Supplementary Information

Self-assembled supramolecular cages containing ruthenium(II) polypyridyl complexes

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S1. General Experimental Methods

The numbering scheme adopted for compound ligands 1 and 2 are shown in Figure S1. $^1$H and $^{13}$C{$_^1$H} NMR spectra were recorded on a Bruker AV-400 spectrometer, Bruker Avance DRX 500, and Bruker Avance III 600M spectrometer; The chemical shifts for the $^1$H and $^{13}$C{$_^1$H} NMR spectra are referenced to residual solvent resonance. Coupling constants ($J$) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, b = broad, ddd = doublet of double doublets. $^1$H and $^{13}$C{$_^1$H} NMR assignments were made using 2D-NMR methods (COSY, ROESY, NOCSY, HSQC, HMBC) and are unambiguous unless stated otherwise.

All mass spectrometry experiments were performed on a hybrid linear quadrupole ion trap mass spectrometer coupled to a high performance orbitrap mass spectrometer (Thermo LTQ Orbitrap XL) that is equipped with an external electrospray ionisation (ESI) source. To generate intact ions of the molecular cages, ESI solutions containing ca. 5 mg/mL of the cages were used. ESI was initiated and maintained by applying a voltage of 5 kV to the ESI emitter relative to the capillary entrance to the mass spectrometer. ESI solutions were infused into the ion source at relatively high flow rates (15 uL/min) and the temperature of the capillary entrance to the mass spectrometer was reduced to 50°C. These conditions were selected to minimise the dissociation of highly charged non-covalently bound assemblies during the ion formation and transfer processes prior to mass analysis using the orbitrap mass spectrometer. The accuracy of this instrument for measuring $m/z$ values is routinely below one part in a million (<ppm).

Compounds Pd(dppp)(OTf)$_2$, Ru(1)$_2$(PF$_6$)$_2$ and Ru(2)$_2$(PF$_6$)$_2$ were prepared by as previously reported.$^2$
Figure S1  Structures of ligands 1 and 2, complexes \([\text{Ru}(1)_2]\)(PF_6)_2 and \([\text{Ru}(2)_2]\)(PF_6)_2; and cages \(\text{3(PF}_6\text{)}_{24}\) and \(\text{4(PF}_6\text{)}_{18}\) and atom number scheme for NMR spectroscopic data.
S2. Reference NMR data for complexes Ru(1)₂(PF₆)₂ and Ru(2)₂(PF₆)₂ in CD₃NO₂

Complexes Ru(1)₂(PF₆)₂ and Ru(2)₂(PF₆)₂ were prepared as previously reported.² NMR data was recorded in CD₃NO₂ for comparison purposes, and is presented below.

2.1.1 NMR characterization of complex Ru(1)₂(PF₆)₂ in nitromethane-d₃

\(^1\)H NMR (600 MHz, CD₃NO₂) δ 9.27 (s, 2H, H^B₃), 8.85 – 8.79 (m, 4H, H^D₂), 8.76 (d, J = 8.1 Hz, 2H, H^A₃), 8.66 (d, J = 1.6 Hz, 2H, H^H₃), 8.42 (t, J = 1.7 Hz, 1H, H^C₂), 8.03 – 7.96 (m, 6H, H^D₃+A₄), 7.64 (dd, J = 5.8, 1.5 Hz, 2H, H^A₅), 7.26 (ddd, J = 7.3, 5.7, 1.3 Hz, 2H, H^A₅).

\(^1\)C\{\(^1\)H\} NMR (151 MHz, CD₃NO₂) δ 159.6 (CA₂), 157.2 (CB₂), 153.7 (CA₆), 151.7 (CD₂), 149.0 (C₃), 148.7 (C₇), 142.0 (C₄), 140.6 (C₄'), 139.5 (C₅), 128.9 (CA₅'), 128.8 (C₃'), 128.4 (C₄'), 125.8 (CA₃'), 123.3 (CD₃'), 123.1 (C₃').

Figure S2  \(^1\)H-NMR (CD₃NO₂, 600MHz, 298K) spectrum of Ru(1)₂(PF₆)₂
Figure S3  $^{13}$C ($^1$H)-NMR (CD$_3$NO$_2$, 151 MHz, 298K) of Ru(1)$_2$(PF$_6$)$_2$
2.1.2 NMR characterization of complex \( \text{Ru}(2)\text{PF}_6\text{)}_2 \) in nitromethane-d₃

\(^1\text{H} \text{NMR} (600 \text{ MHz, CD}_3\text{NO}_2) \delta 9.17 (s, 2H, H^{\text{B3}}), 8.75 (d, J = 8.1 \text{ Hz, } 2H, H^{\text{A3}}), 8.68 (d, J = 5.1 \text{ Hz, } 4H, H^{\text{D2}}), 8.47 (d, J = 1.5 \text{ Hz, } 2H, H^{\text{C4}}), 8.12 (d, J = 1.5 \text{ Hz, } 1H, H^{\text{C2}}), 8.01 (td, J = 7.8, 1.5 \text{ Hz, } 2H, H^{\text{A4}}), 7.66 – 7.57 (m, 6H, H^{\text{D3+6A}}), 7.26 (ddd, J = 7.3, 5.7, 1.3 \text{ Hz, } 2H, H^{\text{A5}}).

\(^{13}\text{C} \{^1\text{H}\} \text{NMR} (151 \text{ MHz, CD}_3\text{NO}_2) \delta 159.5 (C^{\text{A2}}), 157.3 (C^{\text{B2}}), 153.7 (C^{\text{A6}}), 151.5 (C^{\text{D2}}), 147.8 (C^{\text{C3}}), 139.9 (C^{\text{B1}}), 139.5 (C^{\text{A4}}), 137.4 (C^{\text{C2}}), 132.8 (C^{\text{C4}}), 131.8 (C^{\text{D4}}), 129.0 (C^{\text{A5}}), 126.9 (C^{\text{D3}}), 125.9 (C^{\text{A3}}), 125.6 (C^{\text{C1}}), 122.8 (C^{\text{B3}}), 92.7 (C-alkyne), 89.5 (D-alkyne).

Figure S4  \(^1\text{H}-\text{NMR (CD}_3\text{NO}_2, 600\text{MHz, 298K)} \text{ of Ru(2)PF}_6\text{)}_2 \)
S3. Synthetic procedures

3.1.1 Synthesis of cage 3(PF₆)₂₄

A DMSO solution (2 mL) of Ru(1)₂(PF₆)₂ (50 mg, 0.038 mmol) and Pd(dppp)(OTf)₂ (62 mg, 0.076 mmol) was stirred at room temperature for 10 min resulting in a blood-red solution. Excess saturated aqueous NH₄PF₆ (10 mL) was added to the solution. A fine suspension of a red material formed which was collected on Celite, thoroughly washed with plenty of water, ethanol (10 mL), DCM (1 mL) and diethylether (10 mL). The red filter cake was dissolved in acetonitrile and concentrated under reduced pressure to give cage 3 as a red powder (85 mg, 76%). Microanalysis analysis found C 45.42, H 3.40; N 4.71 %. Calculated for C₄₆H₃₇F₁₄₄N₄₀P₄₀Pd₈Ru₄(H₂O)₂₅: C 45.71; H 3.52; N 4.60 %. NMR and ESI-MS characterisation is given below.

3.1.2 Synthesis of cage 4(PF₆)₁₈

A sample of Ru(2)₂(PF₆)₂ (4.0 mg, 0.0028 mmol) was dissolved in CD₃NO₂ (0.5 mL) in an NMR tube with a magnetic stirring bar inside. After stirring for 2 min Pd(dppp)(OTf)₂ (4.6 mg, 0.0057 mmol) was added. The ¹H-NMR and ³¹P{¹H} spectra of this solution is consistent with the proposed structure of cage 4¹⁸⁺.

A sample of Ru(2)₂(PF₆)₂ (8.0 mg, 0.0057 mmol) was dissolved in CH₃NO₂ (2 mL) in a 5 mL flask with a magnetic stirring bar inside. After stirring for 2 min Pd(dppp)(OTf)₂ (9.3 mg, 0.011 mmol) was added. The formed blood-red solution was washed with...
aqueous NH₄PF₆ twice to ensure complete exchange of anions for PF₆⁻. The CH₃NO₂ layer was dried with NaSO₄ and the solvent removed to give cage 4(PF₆)₁₈ as a red powder (12 mg, 0.0040 mmol, 70%). Microanalysis analysis found C 46.52; H 3.35; N 4.87 %. C₃₇₂H₂₈₂F₁₀₈N₃₀P₃₀Pd₆Ru₃(H₂O)₂₅ requires C 46.81; H 3.51; N 4.40 %. NMR and ESI-MS characterisation is given below.

S4. Characterisation of cage 3(PF₆)₂₄ in CD₃NO₂ by NMR

4.1.1 ¹H, ¹³C and ³¹P NMR characterization of cage 3(PF₆)₂₄ in CD₃NO₂

¹H NMR (600 MHz, CD₃NO₂) δ 8.84 – 8.60 (m, 6H, H⁴⁺⁺D₂), 8.29 (m, 4H, H³⁺⁺C₄), 8.01 (s.1H, H⁵⁺⁺), 7.94 – 7.70 (m, 12H, H⁶⁺⁺D₁), 7.69 – 7.42 (m, 12H, H⁶⁺⁺), 7.19 – 6.83 (m, 4H, H⁴⁺⁺⁻⁴⁺⁺), 5.92 (s, 2H, H⁵⁺⁺), 3.30 (s, 4H, H⁴⁺⁺⁻⁴⁺⁺), 2.66 – 2.37 (m, 2H, H⁴⁺⁺⁻⁴⁺⁺).

¹³C{¹H} NMR (151 MHz, CD₃NO₂) δ 159.2 (CA₂), 156.2 (CB₂), 153.1 (CA₆), 151.2 (CD₂), 150.8 (C¹), 148.2 (C¹), 140.9 (C⁵⁺⁺), 138.9 (C⁴⁺⁺), 138.4 (C⁴⁺⁺), 134.5-134.0 (C⁶⁺⁺), 131.2-131.1 (C⁵⁺⁺), 129.6 (C¹), 127.9 (C¹), 127.8 (C³⁻¹⁻⁴⁺⁺), 126.0 (C³⁻¹⁻⁴⁺⁺), 123.3 (C⁵⁺⁺), 23.0-22.7 (C⁴⁺⁺⁻⁴⁺⁺), 18.7 (C⁴⁺⁺⁻⁴⁺⁺).

³¹P{¹H} NMR (243 MHz, CD₃NO₂) δ 8.8 (s, 2P, PdPPP), -144.0 (hept, 3P, JₚF = 709 Hz, PP₆).

Figure S6 ¹H-NMR (CD₃NO₂, 600 MHz, 298K, approx. 1.5 mM) spectrum of cage 3(PF₆)₂₄.
Figure S7  $^{13}$C($^1$H)-NMR (CD$_3$NO$_2$, 151 MHz, 298K, approx. 1.5 mM) spectrum of cage $3$(PF$_6$)$_{24}$.

$^{31}$P-$^{13}$C coupling from the dppp ligand is observed as well as two non-equivalent phenyl ring conformations.

Figure S8  $^{31}$P($^1$H)-NMR (CD$_3$NO$_2$ 243 MHz, 298K, 1.5 mM) spectrum of cage $3$(PF$_6$)$_{24}$
4.1.2 $^1$H-$^1$H COSY NMR spectrum of cage $3(PF_6)_{24}$ in $CD_3NO_2$ at 298K

Figure S9 $^1$H-$^1$H COSY NMR ($CD_3NO_2$, 600 MHz, 298K) spectrum of cage $3(PF_6)_{24}$. 
4.1.3 $^1$H-$^1$H NOESY NMR spectrum of cage $3(PF_6)_{24}$ in CD$_3$NO$_2$ at 298K

Figure S10  $^1$H-$^1$H NOESY NMR {CD$_3$NO$_2$, 600 MHz, 298K} spectrum of cage $3(PF_6)_{24}$. 
4.1.4 $^1$H-$^{13}$C HSQC correlation NMR spectrum of cage 3(PF$_6$)$_{24}$ in CD$_3$NO$_2$ at 298K

Figure S11 $^1$H-$^{13}$C HSQC NMR (CD$_3$NO$_2$, 600 MHz, 298K) spectrum of cage 3(PF$_6$)$_{24}$.
4.1.5 $^1$H-$^{13}$C HMBC correlation NMR spectrum of cage 3(PF$_6$)$_{24}$ in CD$_3$NO$_2$ at 298K

Figure S12  $^1$H-$^{13}$C HMBC NMR (CD$_3$NO$_2$, 600 MHz, 298K) spectrum of cage 3(PF$_6$)$_{24}$. 
S5. Characterisation of cage 3(PF\textsubscript{6})\textsubscript{24} in CD\textsubscript{3}NO\textsubscript{2} by NMR at 348K

5.1.1 1D \textsuperscript{1}H, \textsuperscript{31}C and \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra and assignment of cage 3(PF\textsubscript{6})\textsubscript{24} in CD\textsubscript{3}NO\textsubscript{2} at 348K

\textsuperscript{1}H NMR (600 MHz, CD\textsubscript{3}NO\textsubscript{2}) $\delta$ 8.76 (s, 2H, H\textsuperscript{B3}), 8.73 (d, $J = 5.9$ Hz, 4H, H\textsuperscript{D2}), 8.35 (s, 2H, H\textsuperscript{C4}), 8.29 (d, $J = 8.0$ Hz, 2H, H\textsuperscript{A3}), 8.03 (s, 1H, H\textsuperscript{C2}), 7.91 – 7.76 (m, 12H, H\textsuperscript{D3}+Ph), 7.73 – 7.44(m, 12H, H\textsuperscript{Ph}), 7.08 (d, $J = 5.9$ Hz, 2H, H\textsuperscript{A6}), 6.98 (t, $J = 7.2$ Hz, 2H, H\textsuperscript{A4}), 6.00 (s, 2H, H\textsuperscript{A5}), 3.34 – 3.20 (m, 4H, H\textsuperscript{CH2-P}), 2.56 (ddt, $J = 31.5$, 16.6, 7.5 Hz, 2H, H\textsuperscript{CH2-C}).

DEPT90 \textsuperscript{13}C NMR (151 MHz, CD\textsubscript{3}NO\textsubscript{2}) $\delta$ 153.0 (CA\textsubscript{6}), 151.3 (CD\textsubscript{2}), 138.4 (CA\textsubscript{4}), 134.4-134.2 (C\textsubscript{Ph}), 131.3-131.1(C\textsubscript{Ph}), 129.6(C\textsuperscript{C4}), 127.9(C\textsuperscript{A3}+C\textsuperscript{C2}), 126.1(C\textsuperscript{A3}), 126.0(C\textsuperscript{D3}), 123.3(C\textsuperscript{B3}).

\textsuperscript{31}P{\textsuperscript{1}H} 9.27 (s, P\textsuperscript{Pdppp}), -143.75 (hept., $J_{P-F} = 708$ Hz, P\textsuperscript{PPF6})

Figure S13. \textsuperscript{1}H-NMR (CD\textsubscript{3}NO\textsubscript{2}, 600MHz, 348K) spectrum of cage 3(PF\textsubscript{6})\textsubscript{24} in CD\textsubscript{3}NO\textsubscript{2}
Figure S14  DEPT90-NMR (CD$_3$NO$_2$, 151MHz, 348K) spectrum of cage 3(PF$_6$)$_{24}$. $^{31}$P-$^{13}$C coupling from the dppp ligand is observed as well as two non-equivalent phenyl ring conformations.

Figure S15  $^{31}$P-$^1$H-NMR (CD$_3$NO$_2$, 243MHz, 348K) spectrum of cage 3(PF$_6$)$_{24}$. 
5.1.2 $^1$H-$^1$H COSY NMR spectrum of cage 3(PF$_6$)$_{24}$ in CD$_3$NO$_2$ at 348K

5.1.3 $^1$H-$^{13}$C HSQC correlation NMR spectrum of cage 3(PF$_6$)$_{24}$ in CD$_3$NO$_2$ at 348K
Figure S17  $^1$H-$^{13}$C-HSQC NMR ($^{13}$CD$_3$NO$_2$, (600, 151) MHz), 348K} spectrum of cage $^3$(PF$_6$)$_{24}$.
S6. Effect of temperature on the $^1$H and $^{31}$P{$^1$H} NMR of cage 3 in CD$_3$NO$_2$ (268-348K)

Figure S18  $^1$H-NMR (Nitromethane-d$_3$, 600MHz) of Cage 3 in CD$_3$NO$_2$ at different temperature (a) 348K, (b) 338K, (c) 328K, (d) 318K, (e) 308K, (f) 298K, (g) 288K, (h) 278K, (i) 268K.

Figure S19  $^{31}$P{$^1$H}-NMR (Nitromethane-d$_3$, 243 MHz) of Cage 3 in CD3NO2 at different temperature (a) 348K, (b) 338K, (c) 328K, (d) 318K, (e) 308K, (f) 298K, (g) 288K, (h) 278K, (i) 268K.
S7. Effect of temperature on the $^1$H NMR spectrum of cage 3 in acetone-$d_6$ (248 – 313K)

**Figure S20** $^1$H-NMR (500 MHz, acetone-$d_6$) spectrum of a sample of cage 3 at variable temperature (from top to bottom): 313K, 308K, 303K, 298K, 293K, 288K, 283K, 278K, 273K, 268K, 263K, 258K, 253K, 248K.
S8. Characterisation of cage $3(F_6)_{24}$ in CD$_3$CN at 298K

8.1.1 $^1$H and $^{13}$C NMR of $3(F_6)_{24}$ in CD$_3$CN at 298K

Figure S21 $^1$H-NMR (CD$_3$CN, 600 MHz, 2 mM, 298K) spectrum of cage $3(F_6)_{24}$.

Figure S22 $^{13}$C($^1$H) (top) and DEPT (bottom) NMR (CD$_3$CN, 151 MHz, 2 mM, 298K) spectrum of cage $3(F_6)_{24}$. 
8.1.2 COSY NMR spectrum of 3(PF₆)₂₄ in CD₃CN

Figure S23 ¹H-¹H COSY-NMR (CD₃CN, 600 MHz, 2 mM, 298K) spectrum of cage 3(PF₆)₂₄.

8.1.3 ¹H-¹³C HSQC correlation NMR spectrum of 3(PF₆)₂₄ in CD₃CN

Figure S24 ¹H-¹³C HSQC-NMR (CD₃CN, 600-151 MHz, 2 mM, 298K) spectrum of cage 3(PF₆)₂₄.
8.1.4 $^1$H-$^{13}$C HMQC correlation NMR spectrum of 3(PF$_6$)$_{24}$ in CD$_3$CN

Figure S25  $^1$H-$^{13}$C HMBC NMR (CD$_3$CN, 600-151 MHz, 2 mM, 298K) spectrum of cage 3(PF$_6$)$_{24}$. 
8.1.5 $^{1}$H-$^{1}$H ROESY correlation of 3(PF$_6$)$_{24}$ in CD$_3$CN

Figure S26  $^{1}$H-$^{1}$H ROESY-NMR (CD$_3$CN, 600 MHz, 2 mM, 298K) spectrum of cage 3(PF$_6$)$_{24}$. 
8.1.6 $^1$H-$^1$H NOESY correlation of $3(\text{PF}_6)_{24}$ in CD$_3$CN

Figure S27 $^1$H-$^1$H NOESY-NMR (CD$_3$CN, 600 MHz, 2 mM, 298K) spectrum of cage $3(\text{PF}_6)_{24}$. 
S9. Concentration dependence of cage 3(PF₆)₂₄ stability

9.1.1 Effect of concentration on the stability of cage 3(PF₆)₂₄ in CD₃CN 0.03 – 1.9 mM

Figure S28 ¹H-NMR (600 MHz, CD₃CN, 298K) of cage 3(PF₆)₂₄ at different concentrations (a) 1.92 mM, (b) 0.48 mM, (c) 0.30 mM, (d) 0.21 mM, (e) 0.14 mM, (f) 0.09 mM, (g) 0.06 mM, (h) 0.03 mM, and (i) 1(PF₆)₂ in CD₃CN. Lower concentrations lead to the disassembly of cage 3(PF₆)₂₄. Titration experiments demonstrates that the cage start to disassemble at 0.3 mM and is completely disassembled at 0.03 mM.
9.1.2 Effect of concentration on the stability of cage 3(PF₆)₂₄ in CD₃NO₂ (0.2 – 1.1 mM)

Figure S29 ¹H-NMR (CD₃NO₂, 600MHz, 298K) of cage 3(PF₆)₂₄ in concentration of (a) 1.13mM, (b) 0.58mM, (c) 0.38mM, (d) 0.29mM, (e) 0.19mM and (f) pure 1(PF₆)₂ in CD₃NO₂. An impurity of DMF is present in the CD₃NO₂, but did not appear to affect the experiment.
S10. Characterisation of cage $4\text{(PF}_6\text{)}_{18}$ by NMR

10.1.1 $^1\text{H}$, $^{13}\text{C}^{(^1\text{H})}$ and $^{31}\text{P}^{(^1\text{H})}$ NMR and assignments for cage $4\text{(PF}_6\text{)}_{18}$ in CD$_3$NO$_2$

$^1\text{H}$ NMR (600 MHz, CD$_3$NO$_2$) δ 8.86 (s, 2H, H$^{\text{B3}}$), 8.73 (d, $J = 5.9$ Hz, 4H, H$^{\text{D2}}$), 8.56 (d, $J = 8.1$ Hz, 2H, H$^{\text{A3}}$), 8.28 (d, $J = 1.3$ Hz, 2H, H$^{\text{C1}}$), 7.95 – 7.91 (m, 1H, H$^{\text{C2}}$), 7.80 – 7.73 (m, 10H, H$^{\text{A4}+\text{Ph}}$), 7.63 – 7.45 (m, 12H, H$^{\text{Ph}}$), 7.40 (dd, $J = 6.0, 1.5$ Hz, 2H, H$^{\text{A6}}$), 7.36 (d, $J = 6.0$ Hz, 4H, H$^{\text{D3}}$), 7.02 (t, $J = 6.7$ Hz, 2H, H$^{\text{A5}}$), 3.29 (s, 4H, H$^{\text{C1}}_{\text{H2}-\text{P}}$), 2.46 (d, $J = 25.8$ Hz, 2H, H$^{\text{C1}}_{\text{H2}-\text{C}}$).

$^{13}\text{C}^{(^1\text{H})}$ NMR (151 MHz, CD$_3$NO$_2$) δ 159.2 (C$^{\text{A2}}$), 156.9 (C$^{\text{B2}}$), 153.6 (C$^{\text{A6}}$), 151.2 (C$^{\text{D2}}$), 147.9 (C$^{\text{C3}}$), 140.7 (C$^{\text{D1}}$), 139.2 (C$^{\text{A4}}$), 137.6 (C$^{\text{C4}}$), 135.4 (C$^{\text{C5}}$), 134.8 (C$^{\text{D4}}$), 134.5 (C$^{\text{Pb}}$), 134.4 (C$^{\text{Ph}}$), 134.1 (C$^{\text{Ph}}$), 131.0 (C$^{\text{Ph}}$), 129.6 (C$^{\text{D1}}$), 128.7 (C$^{\text{A5}}$), 126.6-126.2 (C$^{\text{Ph}}$), 125.9 (C$^{\text{A3}}$), 123.5 (C$^{\text{C1}}$), 123.3 (C$^{\text{B1}}$), 97.2 (C$^{\text{alkene}}$), 88.0 (C$^{\text{alkene}}$), 22.6 (C$^{\text{C1}}_{\text{H2}-\text{P}}$), 18.8 (C$^{\text{C1}}_{\text{H2}-\text{C}}$).

$^{31}\text{P}^{(^1\text{H})}$ NMR (243 MHz, CD$_3$NO$_2$) δ 8.9 (s, 2P, P$_{\text{PPP}}$), -144.0 (hept, 3P, $J_{\text{P-F}} = 709$ Hz, P$^{\text{PF6}}$).

Figure S30 $^1\text{H}$-NMR (CD$_3$NO$_2$, 600 MHz, 1.5 mM, 298K) cage $4\text{(PF}_6\text{)}_{18}$ at 298K.
Figure S31  $^{13}$C{'1H}-NMR (CD$_3$NO$_2$, 151 MHz, 1.5 mM, 298K) cage 4(PF$_6$)$_{18}$

Figure S32  $^{31}$P{'1H}-NMR (CD$_3$NO$_2$, 1.5 mM, 243 MHz, 298K) spectrum of cage 4(PF$_6$)$_{18}$.
10.1.2 Comparison of $^1$H NMR of cage 4$^{18+}$ with its parent Ru(II) complex in CD$_3$CN

Figure S33  $^1$H-NMR (CD$_3$CN, 600 MHz, 298K) spectra of (a) Ru(2)$_2$(PF$_6$) and (b) cage 4(PF$_6$)$_{18}$. The observed broad signals suggest slow exchange of pyridyl ligands (on the NMR timescale) by acetonitrile solvent molecules.
S11. Concentration dependence of cage $4\text{(PF}_6\text{)}_{18}$

11.1.1 Concentration dependence of a sample of cage $4\text{(PF}_6\text{)}_{18}$ in $\text{CD}_3\text{NO}_2$ ($0.2 - 1.1 \text{ mM}$)

![NMR Spectra](image_url)

**Figure S34** $^1\text{H-NMR (CD}_3\text{NO}_2, 600\text{MHz, 298K)}$ of Cage 3 at concentrations of (a) 1.13mM, (b) 0.58mM, (c) 0.38mM, (d) 0.29mM, (e) 0.19mM and (f) pure 2 in $\text{CD}_3\text{NO}_2$, indicating cage $4\text{(PF}_6\text{)}_{18}$ is stable in $\text{CD}_3\text{NO}_2$ over this concentration range.
S12. Comparison of $^{31}\text{P}^{1\text{H}}$ NMR of cage 3(PF$_6$)$_{24}$ and 4(PF$_6$)$_{18}$ with the parent Pd(dppp)(OTf)$_2$ complex in CD$_3$NO$_2$

Figure S35 $^{31}\text{P}^{1\text{H}}$-NMR (CD$_3$NO$_2$, 243 MHz, 298K) spectra of (a) Pd(dppp)(OTf)$_2$, (b) cage 3(PF$_6$)$_{24}$, (c) cage 4(PF$_6$)$_{18}$.
S13. Comparison of $^{13}$C-$^1$H NMR spectra in CD$_3$NO$_2$

Figure S36  $^{13}$C-$^1$H-NMR (Nitromethane-d$_3$, 151MHz) spectra of Cage 3 and cage 4 compared with 1 and 2 in CD$_3$NO$_2$. (a) cage 3 in CD$_3$NO$_2$ (b) 1 in CD$_3$NO$_2$, (c) cage 4 in CD$_3$NO$_2$, (d) 2 in CD$_3$NO$_2$. An unidentified quaternary carbon, assumed to be an impurity, is marked with an asterisk.
13.1.1 Comparison of $^{13}\text{C}^{[1\text{H}]}$ NMR of cages $3^{24+}$ and $4^{18+}$ with their parent Ru(II) complexes in CD$_3$CN

**Figure S37** $^{13}\text{C}^{[1\text{H}]}$-NMR (CD$_3$NO$_2$, 151MHz, 1.5 mM, 298K) spectra of cage $3$(PF$_6$)$_{24}$ and cage $4$(PF$_6$)$_{18}$ compared with Ru($1$)$_2$(PF$_6$)$_2$ and Ru($2$)$_2$(PF$_6$)$_2$. Top to bottom: (a) cage $3$(PF$_6$)$_{24}$; (b) Ru($1$)$_2$(PF$_6$)$_2$; (c) cage $4$(PF$_6$)$_{18}$; (d) Ru($2$)$_2$(PF$_6$)$_2$. 
S14. High Resolution Electrospray Mass Spectrometry (HR-ESI-MS) of cages $3(PF_6)_{24}$ and $4(PF_6)_{18}$

14.1.1 HR-ESI-MS of cage $3(PF_6)_{24}$

![Graph showing mass spectrometry data for cage $3(PF_6)_{24}$ with peaks labeled with their respective charges and masses.]

**Chemical Impressions:**
- $3^{10+}$ or $3^{10+}$
- $3^{12+}$ or $3^{12+}$
- $3^{14+}$ or $3^{14+}$
- $3^{15+}$ or $3^{15+}$
- $3^{16+}$ or $3^{16+}$
- $3^{18+}$ or $3^{18+}$
- $3^{20+}$ or $3^{20+}$
- $3^{22+}$ or $3^{22+}$
- $3^{24+}$ or $3^{24+}$

**Equations:**
- $3^{n+} = |cage 3 - n(PF_6)|^{+}$
- $3^{n+} = |cage 3a - n(PF_6)|^{+}$

**Additional Notes:**
- The graphical representation shows the relative abundance of various ions with different charges and masses. The peaks indicate the presence of ions with specific charges and masses, which are labeled in the figure.

![Graphs showing mass spectrometry data for cage $4(PF_6)_{18}$ with peaks labeled with their respective charges and masses.]

**Graphical Analysis:**
- The graphs illustrate the distribution of ions across different charge states, highlighting the spectral information for $3(PF_6)_{24}$ and $4(PF_6)_{18}$ with a focus on the charge distribution and mass accuracy.

**Interpretation:**
- The data suggest a rich spectrum of ionization states, which can be crucial for understanding the structural and chemical properties of the cages.

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**References:**
- Additional references or citations related to HR-ESI-MS for cages $3(PF_6)_{24}$ and $4(PF_6)_{18}$ are provided in the supplementary material or cited within the main text.
Figure S38  ESI-MS of cage 3(PF₆)₂₄ with selected peak expansions and calculated patterns below in red.

a) Full spectrum with peaks corresponding to cage 3⁹⁺ and 3a²⁺,  
   b) [3-10PF₆]¹⁰⁺ overlapping with a 5⁺ peak corresponding to a fragment of half the cage, confirmed by collision-induced dissociation (CID) experiments;  
   c) [3-9PF₆]⁹⁺, d) [3-7PF₆]⁷⁺, e) [3-7PF₆]⁷⁺, f) [3-6PF₆]⁶⁺ and g) [3-5PF₆]⁵⁺ Compound 3a²⁺ corresponds to cage 3²⁺ with the loss of one Pd(dppp)²⁺ unit, which was confirmed by collision-induced dissociation (CID) experiments.
14.1.2 HR-ESI-MS of cage 4(PF₆)₁₈

![Image of mass spectrum showing various peaks and formulas]

Figure S39  ESI-MS of cage 4(PF₆)₁₈, a) Full spectrum of cage 4(PF₆)₁₈, b) expansion of peak [4-8PF₆]⁸⁺, c) [4-7PF₆]⁷⁺, d) [4-6PF₆]⁶⁺ and e) [4-5PF₆]⁵⁺ with calculated patterns red below.
S15. Single crystal X-ray structure data for 
[3](PF₆)_{17.5^-}(CH₃NO₂)

15.1.1 X-ray experimental for [3](PF₆)_{17.5^-}(CH₃NO₂)

Crystals of [3](PF₆)₂₄ were grown by slow diffusion of toluene into a nitromethane solution of the complex. Wine red crystals with a morphology having well defined faces making a parallelohedron were grown in a sealed NMR tube. Crystals started cracking instantly upon cut opening the NMR tube. However, one crystal of dimensions 0.076 X 0.070 X 0.029 mm, coated in paraffin oil, could be transferred quickly to the goniometer under the flow of liquid nitrogen cold stream (150 K). With the MoK microsource installed on the Bruker APEXII CCD diffractometer, the diffraction data could be acquired over ~ 7h. Integration, data reduction and scaling was carried out with the programs SAINT and SADABS in the Bruker’s APEXII suite of software (crystallographic data is summarized in Table 1). The structure was solved by Patterson method, which showed all the heavy atoms (Ru and Pd); the successive refinement and difference Fourier maps revealed the rest of the non-H atoms of the cage. The phenyl ring atoms of the ligands coordinated to the edge of the barrel shaped cage showed very high thermal anisotropies. Most PF₆ anions (total accounting to 8.75 per ½ cage molecule = 17.5 per cage) and a nitromethane solvent molecule (half occupancy) could be located, their occupancies were optimized based on the peak heights and thermal anisotropic behavior. The least-squares refinement was carried out with the latest version of SHELXL, with appropriate constraints applied to the different parts of the cage assembly. The six membered (phenyl) rings were constrained using AFIX66, SADI constraints were used to keep the P-F distances similar in PF₆ anions, RIGU (the new constraint introduced in this version of SHELXL) constraints were used to keep the ADPs of the bonded atoms physically reasonable. However, the diffraction at higher angles faded gradually over the data collection, resulting in the high Rint as well as lower ratio (31%) of observed reflections. The flexibility of the moieties (end phenyl groups and anions) in this large asymmetric unit created alerts at level B and many at level C. The refinement was carried out in Olex-2 using solvent mask (similar to SQUEEZE approach in PLATON) that resulted in the final R value of 0.11.
15.1.2 Table of X-ray data for [3](PF$_6$)$_{17.5}$·(CH$_3$NO$_2$)

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Data collection

| Diffractometer                | Bruker APEX-II CCD           |
| Absorption correction        | –                            |
| No. of measured              | 231819, 57493, 18054         |
| $R_{int}$                    | 0.215                        |
| $(\sin \theta \lambda)_{max}$ (Å$^{-1}$) | 0.595 |

Refinement

| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.113, 0.320, 1.11 |
| No. of reflections             | 57493                      |
| No. of parameters              | 3008                        |
| No. of restraints              | 1988                        |
| H-atom treatment              | H-atom parameters constrained |
| $\Delta \varphi_{max}$, $\Delta \varphi_{ave}$ (e Å$^{-3}$) | 2.60, -2.44 |
15.1.3 Additional figure of the crystal structure of $[3](\text{PF}_6)_{17.5}\cdot(\text{CH}_3\text{NO}_2)$.

**Figure S40** A molecule of $[3]^{2+}$ in the crystal structure of $[3](\text{PF}_6)_{17.5}\cdot(\text{CH}_3\text{NO}_2)$. The back half of the cage is displayed in CPK representation and the front half in sticks. The $\pi-\pi$ stacking between adjacent $\{\text{Ru(tpy)}_2\}$ units is evident between the complexes at the back and front in CPK and line representation respectively. Hydrogens, dppp ligands, solvent and anions omitted for clarity. Pd(II) centres are shown in teal, Ru(II) in red.
**Figure S41** Connectivity of Ru(II) and Pd(II) centres in the structure of [3]$_{24}^{4+}$.

**Figure S42** Crystal packing of [3]$_{24}^{4+}$ cages along the crystallographic $a$ axis. Terminal pyridyl rings are displayed in CPK representation to highlight the interlocked embraces between adjacent complexes. Hydrogens, anions and solvent omitted for clarity.
S16. X-ray experimental for Ru(1)$_2$][PF$_6$)$_{1.5}$·CH$_3$NO$_2$

We have previously reported the X-ray crystal structure of [Ru(1)$_2$][PF$_6$]$_2$, although the data has been recollected on a synchrotron source to give a better quality structure. This data is included here for completeness and has been submitted to the CSD Database (CCDC 1045515).

Crystals of RuC$_{42}$H$_{42}$N$_{10}$[PF$_6$]$_2$ were grown by slow diffusion of toluene into a nitromethane solution of the complex. Dark red crystals were grown in a sealed NMR tube. A crystal of dimensions 0.02 X 0.02 X 0.015 mm, coated in paraffin oil could be transferred to the goniometer under the flow of liquid nitrogen cold stream (100 K). Diffraction measurements were carried out using Si<111> monochromated synchrotron X-ray radiation (λ = 0.71023 Å) (MX1 Beamline at Australian Synchrotron) the complete diffraction data could be acquired within 20 minutes. Data collection was carried out using BluIce$^6$ suite of software$^3$ and unit cell refinement, data reduction and processing was carried out with program XDS.$^7$ The structure was solved using the new version that uses intrinsic phasing in program SHLEXT$^8$ The least-squares refinement was carried out with the latest version of SHELXL$^9$. Only one of the anions of PF$_6$ could be located that has full occupancy. The second PF$_6$ is disordered extensively, only half contribution from this (two symmetry generated positions with 0.25 occupancy each) could be identified in the difference Fourier. One molecule of solvent nitromethane could be well identified and was included in the refinement. One of the pyridines showed orientation disorder over two positions (0.65:0.35) that were included with appropriate PART instructions. The ‘rugby ball’ shaped complex molecule in its packing in the crystal lattice creates voids that are occupied by solvent molecules, possibly a few water molecules and also unaccounted anionic contribution. Solvent mask was used in Olex2$^5$ (similar to SQUEEZE procedure in PLATON) as the peaks in the difference Fourier could not be assigned unambiguously to solvent molecules or waters that made meaningful H-bonding contacts. Low occupied PF$_6$ has been restrained to have similar P-F bonds (using SADI) and similar ADPs (using RIGU), option available in the new SHELXL.

Crystallographic data is summarized in Table 1.
16.1.1 Table of X-ray data for Ru(1)₂[(PF₆)₁.₅·CH₃NO₂

Crystal data

Identification code Ru(1)₂
Empirical formula C₆₃H₄₅F₇.₅N₁₁O₂P₁.₂₅Ru
Formula weight 1270.38
Temperature/K 100
Crystal system Monoclinic
Space group C2/c

a/Å 31.584(6)
b/Å 16.937(3)
c/Å 26.449(5)
α/° 90
β/° 105.27(3)
γ/° 90
Volume/Å³ 13649(5)
Z 8
Radiation type Synchrotron
ρ calcg/cm³ 1.236
μ/mm⁻¹ 0.327
F(000) 5170.0
Crystal size (mm) 0.02 × 0.02 × 0.015

Data collection

Diffractometer MX1 Beamline Australian Synchrotron
Absorption correction None
Radiation wavelength 0.71073

Refinement

Index ranges -41 ≤ h ≤ 41, -22 ≤ k ≤ 22, -34 ≤ l ≤ 34
Reflections collected 113586
Independent reflections 15544 [R(int) = 0.0217, R(sigma) = 0.0107]
Data/restraints/parameters 15544/123/867
Goodness-of-fit on F² 1.055
Final R indexes [I>2σ(I)] R₁ = 0.0564, wR₂ = 0.1772
Final R indexes [all data] R₁ = 0.0592, wR₂ = 0.1805
Largest diff. peak/hole / e Å⁻³ 1.59/-0.65
**Figure S43** Single crystal X-ray structure of Ru(1)₂(PF₆)₁.₅·CH₃NO₂ with thermal ellipsoids drawn at 50% probability.
S17. MMFF model of 4(PF₆)₁₈

Simple molecular modelling was performed using Spartan (Wavefunction Inc.) which confirmed a trimeric structure is a reasonable assignment for cage 4(PF₆)₁₈.

Figure S44  Molecular Mechanics Force Field model of cage 4(PF₆)₁₈
S18. Photophysical data

Solutions at ca. $10^{-5}$ M were prepared using CH$_3$NO$_2$ as the solvent. Absorption spectra were measured using a Cary Bio50 UV-Vis spectrometer. The resulting normalized absorption data for the complexes are shown in Fig. 45. Each of the complexes display an essentially identical 1MLCT absorption band centered at ca. 490 nm. At shorter wavelength (less than 380 nm), more intense $\pi\pi^*$ absorption attributable to the terpyridine chromophores are observed.

![Normalized absorption spectra](image.png)

**Figure S45** Normalised absorption spectra of [Ru(1)$_2$](PF$_6$)$_2$ (black), [Ru(1)$_2$Pd$_6$(dppp)$_6$](PF$_6$)$_{18}$ (blue), [Ru(2)$_2$](PF$_6$)$_2$ (red) and [Ru(3)$_2$Pd$_6$(dppp)$_6$](PF$_6$)$_{18}$ (green) complexes in CH$_3$NO$_2$ solution.

The emission lifetimes for the four complexes were measured by the Time Correlated Single Photo Counting (TCSPC) technique using an ultrafast laser setup. The excitation source was an amplified laser system (Spitfire ACE, Spectra Physics) coupled to a tunable OPA (Topas Prime, Light Conversion) delivering ca. 150 fs excitation pulses at 490 nm. The detection system was a commercially available time resolved fluorescence spectrometer (Haleyone, Ultrafast Systems, LLC) operating in TCSPC mode. The Instrument Response Function (IRF) of this setup had a full width at half maximum (FWHM) of ca. 0.22 ns, as measured experimentally by a Gaussian fit to the scattered laser excitation profile.

As shown in Fig. 46, the luminescence decay profiles gave satisfactory fits to a mono-exponential decay function for each of the [Ru(1)$_2$](PF$_6$)$_2$, [3](PF$_6$)$_{24}$, [Ru(2)$_2$](PF$_6$)$_2$ and [4](PF$_6$)$_{18}$ complexes. Resulting lifetime values determined from the best fit were $\tau = 1.59 \pm 0.01$ ns, $2.04 \pm 0.02$ ns, $1.95 \pm 0.02$ ns and $2.53 \pm 0.02$ ns respectively. Notably, in
both cases, the luminescence lifetimes obtained for the supramolecular cages are slightly longer (by 30 %) suggesting a decrease in the non-radiative decay rate upon formation of the more rigid cage.

**Figure S46** Observed emission lifetimes for the $^3$MLCT emission peak of [Ru(I)$_2$(PF$_6$)$_2$ (black), [3](PF$_6$)$_{24}$ (blue), [Ru(2)$_2$(PF$_6$)$_2$ (red) and [4](PF$_6$)$_{18}$ (green) complexes in CH$_3$NO$_2$ solution measured by TCSPC ($\lambda_{ex} = 490$ nm, $\lambda_{em} = 640$ nm), together with Instrument Response Function (IRF) (pink).

The measured lifetimes are also quite similar to those previously reported for a simple [Ru(TolTpy)(BisTpy)]$^{2+}$ complex which was determined to be $1.3 \pm 0.08$ ns in CH$_3$CN solution.$^{10}$
S19. Electrochemical data for cage 3

Table S1 Electrochemical data\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>(M^{2+/3+})</th>
<th>Ligand reductions(^b) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="PF_6">\text{Ru(tpy)}_2</a>_2)(^{11})</td>
<td>+0.92</td>
<td>-1.67</td>
</tr>
<tr>
<td>(<a href="PF_6">\text{Ru(tpyPh)}_2</a>_2)(^{11-12})</td>
<td>+0.90</td>
<td>-1.66</td>
</tr>
<tr>
<td>(<a href="PF_6">\text{Ru(1)}_2</a>_2)(^2)</td>
<td>+0.89</td>
<td>-1.60, -1.84, -1.77(^g), -1.56(^h)</td>
</tr>
<tr>
<td>(<a href="PF_6">\text{Ru(2)}_2</a>_2)(^2)</td>
<td>+0.91</td>
<td>-1.55, -1.77(^g), -1.63(^d), -1.77(^f)</td>
</tr>
<tr>
<td>Cage 3 (this work)</td>
<td>+0.90</td>
<td>-1.53(^f), -1.77(^g)</td>
</tr>
</tbody>
</table>

\(^{a}\) All measurements in MeCN with 0.1 M \([n\text{BuN}]PF_6\), with a glassy carbon working electrode, platinum counter electrode, Ag+/AgCl reference and potentials quoted are versus Fc+/Fc. tpy = 2,2':6',2''-terpyridine; tpyPh = 4'-phenyl-2,2':6',2''-terpyridine. \(^b\) All processes are reversibly, except where noted qr = quasi-reversible, irr = irreversible. \(^c\)

Figure S47  Cyclic voltammogram (2.5 mM, MeCN, 0.1M TBAPF\(_6\)) of \([\text{Ru(1)}_2](PF_6)_2\) and cage 3. Several irreversible processes were observed at negative potentials.
S20. Supplementary References