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## Photochemistry of P3HT and PC<sub>60</sub>BM in toluene solution: Evidence of T–T energy transfer



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### ABSTRACT

Photochemical properties of regioregular poly(3-hexylthiophene) (P3HT), fullerene derivative [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PC<sub>60</sub>BM) and their 1:1 mixture in argon-saturated toluene solution were studied by optical spectroscopy and nanosecond laser flash photolysis ( $\lambda_{\text{ex}} = 532 \text{ nm}$ ). Separate excitation of components leads to formation of corresponding triplet state of fullerene ( $^3\text{PC}_{60}\text{BM}^*$ ,  $\lambda_{\text{max}} = 710 \text{ nm}$ ,  $\epsilon_{\text{max}} = 22400 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\varphi_{\text{T}} = 0.29$ ) and polymer ( $^3\text{P3HT}^*$ ,  $\lambda_{\text{max}} = 850 \text{ nm}$ ,  $\epsilon_{\text{T}}^{750 \text{ nm}} \leq 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\varphi_{\text{T}} \geq 0.19$ ). Excitation of P3HT/PC<sub>60</sub>BM mixture leads to effective energy transfer from  $^3\text{P3HT}^*$  to the ground state of fullerene with a formation of  $^3\text{PC}_{60}\text{BM}^*$ . No evidence of ion-radical P3HT<sup>•+</sup> and PC<sub>60</sub>BM<sup>•-</sup> formation was obtained though electron transfer between  $^3\text{P3HT}^*$  and  $^1\text{PC}_{60}\text{BM}$  is energetically favorable in studied system. Presumably ultrafast back electron transfer takes place in geminate P3HT<sup>•+</sup>/PC<sub>60</sub>BM<sup>•-</sup> pair with regeneration of the ground states of P3HT and PC<sub>60</sub>BM.

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### 1. Introduction

Conductive polymers and fullerenes attract undiverted attention now because of possible use of these materials in organic photovoltaics [1–5]. Photochemical processes involving these materials are widely studied mostly in solid polymer/fullerene composites, which are used as active layer of organic solar cells [6]. The majority of transient absorption studies of such composites are devoted to charge formation [7,8] and recombination [9–13]. In some works the triplet state [14] formation is studied [7,15–18]. Ultrafast transient absorption spectroscopy also allows to observe excitation dynamics in polymer/fullerene blends [19,20].

Light-induced processes in liquid solutions of conductive polymers, mainly poly(3-hexylthiophene) (P3HT) [21,22], the benchmark polymer for organic photovoltaics, and fullerenes [23] were addressed only in few works where dynamics of the excited states of these molecules was studied. Also, photo-degradation of polymers was observed in several works [24,25], but possible influence of fullerene on this process was not studied.

The laser flash photolysis study of the solutions containing conjugated polymer and C<sub>60</sub> revealed the efficient triplet states

formation and energy transfer from triplet states of polymer to fullerene [26]. Photochemical processes in solutions containing fullerenes C<sub>60</sub>/C<sub>70</sub> and oligothiophenes of different length/polythiophene were studied in Ref. [27]. The electron transfer involving either triplet state of fullerene or triplet state of oligothiophenes/polythiophene and triplet–triplet energy transfer between fullerene and oligothiophenes/polythiophene were observed. The solvent dependence of the reaction pathway was observed in Ref. [27] in C<sub>60</sub>/polythiophene solution. In polar solvent the electron transfer was dominant; while in nonpolar solvent mainly energy transfer took place. The reason is the smaller stabilization energy of radical-ion pair in nonpolar solvent [27].

Nevertheless, to our knowledge, photochemical processes in solutions containing both P3HT and PC<sub>60</sub>BM, the most popular combination in organic photovoltaics, have not been reported yet. However, these processes may be of importance for production of organic solar cells. This is because polymer/fullerene thin film blends for these devices are usually casted from such solutions [28–30], and during the preparation and production they are illuminated for some extent. Therefore, the possibility of photochemical processes in solutions should be studied.

In the present work light-induced formation of the triplet state of P3HT and PC<sub>60</sub>BM, as well as triplet–triplet energy transfer in this system were studied by nanosecond laser flash photolysis method. The rates of the corresponding processes, the quantum

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yields of the triplet states of P3HT and PC<sub>60</sub>BM and their absorption spectra are determined. The extinction coefficients for these triplet states are accurately measured.

## 2. Materials and methods

PC<sub>60</sub>BM was purchased from Aldrich. Regioregular P3HT with molecular weight approximately 20–40 kDa was received from BASF (Sepiolid P200). Both PC<sub>60</sub>BM and P3HT were used without further purification. Unless otherwise specified, all photochemical experiments were performed in a 1 cm quartz cell in argon-saturated toluene (HPLC grade) solutions, temperature 298 K and atmospheric pressure.

UV absorption spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies). The fluorescence spectra and kinetics were measured on a FLS920 spectrofluorimeter (Edinburg Instrument). As excitation sources ozone free xenon lamp Xe900 ( $\lambda_{\text{ex}} = 375$  nm) and diode laser EPL-375 ( $\lambda_{\text{ex}} = 375$  nm, pulse duration of 75 ps, Edinburg Instruments) were used, correspondingly. Kinetic curves were fitted by iterative reconvolution of one exponential function with the instrument response function, which allows to determine fluorescence lifetimes as short as 50 ps.

The laser flash photolysis setup based on LS-2137U Nd:YAG laser (Lotis TII, Belarus) with excitation wavelength of 532 nm, pulse duration of 5–6 ns, illumination spot area of 0.07 cm<sup>2</sup>, and energy per pulse up to 5 mJ was used for the time-resolved measurements in visible region (400–800 nm); the device was similar to that described in previous work [31]. Time resolution of the setup was ca. 50 ns. Laser intensity was measured by means of SOLO 2 laser power meter (Gentec EO).

Nanosecond time-resolved absorption spectroscopy experiments in near-IR (940–1200 nm) were performed using the original experimental set-up constructed recently in Institute of Chemistry of Saint Petersburg State University. The excitation source was the second harmonic (532 nm, 7 ns, 1.5 mJ per pulse, 10 Hz) of an Nd:YAG laser (SOL instruments Ltd. LF117). A 150 W xenon arc lamp (Newport) was used as the probe source. Transient absorption signals were measured in the transverse geometry in which the probe was made to pass through a 1 cm quartz cell filled with the sample solution. The probe and pump beams had square profiles of 7 × 7 mm size at the sample position. After passage through the samples, the probe beam was dispersed through a double monochromator (Standa MSA-130) and detected using a photomultiplier tube (Hamamatsu H10330A-75) connected to a digital oscilloscope (Agilent Technologies InfiniiVision DS07054B). Data from the digital oscilloscope (3000 averaged scans) were analyzed using Origin 9.0 software.

## 3. Results and discussion

### 3.1. Absorption spectra of P3HT, PC<sub>60</sub>BM and their mixture in toluene solution

Absorption spectra of toluene solutions of P3HT, PC<sub>60</sub>BM and 1:1 mixture of P3HT/PC<sub>60</sub>BM at room temperature are shown in Fig. S1. P3HT exhibit broad single band at 450 nm with absorption coefficient (referred to moles of the P3HT monomer unit, Mw = 169) equals to 6700 M<sup>-1</sup> cm<sup>-1</sup>. Close value was obtained by Cook et al. [22] in chlorobenzene ( $\lambda_{\text{max}} = 455$  nm,  $\epsilon_{\text{max}} = 7800$  M<sup>-1</sup> cm<sup>-1</sup>). PC<sub>60</sub>BM spectrum coincides well with published in [23] with  $\lambda_{\text{max}} = 500$  nm and  $\epsilon_{\text{max}} = 1500$  M<sup>-1</sup> cm<sup>-1</sup>. Absorption spectrum of the P3HT/PC<sub>60</sub>BM 1:1 mixture is an algebraic sum of spectra of separate reagents which indicates absence of interaction between unexcited components (similar to that shown in [27] for

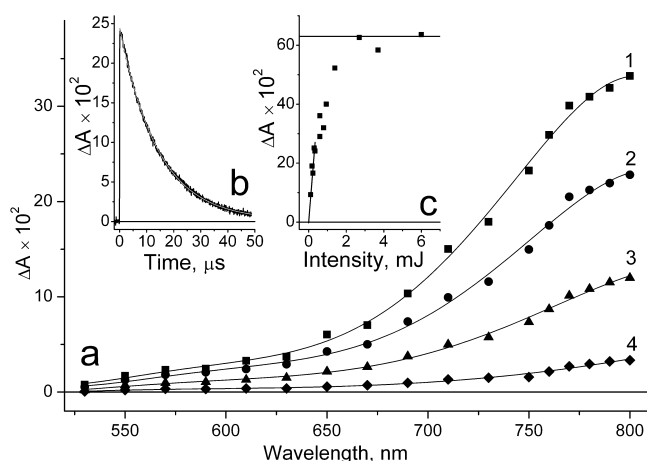
C<sub>60</sub>-P3HT mixture). It worth to note, that the main part of 532 nm light in mixture was absorbed by P3HT (80%).

### 3.2. Quenching of P3HT fluorescence by PC<sub>60</sub>BM

In order to estimate probability of <sup>1</sup>P3HT\* interaction with PC<sub>60</sub>BM in toluene solution the quenching of P3HT (0.25 mg/ml) fluorescence by PC<sub>60</sub>BM (0–7.4 mM) were studied (Fig. S2a,b). The P3HT fluorescence decay without PC<sub>60</sub>BM is practically mono-exponential with the characteristic time of 500 ps in a good agreement with literature data [22]. Linear increase of P3HT fluorescence decay rate with the increase of PC<sub>60</sub>BM concentration allow one to determine corresponding quenching rate constant,  $k_q = 1.3 \times 10^{11}$  M<sup>-1</sup> s<sup>-1</sup> (Fig. S2c). This value is an order of magnitude larger than diffusion-limited reaction rate for small molecules in toluene. Such a large value of apparent quenching rate constant is often explained by association of fluorophore and quencher molecules. However, strong interaction between P3HT and PC<sub>60</sub>BM molecules in toluene solution is unlikely because no new bands or shift of existing bands were observed in absorption spectra upon mixing P3HT and PC<sub>60</sub>BM solutions (data not shown). High quenching rate constant can be caused by large size of P3HT molecule and fast intramolecular excitation diffusion within P3HT chain. The reaction rate constant of similar magnitude was observed for diffusion-controlled triplet energy transfer from biphenyl to conjugated polymer MEH-PPV [32]. Overall, this data allow one to conclude that at concentration of PC<sub>60</sub>BM used in laser flash photolysis experiments ( $< 1.5 \times 10^{-4}$  M) energy and electron transfer from <sup>1</sup>P3HT\* to PC<sub>60</sub>BM could be neglected.

### 3.3. Laser flash photolysis of P3HT

Excitation of argon-saturated solution of P3HT in toluene leads to instant formation of wide transient absorption (TA) band with maximum in near-IR region (>800 nm, Fig. 1a) which decays in microsecond time scale with characteristic time about 14  $\mu$ s (Fig. 1b). The presence of dissolved oxygen decreases the transient lifetime up to 0.16  $\mu$ s. This fact and results of Cook et al. [22] allows to assign this wide band to T–T absorption of polymer (<sup>3</sup>P3HT\*,  $\lambda_{\text{max}} = 850$  nm in dichlorobenzene [22,27]). The monoexponential TA decay kinetics typical for triplet states on conjugated polymers [33] was observed. Yield of T–T absorption at 750 nm exhibits linear dependence on excitation energy at laser intensity less than



**Fig. 1.** (a) TA spectra of P3HT (0.25 g/L) in argon-saturated toluene solution recorded at 0.05 (1), 4 (2), 10 (3) and 22 (4)  $\mu$ s after the laser excitation (532 nm, 0.23 mJ/pulse, 95% of light was absorbed by P3HT). (b) The kinetic curve of transient absorption decay at 750 nm with the best exponential fit with  $\tau = 14$   $\mu$ s. (c) Dependence of the yield of T–T absorption at 750 nm upon laser excitation energy.

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