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Supporting Information (6 pages)

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Pillar[5]arene 1-A and guest 2 were prepared according to the published procedure. NMR spectra were recorded on a BRUKER AVANCE III HD 400MHz spectrometer. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. ITC was carried out on a MicroCal VP-ITC instrument. Scanning electron microscopy (SEM) investigations were carried out on a Hitachi S-3400 SEM instrument. Dynamic light scattering measurements were performed on a goniometer ALV/CGS-3 using a UNIPHASE He-Ne laser operating at 632.8 nm. Viscosity was measured by Ubbelohde viscometer.


1-A (0.20 g, 0.23 mmol), ferrocene-dicarboxylic acid (0.031 g, 0.10 mmol), HOBT(0.038 g, 0.25 mmol) and EDCL (0.055 g, 0.25 mmol) were stirred in 10 mL dry CHCl₃ over night at room temperature. The reaction solvent was evaporated and the residue was purified by flash column chromatography on silica gel (CH₂Cl₂/CH₃OH, v/v 15:1) to give 1 as a yellow solid (0.149 g, yield: 66.0 %), m.p. 118.2 – 120.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (s, 4 H, NH), 6.81 – 6.63 (m, 20 H, ArH), 4.49 (t, J = 1.9 Hz, 4 H, CH₂), 4.32 (t, J = 1.8 Hz, 8 H, ArH) , 3.86 – 3.54 (m, 72 H, 48 OCH₃, 24 CH₂), 3.33 (s, 8 H, CH₂), 1.73 (dt, J = 14.5, 6.5 Hz, 4 H, CH₂), 1.46 (dt, J = 14.8, 7.5 Hz, 4 H, CH₂), 0.93 (t, J = 7.3 Hz, 6 H, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 170.66, 170.31, 151.17, 150.94, 150.87, 150.80, 150.74, 150.72, 150.69, 150.67, 148.40, 129.03, 128.49, 128.43, 128.25, 128.17, 128.08, 127.95, 127.79, 115.10, 115.04, 114.18, 114.03, 113.93, 78.06, 71.13, 70.59, 68.26, 68.20, 56.46, 56.04, 55.96, 55.80, 40.71, 31.76, 30.02, 29.76, 29.69, 29.60, 29.02, 19.44, 13.92; MS (m/z): HRMS (ESI) Calcd. for C₁₁₄H₁₃₆Fe₄N₂O₂₄⁺ ([M + Na]⁺): 2018.8416, found: 2018.8356. Elemental analysis: N, 2.76 %; C, 68.32 %; H, 6.42 %.

Fig. S1 ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of 1.
Fig. S2 ¹³C NMR spectrum (CDCl₃, room temperature, 101 MHz) of 1.

Fig. S3 Mass spectra of 1 C₁₁₁₄H₁₃₀FeN₄NaO₂₄⁺ ([M + Na]⁺): 2018.8356.
3. Construction of supra-molecular polymers

**Fig. S4** Partial NOESY spectrum of 1∶2 in CDCl₃.

**Fig. S5** ITC study of 1∶2 in CHCl₃, the $K_a$ value of 1∶2 was determined to be $(2.34 \pm 0.07) \times 10^4$ M$^{-1}$ in the 1:1 complexation pattern.
4. Application in Fenton-like reaction

**Fig. S6** Photo pictures of (a) TMB and H₂O₂ and (b) TMB, H₂O₂ and 1>2 after reaction 6h.

**Fig. S7** UV-visible spectra the solution containing TMB (black line), TMB, H₂O₂ and pillar[5]arene 1 (blue line), and supramolecular materials, H₂O₂, and TMB (red line).

**Fig. S8** UV-visible spectra the solution containing H₂O₂, and TMB and supramolecular materials with different recycle time.