

Förster resonance energy transfer and charge transfer dynamics in ternary organic nanoparticles

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ABSTRACT

Binary and ternary organic nanoparticles (NPs) comprising 7,7-(4,4-bis(2-Ethylhexyl)-4H-silolo [3,2-b:4,5-b'] dithiophene-2,6-diyl)bis (6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo-[c] [1,2,5]thiadiazole) (p-DTS (FBTTH₂)₂), poly (3-hexylthiophene) (P3HT) or/and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) were prepared by precipitation method. The formation of the organic NPs is confirmed by the atomic force microscope (AFM). The absorption spectra show that the blended organic NPs display increased interchain interactions compared to the polymer blends dissolved in the solution. The processes of exciton separation and charge transfer in the organic NPs have been investigated using time-resolved photoluminescence (TRPL) spectroscopy and anisotropy measurements. The results demonstrate that the charge transfer efficiency is improved in the NPs in comparison with that in solution, due to the enhanced interchain interactions and intimate contact between the donor and acceptor materials in NPs. Due to Förster resonance energy transfer (FRET) between P3HT and p-DTS(FBTTH₂)₂, the photodetectors with ternary NPs in the active layers exhibit improved on/off ratios and enhanced detectivity compared with the binary system, demonstrating the promising applications of organic NPs in the ecofriendly fabrication of organic optoelectronic devices.

1. Introduction

Organic photodetectors have been widely applied in sensing and optical communications [1]. However, one critical concern of such organic devices is the need for conventional flammable and toxic chlorinated solvents such as chloroform, chlorobenzene or *o*-dichlorobenzene to process the photoactive layer. Recently, increased efforts have been devoted to developing devices based upon organic nanoparticulate, which offers advantages over customary solution processing, e.g. the opportunity to print active layers from environmental-benign ethanol or aqueous dispersions rather than the hazardous organic solvents. D'Olieslaeger et al. has achieved a power conversion efficiency of 3.8% using water-based PBDTPD:PC₇₁BM nanoparticles (NPs) dispersions [2], implying the possibility of ecofriendly organic optoelectronic devices by large area roll-to-roll printing technique [3–5].

For the organic fluorescence photodetectors/sensors, it is challenging to achieve broadband coverage when only a single donor polymer is used in a binary system, due to the typically discrete band structure of

organic polymers. A paradigm of ternary phases is a feasible approach to fulfill the wide-range absorption requirements. In the ternary architecture, a third component with complementary absorption is incorporated into a binary donor: acceptor blend, leading to a broad absorption range [6]. In addition, Förster resonance energy transfer (FRET) may also be introduced into the ternary organic semiconductor systems to further boost the photo-response performance if the two donors can serve appropriately as energy donor and energy acceptor, respectively. Using the precipitation method, Shimizu et al. prepared stable aqueous dispersion of poly (3-hexylthiophene) (P3HT) [7]. Darwis et al. obtained NPs suspension comprising P3HT and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) in ethanol and achieved a power conversion efficiency of 1.1% in organic solar cells [8].

In this work, an organic small molecule material (p-DTS(FBTTH₂)₂) was selected to form NPs, individually or together with P3HT and PC₇₁BM. Unitary NPs composed of p-DTS(FBTTH₂)₂ or P3HT, binary NPs comprising p-DTS(FBTTH₂)₂:P3HT or p-DTS(FBTTH₂)₂:PC₇₁BM, and p-DTS(FBTTH₂)₂:P3HT:PC₇₁BM ternary NPs have been fabricated. The influence of the involvement of p-DTS(FBTTH₂)₂, which has a

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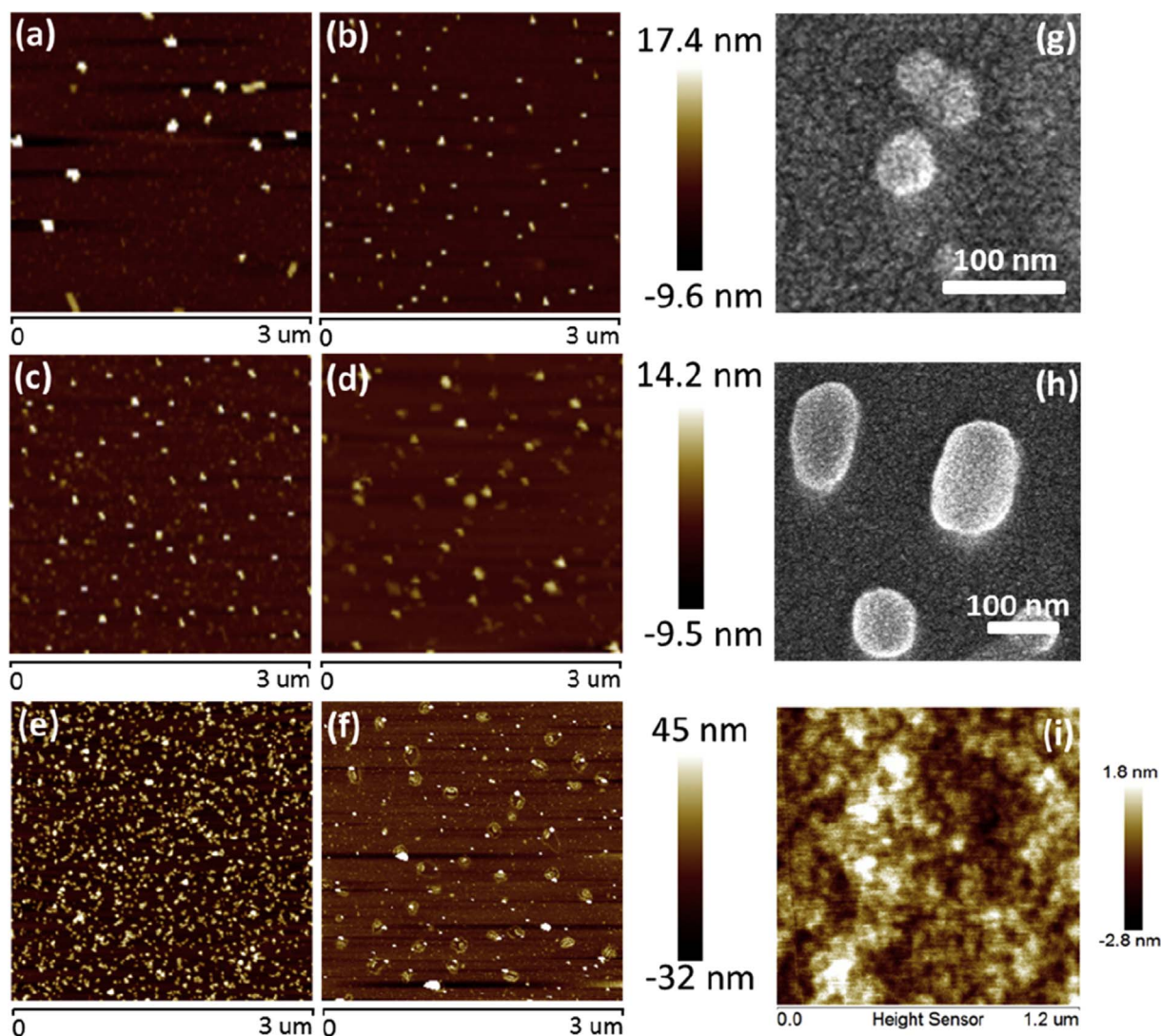


Fig. 1. AFM images of (a) larger and (b) smaller p-DTS(FBTTH₂)₂ NPs, (c) P3HT NPs, (d) p-DTS(FBTTH₂)₂:P3HT NPs, (e) p-DTS(FBTTH₂)₂:PC₇₁BM NPs and (f) ternary p-DTS(FBTTH₂)₂:P3HT:PC₇₁BM NPs. (g) and (h) SEM images of smaller/larger p-DTS(FBTTH₂)₂ NPs. (i) AFM image showing the coverage of the ternary NPs film after spincoating.

complementary absorption with respect to the P3HT and PC₇₁BM system, to the fluorescence sensors based on the ternary NPs has been studied. The energy transfer and charge transfer dynamics of the NPs were investigated by time-resolved photoluminescence (TRPL) spectroscopy and anisotropy.

2. Experimental

2.1. Nanoparticle preparation

p-DTS(FBTTH₂)₂, P3HT and PC₇₁BM were purchased from 1-Material, Sigma Aldrich, Nano-C Inc., respectively, and used as received without further purification. The P3HT had a M_w of ~40 kDa and a polydispersity of 2.4. The organic NPs were obtained using a precipitation method, which has been described elsewhere [9,10]. 5 mg of P3HT, p-DTS(FBTTH₂)₂ and PCBM were dissolved in 2 ml of chloroform, respectively. Unitary NPs were obtained by introducing 1 ml of the P3HT (or p-DTS(FBTTH₂)₂) solution into 5 ml of the poor solvent water under vigorous stirring. To prepare p-DTS(FBTTH₂)₂:P3HT binary NPs, P3HT solution was first added into p-DTS(FBTTH₂)₂ solution. Subsequently, 1 ml of the mixed solution was dropped into 5 ml of water. The p-DTS(FBTTH₂)₂:P3HT:PC₇₁BM ternary NPs were fabricated likewise with a weight ratio of 0.2:1:1. Sonication was applied to all of

the resultant NPs solutions for 3 min.

2.2. Physical characterization of the nanoparticles

Atomic force microscopy (AFM, NanoScope IIIA) measurements were performed on films spin-cast on glass substrates to confirm the formation and analyze the topography of the organic NPs. The absorption spectra were recorded using an UV–visible dual beam spectrophotometer (TU-1900, PG Instruments, Ltd.). The steady-state PL spectra were obtained by an emission spectrometer (PG2000 Pro, Idea Optics Inc.). Time-resolved photoluminescence (TRPL) decay profiles were measured by means of the fluorescence time correlated single photon counting (TCSPC) technique. The excitation light with wavelength of 400 nm was generated from the frequency doubling of a femtosecond Ti:sapphire (Maitai HP, Spectra Physics) at 80 MHz.

3. Results and discussion

In this work, the small molecule material p-DTS(FBTTH₂)₂ was selected to function synergistically with the polymer P3HT both as donors because their absorption ranges are complementary and the energy transfer between them may promote the exciton dissociation and free charge carrier generation [11]. Furthermore, the addition of small

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