

# Photoinduced electron transfer reactions in mixed films of $\pi$ -conjugated polymers and a homologous series of tetracyano-*p*-quinodimethane derivatives

René A. J. Janssen,<sup>a)</sup> Marwijn P. T. Christiaans,<sup>a)</sup> Casey Hare, Nazario Martin,<sup>b)</sup> N. Serdar Sariciftci, Alan J. Heeger, and Fred Wudl

*Institute for Polymers and Organic Solids, University of California, Santa Barbara, California 93106-5090*

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Near-steady-state photoinduced absorption (PIA) and photoluminescence studies are presented on photoinduced electron transfer reactions from poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and poly[3-(2-(3-methylbutoxy)ethyl)thiophene] (P3MBET) as donors (*D*) onto a homologous series of tetracyano-*p*-quinodimethane (TCNQ) derivatives containing fused aromatic rings as acceptors (*A*) to systematically study the effect of acceptor electron affinity. We observe that composite films of these *D/A* couples give rise to long-lived charge separated states upon photoexcitation, as evidenced from the formation of polaron bands (radical cation absorption) in the PIA and the concomitant loss of the metastable triplet PIA and photoluminescence that are observed in pristine MEH-PPV and P3MBET. We find that the efficiency of the photoinduced electron transfer reaction correlates with the reduction potential of the acceptors. © 1995 American Institute of Physics.

## I. INTRODUCTION

Photoinduced electron transfer between semiconducting, conjugated polymers and Buckminsterfullerene ( $C_{60}$ ) has been studied extensively using (time-resolved) photoinduced absorption (PIA) spectroscopy, light-induced electron spin resonance (LESER) spectroscopy, photoinduced Fourier transform infrared (FTIR), and (time-resolved) photoconductivity.<sup>1-4</sup> It is well established that photoexcitation of  $\pi$ -conjugated polymers in composite films with  $C_{60}$  gives rise to an extremely fast (on the order of 300 fs) and efficient electron transfer reaction, producing a long-lived (on the order of ms) charge-separated state. The remarkable metastability of the charge-separated state results from the extended  $\pi$ -electron delocalization of the conjugated polymer, the excellent acceptor properties of  $C_{60}$ , and structural distortions that form on the polycation and the  $C_{60}$  anion. The efficient generation of long-lived charge carriers in the donor-acceptor couple of a semiconducting polymer and  $C_{60}$  has been successfully incorporated in photoelectric devices such as photodiodes and photovoltaic cells.<sup>5</sup>

Different types of  $\pi$ -conjugated polymers have been examined as donors and exhibit electron transfer to  $C_{60}$  upon photoexcitation, viz., poly(3-alkylthiophene)s, poly(2,5-dialkoxy-1,4-phenylene)s, poly(9,9-dihexylfluorene), and poly(*o*-trimethylsilylphenyl-acetylene),<sup>1-9</sup> as well as alkyl substituted oligothiophenes.<sup>10</sup> Polydiacetylene derivatives, however, do not transfer an electron to  $C_{60}$  under similar conditions.<sup>11</sup>

The acceptor side, however, has received less attention until now. Recently, we showed that  $C_{60}$  functionalized with

solubilizing side chains, [5,6] (fulleroid) or [6,6] (methanofullerene), are efficient electron acceptors toward photoexcited poly(2,5-dialkoxy-1,4-phenylene).<sup>12</sup> Antoniadis *et al.* observed a decrease of photoluminescence of soluble poly(*p*-phenylene vinylene) (PPV) derivatives in films doped with (4-*n*-butoxycarbonyl-9-fluoronylidene)-malonitrile (BCFM) and in bilayer devices comprised of fully converted PPV and BCFM/poly(4,4'-cyclohexylidene-diphenylcarbonate) layers, which was attributed to efficient photoinduced electron transfer.<sup>13</sup>

In this paper we describe our studies using PIA and photoluminescence on photoexcitation of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and poly[3-(2-(3-methylbutoxy)ethyl)thiophene] (P3MBET) in composite films with a series of tetracyano-*p*-quinodimethane (TCNQ) derivatives containing fused aromatic rings as acceptors (Fig. 1) and compare the results of the photophysical studies with those obtained with  $C_{60}$ . The photoinduced electron transfer efficiency depends on the reduction potential (i.e., electron affinity) of these acceptor molecules. The quenching of luminescence as well as the intersystem crossing of the conjugated polymer donors show a maximum as function of the reduction potential of the acceptor.

## II. EXPERIMENT

MEH-PPV<sup>14</sup> (UNIAX Corporation) and tetracyano-*p*-quinodimethane (**1**) (Aldrich), were used as received. The synthesis of highly regioregular P3MBET, with no detectable irregularities (head-to-tail coupling  $\geq 98\%$ ), has been previously described by Bouman and Meijer.<sup>15</sup> The preparation and electrochemical properties of 11,11,12,12-tetracyano-9,10-anthraquinodimethane (**2**), 13,13,14,14-tetracyano-5,12-naphthacenequinodimethane (**3**), 8,9-dimethoxy-13,13,14,14-tetracyano-5,12-naphthacenequinodi-

<sup>a)</sup>Permanent address: Laboratory of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

<sup>b)</sup>Permanent address: Departamento Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense, 28040, Madrid, Spain.

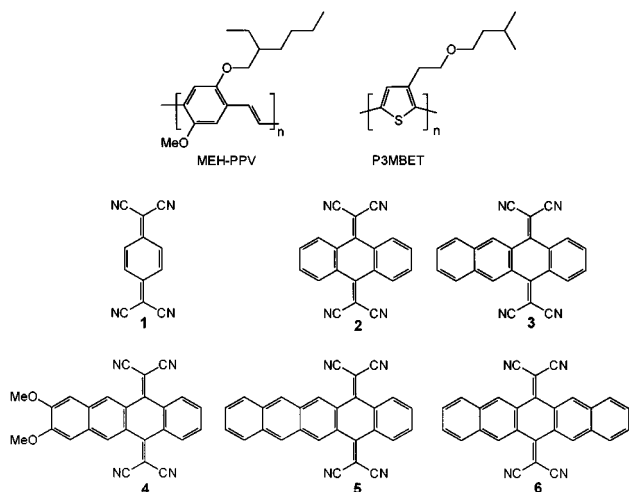


FIG. 1. Molecular structures of MEH-PPV, P3MBET, and tetracyano-*p*-quinodimethane derivatives **1–6**.

methane (**4**), 15,15,16,16-tetracyano-5,14-pentacenequinodimethane (**5**), and 15,15,16,16-tetracyano-6,13-pentacenequinodimethane (**6**) have been reported by Martin *et al.*<sup>16</sup>

PIA experiments were performed using an argon-ion cw laser as a pump beam (514.5 nm, 25 mW, 2 mm pump diameter) and a tungsten-halogen probe beam. The pump beam was mechanically chopped (typically at 275 Hz) and the resulting modulation of the probe light transmission ( $\Delta T$ ) was phase sensitively recorded after dispersion by a grating monochromator using a lock-in amplifier and a two-color (Si/PbS) detector. The probe beam transmission ( $T$ ) was recorded separately and the PIA ( $-\Delta T/T \approx \Delta\alpha \cdot d$ ) was obtained after correction for luminescence. Films were prepared by casting from hot (80 °C) xylenes or benzonitrile solutions onto sapphire substrates. Absorption spectra give no indication that charge transfer occurs in the ground state. The substrates were mounted on a cryostat held at 80 K in a dynamical vacuum on the order of  $10^{-5}$  Torr.

### III. RESULTS AND DISCUSSION

#### A. MEH-PPV/acceptor composites

In order to allow for a direct comparison of the effects observed in the photophysics of conjugated polymer donors in composite films with TCNQ derivatives, we summarize the results of conjugated polymer/ $C_{60}$  composites, where photoinduced electron transfer reactions are well established. The PIA spectrum of a pristine MEH-PPV film and a MEH-PPV/ $C_{60}$  (5 mol %) composite film recorded at 80 K are shown in Fig. 2. Compared to the triplet state photoexcitation observed at 1.34 eV in MEH-PPV, several new features are observed in the PIA of the mixed film, viz., the onset of a band at 0.7 eV, a distinct shoulder at 1.18 eV, and a plateau from 1.5 to 2.0 eV.<sup>1</sup> Absorption detected magnetic resonance (ADMR) experiments on MEH-PPV and MEH-PPV/ $C_{60}$  have shown that the nature of the absorption at 1.34 eV is different in the presence of  $C_{60}$ , being associated with a triplet state ( $S=1$ ) in a pristine MEH-PPV film to a doublet state ( $S=\frac{1}{2}$ ) in the mixed film.<sup>17</sup> The shoulder at

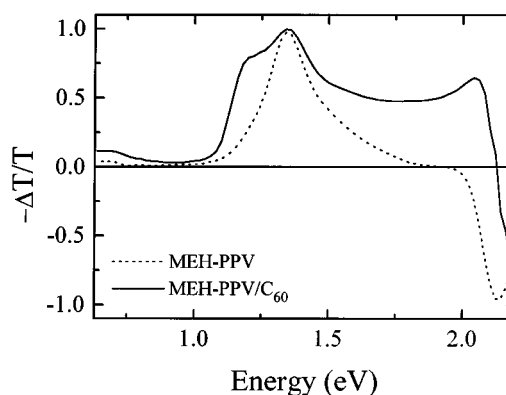


FIG. 2. PIA spectra of pristine MEH-PPV film and a MEH-PPV/ $C_{60}$  (5 mol %) composite film. Spectra were recorded at 80 K by pumping at 2.41 eV with 25 mW and a modulation frequency of 275 Hz. Spectra are normalized to allow for direct comparison.

1.18 eV is generally associated with the  $C_{60}^{\cdot-}$  radical anion.<sup>1,3</sup> In addition to the changes in the PIA, the photoluminescence of MEH-PPV is quenched dramatically upon mixing with  $C_{60}$  (Fig. 3). Finally, the radical ions of polymer and  $C_{60}$  have been identified after photoexcitation using LESR.<sup>1</sup>

The PIA spectra of composite films of MEH-PPV with each of the TCNQ derivatives **1–6** (5 mol %, films cast from benzonitrile) are shown in Fig. 4. Mixing MEH-PPV with either **2**, **3**, **4**, or **5** results in similar PIA features, as observed for MEH-PPV/ $C_{60}$ , exhibiting a new shoulder at 1.22 eV and a plateau from 1.5 to 2.0 eV. The quenching of the photoluminescence is of the same order of magnitude for MEH-PPV/**3**, MEH-PPV/**4**, and MEH-PPV/**5** as compared to MEH-PPV/ $C_{60}$ , but notably less for MEH-PPV/**2** (Fig. 5). The PIA spectra of MEH-PPV/**1** and MEH-PPV/**6** (Fig. 4), on the other hand, show only moderate differences as compared to that of pristine MEH-PPV, and photoluminescence is quenched by a modest factor of 5–10 only (Fig. 5). Figure

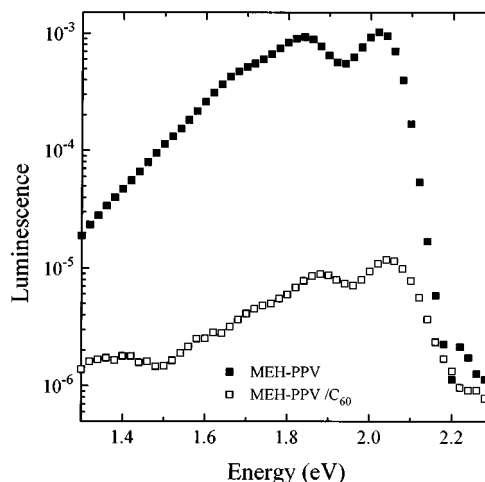


FIG. 3. Luminescence intensity of a pristine MEH-PPV film and a MEH-PPV/ $C_{60}$  (5 mol %) composite film. Spectra were recorded at 80 K by excitation at 2.41 eV with a 25 mW pump beam.

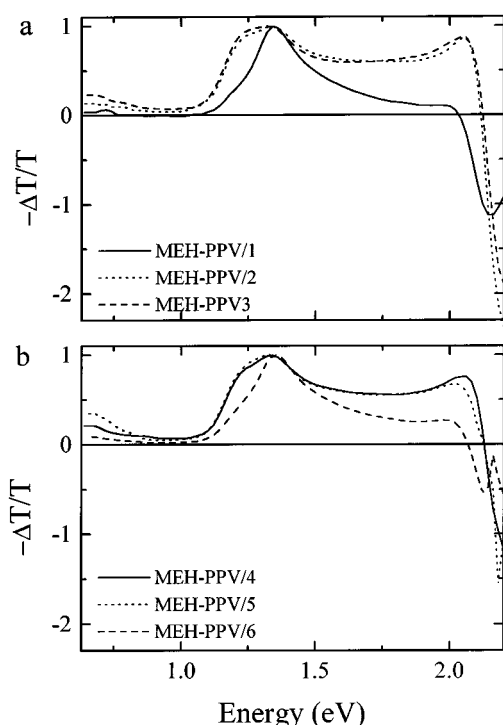


FIG. 4. PIA spectra of composite films of MEH-PPV with TCNQ acceptors (5 mol %): (a) **1–3**; (b) **4–6**. Spectra were recorded at 80 K by pumping at 2.41 eV with 25 mW and a modulation frequency of 275 Hz. Spectra are normalized to allow for direct comparison.

5 shows that the quenching of MEH-PPV luminescence and the ratio of the PIA signal intensity at 1.34 eV to the new band at 1.22 eV are related to the electrochemical reduction potential of the different acceptors. From these results we conclude that photoinduced electron transfer from MEH-PPV to TCNQ derivatives **3**, **4**, and **5** occurs with a high efficiency, similar to  $C_{60}$ . For **1**, **2**, and **6**, electron transfer occurs to a lesser extent.

In order to assess the relaxation behavior of the photoexcitations, the PIA intensity ( $-\Delta T$ ) was measured as function of pump intensity ( $I$ ) at 0.64, 1.22, 1.34, and 2.04 eV.

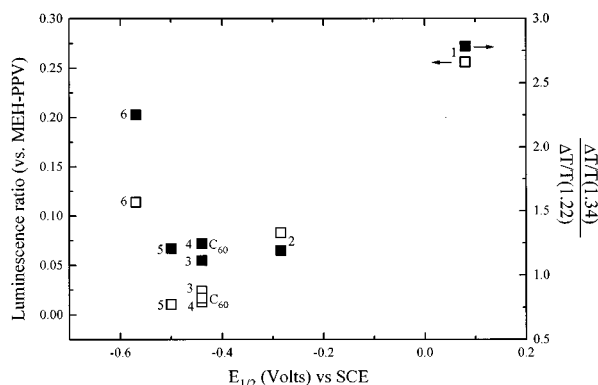


FIG. 5. Relative luminescence intensity (open markers) as compared to pristine MEH-PPV of composite films of MEH-PPV with  $C_{60}$  and acceptors **1–6** as a function of their reduction potentials (Ref. 16) at 80 K. Right-hand axis shows the ratio of the PIA intensity of the bands at 1.34 and 1.22 eV (solid markers).

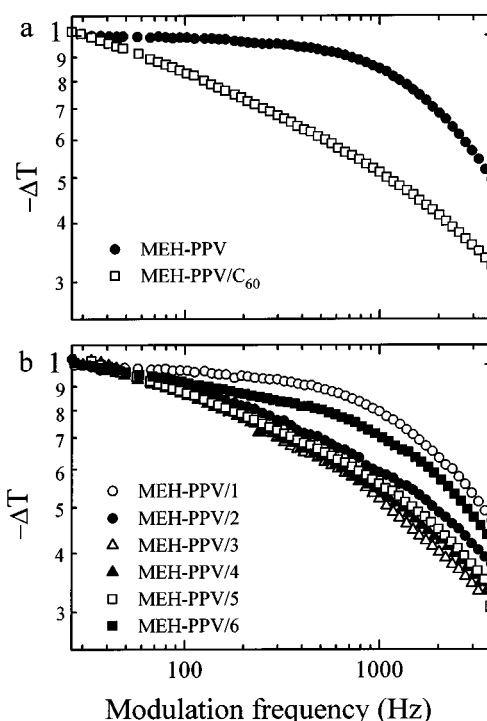


FIG. 6. Normalized intensity dependence of the PIA signal at 1.34 eV as a function of the modulation frequency in (a) MEH-PPV and MEH-PPV/ $C_{60}$  and (b) MEH-PPV with acceptors **1–6**. Data were recorded at 80 K by pumping at 2.41 eV with a 25 mW excitation beam.

We find that the PIA spectra of the pristine and mixed MEH-PPV films generally increase sublinearly with pump intensity according to a  $-\Delta T \sim I^\alpha$  power law, where  $\alpha$  is in the range from 0.46 to 0.54. A square-root behavior is usually associated with a bimolecular decay mechanism.<sup>18</sup>

By varying the modulation frequency ( $\omega$ ) of the pump beam and monitoring the PIA intensity an indication on the lifetime of the photoexcited states can be obtained. The relaxation behavior of the PIA signal at 1.34 eV is shown for pristine and mixed MEH-PPV films in Fig. 6. For pristine MEH-PPV, the decay curve can be fitted to the theoretical expression for bimolecular decay,<sup>18</sup> giving a lifetime of about 0.7 ms at 80 K. For MEH-PPV/ $C_{60}$  the decay of  $-\Delta T$  follows more closely a power-law dependence on  $\omega$ , even at the lowest chopping frequencies. Such power-law decay is typically found for trapped charged excitations,<sup>19</sup> although under similar conditions bimolecular decay has been observed for the charge separated state in photoexcited oligothiophenes/ $C_{60}$  composite films.<sup>10</sup> The relaxation behavior in composite films of MEH-PPV with acceptors **3**, **4**, and **5** is virtually identical to that of MEH-PPV/ $C_{60}$ , while acceptors **1**, **2**, and **6** exhibit a decay intermediate to MEH-PPV and MEH-PPV/ $C_{60}$ . These results give further evidence to our conclusion that photoinduced electron transfer is more efficient for **3**, **4**, and **5** than for **1**, **2**, and **6**.

## B. P3MBET/acceptor composites

The PIA spectrum of P3MBET (Fig. 7) exhibits a broad-band from 1.00 to 1.40 eV. Although there is a close similarity in the pump intensity of the PIA bands at 1.10 eV

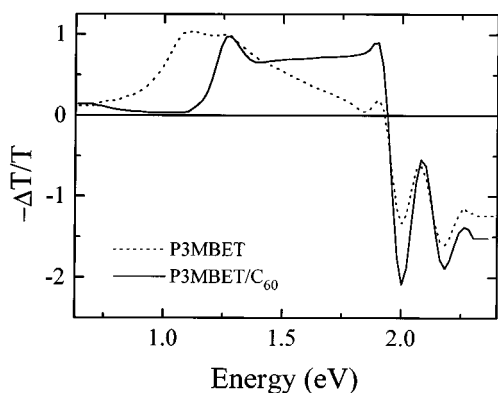


FIG. 7. PIA spectra of a pristine P3MBET film and a P3MBET/C<sub>60</sub> (5 mol %) composite film. Spectra were recorded at 80 K by pumping at 2.41 eV with 25 mW and a modulation frequency of 275 Hz. Spectra are normalized to allow for direct comparison.

( $-\Delta T \sim I^{0.69}$ ) and 1.24 eV ( $-\Delta T \sim I^{0.66}$ ), their relaxation behavior as determined from the modulation frequency dependence is different (Fig. 8). This indicates that two different photoexcitations are present. Using the theoretical expression for monomolecular decay, a lifetime of approximately 150  $\mu$ s is found for the excitation associated with the 1.10 eV band. We attribute the 1.10 eV band to a triplet state photoexcitation in agreement with previous studies on poly(3-alkylthiophenes),<sup>1b,20</sup> since the peak position and lifetime are similar to those of triplet states observed for medium sized alkyl-substituted oligothiophenes.<sup>21</sup> For the

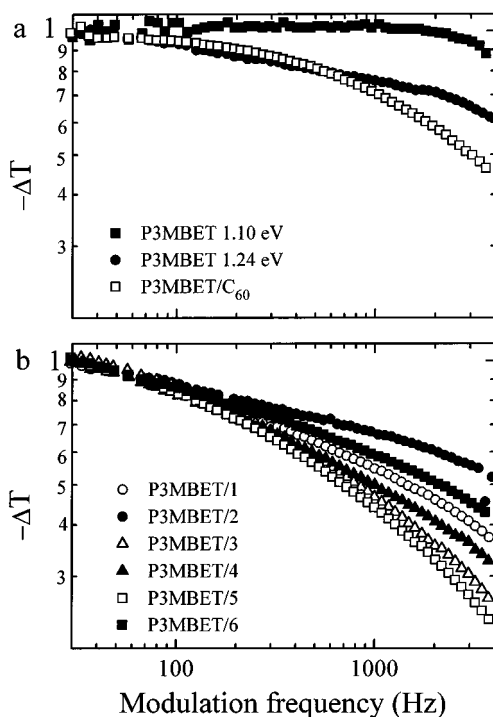


FIG. 8. Normalized intensity dependence of the PIA signal at 1.26 eV as a function of the modulation frequency in (a) P3MBET (also for the 1.10 eV signal) and P3MBET/C<sub>60</sub> and (b) P3MBET with acceptors **1–6**. Data were recorded at 80 K by pumping at 2.41 eV with a 25 mW excitation beam.

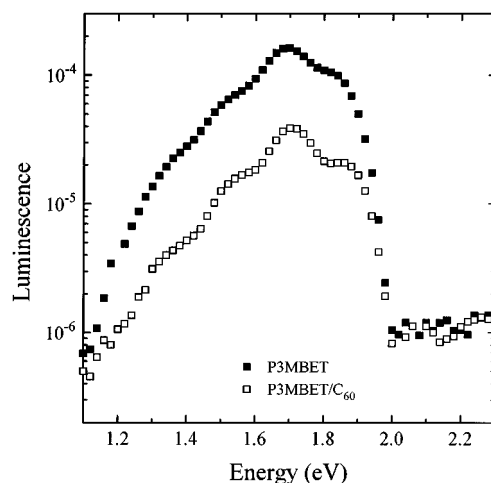


FIG. 9. Luminescence intensity of a pristine P3MBET film and a P3MBET/C<sub>60</sub> (5 mol %) composite film. Spectra were recorded at 80 K by excitation at 2.41 eV with a 25 mW pump beam.

1.26 eV band, no reasonable fit to either mono- or bimolecular decay could be obtained, likely due to spectral overlap in that region.

The PIA of a P3MBET/C<sub>60</sub> (5 mol %) composite film (Fig. 7) reveals the loss of the triplet state photoexcitation at 1.10 eV, while the band at 1.26 eV remains. In addition, a number of new features appear in the spectrum, viz., the onset of a PIA band in the NIR at 0.7 eV, a small shoulder at 1.18 eV, and a plateau from 1.4–1.9 eV. The luminescence efficiency of P3MBET/C<sub>60</sub> is quenched by a factor of about 4 (Fig. 9), remarkably less than in the case of MEH-PPV.

The PIA bands in the NIR region (<0.7 eV) and at 1.26 eV are readily associated with the low- and high-energy sub-gap absorptions of a P3MBET polaron and/or bipolaron.<sup>1</sup> In a dichloromethane solution, these bands are observed at 0.64 and 1.52 eV,<sup>22</sup> the blueshift in solution being caused by the well-known solvatochromic effect associated with poly(3-alkylthiophenes).<sup>23</sup> In combination with the small C<sub>60</sub><sup>•−</sup> signal at 1.18 eV, the observation of polaron/bipolaron bands in the PIA of P3MBET/C<sub>60</sub> gives spectral evidence for a photoinduced electron transfer reaction. Although the relaxation behavior of the 1.26 eV band changes only slightly in the mixed film as compared to the pristine film, the pump intensity dependence is significantly different:  $-\Delta T \sim I^{0.38}$ . Similar power-law exponents are found in the plateau at 1.54 ( $\alpha=0.37$ ) and at 1.92 eV ( $\alpha=0.37$ ).

In Fig. 10, the PIA spectra of P3MBET mixed with TCNQ derivatives **1–6** (5 mol %, cast from benzonitrile) are shown. The PIA spectra are a superposition of the spectra associated with pristine P3MBET and P3MBET/C<sub>60</sub> with a different weight ratio, depending on the nature of the acceptor. This indicates that photoinduced electron transfer to the TCNQ acceptors occurs with variable efficiency. From the partial quenching of the triplet PIA band at 1.10 eV, we infer that electron transfer is most efficient for **3**, **5**, and C<sub>60</sub>, while acceptors **1**, **2**, **4**, and **6** are less effective in this respect. The relaxation behavior of the 1.26 eV PIA band in composite

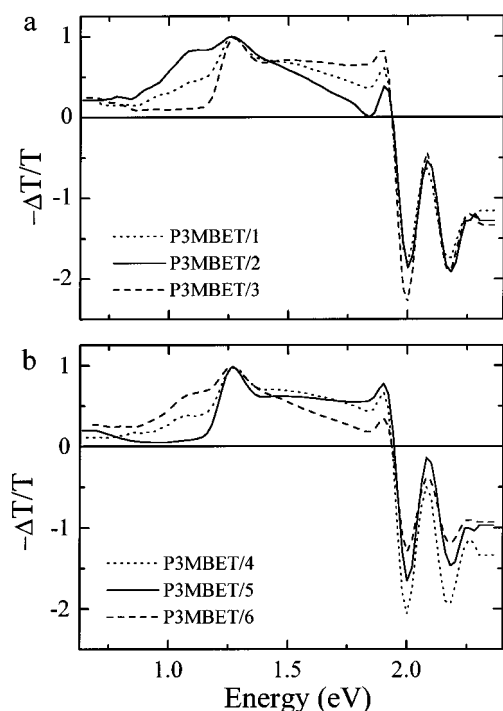


FIG. 10. PIA spectra of composite films of P3MBET with TCNQ acceptors (5 mol %): (a) 1–3; (b) 4–6. Spectra were recorded at 80 K by pumping at 2.41 eV with 25 mW and a modulation frequency of 275 Hz. Spectra are normalized to allow for direct comparison.

films of P3MBET with 1–6 shows the same effect (Fig. 8) and is consistent with this conclusion.

#### IV. CONCLUDING REMARKS

By measuring near-steady-state PIA and photoluminescence we have demonstrated that photoinduced electron transfer occurs from MEH-PPV and P3MBET to various tetracyano-*p*-quinodimethane derivatives containing fused aromatic rings as acceptors with different efficiencies.

A first approximation to the relative rates of electron transfer for the different acceptors can be obtained from the degree of quenching of the luminescence in MEH-PPV (Fig. 5) and the degree of quenching of the triplet PIA band at 1.10 eV in P3MBET. For acceptors 3, 4 (in combination with MEH-PPV), and 5, the results are similar to those obtained for C<sub>60</sub>, which is known to give rise to an ultrafast electron transfer reaction with photoexcited  $\pi$ -conjugated polymers.<sup>1–12</sup> For acceptors 1, 2, 4 (in combination with P3MBET), and 6 photoinduced electron transfer is appreciably less efficient. In this respect, it is important to note that under identical experimental conditions no photoinduced electron transfer reaction has been observed from MEH-PPV to either 1,4-benzoquinone, 1,4-naphthoquinone, or 9,10-anthraquinone. When these quinones are mixed with MEH-PPV we do not observe any effect in the PIA spectrum or a quenching of the MEH-PPV luminescence.<sup>24</sup> Apparently, 1,4-benzoquinone is not an efficient acceptor, despite the fact that the reduction potential (−0.51 eV vs SCE) is similar to that of 3, 4, 5, and C<sub>60</sub>.<sup>25</sup> Interestingly, similar differences in photoinduced electron transfer efficiency have

been observed for tris(2,2′-bipyridyl)ruthenium(II) compounds when linked to fullerene or quinones.<sup>26</sup>

To provide a possible rationale to these differences in efficiency of photoinduced charge transfer reactions, several factors should be taken into account. A first criterion is that  $I_{D^*} - A_A - U_C < 0$ , where  $I_{D^*}$  is the ionization potential of the excited state donor ( $D^*$ ),  $A_A$  is the electron affinity of the acceptor ( $A$ ), and  $U_C$  is the Coulomb energy of the separated radical ions (including polarization effects).<sup>1</sup> Although this provides an energetic criterion, the rate and quantum yield of photoinduced electron transfer in composite films of  $\pi$ -conjugated materials and acceptors depends on the activation barrier and can be low despite favorable energetics, e.g., due to a potential energy barrier preventing charge separation<sup>11</sup> or due to the morphology of the film, which may prevent the necessary overlap between the initially occupied orbital of the donor and the eventually occupied orbital of the acceptor.<sup>10</sup>

For the present case, we find that acceptors 1 and 2, which are reduced more easily than either 3, 5, or C<sub>60</sub>,<sup>16</sup> exhibit a significantly lower rate for photoinduced electron transfer (Fig. 5). Such behavior is predicted from the Marcus theory for electron transfer and referred to as the “inverted region.” As the exothermicity of a charge transfer process continues to increase, a “crossing point” may be reached where the transfer rate actually starts to decrease.<sup>27</sup> Although this phenomenon qualitatively provides an interpretation to the decreased efficiency of acceptors 1 and 2, further experimental work will be necessary to show the correlation quantitatively. On the other hand, the efficient photoinduced charge transfer of MEH-PPV in combination with 3, 4, 5, and C<sub>60</sub> as compared to the lack of activity with 1,4-benzoquinone as an acceptor demonstrates that the reduction potential is not the only parameter that affects the electron transfer rate. Particularly, phase segregation and solubility of molecules 1–6 within the conjugated polymer matrix can cause a problem in interpreting the observed results as being solely due to differences in electron affinity.

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