

Ultrafast Electron and Hole Dynamics in Novel Conjugated Star-Shaped Molecules

Oleg V. Kozlov^{1,2}, Yuriy N. Luponosov³, Sergei A. Ponomarenko³, Dmitry Yu. Paraschuk²,
Nina Kausch-Busies⁴, Maxim S. Pshenichnikov¹

¹Zernike Institute for Advanced Materials, University of Groningen, Groningen, The Netherlands

²International Laser Center and Faculty of Physics, Moscow State University, Moscow, Russian Federation

³Institute of Synthetic Polymeric Materials of the Russian Academy of Science, Moscow, Russian Federation

⁴Heraeus Precious Metals GmbH & Co. KG, Conductive Polymers Division, Leverkusen, Germany

email: o.kozlov@rug.nl

Abstract: Charge dynamics in organic photovoltaic blends based on novel star-shaped molecules are studied by ultrafast visible-IR spectroscopy. Pathways of intra- and intermolecular electron and hole transfer and their recombination are identified and discussed.

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1. Introduction

Bulk heterojunction organic solar cells (OSCs) based on small molecules (SMs) have recently attracted much attention as a promising alternative to conventional polymer-based OSCs, with the latest sunlight-to-power efficiency of ~10% [1]. SMs-based OSCs combine advantages of polymer OSCs with benefits of small molecules like excellent batch-to-batch reproducibility, well-defined molecular structure and molecular weight, easy mass-scale production, etc. However, because of the novelty of such OSCs, the ultrafast photophysics of initial photogeneration of charges and their subsequent recombination is barely known.

In this contribution, charge generation and recombination processes are studied in photovoltaic blends based on a series of novel star-shaped small molecules [2] as donors and PC70BM as acceptor (Fig 1a). The conjugation length of the star arms is systematically varied by including 1-3 thiophene rings. Charge dynamics are investigated by ultrafast photoinduced absorption (PIA) spectroscopy, using a visible pump to mimic the sun photons and broadly-tunable IR probe to monitor concentration of hole polarons at the SM's conjugated system. We show that the charges in blends with PC70BM recombine via two different channels (intra- and intermolecular), and the efficiency of long-time charge survival depends strongly on the donor:acceptor ratio.

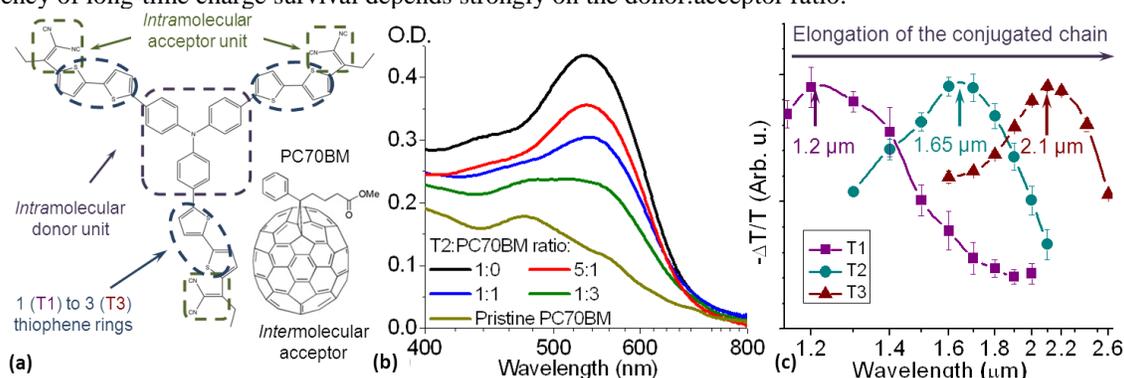


Fig 1 (a) Structure of the star-shaped molecules [2] and the fullerene acceptor. The number of thiophene rings is indicated by a digit after the “T”. (b) Representative absorption spectra of T2-based blends with different donor:acceptor weight content; absorption spectrum of PC70BM film is also shown for comparison. (c) Normalized polaronic spectra of thin films at 3 ps pump-probe delay.

2. Experimental and Results

Blend films were prepared by spin-casting from solutions on a glass substrate. Absorption spectra exhibit a strong absorption peak at ~550 nm (Fig.1b) which is assigned to the intramolecular charge transfer state [3]. For the pump-probe experiments, the wavelength of the pump pulse was set at 550 nm. Fig. 1c shows polaronic spectra [4] of the molecules in the IR region. A red-shift and contraction of the spectra are observed with elongation of the conjugated arm. Importantly, spectral shapes remain unchanged with pump-probe delay time which indicates absence of solvation effects in films (those nonetheless were observed in dichlorobenzene solution but not shown here). This allows us to choose the probe wavelength near the polaronic absorption maxima and consider the PIA response be proportional to the concentration of photogenerated charges.

Figure 2a shows the PIA transients for the T3:PC70BM blends and T3 in toluene solution. In all samples, a fast build-up of the PIA response is observed within the apparatus temporal resolution ($SD \sim 100$ fs) indicating almost instantaneous electron transfer. The PIA response of isolated star-shaped molecules dissolved in toluene decays monoexponentially with ~ 900 ps time which is assigned to *intramolecular* charge recombination. This decay time is strongly solvent-dependent: for instance, it decreases to 500 ps in dichlorobenzene (not shown here).

In the pristine T3 films, PIA decays biexponentially with characteristic timescales of 30 ps and 350 ps, which suggests charge recombination via two independent channels. The contribution of the 30 ps component depends strongly on the PC70BM acceptor content, vanishes completely at high acceptor concentrations, and is independent on the pump flux excluding non-geminate recombination. We assign the 30-ps decay to *intermolecular* (“interstar”) recombination of charges initially separated onto neighboring molecules. The slow 350-ps decay is related to *intramolecular* (“intrastar”) recombination of the charges separated within the same molecule, similarly to the solution case.

In blends with PC70BM, the short-time PIA amplitudes substantially increase (compare neat and 5:1 transients in Fig.2a) but keep on growing only slightly for higher PC70BM concentrations. The abrupt increase indicates a change in the branching ratio between excitons (which are not visible for the IR probe) and polarons. This conclusion was strengthened by time-resolved fluorescence experiments (not shown here). Furthermore, in the blends with high PC70BM concentration the 30-ps decaying component inherited from the pristine phase, is replaced by the ingrowing component with a characteristic time of ~ 3 ps (two upper transients in Fig.2a). Taking into consideration substantial PC70BM absorption (Fig. 1b), we attribute this growth to exciton migration within PC70BM domains with its subsequent dissociation at the donor:acceptor interface, i.e. to the hole-transfer process. This also indicates good intercalation of donor and acceptor domains because otherwise the PC70BM exciton cannot be efficiently harvested (its lifetime is ~ 500 ps).

Figure 2b presents schematics of the charge separation and recombination processes that emerged from our experiments. In pristine T3 films (lower diagram), there are two recombination pathways after charge creation: the interstar one where the charges at two different star-shaped molecules are involved, and the intrastar one where the charges are generated and recombined within the same molecule. When PC70BM is added to the blends (upper diagram), the electron is preferentially transferred to the PC70BM acceptor thereby making the 30-ps interstar channel ineffective. At the same time, the new hole-transfer channel opens due to direct excitation of PC70BM molecules; both processes lead to long-lived separated charges. The unwanted 350 ps component remains even at high PC70BM concentrations albeit with a lower amplitude.

The share of long-lived charges for different PC70BM loading is summarized in Fig.2c. A $>50\%$ survival probability of charges demonstrates that the T2 and T3 star-shaped donors do provide efficient charge separation in blends with PC70BM which makes them prospectively promising donor materials in OSCs.

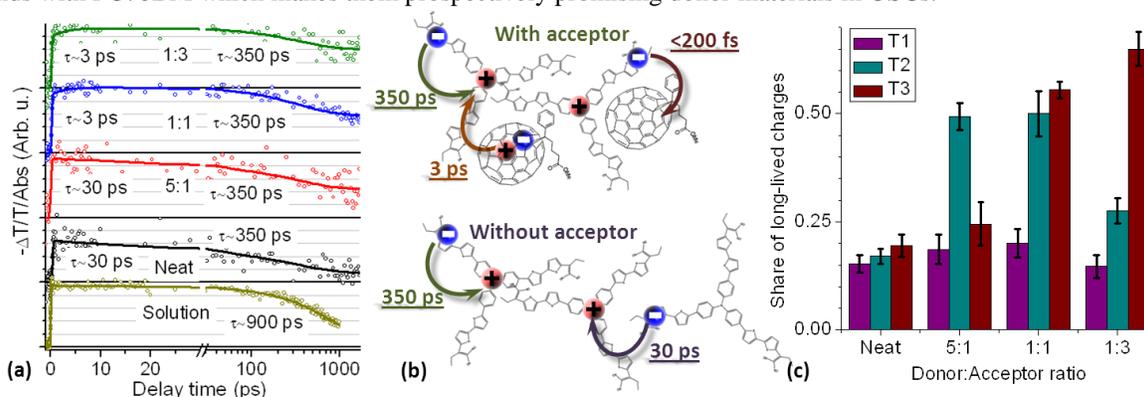


Fig. 2. (a) PIA isotropic transients for films of T3:PC70BM blends with different donor:acceptor concentrations, and for T3 molecule in toluene solution. Transient amplitudes are normalized by film absorption for direct comparison of the amount of generated charges per absorbed photon. Experimental data and biexponential global fits are shown by open circles and solid lines, respectively; the relaxation times are indicated next to the transients. Similar transients were obtained for T1 and T2 molecules. (b) Pictorial representations of charge separation and recombination processes with (upper) and without (lower) PC70BM acceptor. (c) Share of long-lived charges at different PC70BM concentrations.

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