ELECTRONIC SUPPLEMENTARY INFORMATION

for

Coupling Between two Ru(bda) Catalysts Bridged by a trans-dicyano Complex

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Fig. S1 500 MHz $^1$H-NMR spectrum of $\text{trans-Ru(tbupy)}_4(\text{CN})_2$ dissolved in $(\text{CD}_3)_2\text{CO}$.

Fig. S2 125 MHz $^{13}$C-NMR spectrum of $\text{trans-Ru(tbupy)}_4(\text{CN})_2$ dissolved in $(\text{CD}_3)_2\text{CO}$. 
Fig. S3 2D $^1$H-$^{13}$C HSQC spectrum of trans-Ru(tbupy)$_4$(CN)$_2$ dissolved in (CD$_3$)$_2$CO.
Fig. S4 500 MHz $^1$H-NMR spectrum of $[\text{RuRu(tbupy)}_4\text{Ru}]$ dissolved in CD$_3$OD.
**Fig. S5** $^1$H-DOSY spectrum of [RuRu(tbupy)$_4$Ru] in CDCl$_3$ at 298K. The diffusion coefficient is $5.31 \times 10^{-6}$ cm$^2$/s.
Fig. S6 500 MHz $^1$H-NMR spectrum of [RuRu(py)$_4$Ru] dissolved in D$_2$O.
Fig. S7 2D $^1$H-$^1$H COSY spectrum of [RuRu(py)$_4$Ru] dissolved in D$_2$O.
**Fig. S8** 125 MHz $^{13}$C-NMR spectrum of [RuRu(py)$_4$Ru] dissolved in D$_2$O.
Fig. S9 2D $^1\text{H}^{13}\text{C}$ HSQC spectrum of [RuRu(py)$_4$Ru] dissolved in D$_2$O.
Fig. S10 2D $^1$H-$^{15}$N HSQC spectrum of $[\text{RuRu(py)}_4\text{Ru}]$ dissolved in D$_2$O.

Fig. S11 $^1$H-DOSY spectrum of $[\text{RuRu(py)}_4\text{Ru}]$ in D$_2$O at 298K. The diffusion coefficient is $2.48 \times 10^{-6}$ cm$^2$/s.
Fig. S12 Absorbance decay monitored at 360 nm in aqueous solution as a function of time for different [RuRu(py)$_4$Ru] concentrations (top) and for different Ce(IV) concentrations (center). Plot of the rate constant vs [RuRu(py)$_4$Ru] concentrations (bottom). Conditions: pH = 1.0 (aqueous 0.1 M triflic acid) and $T = 298$ K.

**Calculation of the number of transferred electrons**

Fig. S13 shows the fit of the plot of $i_p$ vs the $v^{1/2}$ used for the calculation of the number of transferred electrons according with the Randles-Ševčík equation (1) where $i_p$ is the anodic peak current $\alpha$, $n$ is the
number of transferred electrons, \( F \) is the Faraday constant (96500 C), \( A \) is the active area of the working electrode (0.0707 cm\(^2\)), \( C \) is the catalyst concentration in mol cm\(^{-3}\), \( v \) is the scan rate in V s\(^{-1}\), \( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)) calculated from \(^1\)H-DOSY experiments, \( T \) is the temperature in kelvin and \( R \) is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)).

\[
    i_p = 0.4463 nFAC \left( \frac{nFvD}{RT} \right)^{1/2}
\]

(1)

**Fig. S13** Left: CV of [RuRu(tbupy)\(_4\)Ru] in CH\(_2\)Cl\(_2\) (0.2 M TBAPF\(_6\)) at different scan rates. Right: plot of the anodic current \( i_p \) (Ru\(^{III/II} \)) vs square root of the scan rate \((v^{1/2})\). Conditions: WE (glassy carbon electrode), CE (platinum wire), RE (Ag wire) and [C] = 0.41 mM.
**Fig. S14** Upper graph: CV of [RuRu(py)$_4$Ru] in 0.1 M triflic acid (pH = 1) at different scan rates. Lower graphs: Plots of the anodic current $i_p$ (Ru$^{III/II}$) vs square root of the scan rate ($v^{1/2}$) for the first oxidation (left) and the second oxidation (right) process. Conditions: WE (glassy carbon electrode), CE (platinum wire), RE (Ag/AgCl 3M NaCl) and [C] = 1.28 mM.

**Fig. S15** SWV of [RuRu(py)$_4$Ru] at different pH’s (left). Potential vs pH diagram (right). Conditions: WE (glassy carbon electrode), CE (platinum wire), RE (Ag/AgCl 3M NaCl). $v$ = 100 mV/s.
Fig. S16 Anodic scan of the CVs for [RuRu(py)$_4$Ru] in H$_2$O and D$_2$O at in 0.1 M triflic acid (pH = 1 and pD = 1). [RuRu(py)$_4$Ru] = 1.20 mM.

Fig. S17 Plot of calculated the $k_{WNA}$ and $k_D$ vs complex concentration [RuRu(py)$_4$Ru].

Fig. S18 UV-visible spectra of complexes trans-Ru(tbupy)$_4$(CN)$_2$ (olive trace) and [RuRu(tbupy)$_4$Ru] (black trace) in CH$_2$Cl$_2$ and [RuRu(py)$_4$Ru] (red trace) in 0.1 M triflic acid (pH = 1) at 298 K.
**Fig. S19** UV-Vis spectroelectrochemistry for $[\text{RuRu(tbupy)}_{4}\text{Ru}]$ in CH$_2$Cl$_2$ (0.2 M TBAH). The arrows indicate observed changes. Conditions: WE (platinum), CE (platinum), RE (Ag/AgCl 3M NaCl).

**Fig. S20** UV-Vis spectroelectrochemistry of $[\text{RuRu(py)}_{4}\text{Ru}]$ in 0.1 M triflic acid (pH = 1). The arrows indicate changes during the reduction process. Conditions: WE (platinum), CE (platinum), RE (Ag/AgCl 3M NaCl).

**Fig. S21** UV-Vis spectroelectrochemistry of $[\text{RuRu(py)}_{4}\text{Ru}]$ in 0.1 M triflic acid (pH = 1). The arrows indicate observed changes. Conditions: WE (platinum), CE (platinum), RE (Ag/AgCl 3M NaCl).
Table S1. Energies values and percentual group contributions of selected MOs of complex [RuRu(tbupy)$_4$Ru] in their singlet ground state.

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Fig. S22 Molecular orbital diagram and partial density of states (PDOS) of complex [RuRu(tbupy)$_4$Ru] in their singlet ground state.
Table S2. Energies values and percentual group contributions of selected alpha MOs of complex [Ru$^{III}$Ru$^{II}$(tbupy)$_4$Ru$^{III}$]$^{2+}$ in their triplet ground state.

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Table S3. Energies values and percentual group contributions of selected beta MOs of complex [Ru\textsuperscript{III}Ru\textsuperscript{II}(tbupy)\textsubscript{4}Ru\textsuperscript{III}]\textsuperscript{2+} in their triplet ground state.

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Fig. S23 Molecular orbital diagram and partial density of states (PDOS) of complex [Ru\textsuperscript{III}Ru\textsuperscript{II}(tbupy)\textsubscript{4}Ru\textsuperscript{III}]\textsuperscript{2+} in their triplet ground state.
Fig. S24 Molecular orbitals of complex [Ru^{III}Ru^{II}(tbupy)_{4}Ru^{III}]^{2+} involved in MM´CT transitions.

Table S4. Energies values and percentual group contributions of selected alpha MOs of complex [Ru^{III}Ru^{III}(tbupy)_{4}Ru^{III}]^{3+} in their quartet ground state.

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<td>41</td>
<td>0</td>
<td>55</td>
</tr>
<tr>
<td>H-5</td>
<td>-8.1</td>
<td>2</td>
<td>36</td>
<td>0</td>
<td>62</td>
</tr>
<tr>
<td>H-6</td>
<td>-8.12</td>
<td>1</td>
<td>8</td>
<td>0</td>
<td>91</td>
</tr>
<tr>
<td>H-7</td>
<td>-8.13</td>
<td>1</td>
<td>15</td>
<td>0</td>
<td>84</td>
</tr>
<tr>
<td>H-8</td>
<td>-8.33</td>
<td>21</td>
<td>49</td>
<td>3</td>
<td>27</td>
</tr>
<tr>
<td>H-9</td>
<td>-8.44</td>
<td>8</td>
<td>53</td>
<td>4</td>
<td>35</td>
</tr>
<tr>
<td>H-10</td>
<td>-8.69</td>
<td>8</td>
<td>1</td>
<td>16</td>
<td>75</td>
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</table>
Table S5. Energies values and percentual group contributions of selected beta MOs of complex \([\text{Ru}^{III}\text{Ru}^{III}(\text{tbupy})_4\text{Ru}^{III}]^{3+}\) in their quartet ground state.

<table>
<thead>
<tr>
<th>Beta orbitals</th>
<th>eV</th>
<th>Ru$_{\text{tbupy}}$</th>
<th>Ru$_{\text{bda}}$</th>
<th>tbupy</th>
<th>bda</th>
</tr>
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<tbody>
<tr>
<td>L+10</td>
<td>-2.83</td>
<td>2</td>
<td>4</td>
<td>92</td>
<td>2</td>
</tr>
<tr>
<td>L+9</td>
<td>-2.89</td>
<td>18</td>
<td>54</td>
<td>3</td>
<td>25</td>
</tr>
<tr>
<td>L+8</td>
<td>-3.29</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>L+7</td>
<td>-3.29</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>L+6</td>
<td>-3.5</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>99</td>
</tr>
<tr>
<td>L+5</td>
<td>-3.5</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>99</td>
</tr>
<tr>
<td>L+4</td>
<td>-3.98</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>96</td>
</tr>
<tr>
<td>L+3</td>
<td>-3.98</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>96</td>
</tr>
<tr>
<td>L+2</td>
<td>-4.94</td>
<td>1</td>
<td>72</td>
<td>0</td>
<td>27</td>
</tr>
<tr>
<td>L+1</td>
<td>-4.95</td>
<td>1</td>
<td>72</td>
<td>0</td>
<td>27</td>
</tr>
<tr>
<td>LUMO</td>
<td>-5.88</td>
<td>79</td>
<td>0</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>HOMO</td>
<td>-7.73</td>
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<td>53</td>
<td>1</td>
<td>34</td>
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<tr>
<td>H-1</td>
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<td>7</td>
<td>49</td>
<td>1</td>
<td>44</td>
</tr>
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<td>H-2</td>
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<td>13</td>
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<td>92</td>
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<td>H-4</td>
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<td>25</td>
<td>46</td>
<td>3</td>
<td>27</td>
</tr>
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<td>H-5</td>
<td>-8.11</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>96</td>
</tr>
<tr>
<td>H-6</td>
<td>-8.12</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>H-7</td>
<td>-8.19</td>
<td>8</td>
<td>55</td>
<td>2</td>
<td>34</td>
</tr>
<tr>
<td>H-8</td>
<td>-8.49</td>
<td>51</td>
<td>5</td>
<td>32</td>
<td>12</td>
</tr>
<tr>
<td>H-9</td>
<td>-8.57</td>
<td>35</td>
<td>12</td>
<td>39</td>
<td>14</td>
</tr>
<tr>
<td>H-10</td>
<td>-8.68</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>98</td>
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</table>

Fig. S25 Molecular orbital diagram and partial density of states (PDOS) of complex \([\text{Ru}^{III}\text{Ru}^{III}(\text{tbupy})_4\text{Ru}^{III}]^{3+}\) in their quartet ground state.
Table S6. (TD)DFT assignments for calculated UV-Vis transitions of complex $[RuRu(tbupy)_4Ru]$ in their singlet ground state.

<table>
<thead>
<tr>
<th>No.</th>
<th>Wavelength (nm)</th>
<th>Osc. Strength</th>
<th>Major contributions</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>516.7</td>
<td>0.0184</td>
<td>H-4-&gt;L+1 (14%)</td>
<td>d(Rubda,Rutbupy)-&gt;π*(bda)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-&gt;L+2 (14%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO-&gt;L+1 (27%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO-&gt;L+3 (19%)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>506.4</td>
<td>0.0108</td>
<td>H-4-&gt;L+1 (17%)</td>
<td>d(Rubda,Rutbupy)-&gt;π*(bda)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-&gt;L+2 (16%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO-&gt;L+1 (10%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO-&gt;L+3 (24%)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>456.0</td>
<td>0.0203</td>
<td>H-5-&gt;LUMO (12%)</td>
<td>d(Ruba) -&gt; π*(bda)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-2-&gt;LUMO (11%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-2-&gt;L+3 (12%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-&gt;L+3 (10%)</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>406.1</td>
<td>0.0255</td>
<td>H-4-&gt;L+5 (30%)</td>
<td>d(Rubda,Rutbupy)-&gt;π*(bda)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO-&gt;L+5 (19%)</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>398.1</td>
<td>0.0338</td>
<td>H-6-&gt;LUMO (10%)</td>
<td>d(Rubtupy,Rutbupy)-&gt;π*(bda,tbupy)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-2-&gt;L+5 (29%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-&gt;L+5 (32%)</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>370.0</td>
<td>0.0432</td>
<td>H-3-&gt;L+6 (37%)</td>
<td>d(Rubtupy)-&gt;π*(tbupy)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>HOMO-&gt;L+6 (17%)</td>
<td>d(Ruba) -&gt; π*(bda)</td>
</tr>
<tr>
<td>53</td>
<td>368.4</td>
<td>0.0702</td>
<td>H-6-&gt;L+2 (11%)</td>
<td>d(Rubtupy)-&gt;π*(tbupy)</td>
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<td></td>
<td>H-3-&gt;L+6 (12%)</td>
<td>d(Ruba) -&gt; π*(bda)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>HOMO-&gt;L+7 (21%)</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>354.8</td>
<td>0.0635</td>
<td>H-3-&gt;L+7 (15%)</td>
<td>d(Rubda,Rutbupy)-&gt;π*(tbupy)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-2-&gt;L+8 (21%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-&gt;L+8 (29%)</td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>352.0</td>
<td>0.1255</td>
<td>H-3-&gt;L+8 (36%)</td>
<td>d(Rubda,Rutbupy)-&gt;π*(tbupy)</td>
</tr>
<tr>
<td>64</td>
<td>351.6</td>
<td>0.1467</td>
<td>H-3-&gt;L+7 (11%)</td>
<td>d(Rubda,Rutbupy)-&gt;π*(tbupy)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-3-&gt;L+8 (16%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td>H-2-&gt;L+9 (12%)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-&gt;L+9 (15%)</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>346.2</td>
<td>0.0995</td>
<td>H-4-&gt;L+6 (57%)</td>
<td>d(Rubda,Rutbupy)-&gt;π*(tbupy)</td>
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<td>HOMO-&gt;L+6 (11%)</td>
<td></td>
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<tr>
<td>141</td>
<td>291.3</td>
<td>0.0693</td>
<td>H-21-&gt;LUMO (10%)</td>
<td>d(Rubda,Rutbupy)-&gt;π*(tbupy)</td>
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<td></td>
<td></td>
<td>H-18-&gt;LUMO (12%)</td>
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<tr>
<td>166</td>
<td>282.9</td>
<td>0.1026</td>
<td>H-8-&gt;L+8 (27%)</td>
<td>d(Rubda,Rutbupy)-&gt;π*(bda,tbupy)</td>
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<td></td>
<td></td>
<td></td>
<td>H-4-&gt;L+15 (17%)</td>
<td>π(bda)&gt;π*(bda)</td>
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<td></td>
<td></td>
<td>HOMO-&gt;L+15 (14%)</td>
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</table>
**Fig. S26** (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex [RuRu(tbupy)₄Ru] in their singlet ground state. Calculated transition are represented by black vertical bars.

**Table S7.** (TD)-DFT assignments for calculated UV-Vis transitions of complex [Ru^{III}Ru^{II}(tbupy)₄Ru^{III}]²⁺ in their triplet ground state.

<table>
<thead>
<tr>
<th>No.</th>
<th>Wavelength (nm)</th>
<th>Osc. Strength</th>
<th>Major contributions</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>817.7</td>
<td>0.0114</td>
<td>H-8β→LUMOβ (13%)</td>
<td>d(Ru_{tbupy}) → d(Ru_{bda})</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>H-7β→LUMOβ (10%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-2β→LUMOβ (53%)</td>
<td></td>
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<tr>
<td>10</td>
<td>811.9</td>
<td>0.0053</td>
<td>H-8β→L+1β (12%),</td>
<td>d(Ru_{tbupy}) → d(Ru_{bda})</td>
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<td></td>
<td></td>
<td></td>
<td>H-7β→L+1β (11%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-2β→L+1β (52%)</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>536.3</td>
<td>0.0075</td>
<td>H-2α→LUMOα (49%)</td>
<td>d(Ru_{tbupy}) → π*(bda)</td>
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<td>H-2β→L+2β (39%)</td>
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<tr>
<td>24</td>
<td>535.2</td>
<td>0.0038</td>
<td>H-2α→L+1α (48%)</td>
<td>d(Ru_{tbupy}) → π*(bda)</td>
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<td></td>
<td></td>
<td>H-2β→L+3β (40%)</td>
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<tr>
<td>102</td>
<td>391.7</td>
<td>0.0122</td>
<td>H-6β→L+2β (21%)</td>
<td>d(Ru_{tbupy}) → π*(bda)</td>
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<td>H-5β→L+3β (27%)</td>
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<tr>
<td>140</td>
<td>355.5</td>
<td>0.0459</td>
<td>HOMO α→L+10α (38%)</td>
<td>d(Ru_{tbupy}) → π*(tbupy)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>HOMO β→L+12β (42%)</td>
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<tr>
<td>159</td>
<td>345.9</td>
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<td>H-1α→L+28α (11%)</td>
<td>d(Ru_{tbupy}) → π*(tbupy)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO α→L+11α (23%)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>HOMO β→L+13β (28%)</td>
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</tr>
<tr>
<td>160</td>
<td>345.8</td>
<td>0.0417</td>
<td>H-1α→L+28α (15%)</td>
<td>d(Ru_{tbupy}) → π*(tbupy)</td>
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<td></td>
<td>HOMO α→L+11α (20%)</td>
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<td>HOMO β→L+13β (17%)</td>
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<td>189</td>
<td>334.7</td>
<td>0.0799</td>
<td>H-2α→L+10α (13%)</td>
<td>d(Ru_{tbupy}) → π*(tbupy)</td>
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<td></td>
<td></td>
<td></td>
<td>HOMO α→L+13α (28%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-2β→L+12β (12%)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO β→L+15β (29%)</td>
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<tr>
<td>218</td>
<td>322.1</td>
<td>0.1031</td>
<td>H-1α→L+13α (42%)</td>
<td>d(Ru_{tbupy}) → π*(tbupy)</td>
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<td></td>
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<td>H-1β→L+14β (32%)</td>
<td></td>
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<tr>
<td>321</td>
<td>290.9</td>
<td>0.2091</td>
<td>HOMO β→L+16β (13%)</td>
<td>d(Ru_{tbupy}) → π*(bda)</td>
</tr>
</tbody>
</table>
**Fig. S27** Left: (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex [Ru\textsuperscript{III}Ru\textsuperscript{II}(tbupy)\textsubscript{4}Ru\textsuperscript{III}]\textsuperscript{2+} in their triplet ground state. Calculated transition are represented by red vertical bars.

**Table S8.** (TD)DFT assignments for calculated UV-Vis transitions of complex [Ru\textsuperscript{III}Ru\textsuperscript{II}(tbupy)\textsubscript{4}Ru\textsuperscript{III}]\textsuperscript{3+} in their quartet ground state.

<table>
<thead>
<tr>
<th>No.</th>
<th>Wavelength (nm)</th>
<th>Osc. Strength</th>
<th>Major contributions</th>
<th>Assignment</th>
</tr>
</thead>
</table>
| 12  | 676.3           | 0.0033        | H-9 $\beta$ ->LUMO $\beta$ (43%)  
H-4 $\beta$ ->LUMO $\beta$ (51%) | d(Ru\textsubscript{tbupy}),$\pi$(bda)->d(Ru\textsubscript{tbupy}) |
| 23  | 521.8           | 0.0066        | H-20 $\beta$ ->LUMO $\beta$ (82%) | $\pi$ (tbupy)->d(Ru\textsubscript{tbupy}) |
| 34  | 481.8           | 0.083         | H-22 $\beta$ ->LUMO $\beta$ (83%) | $\pi$(tbupy)->d(Ru\textsubscript{tbupy}) |
| 35  | 478.7           | 0.0733        | H-21 $\beta$ ->LUMO $\beta$ (75%) | $\pi$(tbupy)->d(Ru\textsubscript{tbupy}) |
| 94  | 373.9           | 0.043         | H-26 $\beta$ ->L+2 $\beta$ (40%)  
H-14 $\beta$ ->L+2 $\beta$ (19%) | $\pi$(tbupy,bda)->d(Ru\textsubscript{tbupy}) |
| 97  | 370.0           | 0.0117        | H-26 $\beta$ ->L+2 $\beta$ (11%)  
H-14 $\beta$ ->L+2 $\beta$ (67%) | $\pi$(tbupy) ->d(Ru\textsubscript{bda}) |
| 257 | 291.2           | 0.0804        | H-12 $\alpha$ ->L+1 $\alpha$ (13%)  
H-2 $\alpha$ ->L+3 $\alpha$ (12%)  
H-4 $\beta$ ->L+8 $\beta$ (10%) | d(Ru\textsubscript{bda}) ->$\pi^*$ (bda) |
| 269 | 288.1           | 0.0869        | H-3 $\beta$ ->L+13 $\beta$ (10%)  
H-2 $\beta$ ->L+9 $\beta$ (16%) | $\pi$(bda) -> d(Ru\textsubscript{bda}) |
Fig. S28 (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $\text{[Ru}^\text{III}_2\text{Ru}^\text{III}(\text{tbupy})_4\text{Ru}^\text{III}]^{3+}$ in their quartet ground state. Calculated transition are represented by green vertical bars.

Table S9. Energies values and percentual group contributions of selected MOs of complex $\text{[Ru}^\text{II}_2\text{Ru}^\text{II}(\text{py})_4\text{Ru}^\text{II}]$ in their singlet ground state.

<table>
<thead>
<tr>
<th>MO’s</th>
<th>Energy (eV)</th>
<th>Ru$_{\text{py}}$</th>
<th>Ru$_{\text{bda}}$</th>
<th>py</th>
<th>bda</th>
</tr>
</thead>
<tbody>
<tr>
<td>L+10</td>
<td>-1.2</td>
<td>1</td>
<td>1</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>L+9</td>
<td>-1.5</td>
<td>6</td>
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<td>94</td>
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**Fig. S29** Molecular orbital diagram and partial density of states (PDOS) of complex $[\text{Ru}^{II}\text{Ru}^{II}(\text{py})_4\text{Ru}^{II}]$ in their singlet ground state.

**Table S10.** Energies values and percentual group contributions of selected alpha MOs of the complex $[\text{Ru}^{III}\text{Ru}^{II}(\text{py})_4\text{Ru}^{III}]^{2+}$ in their triplet ground state.

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Table S11. Energies values and percentual group contributions of selected beta MOs of the complex [Ru\textsuperscript{III}Ru\textsuperscript{II}(py)\textsubscript{4}Ru\textsuperscript{III}]\textsuperscript{2+} in their triplet ground state.

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Fig. S30 Molecular orbital diagram and partial density of states (PDOS) of complex [Ru\textsuperscript{III}Ru\textsuperscript{II}(py)\textsubscript{4}Ru\textsuperscript{III}]\textsuperscript{2+} in their triplet ground state.
Fig. S31 Molecular orbitals of complex \([\text{Ru}^{\text{III}}\text{Ru}^{\text{II}}(\text{py})_4\text{Ru}^{\text{III}}]^{2+}\) involved in MM’CT transitions #9 and #10.

Table S12. Energies values and percentual group contributions of selected alpha MOs of the complex \([\text{Ru}^\text{IV}\text{Ru}^{\text{III}}(\text{py})_4\text{Ru}^{\text{IV}}]^{2+}\) in their doublet ground state.

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Table S13. Energies values and percentual group contributions of selected beta MOs of the complex [RuVII(py)₄RuIV]²⁺ in their doublet ground state.

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Fig. S32 Molecular orbital diagram and partial density of states (PDOS) of complex [RuVII(py)₄RuIV]²⁺ in their doublet ground state.
Fig. S33 Molecular orbitals of complex $[\text{Ru}^\text{VI}\text{Ru}^\text{II}(\text{py})_4\text{Ru}^\text{IV}]^{2+}$ involved in MM’CT transitions #3.
Table S14. (TD)DFT assignments for calculated UV-Vis transitions of complex \([\text{Ru}^\text{II}\text{Ru}^\text{II}(\text{py})_4\text{Ru}^\text{II}]\) in their singlet ground state.

<table>
<thead>
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<th>No.</th>
<th>Wavelength (nm)</th>
<th>Osc. Strength</th>
<th>Major contributions</th>
<th>Assignment</th>
</tr>
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<tr>
<td>6</td>
<td>498.3</td>
<td>0.0151</td>
<td>H-3-&gt;L+1 (10%)</td>
<td>(d(\text{Ru}<em>{\text{bda}},\text{Ru}</em>{\text{py}}))-&gt;(\pi^*(\text{bda}))</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-&gt;L+2 (22%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO-&gt;L+1 (18%)</td>
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<td></td>
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<td>HOMO-&gt;L+3 (24%)</td>
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<td>8</td>
<td>489.7</td>
<td>0.0193</td>
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<td>(d(\text{Ru}<em>{\text{bda}},\text{Ru}</em>{\text{py}}))-&gt;(\pi^*(\text{bda}))</td>
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<td></td>
<td></td>
<td></td>
<td>H-1-&gt;L+2 (10%)</td>
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<td>HOMO-&gt;L+3 (16%)</td>
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<td>H-2-&gt;L+2 (23%)</td>
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<td>H-2-&gt;L+3 (17%)</td>
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<td>H-1-&gt;L+5 (16%)</td>
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<td>60</td>
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<td>H-4-&gt;L+7 (13%)</td>
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<td>H-4-&gt;L+8 (41%)</td>
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<td>HOMO-&gt;L+9 (11%)</td>
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<td>0.0839</td>
<td>H-4-&gt;L+5 (10%)</td>
<td>(d(\text{Ru}<em>{\text{py}},\text{Ru}</em>{\text{bda}}))-&gt;(\pi^*(\text{py}))</td>
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<td>H-4-&gt;L+7 (28%)</td>
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<td>H-4-&gt;L+8 (10%)</td>
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<td>H-1-&gt;L+6 (22%)</td>
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<td>0.0474</td>
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<td>H-5-&gt;L+5 (29%)</td>
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<td>H-3-&gt;L+4 (10%)</td>
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<td>105</td>
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<td>0.0376</td>
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<td>(d(\text{Ru}<em>{\text{py}},\text{Ru}</em>{\text{bda}}))-&gt;(\pi^*(\text{py}))</td>
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<td>H-1-&gt;L+11 (12%)</td>
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<tr>
<td>147</td>
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<td>(\pi(\text{bda}))-&gt;(\pi^*(\text{bda}))</td>
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<td>H-18-&gt;L+1 (11%)</td>
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<td>H-17-&gt;LUMO (11%)</td>
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<td>H-17-&gt;L+1 (12%)</td>
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<td>H-10-&gt;L+4 (13%)</td>
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<td>(\pi(\text{bda}))-&gt;(\pi^*(\text{bda}))</td>
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<td>H-10-&gt;L+5 (14%)</td>
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<td>H-9-&gt;L+5 (25%)</td>
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<td>H-2-&gt;L+20 (10%)</td>
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**Fig. S34** (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $[\text{Ru}^{II}\text{Ru}^{II}(\text{py})_4\text{Ru}^{II}]$ in their singlet ground state. Calculated transition are represented by red vertical bars.

**Table S15.** (TD)DFT assignments for calculated UV-Vis transitions of the complex $[\text{Ru}^{III}\text{Ru}^{II}(\text{py})_4\text{Ru}^{III}]^{2+}$ in their triplet ground state.

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<td>9</td>
<td>604.0</td>
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<td>H-8 $\beta \rightarrow$LUMO $\beta$(15%)&lt;br&gt;H-1 $\beta \rightarrow$LUMO $\beta$(61%)</td>
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<tr>
<td>10</td>
<td>603.8</td>
<td>0.0003</td>
<td>H-8 $\beta \rightarrow$L+1 $\beta$(13%)&lt;br&gt;H-1 $\beta \rightarrow$L+1 $\beta$(54%)</td>
<td>$d(\text{Ru}<em>{\text{py}}) \rightarrow d(\text{Ru}</em>{\text{bda}})$</td>
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<td>11</td>
<td>582.2</td>
<td>0.0056</td>
<td>H-4 $\alpha \rightarrow$L+4 $\alpha$(13%)&lt;br&gt;H-4 $\alpha \rightarrow$L+6 $\alpha$(62%)&lt;br&gt;H-3 $\alpha \rightarrow$L+6 $\alpha$(11%)</td>
<td>$d(\text{Ru}<em>{\text{bda}}) \rightarrow d(\text{Ru}</em>{\text{bda}})$</td>
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<tr>
<td>12</td>
<td>579.5</td>
<td>0.0059</td>
<td>H-4 $\alpha \rightarrow$L+7 $\alpha$(12%)&lt;br&gt;H-3 $\alpha \rightarrow$L+5 $\alpha$(10%)&lt;br&gt;H-3 $\alpha \rightarrow$L+7 $\alpha$(65%)</td>
<td>$d(\text{Ru}<em>{\text{bda}}) \rightarrow d(\text{Ru}</em>{\text{bda}})$</td>
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<td>28</td>
<td>504.6</td>
<td>0.005</td>
<td>H-1 $\alpha \rightarrow$L+1 $\alpha$(36%)&lt;br&gt;H-1 $\beta \rightarrow$L+3 $\beta$(33%)</td>
<td>$d(\text{Ru}_{\text{py}}) \rightarrow \pi^*(\text{bda})$</td>
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<tr>
<td>99</td>
<td>375.8</td>
<td>0.0159</td>
<td>H-6 $\alpha \rightarrow$LUMO $\alpha$(14%)&lt;br&gt;H-6 $\beta \rightarrow$L+2 $\beta$(31%)&lt;br&gt;H-5 $\beta \rightarrow$L+2 $\beta$(13%)</td>
<td>LLCT (DMSO$\rightarrow$bd)</td>
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<td>$d(\text{Ru}_{\text{py}}) \rightarrow \pi^*(\text{py})$</td>
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<td>124</td>
<td>356.5</td>
<td>0.0444</td>
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<td>$d(\text{Ru}_{\text{py}}) \rightarrow \pi^*(\text{py})$</td>
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<td>180</td>
<td>334.2</td>
<td>0.1576</td>
<td>H-1 $\alpha \rightarrow$L+12 $\alpha$(15%)&lt;br&gt;H-1 $\alpha \rightarrow$L+13 $\alpha$(14%)&lt;br&gt;H-1 $\beta \rightarrow$L+14 $\beta$(12%)&lt;br&gt;H-1 $\beta \rightarrow$L+15 $\beta$(14%)</td>
<td>$d(\text{Ru}_{\text{py}}) \rightarrow \pi^*(\text{py})$</td>
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<td>$d(\text{Ru}_{\text{py}}) \rightarrow \pi^*(\text{py})$</td>
</tr>
<tr>
<td>309</td>
<td>287.7</td>
<td>0.107</td>
<td>H-1 $\beta \rightarrow$L+19 $\beta$(12%)</td>
<td>$d(\text{Ru}_{\text{py}}) \rightarrow \pi^*(\text{py})$</td>
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<tr>
<td>380</td>
<td>273.3</td>
<td>0.1078</td>
<td>H-6 $\beta \rightarrow$L+10 $\beta$(23%)&lt;br&gt;H-5 $\beta \rightarrow$L+11 $\beta$(14%)</td>
<td>LMCT (DMSO$\rightarrow$Ru$_{bda}$)&lt;br&gt;LLCT (DMSO$\rightarrow$bd)</td>
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**Fig. S35** (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex [Ru$_{III}$Ru$_{II}$(py)$_4$Ru$_{III}$]$^{2+}$ in their triplet ground state. Calculated transition are represented by red vertical bars.

**Fig. S36** Left: (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex [Ru$_{IV}$Ru$_{II}$(py)$_4$Ru$_{IV}$]$^{2+}$ in their singlet ground state. Calculated transition are represented by red vertical bars.
Table S16. (TD)DFT assignments for calculated UV-Vis transitions of the complex [RuVII(py)₄RuIV]²⁺ in their doublet ground state.

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<th>Major contributions</th>
<th>Assignment</th>
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<td>3</td>
<td>1092.7</td>
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<td>H-2β-&gt;LUMOβ (88%)</td>
<td>d(Rup) -&gt; d(RubdaO)</td>
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<td>H-1β-&gt;LUMOβ (10%)</td>
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<tr>
<td>25</td>
<td>616.1</td>
<td>0.0078</td>
<td>H-4β-&gt;LUMOβ (91%)</td>
<td>π(bdaO) -&gt; d(RubdaO)</td>
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<tr>
<td>125</td>
<td>397.2</td>
<td>0.0482</td>
<td>H-4α-&gt;L+2α (21%)</td>
<td>π(bdaO) -&gt; d(RubdaO)</td>
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<td>H-4β-&gt;L+3β (48%)</td>
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<tr>
<td>210</td>
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<td>d(Rup) -&gt; π*(py)</td>
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<td>HOMOβ-&gt;L+13β (43%)</td>
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<td>HOMOα-&gt;L+13α (45%)</td>
<td>d(Rup) -&gt; π*(py)</td>
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<td>HOMOβ-&gt;L+14β (46%)</td>
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<tr>
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<td>320.5</td>
<td>0.0477</td>
<td>H-1α-&gt;L+15α (10%)</td>
<td>d(Rup) -&gt; π*(py)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-4β-&gt;L+5β (11%)</td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>320.2</td>
<td>0.0971</td>
<td>H-2α-&gt;L+14α (18%)</td>
<td>d(Rup) -&gt; π*(py)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-29β-&gt;LUMOβ (20%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-2β-&gt;L+15β (13%)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. S37 Left: (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex [RuVII(py)₄RuIV]²⁺ in their triplet ground state. Calculated transition are represented by red vertical bars.