# Taco Complex-Templated Dynamic Clipping to Cryptand-Based [2]Rotaxane- and [2]Catenane-Type Mechanically Interlocked Structures

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**Supporting Information (18 pages)**

*1. Materials and methods*

Diamine appended BMP32C10 derivative **4**[S1], paraquat **6**[S2], paraquat derivative **7**[S3] and cyclophane **8**[S4] were synthesized according to literature procedures. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. The crystal data were collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra. The crystal structures were solved by SHELXS-97[S5] and refined by SHELXL-97.[S6]

*2. $^1$H NMR spectra of **4**, **6**, **7** and **8***

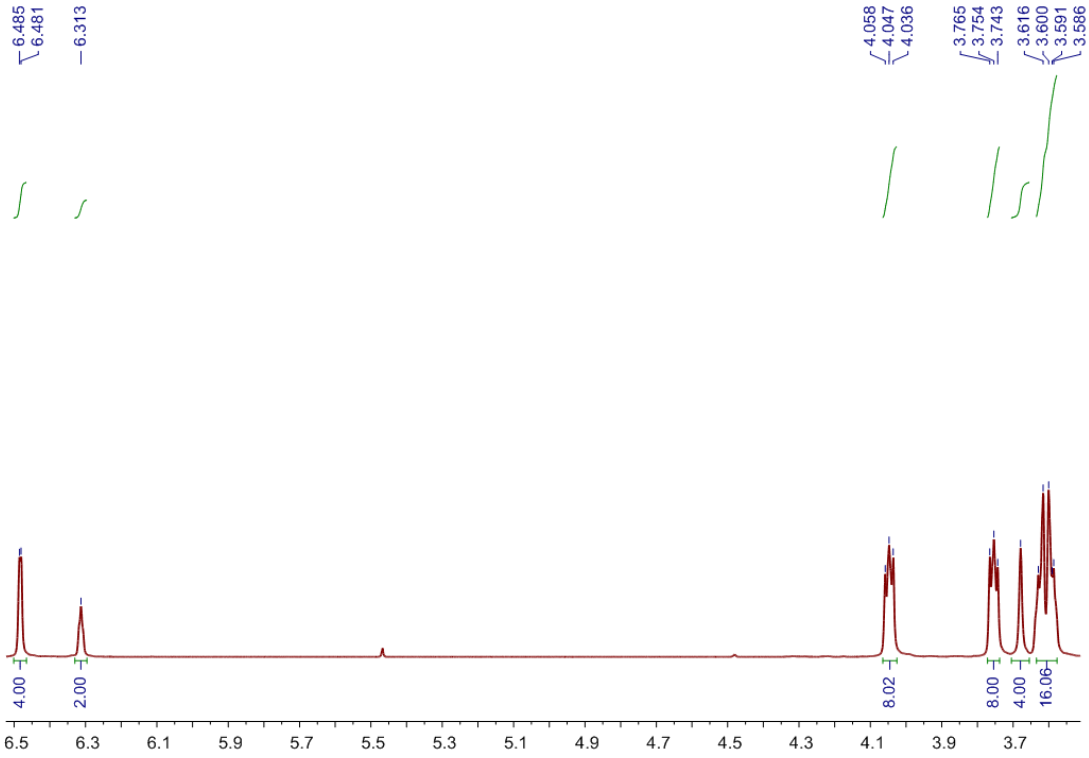



***Figure S1.*** $^1$H NMR spectrum (400 MHz, $CD_3CN$, 20 °C) of **4**.

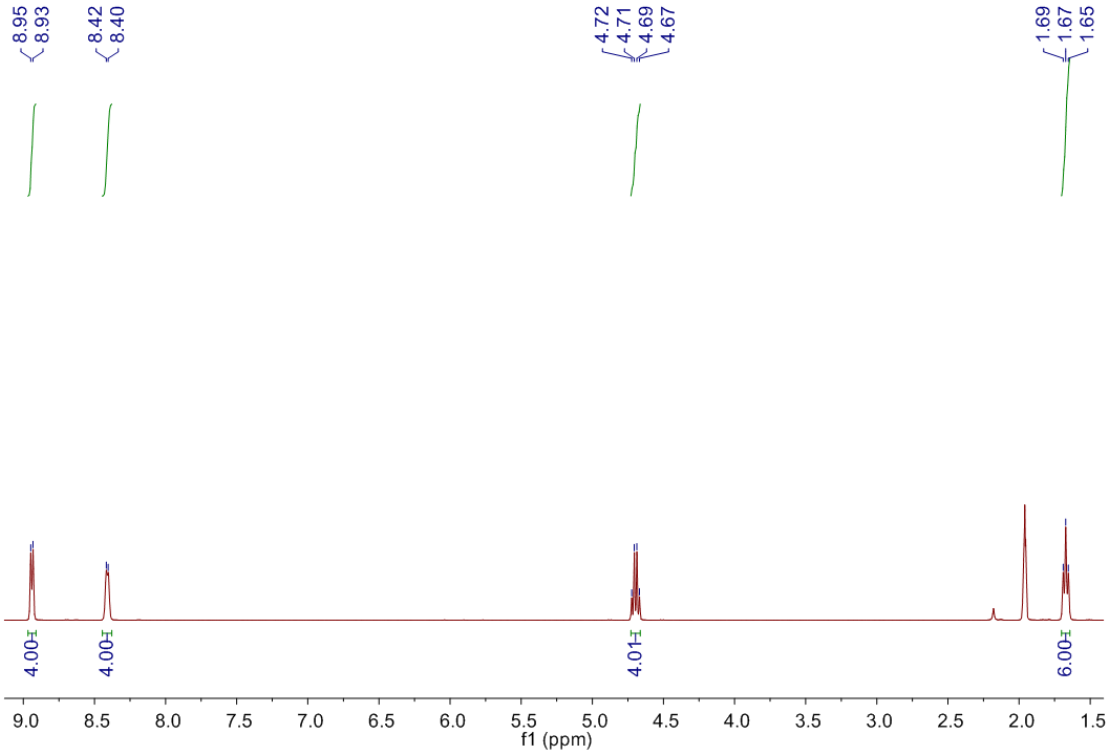



***Figure S2.*** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$, 20 °C) of **6**.

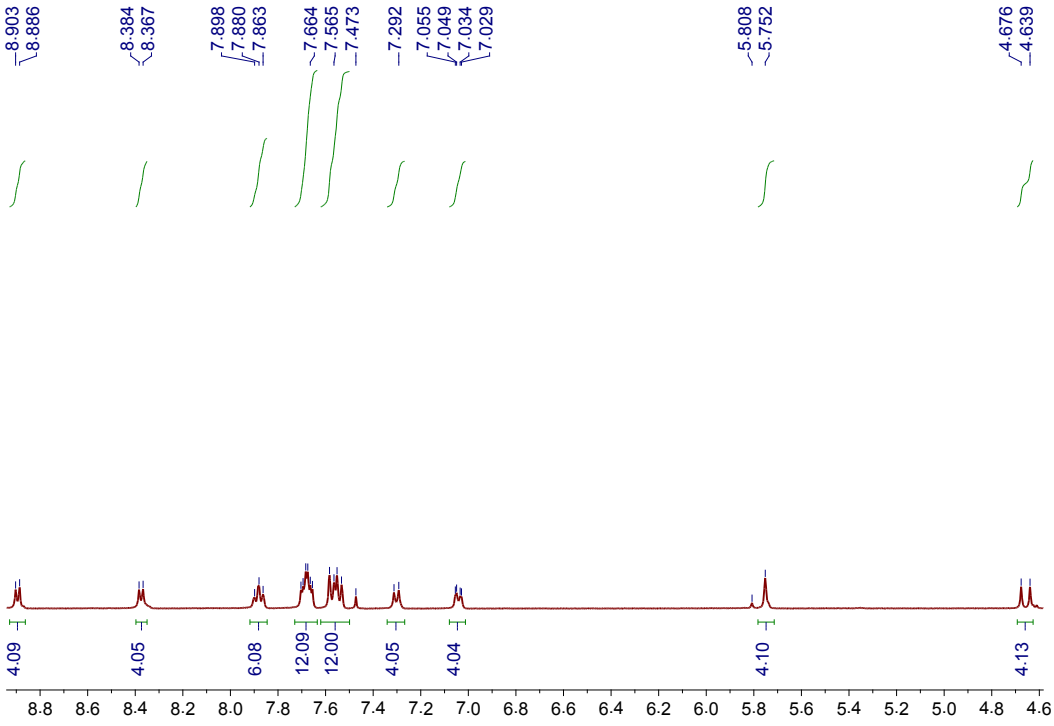



***Figure S3.*** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$, 20 °C) of **7**.

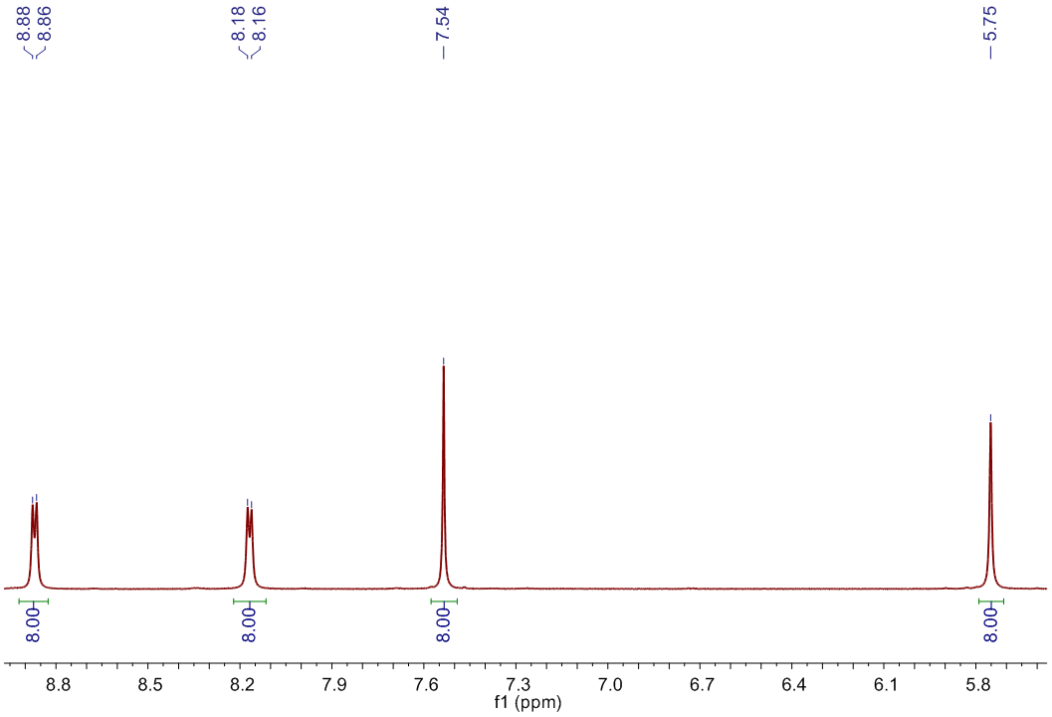
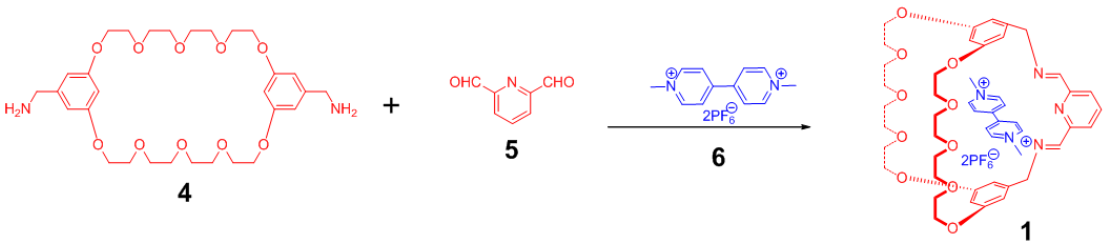



***Figure S4.*** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$, 20 °C) of **8**.

*3. Synthesis of dynamic [2]pseudorotaxane **1***




Equimolar (20.0 mM) diamine appended BMP32C10 derivative **4**, pyridine-2,6-dicarbaldehyde **5**, and paraquat **6** were mixed together in $CD_3CN$ at 25 °C to give the dynamic [2]pseudorotaxane **1** almost quantitative within several minutes. $^{1}$H NMR (400 MHz, $CD_3CN$, room temperature) $\delta$ (ppm) for **1**: 8.63–8.65 (d, 4H, $J$ = 8.0 Hz), 8.49–8.50 (d, 4H, $J$ = 4.0 Hz), 8.47 (s, 2H), 8.13–8.17 (t, 1H, $J$ = 8.0 Hz), 7.81–7.83 (d, 2H, $J$ = 8.0 Hz), 5.86–5.88 (t, 2H, $J$ = 4.0 Hz), 5.71–5.72 (d, 4H, $J$ = 4.0 Hz), 4.48 (s, 4H), 4.36 (s, 6H), 3.60–3.80 (m, 28H), 3.16–3.20 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$, 22 °C) $\delta$ (ppm) for **1**: 159.8, 158.8, 153.3, 145.9, 145.6, 140.8, 138.4, 126.3, 125.5, 106.8, 99.3, 70.1, 70.0, 69.1, 68.9, 67.1, 64.0, 47.5. Low-resolution ESI-MS for **1**: $m/z$ 1024.41 (25%) $[M - PF_6]^+$.

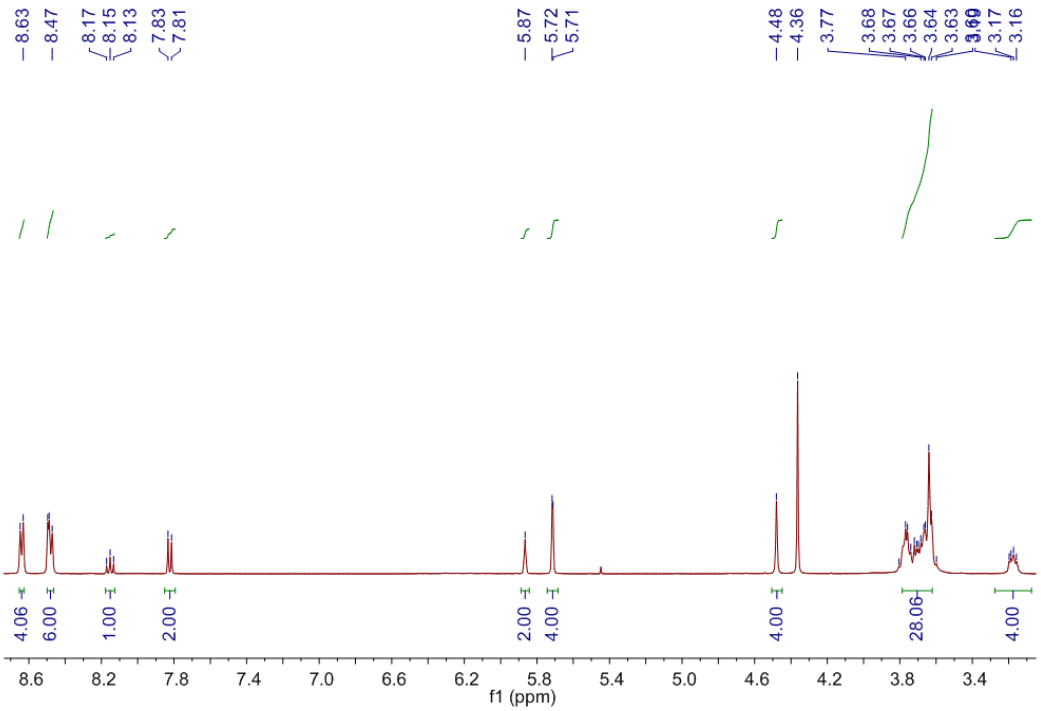



***Figure S5.*** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$, 20 °C) of **1**.

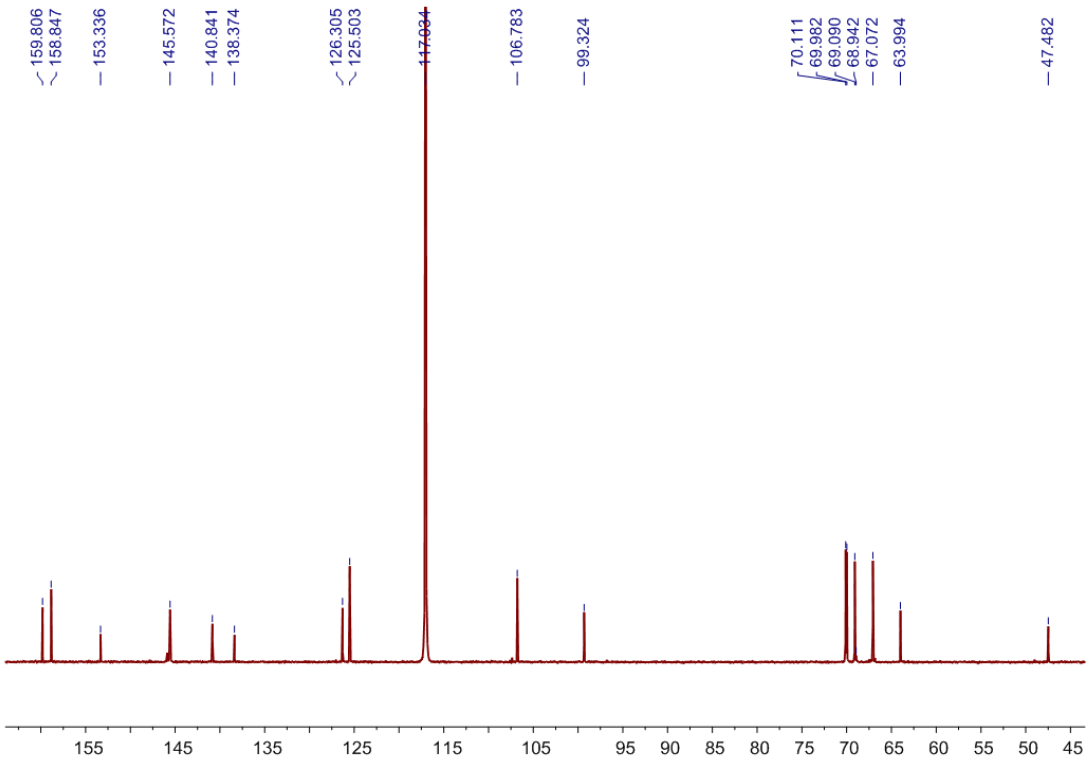
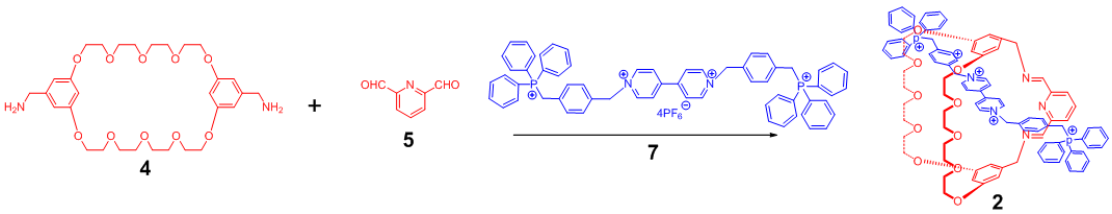



***Figure S6.*** $^{13}$C NMR spectrum (125 MHz, $CD_3CN$, 20 °C) of **1**.

4. *Synthesis of dynamic [2]rotaxane* ***2***




Equimolar (20.0 mM) diamine appended BMP32C10 derivative **4**, pyridine-2,6-dicarbaldehyde **5**, and paraquat derivative **7** were mixed together in $CD_3CN$ at 25 °C to give the dynamic [2]rotaxane **2** almost quantitative within several minutes. $^1$H NMR (500 MHz, $CD_3CN$, room temperature) $\delta$ (ppm) for **2**: 8.89–8.91 (d, 2H, $J$ = 10.0 Hz), 8.56–8.62 (m, 6H), 8.36–8.38 (m, 5H), 7.83–7.89 (m, 6H), 7.40–7.70 (m, 28H), 7.08–7.10 (m, 4H), 5.93–5.94 (t, 2H, $J$ = 2.5 Hz), 5.76 (s, 6H), 5.20–5.21 (d, 2H, $J$ = 5.0 Hz), 4.67–4.71 (m, 4H), 4.11 (s, 4H), 3.55–3.79 (m, 28H), 3.31–3.34 (m, 4H). $^{13}$C NMR (125 MHz, $CD_3CN$, 22 °C) $\delta$ (ppm) for **2**: 159.6, 158.9, 153.2, 145.5, 145.3, 144.5, 140.7, 138.6, 135.1, 133.8, 131.5, 129.8, 127.1, 126.5, 107.4, 97.9, 70.2, 69.8, 69.3, 67.2, 63.7, 62.9. Low-resolution ESI-MS for **2**: $m/z$ 935.4 (100%) $[M - 2PF_6]^{2+}$.

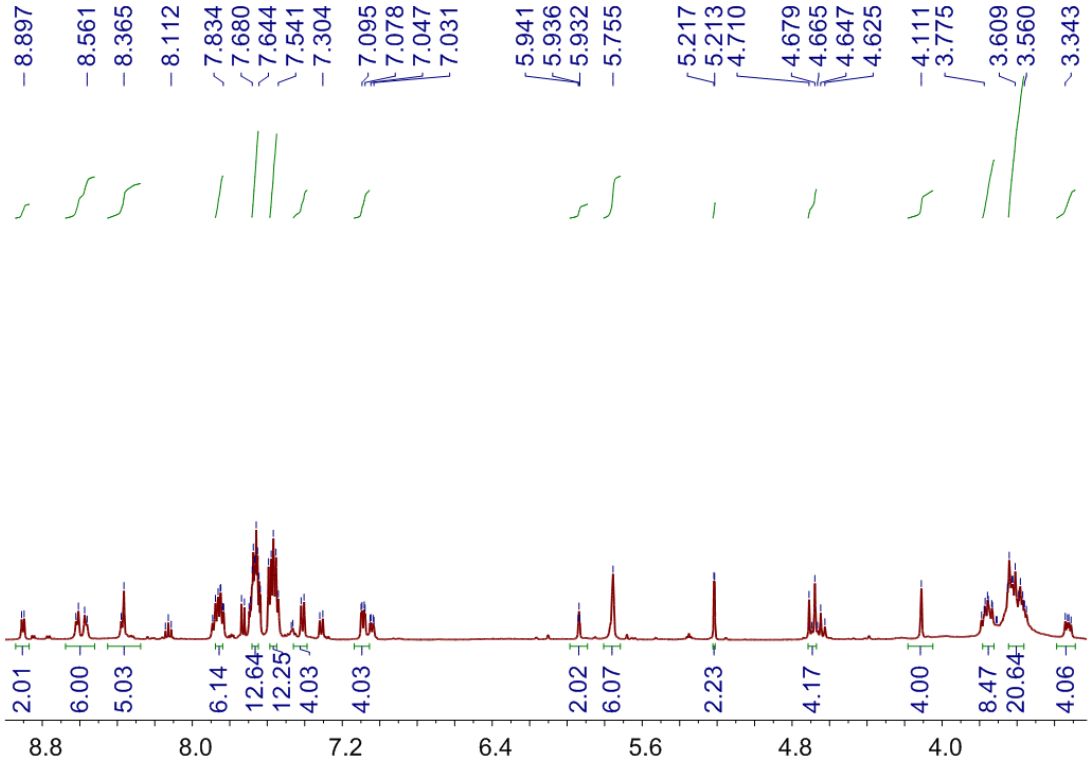



***Figure S7.*** $^{1}$H NMR spectrum (500 MHz, $CD_3CN$, 20 °C) of **2**

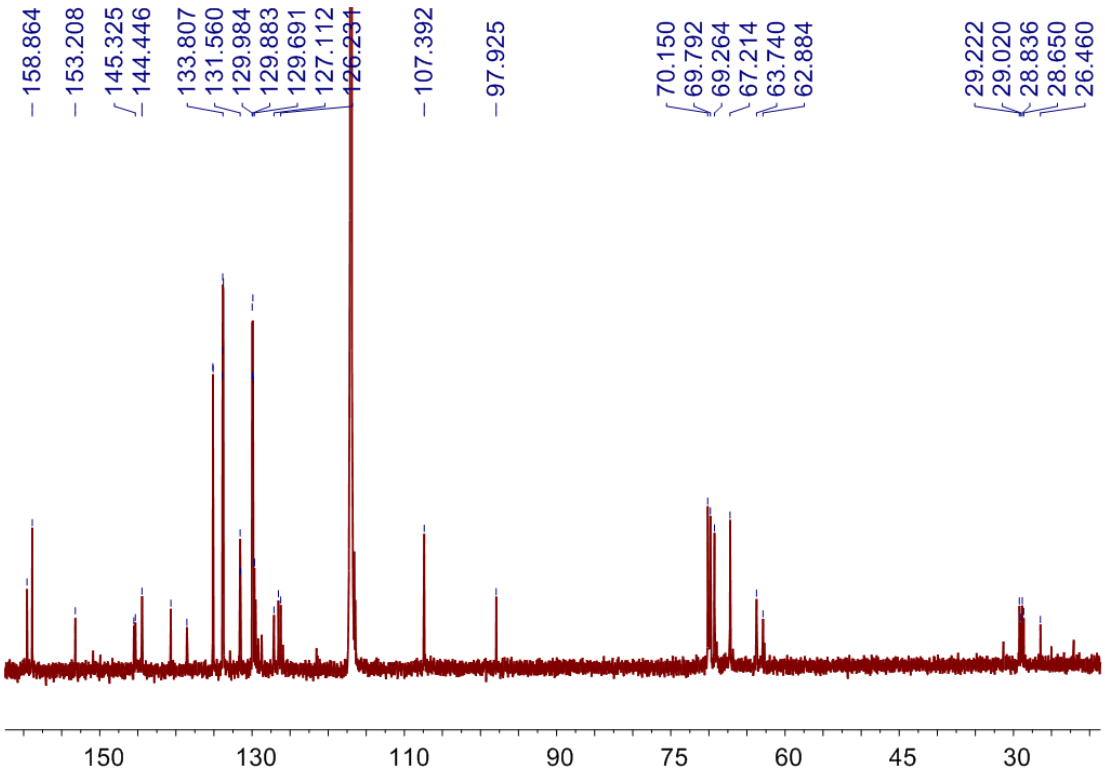
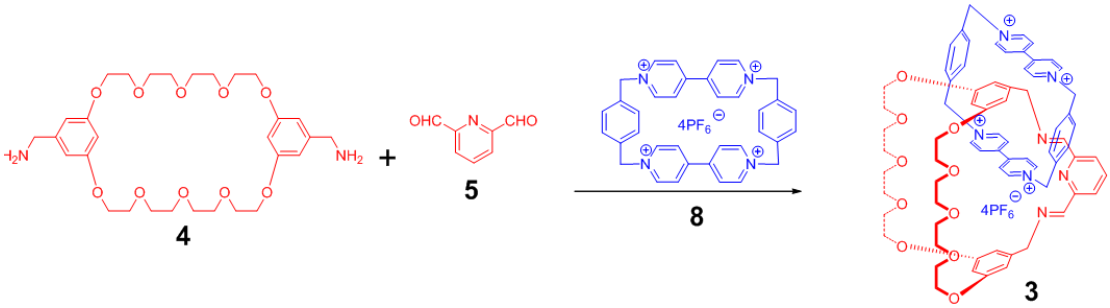



***Figure S8.*** $^{13}$C NMR spectrum (125 MHz, $CD_3CN$, 20 °C) of **2**.

5. *Synthesis of dynamic [2]catenane* ***3***




Equimolar (20.0 mM) diamine appended BMP32C10 derivative **4**, pyridine-2,6-dicarbaldehyde **5**, and cyclophane **8** were mixed together in $CD_3CN$ at 25 °C to give the dynamic [2]catenane **3** almost quantitative within several minutes. $^1$H NMR (500 MHz, $CD_3CN$, room temperature) $\delta$ (ppm) for **3**: 7.49–8.90 (br, 26H), 8.25–8.28 (t, 1H, $J$ = 10.0 Hz), 7.91–7.93 (d, 2H, $J$ = 10.0 Hz), 5.64–6.33 (br, 12H), 4.59–4.74 (br, 2H), 3.57–3.81 (m, 36H). $^{13}$C NMR (125 MHz, $CD_3CN$, 22 °C) $\delta$ (ppm) for **3**: 159.9, 158.8, 150.6, 144.5, 139.0, 135.9, 130.1, 127.0, 107.4, 106.4, 96.8, 70.1, 70.0, 69.5, 69.0, 66.8, 63.7. Low-resolution ESI-MS for **3**: *m/z* 1502.2 (100%) $[M - HPF_6 - PF_6]^+$, *m/z* 1648.2 (90%) $[M - PF_6]^+$, *m/z* 1356.4 (20%) $[M - 2HPF_6 - PF_6]^+$.

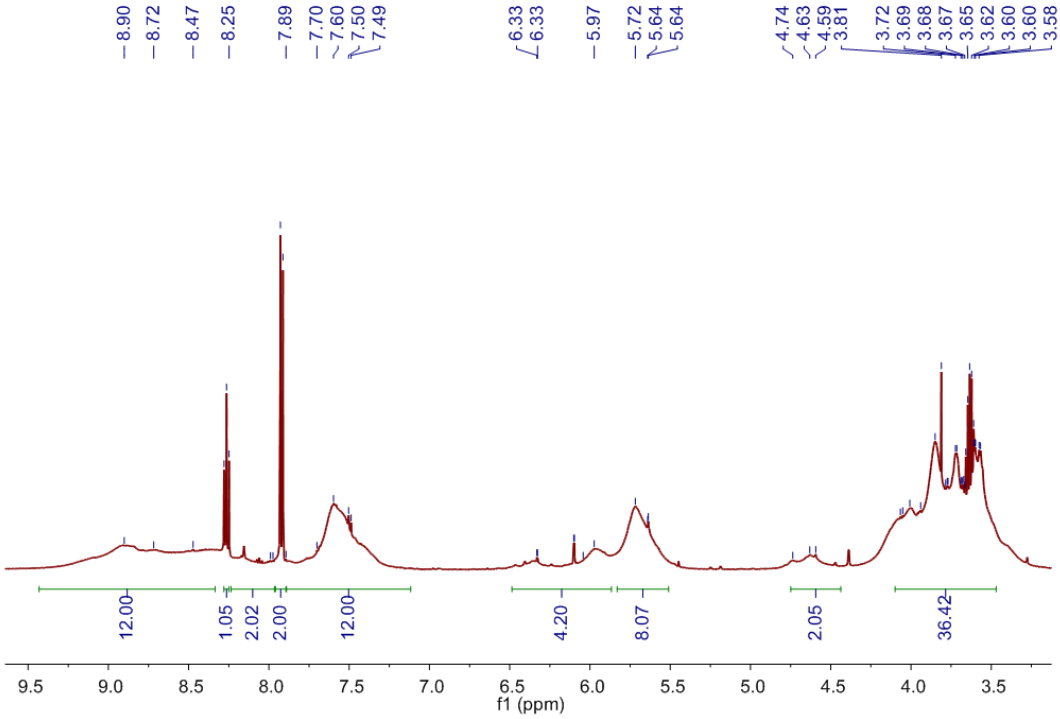



***Figure S9.*** $^{1}$H NMR spectrum (500 MHz, $CD_3CN$, 20 °C) of **3**.

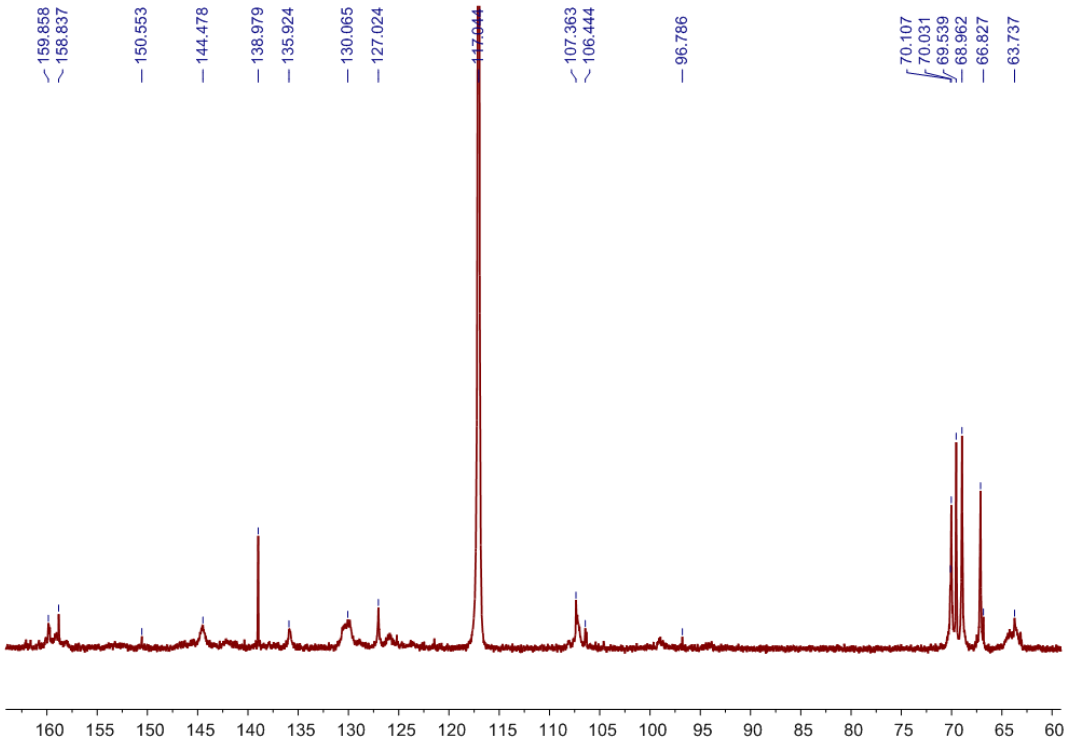



***Figure S10.*** $^{13}$C NMR spectrum (125 MHz, $CD_3CN$, 20 °C) of **3**.

6. *LRESIMS spectra of* ***1*** *,* ***2*** *and* ***3***

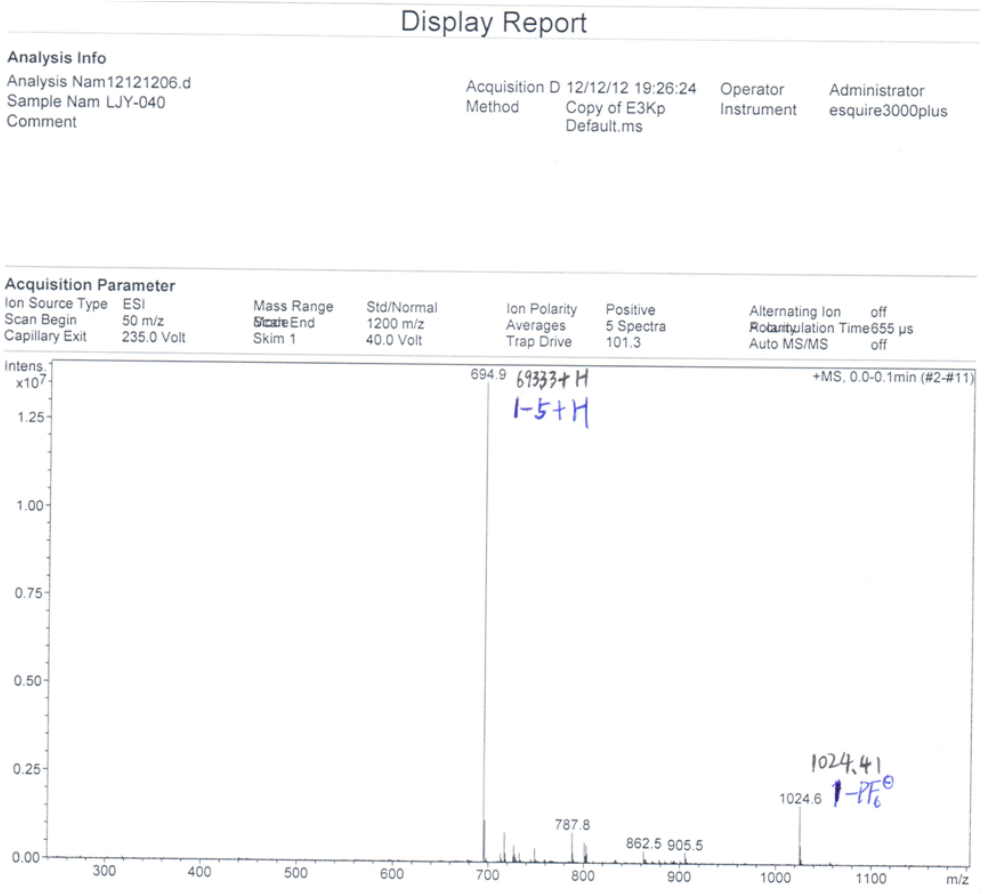



***Figure S11.*** Electrospray ionization mass spectrum of **1**.

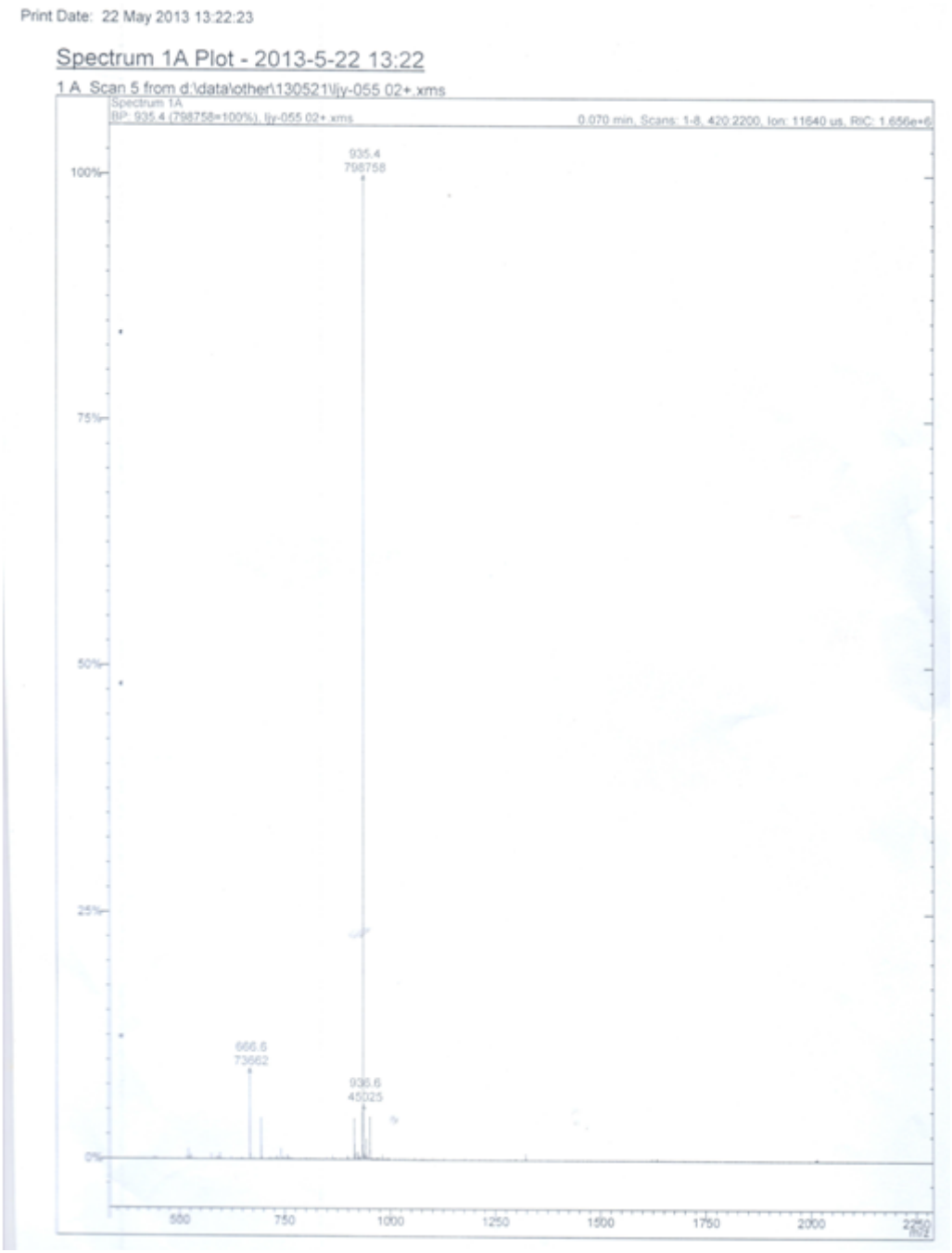



***Figure S12.*** Electrospray ionization mass spectrum of **2**.

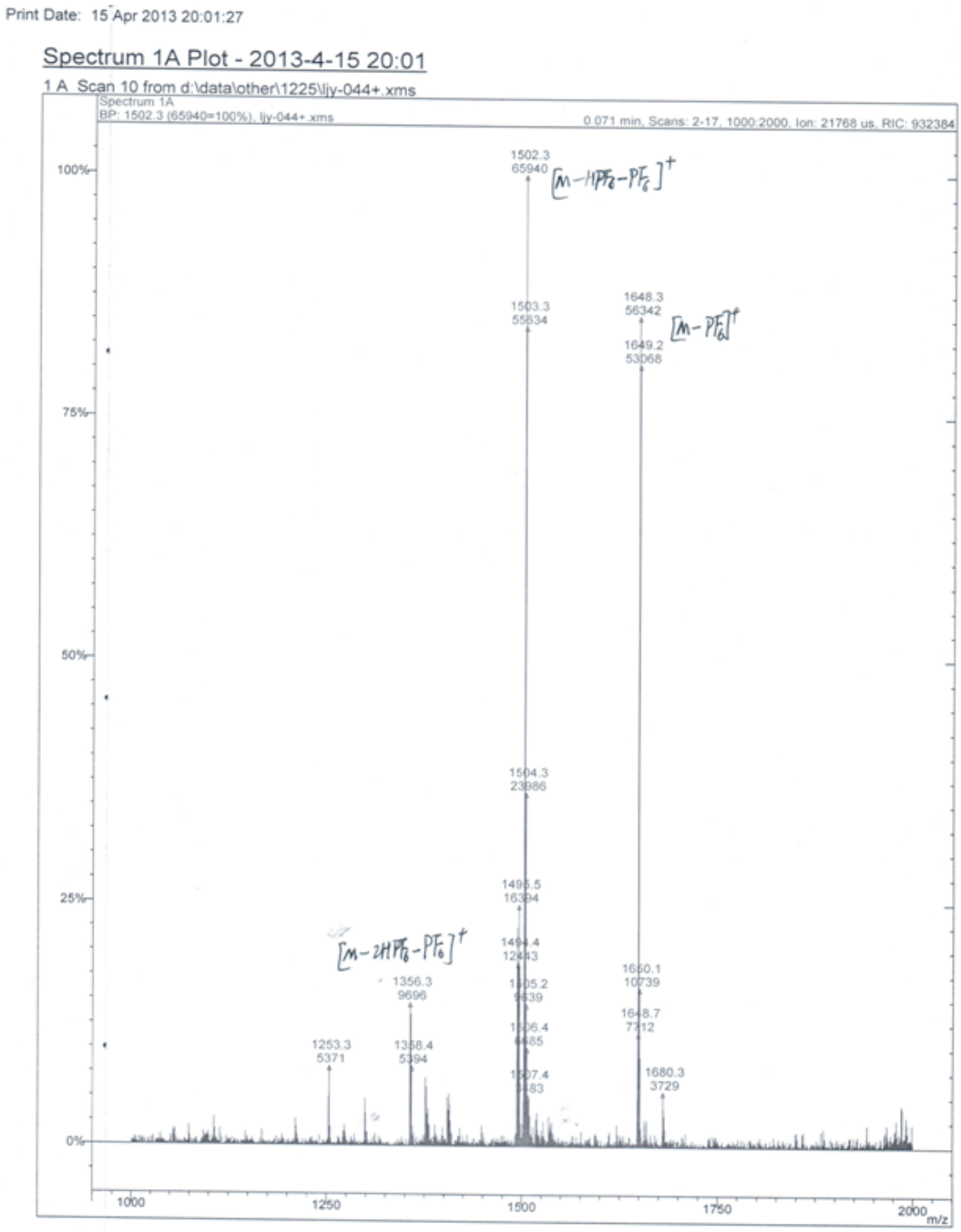



***Figure S13.*** Electrospray ionization mass spectrum of **3**.

## 7. *Partial NOESY NMR spectra of **1, 2** and **3***

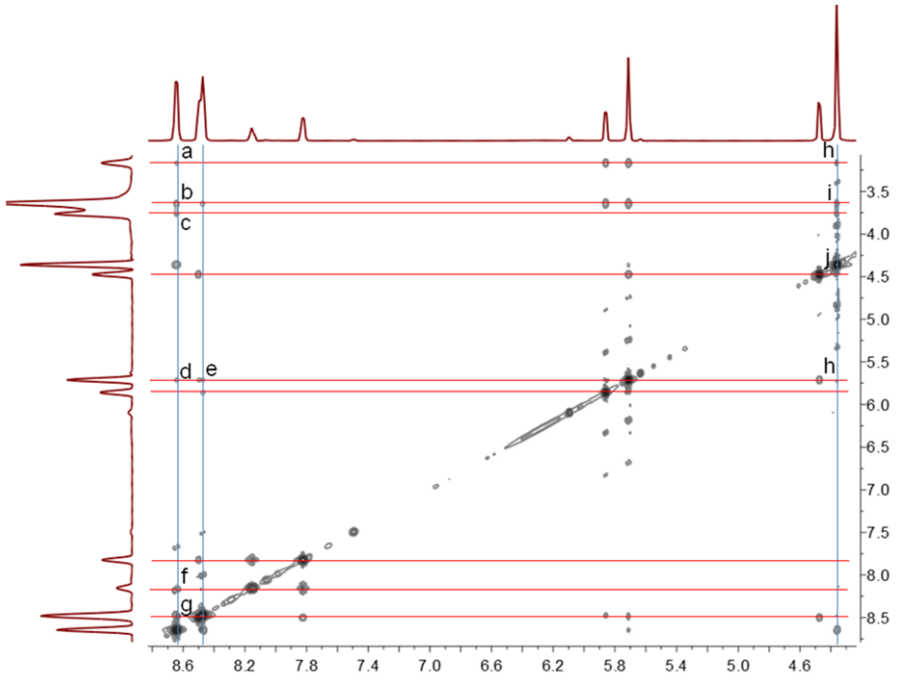



***Figure S14.*** Partial NOESY NMR spectrum of **1** (20.0 mM) in $CD_3CN$ (500 MHz, 20 °C).

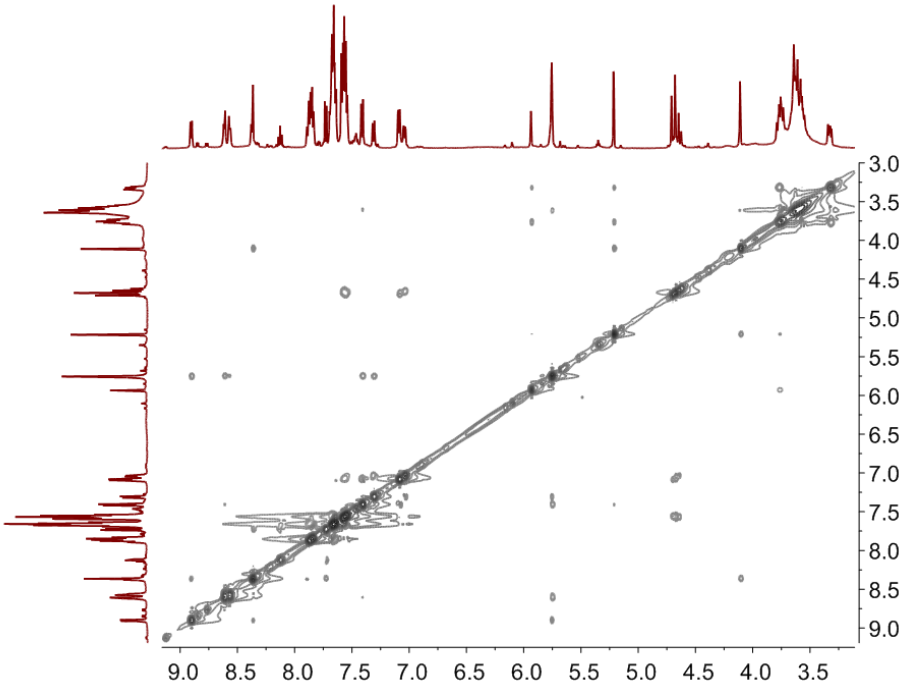



***Figure S15.*** Partial NOESY NMR spectrum of **2** (20.0 mM) in $CD_3CN$ (500 MHz, 20 °C).

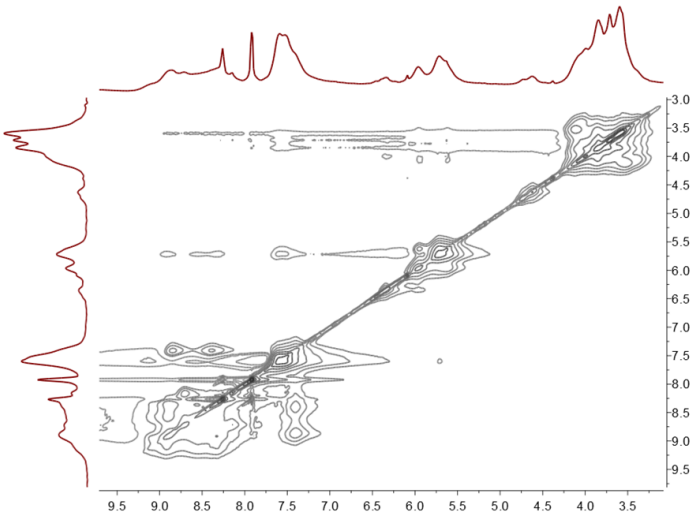


***Figure S16.*** Partial NOESY NMR spectrum of **3** (20.0 mM) in $CD_3CN$ (500 MHz, 20 °C).

8. *Partial COSY NMR spectra of **1, 2** and **3***

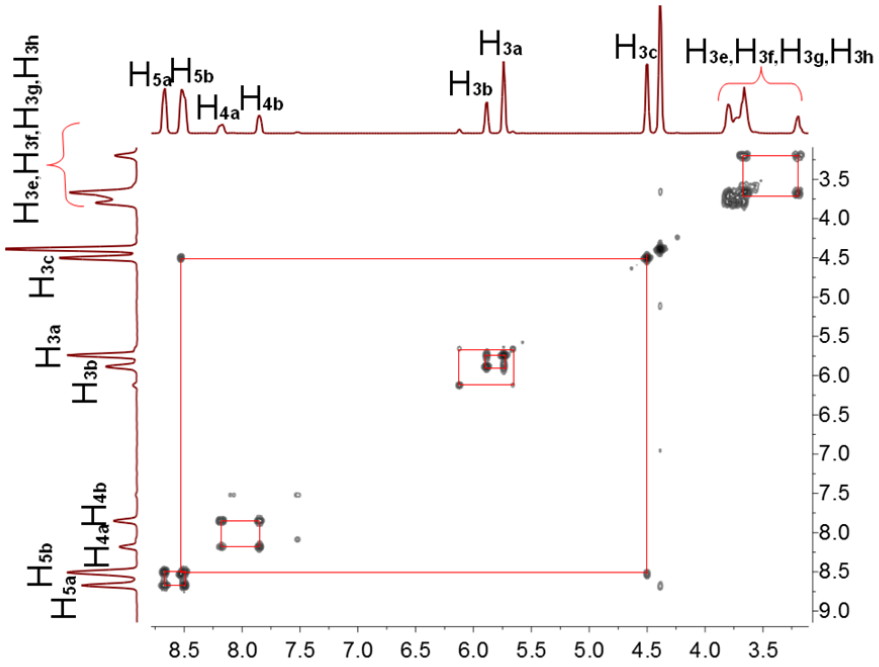



***Figure S17.*** Partial COSY spectrum (500 MHz, $CD_3CN$, 20 °C) of **1** (20.0 mM).

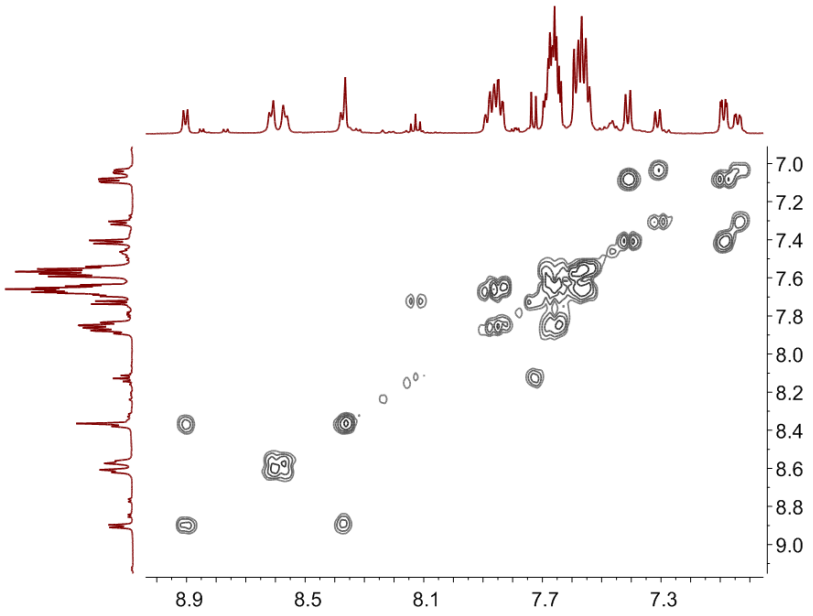



***Figure S18.*** Partial COSY spectrum (500 MHz, $CD_3CN$, 20 °C) of **2** (20.0 mM).

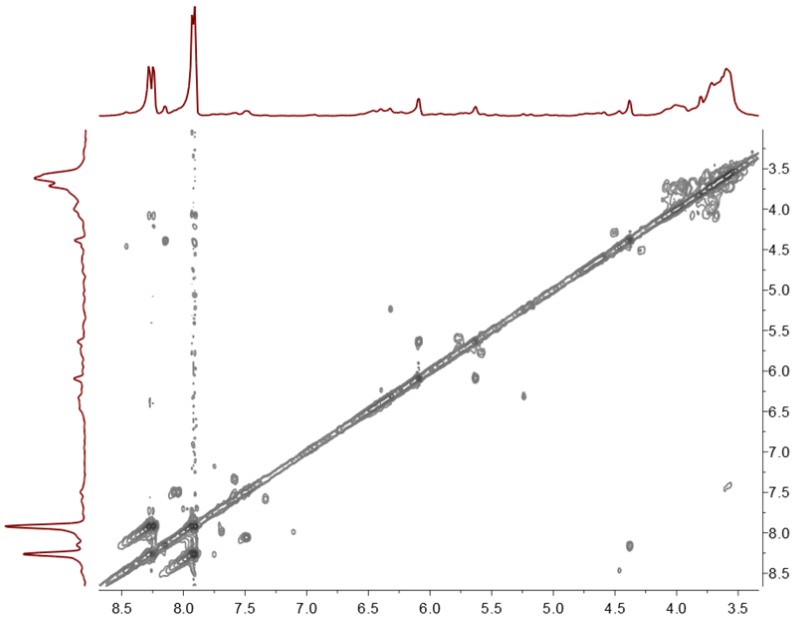



***Figure S19.*** Partial COSY spectrum (500 MHz, $CD_3CN$, 20 °C) of **3** (20.0 mM).

*9. X-ray analysis data of [2]catenane **3***

Crystal data of **3**: block, pale red, 0.48 × 0.40 × 0.32 $mm^3$, $C_{73}H_{79}F_{24}N_7O_{10}P_4$, *FW* 1793.30, triclinic, space group *P* 1, $a$ = 13.9994(6), $b$ = 14.0662(6), $c$ = 15.3078(7) Å, $\alpha$ = 108.714(4)°, $\beta$ = 107.270(4)°, $\gamma$ = 96.152(3)°, $V$ = 2657.17(19) $Å^3$, $Z$ = 1, $D_c$ = 1.121 g $cm^{-3}$, $T$ = 140(2) K, $\mu$ = 1.433 $mm^{-1}$, 9013 measured reflections, 11854 independent reflections, 1063 parameters, 9 restraints, $F(000)$ = 921, $R_1$ = 0.0783, $wR_1$ = 0.2111 (all data), $R_2$ = 0.0717, $wR_2$ = 0.1983 [$I > 2\sigma(I)$], max. residual density 0.366 e•$Å^{-3}$, and goodness-of-fit ($F^2$) = 1.061. CCDC 936994.

*10. Partial $^1$H NMR of the mixture of compounds **4** and **5** without paraquat*

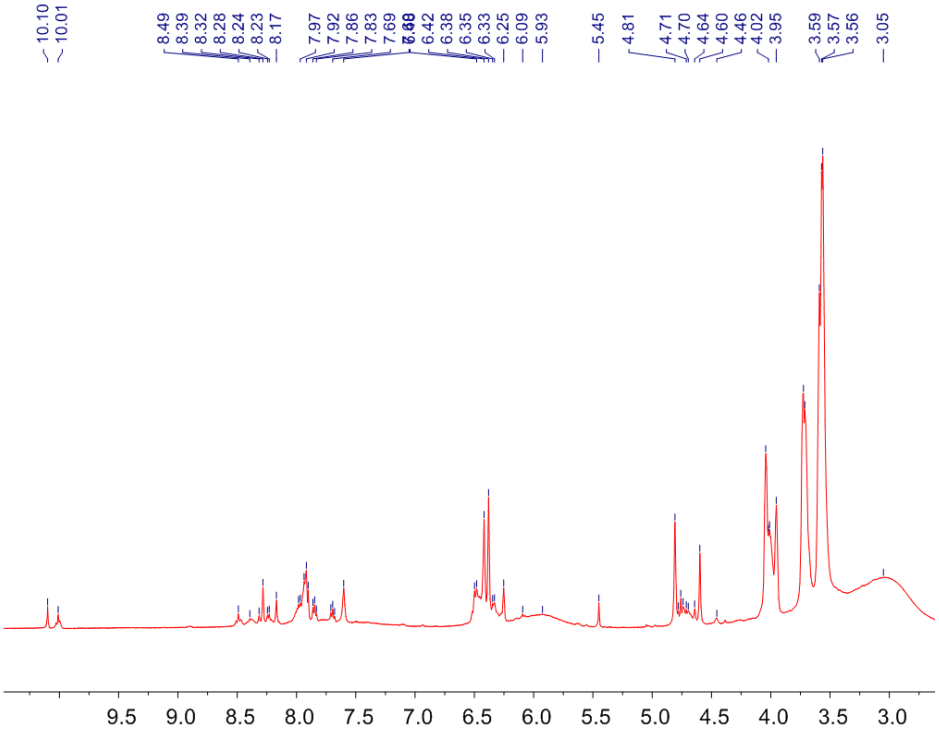



***Figure S20.*** Partial $^1$H NMR spectrum (500 MHz, $CD_3CN$, 20 °C) of equimolar **4** and **5** (20.0 mM).

From Figure S20, we can confirm that in the absence of paraquat template, the mixture of **4** and **5** preferred to form dynamic polymer instead of discrete cryptand as indicated by lots of broad peaks.

*11. UV-Vis spectrum of [2]rotaxane* ***2***

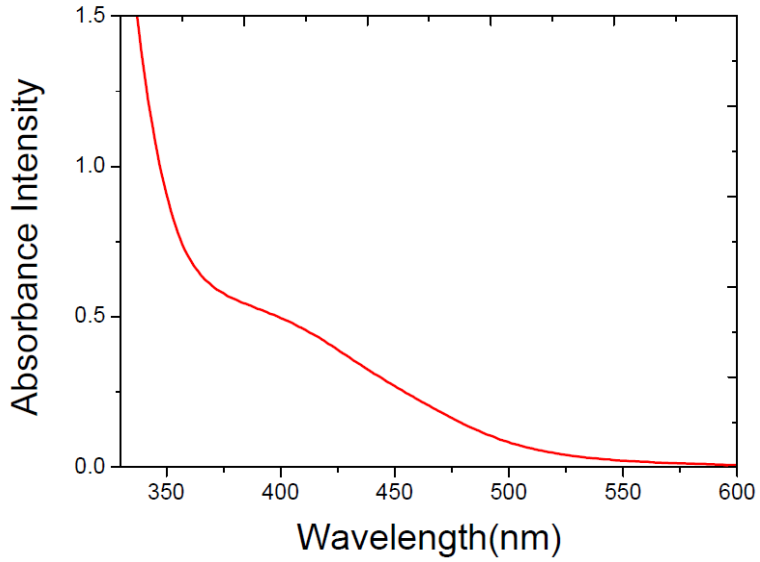



***Figure S21.*** UV-Vis absorption spectrum of dynamic cryptand-based [2]rotaxane **2** at 1.00 mM in $CD_3CN$.

*References:*

S1. K. Zhu, S. Li, F. Wang, F. Huang, *J. Org. Chem.* 2009, **74**, 1322–1328.

S2. W. S. Bryant, J. W. Jones, P. E. Mason, I. Guzei, A. L. Rheingold, D. S. Nagvekar and H. W. Gibson, *Org. Lett.*, 1999, **1**, 1001–1004.

S3. S. Li, M. Liu, J. Zhang, B. Zheng, C. Zhang, X. Wen, N. Li, F. Huang, *Org. Biomol. Chem.* 2008, 6, 2103–2107.

S4. B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, and D. J. Williams, *Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 1547–1550.

S5. S G. M. Sheldrick, *SHELXS-97*, *Program for solution of crystal structures*, University of Göttingen, Germany, 1990.

S6. G. M. Sheldrick, *SHELXS-97*, *Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.