Supporting Information for

Photoisomerization and Thermal isomerization of Ruthenium Aqua Complexes with Chloro Substituted Asymmetric Bidentate Ligands

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Figure S1A $^1$H NMR spectrum of 2-(2’-pyridyl)-4-chloroquinoline in CDCl$_3$.

Figure S1B $^{13}$C NMR spectrum of 2-(2’-pyridyl)-4-chloroquinoline in CDCl$_3$. 
Figure S2A. $^1$H NMR spectrum of $p$-[2Cl]Cl in CD$_3$OD (10%) and CDCl$_3$ (90%).

Figure S2B. $^{13}$C NMR spectrum of $p$-[2Cl]Cl in CD$_3$OD (10%) and CDCl$_3$ (90%).
Figure S3A. $^1$H NMR spectrum of $p$-[3Cl]Cl in CD$_3$OD (10%) and CDCl$_3$ (90%).

Figure S3B. $^{13}$C NMR spectrum of $p$-[3Cl]Cl in CD$_3$OD (10%) and CDCl$_3$ (90%).
Figure S4A. $^1$H NMR spectrum of $\textit{p-}[\text{4Cl}]\text{Cl}$ in CD$_3$OD (10%) and CDCl$_3$ (90%).

Figure S4B. $^{13}$C NMR spectrum of $\textit{p-}[\text{4Cl}]\text{Cl}$ in CD$_3$OD (10%) and CDCl$_3$ (90%).
Figure S5A. $^1$H NMR spectrum of $p$-[2H$_2$O]Cl$_2$ in D$_2$O (80%) and CD$_3$OD (20%).

Figure S5B. $^{13}$C NMR spectrum of $p$-[2H$_2$O]Cl$_2$ in D$_2$O (80%) and CD$_3$OD (20%).
Figure S6A. $^1$H NMR spectrum of $p$-[3H$_2$O]Cl$_2$ in D$_2$O.
Figure S7A. $^1$H NMR spectrum of $p$-[4H$_2$O]Cl$_2$ in D$_2$O.

Figure S7B. $^{13}$C NMR spectrum of $p$-[4H$_2$O]Cl$_2$ in D$_2$O.
| compounds | $p$-[2Cl]([PF$_6$]) | $p$-[3Cl]([BF$_4$]) | $p$-[4Cl]([PF$_6$]) · EtOH | $p$-[2OH]$_2$([PF$_6$]) · 2H$_2$O | $p$-[3OH]$_2$([CF$_3$SO$_3$]) · H$_2$O | $p$-[4OH]$_2$([NO$_3$]) · 2H$_2$O |
|-----------|---------------------|---------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| empirical formula | RuPF$_6$Cl$_2$N$_5$C$_{29}$H$_{20}$ | RuBF$_4$Cl$_2$N$_5$C$_{29}$H$_{20}$ | RuPF$_6$Cl$_2$N$_5$C$_{29}$H$_{20}$ | RuP$_2$F$_{12}$Cl$_2$N$_5$O$_3$C$_{31}$H$_{26}$ | RuS$_2$F$_6$Cl$_2$N$_5$O$_8$C$_{31}$H$_{26}$ | RuClN$_7$O$_9$C$_{29}$H$_{26}$ |
| fw | 755.45 | 697.30 | 801.51 | 919.01 | 909.19 | 753.09 |
| radiation | Mo Kα | Mo Kα | Mo Kα | Mo Kα | Mo Kα | Mo Kα |
| crystal system | monoclinic | triclinic | monoclinic | triclinic | monoclinic | triclinic |
| space group | $P2_1/c$ | $P1$ | $P2_1/c$ | $P1$ | $P2_1/c$ | $P1$ |
| $a$, Å | 20.524(4) | 7.7286(12) | 8.7151(13) | 11.910(2) | 16.770(6) | 8.599(3) |
| $b$, Å | 8.2372(14) | 12.0747(18) | 13.061(2) | 11.910(3) | 17.343(7) | 8.943(3) |
| $c$, Å | 25.346(5) | 14.592(2) | 27.254(4) | 18.237(6) | 11.916(5) | 20.080(6) |
| $α$, deg | 90 | 81.760(2) | 90 | 102.237(5) | 90 | 77.361(3) |
| $β$, deg | 137.909(3) | 89.511(2) | 94.409(2) | 97.412(5) | 101.073(6) | 79.622(3) |
| $γ$, deg | 90 | 77.947(2) | 90 | 111.015(3) | 90 | 89.260(4) |
| $V$, Å$^3$ | 2872.2(9) | 1317.7(4) | 3093.1(8) | 1739.7(9) | 3401(2) | 1481.6(7) |
| $Z$ | 4 | 2 | 4 | 2 | 4 | 2 |
| $μ$, mm$^{-1}$ | 0.858 | 0.858 | 0.804 | 0.724 | 0.755 | 0.682 |
| $T$, K | 293 | 100 | 100 | 100 | 100 | 100 |
| $d_{cal}$, g/cm$^3$ | 1.747 | 1.7574 | 1.721 | 1.7504 | 1.776 | 1.643 |
| $T_{min}$, $T_{max}$ | 0.4333, 1 | 0.647301, 1 | 0.427, 1 | 0.620, 0.986 | 0.9493, 0.9870 | 0.623220, 1 |
| $N_{ref}$ | 6426 | 12164 | 7136 | 7682 | 7623 | 5319 |
| $R[F^2 > 2σ(F^2)]$ | 0.0483 | 0.0312 | 0.0709 | 0.0628 | 0.0843 | 0.0707 |
| $wR[F^2 > 2σ(F^2)]$ | 0.1080 | 0.0728 | 0.1983 | 0.1530 | 0.1839 | 0.2041 |
| GOF | 0.972 | 1.0393 | 0.907 | 1.0143 | 0.930 | 1.080 |
Figure S8. Absorption spectra of ruthenium complexes having R-pyqu ligands in methanol. $p$-1Cl (black), $p$-2Cl (red), $p$-3Cl (blue), and $p$-4Cl (green).
Figure S9 DFT optimized structures of $p$-$nH_2O$ ($n = 1$-$4$), which were optimized at the B3LYP level of DFT using LanL2DZ basis set in Gaussian 09.
Figure S10 Frontier molecular orbitals of a fully optimized $p$-H$_2$O. The structure was obtained by using B3LYP level of DFT and LANL2DZ basis set in Gaussian 09.
Figure S10 (Continued)

128 (LUMO) -2.911 eV
129 (LUMO+1) -2.865 eV
130 (LUMO+2) -2.637 eV

131 (LUMO+3) -1.789 eV
132 (LUMO+4) -1.747 eV
133 (LUMO+5) -1.700 eV

134 (LUMO+6) -1.558 eV
135 (LUMO+7) -0.919 eV
136 (LUMO+8) -0.794 eV
Figure S11 Frontier molecular orbitals of a fully optimized $p$-$2\text{H}_2\text{O}$. The structure was obtained by using B3LYP level of DFT and LANL2DZ basis set in Gaussian 09.
Figure S11 (Continued)

131 (LUMO) -3.082 eV
132 (LUMO+1) -2.862 eV
133 (LUMO+2) -2.628 eV

134 (LUMO+3) -1.974 eV
135 (LUMO+4) -1.881 eV
136 (LUMO+5) -1.698 eV

137 (LUMO+6) -1.639 eV
138 (LUMO+7) -1.132 eV
139 (LUMO+8) -0.917 eV
Figure S12 Frontier molecular orbitals of a fully optimized $p$-$3\text{H}_2\text{O}$. The structure was obtained by using B3LYP level of DFT and LANL2DZ basis set in Gaussian 09.
Figure S12 (Continued)

131 (LUMO) -3.018 eV  132 (LUMO+1) -2.922 eV  133 (LUMO+2) -2.660 eV

134 (LUMO+3) -1.979 eV  135 (LUMO+4) -1.851 eV  136 (LUMO+5) -1.720 eV

137 (LUMO+6) -1.631 eV  138 (LUMO+7) -0.940 eV  139 (LUMO+8) -0.841 eV
Figure S13 Frontier molecular orbitals of a fully optimized \( p-4\text{H}_2\text{O} \). The structure was obtained by using B3LYP level of DFT and LANL2DZ basis set in Gaussian 09.
Figure S13 (Continued)

131 (LUMO) -3.032 eV
132 (LUMO+1) -2.921 eV
133 (LUMO+2) -2.658 eV
134 (LUMO+3) -1.996 eV
135 (LUMO+4) -1.817 eV
136 (LUMO+5) -1.718 eV
137 (LUMO+6) -1.599 eV
138 (LUMO+7) -0.937 eV
139 (LUMO+8) -0.833 eV
Figure S14 The calculated absorption spectra of \( p-\text{H}_2\text{O} \) (A), \( p-\text{H}_2\text{O} \) (B), \( p-\text{H}_2\text{O} \) (C), and \( p-\text{H}_2\text{O} \) (D) by using the time-dependent DFT calculations in PCM method (solvent: water). The singlet excitations, simulated with Gaussian functions, are shown as vertical bars with heights equal to oscillator strength.
**Table S2.** Selected list of TD-DFT energies of \( p-1\text{H}_2\text{O} \) (in water)

| Excited State | \( \lambda / \text{nm} \) | \( f \) | Major contributions |
|---------------|-----------------|------|-------------------|
| 6             | 462.35          | 0.1392 | H-1->LUMO (13%), H-1->L+1 (49%), HOMO->L+2 (28%) |
| 27            | 309.80          | 0.1606 | H-5->LUMO (12%), H-4->L+1 (16%), H-3->L+2 (10%), H-2->L+6 (20%), H-1->L+6 (10%) |
| 30            | 308.06          | 0.5005 | H-5->LUMO (34%), H-5->L+1 (12%), H-4->L+1 (12%) |
| 31            | 305.56          | 0.3438 | H-5->L+1 (46%), H-4->L+1 (12%) |
| 32            | 299.85          | 0.0589 | H-2->L+6 (21%), H-1->L+6 (35%), HOMO->L+6 (16%) |
| 35            | 278.33          | 0.0703 | H-5->L+2 (53%), HOMO->L+7 (25%) |
| 36            | 277.91          | 0.0524 | H-5->L+2 (31%), H-2->L+11 (14%), HOMO->L+7 (38%) |
| 39            | 262.53          | 0.372  | H-3->L+3 (14%), H-3->L+4 (39%), HOMO->L+9 (10%) |
| 42            | 257.37          | 0.0828 | H-3->L+3 (63%), H-3->L+4 (14%), HOMO->L+9 (11%) |
| 44            | 253.20          | 0.2267 | H-6->LUMO (33%), H-6->L+1 (17%), H-2->L+7 (16%) |

**Table S3.** Selected list of TD-DFT energies of \( p-2\text{H}_2\text{O} \) (in water)

| Excited State | \( \lambda / \text{nm} \) | \( f \) | Major contributions |
|---------------|-----------------|------|-------------------|
| 3             | 503.42          | 0.0448 | H-1->LUMO (44%), H-1->L+1 (48%) |
| 5             | 475.58          | 0.1123 | H-2->L+1 (14%), H-1->LUMO (45%), H-1->L+1 (31%) |
| 22            | 322.78          | 0.0515 | H-5->LUMO (16%), H-1->L+5 (36%) |
| 25            | 315.78          | 0.3942 | H-4->LUMO (33%), H-1->L+3 (13%) |
| 27            | 311.38          | 0.0986 | H-4->L+1 (36%), H-2->L+4 (23%) |
| 28            | 309.63          | 0.1885 | H-5->L+1 (20%), H-4->L+1 (39%), H-2->L+5 (11%) |
| 29            | 306.79          | 0.1432 | H-5->L+1 (21%), H-2->L+6 (29%), H-1->L+6 (23%) |
| 30            | 301.97          | 0.2108 | H-5->L+1 (16%), H-2->L+5 (60%), H-2->L+6 (12%) |
| 35            | 277.70          | 0.1264 | H-5->L+2 (82%) |
| 37            | 271.89          | 0.0579 | H-6->LUMO (46%), HOMO->L+8 (16%) |
| 39            | 268.57          | 0.0749 | H-7->LUMO (16%), H-6->LUMO (25%), H-3->L+3 (20%), H-3->L+4 (11%) |
| 42            | 259.54          | 0.0658 | H-3->L+4 (32%), HOMO->L+9 (41%) |
| 47            | 251.02          | 0.1615 | H-4->L+3 (15%), H-3->L+4 (20%), H-1->L+9 (26%) |
| 48            | 250.12          | 0.0839 | H-7->L+1 (36%), H-2->L+8 (44%) |
Table S4. Selected list of TD-DFT energies of $p\text{-}3\text{H}_2\text{O}$ (in water)

| Excited State | $\lambda$/nm | f     | Major contributions                                      |
|---------------|--------------|-------|----------------------------------------------------------|
| 5             | 475.43       | 0.1669| H-2->L+1 (31%), H-1->LUMO (59%)                          |
| 27            | 311.19       | 0.2242| H-5->LUMO (22%), H-4->LUMO (14%), H-4->L+1 (36%)         |
| 28            | 309.83       | 0.1149| H-4->L+1 (26%), H-2->L+6 (20%), H-1->L+6 (12%)           |
| 29            | 308.59       | 0.373 | H-5->LUMO (18%), H-4->L+1 (13%), H-2->L+6 (10%)          |
| 31            | 305.61       | 0.3961| H-5->L+1 (61%)                                          |
| 35            | 278.02       | 0.12  | H-5->L+2 (60%), H-4->L+2 (26%)                          |
| 41            | 263.87       | 0.3776| H-3->L+3 (23%), H-3->L+4 (30%)                          |
| 44            | 256.74       | 0.0848| H-7->LUMO (28%), H-4->L+3 (30%), H-1->L+9 (15%)          |
| 46            | 252.65       | 0.2194| H-6->L+1 (20%), H-5->L+3 (19%), H-2->L+7 (23%)           |
| 47            | 252.13       | 0.061 | H-6->L+1 (19%), H-5->L+3 (38%), H-4->L+3 (23%)           |

Table S5. Selected list of TD-DFT energies of $p\text{-}4\text{H}_2\text{O}$ (in water)

| Excited State | $\lambda$/nm | f     | Major contributions                                      |
|---------------|--------------|-------|----------------------------------------------------------|
| 5             | 476.40       | 0.1841| H-2->L+1 (31%), H-1->LUMO (62%)                          |
| 27            | 310.01       | 0.3371| H-5->LUMO (46%), H-1->L+6 (10%)                          |
| 28            | 307.83       | 0.3976| H-4->L+1 (44%), H-2->L+5 (11%), H-1->L+5 (10%)           |
| 29            | 306.87       | 0.1609| H-4->L+1 (14%), H-2->L+6 (26%)                          |
| 30            | 303.38       | 0.0903| H-5->L+1 (89%)                                          |
| 32            | 298.74       | 0.0594| H-2->L+6 (20%), H-1->L+6 (28%), HOMO->L+6 (27%)          |
| 35            | 278.06       | 0.1136| H-4->L+2 (79%)                                          |
| 39            | 266.32       | 0.4272| H-6->LUMO (12%), H-3->L+3 (51%)                          |
| 40            | 265.54       | 0.0656| H-6->LUMO (83%)                                          |
| 45            | 252.43       | 0.2579| H-6->L+1 (42%), H-2->L+7 (33%)                          |
| 46            | 251.63       | 0.062 | H-7->LUMO (11%), H-3->L+4 (71%)                          |
Figure S15. Energy level diagram of molecular orbitals of $d\text{H}_2\text{O}$ (n= 1-4). The energy level of Ru-N antibonding $d\sigma^*$ orbitals (LUMO+7) are marked in red.
### Table S6. Energies of optimized distal and proximal isomers (in water)

| Complex | Proximal isomer / Hartree | Distal isomer / Hartree | Differences / kcal mol⁻¹ |
|---------|---------------------------|-------------------------|-------------------------|
| 1H₂O    | -1561.059453              | -1561.055725            | -2.34                   |
| 2H₂O    | -1575.389636              | -1575.389304            | -0.21                   |
| 3H₂O    | -1575.404388              | -1575.400461            | -2.46                   |
| 4H₂O    | -1575.403173              | -1575.399308            | -2.43                   |
