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Supporting Information

Poly(*p*-phenylene ethynylene)s with Facially Amphiphilic Pendant Groups: Solvatochromism and Supramolecular Assemblies

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1. Instrument

^{1}H NMR spectra were recorded at 300 MHz for protons on JOEL JNM-ECA 300 spectrometers. Chemical shifts (δ) are given in ppm relative to TMS (δ =0.0). High-resolution electrospray ionization mass spectrometry (HRMS) was measured on Bruker APEX spectometer in positive mode. Elemental analysis was performed on Carlo-Erba-1106 instrument. The molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured with a Waters 515GPC instrument equipped with Stygel columns (101-, 102-, and 103-nm pore sizes) with polystyrene as a calibration. UV/Vis characterization was carried out on a Perkin-Elmer Lambda35 spectrometer. The fluorescence emission measurements were carried out using a fluorescence spectrometer (Hitachi, F-4500). IR spectra were recorded on AVATAR 360 ESP FTS spectrophotometer with KBr pellets. Dynamic light scattering (DLS) measurement was carried out using Malvern Zetasizer 3000HS instrument, which supplies vertically polarized light with a wavelength of 633 nm. Scanning electron microscope (SEM) experiments were performed with LEO-1530 scanning electron microscope. Transmission electron microscopy (TEM) was performed on a MODEL H-800. All the samples were stained with 1.5% phosphotungstic acid hydrate before observed under TEM. X-ray diffraction (XRD) measurements were performed on a D/max-RB diffractometer with a Cu Kα X-ray irradiation source. X-ray diffractograms were recorded over the range of 3-30º in 2θ degrees and the scanning rate is kept at 1º min^{-1}.

2. The UV/Vis and fluorescence characterization of bile acid derived PPEs and the model compound P3

For fluorescent characterization, the slit widths were set to 2.5 nm bandpass and all samples were excited at wavelength 365 nm at 20 ^{o}C. The quantum yield (Φ_f) of PPEs for emission was measured in dilute THF solution in which UV absorbance was less than 0.1 so that inner filter effects were minimal. Quinine sulfate ($9.98*10^{-10}$ M in 2.0 M H_2SO_4) was used as the reference standard.[1, 2]

Table S1. Absorption and emission characterizations of bile acid derived PPEs and the model compound **P3**.

Polymer	λ_{abs}[a]/nm (THF)	λ_{abs}[a]/nm (film[b])	λ_{em}[a]/nm (THF)	λ_{em}[a]/nm (film[b])	Φ_f (THF)
P1	411	426	446	469	0.93
P2	413	422	447	467	0.91
P3	412	425	443	482, 517	0.86

[a] λ_{max} of absorption and emission bands, respectively.

[b] The experiment was carried out on a polymer spin-cast film.

3. Dynamic light scattering spectra of P1

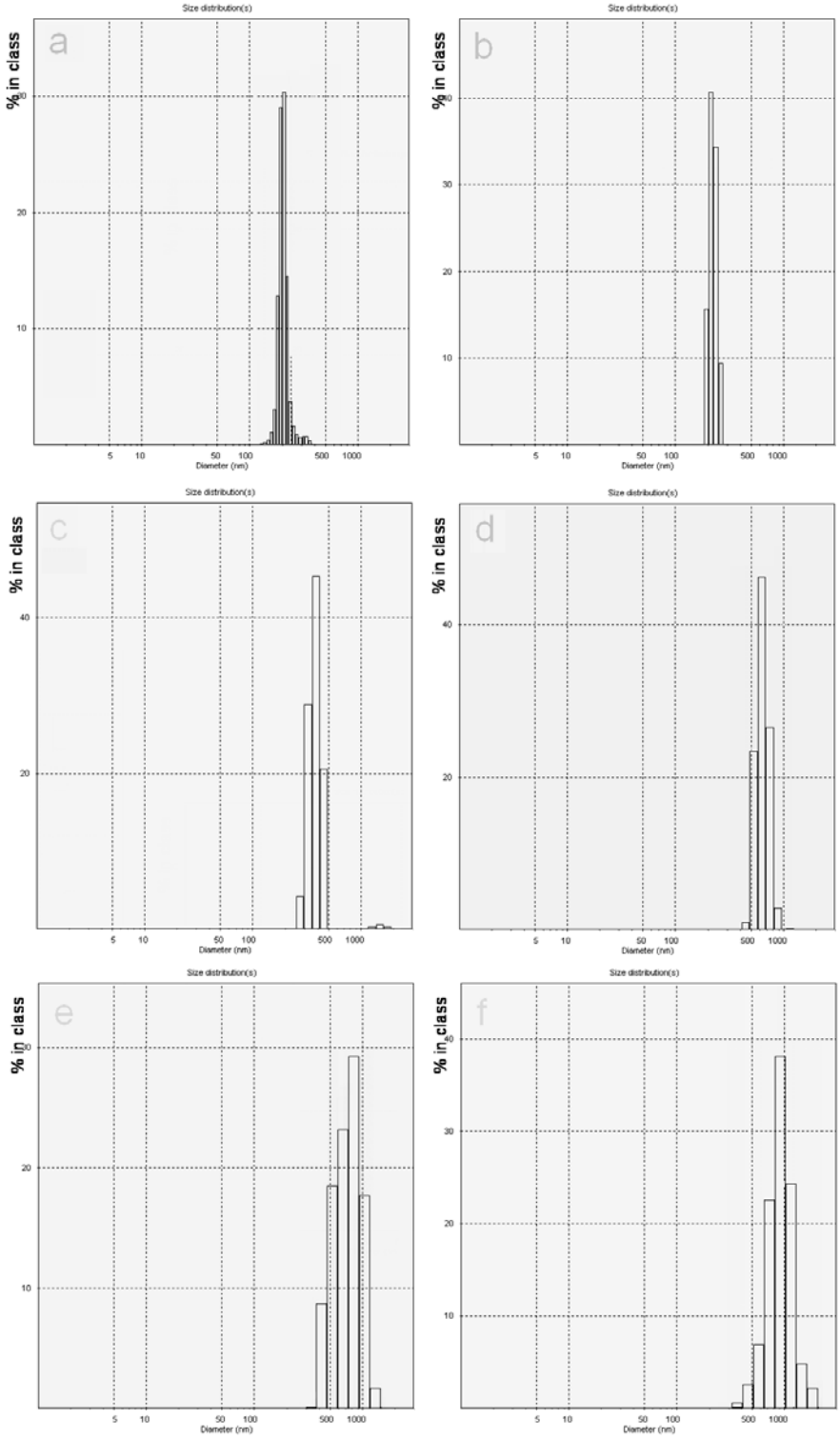


Figure S1. Dynamic light scattering spectra of polymer **P1** in water/dioxane system with the volume fraction of water (a): 10% (ED=194 nm, PD=0.08), (b): 20% (ED=227 nm, PD=0.11), (c): 30% (ED=437 nm, PD=0.21); (d): 40% (ED= 652 nm, PD= 0.27), (e): 50% (ED=778 nm, PD=0. 42) and (f): 60% (ED=902 nm, PD=0. 48). This study is performed not only to measure the particle size but also to prove that the particles are formed in solution and the glass surface used for the SEM analysis has no role in the aggregation formation.

4. Full TEM images

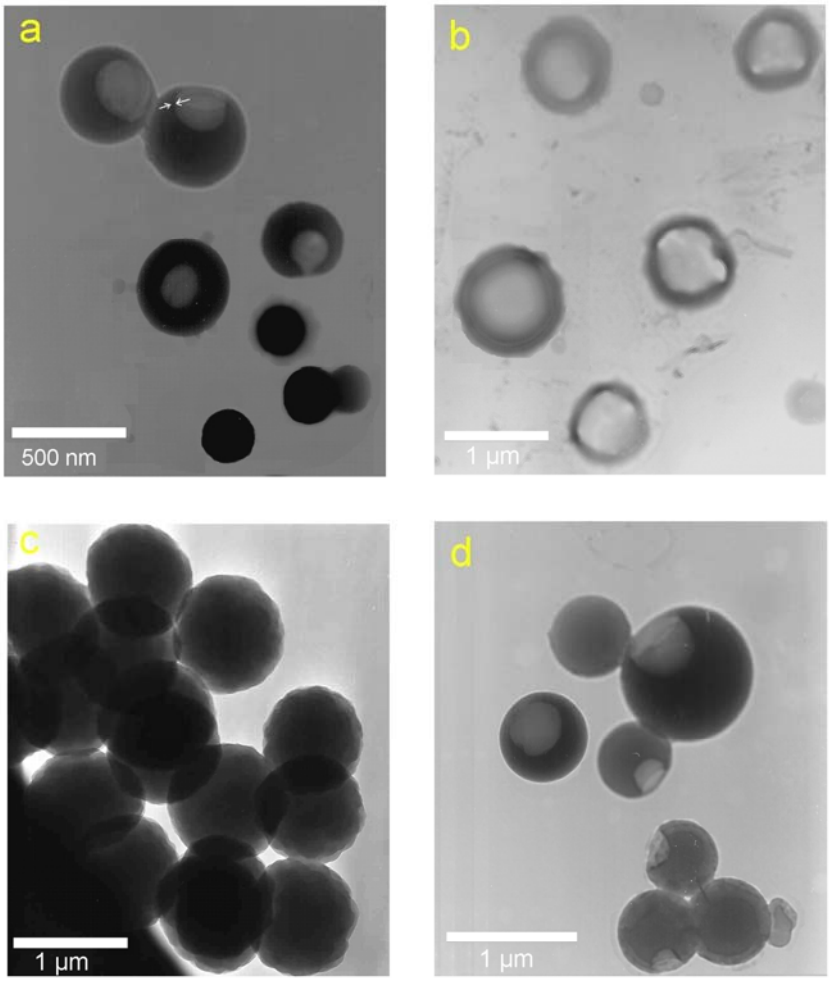


Figure S2. Full TEM images of the formed supramolcular aggregates from **P1** using water/dioxane system with the volume fraction of water (a): 25% and (b): 50%; supramolcular aggregate from **P1** using cyclohexane/dioxane system with the volume fraction of cyclohexane 60%; supramolcular aggregate from **P2** using water/dioxane system with the volume fraction of water 40%.

5. The solvatochromic and self-assembly properties of P3

With the incremental addition of water to dioxane solution of **P3**, significant decrease of the molar absorbance was observed, accompanied by a very weak solvatochromic behavior as shown in Figure S4. In contrast to **P1** and **P2**, the model compound **P3** can be dissolved quite well in cyclohexane/dioxane mixture, forming a transparent solution even when the volume fraction of cyclohexane beyond 70%. No solvatochromic behavior was observed in the non-polar media.

Though weak solvatochromic behavior and Tyndall effect was also observed when water was just added to the dioxane solution of **P3**, this model compound did not show any regular self-assembling as **P1** and **P2** under the investigation of SEM (Figure S5).

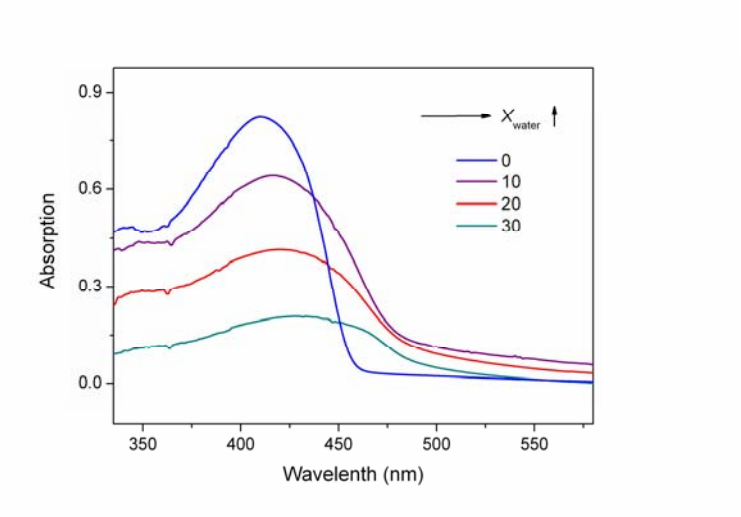


Figure S3. UV/Vis absorption spectrum of **P3** in dioxane at 20°C as function of added water (inset is the content of non-solvent in %).

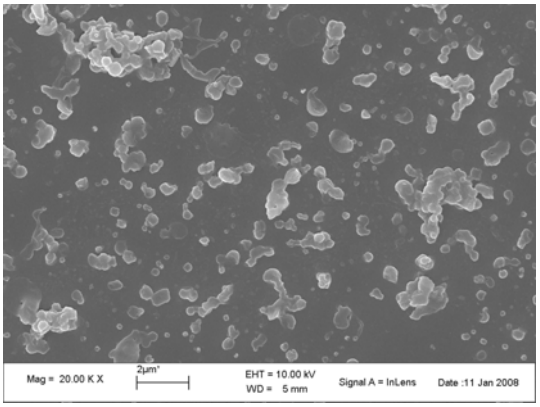
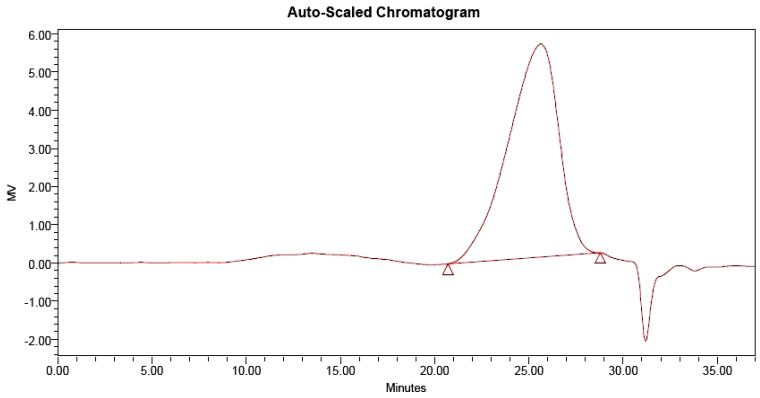


Figure S4. SEM images of the formed supramolcular aggregate from **P3** using dioxane/water solvent mixture with the volume fraction of water 20%.

6. GPC experiment

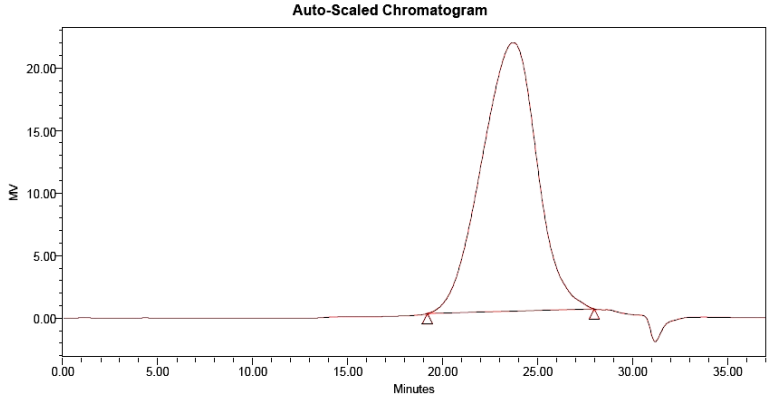
GPC spectra of **P1**



GPC Results

	Dist Name	Mn	Mw	MP	Polydispersity
1		20927	30422	22012	1.453720

GPC spectra of **P2**



GPC Results

	Dist Name	Mn	Mw	MP	Polydispersity
1		21138	32901	27770	1.556486

References

1. H. Li, D. R. Powell, R. K. Hayashi, R. West, *Macromolecules* **1998**, *31*, 52-58.

2. A. Khan, S. Mullera, S. Hecht, *Chem. Commun.* **2005**, 584-586.