)] two PIA features are observed at approximately 1.2 and 1.55 eV. This spectrum changes then rapidly over to a single maximum PIA at 1.55 eV. This observation is also consistent with earlier data from PDA-3BCMU which show that at early times a 1.2-eV feature is visible which evolves to a single maximum at 1.4 eV after several picoseconds.[22] The PIA peak at 1.8 eV for intermediate time scales is not as pronounced in our data on PDA-4BCMU [Fig. 8(b)] as in PDA-3BCMU.[22] The possibility that this 1.8-eV peak is buried under the broad PIA tail of the 1.5-eV band cannot, however, be excluded. Detailed analysis of the subpicosecond photoinduced absorption spectra on the PDA's will be presented separately.[23]

The assignment of these subpicosecond PIA features is difficult due to the fact that the singlet exciton absorptions and triplet-triplet absorptions are close in energy in these materials.[22] Nevertheless, the early time spectra can be assigned to singlet exciton absorptions whereas at later times the intersystem crossing may take over and yield the spectrum observed at millisecond time domain (as shown in Fig. 7), which has been assigned to triplet-triplet absorption.

The addition of C_{60}, however, does not affect the subpicosecond photoinduced absorption spectra of PDA's at all (Fig. 9). The relaxation curves of the different PIA bands observed in PDA/ClCin22 with and without C_{60} are identical, as displayed in Fig. 10. Equivalent results were obtained for PDA-4BCMU. Thus the photoinduced electron transfer is indeed fully inhibited in all time
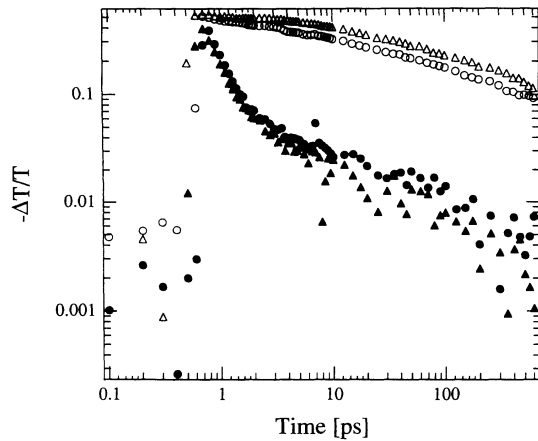
FIG. 10. The time decay of the subpicosecond photoinduced absorption of the two bands observed in PDA-ClCin22: the 1.5-eV band for PDA-ClCin22 (open triangles) and PDA-ClCin22:C_{60} (1%) (open circles) and the 1.2-eV band for PDA/ClCin22 (full triangles) and PDA-ClCin22:C_{60} (1%) (full circles).

domains, ruling out the possibility of a rapid photoinduced electron transfer accompanied by a rapid back-relaxation process (which could in principle explain the absence of photoinduced charge transfer in the millisecond time domain).

The PPV's, however, undergo ultrafast photoinduced electron transfer onto C_{60} upon photoexcitation of their π electrons, as demonstrated in great detail.[1-7] In Fig. 11, we demonstrate this effect in BCHA-PPV and compare the data with results obtained from BCHA-PPV:C_{60} (1%). Even at time scales as early as 700 fs, it is clearly
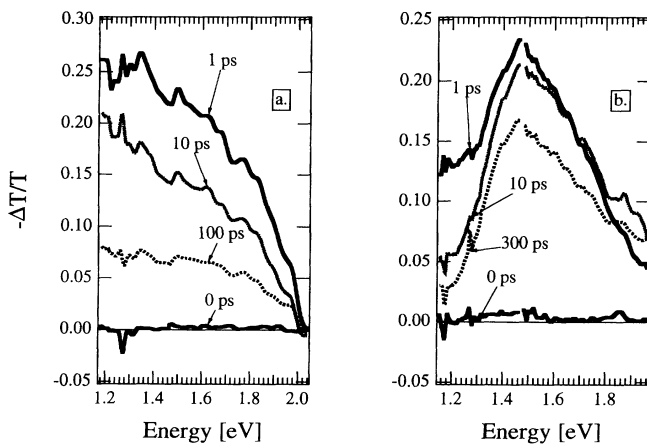

FIG. 11. (a) Subpicosecond photoinduced absorption spectrum of BCHA-PPV at various delay times after the excitation by an 80-fs pump pulse with $\hbar\omega = 2.01$ eV. (b) Subpicosecond photoinduced absorption spectrum of BCHA-PPV:C_{60} (1%) at various delay times after excitation by an 80-fs pump pulse with $\hbar\omega = 2.01$ eV.

observable that the spectrum has changed upon addition of 1% C_{60} and that positive polarons are formed on the PPV backbone (with associated formation of the anion of C_{60}).[4,7,23] Details of the subpicosecond photoinduced electron transfer obtained with time-resolved femtosecond photoinduced absorption techniques are published elsewhere.[4,7,23]

IV. CONCLUSION

The results of absorption and emission spectroscopy, subpicosecond and millisecond photoinduced absorption spectroscopy, and picosecond transient and near-steady-state photoconductivity show clearly that in contrast to the high quantum efficiency photoinduced electron transfer discovered earlier in the PPV's and the P3AT's, photoinduced electron transfer from PDA onto C_{60} is inhibited.

The structure and morphology of the composite samples might be relevant to the absence of the photoinduced electron transfer. The solubility of C_{60} in films of PDA's, PPV's, and P3AT's is unknown and a possible decreased solubility in PDA's compared to the other conjugated polymers might be relevant. On the other hand, in the heavily C_{60} loaded samples of PPV's and P3AT's, which exhibit partial phase segregation due to the lower solubility of the C_{60} component, the ultrafast photoinduced electron transfer process is still clearly observable. Therefore, we cannot attribute the complete absence of the electron transfer in PDA/C_{60} composites to sample morphology effects. Moreover, since all the data from the PDA's were obtained from disordered films cast from solution (rather than from single crystal samples), disorder in the PPV's and the P3AT's can no longer be invoked as the origin of the qualitatively different phenomena. The exciton binding energy of approximately 0.4–0.5 eV, as determined by the energy separation between the onset of absorption and the onset of photoconductivity, is clearly and unambiguously evident in PDA films cast from solution.

Why is the photoinduced electron transfer so strongly inhibited in polydiacetylenes? The energetics of the donor and acceptor components and the relative positions of the various energy levels are important parameters of the photoinduced electron transfer mechanism.[11,24] The ionization potentials of the polydiacetylenes are around 5.5 eV,[20] nearly identical to the ionization potentials of polythiophenes [5.2 eV (Ref. 25 and 26)] and very close to those of the PPV's [5.11 eV (Ref. 26)]. The optical absorption gaps are comparable. Furthermore, the effect of the dielectric constant cannot provide a decisive difference between the PPV's and PDA's because they have nearly identical magnitudes for the real part of the dielectric function as $\omega \rightarrow 0$ (see, for example, Refs. 17 and 27). Thus the extraordinary difference — ultrafast photoinduced electron transfer in the PPV's and P3AT's (Refs. 1–7) and the complete inhibition of ultrafast photoinduced electron transfer in the PDA's — must have had its origin in the photophysics of polydiacetylene.

To achieve photoinduced electron transfer and com-

plete charge separation, the Coulomb barrier (i.e., Coulomb attraction between the electron and hole on the excited donor) must be overcome. The electron-hole (exciton) binding energy is indeed very strong in the PDA's (0.4–0.5 eV) (see Refs. 12–15, 20, 19, and 22 and references therein). The formation of excitons is an ultrafast process which occurs at times faster than our limits of detection. Once the exciton is formed, charge separation can occur either by electron hopping over the Coulomb barrier or by electron tunneling through the barrier. Hopping over the barrier would be thermally activated and would require an excess of energy of the order of the Coulomb binding energy of the exciton. Tunneling through the barrier might be expected, although with a transfer rate that is exponentially small compared to the direct transfer rate determined by the wave-function overlap without the barrier.

Even after the exciton had been broken apart and an electron transferred onto C_{60}, the stabilization of this charge-separated state would require delocalization of the charge to overcome the rapid recombination. In the hypothetical case that the electron transfers over to C_{60} resulting in unstable products, this scenario would display a forward photoinduced electron transfer (within several picoseconds) accompanied by a very rapid back transfer (tens of picoseconds up to nanoseconds) as observed in several small molecule donor-acceptor systems.[24] Apparently this is not the case, as demonstrated by the subpicosecond photoinduced absorption and picosecond photoconductivity data, which clearly show that there is

no forward photoinduced electron transfer in the PDA:C_{60} composites. The logical answer is that the binding energy of excitons in PDA's is sufficiently large that photoinduced electron transfer is inhibited by the Coulomb barrier.

Indirectly, therefore, these results imply that the Coulomb interaction in the P3AT's and the PPV's is sufficiently well screened in comparison with the bandwidth that ultrafast photoinduced electron transfer can occur. Thus any possible exciton binding energy in the P3AT's or the PPV's must be much less than the 0.4–0.5 eV value characteristic of the polydiacetylenes.

The origin of the relatively large exciton binding energy in the PDA's is somewhat of a puzzle since the π-electron densities are comparable. We note, however, that valence bond arguments imply that the triple bonds in the PDA's tend to confine the charged excitations and thereby prevent separation of the electron-hole pair.[28] Such confinement effects will increase the magnitude of the Coulomb binding energy of the exciton and thereby inhibit the photoinduced electron transfer.

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