Electronic Supplementary Material (ESI) for ChemComm.

An anthracene-appended 2:3 copillar[5]arene: synthesis, computational studies, and application in highly selective fluorescent sensing for Fe(III) ion

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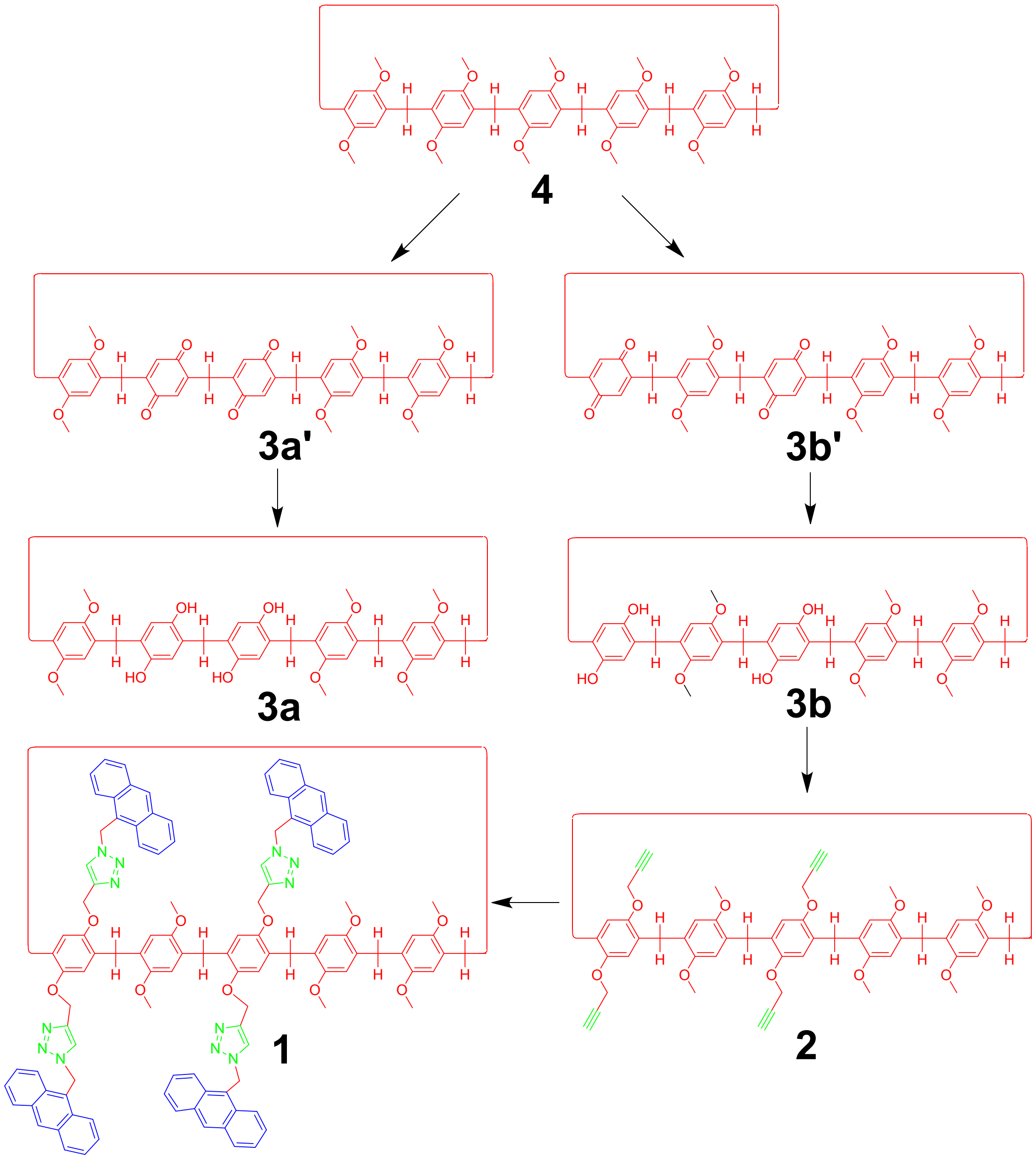
Electronic Supplementary Information (16 pages)

1. Materials and Methods

Compounds **3a′**,[S1] **3b′**,[S1] **4**,[S2] and 9-azidomethylanthracene[S3] were synthesized according to literature procedures. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals. 2D COSY NMR spectra were recorded on a Bruker DRX500 spectrometer. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system or a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH, Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. Solutions of metal ions were prepared from the perchlorate salts of Fe^{3+}, Cr^{3+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pd^{2+}, Zn^{2+}, Mg^{2+}, Hg^{2+}, and Ag^{+}. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). The melting point was collected on a SHPSIC WRS-2 automatic melting point apparatus. The crystal data was collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra instrument. The crystal structure was solved by SHELXS-97[S4] and refined by SHELXL-97.[S5]

*2. Synthesis of **1***

Scheme S1. Synthesis of 2:3 copillar[5]arene **1**



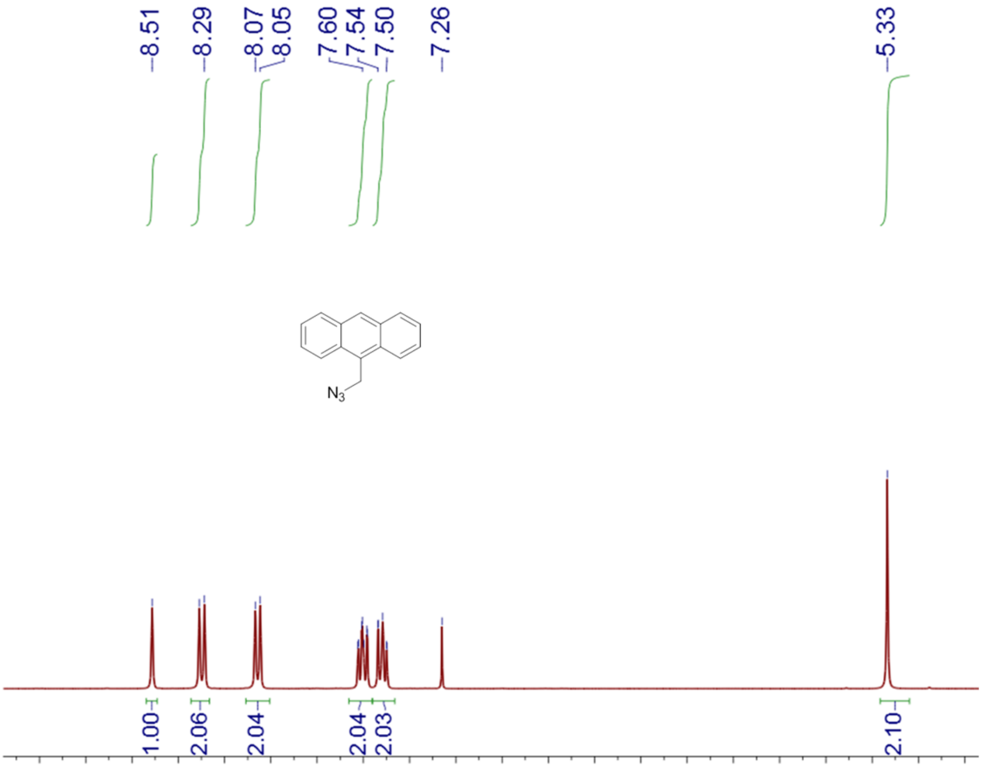


Figure S1. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 293 K) of 9-azidomethylanthracene.

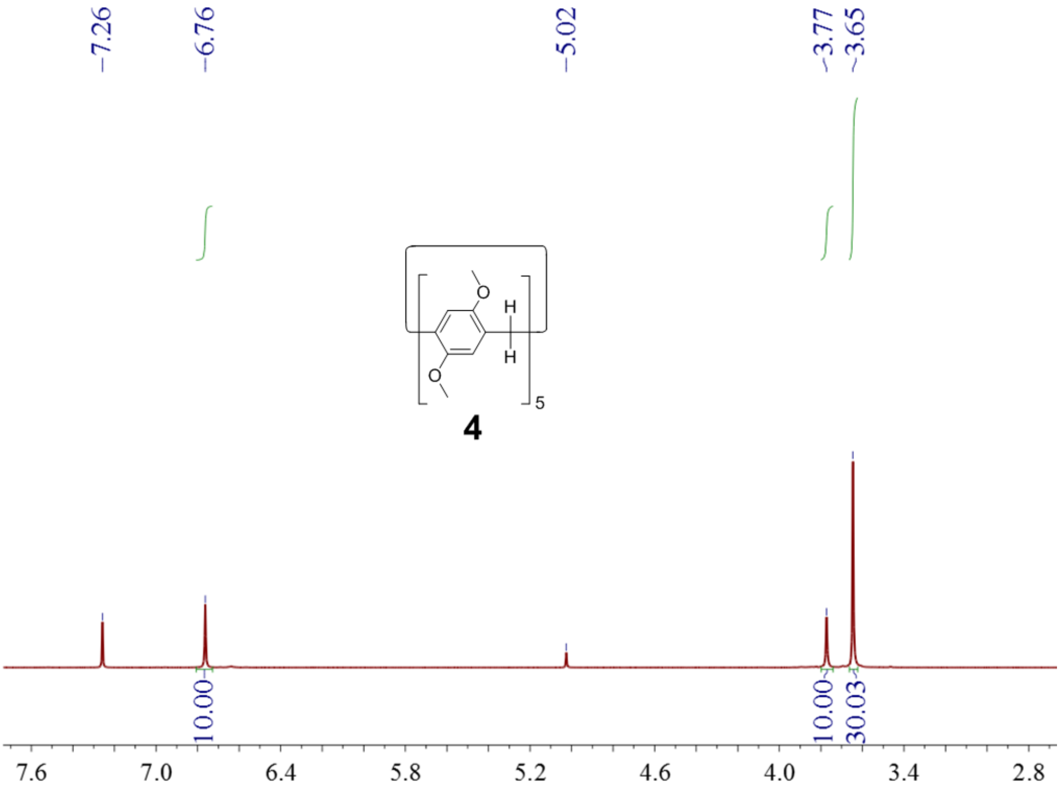


Figure S2. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 293 K) of **4**.

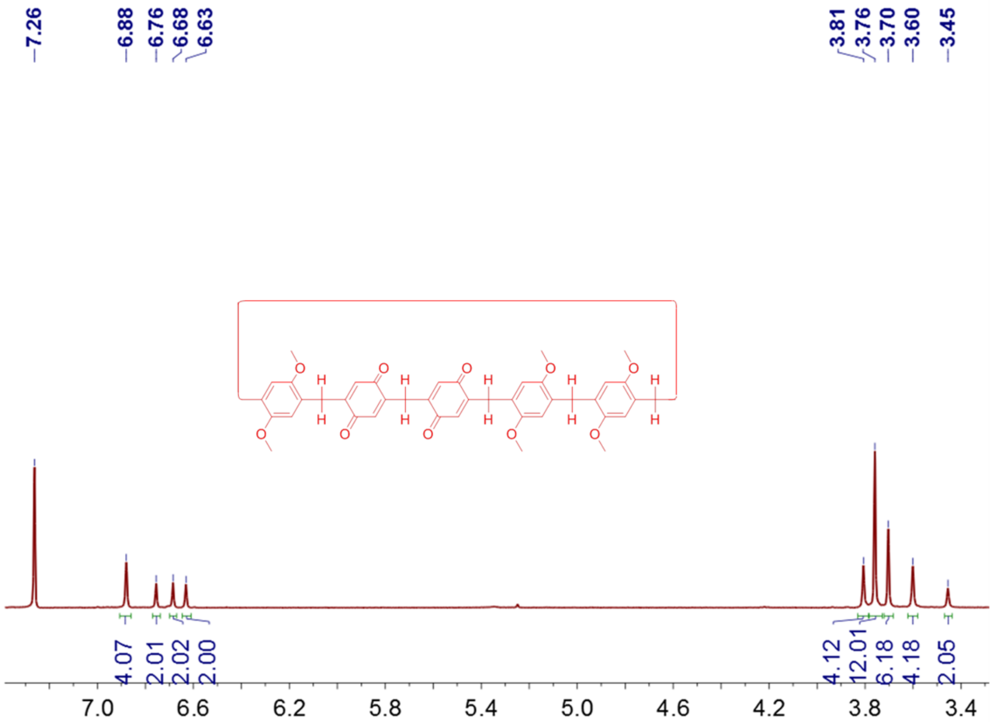


Figure S3. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 293 K) of **3a′**.

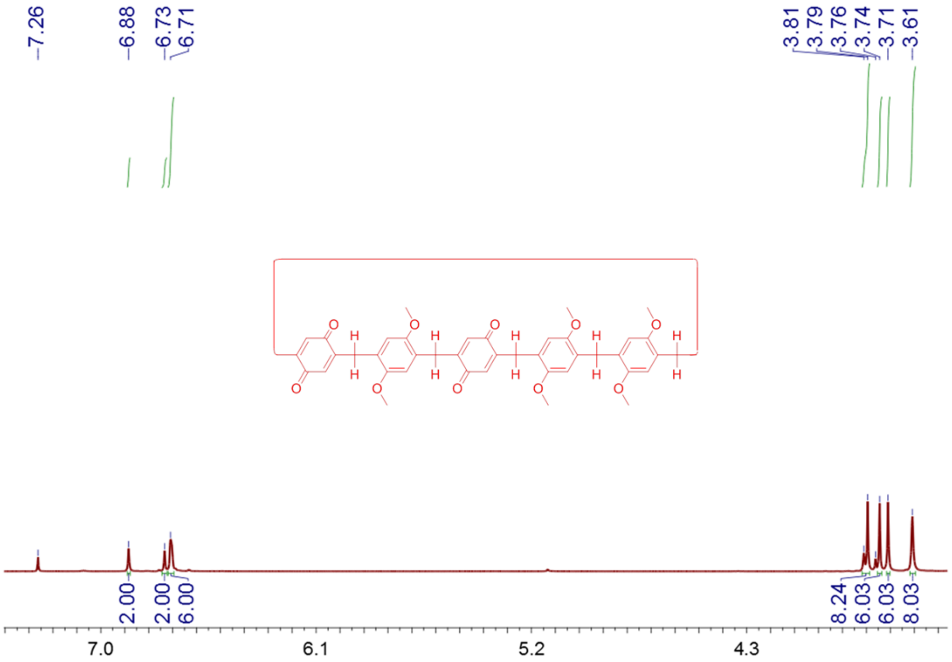


Figure S4. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 293 K) of **3b′**.

A solution of **3b′** (260 mg, 0.370 mmol) in CH_2Cl_2 (30.0 mL) was stirred in a 50.0 mL round–bottom flask. An aqueous solution of $Na_2S_2O_4$ (513 mg, 1.47 mmol) was added. The mixture was stirred roughly at room temperature for 1.5 h. The water layer was extracted by CH_2Cl_2 (25.0 mL × 3). The combined organic phase was washed with water (50.0 mL) and saturated NaCl solution (50.0 mL), dried over anhydrous Na_2SO_4. After being filtered and evaporated, **3b** was obtained quantitatively as a white solid. To a solution of **3b** (250 mg, 0.350 mmol) in acetonitrile (50.0 mL) was added K_2CO_3 (483 mg, 3.50 mmol) and 3-bromopropyne (417 mg, 3.50 mmol). The resulting mixture was stirred at reflux overnight and the reaction was stopped by filtration and evaporation under vacuum. The residue was purified by chromatography on silica gel (petroleum ether/dichloromethane, *v*/*v* 1:3) to obtain **2** as a white solid (280 mg, 95%). Mp. 78.1−79.4 °C. The ^{1}H NMR spectrum of **2** is shown in Figure S5. ^{1}H NMR (400 MHz, chloroform-*d*, 293 K) (ppm): 6.81 (s, 4H), 6.76 (d, 4H, J = 1.60 Hz), 6.71 (s, 2H), 4.47–4.50 (m, 8H), 3.78 (s, 10H), 3.68 (d, 12H, J = 1.60 Hz), 3.63 (s, 6H), 2.13 (t, 2H, J = 4.00 Hz), 2.07 (t, 2H, J = 4.00 Hz). The ^{13}C NMR spectrum of **2** is shown in Figure S6. ^{13}C NMR (125 MHz, chloroform-*d*, 293 K) (ppm): 150.76, 150.72, 150.65, 149.42, 129.28, 129.06, 128.52, 128.06, 127.84, 115.78, 115.63, 114.19, 113.82, 79.06, 79.00, 74.77, 74.75, 56.51, 56.46, 55.88, 55.87, 55.75, 29.87, 29.72, 29.68, 29.57. The LRESI-MS of **2** is shown in Figure S7. LRESI-MS: *m*/*z* 845.7 $[M + H]^+$ (100%), 868.6 $[M + Na]^+$ (20%), 884.6 $[M + K]^+$ (15%). HRESI-MS: *m*/*z* calcd for $[M + NH_4]^+$ $C_{53}H_{54}NO_{10}$ 864.3748, found 864.3764, error 1.9 ppm.

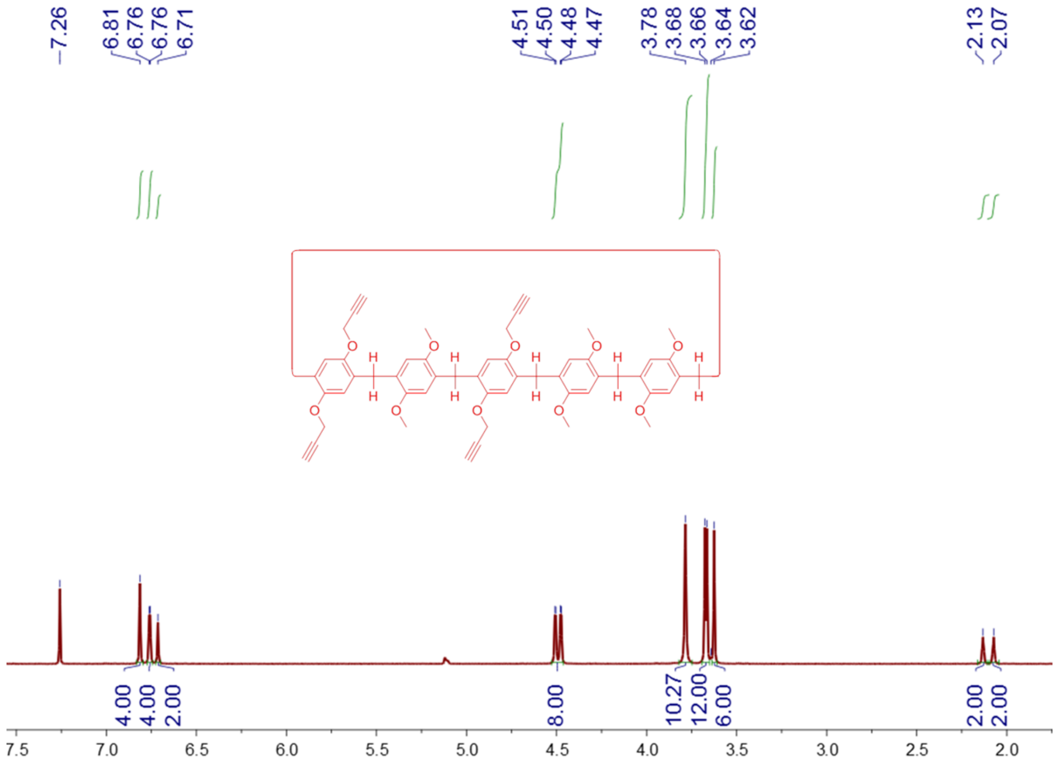


Figure S5. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 293 K) of **2**.

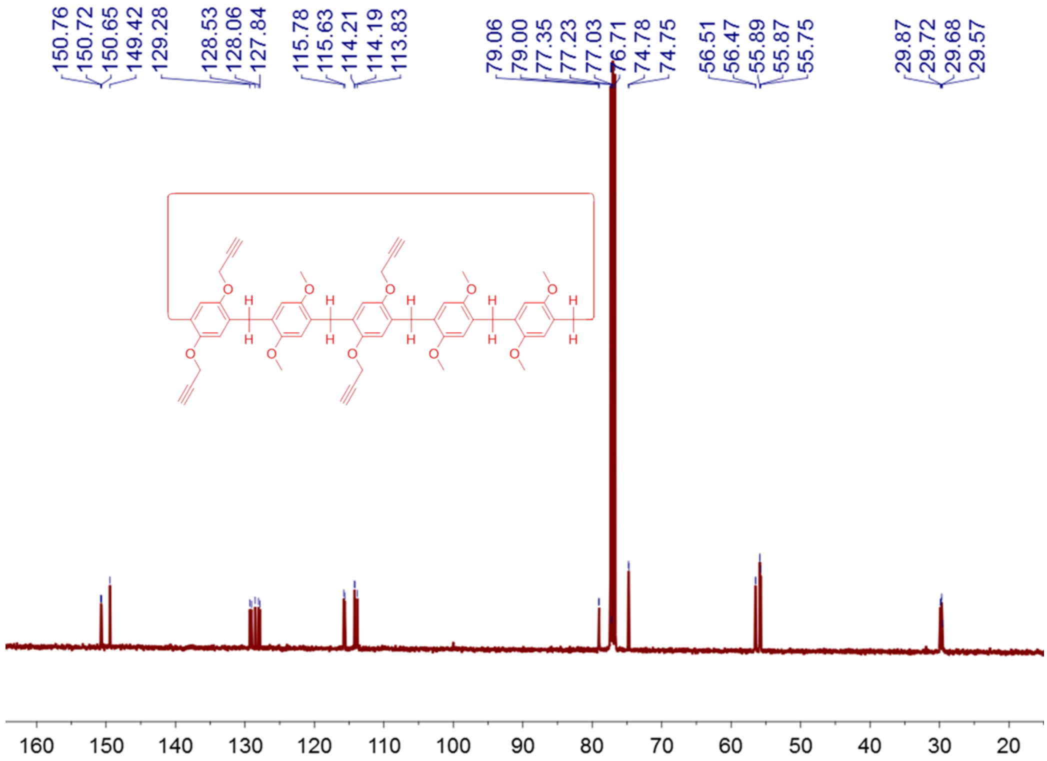


Figure S6. ^{13}C NMR spectrum (125 MHz, chloroform-*d*, 293 K) of **2**.

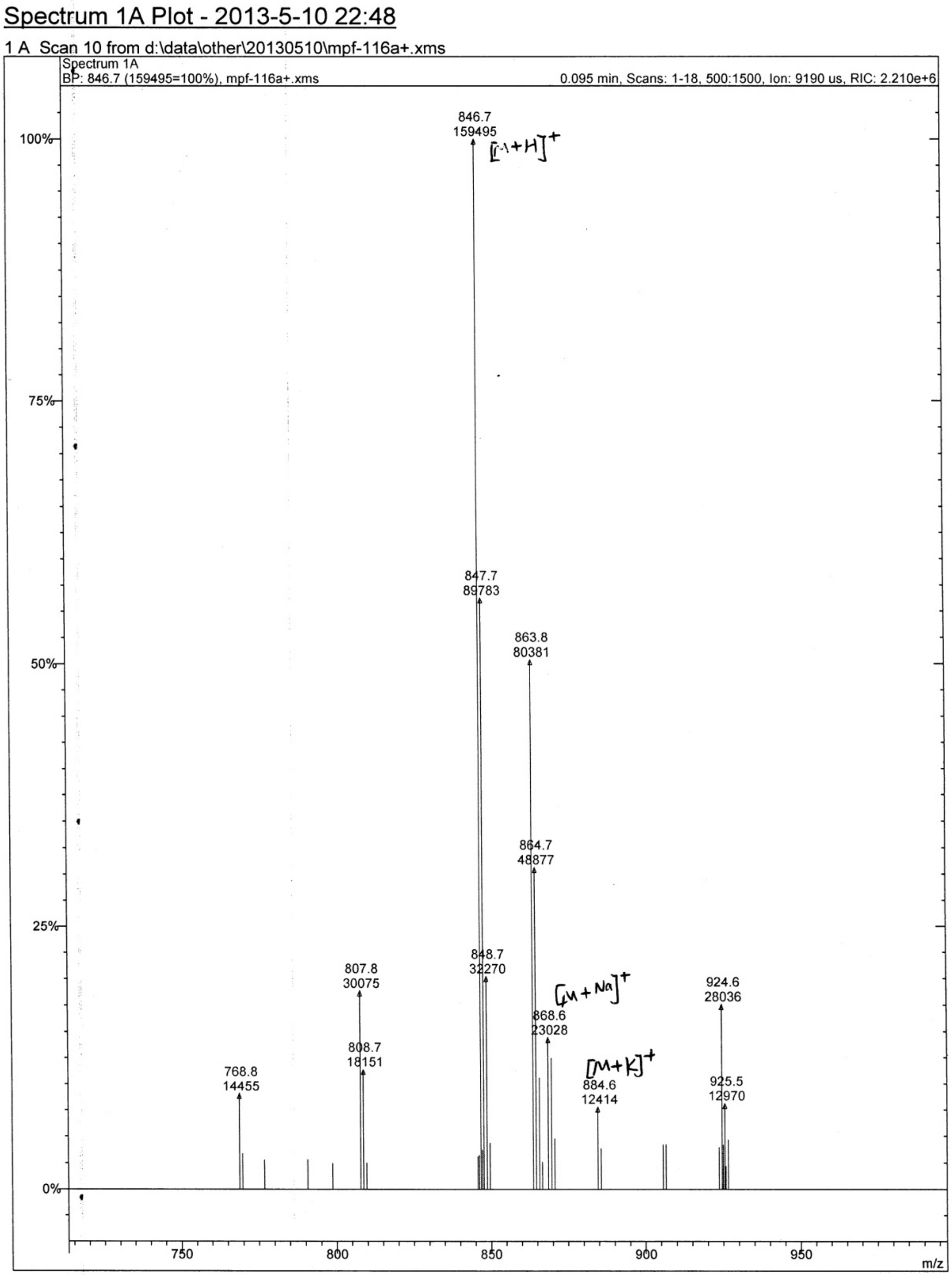


Figure S7. LRESI mass spectrum of **2**.

A mixture of **2** (250 mg, 0.300 mmol), 9-azidomethylanthracene (69.0 g, 3.00 mmol), $CuSO_4•5H_2O$ (75.0 mg, 0.300 mmol), and sodium ascorbate (178 mg, 0.900 mmol) in DMF/H_2O (5:1) (50.0 mL) was refluxed under N_2 atmosphere for 24 hours. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (dichloromethane/ethyl acetate, *v*/*v* 5:1) to yield a brown solid (1.00 g, 48%). Mp 143.4–145.7 °C. The ^{1}H NMR spectrum of **1** is shown in Figure S8. ^{1}H NMR (400 MHz, chloroform-*d*, 293 K) (ppm): 8.55 (d, 4H, *J* = 12.0

Hz), 8.28–8.33 (m, 8H), 8.01–8.06 (m, 8H), 7.45–7.59 (m, 16H), 7.21 (d, 4H, *J* = 8.00 Hz), 6.63 (d, 4H, *J* = 20.0 Hz), 6.49–6.54 (m, 10H), 6.35 (s, 2H), 6.29 (s, 2H), 4.68–4.76 (m, 8H), 3.39–3.57 (m, 10H), 3.96 (s, 6H), 3.03 (d, 12H, *J* = 28.0 Hz). The ^{13}C NMR spectrum of **1** is shown in Figure S9. ^{13}C NMR (125 MHz, chloroform-*d*, 293 K) (ppm): 150.55, 150.38, 149.77, 144.81, 131.43, 130.77, 130.74, 129.92, 129.51, 128.69, 127.73, 127.56, 125.46, 123.78, 123.72, 122.92, 122.88, 122.00, 121.96, 62.79, 55.66, 55.27, 55.22, 46.46, 46.42, 29.37, 29.25. LRESI-MS: *m*/*z* 1780.4 (50%) $[M + H]^+$, 1802.5 (100%) $[M + Na]^+$ and 1818.4 (20%) $[M + K]^+$. HRESI-MS *m*/*z* calcd for $[M + H]^+$ $C_{113}H_{95}N_{12}O_{10}$ 1779.7294, found 1779.7347, error 3.0 ppm.

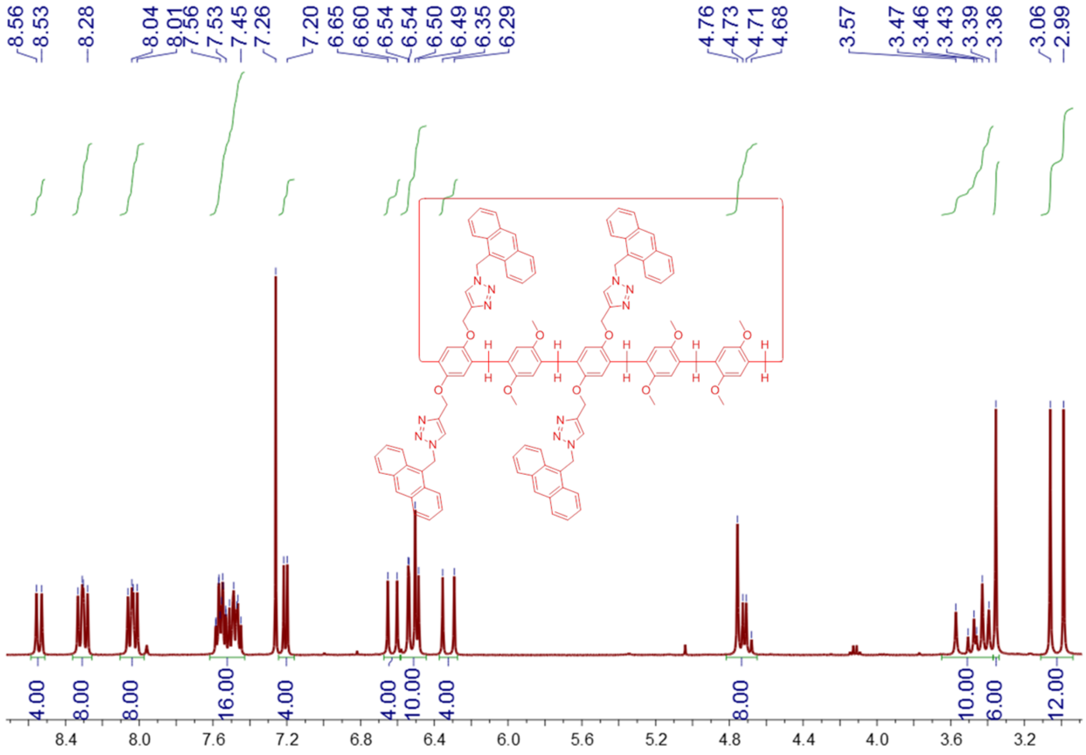


Figure S8. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 293 K) of **1**.

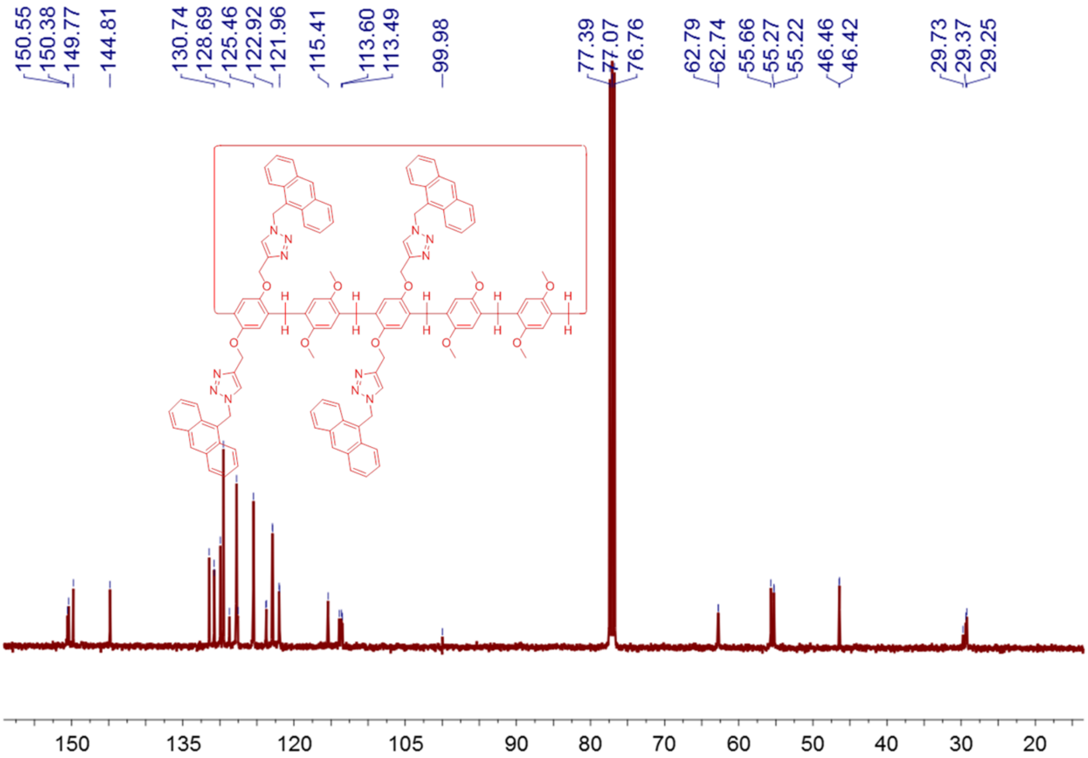


Figure S9. ^{13}C NMR spectrum (125 MHz, chloroform-*d*, 293 K) of **1**.

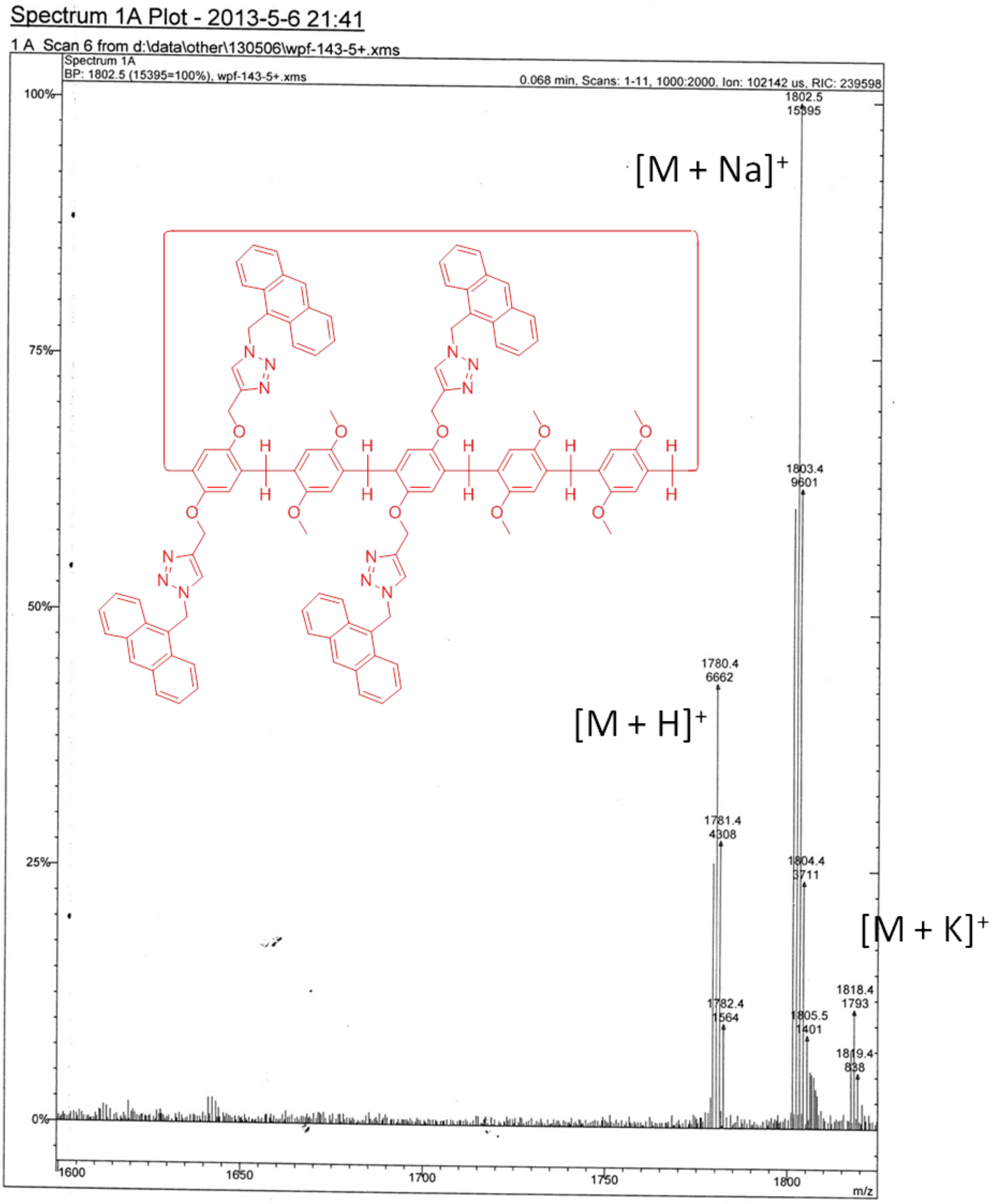


Figure S10. LRESI mass spectrum of **1**.

3. Partial ^{1}H NMR and COSY NMR spectra to identify the protons of ***1***

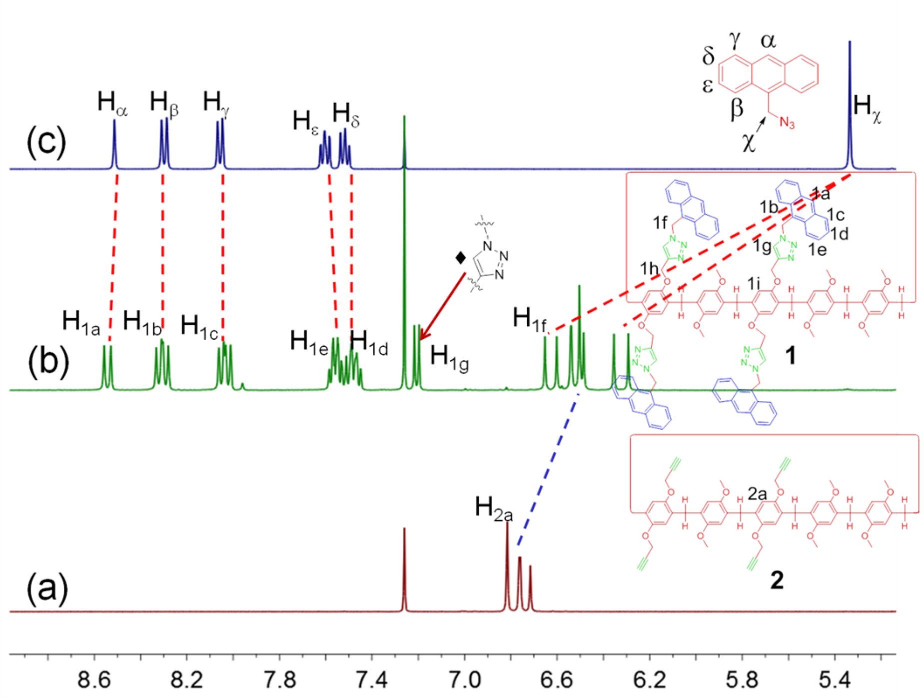


Figure S11. Partial ^{1}H NMR spectra (500 MHz, chloroform-*d*, 293 K): (a) 9-azidomethylanthracene; (b) **1**; (c) **2**.

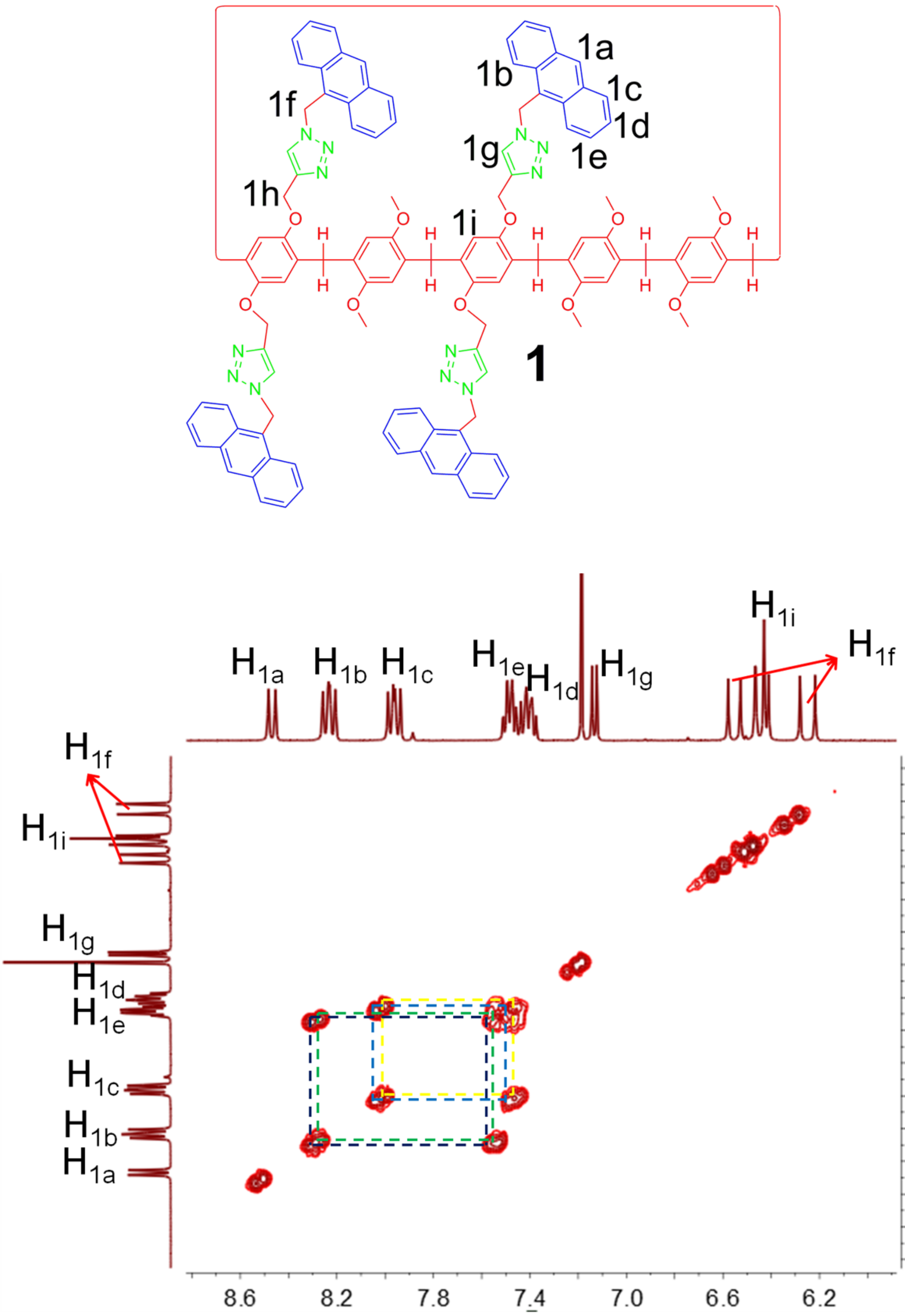


Figure S12. Partial 2D COSY NMR spectrum (500 MHz, chloroform-*d*, 293 K) of **1**.

*4. UV-vis spectra of **1** before and after the addition of* Fe^{3+}

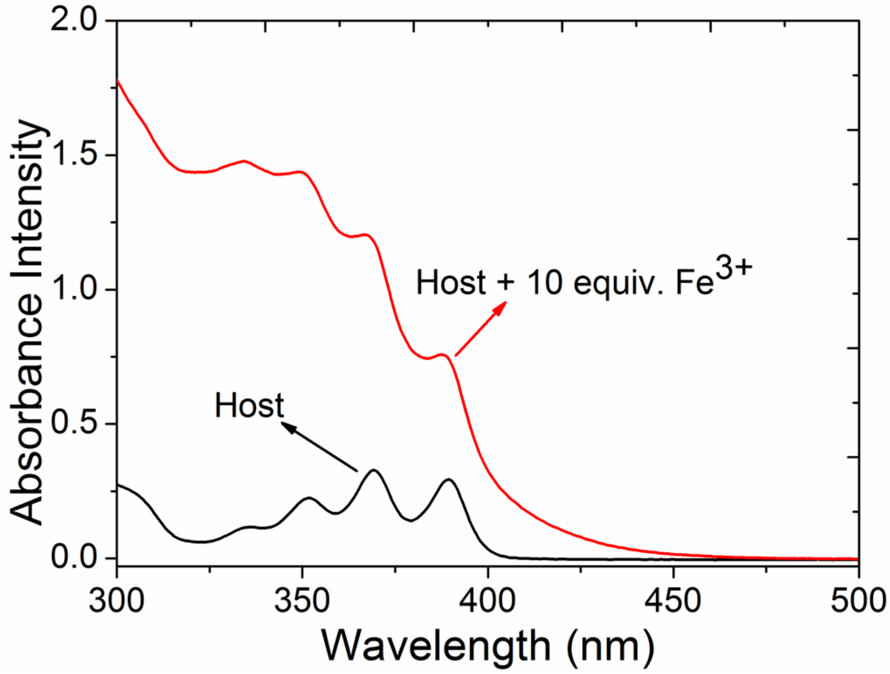


Figure S13. Absorption spectra of the DMSO solution of host **1** (20 μM) before and after the addition of 10 equiv of Fe^{3+}.

*5. Fluorescence titration studies of **1** with* Fe^{3+} *in DMSO*

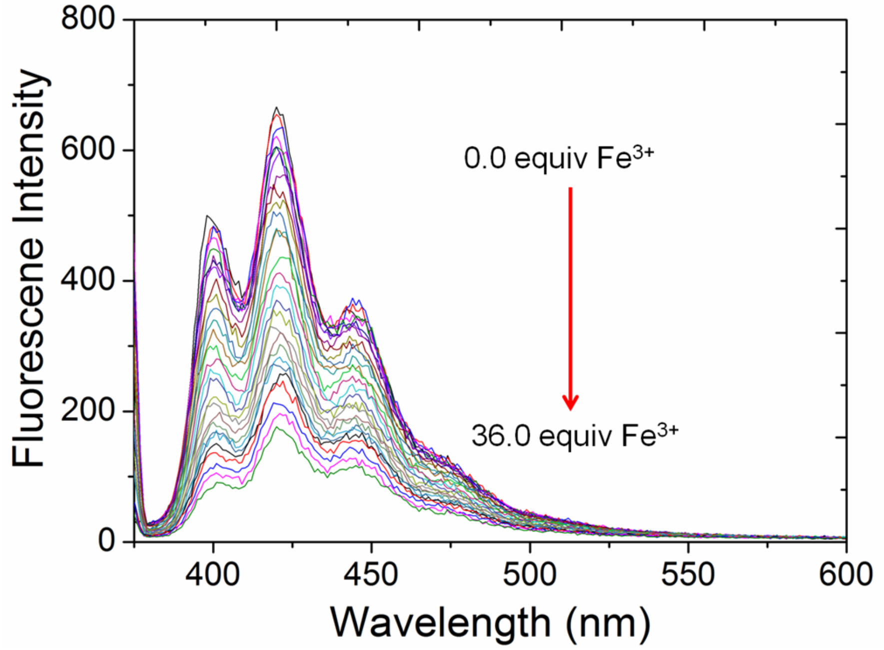


Figure S14. Fluorescence spectra of **1** (20 μM) in the presence of different concentrations of Fe^{3+} in DMSO (excitation wavelength = 370 nm).

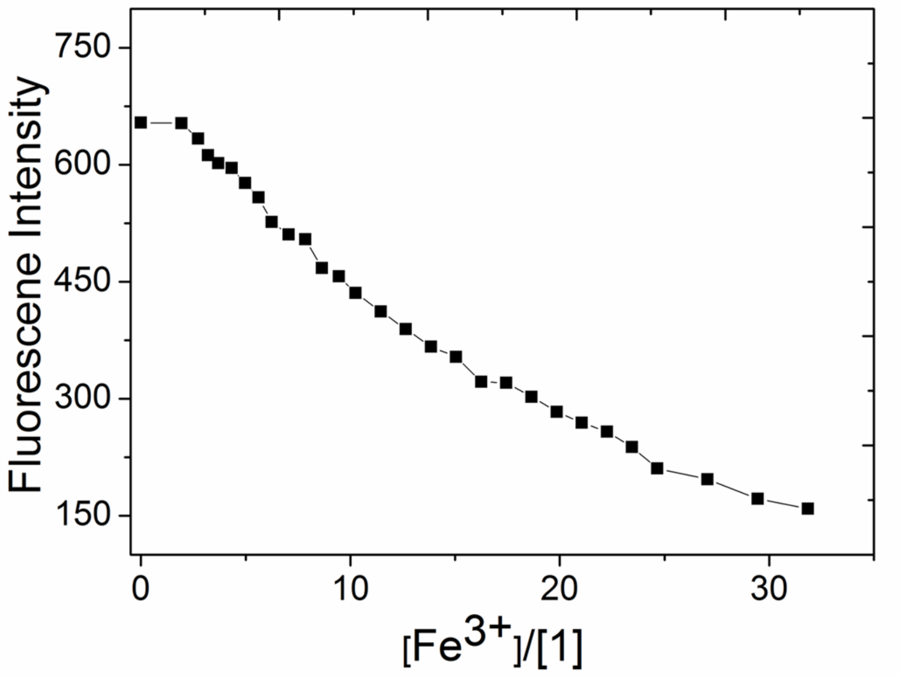


Figure S15. A plot of fluorescence intensity depending on the concentration of Fe^{3+} in the range from 0.0 to 36.0 equivalents at $\lambda = 420$ nm.

6. The snapshots of molecular dynamic simulations

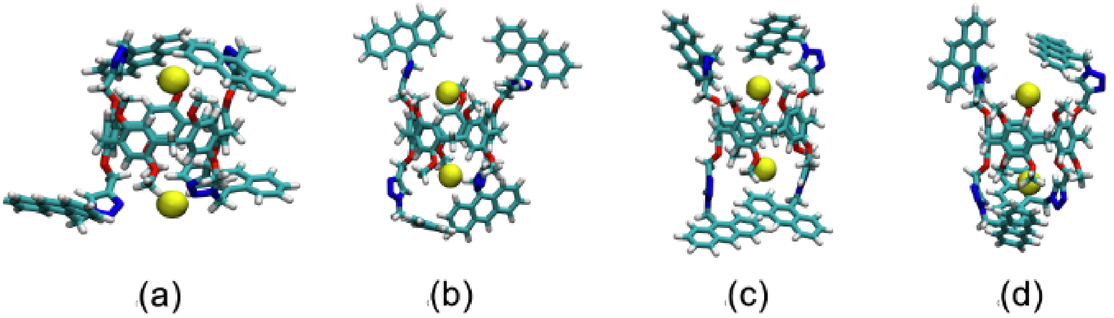


Figure S16. The snapshots of molecular dynamic simulations: (a) 0 ns, (b) 2 ns, (c) 4 ns, (d) 6 ns.

*7. X-ray crystal data of **2***

Crystal data of **2**: block, colorless, 0.42 × 0.40 × 0.35 mm^3, $C_{53}H_{50}O_{10}$•CH_2Cl_2, *FW* 931.86, Triclinic, space group *P*–1, a = 12.0078(5), b = 19.6299(9), c = 20.8822(8) Å, α = 97.198(4)°, β = 98.706(3)°, γ = 96.895(3)°, V = 4778.4(3) Å^3, Z = 4, D_c = 1.295 g cm^{-3}, T = 170(2) K, μ = 0.195 mm^{-1}, 17427 measured reflections, 7260 independent reflections, 1213 parameters, 39 restraints, $F(000)$ = 1960, R_1 = 0.1515, wR_1 = 0.3380 (all data), R_2 = 0.1094, wR_2 = 0.2949 [$I > 2\sigma(I)$], max. residual density 2.473 e•Å^{-3}, and goodness-of-fit (F^2) = 1.045. CCDC 1412286.

References:

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S5. G. M. Sheldrick, *SHELXS-97*, *Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.