Transient optical studies of charge recombination dynamics in a polymer/fullerene composite at room temperature
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Published in:
Applied Physics Letters

DOI:
10.1063/1.1512943

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2002

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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The recombination kinetics of photogenerated charge carriers in a composite of poly[2-methoxy-5-(3′,7′-dimethoxyloxy)-1-4-phenylene vinylene], (MDMO–PPV) and the functionalised fullerene 1-(3-methoxy carbonyl)-propyl-1-phenyl-(6,6)C_{60} are investigated at room temperature by transient absorption spectroscopy. The decay dynamics of positively charged MDMO–PPV polarons were found to be either monophasic or biphasic, depending upon the laser excitation density employed. The slower, power law, decay phase (100 ns–10 ms) is attributed to recombination dynamics of localized polarons, while the fast decay component (<20 ns) is attributed to recombination of relatively mobile polarons observed when the density of localized states is exceeded by the density of photogenerated polarons (≈10^{17} cm^{-3}). The implications of these observations are discussed in relation to polymer/C_{60} photovoltaic cells. © 2002 American Institute of Physics.
TAS signal measured at 296 K at a time delay of 125 ns resulted in a broad, long-lived photoinduced absorption signal. Pulsed laser excitation of the MDMO–PPV/PCBM was taken to subtract contributions from laser scatter and during any of the experiments reported here. Particular care was taken to subtract contributions from laser scatter and sample emission from the data.

We consider first the assignment of the transient optical signal. Pulsed laser excitation of the MDMO–PPV/PCBM resulted in a broad, long-lived photoinduced absorption increase in the red/near-infrared. The transient spectrum of this TAS signal measured at 296 K at a time delay of 125 ns, is displayed in Fig. 1(a). As a comparison, Figs. 1(b) and 1(c) show the frequency domain photoinduced absorption spectra of a pristine MDMO–PPV and (△) of a MDMO–PPV/PCBM blend (∆2) employing excitation at 488 nm with 40 mW and 132 Hz modulation, T = 100 K. Note that ΔOD and ΔT/T are related by ΔOD = 1/2.303 (ΔT/T).

PIA spectra in Fig. 1(b) clearly shows that the transient spectrum closely matches that observed in the frequency domain PIA studies of the blend, and is therefore also assigned to positive MDMO–PPV polarons generated by photoinduced electron transfer from MDMO–PPV to PCBM.

We now consider the decay dynamics of the MDMO–PPV polaron transient absorption signal. Figure 2 shows the kinetics for the MDMO–PPV/PCBM blend on the nanosecond time scale using excitation densities ranging from 1.5 to 70 μJ cm⁻² per pulse (4 – 180×10¹² photons cm⁻² per pulse). It is apparent that the decay dynamics are strongly dependent upon laser intensity. At high laser intensities, they are dominated by a fast, instrument response limited (∼20 ns) decay phase. The amplitude of this fast phase is excitation density dependent and reduces in amplitude by at least 20-fold over the range of excitation densities employed. In contrast, as shown in Fig. 3 the longer timescale data is relatively insensitive to laser power, e.g., the signal in the 50–100 ns time window reducing in amplitude by only ∼50% over the same range. At the lowest excitation power employed, (1.5 μJ cm⁻² per pulse), the instrument response limited (<20 ns) decay is negligible, and the slower timescale dynamics dominate the decay.

In Fig. 4 we show an extension of our data to millisecond time scales on log/log axes. The long lived residual sig-

FIG. 1. (a) Transient absorption spectra of a MDMO–PPV/PCBM blend obtained 125 μs after excitation at 500 nm (80 μJ cm⁻² per pulse), T = 296 K. (b) frequency domain photoinduced absorption spectra of (■) pristine MDMO–PPV and (△) of a MDMO–PPV/PCBM blend (∆2) employing excitation at 488 nm with 40 mW and 132 Hz modulation, T = 100 K. Note that ΔOD and ΔT/T are related by ΔOD = 1/2.303 (ΔT/T).

FIG. 2. Transient absorption kinetics observed for the MDMO–PPV/PCBM blend on the nanosecond time scale using different excitation densities. The excitation densities ranged between 1.5 and 70 μJ cm⁻² per pulse. The decay is assigned to charge recombination between electrons in the fullerene and the positive polarons in the conjugated polymer. The sample was excited at 500 nm at a repetition rate of 4 Hz and probed using a laser diode at 830 nm, T = 296 K.

FIG. 3. Relative amplitude of the transient absorption signal for the MDMO–PPV/PCBM blend as a function of laser excitation power: (●) amplitude of instrument response (20 ns) limited decay; (△) transient signal at 50–100 μs; (■) transient signal at 100–400 μs. Other experimental conditions as for Fig. 2.
sient photoconductivity and LESR studies of PPV/C60 materials, below the mobility edge for the material. The pres-
dynamics are consistent with pico- to nanosecond relaxation
pulse, the amplitude of this long lived signal starts to become
et al.
for time delays
this analysis, the fast,
onds. As observed in Fig. 2, at longer time delays the
signal becomes increasingly less sensitive to the
excitation density down to
transient signal becomes increasingly less sensitive to the
excitation intensity employed. Indeed, for time delays greater
than ~300 ns, the transient signal is independent of excita-
tion density for excitation densities employed down to <1.5
µJ cm−2 per pulse [for excitation densities <1 µJ cm−2 per
pulse, the amplitude of this long lived signal starts to become
smaller, as shown in Fig. 3 (--■--)]. It is furthermore apar-
tent that the slow time scale transient decay dynamics exhib-
ts a power law type behavior
\[ \Delta O.D. \propto t^{-\alpha}. \]  
From the gradient of the decays, we obtain \( \alpha = 0.4 \pm 0.02 \).

We conclude from the data shown in Figs. 2 and 4 that the decay dynamics of MDMO–PPV positive polarons in
photoexcited MDMO–PPV/PCBM blends can be approxi-
mated by a fast (instrument response limited, <20 ns) com-
ponent dependent upon excitation density and a slow com-
ponent that exhibits a power law decay and is independent of excitation density down to ~1 µJ cm−2 per pulse.

The power law type recombination dynamics observed for time delays >300 ns are indicative of localized carriers, as has previously been suggested by Meskers et al.8 These dynamics are consistent with pico- to nanosecond relaxation of the charge carriers down to the lowest energy states of the inhomogeneously broadened density of states typical of such materials, below the mobility edge for the material. The presence of localized states is furthermore consistent with transient photoconductivity and LESR studies of PPV/C60 films.15 The saturation of the amplitude of the power law decay observed here for excitation intensities >1 µJ cm−2 per pulse is consistent with saturation of the density of available localized states. Taking account of the sample absorption at the excitation wavelength (transmission ~40%) and assuming a unity quantum yield of polaron formation per absorbed photon,4 this threshold excitation density corre-
sponds to ~1017 photogenerated polarons cm−3. This calcula-
tion neglects any charge recombination occurring on time scales <<20 ns, in agreement with the data shown in Fig. 2 for the low excitation densities employed. Following from this analysis, the fast, <20 ns decay phase observed for laser intensities >1.5 µJ cm−2 per pulse can be assigned to rela-
tively mobile polarons present when the density of photoge-
genated polarons exceeds the density of localized states be-
low the PPVs mobility edge. We note that the laser power
dependence we observe is not consistent with the assignment of the <20 ns phase to geminate recombination.8

We conclude by noting that the recombination dynamics in photovoltaic device fabricated from polymer/C60 cells un-
der solar illumination can be expected to be dominated by the slower decay phase we report here. The rate of carrier
generation under steady state solar illumination is \( \sim 3 \times 10^{16} \) polarons s−1 cm−2 (estimated from the optimum
short circuit current of 5 mA cm−2).4 Given the ns–μs re-
combination dynamics reported here for localized polarons, the polaron density generated by steady state solar illumination is not expected to exceed the estimated density of localized states (~1017 cm−3), and the recombination dynamics will most probably be dominated by the slow, power law decay we assign to recombination dynamics of localized MDMO–PPV polarons with C60 anions. More quantitative analysis of these recombination dynamics and their compe-
tition with carrier collection dynamics in complete photovoltaic cells will be presented elsewhere.16

The authors are grateful to Richard Monkhouse for technical
assistance with transient laser experiments, Gerald Zerza for
providing the PIA data, Covion Ltd., and Kees Hummelen for
supplying MDMO–PPV and PCBM, respectively, and
the EPSRC for financial support I.M. acknowledges the
financial support of a Marie Curie Fellowship from the EU. N.S.S. gratefully acknowledges the financial support of the Christian Doppler Society.

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