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Highly Tunable Photoluminescent Properties of Amphiphilic Conjugated Block Copolymers

Sang-Jae Park, Seung-Gu Kang, Michael Fryd, Jeffery G. Saven, and So-Jung Park*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Received January 18, 2010; E-mail: sojungp@sas.upenn.edu

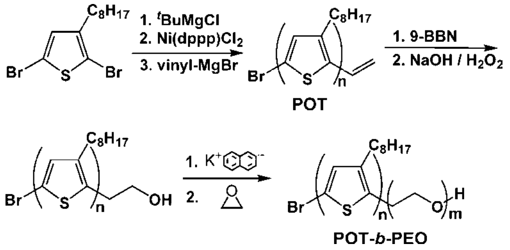
Abstract: We report a novel class of amphiphilic conjugated block copolymers composed of poly(3-octylthiophene) and poly(ethylene oxide) (POT-*b*-PEO) that exhibit highly tunable photoluminescence colors spanning from blue to red. POT-*b*-PEO self-assembles into various well-defined core/shell-type nanostructures as a result of its amphiphilicity. The self-assembly structure can be readily controlled by altering the solvent composition or by other external stimuli. The color change was completely reversible, demonstrating that the strategy can be used to manipulate the light-emission properties of conjugated polymers in a highly controllable manner without having to synthesize entirely new sets of molecules.

Conjugated polymers have emerged as an important class of materials that can replace inorganic semiconductors for a range of applications, including solar cells and light-emitting diodes owing to their excellent optoelectronic properties and processability.[1] In contrast to their inorganic counterparts, conjugated polymers exhibit complicated optical and transport properties that are highly dependent on their nanometer-scale morphology and impurities.[2] While these phenomena open critical problems for device fabrication, they offer a unique opportunity for creating new tunable and responsive materials.

Here, we synthesized a novel amphiphilic block copolymer composed of a widely used conjugated polymer, poly(3-octylthiophene), and a hydrophilic polymer, poly(ethylene oxide) (POT-*b*-PEO), in order to manipulate the morphology and properties of polythiophene in a highly controllable manner. In this approach, the molecular packing and nanoscale morphology of polythiophene can be controlled by utilizing the ability of block copolymers to self-assemble into a variety of well-defined nanostructures. Importantly, the supramolecular assemblies of POT-*b*-PEO exhibit highly tunable photoluminescence (PL) colors spanning from blue to red depending on the self-assembly structure. Various rod−coil block copolymers containing π-conjugated oligomers and polymers have been synthesized previously.[3−10] However, most previously reported amphiphilic molecules, including block copolymers of oligothiophenes and polyethylene oxides, show spectral red shifts associated with polymer aggregation, which are usually accompanied by significant PL intensity drops.[11] We believe our work is the first to report a wide range of PL colors obtained through the self-assembly of conjugated block copolymers.

The POT-*b*-PEO block copolymers were synthesized by initiating the anionic ring-opening polymerization of ethylene oxide (EO) at the end of hydroxyl-terminated POT (Scheme 1). The hydroxyl-terminated POT was synthesized following a literature procedure developed by McCullough and co-workers.[12] The number-average molecular weight (M_n) and polydispersity index (PDI) of POT were determined to be 3017 g/mol and 1.24 by matrix-assisted laser desorption/ionization (MALDI) spectroscopy. Subsequently, the anionic ring-opening polymerization of EO was initiated at the hydroxyl end group of POT using potassium naphthalide as an initiator, producing POT-*b*-PEO. The final product was purified by precipitation with cold diethyl ether (4 °C) and filtration. The M_n of POT-*b*-PEO was 4700 g/mol by ^{1}H NMR analysis, and the PDI was 1.45 by gel-permeation chromatography. The degree of polymerization (DP) was calculated to be 15 and 38 for POT and PEO, respectively.

Scheme 1. Synthesis of POT-*b*-PEO Block Copolymers



The synthesized POT-*b*-PEO block copolymers were dispersible in a wide range of solvents because of the amphiphilic nature of the polymers (Figure 1). In nonselective good solvents such as tetrahydrofuran (THF), POT-*b*-PEO exists mostly as isolated

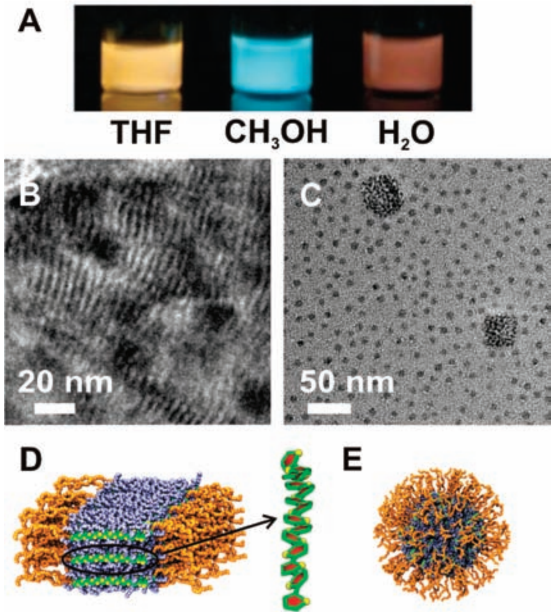


Figure 1. (A) Distinct emission colors of POT-*b*-PEO in three different solvents under UV illumination. (B, C) TEM images of POT-*b*-PEO assemblies in (B) methanol and (C) water. (D, E) Structural models showing PEO (orange), the octyl side chain (blue), and the polythiophene backbone (carbon, green; sulfur, yellow) for (D) methanol and (E) water samples.

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molecules and shows emission properties similar to those of homopolymers of POT, emitting orange-colored light under UV illumination (Figure 1A). In selective polar solvents such as water and methanol, POT-*b*-PEO self-assembled into core/shell-type nanostructures with POT in the core and PEO in the shell, exposing hydrophilic PEO at the exterior. As shown in Figure 1C, spherical assemblies were formed in water along with ordered superstructures of the spherical assemblies. In methanol, POT-*b*-PEO self-assembled into a fiberlike structure (Figure 1B). Both isolated and bundled fibers were observed. The distinct morphologies observed in water and methanol can be explained by the relative volume change in different solvents: as the relative volume of PEO becomes smaller in methanol,[13] POT-*b*-PEO forms fiberlike assemblies with less interfacial area.[14]

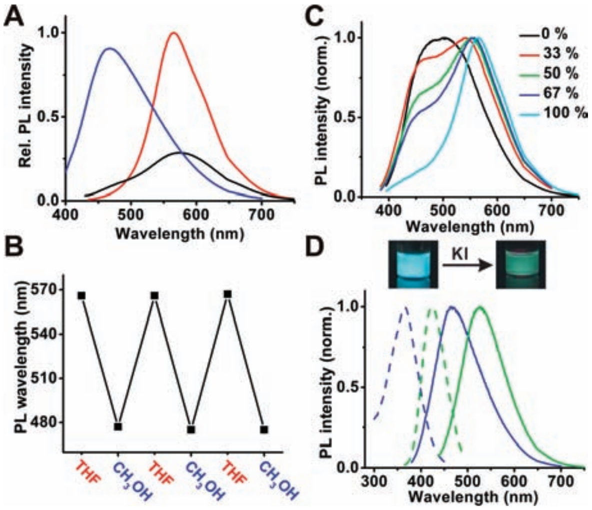

Figure 2. (A) PL spectra of POT-*b*-PEO (0.35 g/L) in THF (red, $\lambda_{\text{exc}} = 419$ nm), methanol (blue, $\lambda_{\text{exc}} = 364$ nm), and water (black, $\lambda_{\text{exc}} = 396$ nm). Each sample was excited at its corresponding excitation maximum. (B) Reversible PL wavelength changes in THF and methanol ($\lambda_{\text{exc}} = 380$ nm). (C) PL spectra of POT-*b*-PEO block copolymers in THF/methanol solvent mixtures at a series of different THF volume percentages ($\lambda_{\text{exc}} = 380$ nm). (D) Excitation (dashed) and emission (solid) spectra of POT-*b*-PEO block copolymers in methanol (blue) without and (green) with KI (0.07 M).

Remarkably, the light-emitting properties of POT-*b*-PEO were highly dependent on the self-assembly structure (Figure 2). Aqueous suspensions of POT-*b*-PEO assemblies showed a red-colored emission under UV illumination (Figure 1A) with a slightly red-shifted spectrum due to energy transfer to low-energy sites[15] in the packed POT strands (Figure 2A). The red shift was accompanied by reduced PL intensity. The spectral red shift and decrease in quantum yield are well-documented phenomena of conjugated polymer aggregates and thin films.[11,16] Interestingly, POT-*b*-PEO showed a drastic color change in methanol and exhibited a strong blue emission (Figures 1A and 2A). The PL quantum yields (QYs) of the assemblies in methanol and isolated molecules in THF were determined to be 12 and 18%, respectively, showing that the QY remains relatively high in the self-assembled structure in methanol. This behavior is distinct from the significantly reduced QYs shown for aggregates of other conjugated amphiphiles.[4,17] In addition, the assemblies in methanol absorb light more strongly than isolated molecules in THF (Supporting Information). Both the relatively high QY and the high absorption coefficient contribute to the strong PL intensity of the assemblies in methanol. The spectral blue shift in the assembly structure is attributed to the reduced conjugation length caused by rotational defects (i.e., disruption of planarity by twists) in the assembly structure. Consistent with this hypothesis, there was no well-defined vibronic structure at the absorption edge, which typically appears in well-packed polythiophene aggregates (Figure S3).[18] The simple solvochromic effect cannot account for the observed spectral shift, as POT homopolymers exhibit a red-shifted spectrum in methanol/THF mixtures because the polymer adopts a more planar conformation in poor solvents (Figures S4 and S5). In addition, the emission wavelength of the methanol sample varied with the excitation wavelength (Figure S6), indicating a distribution in conjugation lengths. This observation also supports our structural model that the POT segment possesses a distorted conformation and reduced conjugation lengths in the fiberlike assemblies (Figure 1D).

The color changes were completely reversible. As shown in Figure 2B, POT-*b*-PEO exhibited reversible color changes when repeatedly dried and redispersed in different solvents. The reversible changes in emission color were also observed when the solvent compositions were gradually altered (Figure 2C). These results clearly indicate that the emission property changes are indeed due to the morphological transitions of the block copolymer assemblies and do not arise as a result of covalent chemical modifications such as photooxidation.

The emission wavelengths of POT-*b*-PEO could be further manipulated by other external stimuli. It is well-known that PEO effectively captures metal ions through ion−dipole interactions.[19] When a KI solution was added to the methanol solution of POT-*b*-PEO, a gradual blue-to-green PL color change was observed (Figure 2D), demonstrating a potential use of POT-*b*-PEO as an analytical tool for metal ions.

In summary, we have developed a versatile way to manipulate the light-emission properties of conjugated polymers through precise control of their assembly structure based on the block copolymer approach. Supramolecular self-assembly has been extensively explored for the past decade as a way to tune the properties of molecule-based materials. However, much of the research has been focused on making complex molecular architectures rather than utilizing the correlation between the structure and properties. The present study has shown that a wide range of PL colors can be obtained without altering the molecular structure, clearly demonstrating that self-assembly can be used as a way to manipulate the properties of materials in a highly controllable fashion.

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Supporting Information Available: Experimental details, ^{1}H NMR data, DLS data, UV−vis extinction spectra, and PL spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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