A supramolecular polymer formed by the combination of crown ether-based and charge-transfer molecular recognitions

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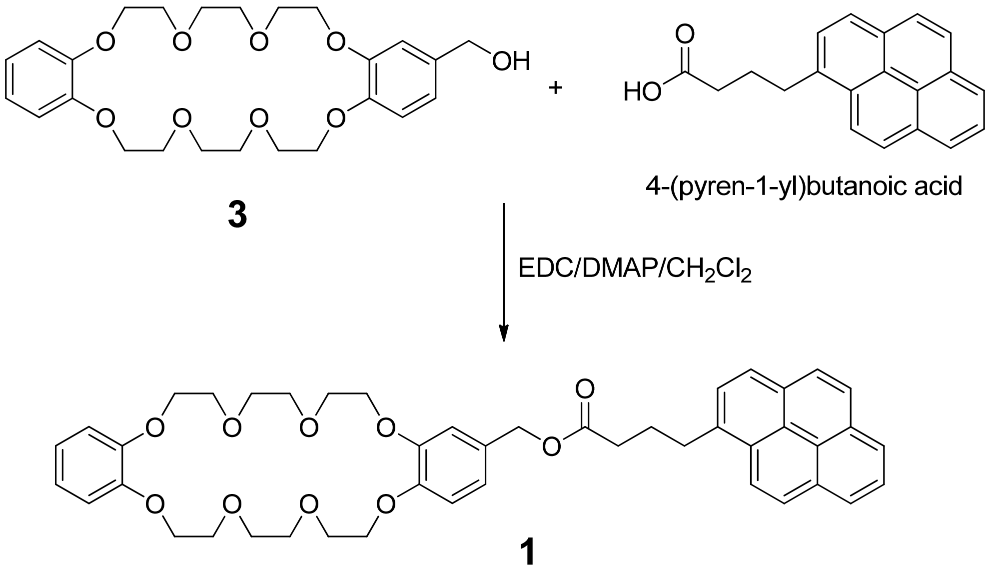
Electronic Supplementary Information (11 Pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **3**,[2a,S1] **4**,[S2] and **5**[S3] were prepared according to the published procedures. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 298 K in CH_3CN. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. Electrospun supramolecular polymer nanofibers were obtained under the following conditions: 15 KV, 2.0 mL/h syringe flow rate, and 20 cm working distance, from a concentrated equimolar solution of 200 mM monomers **1** and **2**.

2. *Syntheses of monomers* **1** *and* **2**

2.1. Synthesis of monomer **1**



A mixture of **3** (4.78 g, 10 mmol), 4-(pyren-1-yl)butanoic acid (2.88 g, 10 mmol), 1-(3’-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 3.85 g, 20 mmol) and 4-dimethylaminopyridine (DMAP, catalytic amount) in CH_2Cl_2 (50 mL) was stirred overnight at room temperature. After filtration, the solution was washed with water and brine. Then the organic layer was dried by $MgSO_4$ overnight. Dichloromethane was removed and the residue was purified by column chromatography (CH_2Cl_2/petroleum ether, 1:1, *v*/*v*) to afford **1** as a yellow solid (3.63 g, 48%). Mp: 144.2–146.5 ºC. The ^{1}H NMR spectrum of compound **1** is shown in Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.15 (d, J = 8.0 Hz, 1H), 8.05 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H), 7.98 (t, J = 8.0 Hz, 2H), 7.91 (s, 2H), 7.88 (d, J = 4.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 6.80–6.70 (m, 7H), 4.94 (s, 2H), 4.04–4.01 (m, 8H), 3.77–3.75 (m, 8H), 3.72 (s, 4H), 3.69 (s, 4H), 3.27 (d, J = 8.0 Hz, 2H), 2.39 (d, J = 8.0 Hz, 2H), 2.10 (d, J = 8.0 Hz, 2H). The ^{13}C NMR spectrum of **1** is shown in Figure S2. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm): 25.74, 31.64, 32.87, 65.18, 68.27, 68.29, 68.36, 68.73, 70.16, 75.80, 76.05, 76.31, 112.54, 112.98, 113.34, 120.36, 123.89, 126.42, 134.60, 147.78, 147.84, 147.91, 172.25. LRESIMS is shown in Figure S3: *m*/*z* 771.5 [M + Na]$^+$ (100%). HRESIMS: *m*/*z* calcd for [M+ H]$^+$ $C_{45}H_{49}O_{10}$, 748.3247; found 748.3242; error –0.7 ppm.

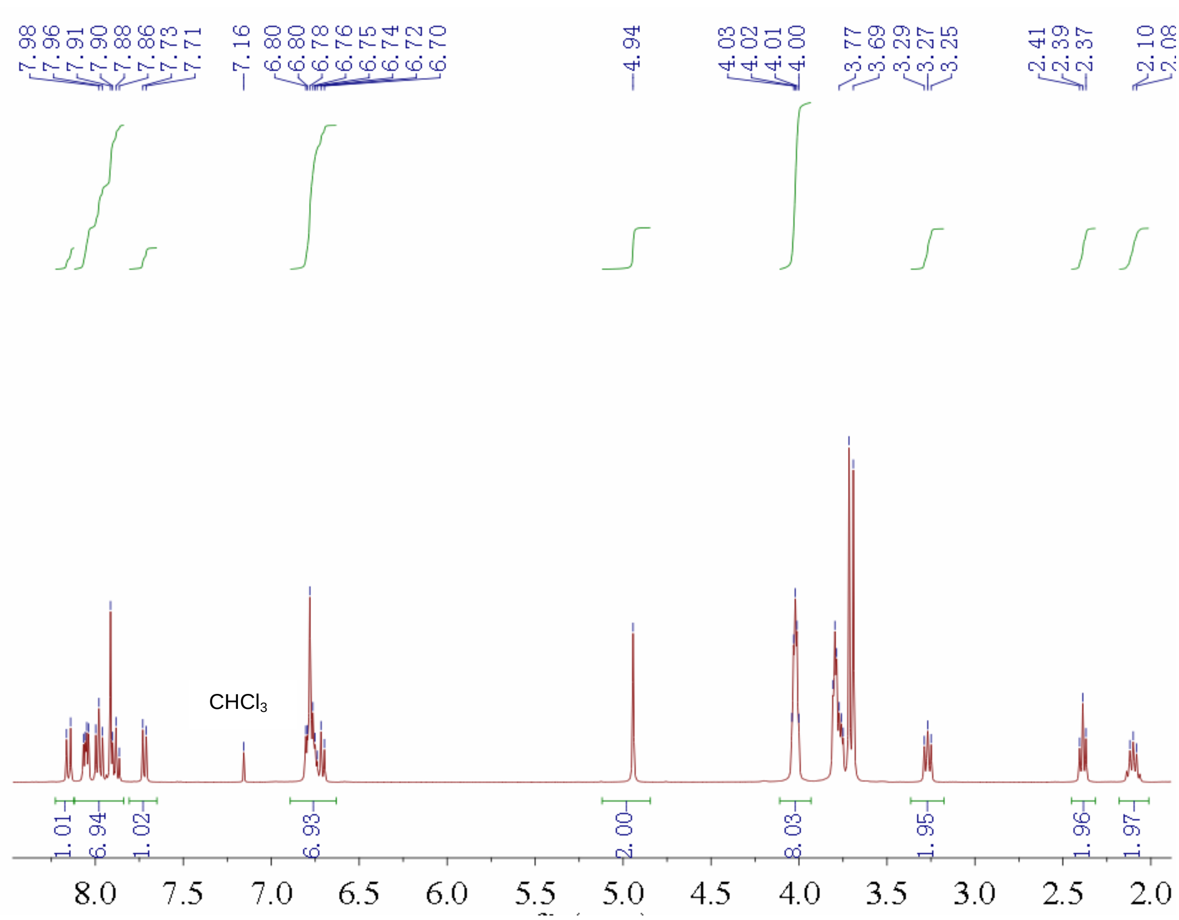


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **1**.

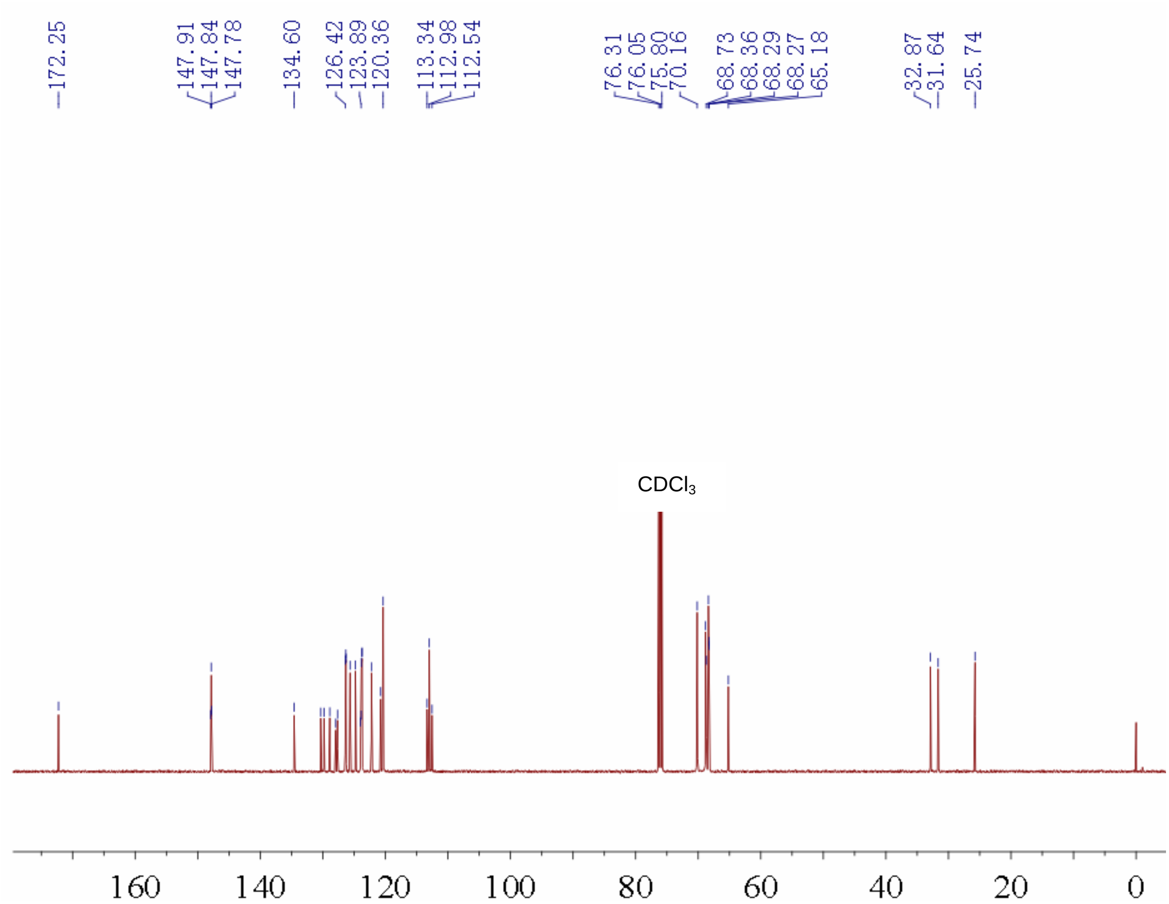


Figure S2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1**.

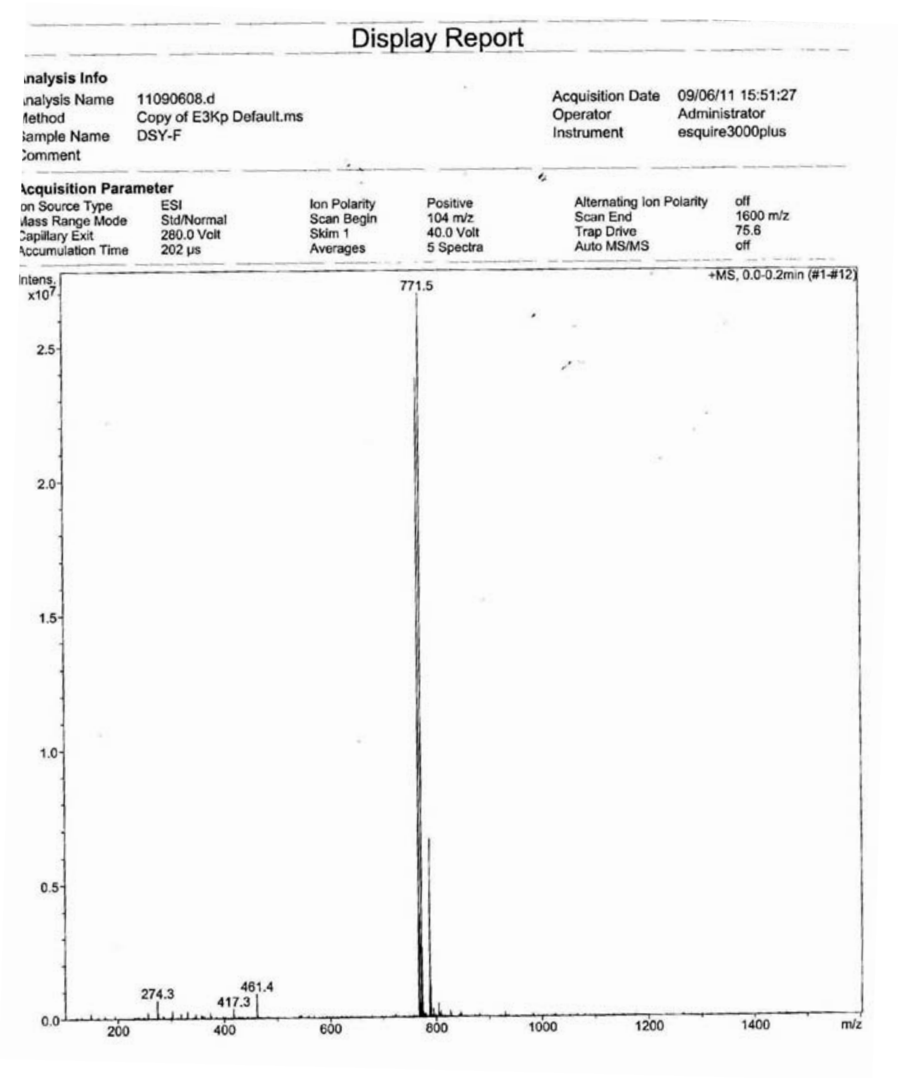


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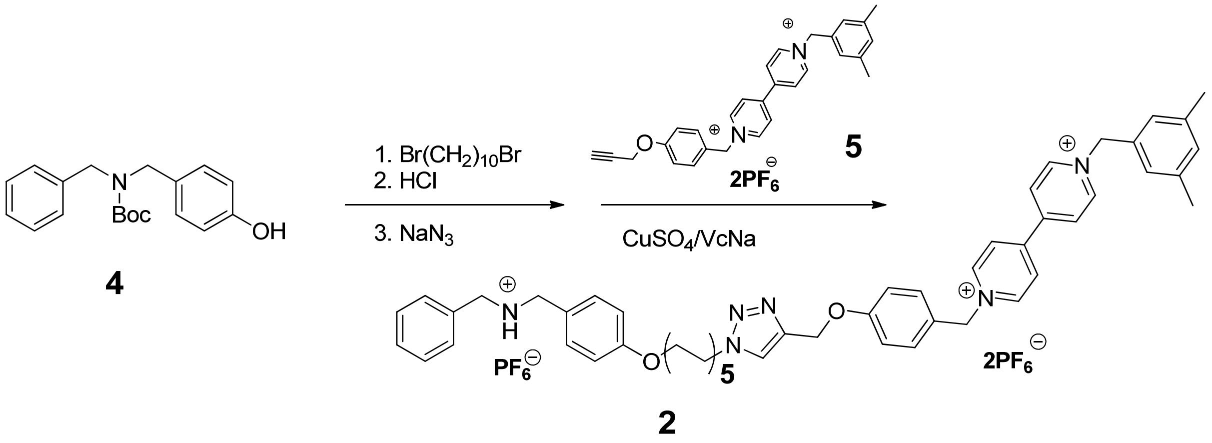
Figure S3. Electrospray ionization mass spectrum of **1**.

*2.2. Synthesis of monomer **2***



A mixture of **4** (3.13 g, 10 mmol), K_2CO_3 (2.76 g, 20 mmol) and 1,10-dibromodecane (6.00 g, 20 mmol) in CH_3CN (100 mL) was stirred under reflux overnight. Then the solvent was removed and the residue was dissolved in 10% HCl/ethyl acetate (50 mL) and the mixture was stirred overnight at room temperature. The white solid was filtered, washed with ethyl acetate thoroughly, and dissolved in warm deionized water/acetonitrile (250 mL, 5:1, *v*:*v*). A saturated aqueous solution of NH_4PF_6 was added to afford a white precipitate, which was filtered and washed with deionized water. This white precipitate was added to a mixture of **5** (6.5 g, 9.1 mmol), $CuSO_4{\bullet}5H_2O$ (0.25 g, 1.0 mmol), Sodium *L*-ascorbate (VcNa, 0.40 g, 2.0 mmol) and DMF (25 mL). The mixture was stirred at 50 ºC overnight. Then the mixture was dropped to cold water to yield a light yellow solid. The solid was filtered and recrystallized from CH_3CN/MeOH/water to afford **2** as a gray solid (4.1 g, 37%). Mp: 189.8–192.3 ºC. The ^1H NMR spectrum of compound **2** is shown in Figure S4. ^1H NMR (400 MHz, CD_3SOCD_3, 298 K) δ (ppm): 9.45 (d, J = 8.0 Hz, 4H), 8.69 (d, J = 8.0 Hz, 4H), 7.59 (d, J = 8.0 Hz, 2H), 7.45–7.36 (m, 8H), 7.21 (s, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.08 (s, 1H), 6.96 (d, J = 8.0 Hz, 2H), 5.83 (d, J = 8.0 Hz, 2H), 5.14 (s, 2H), 4.34 (t, J = 8.0 Hz, 2H), 3.95 (t, J = 8.0 Hz, 2H), 2.27 (s, 6H), 1.79–1.69 (m, 4H), 1.39–1.25 (m, 12H). The ^{13}C NMR spectrum of **2** is shown in Figure S5. ^{13}C NMR (125 MHz, CD_3CN, 298 K) δ (ppm): 21.37, 26.85, 27.25, 29.79, 30.06, 30.16, 30.22, 30.31, 31.06, 51.27, 51.87, 52.00, 62.68, 65.54, 66.03, 69.21, 116.09, 116.92, 118.62, 123.67, 125.25, 126.07, 128.12, 128.53, 130.30, 130.76, 131.13, 132.13, 132.46, 132.64, 132.83, 133.68, 140.76, 144.13, 146.51, 146.69, 151.45, 151.50, 160.94, 161.36. LRESIMS is shown in Figure S6: *m*/*z* 270.2 $[M - 3PF_6]^{3+}$ (100%), 480.1 $[M - 2PF_6]^{2+}$ (100%). HRESIMS: *m*/*z* calcd for $[M - PF_6]^+$ $C_{53}H_{63}F_{12}N_6O_2P_2$, 1105.4296; found 1105.4280; error –1.4 ppm.

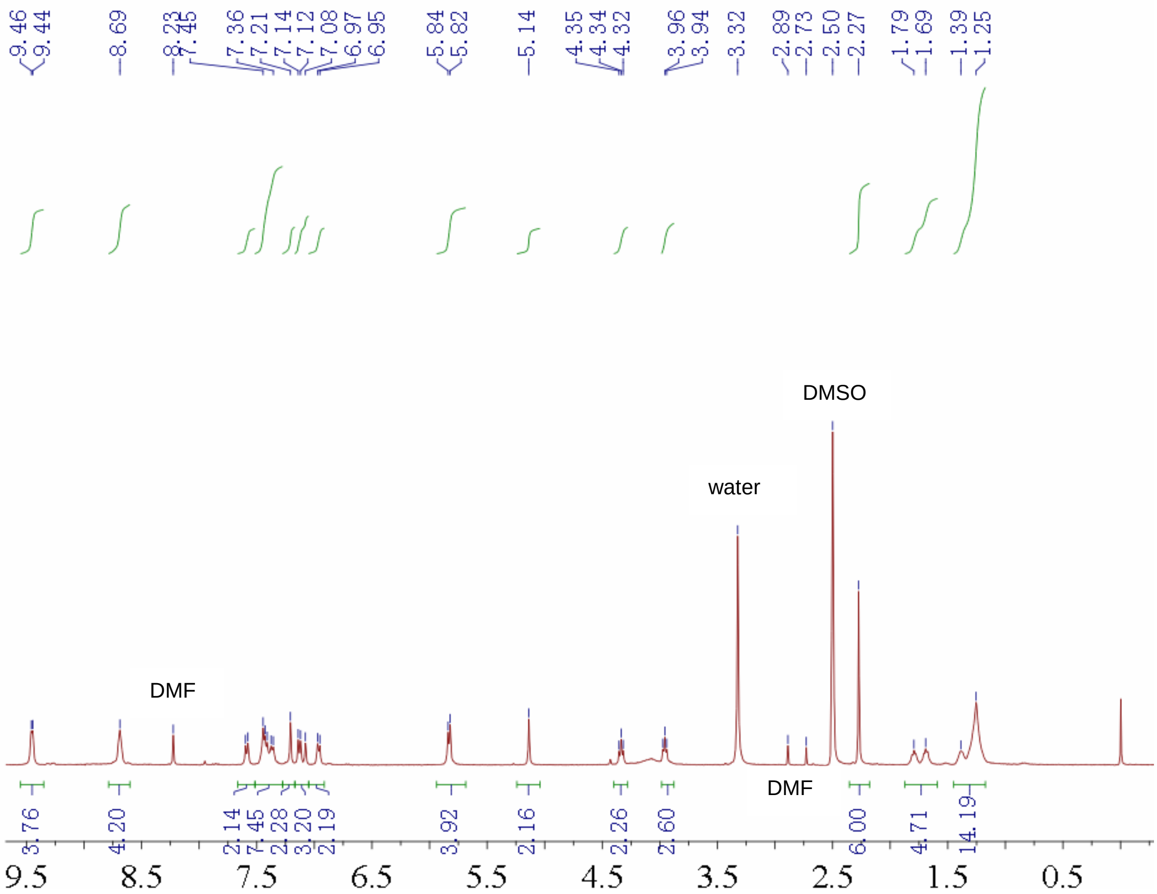


Figure S4. ^{1}H NMR spectrum (400 MHz, CD_3SOCD_3, 298 K) of **2**.

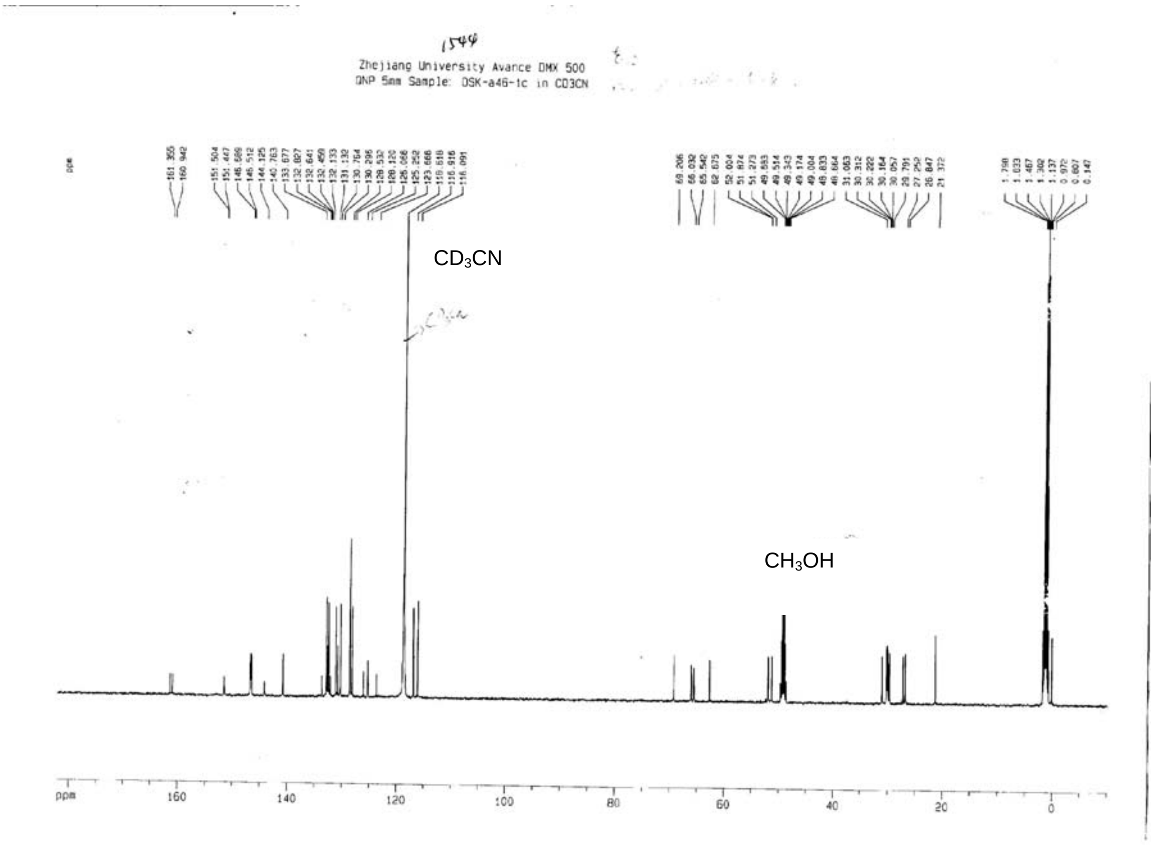


Figure S5. ^{13}C NMR spectrum (125 MHz, CD_3CN, 298 K) of **2**.

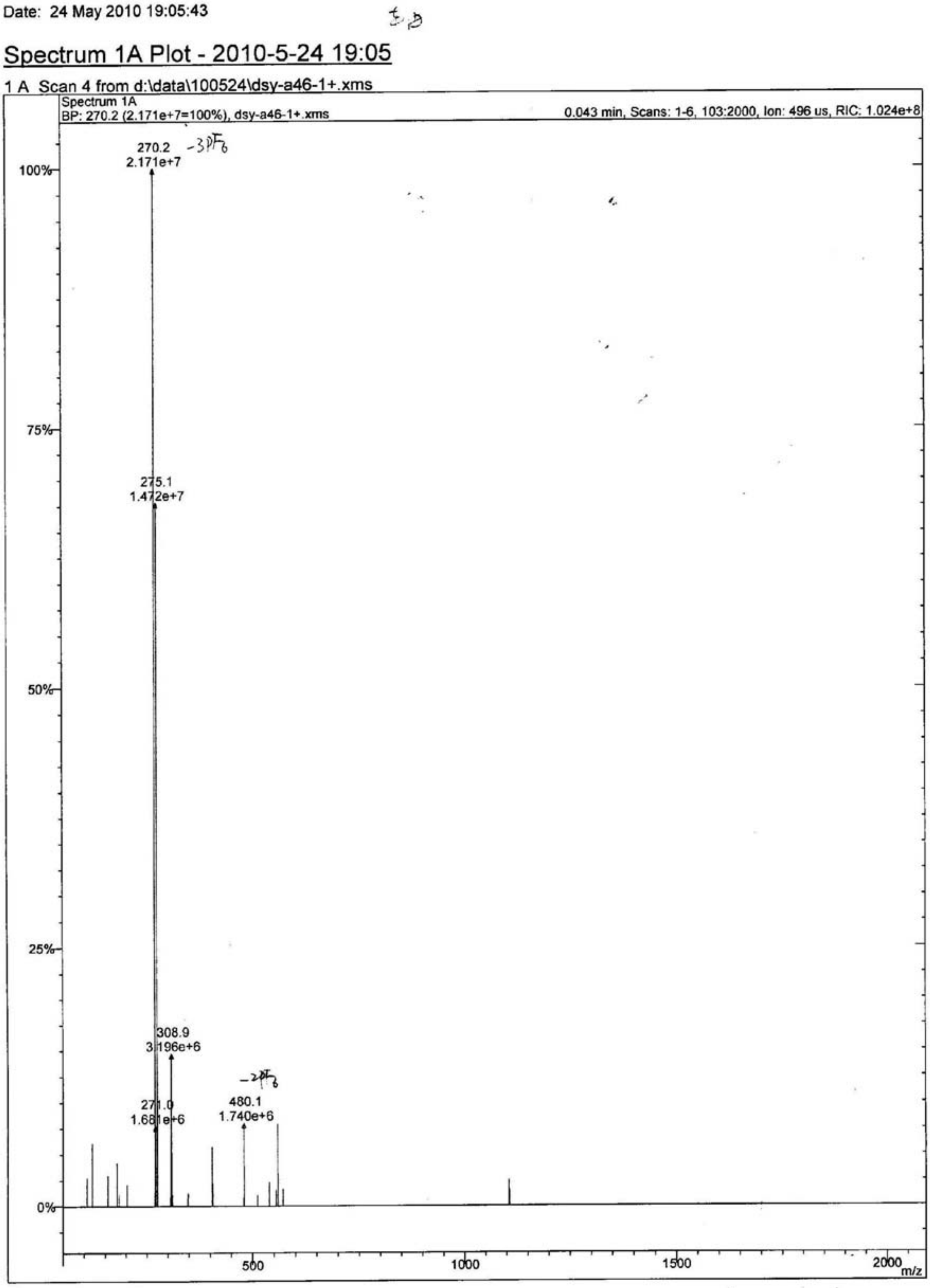


Figure S6. Electrospray ionization mass spectrum of **2**.

3. ^{1}H NMR spectra and UV/vis spectra of model compounds

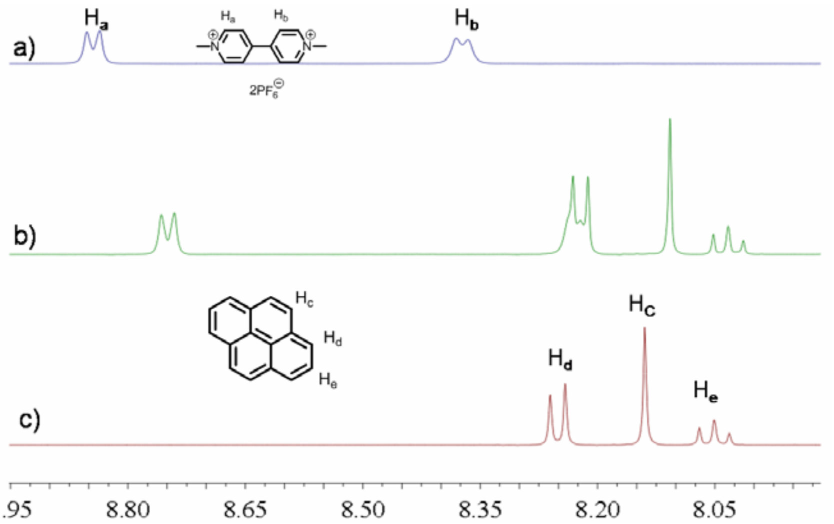


Figure S7. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K): a) paraquat (5.00 mM); b) paraquat and pyrene (both 5.00 mM); c) pyrene (5.00 mM).

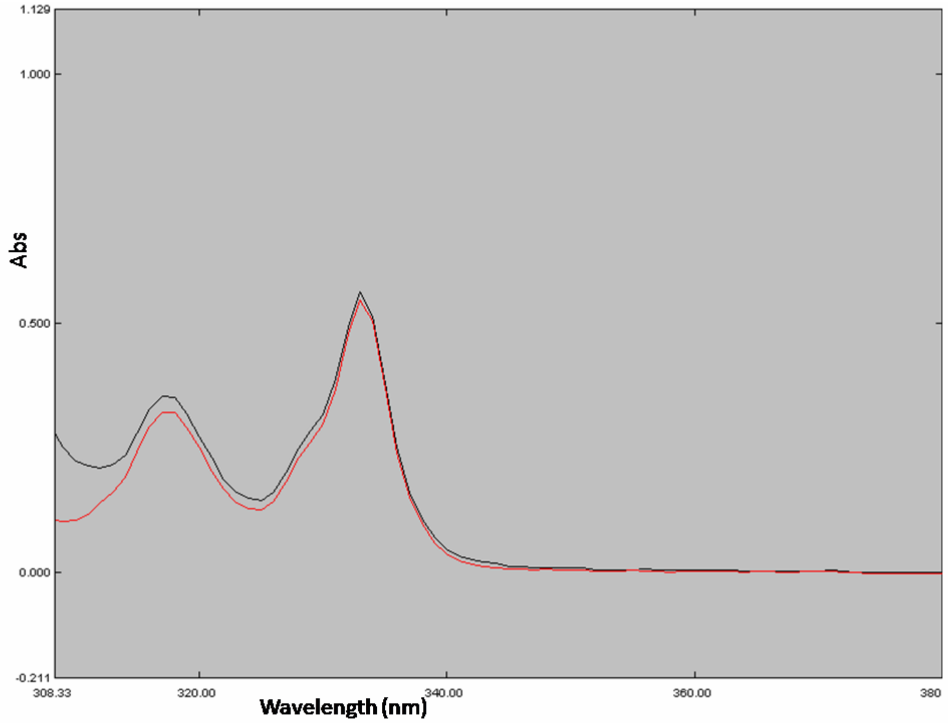


Figure S8. UV/Vis spectroscopy of pyrene (red line) and pyrene-paraquat complexes (black line). The concentrations of pyrene and paraquat are 0.45×10^{-4} M.

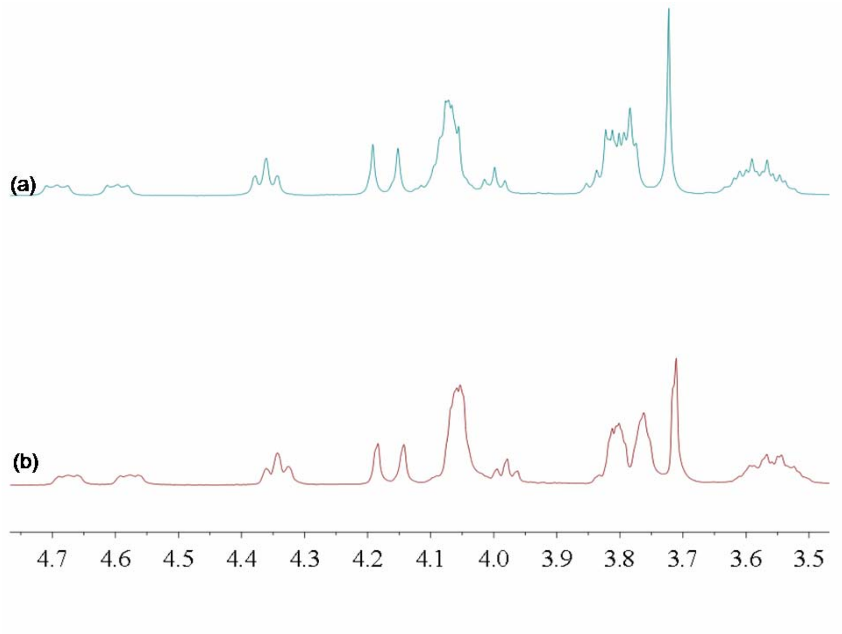


Figure S9. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K): a) dibenzo-24-crown-8 and monomer **2** (1.00 mM for each); b) after adding pyrene (1.00 mM).

References:

S1. F. Wang, C. Han, C. He, Q. Zhou, J. Zhang, C. Wang, N. Li and F. Huang, *J. Am. Chem. Soc.*, 2008, **130**, 11254–11255.

S2. L. Wu, Y.-M. He and Q.-H. Fan, *Adv. Synth. Catal.*, 2011, **353**, 2915–2919.

S3. S. Dong, X. Yan, B. Zheng, J. Chen, X. D, X. Y, D. Xu, M. Zhang and F. Huang, *Chem. Eur. J.*, 2012, **18**, 4195–4199.