Electronic Supplementary Information

Construction of [2]Rotaxane-Based Supramolecular Polymers Driven by Wheel–Stopper π•••π Interactions

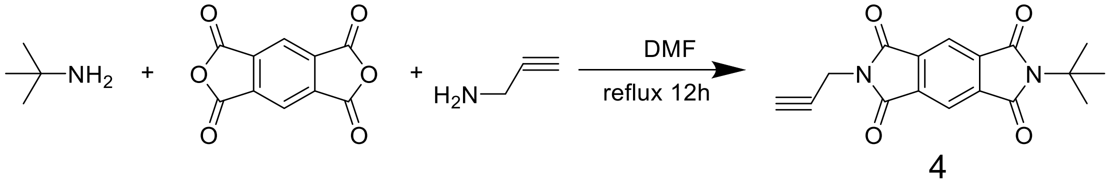
Contents

Materials and methods.

Per-ethyl pillar[5]arene[S1] (**2**) and 1,8-Diazidooctane[S2] (**3**) were prepared by literature methods. Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AV500 instrument. Variable-concentration ^{1}H NMR, 2D ROESY and DOSY experiments were recorded on a Bruker AV600 instrument. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Viscosity measurements were carried out with Ubbelohde micro dilution viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) in chloroform. Scanning electron microscopy (SEM) investigation was carried out on a Hitachi-S4800 instrument.

Synthesis and characterization.

A. Synthesis of **4.**



Scheme S1. Synthesis of **4**.

Pyromellitic dianhydride (2.2 g, 10 mmol) in 100 ml of DMF was added propargylamine (550 mg, 10 mmol) and tert-butylamine (730 mg, 10 mmol). The reaction mixture was stirred at reflux for 12 h. The reaction solution was added to ice water, filtered and dried. The resulting solution was concentrated under vacuo. Column chromatography (eluent: petroleum ether/ethyl acetate 10:1) afforded a colorless solid (1780 mg, 57%). m.p. 191-192 °C. ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 8.22 (s, 2H), 4.50-4.49 (d, *J*=2.56 Hz, 2H), 2.27-2.26 (t, *J*=2.56 Hz, 1H), 1.70 (s, 9H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ (ppm): 167.3, 165.0, 137.4, 136.8, 118.1, 76.4, 72.1, 59.1, 28.9, 27.6. HRMS: Calcd for $C_{17}H_{15}N_2O_4$ [M+H]$^+$ 311.1032, Found 311.1025.

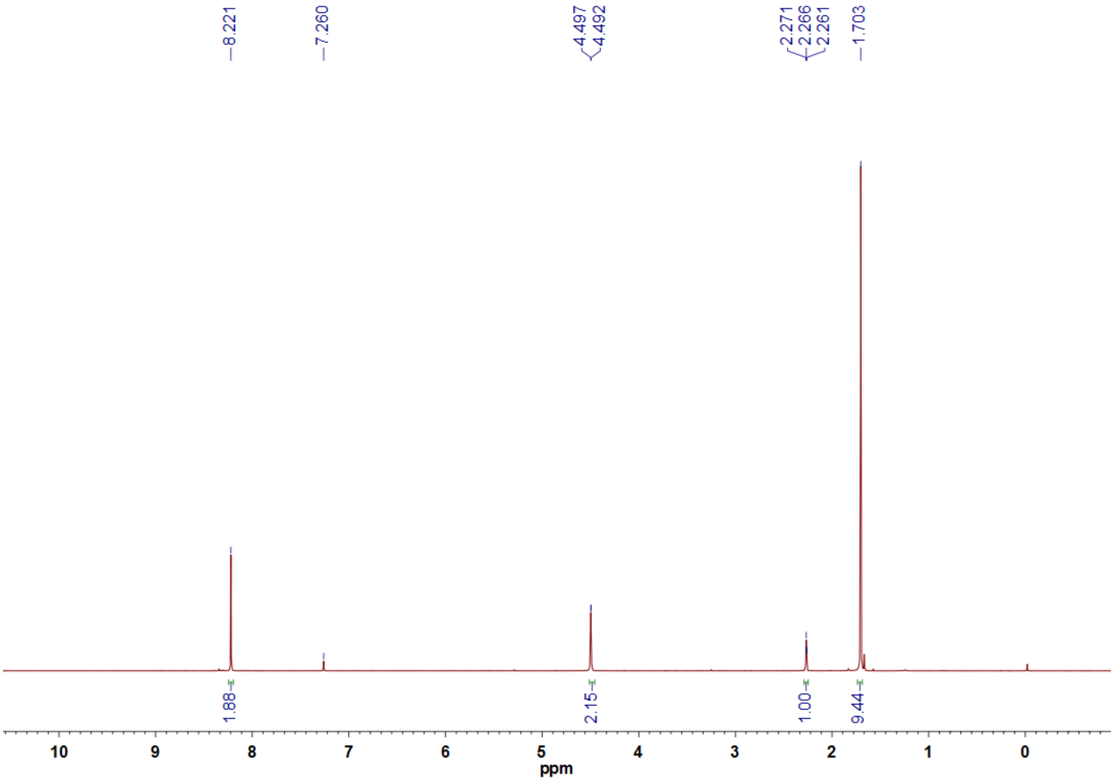


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4**.

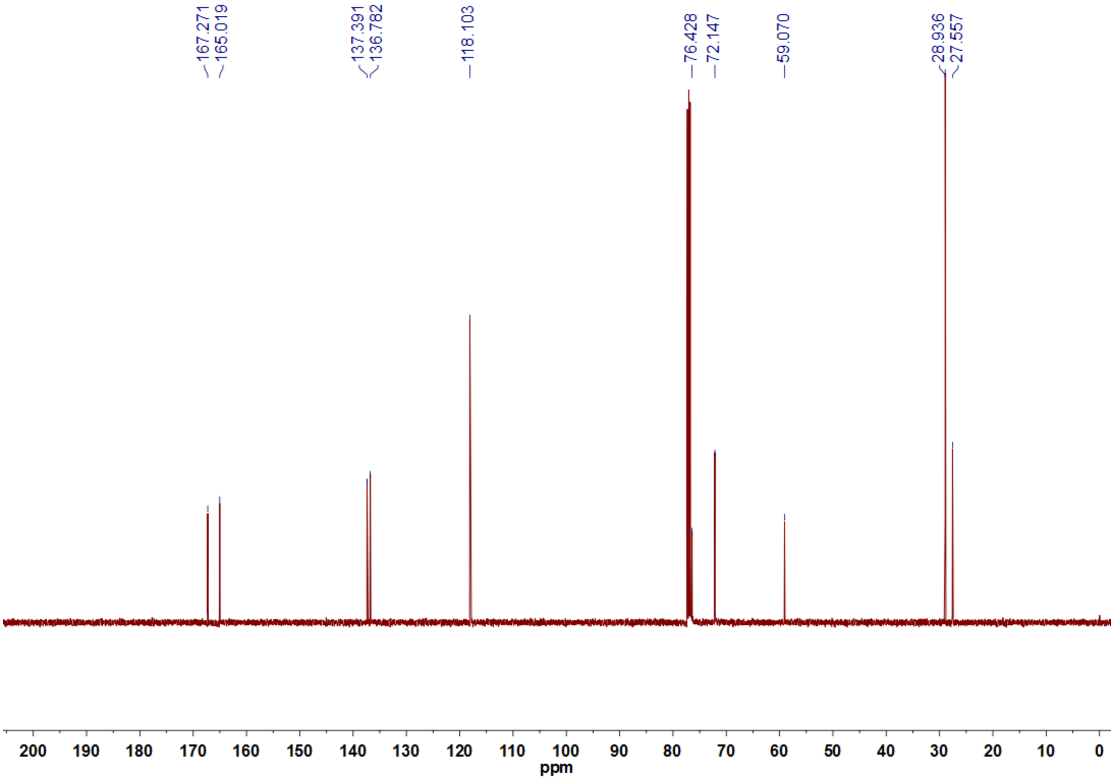


Figure S2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4**.

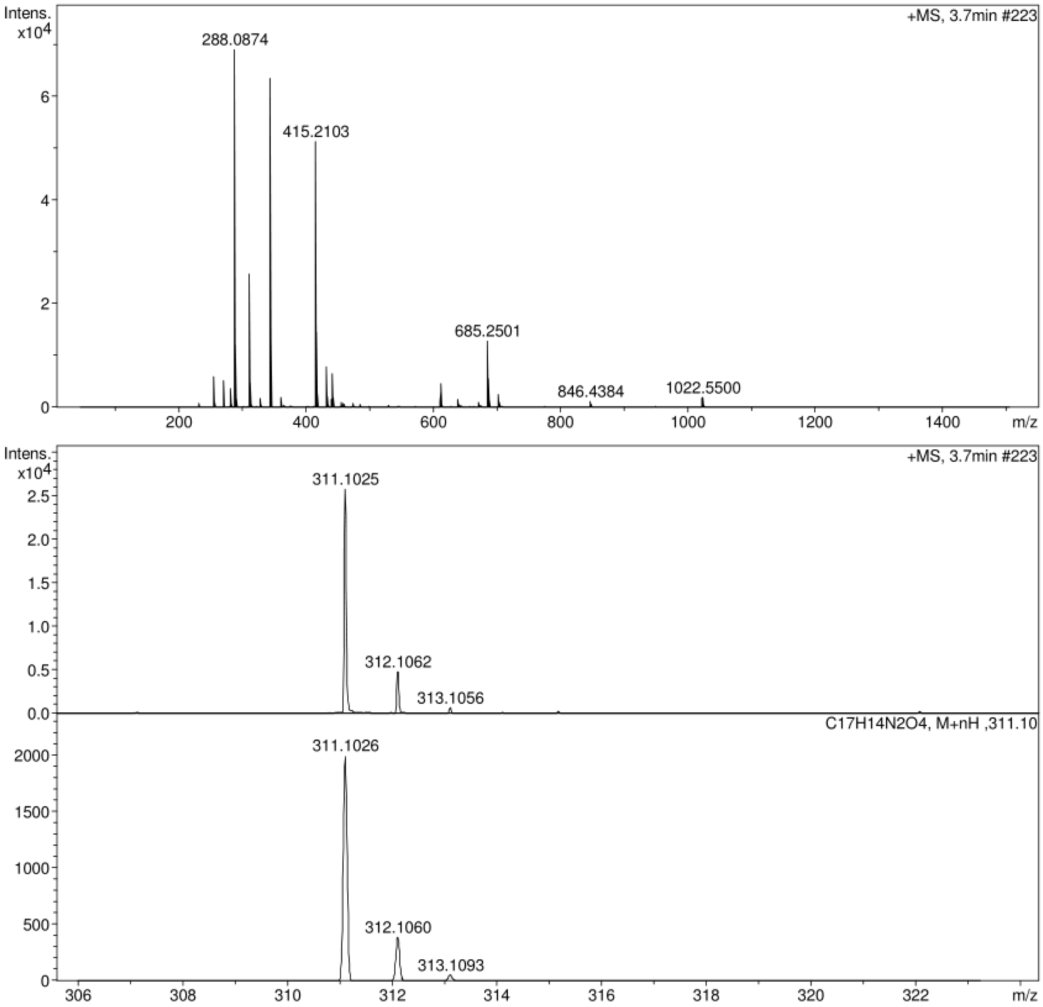
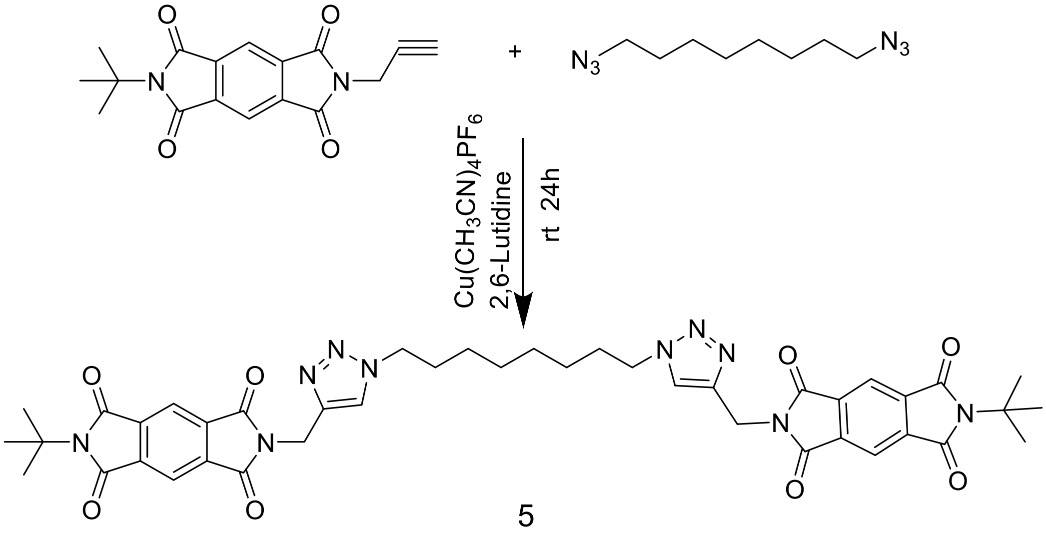


Figure S3. HRMS spectrum of stopper **4**.

B. Synthesis of dumbbell **5**.



Scheme S2. Synthesis of dumbbell **5.**

The chloroform (5 mL) solution of **3** (76 mg, 0.34 mmol) and **4** (320 mg,1.0 mmol) was added 2,6-Lutidine (4.3 mg, 0.040 mmol). $Cu(CH_3CN)_4PF_6$ (15 mg, 0.040 mmol) was then added to the mixture and then stirred at 25°C for 24 h. The resulting solution was concentrated under vacuo. Column chromatography (eluent: petroleum ether/ethyl acetate 1：1) afforded a white solid (222 mg, 0.27 mmol, Yield: 80%). m.p. 227-228 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) :8.19 (s, 4H), 7.60 (s, 2H), 5.02 (s, 1H), 4.31-4.28 (t, *J*=7.10 Hz, 4H), 1.88-1.82 (m, 4H), 1.71 (s, 18H), 1.28-1.25 (m, 8H), ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 167.4, 165.7, 137.3, 136.9, 117.9, 68.0, 59.0, 50.3, 33.5, 30.1, 28.9, 28.6, 26.2, 25.6. HRMS: Calcd for $C_{42}H_{44}N_{10}O_8$ $[M+H]^+$ 817.3422, Found 817.3418.

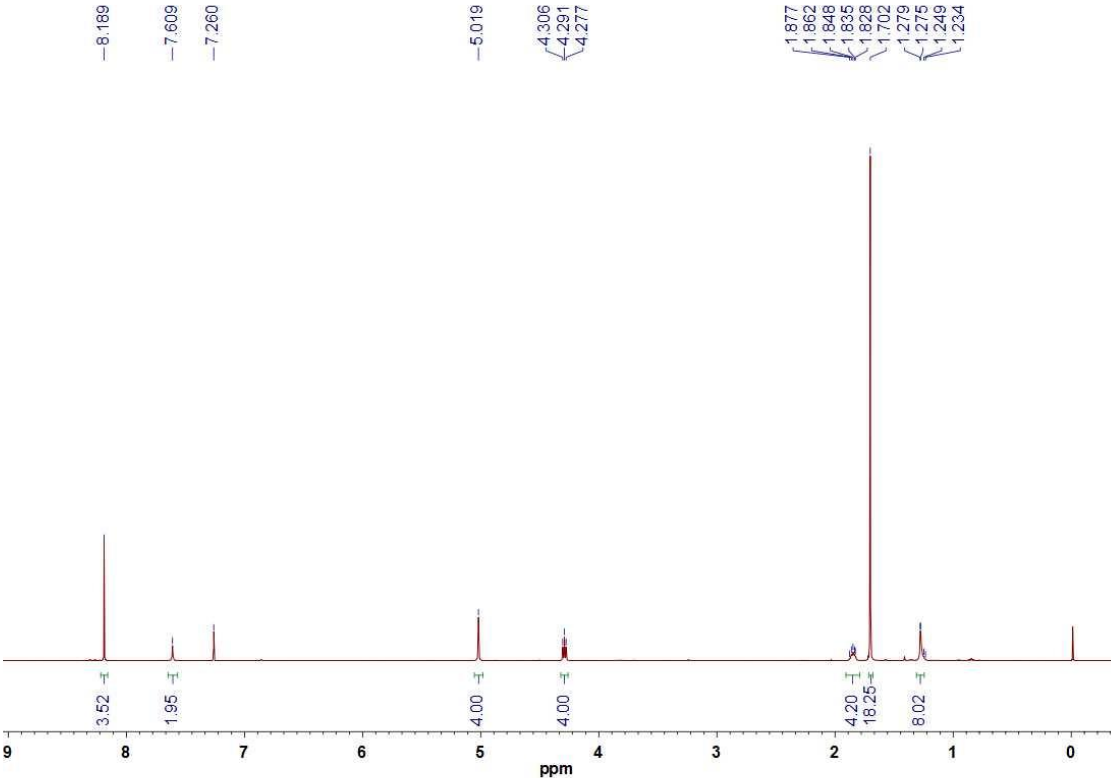


Figure S4. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of dumbbell **5**.

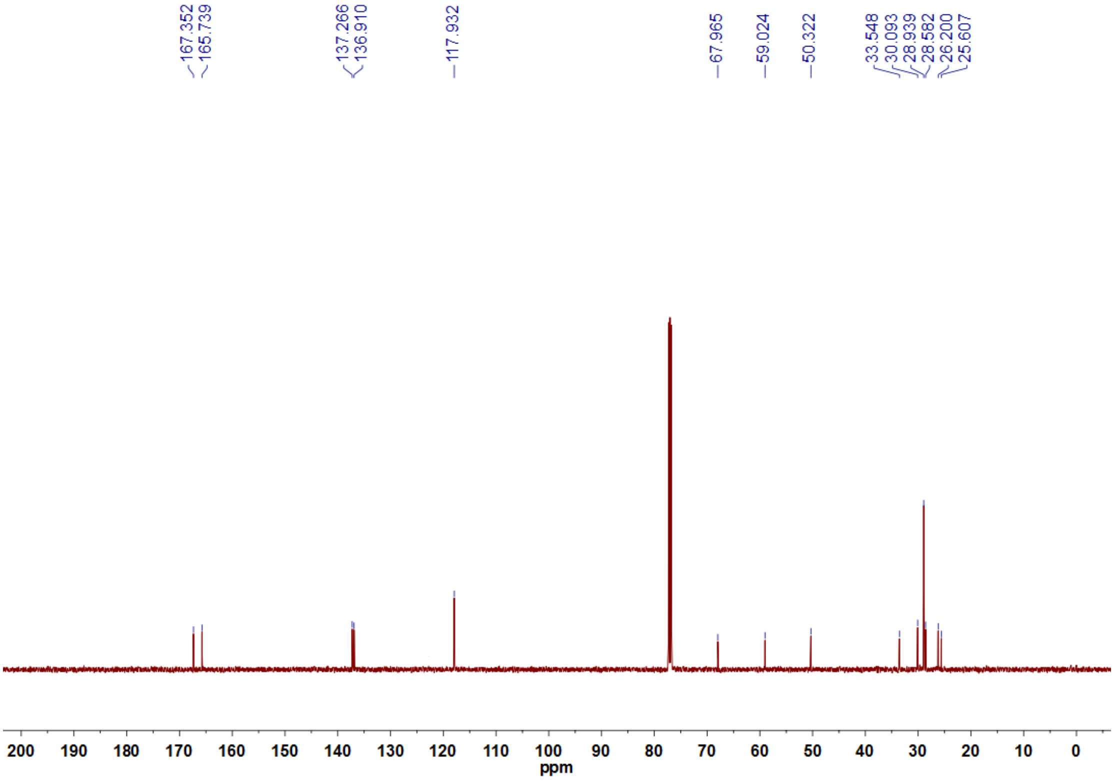


Figure S5. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of dumbbell **5**.

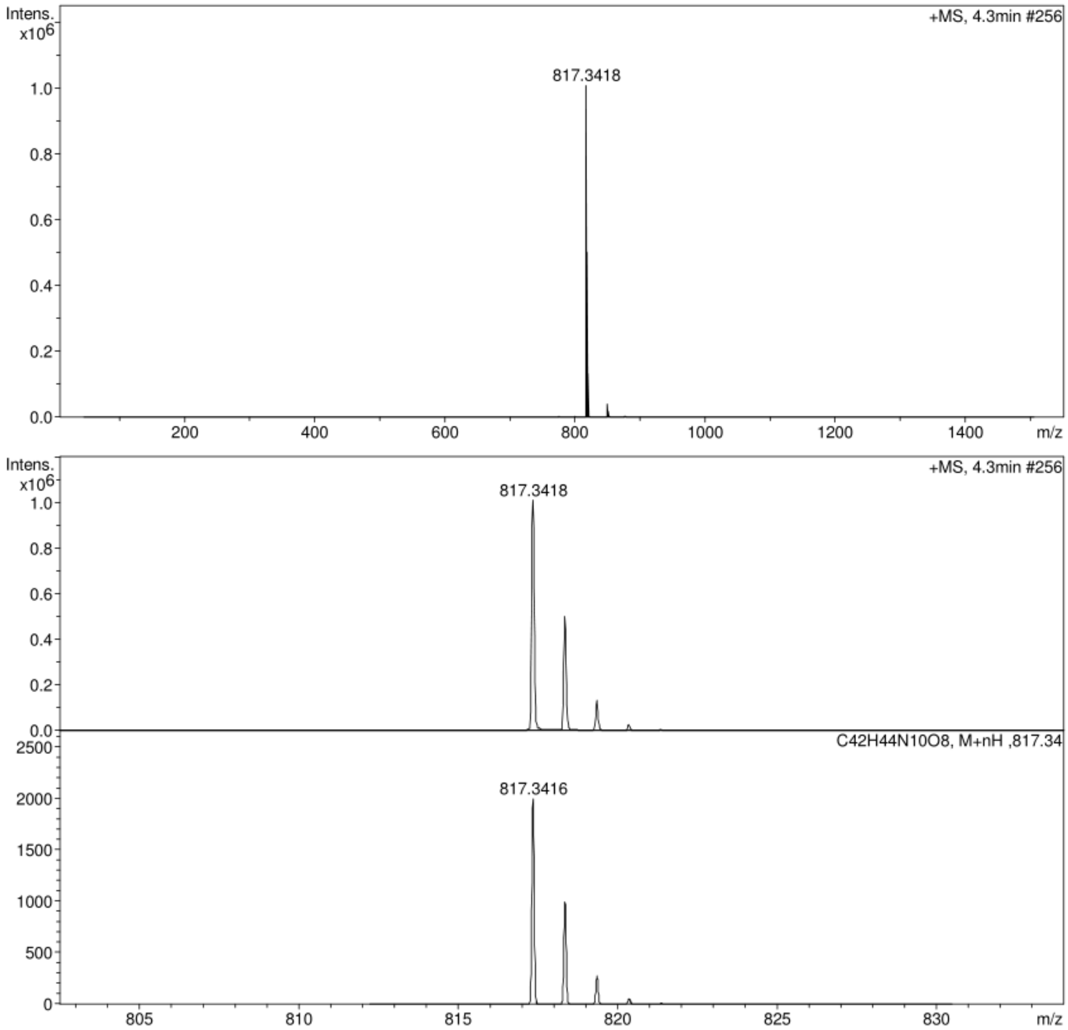
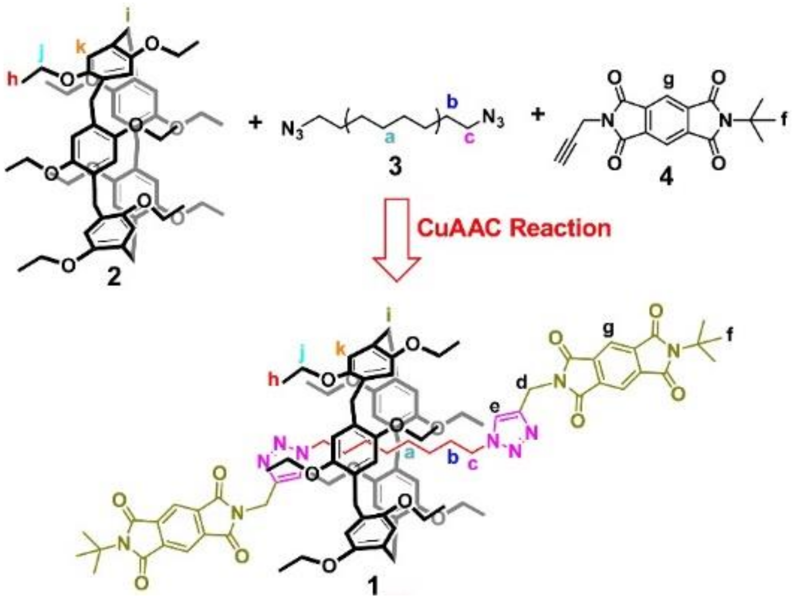


Figure S6. HRMS spectrum of dumbbell **5**.

C. Synthesis of [2]Rotaxane **1.**



To the dried chloroform (5 mL) solution of **3** (76 mg, 0.34 mmol), **2** (1.5 g, 1.7 mmol) and **4** (320 mg, 1.0 mmol) was added. 2,6-Lutidine (4.3 mg, 0.040 mmol). $Cu(CH_3CN)_4PF_6$ (15 mg, 0.040 mmol) was then added to the mixture and stirred at 25 ºC for 24 h. The resulting solution was concentrated under vacuo. Column chromatography (eluent: from dichloromethane to dichloromethane/ethyl acetate 10:1) afforded a red solid (220 mg, 0.13 mmol, Yield: 37%). m.p.155-157 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 8.23 (s, 4H), 7.58 (s, 2H), 6.88 (s, 10H), 5.08-5.07 (br, 4H), 3.89-3.79 (m, 20H), 3.72 (s, 10H), 3.45-3.41 (t, *J*=8.53 Hz, 4H), 1.73 (s, 18H), 1.78-1.35 (t, *J*=6.98 Hz, 30H), 0.49-0.45 (br, 4H), -0.61 ~ -0.67 (br, 8H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 167.4, 165.7, 149.8, 141.1, 137.3, 137.0, 128.8, 121.9, 117.9, 114.9, 64.0, 59.1, 58.5, 50.2, 33.6, 29.5, 29.2, 29.0, 28.2, 25.4, 18.4, 15.5. HRMS: Calcd for $C_{97}H_{114}N_{10}O_{18}$ $[M+H]^+$: 1707.8391, Found 1707.8366.

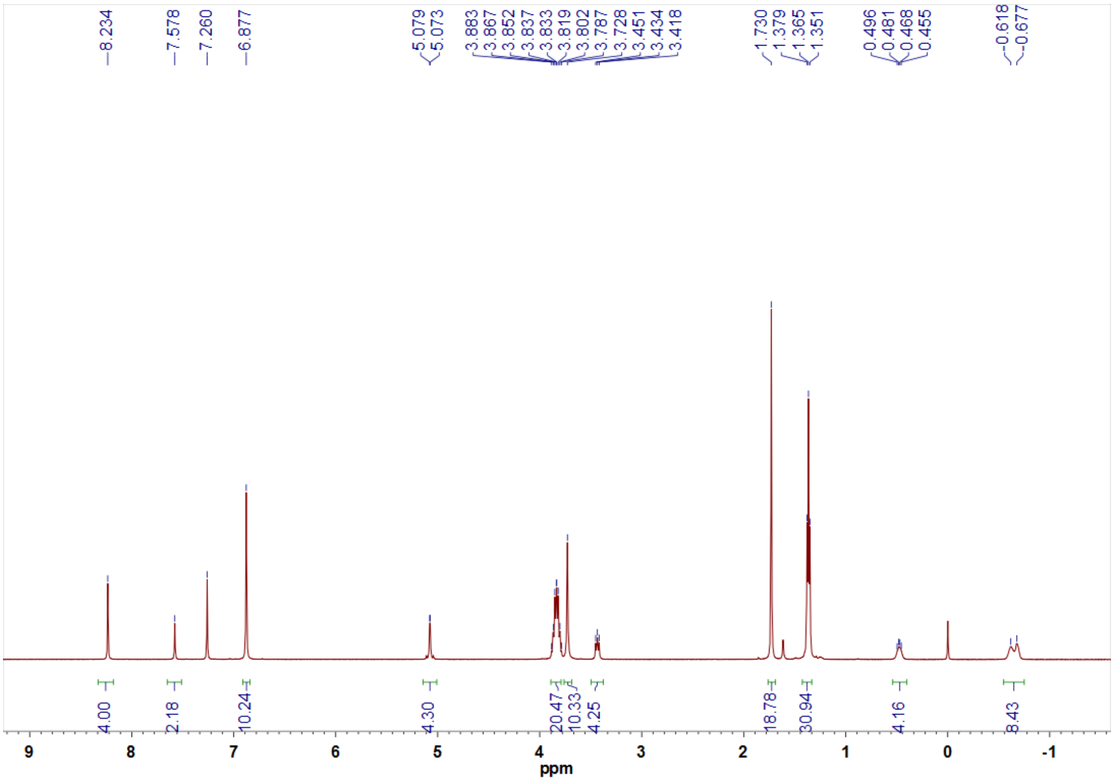


Figure S7. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of [2]rotaxane **1**.

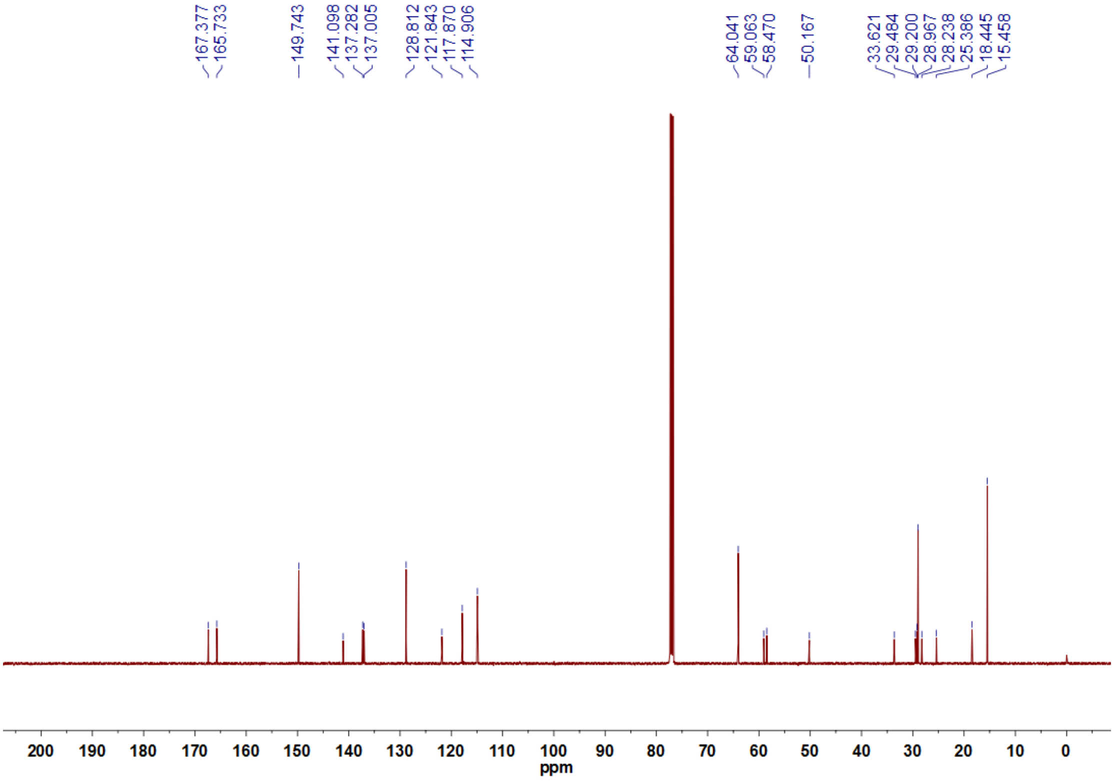


Figure S8. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of [2]rotaxane **1**.

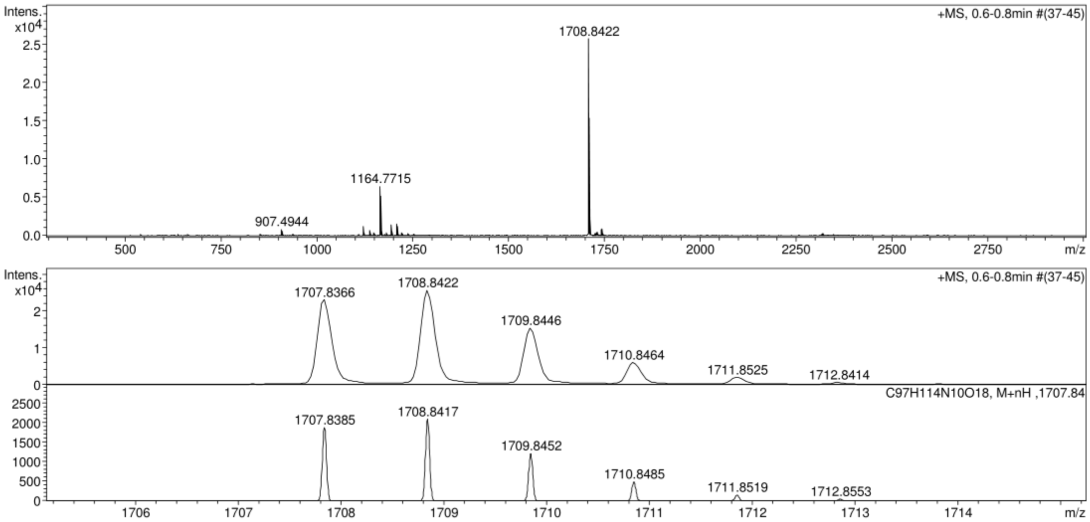


Figure S9. HRMS spectrum of [2]rotaxane **1**.

2D ROESY spectrum of 1.

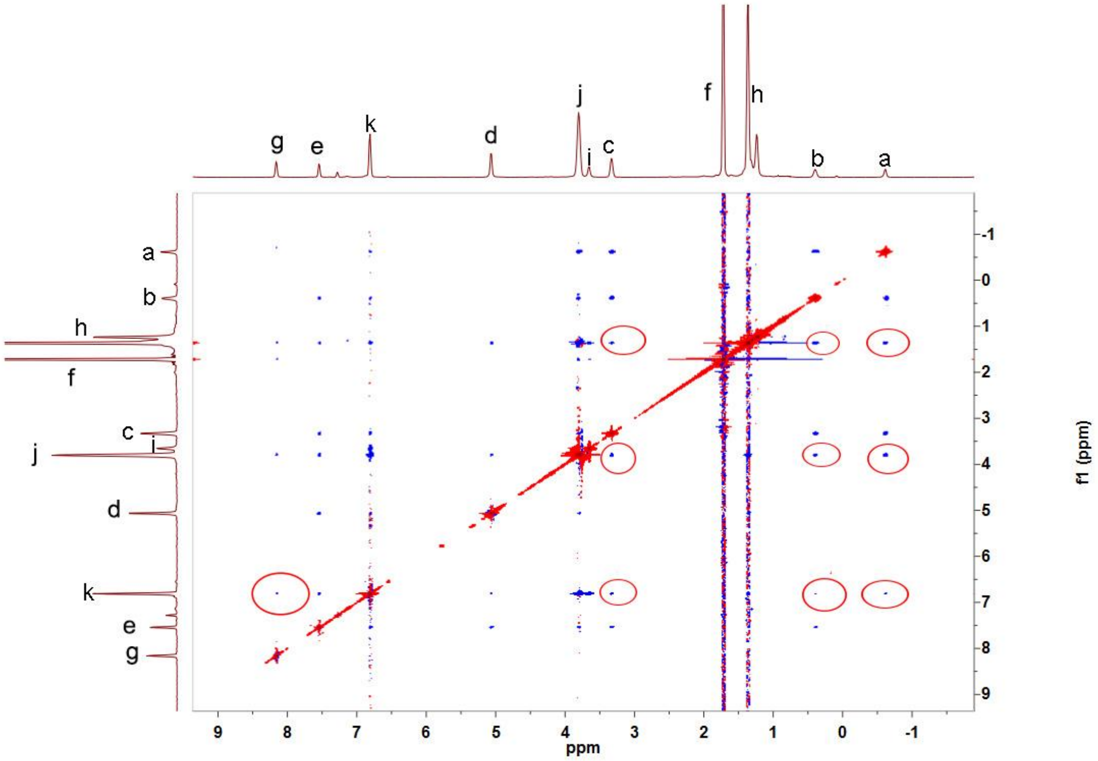


Figure S10. 2D ROESY NMR spectrum (600 MHz) of **1** (40 mM) in $CDCl_3$.

^{1}H NMR spectra of 1 in DMSO-*d*$_6$.

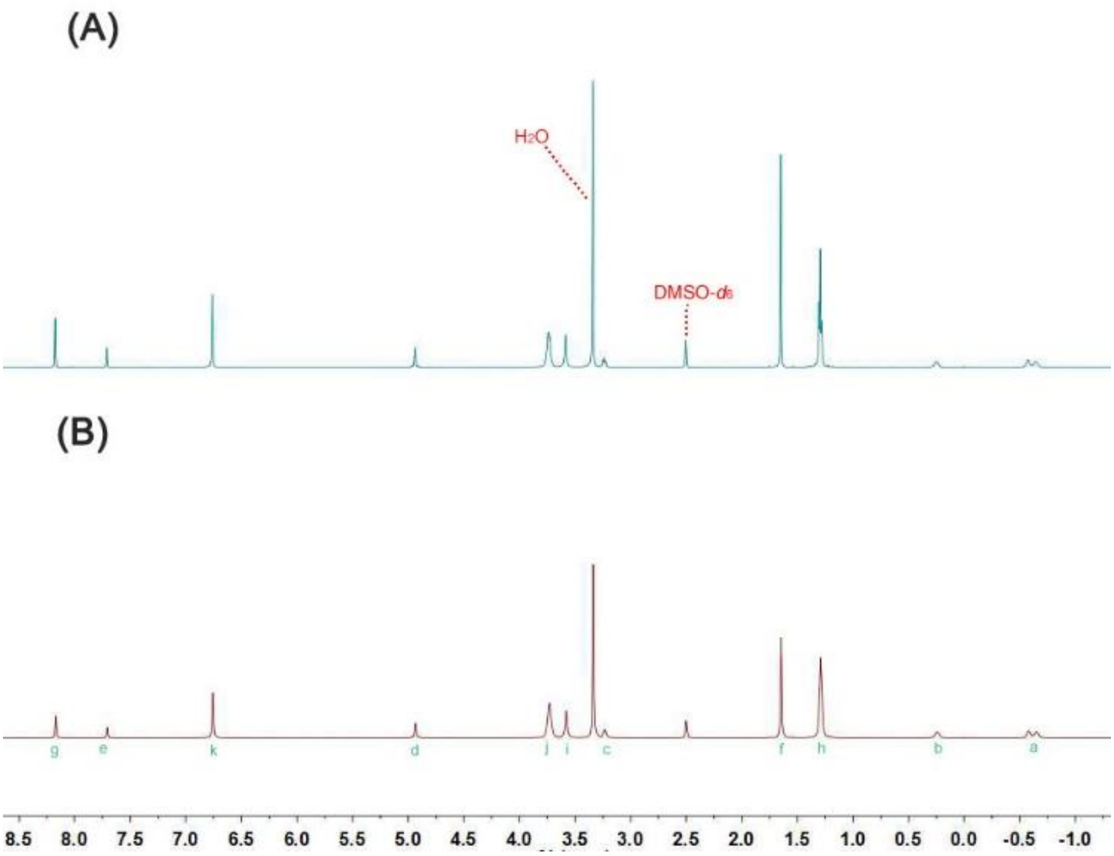


Figure. S11 ^{1}H NMR experiments of **1** (10 mM) in DMSO-*d*$_6$. **(A)** ^{1}H NMR spectrum of **1** in DMSO-*d*$_6$. (B) ^{1}H NMR spectrum of **1** in DMSO-*d*$_6$ after heating at 80 °C for 5 hours.

UV-vis spectra and color changes.

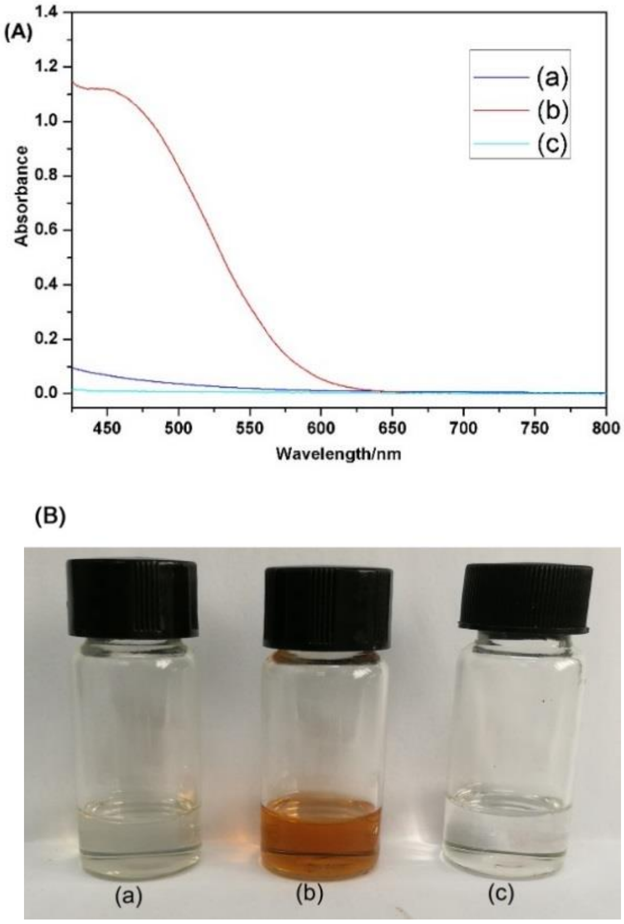


Figure S12. UV-vis spectra (A) and color changes (B) of **5**, **1** and **2** (40 mM) in chloroform at 298 K. (a) **5** (b) **1** and (c) **2**.

Solution colors of the supramolecular polymers at different concentrations.

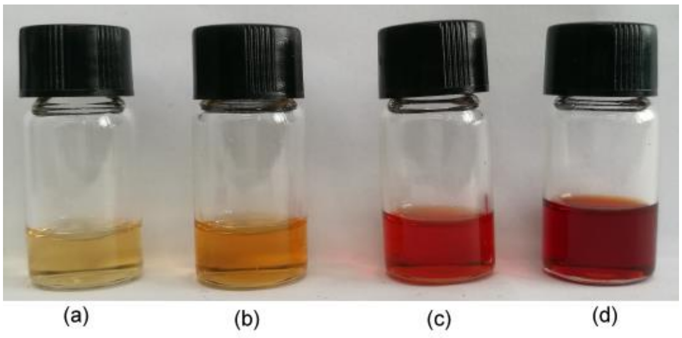


Figure S13. Concentration-dependent color changes of **1** in chloroform. (a) 25 mM; (b) 50 mM; (c) 100 mM; (d) 250 mM.

X-ray crystal data and crystal structure of 1.

Crystallographic data: red, $C_{97}H_{114}N_{10}O_{18}$, *FW* 1707.98, Triclinic, space group P-1, *a*=15.635(16), *b*=15.853(16), *c*=20.76(2), *α*= 76.822(14)°, *β*=87.310(14)°, *γ*= 85.630(14)°, *V*=4994(9) Å^3, *Z*=2, D_c= 1.136 g cm^{-3}, *T*=296 K, *μ*=0.079 mm^{-1}, 19220 measured reflections, 19220 independent reflections, 1127 parameters, 1 restraint, *F*(000) = 1820, R_1 = 0.1585, wR_2 = 0.2077 ((all data), R_1 = 0.0658, wR_2 = 0.1737 [$I > 2\sigma(I)$], max. residual density 0.522 e·Å^{-3}, and goodness-of-fit (F^2) = 0.908 . CCDC 1811542.

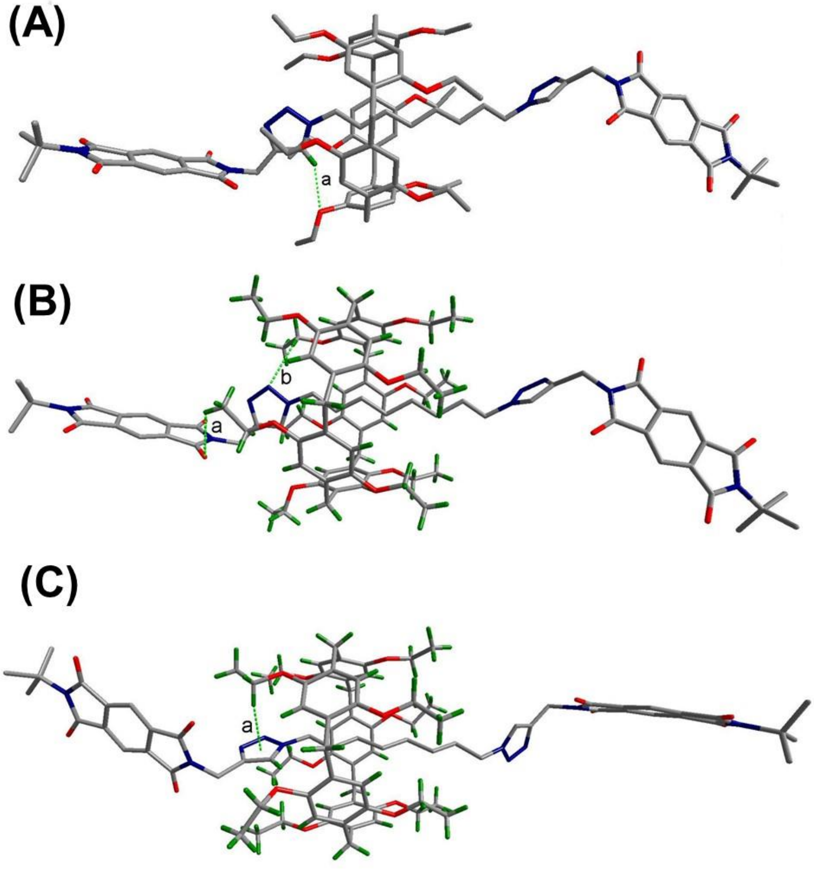


Figure S14. Crystal structure of **1**. Oxygens are shown in red, nitrogens in dark blue, carbons in gray, and hydrogens as green. Dashed lines represent C–H•••O(N) hydrogen bonds or C−H•••π interactions. (A) C–H•••O hydrogen-bond parameters: H•••O distances (Å), C–H•••O angles (deg) a, 2.40, 147. (B) C–H•••O (N) hydrogen-bond parameters: H•••O (N) distances (Å), C–H•••O (N) angles (deg) a, 2.80, 125; b, 2.83, 147. (C) C−H•••π parameters: H•••ring centre distances (Å), C−H•••ring angles (deg) a, 2.89, 147.

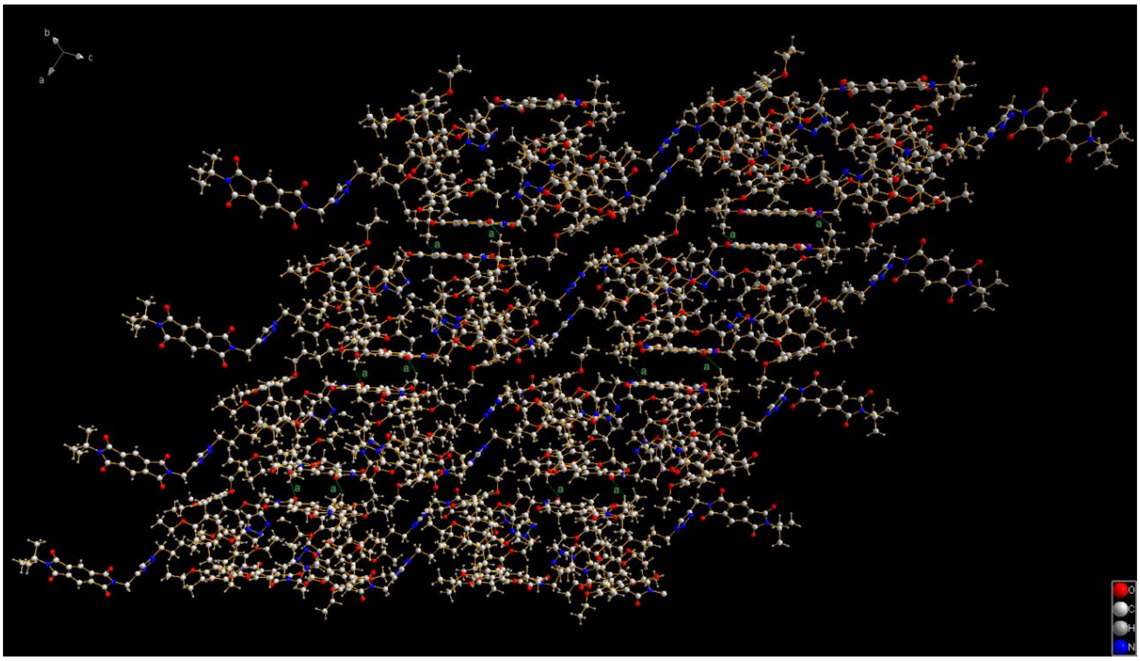


Figure S15. The packing structure of **1**. Dashes represent intermolecular C−H•••O hydrogen bonds. H•••O distance is 2.78 Å and C−H•••O angle is 149 deg.

References

[S1] T. Ogoshi, K. Kitajima, T. Aoki, S. Fujinami and T. Yamagishi, *J. Org. Chem.*, 2011, **75**, 3268.

[S2] C. Lang, P. Kai, C. Kiefer, A. S. Goldmann, P. W. Roesky and C. Barnerkowollik, *Polym. Chem.*, 2013, **4**, 5456.