Supporting information

A hyperbranched supramolecular polymer constructed by orthogonal triple hydrogen bonding and host-guest interactions

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Experimental section

General: $^1$H NMR and $^{13}$C NMR spectra were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a Micrimass LCTTM mass spectrometer. Viscosity measurements were carried out with Ubbelohde microdilution viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 298 K in dichloromethane. DLS were measured on MALV RN, ZETA SIZER, Model ZEN3600, 303K. AFM images were measured on Solver P47-PRO, NT-MDT. SEM images were recorded on a JSM-6360LV apparatus.

Materials: Chemicals were used as received from Adamas, Acros, Aldrich, Fluka, or Merck. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. The molecular structures of the unknown compounds were confirmed via $^1$H NMR, $^{13}$C NMR and High Resolution ESI mass spectroscopy.

Synthesis:

Synthesis of 1 and 3 have been synthesized according to the procedure described in the literature.$^{1,2}$

Synthesis of 2:

4, 5-dicyano dibenzo-24-crown-8(a) has been synthesized according to the procedure described in the literature.$^3$

Synthesis of 4, 5-dicarboxyl dibenzo-24-crown-8 (b): a (0.43 g, 0.9 mmol) in ethanol (15 mL) and potassium hydroxide (0.5 g, 9 mmol) in H$_2$O (15 mL) were mixed and refluxed for 20 h under argon atmosphere. The reaction mixture was cooled down to room temperature, then adjusted pH to 2 using hydrochloric acid. After the mixture was extracted by DCM (3×30 mL), the solvent was removed under reduced pressure. The remaining solid was further purified by chromatography on silica gel using DCM/MeOH (10:1) as the eluent to give a white solid b (0.22 g, 48%).$^3$$^4$$^5$-$^6$H-NMR (400 MHz, DMSO, 298 K): $\delta$ 9.39 (s, 1H), 8.87 (s, 1H), 7.31 (s, 1H), 7.19 (s, 1H), 6.89-6.94 (m, 4H), 4.14 (t, $J$=3.6 Hz, 4H), 4.07 (t, $J$=4.4 Hz, 4H), 3.74-3.80 (m, 8H), 3.66 (s, 8H). HRMS (ESI) m/z:
[M+Na]$^+$ calcd for C$_{26}$H$_{32}$NaO$_{12}$ 559.1791, found 559.1795. Because of the poor solubility of b, even in d$_6$-DMSO, we can not get the $^{13}$C-NMR spectrum suitable for analysis.

Synthesis of 4, 5-dicarboximide dibenzo-24-crown-8 (2): b (0.4 g, 0.75 mmol) and ethanoic anhydride (25 mL) were refluxed for 5 h under argon atmosphere. The reaction mixture was cooled down to room temperature, poured into H$_2$O (50 mL), and extracted by DCM (3×30 mL). The organic phase was then washed by H$_2$O (3×50 mL) and dried. The solvent was removed under reduced pressure. The remaining solid was further purified by chromatography on silica gel using DCM/MeOH (30:1) as the eluent to give a white solid. Mixed the white solid and urea (0.45 g, 7.5 mmol) in toluene (30 mL). The mixture was refluxed for 2 h under argon atmosphere. After it was cooled down to room temperature, a white precipitate was generated. The solid was collected by filtration, washed with ortho-xylene and dried under reduced pressure to afford e (0.2 g, 56 %).

$^1$H-NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ 7.51 (s, 1H), 7.23 (s, 2H), 6.83-6.92 (m, 4H), 4.24 (t, J=4.0 Hz, 4H), 4.15 (t, J=4.0 Hz, 4H), 3.92-3.96 (m, 8H), 3.84 (s, 8H). $^{13}$C-NMR (100 MHz, CDCl$_3$, 298 K): $\delta$ 168.16, 153.67, 148.77, 126.02, 121.41, 113.83, 106.53, 71.53, 71.29, 69.92, 69.78, 69.43, 69.24. HRMS (ESI) m/z: [M+Na]$^+$ calcd for C$_{26}$H$_{31}$NO$_{10}$Na 540.1846, found 540.1833.

Reference
$^1$H NMR spectrum of b

Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Isotope cluster parameters: Separation = 1.0, Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
4556 formula(s) evaluated with 7 results within limits (up to 50 closest results for each mass)

ESI-Mass spectrum of b
$^1$H NMR spectrum of 2

$^{13}$C NMR spectrum of 2
**ESI-Mass spectrum of 2**

Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
10881 formula(s) evaluated with 20 results within limits (up to 50 closest results for each mass)

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