Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Info

Content:

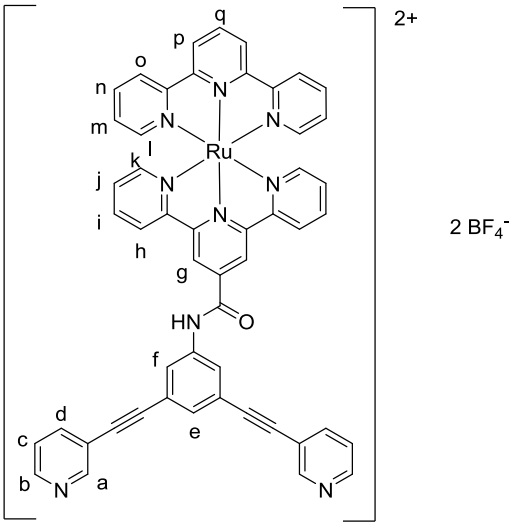
1. Experimental section

1.1 General remarks

All reagents were purchased from commercial sources and used without further purification. Chromatographic separations were performed using silica gel (63-200 µm). NMR spectra were recorded with a Bruker Avance DPX 400 or a Bruker Avance III 400 or a Bruker Avance I 500 spectrometer at a temperature of 298 K. The spectra were referenced to the residual ^{1}H and $^{13}C\{^{1}H\}$ signals of the solvents in parts per million (ppm). Abbreviations for NMR multiplicities are: singlet (s), doublet (d), triplet (t), multiplet (m). Coupling constants *J* are given in Hz. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker HR-QTOF maXisPlus or Thermo Scientific LCQ/Fleet mass spectrometer. UV/vis absorption spectra were acquired with a Jasco V-550 UV/vis spectrometer. Emission spectra and quantum yields were measured on a Hamamatsu Absolute PL Quantum Yield C11347 spectrometer. [Ru(terpy)(terpy-4-COOH)]$(PF_6)_2$ **R1**,[1] ligand **L-NH$_2$**,[2] **C-NH$_2$**,[2] and 4'-methyl-2,2'-bipyridine-4-propionic acid[3] were prepared according to literature procedures.

1.2 Synthetic procedures

Ligand **L1**:



A mixture of [Ru(terpy)(terpy-COOH)]$(PF_6)_2$ **R1** (180 mg, 0.2 mmol, 1 equiv.), ligand **L-NH$_2$** (59.1 mg, 0.2 mmol, 1 equiv.), 2-chloro-1-methylpyridinium iodide (CMPI, 204 mg, 0.8 mmol, 4 equiv.) and 4-(dimethylamino)pyridine (DMAP, 244 mg, 2.0 mmol, 10 equiv.) in dry DMF (10 mL) was stirred under an argon atmosphere at 130 °C for 24 h. Dichloromethane (50 mL) was added to the reaction mixture and the organic phase was extracted five times with water (40 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. After precipitation by addition of diethyl ether to the DMF residue, the red solid was filtered, dissolved in acetonitrile and further purified by column chromatography (acetonitrile/water/KNO_3(sat.) = 7:1:1). The collected band was reduced in volume and treated with $NaBF_4$ to precipitate the product. The precipitate was filtered, washed with water and

diethyl ether and dried under reduced pressure to give ligand **L1** as red solid (146 mg, 0.14 mmol, 68%).

^{1}H NMR (400 MHz, CD_3CN): δ[ppm] = 10.62 (s, 1 H, NH), 9.34 (s, 2 H, H_g), 8.81 (d, *J* = 1.6 Hz, 2 H, H_a), 8.76 (d, *J* = 8.2 Hz, 2 H, H_p), 8.70 (d, *J* = 8.1 Hz, 2 H, H_h), 8.60 (dd, *J* = 4.9, 1.6 Hz, 2 H, H_b), 8.49 (d, *J* = 8.1 Hz, 2 H, H_o), 8.44 (t, *J* = 8.3 Hz, 1 H, H_q), 8.27 (s, 2 H, H_f), 7.98-7.90 (m, 6 H, H_i/H_n/H_d), 7.65 (s, 1 H, H_e), 7.43-7.36 (m, 6 H, H_k/H_l/H_c), 7.22-7.15 (m, 4 H, H_j/H_m).

DOSY NMR (400 MHz, CD_3CN): *log D* = -9.16.

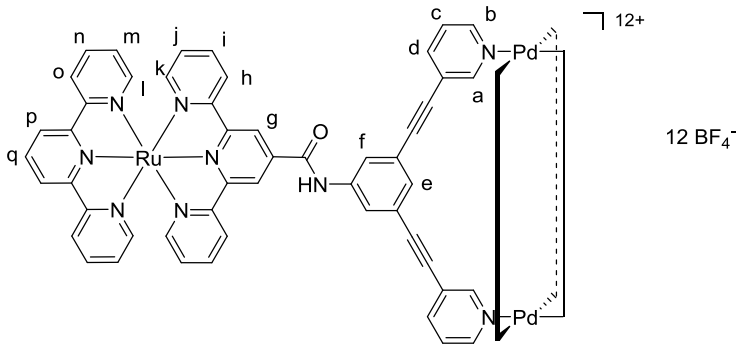
^{13}C NMR (101 MHz, CD_3CN): δ[ppm] = 164.1, 158.8, 158.6, 156.9, 155.9, 153.6, 153.5, 153.0, 150.3, 142.1, 141.6, 140.2, 139.6, 139.3, 137.4, 131.6, 128.8, 128.5, 125.7, 125.5, 124.8, 124.8, 124.5, 124.5, 122.7, 120.5, 91.6, 88.1.

^{11}B NMR (128 MHz, CD_3CN): δ[ppm] = -1.18.

^{19}F NMR (377 MHz, CD_3CN): δ[ppm] = -151.58 ($^{10}BF_4^-$), -151.64 ($^{11}BF_4^-$).

MS (ESI, MeCN): *m/z* = 444.78 $[M - 2BF_4^-]^{2+}$ (calcd for $RuC_{51}H_{33}N_9O$: 444.60), 976.04 $[M - BF_4^-]^+$ (calcd for $RuC_{51}H_{33}N_9OBF_4$: 976.19).

Cage **C1**:



A solution of $[Pd(NCCH_3)_4](BF_4)_2$ (6.7 mg, 15 μmol, 2 equiv.) and ligand **L1** (32 mg, 30 μmol, 4 equiv.) in DMSO (1 mL) was stirred at r.t. for one hour. After precipitation by addition of acetone and diethyl ether, the solid was filtered and washed with diethyl ether to yield the cage compound **C1** as red solid (24 mg, 5 μmol, 67%).

^{1}H NMR (400 MHz, CD_3CN): δ[ppm] = 9.92 (s, 1 H, NH), 9.65 (s, 2 H, H_a), 9.25-9.17 (m, 4 H, H_b/H_g), 8.76 (d, *J* = 8.0 Hz, 2 H, H_p), 8.65 (d, *J* = 7.6 Hz, 2 H, H_h), 8.50-8.42 (m, 3 H, H_o/H_q), 8.35 (s, 2 H, H_f), 8.23 (d, *J* = 7.9 Hz, 2 H, H_d), 7.96-7.87 (m, 5 H, H_i/H_n/H_e), 7.72 (dd, *J* = 7.9, 5.8 Hz, 2 H, H_c), 7.38 (d, *J* = 5.9 Hz, 2 H, H_k), 7.33 (d, *J* = 5.3 Hz, 2 H, H_l), 7.20 (dd, *J* = 7.1, 5.6 Hz, 2 H, H_j), 7.12 (dd, *J* = 7.2, 5.2 Hz, 2 H, H_m).

DOSY NMR (400 MHz, CD_3CN): *log D* = -9.49.

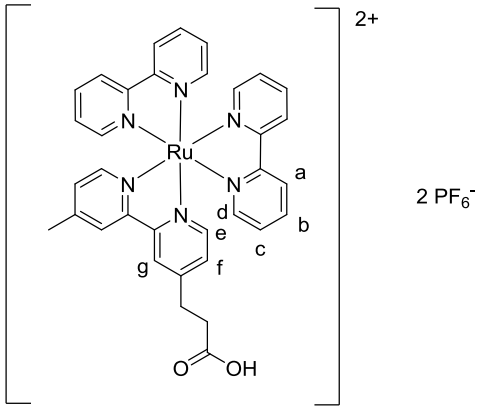
^{13}C NMR (101 MHz, CD_3CN): δ[ppm] = 158.8, 158.5, 156.9, 155.9, 154.2, 153.6, 153.5, 153.4, 151.3, 139.4, 139.3, 139.2, 139.1, 128.8, 128.5, 128.4, 125.7, 125.5, 125.5, 124.8, 124.6, 124.1, 122.5, 94.7, 85.8.

^{11}B NMR (128 MHz, CD_3CN): δ[ppm] = -1.06.

^{19}F NMR (377 MHz, CD_3CN): δ[ppm] = -151.04 ($^{10}BF_4^-$), -151.09 ($^{11}BF_4^-$).

MS (ESI, MeCN): *m/z* = 715.1 $[M - 6BF_4^-]^{6+}$ (calcd for $Pd_2C_{204}H_{132}N_{36}O_4Ru_4B_6F_{24}$: 714.9), 875.1 $[M - 5BF_4^-]^{5+}$ (calcd for $Pd_2C_{204}H_{132}N_{36}O_4Ru_4B_7F_{28}$: 875.3), 1116.2 $[M - 4BF_4^-]^{4+}$ (calcd for $Pd_2C_{204}H_{132}N_{36}O_4Ru_4B_8F_{32}$: 1115.9).

$[Ru(bipy)_2(bipy\text{-}4'\text{-}CH_3\text{-}4\text{-}(CH_2)_2\text{-}COOH)](PF_6)_2$ **R2**:



$[RuCl_2(bipy)_2]$ (484 mg, 1 mmol, 1 equiv.) and 4'-methyl-2,2'-bipyridine-4-propionic acid (242 mg, 1 mmol, 1 equiv.) were dissolved in dry ethanol (15 mL). The mixture was heated to reflux under an argon atmosphere for 16 h. After cooling to r.t., the solvent was removed under reduced pressure and the residue dissolved in water. The red solution was treated with KPF_6, the resulting precipitate was filtered, washed with water and chloroform and dried under reduced pressure to obtain the Ru complex **R2** as orange solid (455 mg, 0.5 mmol, 48%).

^{1}H NMR (400 MHz, CD_3CN): δ[ppm] = 8.48 (d, *J* = 7.9 Hz, 4 H, H_a), 8.39-8.35 (m, 2 H, H_g), 8.08-8.00 (m, 4 H, H_b), 7.75-7.67 (m, 4 H, H_d), 7.54 (dd, *J* = 14.1, 5.9 Hz, 2 H, H_e), 7.43-7.34 (m, 4 H, H_c), 7.29-7.20 (m, 2 H, H_f), 3.06 (t, *J* = 7.1 Hz, 2 H, CH_2), 2.74 (t, *J* = 7.4 Hz, 2 H, CH_2),2.53 (s, 3 H, CH_3).

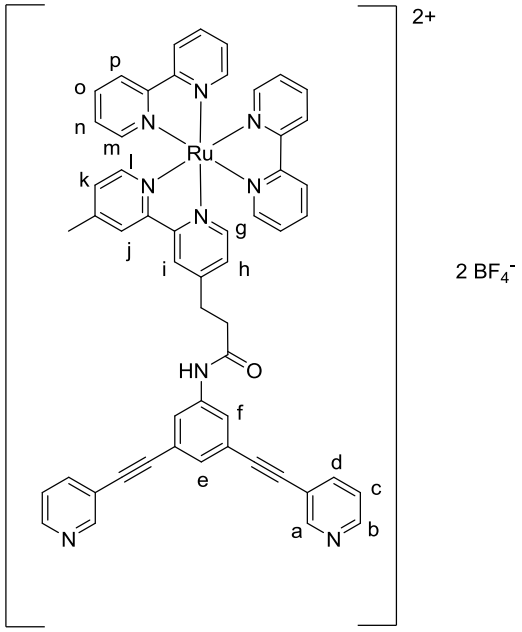
^{13}C NMR (101 MHz, CD_3CN): δ[ppm] = 158.00, 157.6, 157.4, 154.0, 152.7, 152.6, 152.5, 152.4, 152.0, 151.7, 151.5, 138.6, 138.6, 129.3, 128.5, 128.5, 126.0, 125.2, 125.1, 30.6, 21.2.

^{31}P NMR (162 MHz, CD_3CN): δ [ppm] = -144.64 (sept, *J* = 704 Hz).

^{19}F NMR (377 MHz, CD_3CN): δ [ppm] = -72.87 (d, *J* = 704 Hz).

MS (ESI, MeCN): *m/z* = 328.24 $[M - 2PF_6^-]^{2+}$ (calcd for $RuC_{34}H_{30}N_6O_2$: 328.08), 801.08 $[M - PF_6^-]^+$ (calcd for $RuC_{54}H_{41}N_9OPF_6$: 801.11).

Ligand **L2**:



A mixture of Ru complex **R2** (378 mg, 0.4 mmol, 1 equiv.), ligand **L-NH$_2$** (118 mg, 0.4 mmol, 1 equiv.), CMPI (409 mg, 1.6 mmol, 4 equiv.) and DMAP (489 mg, 4.0 mmol, 10 equiv.) in dry DMF (15 mL) was stirred under an argon atmosphere at 130 °C for 24 h. Dichloromethane (50 mL) was added to the reaction mixture and the organic phase was extracted five times with water (40 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. After precipitation by addition of diethyl ether to the DMF residue, the red solid was filtered, dissolved in acetonitrile and further purified by column chromatography (acetonitrile/KNO_3(sat.) = 10:1). The collected band was reduced in volume and treated with $NaBF_4$ to precipitate the product. The precipitate was filtered, washed with water and diethyl ether and dried under reduced pressure to give ligand **L2** as orange solid (248 mg, 0.22 mmol, 56%).

^{1}H NMR (400 MHz, CD_3CN): δ [ppm] = 8.95 (s, 1 H, NH), 8.72 (d, *J* = 1.6 Hz, 2 H, H_a), 8.58 (dd, *J* = 4.7, 1.6 Hz, 2 H, H_b), 8.48-8.43 (m, 4 H, H_p), 8.42 (s, 1 H, H_i), 8.35 (s, 1 H, H_j), 8.04-7.97 (m, 4 H, H_o), 7.87 (dt, *J* = 7.8, 1.6 Hz, 2 H, H_d), 7.74-7.69 (m, 6 H, H_f/H_m), 7.57 (d, *J* = 5.8 Hz, 1 H, H_g), 7.50 (d, *J* = 5.8 Hz, 1 H, H_l), 7.44 (s, 1 H, H_e), 7.41-7.34 (m, 6 H, H_c/H_n), 7.31 (dd,

J = 1.6, 5.8 Hz, 1 H, H_h), 7.20 (dd, J = 1.6, 5.4 Hz, 1 H, H_k), 3.18 (t, J = 7.1 Hz, 2 H, CH_2), 2.82 (t, J = 7.0 Hz, 2 H, CH_2), 2.50 (s, 3 H, CH_3).

DOSY NMR (400 MHz, CD_3CN): *log D* = -9.16.

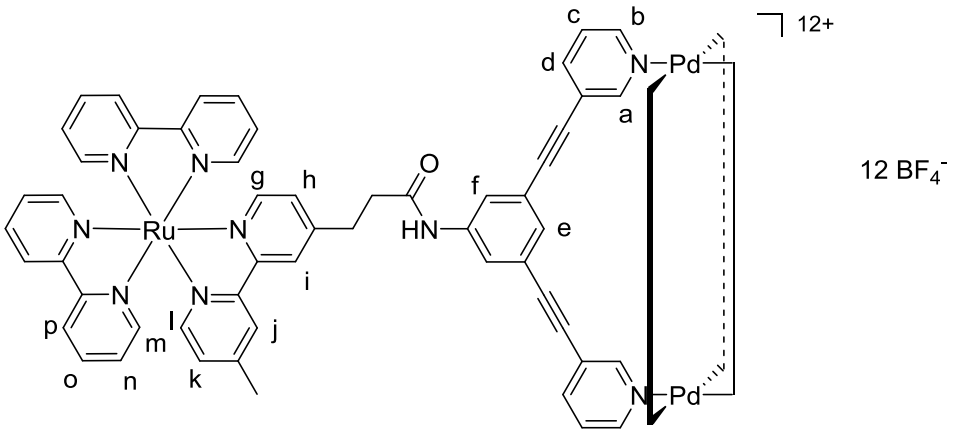
^{13}C NMR (101 MHz, CD_3CN): δ[ppm] = 171.5, 158.0, 157.9, 157.6, 157.4, 154.0, 152.9, 152.7, 152.6, 152.5, 152.0, 151.7, 151.5, 150.2, 140.6, 139.5, 138.6, 130.3, 129.3, 128.7, 128.5, 128.4, 126.0, 125.3, 125.2, 125.1, 124.4, 124.3, 123.4, 120.5, 91.7, 87.6, 37.4, 31.3, 21.3.

^{11}B NMR (128 MHz, CD_3CN): δ[ppm] = -1.16.

^{19}F NMR (377 MHz, CD_3CN): δ[ppm] = -151.53 ($^{10}BF_4^-$), -151.59 ($^{11}BF_4^-$).

MS (ESI, MeCN): *m/z* = 466.96 [M - $2BF_4^-$]$^{2+}$ (calcd for $RuC_{54}H_{41}N_9O$: 466.63), 1020.21 [M - BF_4^-]$^+$ (calcd for $RuC_{54}H_{41}N_9OBF_4$: 1020.25).

Cage **C2**:



A solution of $[Pd(NCCH_3)_4](BF_4)_2$ (6.7 mg, 15 μmol, 2 equiv.) and ligand **L2** (33 mg, 30 μmol, 4 equiv.) in DMSO (1 mL) was stirred at r.t. for one hour. After precipitation by addition of acetone and diethyl ether, the solid was filtered and washed with diethyl ether to yield the cage compound **C1** as red solid (28 mg, 6 μmol, 75%).

^{1}H NMR (400 MHz, CD_3CN): δ[ppm] = 9.58 (s, 2 H, H_a), 9.21 (d, J = 5.3 Hz, 2 H, H_b), 9.01 (s, 1 H, NH), 8.47-8.39 (m, 6 H, H_p/H_i/H_j), 8.08 (d, J = 8.1 Hz, 2 H, H_d), 8.04-7.97 (m, 4 H, H_o), 7.87 (s, 2 H, H_f), 7.69-7.60 (m, 7 H, H_c/H_e/H_m), 7.53 (d, J = 5.9 Hz, 1 H, H_g), 7.48 (d, J = 5.9 Hz, 1 H, H_l), 7.38-7.32 (m, 4 H, H_n), 7.26 (d, J = 5.9 Hz, 1 H, H_h), 7.19 (d, J = 5.7 Hz, 1 H, H_k), 3.12 (t, J = 7.5 Hz, 2 H, CH_2), 2.78 (t, J = 7.5 Hz, 2 H, CH_2), 2.49 (s, 3 H, CH_3).

DOSY NMR (400 MHz, CD_3CN): *log D* = -9.48.

^{13}C NMR (101 MHz, CD_3CN): δ [ppm] = 171.5, 158.0, 157.9, 157.6, 157.4, 154.2, 153.9, 152.6, 152.5, 152.4, 152.0, 151.6, 151.5, 151.2, 143.8, 140.9, 138.5, 130.2, 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 125.9, 125.2, 125.1, 125.1, 124.4, 123.6, 94.7, 85.4, 37.2, 31.1, 21.2.

^{11}B NMR (128 MHz, CD_3CN): δ [ppm] = -1.08.

^{19}F NMR (377 MHz, CD_3CN): δ [ppm] = -151.18 ($^{10}BF_4^-$), -151.23 ($^{11}BF_4^-$).

MS (ESI, MeCN): *m/z* = 744.3 $[M - 6BF_4^-]^{6+}$ (calcd for $Pd_2C_{216}H_{164}N_{36}O_4Ru_4B_6F_{24}$: 744.3), 910.6 $[M - 5BF_4^-]^{5+}$ (calcd for $Pd_2C_{216}H_{164}N_{36}O_4Ru_4B_7F_{28}$: 910.6), 1160.3 $[M - 4BF_4^-]^{4+}$ (calcd for $Pd_2C_{216}H_{164}N_{36}O_4Ru_4B_8F_{32}$: 1160.0).

2. NMR spectra

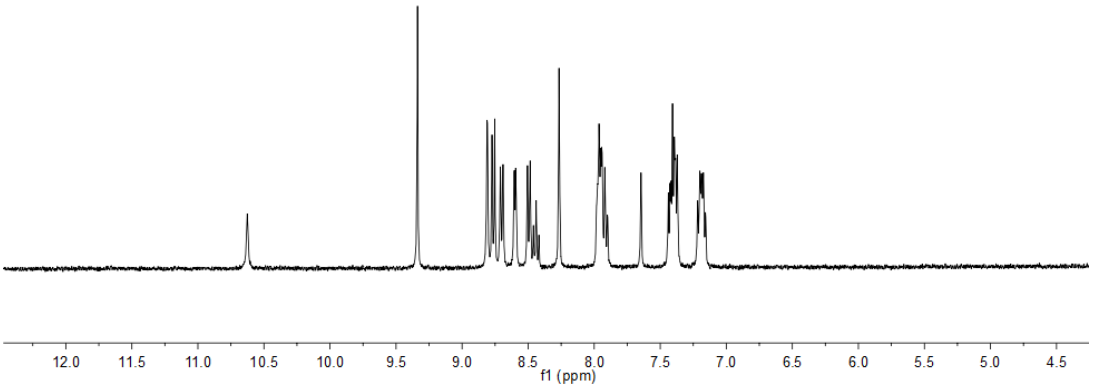


Figure S1. ^{1}H NMR (400 MHz, CD_3CN) spectrum of ligand **L1**.

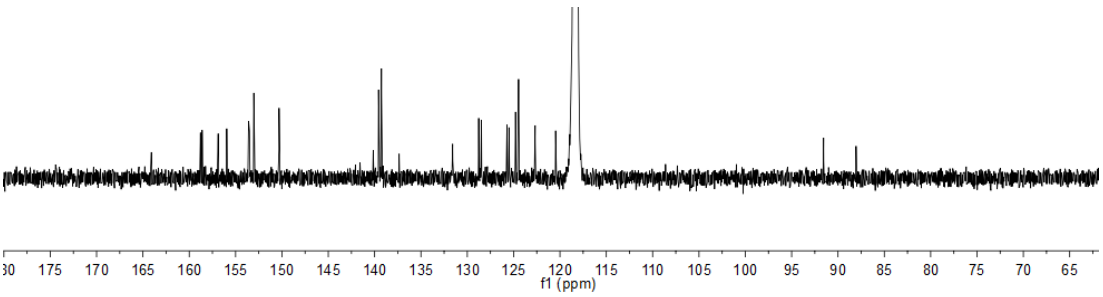


Figure S2. ^{13}C NMR (101 MHz, CD_3CN) spectrum of ligand **L1**.

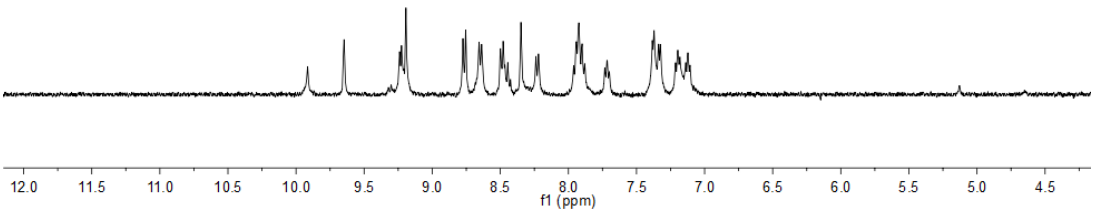


Figure S3. ^{1}H NMR (400 MHz, CD_3CN) spectrum of ligand **C1**.

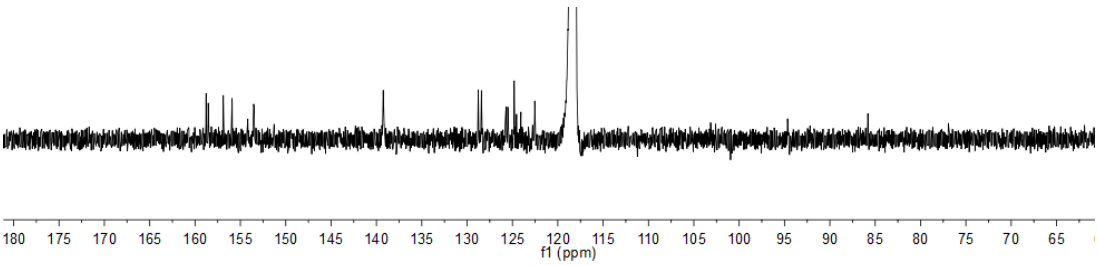


Figure S4. ^{13}C NMR (101 MHz, CD_3CN) spectrum of ligand **C1**.

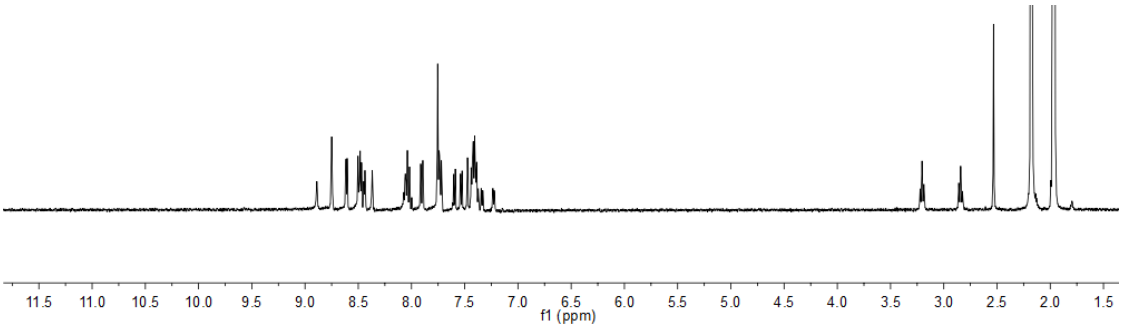


Figure S5. ^{1}H NMR (400 MHz, CD_3CN) spectrum of ligand **L2**.

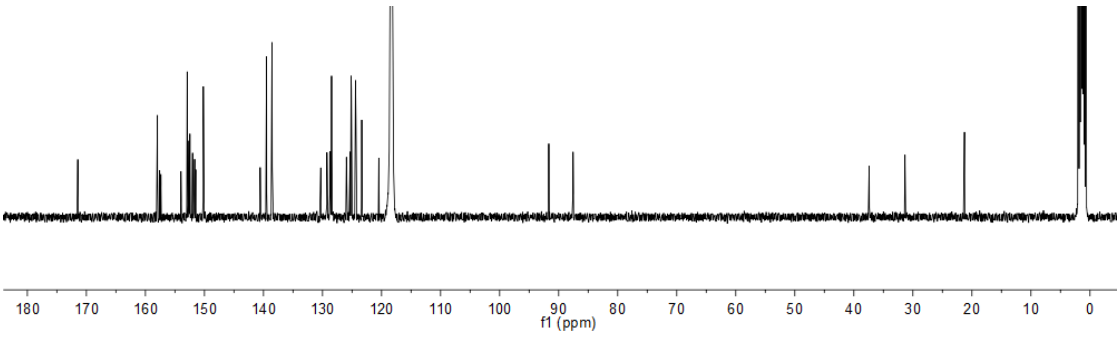


Figure S6. ^{13}C NMR (101 MHz, CD_3CN) spectrum of ligand **L2**.

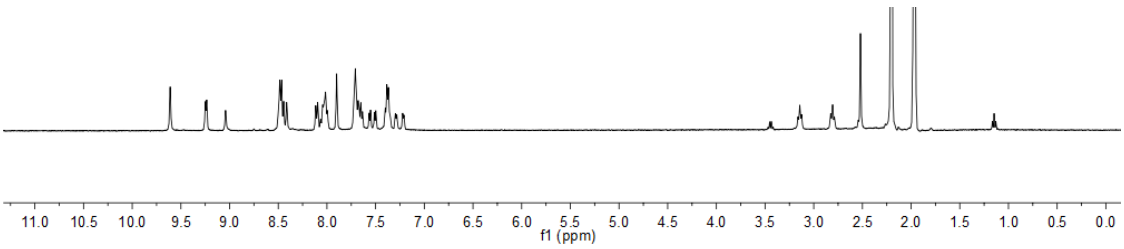


Figure S7. ^{1}H NMR (400 MHz, CD_3CN) spectrum of ligand **C2**.

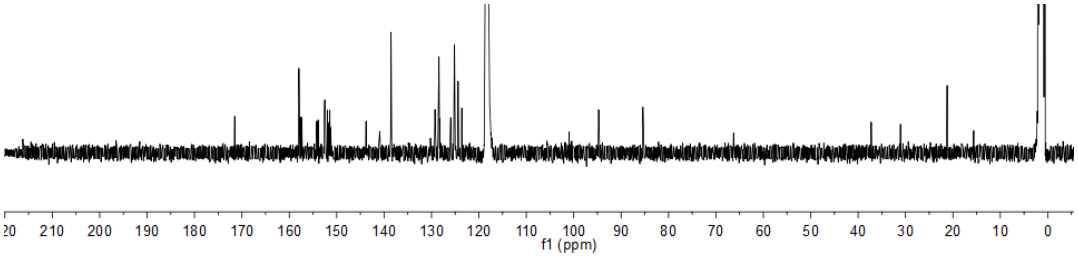


Figure S8. ^{13}C NMR (101 MHz, CD_3CN) spectrum of ligand **C2**.

3. ^{1}H DOSY NMR spectroscopy

Table S1. Comparison of diffusion coefficients (D, x 10^{-10} m^2 s^{-1}) of ligands and palladium cages obtained by ^{1}H DOSY NMR (400 MHz, CD_3CN).

Ligand	D of ligand	Cage	D of cage	Ratio
L1	6.94	**C1**	3.27	2.12
L2	6.91	**C2**	3.31	2.09

In diffusion experiments, the molecular size of the metallocages is estimated by the Stokes-Einstein equation:[4]

$$r_S = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot D}$$

With r_S = hydrodynamic or Stokes radius of the molecule or aggregate being investigated which is assumed to exhibit a spherical shape, k_B = Boltzmann constant, T = temperature, η =viscosity of solution, D = diffusion coefficient.

Table S2. Stokes radii r_S of metallocages obtained by diffusion coefficients with viscosity of acetonitrile = 0.44 mPa·s and a temperature of 298 K.

Cage	D [x 10^{-10} m^2 s^{-1}]	r_S [nm]
C1	3.27	1.52
C2	3.31	1.50

4. Crystallographic details

Data were collected on a single-crystal X-ray diffractometer equipped with a CCD detector (Bruker APEX II, κ-CCD), a fine-focus sealed tube with MoKα radiation (λ = 0.71073 Å) and a graphite monochromator by using the *APEX2* software package.[5] The measurements were performed on a single crystal coated with perfluorinated ether. The crystal was fixed on the top of a glass fiber and transferred to the diffractometer. The crystal was frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using *SAINT*.[6] Absorption corrections, including odd- and even-ordered spherical harmonics were performed using *SADABS*.[6] Space-group assignments were based on systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods as implemented in the *APEX2* software package,[5] based on *SHELXS-97*[7] and were refined against all data using *SHELXLE*[8] in conjunction with *SHELXL-2014*.[9] Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(Fo^2-Fc^2)^2$ with *SHELXL-97*[10] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[11] Images of the crystal structures were generated by PLATON.[12]

CCDC 1484108 (**L1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound L1 (CCDC 1484108)

Suitable single crystals for diffraction experiments of **L1** (PF_6^- as counterions) were grown by vapor diffusion of diethyl ether into an acetone solution of the ligand **L1**.

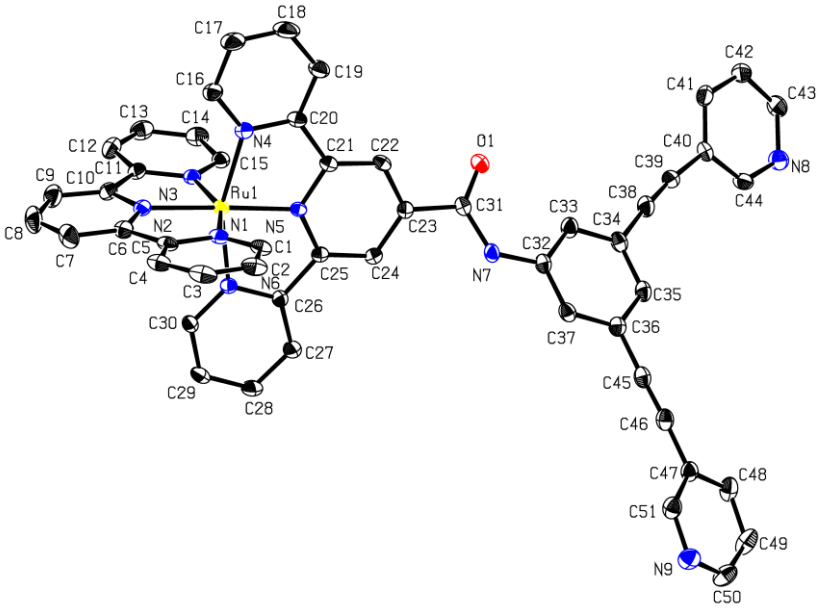


Figure S9. ORTEP style representation of the molecular structure of **L1** in the solid state. Ellipsoids are shown at 50% probability. Hydrogen atoms, counterions and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–N1 2.0729(2), Ru1–N2 1.9796(2), Ru1–N3 2.0683(1), Ru1–N4 2.0690(1), Ru1–N5 1.9694(2), Ru1–N6 2.0703(2), C31–N7 1.3631(1).

Diffractometer operator Manuela Hollering

scanspeed 2 s per frame

dx 63 mm XYZ frames measured in XYZ data sets

phi-scans with delta_phi = 0.5

omega-scans with delta_omega = 0.5

Crystal data

$C_{51}H_{33}N_9ORu \cdot 2(F_6P) \cdot C_2H_3N$ $F(000) = 1228$

$M_r = 1219.93$

Triclinic, *P*

Hall symbol: -P 1

a = 8.9134 (8) Å

b = 9.3811 (7) Å

c = 30.975 (3) Å

α = 95.760 (4)°

β = 97.978 (5)°

γ = 96.792 (4)°

V = 2529.0 (4) Å^3

Z = 2

D_x = 1.602 Mg m^{-3}

Melting point: ? K

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 9450 reflections

θ = 2.3–26.0°

μ = 0.47 mm^{-1}

T = 100 K

Fragment, clear dark red

0.26 × 0.19 × 0.15 mm

Data collection

Bruker APEX-II CCD diffractometer

Radiation source: fine-focus sealed tube

Triumph Optic monochromator

Detector resolution: 16 pixels mm^{-1}

phi– and ω–rotation scans

Absorption correction: multi-scan *SADABS*, Bruker, 2008b

T_{min} = 0.681, T_{max} = 0.745

52760 measured reflections

10330 independent reflections

8489 reflections with $I > 2\sigma(i)$

R_{int} = 0.061

θ_{max} = 26.4°, θ_{min} = 2.0°

h = −11 11

k = −11 11

l = −38 38

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.082$	$W = 1/[\Sigma^2(FO^2) + (0.0255P)^2 + 2.5391P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.002$
10330 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
842 parameters	$\Delta\rho_{min} = -0.59$ e Å^{-3}
270 restraints	Extinction correction: none
? constraints	Extinction coefficient: ?
Primary atom site location: structure-invariant direct methods	

5. Computational details

Semi-empirical PM6 calculations implemented in Gaussian09 D.01 were done.[13,14] All obtained geometries have been identified *via* the numbers of negative frequencies as minima (NImag = 0). A text file of all computed molecule Cartesian coordinates in a format for convenient visualization is included. Calculated bond lengths and angles correspond well to data obtained from the crystal structure.

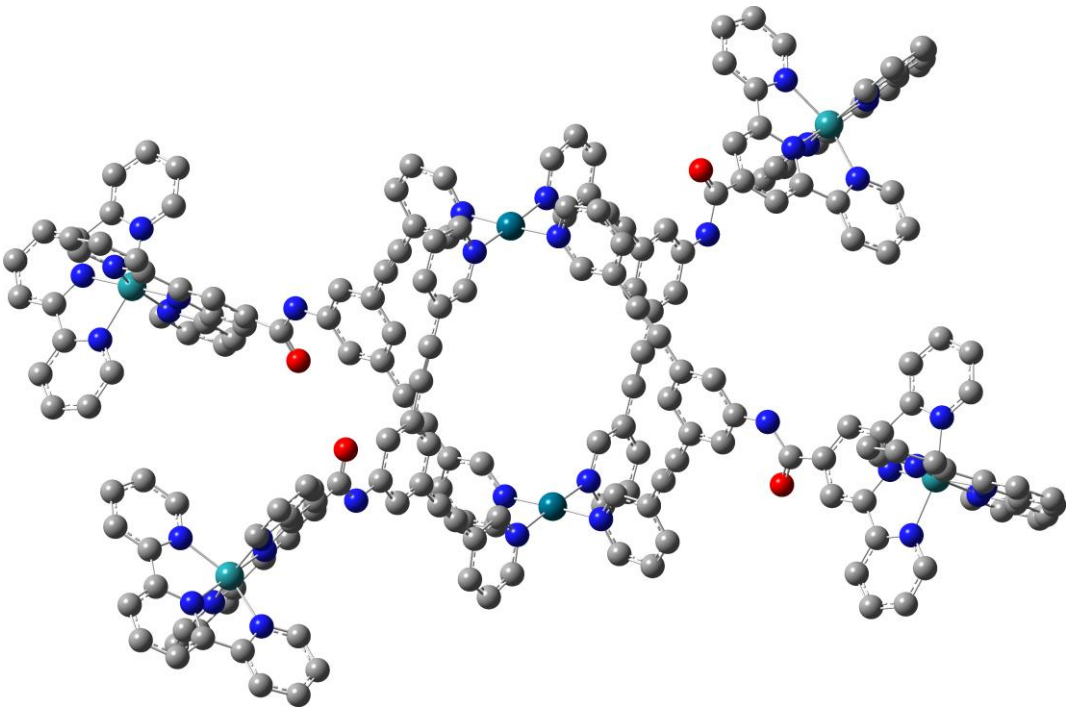


Figure S 10. Molecular model of cage **C1** (C grey, N blue, O red, Pd turquoise, Ru green). Calculated bond lengths and distances (Å): Ru–N 1.93302 – 2.12342, Pd–N 2.05894 – 2.06110, Pd···Pd 10.91408. The span of the cage is 44.17090 Å and the opposing inner C-atoms have a distance of 11.82282 Å.

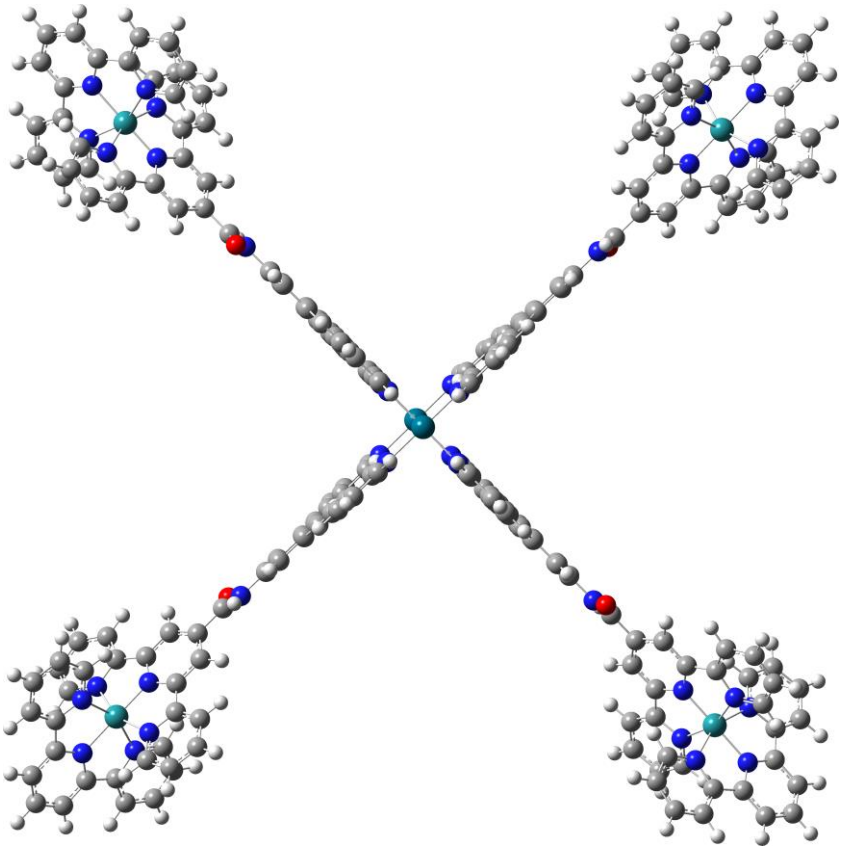


Figure S 11. Molecular model of cage **C1** (view through Pd···Pd axis, C grey, N blue, O red, Pd turquoise, Ru green).

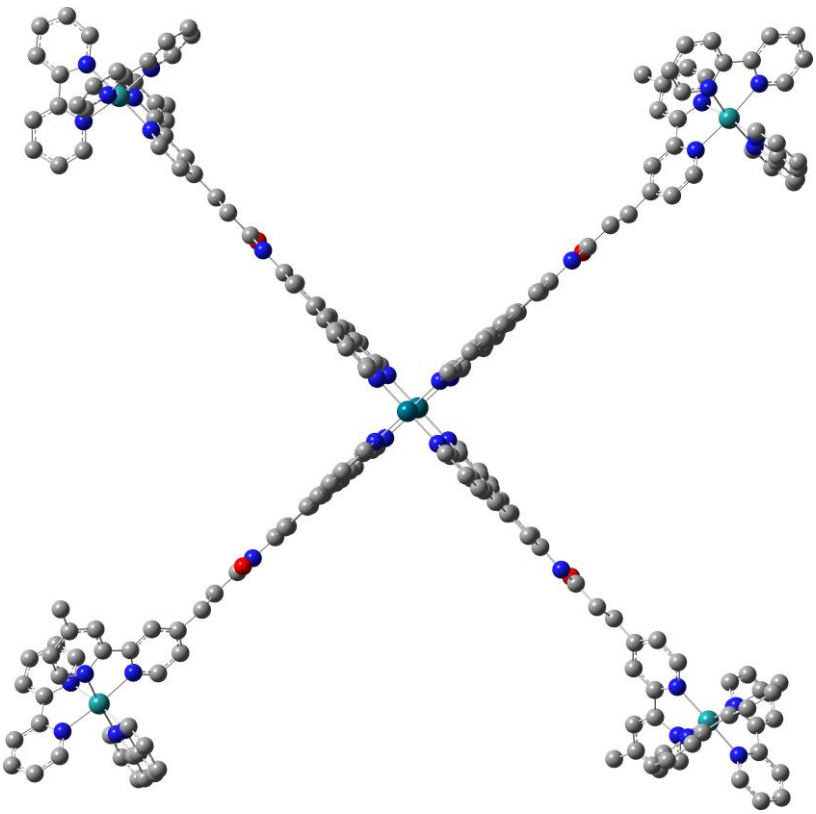


Figure S 12. Molecular model of cage **C2** (view through Pd···Pd axis, C grey, N blue, O red, Pd turquoise, Ru green). Calculated bond lengths and distances (Å): Ru–N 2.11481 – 2.13877, Pd–N 2.05446 – 2.05933, Pd···Pd 11.05782. The span of the cage is 49.44370 Å and the opposing inner C-atoms have a distance of 11.69400 Å.

6. UV/vis, excitation and emission spectroscopy

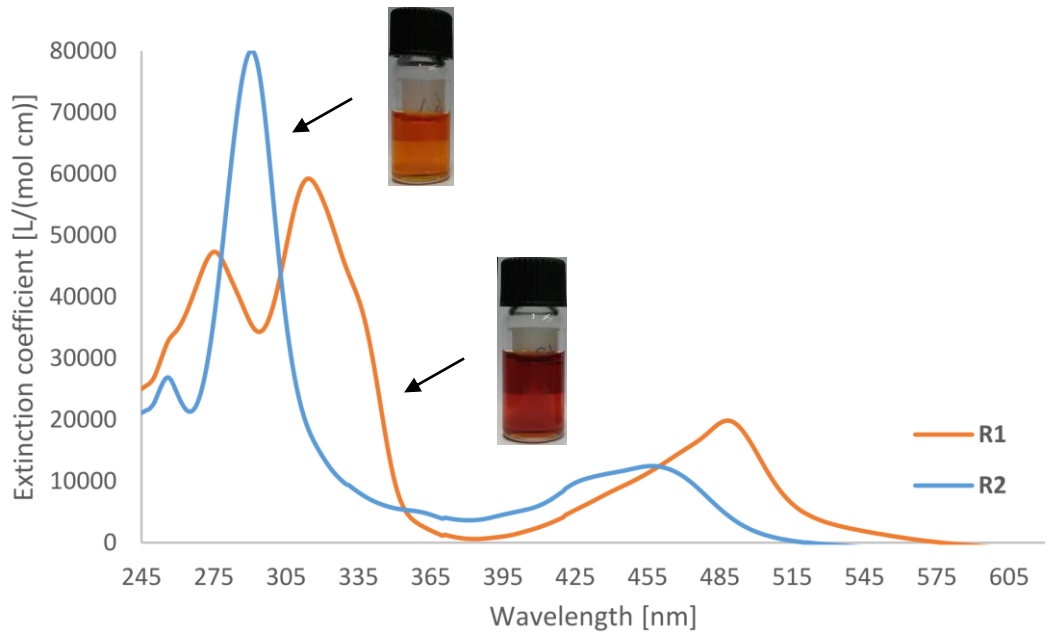


Figure S 13. UV-Vis spectra of ruthenium complexes **R1** and **R2** in DMSO (c = 10^{-5} M). Insets: Photographs of DMSO solutions.

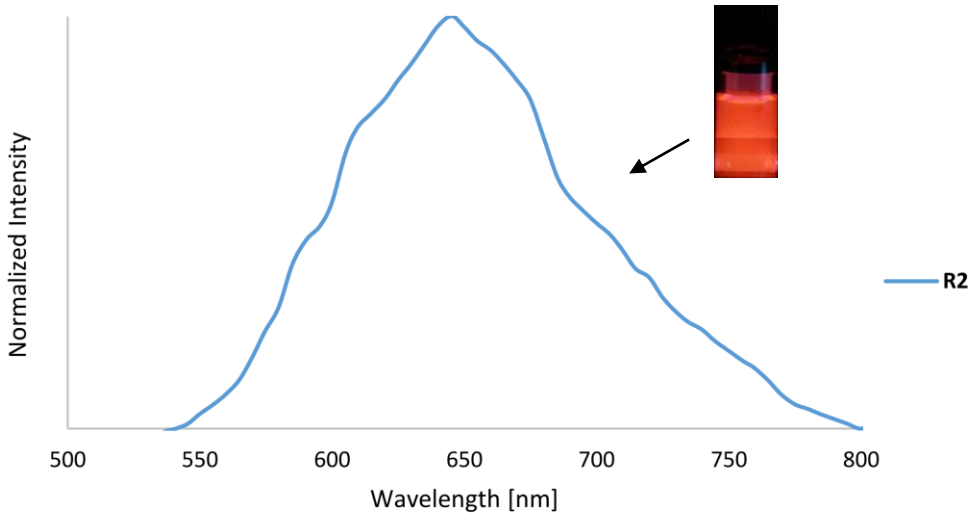


Figure S 14. Emission spectrum of ruthenium complex **R2** in DMSO (c = 10^{-5} M, λ_{ex} = 260 nm). Insets: Photographs of DMSO solutions with UV light irradiation (λ_{ex} = 365 nm).

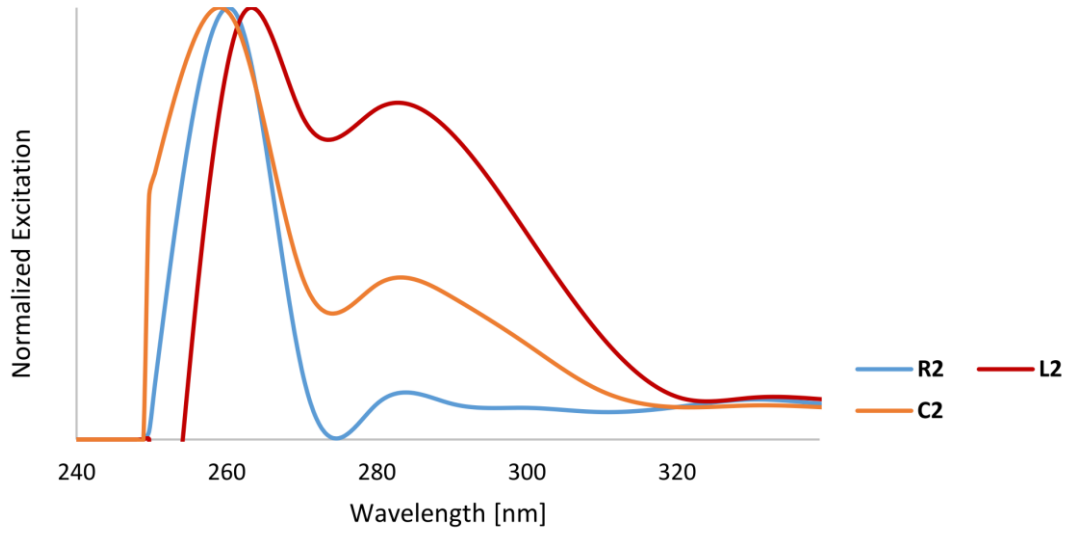


Figure S 15. Excitation spectra of ruthenium complex **R2**, ligand **L2** and cage **C2** in DMSO (c = 10^{-5} M).

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