Electronic Supplementary Information

Continuous Fibrils from the Self-Assembly of Monochelic Polymeric Porphyrin and PEGylated Fullerene

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Materials

Pyrrole, benzaldehyde, p-hydroxybenzaldehyde and azobisisobutyronitrile (AIBN, 99%), were purchased from Sigma-Aldrich. *N*, *N*-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), polyethylene oxide (PEO, M_n = 2000 g mol^{-1}), styrene were purchased from Aladdin-chemicals and used as received. AIBN was recrystallized from acetone twice. Styrene was used after washing with NaOH aq., drying with CaH_2 and finally distilling at 30˚C under reduced pressure. Fullerene (C_{60}, 99.5%) was purchased from Bucky, USA and used as received. All the solvents and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.

Characterization

^{1}H-NMR spectra were recorded at 400 MHz, using BRUKER AV400 spectrophotometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference. TOF-MS was performed using a Waters LCT Premier XE spectrometer, while the vario EL III Element Analyzer was used for Elemental analysis. Gel permeation chromatography (GPC) measurements were performed with Styragel HR3-HR4 (7.8×300 mm) columns equipped with Waters 1515 isocratic HPLC pump and Waters 2414 Refractive Index Detector with flow rate of 1 mL/min, and the instrument was calibrated using polystyrene standards. Absorption spectra were recorded at SHIMADZU UV-2550 UV spectrophotometer using in quartz Cuvette with 1 cm beam path length, and emission spectra were recorded at Varian's Cary Eclipse fluorescence spectrophotometer at 420 nm as excitation wavelength. Dynamic light scattering (DLS) measurements were carried out on NICOMP TM 380ZLS of PSS-NICOMP particle sizer systems, USA.Transmission electron

microscopy (TEM) images were taken on a JEOL JEM1400 / JEOL JEM2100 electron microscopes operated at 100 / 200 KV with carbon-coated copper grid and the HRTEM. Scanning electron microscopy (SEM) images were recorded with Hitachi S-4800, Japan. The SEM sample were prepared by drying 10 μL droplet of solution onto freshly cleaved mica, and were coated with gold nanoparticles before analysis for SEM. Thermo gravimetric analysis (TGA) were performed over PerkinElmer Pyris Diamond TG/DTA analyzer. The sample (3–5 mg) was heated in nitrogen at a rate of 10 °C/min from 100 to 900 °C. Fourier transform infrared (FTIR) spectroscopy was carried out on Nicolet Nexus 670 FTIR spectrometer using KBr pellets.

Synthesis

Synthesis of 5-(4'-hydroxyphenyl)-10, 15, 20-triphenyl porphyrin, TPP-OH

Porphyrin derivative TPP-OH was synthesized by condensation of freshly distilled pyrrole (5 mL, 72 mmol), benzaldehyde (5.49 mL, 54 mmol) and 4-hydroxybenzaldehyde (2.19 g, 18 mmol) in refluxing propionic acid according to the literature.[1] After washing with methanol the bluish color filtrate was purified by silica gel column with chloroform/methanol (95/5) to afford 0.41 g, yield 3.6%. ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 8.86 (m, 8H), 8.21 (m, 8H), 8.08 (d, 2H), 7.75 (m, 9H), 7.22 (d, 2H), -2.77 (s, 2H).

Synthesis of monochelic triphenyl porphyrin chain transfer agent (MTPP-DDAT)

S-1-dodecyl-*S*´-(α,α´-dimethyl-α"-acetic acid) trithiocarbonate (DDAT) was synthesized by reported method.[2] DDAT (0.232 g, 0.635 mmol) and TPP-OH (0.1 g, 0.16 mmol) were then dissolved in dichloromethane (DCM) (20 mL) and dimethylformamide (DMF) (1 mL) under N_2. After 30 min, 4-dimethylaminopyridine (DMAP, 0.019 g, 0.16 mmol) was added into the reaction mixture in ice-bath, and stirred for another 30 min, and then DCM solution of *N*, *N*-dicyclohexylcarbodiimide (DCC, 0.131 g, 0.635 mmol) was added in portions and allowed to stir at room temperature for 15 h under nitrogen atmosphere. The mixture was then washed with DCM/H_2O and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography using DCM as eluent and dried under vacuum at room temperature for 24 h to afford 0.08 g, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm: 8.85 (s, 8H), 8.21 (d, 8H), 7.76 (m, 8H), 7.51 (m, 3H), 3.39 (t, 2H), 2.01 (s, 6H), 1.22 (m, 20H), 0.83 (t, 3H), -2.7 (s, 2H). TOF-MS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{61}H_{61}N_4O_2S_3$, 977.3957; found, 977.3967. Anal. Calcd: C,

74.96; H, 6.19; N, 5.73. Found: C, 73.70; H, 6.77; N, 4.47.

Synthesis of monochelic porphyrinic polystyrene by RAFT polymerization of styrene, MPPS

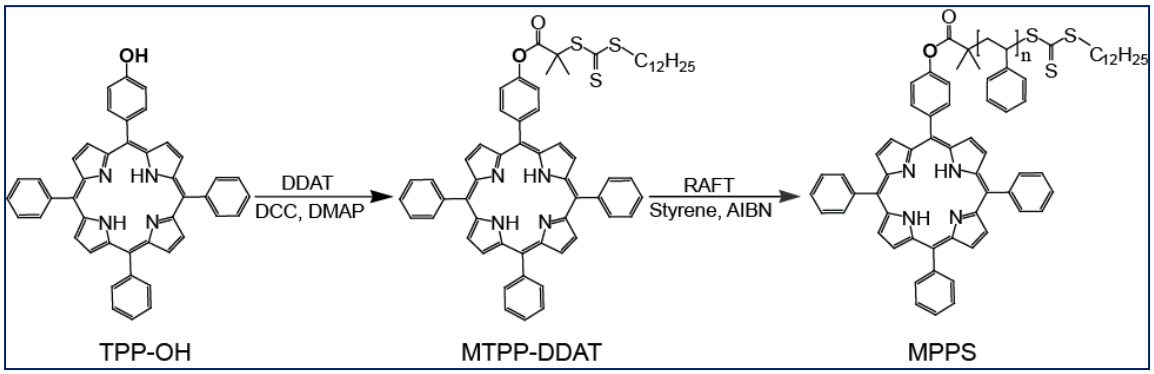
Monochelic porphyrinic polystyrene was synthesized by typical RAFT polymerization with AIBN as initiator.[3] MTPP-DDAT (0.2 g, 0.204 mmol) was dissolved in toluene (3 mL) followed by the addition of styrene (0.45 g, 4.36 mmol) and AIBN (0.003 g, 0.02 mmol). The flask was sealed and degassed with three freeze-thaw cycles and back filled with nitrogen at room temperature. The mixture was then immersed into a preheated oil bath at 68 ˚C for 20 h. The polymer product was precipitated in 300 mL of methanol, dried under vacuum. M_n (GPC) = 2761 g·mol^{-1}, PDI = 1.11, M_n (NMR) = 2957 g·mol^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm: 8.85 (s, 8H), 8.21 (d, 8H), 7.76 (m, 8H), 7.18 (bm, 57H), 6.5 (bm, 38H), 7.51 (m, 3H), 3.39 (t, 2H), 2.01 (s, 6H), 1.8 (bm, 19H), 1.4 (bm, 38H), 1.22 (m, 20H), 0.83 (t, 3H), -2.7 (s, 2H).

Synthesis of 2-(4-ethynyloxyphenyl)-3,4-fulleropyrrolidine, C_{60}-alkynyl

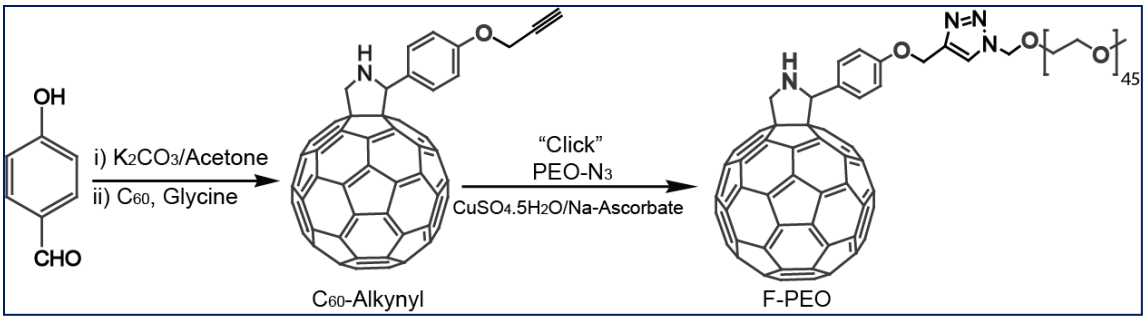
C_{60}-alkynyl was synthesized by the reaction of C_{60} with 4-prop-2-ynyloxybenzaldehyde according to the literature.[4] First, 4-prop-2-ynyloxybenzaldehyde was prepared by reacting 4-hydroxybenzaldehyde and propargyl bromide in presence of K_2CO_3 in acetone under nitrogen. Then 4-prop-2-ynyloxybenzaldehyde (0.27 g, 1.75 mmol) and C_{60} (0.252 g, 0.35 mmol) were dissolved in dichlorobenzene and refluxed at 135 ºC for 8 h. Product was purified with silica column by toluene as eluent, 0.408 g, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm: 7.87 (d, 2H), 7.08 (d, 2H), 5.76 (s, 1H), 5.08 (d, 1H), 4.75 (m, 1H), 4.70 (d, 2H), 2.56 (t, 1H), and 1.56 (s, 1H).

Synthesis of fullerene end capped poly(ethylene oxide), F-PEO

Azido-functionalized poly(ethylene oxide) (PEO-N_3) was first synthesized according to the literature.[5] C_{60}-alkynyl (0.066 g, 0.077 mmol) was then dissolved in 5 mL of DCM for click reaction with PEO-N_3 (1 mL water solution, 0.077 mmol) in presence of $CuSO_4$•$5H_2O$ (0.002 g, 0.007 mmol) and Na-ascorbate (0.006 g, 0.03 mmol) at room temperature. The mixture was stirred at room temperature for two days, and followed by washing with excess of H_2O/DCM. The organic phase was dried and obtained 0.185 g, 91% yield, M_n (GPC) = 2805 g·mol^{-1}, PDI = 1.05.



Scheme S1. Synthesis of monochelic porphyrinic RAFT agent (MTPP-DDAT) and monochelic porphyrinic polystyrene (MPPS), M_n = 2760 g mol^{-1} for MPPS.



Scheme S2. Synthesis of monochelic fullerene-containing poly(ethylene oxide) (F-PEO), M_n = 2000 g mol^{-1} for PEO, while M_n = 2800 g mol^{-1} for F-PEO.

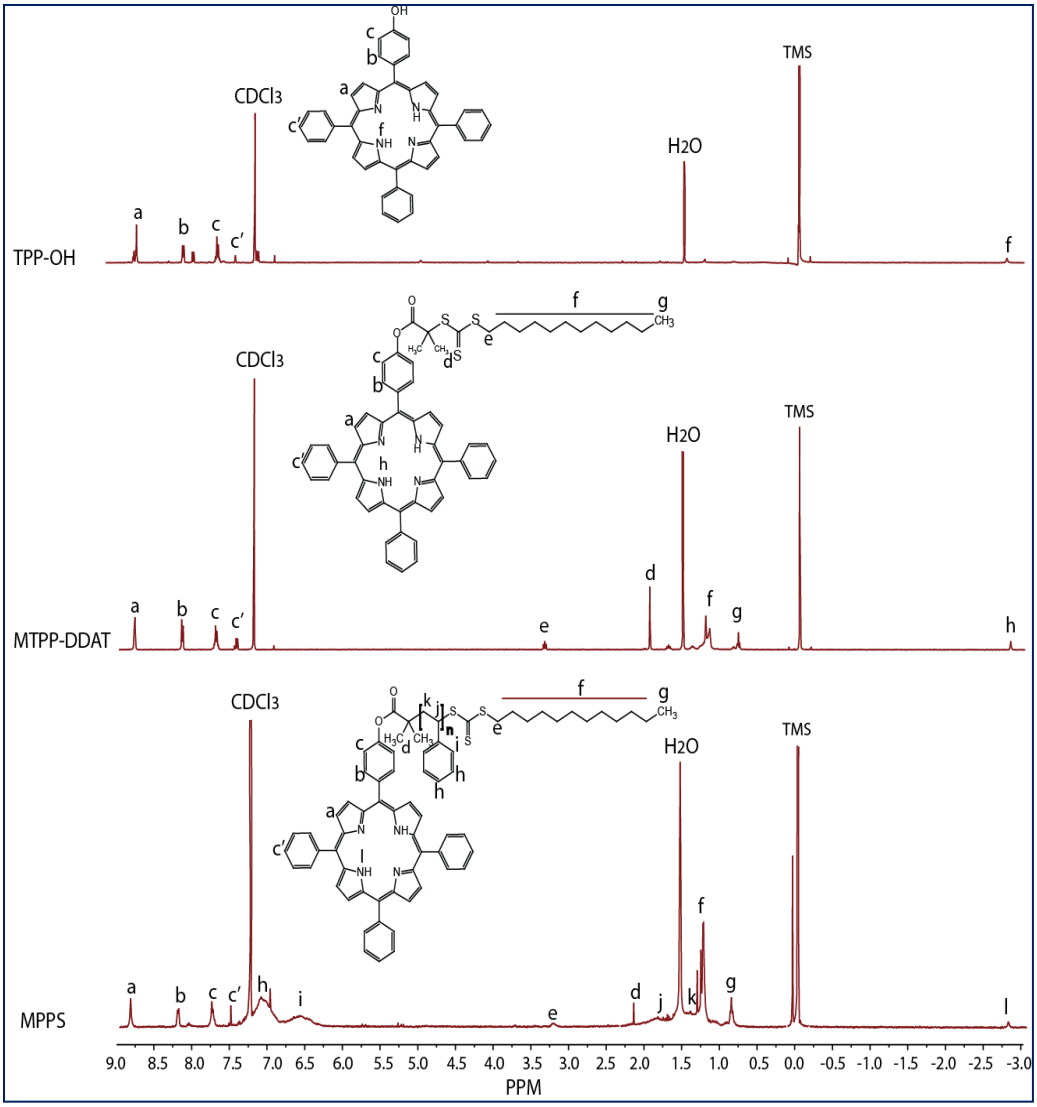


Figure S1. ^{1}H NMR spectra of TPP-OH, MTPP-DDAT and MPPS.

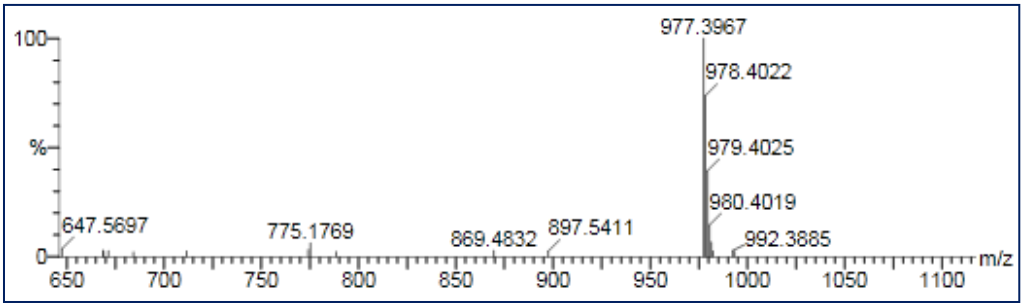


Figure S2. TOF-MS spectrum for MTPP-DDAT, calcd for $C_{61}H_{61}N_4O_2S_3$, 977.3957; found, 977.3967.

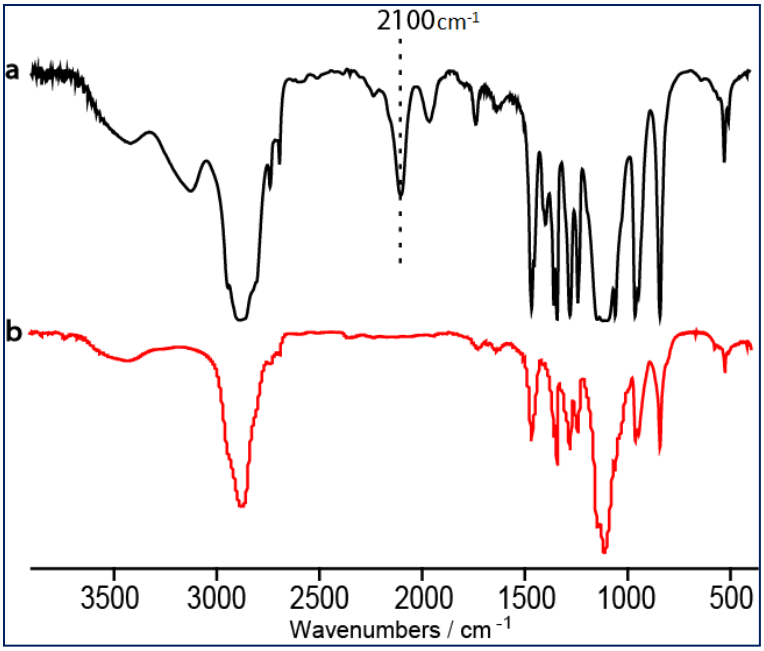


Figure S3. FTIR spectra for azido-functionalized PEO (a) and F-PEO (b), obtained by the click reaction of PEO-N_3 with C_{60}-alkynyl.

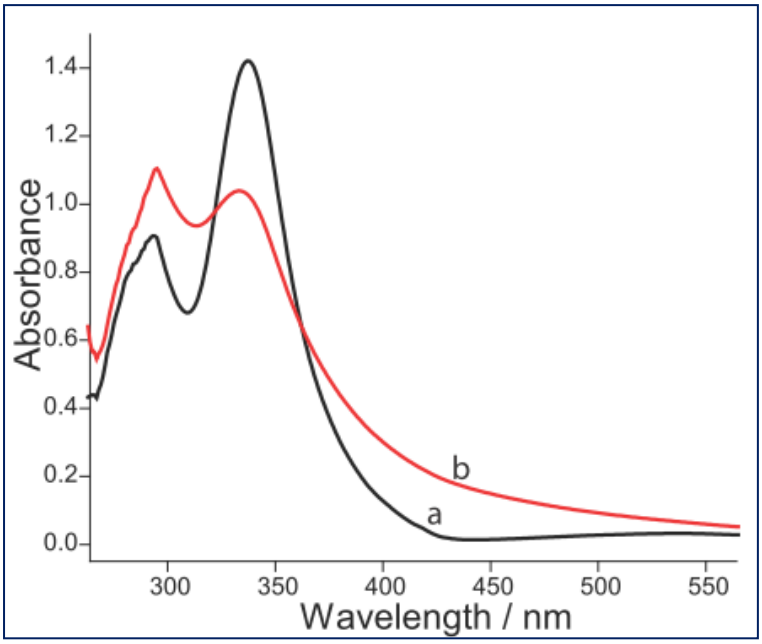


Figure S4. UV/vis. spectra of pristine C_{60} (a) and F-PEO (b) in toluene and THF, respectively.

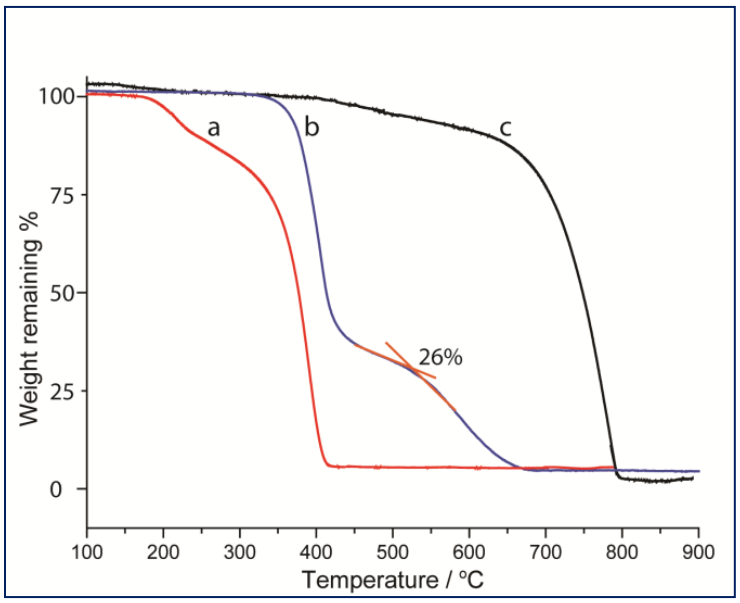


Figure S5. TGA curves for PEO (a), F-PEO (b), and C_{60} (c) under nitrogen.

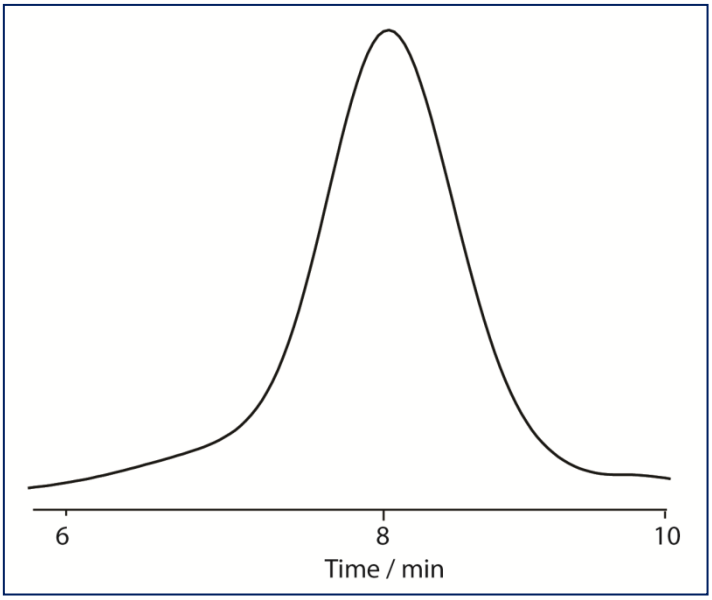


Figure S6. GPC curve for F-PEO, average molecular weight is 2805 g mol^{-1} with PDI=1.05.

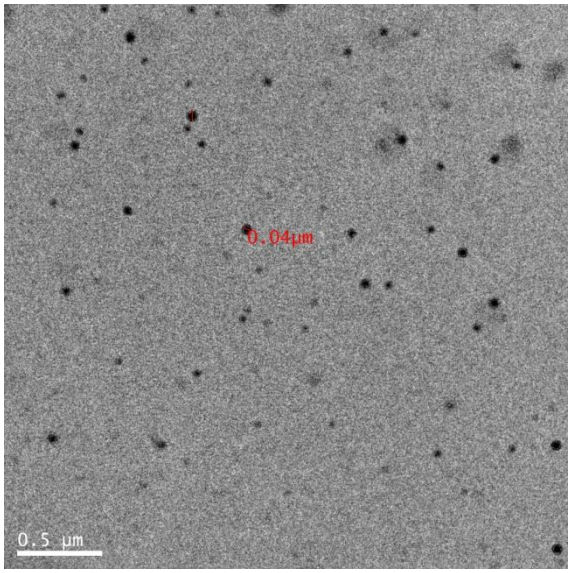


Figure S7. TEM micrographs of spherical aggregates formed by MPPS and F-PEO (M_n = 1000 g mol^{-1}) complexation in THF (5 µM).

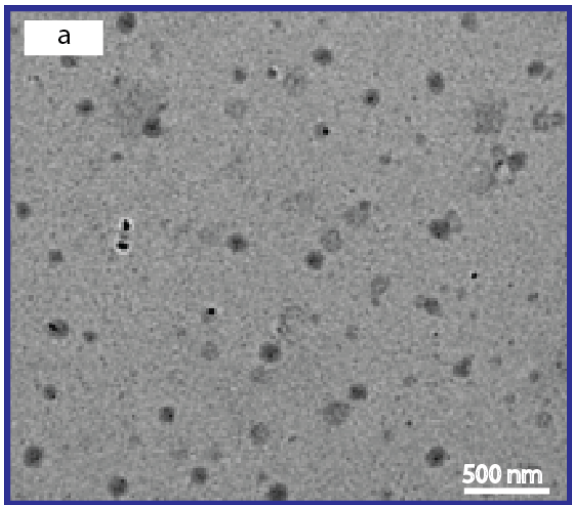


Figure S8. TEM micrographs of spherical aggregates formed by complexation between TPP and F-PEO (M_n = 2800 g mol^{-1}) in THF (5 µM).

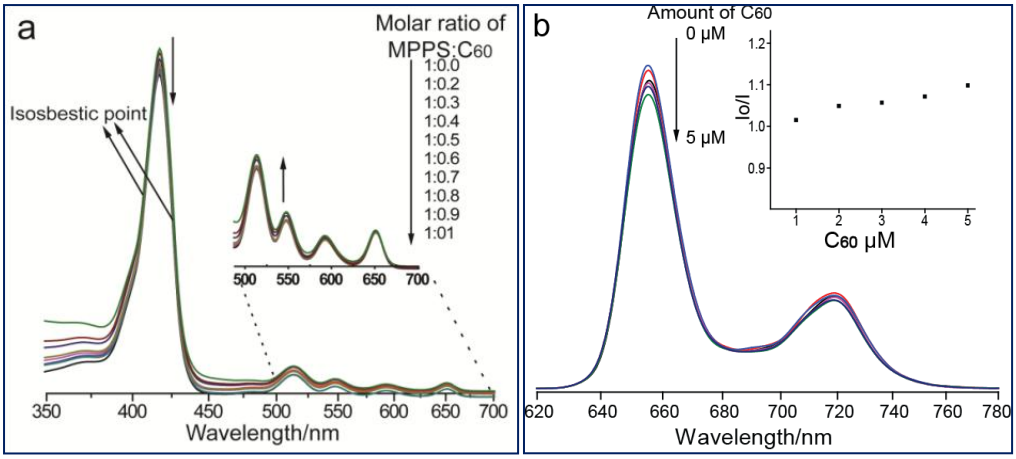


Figure S9. UV-vis (a) and fluorescence (b) spectra of MPPS with pristine C_{60} in THF. (inset of b) Stern-Volmer plot of the fluorescence ratios and [C_{60}].

References

1) F. D'Souza, G. R. Deviprasad, M. E. El-Khouly, M. Fujitsuka and O. Ito, *J. Am. Chem. Soc.*, **2001**, 123, 5277-5284.

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