Panchromatic Ru(II)-polypyridyl complexes as NIR emitters

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Supporting Information
**Materials, methods and instrumentation**

Nuclear magnetic resonance (NMR) spectra were recorded in CD$_3$CN at room temperature (r.t.) on a Bruker AV400 (400 MHz) spectrometer for $^1$H NMR, at 100 or 125 MHz for $^{13}$C NMR, respectively, as mentioned in the experimental section. The following abbreviations have been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “m” for multiplet, and “br” for broad. Chemical shifts are reported in parts per million (ppm) relative to respective residual solvent protons. Chromatography was performed on columns with an i.d. of 25-30 mm on silica gel (Silicagel 60, 40-63 μm). The progress of the catalytic photoredox reactions and the elution of the products were followed by TLC (silica gel on plastic sheets, 250 μm with indicator F-254). Compounds were visualized under UV light.

Accurate mass measurements were performed on a LTQ Orbitrap XL1 mass spectrometer in positive nanospray mode. Appropriate [M-n(PF$_6$)]$^{n+}$ species were used for empirical formula determination, and exact masses were calculated using Analyst® QS Software from Applied Biosystems by EPSRC National Mass Spectrometry Service Centre, Swansea University. Elemental analyses of complexes 1 and 2 were performed by Mr. Stephen Boyer, London Metropolitan University. All photophysical measurements were carried out in deaerated acetonitrile at r.t. in septa-sealed quartz cells. Absorption spectra were measured on a Cary 500i UV-Vis-NIR Spectrophotometer. The sample solutions for the emission spectra were prepared in HPLC grade MeCN and degassed by three freeze-pump-thaw N$_2$/vacuum cycles. Steady state emission and time-resolved emission spectra were recorded at 298 K using a Shimadzu RF-6000 and an Edinburgh Instruments F980, respectively. Samples for steady state measurements were excited at 550 nm or 500 nm, as mentioned in the footnote of Table S11, while samples for time-
resolved measurements were excited at 378 nm using a PDL 800-D pulsed diode laser. The emission profiles were checked at different excitations at 460, 500, 650 nm, except at 550 nm and the emissions of these complexes were found to be centred at ~ 835 nm in all cases. Emission quantum yields were determined using the optical dilution method.\(^1\) A stock solution with absorbance of ca. 1 was prepared and then four dilutions were prepared to obtain solutions with absorbances of ca. 0.1 0.075, 0.05 and 0.025, respectively. The Beer-Lambert law was found to be linear at the concentrations of the solutions. The steady state emission spectra (\(\lambda_{\text{exc}} = 500\) nm) were then measured after the solutions were degassed by three freeze-pump-thaw \(\text{N}_2/\text{vacuum}\) cycles per sample prior to spectrum acquisition. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis and additional measurements were acquired until the Pearson regression factor (\(R^2\)) for the linear fit of the data set surpassed 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope value. The equation \(\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2\) was used to calculate the relative quantum yield of each of the sample, where \(\Phi_r\) is the absolute quantum yield of the reference, \(n\) is the refractive index of the solvent, \(A\) is the absorbance at the excitation wavelength, and \(I\) is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. Acetonitrile solution of \([\text{Ru(bpy)}_3]\text{Cl}_2\) (bpy = 2,2'-bipyridine) (\(\Phi_r = 9.5\%\)) was used as the external reference.\(^2\) Electrochemical measurements were carried out in argon-purged purified acetonitrile at room temperature with a BAS CV50W multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using an internal 1 mM ferrocene/ferrocinium sample at 380 mV vs. SCE in acetonitrile. The concentration of the compounds was about 1 mM. Tetrabutylammonium hexafluorophosphate
(TBAP) was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms of 1 and 2 were obtained at a scan rate of 100 mVs\(^{-1}\). The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. Differential pulse voltammetry was conducted with a sweep rate of 20 mVs\(^{-1}\) and a pulse amplitude, width and period of 50 mV, 50 ms and 200 ms, respectively.

Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV, emission maxima, ±2 nm, quantum yield, ±5%.

1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidine (H-hpp), 2,6-dibromopyridine, 2,6-dichloropyrazine, (±)BINAP, BuOK\(_t\), ammonium hexafluorophosphate, potassium nitrate were purchased from Aldrich and used as received. 2-Acetylpyridine, n-butanol and 4-formylbenzoic acid were purchased from Fluorochem and used as received. Pd(OAc)\(_2\), hydrated RuCl\(_3\) were purchased from Pressure Chemicals. Ligands L\(_1\) (or dgpy),\(^3\) L\(_2\) (or dgpz)\(^4\) and CO\(_2\)HPh-tpy (CO\(_2\)HPh-tpy = 4-([2,2':6',2''-terpyridin]-4'-yl)benzoic acid)\(^5\) were synthesized following literature procedures.

\[
[Ru(L1)(CO_2HPh-tpy)][(PF_6)_2] \text{ (1):}
\]

A mixture of [Ru(CO\(_2\)HPh-tpy)Cl\(_3\)] (100 mg, 0.178 mmol), L\(_1\) (76 mg, 0.214 mmol, 1.2 equiv.) in nitrogen-degassed n-butanol was heated to reflux for 20 h to give a red-brown solution. After cooling of the mixture to ambient temperature, the solution was filtered under vacuum and the filtrate was evaporated to dryness. To the resulting purple solid was added an aliquot of (20 mL) saturated aqueous NH\(_4\)PF\(_6\) solution and the mixture was sonicated for 5 minutes with stirring. The purple solid was filtered, washed with water (2 x 30 mL) and then dried under vacuum. The
crude product was purified by silica column chromatography using 7:1 (v/v) CH$_3$CN: aqu. saturated KNO$_3$ as the eluant. The second purple band was collected, solvent was evaporated to dryness and the nitrate anion was again metathesized with hexafluorophosphate by addition of an aliquot of saturated aqu. NH$_4$PF$_6$. The product was obtained as a purple solid after filtration and drying under vacuum. Crystals suitable for X-ray crystallography of 1 could be grown by diffusing diethyl ether into a concentrated acetonitrile-acetone solution of the title compound. Yield = 115 mg (59%). R$_f$: 0.45 in 7:1 (v/v) CH$_3$CN:satd. aqu. KNO$_3$. $^1$H NMR (400 MHz, acetonitrile-$d_3$): $\delta$/ppm = 8.73 (s, 2H), 8.57 (d, $J = 8.1$ Hz, 2H), 8.29 (d, $J = 8.4$ Hz, 2H), 8.15 (dd, $J = 9.3$, 8.3 Hz, 3H), 8.05 (d, $J = 5.5$ Hz, 2H), 8.00 (td, $J = 7.8$, 1.5 Hz, 2H), 7.51 – 7.44 (m, 4H), 4.05 (s, 2H), 3.20 (s, 6H), 2.36 (m, 8H), 1.66 (s, 2H), 1.46 (s, 2H), 1.19 (s, 2H), 0.87 (s, 2H). $^{13}$C NMR (100 MHz, acetonitrile-$d_3$): $\delta$/ppm = 167.23, 159.72, 158.96, 155.90, 154.07, 154.03, 142.70, 142.04, 140.98, 137.25, 131.65, 131.51, 128.37, 126.97, 124.02, 121.08, 112.91, 49.63, 48.82, 48.46, 43.89, 23.39, 23.13. HRMS (ESI), m/z: 404.1252 [M-2PF$_6$]$^{2+}$ (C$_{41}$H$_{42}$N$_{10}$O$_2$Ru requires 404.1265), 953.2140 [M-PF$_6$]$^+$ (C$_{41}$H$_{42}$N$_{10}$O$_2$RuPF$_6$ requires 953.2177). Anal. Calc. for C$_{41}$H$_{42}$N$_{10}$O$_2$RuPF$_2$: C, 44.86; H, 3.86; N, 12.76. Found: C, 45.02; H, 3.86; N, 12.74.

[Ru(L2)(CO$_2$HPh-tpy)][(PF$_6$)$_2$] (2):

A mixture of [Ru(CO$_2$HPh-tpy)Cl$_3$] (100 mg, 0.178 mmol), L2 (76 mg, 0.214 mmol, 1.2 equiv.) in nitrogen-degassed n-butanol was heated to reflux for 20 h to give a red-brown solution. After cooling of the mixture to ambient temperature, the solution was filtered under vacuum and the filtrate was evaporated to dryness. To the resulting purple solid was added an aliquot of (20 mL) saturated aqueous NH$_4$PF$_6$ solution and the mixture was sonicated for 5 minutes with stirring. The purple solid was filtered, washed with water (2 x 30 mL) and then dried under vacuum. The crude product was purified by silica column chromatography using 7:1 (v/v) CH$_3$CN: aqu.
saturated KNO$_3$ as the eluant. The second purple band was collected, solvent was evaporated to dryness and the nitrate anion was again metathesized with hexafluorophosphate by addition of an aliquot of saturated aqu. NH$_4$PF$_6$. The product was obtained as a purple solid after filtration and drying under vacuum. Yield = 99 mg (51%). R$_f$: 0.40 in 7:1 (v/v) CH$_3$CN:satd. aqu. KNO$_3$. $^1$H NMR (400 MHz, acetonitrile-$d_3$): $\delta$/ppm = 8.75 (s, 2H), 8.59 (d, $J$ = 17.0 Hz, 4H), 8.29 (d, $J$ = 8.3 Hz, 2H), 8.15 – 8.10 (m, 4H), 8.06 – 7.99 (m, 2H), 7.48 (ddd, $J$ = 7.4, 5.7, 1.3 Hz, 2H), 4.15 (br, s, 2H), 3.19 (m, 6H), 2.36 (m, 8H), 1.60 (d, $J$ = 44.3 Hz, 6H), 0.91 (s, 2H). $^{13}$C NMR (100 MHz, acetonitrile-$d_3$): $\delta$/ppm = 159.53, 158.27, 154.06, 153.61, 151.26, 149.91, 148.06, 146.32, 144.32, 137.71, 133.15, 131.27, 127.99, 127.09, 124.31, 121.16, 49.45, 48.94, 48.47, 47.38, 23.48, 23.02. HRMS (ESI), m/z: 404.6238 [M-2PF$_6$]$^{2+}$ (C$_{40}$H$_{41}$N$_{11}$O$_2$Ru requires 404.6244), 954.2114 [M-PF$_6$]$^+$ (C$_{40}$H$_{41}$N$_{11}$O$_2$RuPF$_6$ requires 954.2130). Anal. Calc. for C$_{40}$H$_{41}$N$_{11}$O$_2$RuPF$_2$: C, 43.72; H, 3.76; N, 14.02. Found: C, 43.61; H, 3.74; N, 13.76.

**Figure S1.** $^1$H NMR spectrum of 1 in CD$_3$CN at 400 MHz at room temperature.
Figure S2. $^{13}$C NMR spectrum of 1 in CD$_3$CN at 100 MHz at room temperature.

Figure S3. $^1$H NMR spectrum of 2 in CD$_3$CN at 400 MHz at room temperature.
**Figure S4.** $^{13}$C NMR spectrum of 2 in CD$_3$CN at 125 MHz at room temperature.

**Figure S5.** $^1$H-$^1$H COSY NMR spectrum of 1 in CD$_3$CN at 400 MHz at room temperature.
Figure S6. $^1$H-$^1$H COSY NMR spectrum of 1 in CD$_3$CN at 400 MHz at room temperature.

Figure S7. High resolution NSI mass spectrum of 2 in CH$_3$CN (insets show the overlay of experimental and theoretical isotropic distribution patterns of [M-2PF$_6$]$^{2+}$ (left) and [M-PF$_6$]$^{+}$ (right)).
**Figure S8.** High resolution NSI mass spectrum of 2 in CH$_3$CN (insets show the overlay of experimental and theoretical isotropic distribution patters of [M-2PF$_6$]$^2^+$ (left) and [M-PF$_6$]$^+$ (right)).
**X-ray diffraction studies:**

X-ray crystallographic data were collected from a single crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker diffractometer equipped with a Bruker APEX-II CCD detector, a Kappa goniometer and a Cu-K$_\alpha$ source ($\lambda = 1.54178$ Å) at 100(2) K. The crystal-to-detector distance was 4.0 cm, and the data collection was carried out in 1024 x 1024 pixel mode. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 110.0 degree scan in 110 frames over three different parts of the reciprocal space.

The diffraction quality of the crystals were checked, revealing in some cases poor diffraction with a large amount of diffuse scattering, signaling extensive crystal disorder. Data collection, cell refinement and data reduction were done using APEX2$^6$ and SAINT.$^7$ Absorption corrections were applied using SADABS.$^8$ Structures were solved by direct methods using SHELXS2012 and refined on $F^2$ by full-matrix least squares using SHELXL2012.$^9$ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. For complex 1, atom C36 in the hpp moiety was found to be disordered over two positions. This minor positional disorder was not taken into account for modelling. The P atom and some fluorine atoms in the PF$_6$ anions of the structure of 1 were also found to be positionally disordered. For complex 1 the highest difference peak is in close proximity to the atom C36, which was found to exhibit positional disorder. In addition, in 1 four more peaks with density around 1 e/Å$^3$ were present essentially due to the positional disorder of the hexafluorophosphate anion in the crystal employed, which was the best available.
Figure S9. ORTEP view of complex 1. Hydrogen atoms, solvated acetone molecule and anions are not shown for clarity. Ellipsoids correspond to a 50% probability level.
Table S1. Crystallographic data for complexes 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CCDC</strong></td>
<td>1843763</td>
</tr>
<tr>
<td><strong>Formula</strong></td>
<td>([\text{C}<em>{41}\text{H}</em>{42}\text{N}<em>{10}\text{O}</em>{2}\text{Ru}]\text{2(PF}<em>{6})\cdot\text{C}</em>{3}\text{H}_{6}\text{O})</td>
</tr>
<tr>
<td><strong>Mw (g/mol); (d_{\text{calc.}}(\text{g/cm}^3))</strong></td>
<td>1153.91; 1.6714</td>
</tr>
<tr>
<td><strong>(T (K)); F(000)</strong></td>
<td>100(2); 1177.66</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>P-1</td>
</tr>
<tr>
<td><strong>Unit Cell:</strong></td>
<td></td>
</tr>
<tr>
<td>(a (\text{Å}))</td>
<td>8.4554(2)</td>
</tr>
<tr>
<td>(b (\text{Å}))</td>
<td>13.7942(4)</td>
</tr>
<tr>
<td>(c (\text{Å}))</td>
<td>20.8461(5)</td>
</tr>
<tr>
<td>(\alpha (°))</td>
<td>97.2010(14)</td>
</tr>
<tr>
<td>(\beta (°))</td>
<td>94.2490(15)</td>
</tr>
<tr>
<td>(\gamma (°))</td>
<td>106.8770(14)</td>
</tr>
<tr>
<td><strong>(V (\text{Å}^3); Z)</strong></td>
<td>2292.64(10); 2</td>
</tr>
<tr>
<td><strong>(\theta) range (°); completeness</strong></td>
<td>2.15-71.58; 0.9721</td>
</tr>
<tr>
<td><strong>(R_{\text{flc}}); collec./indep.; (R_{\text{int}})</strong></td>
<td>47548/8587; 0.0250</td>
</tr>
<tr>
<td><strong>(\mu (\text{mm}^{-1}))</strong></td>
<td>4.35</td>
</tr>
<tr>
<td><strong>R1(F); wR(F(^2)); GoF(F(^2))(^a)</strong></td>
<td>0.0399; 0.1040; 1.036</td>
</tr>
<tr>
<td><strong>Residual electron density</strong></td>
<td>1.83; -1.03</td>
</tr>
</tbody>
</table>

\(^a\)R1(F) based on observed reflections with \(I>2\sigma(I)\) for 1; wR(F\(^2\)) and GoF(F\(^2\)) based on all data for all compounds.
Table S2. Comparison of bond distances and angles in 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Length</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Obs. (X-ray)</td>
<td>Calc. (DFT)</td>
</tr>
<tr>
<td>Ru1-N1</td>
<td>2.066(3)</td>
<td>2.15071</td>
</tr>
<tr>
<td>Ru1-N2</td>
<td>1.939(2)</td>
<td>2.00868</td>
</tr>
<tr>
<td>Ru1-N3</td>
<td>2.087(3)</td>
<td>2.15135</td>
</tr>
<tr>
<td>Ru1-N4</td>
<td>2.070(2)</td>
<td>2.12726</td>
</tr>
<tr>
<td>Ru1-N7</td>
<td>2.059(3)</td>
<td>2.15135</td>
</tr>
<tr>
<td>Ru1-N10</td>
<td>2.089(3)</td>
<td>2.15622</td>
</tr>
</tbody>
</table>
Table S3. Electrochemical data for L1, L2, 1 and 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_{1/2}(\text{ox})^a/V)</th>
<th>(E_{1/2}(\text{red})^c/V)</th>
<th>(\Delta E_{1/2}/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1(dgpy)(^b)</td>
<td>1.11 (308)</td>
<td>0.77 (irr)(^c)</td>
<td>----</td>
</tr>
<tr>
<td>L2(dgpz)(^b)</td>
<td>1.14 (189)</td>
<td>0.77 (irr)(^c)</td>
<td>-1.99 (irr)(^c)</td>
</tr>
<tr>
<td>1</td>
<td>0.52 (66)</td>
<td>-1.49 (61)</td>
<td>-2.03 (72)</td>
</tr>
<tr>
<td>2</td>
<td>0.59 (59)</td>
<td>-1.44 (66)</td>
<td>-1.89 (101)</td>
</tr>
</tbody>
</table>

\(^a\)Potentials are in volts vs. SCE for acetonitrile solutions, 0.1 M in \([n-\text{Bu}_4\text{N}]\text{PF}_6\), recorded at 25 \(\pm\) 1 °C at a sweep rate of 100 mVs\(^{-1}\) for cyclic voltammetry and 20 mVs\(^{-1}\) for differential pulsed voltammetry. The difference between cathodic and anodic peak potentials (mV) is given in parentheses. \(^b\)From ref 4. \(^c\)Irreversible; oxidation potential is given for anodic wave, while reduction potential is given for cathodic wave.

Figure S10. Cyclic voltammograms of 1 (maroon) and 2 (blue) in bold lines in dry, degassed CH\(_3\)CN. Differential pulse voltammograms of 1 (maroon) and 2 (blue) are presented in dotted lines. Vertical line at 0.38 mV represents the Fc\(^+\)/Fc couple in both the voltammograms.
Figure S11. Cyclic voltammograms of 1 (maroon) and 2 (blue) in bold lines in dry, degassed CH$_3$CN in the negative potential only. Differential pulse voltammograms of 1 (maroon) and 2 (blue) are presented in dotted lines.

DFT Calculations:

All calculations were performed with the Gaussian09$^{10}$ suite of programs employing the DFT method, the Becke three-parameter hybrid functional,$^{11}$ and Lee-Yang-Parr’s gradient-corrected correlation functional (B3LYP).$^{12}$ Singlet ground state geometry optimizations for [1]$^{2+}$ and [2]$^{2+}$ were carried out at the (R)B3LYP level in the gas phase, using their respective crystallographic structures as starting points. All elements except cobalt were assigned the 6-31G(d,p) basis set.$^{13}$ The double-$\zeta$ quality SBKJC-VDZ basis set$^{14}$ with an effective core potential and one additional f-type polarization was employed for the Ru(II)-ion. Vertical electronic excitations based on (R)B3LYP-optimized geometries were computed for [1]$^{2+}$ and [2]$^{2+}$ using the TD-DFT formalism$^{15a,b}$ in acetonitrile using conductor-like polarizable continuum model (CPCM).$^{16a-c}$ Vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues. The electronic distribution and localization of the singlet excited states were visualized using the electron density.
difference maps (ED-DMs).\textsuperscript{17} \textit{Gausssum 2.2} and \textit{Chemissian} were employed to visualize the absorption spectra (simulated with Gaussian distribution with a full-width at half maximum (fwhm) set to 3000 cm\(^{-1}\)) and to calculate the fractional contributions of various groups to each molecular orbital. All calculated structures and Kohn-Sham orbitals were visualized with ChemCraft.\textsuperscript{18}

\textbf{Table S4.} M.O. Composition of [1]\textsuperscript{2+} in Singlet (\(S = 0\)) Ground State (b3lyp/SBKJC-VDZ[Ru]6-31G**[C,H,N,O]).

<table>
<thead>
<tr>
<th>MO</th>
<th>Energy (eV)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ru</td>
</tr>
<tr>
<td>LUMO+4</td>
<td>-5.84</td>
<td>5</td>
</tr>
<tr>
<td>LUMO+3</td>
<td>-5.91</td>
<td>2</td>
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<tr>
<td>LUMO+2</td>
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<td>LUMO</td>
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<tr>
<td>HOMO</td>
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<td>49</td>
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<tr>
<td>HOMO-1</td>
<td>-9.93</td>
<td>54</td>
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<tr>
<td>HOMO-2</td>
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<tr>
<td>HOMO-3</td>
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<td>0</td>
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<tr>
<td>HOMO-4</td>
<td>-10.89</td>
<td>3</td>
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\textbf{Table S5.} M.O. Composition of [2]\textsuperscript{2+} in Singlet (\(S = 0\)) Ground State (b3lyp/SBKJC-VDZ[Ru]6-31G**[C,H,N,O]).

<table>
<thead>
<tr>
<th>MO</th>
<th>Energy (eV)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ru</td>
</tr>
<tr>
<td>LUMO+4</td>
<td>-5.97</td>
<td>5</td>
</tr>
<tr>
<td>LUMO+3</td>
<td>-6.03</td>
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<td>LUMO+2</td>
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<td>LUMO+1</td>
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<td>LUMO</td>
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<tr>
<td>HOMO</td>
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<tr>
<td>HOMO-1</td>
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<tr>
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<td>HOMO-3</td>
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<tr>
<td>HOMO-4</td>
<td>-11</td>
<td>5</td>
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</table>
Table S6. UV-vis absorption data of L1, L2, 1, 2 and benchmark complex [Ru(tpy)2]2+.a

<table>
<thead>
<tr>
<th>Compound</th>
<th>λmax, nm (ε x 10³, M⁻¹cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1 (dgpy)</td>
<td>228 (29.0), 311 (12.8)</td>
</tr>
<tr>
<td>L1 (dgpz)</td>
<td>224 (26.9), 340 (14.1)</td>
</tr>
<tr>
<td>1</td>
<td>226 (40.7), 246 (37.3), 282 (40.7), 289 (44.2), 317 (23.6), 395 (10.9), 541 (9.5), 620 (6.1)</td>
</tr>
<tr>
<td>2</td>
<td>224 (37.5), 245 (31.8), 279 (31.8), 288 (36.6), 320 (26.7), 396 (9.5), 538 (8.8), 612 (6.9)</td>
</tr>
<tr>
<td>[Ru(tpy)2]2+b</td>
<td>474 (10.4)</td>
</tr>
</tbody>
</table>

a data in dry acetonitrile at room temperature. b from 19.

Table S7. Selected Transitions from TD-DFT calculations of [1]2+ in the Singlet Ground State (b3lyp/SBKJC-VDZ[Ru]6-31G**[C,H,N,O], CPCM (CH₃CN)).

<table>
<thead>
<tr>
<th>state</th>
<th>λ/nm</th>
<th>λ/nm (ε x 10³ M⁻¹cm⁻¹) [expt.]</th>
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<td>CO₂HPh-tpy(π) to CO₂HPh-tpy(π*) (major) + hpp(π) to CO₂HPh-tpy(π*) (minor)</td>
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<td>H-6-&gt;L (57%), H-4-&gt;L+1 (12%), H-2-&gt;L+5 (16%)</td>
<td>hpp(π) to CO₂HPh-tpy(π*) (major) + CO₂HPh-tpy(π) to CO₂HPh-tpy(π*) (minor) + Ru(dπ) to Py(π*) (minor)</td>
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Table S8. Selected Transitions from TD-DFT calculations of [2]^{2+} in the Singlet Ground State (b3lyp/SBKJC-VDZ[Ru]6-31G**[C,H,N,O], CPCM (CH3CN)).

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**Figure S12.** UV-vis absorption spectra of 1 and 2 in dry MeCN at r.t.
**Figure S13.** Overlay of experimental (curved line) absorption spectra and TD-DFT calculated oscillator strengths (red bars) at different wavelengths of 1, at ambient temperature in dry acetonitrile.

**Figure S14.** Overlay of experimental (curved line) absorption spectra and TD-DFT calculated oscillator strengths (red bars) at different wavelengths of 2, at ambient temperature in dry acetonitrile.
Table S9. Relevant photophysical data of complexes 1 and 2 in dry, degassed MeCN solution at 298 K.

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<th>$\tau_{PL}$ (ns) $^d$</th>
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$^a$In dry, degassed MeCN solution; $^b$$\lambda_{exc} = 550$ nm; $^c$Using [Ru(bpy)$_3$]Cl$_2$ in MeCN ($\Phi_{PL} = 9.5\%$, $\lambda_{exc} = 500$ nm); $^d$$\lambda_{exc} = 378$ nm ($\chi^2$ denotes the fitting value); $^e$calculated using $K_r = \Phi_{PL} / \tau_{PL}$; $^f$calculated using $K_{nr} = (1 - \Phi_{PL}) / \tau_{PL}$.

Figure S15. Photoluminescence decay profiles of complexes 1 and 2 at r.t. in dry, degassed acetonitrile ($\lambda_{exc} = 378$ nm).

Figure S16. Triplet spin density profiles of [1]$^{2+}$ and [2]$^{2+}$ using unrestricted DFT calculations ((rb3lyp/SBKJC-VDZ[Ru]6-31G**[C,H,N,O], CPCM (CH$_3$CN)).
Table S10. Optimized Atomic coordinates obtained from DFT calculations of [I]^{2+}

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Table S11. Optimized Atomic coordinates obtained from DFT calculations of [2]^{2+}

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