Electronic Supplementary Material (ESI) for Dalton Transactions.

# Supporting Information

# Tuning the Excited-State Deactivation Pathways of Binuclear Ruthenium(II) 2,2'-Bipyridine Complexes Through Bridging Ligand Design

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# Experimental Section

Acetonitrile ≥ 99.9% (VWR), Dry acetonitrile ≥ 99.8% (Sigma-Aldrich), Dry N,N-dimethylformamide ≥ 99.8% (Sigma-Aldrich), $CH_2Cl_2$ 99% (VWR), Ethylene glycol ≥ 99% (Roth), n-Butyronitrile 99%, aqueous HCl 37% for analysis (VWR), aqueous $NH_3$ 25% for analysis (Roth), NaOH pellet for analysis (VWR), $NH_4PF_6$ 99% (Fluorochem), $[Ni(PPh_3)_2Cl_2]$ 98% (Acros Organics), Zn powder 40 mesh 99.999% (Acros Organics), $AgNO_3$ 99% (Acros Organics) were purchased from commercial suppliers and used as received. 4-bromo-2,2'-bipyridine[1], 5-bromo-2,2'-bipyridine[2] and $[Ru(bpy)_3](PF_6)_2$[3] were synthesized according to literature procedures. Water was purified with a Millipore Milli-Q system. The precipitates were isolated by centrifuging at 6000 rpm for five minutes in a Hettich Universal 320 centrifuge.

**Microwave synthesis.** Microwave (MW) syntheses were performed on a Milestone MicroSYNTH labstation under magnetic stirring. Typically, the conditions allowed the vessels to reach the desired temperature in 5 minutes and the vessels were held at the desired temperature for the indicated period of time.

**Nuclear Magnetic Resonance**. Characteristic NMR spectra were obtained at room temperature using a Bruker AC-300 Avance II (300 MHz) or Bruker AM-500 (500 MHz) at 20 °C. Solvent residual peaks were used as internal standards for $^1H$ ($\delta$ =7.26 ppm for $CDCl_3$ and $\delta$ = 1.94 ppm for $CD_3CN$) chemical shift referencing. NMR spectra were processed using MNOVA.

**Mass Spectrometry**. Compounds were analyzed using a Q-Extractive orbitrap from ThermoFisher and were ionized by atmospheric-pressure chemical ionization (APCI) or electrospray ionization (ESI).

**UV−Visible Absorption**. UV−vis absorption spectra were recorded on a Shimadzu UV-1700 with 1 cm path length quartz cell.

**Steady-State Photoluminescence**. Room temperature and 77 K steady-state photoluminescence (PL) spectra were recorded on a Horiba Scientific-FL-1000 fluorimeter and were corrected by calibration of the instrument's response with a standard tungsten-halogen lamp. The photoluminescence intensity was integrated for 0.1 s at 1 nm resolution and averaged over 3 scans. The PL quantum yield, $\Phi_{PL}$, was measured by comparative actinometry using $[Ru(bpy)_3]^{2+}.2PF_6^-$ in acetonitrile ($\Phi = 0.018$) as a quantum yield standard.[4] 77 K photoluminescence measurements were performed using a Janis Dual Reservoir VPF system with a four-way fused quartz windows. 77 K photoluminescence measurements were obtained using the same parameters as the room temperature photoluminescence measurements, and were performed on the complexes in butyronitrile glasses.

**Time-Resolved Photoluminescence**. Time-resolved PL data were acquired on a nitrogen dye laser with excitation centered at 445 nm, as described previously.[5] Pulsed light excitation was achieved with a Photon Technology International (PTI) GL-301 dye laser that was pumped by a PTI GL-3300 nitrogen laser. The PL was detected by a Hamamatsu R928 PMT optically coupled to a ScienceTech Model 9010 monochromator terminated into a LeCroy Waverunner LT322 oscilloscope. Decays were monitored at the photoluminescence maximum and averaged over 180 scans. Non-radiative and radiative rate constants were calculated from the quantum yields, $\Phi_{PL} = k_r/(k_r + k_{nr})$ and lifetimes, $\tau = 1/(k_r + k_{nr})$.

**Transient Absorption.** Nanosecond transient absorption measurements were acquired on a setup published previously.[6] Briefly, a Q-switched, pulsed Nd:YAG laser (Quantel U.S.A. (BigSky) Brilliant B 5-6 ns full width at half-maximum (fwhm), 1 Hz, ~10 mm in diameter) doubled to 532 nm was used. The laser irradiance at the sample was attenuated to ~2 mJ/pulse. A 150 W Xenon arc probe lamp was pulsed at 1 Hz during the experiment. Signal detection was achieved using a monochromator (SPEX 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu) at a right angle to the excitation laser. Transient data were acquired with a computer-interfaced digital oscilloscope (LeCroy 9450, Dual 330 MHz) with an overall instrument response time of ~10 ns. 30 laser pulses were acquired and averaged at each wavelength over the 380-800 nm range. Intervals of 10 nm were used for wavelength between 380 and 600 nm and intervals of 20 nm were used between 600 and 800 nm. Transient absorption changes were corrected for photoluminescence at relevant wavelengths.

**Electrochemistry**. Cyclic voltammetry was performed with an Autolab PGSTAT 100 potentiostat using a standard three-electrode-cell, *i.e.* a glassy carbon disk working electrode (approximate area = 0.03 $cm^2$), a platinum wire counter electrode and an aqueous Ag/AgCl reference electrode. Experiments were performed in dry 0.1 M $TBAPF_6$ acetonitrile or dimethylformamide (DMF) electrolyte.

**Variable Temperature Measurements.** Variable temperature measurements were obtained using the steady-state or time-resolved photoluminescence equipment described above mounted with a liquid nitrogen CoolSpek UV USP-203 four-window cryostat (Unisoku).

**Data analysis.** Data analysis for all experiments was performed using *OriginLab, version 9.0.* Data fitting was preformed using a Levenberg-Marquardt iteration method. Franck Condon line-shape analysis was performed by using a single mode fitting procedure as has been described previously.[7-12]

**Calculation procedure.** Our computational methodology is based on Density Functional Theory (DFT) and time dependent DFT (TD-DFT) methods. All calculations were performed using the Gaussian 16 computational chemistry package[13] while applying default procedures, integration grids, algorithms and parameters. As a first step, the equilibrium geometries of the singlet and triplet states of the two binuclear Ru(II) complexes ($\mathbf{D_p}$ and $\mathbf{D_m}$) were optimized in acetonitrile using the integral equation formalism model (IEFPCM).[14] These calculations were performed using the hybrid B3LYP exchange-correlation functional.[15-17] The 6-31+G(d,p) basis set[18-20] was used for the C, N and H atoms while the def2-SVP relativistic effective core potential and associated basis set[21-22] was employed to describe the Ru atoms. This potential has been shown to allow an accurate description of the electronic and bonding properties of Ru complexes.[23] The harmonic vibrational frequencies of each complex were calculated to the same level, and it was verified that all structures correspond to true minima of the potential energy surface. Cartesian coordinates for all atoms in optimized structures of the complexes $\mathbf{D_p}$ and $\mathbf{D_m}$ are provided in **Tables S2-S5**.

A time-dependent DFT (TD-DFT) method was employed to investigate the excited state electronic structure of each of the two complexes $\mathbf{D_p}$ and $\mathbf{D_m}$. The first 100 lowest-lying excited states of the two complexes at their ground state singlet and triplet geometries were evaluated within the vertical TD-DFT approximation, using the same level of theory in the optimization and frequency calculations. The modeling of solvent effects (here acetonitrile) was included through the IEF-PCM model. In order to discuss the excited-states characteristics, it was favorable to analyze the frontier orbitals. However, because the canonical orbitals created by the DFT method were not a good representation of the excited-state transitions (due to the fact that interacting configurations were present in many cases), the natural transition orbitals (NTOs)[24] were used instead. NTOs can be interpreted similarly to DFT orbitals, with the exception that they are specifically adapted to the excited state of interest.

**Synthesis**

The synthesis of $\mathbf{L_p}$ and $\mathbf{D_p}$ was reported elsewhere.[25] Synthesis of quaterpyridine $\mathbf{L_m}$: [$Ni(PPh_3)_2Cl_2$] (0.7816 g, 1.195 mmol, 1 eq.) was dissolved in 15 mL of anhydrous DMF and then zinc powder (40 mesh, 0.0782 g, 1.195 mmol, 1 eq.) was added to the reaction mixture which was stirred at room temperature during 90 minutes under argon atmosphere to allow the complete disappearance of the zinc powder. The corresponding 5-bromo-2,2'-bipyridine (0.3000 g, 1.195 mmol, 1 eq.) was added and the reaction mixture was then stirred at room temperature for 10 hours. After quenching by the addition of 225 mL of aqueous ammonia 2M, the medium was extracted with $CH_2Cl_2$. The organic phase was then extracted with 1M aqueous hydrochloric acid (3 x 20 mL). The aqueous layers were combined and neutralized with aqueous 10 M sodium hydroxide. The product was finally collected by filtration, washed with water and dried under vacuum.

*2,2':5',3'':6'',2'''-quaterpyridine (**L$_m$**):* white powder (0.1469 g, 79%). $^1$H NMR ($CDCl_3$, 300 MHz): δ (ppm), 9.00 (dd, 2H, $H_c$, $J_{Hc\text{-}Hb}$ = 2.3 Hz, $J_{Hc\text{-}Ha}$ = 0.7 Hz), 8.72 (ddd, 2H, $H_6$, $J_{H6\text{-}H5}$ = 4.8 Hz, $J_{H6\text{-}H4}$ = 1.7 Hz, $J_{H6\text{-}H3}$ = 0.9 Hz), 8.56 (dd, 2H, $H_a$, $J_{Ha\text{-}Hb}$ = 8.3 Hz, $J_{Ha\text{-}Hc}$ = 0.7 Hz), 8.47 (dt, 2H, $H_3$, $J_{H3\text{-}H4}$ = 7.8 Hz, $J_{H6\text{-}H4}$ = 1.1 Hz), 8.10 (dd, 2H, $H_b$, $J_{Hb\text{-}Ha}$ = 8.3 Hz, $J_{Hb\text{-}Hc}$ = 2.3 Hz), 7.86 (td, 2H, $H_4$, $J_{H4\text{-}H3(H5)}$ = 7.8 Hz, $J_{H4\text{-}H6}$ = 1.7 Hz), 7.35 (ddd, 2H, $H_5$, $J_{H5\text{-}H4}$ = 7.8 Hz, $J_{H5\text{-}H6}$ = 4.8 Hz, $J_{H5\text{-}H3}$ = 1.1 Hz). $^1$H NMR data were in agreement with those reported.[26]

Synthesis of **D$_m$**: **L$_m$** (0.025 g, 0.0806 mmol, 1eq.), [Ru(bpy)$_2$Cl$_2$] (0.1038 g, 0.214 mmol, 2.66 eq.) and $AgNO_3$ (0.1368 g, 0.805 mmol, 10 eq.) were transferred in a microwave tube. A 9:1 ethylene glycol/water (27 mL) mixture was then added and subsequently purged with argon for 15 minutes. The reaction mixture was heated at 180°C for 1 hour in a microwave reactor. After reaction completion and cooling down to room temperature, an excess of saturated aqueous ammonium hexafluorophosphate solution was added. The resulting precipitate was collected by filtration and washed thoroughly with water. The solid was purified by flash chromatography on $SiO_2$ (acetonitrile/saturated aqueous $KNO_3$/water: v/v/v: 7/1/0.5). The desired fractions were collected and evaporated under reduced pressure. The resulting solid was dissolved in water and precipitated by addition of an excess of saturated aqueous ammonium hexafluorophosphate. The precipitate was collected by centrifugation and washed three times with water to afford a red powder. The powder was dissolved in acetonitrile, filtered through a 0.45 μm PTFE syringe filter and the solvent was removed under reduced pressure to yield the pure complexes.

*$[Ru_2(L_M)(bpy)_4].(PF_6)_4$* (***D$_m$***)*:* a red solid (0.1596 g, 77%), $^1$H NMR (CD$_3$CN, 500 MHz): δ (ppm), 8.54-8.38 (m, 12H, H$_a$, H$_3$ and H$_{A3}$), 8.13-7.91 (m, 12H, H$_b$, H$_4$ and H$_{A4}$), 7.74-7.58 (m, 12H, H$_c$ ,H$_6$ and H$_{A6}$), 7.45-7.30 (m, 10H, H$_5$ and H$_{A5}$). HRMS (ESI): *m/z* calculated for $[C_{60}H_{46}N_{12}{}^{96}Ru_2P_2F_{12}]^{2+}$, 708.06965; found: 708.0693.

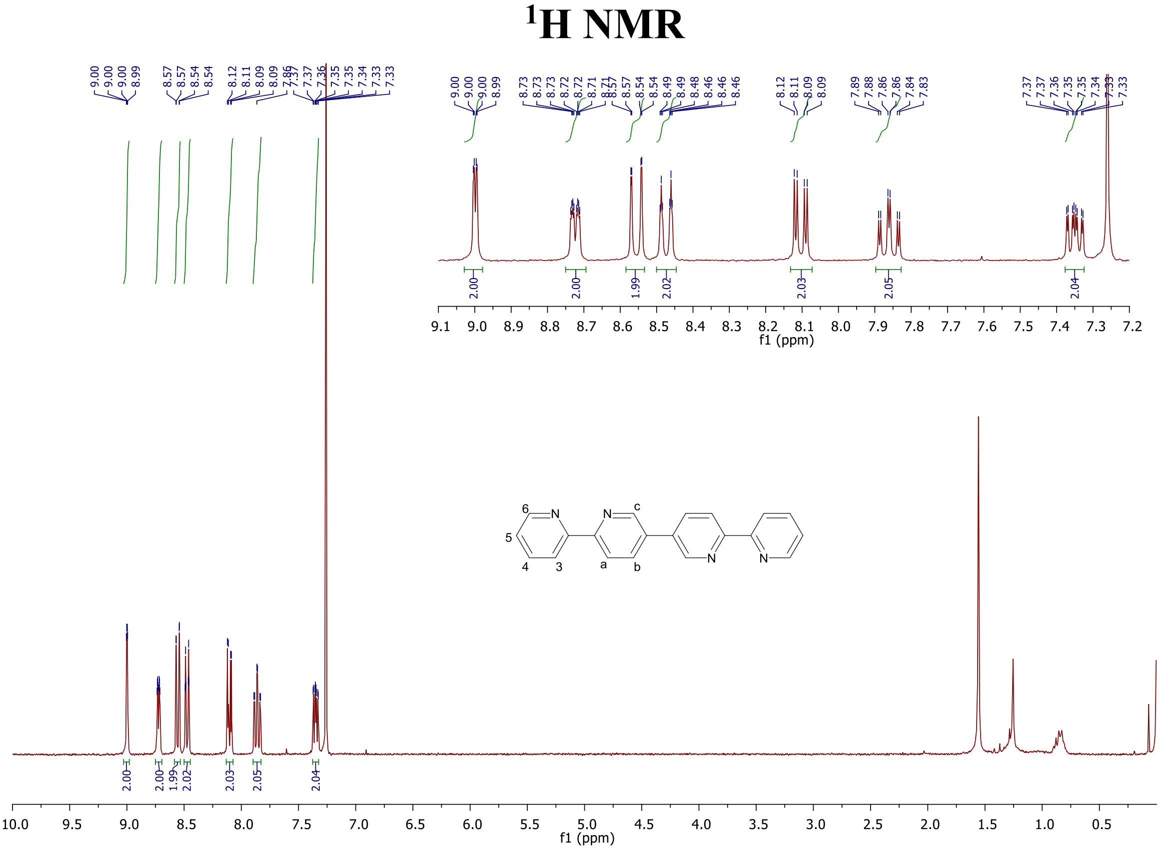


**Figure S1** : $^1$H NMR spectrum of **L$_m$** recorded at 300MHz in CDCl$_3$ at 298 K.

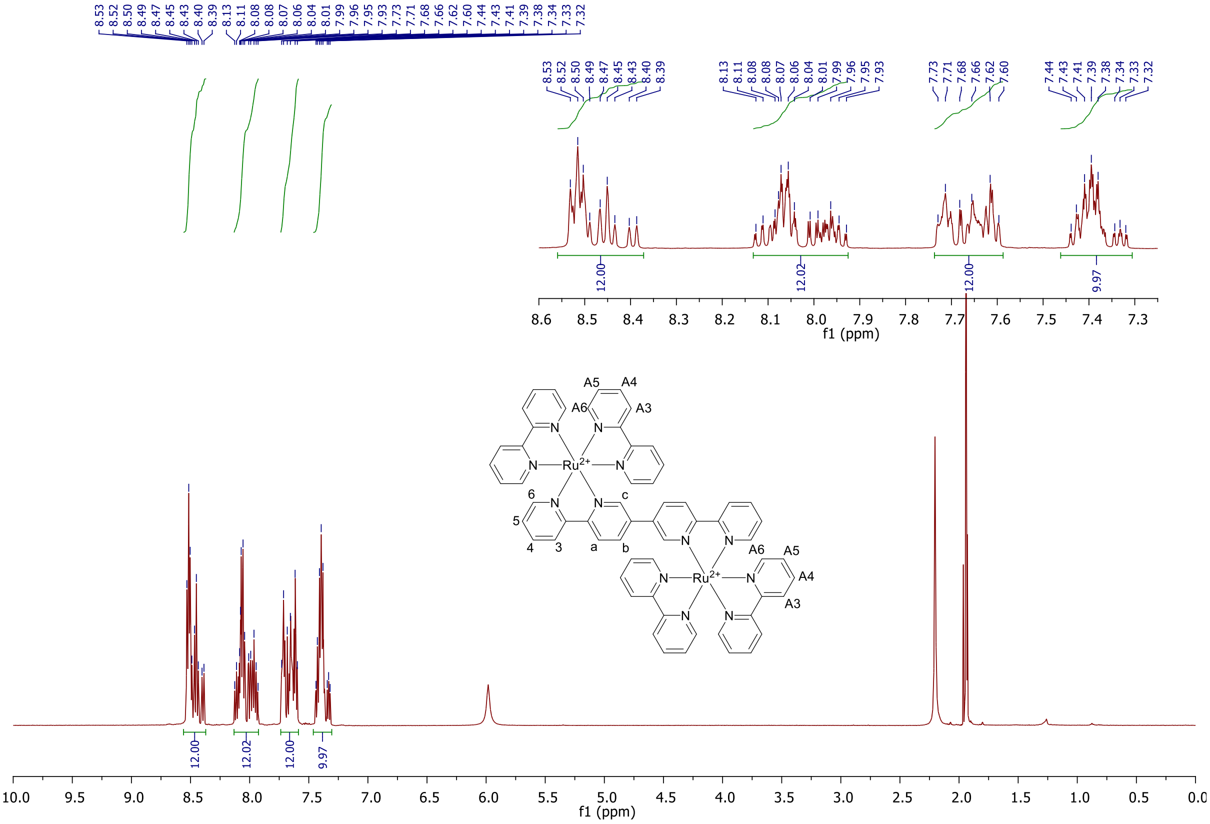


**Figure S2** : $^1$H NMR spectrum of $\mathbf{D_m}$ recorded at 500MHz in $CD_3CN$ at 298 K.

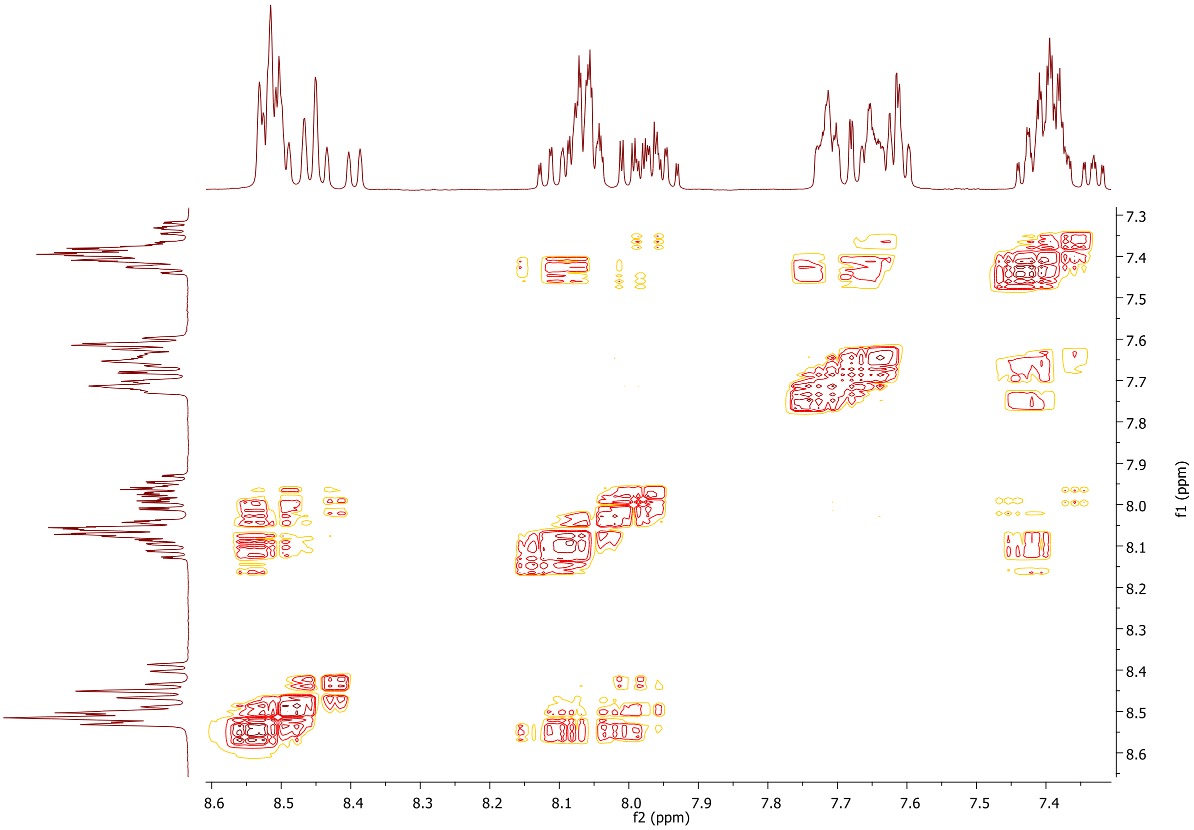
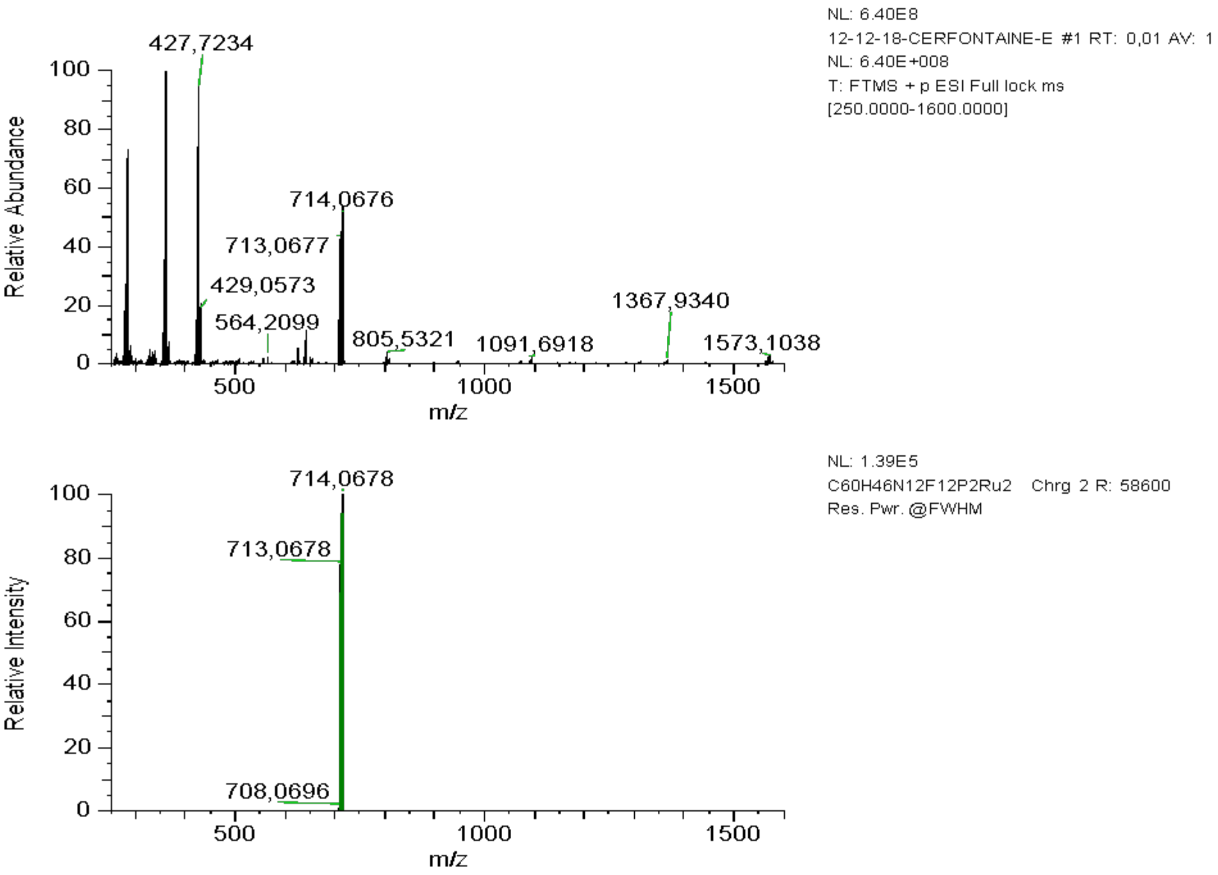
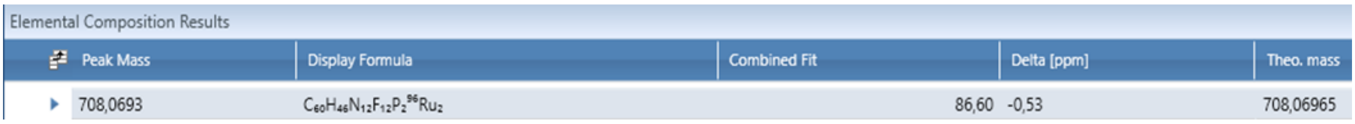


**Figure S3** : $^1$H-$^1$H COSY NMR spectrum of $\mathbf{D_m}$ recorded at 500 MHz in $CD_3CN$ at 298 K.

# Mass Spectrometry




Elemental Composition Results

| Peak Mass | Display Formula | Combined Fit | Delta [ppm] | Theo. mass |
|---|---|---|---|---|
| 708,0693 | $C_{60}H_{46}N_{12}F_{12}P_2{}^{96}Ru_2$ | 86,60 | -0,53 | 708,06965 |

**Figure S4** : Mass spectrometry analysis of **D$_m$** recorded by ESI ionization in positive mode

# Electrochemical and Photophysical Characterization

The electrochemical data for the two binuclear complexes (**D$_p$-D$_m$**) and the reference compound [Ru(bpy)$_3$]$^{2+}$ are gathered in **Table S1.** Both binuclear complexes underwent a reversible two-electron oxidation at 1.33 V vs Ag/AgCl. A one-electron oxidation of [Ru(bpy)$_3$]$^{2+}$ is observed at a similar potential (1.30 V vs Ag/AgCl). Interestingly, the first one-electron ligand-centered reduction wave occurred at a potential 300 mV more positive than in the parent [Ru(bpy)$_3$]$^{2+}$ complex.

The presence of a single reversible Ru$^{III/II}$ oxidation wave for both binuclear complexes was indicative of a simultaneous oxidation of the two Ru(II) centers, in agreement with weak intermetal communication.[27-29] In contrast, the bridging-ligand-centered reduction showed some influence of the two metallic centers, as it occurred 300 mV more positive than that of [Ru(bpy)$_3$]$^{2+}$. The geometrical arrangement of the bridging ligands did not yield any significant differences in redox potentials between the two binuclear complexes, but had drastic influence on the ground-state absorption features.

| **Complex** | **E$_{1/2}$(Ru$^{III/II}$)[a]** V vs A/AgCl | **E$_{1/2}$(L$^{n/n-1}$)[b]** V vs A/AgCl |
|---|---|---|
| **D$_p$** | +1.33 | –0.99, -1.36, -1.44 |
| **D$_m$** | +1.33 | –0.99, -1.17, -1.47 |
| **[Ru(bpy)$_3$]$^{2+}$** | +1.30 | –1.31, -1.50, -1.75 |

**Table S1**: Oxidation and reduction potential (V vs Ag/AgCl). Redox potential can be estimated vs NHE by adding 0.2 V. [a] Cyclic voltammetry in acetonitrile. [b] Differential pulse voltammetry in DMF.

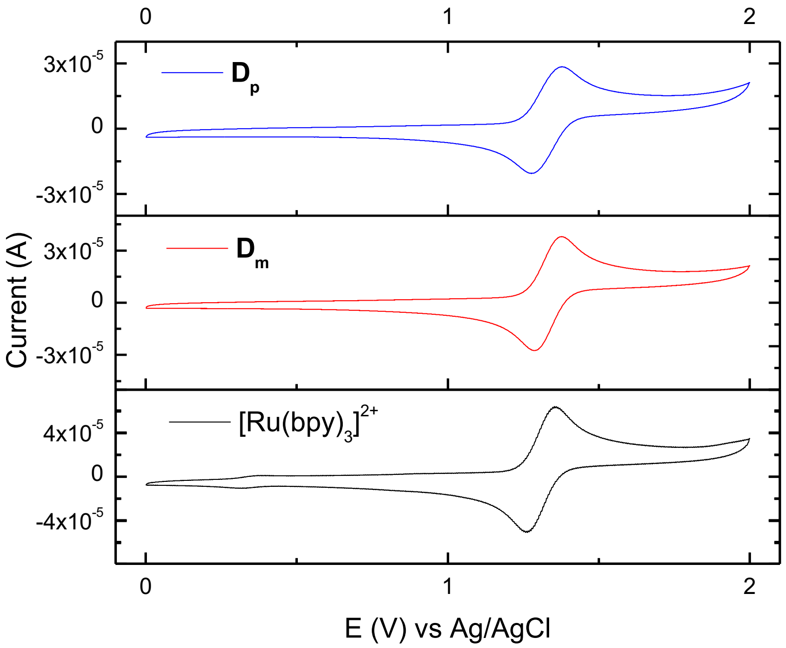


**Figure S5** : Cyclic voltammograms of the indicated complexes recorded in dry $CH_3CN$.

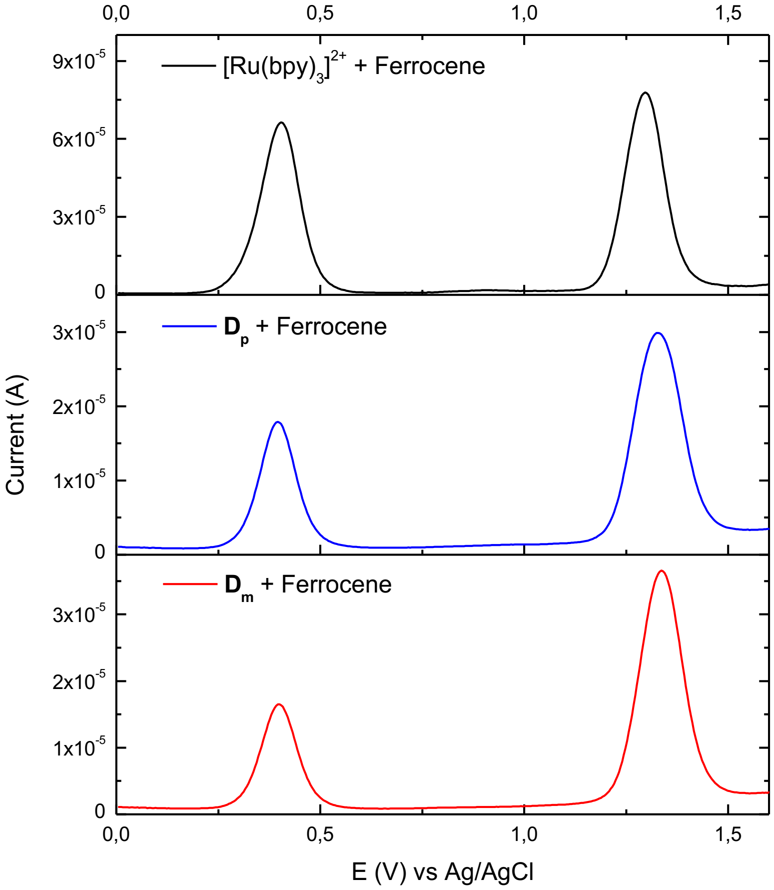


**Figure S6**: Differential pulse voltammograms of the indicated complexes recorded in dry $CH_3CN$ with equimolar concentration of complexes and ferrocene.

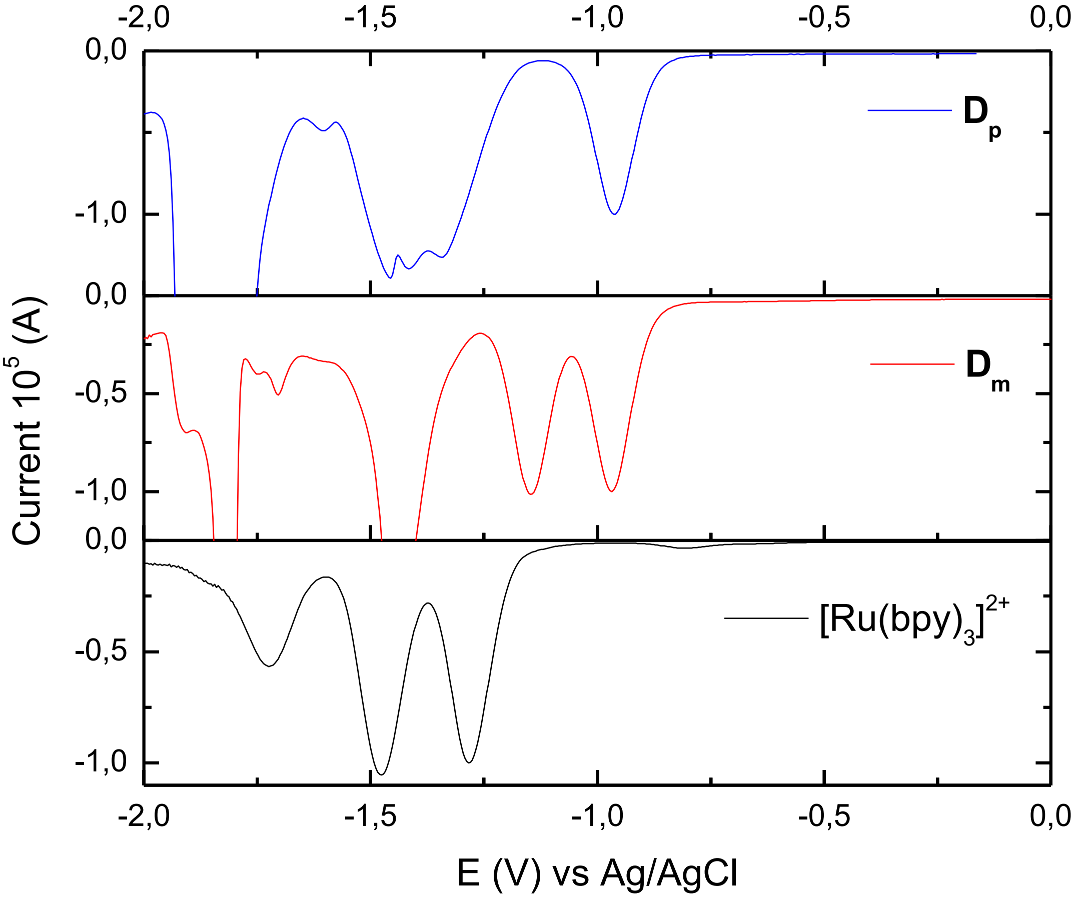


**Figure S7** : Differential pulse voltammograms of the indicated complexes recorded in dry DMF.

# Franck-Condon lineshape analysis

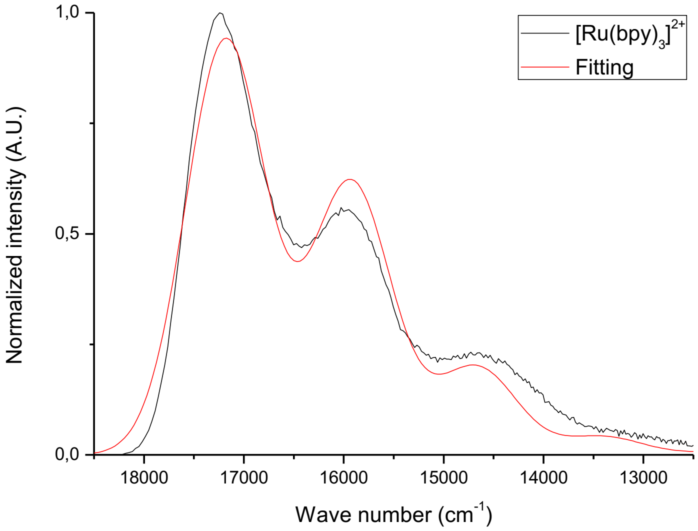


**Figure S8** : Franck-Condon lineshape analysis of the photoluminescence spectrum of [Ru(bpy)$_3$]$^{2+}$ at 77K in butyronitrile matrix.

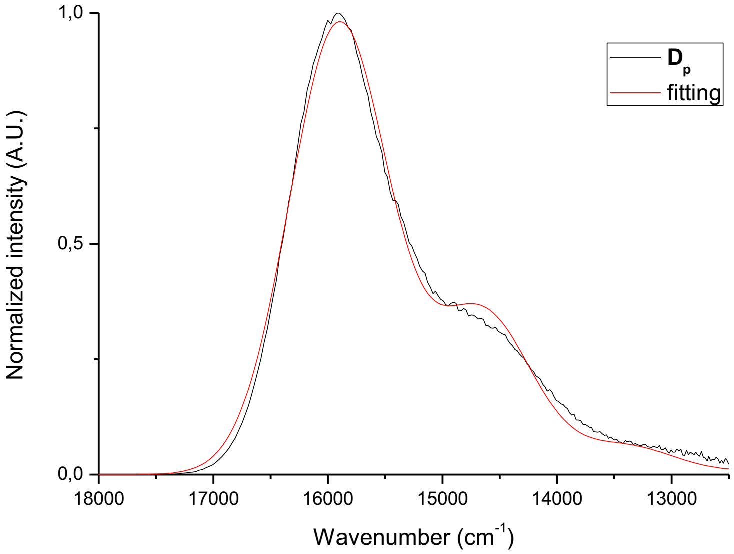


**Figure S9** : Franck-Condon lineshape analysis of the photoluminescence spectrum of $\mathbf{D_p}$ at 77K in butyronitrile matrix.

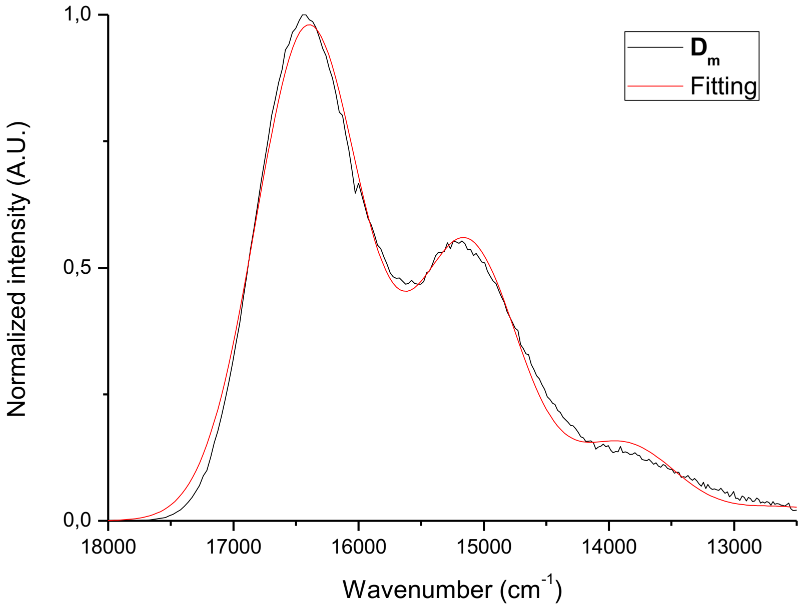


**Figure S10** : Franck-Condon lineshape analysis of the photoluminescence spectrum of $\mathbf{D_m}$ at 77K in butyronitrile matrix.

# Photoluminescence at variable temperature

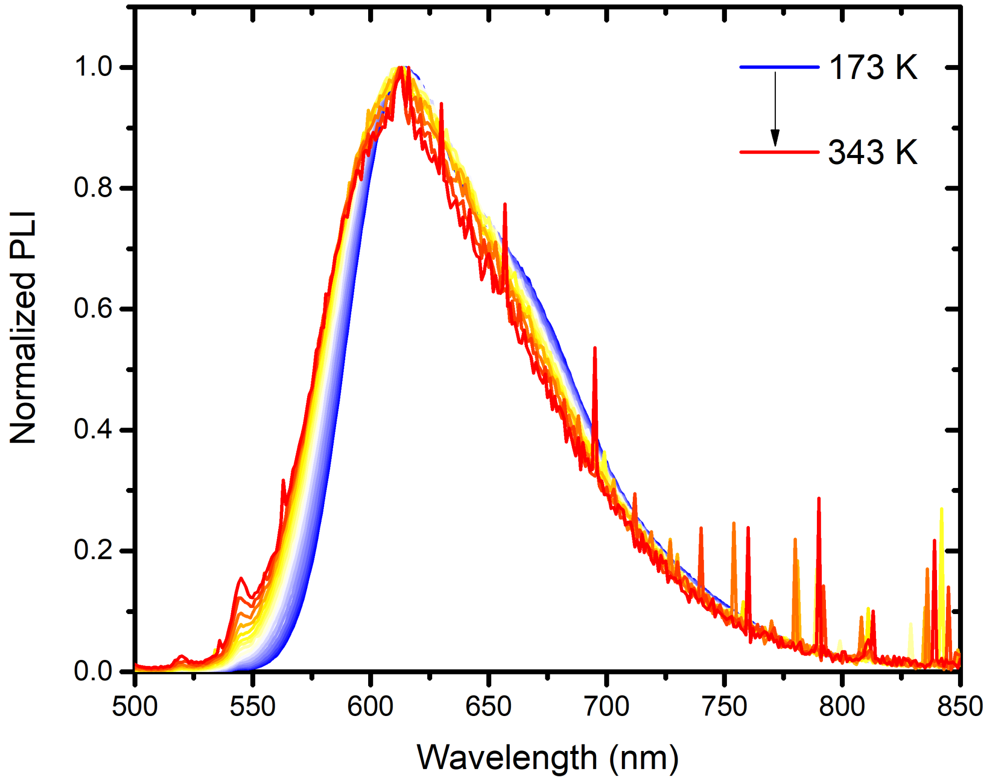


**Figure S11**: Normalized steady-state photoluminescence of $[Ru(bpy)_3]^{2+}$ in fluid butyronitrile as a function of temperature.

# Time-resolved photoluminescence

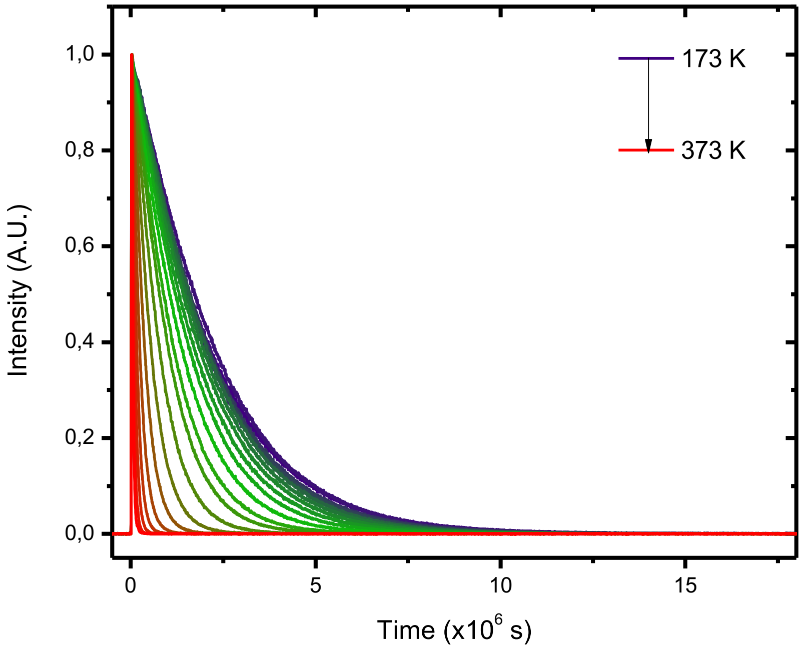


**Figure S12**: Time-resolved photoluminescence of **[Ru(bpy)$_3$]$^{2+}$** in butyronitrile as a function of temperature.

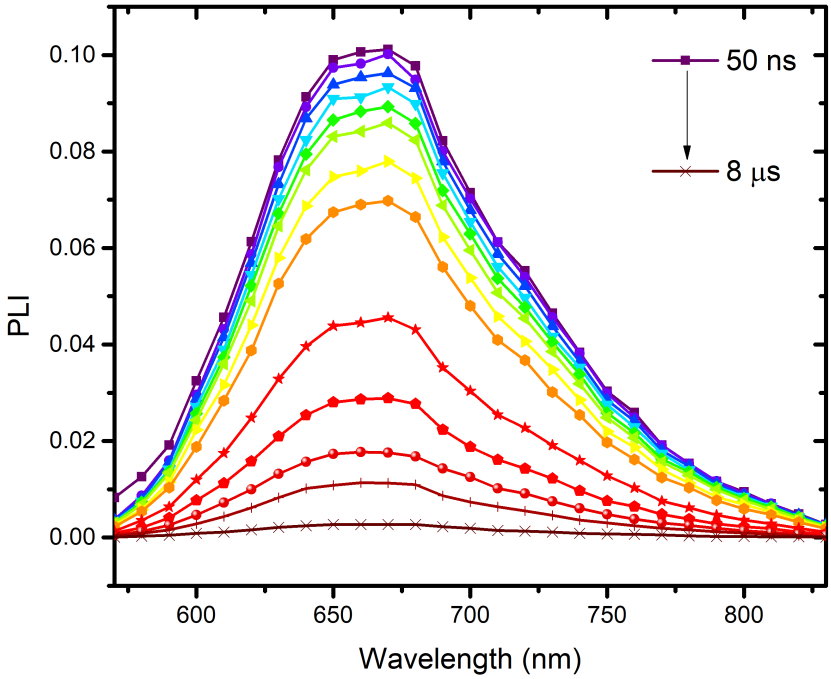


**Figure S13**: Time-resolved photoluminescence spectra of **D$_p$** at 298 K in butyronitrile.

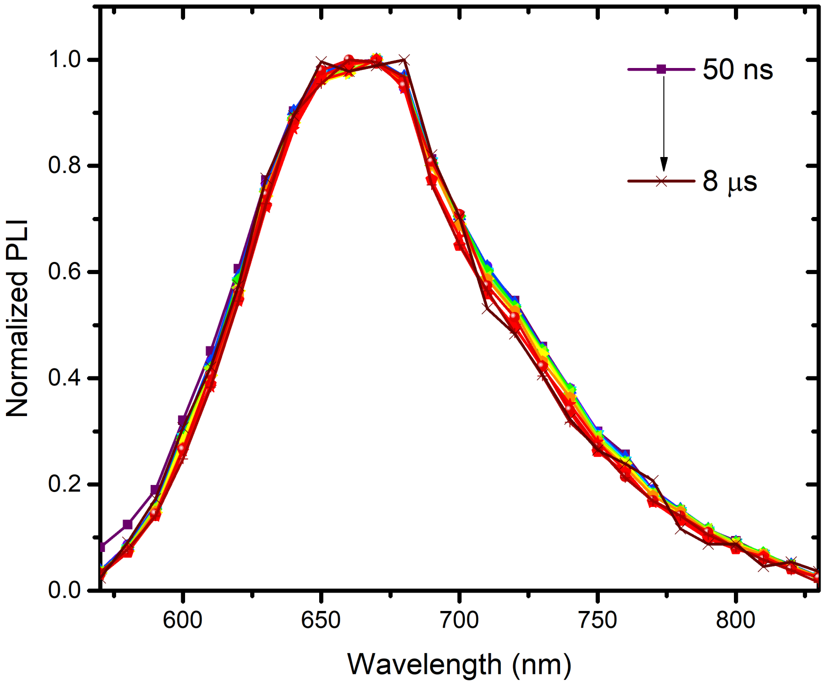


**Figure S14**: Normalized time-resolved photoluminescence spectra of $\mathbf{D_p}$ at 298 K in butyronitrile.

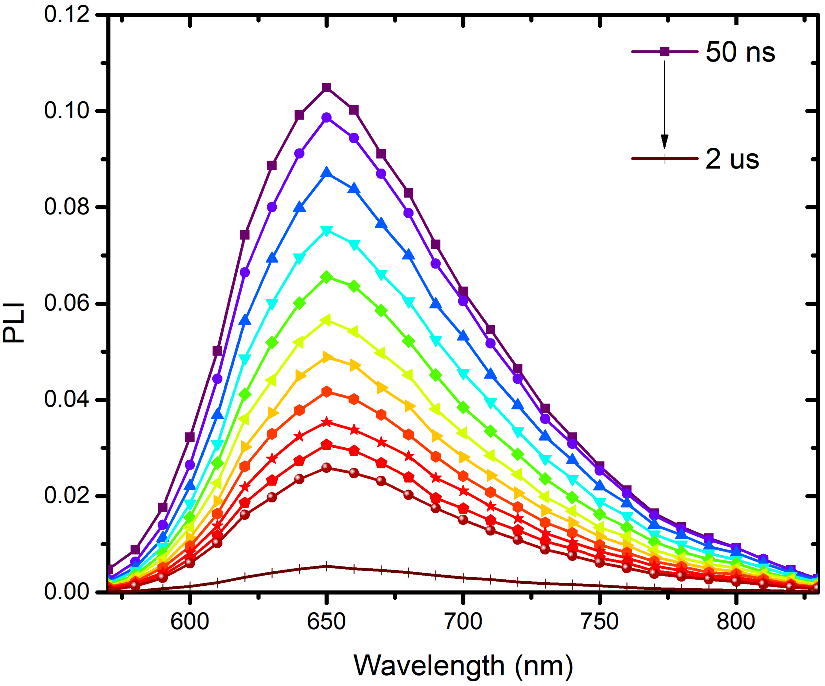


**Figure S15**: Time-resolved photoluminescence spectra of $\mathbf{D_m}$ at 298 K in butyronitrile.

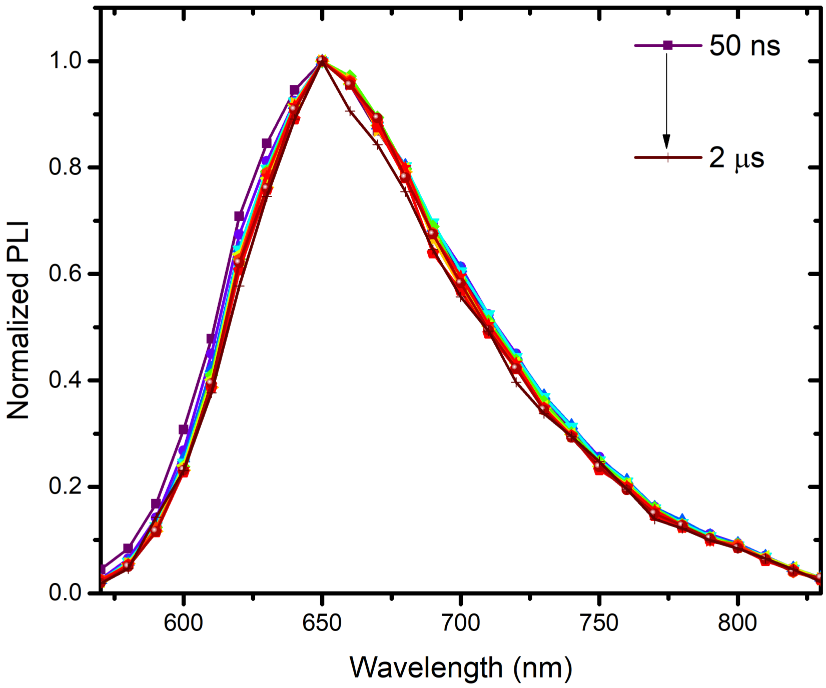


**Figure S16**: Normalized time-resolved photoluminescence spectra of $\mathbf{D_m}$ at 298 K in butyronitrile.

# Fitting of the excited-state lifetime with temperature

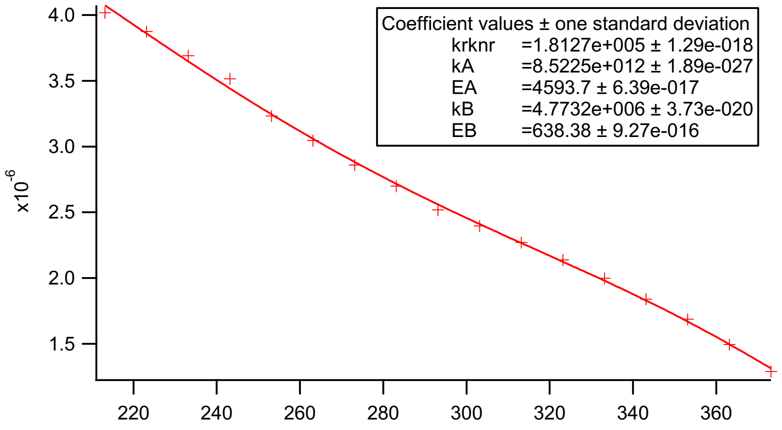


**Figure S17** : Fitting of the excited-state lifetime with temperature for $\mathbf{D_p}$.

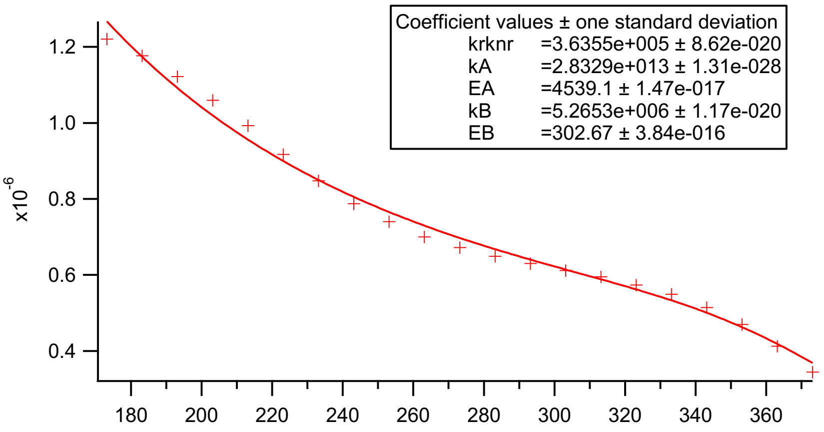


**Figure S18**: Fitting of the excited-state lifetime with temperature for $\mathbf{D_m}$.

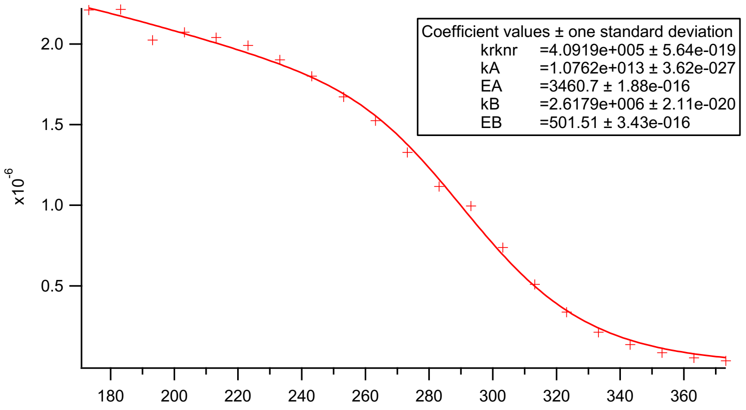


**Figure S19**: Fitting of the excited-state lifetime with temperature for $\mathbf{[Ru(bpy)_3]^{2+}}$.

# DFT Calculations

**Table S2.** Cartesian Coordinates (in Å) of the equilibrium geometry of the singlet state of binuclear Ru(II) complexes **$D_p$**.

| Atom | X | Y | Z |
|---|---|---|---|
| Ru | -5.631873 | 0.066051 | 0.002499 |
| C | -2.843330 | -1.161706 | -0.366049 |
| C | -8.549611 | 0.151232 | 0.969665 |
| C | -5.330409 | -0.081655 | 3.057766 |
| C | -2.883634 | 1.098526 | 0.279511 |
| C | -8.188661 | 0.847240 | -1.252707 |
| C | -5.785479 | -2.125518 | 1.975068 |
| C | -3.736790 | 2.249413 | 0.602798 |
| C | -6.049025 | -2.775985 | 0.685181 |
| C | -7.182797 | 1.084344 | -2.295690 |
| C | -5.956458 | 3.000616 | 0.852201 |
| C | -6.233405 | -2.460021 | -1.643125 |
| C | -4.896940 | 0.947092 | -2.851451 |
| C | -1.454875 | -1.178134 | -0.364931 |
| C | -9.922650 | 0.350367 | 0.849635 |
| C | -5.279378 | -0.707559 | 4.300668 |
| C | -1.487065 | 1.130393 | 0.297233 |
| C | -5.743161 | -2.799362 | 3.201610 |
| C | -9.562077 | 1.058620 | -1.423006 |
| C | -3.254695 | 3.521680 | 0.932039 |
| C | -7.473897 | 1.596500 | -3.565837 |
| C | -6.326582 | -4.139969 | 0.534924 |
| C | -5.524941 | 4.281529 | 1.187924 |
| C | -6.512329 | -3.809677 | -1.842867 |
| C | -5.137409 | 1.450066 | -4.127441 |
| H | -5.179452 | 0.983055 | 2.957251 |
| H | -8.111290 | -0.200870 | 1.891488 |
| H | -3.409777 | -2.041565 | -0.631851 |
| H | -6.184063 | -1.767443 | -2.470284 |
| H | -3.900674 | 0.678010 | -2.533107 |
| H | -7.006976 | 2.753367 | 0.812876 |
| H | -10.568082 | 0.146610 | 1.694377 |
| H | -5.080492 | -0.119596 | 5.187492 |
| H | -0.944350 | -2.088496 | -0.650921 |
| H | -6.687542 | -4.176541 | -2.846052 |
| H | -4.311846 | 1.577862 | -4.815809 |
| H | -6.254356 | 5.049403 | 1.411433 |
| N | -3.561097 | -0.050935 | -0.055340 |
| N | -5.578297 | -0.767382 | 1.911740 |
| N | -7.690625 | 0.391557 | -0.054633 |
| N | -5.088341 | 1.996786 | 0.563616 |
| N | -5.892215 | 0.763308 | -1.945488 |
| N | -6.003794 | -1.943044 | -0.408261 |
| C | -6.446443 | 1.782100 | -4.491308 |
| H | -6.664345 | 2.178374 | -5.475397 |
| H | -8.490562 | 1.852713 | -3.831340 |
| H | -9.946956 | 1.410236 | -2.370538 |
| C | -10.438750 | 0.809292 | -0.366555 |
| H | -11.502466 | 0.969933 | -0.491411 |
| C | -4.152669 | 4.548167 | 1.227265 |
| C | -0.740570 | -0.012750 | -0.029200 |
| H | -3.787307 | 5.535297 | 1.482162 |
| H | -0.978460 | 2.038828 | 0.588830 |
| H | -2.190906 | 3.715481 | 0.955386 |
| C | -5.488020 | -2.088645 | 4.374921 |
| C | -6.560982 | -4.664305 | -0.736724 |
| H | -5.453858 | -2.603202 | 5.327298 |
| H | -6.777653 | -5.718208 | -0.860145 |
| H | -5.905834 | -3.867771 | 3.243729 |
| H | -6.362806 | -4.787864 | 1.400079 |
| C | 0.740562 | 0.012817 | -0.029208 |
| C | 1.454872 | 1.178145 | -0.365125 |
| C | 1.487056 | -1.130278 | 0.297410 |
| C | 2.843325 | 1.161715 | -0.366226 |
| H | 0.944349 | 2.088456 | -0.651276 |
| C | 2.883626 | -1.098412 | 0.279722 |
| H | 0.978447 | -2.038670 | 0.589129 |
| H | 3.409787 | 2.041514 | -0.632200 |
| N | 3.561090 | 0.050995 | -0.055325 |
| C | 3.736775 | -2.249243 | 0.603225 |

| | | | |
|---|---|---|---|
| C | 3.254679 | -3.521433 | 0.932757 |
| C | 5.956448 | -3.000407 | 0.852750 |
| C | 4.152653 | -4.547861 | 1.228193 |
| H | 2.190891 | -3.715224 | 0.956183 |
| C | 5.524926 | -4.281243 | 1.188762 |
| H | 7.006965 | -2.753177 | 0.813337 |
| H | 3.787289 | -5.534931 | 1.483319 |
| H | 6.254340 | -5.049076 | 1.412415 |
| N | 5.088330 | -1.996632 | 0.563972 |
| Ru | 5.631836 | -0.066007 | 0.002505 |
| C | 4.896824 | -0.947497 | -2.851310 |
| C | 7.182668 | -1.084839 | -2.295521 |
| C | 5.137232 | -1.450848 | -4.127165 |
| H | 3.900592 | -0.678190 | -2.533045 |
| C | 7.473704 | -1.597382 | -3.565525 |
| C | 6.446224 | -1.783140 | -4.490938 |
| H | 4.311653 | -1.578720 | -4.815500 |
| H | 8.490339 | -1.853778 | -3.830959 |
| H | 6.664077 | -2.179737 | -5.474906 |
| C | 6.049267 | 2.776068 | 0.684783 |
| C | 6.233550 | 2.459801 | -1.643490 |
| C | 6.327264 | 4.139946 | 0.534389 |
| C | 6.512830 | 3.809364 | -1.843380 |
| H | 6.184004 | 1.767143 | -2.470572 |
| C | 6.561791 | 4.664082 | -0.737323 |
| H | 6.363808 | 4.787897 | 1.399492 |
| H | 6.688087 | 4.176082 | -2.846611 |
| H | 6.778824 | 5.717898 | -0.860850 |
| N | 5.892112 | -0.763597 | -1.945396 |
| N | 6.003830 | 1.943020 | -0.408570 |
| C | 8.188571 | -0.847564 | -1.252616 |
| C | 9.561979 | -1.058994 | -1.422924 |
| C | 10.438691 | -0.809448 | -0.366557 |
| H | 9.946824 | -1.410824 | -2.370393 |
| C | 8.549612 | -0.151057 | 0.969587 |
| C | 9.922644 | -0.350249 | 0.849551 |
| H | 11.502402 | -0.970121 | -0.491420 |
| H | 8.111324 | 0.201254 | 1.891349 |
| H | 10.568112 | -0.146319 | 1.694223 |
| N | 7.690590 | -0.391592 | -0.054627 |
| C | 5.785504 | 2.125825 | 1.974738 |
| C | 5.742995 | 2.799907 | 3.201140 |
| C | 5.487705 | 2.089417 | 4.374558 |
| H | 5.905581 | 3.868335 | 3.243051 |
| C | 5.330285 | 0.082170 | 3.057766 |
| C | 5.279102 | 0.708315 | 4.300543 |
| H | 5.453376 | 2.604164 | 5.326824 |
| H | 5.179305 | -0.982553 | 2.957446 |
| H | 5.080105 | 0.120522 | 5.187456 |
| N | 5.578307 | 0.767674 | 1.911637 |

**Table S3.** Cartesian Coordinates (in Å) of the equilibrium geometry of the triplet state of the binuclear Ru(II) complexes $\mathbf{D_p}$.

| Atom | X | Y | Z |
|---|---|---|---|
| Ru | 5.629304 | 0.058685 | -0.033341 |
| C | 2.855156 | -1.185173 | 0.393582 |
| C | 8.573147 | -0.026861 | -0.968442 |
| C | 5.191301 | -0.205869 | -3.043819 |
| C | 2.899247 | 1.117573 | -0.242856 |
| C | 8.215065 | 0.912859 | 1.168205 |
| C | 5.709618 | -2.215447 | -1.907709 |
| C | 3.733331 | 2.235526 | -0.618897 |
| C | 6.021958 | -2.814803 | -0.604535 |
| C | 7.207065 | 1.251872 | 2.181313 |
| C | 5.970588 | 2.967027 | -0.967785 |
| C | 6.323672 | -2.391535 | 1.698464 |
| C | 4.907573 | 1.194119 | 2.722262 |
| C | 1.486663 | -1.192512 | 0.409003 |
| C | 9.947535 | 0.171702 | -0.865843 |
| C | 5.095897 | -0.876529 | -4.259669 |
| C | 1.507790 | 1.139858 | -0.232540 |
| C | 5.620069 | -2.930448 | -3.105788 |
| C | 9.588635 | 1.129606 | 1.317986 |
| C | 3.267317 | 3.524642 | -0.954704 |
| C | 7.492885 | 1.868294 | 3.403710 |
| C | 6.298249 | -4.171417 | -0.406928 |

| | | | |
|---|---|---|---|
| C | 5.546968 | 4.241643 | -1.308861 |
| C | 6.602944 | -3.733848 | 1.944646 |
| C | 5.145815 | 1.803631 | 3.951546 |
| H | 5.029938 | 0.859191 | -2.968493 |
| H | 8.134639 | -0.473698 | -1.848349 |
| H | 3.416158 | -2.074205 | 0.644159 |
| H | 6.321385 | -1.661683 | 2.494857 |
| H | 3.913551 | 0.908393 | 2.412117 |
| H | 7.018902 | 2.705201 | -0.964862 |
| H | 10.593191 | -0.129543 | -1.680110 |
| H | 4.854546 | -0.323562 | -5.157756 |
| H | 0.986379 | -2.108496 | 0.691018 |
| H | 6.825223 | -4.057078 | 2.953042 |
| H | 4.316855 | 2.002568 | 4.617867 |
| H | 6.274410 | 4.997033 | -1.575101 |
| N | 3.598261 | -0.061042 | 0.099146 |
| N | 5.497603 | -0.857043 | -1.893144 |
| N | 7.721762 | 0.339934 | 0.021973 |
| N | 5.095118 | 1.977805 | -0.636000 |
| N | 5.914849 | 0.919706 | 1.856126 |
| N | 6.033896 | -1.938742 | 0.453666 |
| C | 6.456360 | 2.146721 | 4.296656 |
| H | 6.670785 | 2.624093 | 5.244647 |
| H | 8.509951 | 2.130749 | 3.659432 |
| H | 9.977267 | 1.580037 | 2.220685 |
| C | 10.462252 | 0.758180 | 0.294214 |
| H | 11.526861 | 0.923013 | 0.403265 |
| C | 4.166421 | 4.522665 | -1.299357 |
| C | 0.739962 | 0.004705 | 0.094510 |
| H | 3.807464 | 5.511816 | -1.557133 |
| H | 1.012562 | 2.056857 | -0.520365 |
| H | 2.206479 | 3.735786 | -0.938687 |
| C | 5.312890 | -2.257916 | -4.290437 |
| C | 6.589828 | -4.636232 | 0.876859 |
| H | 5.242668 | -2.805954 | -5.221719 |
| H | 6.804557 | -5.685174 | 1.038240 |
| H | 5.785822 | -3.998669 | -3.119309 |
| H | 6.289221 | -4.859135 | -1.241177 |
| C | -0.713254 | 0.037420 | 0.094815 |
| C | -1.457284 | 1.249262 | 0.031827 |
| C | -1.484833 | -1.150309 | 0.160442 |
| C | -2.838358 | 1.229539 | 0.026142 |
| H | -0.965791 | 2.212657 | 0.009245 |
| C | -2.875077 | -1.116309 | 0.151769 |
| H | -0.990348 | -2.109983 | 0.191835 |
| H | -3.404754 | 2.148720 | -0.013537 |
| N | -3.566403 | 0.076305 | 0.082895 |
| C | -3.723595 | -2.314824 | 0.213608 |
| C | -3.239217 | -3.624018 | 0.333575 |
| C | -5.940320 | -3.121699 | 0.192873 |
| C | -4.131626 | -4.694683 | 0.381753 |
| H | -2.175199 | -3.808901 | 0.392704 |
| C | -5.505457 | -4.438636 | 0.309149 |
| H | -6.991124 | -2.879385 | 0.131367 |
| H | -3.761751 | -5.708495 | 0.474548 |
| H | -6.231158 | -5.241177 | 0.342626 |
| N | -5.076424 | -2.073927 | 0.143915 |
| Ru | -5.636200 | -0.069092 | 0.015279 |
| C | -4.964683 | 0.073047 | 3.009164 |
| C | -7.233934 | -0.294025 | 2.488593 |
| C | -5.229937 | 0.020984 | 4.375100 |
| H | -3.966246 | 0.242724 | 2.634036 |
| C | -7.549586 | -0.356280 | 3.851418 |
| C | -6.542972 | -0.199061 | 4.804613 |
| H | -4.420673 | 0.150062 | 5.082418 |
| H | -8.569260 | -0.526807 | 4.169040 |
| H | -6.779867 | -0.246773 | 5.860395 |
| C | -6.015163 | 2.379070 | -1.587875 |
| C | -6.268049 | 2.855156 | 0.706561 |
| C | -6.283431 | 3.715827 | -1.907321 |
| C | -6.538368 | 4.194485 | 0.438506 |
| H | -6.249218 | 2.476105 | 1.717483 |
| C | -6.547744 | 4.633018 | -0.889909 |
| H | -6.290004 | 4.039782 | -2.939214 |
| H | -6.737583 | 4.874084 | 1.257226 |
| H | -6.756841 | 5.668254 | -1.130007 |
| N | -5.939523 | -0.080566 | 2.075535 |
| N | -6.009784 | 1.956402 | -0.278965 |
| C | -8.216529 | -0.436098 | 1.406843 |
| C | -9.590249 | -0.615004 | 1.610884 |

|  |  |  |  |
|---|---|---|---|
| C | -10.444394 | -0.738408 | 0.514641 |
| H | -9.992724 | -0.654912 | 2.613898 |
| C | -8.533296 | -0.502022 | -0.927660 |
| C | -9.905775 | -0.681188 | -0.775087 |
| H | -11.508093 | -0.876003 | 0.664947 |
| H | -8.077793 | -0.455935 | -1.905859 |
| H | -10.533663 | -0.772942 | -1.652084 |
| N | -7.695267 | -0.381927 | 0.134994 |
| C | -5.722495 | 1.335840 | -2.578409 |
| C | -5.642510 | 1.560139 | -3.958333 |
| C | -5.364468 | 0.498061 | -4.819153 |
| H | -5.793101 | 2.553313 | -4.359430 |
| C | -5.257473 | -0.952104 | -2.902302 |
| C | -5.170142 | -0.778623 | -4.281046 |
| H | -5.301461 | 0.664368 | -5.887502 |
| H | -5.116280 | -1.921069 | -2.446662 |
| H | -4.953715 | -1.629598 | -4.914199 |
| N | -5.529036 | 0.077196 | -2.057942 |

**Table S4.** Cartesian Coordinates (in Å) of the equilibrium geometry of the singlet state of the binuclear Ru(II) complexes **D$_{\mathbf{m}}$**.

| Atom | X | Y | Z |
|---|---|---|---|
| Ru | 4.881596 | -0.106635 | 0.002748 |
| C | 1.856810 | 0.027614 | -0.494877 |
| C | 7.507137 | 0.444978 | 1.502097 |
| C | 4.404289 | -1.471217 | 2.715965 |
| C | 2.850990 | -2.085165 | -0.812053 |
| C | 7.579690 | 0.754257 | -0.833289 |
| C | 3.980584 | 0.846617 | 2.648657 |
| C | 4.101621 | -2.848100 | -0.765988 |
| C | 3.996659 | 2.053358 | 1.812049 |
| C | 6.818033 | 0.674262 | -2.086088 |
| C | 6.408587 | -2.758021 | -0.295162 |
| C | 4.404565 | 2.910612 | -0.345322 |
| C | 4.723018 | 0.197450 | -3.054212 |
| C | 0.584764 | -0.453396 | -0.836057 |
| C | 8.840604 | 0.824508 | 1.632501 |
| C | 4.032236 | -1.539050 | 4.056138 |
| C | 1.606430 | -2.625246 | -1.156270 |
| C | 3.595207 | 0.828134 | 3.994561 |
| C | 8.922324 | 1.143048 | -0.752618 |
| C | 4.203678 | -4.209355 | -1.077703 |
| C | 7.352853 | 0.951008 | -3.350111 |
| C | 3.667220 | 3.333851 | 2.272604 |
| C | 6.560109 | -4.109987 | -0.594393 |
| C | 4.083533 | 4.201880 | 0.065637 |
| C | 5.209727 | 0.461741 | -4.331796 |
| H | 4.732675 | -2.348385 | 2.178249 |
| H | 6.918029 | 0.158924 | 2.360686 |
| H | 2.005625 | 1.056711 | -0.203798 |
| H | 4.697694 | 2.701488 | -1.363444 |
| H | 3.696477 | -0.098141 | -2.896003 |
| H | 7.247228 | -2.154797 | 0.019412 |
| H | 9.298798 | 0.838372 | 2.613060 |
| H | 4.067380 | -2.489465 | 4.573037 |
| H | 4.129702 | 5.016234 | -0.646012 |
| H | 4.550450 | 0.367359 | -5.185113 |
| H | 7.537531 | -4.568151 | -0.514788 |
| N | 2.963360 | -0.752866 | -0.489386 |
| N | 4.383818 | -0.306684 | 2.016744 |
| N | 6.879293 | 0.406457 | 0.298161 |
| N | 5.207693 | -2.128895 | -0.375564 |
| N | 5.501813 | 0.300452 | -1.945929 |
| N | 4.364747 | 1.849859 | 0.502409 |
| C | 6.546162 | 0.845063 | -4.483526 |
| H | 6.953797 | 1.056875 | -5.464266 |
| H | 8.388487 | 1.245067 | -3.452339 |
| H | 9.467034 | 1.415512 | -1.646330 |
| C | 9.560619 | 1.180387 | 0.487529 |
| H | 10.598858 | 1.480552 | 0.557195 |
| C | 5.441152 | -4.848340 | -0.993227 |
| C | 0.475440 | -1.815629 | -1.174247 |
| H | 5.528746 | -5.900696 | -1.233347 |
| H | 1.517644 | -3.670185 | -1.419431 |
| H | 3.329322 | -4.767524 | -1.383993 |
| C | 3.620004 | -0.371467 | 4.706750 |
| C | 3.710353 | 4.418609 | 1.396129 |
| H | 3.324173 | -0.393084 | 5.748367 |
| H | 3.459004 | 5.412270 | 1.746002 |
| H | 3.277108 | 1.738634 | 4.483927 |
| H | 3.383836 | 3.486148 | 3.305179 |
| C | -0.475457 | 1.815926 | -1.173736 |
| C | -0.584774 | 0.453602 | -0.835915 |
| C | -1.606448 | 2.625533 | -1.155532 |
| C | -1.856816 | -0.027506 | -0.494851 |
| C | -2.851004 | 2.085356 | -0.811450 |
| H | -1.517669 | 3.670543 | -1.418412 |
| H | -2.005613 | -1.056695 | -0.204083 |
| N | -2.963372 | 0.752969 | -0.489137 |
| C | -4.101636 | 2.848276 | -0.765173 |
| C | -4.203702 | 4.209613 | -1.076526 |
| C | -6.408598 | 2.758063 | -0.294347 |
| C | -5.441177 | 4.848573 | -0.991859 |
| H | -3.329352 | 4.767864 | -1.382681 |
| C | -6.560128 | 4.110111 | -0.593208 |
| H | -7.247229 | 2.154746 | 0.020080 |
| H | -7.537550 | 4.568250 | -0.513460 |

| | | | |
|---|---|---|---|
| N | -5.207702 | 2.128968 | -0.374927 |
| Ru | -4.881607 | 0.106598 | 0.002807 |
| C | -4.723015 | -0.196590 | -3.054242 |
| C | -6.818063 | -0.673580 | -2.086281 |
| C | -5.209725 | -0.460471 | -4.331910 |
| H | -3.696463 | 0.098916 | -2.895941 |
| C | -7.352889 | -0.949907 | -3.350394 |
| C | -6.546181 | -0.843670 | -4.483770 |
| H | -4.550433 | -0.365871 | -5.185191 |
| H | -8.388542 | -1.243865 | -3.452720 |
| H | -6.953819 | -1.055164 | -5.464577 |
| C | -3.996580 | -2.053880 | 1.811479 |
| C | -4.404629 | -2.910563 | -0.346087 |
| C | -3.667035 | -3.334478 | 2.271658 |
| C | -4.083512 | -4.201930 | 0.064497 |
| H | -4.697862 | -2.701186 | -1.364126 |
| C | -3.710190 | -4.419002 | 1.394893 |
| H | -3.383547 | -3.487036 | 3.304167 |
| H | -4.129723 | -5.016095 | -0.647366 |
| H | -3.458747 | -5.412743 | 1.744472 |
| N | -5.501820 | -0.299892 | -1.945995 |
| N | -4.364771 | -1.850034 | 0.501919 |
| C | -7.579730 | -0.753928 | -0.833510 |
| C | -8.922385 | -1.142671 | -0.752962 |
| C | -9.560678 | -1.180382 | 0.487174 |
| H | -9.467116 | -1.414802 | -1.646763 |
| C | -7.507153 | -0.445417 | 1.501979 |
| C | -8.840640 | -0.824920 | 1.632262 |
| H | -10.598933 | -1.480511 | 0.556744 |
| H | -6.918023 | -0.159673 | 2.360657 |
| H | -9.298832 | -0.839083 | 2.612818 |
| N | -6.879314 | -0.406537 | 0.298052 |
| C | -3.980506 | -0.847372 | 2.648421 |
| C | -3.595075 | -0.829253 | 3.994311 |
| C | -3.619917 | 0.370143 | 4.706845 |
| H | -3.276906 | -1.739876 | 4.483403 |
| C | -4.404350 | 1.470417 | 2.716408 |
| C | -4.032257 | 1.537886 | 4.056589 |
| H | -3.324046 | 0.391478 | 5.748457 |
| H | -4.732817 | 2.347715 | 2.178949 |
| H | -4.067453 | 2.488147 | 4.573767 |
| N | -4.383815 | 0.306087 | 2.016852 |
| H | 0.477043 | 2.237708 | -1.469794 |
| H | -0.477069 | -2.237336 | -1.470385 |
| H | -5.528779 | 5.900991 | -1.231703 |

**Table S5.** Cartesian Coordinates (in Å) of the equilibrium geometry of the triplet state of the binuclear Ru(II) complexes $\mathbf{D_m}$.

| Atom | X | Y | Z |
|---|---|---|---|
| Ru | -4.930090 | 0.101223 | -0.000563 |
| C | -1.886321 | -0.032035 | -0.282579 |
| C | -7.639262 | -0.662065 | 1.242229 |
| C | -4.565582 | 1.168453 | 2.849337 |
| C | -2.846612 | 2.134991 | -0.411191 |
| C | -7.570847 | -0.619244 | -1.115437 |
| C | -4.194388 | -1.146233 | 2.571976 |
| C | -4.072463 | 2.886793 | -0.375211 |
| C | -4.187370 | -2.261116 | 1.615781 |
| C | -6.732156 | -0.361793 | -2.293322 |
| C | -6.433449 | 2.776572 | -0.142102 |
| C | -4.503961 | -2.881231 | -0.638139 |
| C | -4.572473 | 0.225473 | -3.044108 |
| C | -0.565382 | 0.452362 | -0.436142 |
| C | -8.974420 | -1.058162 | 1.233470 |
| C | -4.265826 | 1.091026 | 4.206914 |
| C | -1.552880 | 2.683595 | -0.570199 |
| C | -3.882309 | -1.272016 | 3.930125 |
| C | -8.910309 | -1.019545 | -1.174994 |
| C | -4.157998 | 4.288255 | -0.531988 |
| C | -7.185875 | -0.435241 | -3.614847 |
| C | -3.908245 | -3.589473 | 1.956433 |
| C | -6.556749 | 4.150865 | -0.292837 |
| C | -4.230274 | -4.215766 | -0.348205 |
| C | -4.977425 | 0.159491 | -4.374772 |
| H | -4.840761 | 2.102820 | 2.383343 |
| H | -7.104593 | -0.506835 | 2.167695 |
| H | -2.077564 | -1.085762 | -0.146507 |
| H | -4.736786 | -2.560366 | -1.642808 |
| H | -3.558030 | 0.478615 | -2.773885 |
| H | -7.298866 | 2.149830 | 0.018351 |
| H | -9.490561 | -1.218873 | 2.171000 |
| H | -4.305079 | 1.985508 | 4.814782 |
| H | -4.255740 | -4.951248 | -1.141718 |
| H | -4.264076 | 0.368217 | -5.161356 |
| H | -7.535721 | 4.610358 | -0.255025 |
| N | -2.974645 | 0.753146 | -0.273801 |
| N | -4.536784 | 0.076164 | 2.043591 |
| N | -6.946477 | -0.443045 | 0.096115 |
| N | -5.228480 | 2.146150 | -0.172345 |
| N | -5.425733 | -0.031585 | -2.020024 |
| N | -4.483011 | -1.918510 | 0.318026 |
| C | -6.304159 | -0.173978 | -4.664926 |
| H | -6.648689 | -0.228872 | -5.690115 |
| H | -8.215343 | -0.689727 | -3.826380 |
| H | -9.396993 | -1.161325 | -2.130120 |
| C | -9.619647 | -1.241089 | 0.006505 |
| H | -10.656450 | -1.551321 | -0.031961 |
| C | -5.393052 | 4.918358 | -0.491117 |
| C | -0.439346 | 1.872681 | -0.585139 |
| H | -5.459346 | 5.993015 | -0.612290 |
| H | -1.434122 | 3.752496 | -0.690603 |
| H | -3.258320 | 4.868580 | -0.687458 |
| C | -3.918354 | -0.147413 | 4.756009 |
| C | -3.929478 | -4.575878 | 0.969161 |
| H | -3.678779 | -0.237770 | 5.808209 |
| H | -3.716045 | -5.606255 | 1.225252 |
| H | -3.612093 | -2.234628 | 4.341878 |
| H | -3.680200 | -3.855647 | 2.979410 |
| C | 0.439354 | -1.872934 | -0.584670 |
| C | 0.565366 | -0.452576 | -0.436036 |
| C | 1.552906 | -2.683824 | -0.569523 |
| C | 1.886300 | 0.031883 | -0.282631 |
| C | 2.846629 | -2.135156 | -0.410657 |
| H | 1.434168 | -3.752758 | -0.689656 |
| H | 2.077526 | 1.085649 | -0.146849 |
| N | 2.974639 | -0.753272 | -0.273656 |
| C | 4.072496 | -2.886921 | -0.374442 |
| C | 4.158063 | -4.288429 | -0.530791 |
| C | 6.433481 | -2.776574 | -0.141372 |
| C | 5.393133 | -4.918489 | -0.489740 |
| H | 3.258396 | -4.868822 | -0.686072 |
| C | 6.556813 | -4.150909 | -0.291706 |
| H | 7.298885 | -2.149764 | 0.018889 |
| H | 7.535797 | -4.610366 | -0.253771 |

|  |  |  |  |
|---|---|---|---|
| N | 5.228495 | -2.146192 | -0.171785 |
| Ru | 4.930065 | -0.101224 | -0.000586 |
| C | 4.572534 | -0.226306 | -3.044107 |
| C | 6.732204 | 0.361124 | -2.293415 |
| C | 4.977524 | -0.160682 | -4.374777 |
| H | 3.558080 | -0.479362 | -2.773841 |
| C | 7.185961 | 0.434219 | -3.614947 |
| C | 6.304271 | 0.172690 | -4.664982 |
| H | 4.264194 | -0.369604 | -5.161327 |
| H | 8.215438 | 0.688639 | -3.826518 |
| H | 6.648830 | 0.227311 | -5.690175 |
| C | 4.187415 | 2.261631 | 1.615049 |
| C | 4.503930 | 2.881040 | -0.639078 |
| C | 3.908398 | 3.590112 | 1.955312 |
| C | 4.230329 | 4.215677 | -0.349539 |
| H | 4.736682 | 2.559857 | -1.643663 |
| C | 3.929640 | 4.576212 | 0.967736 |
| H | 3.680426 | 3.856621 | 2.978219 |
| H | 4.255785 | 4.950914 | -1.143280 |
| H | 3.716289 | 5.606682 | 1.223522 |
| N | 5.425770 | 0.031010 | -2.020067 |
| N | 4.482988 | 1.918614 | 0.317387 |
| C | 7.570865 | 0.618888 | -1.115578 |
| C | 8.910344 | 1.019121 | -1.175210 |
| C | 9.619651 | 1.240988 | 0.006247 |
| H | 9.397065 | 1.160597 | -2.130363 |
| C | 7.639204 | 0.662401 | 1.242078 |
| C | 8.974375 | 1.058452 | 1.233245 |
| H | 10.656467 | 1.551169 | -0.032276 |
| H | 7.104501 | 0.507459 | 2.167572 |
| H | 9.490492 | 1.219422 | 2.170744 |
| N | 6.946450 | 0.443066 | 0.096005 |
| C | 4.194356 | 1.147024 | 2.571569 |
| C | 3.882233 | 1.273213 | 3.929670 |
| C | 3.918167 | 0.148842 | 4.755876 |
| H | 3.612055 | 2.235956 | 4.341139 |
| C | 4.565370 | -1.167611 | 2.849601 |
| C | 4.265568 | -1.089777 | 4.207146 |
| H | 3.678556 | 0.239515 | 5.808041 |
| H | 4.840490 | -2.102134 | 2.383886 |
| H | 4.304729 | -1.984091 | 4.815267 |
| N | 4.536686 | -0.075548 | 2.043545 |
| H | -0.531075 | -2.327227 | -0.737244 |
| H | 0.531090 | 2.326918 | -0.737834 |
| H | 5.459451 | -5.993182 | -0.610587 |

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