Ru(II)-cornered coordination cage that senses guest inclusion by color change

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General

All the chemicals were of reagent grades and used without any further purification. D_2O was acquired from Cambridge Isotopic Laboratories.

All NMR spectral data were recorded on Bruker DRX-500 (500 MHz) spectrometer or Bruker AXL-500 (500 MHz) spectrometer. These data were collected at ambient temperature (300 K) unless otherwise noted and the chemical shift values reported here are with respect to external TMS ($CDCl_3$ solution) standard. CSI-MS (Coldspray ionization mass spectroscopy) data were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with the CSI source. X-ray diffraction data were measured on a Bruker APEX-II CCD diffractometer equipped with a micro-focused rotating anode system combined with an X-ray focusing mirror (MoKa radiation, λ = 0.71073 Å) with a cryostat system equipped with a N_2 generator (XR-HR 10K, Japan Thermal Eng. Co., Ltd.). Structures were solved by direct methods (SHELXS 97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) using the SHELX-TL program package. IR measurements were carried out as KBr pellets using a DIGILAB Scimitar FTS2000 instrument. UV-Vis spectral data were recorded on SHIMADZU UV-3150 spectrometer. Melting points were determined on a Yanaco MF-500 V melting point apparatus.

Preparation of Ru(II)-cage **1**: To a aqueous solution (2 mL) of $[Ru([12]aneS_4)(dmso)(H_2O)](NO_3)_2$ (67.4 mg, 0.12 mmol), 2,4,6-tris(4-pyridyl)-1,3,5-triazine (24.5 mg, 0.08 mmol) was suspended, and the resulting mixture was stirred at 100 °C for 2 h. After removal of precipitate by filtration, excess amount of THF was added to the resulting red solution, and the orange precipitate was corrected by filtration, and dried under vacuum to give **1** as orange powder (79.9 mg, 0.019 mmol, 98%). ^{1}H NMR (500 MHz, D_2O, r.t.) δ (ppm) = 9.01 (br, PyH_α), 8.86 (br, PyH_α), 8.53 (br, PyH_β), 8.35 (br, PyH_β), 4.46 (br, $[12]aneS_4$), 4.07 (d, J = 14.3 Hz, $[12]aneS_4$), 3.87 (d, J = 13.3 Hz, $[12]aneS_4$), 3.58-3.16 (m, $[12]aneS_4$) 3.02 (br, $[12]aneS_4$), 2.63 (d, $[12]aneS_4$). ^{13}C NMR (125 MHz, D_2O, r.t.) δ (ppm) = 170.5 (*C*q), 169.7 (*C*q), 156.2 (*C*H$_\alpha$), 155.4 (*C*H$_\alpha$), 154.5 (*C*H$_\alpha$), 143.8 (*C*q), 125.5 (*C*H$_\beta$), 125.3 (*C*H$_\beta$), 125.0 (*C*H$_\beta$), 43.1 (*C*H$_2$), 42.6 (*C*H$_2$), 39.5 (*C*H$_2$), 36.2 (*C*H$_2$), 33.8

(CH_2), 33.8 (CH_2). IR (KBr, cm^{-1}): 3435 (br), 2968, 2916, 1626, 1572, 1518, 1382, 805. m.p.: ~210 ºC (decomposed). CSI-MS (H_2O-DMSO): *m/z* = 451.7 $[\mathbf{1}-(NO_3^-)_{10}+(dmso)_{14}]^{10+}$, 459.8 $[\mathbf{1}-(NO_3^-)_{10}+(dmso)_{15}]^{10+}$, 467.4 $[\mathbf{1}-(NO_3^-)_{10}+(dmso)_{16}]^{10+}$, 475.4 $[\mathbf{1}-(NO_3^-)_{10}+(dmso)_{17}]^{10+}$, 483.0 $[\mathbf{1}-(NO_3^-)_9+(dmso)_{11}]^{9+}$, 491.4 $[\mathbf{1}-(NO_3^-)_9+(dmso)_{12}]^{9+}$, 500.2 $[\mathbf{1}-(NO_3^-)_9+(dmso)_{13}]^{9+}$, 509.0 $[\mathbf{1}-(NO_3^-)_9+(dmso)_{14}]^{9+}$, 517.8 $[\mathbf{1}-(NO_3^-)_9+(dmso)_{15}]^{9+}$, 521.6 $[\mathbf{1}-(NO_3^-)_8+(dmso)_7]^{8+}$, 531.7 $[\mathbf{1}-(NO_3^-)_8+(dmso)_8]^{8+}$, 541.2 $[\mathbf{1}-(NO_3^-)_8+(dmso)_9]^{8+}$, 551.3 $[\mathbf{1}-(NO_3^-)_8+(dmso)_{10}]^{8+}$, 561.1 $[\mathbf{1}-(NO_3^-)_8+(dmso)_{11}]^{8+}$, 570.7 $[\mathbf{1}-(NO_3^-)_8+(dmso)_{12}]^{8+}$ and $[\mathbf{1}-(NO_3^-)_7+(dmso)_5]^{7+}$, 582.7 $[\mathbf{1}-(NO_3^-)_7+(dmso)_6]^{7+}$, 593.7 $[\mathbf{1}-(NO_3^-)_7+(dmso)_7]^{7+}$, 605.0 $[\mathbf{1}-(NO_3^-)_7+(dmso)_8]^{7+}$, 616.3 $[\mathbf{1}-(NO_3^-)_7+(dmso)_9]^{7+}$, 638.7 $[\mathbf{1}-(NO_3^-)_6+(dmso)_2]^{6+}$, 650.9 $[\mathbf{1}-(NO_3^-)_6+(dmso)_3]^{6+}$, 664.1 $[\mathbf{1}-(NO_3^-)_6+(dmso)_4]^{6+}$, 677.2 $[\mathbf{1}-(NO_3^-)_6+(dmso)_5]^{6+}$, 746.4 $[\mathbf{1}-(NO_3^-)_5]^{5+}$, 762.4 $[\mathbf{1}-(NO_3^-)_5+dmso]^{5+}$, 778.0 $[\mathbf{1}-(NO_3^-)_5+(dmso)_2]^{5+}$, 794.3 $[\mathbf{1}-(NO_3^-)_5+(dmso)_3]^{5+}$, 948.9 $[\mathbf{1}-(NO_3^-)_4]^{4+}$. Elemental analysis: calcd. for $C_{120}H_{144}N_{36}O_{36}Ru_6S_{24}\cdot 26H_2O$: C, 31.95; H, 4.38; N, 11.18; found: C, 32.18; H, 4.16; N, 10.97.

Guest encapsulation experiment

Excess amount of guest molecule (ca. 10 equiv.) was suspended to an aqueous solution of **1**, and the resulting solution was stirred at room temperature for 30 min.

Physical properties of $\mathbf{1}\supset(\mathbf{6})_4$: ^{1}H NMR (500 MHz, D_2O, r.t.) δ(ppm) = 9.26 (br, PyH_α), 9.11 (br, PyH_α), 9.07 (br, PyH_α), 8.73 (br, PyH_β), 8.63 (br, PyH_β), 4.47 (br, [12]aneS_4), 4.11 (d, *J* = 13.2 Hz, [12]aneS_4), 3.89 (d, *J* = 13.7 Hz, [12]aneS_4), 3.57-3.15 (m, [12]aneS_4) 3.05 (br, [12]aneS_4), 2.60 (d, [12]aneS_4), 1.36 (br, **6**), 0.44 (br, **6**), 0.30 (br, **6**), -0.36 (br, **6**),. ^{13}C NMR (125 MHz, D_2O, r.t.) δ(ppm) = 169.7 (*C*q), 169.3 (*C*q), 156.6 (CH_α), 155.6 (CH_α), 154.7 (CH_α), 142.8 (*C*q), 142.6 (*C*q), 125.5 (CH_β), 125.2 (CH_β), 125.0 (CH_β), 43.8 (**6**, CH_2), 42.9 (CH_2), 42.4 (CH_2), 39.2 (CH_2), 36.3 (CH_2), 35.2 (**6**, CH_2), 33.7 (CH_2), 32.3 (CH_2), 29.9 (**6**, *C*H).

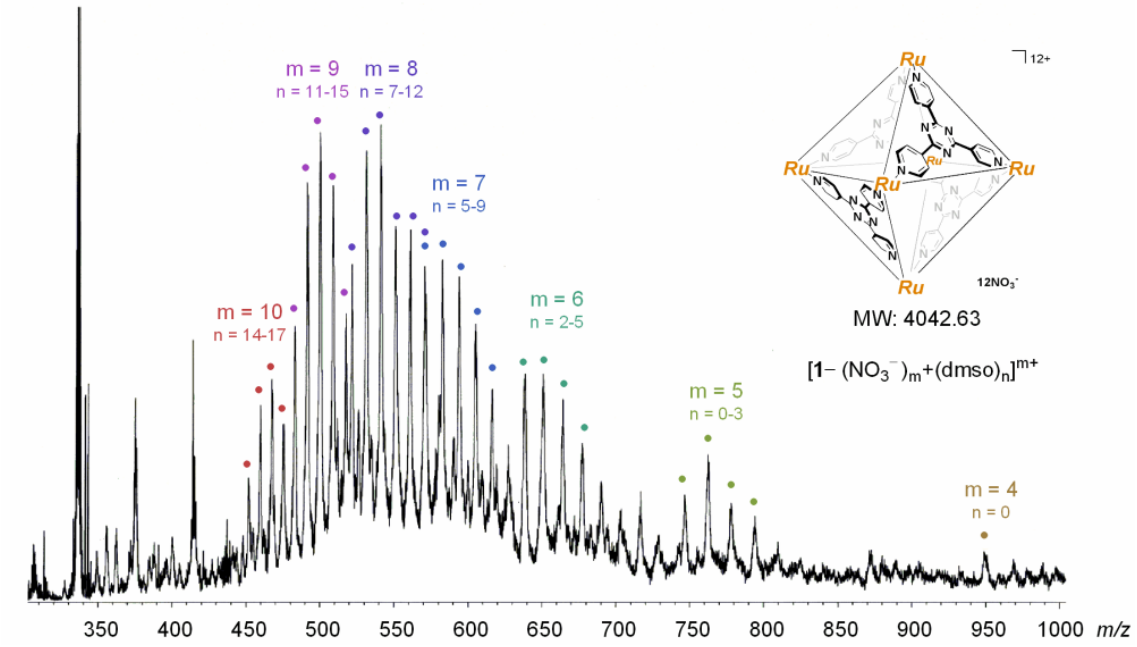

Figure S1. CSI-MS spectrum of **1**.

Table 1. Crystal data and structure refinement for **1**·$(H_2O)_m$.

Identification code	cage1	
Empirical formula	C120 H 281 N31 O91.50 Ru6 S24	
Formula weight	4990.59	
Temperature	80(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 28.043(5) Å	α= 81.553(2)°.
	b = 28.463(5) Å	β= 70.715(2)°.
	c = 37.746(6) Å	γ= 72.193(2)°.
Volume	27040(8) Å^3	
Z	4	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	0.587 mm^{-1}	
F(000)	10392	
Crystal size	0.15 x 0.11 x 0.04 mm^3	
Theta range for data collection	1.53 to 27.90°.	
Index ranges	-36<=h<=36, -37<=k<=37, -48<=l<=49	
Reflections collected	315324	
Independent reflections	125585 [R(int) = 0.0741]	
Completeness to theta = 27.90°	97.1 %	
Absorption correction	Semi-empirical	
Max. and min. transmission	0.9769 and 0.9172	
Refinement method	userblock least-squares on F^2	
Data / restraints / parameters	125585 / 5351 / 5055	
Goodness-of-fit on F^2	1.218	
Final R indices [I>2sigma(I)]	R_1 = 0.1217, wR_2 = 0.3486	
R indices (all data)	R_1 = 0.2492, wR_2 = 0.4245	
Absolute structure parameter	0.07(2)	
Largest diff. peak and hole	2.090 and -0.946 e.Å^{-3}	

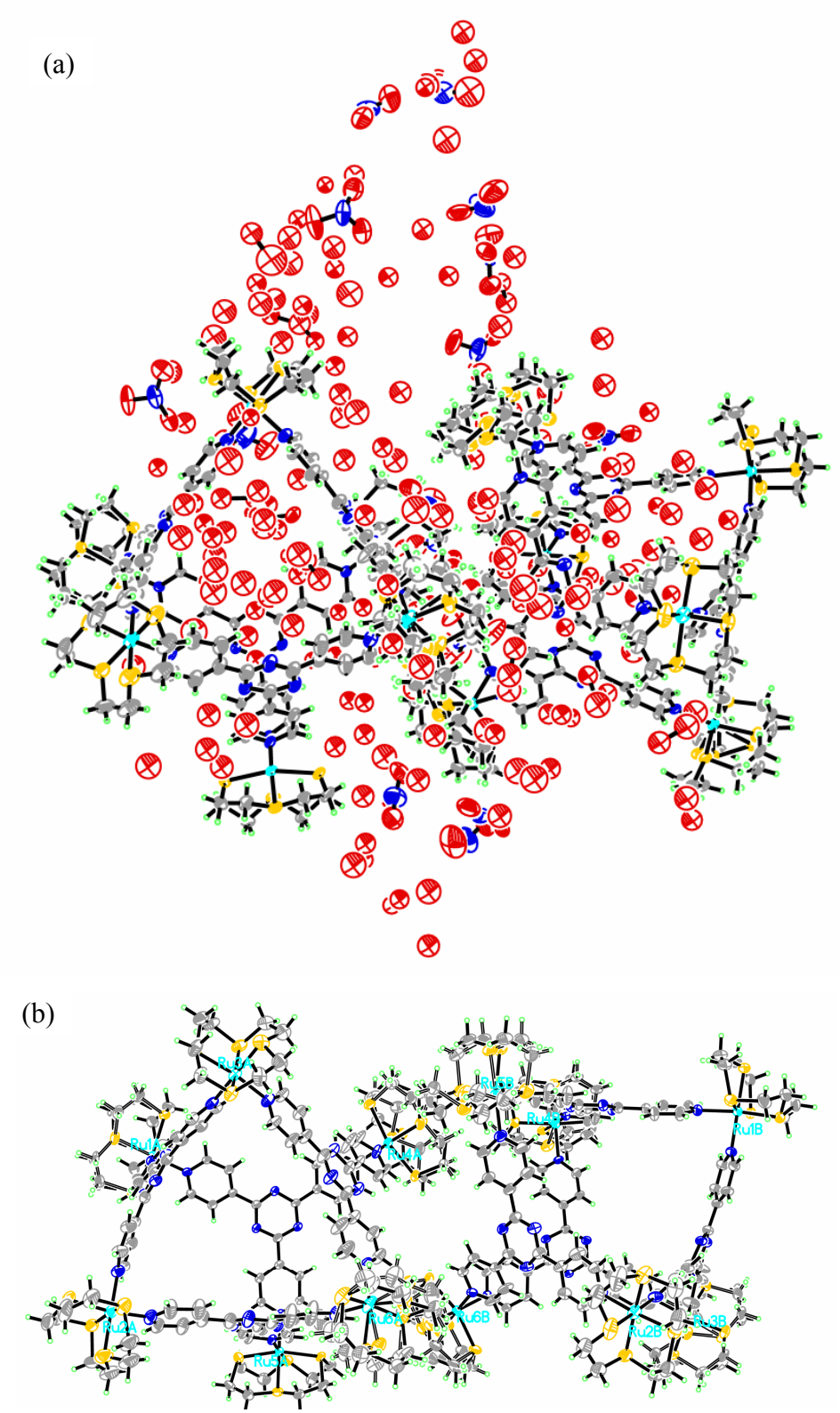

Figure S2. ORTEP views (30% probability level) of **1**·$(H_2O)_m$: (a) Independent molecular structure. Water molecules and nitrate anions are severely disordered. (b) Molecules of **1**.

Table 2. Crystal data and structure refinement for $[\mathbf{1}\cdot(\mathbf{6})_4]\cdot(\mathbf{5})\cdot(H_2O)_m$.

Identification code	cage1.6	
Empirical formula	C178 H334.5 N37 O85.25 Ru6 S24	
Formula weight	5728.7	
Temperature	80(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Ccc*2	
Unit cell dimensions	a = 37.576(5) Å	α= 90°.
	b = 44.413(6) Å	β= 90°.
	c = 35.800(5) Å	γ= 90°.
Volume	59747(14) Å^3	
Z	8	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	0.539 mm^{-1}	
F(000)	23932	
Crystal size	0.16 x 0.09 x 0.06 mm^3	
Theta range for data collection	1.57 to 27.92°.	
Index ranges	-49<=h<=49, -58<=k<=57, -47<=l<=46	
Reflections collected	344836	
Independent reflections	71025 [R(int) = 0.0725]	
Completeness to theta = 27.92°	99.7 %	
Absorption correction	Semi-empirical	
Max. and min. transmission	0.9684 and 0.9187	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	71025 / 1748 / 3564	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R_1 = 0.0774, wR_2 = 0.1919	
R indices (all data)	R_1 = 0.1470, wR_2 = 0.2440	
Absolute structure parameter	0.07(2)	
Largest diff. peak and hole	2.009 and -1.281 e.Å^{-3}	

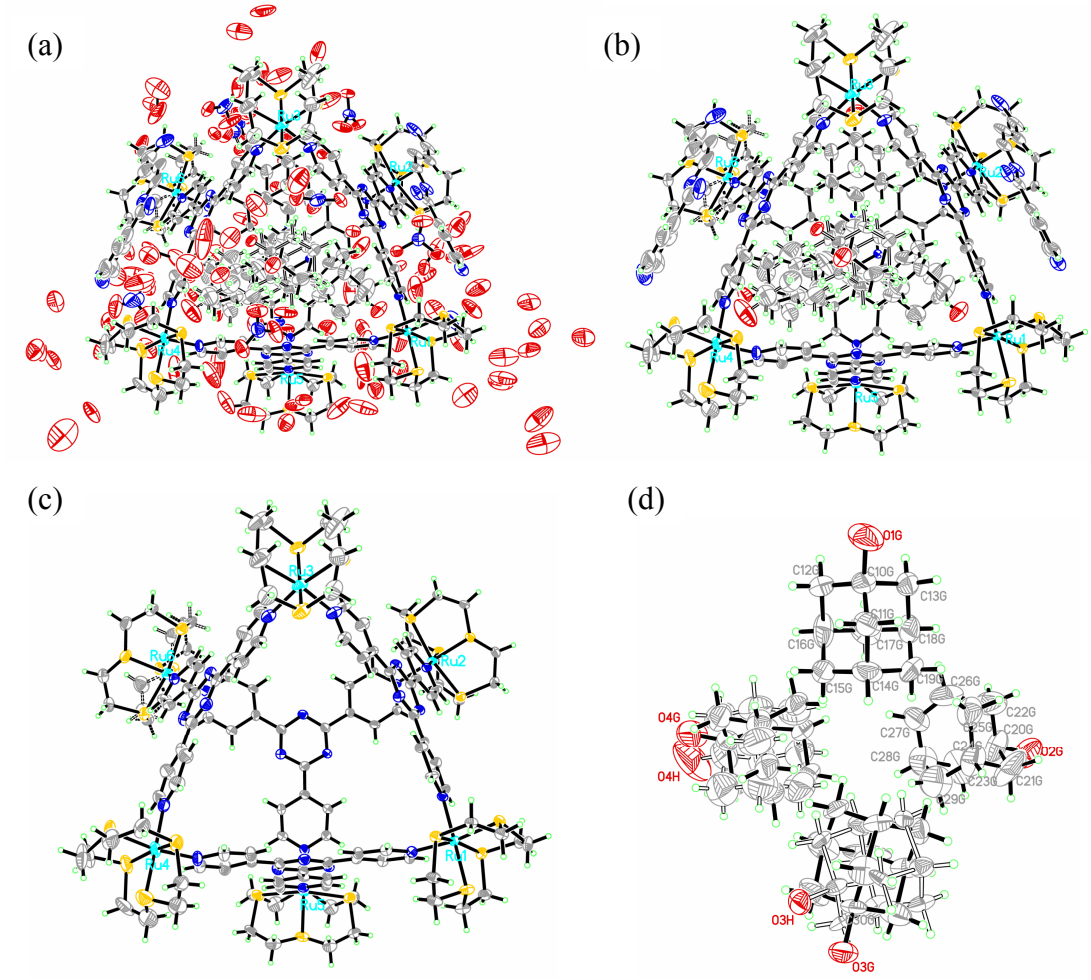

Figure S3. ORTEP views (30% probability level) of $[\mathbf{1}\cdot(\mathbf{6})_4]\cdot(\mathbf{5})\cdot(H_2O)_m$: (a) Independent molecular structure. Water molecules and nitrate anions are severely disordered. (b) Molecule of $[\mathbf{1}\supset(\mathbf{6})_4]\cdot(\mathbf{5})$. (c) Molecule of **1**. (d) Molecules of encapsulated **6**.

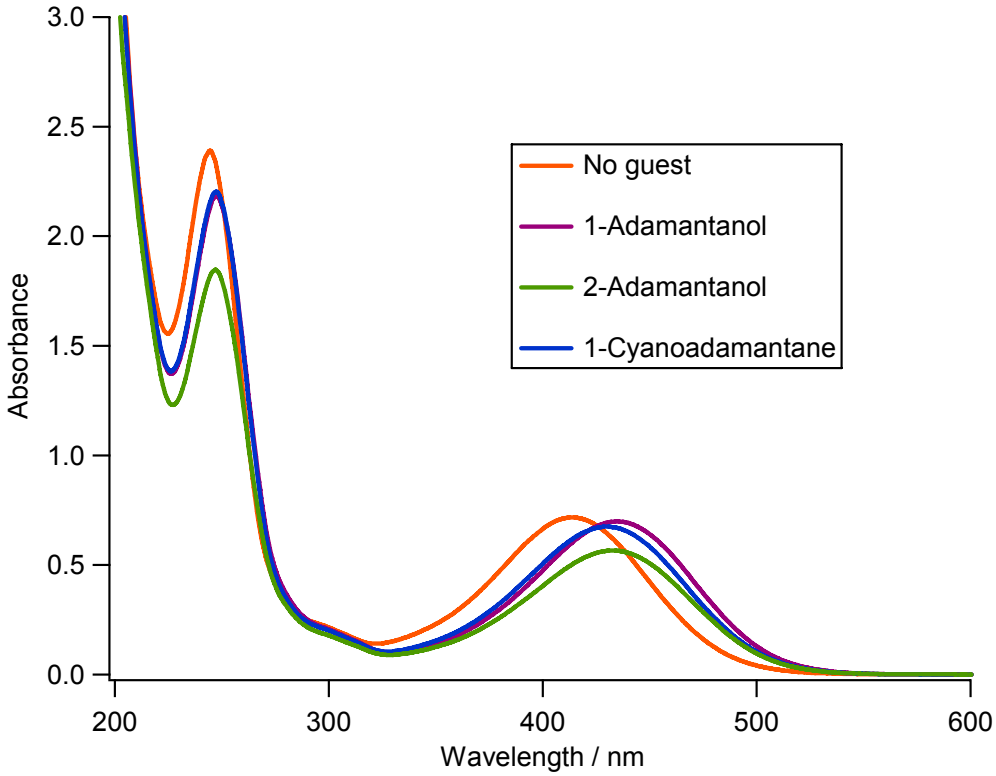

Figure S4. UV-Vis spectra of Ru(II)-cage **1** encapsulating adamantane derivatives (0.1 mM in H_2O).