

Electronic Supplementary Information

Tetraphenylethene-containing supramolecular hyperbranched polymers: aggregation-induced emission by supramolecular polymerization in aqueous solution

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1. Experimental Section

The synthetic method of TPE derivative **1** is depicted in Scheme 2. Tetra-imidazole-appended tetrakis(p-phenylene)ethylene (TITPE) (0.2 g, 0.34 mmol) and 2-(bromomethyl) naphthalene (0.59 g, 2.68 mmol) were dissolved in acetonitrile (20 mL). The mixture was stirred at 90 °C for 48 h. After that, the solution was added dropwise to 400 mL of diethyl ether and filtered. The product was a yellow-green powder. The yield was 85%. ¹H NMR (400 MHz, DMSO) δ 10.14 (s, 4H), 8.35 (s, 4H), 8.10 (s, 4H), 8.04 (s, 4H), 8.01-7.89 (m, 12H), 7.74 (d, *J* = 8.2 Hz, 8H), 7.65-7.55 (m, 12H), 7.39 (d, *J* = 8.6 Hz, 8H), 5.67 (s, 8H). HRESI-MS: *m/z* = 1161.44 [M-4Br]⁴⁺.

Materials. Tetra-imidazole-appended tetrakis(p-phenylene)ethylene (TITPE) was synthesized according to the literatures report.^[S1-S2] 2-(bromomethyl) naphthalene was obtained from Acros. Acetonitrile and diethyl ether were purchased from Sinopharm Chemical Reagent Co., Ltd.

Dynamic light scattering (DLS) measurement. DLS data were collected on a DynaPro NanoStar (Wyatt Technology) with a gallium-arsenide diode laser of 658 nm emission. The instrument has a temperature-controlled sample holder (precision of 0.1 °C) for a quartz cuvette of 10 μL. Scattering data were collected at an angle of $\theta = 90^\circ$ and processed using the software program DYNAMICS V6, version 6.3.40. The autocorrelation functions were analyzed with the CONTIN method.

¹H NMR spectra. ¹H-NMR spectra was recorded on a Bruker Avance 400 spectrometer (400 MHz). DOSY experiments were carried out with a BRUKER AVANCE 600 NMR Spectrometer.

UV-vis spectra. UV-vis spectra were obtained on a Shimadzu UV-1601PC spectrophotometer.

Fluorescence spectroscopy. Steady-state fluorescence measurements were carried out using a Hitachi 4500 spectrophotometer. The Integrating Sphere (IS) consists of a 120mm inside diameter spherical cavity, which is machined from BENFLEC block. This is then surrounded by an aluminium shell for handling and protection. The internal reflection material was suppressed polytetrafluoroethylene (PTFE, 90% reflectivity), and the wavelength range was from 250 nm to 2500 nm. To determine the absolute quantum yield of the compound, the excitation wavelength was set at 340 nm. The scattering spectral range of blank and sample was from 320 nm to 360 nm, and the emission spectral range was from 360 nm to 660 nm.

Transmission electron microscopy (TEM) measurements. TEM images were obtained on a JEM

2100 and JEM 2100F operating at 200 kV. Samples for TEM measurement were prepared by dropping the mixture aqueous solution on carbon-coated copper grid (300 mesh) and drying by slow evaporation.

Viscosity measurements. Viscosity measurements were carried out with a micro-Ubbelohde dilution viscometer at 25 °C in water.

2. ^1H NMR for TPE derivative 1, CB[8] and [1-2CB[8]]

Upon addition of CB[8], signals corresponding to the hydrogen atoms of the naphthalene group moved to the high field and broadened, indicating that the naphthalene groups are encapsulated in the cavity of CB[8].

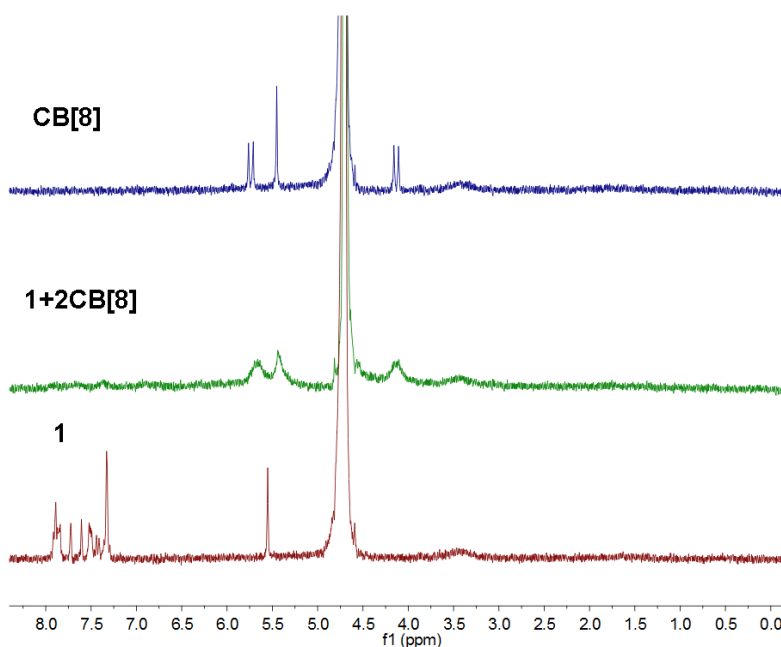


Fig. S1. ^1H NMR spectra of 67.6 μM TPE derivative 1, 226 μM CB[8] and 33.8 μM [1-2CB[8]].

3. DLS for the Assembly of 1-2CB[8]

Dynamic light scattering (DLS) experiments support the formation of large supramolecular hyperbranched polymers. The average radius of the aggregates in solution of 1-2CB[8] is measured to be around 300 nm.

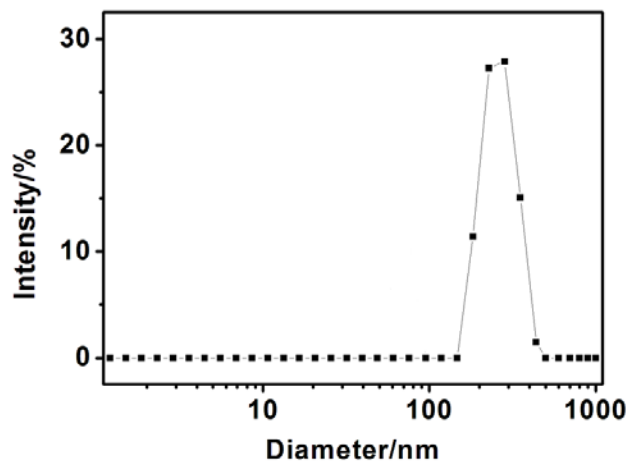


Fig. S2. DLS data of 67.6 μM [1-2CB[8]]; the DLS data are shown as the size probability distribution obtained by a CONTIN analysis.

4. Diffusion-ordered NMR Spectroscopy data

The average diffusion coefficients of **1** and CB[8] were measured to be $8.17 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ and $8.12 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, respectively. However, after complexation in 1:2 ratio, the diffusion coefficient gradually decreases, meanwhile the NMR signals of both **1** and CB[8] finally show a single diffusion coefficient with a value of $3.01 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, which suggests the two building blocks diffuse as one entity, indicating naphthalene moieties are efficiently encapsulated by CB[8] to form hyperbranched supramolecular polymers.

5. Transmission electron microscopy (TEM) measurements.

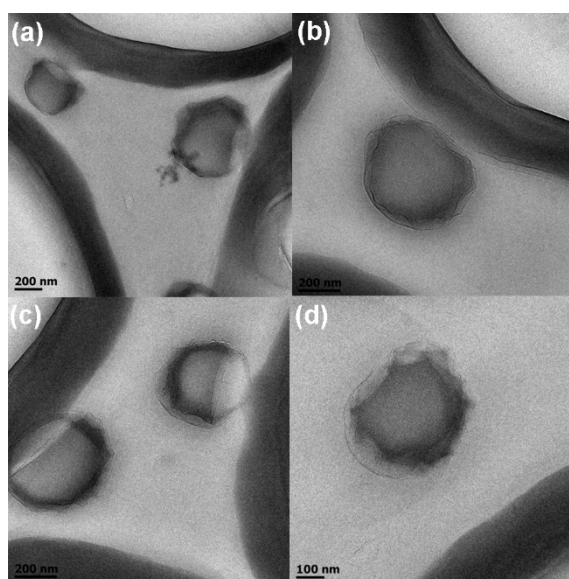


Fig. S3. TEM images of supramolecular hyperbranched polymers formed by **1** and CB[8] (67.6 μM).

References:

- [S1] K. Y. Kim, S. H. Jung, J.-H. Lee, S. S. Lee and J. H. Jung, *Chem. Commun.*, 2014, **50**, 15243.
- [S2] H.-L. Zhang, B. Zhao, W.-G. Yuan, W. Tang, F. Xiong, L.-H. Jing and D.-B. Qin, *Inorg. Chem. Commun.*, 2013, **35**, 208.