Supplementary Material (ESI) for Chemical Communications

Supporting Information

Polymeric Vesicles with a Hydrophobic Interior Formed by Thiophene-Based All-Conjugated Amphiphilic Diblock Copolymer

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1. Experimental Details

Materials. 2-bromo-3-hexyl-5-iodothiophene and 3-(3,6,9,12-tetraoxatridecanyl)thiophene were synthesized following previous literatures.[a,b] All other chemicals were phased from Sigma-Aldrich Co, Junsei Co and used without purification except tetrahydrofuran (THF) which was purified using a J. C. Meyer solvent dispensing system.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 (300 MHz) FT NMR system operating at 300 MHz and 75 MHz, respectively. High resolution mass spectra were obtained from Deagu Branch Analytical Laboratory of the Korea Basic Science Institute (high resolution mass spectrometer; JEOL JMS 700 model). Elemental analyses were performed by Organic Chemistry research center (Elemental analyzer; CE Instruments Flash EA 1112 series). Differential scanning calorimetric (DSC) measurements of the polymers were performed using a Perkin-Elmer Pyris 1 DSC instrument under a nitrogen atmosphere at a heating and cooling rate of 10 °C/min and only that of BP3 was 3 °C/min due to slow thermal behavior of this polymer. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a gel permeation chromatography (GPC) with SHIMADZU LC solution with chloroform eluent using a calibration curve of polystyrene standards. The UV-Vis absorption spectra were measured with a Mecasys Optizen Pop UV/Vis spectrophotometer and photoluminescence (PL) spectra of the copolymers were measured on a Jasco FP-6500 spectrometer. Transmission electron microscopy (TEM) (S-7600, Hitachi) was operated at 60kV. For laser scanning confocal microscopy, fixed cells were examined with a Zeiss LSM 510 META laser scanning confocal microscope (Jena) using C-APOCHROMAT (×40/1.2 W numerical aperture water immersion lens) in the multitrack mode. Excitation/emission wavelengths were 488nm. Transmitted light reference images were captured using differential interference contrast optics and argon laser illumination at 488 nm. The atomic force microscope was measured using DI, Nanoscope III with tapping mode.

2. Synthesis of Monomers and Copolymers.

2-bromo-3-(3,6,9,12-tetraoxatridecanyl)thiophene (2). 3-(3,6,9,12-Tetraoxatridecanyl) thiophene (10.0g, 36.4mmol) were dissolved in 200ml of tetrahydrofuran (THF) and temperature of the solution was decreased to 0°C. To this solution, N-bromosuccinimide (NBS) (6.49g, 36.4mmol) dissolved in 50ml of THF was dropwised and stirred overnight at 0°C. The THF was removed under reduced pressure and residue was poured into water and extracted three times with ethyl acetate. The organic layer was washed with 10% $NaHCO_3$ aq. and dried by $MgSO_4$. Solvent was removed by evaporation under reduced pressure and remaining yellow colored liquid was purified by silica gel column chromatography (hexane : ethyl acetate (v/v) = 6:4) to give pure product (10.4g, yield : 80.9%). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) : δ 7.17 (d, *J*=5.7 Hz, 1H); 6.86 (d, *J*=5.7 Hz, 1H); 3.58-3.46 (m, 14H); 3.29 (s, 1H); 2.78 (t, *J*=6.9 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): δ 138.74; 129.08; 125.69; 110.18; 72.31; 71.00; ; 70.95; 70.88; 70.62; 70.54; 59.36; 30.29. MS (EI+,m/z) [M]+ calcd for $C_{13}H_{21}BrO_4S$ 353.27, found 353.29. Elemental analysis calcd (%) for $C_{13}H_{21}BrO_4S$: C 44.20, H 5.99, S 9.08 ; found : C 44.20, H 6.04, S 9.01.

2-bromo-5-iodo-3-(3,6,9,12-tetraoxatridecanyl)thiophene (M2). 2-Bromo-3-(3,6,9,12-tetraoxatridecanyl)thiophene (7.21g, 20.4mmol) were dissolved in 200ml of dichloromethane and temperature of the solution was decreased to 0 °C. To this solution, iodine (2.69g, 10.6mmol) and iodobenzene diacetate (3.69g, 10.6mmol) were successively added and mixture was stirred overnight at room temperature. The reaction was quenched by adding $Na_2S_2O_3$ aq. and extracted three times with dichloromethane and washed with distilled water. Organic layer was dried by $MgSO_4$ and solvent was removed by evaporation under reduced pressure. Residue was purified by silica gel column chromatography (hexane : ethyl acetate (v/v) = 6:4) to give slightly yellow liqiud (7.43g, yield : 76.0%). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) : δ 7.05 (s, 1H); 3.65-3.52 (m, 14H); 3.36 (s, 1H); 2.81 (t, *J*=6.6 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): δ 141.17; 138.85; 113.12; 72.35; 71.55; 71.07; 71.05; 70.98; 70.93; 70.69; 70.34; 59.44; 30.05. MS (EI+,m/z) [M]+ calcd for $C_{13}H_{20}BrIO_4S$ 479.17, found 479.19. Elemental analysis calcd (%) for $C_{13}H_{20}BrIO_4S$: C 32.59, H 4.21, S 6.69 ; found : C 32.48, H 4.19, S 6.71.

P3HT. To a 50 mL one-neck flask containing compound M1 (746 mg, 2 mmol) and lithium chloride (84.8 mg, 2 mmol) in anhydrous THF (20 mL), was added 2M isopropyl magnesium chloride in THF(1 mL, 2mmol) and the mixture was stirred at room temperature. After 1h, $Ni(dppp)Cl_2$ catalyst (10.8mg, 0.02mmol) dispersed in THF (20 mL) was added in one portion and mixture was heated up to 50 °C and stirred for 12h. All this procedures were performed in a glove box filled with N_2 atmosphere. The reaction was quenched by adding 5M of HCl aq. and extracted three times with chloroform. The organic layer was dried by

$MgSO_4$ and solvent was removed by evaporation under reduced pressure. The cold hexane was added and the insoluble residue was collected to give purple solid (232mg, 68.9%). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) : δ 6.98 (s, 1H); 2.81 (t, *J*=7.5 Hz, 2H); 1.71 (br, 2H); 1.36 (br, 6H); 0.91 (t, *J*=6.6 Hz, 3H).

PEGT. Following the procedure described above, M2 (0.958 mg, 2 mmol) afforded the yellow oil (201 mg, 36.6%). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) : δ 7.07 (s, 1H); 3.65 (br, 12H); 3.55 (br, 2H); 3.35 (br, 3H); 3.10 (br, 2H).

BP26. To a 50 mL one-neck flask containing compound M1 (187 mg, 0.500 mmol) and lithium chloride (21.2 mg, 0.500 mmol) in anhydrous THF (5 mL), was added 2M isopropyl magnesium chloride in THF(0.250 mL, 0.500mmol) and the mixture was stirred at room temperature for 1h (solution A). In the other flask, M2 (719mg, 1.50mmol) was reacted with 2M isopropyl magnesium chloride in THF (0.750mL, 1.50mmol) following the same means with solution A (solution B). Ni(dppp)Cl_2 catalyst (10.8mg, 0.02mmol) dispersed in THF (20 mL) was added in one portion to solution A and mixture was stirred for 1h. Prepared solution B was added to solution A through syringe and resulting solution was heated up to 50 °C and stirred for 12h. All this procedures were performed in a glove box filled with N_2 atmosphere. The reaction was quenched by adding 5M of HCl aq. and extracted three times with chloroform. The organic layer was dried by $MgSO_4$ and solvent was removed by evaporation under reduced pressure. The cold hexane was added and the insoluble residue was collected to give dark brown sticky solid (187 mg, 37.4%). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) : (based on integral of proton at 4-position of P3HT block = 1) δ 7.07 (br, 3.07H); 6.98 (br, 1H); 3.67 (br, 37.96H); 3.54 (br, 7.54H); 3.35 (br, 9.83H); 3.10 (br, 5.687H); 2.81 (t, *J*=7.5 Hz, 2H); 1.71 (br, 2H); 1.36 (br, 6H); 0.91 (t, *J*=6.6 Hz, 3H).

RP. To a 50 mL one-neck flask containing compound M1 (187 mg, 0.500 mmol), M2 (719mg, 1.5 mmol) and lithium chloride (84.8 mg, 2 mmol) in anhydrous THF (20 mL), was added 2M isopropyl magnesium chloride in THF(1 mL, 2mmol) and the mixture was stirred at room temperature. After 1h, Ni(dppp)Cl_2 catalyst (10.8mg, 0.02mmol) dispersed in THF (20 mL) was added in one portion and mixture was heated up to 50 °C and stirred for 12h. All this procedures were performed in a glove box filled with N_2 atmosphere. The reaction was quenched by adding 5M of HCl aq. and extracted three times with chloroform. The organic layer was dried by $MgSO_4$ and solvent was removed by evaporation under reduced pressure. The cold hexane was added and the insoluble residue was collected to give purple solid (220mg, 44.4%). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) : δ 7.07-6.98 (m, 2H); 3.77 (br, 2.63H);

3.67-3.60 (br, 15.0H); 3.52 (br, 3.03H); 3.35 (br, 4.40H), 3.11 (br, 2.25H); 2.79 (br, 1.33H); 1.69 (br, 1.39H); 1.48-1.30 (br, 4.13H); 0.91 (br, 2.08H).

3. Additional TEM images and UV and PL Spectra.

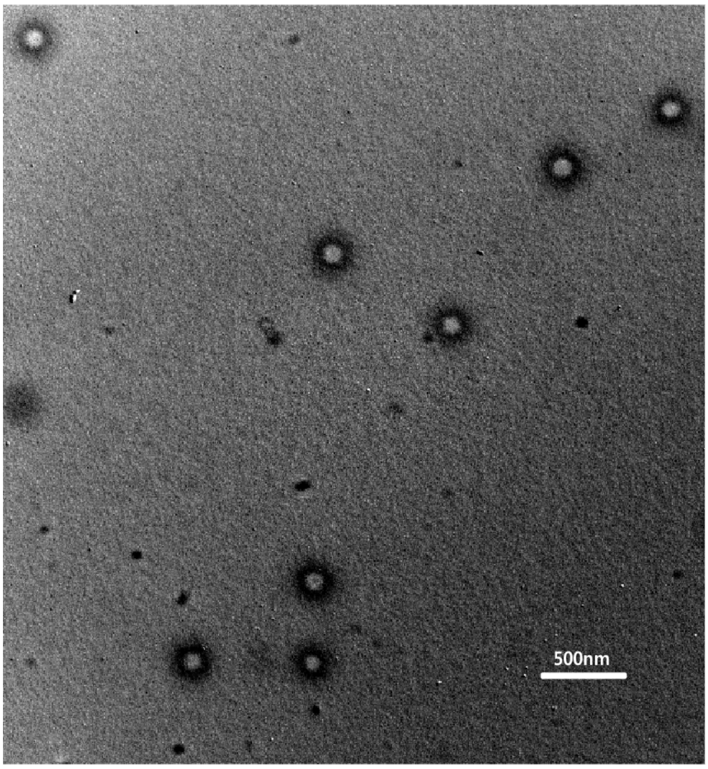

Fig. S1 TEM image of self-assembled aggregates from **BP26** in methanol.

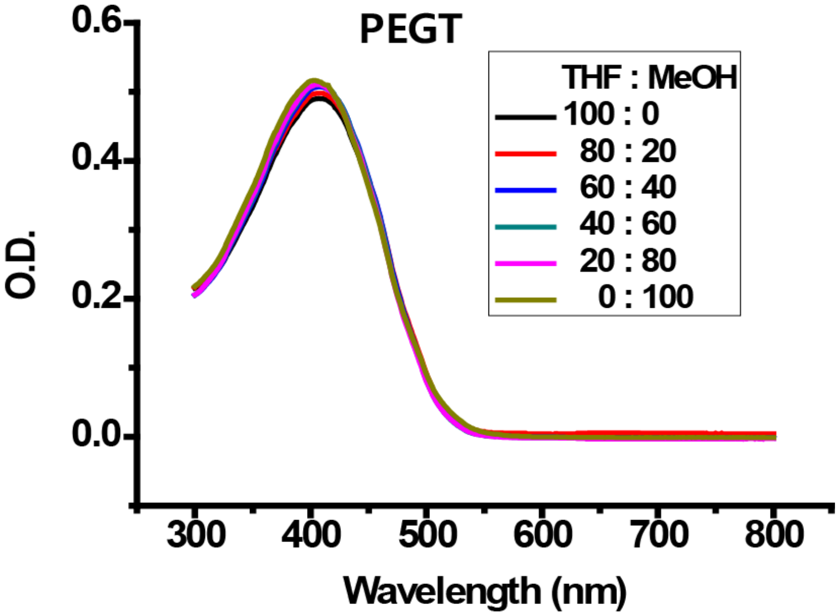

Fig. S2 Absorption spectra obtained from titration of THF solution of **PEGT** with methanol.

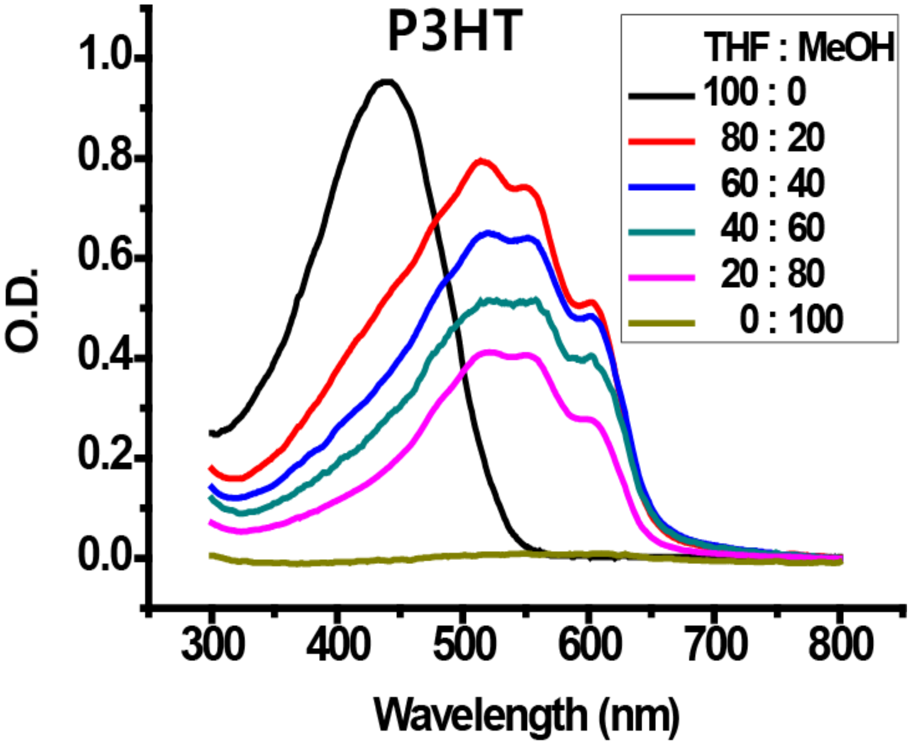

Fig. S3 Absorption spectra obtained from titration of THF solution of **P3HT** with methanol.

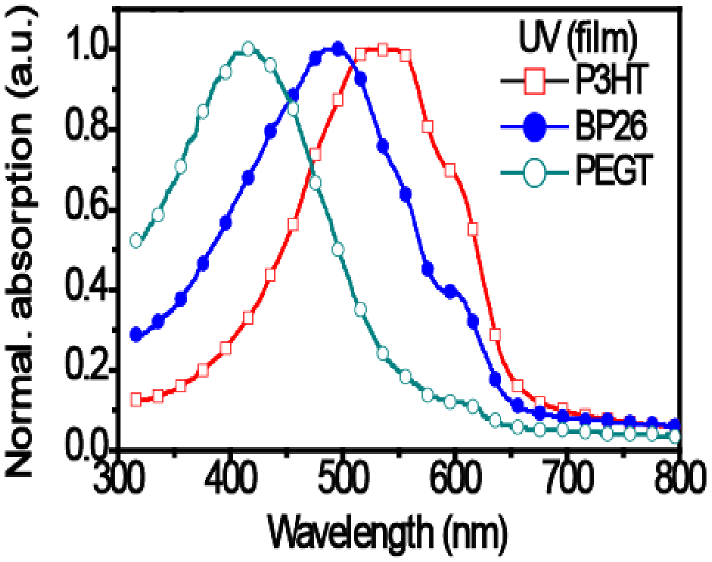

Fig. S4 Absorption spectra of **P3HT** (—□—), BP26 (—●—) and **PEGT**(—○—) in film.

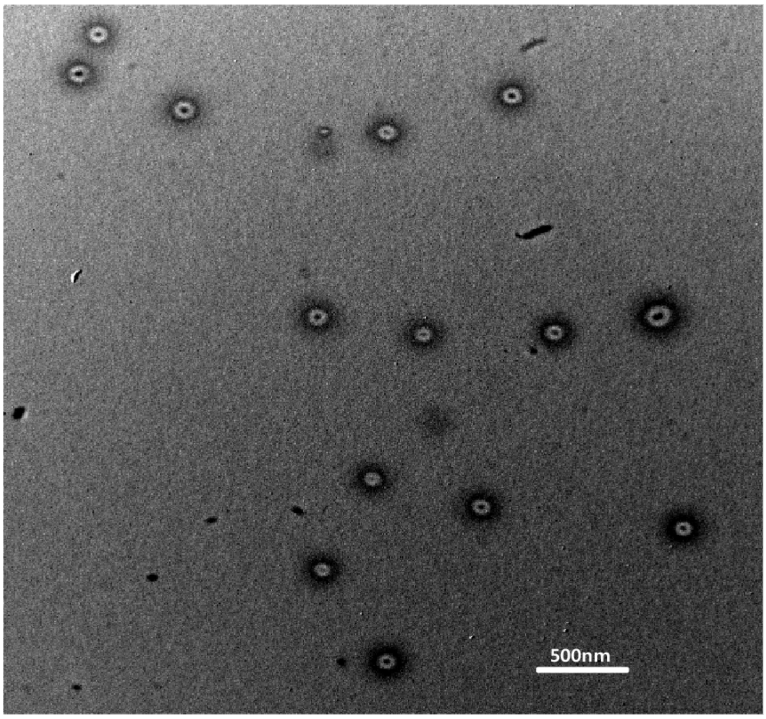

Fig. S5 TEM image of self-assembled co-aggregates from a mixture solution of **BP26** and **PF** in methanol.