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Molecular self-assembly of arene-Ru based interlocked catenane metallacages

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Materials and methods

The acceptor clips (A**1**),[1] (A**2**),[2] (A**3**),[3] and (A**4**)[4] and 3-(4-Pyridyl)pyrazole[5] were synthesized under a dry nitrogen atmosphere by means of a standard Schlenk technique following the reported procedures. The solvents were dried and distilled according to the standard literature procedures. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer. The chemical shifts (δ) in ^{1}H NMR spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization (ESI) with the MassLynx software suite. Elemental analyses were performed using an Elemental GmbH Vario EL-3 instrument. Absorption spectra were recorded using a CARY 100 Conc UV-Visible spectrophotometer.

Synthesis of 1,3,5-tris(3-(pyridin-4-yl)-1H-pyrazol-1-yl)benzene (D1):

In a round bottomed flask 1,3,5-tribromobenzene (0.40 g, 1.27 mmol), 3-(4-Pyridyl)pyrazole (1.10 g, 7.62 mmol), K_2CO_3 (1.05 g, 7.62 mmol) and CuI (0.60 g, 3.17 mmol) were mixed in 10 mL of nitrobenzene. The mixture was refluxed for 6 h under nitrogen, and then reaction mixture was allowed to cool to room temperature. Hexane was added to the reaction mixture to precipitate out the product. Precipitate was filtered and washed with hexane (3 x 20 ml) to remove remaining nitrobenzene. Then, precipitate was washed with dichloromethane: methanol (8:2, 100 mL), filtrate was collected and solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, CH_2Cl_2/MeOH (96:4 v/v) to yield desired product as a pale yellow solid. Yield: 322 mg, 50%. M.P. = 122-124°C. MS (*m*/*z*): calcd = 507.19, found = 508.13. Anal. Calcd for $C_{30}H_{21}N_9$: C, 70.99; H, 4.17; N, 24.84. Found: C, 70.87; H, 4.27; N, 24.81. ^{1}H NMR (methanol-d_4, 300 MHz, δ, ppm): 8.67 (d, *J* = 2.65 Hz, 3H), 8.63 (d, *J* = 6.3 Hz, 6H), 8.43 (s,

3H), 8.05 (d, J = 6.3 Hz, 6H), 7.20 (d, 2H, J = 2.65, 3H). ^{13}C NMR (Methanol-d_4, 300 MHz, δ, ppm):153.4, 145.5, 143.5, 138.2, 130.2, 123.7, 122.2, 109.2 .

Synthesis of intercalated metalla-cage 1. A mixture of starting complex **A1** (13.14 mg, 0.018 mmol) and $AgCF_3SO_3$ (8.85 mg, 0.040 mmol) in nitromethane-methanol (1:1) was stirred at room temperature for 4 h and filtered to remove AgCl. The corresponding donor **D1** (6.00 mg, 0.012 mmol) was added to the filtrate. The mixture was then stirred at room temperature for 24 h, and the solvent was removed under reduced pressure. The reaction mixture was filtered, followed by the removal of the solvent under reduced pressure. The resulting solid was washed with diethyl ether followed by drying to furnish **1** as a sea-green sea green colored crystalline solid. Isolated Yield: 17 mg (74%); MS (ESI) calcd for $[M - 4OTf]^{4+}$ m/z 1793.91, found 1793.87; Anal. Calcd for $C_{312}H_{288}F_{36}N_{36}O_{54}Ru_{12}S_{12}$: C, 48.75; H, 3.78; N, 6.56. Found: C, 48.80; H, 3.77; N, 6.21.

Synthesis of intercalated metalla-cage 2. A mixture of starting complex **A2** (14.95 mg, 0.018 mmol) and $AgCF_3SO_3$ (8.85 mg, 0.040 mmol) in nitromethane-methanol (1:1) was stirred at room temperature for 4 h and filtered to remove AgCl. The corresponding donor **D1** (6.00 mg, 0.012 mmol) was added to the filtrate. The mixture was then stirred at room temperature for 24 h, and the solvent was removed under reduced pressure. The reaction mixture was filtered, followed by the removal of the solvent under reduced pressure. The resulting solid was washed with diethyl ether followed by drying to furnish **2** as a dark green colored crystalline solid. Isolated Yield: 19 mg (76%); MS (ESI) calcd for $[M - 3OTf]^{3+}$ m/z 1246.82, found 1246.86; calcd for $[M - 4OTf]^{4+}$ m/z 1944.71, found 1944.64; Anal. Calcd for $C_{360}H_{300}F_{36}N_{36}O_{54}Ru_{12}S_{12}$: C, 52.25; H, 3.65; F, 8.26; N, 6.09; O, 10.44; Ru, 14.65; S, 4.65. Found: C, 52.17; H, 3.77; N, 6.01.

Synthesis of metalla-cage 3. A mixture of starting complex **A3** (13.96 mg, 0.018 mmol) and $AgCF_3SO_3$ (8.85 mg, 0.040 mmol) in nitromethane-methanol (1:1) was stirred at room temperature for 2 h and filtered to remove AgCl. The corresponding donor **D1** (6.00 mg, 0.012 mmol) was added to the filtrate. The mixture was then stirred at room temperature for 24 h, and the solvent was removed under reduced pressure. The reaction mixture was filtered, followed by the removal of the solvent under reduced pressure. The resulting solid was washed with diethyl ether followed by drying to furnish **3** as light yellow colored crystalline solid. Isolated Yield: 12 mg (80%); ^{1}H NMR (methanol-d_4, 300 MHz, δ, ppm): 8.20 (m, 18H, Ha/H_d), 7.80-7.76 (m, 15H, Har/ He), 7.68 (broad, 12H, H_b), 7.38 (m, 18H, Har/Hc), 6.97 (d, J = 6.0 Hz, 6H, Hc), 6.67 (m, 12H, Hcym), 6.25 (m, 12H, Hcym), 2.60 (m, 6H, $CH(CH_3)_2$), 1.76 (s, 18H, CH_3), 1.00 (d, J = 6.1 Hz, 36H,$CH(CH_3)_2$); MS (ESI) calcd for $[M - 3OTf]^{3+}$ m/z 1190.25, found 1190.32; calcd for $[M - 4OTf]^{4+}$ m/z 855.42, found 855.18; calcd for $[M - 5OTf]^{5+}$ m/z 654.52, found 654.67; Anal. Calcd for $C_{168}H_{156}F_{18}N_{30}O_{18}Ru_6S_6$: C, 50.14; H, 3.91; N, 10.44. Found: C, 50.08; H, 3.82; N, 10.24.

Synthesis of metalla-cage 4. A mixture of starting complex **A4** (12.57 mg, 0.018 mmol) and $AgCF_3SO_3$ (8.85 mg, 0.040 mmol) in nitromethane-methanol (1:1) was stirred at room temperature for 2 h and filtered to remove AgCl. The corresponding donor **D1** (6.00 mg, 0.012 mmol) was added to the filtrate. The mixture was then stirred at room temperature for 24 h, and the solvent was removed under reduced pressure. The reaction mixture was filtered, followed by the removal of the solvent under reduced pressure. The resulting solid was washed with diethyl ether followed by drying to furnish **3** as light yellow colored crystalline solid. Isolated Yield: 18 mg (80%); ^{1}H NMR [300 MHz, acetone-d_6, δ, ppm]: 11.36 (s, 3H, NH-$H_{oxonato}$), 8.75 (m, 12H, Ha), 8.24 (broad, 6H, Hd), 8.07 (m, 6H, He/Hb), 6.97 (d, 6H, Hc), 6.39 (m, 12H, Hcym), 6.28 (m, 12H, Hcym), 3.39 (m, 6H, $CH(CH_3)_2$), 2.98 (s, 18H, CH_3), 1.40 (d, 36H,$CH(CH_3)_2$); MS (ESI) calcd for $[M - 3OTf]^{3+}$ m/z 1113.08, found

1113.18; calcd for $[M - 4OTf]^{4+}$ m/z 797.54, found 797.89; calcd for $[M - 5OTf]^{5+}$ m/z 608.22, found 608.25; Anal. Calcd for $C_{138}H_{135}F_{18}N_{27}O_{30}Ru_6S_6$: C, 43.70; H, 3.59; N, 9.97. Found: C, 44.08; H, 3.62; N, 10.14.

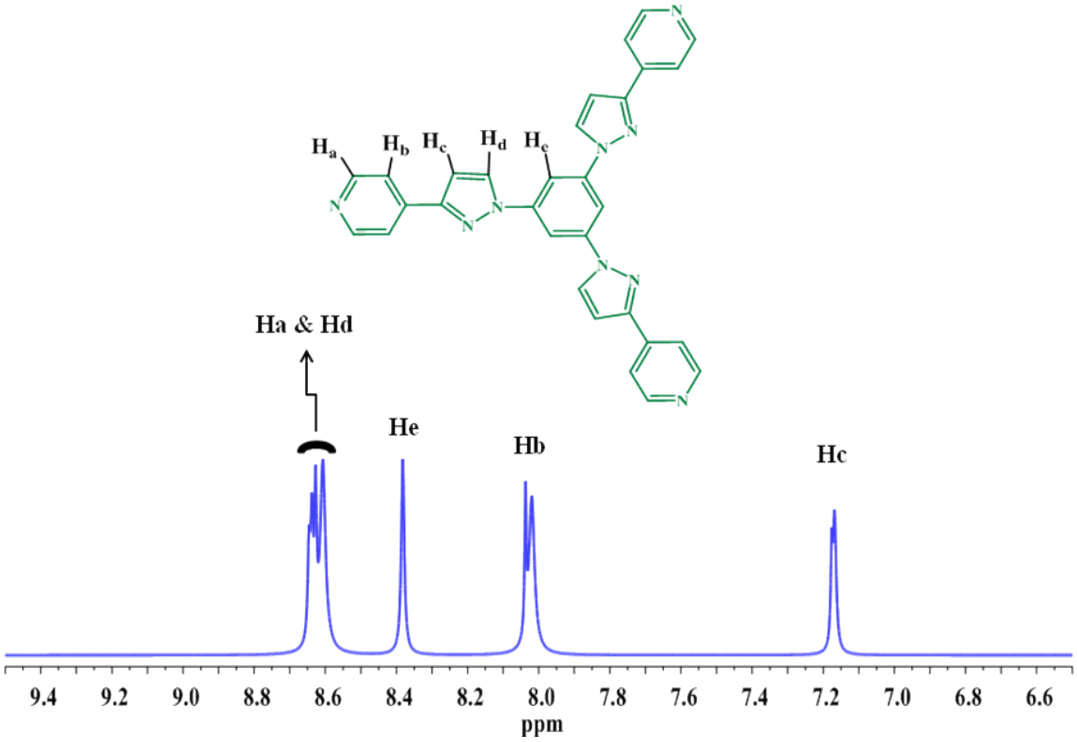

Figure S1. ^{1}H NMR spectrum of ligand **D1** recorded in CD_3OD.

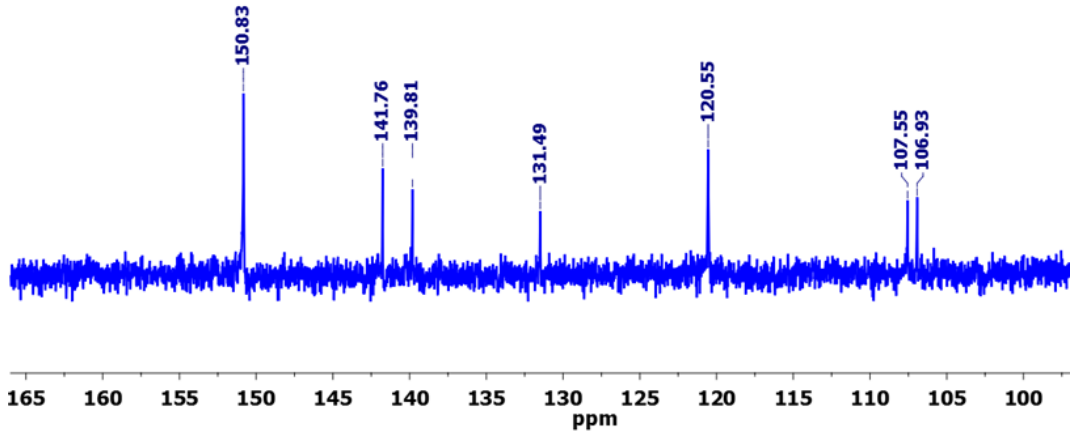

Figure S2. ^{13}C NMR spectrum of ligand **D1** recorded in CD_3OD.

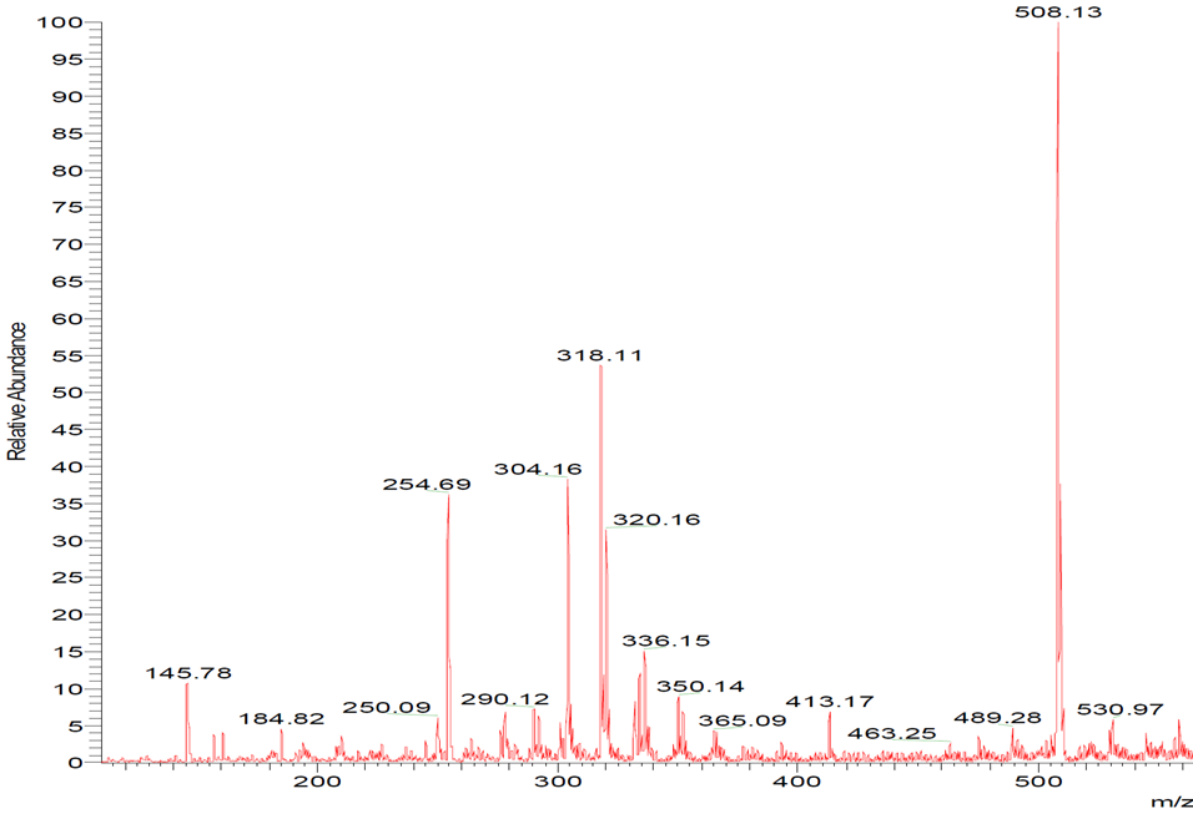

Figure S3. ESI-MS spectrum of ligand **D1** in CH_3OH.

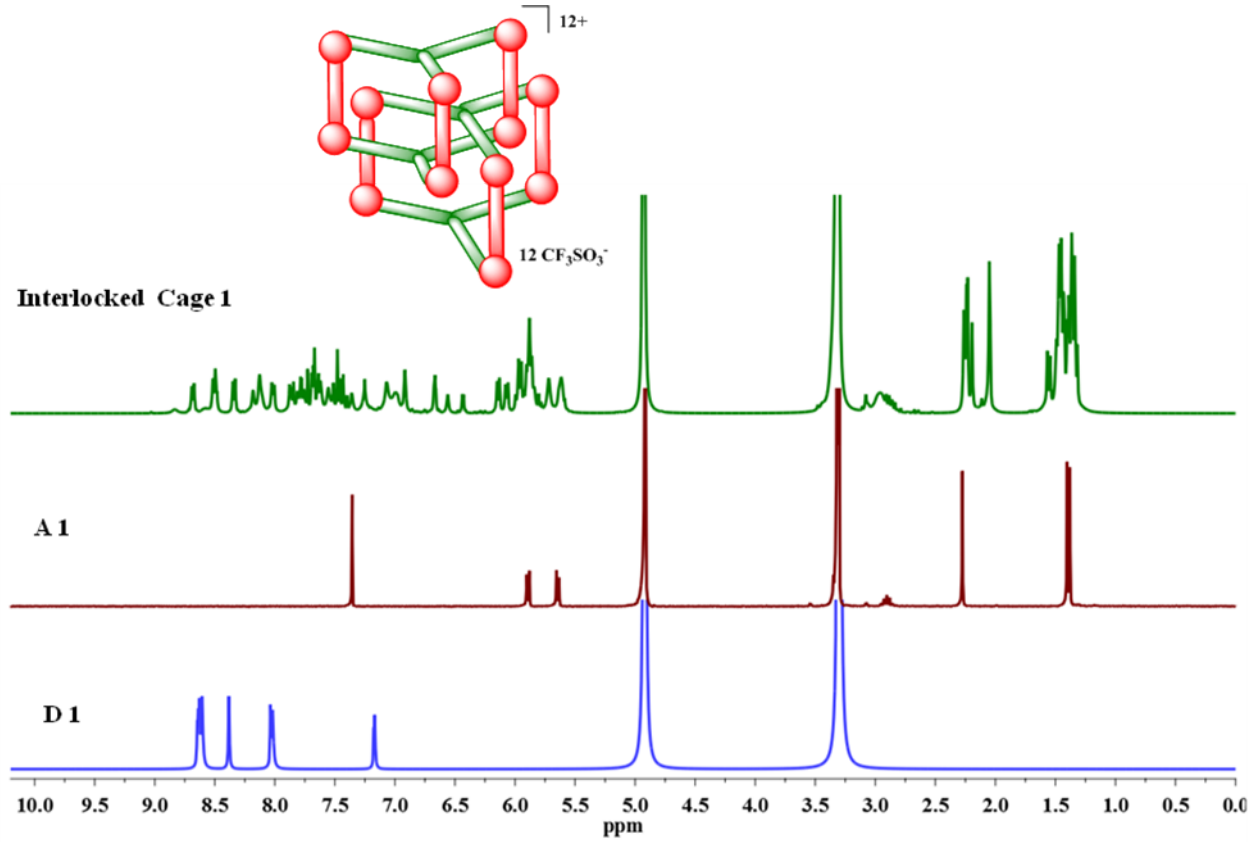

Figure S4. Comparison of the ^{1}H NMR spectra of (a) ligand **D1**, (b) Ru acceptor **A1,** and (c) self-assembled [2+3] interlocked cage **1** in CD_3OD solvent.

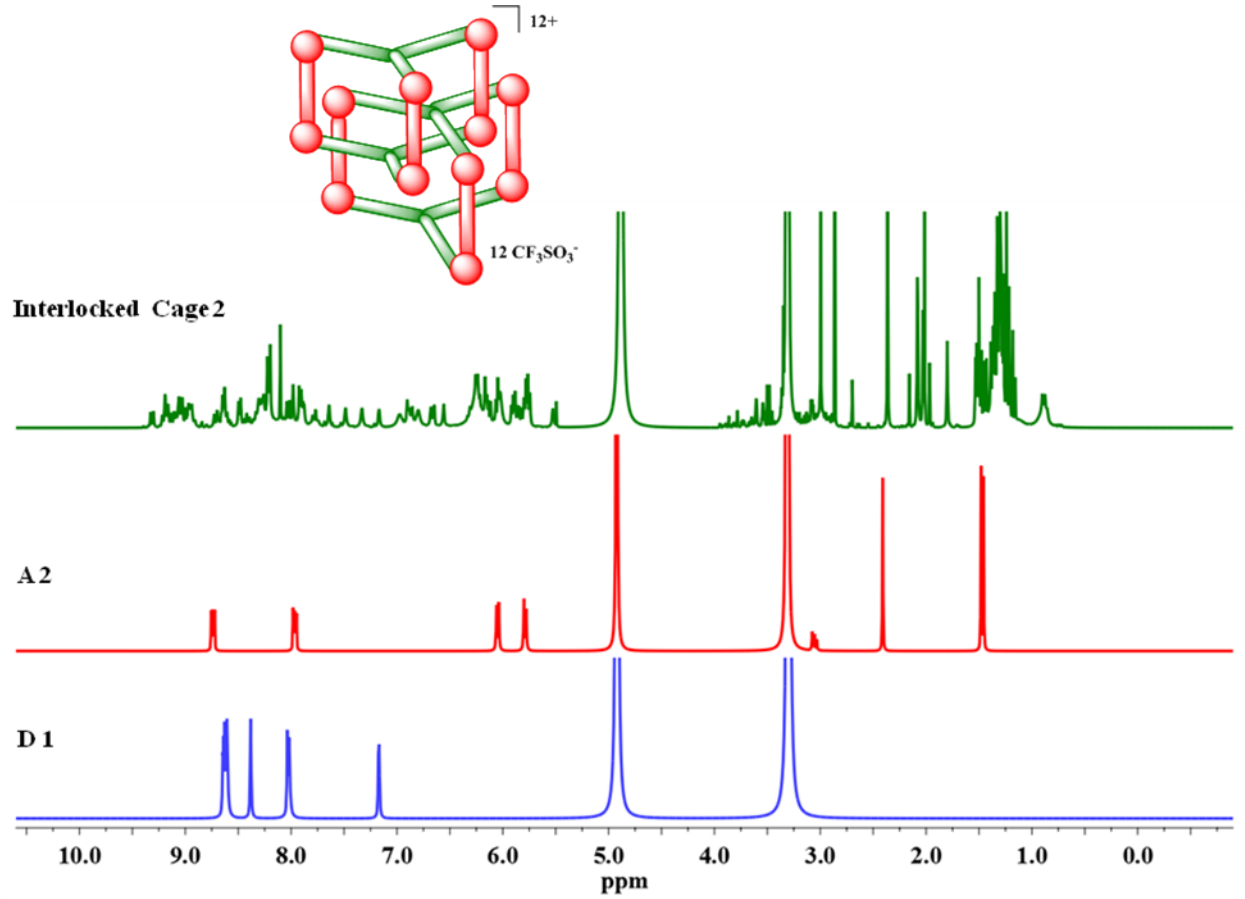

Figure S5. Comparison of the ^{1}H NMR **spectra** of (a) ligand **D1**, (b) Ru acceptor **A2,** and (c) self-assembled [2+3] interlocked cage **2** in CD_3OD solvent.

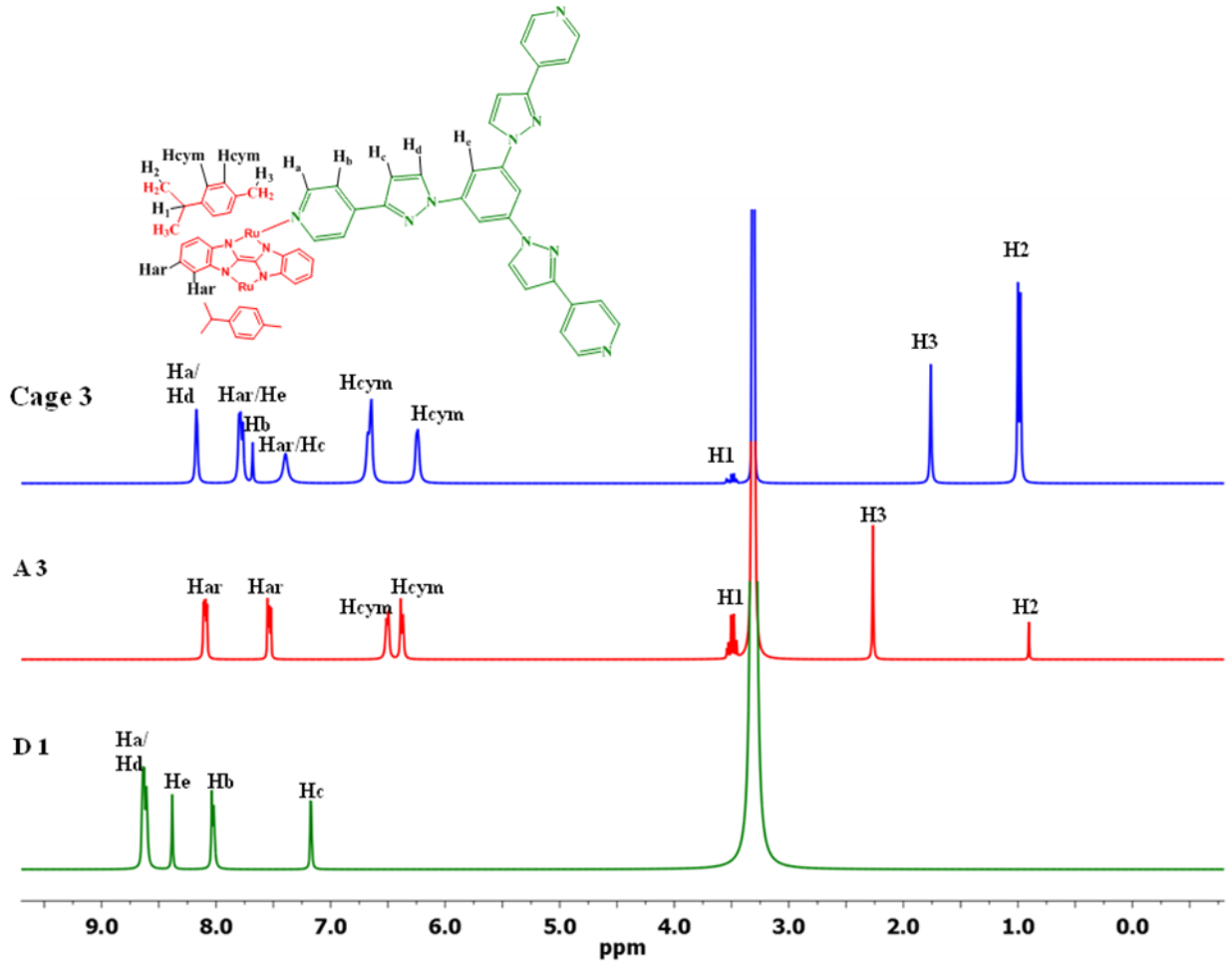

Figure S6. Comparison of the ^{1}H NMR spectra of (a) ligand **D1**, (b) Ru acceptor **A3,** and (c) self-assembled [2+3] cage **3** in CD_3OD solvent.

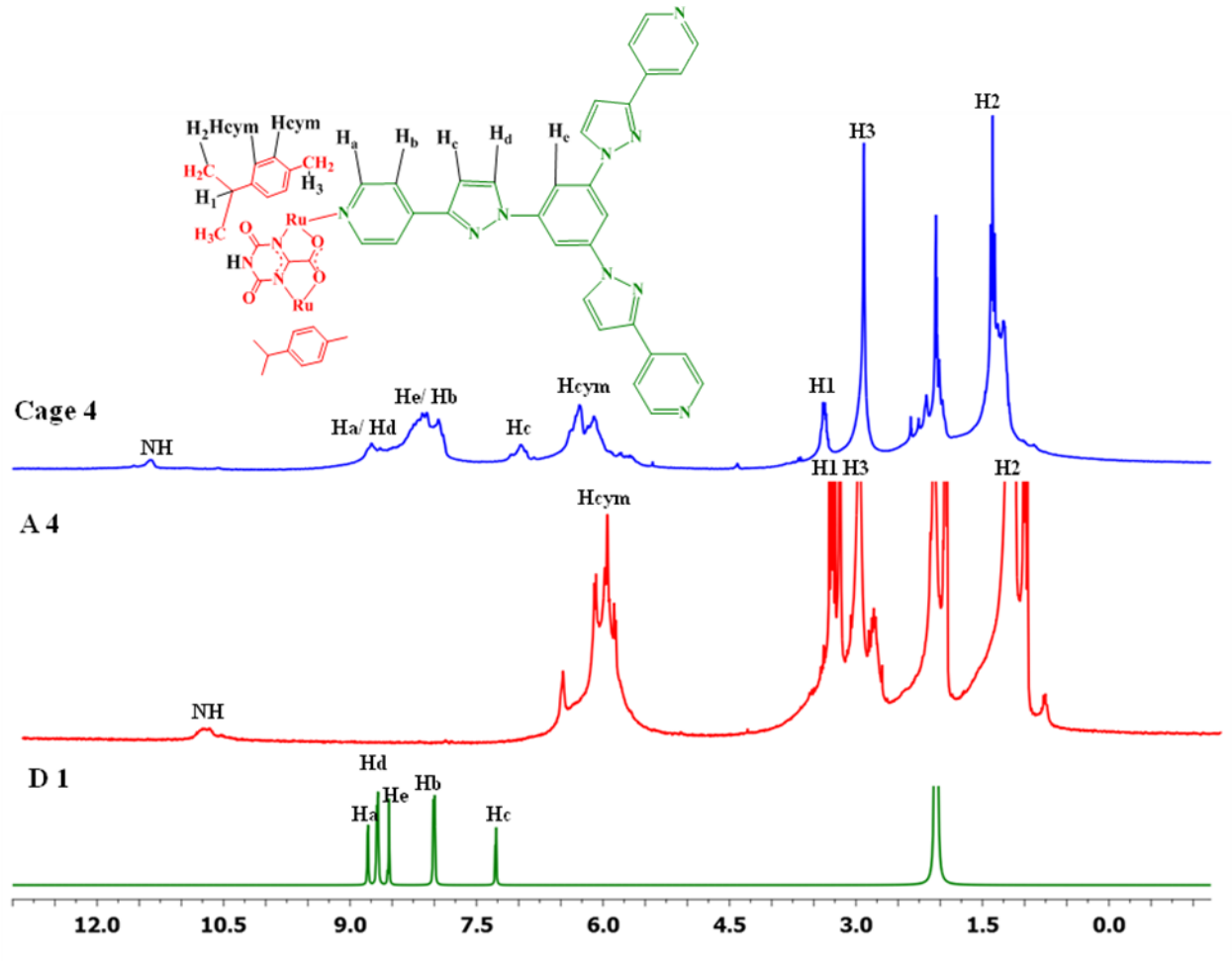

Figure S7. Comparison of the ^{1}H NMR spectra of (a) ligand **D1**, (b) Ru acceptor **A4,** and (c) self-assembled [2+3] cage **4** in acetone-d_6 solvent.

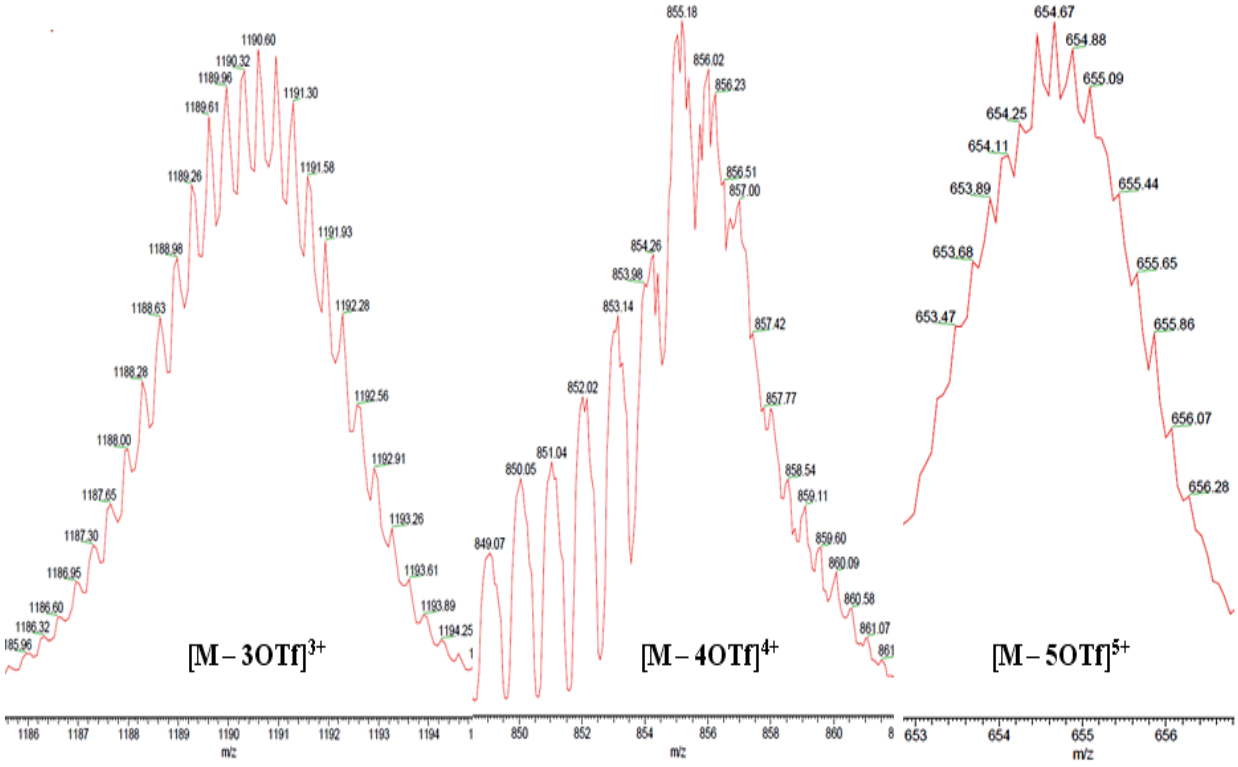

Figure S8. ESI-MS spectra of self-assembled cage **3**.

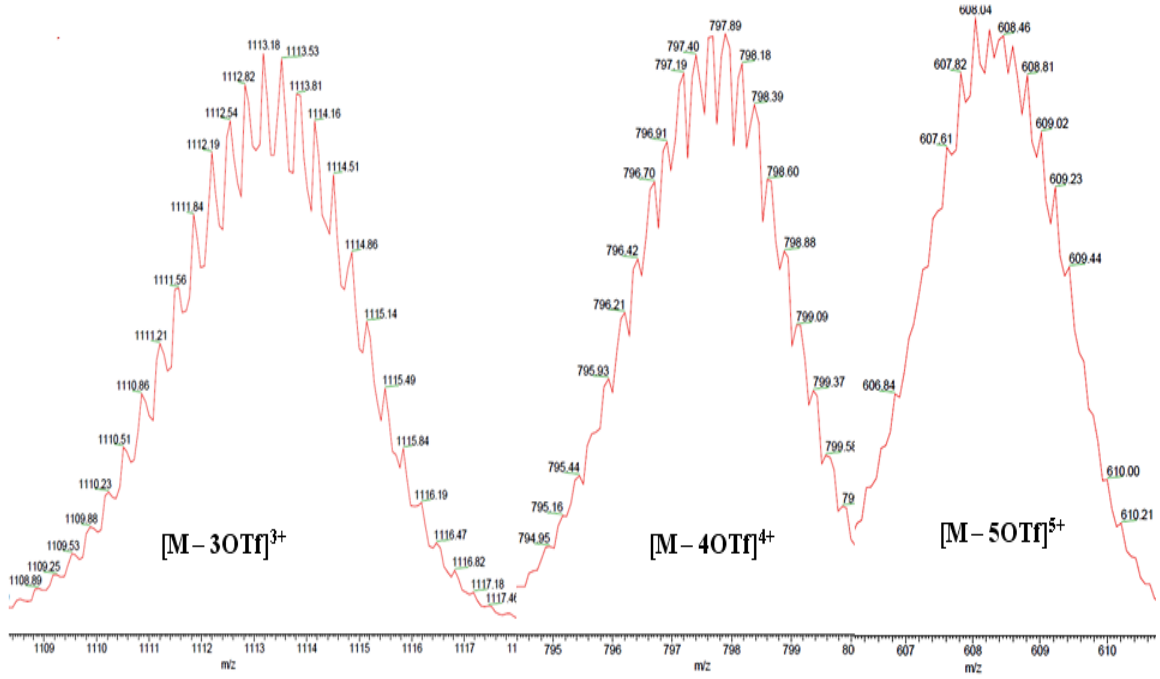

Figure S9. ESI-MS spectra of self-assembled cage **4**.

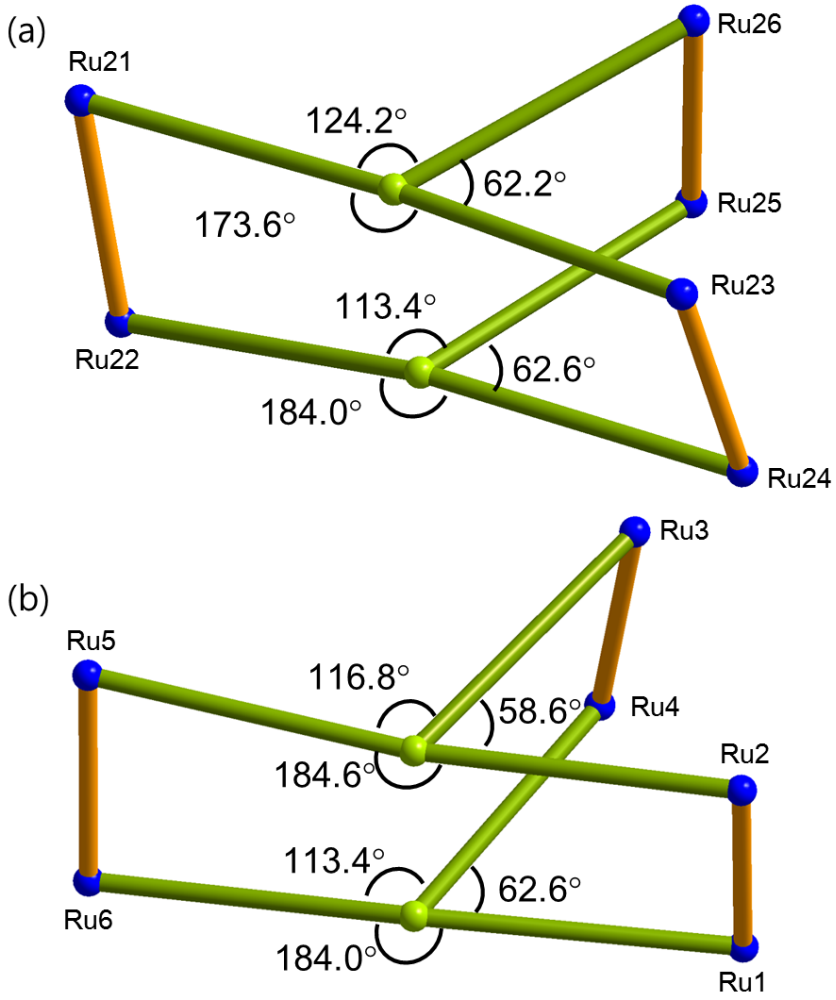

Figure S10. Two distorted trigonal prisms of a catenated cage. Ru centers are connected by simplified coordinating ligands

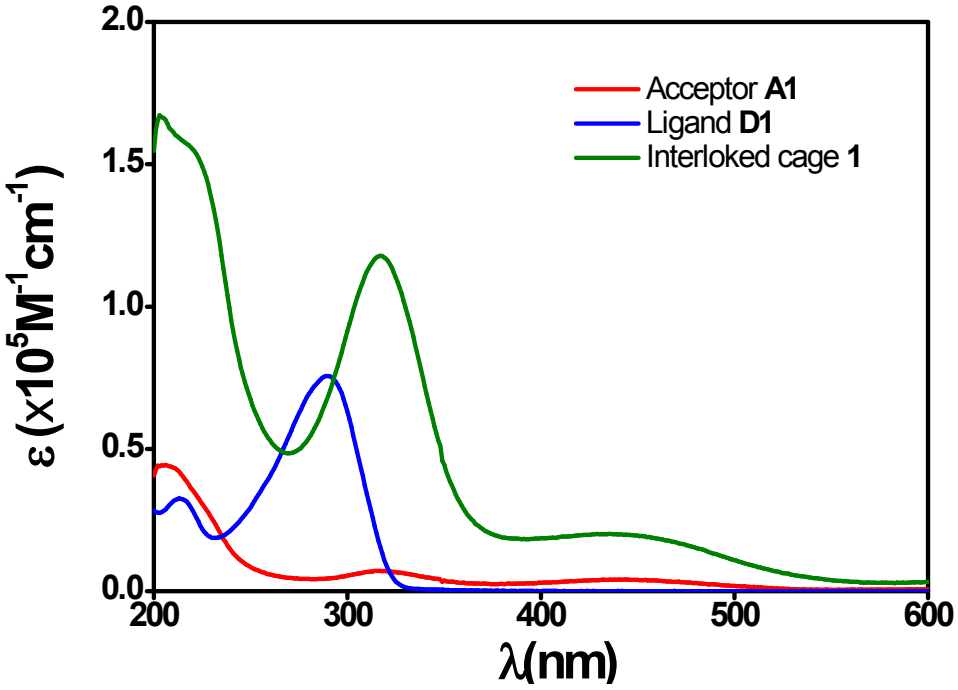

Figure S11. Electronic absorption spectra of **A1, D1** and interlocked cage **1** in methanol.

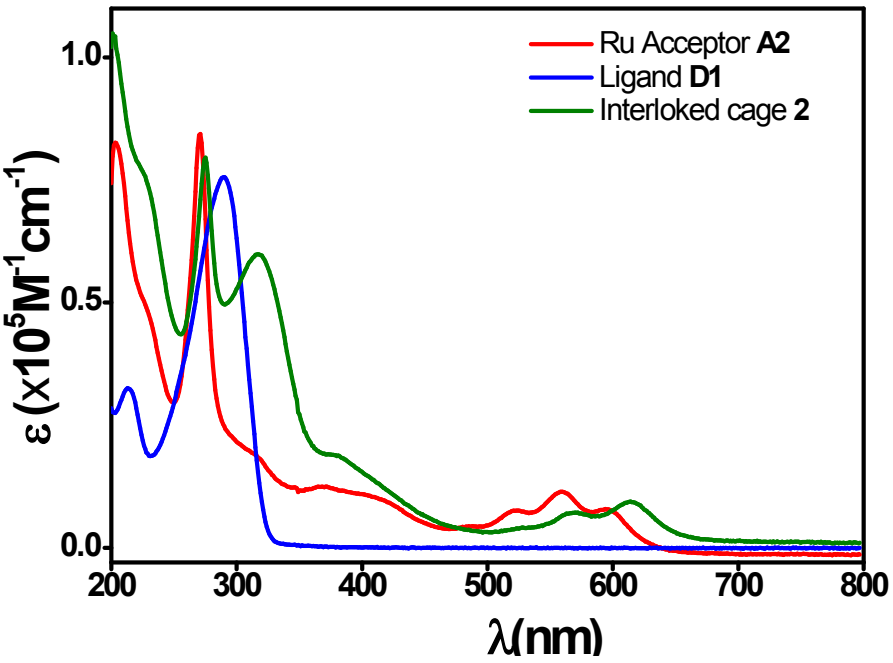

Figure S12. Electronic absorption spectra of **A2, D1** and interlocked cage **2** in methanol.

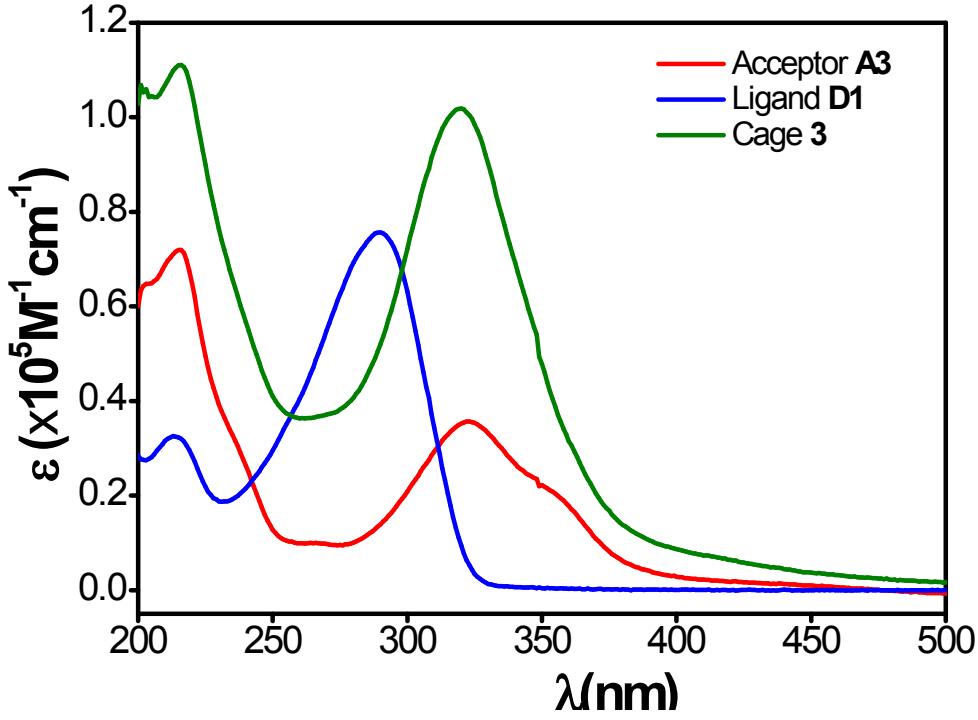

Figure S13. Electronic absorption spectra of **A3, D1** and cage **3** in methanol.

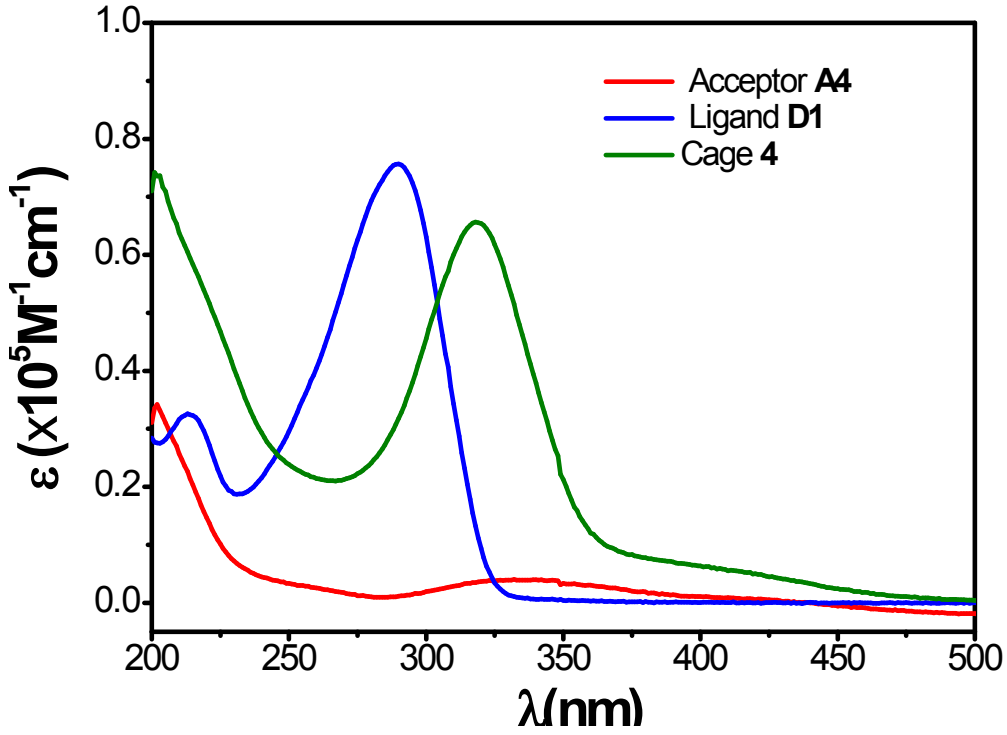

Figure S14. Electronic absorption spectra of **A4, D1** and cage **4** in methanol.

X-ray crystallography:

The diffraction data from single crystals of intercalated metalla-cage **2** were collected at 100

K on an ADSC Quantum 210 CCD diffractometer with a synchrotron radiation (λ = 0.80003 Å) at Supramolecular Crystallography Beamline 2D, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The raw data were processed and scaled using the program HKL2000. The structure was solved by direct methods, and the refinements were carried out with full-matrix least-squares on F^2 with appropriate softwares implemented in SHELXTL program package. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions. The crystallographic data are summarized in Table S1. CCDC- 991298 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

Table S1. Crystal data and structure refinement for intercalated metalla-cage **2**.

Empirical formula	C182 H172.5 F18 N18 O35 Ru6 S6	
Formula weight	4312.66	
Temperature	100(2) K	
Wavelength	0.80003 Å	
Crystal system	Monoclinic	
Space group	*Cc*	
Unit cell dimensions	a = 44.175(9) Å	□ α = 90°
	b = 31.227(6) Å	□ β = 115.67(3)°
	c = 32.536(7) Å	□ γ = 90°
Volume	40453(14) Å^3	
Z	8	
Density (calculated)	1.416 g/cm^3	
Absorption coefficient	0.795 mm^{-1}	
F(000)	17540	
Crystal size	0.30 × 0.20 × 0.20 mm^3	
Theta range for data collection	1.87 to 32.05°	
Index ranges	-56≤h≤54, -38≤k≤38, -35≤l≤36	
Reflections collected	137103	
Independent reflections	73935 [R(int) = 0.0589]	
Completeness to theta = 25.00°	95.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8572 and 0.7964	

Refinement method	Full-matrix-block least-squares on F^2
Data / restraints / parameters	73935 / 1172 / 4748
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R_1 = 0.0950, wR_2 = 0.2487
R indices (all data)	R_1 = 0.1107, wR_2 = 0.2649
Absolute structure parameter	0.044(17)
Extinction coefficient	0.00175(4)
Largest diff. peak and hole	1.864 and -1.124 e.Å^{-3}

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