Precursor Control Over the Self-Assembly of [2]Catenanes via

Hydrazone Condensation in Water

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Supporting Information

Table of Contents

- 1. General Methods
- 2. Synthetic Procedures
- 3. Characterization of 3b⁴⁺ and 3d⁴⁺ in D₂O by NMR and HRMS

4. Characterization of 3f⁴⁺ in both D₂O and CD₃CN by NMR and HRMS

- 5. Thermodynamic Stability Investigations
- 6. Yields of the Formation of $3b^{4+}$, $3d^{4+}$ and $3f^{4+}$ in Solutions.
- 7. X-ray Crystallography
- 8. References

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 for ¹H and 100/125/150 MHz for ¹H and ¹³C, respectively. Chemical shifts are reported in ppm relative to the residual internal non-deuterated solvent signals (D₂O: $\delta = 4.79$ ppm, DMSO-d₆: $\delta = 2.50$ ppm, CD₃CN: $\delta = 1.94$ ppm). High-resolution mass spectra were measured by using either a SHIMADZU liquid chromatograph mass spectrometry ion trap time of flight (LCMS-IT-TOF) instrument, or a gas chromatography time of flight (GCTOF-HRMS) GCT premier (Waters, USA) instrument. X-ray crystallographic data were collected on a Bruker D8 Venture.

2. Synthetic Procedures

The dihydrazine linkers, including 2a, 2b, 2c, 2d, 2e, were prepared according to literature procedures.¹



Scheme S1. Synthesis of 1²⁺·2Cl⁻

1²⁺·2Cl⁻: α,α'-dibromo-p-xylene (263 mg, 1.0 mmol) and 4-(4-formylphenyl)pyridine (366 mg, 2.0 mmol) were dissolved in 15 ml MeCN in a sealed tube. The reaction mixture was stirred at 85 °C for 8 h, during which a light yellow precipitate was formed. After cooling the reaction system to room temperature, the precipitate was filtered and collected, which was washed with petroleum ether and ethyl acetate to give a light yellow solid 1²⁺·2Br⁻ (649 mg, >99 %). Small amount of solvent might be contained in the solid products. 1²⁺·2Br⁻ was changed into its more water soluble counterpart 1²⁺·2Cl⁻ (486 mg, 90 %) as a white powder by means of counteranion exchange. ¹H NMR (400 MHz, D₂O): δ = 9.95 (s, 2H), 8.90 (d, J = 6.7 Hz, 4H), 8.31 (d, J = 6.7 Hz, 4H), 8.05 (d, J = 8.3 Hz, 4H), 8.00 (d, J = 8.3 Hz, 4H), 7.54 (s, 4H), 5.83 (s, 4H). ¹³C NMR (100 MHz, CD₃CN): δ = 195.4, 155.8, 144.5, 139.5, 137.6, 134.5, 130.7, 129.9, 128.8, 126.0, 63.3. MS (LCMS-IT-TOF): *m/z* [M–2Cl]²⁺ calcd for C₃₂H₂₆O₂N₂²⁺: 235.0992; found: 235.0975.



Scheme S2. Synthesis of 2f

2f: A mixture of 1,4-phenylenediacetic acid dimethyl ester (222 mg, 1.0 mmol) and hydrazine

hydrate (0.75 ml, 10.0 mmol) was refluxed in ethanol (15 mL) in a round flask for 8 h, during which a white solid was precipitated. After cooling the reaction system to room temperature, the precipitate was filtered and collected, which was washed with ethanol and petroleum ether to give a white solid **2f** (213 mg, 96 %). ¹**H NMR** (400 MHz, D₂O): $\delta = 7.15$ (s, 4H), 3.43 (s, 4H). ¹³**C NMR** (100 MHz, D₂O): $\delta = 173.4$, 133.5, 129.4, 39.9. **MS (GCTOF-HRMS)**: *m/z* [M]⁺ calcd for C₁₀H₁₄N₄O₂: 222.1117, found: 222.1123.



Scheme S3. Synthesis of 3b⁴⁺ and 3d⁴⁺ (the counteranion could be either Cl⁻ or CF₃COO⁻).

We combined $1^{2+} \cdot 2Cl^-$ (0.54 mg, 0.001 mmol) with each of the dihydrazine linkers **2a-2e** (0.001 mmol) in a 1:1 ratio, in D₂O (0.5 mL) in the presence of catalytic amount of TFA (5 µL). After heating the corresponding solutions at 50 °C for 8 h, the ¹H NMR and mass spectra of the corresponding solutions were recorded. It was demonstrated that in the case of **2b** and **2d**, the [2]catenanes **3b**⁴⁺ and **3d**⁴⁺ (counteranions could be either Cl⁻ or CF₃COO⁻) were produced as the major products, as inferred from the corresponding ¹H NMR spectroscopic results (Figure S1 B,

3. Characterization of 3b⁴⁺ and 3d⁴⁺ in D₂O by NMR and HRMS



Figure S1. The ¹H NMR spectra (600 MHz, D₂O, 298 K) of the self-assembled products by condensing $1^{2+} \cdot 2Cl^-$ with A) **2a**, B) **2b**, C) **2c**, D) **2d**, E) **2e**. The counteranion could be either Cl⁻ or CF₃COO⁻.

In the case of 2a, 2c, and 2e, ¹H NMR spectroscopy indicated (Figure S1 A, C, E) that hydrazone

condensation produces a library of mixture products that is hard to characterize, although mass

spectrometry (Figure S6, S7, S8) shows the presence of the catenane products as the minor products. We tried to increase the yields of catenane by adding NaCl into the corresponding NMR samples, which might strengthen hydrophobic interactions. However, in the case of **2a**, **2c** and **2e**, addition of NaCl (0.5 mg) led to nearly complete precipitation of the self-assembled products in the NMR tubes. In the case of both **3b**⁴⁺ and **3d**⁴⁺, addition of NaCl (0.5 mg) into the NMR samples (All of these NMR samples contain 0.54 mg **1**^{2+.}2Cl⁻ resolved in 0.5 ml D₂O.) led to diminish of the resonances of byproducts, as inferred from the corresponding ¹H NMR spectra (Figure S2 B, D). The yields of **3b**⁴⁺ and **3d**⁴⁺ (counteranions could be either Cl⁻ or CF₃COO⁻) were determined by using an internal standard in the corresponding ¹H NMR samples (Figure S35, S36). The structures of **3b**⁴⁺ and **3d**⁴⁺ were further convinced by using mass spectrometry (Figure S4, S5) and NMR spectroscopy. DOSY spectra provided evidence that a single species was formed. Two-dimensional NMR spectra, including COSY and NOESY, were used to make peak assignments for the ¹H NMR spectra.



Figure S2. The ¹H NMR spectra (600 MHz, D₂O, 298 K) of the [2]catenanes $3b^{4+}$ and $3d^{4+}$ (The counteranion could be either Cl⁻ or CF₃COO⁻). Spectra A) and B) are the spectra of $3b^{4+}$, which were recorded before A) and after B) (0.5 mg NaCl) was added into the NMR sample; Spectra C) and D) are the spectra of $3d^{4+}$, which were recorded before C) and after D) (0.5 mg NaCl) was added into the NMR sample.

In the ¹H NMR spectrum (Figure S3 A) of the catenane $3d^{4+}$, the resonances of the phenyl protons e and f in the 4-phenylpyridinium residues undergo remarkable upfield shift, indicating that the phenyl units, instead of the polymethylene chains, are located within the cavity of another macrocycle and thus experience a shielded magnetic environment. This co-conformation reflects the fact that the polymethylene chains cannot provide strong enough hydrophobic effect to drive their formation of $3d^{4+}$. Each of its two macrocycles therefore chooses to encircle the phenyl group in one of the two 4-phenylpyridinium residues. The two phenylpyridinium residues in each of the two macrocycles of 3d⁴⁺ are equivalent in the ¹H NMR spectrum (Figure S3 A), an observation indicating the occurrence of fast circumvolution of the two interlocked rings with respect to each other on the ¹H NMR timescale. In the ¹H NMR spectrum (Figure S3 C) of the [2] catenane $3b^{4+}$, however, the resonances of the corresponding protons d, f and e, become remarkably broad. This observation indicates circumvolution motion in the case of $3b^{4+}$ are relatively slower than that of $3d^{4+}$. This is because $3b^{4+}$ is composed of two smaller macrocycles bearing two shorter $(CH_2)_5$ chains than the $(CH_2)_7$ chains in $3d^{4+}$. We also recorded the ¹H NMR spectrum (Figure S3 B) of **3b**⁴⁺ at 60 °C, in which the corresponding resonances become sharper, an observation indicating that circumvolution was speeded up at elevated temperatures. The effort to calculate the activation energy barrier of this circumvolution by means of Eyring equation is unsuccessful, on account of the relatively high freezing point of D_2O . The structures of both $3b^{4+}$ and $3d^{4+}$ are further confirmed by using a variety of two-dimensional NMR spectroscopy (see Fig. S9-S14 in SI).



Fig. S3 Partial ¹H NMR spectra (600 MHz, D₂O, 0.5 mg NaCl) of A) $3d^{4+}$, B) $3b^{4+}$, and C) $3b^{4+}$. Counteranions are either CF₃CO₂⁻ or Cl⁻. The spectra in A) and C) were recorded at 298 K, while that in B) was taken at 333 K.



Figure S4. LCMS-IT-TOF of $3b^{4+}$ (The counteranion could be either Cl⁻ or CF₃COO⁻). The signal labeled in the spectrum correspond to molecular cations that contain four, three, and two positive charges, respectively, which reflects losing varying numbers of (between 0 and 2) protons.



Figure S5. LCMS-IT-TOF of $3d^{4+}$ (The counteranion could be either Cl⁻ or CF₃COO⁻). The signal labeled in the spectrum correspond to molecular cations that contain four, three, and two positive charges, respectively, which reflects losing varying numbers of (between 0 and 2) protons.



Figure S6. LCMS-IT-TOF of the self-assembled products of 1^{2+} and 2a in D₂O. (The counteranion could be either Cl⁻ or CF₃COO⁻). $3a^{4+}$ was not observed in an appreciable yield in mass spectrometry.



Figure S7. LCMS-IT-TOF of $3c^{4+}$ (The counteranion could be either Cl⁻ or CF₃COO⁻). The signal labeled in the spectrum correspond to molecular cations that contain four, three, and two positive charges, respectively, which reflects losing varying numbers of (between 0 and 2) protons.



Figure S8. LCMS-IT-TOF of $3e^{4+}$ (The counteranion could be either Cl⁻ or CF₃COO⁻). The signal labeled in the spectrum correspond to molecular cations that contain four and three positive charges, respectively, which reflects losing varying numbers of (between 0 and 1) proton.



Figure S9. ¹H-¹H COSY spectrum of $3b^{4+}$ (600 MHz, D₂O, 333 K). Key correlation peaks are labeled in the spectrum. The counteranion could be either Cl⁻ or CF₃COO⁻.



Figure S10. ¹H-¹H NOESY spectrum of **3b**⁴⁺ (500 MHz, D₂O, 333 K). Key correlation peaks are labeled in the spectrum. The counteranion could be either Cl⁻ or CF₃COO⁻.



Figure S11. DOSY spectrum of $3b^{4+}$ (500 MHz, D₂O, 333 K). The counteranion could be either Cl⁻ or CF₃COO⁻.



Figure S12. ¹H–¹H gradient-selected double-quantum filtered phase-sensitive COSY spectrum of $3d^{4+}$ (500 MHz, D₂O, 298 K). The counteranion could be either Cl⁻ or CF₃COO⁻.



Figure S13. ¹H-¹H NOESY spectrum of **3d**⁴⁺ (500 MHz, D₂O, 298 K). The counteranion could be either Cl⁻ or CF₃COO⁻. Key correlation peaks are labeled in the spectrum.



Figure S14. DOSY spectrum of $3d^{4+}$ (500 MHz, D₂O, 298 K). The counteranion could be either Cl⁻ or CF₃COO⁻.

4. Characterization of **3f**⁴⁺ in both D₂O and CD₃CN by NMR and HRMS



Figure S15. LCMS-IT-TOF of $3f^{4+}$ (The counteranion could be either Cl⁻ or CF₃COO⁻). The signal labeled in the spectrum correspond to molecular cations that contain four, three, and two charges, respectively, reflecting varying numbers of (between 2 and 0) attached protons.

We combined $1^{2+} 2Cl^-$ (0.54 mg, 0.001 mmol) with **2f** (0.22 mg, 0.001 mmol) in a 1:1 ratio, in 0.5 ml D₂O in the presence of catalytic amount of TFA (5 µL). After heating the corresponding solutions at 50 °C for 8 h, the ¹H NMR (see Figure 2C in the main text) and mass spectrum (Figure S15) of the corresponding solution were recorded. To our delight, a new set of sharp resonances was observed in the ¹H NMR spectrum, indicating the formation of a single thermodynamically stable product, namely the [2]catenane **3f**⁴⁺, whose counteranions are either CF₃CO₂⁻ or Cl⁻.



Figure S16. Partial ¹H NMR spectrum (500 M Hz, 298 K, 1:1 D₂O/DMSO-d₆) of **3f**⁴⁺, which was self-assembled in a 1:1 D₂O/DMSO-d₆ solution. Counteranions are either $CF_3CO_2^-$ or Cl^- . Unreacted **2f** was also observed in the ¹H NMR spectrum.

The [2]catenane **3f**⁴⁺, whose counteranions are either CF₃CO₂⁻ or Cl⁻, could also be selfassembled by performing the condensation of **1**^{2+.}2Cl⁻ (0.54 mg, 0.001 mmol) with **2f** (0.22 mg, 0.001 mmol) in a 1:1 ratio, in the mixture solution containing 1:1 D₂O/DMSO-d₆ (0.25 mL/0.25 mL) in the presence of catalytic amount of TFA (5 μ L), as indicated by the ¹H NMR spectrum (Figure S16). This experiment indicates that the formation **3f**⁴⁺ is thermodynamically favored even in the less polar media where hydrophobic interactions are suppressed.



Figure S17. ¹H–¹H gradient-selected double-quantum filtered phase-sensitive COSY spectrum of **3f**⁴⁺ (600 MHz, D₂O, 333 K). (The counteranion could be either Cl⁻ or CF₃COO⁻).

The structure of **3f**⁴⁺ was further convinced two dimensional NMR spectroscopy. Twodimensional NMR spectra, including COSY (Figure S17) and NOESY (Figure S18), were used to make peak assignments for the ¹H NMR spectra. DOSY spectra (Figure S19) provided evidence that a single species was formed.



Figure S18. ¹H-¹H NOESY spectrum of **3f**⁴⁺(500 MHz, D₂O, 333 K). Key correlation peaks are labeled in the spectrum. (The counteranion could be either Cl⁻ or CF₃COO⁻).



Figure S19. DOSY spectrum of $3f^{4+}$ (500 MHz, D₂O, 332 K). (The counteranion could be either Cl⁻ or CF₃COO⁻).





Figure S20. ¹H NMR spectra of $3f^{4+}$ (The counteranion could be either Cl⁻ or CF₃COO⁻) at variable temperatures in D₂O (600 M Hz).

The ¹H NMR spectrum of **3f**⁴⁺ is temperature dependent in D₂O. At room temperature (25 °C), the resonances of the protons g and i (see Figure S20) are remarkably broad. 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, indicating that the circumvolution motion is "speeded up" at higher temperatures.



Figure S21. Partial ¹H NMR spectrum (500 M Hz, 298 K, CD₃CN) of $3f^{4+.}4PF_6^{-}$.



Figure S22. ¹³C NMR spectrum (500 M Hz, 298 K, CD₃CN) of $3f^{4+}\cdot 4PF_6^-$.



Figure S23. ¹H–¹H gradient-selected double-quantum filtered phase-sensitive COSY spectrum of $3f^{4+} \cdot 4PF_6^-$ (500 MHz, D₂O, 298 K).

The [2]catenane **3f**⁴⁺, whose counteranions are either CF₃CO₂⁻ or Cl⁻, could be transformed to its organic solvent soluble counterpart with PF₆⁻ salt by means of counteranion exchange. The structure of **3f**^{4+.4}PF₆⁻ was fully characterized by ¹H (see Figure S21) and ¹³C (see Figure S22) NMR spectroscopy. Two-dimensional NMR spectra, including COSY (Figure S23), NOESY (Figure S24) and DOSY (Figure S25), were used to make peak assignments for the ¹H NMR spectra. It is noteworthy that the NMR spectroscopy indicates that the co-conformation of **3f** ^{4+.4}PF₆⁻ in CD₃CN is essentially the same as **3f**^{4+.4}Cl⁻ in D₂O. Once dissolved in CD₃CN, **3f**^{4+.4}PF₆⁻ is relatively stable.



Figure S24. ¹H-¹H NOESY spectrum of $3f^{4+.}4PF_6^-$ (500 MHz, CD₃CN, 298 K). Key correlation peaks are labeled in the spectrum.



Figure S25. DOSY spectrum of $3f^{4+.}4PF_6^-$ (500 MHz, D₂O, 298 K).

5. Thermodynamic Stability Investigations



Figure S26. Partial ¹H NMR spectra (600 M Hz, D₂O, 298 K) of A) $3d^{4+}$, B) 1:1:2 mixture of 2b, 2d and 1^{2+} , and C) $3b^{4+}$. The counteranions could be either Cl⁻ or CF₃COO⁻.

When $1^{2+} \cdot 2Cl^-$, **2b** and **2d** were combined in D₂O in a 2:1:1 ratio, heating the mixture solution produces a library of three catenane products, namely **3b**⁴⁺ and **3d**⁴⁺, as well as their hybridized catenane **3b/d**⁴⁺, as indicated by both ¹H NMR (Figure S26) and mass spectrum (Figure S27).



Figure S27. Partial LCMS-IT-TOF spectrum of the self-assembled products of 1:1:2 mixture of **2b**, **2d** and 1^{2+} . The counteranion could be either Cl⁻ or CF₃COO⁻.



Figure S28. Partial ¹H NMR spectra (600 M Hz, D₂O, 298 K) of A) $3f^{4+}$, B) 1:1:2 mixture of 2f, 2d and 1^{2+} , and C) $3d^{4+}$. The counteranions could be either Cl⁻ or CF₃COO⁻.



Figure S29. Partial LCMS-IT-TOF spectrum of the self-assembled products of 1:1:2 mixture of 2f, 2d and 1^{2+} . The counteranion could be either Cl⁻ or CF₃COO⁻.

However, when the same experiment was performed by mixing $1^{2+} \cdot 2Cl^{-}$, 2d and 2f in D₂O, we observed that $3d^{4+}$ and $3f^{4+}$ were produced as the major products, while very little amount of hybridized catenane $3d/f^{4+}$ was observed by both ¹H NMR spectroscopy (Figure S28) and mass spectrum (Figure S29).



Figure S30. The ¹H NMR spectrum (D₂O, 298 K) of the [2]catenanes $3b^{4+}$, A) before and B) after 2f was added into the ¹H NMR solution. The spectrum in B) indicates that $3b^{4+}$ was transformed to $3f^{4+}$, after adding 2f.

We added **2f** into the solution of **3b**⁴⁺ (Figure S30 A) in D₂O. After heating the solution for 8 h, we observed (Figure S30 B) that **3b**⁴⁺ was transformed into the [2]catenane **3f**⁴⁺, during which **2b** was released. This experiment indicates that the [2]catenane **3f**⁴⁺ is more thermodynamically favored than **3b**⁴⁺.



Figure S31. ¹H NMR spectrum (600 MHz, D₂O, 333K) of $3f^{4+}$ A) before and after a potential template **4** was added into the solution. The spectrum in B) was recorded after heating the solution for 2 days, which indicates that $3f^{4+}$ does not undergo decomposition in the presence of **4**. The resonances of the aromatic protons of **4** were marked with arrows in the spectrum B. The counteranion could be either Cl⁻ or CF₃COO⁻.

We added guest **4** into the solutions of both $\mathbf{3d}^{4+}$ and $\mathbf{3f}^{4+}$ in D₂O. After heating the solution for 8 h, we observed (Figure S31) that $\mathbf{3f}^{4+}$ was remarkably stable in the presence of **4**. In contrast, $\mathbf{3b}^{4+}$ underwent decomposition and form a pseudorotaxane $\mathbf{4} \subset \mathbf{5d}^{2+}$ (Figure S32). This experiment indicates that the [2]catenane $\mathbf{3f}^{4+}$ is more thermodynamically favored than $\mathbf{3d}^{4+}$. DOSY spectrum was also recorded, indicating the formation of $\mathbf{4} \subset \mathbf{5d}^{2+}$ (Figure S33)



Figure S32. ¹H NMR spectrum (600 MHz, D₂O, 298K) of $3d^{4+}$ A) before and after a potential template **4** was added into the solution. The spectrum in B) was recorded after heating the solution for 2 days, which indicates that $3d^{4+}$ does undergo dissociation and form a pseudo-rotaxane **4**-**5** d^{2+} . The counteranion could be either Cl⁻ or CF₃COO⁻.



Figure S33. DOSY spectrum of $4 \subset 5d^{2+}$ (500 MHz, D₂O, 298 K). The counteranion could be either Cl⁻ or CF₃COO⁻.



6. Yields of the formation of 3b⁴⁺, 3d⁴⁺ and 3f⁴⁺ in solutions.

Figure S34. ¹H NMR spectra (400 MHz, D₂O, 298 K) of $1^{2+}2Cl^{-}$ (top) and $3f^{4+}$ (bottom; the counteranion could be either cl⁻ or CF₃COO⁻).

The yields of [2]catenanes $3b^{4+}$, $3d^{4+}$ and $3f^{4+}$ (the counteranion could be either Cl⁻ or CF₃COO⁻) were obtained from peak integrations using DMSO or EtOH at a fixed concentration as the internal standard in the corresponding solutions of [2]catenanes or parent aldehyde $1^{2+}2Cl^-$ in D₂O. The integrated intensity of the resonance of internal standard was normalized to 1, allowing the concentration ratios of the catenane products relative to their corresponding aldehyde precursors to be calculated. For example, in the ¹H NMR spectra of 1^{2+} (0.54 mg dissolved in 0.5 mL) and $3f^{4+}$, whose spectra were recorded before and after the reaction was allowed to proceed by adding 2f, the resonances of the phenyl units integrated as 1.18 and 1.11, respectively, relative to the standard; the yield of $3f^{4+}$ was thus 94% (1.11/1.18). Using this method, the NMR yields of $3b^{4+}$ and $3d^{4+}$ self-assembled in the same concentration were calculated to be 57 % and 29 %, respectively.



Figure S35. ¹H NMR spectra (400 MHz, D₂O, 298 K) of $1^{2+.2}Cl^{-}$ (top) and $3b^{4+}$ (bottom; the counteranion could be either Cl⁻ or CF₃COO⁻).



Figure S36. ¹H NMR spectra (400 MHz, D₂O, 298 K) of $1^{2+} \cdot 2Cl^{-}$ (top) and $3d^{4+}$ (bottom; the counteranion could be either Cl⁻ or CF₃COO⁻).

7. X-ray Crystallography

1) $3b^{4+.}4PF_{6}^{--}$

1.1) Methods

Single crystals of the [2]catenane $3b^{4+.}4PF_6^-$ was obtained by slow vapor diffusion of isopropyl ether into their MeCN solutions under room temperature. A suitable crystal was selected on a Bruker D8 Venture diffractometer. The crystal was kept at 170.0 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1.2) Crystal data

3b·4PF₆: $[(C_{39}H_{38}N_6O_2)_4 \cdot (PF6)_{10}] \cdot (PF_5)_1 \cdot (CH_3CN)_1 (M = 4107.73 g/mol)$: triclinic, space group P-1 (no. 2), a = 18.275(3) Å, b = 22.178(4) Å, c = 26.090(4) Å, $a = 100.067(10)^\circ$, $\beta = 91.197(10)^\circ$, $\gamma = 90.025(10)^\circ$, V = 10409(3) Å³, Z = 2, T = 170.0 K, $\mu(GaK\alpha) = 1.190$ mm⁻¹, Dcalc = 1.311 g/cm³, 156365 reflections measured (5.914° $\leq 2\Theta \leq 112.364^\circ$), 39674 unique ($R_{int} = 0.0950$, $R_{sigma} = 0.0942$) which were used in all calculations. The final R_1 was 0.1828 (I > 2 σ (I)) and wR_2

was 0.5211 (all data). CCDC number: 1820482.

Table S1 (Crystal	data a	nd structure	refinement f	for 3b44	$\cdot 4PF_6^{-}$
	•/					0

$C_{158}H_{155}F_{65}N_{25}O_8P_{11}$
4107.73
170.0
triclinic
P-1
18.275(3)
22.178(4)
26.090(4)
100.067(10)
91.197(10)
90.025(10)
10409(3)

Z	2		
$\rho_{calc}g/cm^3$	1.311		
μ/mm^{-1}	1.190		
F(000)	4184.0		
Crystal size/mm ³	0.2 imes 0.15 imes 0.1		
Radiation	$GaK\alpha (\lambda = 1.34139)$		
2Θ range for data collection/°	5.914 to 112.364		
Index ranges	$-22 \le h \le 22, -27 \le k \le 26, -31 \le l \le 31$		
Reflections collected	156365		
Independent reflections	$39674 [R_{int} = 0.0950, R_{sigma} = 0.0942]$		
Data/restraints/parameters	39674/0/2406		
Goodness-of-fit on F ²	1.774		
Final R indexes [I>= 2σ (I)]	$R_1 = 0.1828, wR_2 = 0.4860$		
Final R indexes [all data]	$R_1 = 0.2410, wR_2 = 0.5211$		
Largest diff. peak/hole / e Å ⁻³	1.18/-0.85		

2) $3f^{4+} \cdot 4PF_6^-$

2.1) Methods

Single crystals of the [2]catenane $3f^{4+} \cdot 4PF_6^-$ was obtained by slow vapor diffusion of isopropyl ether into their MeCN solutions under room temperature. A suitable crystal was selected on a Bruker APEX-II CCD diffractometer. The crystal was kept at 169.99 K during data collection. Using Olex2², the structure was solved with the ShelXT³ structure solution program using Intrinsic Phasing and refined with the ShelXL⁴ refinement package using Least Squares minimisation.

2.2) Crystal data

3f⁴⁺·4PF₆: [(C₄₂H₃₆N₆O₂)₄·(PF6)₈] ·(CH₃CN)₁₂·(O)₂ (*M*=4311.47 g/mol); monoclinic, space group C2/c (no. 15), a = 34.3375(10) Å, b = 27.6556(8) Å, c = 43.5292(12) Å, $\beta = 105.457(2)^{\circ}$, V = 39841(2) Å³, Z = 8, T = 169.99 K, μ (GaK α) = 1.055 mm⁻¹, *Dcalc* = 1.438 g/cm³, 216258 reflections measured (5.576° $\leq 2\Theta \leq 110.006^{\circ}$), 37789 unique ($R_{int} = 0.0606$, $R_{sigma} = 0.0450$) which were used in all calculations. The final R_1 was 0.0806 (I > 2 σ (I)) and wR_2 was 0.2467 (all data). CCDC number: 1820483.

Empirical formula	$C_{192}H_{180}F_{48}N_{36}O_{10}P_8$			
Formula weight	4311.47			
Temperature/K	169.99			
Crystal system	monoclinic			
Space group	C2/c			
a/Å	34.3375(10)			
b/Å	27.6556(8)			
c/Å	43.5292(12)			
α/°	90			
β/°	105.457(2)			
$\gamma/^{\circ}$	90			
Volume/Å ³	39841(2)			
Z	8			
$\rho_{calc}g/cm^3$	1.438			
μ/mm^{-1}	1.055			
F(000)	17728.0			
Crystal size/mm ³	$0.1\times0.08\times0.06$			
Radiation	GaK α ($\lambda = 1.34139$)			
2Θ range for data collection/°	5.576 to 110.006			
Index ranges	$\textbf{-41} \leq h \leq \textbf{41}, \textbf{-28} \leq k \leq \textbf{33}, \textbf{-53} \leq \textbf{l} \leq \textbf{52}$			
Reflections collected	216258			
Independent reflections	37789 [$R_{int} = 0.0606, R_{sigma} = 0.0450$]			
Data/restraints/parameters	37789/0/2661			
Goodness-of-fit on F ²	1.023			
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0806, wR_2 = 0.2274$			
Final R indexes [all data]	$R_1 = 0.1056, wR_2 = 0.2467$			
Largest diff. peak/hole / e Å-3	1.38/-0.91			

Table S2	Crystal	data and	structure	refinement	for 3f4+	•4PF ₆ ⁻ .
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8. References

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