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Supramolecular polymer networks based on pillar[5]arene: synthesis, characterization and application in Fenton reaction

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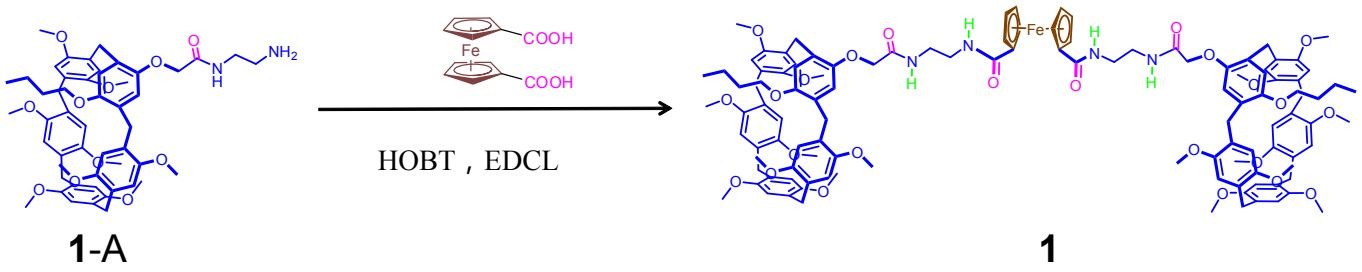
Supporting Information (6 pages)

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.[S1,S2] 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.

*2. Synthesis of Pillar[5]arene dimer **1***



Scheme 1. Synthetic route to pillar[5]arene **1**.

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，0.25mmol) were stirred in 10 mL dry $CHCl_3$ over night at room temperature. The reaction solvent was evaporated and the residue was purified by flash column chromatography on silica gel (CH_2Cl_2/CH_3OH, *v*/*v* 15:1) to give **1** as a yellow solid (0.149 g, yield: 66.0 %), m.p. 118.2 – 120.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 4 H, NH), 6.81 – 6.63 (m, 20 H, ArH), 4.49 (t, *J* = 1.9 Hz, 4 H, CH_2), 4.32 (t, *J* = 1.8 Hz, 8 H, ArH) , 3.86 – 3.54 (m, 72 H, 48 OCH_3, 24 CH_2), 3.33 (s, 8 H, CH_2), 1.73 (dt, *J* = 14.5, 6.5 Hz, 4 H, CH_2), 1.46 (dt, *J* = 14.8, 7.5 Hz, 4 H, CH_2), 0.93 (t, *J* = 7.3 Hz, 6 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) 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, 39.12, 31.76, 30.02, 29.76, 29.69, 29.60, 29.02, 19.44, 13.92; MS (m/z): HRMS (ESI) Calcd. for $C_{114}H_{130}FeN_4NaO_{24}^+$ ([M + Na]$^+$): 2018.8416, found: 2018.8356. Elemental analysis: N, 2.76 % ; C, 68.32 %; H, 6.42 %.

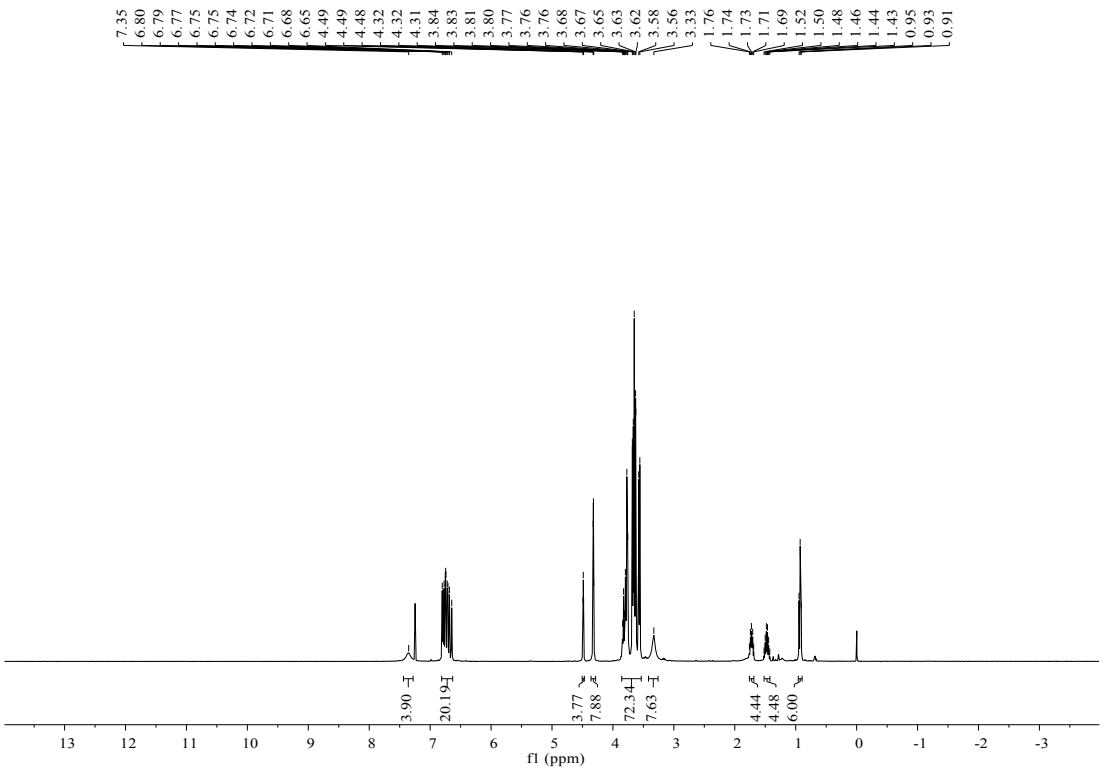


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **1**.

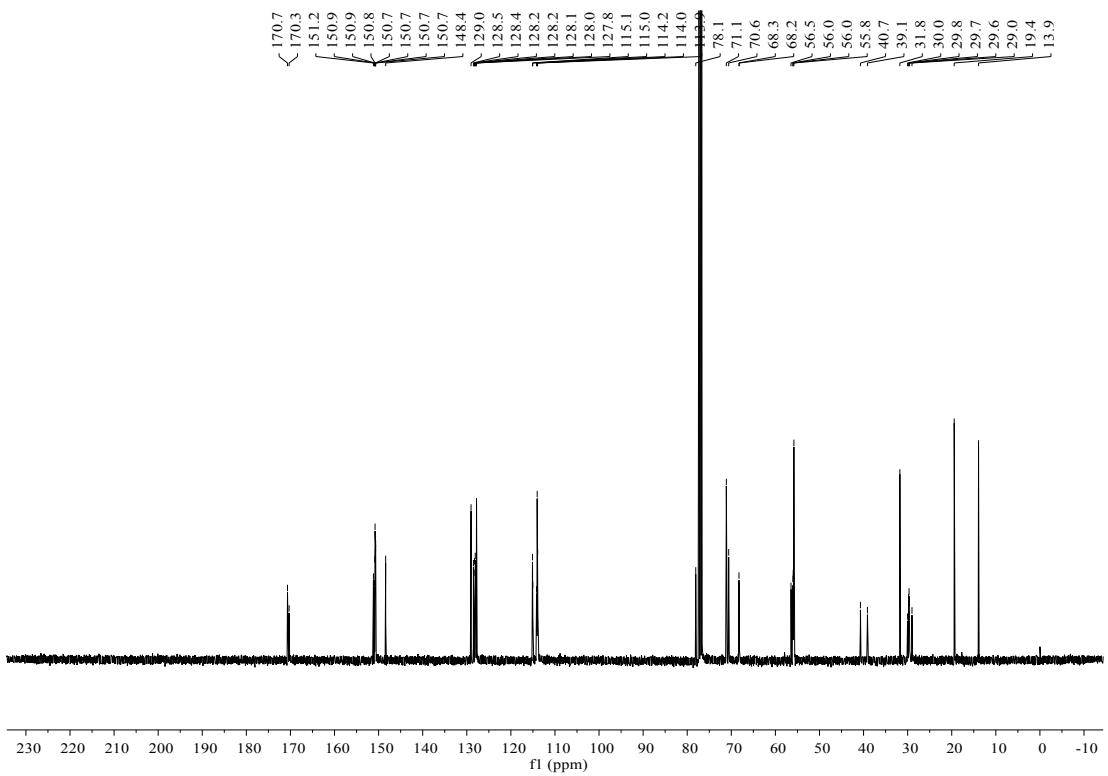


Fig. S2 ^{13}C NMR spectrum ($CDCl_3$, room temperature, 101 MHz) of **1**.

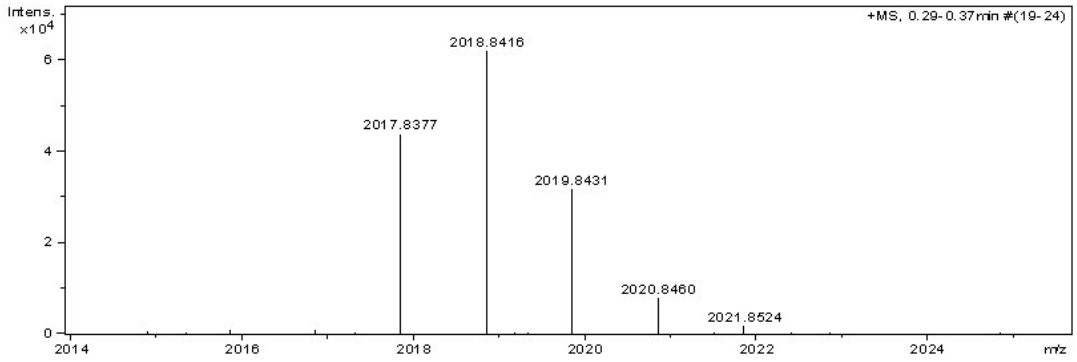


Fig. S3 Mass spectra of **1** $C_{114}H_{130}FeN_4NaO_{24}^+$ ($[M + Na]^+$): 2018.8356.

3. Construction of supra-molecular polymers

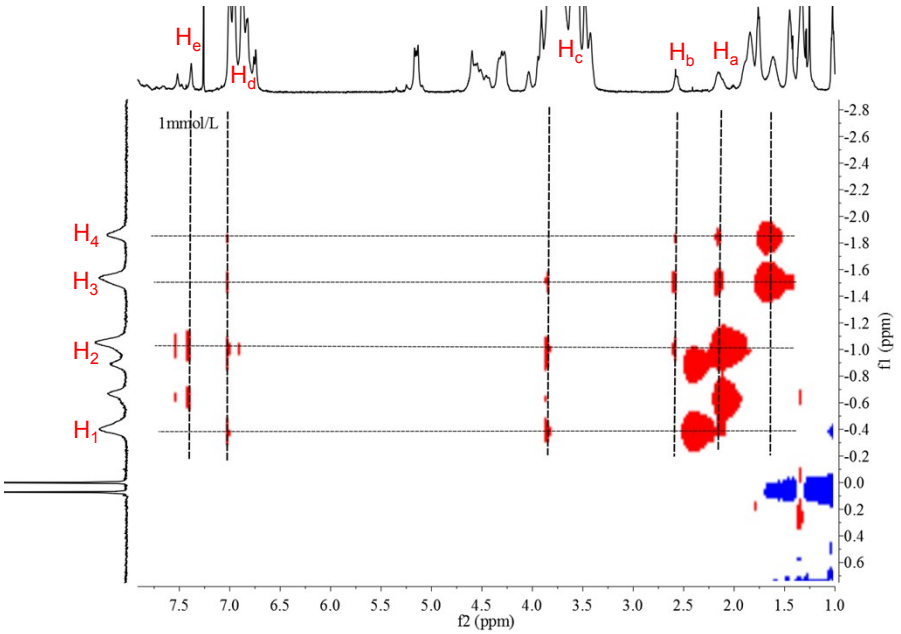


Fig. S4 Partial NOESY spectrum of **1** ⊃ **2** in $CDCl_3$.

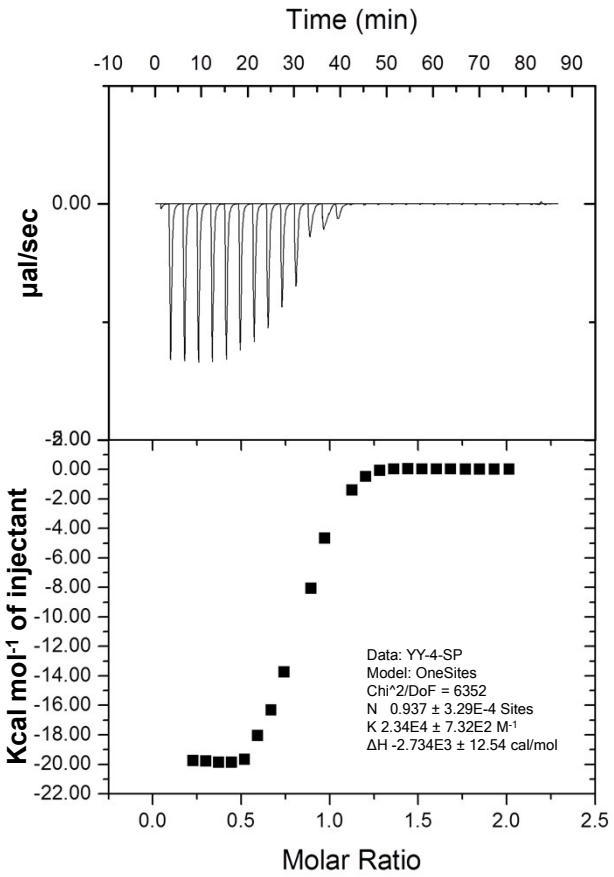


Fig. S5 ITC study of **1** ⊃ **2** in $CHCl_3$, the *K*a value of **1** ⊃ **2** was determined to be (2.34 ± 0.07) × 10^4 M^{-1} in the 1:1 complexation pattern.

4. Application in Application in Fenton-like reaction

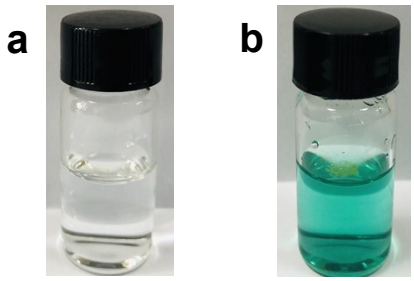


Fig. S6 Photo pictures of (a) TMB and H_2O_2 and (b) TMB, H_2O_2 and **1⊃2** after reaction 6h.

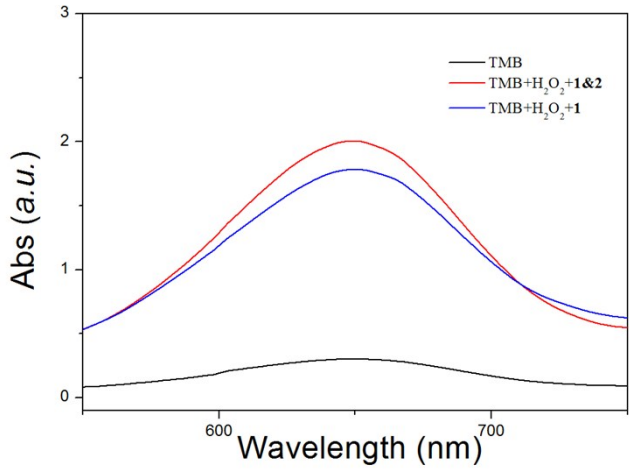


Fig. S7 UV-visible spectra the solution containing TMB (black line), TMB, H_2O_2 and pillar[5]arene **1** (blue line), and supramolecular materials, H_2O_2, and TMB (red line).

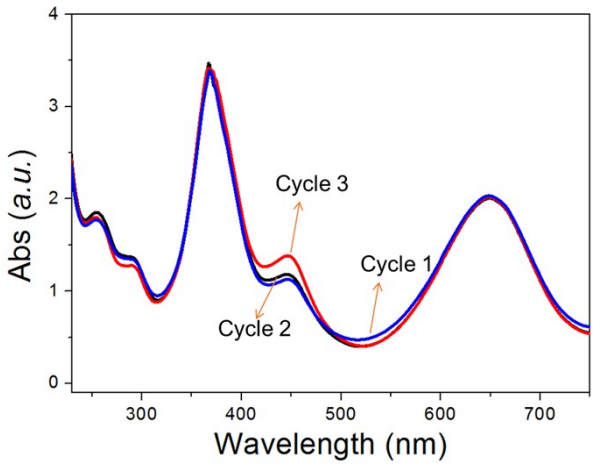


Fig. S8 UV-visible spectra the solution containing H_2O_2, and TMB and supramolecular materials with different recycle time.

S1. X. Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia and C. Li, *Chem. Commun.*, **2012**, 48, 2967.

S2. Y. Liu, L. Sgangguan, H. Wang, D. Xia and B. Shi, *Polym. Chem.*, **2017**, 8, 3783.