Photoinduced charge separation in blends of MEH-PPV with $(Pt_{0,75}C_{60})_n$

A.A. Bakulin, S.G. Elizarov, A.E. Ozimova, and D.Yu. Paraschuk[*]
International Laser Center, Moscow State University, Moscow 119992, Russia

M.V. Tsikalova and Yu.N. Novikov
Institute of Organoelement Compounds, RAS, Vavilov St. 28, Moscow 119991, Russia

S.A. Arnautov and E.M. Nechvolodova
Institute of Chemical Physics, RAS, Kosygin St. 4, Moscow 119991, Russia

Fullerenes and their derivatives in blends with conjugated polymers are well known to be the most effective acceptors in photoinduced charge transfer reaction. In addition, fullerenes in these blends can form a highly conductive network for collection of photoinduced charges that makes fullerenes indispensable in polymer solar cells. However, the active layer of such an optimized cell contains from 45% [1] to 80% [2] of metanofullerene by weight, which weakly absorbs the solar light. In this work, we study a recently synthesized fullerene-based coordination oligomer $(Pt_{0,75}C_{60})_n$ (Fig. 1) as an acceptor for the photoinduced charge separation in the bulk heterojunction. We were motivated that $(Pt_{0,75}C_{60})_n$ chains could facilitate the charge transport in the bulk heterojunction allowing decreasing the fullerene content in it. Here we report on comparative studies of optical and photophysical properties of MEH-PPV/$Pt_{0,75}C_{60}$ and MEH-PPV/C_{60} blends.

$(Pt_{0,75}C_{60})_n$ was synthesized by reaction of C_{60} with $Pt(dba)_2$ (dba=dibenzylideneacetone) at molar ratio $Pt(dba)_2/C_{60}=¾$ according to [3]. The compound was characterized by elemental analysis, IR and Raman spectroscopies. Drop-cast films of MEH-PPV/$Pt_{0,75}C_{60}$ and MEH-PPV/C_{60} blends were prepared from chlorobenzene for various molar donor-acceptor ratio.

Optical absorption spectra of MEH-PPV/$Pt_{0,75}C_{60}$ blends are similar to those of MEH-PPV/C_{60} indicating the absence of essential donor-acceptor interaction in the electronic ground state. Fig. 2 compares the photoluminescence (PL) quenching efficiency in MEH-PPV/$Pt_{0,75}C_{60}$ and MEH-PPV/C_{60} blends. Fig. 2 shows that PL quenching at acceptor content less than 10% is essentially more efficient in MEH-PPV/C_{60} blends implying more efficient initial charge separation.
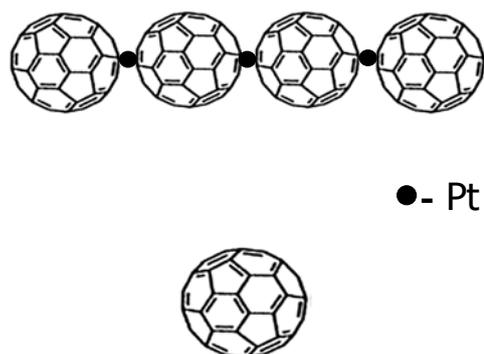

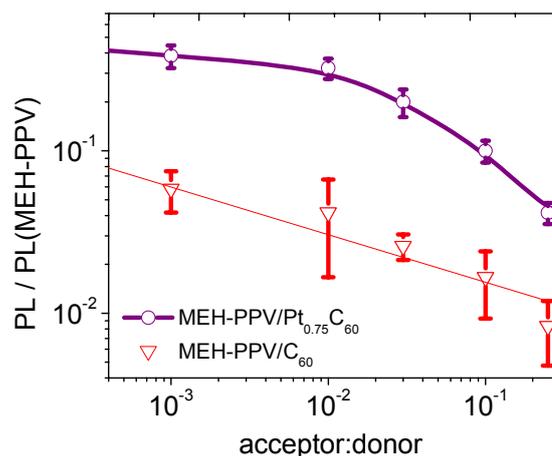Fig. 1. Chemical structure of $(Pt_{0,75}C_{60})_n$ (top) and C_{60} (bottom).

Fig. 2. PL quenching in MEH-PPV/$Pt_{0,75}C_{60}$ and MEH-PPV/C_{60} blends vs acceptor:donor molar ratio referenced to pristine MEH-PPV PL. All values are normalized to absorbed pump power at 532 nm.
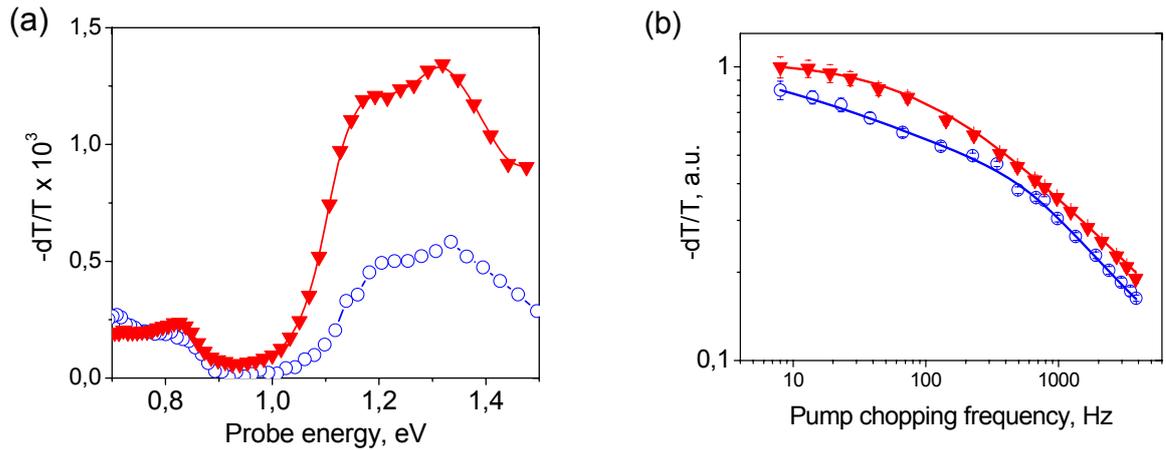
[*] paras@polys.phys.msu.su

Fig. 3. PIA data for 1:0.03 MEH-PPV/Pt$_{0,75}$C$_{60}$ (o) and MEH-PPV/C$_{60}$ (▼) blends photoexcited at 532 with pump intensity 1 W/cm^2 at 110 K. Almost all the pump power was absorbed in the films. (a) PIA spectra for chopping frequency 70 Hz. The lines are a guide to the eye. (b) Normalized frequency dependences for the 1.3 eV band. Solid lines are fits to the data (see the text).

Fig. 3 compares photoinduced absorption (PIA) data in MEH-PPV/Pt$_{0,75}$C$_{60}$ and MEH-PPV/C$_{60}$ blends. Fig. 3a shows that both blends give very similar spectra in which the MEH-PPV polaron band at 1.3 eV dominates indicating that charge separated states are effectively excited in MEH-PPV/Pt$_{0,75}$C$_{60}$ blends. However, the PIA at 1.3 eV in MEH-PPV/C$_{60}$ is ~2 times higher compared to MEH-PPV/Pt$_{0,75}$C$_{60}$ indicating some difference in charge generation efficiency and/or charge recombination in these blends. Fig. 3b shows that the chopping frequency dependencies in MEH-PPV/Pt$_{0,75}$C$_{60}$ and MEH-PPV/C$_{60}$ blends are qualitatively different. The MEH-PPV/C$_{60}$ blend demonstrates a typical "dispersive" frequency dependency fitted by $1/(1+i(2\pi f\tau)^{\alpha})$, where $\alpha=0.44$ and $\tau=12$ ms. In contrast, the frequency dependence in the MEH-PPV/Pt$_{0,75}$C$_{60}$ blend has a characteristic knee (Fig. 3b), and any single "dispersive" kinetics does not give a satisfactory fit to the experimental data. We relate this to the contribution of MEH-PPV triplet excitons in the PIA band at 1.3 eV. In fact, a superposition of "dispersive" ($\alpha=0.35$, $\tau=11$ ms) and monomolecular ($\alpha=1$, $\tau=1.5$ ms) kinetics gives a good approximation to the observed frequency dependence in MEH-PPV/Pt$_{0,75}$C$_{60}$ blend (Fig. 3b). Therefore, our PIA data suggest that MEH-PPV triplet excitons in MEH-PPV/Pt$_{0,75}$C$_{60}$ blends are not completely quenched in contrast to MEH-PPV/C$_{60}$ blends. This is also supported by the PL quenching data in Fig. 2 implying that a part of singlet excitons lives a sufficient time to be converted into triplet excitons via intersystem crossing.

We discuss two factors that could explain the observed difference in photoinduced charge transfer in MEH-PPV/Pt$_{0,75}$C$_{60}$ and MEH-PPV/C$_{60}$ blends: (i) lower electron affinity of (Pt$_{0,75}$C$_{60}$)$_n$ than C$_{60}$ and (ii) more enhanced phase separation observed in MEH-PPV/Pt$_{0,75}$C$_{60}$ blends as compared with MEH-PPV/C$_{60}$ blends.

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3. H. Nagashima, Y. Kato, H. Yamaguchi *et al.*, Chem. Lett., iss.7, 1207 (1994).