Electronic Supplementary Information (ESI)


Consequences for biological applications

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A. Structure of [Ru\(^{II}\)(terpy)(bipy)Cl]Cl in solution as determined by NMR spectroscopy

Numbering scheme of terpy and bipy ligands used for NMR characterization

\(^1\)H NMR (DMSO\(_d\)-6): \(\delta\) 10.09 (d, 1H, J = 5.6 Hz, Ha), 8.92 (d, 1H, J = 8.2 Hz, Hd), 8.82 (d, 2H, J = 8.1 Hz, H3'/H5'), 8.70 (d, 2H, J = 8.1 Hz, H3/H3'), 8.64 (d, 1H, J = 8.1 Hz, Hg), 8.35 (td, 1H, J = 8.0 Hz, J2 = 1.4 Hz, Hc), 8.21 (t, 1H, J = 8.0 Hz, H4'), 8.06 (ddd, J1 = 7.0 Hz, J2 = 5.6 Hz, J3 = 1.3 Hz, 1H, Hb), 7.98 (td, 2H, J1 = 7.6 Hz, J2 = 1.4 Hz, H4/H4'), 7.77 (td, 1H, J1 = 7.6 Hz, J2 = 1.5 Hz, Hh), 7.61 (d, 2H, J = 5.6 Hz, H6/H6''), 7.37 (ddd, J1 = 7.1 Hz, J2 = 5.5 Hz, J3 = 1.3 Hz, 2H, H5/H5''), 7.31 (d, 1H, J = 5.6 Hz, Hj), 7.08 (ddd, J1 = 7.3 Hz, J2 = 5.8 Hz, J3 = 1.4 Hz, 1H, Hi)

\(^{13}\)C NMR (DMSO\(_d\)-6): \(\delta\) 158.9 (C2/C2''), 158.8 (Cf), 158.0 (C2'/C6'), 156.2 (Ce), 152.4 (Ca), 152.3 (C6/C6''), 152.0 (Cj), 137.5 (C4/C4''), 137.1 (Cc), 136.0 (Ch), 134.3 (C4'), 127.9 (C5/C5''), 127.4 (Cb), 126.9 (Ci), 124.2 (C3/C3''), 124.2 (Cd), 124.0 (Cg), 123.1 (C3'/C5')
$^{15}$N NMR (DMSO$_{d-6}$): $\delta$ $-91.9$ N(IV), $-117.2$ N(II), $-127.6$ N(I), $-129.6$ N(III)/N(V)

Coordination shift of terpy N signals vs free ligand in dmoso:
\[ \Delta N_{III/V} = -56.6 \text{ ppm} \]
\[ \Delta N_{IV} = -8.3 \text{ ppm} \]

NMR spectra

$^1$H NMR

$^{13}$C NMR
$^{1}H^{13}C$ HMBC NMR

$^{1}H^{13}C$ HMQC NMR
\(^1\)H-\(^{15}\)N HMQC NMR

B. Structure of [Ru\(^{11}\)(terpy)(en)Cl]Cl in solution as determined by NMR spectroscopy

Numbering scheme of terpy and en ligands used for NMR characterization

\(^1\)H NMR (DMSO\(_{d-6}\)): \(\delta\) 9.15 (d, 2H, J = 5.5 Hz, H6/H6”), 8.60 (d, 2H, J = 8.0 Hz, H3/H3”), 8.56 (d, 2H, J = 8.0 Hz, H3’/H5”), 8.02 (td, 2H, J\(_1\) = 7.7 Hz, J\(_2\) = 1.4 Hz, H4/H4”), 7.77 (t, 1H, J = 7.9 Hz, H4’), 7.71 (ddd, 2H, J\(_1\) = 7.1 Hz, J\(_2\) = 5.6 Hz, J\(_3\) = 1.3 Hz, H5/H5”), 6.20 (t, br, 2H, J = 5.8 Hz, NH\(_2\)(II)), 3.02 (m, 2H, Hb), 2.78 (t, br, J = 5.2 Hz, NH\(_2\)(I)), 2.11 (m, 2H, Ha)

\(^{13}\)C NMR (DMSO\(_{d-6}\)): \(\delta\) 161.5 (C2/C2”), 161.5 (C2’/C6”), 154.4 (C6/C6”), 136.5 (C4/C4”), 129.1 (C4’), 127.7 (C5/C5”), 123.7 (C3/C3”), 122.4 (C3’/C5’), 46.5 (Cb), 46.2 (Ca) \(^*\)split

\(^{15}\)N NMR (DMSO\(_{d-6}\)): \(\delta\) -78.7 N(IV), -128.5 N(III)/N(V), -375.4 N(II), -399.2 N(I)

Coordination shift of terpy N signals vs free ligand in dmso:
\(\Delta N_{\text{III/V}} = -55.5\) ppm
$\Delta N_{IV} = 4.1$ ppm

NMR spectra

$^1H$ NMR

$^{13}C$ NMR
$^1$H-$^{13}$C HMBC NMR

$^1$H-$^{13}$C HMQC NMR
$^1$H-$^{15}$N HMQC NMR
Table S1. Dependence of $k_{obs}$ on temperature for the reaction of [Ru(terpy)(bipy)(H$_2$O)]$^{2+}$ with chloride$^a$

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$10^3 k_{obs}$, s$^{-1}$</th>
<th>$10^3 k_1$, M$^{-1}$s$^{-1}$</th>
<th>$\Delta H^\circ$, kJ mol$^{-1}$</th>
<th>$\Delta S^\circ$, J K$^{-1}$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2</td>
<td>0.53 ± 0.03</td>
<td>0.211</td>
<td>78 ± 2</td>
<td>−46 ± 5</td>
</tr>
<tr>
<td>29.6</td>
<td>1.66 ± 0.03</td>
<td>0.666</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.4</td>
<td>4.94 ± 0.02</td>
<td>1.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>49.3</td>
<td>12.5 ± 0.1</td>
<td>5.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Experimental conditions: [Ru(II)] = 7.1 x 10$^{-5}$ M, [Cl$^-$] = 2.5 M, $I$ = 2.5 M (NaCl).

Table S2. Dependence of $k_{obs}$ on temperature for the reaction of [Ru(terpy)(bipy)(H$_2$O)]$^{2+}$ with thiourea$^a$

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$10^3 k_{obs}$, s$^{-1}$</th>
<th>$10^3 k_2$, M$^{-1}$s$^{-1}$</th>
<th>$\Delta H^\circ$, kJ mol$^{-1}$</th>
<th>$\Delta S^\circ$, J K mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.4</td>
<td>0.18 ± 0.02</td>
<td>0.60</td>
<td>82.9 ± 0.8</td>
<td>−29 ± 2</td>
</tr>
<tr>
<td>30.9</td>
<td>0.35 ± 0.03</td>
<td>1.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36.3</td>
<td>0.62 ± 0.04</td>
<td>2.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43.6</td>
<td>1.33 ± 0.01</td>
<td>4.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>51.8</td>
<td>3.01 ± 0.02</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Experimental conditions: [Ru(II)] = 5.9 x 10$^{-5}$ M, [TU] = 0.3 M, $I$ = 0.1 M (NaNO$_3$).

Table S3. Dependence of $k_{obs}$ on temperature for the reaction of [Ru(terpy)(en)(H$_2$O)]$^{2+}$ with thiourea$^a$

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$10^3 k_{obs}$, s$^{-1}$</th>
<th>$10^3 k_2$, M$^{-1}$s$^{-1}$</th>
<th>$\Delta H^\circ$, kJ mol$^{-1}$</th>
<th>$\Delta S^\circ$, J K mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.8</td>
<td>1.53 ± 0.02</td>
<td>7.64</td>
<td>65 ± 2</td>
<td>−55 ± 6</td>
</tr>
<tr>
<td>16.0</td>
<td>2.76 ± 0.01</td>
<td>13.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.5</td>
<td>4.29 ± 0.05</td>
<td>21.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.5</td>
<td>7.53 ± 0.01</td>
<td>37.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.5</td>
<td>11.2 ± 0.2</td>
<td>56.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.8</td>
<td>16.0 ± 0.2</td>
<td>80.1</td>
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<td></td>
</tr>
</tbody>
</table>

$^a$ Experimental conditions: [Ru(II)] = 1.2 x 10$^{-4}$ M, [TU] = 0.2 M, $I$ = 0.1 M (NaNO$_3$).
Table S4. Dependence of $k_{\text{obs}}$ on temperature for the reaction of $[\text{Ru(terpy)(en)(H}_2\text{O)}]^2+$ with cyanide$^a$

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$10^4 k_{\text{obs}}$, s$^{-1}$</th>
<th>$10^3 k_3$, M$^{-1}$ s$^{-1}$</th>
<th>$\Delta H^\circ$, kJ mol$^{-1}$</th>
<th>$\Delta S^\circ$, J K$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.5</td>
<td>2.28 ± 0.03</td>
<td>4.55</td>
<td>83 ± 2</td>
<td>+2 ± 6</td>
</tr>
<tr>
<td>17.7</td>
<td>4.50 ± 0.01</td>
<td>9.00</td>
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<td></td>
</tr>
<tr>
<td>22.4</td>
<td>7.90 ± 0.01</td>
<td>15.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.7</td>
<td>15.4 ± 0.2</td>
<td>30.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.3</td>
<td>22.4 ± 0.5</td>
<td>44.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Experimental conditions: $[\text{Ru(II)}] = 1.9 \times 10^{-4}$ M, $[\text{CN}^-] = 0.05$ M, pH = 10.5, $I = 1$ M (NaNO$_3$).
Table S5. Summary of computational data for water exchange reactions on complexes of the type [Ru(terpy)(N^N)(OH$_2$)]$^{2+}$. All ZPE corrections were derived from the B3LYP/def2svp-calculations; GS: ground state, TS: transition state

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{\text{tot}}$ (GS) [a.u.]</th>
<th>ZPE (TS) [kcal mol$^{-1}$]</th>
<th>$E_{\text{tot}}$ (TS) [a.u.]</th>
<th>ZPE (TS) [kcal mol$^{-1}$]</th>
<th>$\Delta E_{\text{tot}}$ [kcal mol$^{-1}$]</th>
<th>$\Delta ZPE$ [kcal mol$^{-1}$]</th>
<th>$\Delta E$ [kcal mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[$Ru(terpy)(bipy)(H$_2$O)]$^{2+}$ + H$_2$O</td>
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<td></td>
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</tr>
<tr>
<td>B3LYP/def2svp</td>
<td>-1484.34842</td>
<td>278.14</td>
<td>-1484.31095</td>
<td>277.08</td>
<td>23.51</td>
<td>-1.06</td>
<td>22.46</td>
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<tr>
<td>B3LYP/def2tzvp/B3LYP/def2svp</td>
<td>-1485.87659</td>
<td>278.14</td>
<td>-1485.84246</td>
<td>277.08</td>
<td>21.42</td>
<td>-1.06</td>
<td>20.36</td>
</tr>
<tr>
<td>B3LYP(CPCM)/def2tzvp/B3LYP/def2svp</td>
<td>-1486.07068</td>
<td>278.14</td>
<td>-1486.03999</td>
<td>277.08</td>
<td>19.26</td>
<td>-1.06</td>
<td>18.20</td>
</tr>
<tr>
<td>$\omega$B97XD/def2tzvp/B3LYP/def2svp</td>
<td>-1485.39353</td>
<td>278.14</td>
<td>-1485.35949</td>
<td>277.08</td>
<td>21.36</td>
<td>-1.06</td>
<td>20.30</td>
</tr>
<tr>
<td>$\omega$B97XD(CPCM)/def2tzvp/B3LYP/def2svp</td>
<td>-1485.58665</td>
<td>278.14</td>
<td>-1485.55585</td>
<td>277.08</td>
<td>19.33</td>
<td>-1.06</td>
<td>18.27</td>
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<tr>
<td>$[$Ru(terpy)(en)(H$_2$O)]$^{2+}$ + H$_2$O</td>
<td></td>
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</tr>
<tr>
<td>(H$_2$O$\cdots$H$_2$NR)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>B3LYP/def2svp</td>
<td>-1179.67674</td>
<td>249.64</td>
<td>-1179.64548</td>
<td>248.92</td>
<td>19.61</td>
<td>-0.72</td>
<td>18.89</td>
</tr>
<tr>
<td>B3LYP/def2tzvp/B3LYP/def2svp</td>
<td>-1180.88637</td>
<td>249.64</td>
<td>-1180.85924</td>
<td>248.92</td>
<td>17.03</td>
<td>-0.72</td>
<td>16.31</td>
</tr>
<tr>
<td>B3LYP(CPCM)/def2tzvp/B3LYP/def2svp</td>
<td>-1181.09945</td>
<td>249.64</td>
<td>-1181.07502</td>
<td>248.92</td>
<td>15.32</td>
<td>-0.72</td>
<td>14.60</td>
</tr>
<tr>
<td>$\omega$B97XD/def2tzvp/B3LYP/def2svp</td>
<td>-1180.52312</td>
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<td>248.92</td>
<td>17.53</td>
<td>-0.72</td>
<td>16.81</td>
</tr>
<tr>
<td>$\omega$B97XD(CPCM)/def2tzvp/B3LYP/def2svp</td>
<td>-1180.73480</td>
<td>249.64</td>
<td>-1180.70959</td>
<td>248.92</td>
<td>15.82</td>
<td>-0.72</td>
<td>15.10</td>
</tr>
<tr>
<td>$[$Ru(terpy)(en)(H$_2$O)]$^{2+}$ + H$_2$O</td>
<td></td>
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</tr>
<tr>
<td>(H$_2$O$\cdots$H$_2$O)</td>
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</tr>
<tr>
<td>B3LYP/def2svp</td>
<td>-1179.68161</td>
<td>249.84</td>
<td>-1179.64548</td>
<td>248.92</td>
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<td>-0.92</td>
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<tr>
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<td>-1180.85924</td>
<td>248.92</td>
<td>20.23</td>
<td>-0.92</td>
<td>19.30</td>
</tr>
<tr>
<td>B3LYP(CPCM)/def2tzvp/B3LYP/def2svp</td>
<td>-1181.10494</td>
<td>249.84</td>
<td>-1181.07502</td>
<td>248.92</td>
<td>18.77</td>
<td>-0.92</td>
<td>17.85</td>
</tr>
<tr>
<td>$\omega$B97XD/def2tzvp/B3LYP/def2svp</td>
<td>-1180.52738</td>
<td>249.84</td>
<td>-1180.49519</td>
<td>248.92</td>
<td>20.20</td>
<td>-0.92</td>
<td>19.28</td>
</tr>
<tr>
<td>$\omega$B97XD(CPCM)/def2tzvp/B3LYP/def2svp</td>
<td>-1180.73959</td>
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<td>-1180.70959</td>
<td>248.92</td>
<td>18.83</td>
<td>-0.92</td>
<td>17.91</td>
</tr>
<tr>
<td>Method</td>
<td>E\text{tot} (GS) [a.u.]</td>
<td>ZPE (TS) [kcal mol(^{-1})]</td>
<td>E\text{tot} (TS) [a.u.]</td>
<td>ZPE (TS) [kcal mol(^{-1})]</td>
<td>(\Delta E\text{tot} ) [kcal mol(^{-1})]</td>
<td>(\Delta ZPE ) [kcal mol(^{-1})]</td>
<td>(\Delta E ) [kcal mol(^{-1})]</td>
</tr>
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<td>--------------------------</td>
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</tr>
<tr>
<td>B3LYP/def2svp</td>
<td>-1258.22194</td>
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<td>-1258.18508</td>
<td>284.40</td>
<td>23.13</td>
<td>-0.70</td>
<td>22.43</td>
</tr>
<tr>
<td>B3LYP/def2tzvp//B3LYP/def2svp</td>
<td>-1259.51685</td>
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<td>284.40</td>
<td>21.50</td>
<td>-0.70</td>
<td>20.80</td>
</tr>
<tr>
<td>B3LYP(CPCM)/def2tzvp//B3LYP/def2svp</td>
<td>-1259.72423</td>
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<td>-1259.69428</td>
<td>284.40</td>
<td>18.79</td>
<td>-0.70</td>
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</tr>
<tr>
<td>ωB97XD/def2tzvp//B3LYP/def2svp</td>
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<td>-1259.10210</td>
<td>284.40</td>
<td>20.98</td>
<td>-0.70</td>
<td>20.28</td>
</tr>
<tr>
<td>ωB97XD(CPCM)/def2tzvp//B3LYP/def2svp</td>
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<td>285.10</td>
<td>-1259.31246</td>
<td>284.40</td>
<td>18.36</td>
<td>-0.70</td>
<td>17.66</td>
</tr>
</tbody>
</table>
Figure S1. ESI-MS spectra of [Ru(terpy)(bipy)(H₂O)]²⁺.
Figure S2. ESI-MS spectra of $[\text{Ru(terpy)(en)}(\text{N}_2)]^{2+}$. 
Figure S3. Plot of $k_{\text{obs}}$ versus thiourea concentration for the reaction of [Ru(II)(terpy)(bipy)(H_2O)]^{2+} with thiourea. Experimental conditions: [Ru(II)] = 5.9 x 10^{-5} \text{ M}, I = 0.1 \text{ M (NaNO_3)}, T = 36.3 ^\circ \text{C}.

Figure S4. Plot of $k_{\text{obs}}$ versus thiourea concentration for the reaction of [Ru(II)(terpy)(en)(H_2O)]^{2+} with thiourea. Experimental conditions: [Ru(II)] = 1.2 x 10^{-4} \text{ M}, I = 0.1 \text{ M (NaNO_3)}, T = 25 ^\circ \text{C}.
Figure S5. Plot of $k_{obs}$ versus cyanide concentration for the reaction of $[\text{Ru}^{II}(\text{terpy})(\text{en})(\text{H}_2\text{O})]^2+$ with cyanide. Experimental conditions: $[\text{Ru(II)}] = 1.9 \times 10^{-4}$ M, pH = 10.25, $I = 1$ M (NaNO$_3$), $T = 25$ °C.

$k_{obs} = (2.91 \pm 0.05) \times 10^{-2}[\text{CN}^-]$
Figure S6. 54.24 MHz $^{17}$O-NMR spectra of 0.03 M [Ru$^{III}$(terpy)(en)(H$_2$O)]$^{2+}$ in aqueous solution containing 30% (v/v) of 10%-enriched $^{17}$OH$_2$ and 0.1 M MnSO$_4$. The spectra were recorded in the temperature range from 313.2 to 372.9 K and are the result of 30k (30720) scans using a relaxation delay of 0.15 s, an acquisition time of 0.1 s and a pulse width of 16.7 µs in the quadratic detection mode.