Electronic Supplementary Material (ESI) for ChemComm.

Ultramacrocyclization via Selective Catenation in Water

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Supporting Information

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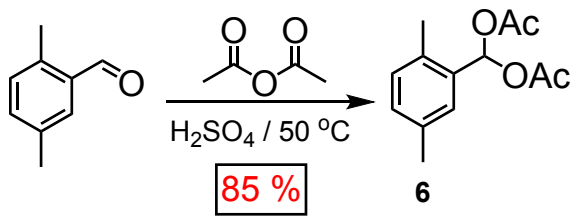
1. General Methods

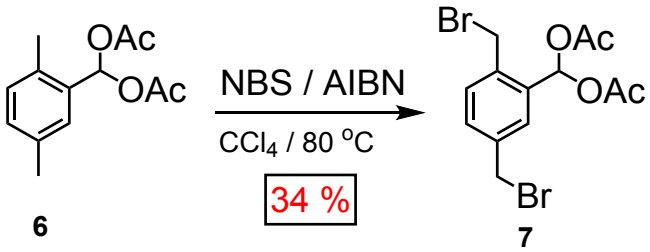
All reagents and solvents were purchased from commercial sources and used without further purification. Manipulations were performed under a normal laboratory atmosphere unless otherwise noted. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature using Bruker AVANCE III 400, Bruker AVANCE III 500, or Agilent DD2 600 spectrometers, with working frequencies of 400/500/600 and 100/125/150 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts are reported in ppm relative to the residual internal non deuterated solvent signals (D_2O: δ = 4.79 ppm, DMSO-d_6: δ = 2.50 ppm, CD_3CN: δ = 1.94 ppm). High-resolution mass spectra (HRMS) were measured by using a SHIMADZU liquid chromatograph mass spectrometry ion trap time of flight (LCMS-IT-TOF) instrument and ESI-Q-TOF-MS. Analytical HPLC-MS experiments were performed on an Agilent 1260 instrument equipped with a diode array detector, an Agilent Zorbax SB-C18 column (2.1 x 50 mm, 5 μm) and an Agilent Zorbax SB-C18 column (4.6 x 150 mm, 5 μm). The analytical HPLC experiments shown in Figure 4 and Figure S6 were performed by using an Agilent Zorbax SB-C18 column (2.1 x 50 mm, 5 μm). Others were performed by using an Agilent Zorbax SB-C18 column (4.6 x 150 mm, 5 μm). The following acetonitrile / water (both containing 0.1% acid) gradient was used: In the beginning, 1/9 acetonitrile/water was used as the fluent phase, followed by gradually increasing the acetonitrile content from 10% to 100% acetonitrile over the course of 20 min. The detection wavelength was 254 nm.

2. Synthetic Procedures



Scheme S1. Synthesis of **6**.

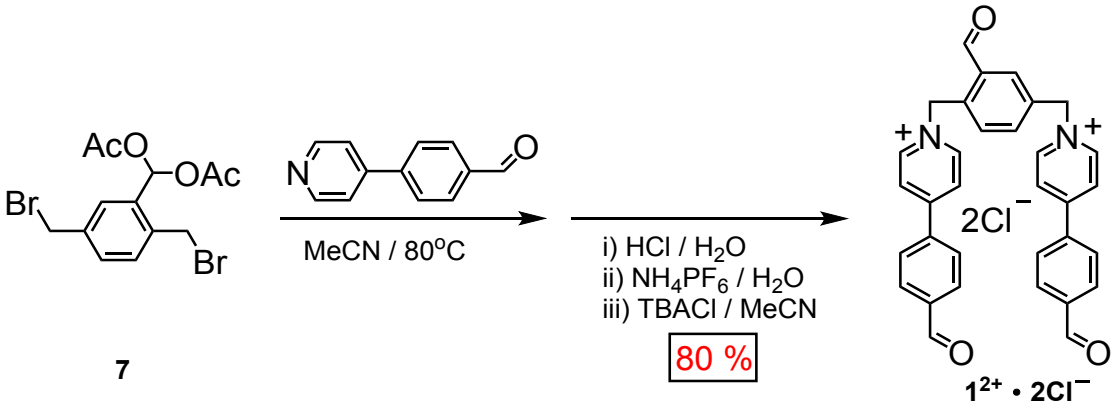
6: 2,5-dimethylbenzaldehyde (500mg, 3.73mmol) were dissolved in 30 ml acetic anhydride in a round flask. Two drops of concentrated sulfuric acid was then added into the solution as the catalyst. The reaction mixture was stirred at 50°C for 12 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was poured into water. The aqueous mixture was then extracted with CH_2Cl_2. The resulting organic extract was washed with water (3 x 50 mL), dried over anhydrous Na_2SO_4, and then concentrated to give the crude product. Purification by flash column chromatography (petroleum ether/ethyl acetate (10:1); silica gel, 200-300 mesh) yielded the white solid-state product **6** (748.5 mg, 85 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.31 (s, 1H), 7.12~7.07 (m, 2H), 2.41 (s, 3H), 2.34 (s, 3H), 2.12 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.7, 133.2, 133.1, 135.2, 130.8, 130.4, 127.6, 88.6, 20.9, 20.8, 18.4. **HRMS**: *m/z* calculated for $C_{13}H_{16}O_4Na^+$ ([M + Na]$^+$): 259.0941; found: 259.0942.



Scheme S2. Synthesis of **7**.

7: In a 250 ml round bottom flask, **6** (619.3mg, 2.62mmol) was dissolved in 30 ml of carbon tetrachloride. N-Bromosuccinimide (1.0g, 5.73mmol) and AIBN (21.5mg, 0.13mmol) were then added into the flask. The mixture was refluxed for 12 h at 77 °C. After the completion of reaction, the solution was cooled to room temperature. The precipitates were removed by filtration. The filtrate was connected and the solvent was removed by distillation to give

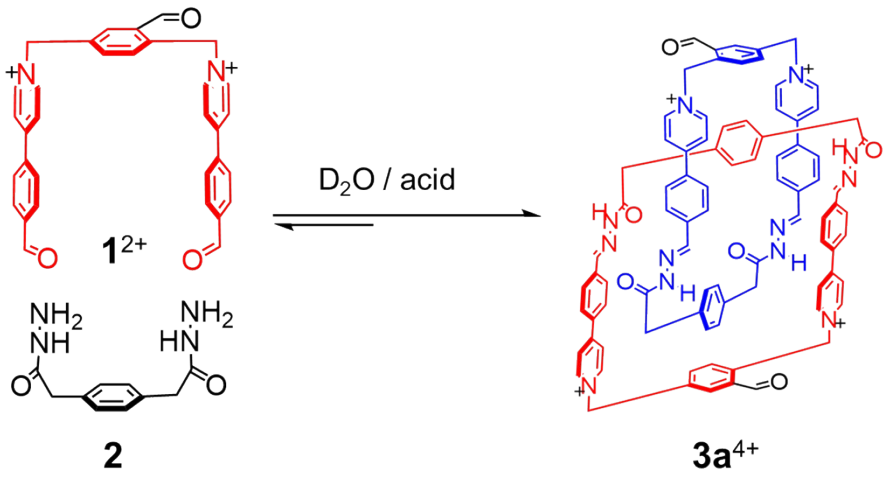
the crude product. Purification by flash column chromatography (petroleum ether/ethyl acetate (20:1); silica gel, 200-300 mesh) yielded the yellow solid-state product **7** (353 mg, 34 %). **^{1}H NMR** (400 MHz, CD3CN): δ = 7.84 (s, H), 7.67 (d, 1H), 7.54~7.49 (m, 2H), 4.74 (s, 2H), 4.62 (s, 2H), 2.10 (s, 6H). **^{13}C NMR** (400 MHz, CD_3CN): δ = 168.4, 139.1, 136.0, 134.1, 131.6, 130.6, 128.0, 86.9, 32.1, 29.2, 19.7. **HRMS**: *m/z* calculated for $C_{13}H_{14}Br_2O_4Na^+$ ([M + Na]$^+$): 414.9149 ; found: 414.9157.



Scheme S3. Synthesis of $\mathbf{1}^{2+}\cdot 2Cl^-$.

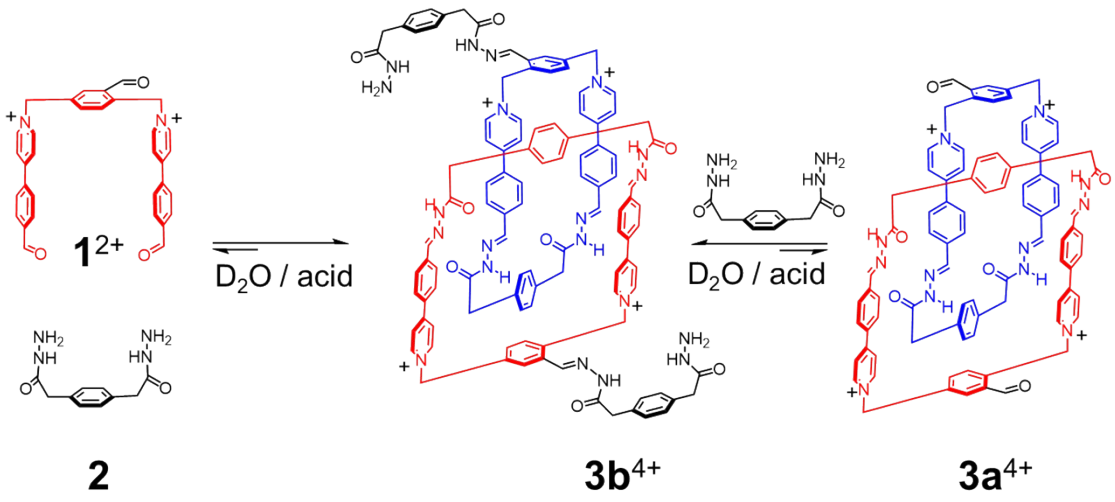
$\mathbf{1}^{2+}\cdot 2Cl^-$: **7** (392.0mg, 1mmol) and 4-(4-formylphenyl)pyridine(458.0mg, 2.5mmol) were dissolved in 15 ml MeCN in a sealed tube. The reaction mixture was stirred at 80 °C for 12 h, during which a light yellow solid precipitated from the reaction mixture. After cooling the reaction mixture to room temperature, the precipitate was collected by filtration. The solid was then dissolved in water (20 mL). Two drops of HCl was added into the aqueous solution, and the corresponding reaction mixture was stirred at 50 °C for 5h, in order to remove the protecting group of the formyl function. Ammonium hexafluorophosphate ($NH_4^+\cdot PF_6^-$) was then added into the aqueous reaction mixture, yielding $\mathbf{1}^{2+}\cdot 2PF_6^-$. The latter compound was then collected by filtration, and then dissolved in MeCN. To the organic solution of $\mathbf{1}^{2+}\cdot 2PF_6^-$, tetrabutylammonium chloride was added, yielding $\mathbf{1}^{2+}\cdot 2Cl^-$ as a white powder (454.4mg, 80%). **^{1}H NMR** (500 MHz, CD_3CN): δ = 10.18 (s, 1H), 10.15 (s, 1H), 9.47 (d, J=5, 2H), 9.20 (d, J=5, 2H), 8.69 (d, J=5, 2H), 8.65 (d, J=5, 2H), 8.40 (d, J=5, 1H), 8.31 (d, J=5, 2H), 8.29 (d,J=5, 2H), 8.17 (d, J=5, 2H), 8.15 (d, J=5, 2H), 8.03 (d, J=10, 1H), 7.44 (d, J=5, 1H), 6.30 (s, 2H), 6.10 (s, 2H). **^{13}C NMR** (500 MHz, CD_3CN): δ =

193.3, 192.8, 154.0, 145.6, 145.3, 138.7, 138.6, 137.9, 136.0, 135.0, 134.9, 134.7, 134.1, 130.8, 130.3, 130.2, 129.1, 129.0, 125.7, 125.4, 61.35, 59.87. **HRMS**: *m/z* calculated for $C_{33}H_{26}N_2O_3^{2+}$ ($[M]^{2+}$): 249.0966; found: 249.1023; *m/z* calculated for $C_{33}H_{26}ClN_2O_3^{+}$ ($[M + Cl]^{+}$): 533.1626; found: 533.1625.



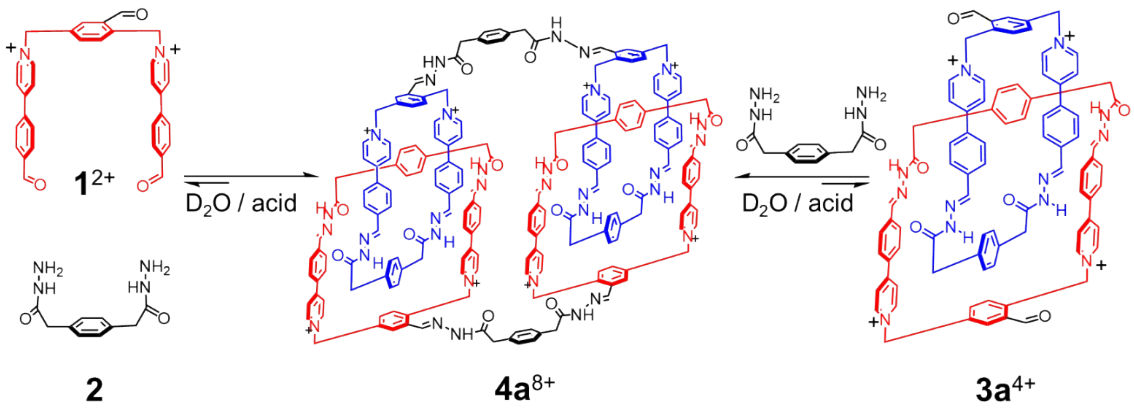
Scheme S4. Synthesis of $\mathbf{3a}^{4+}\cdot 4Cl^{-}$.

$\mathbf{3a}^{4+}\cdot 4Cl^{-}$: A 1:1 mixture of $\mathbf{1}^{2+}\cdot 2Cl^{-}$ (5.68 mg, 0.01 mmol) and **2** (2.2. mg, 0.01 mmol) was dissolved in D_2O (3 mL) in the presence of catalytic amount of DCl (10 μL). After heating the corresponding solutions at 60 °C for 8 h, the ^1H NMR (Figure S2 A and B) and mass spectrum (Figure S1) of the corresponding solution were recorded. To our delight, a new set of sharp resonances were observed in the ^1H NMR spectrum, indicating the formation of a thermodynamically stable product, namely the [2]catenane $\mathbf{3a}^{4+}\cdot 4Cl^{-}$. The structure of $\mathbf{3a}^{4+}\cdot 4Cl^{-}$ was further convinced by $^1H-^1H$ COSY spectra (Figure S3), $^1H-^1H$ NOESY spectra (Figure S4), DOSY spectra (Figure S5) and HPLC analysis (Figure S6). The more soluble counterpart in organic solvent, namely $\mathbf{3a}^{4+}\cdot 4PF_6^{-}$, could be obtained by means of counteranion exchange, by adding ammonium hexafluorophosphate ($NH_4^{+}\cdot PF_6^{-}$) into a water solution of $\mathbf{3a}^{4+}\cdot 4Cl^{-}$, yielding a solid that was collected by filtration. The ^1H NMR spectrum (Figure S2 C) of $\mathbf{3a}^{4+}\cdot 4PF_6^{-}$ was recorded, indicating that the catenane underwent partial decomposition during couteranion exchange.



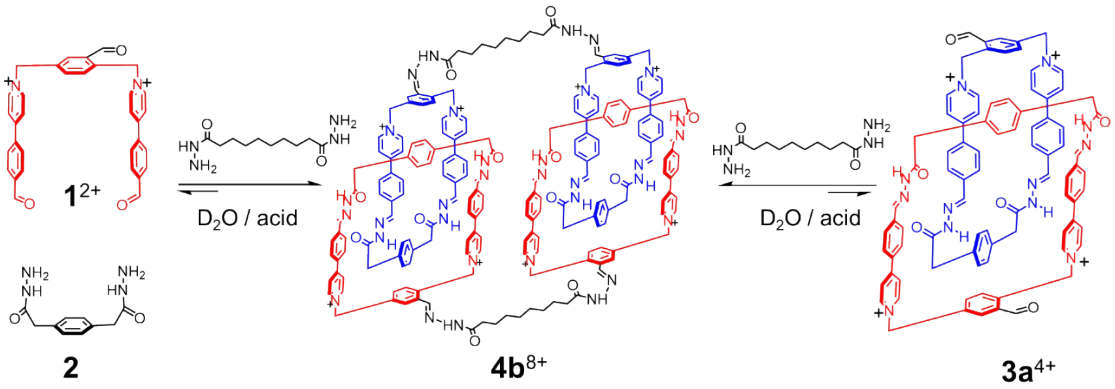
Scheme S5. Synthesis of **3b**$^{4+}$·4Cl^{-}.

3b^{4+}·4Cl^{-}: A 1:1 mixture of **1**$^{2+}$ • 2Cl^{-} (5.68 mg, 0.01 mmol) and **2** (4.44 mg, 0.02 mmol) was dissolved in D_2O (5 mL) in the presence of catalytic amount of DCl (20 μL). After heating the corresponding solutions at 60 °C for 8 h, to our delight, a new set of sharp resonances were observed in the ^{1}H NMR spectrum (Figure S8), indicating the formation of a thermodynamically stable product, namely the [2]catenane **3b**$^{4+}$·4Cl^{-}. The structure of **3b**$^{4+}$·4Cl^{-} was further convinced by the ^{1}H−^{1}H COSY spectra (Figure S9), ^{1}H−^{1}H NOESY spectra (Figure S10), DOSY spectra (Figure S11) and mass spectrum (Figure S7). **3b**$^{4+}$·4Cl^{-} could also be obtained a post-functionalization manner. That is, adding **2** (0.44mg, 0.002mmol) into **3a**$^{4+}$·4Cl^{-} (0.001mmol) in 1.2 ml D_2O in the presence of catalytic amount of DCl (5 μL) also yielded the same product.



Scheme S6. Synthesis of $\mathbf{4a}^{8+}\cdot 8Cl^{-}$.

$\mathbf{4a}^{8+}\cdot 4Cl^{-}$: A 1:1 mixture of $\mathbf{1}^{2+}\cdot 2Cl^{-}$ (5.68 mg, 0.01 mmol) and **2** (3.33 mg, 0.015 mmol) was dissolved in D_2O (4 mL) in the presence of catalytic amount of DCl (15 μL). The reaction mixture was heated at 60 °C for 8 h, yielding $\mathbf{4a}^{8+}\cdot 4Cl^{-}$ as the major product. $\mathbf{4a}^{8+}\cdot 4Cl^{-}$ could also be obtained a post-functionalization manner. That is, adding **2** (0.11mg, 0.0005mmol) into $\mathbf{3a}^{4+}\cdot 4Cl^{-}$ (0.001mmol) in 1.2 ml D_2O in the presence of catalytic amount of DCl (5 μL) produced the same product. The structure of $\mathbf{4a}^{8+}\cdot 4Cl^{-}$ was characterized by the ^{1}H NMR spectrum (Figure S13), DOSY spectra (Figure S14), mass spectrum (Figure S12) and HPLC analysis (Figure 4E). The ^{1}H NMR spectrum of the catenane dimer $\mathbf{4a}^{8+}\cdot 8Cl^{-}$ seemed remarkably complicated, making it impossible to assign each of the peaks. The DOSY spectrum and HPLC analysis convinced that under acidic aqueous conditions, the [2]catenane dimer $\mathbf{4a}^{8+}\cdot 8Cl^{-}$ was formed successfully as the main product.



Scheme S7. Synthesis of $\mathbf{4b}^{8+}\cdot 4Cl^{-}$.

$\mathbf{4b}^{8+}\cdot 4Cl^{-}$: A 1:1:0.5 of mixture of $\mathbf{1}^{2+}\cdot 2Cl^{-}$ (5.68 mg, 0.01 mmol), **2** (2.22 mg, 0.01 mmol) and **5** (1.15 mg, 0.005 mmol) was dissolved in 4 ml D_2O in the presence of catalytic amount of DCl (15 μL). The reaction mixture was heated at 60 °C for 8 h, yielding $\mathbf{4b}^{8+}\cdot 4Cl^{-}$ as the major product. $\mathbf{4b}^{8+}\cdot 4Cl^{-}$ could also be obtained by a post-functionalization manner. That is, adding **5** (0.12mg, 0.0005mmol) into $\mathbf{3a}^{4+}\cdot 4Cl^{-}$ (0.001mmol) in 1.2 ml D_2O in the presence of catalytic amount of DCl (5 μL) produced the same product. The structure of $\mathbf{4b}^{8+}\cdot 4Cl^{-}$ was characterized by mass spectrum (Figure S15) and HPLC analysis (Figure S17). The DOSY spectrum and HPLC analysis convinced that under acidic aqueous conditions, the [2]catenane dimer $\mathbf{4b}^{8+}\cdot 8Cl^{-}$ was formed successfully as the main product.

3. Characterization of $3a^{4+}$ by ^{1}H NMR and HRMS, and HPLC

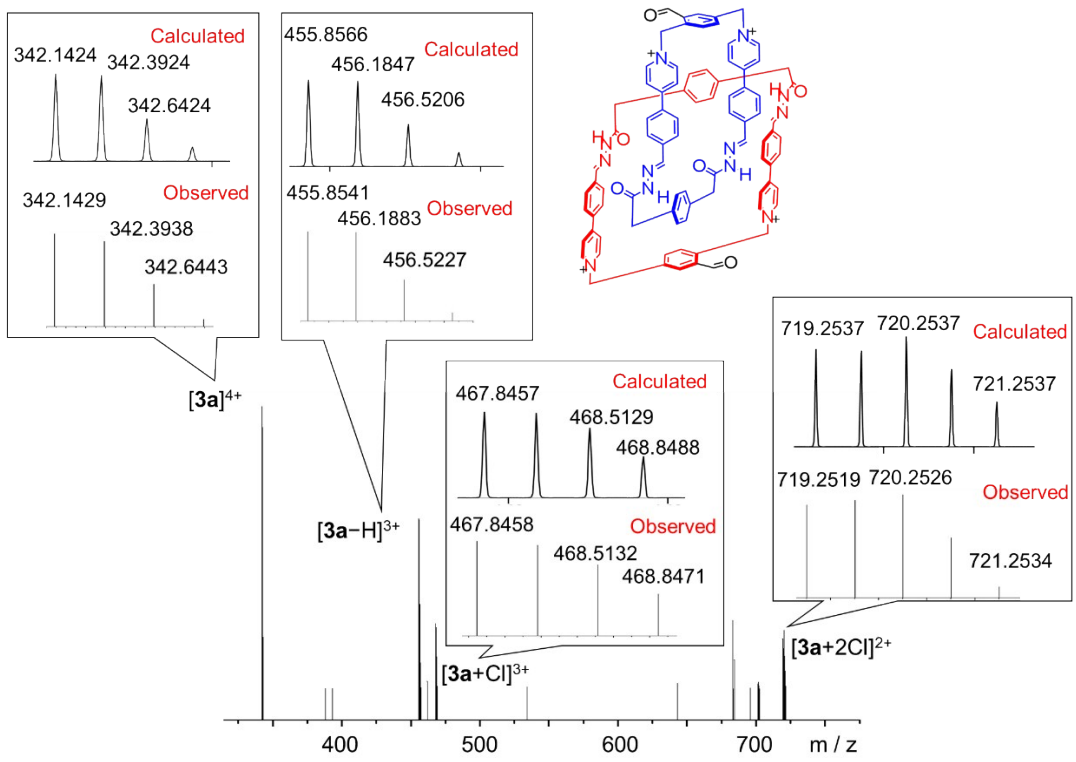


Figure S1. High-resolution ESI-Q-TOF-mass spectrum of $\mathbf{3a}^{4+}\cdot 4Cl^{-}$. The signals labeled in the spectrum correspond to molecular cations that contain four, three, and two positive charges, respectively, by either losing protons or obtaining chloride counteranions. *m/z* $[\mathbf{3a}]^{4+}$ calculated for $C_{86}H_{72}N_{12}O_6^{4+}$: 342.1424; found: 342.1429. $[\mathbf{3a} - H]^{3+}$ calculated for $C_{86}H_{71}N_{12}O_6^{3+}$: 455.8566; found: 455.8541. $[\mathbf{3a} + Cl]^{3+}$ calculated for $C_{86}H_{72}ClN_{12}O_6^{3+}$: 467.8457; found: 467.8458. $[\mathbf{3a} + 2Cl]^{2+}$ calculated for $C_{86}H_{72}Cl_2N_{12}O_6^{2+}$: 719.2537; found 719.2519.

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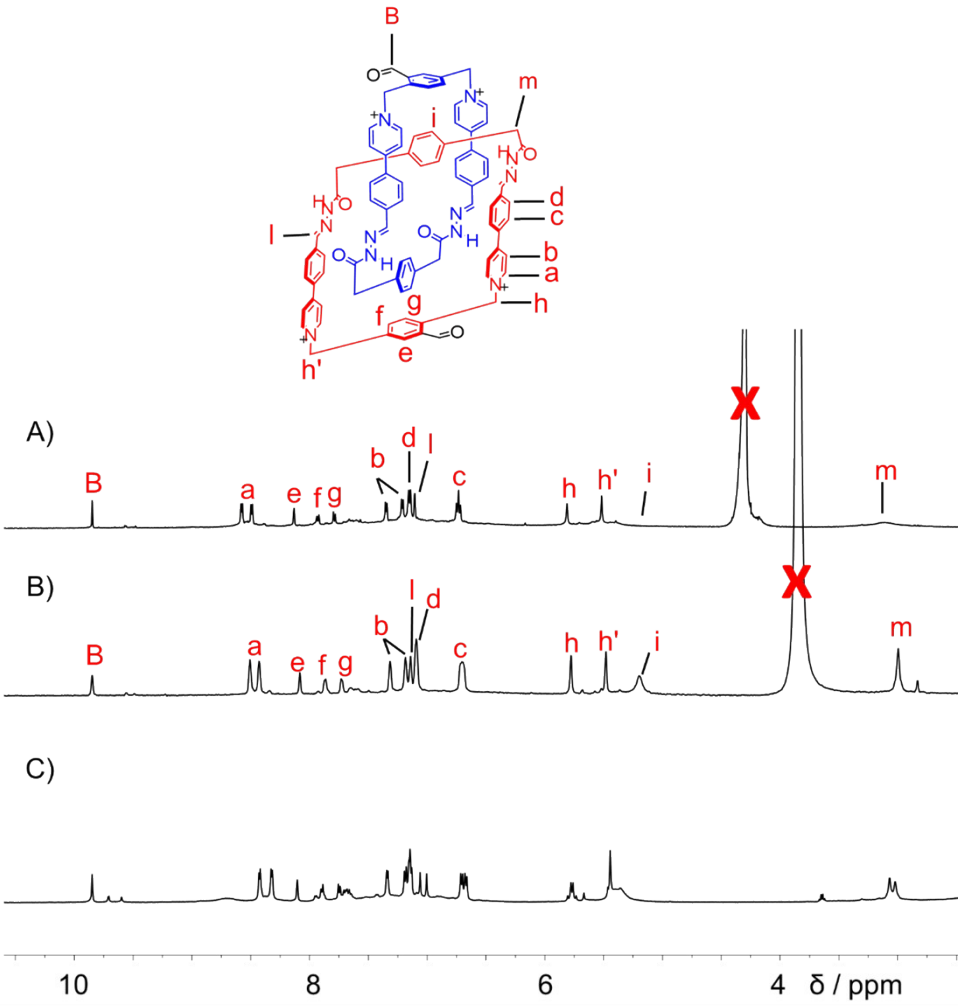

Figure S2. Partial ^{1}H NMR spectra of A) **3a**$^{4+}$·4Cl$^-$ (600 MHz, D_2O, 298 K), B) **3a**$^{4+}$·4Cl$^-$ (600 MHz, D_2O, 333 K), and C) **3a**$^{4+}$·4PF_6^- (500 MHz, CD_3CN, 298 K).

At room temperature (i.e., 25 °C), the resonances of the protons i and m are remarkably broad (see Figure S2 A). This observation could be explained by the fact that, within the cavity of one of the two interlocked rings, the circumvolution movement of the *p*-xylene units around the C−C bond between the methylene and the phenyl unit is significantly slowed down. At elevated temperature such as 60 °C, these two peaks become sharper (see Figure S2 B), indicating that the circumvolution motion is ”speeded up” at higher temperatures. **3a**$^{4+}$·4PF_6^- was obtained by means of counteranion exchange. ^{1}H NMR spectrum recorded in CD_3CN indicated that the catenane underwent partial decomposition via hydrazone exchange during precipitation when hydrophobic effect was absent.

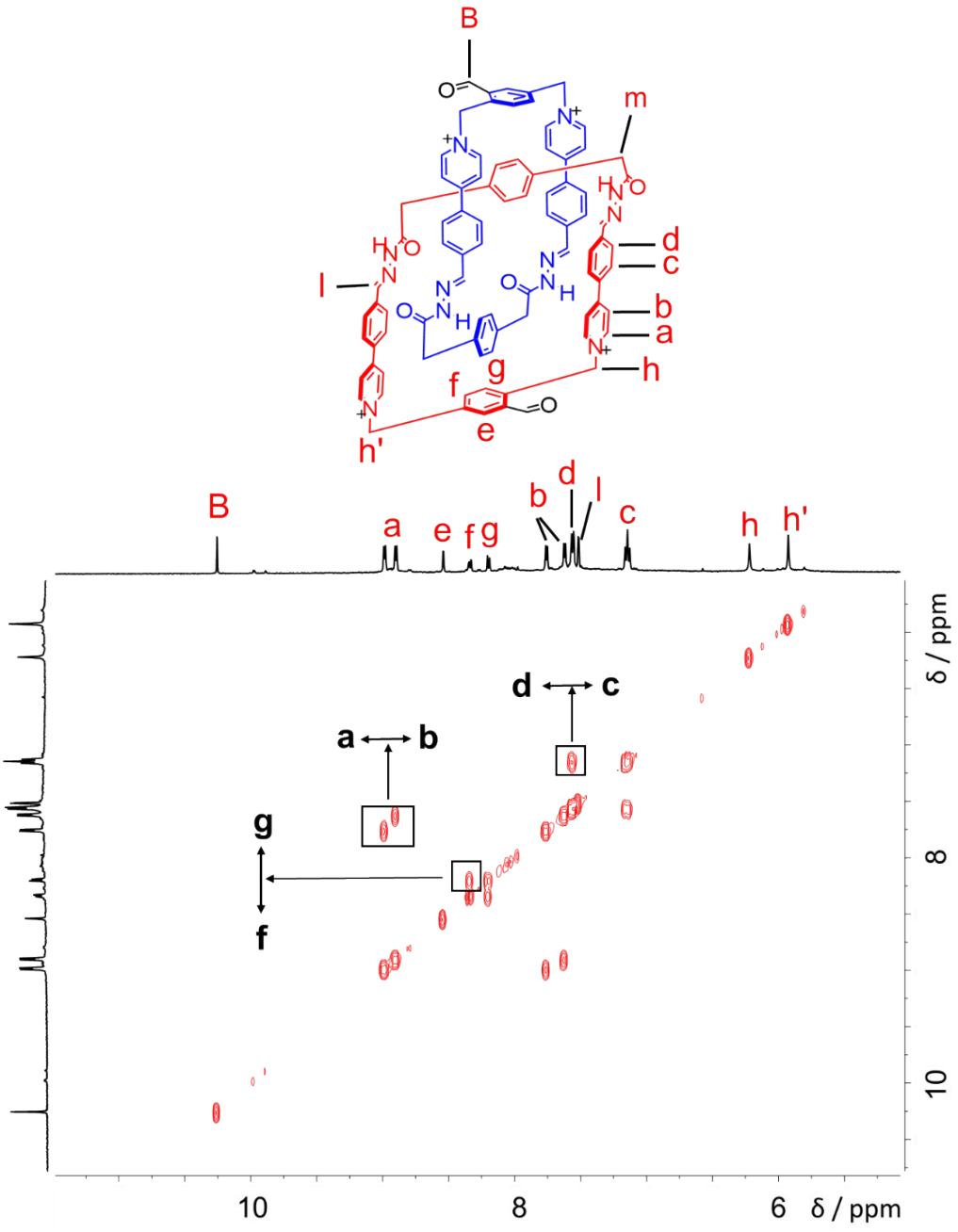

Figure S3. $^{1}H-^{1}H$ COSY spectrum (500 MHz, D_2O, 298 K) of **3a**$^{4+}$·4Cl^{-}. Key correlation peaks are labeled in the spectrum.

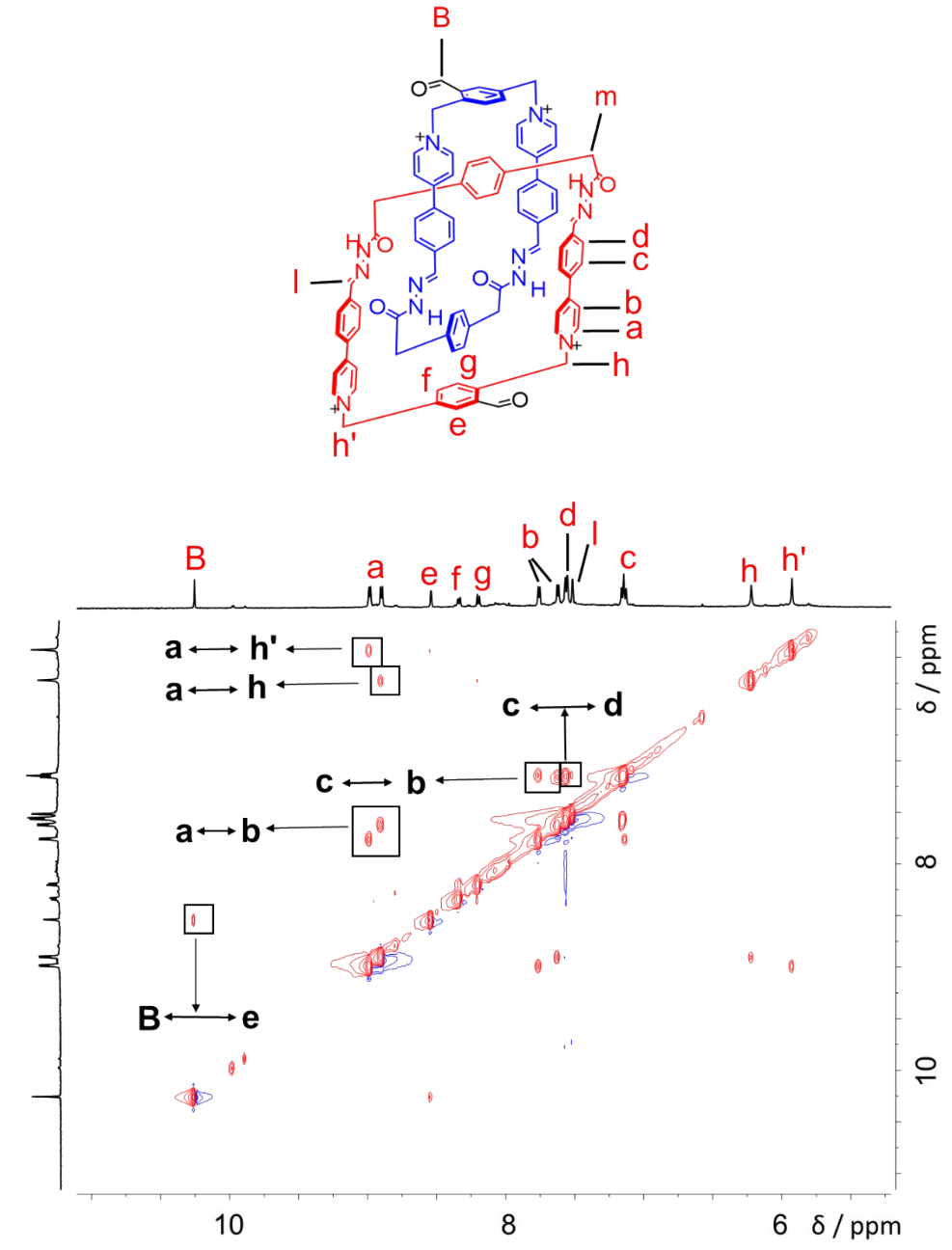

Figure S4. $^{1}H-^{1}H$ NOESY spectrum (500 MHz, D_2O, 298 K) of **3a**$^{4+}$·4Cl^{-}. Key correlation peaks are labeled in the spectrum.

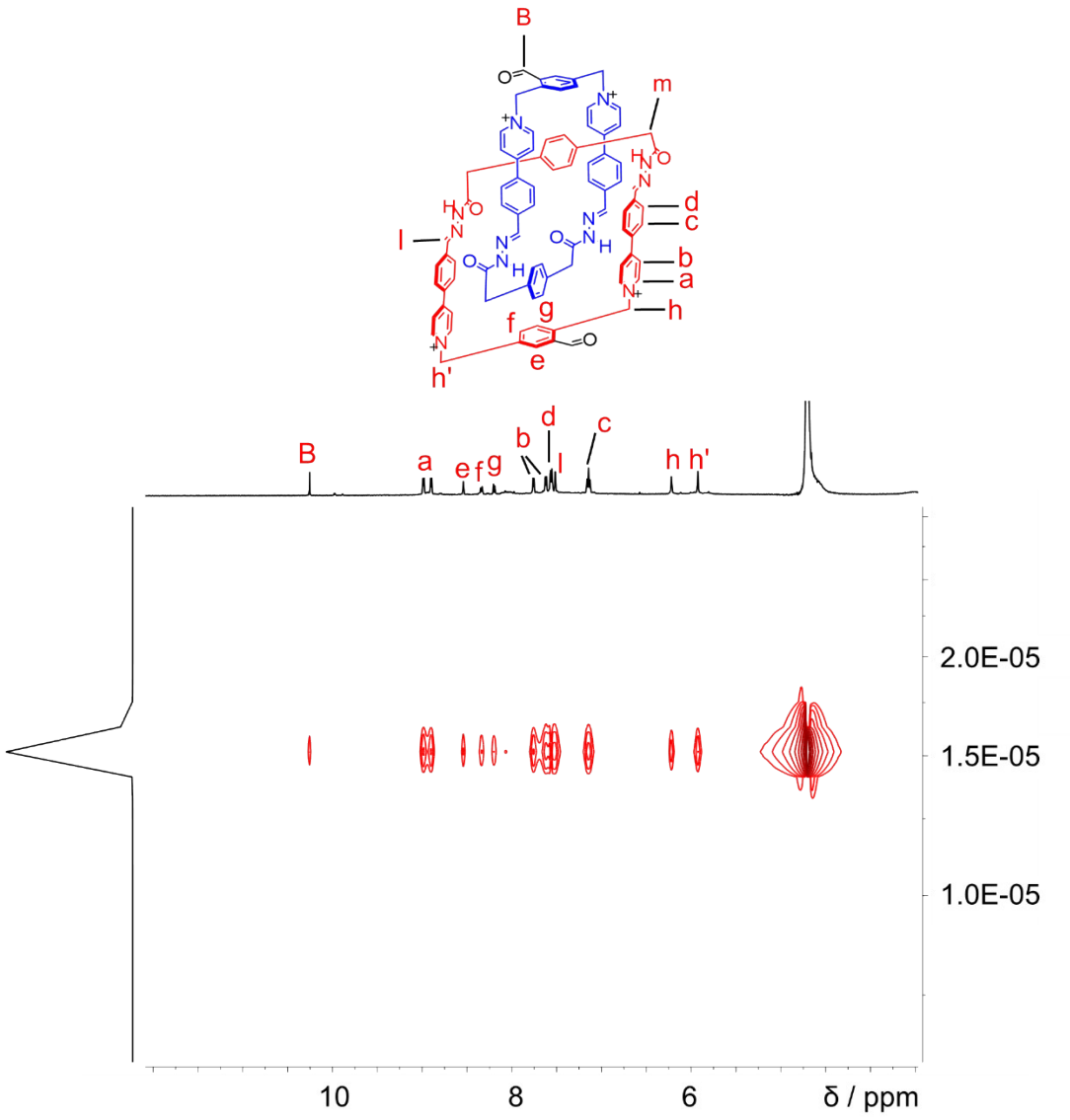

Figure S5. DOSY spectrum (500 MHz, D_2O, 298 K) of **3a**$^{4+}$·4Cl^{-}.

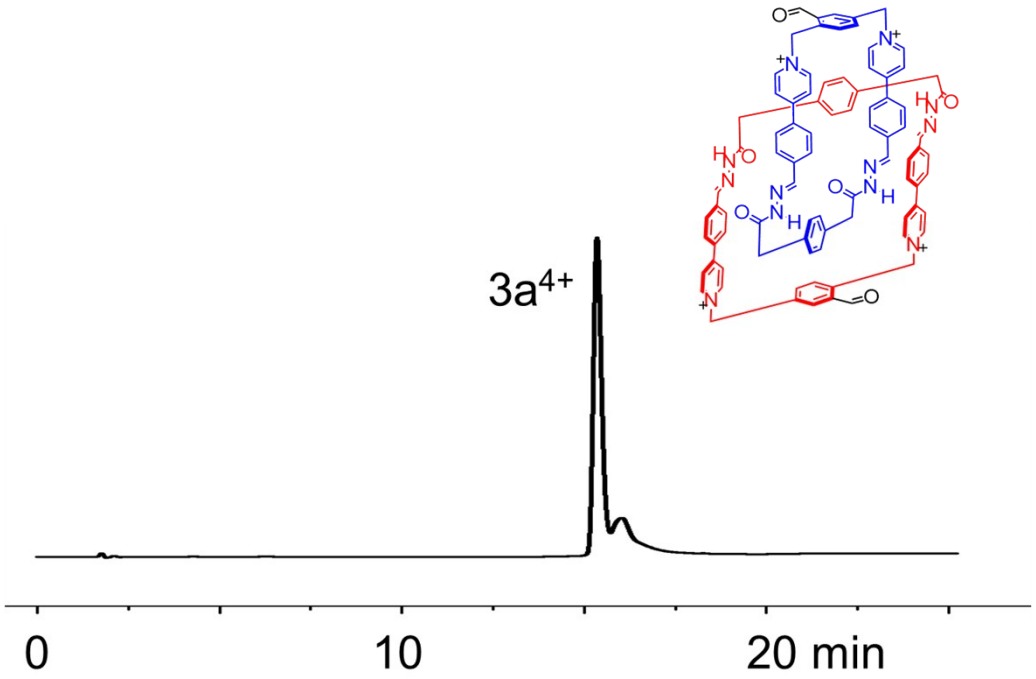

Figure S6. Reversed-phase HPLC analysis of the [2]catenane **3a**$^{4+}$·4Cl^{-}. The HPLC trace was recorded on an Agilent 1260 instrument. The following acetonitrile /water (both containing 0.1% trifluoroacetate acid) gradient was used. In the beginning, 1/9 acetonitrile/water was used as the fluent phase, followed by gradually increasing the acetonitrile content from 10% to 100% acetonitrile over the course of 20 min. The detection wavelength was 254 nm. A side-peak was also observed, probably corresponding to oligomeric or polymeric byproducts.

4. Characterization of $3b^{4+}\cdot 4Cl^-$ in D_2O by NMR and HRMS

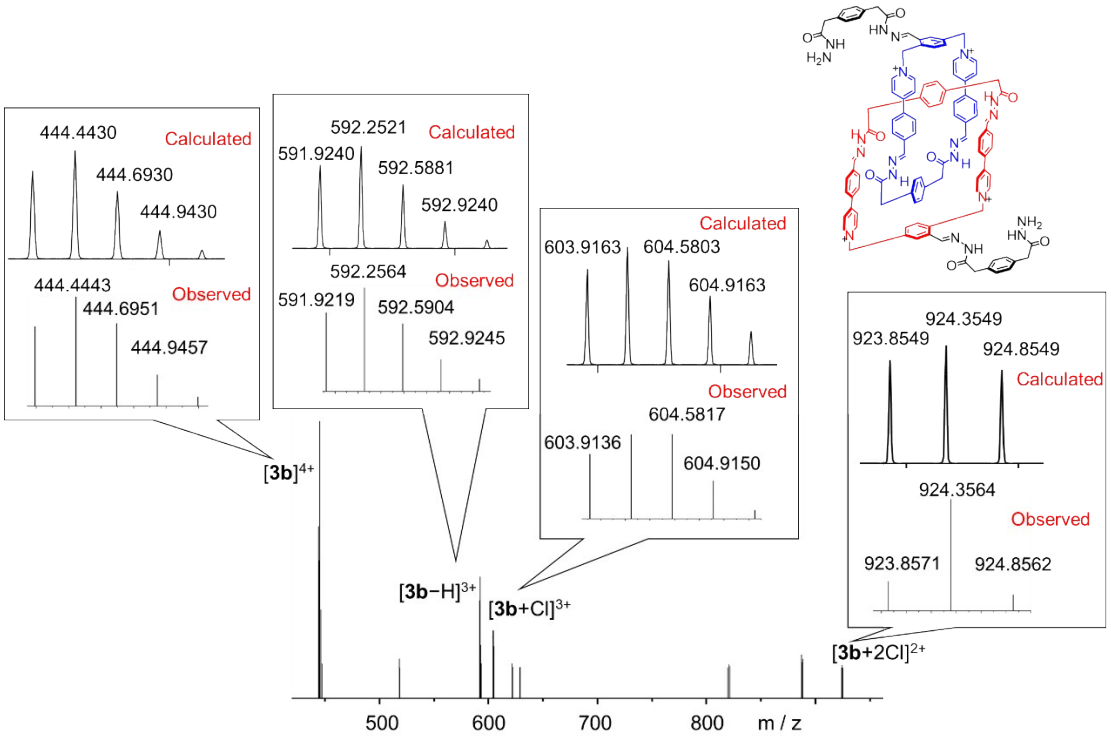

Figure S7. High-resolution ESI-Q-TOF-mass spectrum of $\mathbf{3b}^{4+}\cdot 4Cl^-$. The signal labeled in the spectrum correspond to molecular cations that contain four, three, and two positive charges, respectively, by either obtaining chloride counteranions or losing protons. *m/z* [**3b**]$^{4+}$ calculated for $C_{106}H_{96}N_{20}O_8^{4+}$: 444.4430; found: 444.4443. [**3a** — H]$^{3+}$ calculated for $C_{106}H_{95}N_{20}O_8^{3+}$: 592.2521; found: 592.2564. [**3a** + Cl]$^{3+}$ calculated for $C_{106}H_{96}ClN_{20}O_8^{3+}$: 603.9163; found: 603.9136. [**3a** + 2Cl]$^{2+}$ calculated for $C_{106}H_{96}Cl_2N_{20}O_8^{2+}$: 923.8549; found 923.8571.

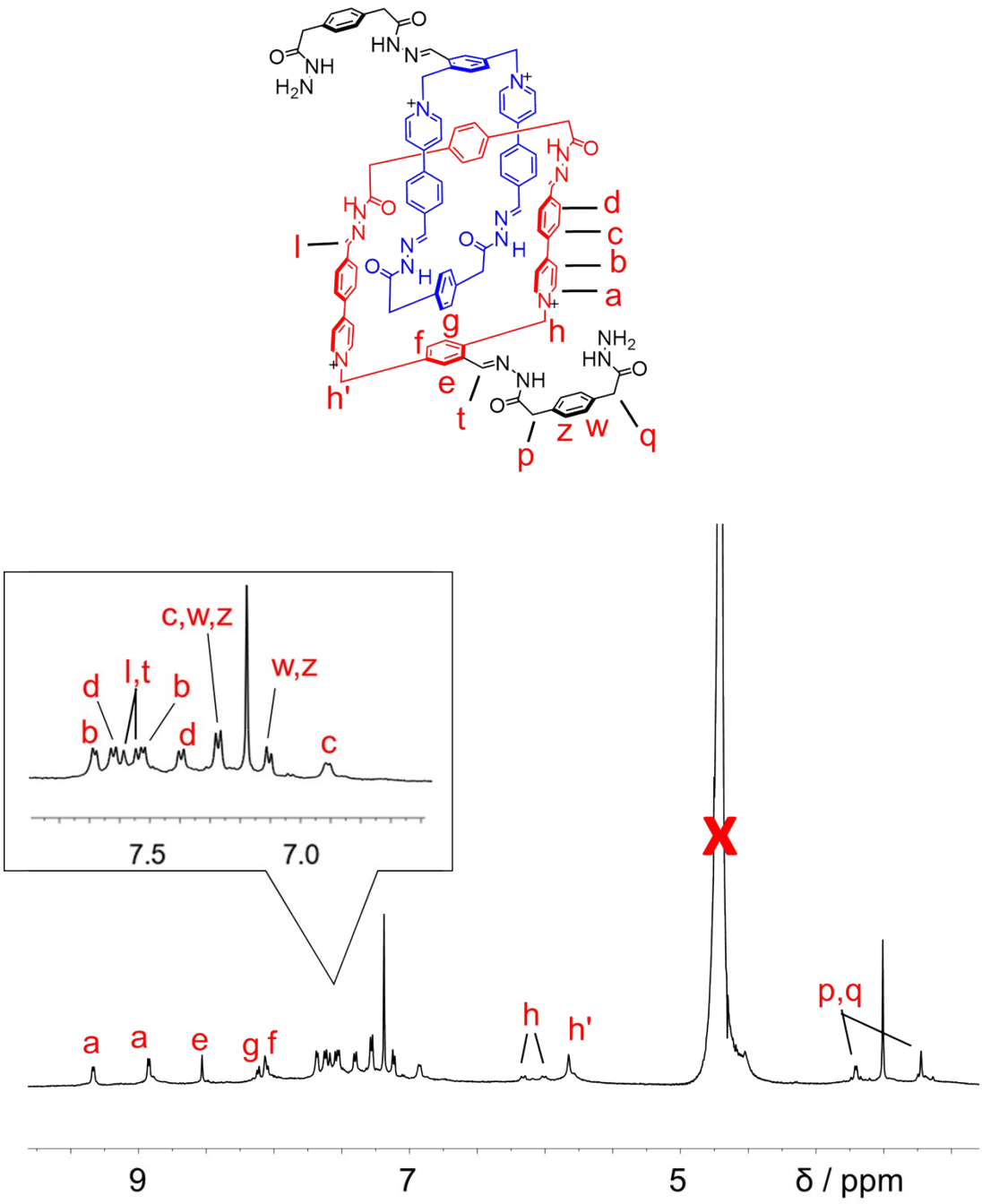

Figure S8. Partial ^{1}H NMR spectra (500 MHz, D_2O, 298 K) of **3b**$^{4+}$·4Cl^{-}. The resonance of protons h splits into two peaks, indicating that these two protons are diastereotopic.

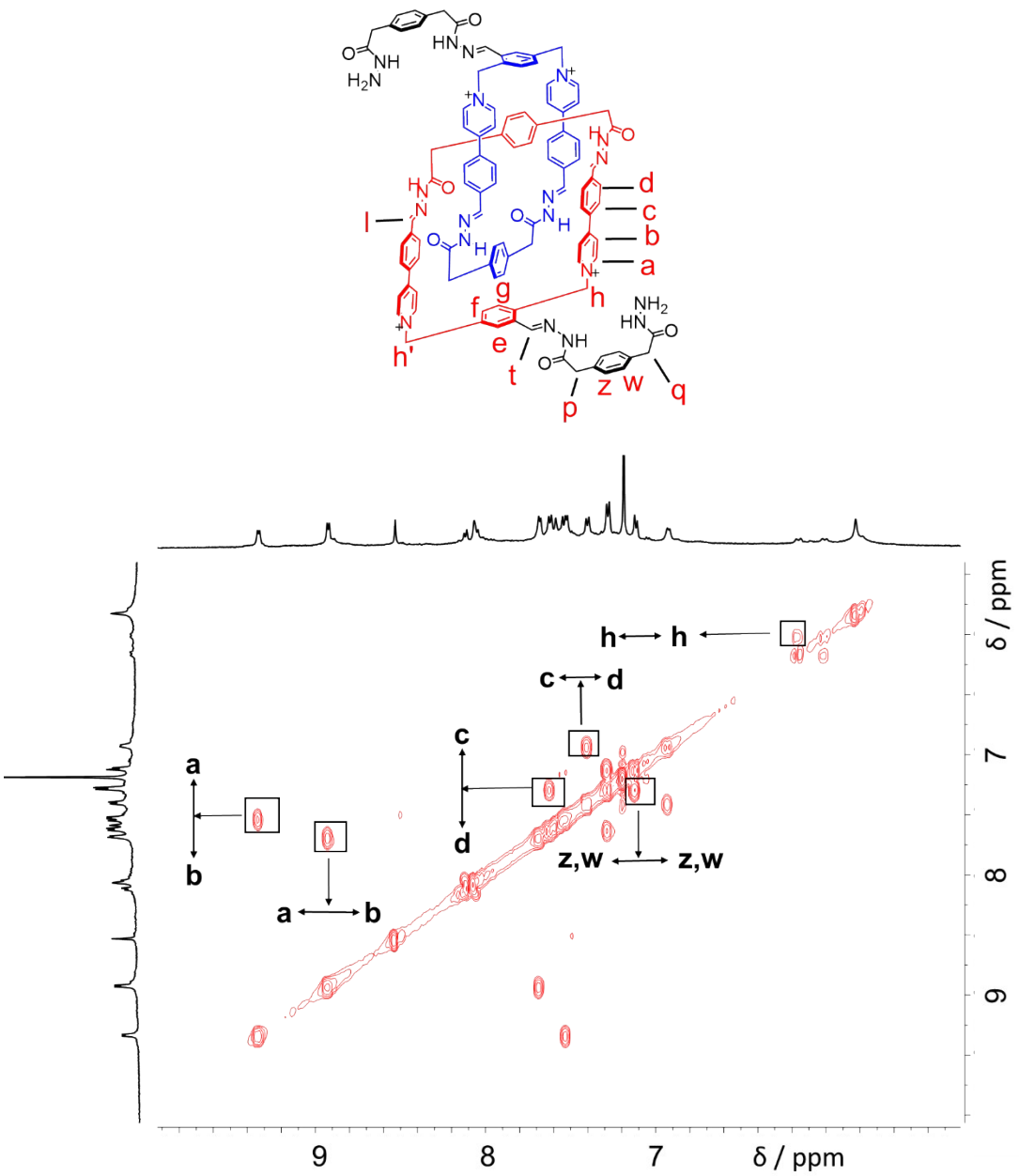

Figure S9. $^{1}H-^{1}H$ COSY spectrum (500 MHz, D_2O, 298 K) of **3b**$^{4+}$·4Cl^{-}. Key correlation peaks are labeled in the spectrum.

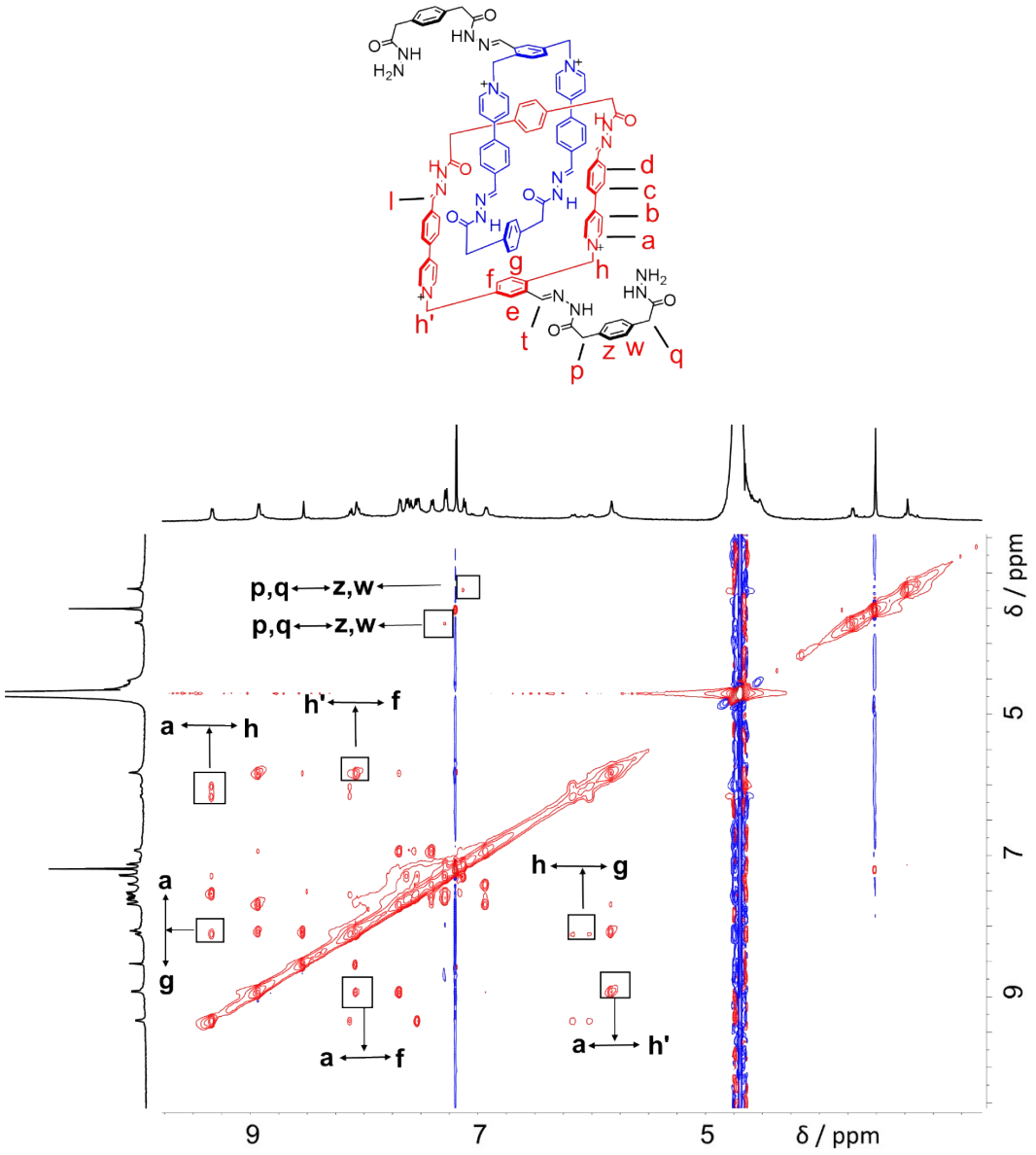

Figure S10. $^{1}H-^{1}H$ NOESY spectrum (500 MHz, D_2O, 298 K) of **3b**$^{4+}$·4Cl^{-}. Key correlation peaks are labeled in the spectrum.

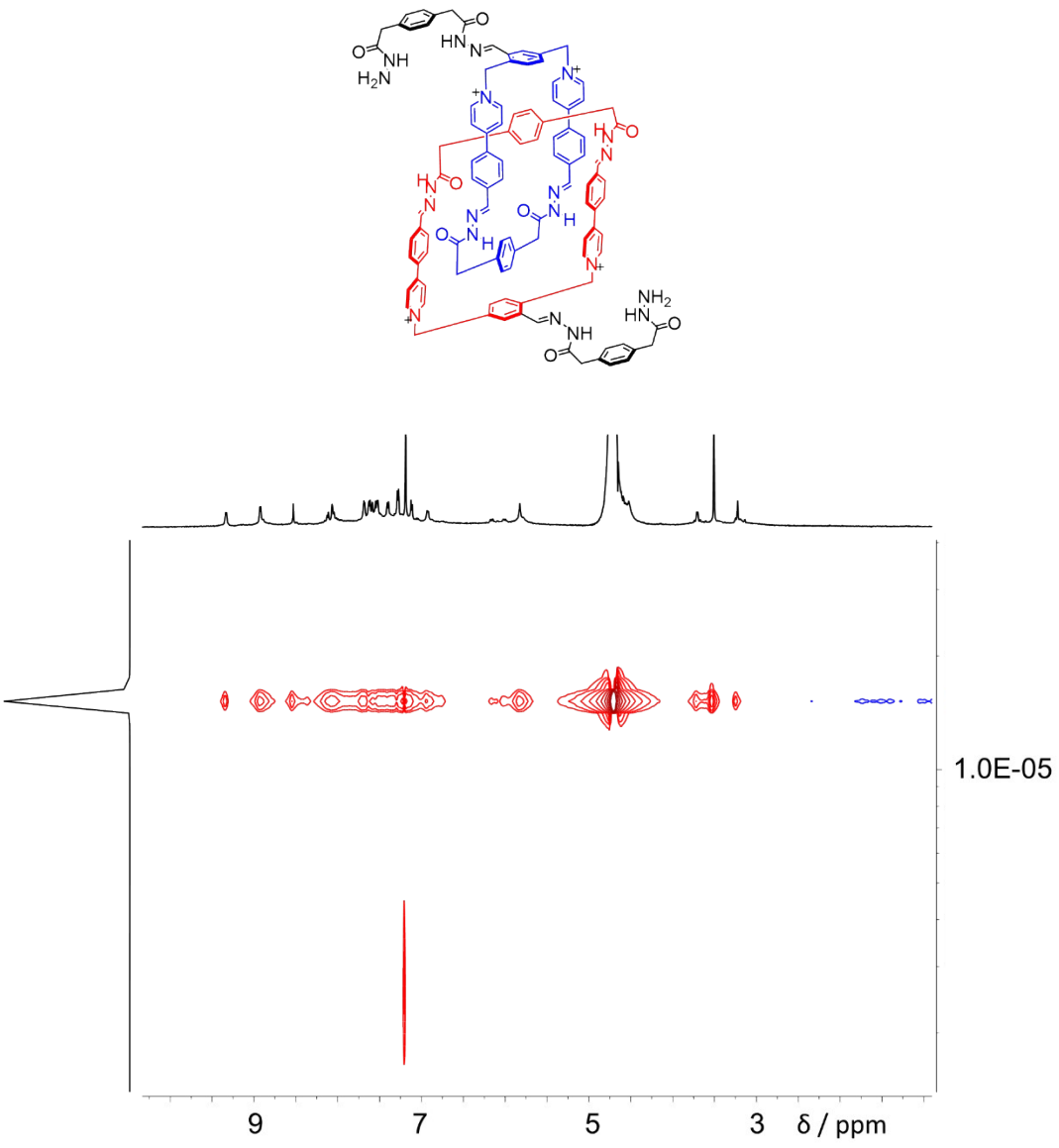

Figure S11. DOSY spectrum (500 MHz, D_2O, 298 K) of **3b**$^{4+}$·4Cl^{-}.

5. Characterization of $4a^{8+}\cdot 8Cl^-$ in D_2O by NMR, HRMS and HPLC.

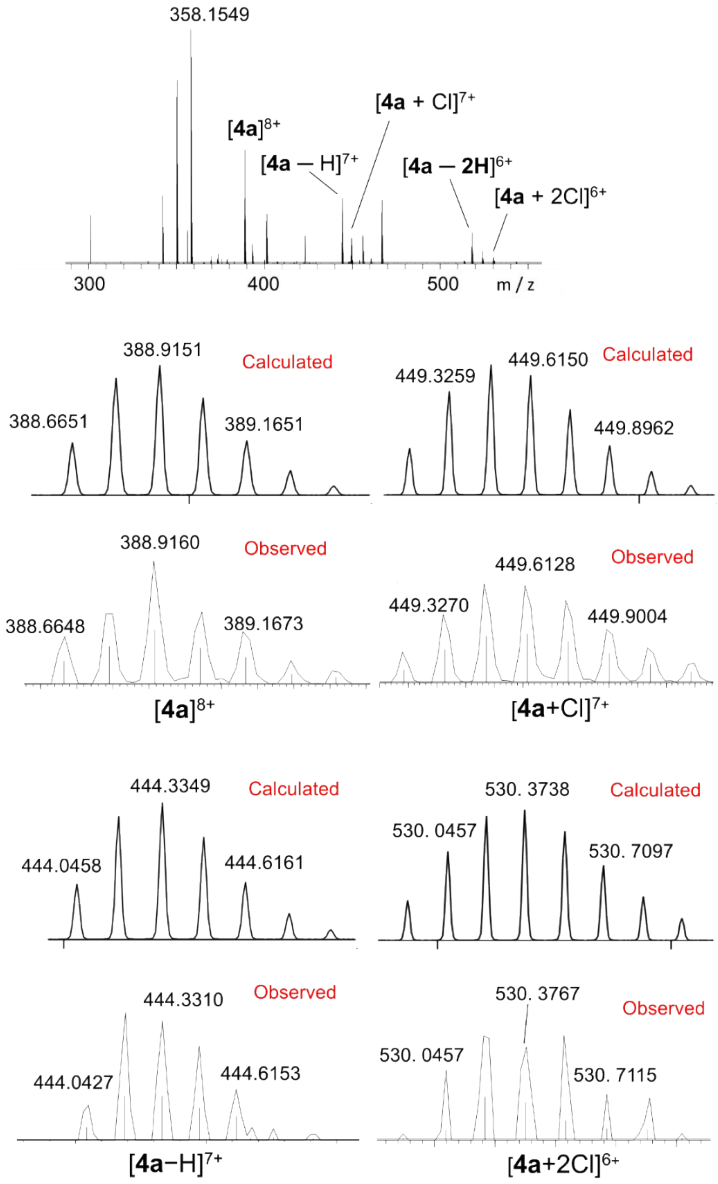

Figure S12. LCMS-IT-TOF mass spectrum of $\mathbf{4a}^{8+}\cdot 8Cl^-$. The signals labeled in the spectrum correspond to molecular cations that contain eight, seven, and six positive charges, respectively, by either obtaining chloride counteranions or losing protons. m/z $[4a]^{8+}$ calculated for $C_{192}H_{164}N_{32}O_{12}^{8+}$: 388.9151; found: 388.9160; *m/z* $[\mathbf{4a} + Cl]^{7+}$ calculated for $C_{192}H_{164}ClN_{32}O_{12}^{7+}$: 449.3259; found: 449.3270; $[\mathbf{4a} - H]^{7+}$ calculated for $C_{192}H_{163}N_{32}O_{12}^{7+}$: 444.3349; found: 444.3310. $[\mathbf{4a} + 2Cl]^{6+}$ calculated for $C_{192}H_{164}Cl_2N_{32}O_{12}^{6+}$: 530.3738; found: 530.3767.

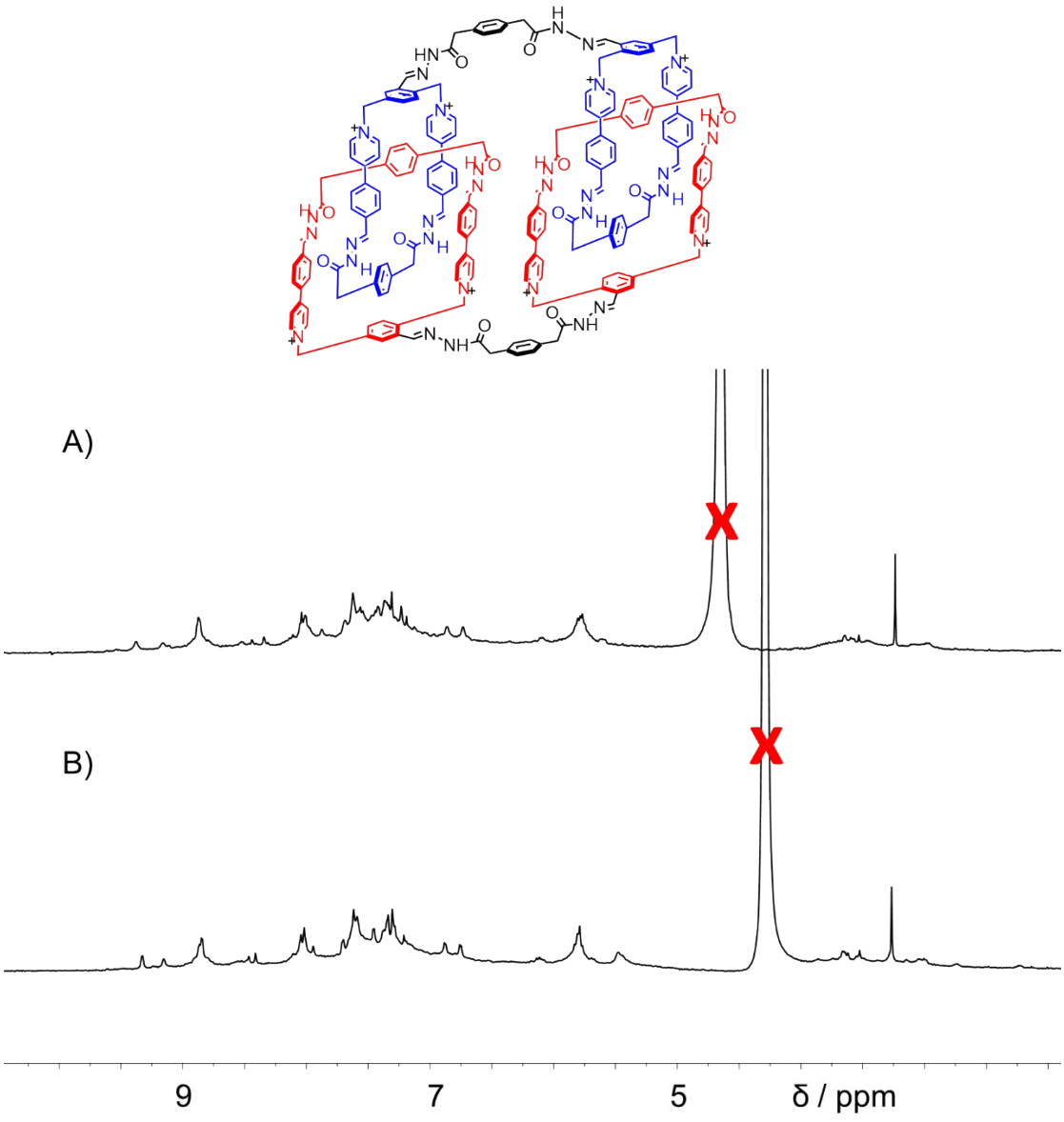

Fig. S13 Partial ^{1}H NMR spectra (600 MHz, D_2O) of **4a**$^{8+}$·8Cl^{-}. The spectra in A) and B) were recorded at 298 K and 333 K, respectively.

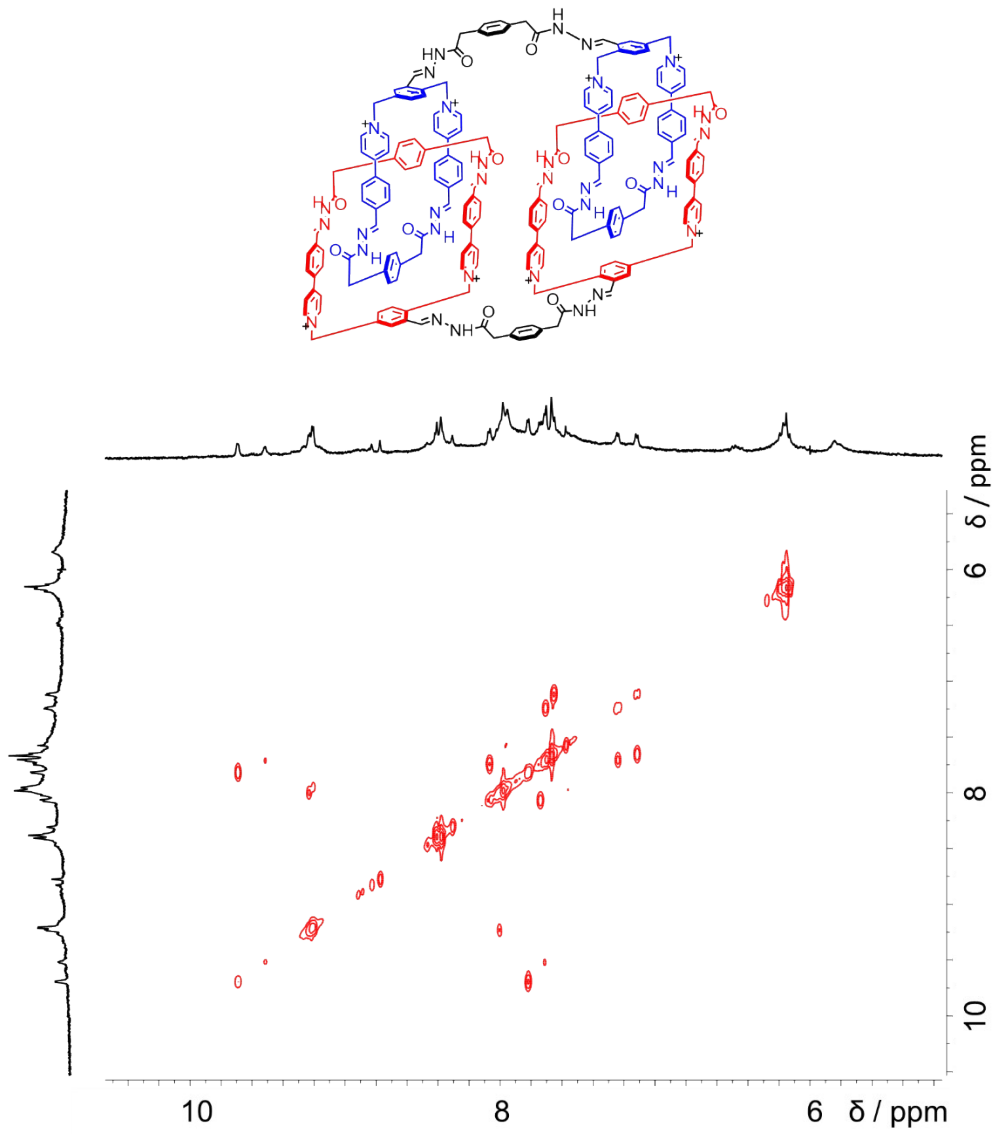

Figure S14. $^{1}H-^{1}H$ COSY spectrum (600 MHz, D_2O, 333 K) of **4a**$^{8+}\cdot 8Cl^{-}$.

6. Characterization of $4b^{8+}\cdot 8Cl^-$ in D_2O by NMR, HRMS and HPLC.

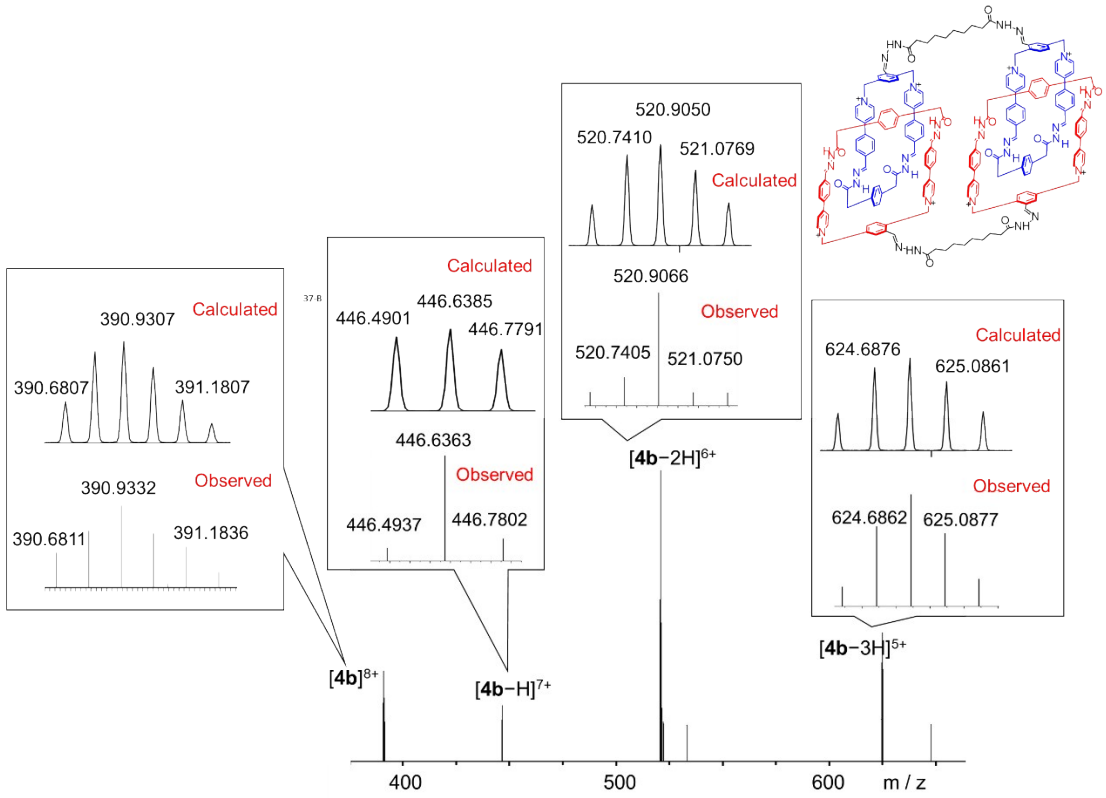

Figure S15. High-resolution ESI-Q-TOF-mass spectrum of $\mathbf{4b}^{8+}\cdot 8Cl^-$. The signal labeled in the spectrum correspond to molecular cations that contain eight, seven, six and five positive charges, respectively. *m/z* [**4b**]$^{8+}$ calculated for $C_{192}H_{180}N_{32}O_{12}^{8+}$: 390.9307; found: 390.9332. [**4b** — H]$^{7+}$ calculated for $C_{192}H_{179}N_{32}O_{12}^{7+}$: 446.6385; found: 446.6363. [**4b** — 2H]$^{6+}$ calculated for $C_{192}H_{178}N_{32}O_{12}^{6+}$: 520.9050; found: 520.9066. [**4b** — 3H]$^{5+}$ calculated for $C_{192}H_{177}N_{32}O_{12}^{5+}$: 624.6876; found: 624.6862.

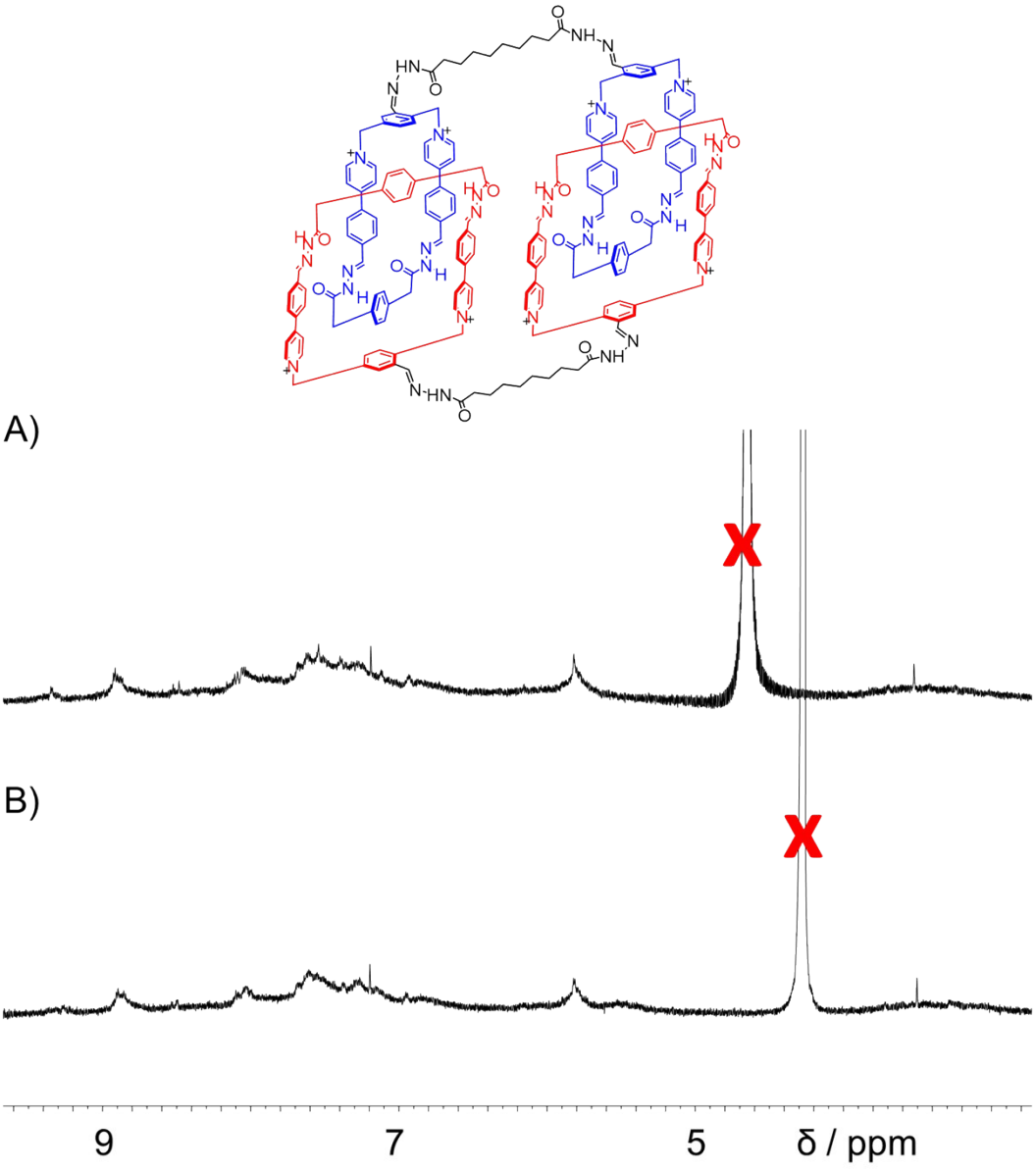

Fig. S16 Partial ^{1}H NMR spectra (600 MHz, D_2O) of **4b**$^{8+}$·8Cl^{-}. The spectra in A) and B) were recorded at 298 K and 333 K, respectively.

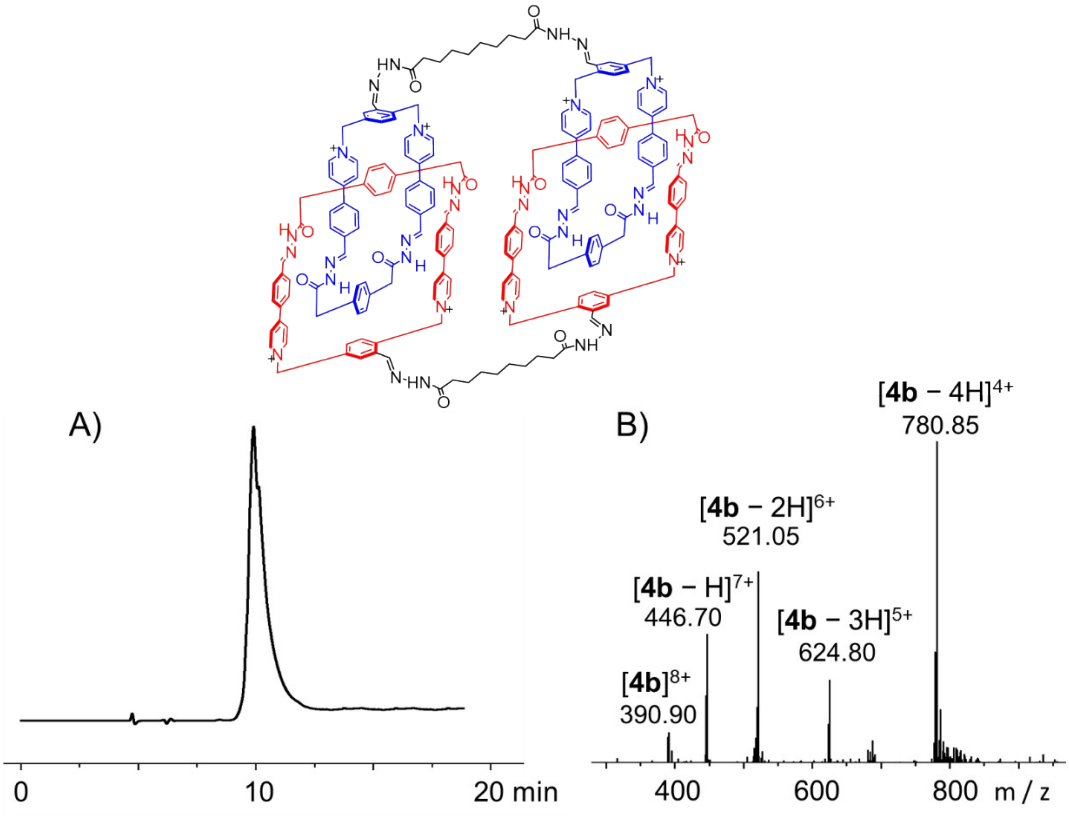

Figure S17. A) Reversed-phase HPLC analysis of the [2]catenane **4b**$^{8+}$·8Cl^{-}; B) corresponding low-resolution MS data, which is associated with the HPLC peak in A). The HPLC analysis was performed on an Agilent 1260 instrument. The following acetonitrile /water (both containing 0.1% acetate acid) gradient was used. In the beginning, 1/9 acetonitrile/water was used as the fluent phase, followed by gradually increasing the acetonitrile content from 10% to 100% acetonitrile over the course of 20 min. The detection wavelength was 250 nm.

7. Confirmation the reactive activity of two types of formyl functions in $\mathbf{1}^{2+}\cdot 2Cl^-$

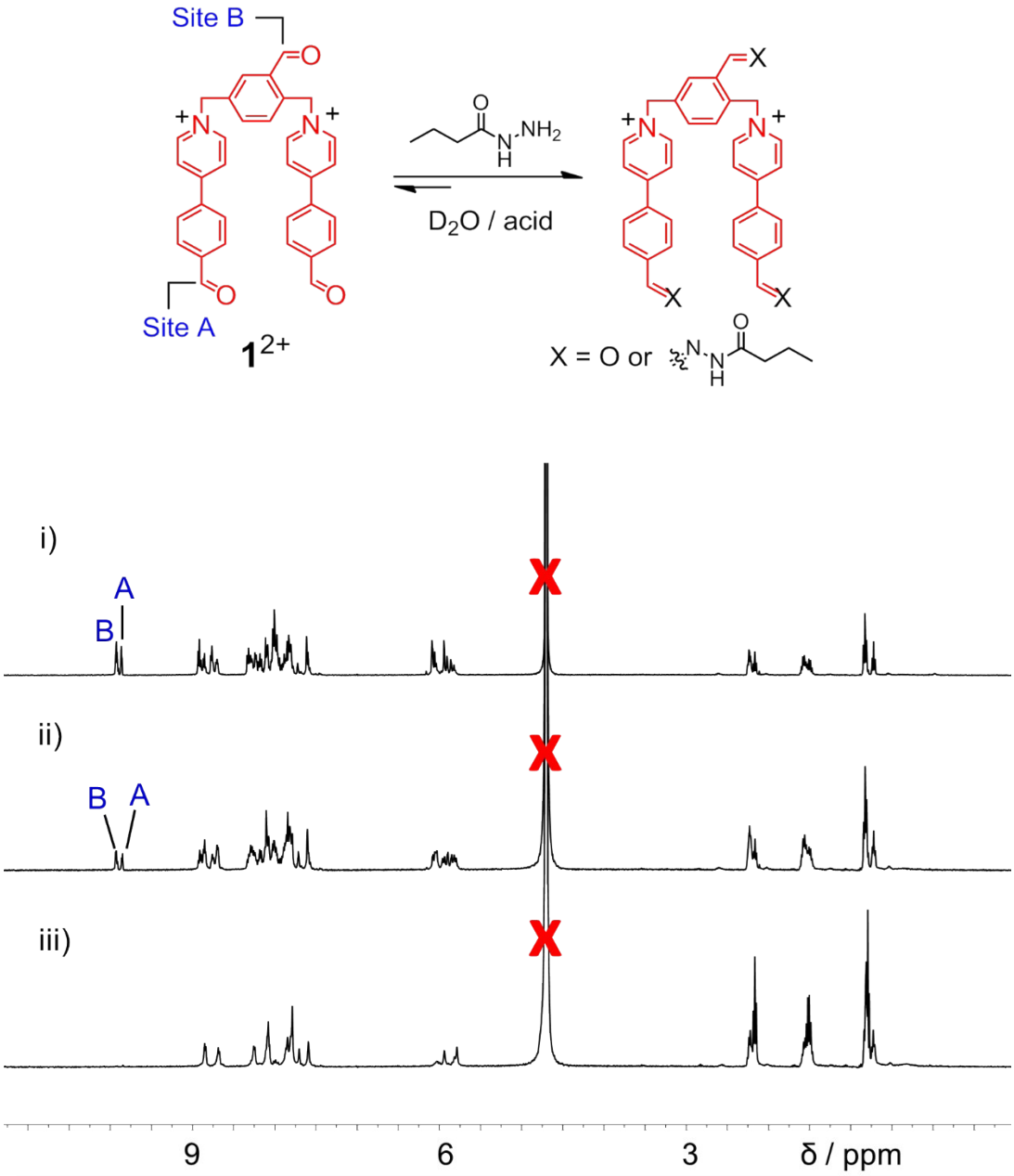

Figure S18. Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of the mixtures of $\mathbf{1}^{2+}\cdot 2Cl^-$ and butanehydrazide (**8**) in D_2O in a catalytic amount of DCl, after heading the solutions at 60 °C for 8 h. The ratios of $\mathbf{1}^{2+}\cdot 2Cl^-$ to **8** are i) 1:1, ii) 1:2, and iii) 1:3, respectively. ^{1}H NMR spectra indicate that two types of formyl functions (site A and site B) in $\mathbf{1}^{2+}\cdot 2Cl^-$ underwent random reaction unselectively, forming a library of mixtures containing both of the two formyl functional groups, in the case of two equiv of **8** (see ii).

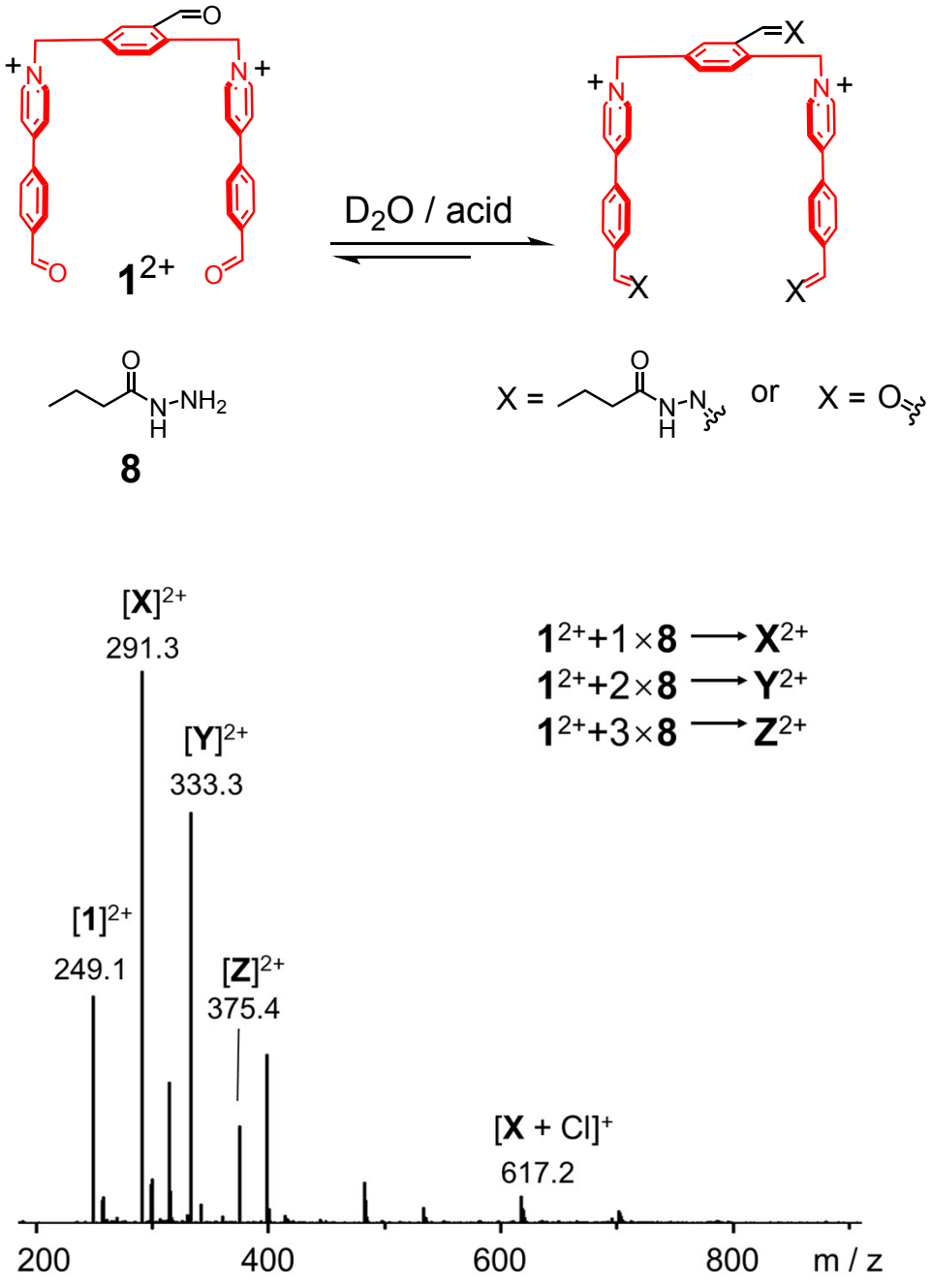

Figure S19. ESI Mass spectrum of a 1:1 mixture of $\mathbf{1}^{2+}\cdot 2Cl^{-}$ and **8**.

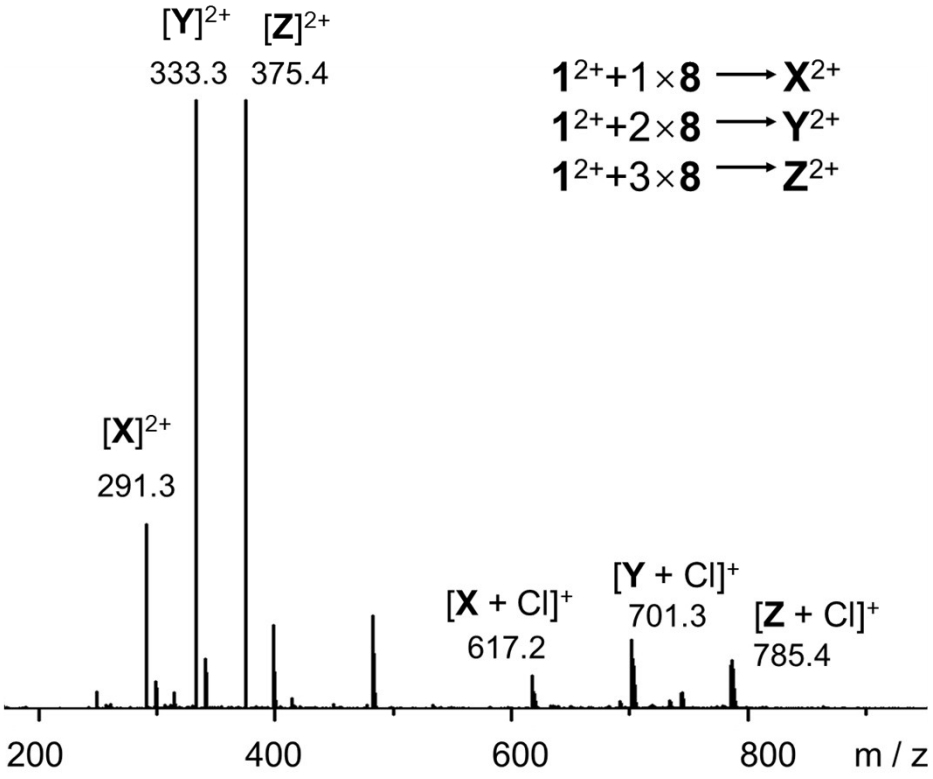

Figure S20. ESI Mass spectrum of a 1:2 mixture of $\mathbf{1}^{2+}\cdot 2Cl^{-}$ and **8**.

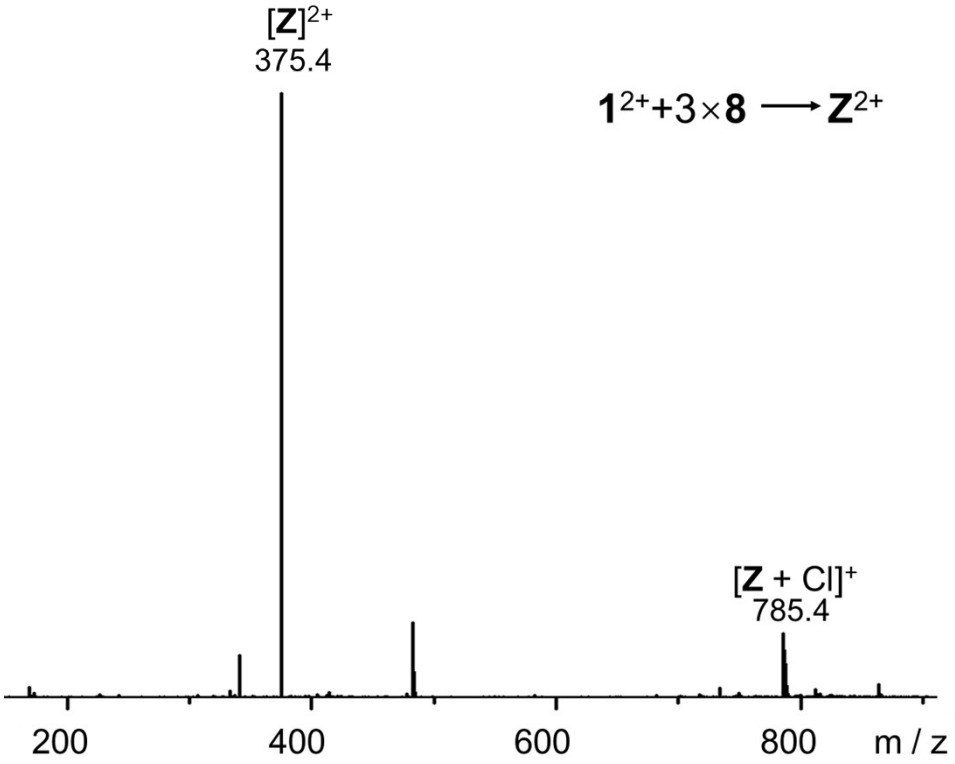

Figure S21. ESI Mass spectrum of a 1:3 mixture of $\mathbf{1}^{2+}\cdot 2Cl^{-}$ and **8**.

8. Complementary HPLC Analyses

The analytical HPLC experiment shown in Supplementary Figure 22-24 was performed on an Agilent 1260 instrument equipped with a diode array detector and an Agilent Zorbax SB-C18 column (4.6 x 150 mm, 5 µm). The following acetonitrile /water (both containing 0.1% acetate acid) gradient was used. In the beginning, 1/9 acetonitrile/water was used as the fluent phase, followed by gradually increasing the acetonitrile content from 10% to 100% acetonitrile over the course of 20 min. The detection wavelength was 254 nm.

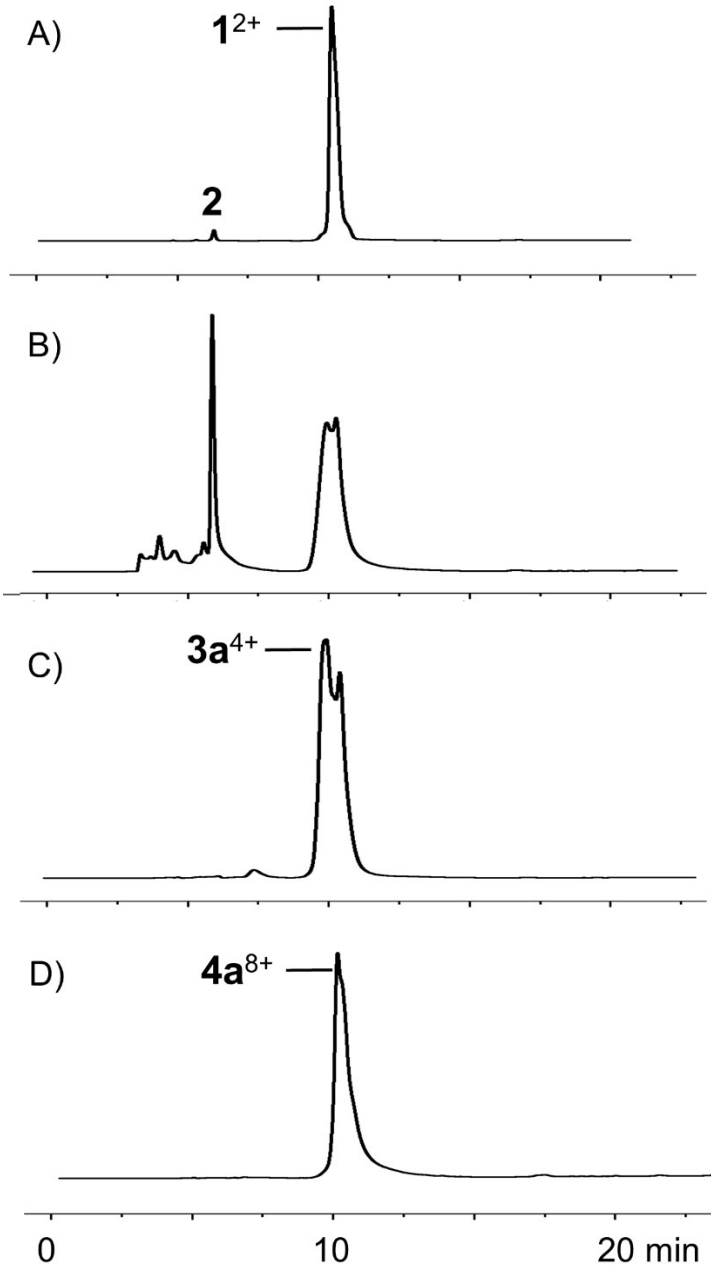

Figure S22. HPLC traces of a 2:3 reaction mixture of $\mathbf{1}^{2+}\cdot 2Cl^{-}$ and **2** when A) they were mixed in water in the absence of acid; B) when DCl was added into the solution and the resulting solution was heated at 60 °C for 1 h; C) when the same solution used in B) continued to be heated at 60 °C for 3 h, showing that a library of mixtures including the [2]catenane $\mathbf{3a}^{4+}$ were formed; and D) when the same solution used in C) continued to be heated for 4 h, showing that the cyclic [2]catenane dimer $\mathbf{4a}^{8+}$ finally became the major product. The corresponding peaks assigned to $\mathbf{1}^{2+}$, **2**, $\mathbf{3a}^{4+}$ and $\mathbf{4a}^{8+}$ are labelled in the HPLC traces in A), C) and D), respectively.

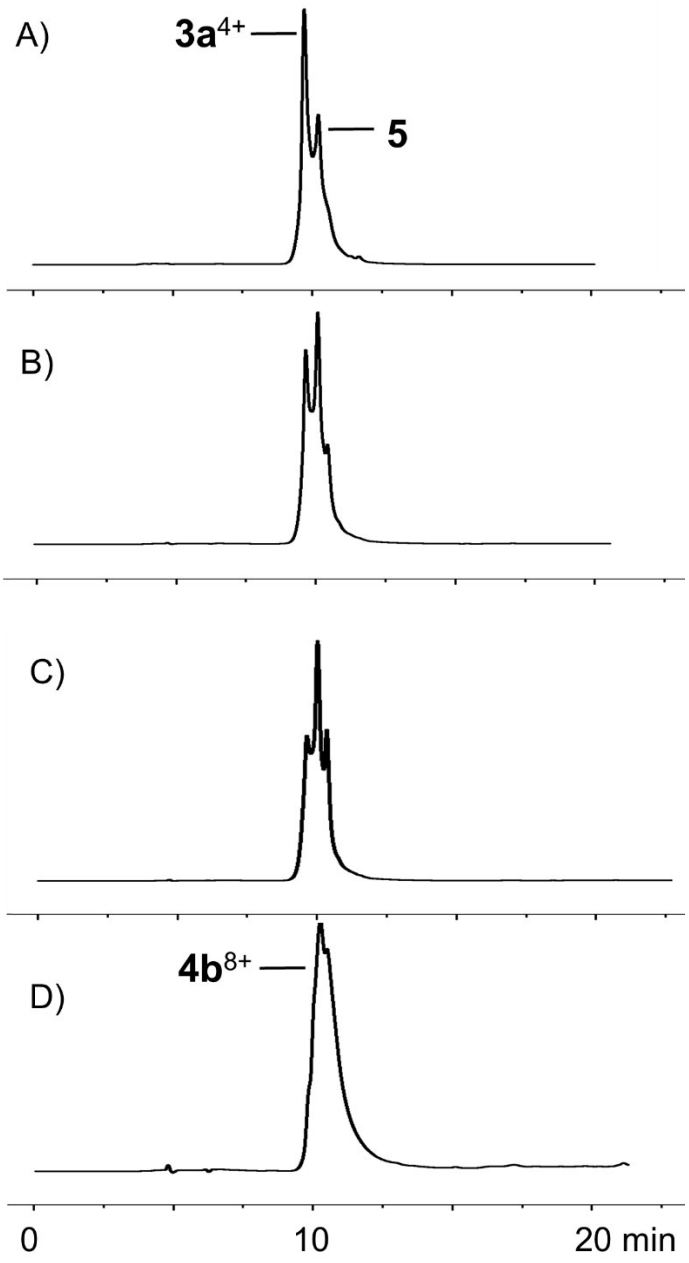

Figure S23. HPLC traces of a 1:1 reaction mixture of **3a**$^{4+}$·4Cl^{-} and **5** when A) they were mixed in water in the absence of acid; B) when DCl was added into the solution and the resulting solution was heated at 60 °C for 1 h; C) when the same solution used in B) continued to be heated at 60 °C for 2 h; and D) when the same solution used in C) continued to be heated for 4 h, showing that the cyclic [2]catenane dimer **4a**$^{8+}$ finally became the major product. The corresponding peaks assigned to **5**, **3a**$^{4+}$ and **4b**$^{8+}$ are labelled in the HPLC traces in A) and D), respectively.

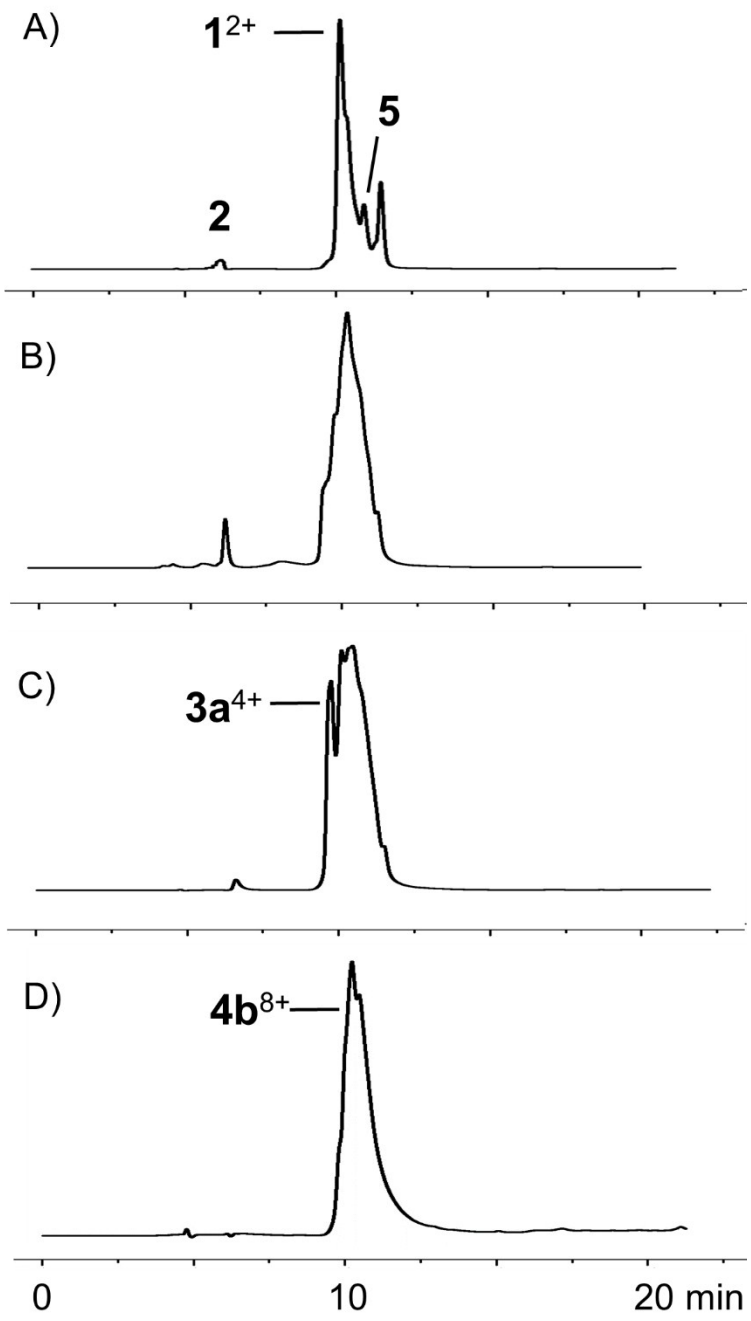

Figure S24. HPLC traces of a 2:2:1 reaction mixture of $\mathbf{1}^{2+}\cdot 2Cl^{-}$, **2** and **5** when A) they were mixed in water in the absence of acid; B) when DCl was added into the solution and the resulting solution was heated at 60 °C for 1 h; C) when the same solution used in B) continued to be heated at 60 °C for 2 h; and D) when the same solution used in C) continued to be heated for 4 h, showing that the cyclic [2]catenane dimer $\mathbf{4b}^{8+}$ finally became the major product. The corresponding peaks assigned to $\mathbf{1}^{2+}$, **2**, **5**, $\mathbf{3a}^{4+}$ and $\mathbf{4b}^{8+}$ are labelled in the HPLC traces in A), C) and D), respectively.