Electronic Supplementary Information

Novel self-assembled dynamic [2]catenanes interlocked by the quadruple hydrogen bonding ureidopyrimidinone motif

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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. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, where $CDCl_3$ and CD_3CN were dried using neutral aluminium oxide. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. Elemental analyses were obtained on Perkin-Elmer 240 instruments. NOESY and DOSY experiments were performed on a Bruker DPX 500 MHz spectrometer. 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 (*v*/*v*, 1/1). Cyclobis(paraquat-*p*-phenylene) tetra(hexafluorophosphate)[S1], **1**[S2], **2**[S3], **M1**[S4], and **M2**[S5] was prepared according to literature procedure.

2. Concentration-dependent ^{1}H NMR spectra of L1 and C1

In order to compare the assembly behavior of **L1** and **C1**, we performed all the ^{1}H NMR experiments in the mixed solvents of acetonitrile and chloroform. The **UPy** N–H signals still showed a large downfield shift (between 10 and 13.5 ppm) in the mixed solvents, giving direct evidence for the **UPy** unit dimerization. According to literature, there are many previous examples showing the strong **UPy** dimerization in acetonitrile or acetonitrile/chloroform (1/1, *v/v*), which could promote the formation of pseudo[2]rotaxane dimer or supramolecular polymers.[S6]

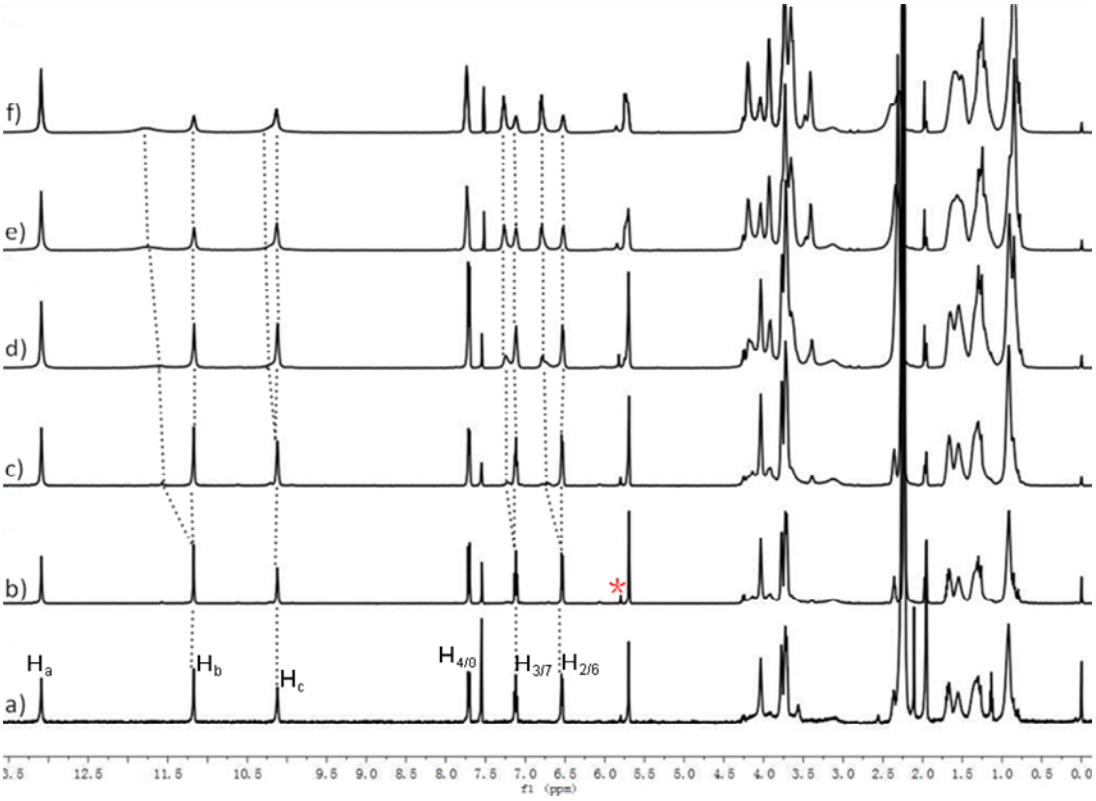


Figure S1 ^{1}H NMR spectra (300MHz, $CDCl_3/CD_3CN$ = 1/1, *v/v*, 298K) of **L1** at different monomer concentrations: (a) 4, (b) 16, (c) 32, (d) 75, (e) 150, and (f) 200 mM. The asterisk symbol stands for minor tautomers arised from competitive intramolecular hydrogen bonding of the ether atoms of the oligo(ethylene oxide) (oligoEO) chain to the hydrogen bond donors of the **UPy** unit.[S7]

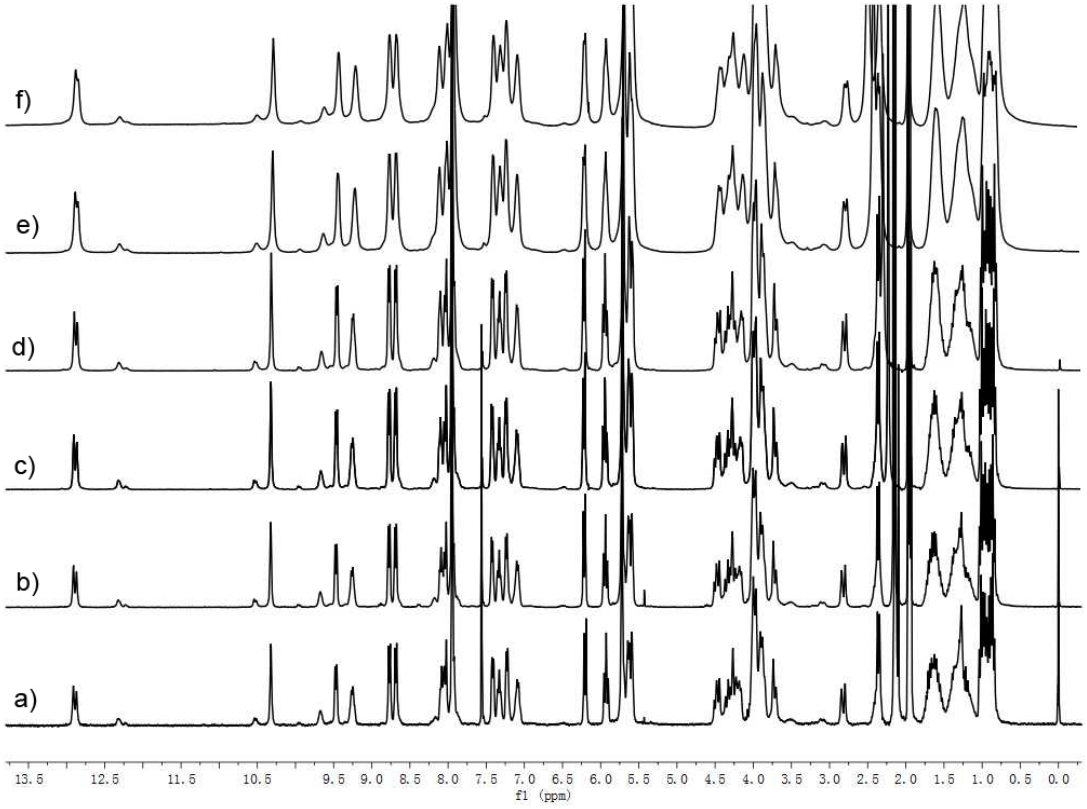


Figure S2 ^{1}H NMR spectra (300MHz, $CDCl_3/CD_3CN$ = 1/1, *v/v*, 298K) of **C1** at different monomer concentrations: (a) 2, (b) 10, (c) 50, (d) 100, (e) 150, and (f) 200 mM.

As can be seen from **Figure S2**, no chemical shift has been occurred upon increasing concentration, indicating no polymerization process happened during the procedure. As we know, substituents on the flexible chain have a large influence on the concentration and polymerizability of cyclic products formed. No doubt, the substituents in cyclic monomer exists less steric repulsion compared to polymer. Consequently, large or multiple substituents can decrease or even prevent polymerization. In our system, the entropy of the polypseudorotaxane should be largely decreased due to its rotational restriction by **CBPQT**$^{4+}$, whereas the entropy of the [2]catenane is not altered much, as compared to **L1**.

3. Variable-temperature ^{1}H NMR spectra of C1

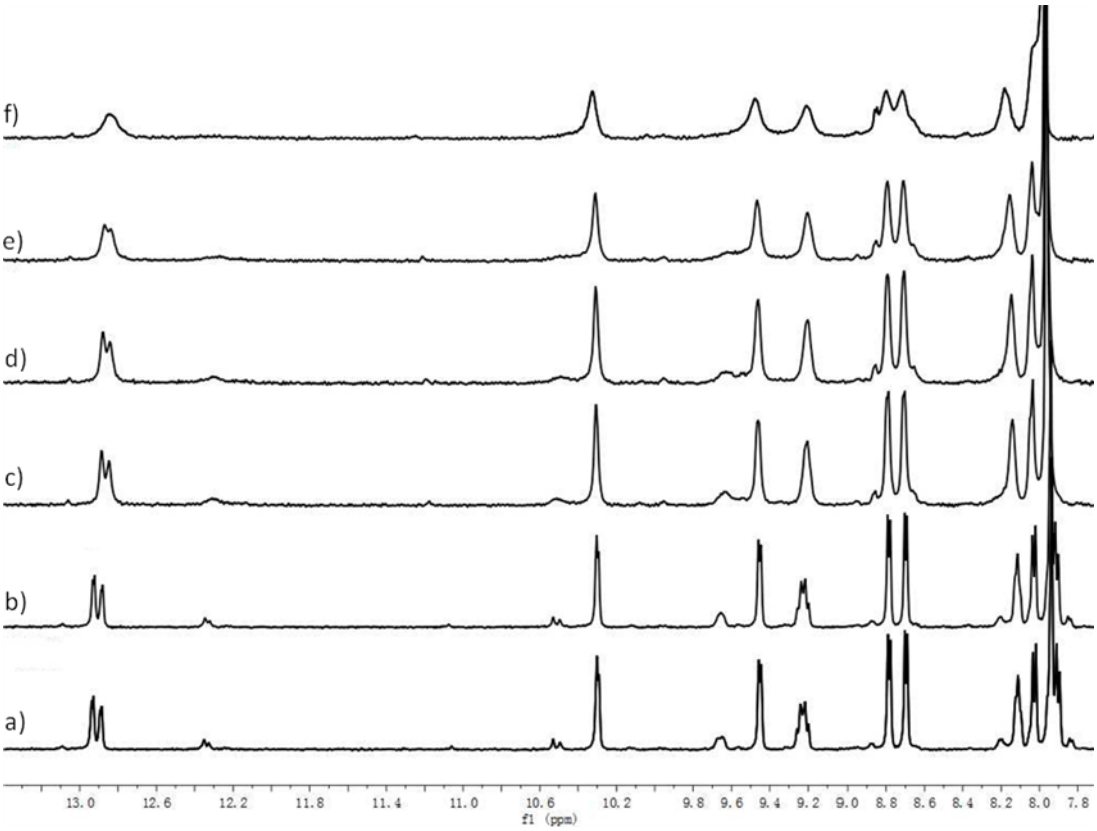


Figure S3(a) Partial ^{1}H NMR spectrum(500MHz, $CDCl_3/CD_3CN$ = 1/1, *v/v*) of **C1** at different temperature: (a) 280, (b) 293, (c) 308, (d) 313, (e) 318, and (f) 328 K.

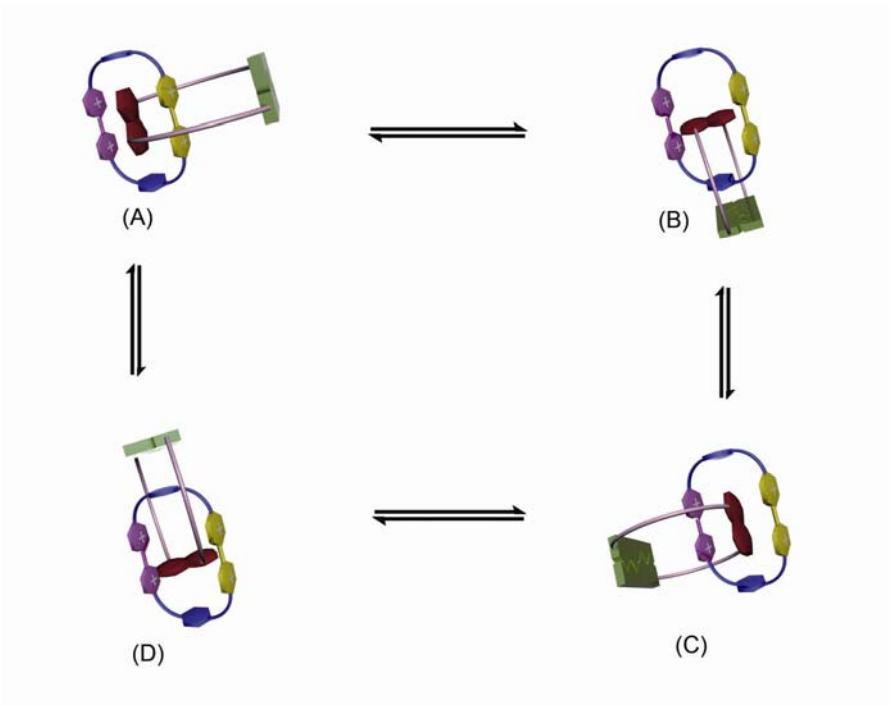


Figure S3(b) The pirouetting rotation model of the [2]catenane **C1**

The minor set of peaks were generated from the state of (B) and (D) (**Figure S3(b)**), which

were relatively less stable than (A) and (C). The disappearance of the smaller one at high temperature can be ascribed to the rapid pirouetting of the neutral component loop around **CBPQT**$^{4+}$ ring.

4. ESI-MS spectra of the [2]Catenane C1 and C2.

(a) ESI-MS of the tetrahexafluorophosphate salt **C1**: calcd for [**C1**−2PF_6^-]$^{2+}$ *m/z* = 851.35, found *m/z* = 851.85; calcd for [**C1**− HPF_6−2PF_6^-]$^{2+}$ *m/z* = 778.36, found *m/z* = 779.00; calcd for [**C1**− 2HPF_6−2PF_6^-]$^{2+}$ *m/z* = 705.38, found *m/z* = 706.20; calcd for [**C1**−3PF_6^-]$^{3+}$ m/z = 519.24, found *m/z* = 519.80.

(b) ESI-MS of the tetrahexafluorophosphate salt **C2**: calcd for [**C2**−2PF_6^-]$^{2+}$ *m/z* = 826.81, found *m/z* = 826.65; calcd for [**C2**−HPF_6−2PF_6^-]$^{2+}$ *m/z* = 753.83, found *m/z* = 753.65; calcd for [**C2**−3PF_6^-]$^{3+}$ *m/z* = 502.89, found *m/z* = 502.55. Signals from the free neutral component is also found: calcd for [**L2**+H]$^+$ *m/z* = 843.49, found *m/z* = 843.45; calcd for [**L2**+Na]$^+$ *m/z* = 865.48, found *m/z* = 865.44.

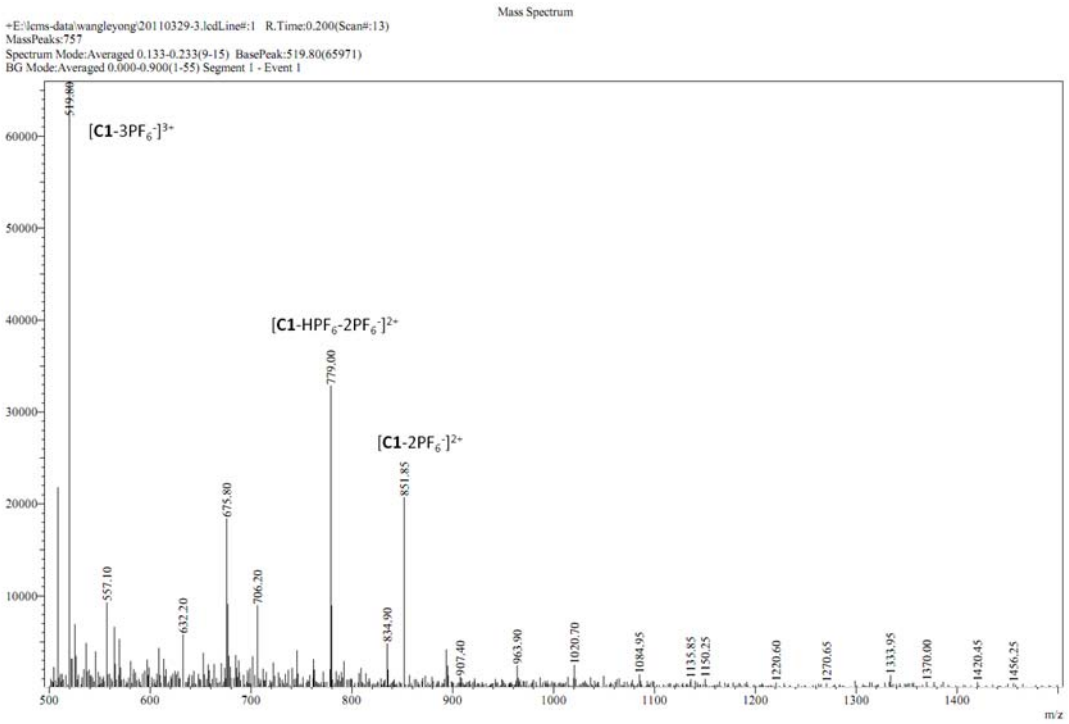


Figure S4(a) ESI-MS spectrum of the [2]catenane **C1**

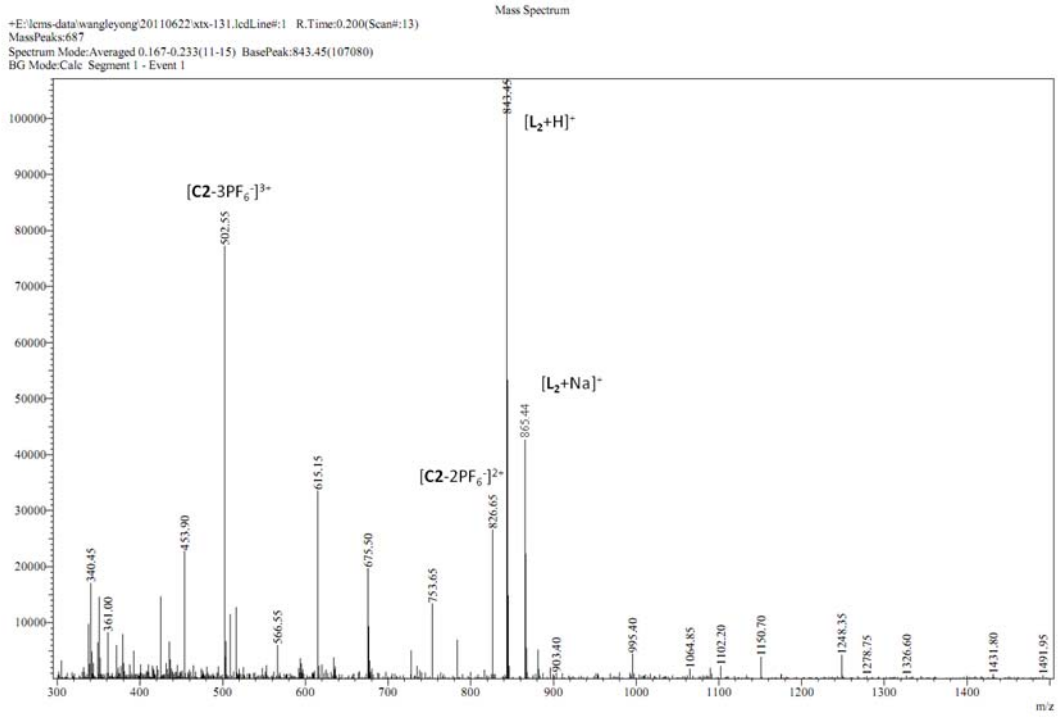


Figure S4(b) ESI-MS spectrum of the [2]catenane **C2**

5. Time-dependent ^{1}H NMR spectra of L1 mixed with CBPQT^{4+}

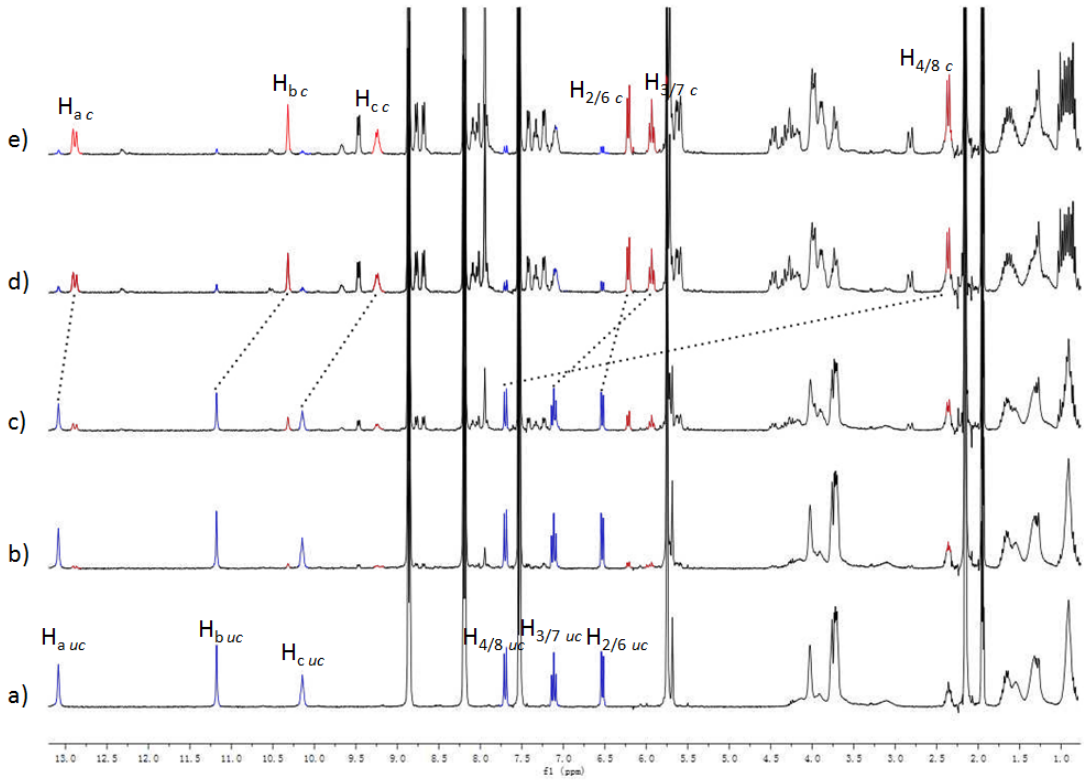


Figure S5 Partial ^{1}H NMR spectrum (300MHz, $CDCl_3/CD_3CN$ = 1/2, *v/v*, 298K) showing the formation of the [2]catenane **C1** from **L1** (8 mM) and **CBPQT^{4+}** (ca. 1.5 equiv.) by using the method of

"threading-followed-by-selective cyclization" with the reaction temperature at 50 ℃. From bottom to top: time = (a) 0, (b) 15 min, (c) 1, (d) 12, and (e) 36 h. Designations *c* = complexed and *uc* = uncomplexed.

Further evidence showed that using excess **L1** could not only shorten the reaction time (within 24 h), but also greatly reduce the purification procedure, where excess **L1** in product can be removed only by rinsing with $CHCl_3$ easily.

6. ^{1}H NMR spectra of C1 and L1 in DMSO-d_6

The quadruple hydrogen bond was completely broken in DMSO due to its strong acceptor nature. So the [2]catenane **C1** was dissociated into a pseudo[2]rotaxane (**R1**) and a certain amount of free **L1** and **CBPQT**$^{4+}$ in DMSO-d_6. The spectrum of **C1** in DMSO-d_6 was complicated because of the overlapping peaks. The figure indicated that one of the N-*H* protons (H_c) was folded with $H_{4/8}$ in naphthylene ring of **L1** (**Figure S6**(a)), and these two peaks were folded again with H_β of **R1** in DMSO-d_6 (**Figure S6**(b) and (c)). In contrast to **L1** in DMSO-d_6, the N-*H* protons of **R1** showed a minor downfield shift, suggesting that the **UPy** motif emanating from naphthalene ring by oligoEO chain was located at the unshielding area of the paraquat moieties. It was wholly different from **C1** in $CDCl_3$ and CD_3CN mixed solvents.

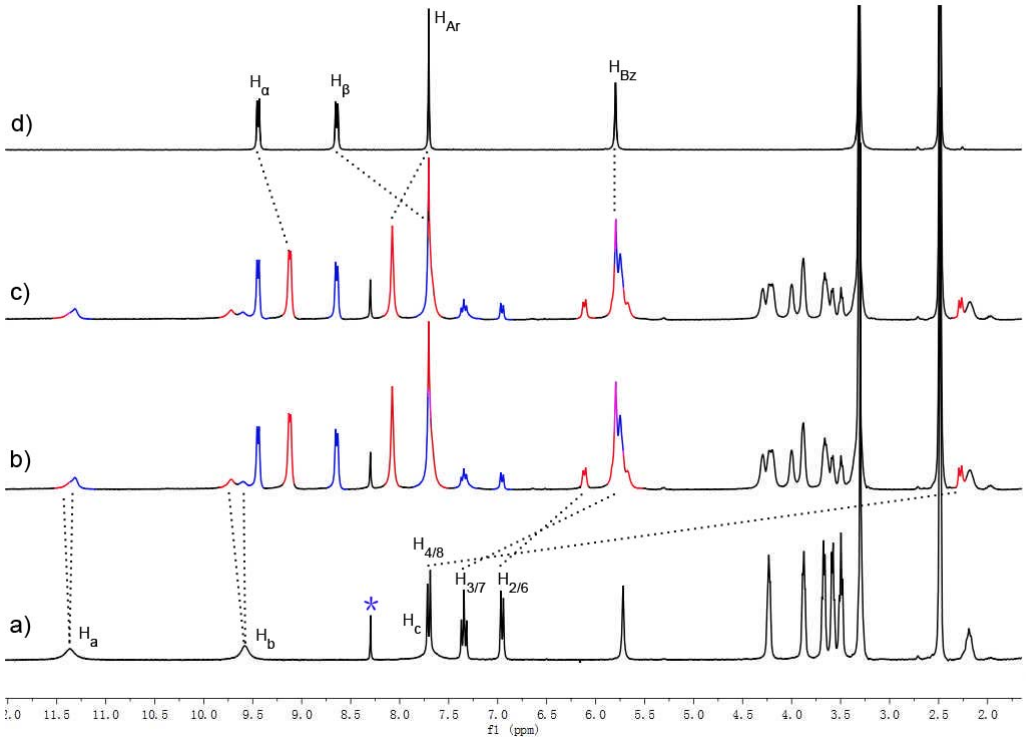
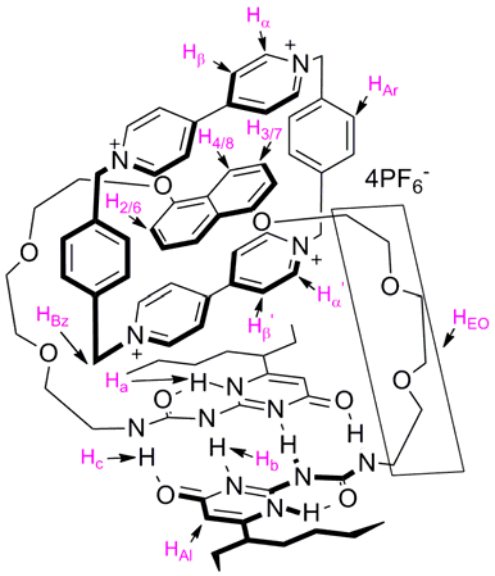


Figure S6 Partial ^{1}H NMR spectra(300MHz, DMSO-d_6, 298K) of (a) **L1**; the [2]catenane **C1** dissolved in

DMSO-d_6 (ca. 12 mM) after: (b) 0.5, (c) 120 min; and d) **CBPQT**$^{4+}$. Designations α = **CBPQT**$^{4+}$ N-C*H*=CH, β = **CBPQT**$^{4+}$ N-CH=C*H*, Ar = **CBPQT**$^{4+}$ Aril -H, Bz = **CBPQT**$^{4+}$ benzyl-H. The chemical shift at 2.50 ppm and 3.33 ppm are solvent peaks for DMSO and H_2O, respectively. The asterisk symbol stands for residual $CHCl_3$. Red peaks represent complexed compound while blue peaks indicate free components.

7. ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY spectrum of C1

The two-dimensional COSY NMR spectrum (**Figure S7**) of **C1** at 50 mM showed the proton H-α was correlated with the protons H-β on the paraquat groups. Noteworthy, similar correlations were observed between $H_{2/6}$, $H_{3/7}$, and $H_{4/8}$ of the naphthalene protons. Hence, $H_{4/8}$ (2.36 ppm) folded with C*H*$(CH_2)_2$ in the alkyl chain of **UPy** could be accurately assigned in the ^{1}H NMR spectra. The two-dimensional NOESY NMR spectrum of **C1** at 50 mM is displayed in **Figure S8**. The spectrum showed the protons $H_{3/7}$ was correlated with H_{Ar}. Similar correlations were observed for oligo(ethylene oxide) (oligoEO) chain with *p*-xylene group of **CBPQT**$^{4+}$ (H_{EO} and H_{Ar}) and **UPy** motif (H_{EO} and H_c). From these information we could accurately assign the ^{1}H NMR spectrum of **C1**.



Scheme S1. Structure of the [2]catenane **C1**

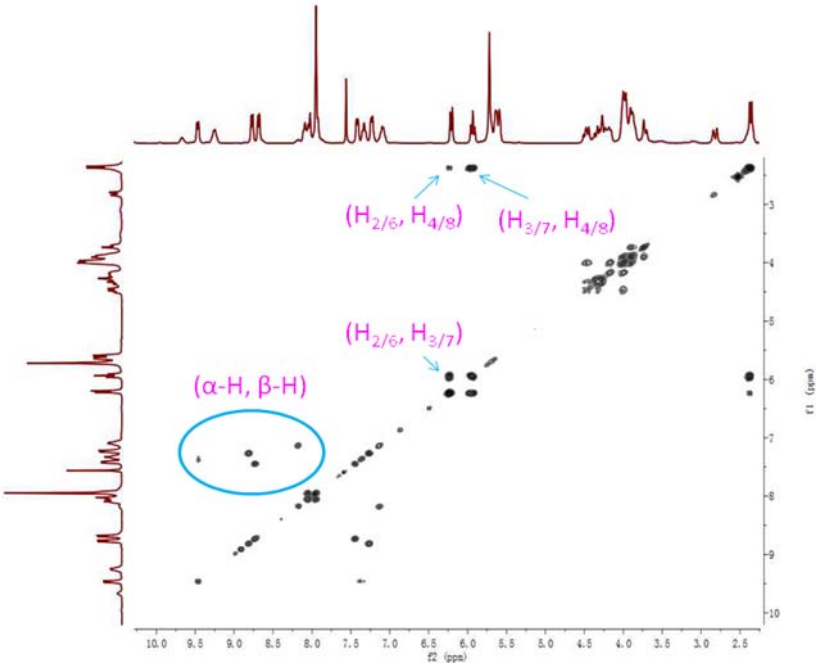


Figure S7 Partial ^{1}H-^{1}H COSY (300MHz, $CDCl_3/CD_3CN$ = 1/1, *v/v*, 298K) of **C1**

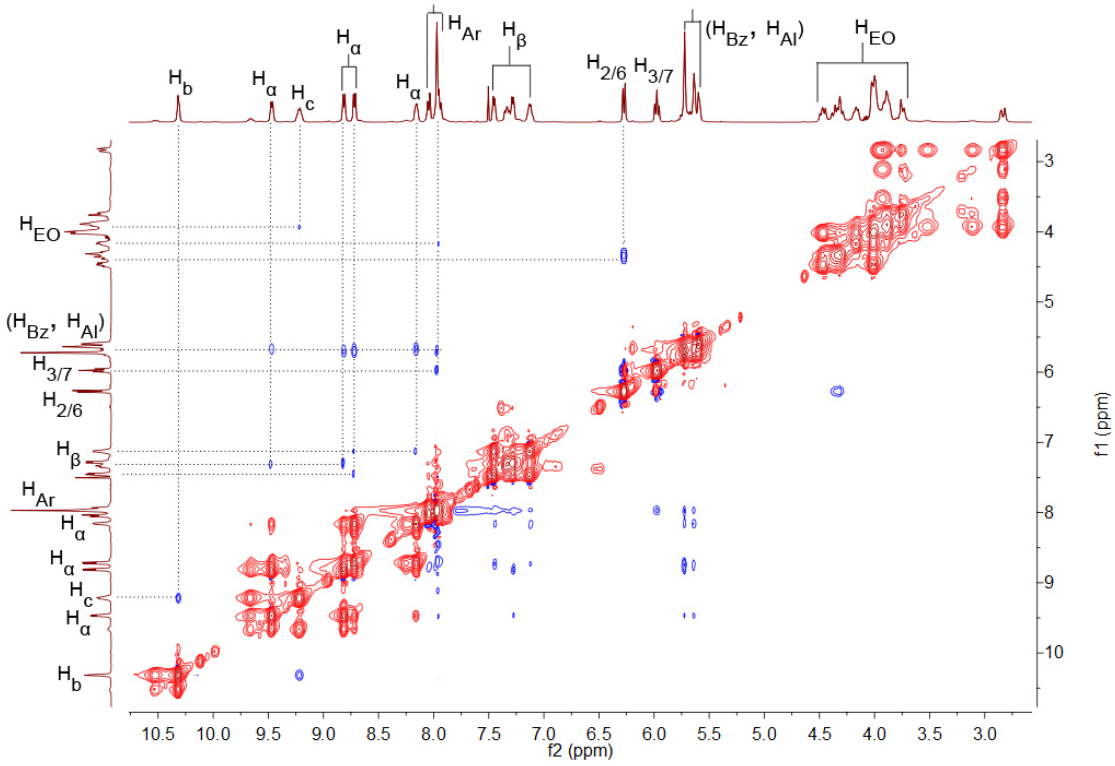
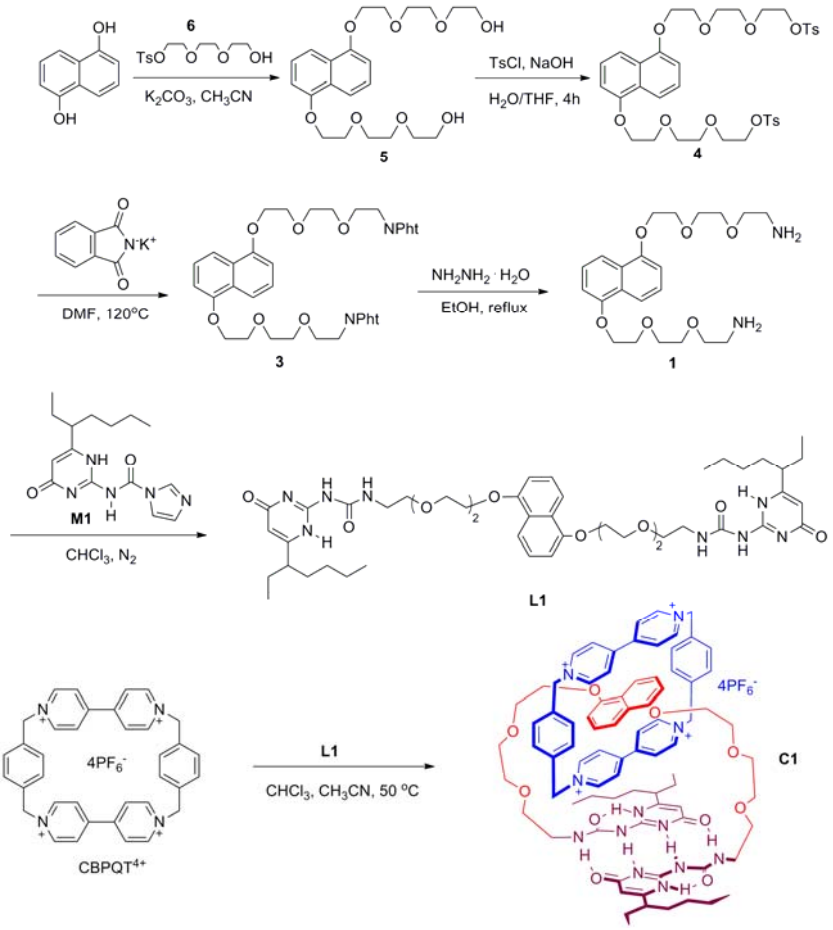
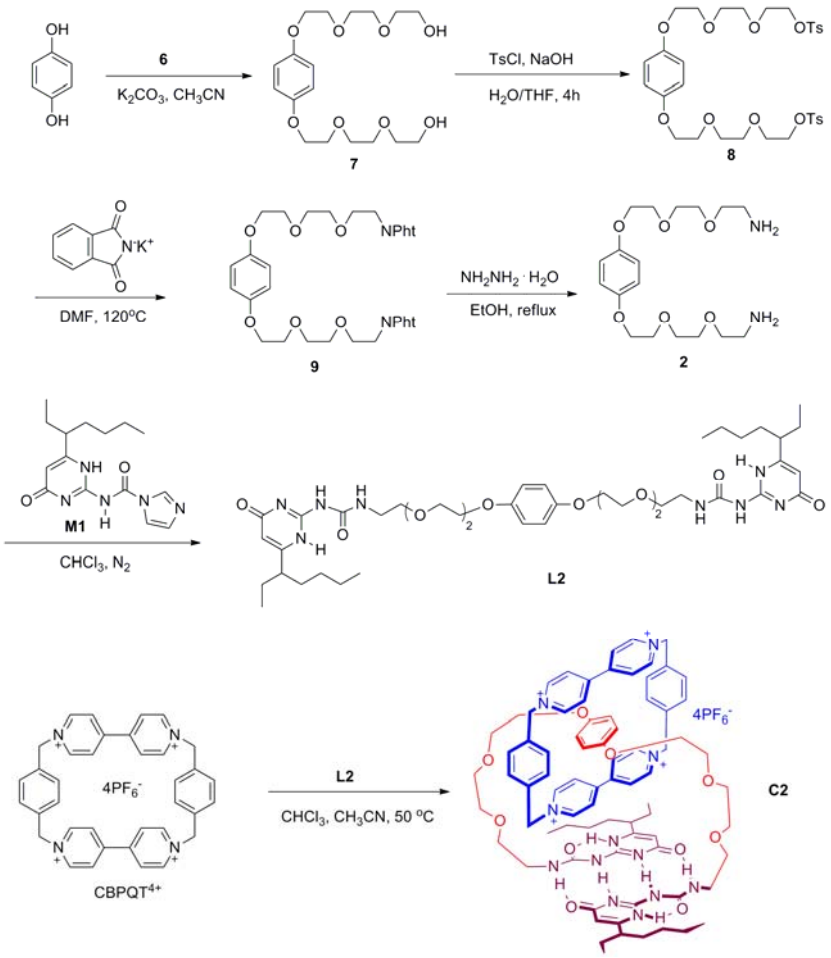


Figure S8 Partial ^{1}H-^{1}H NOESY(400MHz, $CDCl_3/CD_3CN$ = 1/1, *v/v*, 298K) of **C1**

8. Synthetic procedures for the title [2]Catenanes



Scheme S2. Synthesis of the [2]catenane **C1**



Scheme S4. Synthesis of the [2]catenane **C2**

8.1 Synthesis of Compound **L1**

Imidazolide **M1** (0.38 g, 1.25 mmol) and **1** (0.21 g, 0.50 mmol) were dissolved in dry $CHCl_3$ (20 mL) and this solution was stirred for three hours under nitrogen at r.t. To the above reaction mixture, $CHCl_3$ (20 mL) was added and the organic layer was washed with 1N HCl (20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), and dried over Na_2SO_4. After the solvent was removed, the resulting residue was subjected to column chromatography ($CHCl_3$/MeOH 150:1 (*v/v*)) to give **L1** (0.32 g, 71%) as a colorless viscous solid. ^{1}H NMR (300MHz, DMSO-d_6): δ 11.37 (*br* s, 2H, N*H*), 9.59 (*br* s, 2H, N*H*), 7.74-7.70 (m, 4H, 2H N*H* and 2H naphthalene *H*-4,8), 7.36 (t, J = 8.0 Hz, 2H, naphthalene *H*-3,7), 6.97 (d, J = 7.7 Hz, 2H, naphthalene *H*-2,6), 5.74 (s, 2H, alkylidene-*H*), 4.25 (m, 4H, OCH_2), 3.89 (m, 4H, OCH_2), 3.69 (m, 4H, OCH_2), 3.60 (m, 4H, OCH_2), 3.51 (m, 4H, OCH_2), 3.32 (m, 4H, CH_2N), 2.21 (m, 2H, CH(CH_2)$_2$), 1.49 (m, 8H, CH_2), 1.34-1.02 (m, 8H, CH_2), 0.82-0.71 (m, 12H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7,

156.9, 155.1, 154.6, 154.5, 126.8, 124.4, 114.6, 105.9, 104.7, 72.0, 70.8, 70.2, 69.9, 67.8, 45.3, 40.3, 32.9, 29.5, 26.6, 22.6, 14.1, 11.8 ppm; ESI-MS: *m/z* 893.17 $[M + H]^+$ (100%); Elemental analysis calcd (%) for **L1** ($C_{46}H_{68}N_8O_{10}$): C 61.86, H 7.67, N 12.55; found C 61.93, H 7.81, N 12.29.

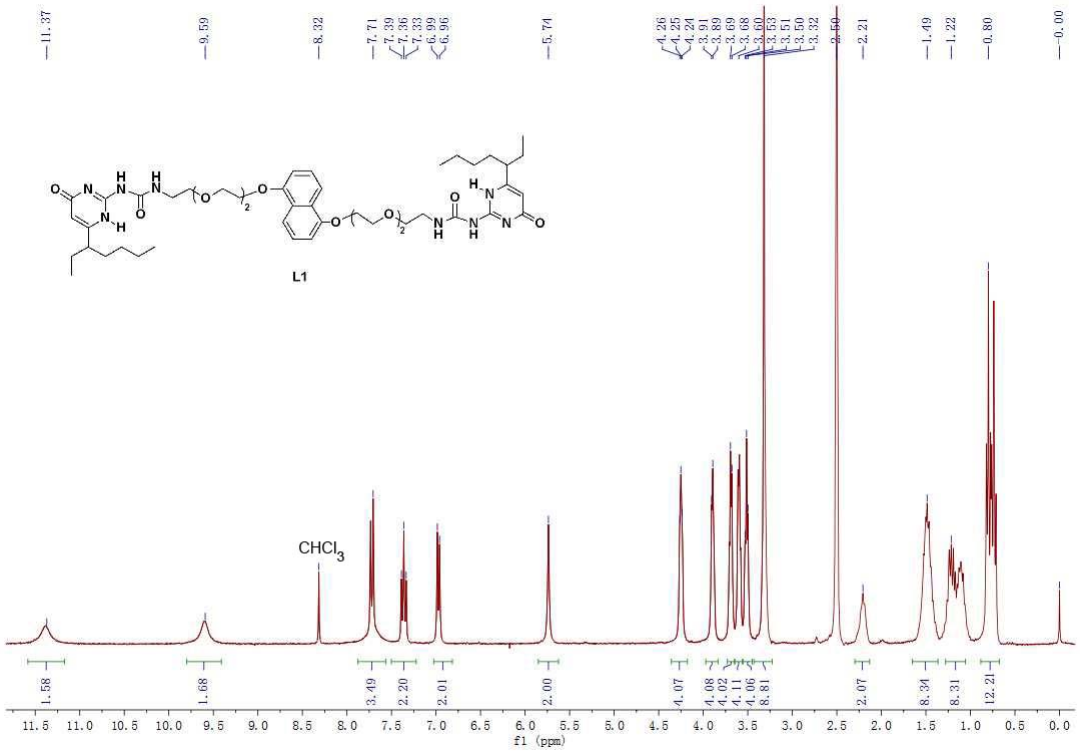


Figure S9(a) ^{1}H NMR spectrum (300MHz, DMSO-d_6, 298K) of **L1**

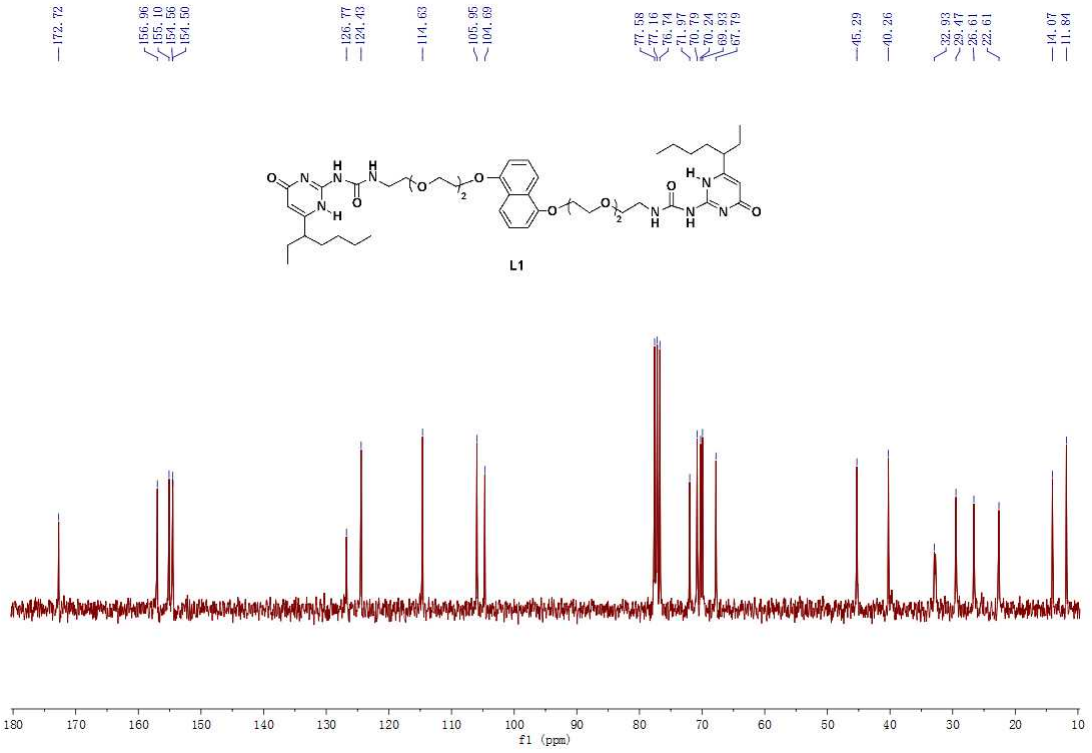


Figure S9(b) ^{13}C NMR spectrum (75MHz, $CDCl_3$, 298K) of **L1**

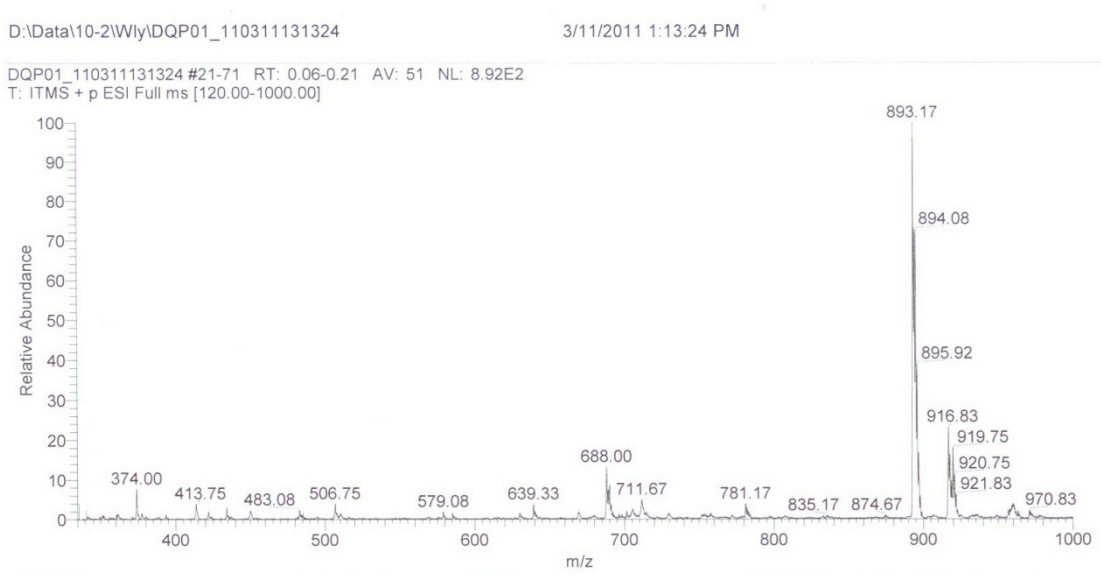


Figure S9(c) Electrospray ionization mass spectrum of **L1**

8.2 Synthesis of Compound **C1**

To a 50 mL three-necked flask, a solution of **CBPQT**$^{4+}$ (0.24 g, 0.22 mmol) in CH_3CN (20 mL) and a solution of **L1** (0.98 g, 1.10 mmol) in $CHCl_3$ (10 mL) were added under nitrogen atmosphere. The resulting mixture was stirred at 50 °C for 24 h. After the solvent was evaporated

by rotary evaporation at 30 °C, the residue was dispersed in $CHCl_3$ (20 mL) and stirred for 15 min. The obtained suspension was centrifuged at 3000 rpm for 30 min, followed by filtration. The solid was rinsed thoroughly with $CHCl_3$ to give the desired product **C1** (0.41 g, 93%) as a purple powder. ^{1}H NMR (300 MHz, $CDCl_3/CD_3CN$ = 1/1, *v/v*): δ 12.89 (d, J = 12.0 Hz, 2H, N*H*-C=N), 10.32 (s, 2H, NH(C=O)N*H*-Ar), 9.47 (d, J = 6.2 Hz, 2H, α-*H* in $CBPQT^{4+}$), 9.33-9.17 (m, 2H, N*H*(C=O)NH-Ar), 8.77 (d, J = 6.3 Hz, 2H, α-*H* in $CBPQT^{4+}$), 8.69 (d, J = 6.5 Hz, 2H, α-*H* in $CBPQT^{4+}$), 8.25-7.80 (m, 10H, α-*H* in $CBPQT^{4+}$-2H and C_6H_4 in $CBPQT^{4+}$-8H), 7.42 (d, J = 5.0 Hz, 2H, β-*H* in $CBPQT^{4+}$), 7.33 (t, J = 5.4 Hz, 2H, β-*H* in $CBPQT^{4+}$), 7.23 (d, J = 5.2 Hz, 2H, β-*H* in $CBPQT^{4+}$), 7.09 (m, 2H, β-*H* in $CBPQT^{4+}$), 6.21 (d, J = 7.8 Hz, 2H, naphthalene *H*-2,6), 5.93 (t, J = 8.0 Hz, 2H, naphthalene *H*-3,7), 5.81-5.54 (m, 10H, (C=O)C*H*=C-2H and CH_2 in $CBPQT^{4+}$-8H), 4.61-2.80 (m, 24H, protons in EO chain), 2.49-2.29 (m, 4H, 2H in naphthalene *H*-4,8 and 2H in $CH(CH_2)_2$), 1.78-1.48 (m, 8H, CH_2), 1.49-1.08 (m, 8H, CH_2), 1.07-0.78 (m, 12H, CH_3) ppm; ESI-MS: *m/z* 519.24 $[M-3PF_6^-]^{3+}$ (100%), 778.36 $[M-HPF_6-2PF_6^-]^{2+}$ (50%), 851.85 $[M-2PF_6^-]^{2+}$ (31%); Elemental analysis calcd (%) for **C1** ($C_{82}H_{100}F_{24}N_{12}O_{10}P_4$): C 49.40, H 5.06, N 8.43; found C 49.24, H 5.28, N 8.21.

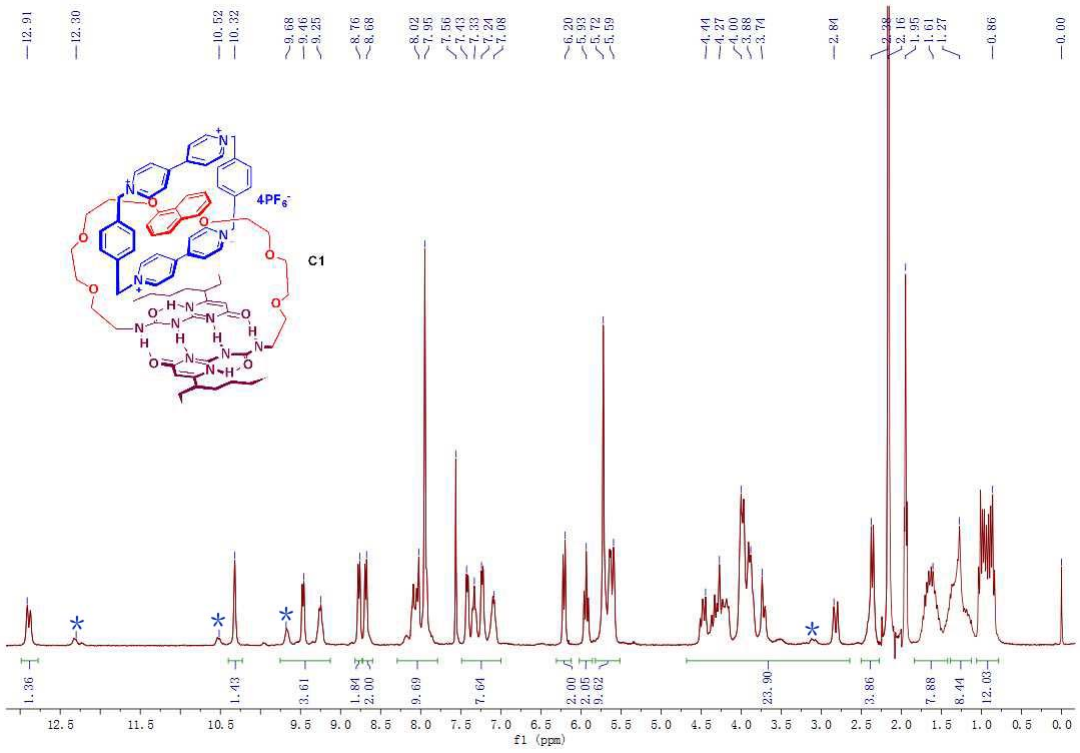


Figure S10 ^{1}H NMR spectrum (300MHz, $CD_3CN/CDCl_3$ = 1/1, *v/v*, 298K) of **C1**, The asterisk symbol stands for another set of signals as a result of a pirouetting motion of the two rings (For detail, please see the variable temperature ^{1}H NMR).

8.3 Synthesis of Compound **L2**

Imidazolide **M1** (0.73 g, 2.42 mmol) and **2** (0.41 g, 1.10 mmol) were dissolved in dry $CHCl_3$ (20 mL) and this solution was stirred for three hours under nitrogen at 25 °C. To the above reaction mixture, $CHCl_3$ (20 mL) was added and the organic layer was washed with 1N HCl (20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL) and dried over Na_2SO_4. After the solvent was removed, the resulting residue was subjected to column chromatography with $CHCl_3$ as eluent to give **L2** (0.59 g, 64%) as a colorless viscous solid. ^{1}H NMR (300MHz, $CDCl_3$): δ 13.20 (br s, 2H, N*H*), 11.92 (br s, 2H, N*H*), 10.36 (br s, 2H, N*H*), 6.72 (s, 4H, Ar-*H*), 5.81 (s, 2H, alkylidene-*H*), 3.96-3.49(m, 24H, OCH_2), 2.28 (m, 2H, CH(CH_2)$_2$), 1.58 (m, 8H, CH_2), 1.25 (m, 8H, CH_2), 0.87(m, 12H, CH_3) ppm; ^{13}C NMR (75MHz, DMSO-d_6): δ 170.7, 161.3, 154.5, 152.5, 151.6, 115.3, 105.2, 69.9, 69.7, 69.2, 69.1, 67.5, 47.9, 39.2, 32.9, 29.1, 26.5, 22.2, 13.8, 11.8 ppm; ESI-MS: *m/z* 843.33 $[M+H]^+$ (53%), 865.33 $[M+Na]^+$ (100%); Elemental analysis calcd (%) for **L2** ($C_{42}H_{66}N_8O_{10}$): C 59.84, H 7.89, N 13.29; found C 59.99, H 7.69, N 13.48.

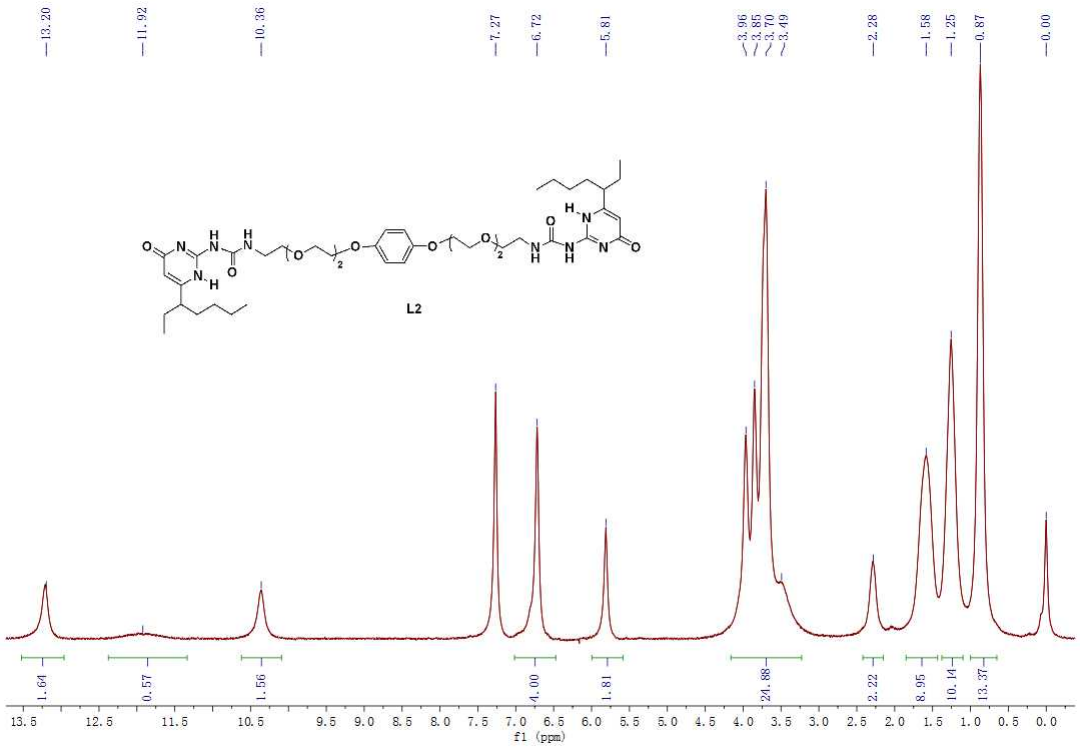


Figure S11(a) ^{1}H NMR spectrum (300MHz, $CDCl_3$, 298K) of **L2**

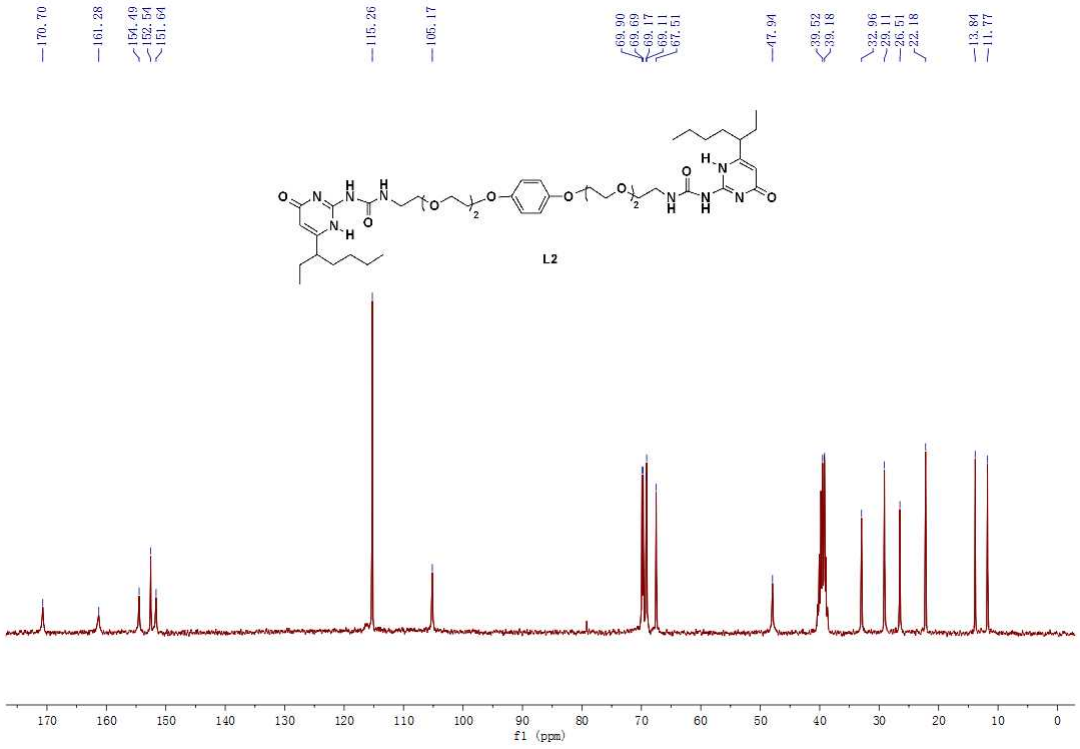


Figure S11(b) ^{13}C NMR spectrum (75MHz, DMSO-d_6, 298K) of **L2**

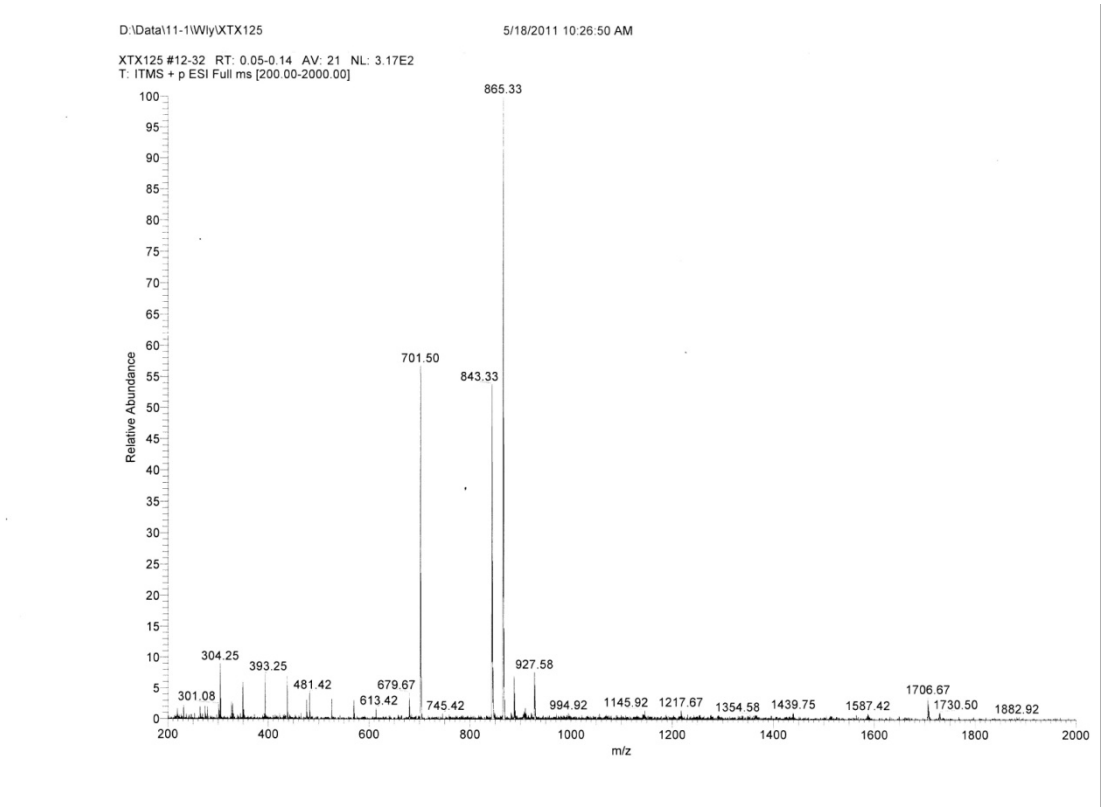


Figure S11(c) Electrospray ionization mass spectrum of **L2**

8.4 Synthesis of Compound **C2**

To a round bottom flask, a solution of **CBPQT**$^{4+}$ (0.060 g, 0.055 mmol) in CH_3CN (10 mL) and a solution of **L2** (0.18 g, 0.22 mmol) in $CHCl_3$ (5 mL) were added under nitrogen atmosphere. The resulting mixture was stirred at 50 °C for 24 h. After the solvent was evaporated by rotary evaporation at 30 °C, the residue was dispersed in $CHCl_3$ (10 mL) and stirred for 15 min. The obtained suspension was centrifuged at 3000 rpm for 30 min, followed by filtration. The solid was rinsed thoroughly with $CHCl_3$ to give the desired product **C1** (0.10 g, 90%) as a magenta powder. ^{1}H NMR (300MHz, $CD_3CN/CDCl_3$ = 1/1, *v/v*, 298 K) of the major component: δ 12.88 (s, 2H, N*H*-C=N), 10.55(s, 2H,C-NH (C=O)N*H*-Ar), 9.54 (s, 2H, C-N*H* (C=O)NH-Ar), 9.11-8.60 (m, 8H, α-*H* in CBPQT^{4+}), 7.95-7.69 (m, 16H, β-*H* and C_6H_4 in CBPQT^{4+}), 5.66(s, 8H, CH_2 in CBPQT^{4+}), 5.64 (s, 2H, (C=O)C*H*=C)), 4.20-3.44 (m, 26H, 22H in OCH_2 and 4H in C_6H_4), 2.92 (*br* s, 2H, OCH_2), 2.41 (s, 2H, C*H*$(CH_2)_2$), 1.91-1.52 (m, 8H, CH_2), 1.45-1.15 (m, 8H, CH_2), 1.08-0.76(m, 12H, CH_3) ppm; ESI-MS: *m/z* 826.65 $[M-2PF_6^-]^{2+}$, 502.55 $[M-3PF_6^-]^{3+}$; Elemental analysis calcd (%) for **C2** ($C_{78}H_{98}F_{24}N_{12}O_{10}P_4$): C 48.20, H 5.08, N 8.65; found C 48.40, H 5.25, N 8.42.

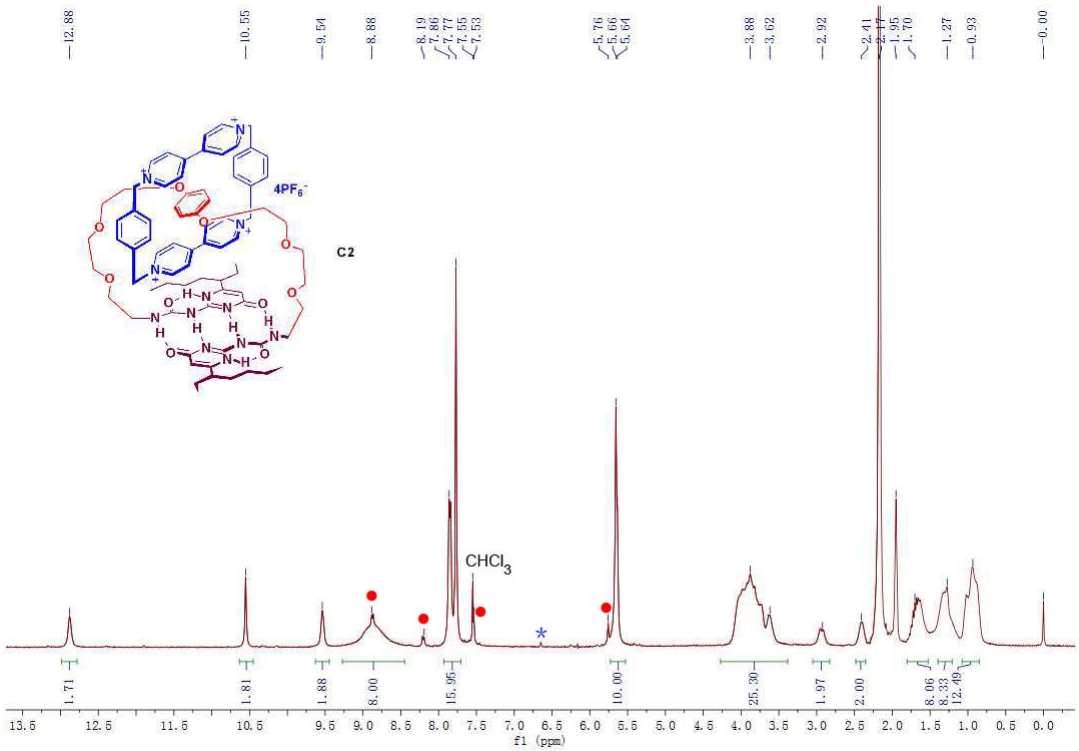


Figure S12 ^{1}H NMR spectrum (300MHz, $CD_3CN/CDCl_3$ = 1/1, *v/v*, 298K) of **C2**

●Signals from the free **CBPQT**$^{4+}$macrocycle, ⁎ Signals from the free neutral component

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