Precursor Control Over the Self-Assembly of [2]Catenanes via Hydrazone Condensation in Water

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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 for $^1$H 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$_2$O: $\delta = 4.79$ ppm, DMSO-d$_6$: $\delta = 2.50$ ppm, CD$_3$CN: $\delta = 1.94$ 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%). \textit{H} NMR (400 MHz, D\textsubscript{2}O): \(\delta = 7.15\) (s, 4H), 3.43 (s, 4H). \textit{C} NMR (100 MHz, D\textsubscript{2}O): \(\delta = 173.4, 133.5, 129.4, 39.9\). MS (GCTOF-HRMS): \(m/z\) [M]\(^+\) calcd for C\textsubscript{10}H\textsubscript{14}N\textsubscript{4}O\textsubscript{2}: 222.1117, found: 222.1123.

![Diagram of 12+ and 3a-3e](image)

**Scheme S3. Synthesis of 3b\textsuperscript{4+} and 3d\textsuperscript{4+} (the counteranion could be either Cl\textsuperscript{−} or CF\textsubscript{3}COO\textsuperscript{−}).**

We combined 1\textsuperscript{2+}\cdot2Cl\textsuperscript{−} (0.54 mg, 0.001 mmol) with each of the dihydrazine linkers 2a-2e (0.001 mmol) in a 1:1 ratio, in D\textsubscript{2}O (0.5 mL) in the presence of catalytic amount of TFA (5 \(\mu\)L). After heating the corresponding solutions at 50 °C for 8 h, the \textit{H} 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\textsuperscript{4+} and 3d\textsuperscript{4+} (counteranions could be either Cl\textsuperscript{−} or CF\textsubscript{3}COO\textsuperscript{−}) were produced as the major products, as inferred from the corresponding \textit{H} NMR spectroscopic results (Figure S1 B, D).
3. Characterization of $3b^{4+}$ and $3d^{4+}$ in D$_2$O by NMR and HRMS

Figure S1. The $^1$H NMR spectra (600 MHz, D$_2$O, 298 K) of the self-assembled products by condensing $1^{2+}$·2Cl$^-$ with A) 2a, B) 2b, C) 2c, D) 2d, E) 2e. The counteranion could be either Cl$^-$ or CF$_3$COO$^-$. 

In the case of 2a, 2c, and 2e, $^1$H 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 \(1^{2+}\cdot2\text{Cl}^{-}\) resolved in 0.5 ml D\(_2\)O.) led to diminish of the resonances of byproducts, as inferred from the corresponding \(^1\text{H}\) NMR spectra (Figure S2 B, D). The yields of \(3b^{4+}\) and \(3d^{4+}\) (counteranions could be either Cl\(^{-}\) or CF\(_3\)COO\(^{-}\)) were determined by using an internal standard in the corresponding \(^1\text{H}\) 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 \(^1\text{H}\) NMR spectra.
Figure S2. The $^1$H NMR spectra (600 MHz, D$_2$O, 298 K) of the [2]catenanes 3b$^{4+}$ and 3d$^{4+}$ (The counteranion could be either Cl$^-$ or CF$_3$COO$^-$). 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 $^1$H 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 3d4+. 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 3b4+, however, the resonances of the corresponding protons d, f and e, become remarkably broad. This observation indicates circumvolution motion in the case of 3b4+ are relatively slower than that of 3d4+. This is because 3b4+ is composed of two smaller macrocycles bearing two shorter (CH2)3 chains than the (CH2)7 chains in 3d4+. We also recorded the 1H NMR spectrum (Figure S3 B) of 3b4+ 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 D2O. The structures of both 3b4+ and 3d4+ are further confirmed by using a variety of two-dimensional NMR spectroscopy (see Fig. S9–S14 in SI).
Fig. S3 Partial $^1$H NMR spectra (600 MHz, D$_2$O, 0.5 mg NaCl) of A) $3d^{4+}$, B) $3b^{4+}$, and C) $3b^{4+}$. Counteranions are either CF$_3$CO$_2^-$ 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 CF_3COO^-). 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$^-\ $or CF$_3$COO$^-\ $). The signal labeled in the spectrum correspond to molecular cations that contain four, three, and two positive charges, respectively, which reflects losing varying numbers of (between 0 and 2) protons.
Figure S6. LCMS-IT-TOF of the self-assembled products of 1$^{\text{2+}}$ and 2a in D$_2$O. (The counteranion could be either Cl$^{-}$ or CF$_3$COO$^{-}$). 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 CF$_3$COO$^-$). 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 CF$_3$COO$^{-}$). 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. $^1$H-$^1$H COSY spectrum of 3b$^{4+}$ (600 MHz, D$_2$O, 333 K). Key correlation peaks are labeled in the spectrum. The counteranion could be either Cl$^-$ or CF$_3$COO$^-$.  

Figure S10. $^1$H-$^1$H NOESY spectrum of 3b$^{4+}$ (500 MHz, D$_2$O, 333 K). Key correlation peaks are labeled in the spectrum. The counteranion could be either Cl$^-$ or CF$_3$COO$^-$. 
Figure S11. DOSY spectrum of 3b$^{4+}$ (500 MHz, D$_2$O, 333 K). The counteranion could be either Cl$^{-}$ or CF$_3$COO$^{-}$.

Figure S12. $^1$H–$^1$H gradient-selected double-quantum filtered phase-sensitive COSY spectrum of 3d$^{4+}$ (500 MHz, D$_2$O, 298 K). The counteranion could be either Cl$^{-}$ or CF$_3$COO$^{-}$. 
Figure S13. $^1$H-$^1$H NOESY spectrum of 3d$^{4+}$ (500 MHz, D$_2$O, 298 K). The counteranion could be either Cl$^-$ or CF$_3$COO$^-$. Key correlation peaks are labeled in the spectrum.
Figure S14. DOSY spectrum of 3d\textsuperscript{4+} (500 MHz, D\textsubscript{2}O, 298 K). The counteranion could be either Cl\textsuperscript{−} or CF\textsubscript{3}COO\textsuperscript{−}.
4. Characterization of 3f\textsuperscript{4+} in both D\textsubscript{2}O and CD\textsubscript{3}CN by NMR and HRMS

**Figure S15.** LCMS-IT-TOF of 3f\textsuperscript{4+} (The counteranion could be either Cl\textsuperscript{−} or CF\textsubscript{3}COO\textsuperscript{−}). 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\textsuperscript{2+}·2Cl\textsuperscript{−} (0.54 mg, 0.001 mmol) with 2f (0.22 mg, 0.001 mmol) in a 1:1 ratio, in 0.5 ml D\textsubscript{2}O in the presence of catalytic amount of TFA (5 μL). After heating the corresponding solutions at 50 °C for 8 h, the \textsuperscript{1}H 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 \textsuperscript{1}H NMR spectrum, indicating the formation of a single thermodynamically stable product, namely the [2]catenane 3f\textsuperscript{4+}, whose counteranions are either CF\textsubscript{3}CO\textsubscript{2}− or Cl\textsuperscript{−}.
Figure S16. Partial $^1$H NMR spectrum (500 MHz, 298 K, 1:1 D$_2$O/DMSO-$d_6$) of 3f$^{4+}$, which was self-assembled in a 1:1 D$_2$O/DMSO-$d_6$ solution. Counteranions are either CF$_3$CO$_2^-$ or Cl$^-$. Unreacted 2f was also observed in the $^1$H NMR spectrum.

The [2]catenane 3f$^{4+}$, whose counteranions are either CF$_3$CO$_2^-$ or Cl$^-$, could also be self-assembled 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 D$_2$O/DMSO-$d_6$ (0.25 mL/0.25 mL) in the presence of catalytic amount of TFA (5 μL), as indicated by the $^1$H 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.
The structure of $3f^{+}$ was further convinced two-dimensional NMR spectroscopy. Two-dimensional NMR spectra, including COSY (Figure S17) and NOESY (Figure S18), were used to make peak assignments for the $^1$H NMR spectra. DOSY spectra (Figure S19) provided evidence that a single species was formed.
Figure S18. $^1$H-$^1$H NOESY spectrum of 3f$^{4+}$(500 MHz, D$_2$O, 333 K). Key correlation peaks are labeled in the spectrum. (The counteranion could be either Cl$^−$ or CF$_3$COO$^−$).

Figure S19. DOSY spectrum of 3f$^{4+}$ (500 MHz, D$_2$O, 332 K). (The counteranion could be either Cl$^−$ or CF$_3$COO$^−$).
Figure S20. $^1$H NMR spectra of 3f$^{4+}$ (The counteranion could be either Cl$^-$ or CF$_3$COO$^-$) at variable temperatures in D$_2$O (600 M Hz).

The $^1$H NMR spectrum of 3f$^{4+}$ is temperature dependent in D$_2$O. 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 $^1$H NMR spectrum (500 M Hz, 298 K, CD$_3$CN) of $3f^{4+}$·4PF$_6^−$.

Figure S22. $^{13}$C NMR spectrum (500 M Hz, 298 K, CD$_3$CN) of $3f^{4+}$·4PF$_6^−$. 
Figure S23. $^1$H–$^1$H gradient-selected double-quantum filtered phase-sensitive COSY spectrum of
3f$^{4+}$·4PF$_6^-$ (500 MHz, D$_2$O, 298 K).

The [2]catenane 3f$^{4+}$, whose counteranions are either CF$_3$CO$_2^-$ or Cl$^-$, could be transformed to its
organic solvent soluble counterpart with PF$_6^-$ salt by means of counteranion exchange. The
structure of 3f$^{4+}$·4PF$_6^-$ was fully characterized by $^1$H (see Figure S21) and $^{13}$C (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 $^1$H NMR
spectra. It is noteworthy that the NMR spectroscopy indicates that the co-conformation of 3f
$^{4+}$·4PF$_6^-$ in CD$_3$CN is essentially the same as 3f$^{4+}$·4Cl$^-$ in D$_2$O. Once dissolved in CD$_3$CN,
3f$^{4+}$·4PF$_6^-$ is relatively stable.
Figure S24. $^1$H-$^1$H NOESY spectrum of 3f$^{4+}$·4PF$_6^-$ (500 MHz, CD$_3$CN, 298 K). Key correlation peaks are labeled in the spectrum.

Figure S25. DOSY spectrum of 3f$^{4+}$·4PF$_6^-$ (500 MHz, D$_2$O, 298 K).
5. Thermodynamic Stability Investigations

![Diagram](image)

**Figure S26.** Partial $^1$H NMR spectra (600 M Hz, D$_2$O, 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 CF$_3$COO$^-$. When 1$^{2+}$·2Cl$^-$, 2b and 2d were combined in D$_2$O 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 $^1$H 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 CF$_3$COO$^-$. 
Figure S28. Partial $^1$H NMR spectra (600 MHz, D$_2$O, 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 CF$_3$COO$^-$.
Figure S29. Partial LCMS-IT-TOF spectrum of the self-assembled products of 1:1:2 mixture of 2f, 2d and 1²⁺. The counteranion could be either Cl⁻ or CF₃COO⁻. However, when the same experiment was performed by mixing 1²⁺·2Cl⁻, 2d and 2f in D₂O, we observed that 3d⁴⁺ and 3f⁴⁺ were produced as the major products, while very little amount of hybridized catenane 3d/f⁴⁺ was observed by both ¹H NMR spectroscopy (Figure S28) and mass spectrum (Figure S29).
Figure S30. The $^1$H NMR spectrum (D$_2$O, 298 K) of the [2]catenanes 3b$^{4+}$, A) before and B) after 2f was added into the $^1$H 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 D$_2$O. 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. $^1$H NMR spectrum (600 MHz, D$_2$O, 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 CF$_3$COO$^-$. We added guest 4 into the solutions of both 3d$^{4+}$ and 3f$^{4+}$ in D$_2$O. After heating the solution for 8 h, we observed (Figure S31) that 3f$^{4+}$ was remarkably stable in the presence of 4. In contrast, 3b$^{4+}$ underwent decomposition and form a pseudorotaxane 4$\subset$5d$^{2+}$ (Figure S32). This experiment indicates that the [2]catenane 3f$^{4+}$ is more thermodynamically favored than 3d$^{4+}$. DOSY spectrum was also recorded, indicating the formation of 4$\subset$5d$^{2+}$ (Figure S33).
Figure S32. $^1$H NMR spectrum (600 MHz, D$_2$O, 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 $4\circ5d^{2+}$. The counteranion could be either Cl$^-$ or CF$_3$COO$^-$. 
Figure S33. DOSY spectrum of 4-5d²⁺ (500 MHz, D₂O, 298 K). The counteranion could be either Cl⁻ or CF₃COO⁻.
6. Yields of the formation of $3b^{4+}$, $3d^{4+}$ and $3f^{4+}$ in solutions.

The yields of [2]catenanes $3b^{4+}$, $3d^{4+}$ and $3f^{4+}$ (the counteranion could be either Cl$^-$ or CF$_3$COO$^-$) 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 D$_2$O. The integrated intensity of the resonance of internal standard was normalized to 1, allowing

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**Figure S34.** $^1$H NMR spectra (400 MHz, D$_2$O, 298 K) of $1^{2+}$·2Cl$^-$ (top) and $3f^{4+}$ (bottom; the counteranion could be either Cl$^-$ or CF$_3$COO$^-$).
the concentration ratios of the catenane products relative to their corresponding aldehyde precursors to be calculated. For example, in the $^1$H NMR spectra of I$^{2+}$ (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.

![Diagram](image)

**Figure S35.** $^1$H NMR spectra (400 MHz, D$_2$O, 298 K) of I$^{2+}$·2Cl$^-$ (top) and 3b$^{4+}$ (bottom; the counteranion could be either Cl$^-$ or CF$_3$COO$^-$).
Figure S36. $^1$H NMR spectra (400 MHz, D$_2$O, 298 K) of 1$^{2+}$·2Cl$^-$ (top) and 3d$^{4+}$ (bottom; the counteranion could be either Cl$^-$ or CF$_3$COO$^-$).
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·4PF$_6$: [(C$_{39}$H$_{38}$N$_6$O$_2$)$_4$·(PF$_6$)$_{10}$·(PF$_3$)$_1$·(CH$_3$CN)$_1$] (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, $\alpha = 100.067(10)^\circ$, $\beta = 91.197(10)^\circ$, $\gamma = 90.025(10)^\circ$, $V = 10409(3)$ Å$^3$, $Z = 2$, $T = 170.0$ K, $\mu$(GaKα) = 1.190 mm$^{-1}$, $D_{calc} = 1.311$ g/cm$^3$, 156365 reflections measured (5.914° ≤ 2Θ ≤ 112.364°), 39674 unique ($R_{int} = 0.0950$, $R_{sigma}$ = 0.0942) which were used in all calculations. The final $R_1$ was 0.1828 (I > 2σ(I)) and $wR_2$ was 0.5211 (all data). CCDC number: 1820482.

Table S1 Crystal data and structure refinement for 3b$^{4+}$-4PF$_6^-$.

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Z & 2 \\
\rho_{\text{calc}}/\text{g/cm}^3 & 1.311 \\
\mu/\text{mm}^{-1} & 1.190 \\
F(000) & 4184.0 \\
\text{Crystal size/mm}^3 & 0.2 \times 0.15 \times 0.1 \\
\text{Radiation} & \text{GaK}\alpha (\lambda = 1.34139) \\
2\Theta \text{ range for data collection/°} & 5.914 \text{ to } 112.364 \\
\text{Index ranges} & -22 \leq h \leq 22, -27 \leq k \leq 26, -31 \leq l \leq 31 \\
\text{Reflections collected} & 156365 \\
\text{Independent reflections} & 39674 \ [R_{\text{int}} = 0.0950, R_{\text{sigma}} = 0.0942] \\
\text{Data/restraints/parameters} & 39674/0/2406 \\
\text{Goodness-of-fit on } F^2 & 1.774 \\
\end{array}
\]

**2) \text{3}^{\text{I}}\text{I}^{+}\cdot4\text{PF}_6^-**

2.1) Methods

Single crystals of the \([2]\)catenane \(\text{3}^{\text{I}}\text{I}^{+}\cdot4\text{PF}_6^-\) 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 Olex2\(^2\), the structure was solved with the ShelXT\(^3\) structure solution program using Intrinsic Phasing and refined with the ShelXL\(^4\) refinement package using Least Squares minimisation.

2.2) Crystal data

\(\text{3}^{\text{I}}\text{I}^{+}\cdot4\text{PF}_6^-\): \([\text{C}_{42}\text{H}_{36}\text{N}_6\text{O}_2]^{\text{I}+}\cdot\text{(PF}_6\text{)}^8\cdot\text{(CH}_3\text{CN})_{12}\cdot\text{(O)}_2 \quad (M = 4311.47 \ \text{g/mol}); \) monoclinic, space group C2/c (no. 15), \(a = 34.3375(10) \ \text{Å}, b = 27.6556(8) \ \text{Å}, c = 43.5292(12) \ \text{Å}, \beta = 105.457(2)^\circ, \)
\(V = 39841(2) \ \text{Å}^3, Z = 8, T = 169.99 \ \text{K}, \mu(\text{GaK}\alpha) = 1.055 \ \text{mm}^{-1}, D_{\text{calc}} = 1.438 \ \text{g/cm}^3, 216258 \)
reflections measured \((5.576^\circ \leq 2\Theta \leq 110.006^\circ), 37789 \ \text{unique} \ (R_{\text{int}} = 0.0606, R_{\text{sigma}} = 0.0450)\)
which were used in all calculations. The final \(R_1\) was 0.0806 \((I > 2\sigma(I))\) and \(wR_2\) was 0.2467 (all
data). CCDC number: 1820483.

**Table S2 Crystal data and structure refinement for 3f^{4+}·4PF_6^{−}**.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{192}H_{180}F_{48}N_{36}O_{10}P_{8}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>4311.47</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>169.99</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>34.3375(10)</td>
</tr>
<tr>
<td>b/Å</td>
<td>27.6556(8)</td>
</tr>
<tr>
<td>c/Å</td>
<td>43.5292(12)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>105.457(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>39841(2)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>ρ_{calc}/cm³</td>
<td>1.438</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>1.055</td>
</tr>
<tr>
<td>F(000)</td>
<td>17728.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.1 × 0.08 × 0.06</td>
</tr>
<tr>
<td>Radiation</td>
<td>GaKα (λ = 1.34139)</td>
</tr>
<tr>
<td>2θ range for data collection/°</td>
<td>5.576 to 110.006</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-41 ≤ h ≤ 41, -28 ≤ k ≤ 33, -53 ≤ l ≤ 52</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>216258</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>37789 [R_{int} = 0.0606, R_{sigma} = 0.0450]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>37789/0/2661</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.023</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ(I)]</td>
<td>R₁ = 0.0806, wR₂ = 0.2274</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.1056, wR₂ = 0.2467</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>1.38/-0.91</td>
</tr>
</tbody>
</table>

8. References