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Photoinduced Electron Transfer Between Conjugated Polymers and a Homologous Series of TCNQ Derivatives

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Abstract. — The results of photoinduced absorption (PIA) and photoluminescence studies of the photoinduced electron transfer reactions from conjugated polymer donors onto a series of acceptors based on TCNQ and benzoquinone derivatives containing fused aromatic rings are summarized. The results are compared to the well-defined photoinduced electron transfer demonstrated from conjugated polymer donors onto buckminsterfullerene, C_{60}. For the TCNQ derivatives, the efficiency of the electron transfer process correlates with the reduction potential of the acceptors. However, photoinduced electron transfer was not observed in the case of the benzoquinone derivatives, although their electrochemical reduction potentials are similar to C_{60}.

1. Introduction

Igor Schegolev was a pioneer in the study of the organic charge transfer salts. His early research had a profound effect and contributed in a significant way to the creation of the field now known as “synthetic metals”. In subsequent years, he continued to provide leadership in the study of the electrical and magnetic properties of the charge transfer salts with a particular focus on these materials as metals and superconductors. As a friend and colleague, Igor will be missed by all who knew him and benefited from interacting with him. The record of his scientific accomplishments speaks for itself.

Although Schegolev was principally interested in the study of materials which exhibit charge transfer in the ground state, we focus here on electron transfer in the excited state. As a continuation of our studies on the conjugated polymer (donor) and buckminsterfullerene, C_{60}, (acceptor) [1–6] we have investigated different types of \pi-conjugated polymers (and oligomers) as photoexcited electron donors [4, 5, 7, 8]. In composites with C_{60}, conjugated polymers such

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Fig. 1. — Molecular structures of MEH-PPV, P3MBET, and TCNQ derivatives 1-6.

as poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (hereafter referred as MEH-PPV), and poly[3-(2-(3-methylbutoxy)ethyl)thiophene] (P3MBET) exhibit ultrafast electron transfer upon photoexcitation (the forward electron transfer occurs in less than 1 picosecond!) [1-8]. The back transfer of the separated electron is, however, inhibited and the charge-separated state is metastable. This high asymmetry in the forward and back electron transfer rates makes possible the utilization of this charge separation in creating efficient "plastic" photovoltaic cells [2,9-11].

Variations of the acceptor have received less attention. Recently, we showed that C_{60} functionalized with solubilizing side chains are also efficient electron acceptors in conjugated polymer matrices [12]. Antoniadis et al. attributed the decrease of the photoluminescence form PPV derivatives in films doped with 4-n-butoxycarbonyl-9-fluoronylidene)-malonitrile (BCFM), to efficient photoinduced electron transfer [13,14]. In this short review, we summarize the results of near-steady-state photoinduced absorption (PIA) and photoluminescence studies on the photoinduced electron transfer reactions from conjugated polymer donors onto a series of acceptors based on TCNQ and benzoquinone derivatives containing fused aromatic rings (Fig. 1). We find the efficiency of the electron transfer correlates with the reduction potential of the acceptors for the TCNQ derivatives.
MEH-PPV [15] (UNIAX Corporation) and tetracyano-p-quinodimethane (TCNQ) (1)(Aldrich) were used as received. The synthesis of regioregular P3MBET, with no detectable irregularities (head-to-tail coupling ≥ 98%), has been previously described by Bouman and Meijer [16]. The preparation and electrochemical properties of 11,11,12,12-tetracyano-9,10-anthraquinodimethane (2), 13,13,14,14-tetracyano-5,12-naphthquinodimethane (3), 8,9-dimethoxy-13,13, 14,14-tetracyano-5,12-naphthacenequinodimethane(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. [17].

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

3. Results and Discussion

MEH-PPV/Acceptor Composites. — In order to allow for a direct comparison of the effects observed in the photophysics of conjugated polymer donors in the composite films with the various TCNQ derivatives, we briefly summarize the results obtained earlier from conjugated polymer/C$_{60}$ composites, where the photoinduced electron transfer reactions are ultrafast and well documented [1, 4, 5]. The PIA spectrum of a pristine MEH-PPV film and a MEH-PPV/C$_{60}$ (5 mol%) composite film recorded at 80 K is shown in Figure 2. Several features are observed in the PIA of the composite 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 [1]. Photo-induced absorption detected magnetic resonance (PIADMR) experiments on MEH-PPV and MEH-PPV/C$_{60}$ films

![Graph showing PIA spectra of MEH-PPV and MEH-PPV/C$_{60}$.

Fig. 2. — PIA spectra of a pristine MEH-PPV film and a MEH-PPV/C$_{60}$ (5 mol%) composite film. The spectra were recorded at 80 K and normalized for direct comparison.

2. Experiment

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have shown that the 1.34 eV PIA band is associated with a triplet ($S = 1$) state in the pristine MEH-PPV film. This triplet excitation is completely quenched in the MEH-PPV/C$_{60}$ films for all PIA bands [18]. In addition to the changes in the PIA, the photoluminescence of MEH-PPV is quenched dramatically upon mixing with C$_{60}$ [1]. Finally, the radical ions on both the polymer and C$_{60}$ have been identified using light induced electron spin resonance (LESR) [1].

Upon mixing each of the TCNQ derivatives (1-6) into the MEH-PPV host (5 mol%, films cast from benzonitrile), the changes in the PIA spectrum are similar to those in the C$_{60}$ composites (Fig. 3). The quenching of the photoluminescence is of the same order of magnitude for acceptors 3-5, but notably less for 1 and 2. If one looks closer to the PIA features and to the luminescence quenching quantitatively and correlates them with the electron affinity of the acceptors (e.g. electrochemical reduction potential) a consistent picture emerges as displayed in Figure 4. Studies of the relaxation in the different composites support the argument of electron transfer being more efficient for 3, 4 and 5 than for 1, 2 and 6 [19].

**P3MBET/Acceptor Composites.** — The PIA spectrum of P3MBET exhibits a broad absorption band extending from 1.0 to 1.4 eV (Fig. 5) Although the pump intensity dependences of the PIA bands at 1.1 eV and 1.24 eV are similar ($-\Delta T \propto I^0$), their relaxation behavior as determined from the modulation frequency dependence is different [19]. The 1.1 eV band was assigned to a triplet state photoexcitation in agreement with previous studies on poly(3-alkylthiophenes) [4].
Fig. 4. — Relative luminescence intensity (open markers) of composite films of MEH-PPV with C₆₀ and acceptors 1-6 as a function of their reduction potentials at 80 K (in each case, the luminescence intensity was referenced to that of pristine MEH-PPV). Right-hand axis shows the ratio of the PIA intensity of the bands at 1.34 eV and 1.2 eV (solid markers).

Fig. 5. — PIA spectra of a pristine P3MBET films and a P3MBET/C₆₀ (5 mol%) composite film. The spectra were normalized for direct comparison.

The PIA of a P3MBET/C₆₀ (5 mol%) composite film reveals the absence of the triplet photoexcitation at 1.1 eV, while the band at 1.26 eV remains (Fig. 5). The luminescence of P3MBET/C₆₀ is quenched by about an order of magnitude, much less than in the case
4. Discussion and Conclusion

By measuring the near-steady-state PIA and photoluminescence, we have demonstrated that photoinduced electron transfer from MEH-PPV and P3MBET to different acceptors occurs with different efficiencies.

A first approximation to the relative degree of electron transfer is displayed in Figure 4 using the quenching of photoluminescence and the ratio for the PIA peaks as a quantitative measure of the electron transfer; the efficiency of electron transfer (arbitrary units) is plotted as a function of the electrochemical reduction potentials of the different acceptors. There is consistency between the electrochemical reduction potentials and the electron transfer efficiency from the conjugated polymer donors onto these acceptors. Surprisingly, however, there is
a clear maximum for the electron transfer rate at around $-0.45$ V near the value for $C_{60}$. Further increase of the electron acceptor capability by increasing the reduction potential does not result in an increase in the electron transfer rate, but a decrease! This non-monotonic behavior is qualitatively similar to that predicted by Marcus theory in the so-called “inverted region” [20,21]. Marcus showed that, as the exothermicity of a charge transfer process continues to increase, a “crossing point” will be reached beyond which the transfer rate actually starts to decrease. Although this qualitatively explains the observation displayed in Figure 4, further experimental work is necessary to demonstrate the details of this correlation with the Marcus theory.

It is clear, however, that the electrochemical reduction potential (the electron affinity of the different acceptors) is not the only parameter determining the electron transfer rate. We carried out similar studies with a series of benzoquinone derivatives mixed with conjugated polymer donors. The results were, however, contrary to those obtained with TCNQ derivatives: Photoinduced electron transfer was not observed in any of the studied benzoquinone derivatives. For example, although 1,4-benzoquinone has a similar reduction potential (-0.51 V/SCE) to that of 3, 4, 5, and $C_{60}$, 1,4-benzoquinone does not show any activity upon mixing into the conjugated polymer donor matrix [19]. The origin of this interesting difference in the role of TCNQ and quinone derivatives upon photoexcitation of the conjugated polymer donor matrix in composite films is yet unknown but may have to do with the degree of stability of the radical anion formed upon one-electron reduction of the acceptor.

Charge transfer continues to be centrally important in the study of organic solids. Charge transfer in the ground state leads to the organic metals and superconductors that Igor Schegolev studied for much of his scientific career. Charge transfer in the excited state is analogous to “artificial photosynthesis”; the asymmetry in forward to reverse transfer, although poorly understood, promises to be useful in a wide range of applications ranging from sensitized photoconductivity [3] and enhanced photo-detector response [11,22] to optical limiting [23].

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