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Excited-state dynamics of an amphiphilic diblock copolymer self-assembled from mixed solvents

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ABSTRACT

An amphiphilic diblock-copolymer consisting of poly(3-hexylthiophene) and poly(4-vinylpyridine) has been synthesized and self-assembled from mixed selective solvents of tetrahydrofuran and methanol to produce nanostructures having photoluminescence spanning from the blue to the red. The emission decay times of the nanostructures have been found to increase with the fraction of methanol, suggesting that the probability of the nongeminate recombination of relaxed S_1 excitons decreases with the increase of medium polarity. The emission decay times are shorter at 690 nm than at 650 nm, indicating that two-dimensional interchain effect is more important for the 0–1 vibronic transition than for the 0-0 transition. The initial intensity percentage of the fast component of biphasic emission decay is much larger with excitation at 532 nm than with excitation at 355 nm, suggesting that other charge carriers such as polarons are generated rapidly from S_1 excitons in competition with vibrational relaxation.

1. Introduction

The fabrication and characterization of nanostructured materials having functional properties have been widely explored due to their potential applications in the field of nanotechnology [1–4]. Among numerous nanostructured materials, conjugated polymers have been extensively studied for applications in optoelectronic devices such as light-emitting diodes, biosensors, and photovoltaic cells because of their advantages such as lightweight, flexibility, processability, roll-to-roll production, low cost, and large area [5–8]. In spite of these diverse advantages, organic solar cells containing active layers based on conjugated polymers have not been commercialized well due to their low power-conversion efficiency [9]. Thus, many research groups have diversely reported solutions such as the synthesis of low-band-gap conjugated polymers [10], the functionality enhancement of conjugated polymers [11], the development of new device-fabrication processes [12], and the fabrication of hybrid nanocomposites composed of inorganic nanoparticles and organic conjugated polymers [13,14] in order to overcome this low-efficiency problem. In particular, amphiphilic diblock copolymers consisting of a rod-shape polymer such as poly(3-hexylthiophene) (P3HT), which is most commonly used in optoelectronic devices, have received intense attention for applications in photovoltaic cells because of their excellent optical and transport properties highly dependent on their nanoscale morphology, which is also tunable facilely with selective solvents [15,16]. Since a rod-shape polymer and a coil-shape polymer are covalently linked in an amphiphilic diblock copolymer, compared to conjugated homo polymers and polymer blends, amphiphilic diblock copolymers can be spontaneously separated into two different transport channels of a well-ordered or amorphous structure on the nano-sized scale, facilitating the migration of charge carriers to improve optoelectronic device performances [17]. Quasi-living polymerization methods such as atom transfer radical polymerization (ATRP) [18], ring-opening metathesis polymerization (ROMP) [19], and reversible addition-fragmentation chain transfer polymerization (RAFT) [20] have been reported numerously as synthetic strategies of amphiphilic diblock copolymers consisting of P3HT.

The aggregates of conjugated polymers can be distinguished by two types of fundamental electronic interactions: intrachain head-to-tail (HT) through-bond interactions lead to J-aggregate behaviors and interchain Coulombic head-to-head (HH) interactions lead to H-aggregate behaviors [21]. When interchain HH order is dominant in H-aggregate nanofibers (NFs), the 0-0 electronic transition is forbidden by symmetry ($\Sigma\mu = 0$) and less intense than the 0–1 vibronic sideband, giving rise to 0–0/0–1 intensity ratios

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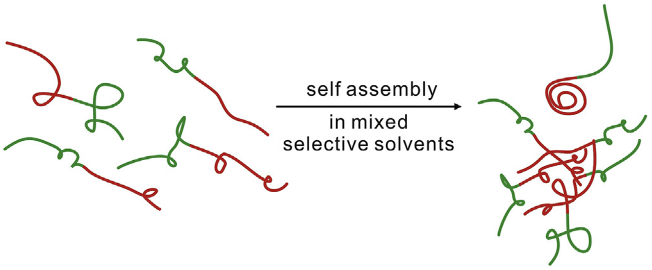
smaller than 1. In contrast, when intrachain HT order is dominant in J-aggregate NFs, the 0-0 transition is allowed ($\Sigma\mu \neq 0$) and more intense than the 0–1 vibronic sideband, thus giving rise to 0–0/0–1 intensity ratios larger than 1 [21–25].

Diverse recent spectroscopic studies on various assembled types of pristine P3HT and amphiphilic diblock copolymers consisting of P3HT have shown that the formation and decay of charge carriers such as excitons and polarons are strongly dependent on the conformation and packing behaviors of P3HT chains [22–24,26–35]. However, many aspects of the photophysical properties of amphiphilic diblock copolymers self-assembled in mixed selective solvents remain still unclear. In this paper, we present that an amphiphilic diblock copolymer (P3HT-*b*-P4VP) consisting of a rod-shape poly(3-hexylthiophene) block and a coil-shape poly(4-vinylpyridine) block has been synthesized by the RAFT polymerization of 4-vinylpyridine using a trithiocarbonate-terminated P3HT as a macro-RAFT agent (Scheme S1) [20]. The mixed-solvent method [36] has been used to fabricate self-assembled nanostructures in a dilute solution by adding methanol (MeOH) as a poor solvent to tetrahydrofuran (THF) (Scheme 1). The emission colors of self-assembled P3HT-*b*-P4VP nanostructures have been facilely tuned from the blue to the red by altering the fraction of MeOH in mixed solvents of MeOH and THF. It has been found that the emission of P3HT-*b*-P4VP around 480 nm is enormously stronger and decays much more slowly in a 5:1 (v/v) mixture solution of MeOH and THF than in a 1:5 (v/v) mixture solution of MeOH and THF, indicating that the conjugation length of P3HT is extensively reduced in a polar solvent. Meanwhile, emission around 650 nm originates from the 0-0 transition of aggregated chains associated with J-type (intrachain) aggregation while emission around 690 nm is due to the 0–1 vibronic transition of aggregated chains associated with H-type (interchain) aggregation. The emission decay times of self-assembled P3HT-*b*-P4VP have been found to be shorter at 690 nm than at 650 nm, indicating that two-dimensional interchain effect inducing the nongeminate recombination of relaxed S_1 excitons is stronger in H-type aggregates than in J-type aggregates.

2. Experiment

2.1. Synthesis

The detailed synthetic and characterization procedures of hydroxypropyl-terminated poly(3-hexylthiophene) (P3HT-OH) with 98% regioregularity ($M_n = 10{,}400$ g mol^{-1}, PDI = 1.13, MALDI-MS $m/z = 6960$) have already been reported [33], and 3-benzylsulfanylthiocarbonylsulfanylpropionic acid chloride (RAFT agent) was synthesized as previously described [20]. Amphiphilic diblock copolymer P3HT-*b*-P4VP consisting of P3HT and poly(4-vinylpyridine) (P4VP) was synthesized *via* the RAFT polymerization of 4-vinyl pyridine using a trithiocarbonate-terminated P3HT as a macro-RAFT agent (Scheme S1), as described in a previous report [20]. Since the molar weights of the repeating units of P3HT and P4VP are 166 and 105 g/mol, respectively, the weight fraction of the P4VP block in P3HT-*b*-P4VP has been estimated as 0.60. The molecular weight of P3HT-*b*-P4VP calculated by the ^{1}H NMR spectrum of Fig. S1 is 16,762 g/mol. For the fabrication of self-assembled nanostructures in mixed solvents, 0.1 mg of P3HT-*b*-P4VP was completely dissolved in 3.0 mL of THF of a nonselective solvent at room temperature. Then, MeOH as a quantitative selective polar solvent of the P4VP block was added into the limpid orange-colored P3HT-*b*-P4VP solution to reach a certain volume ratio of MeOH to THF (*R*). The mixture solution was turned into a homogeneous transparent violet-colored solution and incubated in an argon glove box at room temperature for a day to generate self-assembled P3HT-*b*-P4VP nanostructures.



Scheme 1. Schematic for the fabrication of P3HT-*b*-P4VP nanostructures self-assembled from mixed selective solvents, where the red and the green indicate P3HT and P4VP, respectively.

2.2. Characterization

^{1}H (500 MHz) and ^{13}C (125 MHz) spectra were acquired in $CDCl_3$ using a Varian/Oxford As-500 spectrometer. Size-exclusion chromatography (SEC) was performed using a Waters system consisting of a 1515 pump and a 2414 refractive-index detector and a Shodex GPC LF-804 column. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded using an Applied Biosystems Voyager-DE STR biospectrometry workstation. Transmission electron microscopy (TEM) images were obtained using a Hitachi H7600 microscope; a TEM sample was prepared by evaporating and drying a colloidal droplet on a carbon-coated copper grid in an argon glove box at room temperature. Absorption spectra were measured with a Scinco S3100 UV/vis spectrophotometer, and emission spectra were obtained using a home-built fluorometer consisting of a 75 W Acton Research XS 432 Xe lamp with an Acton Research Spectrapro150 monochromator of 0.15 m and an Acton Research PD438 photomultiplier tube attached to an Acton Research Spectrapro300 monochromator of 0.30 m. Picosecond emission kinetic profiles with excitation of 355 or 532 nm pulses from a mode-locked Quantel YG901-10 Nd:YAG laser of 25 ps were detected using a Hamamatsu C2830 streak camera of 10 ps attached to a Princeton Instruments RTE128H CCD detector. Emission wavelengths were selected using combined band-pass and cut-off filters. Emission kinetic constants were extracted by fitting measured kinetic profiles to computer-simulated kinetic curves convoluted with instrument temporal response functions.

3. Results and discussion

The molar and weight fractions of the P4VP block in P3HT-*b*-P4VP were estimated by measuring ^{1}H NMR spectra (Fig. S1) [15b]. The measured integration value of the two aromatic protons of the P4VP signal in the range of 6.70–6.10 ppm (4.82) relatively to the integration value of the aromatic proton of the P3HT signal at 6.98 ppm has indicated that the mole fraction of the P4VP block in P3HT-*b*-P4VP is 0.69. Fig. 1 shows that P3HT-*b*-P4VP chains in a 1: 1 (v/v) mixed solvent of MeOH and THF are self-assembled into nanoparticles having an average diameter of 14.5 ± 1.5 nm. It is suggested that the nanoparticles have P3HT@P4VP core-shell nanostructures because, in mixed solvents of MeOH and THF, the hydrophilic P4VP block is likely to be exposed at the exterior positions and the hydrophobic P3HT block is likely to be aggregated at the interior positions. Fig. S2 shows TEM images of P3HT-*b*-P4VP nanostructures self-assembled in mixed solvents of *R* = 2.0 and 5.0. TEM images of P3HT-*b*-P4VP nanostructures self-assembled in mixed solvents of *R* = 1.0, 2.0, and 5.0 (Fig. 1 and S2) indicate that an