

## Supporting Information

### 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

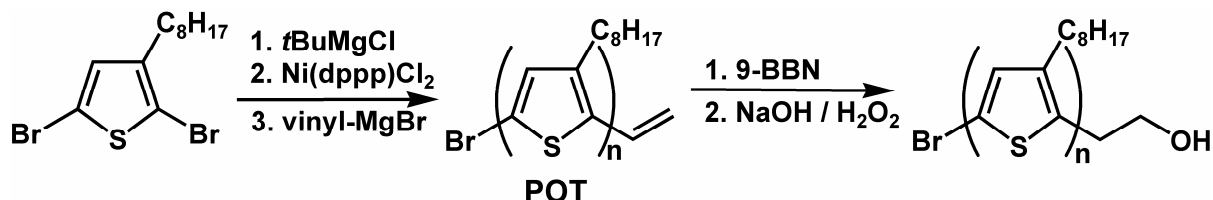
#### Detailed synthetic procedures for the block-copolymer composed of poly(3-octylthiophene) (POT) and polyethylene oxide (PEO)

**Materials:** Methanol, hexanes, and chloroform were purchased from Fisher Scientific. All other reagents were purchased from Aldrich. Distilled THF was used for the synthesis of poly(3-octylthiophene) to ensure anhydrous reaction conditions, and all other reagents were used without further purification.

**Instrumentation:**  $^1\text{H}$  NMR spectra were obtained using Bruker 500 MHz spectrometer in  $\text{CDCl}_3$  solvent. Chemical shifts were reported in ppm relative to the solvent residual proton ( $\delta = 7.24$ ). GPC measurements were carried out at room temperature on a Shimadzu LC-10AT liquid chromatography system equipped with a PLgel 10 $\mu\text{m}$  10E6A column and SPD-10AVvp absorbance UV/VIS detector. THF was used as the eluent at a flow rate of 1.0 mL/min. Calibration was based on polystyrene standards (Polymer Standards Service). MALDI-TOF MS (Voyager) was used to measure molecular weights in positive mode. The matrix used was 2, 2':5, 2''-terthiophene (Aldrich). Fluorescence emission measurements were recorded with a Fluorolog<sup>®</sup>-3 spectrofluorometer (HORIBA Jobin Yvon, Inc.) utilizing an R928 PMT detector. Transmission electron microscopy (TEM) was performed on a JEOL TEM-2010F operating at 200 kV accelerating voltage.

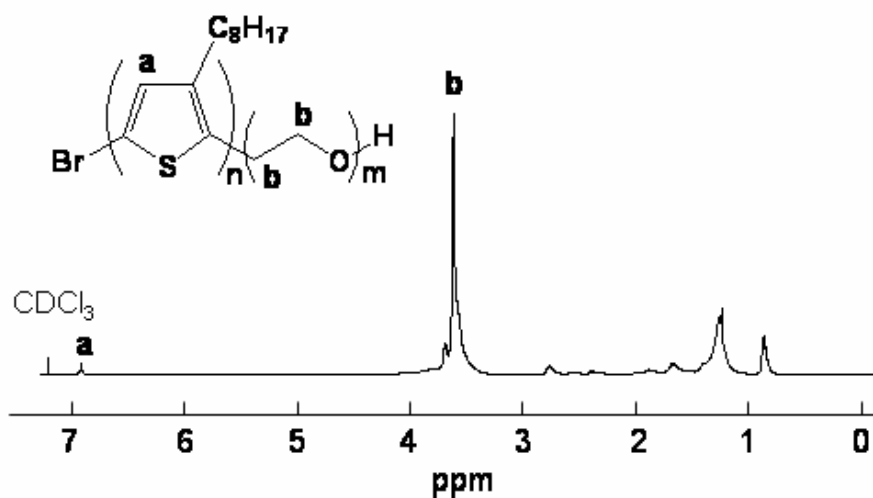
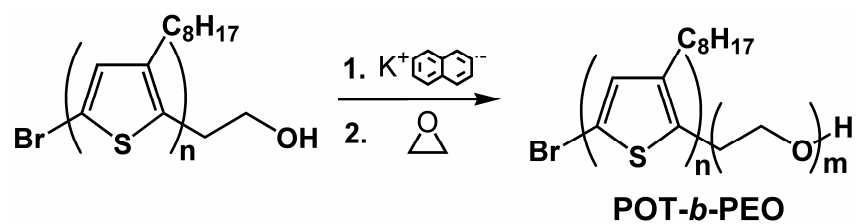
**Synthesis of hydroxyl-terminated POT:** The hydroxyl-terminated POT was synthesized following a previously reported method (Scheme S1).<sup>[1, 2]</sup>

**Scheme S1.** Synthesis of hydroxyl-terminated POT.

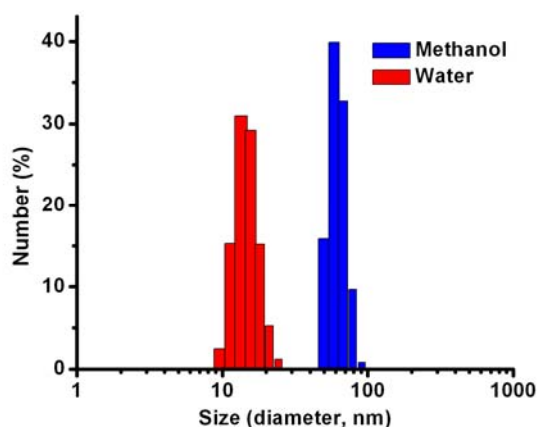


**Synthesis of POT-*b*-PEO block-copolymers:** The POT-*b*-PEO was synthesized by initiating the anionic ring-opening polymerization of ethylene oxide (EO) at the end of hydroxyl-terminated POT (Scheme S2). The hydroxyl-terminated POT (55 mg) was dissolved in 15 mL of anhydrous THF in a 100 mL reaction flask under inert atmosphere. Potassium naphthalide (0.02 mL, 0.95 M in THF) was added to the solution via syringe. After stirring the mixture for 20 min, the solution was cooled to 0 °C in an ice bath. Liquid ethylene oxide (10 mL) was transferred via cannula to the reaction mixture and the mixture was slowly warmed up to room temperature. After stirring the solution for 48 h at room temperature, the reaction was terminated by the addition of HCl (0.02 mL, 1.0 M in diethyl ether). Excess cold diethyl ether was poured into the solution to precipitate the product. The precipitates were recovered by filtration and redissolved in chloroform. The undissolved solid in chloroform was removed by filtration. Chloroform was then removed via rotary evaporator, and the remaining POT-*b*-PEO product was dried in a vacuum oven overnight. Yield: 40 %, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 0.87 (t, 3H, *J* = 6.85 Hz), 1.27 (m, 10H), 1.67 (m, 2H), 2.78 (t, 2H, *J* = 6.75 Hz), 2.98 (t, 2H, *J* = 7.09 Hz), 3.60 (s, 214H), 4.29 (2H, t, *J* = 4.18 Hz), 6.97 (1H, s).

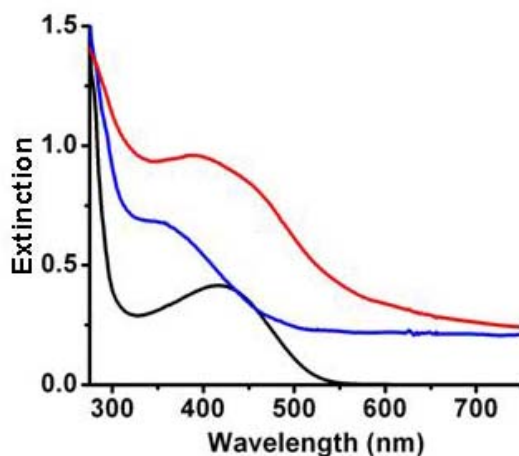
**Scheme S2.** Synthesis of POT-*b*-PEO block-copolymers.



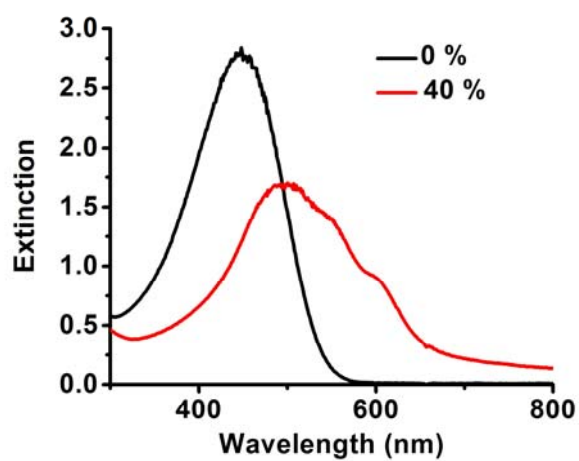
**Figure S1.** <sup>1</sup>H NMR spectrum of POT-*b*-PEO in CDCl<sub>3</sub>. The unlabeled peaks upfield of 3.0 ppm are associated with the octyl side chain of the polymer.



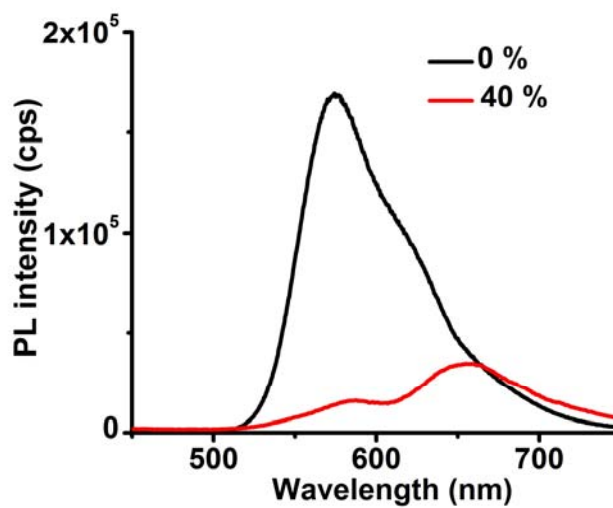
**Figure S2.** Number distributions of POT-*b*-PEO assemblies in methanol and water measured by dynamic light scattering (DLS). The samples were filtered with syringe filters (0.2  $\mu\text{m}$  pore size, Cellulose Acetate filter media) prior to the DLS measurements. Intensity distributions indicated the presence of larger aggregates with multiple peaks at 17 nm, 64 nm, and 370 nm for the water sample and 65 nm and 330 nm for the methanol sample.



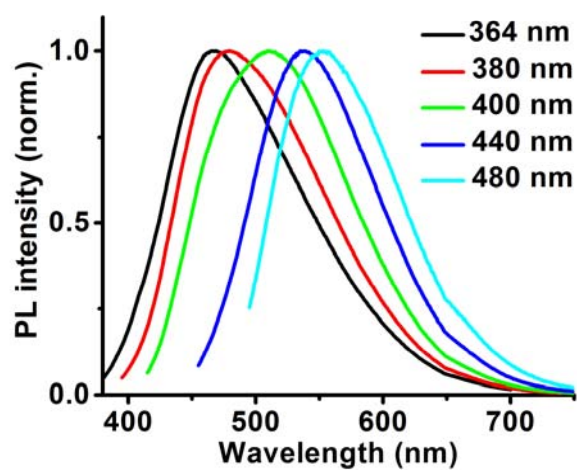
**Figure S3.** UV/Vis extinction spectra of POT-*b*-PEO (3.2 g/L) in THF (black), methanol (blue), and water (red). The absorption peak position is blue-shifted for the methanol sample due to the reduction of the conjugation length. The tails in the long wavelength range of the methanol and the water samples indicate the formation of large assemblies of conjugated block-copolymers and are consistent with TEM and DLS results.



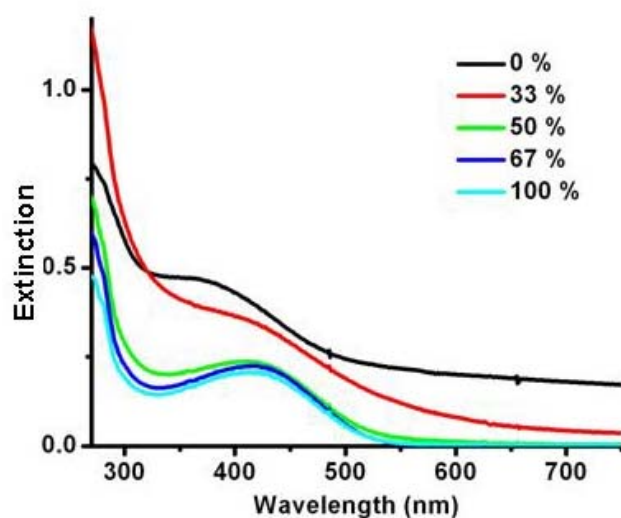
**Figure S4.** UV/Vis extinction spectra of POT homopolymers (1.5 g/L) in THF/methanol mixtures at different methanol volume percents.



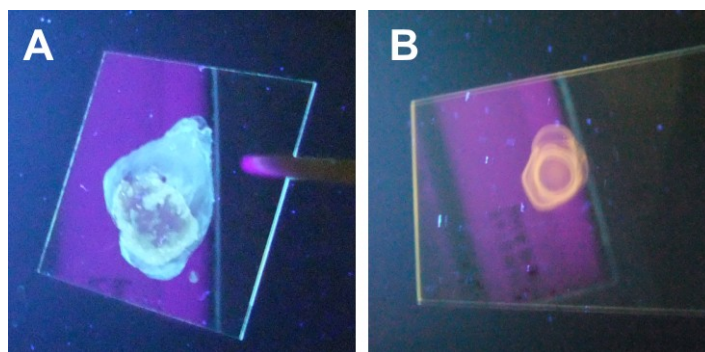
**Figure S5.** PL spectra of POT homopolymers in THF/methanol solvent mixtures at different methanol volume percents.



**Figure S6.** PL spectra of POT-*b*-PEO assemblies in methanol at a series of different excitation wavelengths. The emission peak position shifts with excitation wavelengths indicating that there is a distribution in conjugation lengths.



**Figure S7.** UV/Vis extinction spectra of POT-*b*-PEO (1.8 g/L) in THF/methanol solvent mixtures at a series of different THF volume percent.

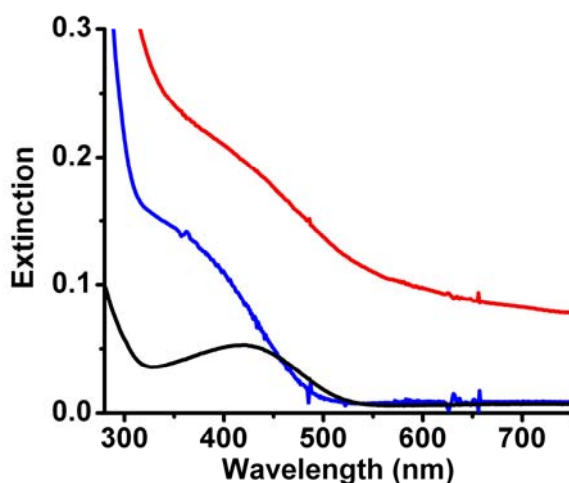


**Figure S8.** Drop-cast films of POT-*b*-PEO assemblies in methanol (A) and water (B). The assemblies in methanol and water were co-deposited with PEO and poly(vinyl alcohol), respectively as matrix materials.

### Quantum Yield Measurements

The quantum yields of POT-*b*-PEO in THF, methanol, and water were determined following the typical procedure described in our previous report.<sup>[3]</sup> Coumarin 102 (ethanol) with QY of 95 %<sup>[4]</sup> was used as a standard for all three samples. UV-vis and PL spectra were obtained for a series of dilute samples of POT-*b*-PEO in different concentrations. The absorbance was kept lower than 0.055 for all QY measurements to avoid the self-quenching. The methanol samples were excited at 364 nm, and THF and water samples were excited at 400 nm. The entire set of measurements was repeated three or four times for each sample. The quantum yields were determined to be  $18 \pm 1.3$ ,  $12 \pm 1.3$ , and  $1.6 \pm 0.33$  % for THF, methanol, and water samples, respectively. The actual QY of the water sample should be somewhat higher than the determined value of 1.6 % because the potential effect of light scattering on the extinction and the PL spectra was ignored in the QY estimation. Scattering was not significant for the methanol sample at low concentrations used for quantum yield measurements as indicated by the low extinction at the long wavelength range (Figure S9). Note that the QY of the assemblies in methanol remains relatively high. In addition, the absorbance measured at the

same concentration is higher for the methanol sample than the THF sample (Figure S9). Thus, both the relatively high QY and high absorption contribute to the strong PL intensity of the assemblies in methanol.



**Figure S9.** UV/Vis extinction spectra of POT-*b*-PEO at a low concentration (0.25 g/L) in THF (black), methanol (blue), and water (red). Extinction coefficients were estimated to be  $1300 \text{ M}^{-1}\text{cm}^{-1}$  at 419 nm and  $3100 \text{ M}^{-1}\text{cm}^{-1}$  at 364 nm for isolated block-copolymers in THF and the assemblies in methanol, respectively.

## References

- [1] M. Jeffries-El, G. Sauve, R. D. McCullough, *Macromolecules* **2005**, 38, 10346.
- [2] M. C. Iovu, M. Jeffries-El, E. E. Sheina, J. R. Cooper, R. D. McCullough, *Polymer* **2005**, 46, 8582.
- [3] T. V. Duncan, S. -J. Park, *J. Phys. Chem. B* **2009**, 113, 13216.
- [4] G. Jones, M. A. Rahman, *J. Phys. Chem.* **1994**, 98, 13028.