Supplementary Information

A cyclic Bis[2]catenane Metallacage

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Supplementary Methods

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Compound 1, 4, p-Terphenyl-3,3′,5,5′-tetracarboxylic acid, 1-iodo-3,5-dimethoxy-benzene was prepared according to the published procedures. ¹H NMR, ¹³C NMR NMR spectra were recorded on a Varian Inova 400 MHz spectrometer and JEOL JNM-ECZ400SL NMR spectrometer. ³¹P(¹H) NMR spectra were recorded on a Varian Unity 300 MHz spectrometer and JEOL JNM-ECZ400SL NMR spectrometer. DOSY spectra were recorded on a Varian Inova 500 MHz spectrometer and Bruker AVANCE III HD 500MHz spectrometer. COSY spectra were recorded on a Bruker AVANCE III HD 600MHz spectrometer. ¹H and ¹³C NMR chemical shifts are reported relative to residual solvent signals, and ³¹P(¹H) NMR chemical shifts are referenced to an external unlocked sample of 85% H₃PO₄ (δ = 0.0). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. The single crystals data were collected on an Oxford Diffraction Xcalibur Atlas Gemini captra.

Supplementary Figure 1. The synthesis of 4-(3,5-dimethoxyphenyl)-pyridine.

Synthesis of 4-(3,5-dimethoxyphenyl)-pyridine. 1-iodo-3,5-dimethoxy-benzene (2.64 g, 10 mmol), 4-Pyridineboronic acid (1.48 g, 12 mmol), CsF (3 g) and tetrakis(triphenylphosphine)palladium(0) (300 mg) were mixed in a 250 mL flask connected to a condenser. The flask was degassed under vacuum for 2 h, and then 100 mL of degassed 1,4-dioxane were added to the flask. The reaction mixture was heated to reflux under nitrogen atmosphere for 48 h. After removal of the organic solvent under vacuum, the residue was washed with water and extracted with CH₂Cl₂ three times. Combined organic layers were dried over MgSO₄ and filtered. The solvent was removed and the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane: 1/5) to give 1.25 g 4-(3,5-dimethoxyphenyl)-pyridine as a white solid. Yield: 58%. The ¹H NMR spectrum of 4-(3,5-dimethoxyphenyl)-pyridine is shown in Supplementary Figure 2. ¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm): 8.64 (d, J = 5.4 Hz, 2H), 7.46 (d, J = 6.0 Hz, 2H), 6.74 (d, J = 2.2 Hz, 2H), 6.53 (t, J = 2.3 Hz, 1H), 3.84 (s, 6H). The ¹³C NMR spectrum of 4-(3,5-dimethoxyphenyl)-pyridine is shown in Supplementary Figure 3. ¹³C NMR (100 MHz, CDCl₃, 298 K) δ (ppm): 161.45, 150.31, 148.48, 140.43, 121.84, 105.40, 100.84, and 55.57. HRMS (ESI-ToF) m/z: [M+H]+ Calc'd for [C₁₃H₁₄NO₂]+, 216.1019; Found 216.1025.
Supplementary Figure 2. $^1\text{H}$ NMR spectrum (400 MHz, CDCl$_3$, 298K) of 4-(3,5-dimethoxyphenyl)-pyridine.

Supplementary Figure 3. $^{13}\text{C}$ NMR spectrum (100 MHz, CDCl$_3$, 298K) of 4-(3,5-dimethoxyphenyl)-pyridine.
Supplementary Figure 4. The synthesis of compound 2.

Synthesis of 2. Boron tribromide (3 mL) was added to a CH$_2$Cl$_2$ (20 mL) solution of 4-(3,5-dimethoxyphenyl)-pyridine (1.08 g, 5 mmol). The mixture was stirred at room temperature for 6 h. Then the mixture was poured into ice water. Combined aqua layers and concentrated, then the pH value of 2·HBr solution was adjusted to 7.0 with standard sodium hydroxide solution. The resulting precipitate was collected by filtration and washed with water to give 870 mg 2 as pale-yellow solid, yield: 93%. The $^1$H NMR spectrum of 2 is shown in Supplementary Figure 5. $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K) δ (ppm): 9.97 (s, 2H), 9.03 (s, 2H), 7.99 (s, 2H), 7.01 (d, $J = 2.1$ Hz, 2H), 6.76 (t, $J = 2.1$ Hz, 1H). The $^{13}$C NMR spectrum of 2 is shown in Supplementary Figure 6. $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K) δ (ppm): 159.50, 150.36, 148.05, 139.51, 121.63, 105.28, and 103.78. HRMS (ESI-ToF) m/z: [M+H]$^+$ Calc’d for [C$_{11}$H$_{10}$NO$_2$]$^+$, 188.0706; Found 188.0712.

Supplementary Figure 5. $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 298K) of compound 2.
Supplementary Figure 6. $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$, 298K) of compound 2.

Supplementary Figure 7. The synthesis of compound 3.

**Synthesis of 3.** 2,7-Dichloro-1,8-naphthyridine (1) (1.33 g, 6.7 mmol, 1 equivalent (eq.)), 2 (1.25 g, 6.7 mmol, 1 eq.), and Cs$_2$CO$_3$ (5.45 g, 16.7 mmol, 2.5 eq.) were combined under an nitrogen atmosphere. DMSO (100 mL) was added, and the reaction was heated to 100 °C and stirred vigorously for 18 hr. The reaction mixture was diluted with 200 mL H$_2$O causing formation of a grey precipitate. The solid was collected by filtration, washed with 100 mL H$_2$O, dissolved in CH$_2$Cl$_2$, dried over anhydrous MgSO$_4$, filtered, and concentrated in vacuum. The product was then purified via column chromatography by silica gel (ethyl acetate) and recrystallization in CH$_2$Cl$_2$/hexane to yield 1.34 g 3 as a pale-yellow solid. Yield: 64%. The $^1$H NMR spectrum of 3 is shown in Supplementary Figure 8. $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K) δ (ppm): 8.55 (d, $J = 5.8$ Hz, 4H), 8.44 (d, $J = 8.6$ Hz, 4H), 7.71 (d, $J = 5.9$ Hz, 4H), 7.56 (d, $J = 1.9$ Hz, 4H), 7.30 (d, $J = 8.6$ Hz, 4H), 7.17 (t, $J = 1.9$ Hz, 2H). The $^{13}$C NMR spectrum of 2 is shown in Supplementary Figure 9. $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K) δ (ppm): 164.20, 154.39, 153.30, 150.02, 145.21, 140.77, 140.06, 121.33, 118.71, 117.57, 116.81 and 111.16. HRMS (ESI-ToF) m/z: [M+H]$^+$ Calc'd
for $[\text{C}_{38}\text{H}_{23}\text{N}_6\text{O}_4]^+$, 627.1775; Found 627.1783.

Supplementary Figure 8. $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 298K) of compound 3.

Supplementary Figure 9. $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$, 298K) of compound 3.
Supplementary Figure 10. The synthesis of compound 8.

Synthesis of 8. p-Terphenyl-3,3''5,5''-tetracarboxylic acid (68 mg, 0.17 mmol) and NaOH (27 mg, 0.67 mmol) were added into a 2-dram vial with 5 mL water. The mixture was stirred at room temperature for 3 h. All solvent was removed by N₂ flow and white solid 7 was dried under vacuum (79 mg, Yield: 99%). The \(^1\)H NMR spectrum of 8 is shown in Supplementary Figure 11. \(^1\)H NMR (400 MHz, D₂O, 298 K) δ (ppm): 8.36 (t, J = 1.3 Hz, 4H), 8.31 (q, J = 1.4 Hz, 2H), 7.96 (d, J = 1.0 Hz, 4H). The \(^13\)C NMR spectrum of 8 is shown in Supplementary Figure 12. \(^13\)C NMR (100 MHz, D₂O, 298 K) δ (ppm): 174.94, 139.87, 139.22, 137.17, 129.57, 128.01, and 127.64.

Supplementary Figure 11. \(^1\)H NMR spectrum (400 MHz, D₂O, 298K) of compound 8.
Supplementary Figure 12. $^{13}$C NMR spectrum (100 MHz, D$_2$O, 298K) of compound 8.

Supplementary Figure 13. The synthesis of NaOTf⊂ 6.

Synthesis of NaOTf⊂ 6. 3 (6.27 mg, 10 μmol), cis-Pt(PET$_3$)$_2$(OTf)$_2$ 4 (14.59 mg, 20 μmol) and dicarboxylate ligand 5 (2.10 mg, 10 μmol), were placed in a 2-dram vial, followed by addition of H$_2$O (0.2 mL) and acetone (1.0 mL). After 3 h of heating at 50 °C, all solvent was removed by N$_2$ flow. Acetone (1.0 mL) was then added into the resultant mixture, and the solution was stirred at 50 °C for 8 h. The resulting product NaOTf⊂ 6 was precipitated with diethyl ether, isolated and dried under reduced pressure and dissolved in acetone-$d_6$ for characterization, white solid: 20.39 mg, Yield: 96%. The $^1$H NMR spectrum of NaOTf⊂ 6 is shown in Supplementary Figure 14. $^1$H NMR (400 MHz, acetone-$d_6$, 298 K) δ (ppm): 9.04 (m, 4H), 8.55 (d, J = 8.7 Hz, 4H), 8.22 (t, J = 1.8 Hz, 1H), 8.06 (d, J = 6.0 Hz, 4H), 7.81 (dd, J = 7.6, 1.7 Hz, 2H), 7.73 (d, J = 2.0 Hz, 4H), 7.36 (d, J = 8.8 Hz, 6H), 7.18 (t, J = 7.7 Hz, 1H), 2.07 – 1.88 (m, 48H), 1.30 (m, 72H). The $^{31}$P$^{[1]}$H NMR spectrum of NaOTf⊂ 6 is shown in Supplementary Figure 15. $^{31}$P$^{[1]}$H NMR (121 MHz, acetone-$d_6$, 298 K) δ (ppm): 6.96 (d, $^2$J$_{P-P}$ = 21.5 Hz, $^{195}$Pt satellites), $^1$J$_{P-P}$ = 3229 Hz), and 1.66 (d, $^2$J$_{P-P}$ = 21.5 Hz, $^{195}$Pt satellites, $^1$J$_{P-P}$ = 3428 Hz). ESI-TOF-MS is shown in Supplementary Figure 16: 912.23 [M+NaOTf–2OTf]$^{2+}$. 2D DOSY NMR spectrum (500 MHz, acetone-$d_6$, 30 mM, 298 K) of NaOTf⊂
Supplementary Figure 17. \( D = 9.00 \times 10^{-10} \text{ m}^2\text{s}^{-1} \).

Supplementary Figure 14. \( ^1\text{H} \) NMR spectrum (400 MHz, acetone-\( d_6 \), 298K) of NaOTf \( \subset 6 \).

Supplementary Figure 15. \( ^{31}\text{P}(^1\text{H}) \) NMR spectrum (121 MHz, acetone-\( d_6 \), 298K) of NaOTf \( \subset 6 \).
Supplementary Figure 16. Experimental (black) and calculated (red) electrospray ionization mass spectrum of NaOTf⊂ 6.

Supplementary Figure 17. DOSY NMR spectra (500 MHz, acetone-d₆, 298 K) of NaOTf⊂ 6 at 2.0 mM.

\[ D = 9.00 \times 10^{-10} \text{ m}^2\text{s}^{-1} \]
Supplementary Figure 18. The synthesis of 6.

Synthesis of 6. NaOTf ☐ 6 (21.24 mg, 10 μmol) was placed in a 2-dram vial, followed by addition of H2O (2.0 mL) and CH2Cl2 (3.0 mL). The mixture was stirred at room temperature for 12 h. Then, organic phase was collected and dried over anhydrous MgSO4, filtered. CH2Cl2 was removed by N2 flow and the solid was dried under vacuum, white solid: 19.40 mg, Yield: 99%. The solid was dissolved in CD2Cl2 for characterization. The 1H NMR spectrum of 6 is shown in Supplementary Figure 19. 1H NMR (400 MHz, CD2Cl2, 298 K) δ (ppm): 8.76 (m, 4H), 8.20 – 8.08 (m, 5H), 7.74 (d, J = 5.9 Hz, 4H), 7.69 (m, 2H), 7.35 (d, J = 2.1 Hz, 4H), 7.14 (d, J = 8.6 Hz, 4H), 7.09 (t, J = 2.1 Hz, 2H), 7.04 (t, J = 7.7 Hz, 1H), 1.98 – 1.65 (m, 48H), 1.29 – 1.19 (m, 72H). The 31P{1H} NMR spectrum of 6 is shown in Supplementary Figure 20. 31P{1H} NMR (121 MHz, CD2Cl2, 298 K) δ (ppm): 5.35 (d, 2Jp,p = 21.4 Hz, 195Pt satellites, 1Jp,P = 3216 Hz), and -0.22 (d, 2Jp,p = 21.7 Hz, 195Pt satellites, 1Jp,P = 3415 Hz). ESI-TOF-MS is shown in Supplementary Figure 21: m/z = 826.24 [M−2OTf]2+. 2D DOSY NMR spectrum (500 MHz, CD2Cl2, 30 Mm, 298 K) of 6 is shown in Supplementary Figure 22, D = 6.47 × 10-10 m2s⁻¹.

Supplementary Figure 19. 1H NMR spectrum (400 MHz, CD2Cl2, 298K) of 6.
**Supplementary Figure 20.** $^{31}$P($^1$H) NMR spectrum (121 MHz, CD$_2$Cl$_2$, 298K) of 6.

**Supplementary Figure 21.** Experimental (black) and calculated (red) electrospray ionization mass spectrum of 6/7. [M-2OTf]$^{2+}$ represents the ESI-TOF-MS of monomeric cage 6. For the experimental and calculated ESI-TOF-MS data of [2M-3OTf]$^{3+}$ (corresponding to catenane 7), please see Figure 3b in the manuscript.
Supplementary Figure 22. DOSY NMR spectra (500 MHz, CD$_2$Cl$_2$, 298 K) of 6 at 2.0 mM.

Supplementary Figure 23. The synthesis of 9.
Synthesis of 9. 3 (6.27 mg, 10 μmol), cis-Pt(PEt$_3$)$_2$(OTf)$_2$ 4 (14.59 mg, 20 μmol) and tetracarboxylate ligand 8 (2.47 mg, 5 μmol), were placed in a 2-dram vial, followed by addition of H$_2$O (0.2 mL) and acetone (1.0 mL). After 3 h of heating at 50 °C, all solvent was removed by N$_2$ flow. Acetone (1.0 mL) was then added into the resultant mixture, and the solution was stirred at 50 °C for 8 h. The resulting product was precipitated with diethyl ether, isolated and dried under reduced pressure and dissolved in CH$_2$Cl$_2$ (3.0 mL). Above solution was placed in a 2-dram vial, followed by addition of H$_2$O (2.0 mL), and stirred at room temperature for 12 h. Organic phase was collected and dried over anhydrous MgSO$_4$, filtered. CH$_2$Cl$_2$ was removed by N$_2$ flow and the solid was dried under vacuum, white solid: 18.27 mg, Yield: 92%. The solid was dissolved in CD$_2$Cl$_2$ for characterization. The $^1$H NMR spectrum of 9 is shown in Supplementary Figure 24. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) δ (ppm): 8.98 – 8.65 (8H), 8.27 – 8.07 (6H), 7.93 (s, 6H), 7.85 – 7.66 (8H), 7.50 – 7.28 (8H), 7.26 (s, 6H), 7.19 – 6.89 (12H), 2.05 – 1.67 (m, 96H), 1.41 – 1.07 (m, 144H). The $^{31}$P($^1$H) NMR spectrum of 9 is shown in Supplementary Figure 25. $^{31}$P($^1$H) NMR (121 MHz, CD$_2$Cl$_2$, 298 K) δ (ppm): 5.48 (d, $^2$J$_{P,P}$ = 21.8 Hz, $^{195}$Pt satellites, $^1$J$_{P,P}$ = 3250 Hz), and -0.10 (d, $^2$J$_{P,P}$ = 21.6 Hz, $^{195}$Pt satellites, $^1$J$_{P,P}$ = 3461 Hz). ESI-TOF-MS is shown in Supplementary Figure 26: 845.13 [M - 4OTf]$^{+}$. 2D DOSY NMR spectrum (500 MHz, CD$_2$Cl$_2$, 15 mM, 298 K) of 9 is shown in Supplementary Figure 27, $D$ = 3.91 x $10^{-10}$ m$^2$s$^{-1}$. 

\[ D = 6.47 \times 10^{-10} \text{ m}^2\text{s}^{-1} \]
Supplementary Figure 24. $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 9.

Supplementary Figure 25. $^{31}$P($^1$H) NMR spectrum (121 MHz, CD$_2$Cl$_2$, 298K) of 9.
Supplementary Figure 26. Experimental (black) and calculated (red) electrospray ionization mass spectrum of \(9/10\). \([M\text{-}4\text{OTf}]^{4+}\) represents the ESI-TOF-MS of bis-metallacage 9. For the experimental and calculated ESI-TOF-MS data of \([2M\text{-}6\text{OTf}]^{6+}\), \([2M\text{-}5\text{OTf}]^{5+}\), and \([2M\text{-}4\text{OTf}]^{4+}\) (corresponding to cyclic bis[2]catenate 10), please see Figure 3c in the manuscript.

Supplementary Figure 27. DOSY NMR spectra (500 MHz, CD$_2$Cl$_2$, 298 K) of 9 at 1.0 mM. 

\[ D = 3.91 \times 10^{-10} \text{ m}^2\text{s}^{-1} \]
### Supplementary Table 1. Crystal data and structure refinement for 3

| Property                                | Value                                      |
|-----------------------------------------|--------------------------------------------|
| Empirical formula                       | C\textsubscript{40}H\textsubscript{26}Cl\textsubscript{4}N\textsubscript{6}O\textsubscript{4} |
| Formula weight                          | 796.47                                     |
| Temperature                             | 173(2) K                                   |
| Wavelength                              | 0.71073 Å                                  |
| Crystal system                          | Orthorhomic                                |
| Space group                             | Cmca                                       |
| Unit cell dimensions                    |                                           |
| \(a\) = 20.2564(11) Å \(\alpha = 90^\circ\). |                                           |
| \(b\) = 19.0787(11) Å \(\beta = 90^\circ\). |                                           |
| \(c\) = 19.8420(11) Å \(\gamma = 90^\circ\). |                                           |
| Volume                                  | 7668.3(7) Å\textsuperscript{3}             |
| \(Z\)                                   | 8                                          |
| Density (calculated)                    | 1.380 Mg/m\textsuperscript{3}              |
| Absorption coefficient                  | 0.358 mm\textsuperscript{-1}              |
| F(000)                                  | 3264                                       |
| Crystal size                            | 0.220 x 0.190 x 0.160 mm\textsuperscript{3} |
| Theta range for data collection         | 2.369 to 25.008°                           |
| Index ranges                            | -24\leq h \leq 24, -16\leq k \leq 22, -23\leq l \leq 22 |
| Reflections collected                   | 22404                                      |
| Independent reflections                 | 3480 [R(int) = 0.0341]                     |
| Refinement method                       | Full-matrix least-squares on \(F^2\)      |
| Data / restraints / parameters           | 3480 / 0 / 256                             |
| Goodness-of-fit on \(F^2\)              | 1.035                                      |
| Final \(R\) indices [\(I\geq2\sigma(I)\)] | \(R_1 = 0.0467, wR_2 = 0.1294\)             |
| \(R\) indices (all data)               | \(R_1 = 0.0555, wR_2 = 0.1369\)            |
| Extinction coefficient                  | n/a                                        |
| Largest diff. peak and hole             | 0.923 and -0.574 e.Å\textsuperscript{-3}   |
| CCDC                                    | 1939272                                    |

**Crystal Structure Determination and refinements** (For 3, NaOTf \(\subset\) 6 and 7). Single-crystal X-ray diffraction data was collected on a Nonius KappaCCD diffractometer equipped with Mo K-alpha radiation (\(\lambda = 0.71073\) Å) and a BRUKER APEXII CCD. Throughout data collection, the crystal was cooled with an Oxford Cryosystem. The APEX3 software suite was used to manage data collection, reduction (SAINT V8.38A1), and absorption correction by the Multi-scan method (SADABS), structure determination via direct methods (SHLEXT) and model refinement (SHELXL). All non-hydrogen atoms were refined anisotropically though many atoms required anisotropic displacement parameter restraints. All hydrogen atoms were refined with isotropic displacement coefficients and their positions ideally constrained.
**Supplementary Figure 28.** Centroid–centroid distance and N···N distance (Å) of two benzene-pyridine arms from tweezer 3 in solid state (hydrogen atoms are omitted).
**Supplementary Table 2.** Crystal data and structure refinement for NaOTf ∂ 6

| Property                        | Value                                      |
|--------------------------------|--------------------------------------------|
| Empirical formula              | C$_{88}$H$_{116}$F$_9$N$_6$NaO$_{22}$P$_4$Pt$_2$S$_3$ |
| Formula weight                 | 2414.09                                    |
| Temperature                    | 103(2) K                                   |
| Wavelength                     | 0.71073 Å                                  |
| Crystal system                 | monoclinic                                 |
| Space group                    | P 1 21/n 1                                 |
| Unit cell dimensions           |                                           |
| a                             | 19.2590(5) Å                              |
| α                             | 90°                                        |
| b                             | 20.6064(5) Å                              |
| β                             | 100.6880(10)°                             |
| c                             | 26.1521(6) Å                              |
| γ                             | 90°                                        |
| Volume                         | 10198.6(4) Å                               |
| Density (calculated)           | 1.572 Mg/m$^3$                            |
| Absorption coefficient         | 2.955 mm$^{-1}$                            |
| F(000)                         | 4872                                       |
| Crystal size                   | 0.060 x 0.145 x 0.165 mm$^3$               |
| Theta range for data collection| 2.13 to 31.01°                             |
| Index ranges                   | -27<=h<=27, -29<=k<=29, -37<=l<=34        |
| Reflections collected          | 161925                                     |
| Independent reflections        | 32493 [R(int) = 0.0735]                    |
| Refinement method              | Full-matrix least-squares on $F^2$         |
| Data / restraints / parameters  | 32493 / 1579 / 1460                        |
| Goodness-of-fit on $F^2$        | 1.014                                      |
| Final $R$ indices [$>2\sigma(I)$]| $R_1 = 0.00365$, $wR_2 = 0.0656$          |
| $R$ indices (all data)         | $R_1 = 0.0670$, $wR_2 = 0.0735$           |
| Extinction coefficient         | n/a                                        |
| Largest diff. peak and hole    | 1.182 and -0.923 e.Å$^{-3}$                |
| CCDC                           | 1939276                                    |
**Supplementary Figure 29.** Solid state structures of NaOTf $\subset 6$: (a) side view and (b) front view (acetone and some of OTf$^-$ are omitted).
**Supplementary Table 3. Crystal data and structure refinement for 7**

| Property                      | Value                              |
|-------------------------------|------------------------------------|
| Empirical formula            | C<sub>81</sub>H<sub>104</sub>F<sub>6</sub>N<sub>6</sub>O<sub>17</sub>P<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub> |
| Formula weight               | 2125.88                            |
| Temperature                  | 103(2) K                           |
| Wavelength                   | 0.71073 Å                          |
| Crystal system               | monoclinic                         |
| Space group                  | C 1 2/c 1                          |
| Unit cell dimensions         |                                     |
| a                             | 36.6185(19) Å                      |
| α                             | 90°                                 |
| b                             | 16.1960(9) Å                       |
| β                             | 119.833(2)°                        |
| c                             | 35.828(3) Å                        |
| γ                             | 90°                                 |
| Volume                        | 18433.0(2) Å³                      |
| Z                             | 8                                   |
| Density (calculated)         | 1.532 Mg/m³                        |
| Absorption coefficient       | 3.224 mm⁻¹                         |
| F(000)                       | 8560                               |
| Crystal size                 | 0.135 x 0.195 x 0.400 mm³          |
| Theta range for data collection | 1.42 to 33.14°                      |
| Index ranges                 | -54<=h<=56, -24<=k<=24, -54<=l<=55 |
| Reflections collected        | 161477                             |
| Independent reflections      | 35120 [R(int) = 0.0593]             |
| Refinement method            | Full-matrix least-squares on F<sup>2</sup> |
| Data / restraints / parameters | 35120 / 86 / 1078                  |
| Goodness-of-fit on F<sup>2</sup> | 1.232                              |
| Final R indices [I>2sigma(I)] |                                     |
| R<sub>i</sub>                | 0.0617, wR<sub>2</sub> = 0.1141    |
| R indices (all data)         |                                     |
| R<sub>i</sub>                | 0.0839, wR<sub>2</sub> = 0.1198    |
| Extinction coefficient       | n/a                                |
| Largest diff. peak and hole  | 2.447 and -3.097 e.Å⁻³              |
| CCDC                          | 1946245                            |
Supplementary Figure 30. Multiple C-H⋯N hydrogen bonds between H atoms from aromatic rings and N atoms from naphthyridyl groups of 7 in solid state: C-H⋯N distances (Å).

Supplementary Figure 31. π⋯π stacking between two of four naphthyridine rings of 7 in solid state: centroid⋯centroid distance (Å) (hydrogen atoms and PEt₃ groups are omitted).
Supplementary Table 4. Containing the Check cif alerts obtained from the checkcif.iucr.org webpage and the authors responses

| Check cif alerts                                      | Response                                                                 |
|------------------------------------------------------|---------------------------------------------------------------------------|
| The value of sine(theta_max)/wavelength is less than 0.550 | The diffraction limit was found to be 1.5 Å and the data was trimmed accordingly |
| Non-Solvent Resd Ueq(max)/Ueq(min) Range             | Disordered moieties remained unmodelled due to the low data/parameter ratio. |
| MainMol' Ueq as Compared to neighbours               | Disordered moieties remained unmodelled due to the low data/parameter ratio. |

Supplementary Table 5. Crystal data and structure refinement for 10

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                            | C_{147}F_{3}N_{12}O_{19}P_{8}Pt_{4}S       |
| Formula weight                               | 3354.73                                    |
| Temperature                                  | 103.15 K                                   |
| Wavelength                                   | 0.71073 Å                                  |
| Crystal system                               | monoclinic                                 |
| Space group                                  | P 1 21/c 1                                 |
| Unit cell dimensions                         | a = 23.2555(8) Å, b = 55.5910(19) Å, c = 29.0761(10) Å |
| Volume                                        | 37452(2) Å³                               |
| Z                                             | 8                                          |
| Density (calculated)                         | 1.190 Mg/m³                                |
| Absorption coefficient                       | 3.112 mm⁻¹                                 |
| F(000)                                        | 12744                                      |
| Crystal size                                 | 0.50 x 0.10 x 0.05 mm³                     |
| Theta range for data collection              | 1.015 to 13.342°                           |
| Index ranges                                 | -15<=h<=15, -36<=k<=36, -18<=l<=18         |
| Reflections collected                        | 106205                                     |
| Independent reflections                      | 10717 [R(int) = 0.1762]                    |
| Refinement method                            | Full-matrix least-squares on F²            |
| Data / restraints / parameters               | 10717 / 1472 / 1089                        |
| Goodness-of-fit on F²                         | 1.031                                      |
| Final R indices [I>2sigma(I)]                | R₁ = 0.0947, wR₂ = 0.2340                  |
| R indices (all data)                         | R₁ = 0.1232, wR₂ = 0.2633                  |
| Extinction coefficient                       | 0.000112(15)                               |
| Largest diff. peak and hole                  | 3.239 and -1.457 e.Å⁻³                     |
| CCDC                                          | 1947413                                    |

Crystal Structure Determination and refinements (for 10). Single crystals of 10 were obtained by slow diffusion of n-hexane into an acetone solution of 10. Single-crystal X-ray diffraction data was collected on a Nonius KappaCCD diffractometer equipped with Mo K-alpha radiation (λ = 0.71073 Å) and a BRUKER APEXII CCD. Throughout data collection, the crystal was cooled with an Oxford Cryosystem. The crystal structure was solved and refined against all F² values using the SHELX and Olex 2 suite of
programmes. Crystals of bis[2]catenane presented a diffraction resolution of 1.5 Å. Only the platinium atoms were refined anisotropically. The rest of the atoms were refined isotropically due to a poor reflexions/parameters ratio. Hydrogen atoms were not placed in the calculated positions. The phenyl, napthyridyl and pyridyl groups were restrained to have idealized geometries using SHELX AFIX commands. The C-O distances in the carboxylate groups, P-C distances and C-C distances in PEt groups were restrained using SHELX DFIX commands. The atomic displacement parameters (adp) of the ligands have been restrained using SHELX DELU, SIMU and REGU commands.

Single crystal of bis[2]catenane presents large voids filled with a lot of scattered electron density. Solvent mask protocol inside Olex 2 software was used to account for the void electron density corresponding to the disordered OTf anions and solvent molecules placed in the intermolecular space in the crystal structure.

A large number of A-alerts and B-alerts were found due to poor resolution (1.5 Å). Rigid Body was used to solve the structure of the bis[2]catenane. Different moieties of the bis[2]catenane were restrained to have idealized geometries and allowed to refine their position and orientation.

Supplementary Figure 32. Two conformations of bis-metallacage 9 (I & II) in solid state: Pt···Pt distances (Å).
Supplementary Figure 33. 2F₀-Fc electronic density map (1.50 electrons per Å³) of 10.
Supplementary Figure 34. $^{31}$P{$^{1}$H} NMR spectra (121 MHz, CD$_2$Cl$_2$, 298K) of NaOTf ⊂ 6 (bottom) and 6 (up).

Supplementary Figure 35. $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298K) of NaOTf ⊂ 6 (bottom) and 6 (top).
Supplementary Figure 36. $^{31}$P($^1$H) NMR (160 MHz, acetone-d$_6$, 298K) spectra of 6 at different concentrations.
Supplementary Figure 37. Partial $^1$H NMR (400 MHz, acetone-$d_6$, 298 K) spectra of 6 at different concentrations.
Supplementary Figure 38. $^{31}$P($^1$H) NMR (160 MHz, acetone-$d_6$, 298K) spectra of 6 (30 mM) with different eq. of NaOTf.
Supplementary Figure 39. Partial $^1$H NMR (400 MHz, acetone-$d_6$, 298K) spectra of 6 (30 mM) with different eq. of NaOTf.
Supplementary Figure 40. $^{31}$P($^1$H) NMR (121 MHz, acetone-$d_6$, 298K) spectra of 6 (30 mM) with 1.5 eq. NaOTf: before and after the addition of 18C6 (1.8 eq.).
Supplementary Figure 41. Partial $^1$H NMR (400 MHz, acetone-$d_6$, 298K) spectra of 6 (30 mM) with 1.5 eq. NaOTf: before and after the addition of 18C6 (1.8 eq.).

Upon addition of 1.5 eq. of NaOTf, the $^{31}$P($^1$H) NMR (Supplementary Figure 38) spectra show a clear transformation from four sets of coupled doublets for 7, into two sets of coupled doublets for NaOTf ⊂ 6. And the $^1$H NMR (Supplementary Figure 39) spectra also indicate a structural transformation from 7 to NaOTf ⊂ 6. Then, we expected that the sodium can be removed from the cavity of 6 with the assistance of 18-crown-6-ether (18C6), resulting in the reassembly of 7. When we added 1.8 eq. 18C6 to the mixture of 6 and NaOTf, the NMR signals almost recovered the resonances of 7 (Supplementary Figure 40 & Supplementary Figure 41), indicating that the NaOTf- and 18C6-triggered structural inversions are reversible.
Supplementary Figure 42. $^{31}$P($^1$H) NMR (121 MHz, 298K) spectra of 6 (30 mM) in mixing solvent of acetone-$d_6$ and CD$_2$Cl$_2$.

Supplementary Figure 43. Partial $^1$H NMR (400 MHz, 298K) spectra of 6 (30 mM) in mixing mixing solvent of acetone-$d_6$ and CD$_2$Cl$_2$. 
When the proportion of CD$_2$Cl$_2$ in a acetone-d$_6$/CD$_2$Cl$_2$ solution of 7 increase, the $^{31}$P{$_^1$H} NMR (Supplementary Figure 42) and $^1$H NMR (Supplementary Figure 43) spectra clearly show that the nuclear resonances of 7 are gradually replaced by the signals for 6. While 6 is dissolved in CD$_2$Cl$_2$ at 30 mM, only the resonances for the monomeric metallacage 6 is observed by NMR spectroscopy (Supplementary Figure 42 & Supplementary Figure 43), indicating that 7 could not be formed in CD$_2$Cl$_2$.

**Supplementary Figure 44.** $^{31}$P{$_^1$H} NMR spectra (160 MHz, 298 K) of 9 in acetone-d$_6$ at different concentrations.
Supplementary Figure 45. Partial $^1$H NMR (400 MHz, acetone-$d_6$, 298K) spectra of 9 in acetone-$d_6$ at different concentrations.
Supplementary Figure 46. $^{31}$P($^1$H) NMR spectra (160 MHz, acetone-d$_6$, 298 K) of 9 (15 mM) with different eq. of NaOTf.
Supplementary Figure 47. Partial $^1$H NMR (400 MHz, acetone-$d_6$, 298K) spectra of 9 (15 mM) with different eq. of NaOTf.
Supplementary Figure 48. Partial $^1$H NMR (400 MHz, acetone-$d_6$, 298K) spectra of 9 (15 mM) with 6.0 eq. NaOTf: before and after the addition of 18C6 (7.0 eq.).
Supplementary Figure 49. $^{31}$P($^1$H) NMR (121 MHz, 298 K) spectra of 9 (15 mM) in a mixing solvent of acetone-$d_6$/CD$_2$Cl$_2$ (v/v).
Supplementary Figure 50. Partial $^1$H NMR (400 MHz, 298K) spectra of 9 (15 mM) in mixing solvent of acetone-$d_6$ and CD$_2$Cl$_2$. 
Supplementary Figure 51. $^{31}\text{P}^{(1}\text{H})$ NMR (160 MHz, 298 K) spectra of 6 in DMSO-$d_6$ (30 mM), acetonitrile-$d_3$ (30 mM), and methanol-$d_4$ (10 mM). Due to the low solubility, 6 in methanol-$d_4$ was tested at the concentration of 10 mM.
Supplementary Figure 52. Partial $^1$H NMR (400 MHz, 298K) spectra of 6 in DMSO-$d_6$ (30 mM), acetonitrile-$d_3$ (30 mM), and methanol-$d_4$ (10 mM). Due to the low solubility, 6 in methanol-$d_4$ was tested at the concentration of 10 mM.
Supplementary Figure 53. $^{31}$P($^1$H) NMR (160 MHz, 298 K) spectra of 9 (15 mM) in DMSO-$d_6$, acetonitrile-$d_3$, and methanol-$d_4$. 
**Supplementary Figure 54.** Partial $^1$H NMR (400 MHz, 298K) spectra of 9 (15 mM) in DMSO-$d_6$, acetonitrile-$d_3$, and methanol-$d_4$.

**Supplementary Table 6.** Proportions of 6/7 at different concentrations of 6 in acetone-$d_6$.

| Concentration of 6 (mM) in acetone-$d_6$ | Percentage of 6  | Percentage of 7 |
|----------------------------------------|------------------|-----------------|
| 2                                      | 89.3             | 10.7            |
| 4                                      | 70.7             | 29.3            |
| 6                                      | 60.1             | 39.9            |
| 8                                      | 47.2             | 52.8            |
| 10                                     | 32.1             | 67.9            |
| 15                                     | 23.1             | 76.9            |
| 20                                     | 19.5             | 80.5            |
| 30                                     | 18.2             | 81.8            |

**Supplementary Table 7.** Proportions of 6/7 in acetone-$d_6$ solution of 6 at 30 mM in the presence of NaOTf.

| Addition of NaOTf (eq.) | Percentage of 6  | Percentage of 7 |
|------------------------|------------------|-----------------|
| 0.2                    | 37.9             | 62.1            |
| 0.4                    | 54.3             | 45.7            |
| 0.6                    | 73.5             | 26.5            |
| 0.8                    | 80.6             | 19.4            |
### Supplementary Table 8. Proportions of 6/7 in different solvents of 6 at 30 mM.

| Solvents                          | Percentage of 6 | Percentage of 7 |
|-----------------------------------|-----------------|-----------------|
| Acetone-$d_6$/CD$_2$Cl$_2$ (v/v, 100/0) | 18.2            | 81.8            |
| Acetone-$d_6$/CD$_2$Cl$_2$ (v/v, 75/25) | 38.5            | 61.5            |
| Acetone-$d_6$/CD$_2$Cl$_2$ (v/v, 50/50) | 61.0            | 39.0            |
| Acetone-$d_6$/CD$_2$Cl$_2$ (v/v, 25/75) | 92.6            | 7.4             |
| methanol-$d_4$                      | 54.3            | 45.7            |
| acetonitrile-$d_3$                  | 92.6            | 7.4             |
| DMSO-$d_6$                         | >95.0           | <5.0            |

*: Due to the lack of solubility, the concentration of 6 in methanol-$d_4$ is 10 mM.

### Supplementary Table 9. Proportions of 9/10 at different concentrations of 9 in acetone-$d_6$.

| Concentration of 9 (mM) in acetone-$d_6$ | Percentage of 9 | Percentage of 10 |
|-----------------------------------------|-----------------|-----------------|
| 1                                       | 35.7            | 64.3            |
| 2                                       | 22.3            | 77.7            |
| 3                                       | 16.2            | 83.8            |
| 4                                       | 13.8            | 86.2            |
| 5                                       | 12.5            | 87.5            |
| 7.5                                     | 9.5             | 90.5            |
| 10                                      | 7.7             | 92.3            |
| 15                                      | 5.1             | 94.9            |

### Supplementary Table 10. Proportions of 9/10 in acetone-$d_6$ solution of 9 at 15 mM in the presence of NaOTf.

| Addition of NaOTf (eq.) | Percentage of 9 | Percentage of 10 |
|-------------------------|-----------------|-----------------|
| 0.4                     | 9.9             | 90.1            |
| 0.8                     | 14.6            | 85.4            |
| 1.2                     | 16.0            | 84.0            |
| 1.6                     | 20.5            | 79.5            |
| 3                       | 78.1            | 21.9            |
| 6                       | >95.0           | <5.0            |

### Supplementary Table 11. Proportions of 9/10 in different solvents of 9 at 15 mM.

| Solvents                          | Percentage of 9 | Percentage of 10 |
|-----------------------------------|-----------------|-----------------|
| Acetone-$d_6$/CD$_2$Cl$_2$ (v/v, 100/0) | 5.1             | 94.9            |
| Acetone-$d_6$/CD$_2$Cl$_2$ (v/v, 75/25) | 29.8            | 70.2            |
| Acetone-$d_6$/CD$_2$Cl$_2$ (v/v, 50/50) | 35.2            | 64.8            |
| Acetone-$d_6$/CD$_2$Cl$_2$ (v/v, 25/75) | >95.0           | <5.0            |


### Supplementary Figure 55

DOSY NMR spectrum (500 MHz, acetone-$d_6$, 298 K) of 6/7. (Concentration of 6: 30 mM)

### Supplementary Figure 56

DOSY NMR spectrum (500 MHz, acetone-$d_6$, 298 K) of 10. (Concentration of 9: 15 mM)
Supplementary Figure 57. $^1$H–$^1$H COSY NMR spectrum (600 MHz, acetone-$d_6$, 298 K) of 6 at 30 mM.
Supplementary Figure 58. $^1$H-$^1$H COSY NMR spectrum (600 MHz, acetone-$d_6$, 298 K) of 9 at 15 mM.
Supplementary Figure 59. The non-linear curve-fitting (NMR titrations) for the complex of NaOTf $\subset$ 6, $K_a$ = $(1270 \pm 30) \text{ M}^{-1}$. 
Supplementary Figure 60. Partial $^1$H NMR spectra (400 MHz, in acetone-d$_6$ at 298 K) of 6 (H$_i$) at a concentration of 0.50 mM upon addition of NaOTf. From bottom to top, the concentration of NaOTf was 0.00, 0.10, 0.20, 0.39, 0.59, 0.96, 1.68, 2.36, 3.60, 5.71, 8.29, 10.3, 13.1 and 15.0 mM.

For the host–guest pairs, chemical exchange is fast on the NMR time scale. To determine the association constant, NMR titrations were done with solutions which had a constant concentration of 6 and varying concentrations of NaOTf. Using the nonlinear curve-fitting method, the association constant was obtained for each host–guest combination from the following equation:

$$A = (A_\infty/[G]_0) (0.5[H]_0 + 0.5([G]_0+1/K_a)-(0.5 ([H]_0^2+2[H]_0(1/K_a-[G]_0)) + (1/K_a + [G]_0^2)^{0.5}))$$ (Supplementary equation 1)

Where $A$ is the chemical shift change of 6, $A_\infty$ is the chemical shift change when the NaOTf is completely complexed, $[H]_0$ is the fixed initial concentration of the 6, and $[G]_0$ is the initial concentration of NaOTf. The association constants ($K_a$) was calculated by using the nonlinear curve-fitting method (Supplementary Figures 59 and 60).

Supplementary References

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