Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information for

Synergistic covalent-and-supramolecular polymers connected by [2]pseudorotaxane moieties

Junjun Wan[#], Zhaoming Zhang[#,*], Yongming Wang, Jun Zhao, Yumeng Qi, Xinhai Zhang, Kai Liu, Chunyang Yu* and Xuzhou Yan*

School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

[#]These authors contributed equally to this work.

*To whom correspondence should be addressed.

E-mail: zhangzhaoming@sjtu.edu.cn; chunyangyu@sjtu.edu.cn; xzyan@sjtu.edu.cn

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. All the solvents were used as received from Adamas-beta with a reagent grade (99%). The compounds **1**[1], **4**[2], **6**[3], and **7**[4] was prepared according to the established methods, and the ^{1}H NMR spectra of the obtained known compounds were consistent with those reported in literatures. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). All reactions were performed at ambient laboratory conditions, and no precautions are taken to exclude atmospheric moisture unless otherwise specified.

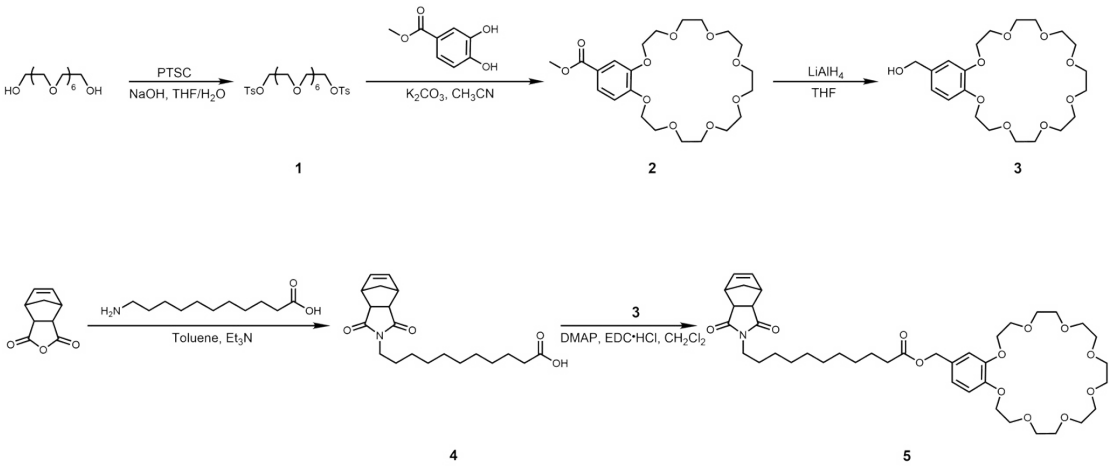
Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance DMX 400 spectrometers with the use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. The transmitter frequency of ^{13}C NMR is 100 MHz.

High resolution mass spectra were obtained on a Bruker SolariX 7.0T FT-ICR MS spectrometer. Gel permeation chromatograph (GPC) was performed on a HLC-8320GPC (TOSOH, Japan) instrument using dimethylformamide (DMF) as the eluent and polystyrene as the standard.

The thermal stability analysis was conducted using a TA Instruments Q500 thermogravimetric analyzer (TGA) under the nitrogen. Each sample (~5 mg) was heated from 50 to 800 °C with a rate of 20 °C/min. Transition temperatures of materials were determined on a TA Instruments Q2000 differential scanning calorimetry (DSC) under the nitrogen. Rheological experiments were carried out using a Kinexus Ultra rotational rheometer (NETZSCH Instruments).

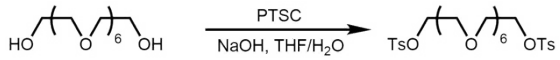
The mechanical properties of the materials were measured using an Instron 3343 machine in standard stress/strain experiments. As for the preparations of the specimens used for the tests, the CP-**1** was dissolved in chloroform and the bis(pyridinium) ligand **6** was dissolved in acetonitrile, then the two solutions were mixed together with fixed ratio of the two solvents ($CH_3CN/CHCl_3$, 3:1 *v*/*v*) and stirred for 1 hour. After that, the $Pd(PhCN)_2Cl_2$ was added into the mixture and stirred. The mixture was transferred to Teflon molds and the solvent was removed by oven at 60 °C. Young's modulus was determined from the initial slope of the stress-strain curves.

2. Synthesis of monomer 5



Scheme S1. Synthetic route of monomer **5**.

*2.1 Synthesis of compound **1***



1

Heptaethylene glycol (20.0 g, 61.3 mmol) was dissolved in THF (60 mL) and then stirred at 0 °C. Sodium hydroxide (12.0 g, 306 mmol) was dissolved in water (40 mL), then cooled into room temperature and added into the THF solution. Tosyl chloride (PTSC, 29.0 g, 153 mmol) was dissolved in THF (60 mL) and added into the mixture of heptaethylene glycol and sodium hydroxide dropwise. After stirring at room temperature for 48 hours, 250 mL H_2O was added into the mixture to dissolve the sodium chloride precipitated, and most of the THF was removed by rotary evaporator. The residual liquid was then extracted by DCM (200 mL × 3), and the combined organic phases was washed by water and brine. The solvent was removed by rotary evaporator to give compound **1** (35.0 g, 90%) as a colorless oil. The ^{1}H NMR spectrum of compound **1** is shown in Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 7.76 (d, J = 8.4 Hz, 4H), 7.31 (d, J = 8.0 Hz, 4H), 4.17–4.09 (m, 4H), 3.68–3.52 (m, 24H), 2.42 (s, 6H).

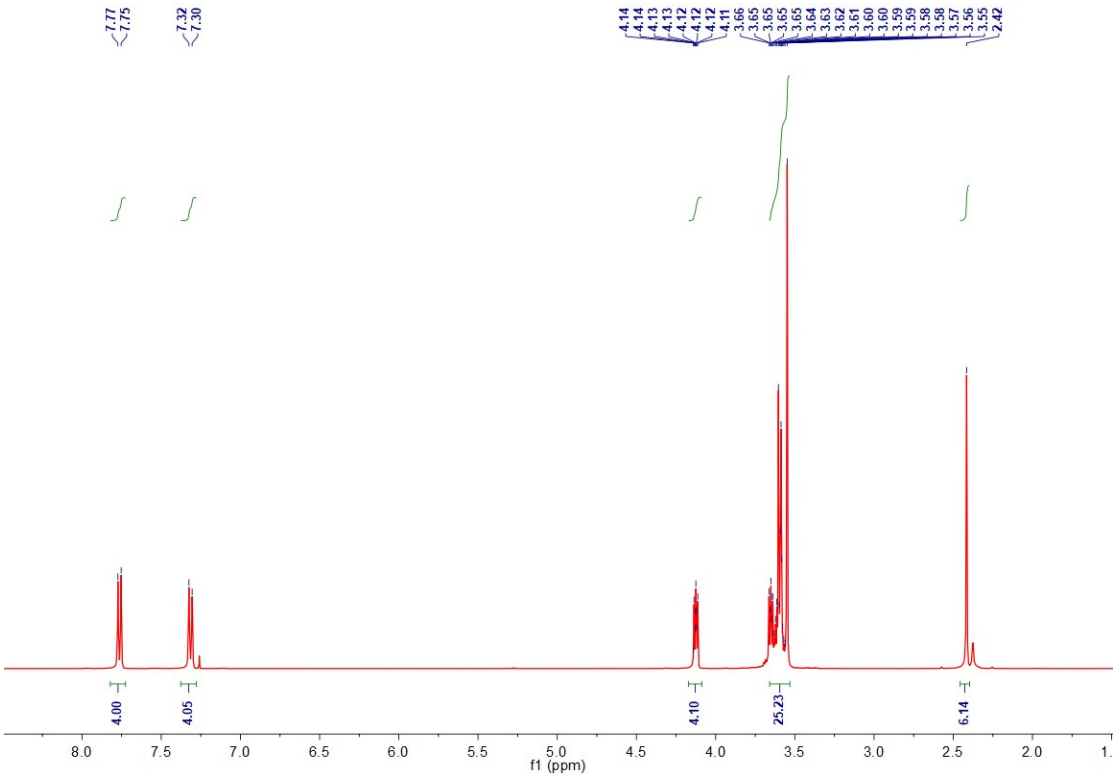
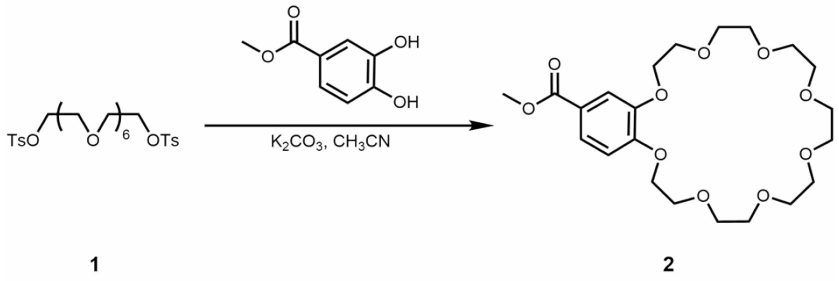


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **1**.

*2.2 Synthesis of compound **2***



1 **2**

A mixture of 3,4-dihydroxy-2-methylbenzoate (5.13 g, 30.5 mmol), K_2CO_3 (12.7 g, 91.5 mmol), and compound **1** (18.0 g, 30.5 mmol) in 300 mL of CH_3CN was stirred and refluxed for three days under nitrogen. After cooling down, the mixture was filtered and CH_3CN was removed with a rotary evaporator, and then chloroform was added. After washing with brine for eight times, the organic phase was dried with Na_2SO_4 and then concentrated. The residue was purified by silica-gel column chromatography to provide **2** (9.78 g, 70%) as a pale yellow oil. The ^{1}H NMR spectrum of **2** is shown in Fig. S2. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 7.63 (dd, J = 8.4, 2.0 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 4.24–4.15 (m, 4H), 3.91 (q, J = 4.4 Hz, 4H), 3.86 (s, 3H), 3.78 (t, J = 4.4 Hz, 4H), 3.70–3.68 (m, 4H), 3.67–3.59 (m, 12H). The ^{13}C NMR spectrum of **2** is shown in Fig. S3. ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ (ppm): 166.79, 152.93, 148.27, 123.93, 122.90, 114.68, 112.36, 71.27, 71.19, 70.92, 70.90, 70.84, 70.83, 70.73, 70.72, 69.70, 69.57, 69.33, 69.11, 51.96. HRESIMS is shown in Fig. S4: m/z calcd for $C_{22}H_{34}O_{10}$, 481.2050 $[M+Na]^+$; found 481.2046 $[M+Na]^+$.

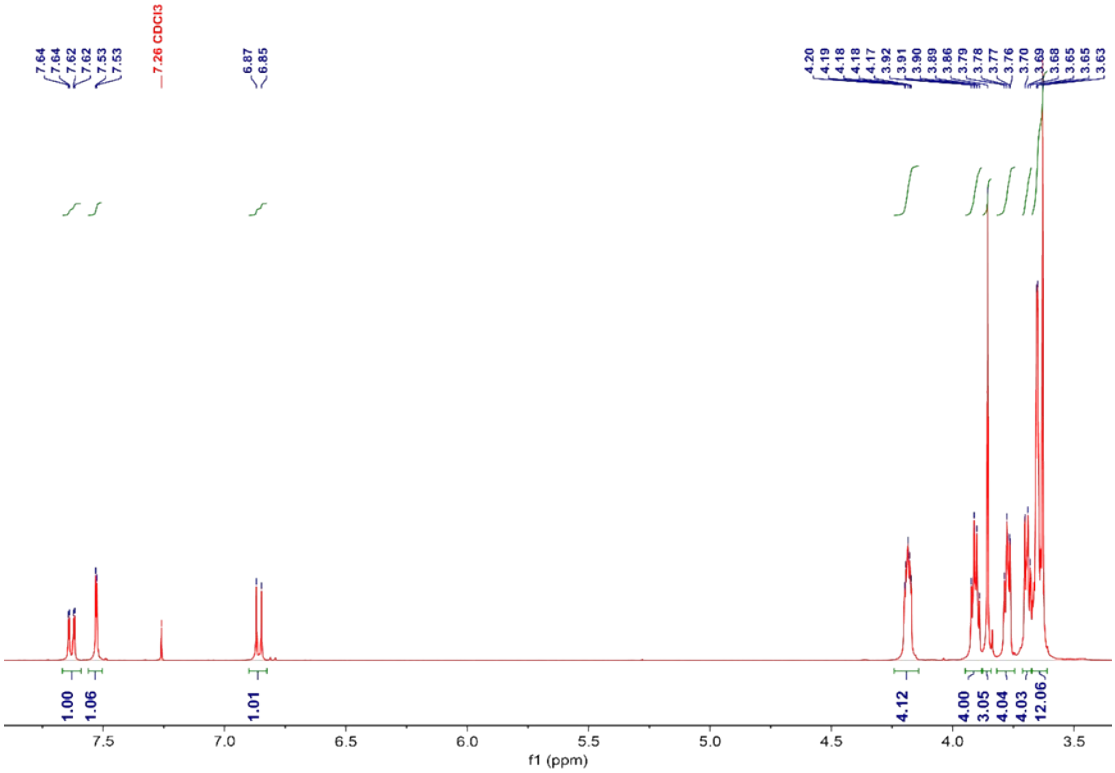


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2**.

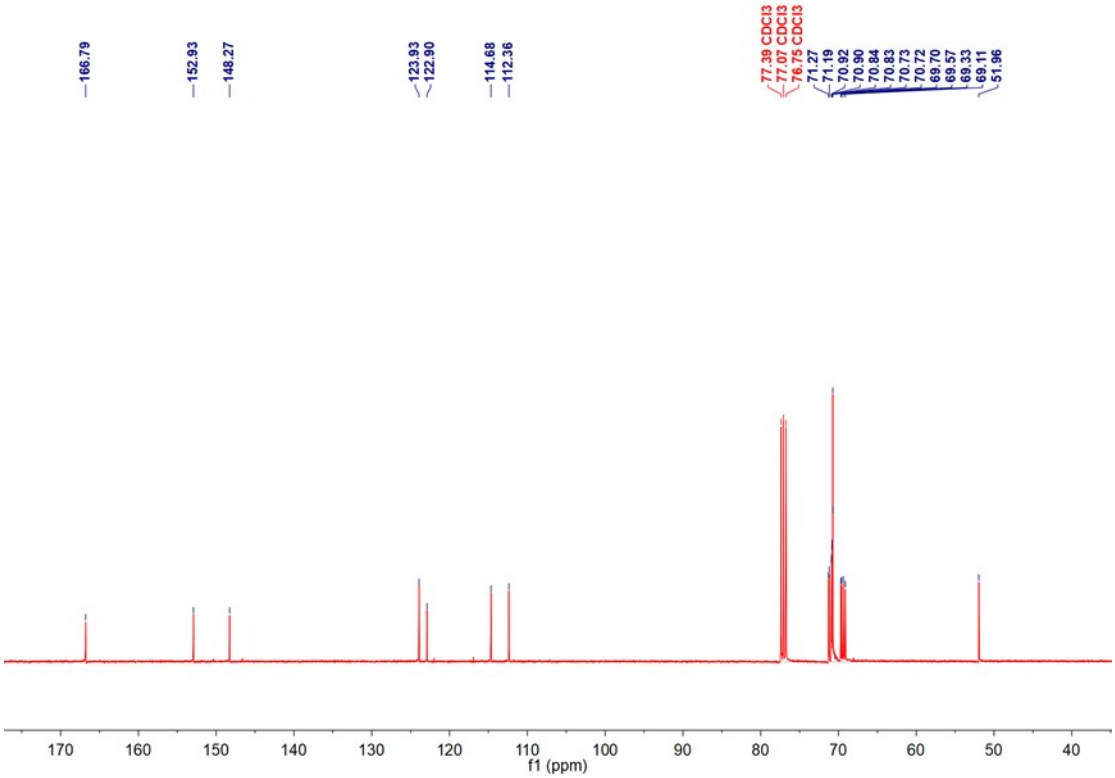


Figure S3. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298K) of **2**.

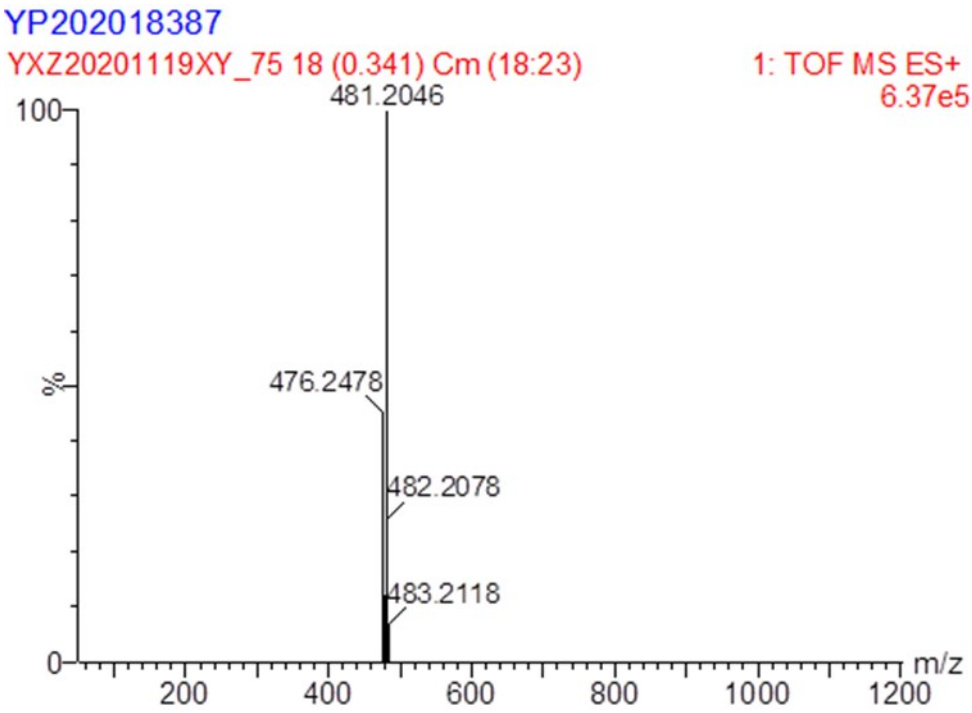
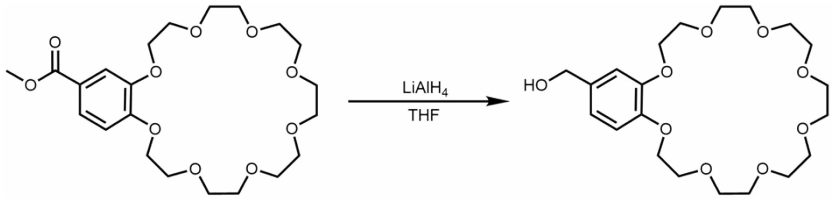


Figure S4. Electrospray ionization mass spectrum of **2**.

*2.3 Synthesis of compound **3***



2 3

Compound **2** (5.00 g, 10.9 mmol) was dissolved in dried THF (100 mL) and then stirred. Lithium aluminium hydride (0.455 g, 12.0 mmol) was added portionwise. The mixture was stirred at room temperature overnight, and then quenched with water (1 mL) and 15% aqueous sodium hydroxide solution (1 mL). The mixture was dried over $MgSO_4$ and filtered. The solvent was removed by a rotary evaporator and the residue was purified by column chromatography on silica gel (DCM/MeOH, 200:1 *v*/*v*) to give compound **3** (4.20 g, 90%) as a colorless oil. The ^{1}H NMR spectrum of compound **3** is shown in Fig. S5. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 6.95 (d, J = 1.6 Hz, 1H), 6.87 (d, J = 2.0 Hz, 2H), 4.59 (d, J = 5.6 Hz, 2H), 4.16 (td, J = 6.0, 4.4 Hz, 4H), 3.94–3.86 (m, 4H), 3.81–3.75 (m, 4H), 3.71 (dt, J = 6.4, 2.8 Hz, 4H), 3.69–3.60 (m, 12H). The ^{13}C NMR spectrum of **3** is shown in Fig. S6. ^{13}C NMR (125 MHz, $CDCl_3$, 298K) δ (ppm): 148.66, 147.91, 134.47, 119.66, 114.03, 113.07, 70.71, 70.51, 70.39, 69.57, 69.03, 68.83, 64.45. HRESIMS is shown in Fig. S7: *m*/*z* calcd for $C_{21}H_{34}O_9$, 453.2203 $[M+Na]^+$; found 453.2089 $[M+Na]^+$.

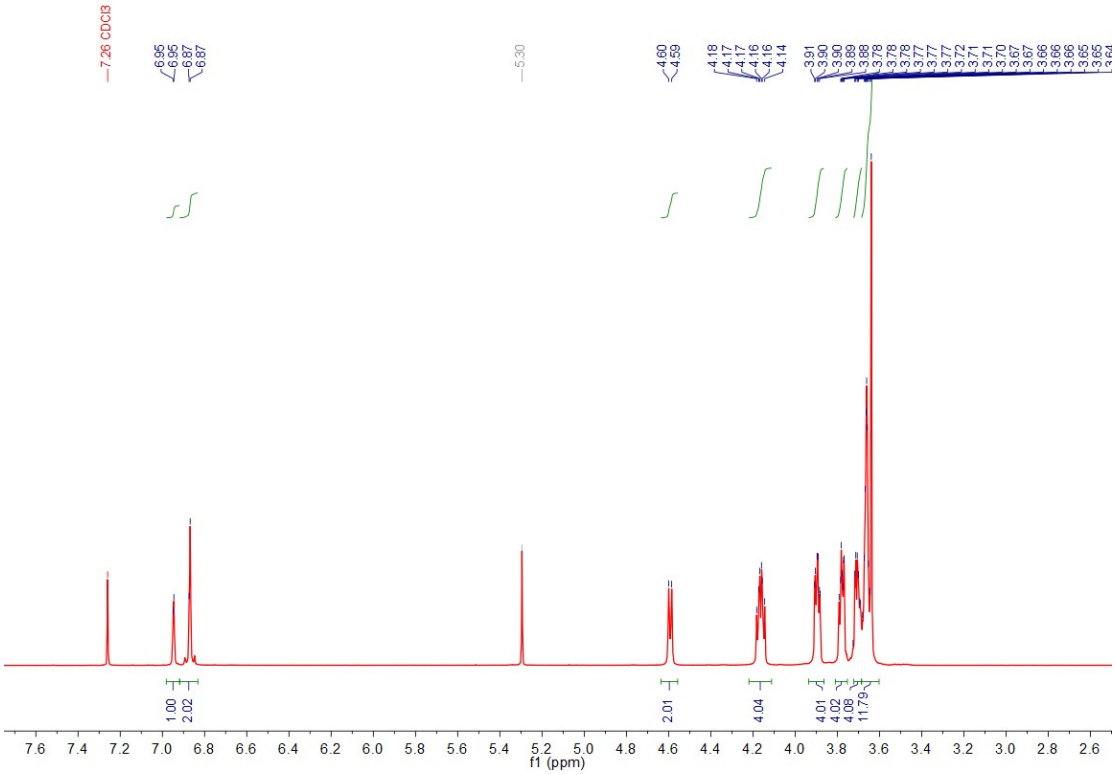


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **3**.

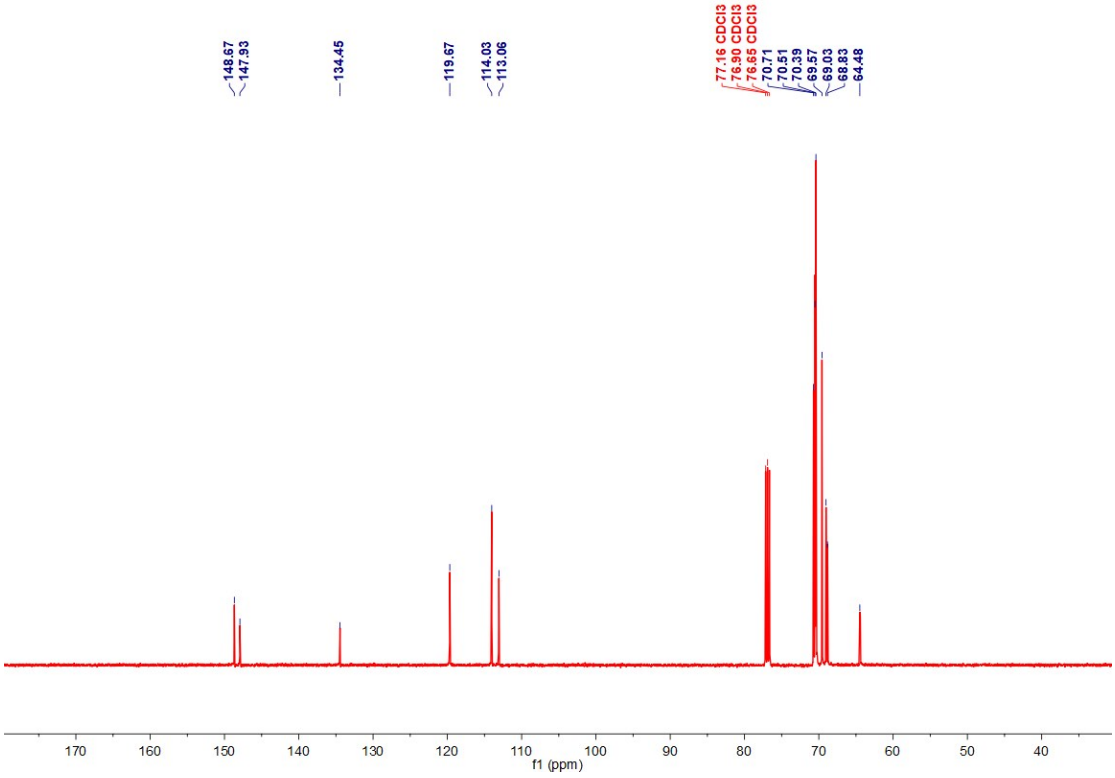


Figure S6. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298K) of **3**.

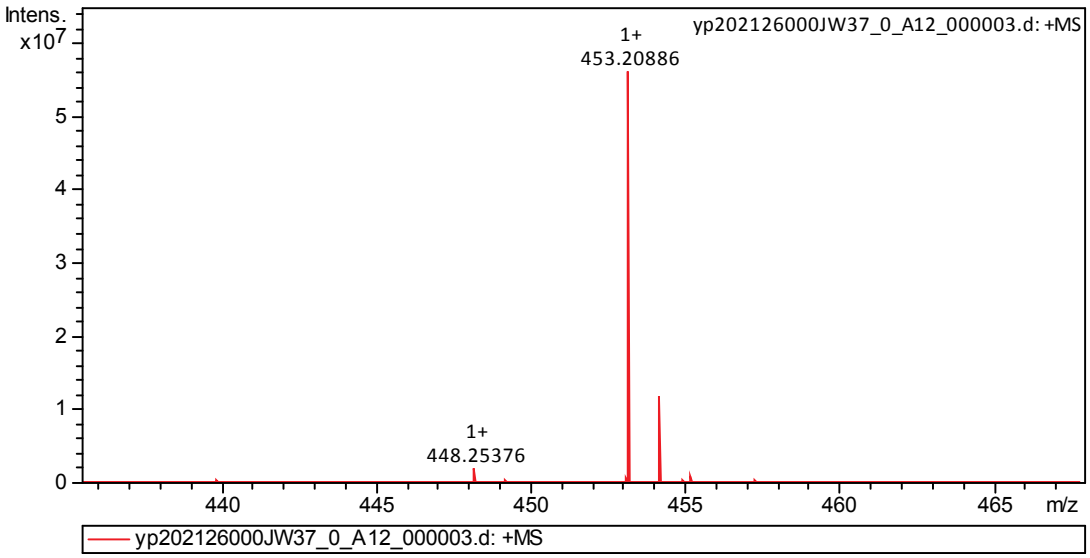
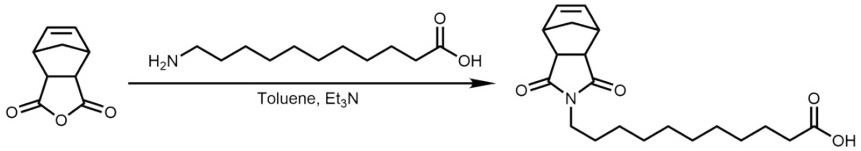


Figure S7. Electrospray ionization mass spectrum of **3**.

*2.4 Synthesis of compound **4***



4

A mixture of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (3.00 g, 18.3 mmol) and 11-aminoundecanoic acid (3.68 g, 18.3 mmol) was dissolved in toluene (150 mL), and then trimethylamine (0.19 mL, 1.83 mmol) was added into the mixture. The mixture was heated to reflux under a nitrogen atmosphere for 20 hours. After that, the solvent was removed by a rotary evaporator and the residue was purified by column chromatography on silica gel (DCM/MeOH, 200:1 *v*/*v*) to give compound **4** (5.66 g, 94%) as a white solid. The ^{1}H NMR spectrum of compound **4** is shown in Fig. S8. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 6.28 (t, J = 2.0 Hz, 2H), 3.51–3.38 (m, 2H), 3.27 (t, J = 1.8 Hz, 2H), 2.67 (d, J = 1.4 Hz, 2H), 2.34 (t, J = 7.6 Hz, 2H), 1.62 (p, J = 7.6 Hz, 2H), 1.56–1.50 (m, 2H), 1.36–1.18 (m, 14H).

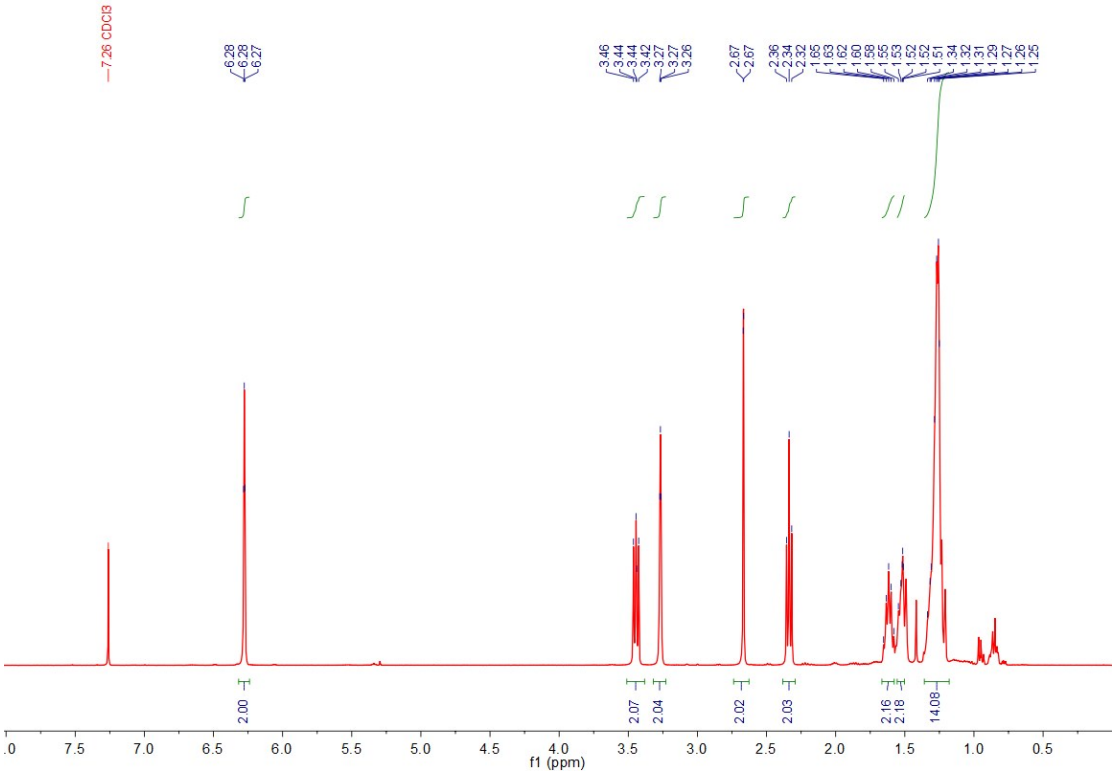
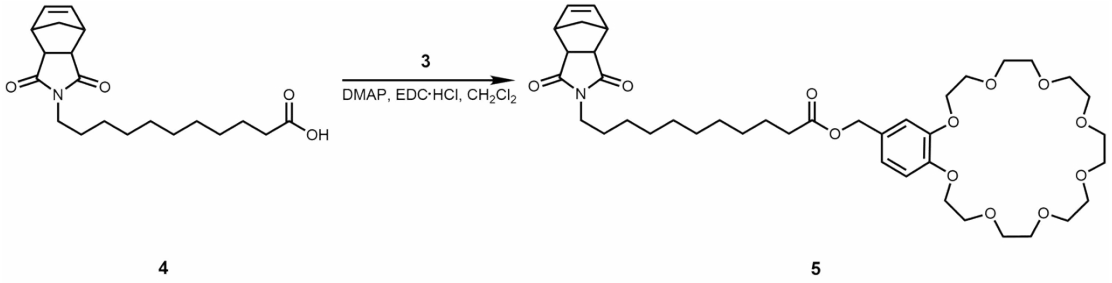


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **4**.

2.5 Synthesis of compound ***5***



4 **5**

A mixture of compound **3** (5.01 g, 11.6 mmol) and compound **4** (4.10 g, 11.8 mmol) was dissolved in DCM and stirred at 0 °C. 4-Dimethylaminopyridine (DMAP, 0.44 g, 3.60 mmol) was then added into the mixture. After DMAP was dissolved in the DCM completely, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (2.49 g, 13.0 mmol) was added into the mixture and stirred at room temperature overnight. The solvent was removed by a rotary evaporator and the residue was purified by column chromatography on silica gel (petroleum ether/acetone, 8:1 *v*/*v*) to give compound **5** (5.20 g, 58%) as a colorless oil. The ^{1}H NMR spectrum of **5** is shown in Fig. S9. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 6.93–6.82 (m, 3H), 6.28 (t, J = 2.0 Hz, 2H), 5.01 (s, 2H), 4.21–4.11 (m, 4H), 3.94–3.86 (m, 4H), 3.79 (m, 4H), 3.71 (m, 4H), 3.69–3.63 (m, 12H), 3.44 (t, J = 7.6 Hz, 2H), 3.27 (p, J = 1.8 Hz, 2H), 2.66 (d, J = 1.2 Hz, 2H), 2.32 (t, J = 7.6 Hz, 2H), 1.61 (t, J = 7.2 Hz, 2H), 1.55–1.50 (m, 2H), 1.32–1.22 (m, 14H). The ^{13}C NMR spectrum of **5** is shown in Fig. S10. ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ (ppm): 178.22, 173.84, 149.12, 137.96, 129.44, 121.89, 114.97, 114.32, 71.31, 71.09, 71.01, 70.92, 70.90, 69.95, 69.94, 69.56, 66.13, 47.92, 45.28, 42.84, 38.86, 34.47, 29.49, 29.45, 29.32, 29.24, 29.22, 27.88, 27.07, 25.05. HRESIMS is shown in Fig. S11: *m*/*z* calcd for $C_{41}H_{61}NO_{12}$, 782.4194 $[M+Na]^+$; found 782.4092 $[M+Na]^+$.

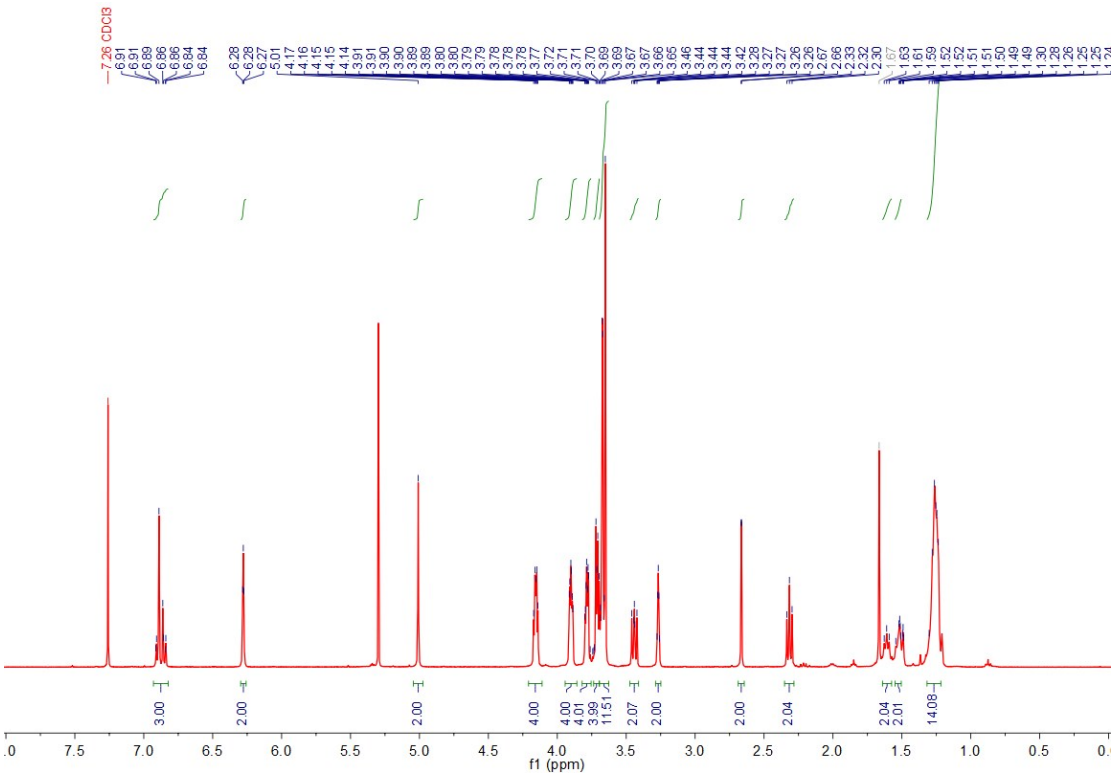


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **5**.

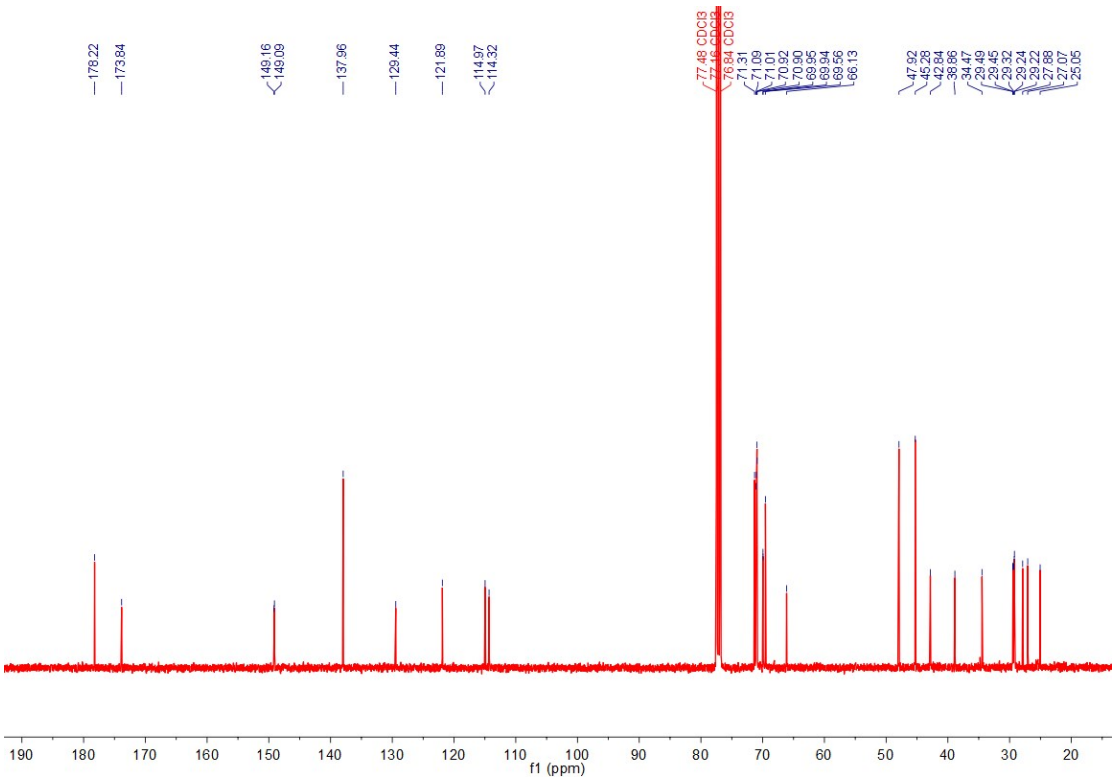


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298K) of **5**.

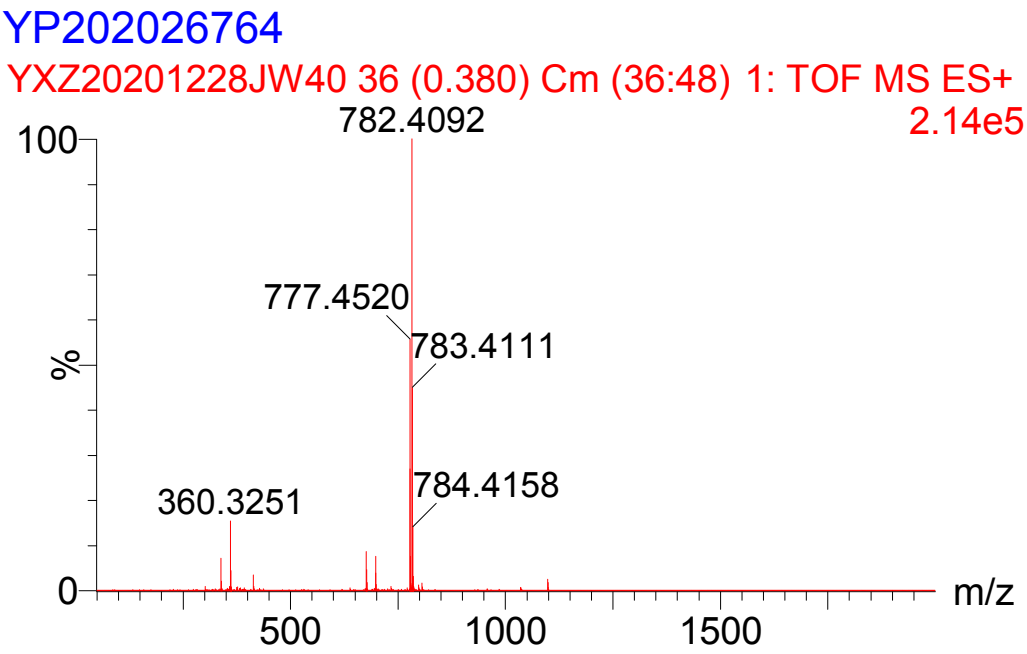
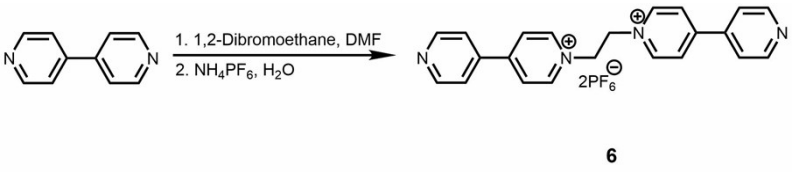


Figure S11. Electrospray ionization mass spectrum of **5**.

3. Synthesis of guest molecule 6



6

A mixture of 4,4'-bipyridine (4.99 g, 32.0 mmol) and 1,2-dibromoethane (2.00 g, 10.7 mmol) was dissolved in DMF and heated at 70 °C for 12 hours. A pale yellow precipitate separated out and filtered, then recrystallized in water and filtered. The residue was dissolved in hot water and a saturated aqueous NH_4PF_6 solution was added to produce a precipitate, which was collected by vacuum filtration to afford compound **6** (1.34 g, 20%) as a pale purple solid. The ^{1}H NMR spectrum of **6** is shown in Fig. S12. ^{1}H NMR (400 MHz, Acetone-d_6, 298K) δ (ppm): 9.39 (d, J = 6.8 Hz, 4H), 8.89 (d, J = 6.0 Hz, 4H), 8.79 (d, J = 7.2 Hz, 4H), 7.99 (d, J = 6.0 Hz, 4H), 5.84 (s, 4H).

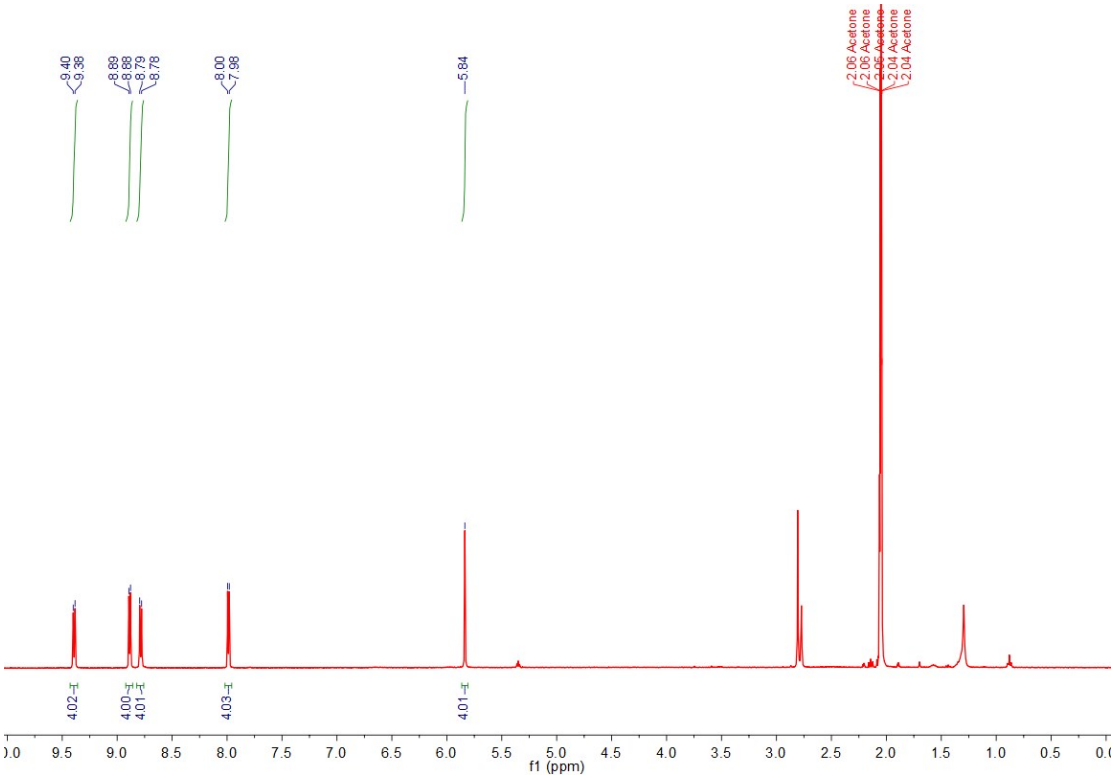
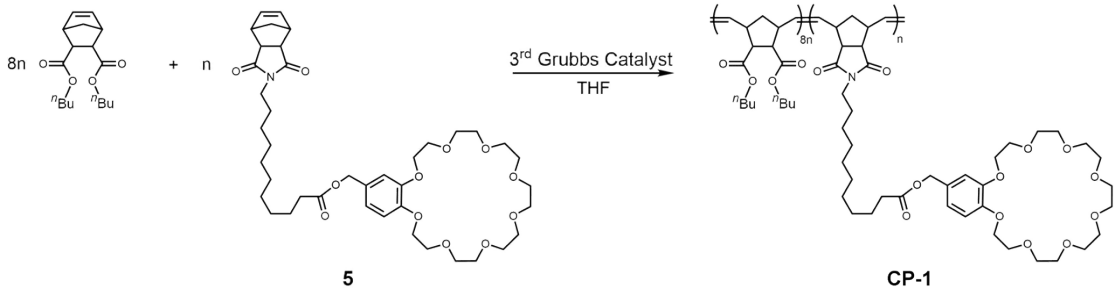


Figure S12. ^{1}H NMR spectrum (400 MHz, Acetone-d_6, 298K) of **6**.

4. Synthesis of CP-1



5 **CP-1**

An oven-dried vial was charged with norbornenyl *exo*-di-*n*-butyl ester (1.62 g, 5.49 mmol), compound **5** (0.52 g, 0.69 mmol) and a stirring bar. The vial was then degassed, and the 50 mL of degassed anhydrous THF was added via syringe under a nitrogen atmosphere to dissolve the monomer. The Ru catalyst (18.9 mg, 0.021 mmol) in 10 mL degassed anhydrous THF was injected into the monomer solution to initiate the polymerization. The solution was stirred for 8 h at room temperature and then quenched by the addition of 0.2 mL of neat ethyl vinyl ether. After stirring for an additional 60 min, the mixture was added dropwise to 1 L of rapidly stirring methanol and a pale grey precipitate formed immediately. The suspension was then centrifuged and collected. The solid was dried under vacuum for 24 h to afford CP-**1** (2.09 g, 97%). The ^{1}H NMR spectrum of CP-**1** is shown in Fig. S13. The SEC curve of CP-**1** is shown in Fig. S14 with M_n = 129000 g/mol and $Đ$ = 2.25.

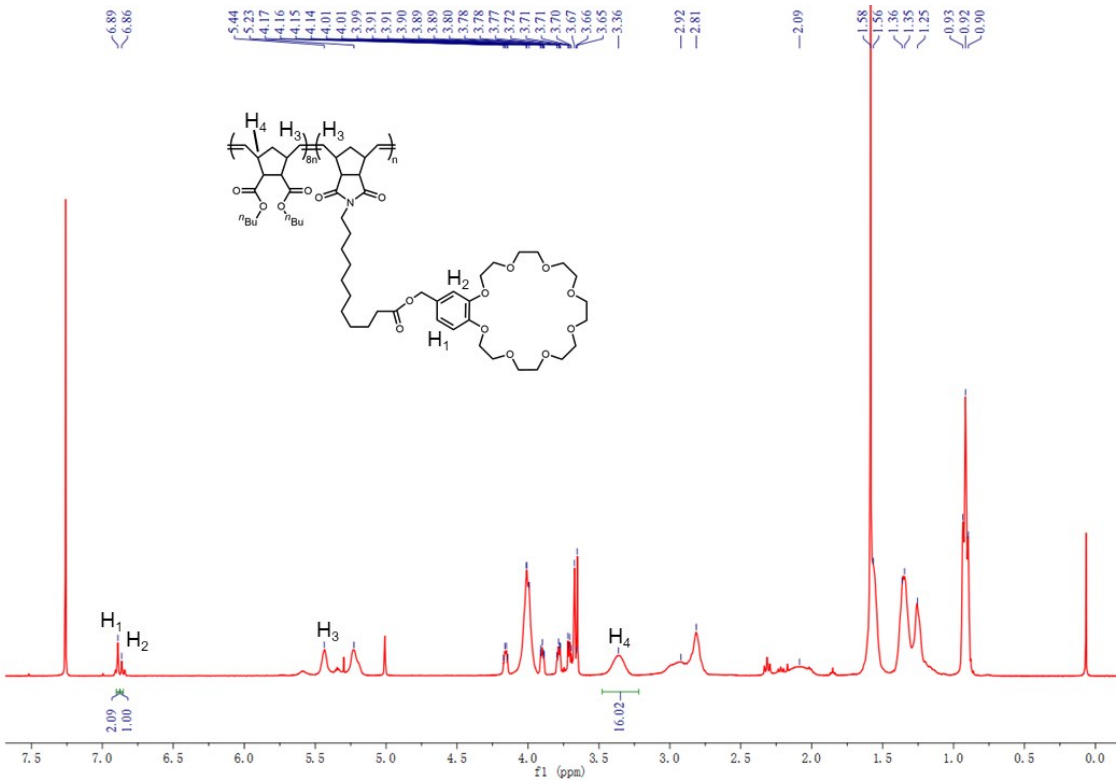


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of CP-**1**.

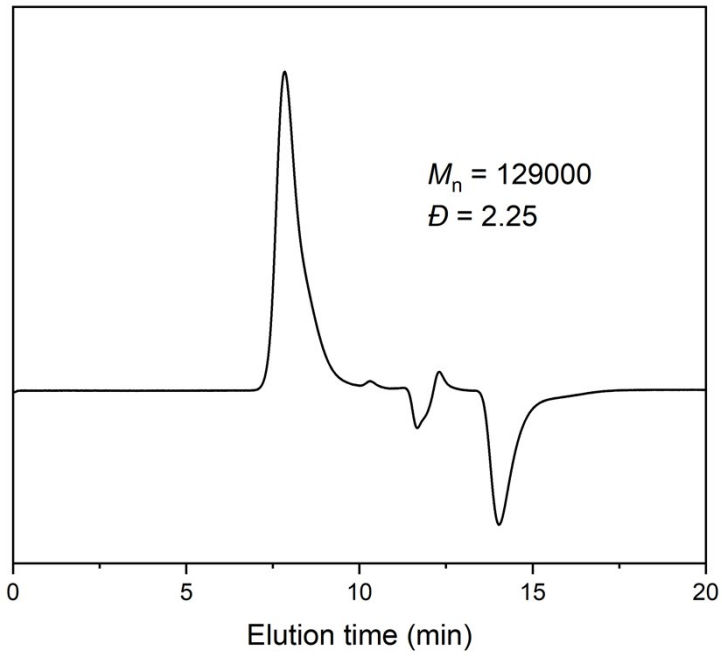


Figure S14. GPC elution curve of CP-**1** with DMF as the eluent and PS as the standard.

5. Partial ^{1}H NMR spectra of model molecules

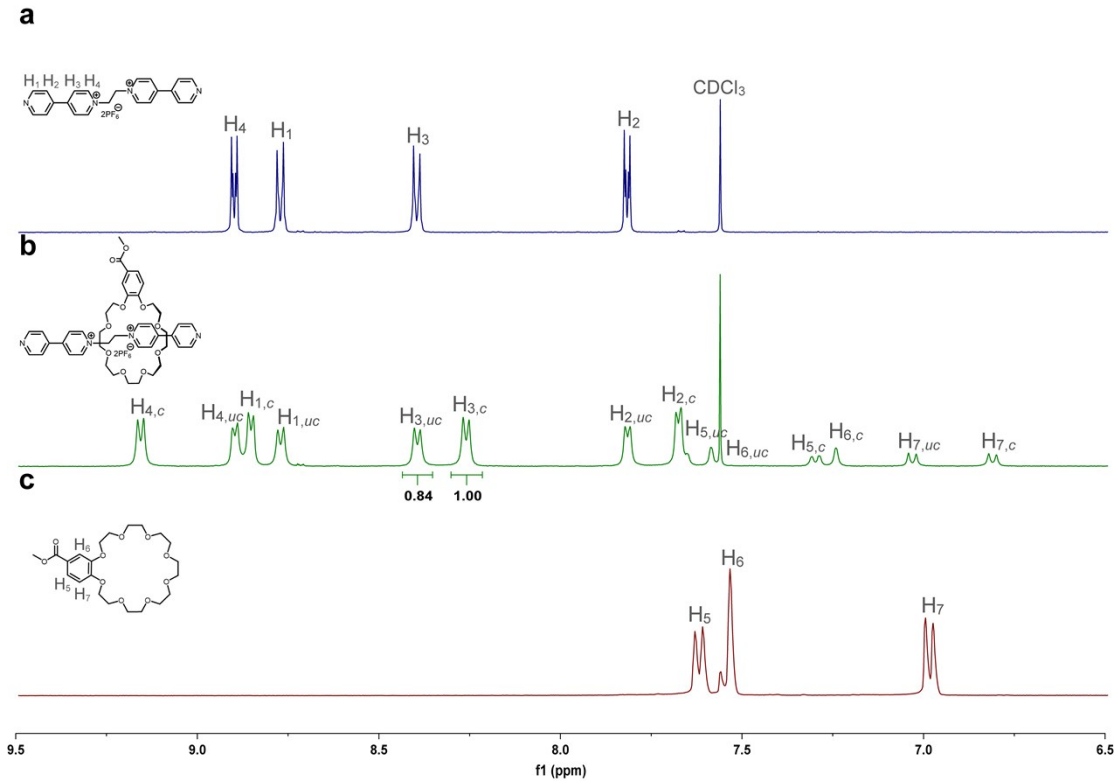


Figure S15. Partial ^{1}H NMR (400 MHz, CD_3CN:$CDCl_3$ = 3:1 *v*/*v*, 298 K) of (a) bis(pyridinium) ligand **6**, (b) host–guest complex and (c) crown ether **2**. Letters "c" and "uc" denote complexed and uncomplexed species, respectively. In the spectrum of host–guest complex, the proton signals on compound **6** and crown ether were split and shifted, indicating the formation of the [2]pseudorotaxane. The association constants (K_a) of complexation was calculated as 220 M^{-1} with a sample concentration of 11.8 mM.

6. Partial 2D COSY NMR spectrum of model [2]pseudorotaxane coordinated with $Pd(PhCN)_2Cl_2$

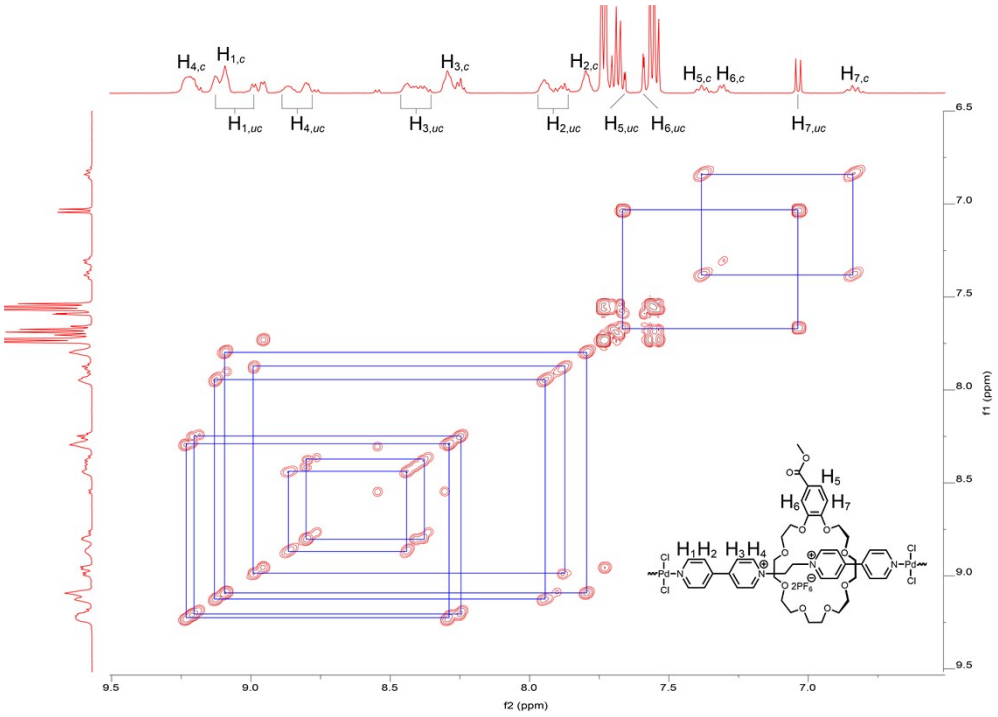


Figure S16. Partial 2D COSY NMR spectrum (500 MHz, CD_3CN:$CDCl_3$ = 3:1 *v*/*v*, 298 K) of model [2]pseudorotaxane coordinated with $Pd(PhCN)_2Cl_2$. Letters "c" and "uc" denote complexed and uncomplexed species, respectively.

7. STEM image of CSP-2

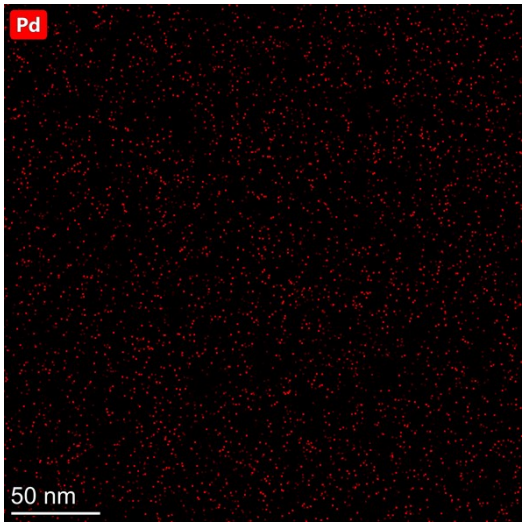


Figure S17. STEM image of CSP-**2**.

8. TGA curves of CPs and CSPs

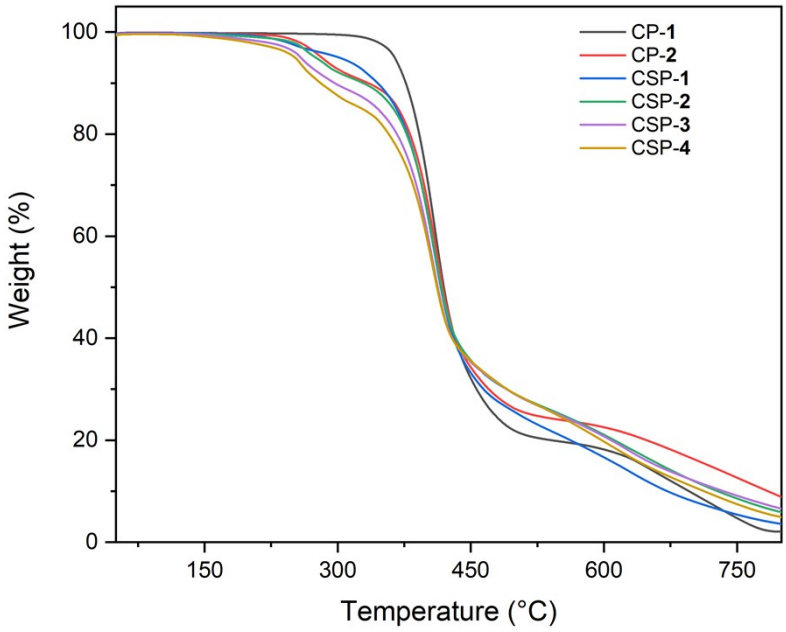


Figure S18. Stack plots of TGA curves of CPs and CSPs.

9. DSC curves of CPs and CSP-2

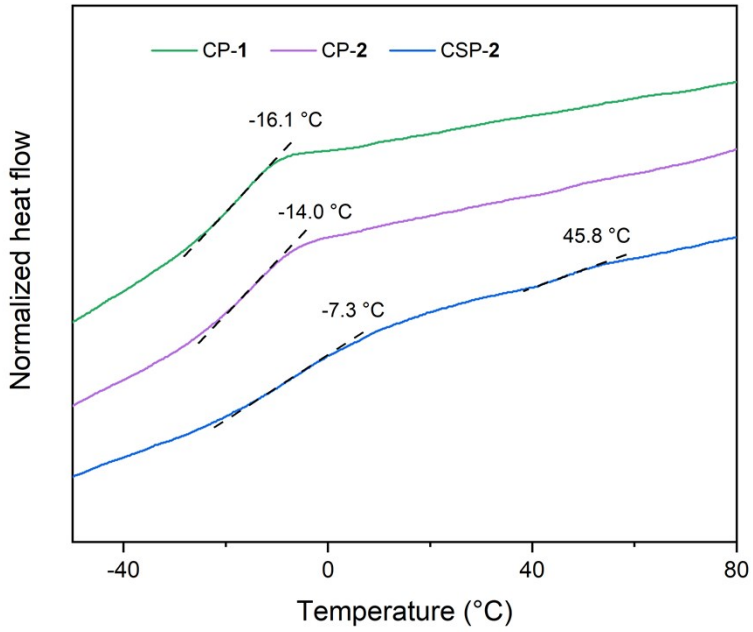


Figure S19. Stack plots of DSC curves of CPs and CSP-**2**.

10. Mechanical properties of CPs and CSPs

Sample	Stress (MPa)	Strain (%)	Young's modulus (MPa)
CP-**1**	0.05	> 800	0.26
CP-**2**	0.12	> 1000	0.48
CSP-**1**	7.10	425	22.9
CSP-**2**	12.3	398	116
CSP-**3**	14.5	214	158
CSP-**4**	17.0	97	270

Table S1. Comparison of the mechanical properties of CPs and CSPs.

11. Young's modulus of CSP-2 under different deformation rates

Deformation rates (mm/min)	0.2	2.0	20	200
Young's modulus (MPa)	73.0	88.5	116	150

Table S2. Comparison of Young's modulus of CSP-**2** under different deformation rates.

12. Young's modulus and elongation at break of CSP-2 after stress relaxation

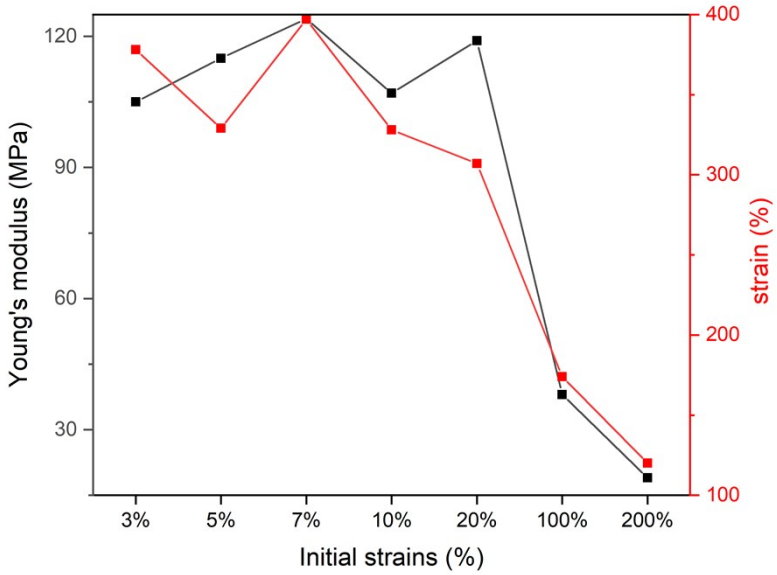


Figure S20. Comparison of Young's modulus and elongation at break of CSP-**2** samples after stress relaxation tests under different initial strains.

13. Stress–strain hysteresis loops of CSP-2 under different strains

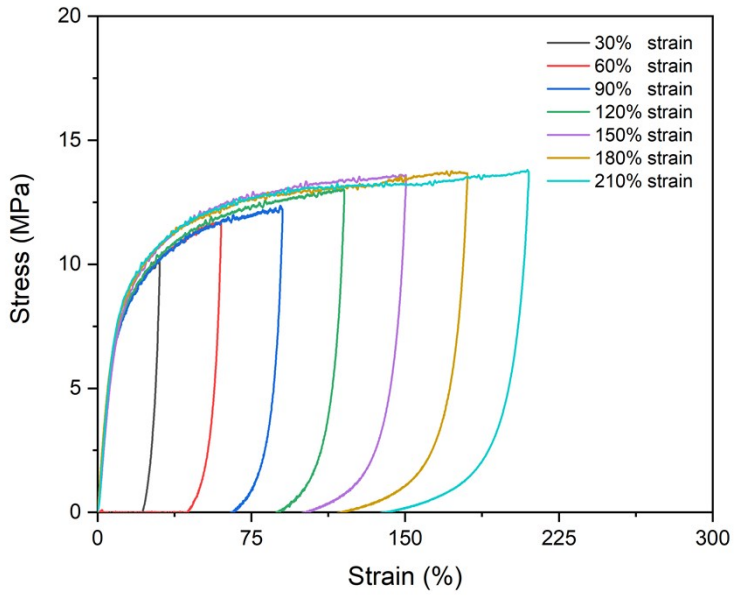


Figure S21. Stack plots of stress–strain hysteresis loops of CSP-**2** under different strains.

14. Dissipation energies of CSP-2 under different strains

Strains (%)	30	60	90	120	150	180	210
Dissipation energies (MJ/m^3)	2.08	5.15	8.72	12.6	16.6	20.4	24.3

Table S3. Comparison of dissipation energies of CSP-**2** under different strains.

15. Strain amplitude sweep test of CSP-2

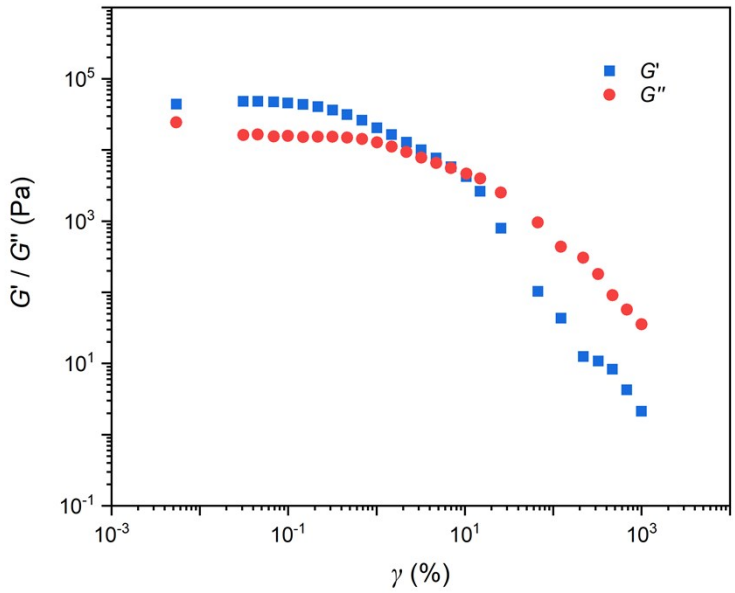


Figure S22. Storage modulus (G') and loss modulus (G'') versus shear strain (γ) for CSP-**2**.

References:

1. H. Sekiguchi, K. Muranaka, A. Osada, S. Ichikawa and A. Matsuda, *Biorg. Med. Chem.*, 2010, **18**, 5732-5737.
2. C. Nicolas, L. Fontaine and V. Montembault, *Polym. Chem.*, 2019, **10**, 5487-5497.
3. S. J. Loeb, J. Tiburcio, S. J. Vella and J. A. Wisner, *Org. Biomol. Chem.*, 2006, **4**, 667-680.
4. A. B. Chang, T.-P. Lin, N. B. Thompson, S.-X. Luo, A. L. Liberman-Martin, H.-Y. Chen, B. Lee and R. H. Grubbs, *J. Am. Chem. Soc.*, 2017, **139**, 17683-17693.