

A fluorescent supramolecular polymer with aggregation induced emission (AIE)

properties formed by crown ether-based host-guest interactions

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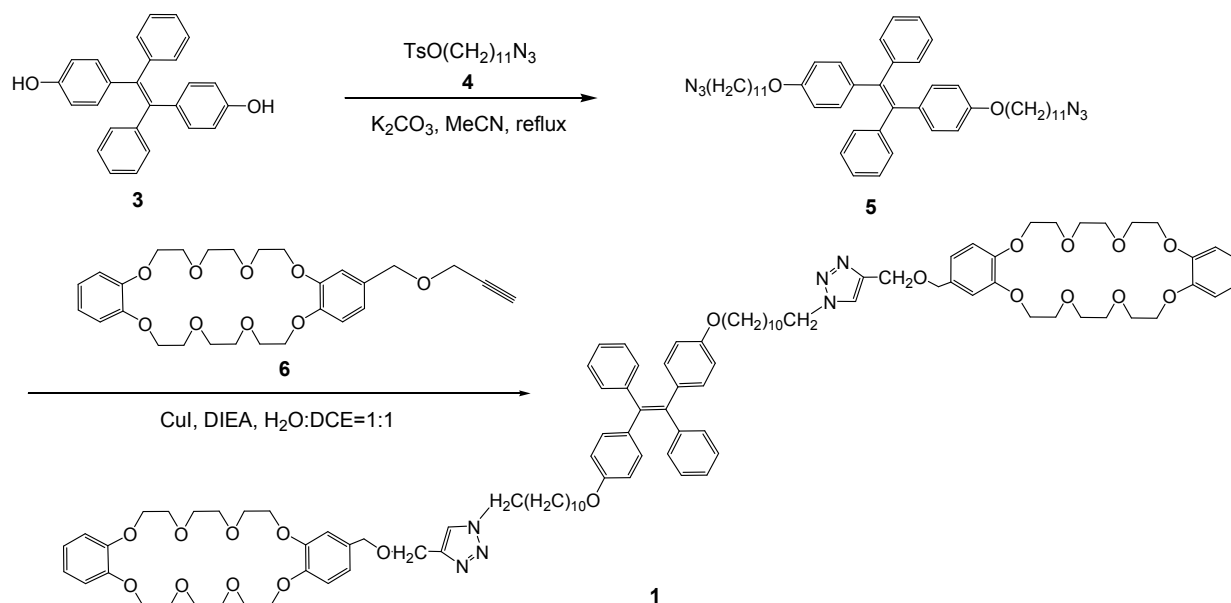
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1. Materials and methods

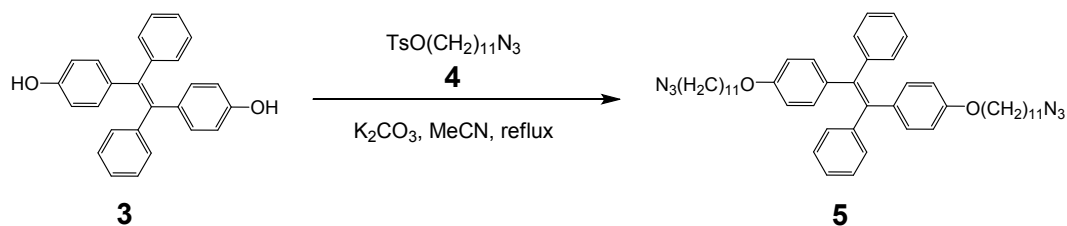
Compounds **3**^{S1}, **4**^{S2} and **6**^{S3} were synthesized according to the published procedure. 1D (¹H, ¹³C) and 2D (¹H-¹H-NOESY, COSY, DOSY) nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker Avance 500 operating at a frequency of 500 MHz for ¹H and 125 MHz for ¹³C. Mass spectra were recorded on a Hewlett-Packard 5989 A mass spectrometer (ESI mode). High-resolution mass data were obtained with a Agilent Technologies 6530 Accurat-Mass Q-TOF LC/MC instrument. Viscosity measurements were carried out with Ubbelohde dilution viscometers (Julabo Technology Corporation visco-170, 0.47 mm inner diameter) in CHCl₃/CH₃CN (1/1, v/v) containing 0.05 mol/L tetrabutylammonium hexafluorophosphate to exclude the polyelectrolyte effect. Scanning electron microscopy (SEM) investigations were carried out on a Carl Zeiss Jena supra55 sapphire instrument. Fluorescent confocal images were recorded on a Zeiss LSM 710 confocal fluorescence microscopy. The fluorescence spectra were recorded on a HITACHI F7000 fluorescence spectrophotometer. The samples for solid-state fluorescence measurements were prepared as follows. A linear supramolecular polymer solution (90 mM in CHCl₃/CH₃CN) was first prepared. Then different metal ions (100 μM in CHCl₃/CH₃CN, 2 μL) were added into linear supramolecular polymer solution (20 μL). After stirring for 10 min, 2 μL of the mixture solution was drop-coated on quart slides to dry.

2. Synthesis of compound 1



Scheme S1 Synthetic routes of monomer 1.

2.1. Synthesis of compound 5



3 (364 mg, 1.00 mmol), **4** (917 mg, 2.50 mmol) and K_2CO_3 (3.40 g, 25.0 mmol) in acetonitrile (100 mL) were refluxed for 24 h. After filtration, the solvent was removed with a rotary evaporator and the residue was extracted with H_2O/CH_2Cl_2 . The organic phase was collected, combined, dried over anhydrous Na_2SO_4 and then the solvent was removed to give a crude product, which was further purified by flash column chromatography (1:2 dichloromethane/hexane, v/v) to afford **5** as a pale yellow liquid (475 mg, 63.0%). 1H NMR (500 MHz, $CDCl_3$, 293K) δ (ppm): 7.02–7.18 (m, 10H), 6.90–7.00 (m, 4H), 6.61–6.71 (m, 4H), 3.85–3.95 (m, 4H), 3.29 (t, $J = 7.0$ Hz, 4H), 1.72–1.84 (m, 4H), 1.58–1.68 (m, 4H), 1.28–1.44 (m, 28H). HRMS $[M+H]^+$: calcd. for $C_{48}H_{63}N_6O_2$ 755.5139, found 755.5007.

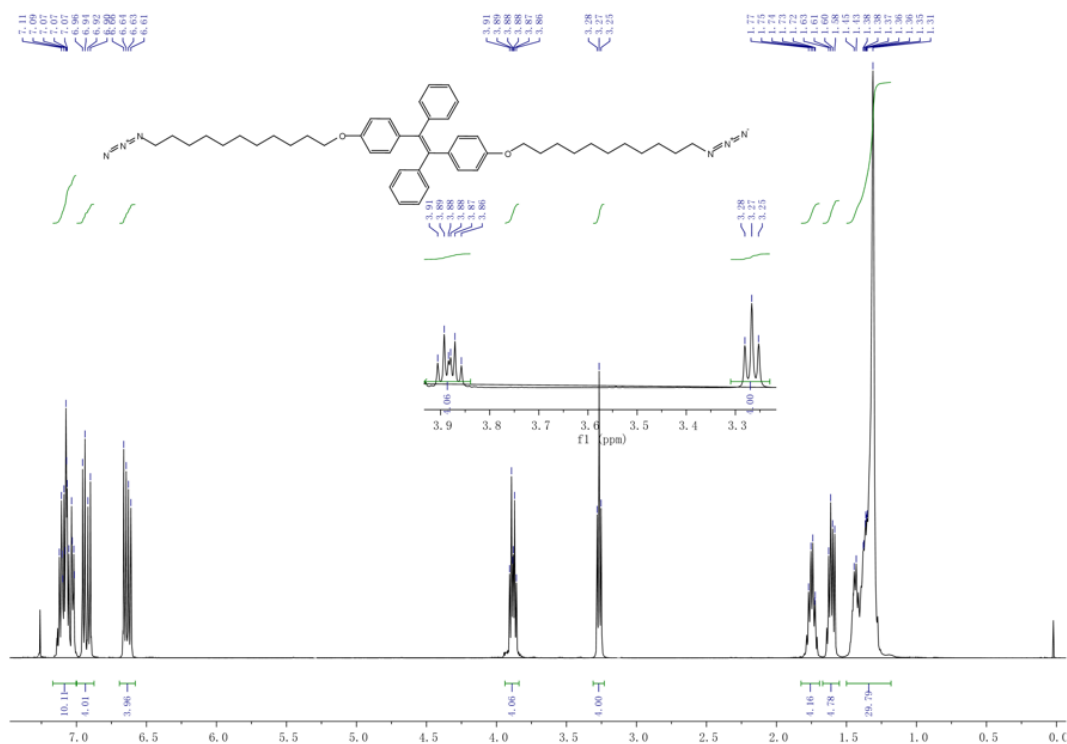


Fig. S1 1H NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **5**.

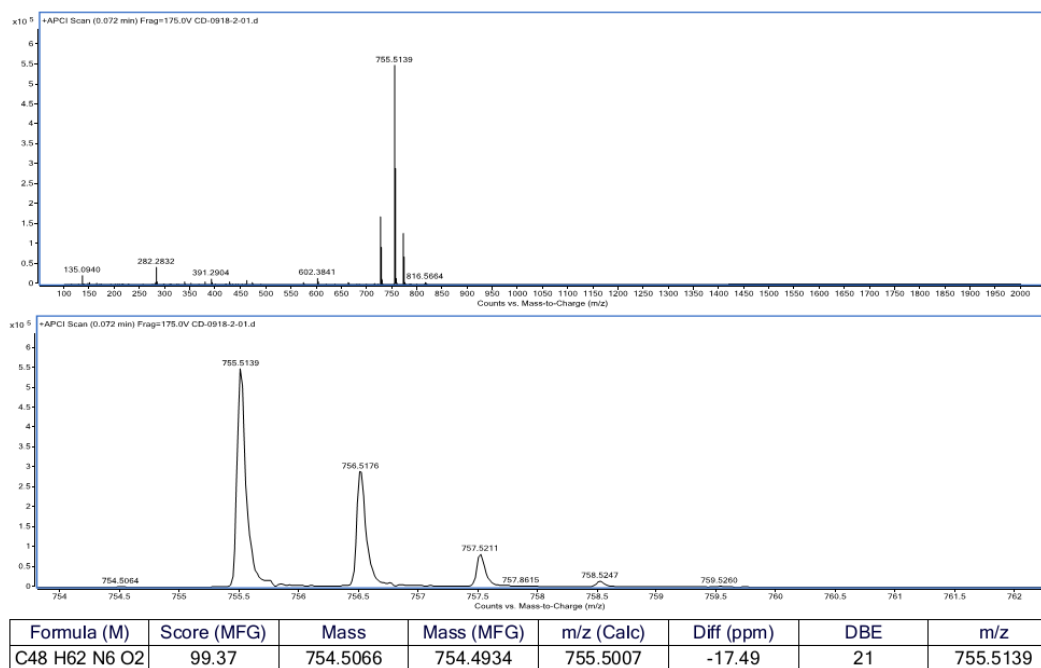
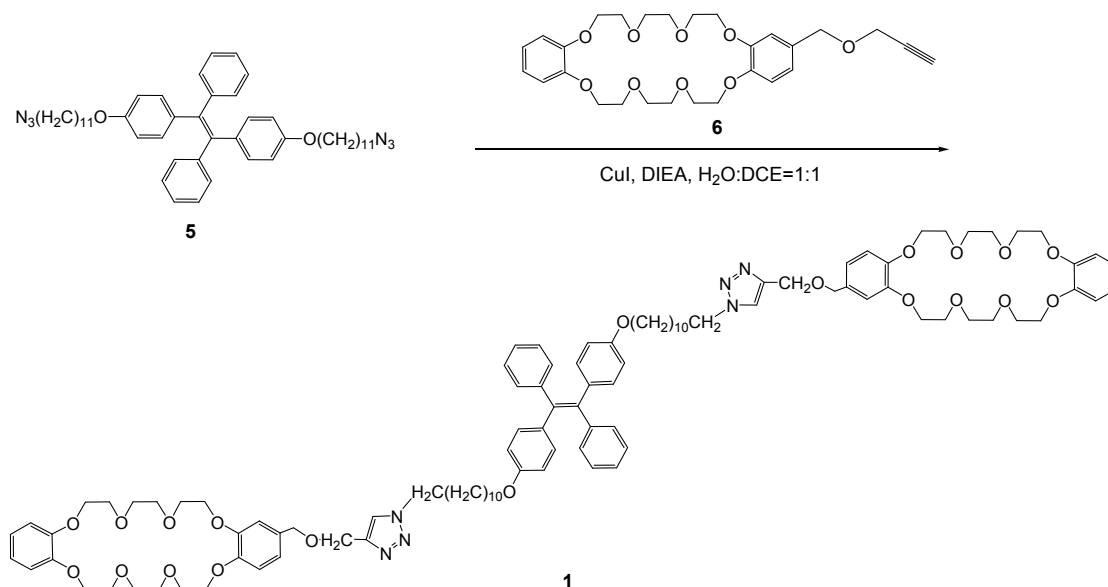


Fig. S2 HRMS spectrum of compound **5**.

2.2. Synthesis of compound **1**



A mixture of **5** (755 mg, 1.00 mmol), **6** (1.29 g, 2.50 mmol), CuI (760 mg, 0.40 mmol), DIEA (103 mg, 0.80 mmol) in DCE/H₂O (1:1, 100 mL) was stirred at 50°C for 24 h. The solvent was removed with a rotary evaporator and the residue was extracted with H₂O/CH₂Cl₂. The combined organic phase was concentrated and purified by flash column chromatography (first ethyl acetate, then 4:1

dichloromethane/MeOH, v/v) to afford the desired product as a solid (1.05 g, 59%). ^1H NMR spectrum (500 MHz, 1:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$, 293K) δ (ppm): 7.52 (s, 2H), 7.00–7.12 (m, 10H), 6.79–6.96 (m, 18H), 6.59–6.68 (m, 4H), 4.63 (s, 4H), 4.50 (s, 4H), 4.31 (t, $J = 7.2$ Hz, 4H), 4.14 (d, $J = 5.0$ Hz, 16H), 3.90 (d, $J = 5.0$ Hz, 16H), 3.83 (m, 20H), 1.91–1.84 (m, 4H), 1.75–1.64 (m, 4H), 1.46–1.13 (m, 28H). ^{13}C NMR (125 MHz, 1:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$, 293K) δ (ppm): 157.6, 157.6, 149.04, 148.9, 148.5, 144.3, 144.2, 139.8, 132.3, 132.2, 131.4, 131.2, 131.1, 127.7, 127.6, 126.2, 121.4, 121.0, 117.0, 114.4, 114.1, 114.0, 113.7, 113.6, 71.8, 70.8, 69.7, 69.7, 69.2, 69.1, 67.8, 63.2, 50.0, 30.1, 29.3, 29.3, 29.2, 29.2, 28.8, 26.3, 25.9, 25.9. ESI-MS: m/z 1809.47 $[\text{M}+\text{Na}]^+$. HRMS $[\text{M}+\text{H}]^+$: calcd. for $\text{C}_{104}\text{H}_{135}\text{N}_6\text{O}_{20}$ 1787.9726, found 1787.9987.

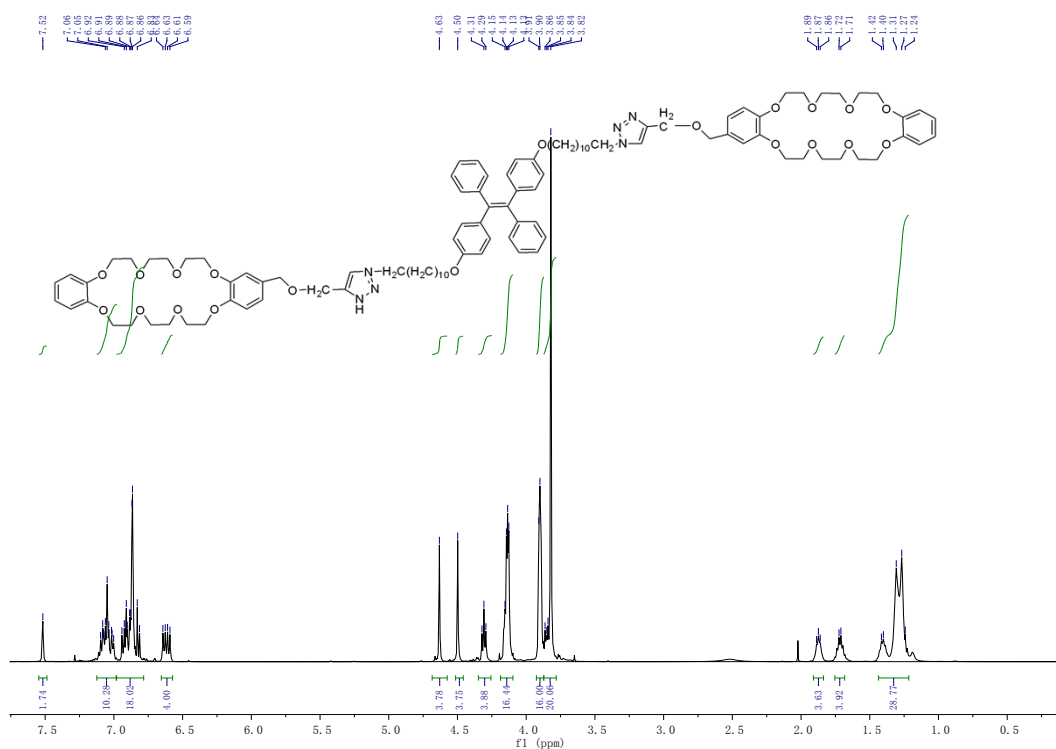


Fig. S3 ^1H NMR spectrum (500 MHz, 1:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$, 293K) of compound **1**.

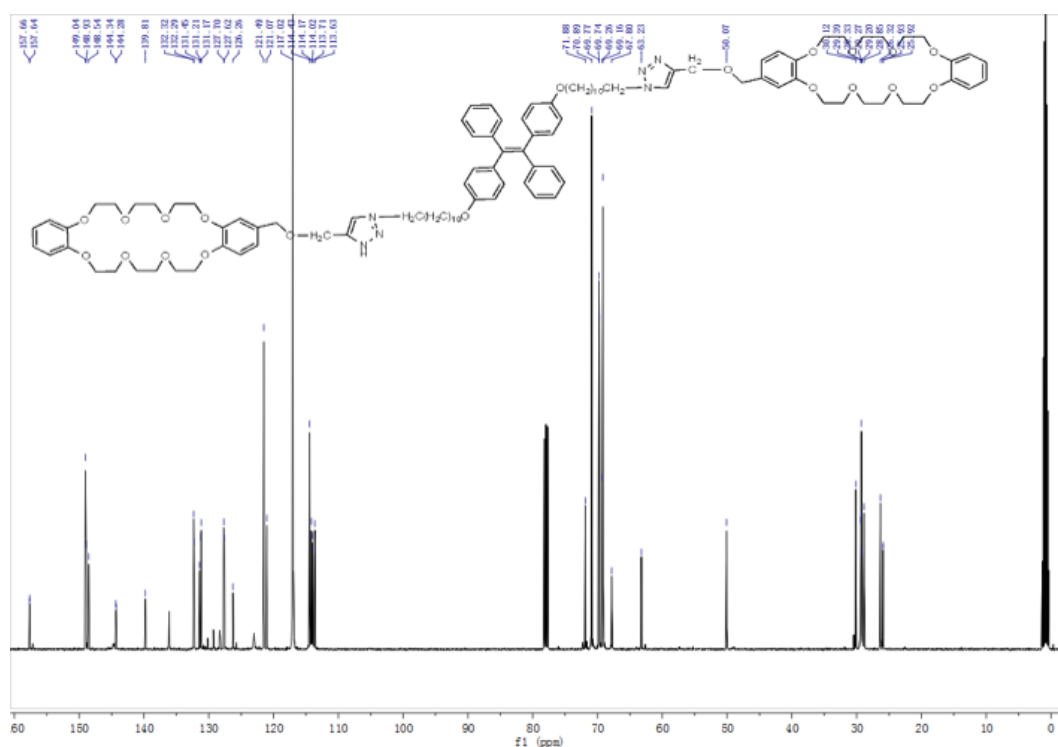


Fig. S4 ^{13}C NMR spectrum (125 MHz, 1:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$, 293K) of compound 1.

ESI-131219-Ib-06_01 #1 RT: 0.03 AV: 1 NL: 1.71E7
T: + c ESI Full ms [100.00-2000.00]

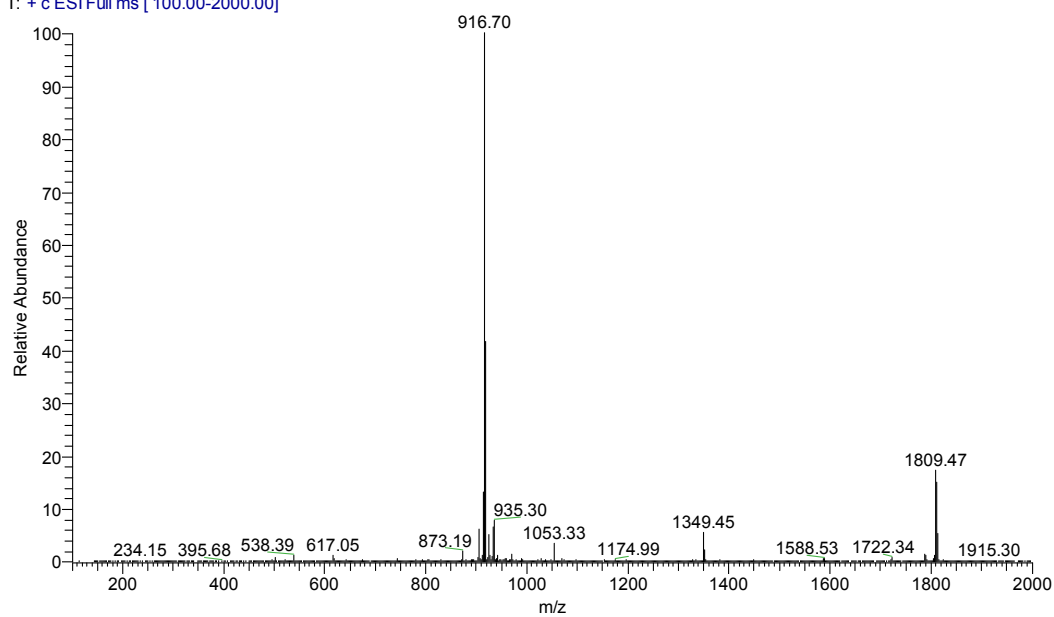


Fig. S5 Electrospray ionization mass spectrum of compound 1.

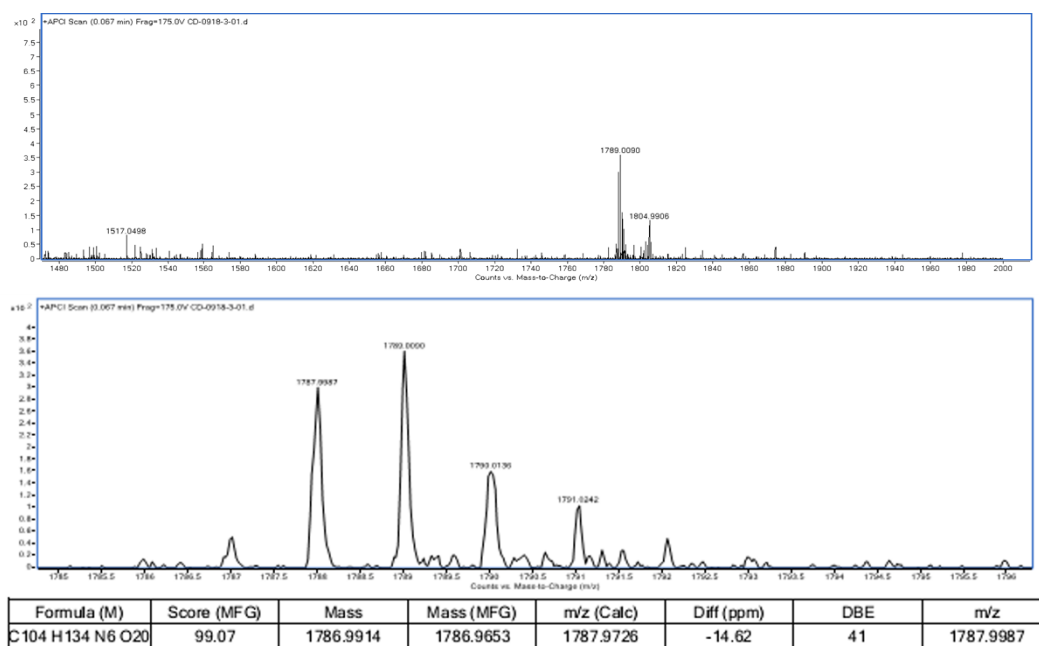


Fig. S6 HRMS spectrum of compound **1**.

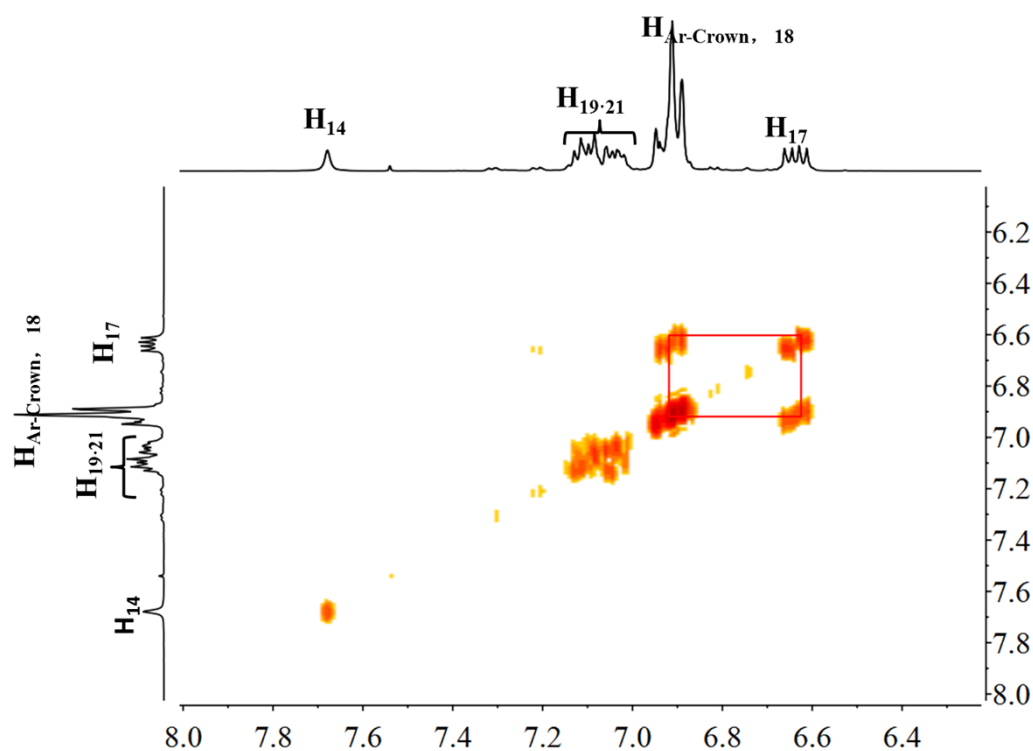


Fig. S7 Partial 2D H-H COSY spectrum (500MHz, 1:1 CDCl₃/CD₃CN, 293K) of compound **1** in the downfield region.

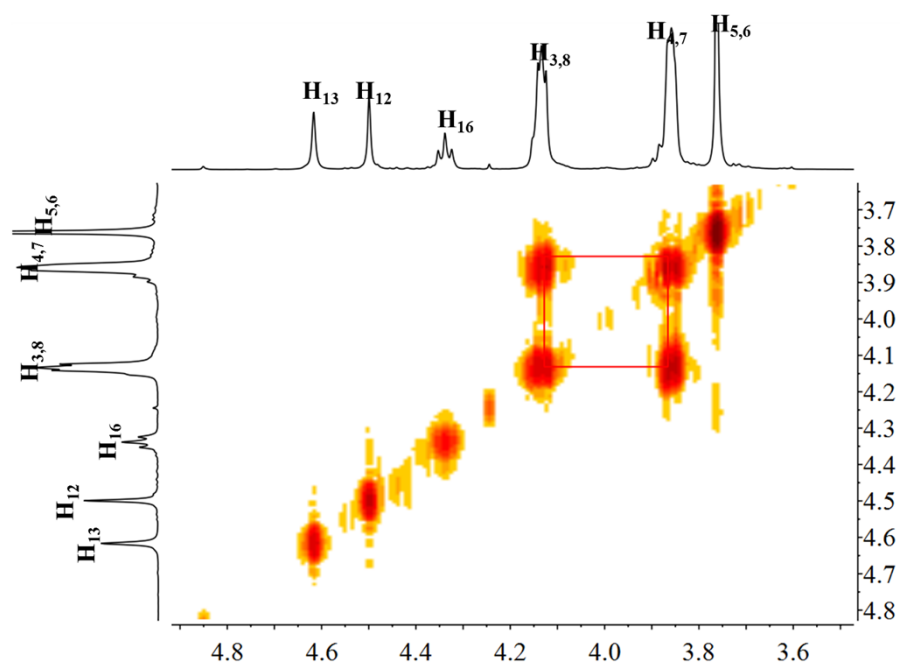


Fig. S8 Partial 2D H-H COSY spectrum (500MHz, 1:1 CDCl₃/CD₃CN, 293K) of monomer **1** in the upfield region.

3. The conversion between supramolecular polymer and monomers

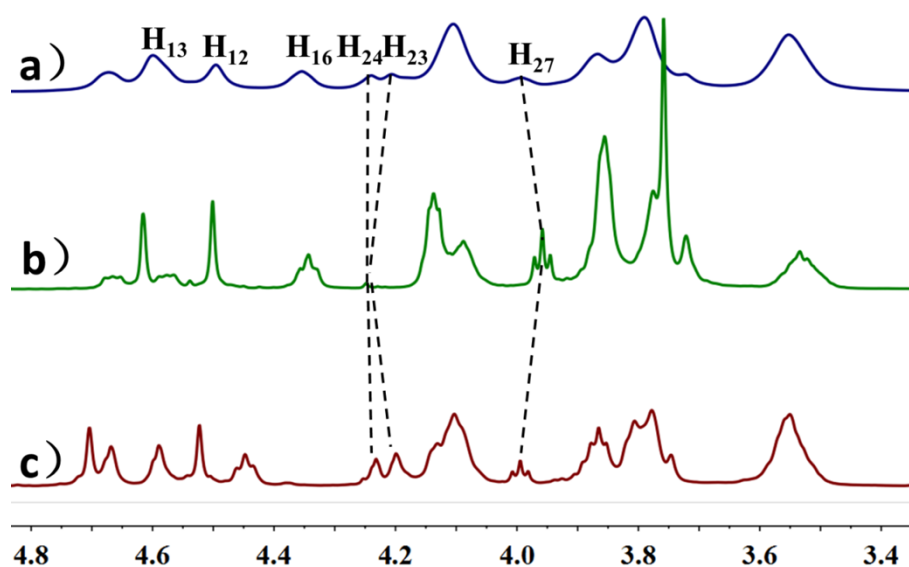


Fig. S9 Partial ¹H NMR spectra (500MHz, 1:1 CDCl₃/CD₃CN, 293K) of (a) 1:1 mixture of **1** and **2** at the concentration of 90 mM; (b) treating the mixture with 1.5 equiv. of Et₃N to (a); (c) subsequent addition of 3.5 equiv. of TFA to (b).

4. Fluorescence spectra of monomer **1** and the linear supramolecular polymer

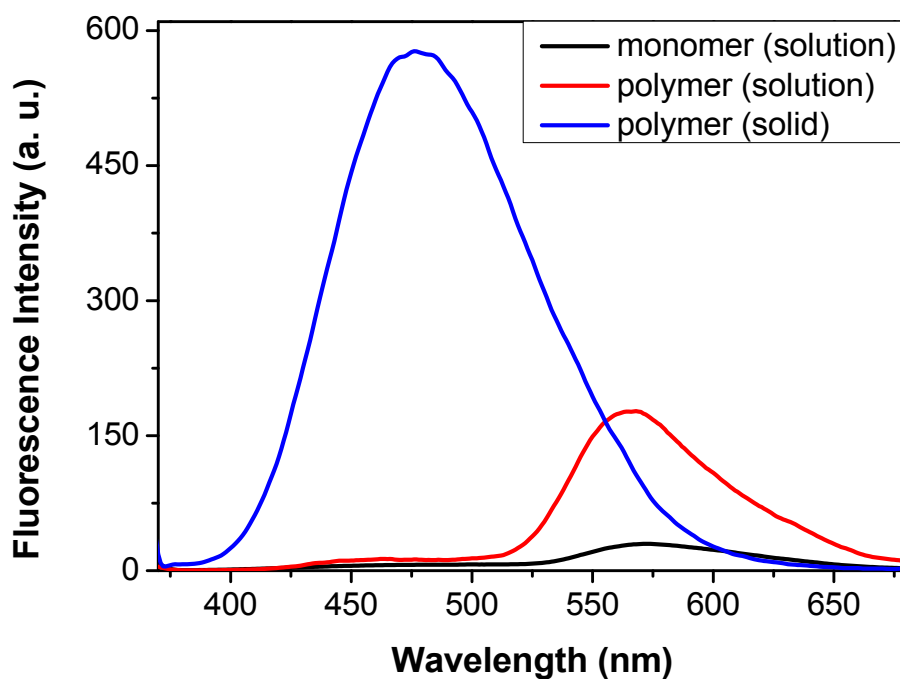


Fig. S10 Fluorescence spectra of monomer **1** (200 mM) and the linear supramolecular polymer in 1:1 CH₃CN/CHCl₃ (200 mM) and in the solid state.

References:

- S1. H. Tong, Y. Hong, Y. Dong, M. Haeussler, J. W. Y. Lam, Z. Li, Z. Guo and B. Z. Tang, *Chem. Commun.* 2006, 3705.
- S2. H. Li, A. C. Fahrenbach, S. K. Dey, S. Basu, A. Trabolsi, Z. Zhu, Y. Y. Botros and J. F. Stoddart, *Angew. Chem., Int. Ed.* 2010, **49**, 8260.
- S3. Y. Koyama, Y. Suzuki, T. Asakawa, N. Kihara, K. Nakazono and T. Takata, *Polym. J.* 2012, **44**, 30.