Electronic Supplementary Material (ESI) for Chemical Communications

Switchable supramolecular polymers from the orthogonal self-assembly of quadruple hydrogen bonding and benzo-21-crown-7/secondary ammonium salt recognition

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Electronic Supplementary Information

1. Materials and methods

All reactions were performed in atmosphere unless noted. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. **M1**[S1], **N1**[S2], **H4**[S1], **G2**[S3], **P1**[S4], and **P2**[S5] were prepared according to literature procedure. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer or a Bruker AVANCE Ⅲ 400MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, where $CDCl_3$ and CD_3CN were dried using neutral aluminium oxide. ^1H-^1H COSY and NOESY experiments were performed on a Bruker AVANCE III 400 MHz spectrometer. ^1H NMR Diffusion measurements (DOSY) were carried out at 298 K on a Bruker AVANCE III 400 spectrometer. The ledbpgp2s pulse sequence from Bruker Biospin was selected for the DOSY NMR by using gradients varied linearly from 5% up to 95% in 32 steps, with 16 scans per step. The diffusion time (Δ) was set at 20 ms, and the gradient length (δ) was set at 2 ms. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. Scanning electron microscopy (SEM) investigations were carried out on a Shimadzu SSX-550 instrument. Transmission electron microscope (TEM) experiments were carried out on a JEM-2100 instrument. Viscosity measurements were carried out with Ubbelohde micro viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm and 0.71 mm inner diameter) at 298 K in chloroform/acetonitrile (1/1, v/v).

2. Concentration-dependent ^{1}H NMR spectra

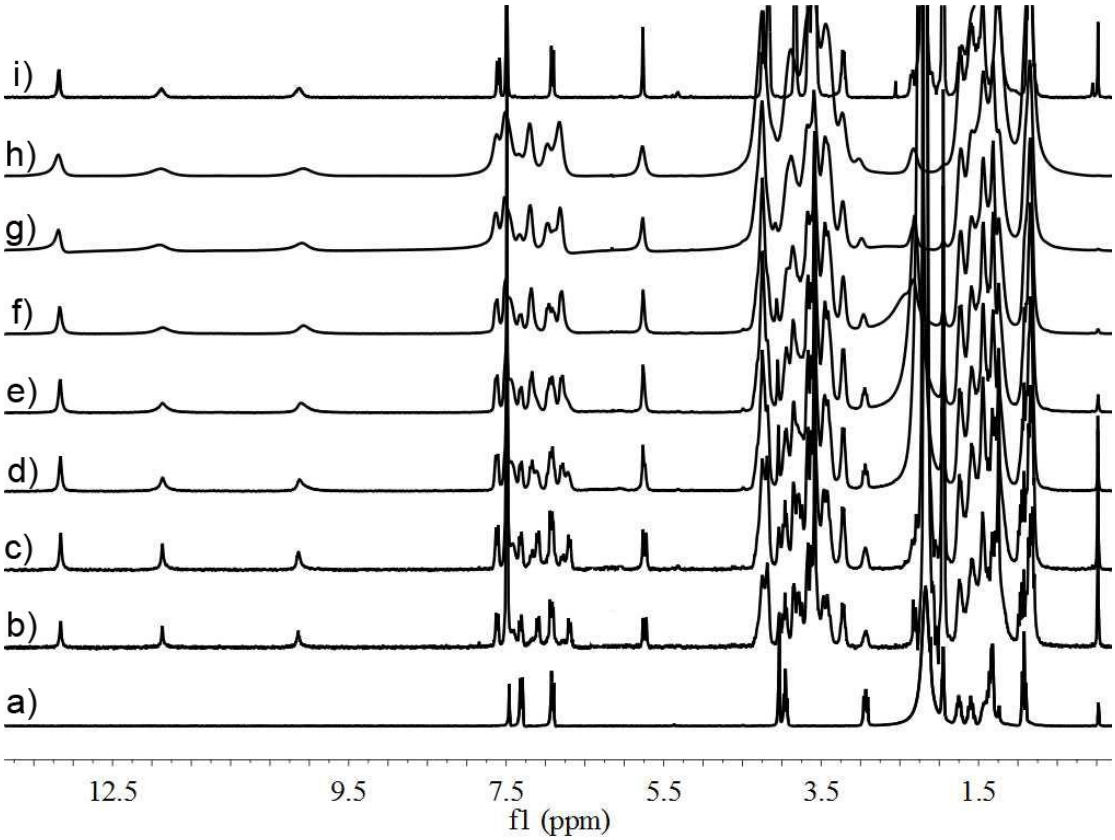


Figure S1 ^{1}H NMR spectra (300MHz, $CDCl_3/CD_3CN$ = 1/1, *v/v*, 298K) of (a) **G1**; mixtures of **H1** and 0.50 equiv. **G1** at different **H1** concentrations: (b) 2.5, (c) 5, (d) 20, (e) 40, (f) 80, (g) 160, (h) 320 mM; and (i) **H1**.

Large downfield shift for the N–*H* protons in **UPy** group was observed (between 10 and 13.5 ppm), giving direct evidence for the involvement of these protons in strong hydrogen bonding. Moreover, no obvious chemical shift change occurs for the **UPy** N-*H* protons upon concentration increasing, demonstrating the quadruple hydrogen bonding complexation was robust enough in this orthogonal self-assembly system.

3. Orthogonality test of the two binding interactions

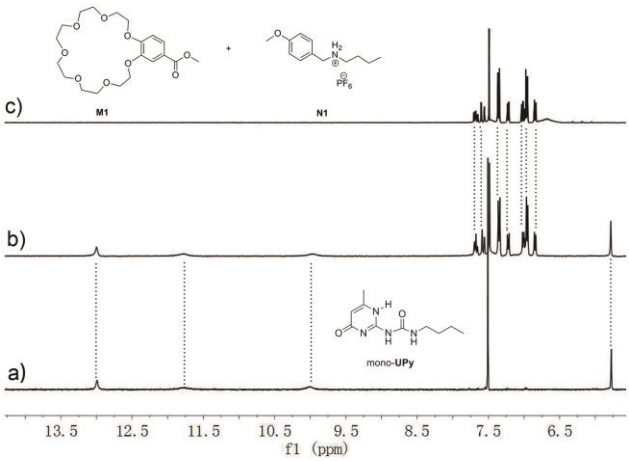
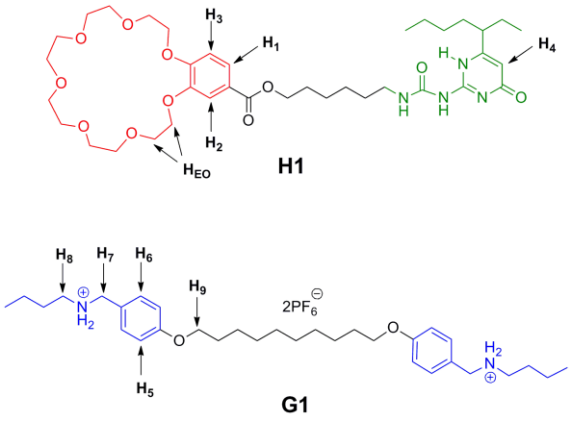


Figure S2 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) of (a) mono-**UPy** (8 mM); (b) mixtures of mono-**UPy** (8 mM), **M1** (8 mM) and **N1** (10 mM)**,** (c) mixtures of **M1** (8 mM) and **N1** (10 mM).

The mono-**UPy** was synthesized from literature report.[S6] As shown from Figure S2, no obvious chemical shift change occurs for both the **UPy** unit and **B21C7**/secondary ammonium salt motif, demonstrating that the quadruple hydrogen bonding complexation was robust enough upon the involvement of **B21C7**/secondary ammonium salt recognition to the system, which proves that these two binding units could act in the "orthogonal" way. These results encourage us to construct novel supramolecular polymers by utilizing the above binding units based on quadruple hydrogen bonding and host-guest interactions.

4. ^{1}H-^{1}H COSY NMR spectrum of H1 (20 mM) and G1 (10 mM) mixtures in $CDCl_3/CD_3CN$



Scheme S1 Structures of **H1** and **G1**

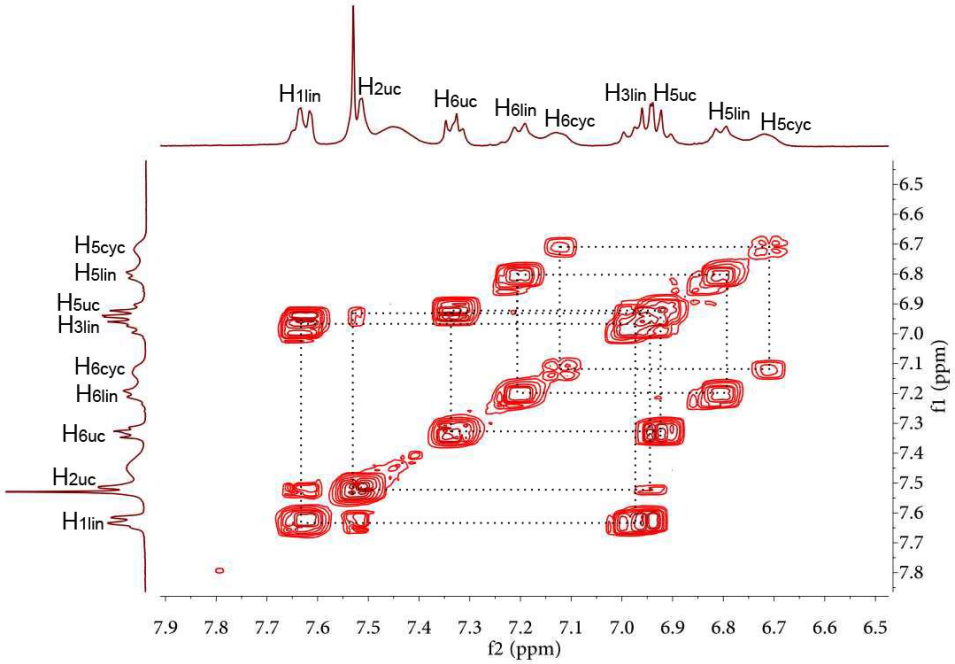


Figure S3 Partial COSY NMR (400 MHz, $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) spectrum of a solution of **H1** (20 mM) and 0.50 equiv **G1** (10 mM). Peaks of linear polymers, cyclic oligomers, and uncomplexed monomer are designated by lin, cyc, and uc, respectively.

The COSY NMR experiment was performed at a concentration of 20.0 mM (**H1**) because the signal peaks belonging to different species, including complexed (linear and cyclic species) and uncomplexed, all appeared. As shown in Figure S3, strong correlations were observed between the aromatic protons H_5 and H_6 in **G1**, such as H_{5cyc} and H_{6cyc}, H_{5uc} and H_{6uc}, and H_{5lin} and H_{6lin}. Meanwhile, the linear correlative peaks between H_{1lin} and H_{3lin} in **H1** were also observed. With the assistance of COSY analysis, assignments of the complicated concentration-dependent ^1H NMR spectra (Fig. 2 and Figure S1) and proof of the formation of the supramolecular polymers constructed by orthogonal assembly were achieved.

5. NOESY NMR spectrum of H1 (80 mM) and G1 (40 mM) mixtures in $CDCl_3/CD_3CN$

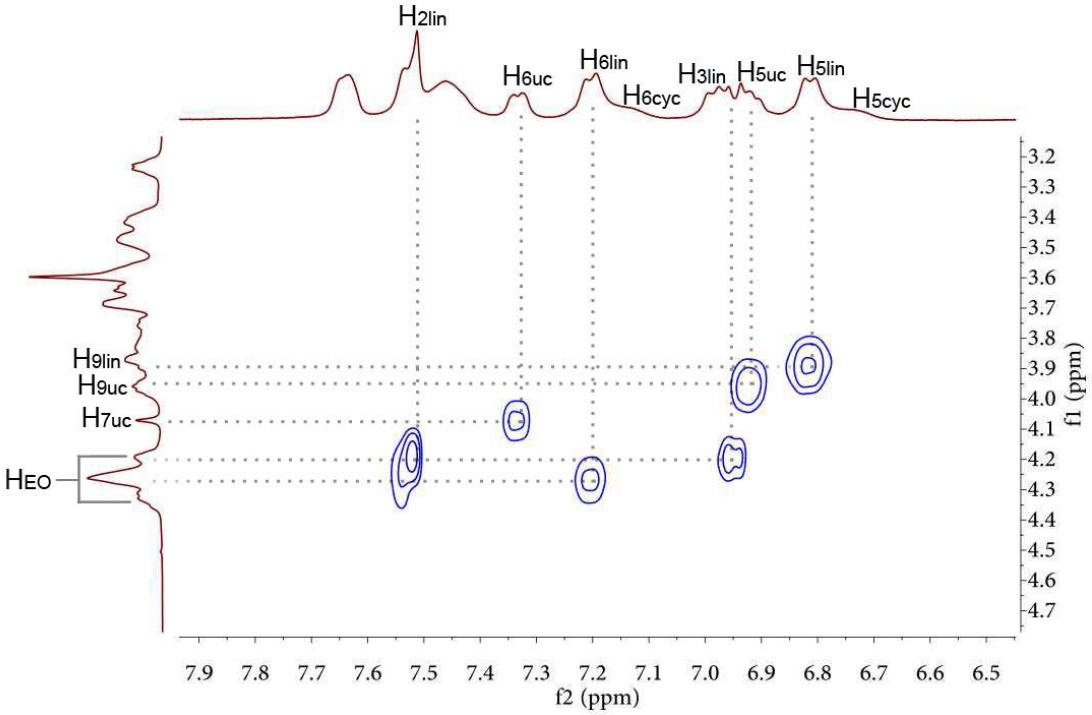
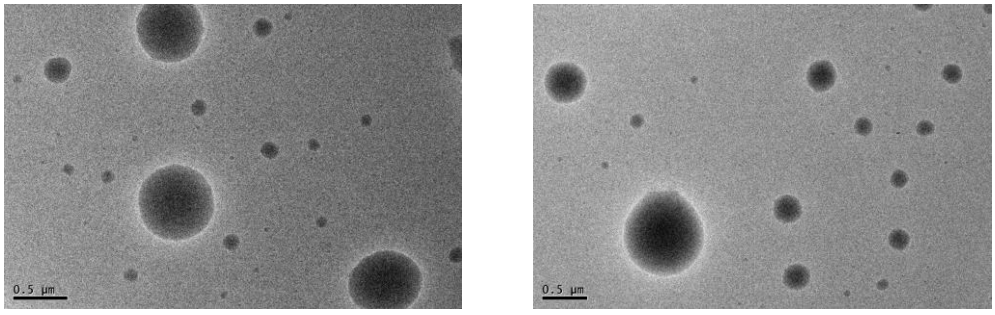


Figure S4 Partial NOESY NMR (400 MHz, $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) spectrum of a solution of **H1** (80 mM) and 0.50 equiv **G1** (40 mM). Peaks of linear polymers, cyclic oligomers, and uncomplexed monomer are designated by lin, cyc, and uc, respectively.

NOESY experiment was recorded at a relatively high concentration (**H1**, 80 mM). On the one hand, NOESY provides great help for us to assign H_{3lin} and H_{5uc}, because these two peaks are too close to identify them. However, through the strong correlation between H_{3lin} and H_{EO}, H_{5uc} and H_{9uc}, these two peaks are clearly identified. On the other hand, the strong correlation between H_{6lin} and H_{EO} indicated the dialkylammonium moiety were complexed tightly with the crown ether moiety in the solution.

6. TEM study of the supramolecular polymers



(a) (b)

Figure S5 Representative TEM images of the supramolecular polymers.

A drop of the solution of the sample (**H1** with 0.5 equiv. **G1**) was placed on a carbon-coated copper grid. After the excess of solvent was evaporated, TEM images were taken. As shown from the representative TEM images, we could observe a further assembly of the linear supramolecular polymers into larger globular aggregates with diameters ranging from 150 to 600 nm. Similar results from linear supramolecular polymers constructed by orthogonal self-assembly were also observed previously on a carbon-coated copper grid surfaces in TEM.[S7]

7. DOSY investigation of the supramolecular polymers

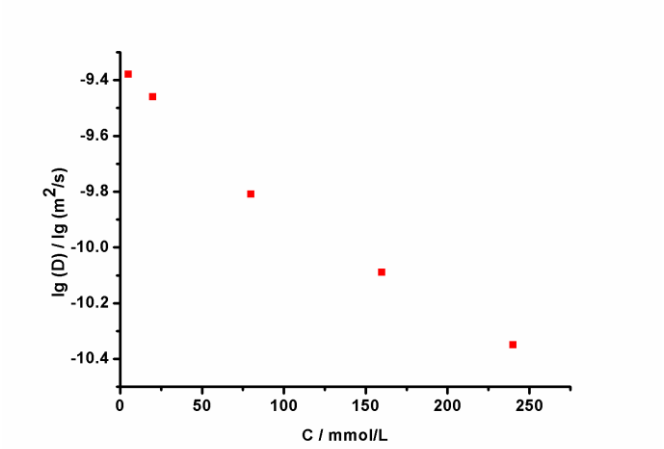


Figure S6 Concentration dependence of diffusion coefficient D (400 MHz, $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) of **H1** and 0.50 equiv. **G1**.

We have studied the diffusion coefficient D of mixtures of **H1** and 0.5 equiv **G1** at different

concentrations (from 5.0 mM to 240.0 mM), suggesting the increase in the average size of the aggregates. As the monomer **H1** concentration increased from 5.0 mM to 240 mM, the measured weight average diffusion coefficient decreased from 4.17×10^{-10} to 4.47×10^{-11} m^2s^{-1}, which means the diffusion constant of the assemblies decreased ~9 fold. By employing the Stokes-Einstein equation ($R_h = k_bT/(6\pi\eta D)$), the diffusion coefficients that were experimentally obtained could be converted to an approximate hydrodynamic radius (or Stokes radius). K_b is Boltzmann's constant and T is the temperature. The viscosity coefficient η of a mixed solution of $CHCl_3$ and CH_3CN (v/v = 1/1) is obtained from literature.[S8] Thus the hydrodynamic radius of the aggregates in different concentration were determined to be 2.4 nm (**H1** = 5 mM) and 22.2 nm (**H1** = 240 mM).

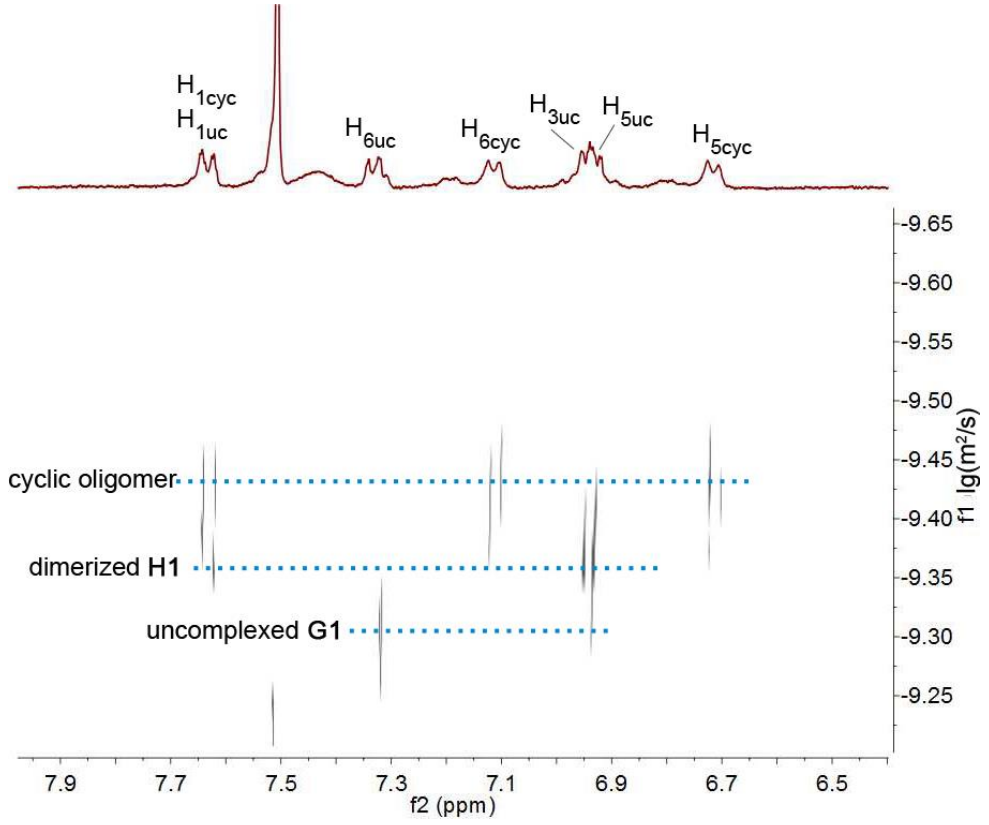


Figure S7 Representative DOSY spectra (400 MHz, $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) of **H1** (5 mM) and 0.50 equiv. **G1**. Peaks of cyclic oligomer and uncomplexed monomer are designated by cyc, and uc, respectively.

According to ring-chain equilibrium mechanism, there exists CPC (critical polymerization concentration) during the polymerization process, below which the cyclic species are predominant, while above which the linear species (polymers) are predominant. In our case, the cyclic

oligomers are mainly referred to 2:1 species (2 **H1** molecules and 1 **G1** molecule). Moreover, the cyclic oligomers also included higher cyclic species. However, the signals of higher cyclic species could not be seen from the DOSY spectra (Figure S7), indicating the 2:1 cyclic species are predominant. Compared to the well-defined super-structures we reported before,[10] the DOSY signals in this case are disordered on accounts of the different species. From the above DOSY spectra (Figure S7), we can see that there are three species in such a low concentration (**H1** = 5 mM), which include the cyclic oligomer (two **H1** and one **G1**, M_n = 2311.8 g/mol), quadruply hydrogen bonded dimer of **H1** (M_n = 1577.4 g/mol), and uncomplexed **G1** (M_n = 788.7 g/mol). It should be noted that the relative diffusion coefficient values of each species are in accordance with their molecular weight.

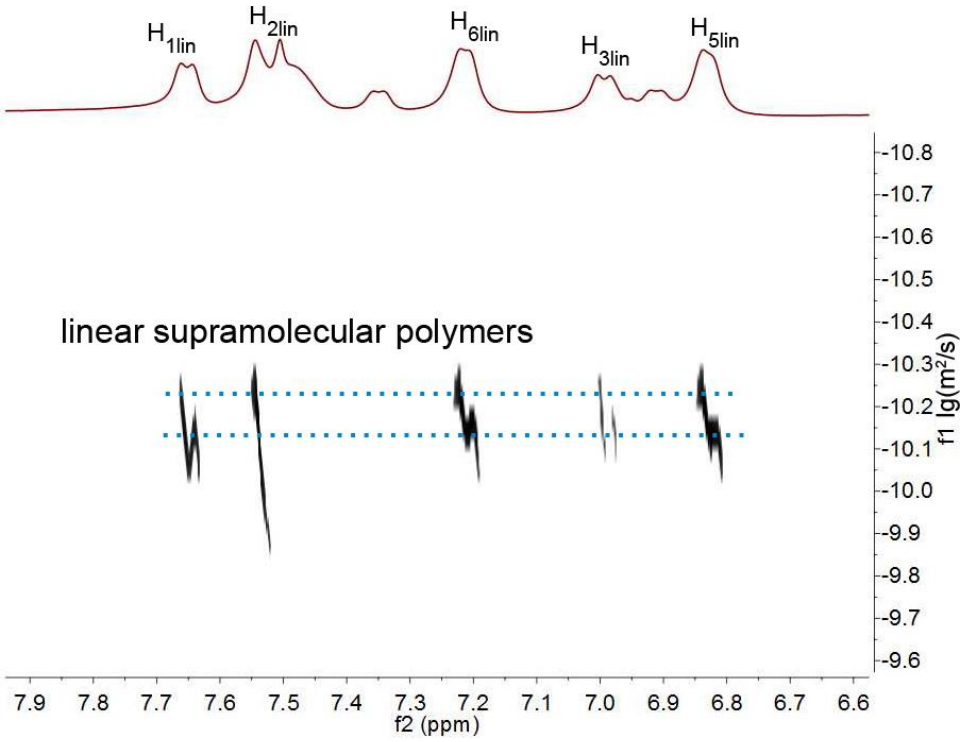
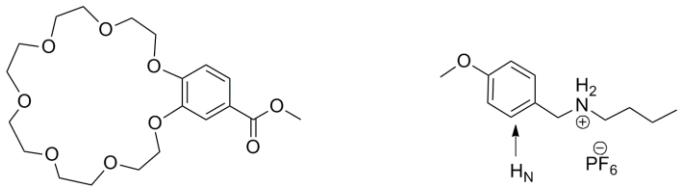


Figure S8 Representative DOSY spectra (400 MHz, $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) of **H1** (160 mM) and 0.50 equiv. **G1**. Peaks of linear supramolecular polymers are designated by lin.

As mentioned above, the linear supramolecular polymers are predominant when the concentration exceeds the CPC. From Figure S8, we can only see DOSY signals of the polymers, which is consistent with the theory of ring-chain mechanism. That means the linear polymers are predominant.

8. Discussion of the association constants of the two orthogonal binding interactions

(1) Benzo-21-Crown-7/Dialkylammonium Salt association: We use the model compound **M1** and **N1** (Scheme S2) to determine the association constant K_a of the **B21C7**/Dialkylammonium recognition according to the reference method.[S1b] **M1**[S1] and **N1**[S2] were synthesized motif by ^{1}H NMR spectroscopy according to literature reports. Because of the slow-exchange complexation properties of **B21C7**-based complexes, the K_a value could be calculated from integrations of complexed and uncomplexed peaks in ^{1}H NMR spectrum. The K_a value was measured at 1.00 mM host and guest in $CDCl_3/CD_3CN$ (1/1, v/v) solution.



Scheme S2 Structures of **M1** and **N1**

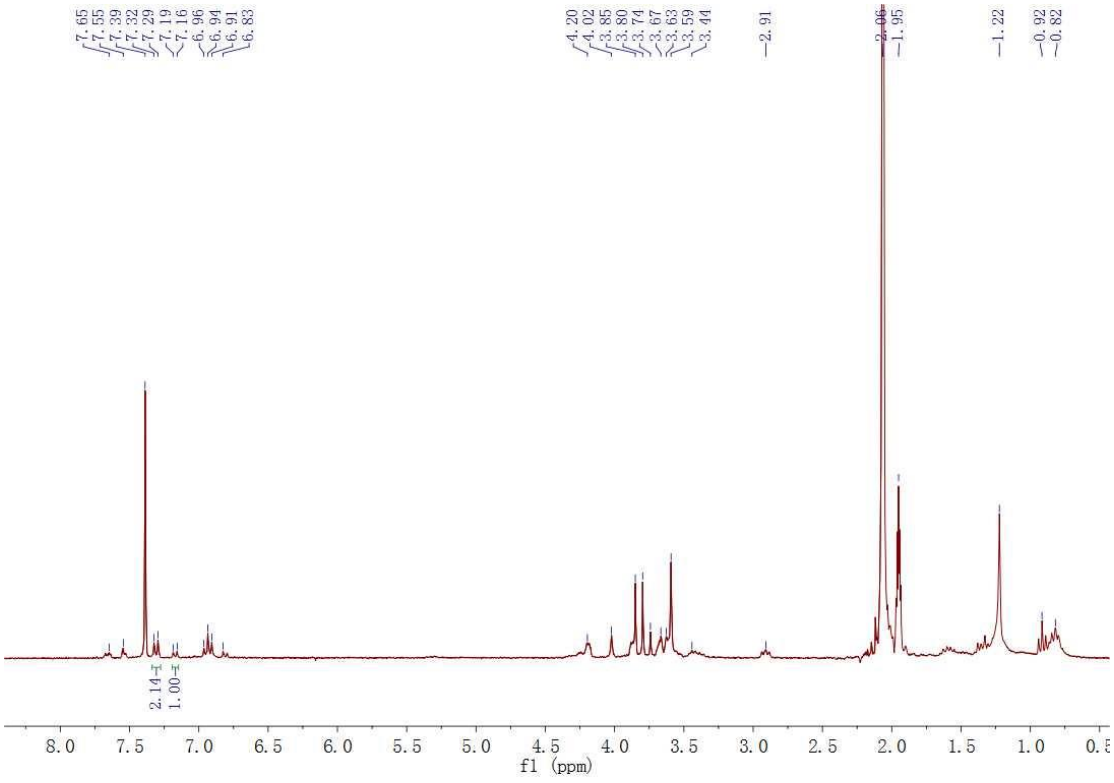


Figure S9 Representative ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) of 1.00 mM **M1** and **N1**.

Using the method reported in literature,[S1b] the K_a value was calculated as below:

$K_{a,\,\mathbf{M1}\cdot\mathbf{N1}} = [HG]/[H][G] = [A_{HG}/(A_{HG}+A_{H\ or\ G})] \times 1 \times 10^{-3}/\{[\ 1- A_{HG}/(A_{HG}+A_{H\ or\ G})] \times 1 \times 10^{-3}\}^2$, [HG], [H], and [G] represent equilibrium concentration of complexed **M1** and **N1**, individual **M1** and individual **N1**, while A stands for the integral area. The association constant $K_{a,\,\mathbf{M1}\cdot\mathbf{N1}}$ value calculated from integrations of complexed and uncomplexed peaks of H_N in **N1** is $[(1/3.14) \times 1 \times 10^{-3}]/[(1 - 1/3.14) \times 1 \times 10^{-3}]^2 = 686\ M^{-1}$. The experiment was repeated for three times and an average value of K_a was determined to be $740 \pm 66\ M^{-1}$, which is close to the literature value.[S1b]

(2) UPy dimerization: For **UPy** dimerization in mixed solution of $CHCl_3$ and CH_3CN (v/v, 1/1), we have elaborately discussed in our previous report,[S9] which pointed out that the K_a value should be larger than $4.75\times10^5\ M^{-1}$. In our case, in the ^1H NMR spectra, there just showed one set of signals for the N*H* protons, indicating the strong dimerization of **UPy** groups. Additionally, the N*H* proton in **UPy** would only shift to very downfield (> 13 ppm) because of the tightly binding condition (quadruply hydrogen bonded dimers). So far, there are also some examples from other groups to illuminate the strong **UPy** dimerization in CH_3CN or $CHCl_3/CH_3CN$ (v/v, 1/1), which can form linear supramolecular polymers[5b] and pseudo[2]rotaxane dimer.[12e] In our system or the cases from literature,[5b, 12e] the supramolecular building block is ionic compound, with the ionic strength of the solution increased, this may decrease the dimerization constant to some extent. But we believe that the K_a of **UPy** dimerization is still large enough for the contribution of the formation of the supramolecular polymers.

9. Switchable behaviors of the supramolecular polymers investigated by DOSY and NOESY experiments

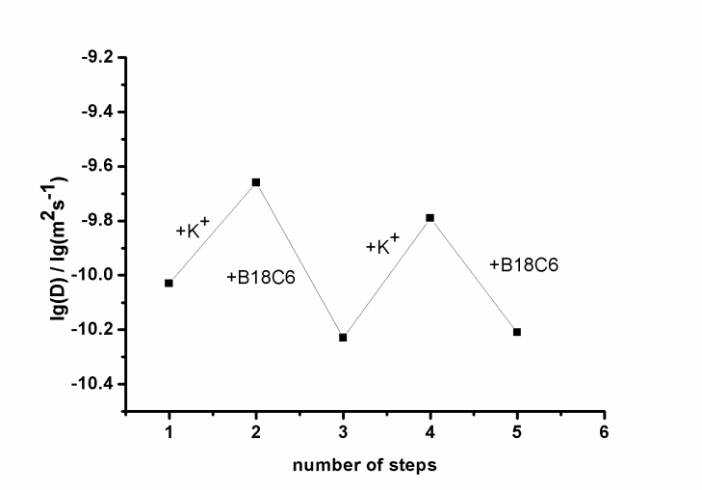


Figure S10 Diffusion coefficient of a solution of supramolecular polymer constructed from **H1** and **G1** ([H1] = 160 mM in $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) upon stepwise addition of equal equiv. K^+ ion or **B18C6**.

The reversible process was investigated by DOSY NMR experiments (**H1** = 160 mM, Figure S10). The diffusion coefficient of the supramolecular polymer increases significantly from 7.41 × 10^{-11} m^2s^{-1} to 2.19 × 10^{-10} m^2s^{-1} after the addition of one equiv. K^+ ion. Upon subsequent addition of the same equiv. **B18C6**, the diffusion coefficient decreases again. This external switching cycle between polymers and dimers could be repeated at least four times with the addition/removal of K^+ monitored by the changes of the diffusion coefficient.

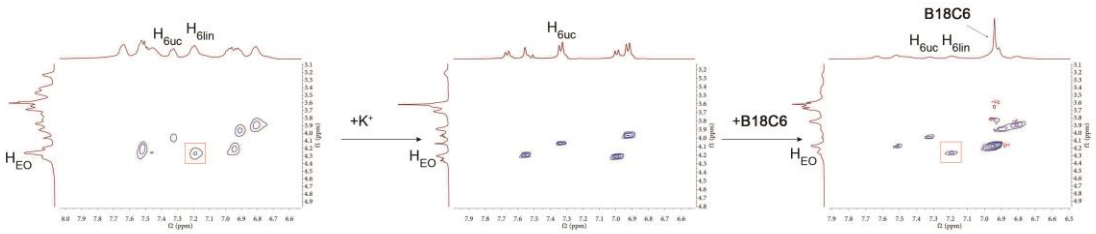


Figure S11 NOESY of the supramolecular polymers constructed from **H1** and **G1** ([H1] = 40 mM in $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) upon stepwise addition of equal equiv. K^+ ion or **B18C6**.

The reversible process was investigated by NOESY NMR experiments (**H1** = 40 mM). As shown from Figure S11, the broad peaks of the ^1H NMR became simple and sharp after the addition of K^+, suggesting that the large aggregates were disassembled into low-molecular-weight

species. It should be noted that the NOE signal between H_{6lin} from **G1** and H_{EO} from **H1** disappeared, indicating that the supramolecular polymer was disassembled and the **B21C7** moiety was occupied by K^+. Upon subsequent addition of **B18C6**, the NOE signal between H_{6lin} from **G1** and H_{EO} from **H1** was recovered and the peaks became broad again, suggesting the supramolecular polymer was reformed.

10. Orthogonal responsiveness of the supramolecular polymers by adding a mono-functional UPy competitor

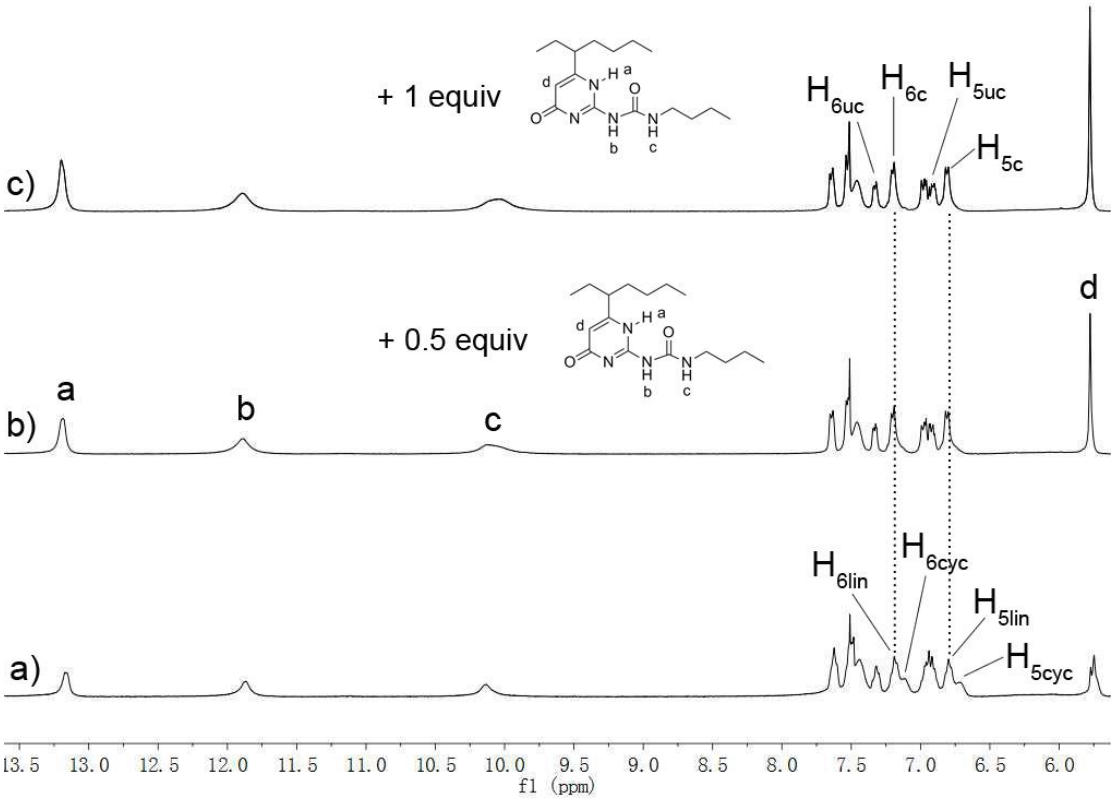
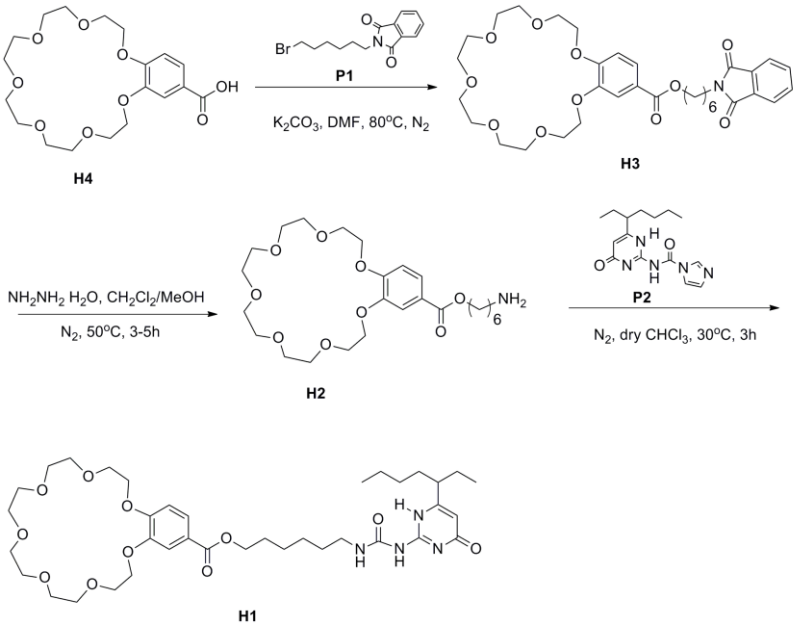


Figure S12 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1/1, v/v, 298 K) of (a) **H1** (40 mM) with 0.5 equiv. **G1** (20 mM), (b) after addition of 0.5 equiv. **UPy** competitor (20 mM), and (c) after addition of 1 equiv. **UPy** competitor (40 mM). Peaks of linear polymers and cyclic oligomers are designated by lin and cyc, respectively. Peaks of complexed species and uncomplexed monomer are designated by c and uc, respectively.

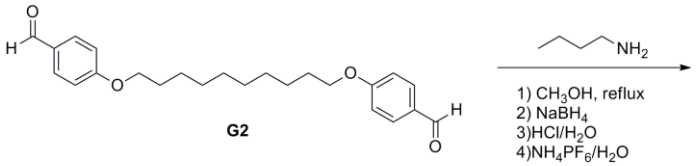
The mono-functional **UPy** competitor was synthesized according to literature reports.[S5] Responsiveness of the supramolecular polymer was studied by adding the mono-functional **UPy**

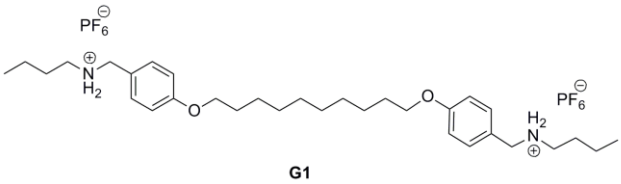
competitor. Much of interesting information can be obtained from Figure S12. On the one hand, the peaks from N*H* protons of **H1** became broad after the addition of the mono-functional **UPy** competitor, suggesting the **UPy** group in **H1** exhibited exchange binding behavior with the mono-functional **UPy** competitor and the mono-functional **UPy** competitor played the role of "stopper". On the other hand, the broad peaks (6.2-7.7 ppm) from **B21C7** group of **H1** and peaks from **G1** became sharp and clear, indicating the supramolecular polymers were disassembled. However, the **B21C7** group was still associated with the dialkylammonium group (H_{6c} and H_{5c}), indicating the orthogonal stimuli-responsive property of the material. It is interesting to note that the chemical shifts of H_{5c} and H_{6c} are the same with the H_{5lin} and H_{6lin} respectively and the peaks H_{5cyc} and H_{6cyc} disappeared. This is because the linear supramolecular polymers were disassembled into short linear supramolecular species probably with the assembly of one **G1** molecule, two **H1** molecules and two stoppers (two mono-functional **UPy** competitors). Thus no cyclic species (cyclic oligomers) existed in the system. Additionally, the conformations of the short linear supramolecular species and the linear supramolecular polymers are very similar, therefore, the chemical environment of H_{5c} and H_{6c} are similar to H_{5lin} and H_{6lin} leading to the same chemical shifts.

11. Synthesis of monomers H1 and G1



Scheme S3 Synthesis of **H1**





Scheme S4 Synthesis of **G1**

11.1. Synthesis of Compound **H3**

To a stirred solution of 2-(6-bromohexyl)isoindoline-1,3-dione (**P1**) (0.79 g，2.54 mmol) and **H4** (0.68 g, 1.69 mmol) in DMF (30 mL) was added potassium carbonate (0.70 g, 1.69 mmol) at room temperature. The mixture was then stirred at 85 ^{o}C for 12 h under N_2 atmosphere. Upon cooling to room temperature, the solution was poured into water (100 mL), exctrated with ethyl acetate (2 × 80 mL). The combined organic phase was washed with water (2 × 80 mL), brine (80 mL), and dried over $MgSO_4$. After the solvent was removed with an evaporator under reduced pressure, the resulting residue was subjected to column chromatography (dichloromethane/CH_3OH 100:1), to give **H3** (0.77 g, 73 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 – 7.80 (m, 2H), 7.73 – 7.68 (m, 2H), 7.64 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 4.23 – 4.17 (m, 4H), 3.97 – 3.89 (m, 4H), 3.84 – 3.77 (m, 4H), 3.76 – 3.71 (m, 4H), 3.70 – 3.60 (m, 10H), 1.80 – 1.65 (m, 4H), 1.54 – 1.37 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 166.3, 152.8, 148.3, 133.9, 132.1, 123.8, 123.2, 123.1, 114.6, 112.3, 71.3, 71.2, 71.1, 71.0, 70.5, 69.6, 69.5, 69.3, 69.1, 64.7, 37.8, 28.6, 28.5, 26.5, 25.7 ppm; ESI-MS: *m/z* calcd for $[M + NH_4]^+$ = 647.32 , found = 647.30 (100%); calcd for $[M + Na]^+$ = 652.27 , found = 652.20 (100%); HR-ESI-MS ($C_{33}H_{43}NO_{11}$): *m/z* calcd for $[M + Na]^+$ = 652.2728, found = 652.2729.

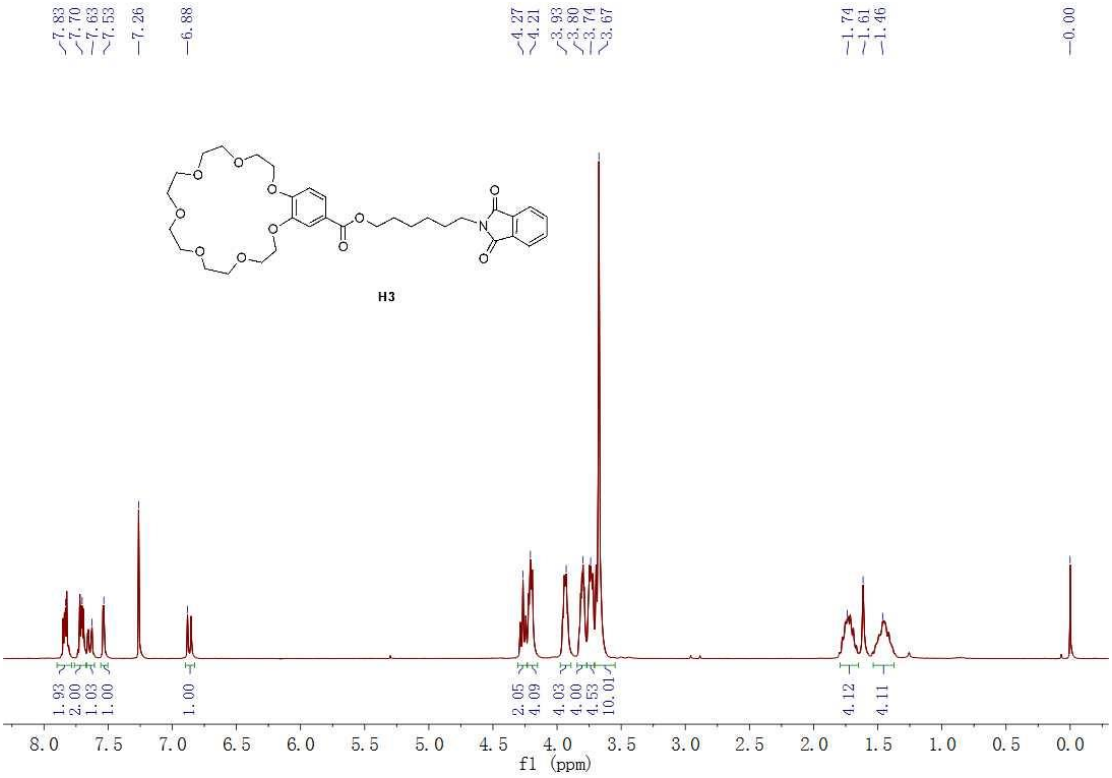


Figure S13 ^{1}H NMR spectrum (300MHz, $CDCl_3$, 298K) of **H3**

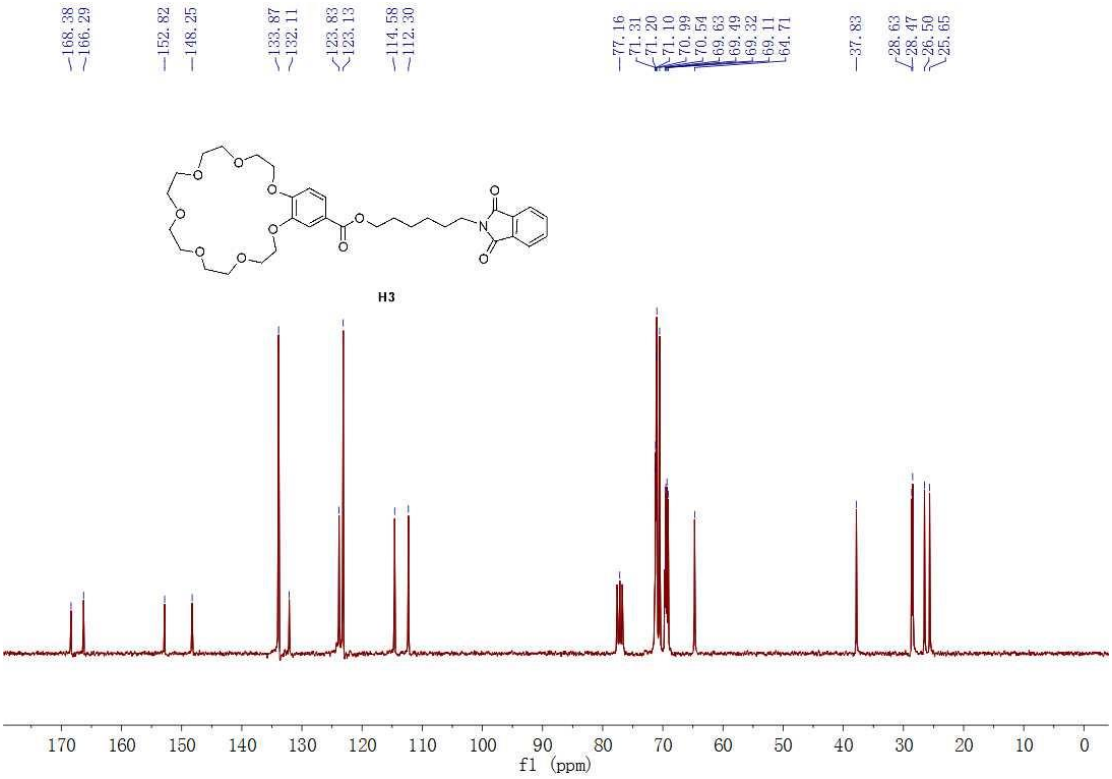


Figure S14 ^{13}C NMR spectrum (75MHz, $CDCl_3$, 298K) of **H3**

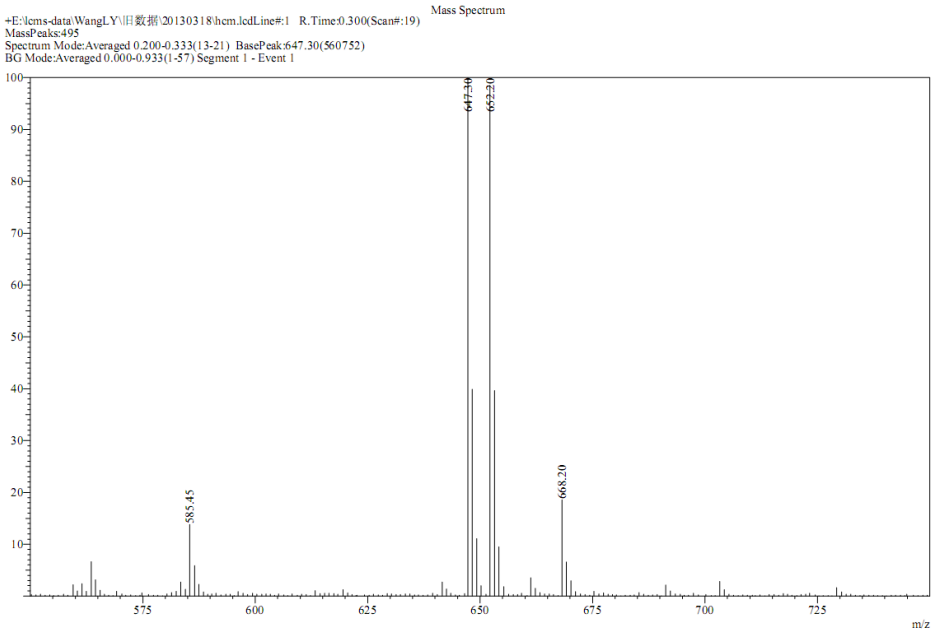


Figure S15 Electrospray ionization mass spectrum of **H3**

11.2. Synthesis of Compound **H2**

To a solution of **H3** (0.6 g, 0.95 mmol) in CH_2Cl_2 (20 mL) and MeOH (10 mL) under N_2 atmosphere, hydrazine monohydrate (0.46 mL, 9.5 mmol) was added and the mixture was stirred at 46 ^oC for 7h. After evaporation, the mixture was dissolved in CH_2Cl_2 (20 mL) and washed with 3M aqueous NaOH (20 mL), water (20 mL), brine (20 mL), and dried over Na_2SO_4. The solvent was removed with an evaporator under reduced pressure to afford **H2** (0.48 g, 97%) as a pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.55 (d, *J* = 1.7 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.36 – 4.14 (m, 6H), 4.00 – 3.90 (m, 4H), 3.85 – 3.78 (m, 4H), 3.78 – 3.71 (m, 4H), 3.71 – 3.61 (m, 8H), 2.73 (t, *J* = 7.0 Hz, 2H), 2.18 (br s, 2H), 1.81 – 1.68 (m, 2H), 1.56 – 1.32 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 152.8, 148.2, 123.9, 123.3, 114.6, 112.3, 71.3, 71.2, 71.0, 70.7, 70.5, 69.7, 69.6, 69.3, 69.1, 65.3, 64.8, 41.9, 32.8, 28.7, 26.5, 25.9 ppm; ESI-MS: *m/z* calcd for $[M + H]^+$ = 500.28 , found = 500.40 (100%); calcd for $[M + Na]^+$ = 522.27 , found = 522.25 (85%); HR-ESI-MS ($C_{25}H_{41}NO_9$): *m/z* calcd for $[M + Na]^+$ = 522.2674, found = 522.2678.

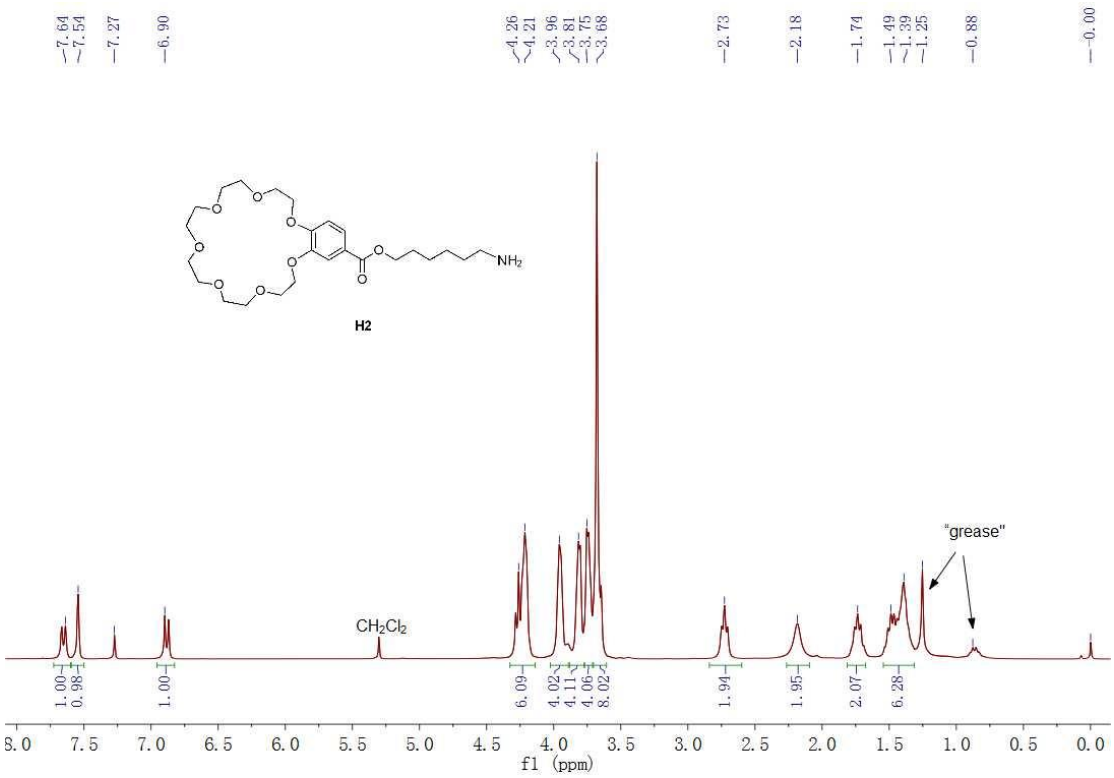


Figure S16 ^{1}H NMR spectrum (300MHz, $CDCl_3$, 298K) of **H2**

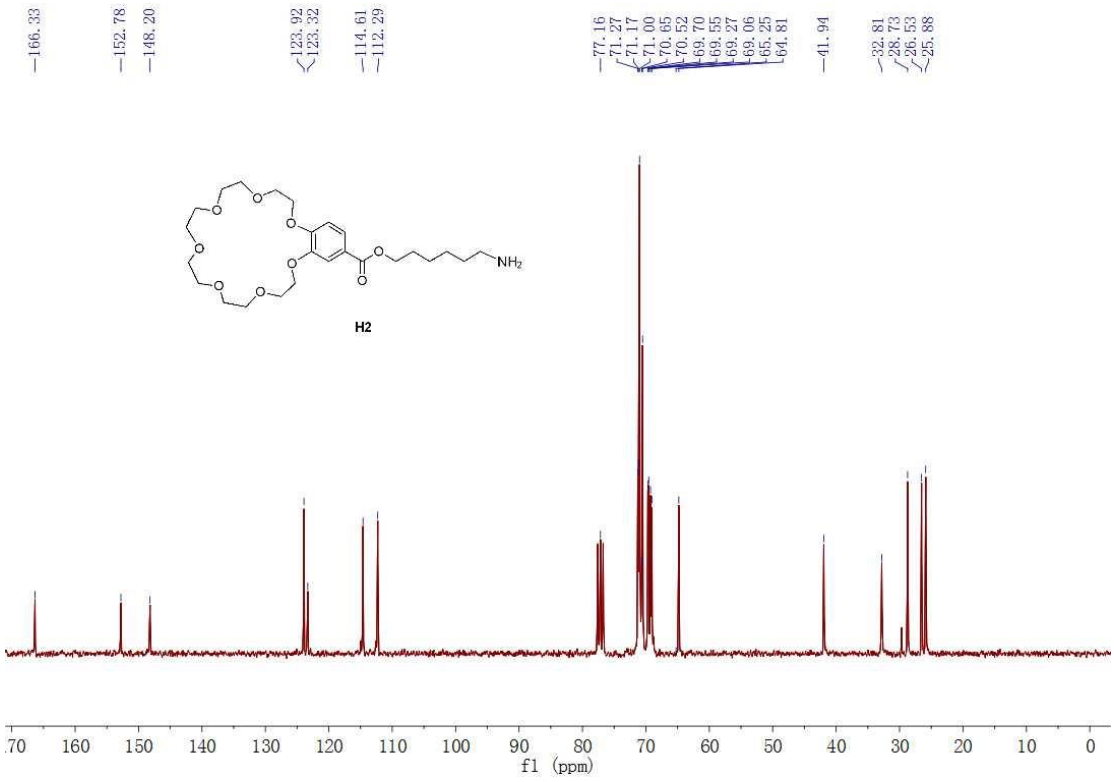


Figure S17 ^{13}C NMR spectrum (75MHz, $CDCl_3$, 298K) of **H2**

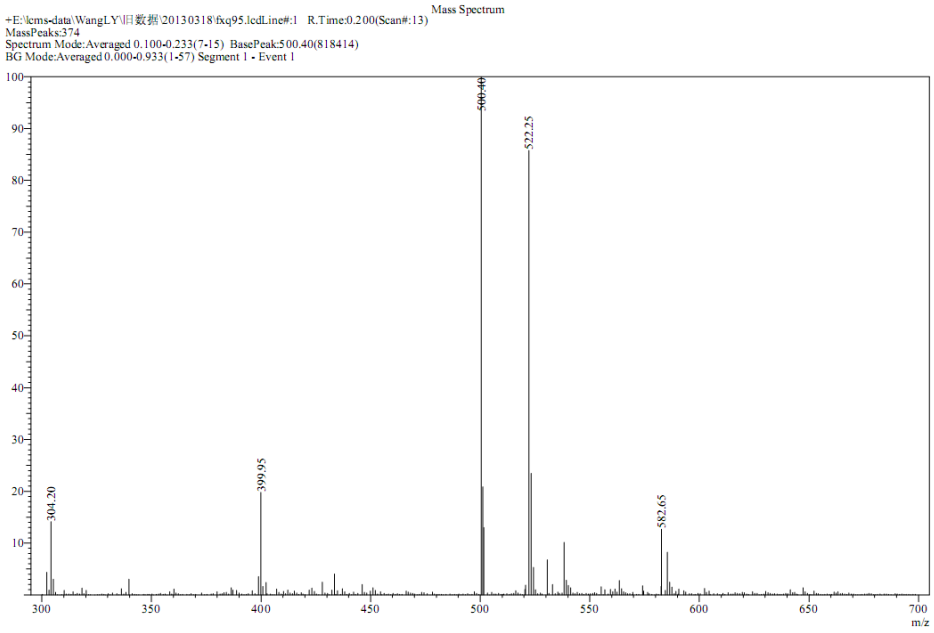


Figure S18 Electrospray ionization mass spectrum of **H2**

11.3. Synthesis of Compound **H1**

Imidazolide **P2** (0.93 g, 3.06 mmol) and **H2** (1.39 g, 2.78 mmol) were dissolved in 60 mL of dry $CHCl_3$ and this solution was stirred for 12 hours under nitrogen at r.t. To the reaction mixture 50 mL of $CHCl_3$ was added and the organic layer was washed with 1N HCl (30 mL), saturated $NaHCO_3$ (30 mL), brine (30 mL) and dried over Na_2SO_4. After the solvent was removed, the resulting residue was subjected to column chromatography $CHCl_3$/MeOH 100:1 (*v*/*v*), to give **H1** (1.23 g, 60%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.24 (s, 1H), 11.91 (s, 1H), 10.22 (s, 1H), 7.65 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 5.82 (s, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 4.23 – 4.15 (m, 4H), 3.98 – 3.90 (m, 4H), 3.85 – 3.77 (m, 4H), 3.80 – 3.70 (m, 4H), 3.70 – 3.63 (m, 8H), 3.33 – 3.21 (m, 2H), 2.34 – 2.22 (m, 1H), 1.82 – 1.72 (m, 2H), 1.71 – 1.52 (m, 6H), 1.51 – 1.37 (m, 4H), 1.34 – 1.17 (m, 4H), 0.94 – 0.81 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 166.4, 156.8, 155.5, 155.0, 152.9, 148.4, 123.9, 123.4, 114.7, 112.4, 106.3, 71.4, 71.3, 71.2, 71.1, 70.6, 69.7, 69.6, 69.4, 69.2, 65.0, 45.4, 39.7, 33.0, 29.4, 28.8, 26.8, 26.7, 25.8, 22.5, 14.0, 11.8 ppm; ESI-MS: *m/z* calcd for $[M + H]^+$ = 735.42 , found = 735.40 (100%); calcd for $[M + NH_4]^+$ = 752.44 , found = 752.45 (79%); HR-ESI-MS ($C_{37}H_{58}N_4O_{11}$): *m/z* calcd for $[M + H]^+$ = 735.4175, found = 735.4175; calcd for $[M + NH_4]^+$ = 752.4440, found =

752.4441.

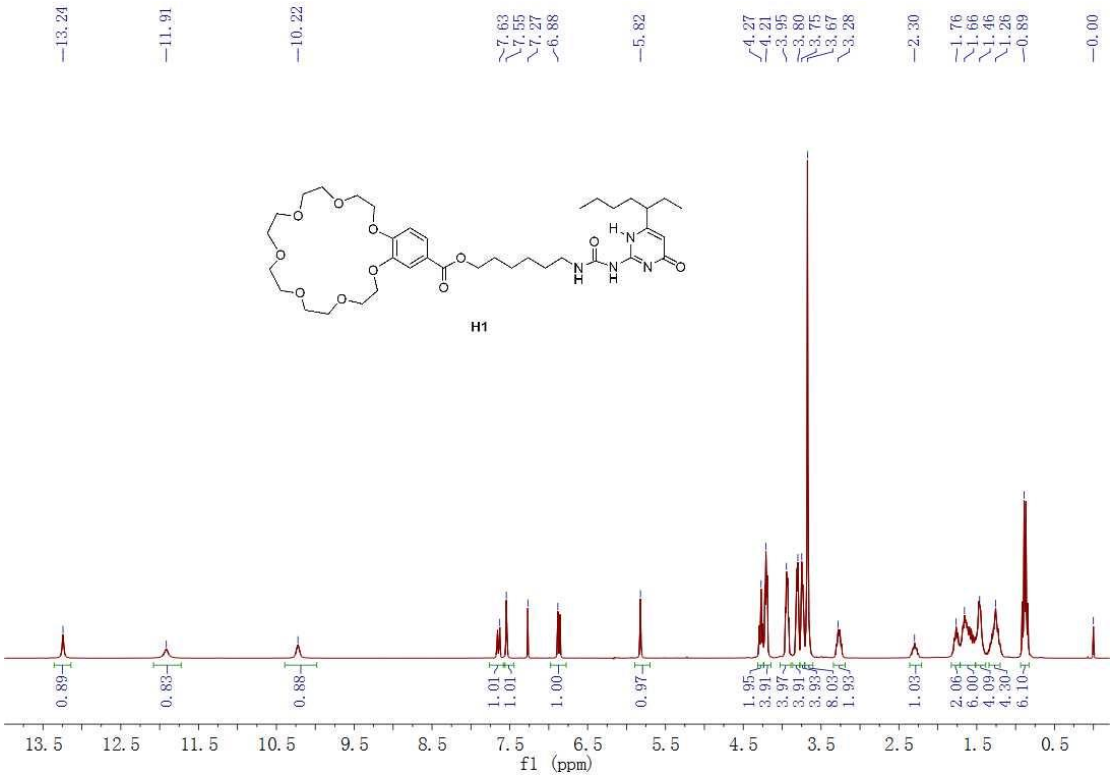


Figure S19 ^{1}H NMR spectrum (300MHz, $CDCl_3$, 298K) of **H1**

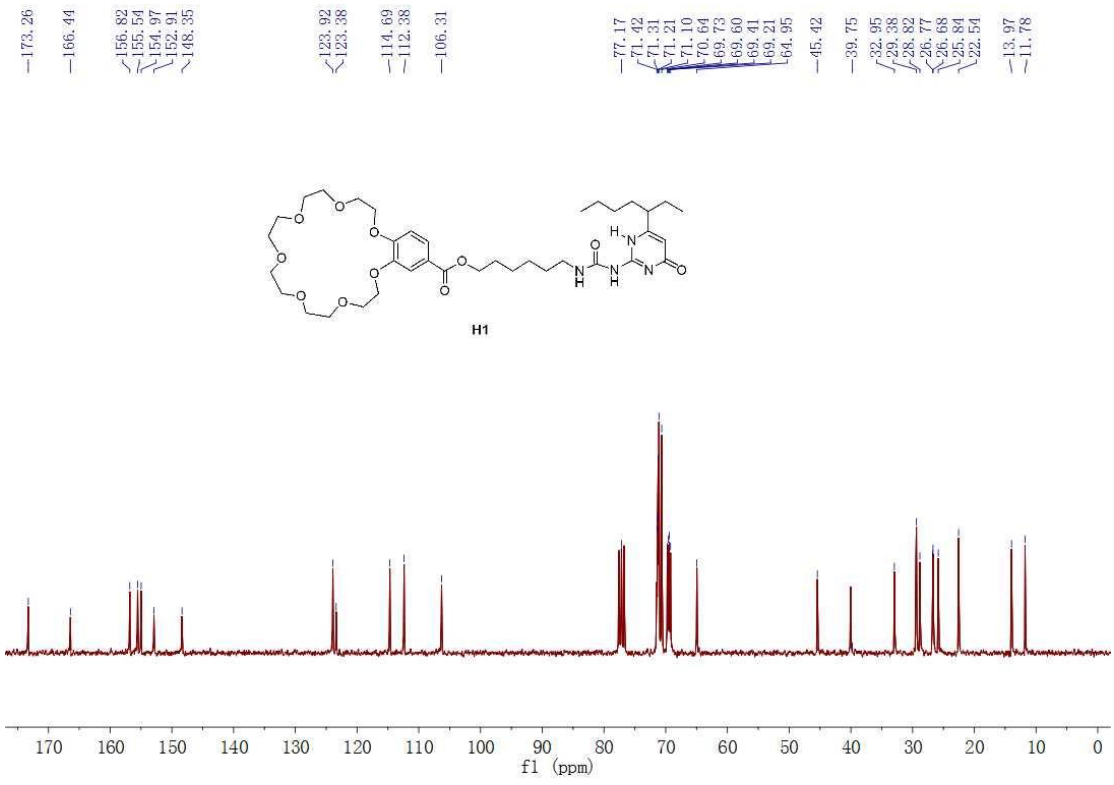


Figure S20 ^{13}C NMR spectrum (75MHz, $CDCl_3$, 298K) of **H1**

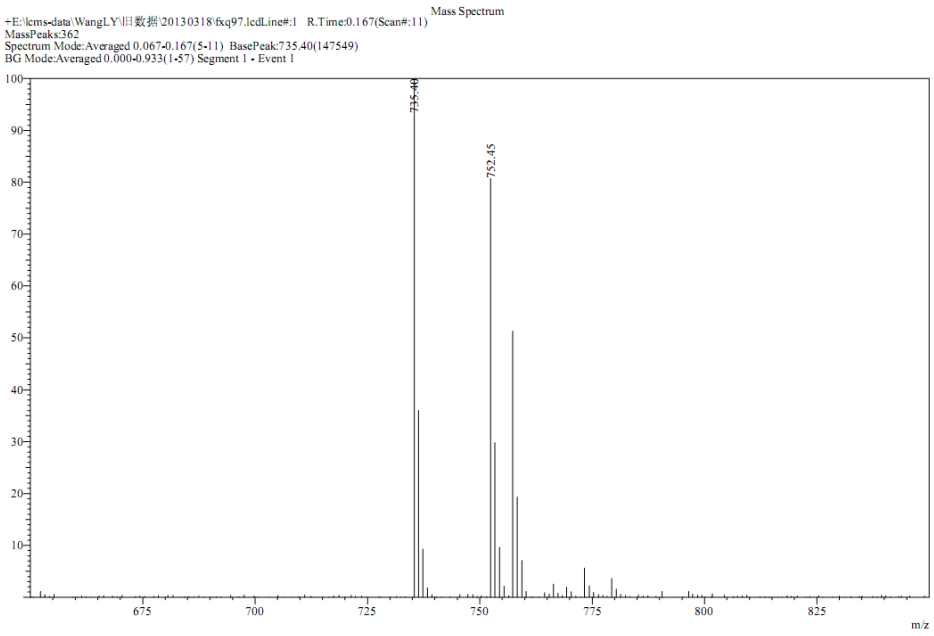


Figure S21 Electrospray ionization mass spectrum of **H1**

11.4. Synthesis of Compound **G1**

Bisaldehyde **G2** (1.97 g, 2.5 mmol) and butylamine (0.36 g, 5.0 mmol) were dissolved in methanol (60 mL) and heated at 70 ^{o}C under N_2 atmosphere overnight. After the reaction mixture was cooled to ambient temperature, $NaBH_4$ (0.38 g, 10.0 mmol) was added to the solution in small portions and the mixture was stirred at room temperature for another 7 h. Water (30 mL) was added to quench the remaining $NaBH_4$ and 2 M HCl was added to acidify the amine. The solvent was removed to give a white solid which was dissolved in deionized water/methanol (200 mL, 5:1, v/v). A saturated aqueous solution of NH_4PF_6 was added to afford a white precipitate which was filtered off and washed with deionized water to afford **G1** as a white solid (0.95 g, 48%). ^{1}H NMR (300 MHz, CD_3CN): δ 7.36 (d, *J* = 8.7 Hz, 4H), 6.96 (d, *J* = 8.7 Hz, 4H), 6.47 (br s, 4H), 4.08 (s, 4H), 4.00 (t, *J* = 6.5 Hz, 4H), 3.07 – 2.91 (m, 4H), 1.84 – 1.68 (m, 4H), 1.68 – 1.57 (m, 4H), 1.49 – 1.40 (m, 4H), 1.43 – 1.28 (m, 12H), 0.93 (t, *J* = 7.3 Hz, 6H) ppm; ^{13}C NMR (75 MHz, CD_3CN): δ 161.2, 132.7, 123.2, 115.9, 69.0, 52.1, 48.4, 30.3, 30.1, 29.9, 28.5, 26.7, 20.3, 13.7 ppm; ESI-MS: *m/z* calcd for $[M\text{-}HPF_6\text{-}PF_6^-]^+$ = 497.41 , found = 497.40 (100%); HR-ESI-MS ($C_{32}H_{54}F_{12}N_2O_2P_2$): *m/z* calcd for $[M\text{-}HPF_6\text{-}PF_6^-]^+$ = 497.4102, found = 497.4104.

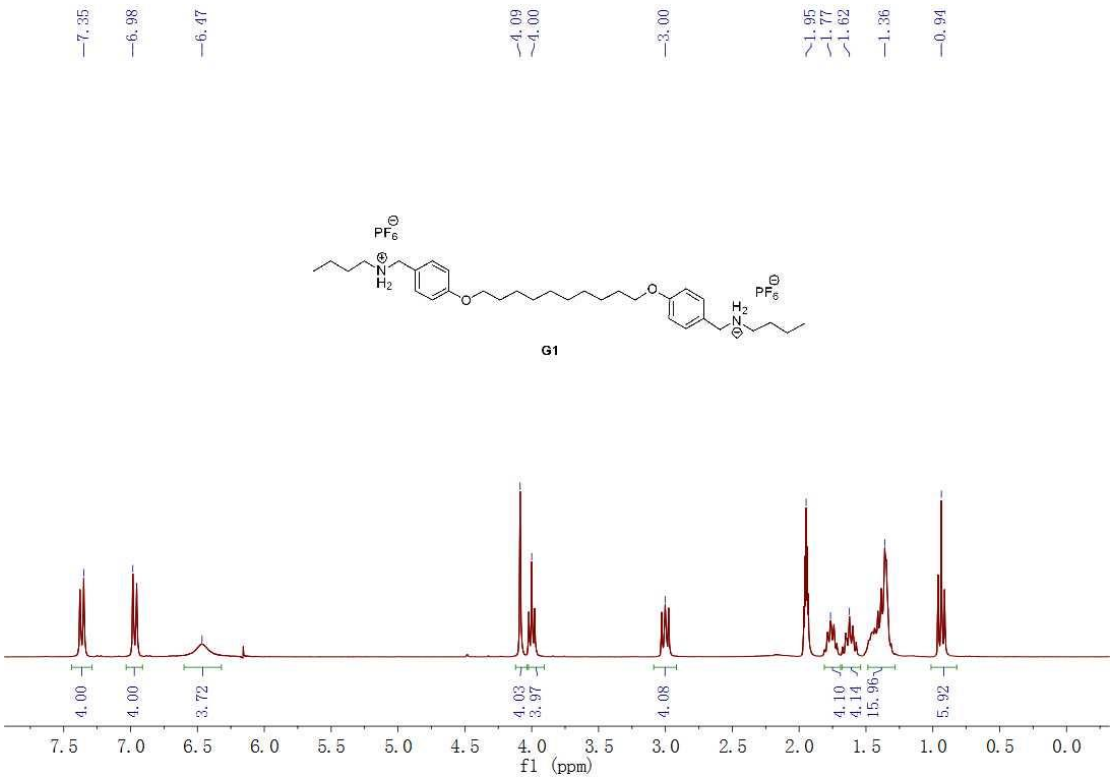


Figure S22 ^{1}H NMR spectrum (300MHz, $CDCl_3$, 298K) of **G1**

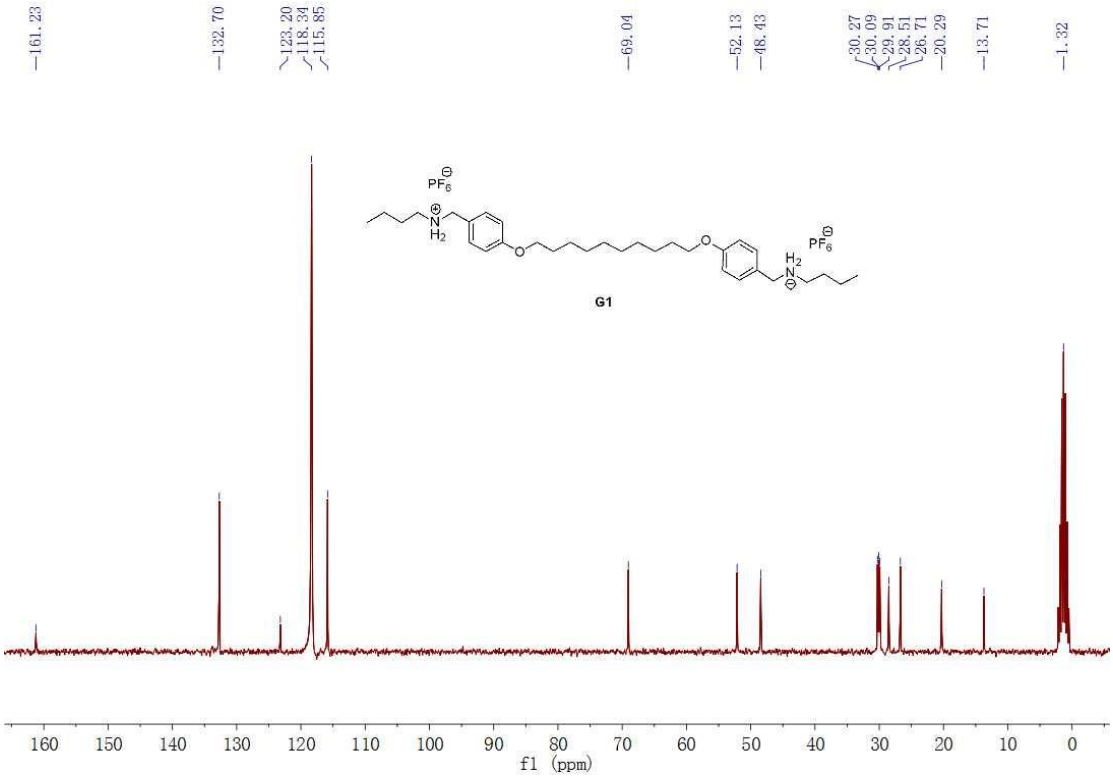


Figure S23 ^{13}C NMR spectrum (75MHz, $CDCl_3$, 298K) of **G1**

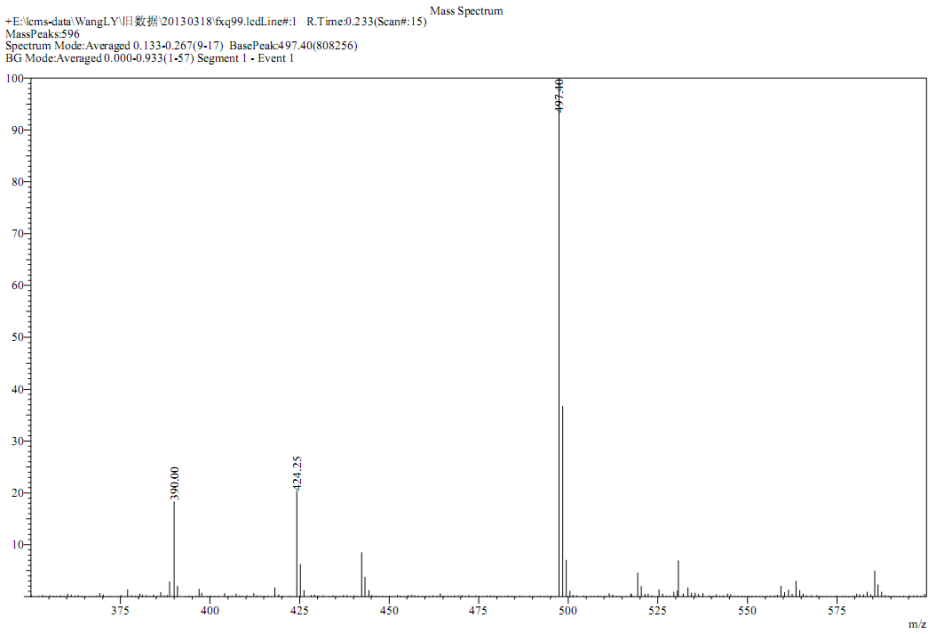


Figure S24 Electrospray ionization mass spectrum of **G1**

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