Electronic Supplementary Material (ESI) for Dalton Transactions.


# A ratiometric sensor for DNA based on a dual emission Ru(dppz) light-switch complex Supplementary information

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## S1. COMPUTATIONAL DETAILS

### S1.1. General Computational Procedure

Density functional theory (DFT) calculations were performed using Gaussian09, version C.01.[S1] Gaussian was compiled using Portland compiler v.8 with Gaussian-supplied versions of BLAS and ATLAS.[S2] The B3LYP[S3] functional was used throughout with the 6-311G** basis set[S4] on all C, N, H, and O. A Stuttgart-Dresden pseudopotential[S5] was used on Ru throughout. This computational procedure was found to give good correlation with experiment in previous work.[S6,S7] The starting atomic coordinates of complex 1 are based on previous, similar systems,[S7] with DMSP based on the crystal structure of the individual ligand. All the calculations performed on these systems were done using water as the solvent via a polarizable continuum model (PCM)[S8] using the standard parameters as supplied by Gaussian. Visualization was done by Gausssum v2.5[S9] for the TD-DFT spectra, Jmol[S10] and Povray[S11] for the geometries. Finally, supporting information was created using in-houe developed software based on the OpenEye toolkit.[S12]

The following procedure was followed. First, complexes [**1**] and [**2**] were optimized in their singlet and triplet ground states. Harmonic frequencies were calculated upon convergence. No imaginary frequencies were found, confirming the structure as a minimum. From the optimized S0 geometry a number of calculations were performed. First, a time-dependent DFT[S13] calculation was performed with 100 states included to obtain the absorption spectrum. Its absorption spectrum and a breakdown of the states is given in sections S4.3 and S4.5.

From the $S_0$ geometry for [**1**] geometry optimizations for the $S_1$ and $S_2$ states were performed. Unfortunately, due to the excessive computational cost, the calculation of frequencies upon convergence was not feasible. These optimizations allow us to calculate emission frequencies (ignoring vibrational contributions) from these states. To get more accurate emission frequencies the electronic (fast) reorganization of the solvent during emission needs to be included (PCM-SS method).[S14] However, these calculations (using the procedure outlined in the Gaussian manual) lead to unphysical results (negative excitation frequencies), presumably due to root crossing. Therefore, all emission frequencies reported are based on the solvent field for the excited state (PCM-LR method).[S14]

From the $T_1$ structure, the $T_2$ state was optimized. Again, emission frequencies are reported in the PCM-LR formalism for the same reasons as above. Also, again no frequencies are available for reasons already stated above.

For [**2**] similar calculations were attempted for $S_1$, $S_2$, and $T_2$ from equivalent starting positions. Unfortunately, due to root crossings these calculations were not successful.

During the course of this project it was found that there are a number of different conformers of [**1**] that could be populated at room temperature. These conformers all differ in the orientation of the OMe groups on top of the DMSP ligand. Our discussion is based upon the conformer for which we have the most excited state information (which is not the lowest conformer, unfortunately). However, it should be noted that the basic conclusions drawn do not differ between different conformers. For example for the lowest energy conformer (whose Gibbs Energy is lower by 2.5 kJ $mol^{-1}$ the $S_0$ to $T_1$ splitting corresponds to a wave length of 639.64 nm, whereas 637 nm is found for the conformer reported on in the main text. Similarly, the excited singlet states (in the $S_0$ geometry) vary in the relative amount of charge transfer on the DMSP vs the dppz ligand. However, the general characteristics are similar to the conformer reported in the main paper with the exception that it is now $S_5$ and $S_6$ that are near-degenerate and $S_5$ has the largest amount of charge transfer onto dppz rather than $S_7$ (See figure S1). These calculations are available upon request from the authors. The optimized structure for the $S_0$ and $T_1$ states of the lowest energy isomer are given at the end of the SI.

### S1.2. Computational References

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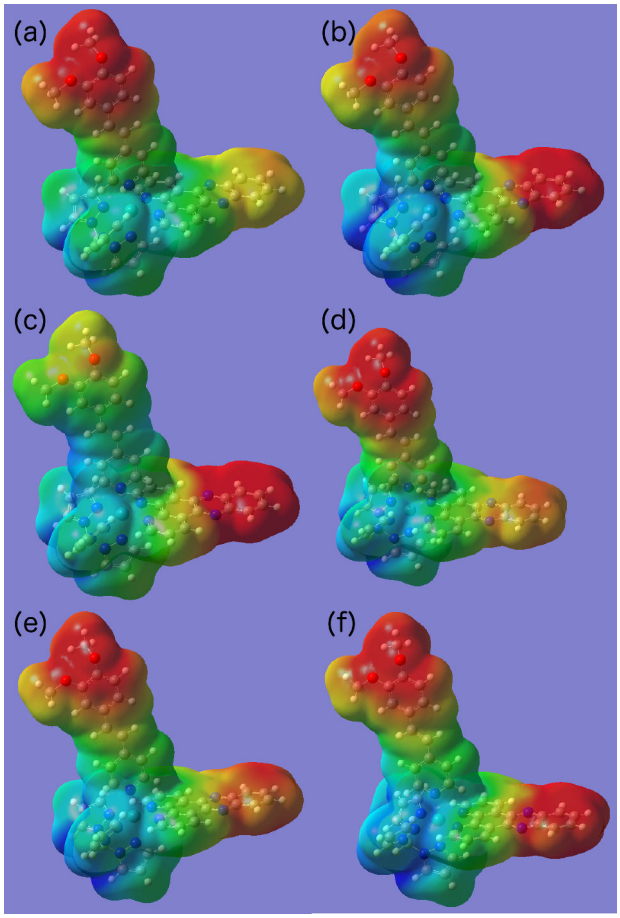


FIG. S1. Mapped electrostatic potential energy surfaces of some states of lowest-energy conformation of [**1**]. All geometries are the $S_0$ geometry. Panel (a): $S_0$. Panel (b): $S_1$. Panel (c): $S_5$. Panel (d): $S_6$. Panel (e): $S_7$. Panel (f): $S_8$.


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## S2. EXPERIMENTAL DETAILS

### S2.1. Materials and Instrumentation

All chemicals and solvents were purchased from commercial sources and were used as supplied unless otherwise stated. $^1$H NMR spectra were carried out on a Bruker AV2-400 or Bruker DRX500 machine, working in Fourier transform mode. ES mass spectra were recorded on a Micromass LCT ES-TOF machine. CHN analysis was determined using a Perkin Elmer 2400 CHNS/O Series II Elemental Analyser. All UV-Visible spectra were recorded on a thermo regulated Varian-Carey Bio-300 UV-Visible spectrometer, using quartz cells of 10 mm path length at 25°C. Spectra were baseline corrected using Cary Win UV software and were diluted accordingly to give readings between 0.2 and 1.0 absorbance units. Luminescence spectra were recorded on a thermo regulated Jobin-Yvon FluoroMax-3 spectrophotometer operating in luminescence wavelength scan mode at 25°C, with excitation and emission slit widths at 5 nm. DNA titrations and viscosity experiments were carried out using previously reported procedures.[1]

### S2.2. References Materials and Instrumentation

1. Foxon, S. P., Metcalfe, C., Adams, H., Webb, M., & Thomas, J. A. (2007). Electrochemical and Photophysical Properties of DNA Metallo-intercalators Containing the Ruthenium(II) Tris(1-pyrazolyl)methane Unit. Inorganic Chemistry, 46(2), 409416.

## S3. ADDITIONAL EXPERIMENTAL DATA I

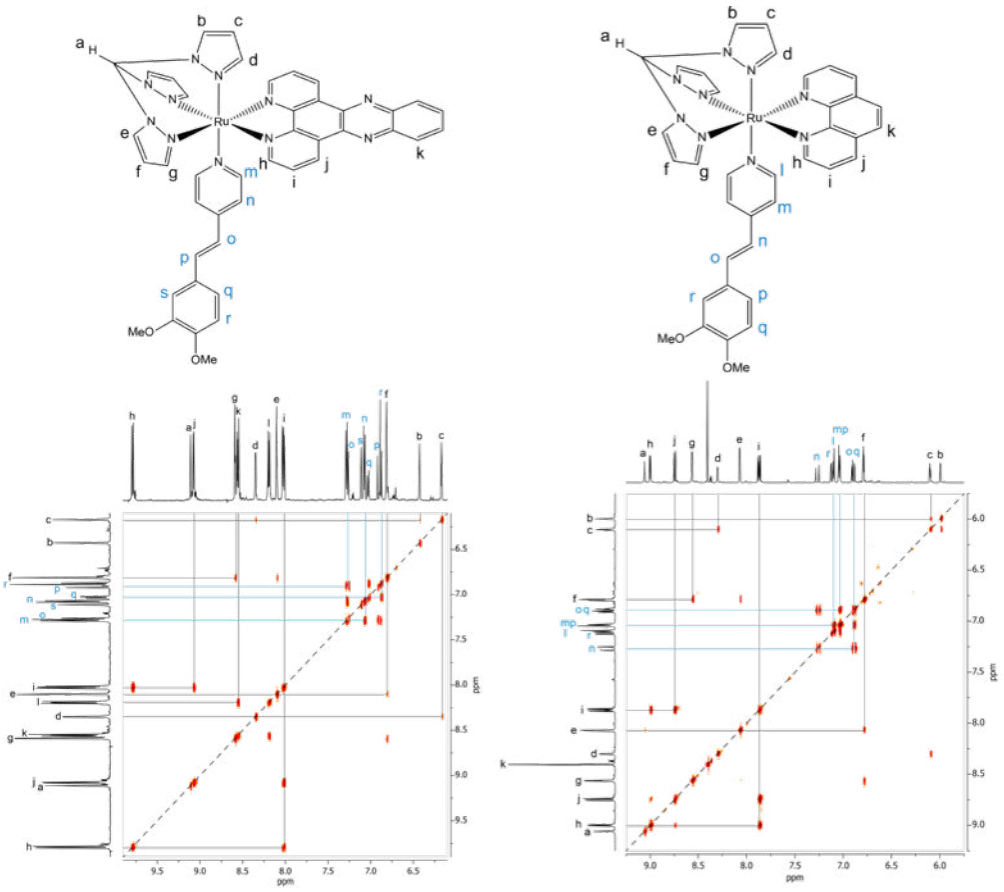



FIG. S2. $^{1}$H NMR COSY of [**1**](PF6)$_2$ (left) and [**2**](PF6)$_2$ (right) in MeCN-d$^3$.

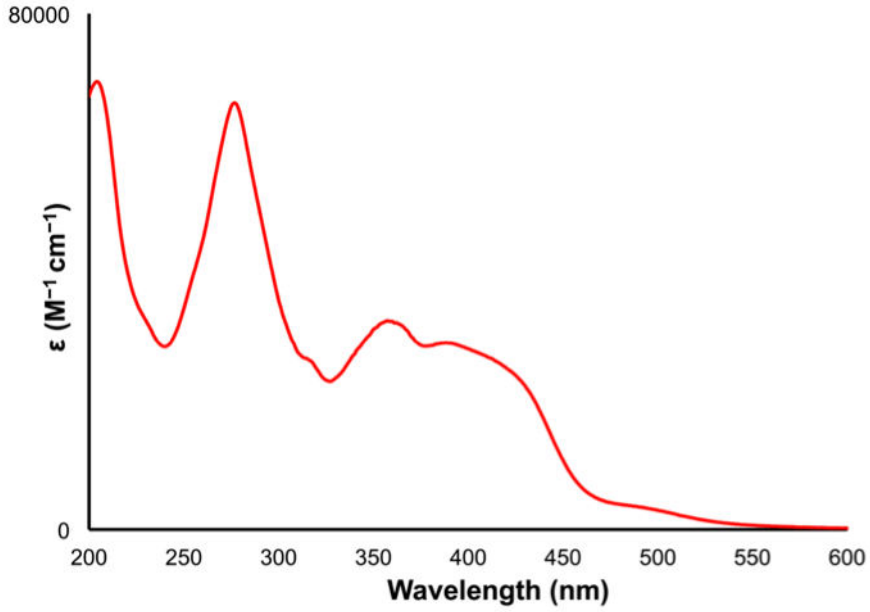



FIG. S3. UV-Visible spectrum of [**1**]$(PF_6)_2$ in acetonitrile

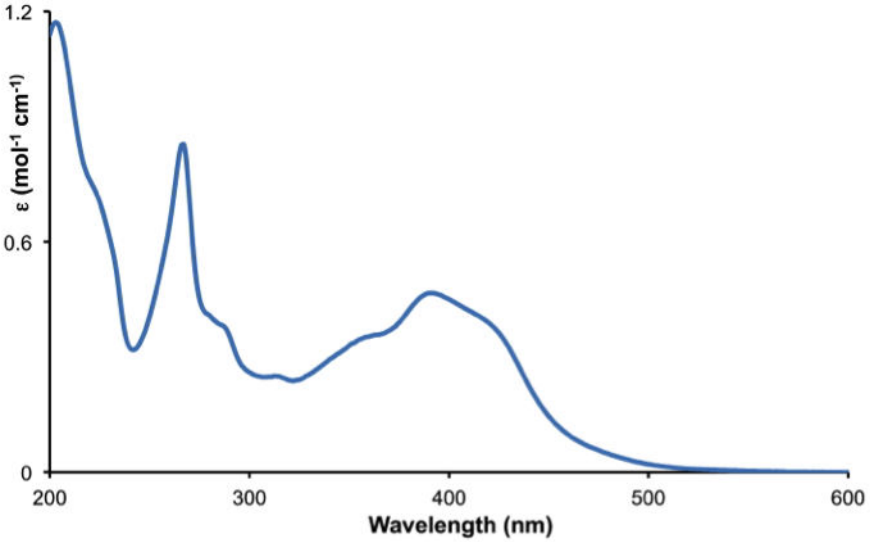



FIG. S4. UV-Visible spectrum of [**2**]$(PF_6)_2$ in acetonitrile

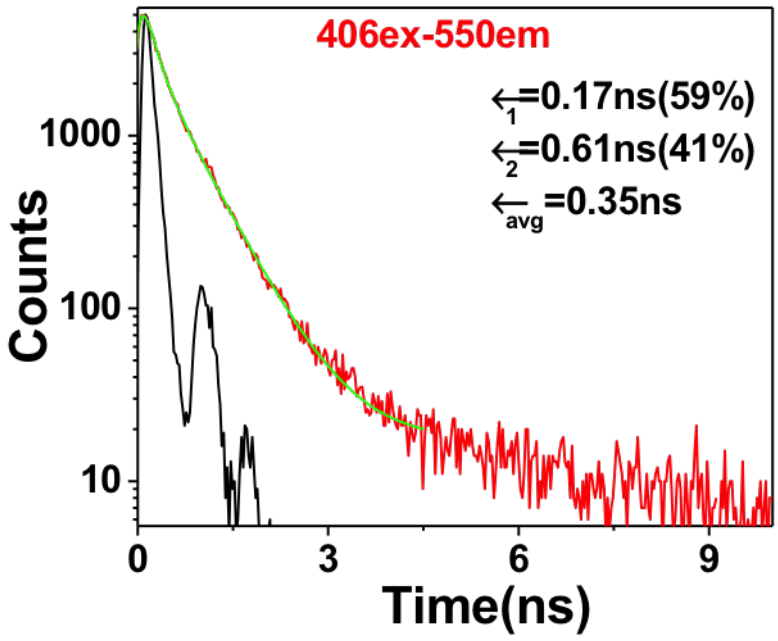



FIG. S5. Emission lifetime of complex $[\mathbf{1}](PF_6)_2$ in air equilibrated HPLC (extra pure) grade acetonitrile. Laser source with $\lambda_{ex}$ = 406 nm and $\lambda_{ex}$ = 550 nm

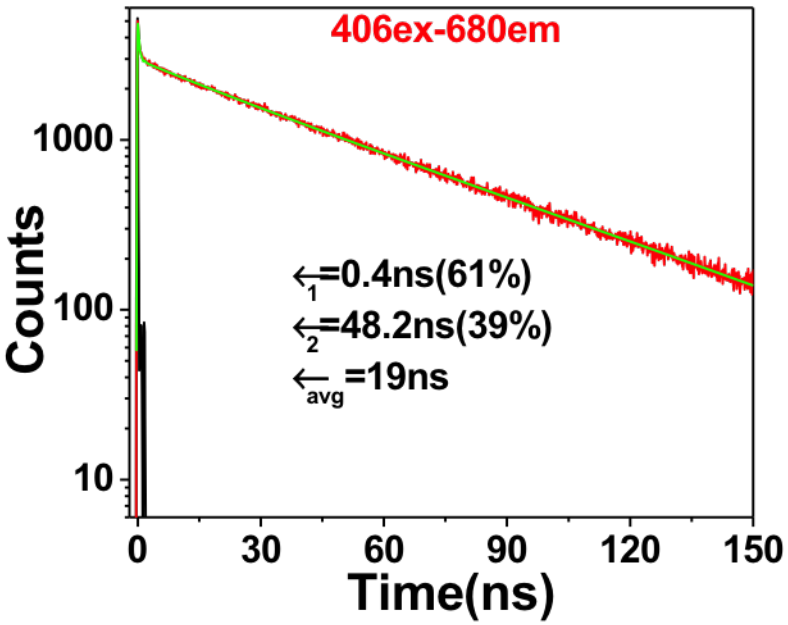



FIG. S6. Emission lifetime of complex $[\mathbf{1}](PF_6)_2$ in air equilibrated HPLC (extra pure) grade acetonitrile. Laser source with $\lambda_{ex}$ = 406 nm and $\lambda_{ex}$ = 680 nm

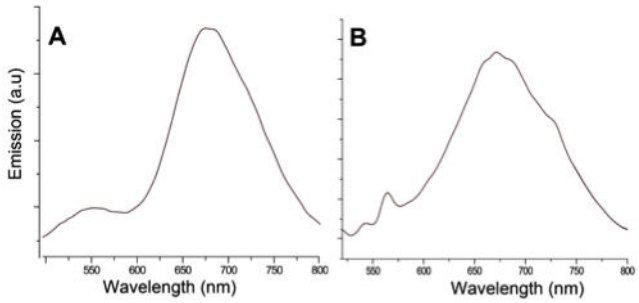



FIG. S7. Comparison of steady-state emission of complex **1** when photo-excited at (A) 410 nm and (B) 500 nm

## S4. ADDITIONAL COMPUTATIONAL DATA

### S4.1. DMSP ($S_0$)

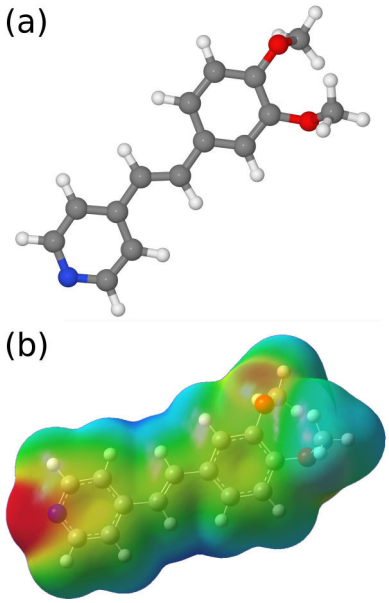



FIG. S8. Structure of DMSP in the $S_0$ state [panel (a)] with the associated electrostatic potential, mapped onto the electron density at $\rho = 0.004$ [panel (b)]. Red corresponds to a charge of -0.05 and blue corresponds to a charge of +0.05.

| | | |
|---|---|---|
| SMILES | : | n1ccc(cc1)/C=C/c1cc(c(cc1)OC)OC |
| Formula | : | $C_{15}H_{15}NO_2$ |
| Charge | : | 0 |
| Multiplicity | : | 1 |
| Energy | : | -785.989278682 a.u. |
| Number of imaginary frequencies | : | 0 |

#### *S4.1.1. Cartesian Co-ordinates (XYZ format)*

33

| | | | |
|---|---|---|---|
| N | -6.22685 | 0.43391 | 0.11332 |
| C | -5.80031 | -0.81015 | -0.13720 |
| C | -5.27658 | 1.36352 | 0.29960 |
| C | -4.45915 | -1.16881 | -0.21066 |
| H | -6.57032 | -1.56181 | -0.28740 |
| C | -3.91378 | 1.10808 | 0.24696 |
| H | -5.62752 | 2.37132 | 0.50331 |
| C | -3.46362 | -0.19764 | -0.01699 |
| H | -4.18755 | -2.19772 | -0.41788 |
| H | -3.22008 | 1.92276 | 0.41227 |
| C | -2.05495 | -0.58698 | -0.09758 |
| H | -1.89120 | -1.64216 | -0.29570 |
| C | -0.99594 | 0.23141 | 0.04770 |
| H | -1.17225 | 1.28562 | 0.24269 |
| C | 0.41915 | -0.13576 | -0.02738 |
| C | 1.38132 | 0.87382 | 0.14177 |
| C | 0.87623 | -1.44345 | -0.27108 |

| | | | |
|---|---|---|---|
| C | 2.74493 | 0.60557 | 0.08750 |
| H | 1.07431 | 1.89880 | 0.31853 |
| C | 2.23488 | -1.72048 | -0.31464 |
| H | 0.17308 | -2.25420 | -0.41533 |
| C | 3.18367 | -0.71200 | -0.12912 |
| H | 2.59089 | -2.72899 | -0.49006 |
| O | 4.51573 | -1.03295 | -0.21022 |
| O | 3.63172 | 1.63856 | 0.28820 |
| C | 4.38254 | 2.03209 | -0.87601 |
| H | 3.70729 | 2.37532 | -1.66548 |
| H | 5.02142 | 2.85561 | -0.56070 |
| H | 4.99608 | 1.20807 | -1.24569 |
| C | 5.26275 | -0.90163 | 1.01525 |
| H | 6.28224 | -1.20335 | 0.78050 |
| H | 5.25310 | 0.12893 | 1.37392 |
| H | 4.85211 | -1.56608 | 1.78115 |

### S4.2. DMSP ($S_1$)

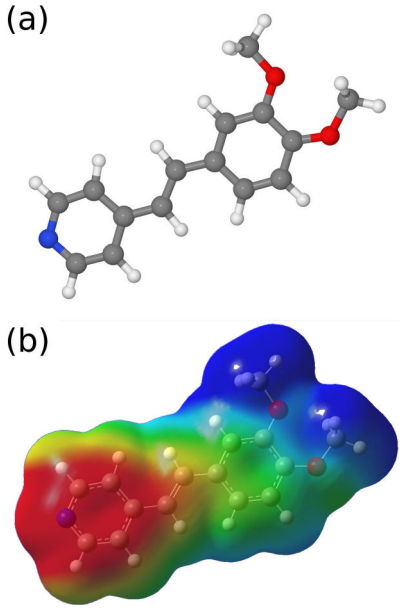



FIG. S9. Structure of DMSP in the $S_1$ state [panel (a)] with the associated electrostatic potential, mapped onto the electron density at $\rho = 0.004$ [panel (b)]. Red corresponds to a charge of -0.05 and blue corresponds to a charge of +0.05.

| | | |
|---|---|---|
| SMILES | : | n1ccc(cc1)/C=C/c1cc(c(cc1)OC)OC |
| Formula | : | $C_{15}H_{15}NO_2$ |
| Charge | : | 0 |
| Multiplicity | : | 1 |
| Energy | : | -785.881737711 a.u. |
| Number of imaginary frequencies | : | 0 |

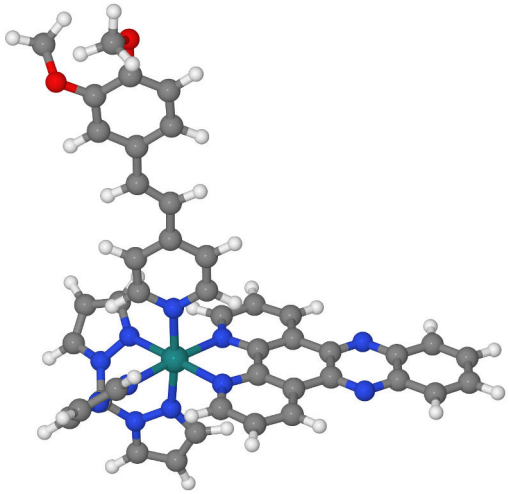
#### *S4.2.1. Cartesian Co-ordinates (XYZ format)*

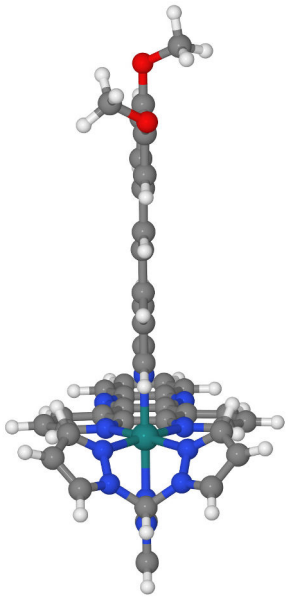
33

| | | | |
|---|---|---|---|
| N | -6.18611 | 0.43146 | 0.00025 |
| C | -5.21754 | 1.37219 | 0.00014 |
| C | -5.74885 | -0.85282 | 0.00033 |
| C | -3.86003 | 1.11682 | 0.00005 |
| H | -5.56365 | 2.40387 | 0.00016 |
| C | -4.42191 | -1.22734 | 0.00023 |
| H | -6.52321 | -1.61625 | 0.00043 |
| C | -3.39045 | -0.23830 | 0.00005 |
| H | -3.16706 | 1.94931 | 0.00008 |
| H | -4.15966 | -2.28067 | 0.00028 |
| C | -2.02292 | -0.61059 | -0.00015 |
| H | -1.83601 | -1.68021 | -0.00008 |
| C | -0.91985 | 0.25616 | -0.00038 |
| H | -1.09320 | 1.32645 | -0.00048 |
| C | 0.44229 | -0.15620 | -0.00040 |
| C | 1.47590 | 0.81612 | -0.00025 |
| C | 0.85061 | -1.53932 | -0.00055 |
| C | 2.82056 | 0.47584 | -0.00014 |
| H | 1.19398 | 1.85977 | -0.00021 |
| C | 2.17808 | -1.88225 | -0.00043 |

| | | | |
|---|---|---|---|
| H | 0.10798 | -2.32531 | -0.00085 |
| C | 3.20239 | -0.91249 | -0.00012 |
| H | 2.48619 | -2.92091 | -0.00054 |
| O | 4.44581 | -1.41195 | 0.00008 |
| O | 3.82589 | 1.37244 | -0.00002 |
| C | 3.52282 | 2.77446 | -0.00011 |
| H | 2.96001 | 3.04811 | 0.89528 |
| H | 4.48631 | 3.27746 | 0.00000 |
| H | 2.96024 | 3.04800 | -0.89568 |
| C | 5.65510 | -0.62858 | 0.00101 |
| H | 6.45422 | -1.36628 | 0.00147 |
| H | 5.71357 | -0.00472 | -0.89048 |
| H | 5.71231 | -0.00491 | 0.89269 |

### S4.3. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ ($S_0$)





| | | |
|---|---|---|
| SMILES | : | COc1ccc(cc1OC)C=Cc2cc[n+](cc2)[Ru]345([n+]6cccc7=c8c(=c9ccc[n+]3c9=c76)nc1ccccc1n8)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 |
| Formula | : | $C_{43}H_{35}N_{11}O_2Ru^{2+}$ |
| Charge | : | 2 |
| Multiplicity | : | 1 |
| Energy | : | -2507.66110303 a.u. |
| Number of imaginary frequencies | : | 0 |

#### *S4.3.1. Cartesian Co-ordinates (XYZ format)*

92

| | | | |
|---|---|---|---|
| Ru | 2.23839259 | 0.02502113 | 0.01327208 |
| N | 0.60996169 | -0.02120190 | 1.33748794 |

| | | | |
|---|---|---|---|
| N | -4.20938730 | -0.13151386 | 1.40500033 |
| N | -4.20344162 | -0.09735123 | -1.40966558 |
| N | 0.61577570 | 0.00782257 | -1.31880891 |
| N | 3.81991839 | -0.05526416 | -1.39572215 |
| N | 4.79279852 | -0.98393136 | -1.18352270 |
| N | 3.81368470 | -0.08483468 | 1.42692685 |
| N | 4.78716469 | -1.00950778 | 1.19987464 |
| N | 2.32634354 | -2.08048701 | -0.00767990 |
| N | 3.55645418 | -2.65932775 | -0.01280926 |
| C | 0.65021497 | -0.07931186 | 2.67297149 |
| H | 1.63013458 | -0.09159181 | 3.12694454 |
| C | 4.73890257 | -1.82358181 | -0.00081293 |
| H | 5.60997677 | -2.47102189 | -0.00588098 |
| C | -0.50288355 | -0.13037005 | 3.45736194 |
| H | -0.40651327 | -0.17220658 | 4.53399658 |
| C | -1.74365449 | -0.12794365 | 2.84785247 |
| H | -2.65911841 | -0.16587962 | 3.42236733 |
| C | -1.81186807 | -0.08387545 | 1.44844055 |
| C | -3.07916093 | -0.09768444 | 0.71782875 |
| C | -5.36711645 | -0.14809984 | 0.71297860 |
| C | -6.60643005 | -0.18394281 | 1.40576780 |
| H | -6.58782864 | -0.19678277 | 2.48857117 |
| C | -7.78177118 | -0.20143206 | 0.70020318 |
| C | -7.77881622 | -0.18384989 | -0.72167349 |
| C | -6.60054636 | -0.14909653 | -1.42171276 |
| H | -6.57751703 | -0.13529126 | -2.50441742 |
| C | -5.36409950 | -0.13050660 | -0.72312242 |
| C | -3.07610846 | -0.08041105 | -0.71711200 |
| C | -1.80563557 | -0.04990100 | -1.44171321 |
| C | -1.73132741 | -0.06146638 | -2.84145713 |
| H | -2.64430928 | -0.08517295 | -3.42065883 |
| C | -0.48790595 | -0.05102517 | -3.44546628 |
| H | -0.38689429 | -0.06795369 | -4.52234888 |
| C | 0.66179937 | -0.01959212 | -2.65509319 |
| H | 1.64364517 | -0.02246350 | -3.10503745 |
| C | -0.60572410 | -0.01731980 | -0.71660185 |
| C | -0.60886854 | -0.03365016 | 0.72952712 |
| C | 4.18140173 | 0.59266812 | -2.50431824 |
| H | 3.57471490 | 1.39871883 | -2.88399625 |
| C | 5.38808203 | 0.07874174 | -3.01227474 |
| H | 5.91617489 | 0.40090424 | -3.89329123 |
| C | 5.75491428 | -0.92408466 | -2.14412069 |
| H | 6.60287857 | -1.58897746 | -2.12953424 |
| C | 5.74608612 | -0.96836209 | 2.16473770 |
| H | 6.59458256 | -1.63223779 | 2.13976765 |
| C | 5.37609673 | 0.01696501 | 3.05133820 |
| H | 5.90109730 | 0.32151309 | 3.94042897 |
| C | 4.17116833 | 0.54088753 | 2.54944372 |
| H | 3.56290245 | 1.33905661 | 2.94303679 |
| C | 3.46538353 | -4.01748943 | -0.03051703 |
| H | 4.34567451 | -4.63844681 | -0.03772910 |
| C | 2.12410617 | -4.32468700 | -0.03623349 |
| H | 1.68316150 | -5.30667782 | -0.04932432 |
| C | 1.45404625 | -3.08757997 | -0.02150958 |
| H | 0.39450011 | -2.89136386 | -0.02056936 |
| N | 2.30668020 | 2.15343237 | 0.03326530 |
| C | 1.19971764 | 2.92494607 | 0.03843987 |
| C | 3.49580479 | 2.80173969 | 0.04029034 |
| C | 1.23862684 | 4.30695963 | 0.04914592 |
| H | 0.24742033 | 2.41612530 | 0.03368019 |
| C | 3.61470318 | 4.17683029 | 0.05081121 |
| H | 4.37936974 | 2.18071866 | 0.03764819 |
| C | 2.46646047 | 4.98911810 | 0.05410301 |
| H | 0.30438873 | 4.85498714 | 0.05207955 |

| | | | |
|---|---|---|---|
| H | 4.60987997 | 4.60076094 | 0.05837062 |
| C | 2.48068333 | 6.44691658 | 0.06258439 |
| H | 1.49829614 | 6.90752840 | 0.08921028 |
| C | 3.58082485 | 7.22554922 | 0.03450114 |
| H | 4.55725288 | 6.75072384 | 0.00024592 |
| C | 3.62486935 | 8.68620968 | 0.03844537 |
| C | 4.87974262 | 9.31655407 | -0.01314774 |
| C | 2.48049378 | 9.50202084 | 0.10267353 |
| C | 5.00528240 | 10.70121288 | -0.01838193 |
| H | 5.78868532 | 8.72616768 | -0.04815953 |
| C | 2.59774184 | 10.88359833 | 0.08635253 |
| H | 1.49252546 | 9.06209183 | 0.15417790 |
| C | 3.84935737 | 11.50127316 | 0.01568912 |
| H | 1.71897900 | 11.51663017 | 0.12346905 |
| O | 3.91000509 | 12.87075520 | 0.03041893 |
| O | 6.26334095 | 11.25166321 | -0.09583876 |
| C | 6.70887709 | 11.92583179 | 1.09676850 |
| H | 6.74690008 | 11.22591400 | 1.93666875 |
| H | 7.71188641 | 12.29075432 | 0.88147330 |
| H | 6.05448294 | 12.76448727 | 1.34269786 |
| C | 4.41091156 | 13.48861980 | -1.17230868 |
| H | 4.38169765 | 14.56198692 | -0.99291122 |
| H | 5.43436384 | 13.17329693 | -1.38074803 |
| H | 3.76503778 | 13.24166679 | -2.01980758 |
| H | -8.72856712 | -0.22892317 | 1.22608674 |
| H | -8.72342491 | -0.19826077 | -1.25199485 |

### *S4.3.2. TD-DFT Results*

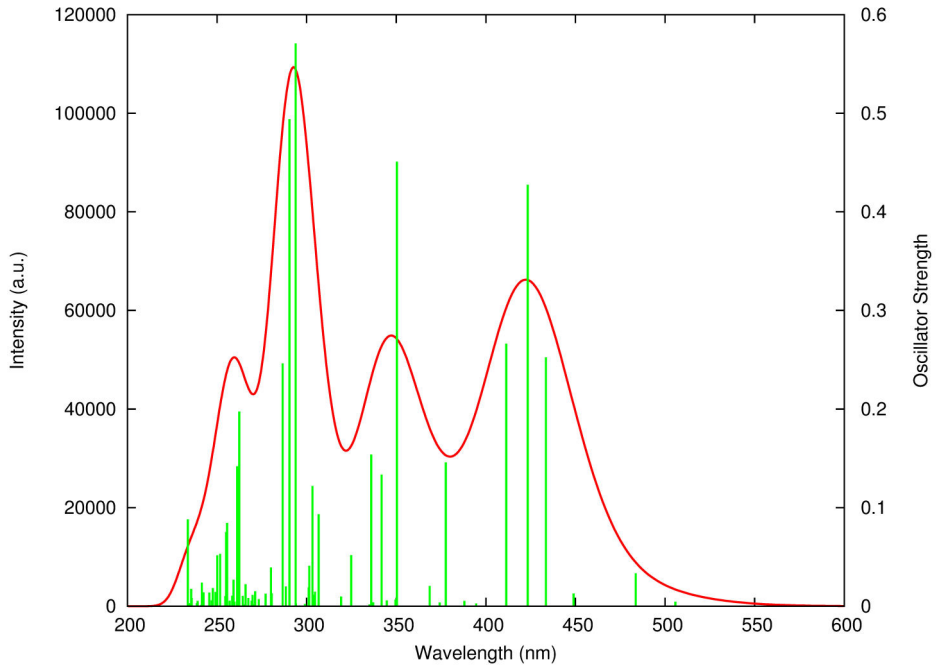



FIG. S10. Absorption Spectrum for $[Ru(tpm)(DMSP)(dppz)]^{2+}$ in water.

TABLE S1: Major transitions ($f > 0.04$) for $[Ru(tpm)(DMSP)(dppz)]^{2+}$ in water. Additionally, the transitions to $S_1$ and $S_2$ are included.

| No. | Energy ($cm^{-1}$) | Wave length (nm) | Osc. Strength | Major contribs |
|---|---|---|---|---|
| 1 | 18168 | 550.43 | 0.00 | HOMO→LUMO (78%), HOMO→L+1 (17%) |
| 2 | 19771 | 505.79 | 0.00 | HOMO→LUMO (19%), HOMO→L+1 (74%) |
| 5 | 23068 | 433.49 | 0.25 | HOMO→L+2 (69%), HOMO→L+3 (25%) |
| 6 | 23621 | 423.35 | 0.43 | H-3→LUMO (37%), H-3→L+1 (16%), HOMO→L+2 (16%), HOMO→L+3 (29%) |
| 8 | 24311 | 411.34 | 0.27 | H-3→LUMO (54%), HOMO→L+2 (10%), HOMO→L+3 (30%) |
| 12 | 26479 | 377.65 | 0.15 | H-3→L+1 (67%) |
| 16 | 28539 | 350.39 | 0.45 | H-2→L+2 (96%) |
| 19 | 29256 | 341.81 | 0.13 | H-2→L+3 (94%) |
| 21 | 29756 | 336.07 | 0.15 | H-6→LUMO (71%), H-4→L+3 (19%) |
| 25 | 30781 | 324.88 | 0.05 | H-4→L+1 (87%) |
| 27 | 32604 | 306.71 | 0.09 | H-5→L+2 (77%), H-5→L+3 (14%) |
| 30 | 32979 | 303.23 | 0.12 | H-6→L+1 (39%), H-1→L+4 (15%), H-1→L+12 (21%) |
| 32 | 33174 | 301.44 | 0.04 | H-6→L+1 (43%), H-1→L+4 (11%), H-1→L+12 (10%), HOMO→L+7 (16%) |
| 38 | 34029 | 293.87 | 0.57 | H-4→L+2 (78%) |
| 40 | 34432 | 290.43 | 0.49 | H-4→L+2 (12%), H-4→L+3 (38%), H-1→L+4 (14%), H-1→L+12 (10%) |
| 42 | 34884 | 286.67 | 0.25 | H-6→LUMO (11%), H-4→L+3 (35%), H-3→L+4 (12%), H-1→L+4 (15%), HOMO→L+8 (10%) |
| 47 | 35702 | 280.09 | 0.04 | H-3→L+4 (10%), H-3→L+12 (13%), H-1→L+6 (19%), HOMO→L+8 (32%) |
| 63 | 38111 | 262.39 | 0.20 | H-14→LUMO (27%), H-10→L+1 (17%), H-6→L+3 (13%), H-1→L+8 (11%) |
| 65 | 38280 | 261.23 | 0.14 | H-14→LUMO (58%), H-10→L+1 (12%) |
| 71 | 39123 | 255.60 | 0.08 | H-12→L+2 (11%), H-9→L+3 (28%), HOMO→L+11 (23%) |
| 73 | 39196 | 255.13 | 0.08 | H-15→LUMO (34%), H-12→L+2 (11%), H-9→L+3 (17%), HOMO→L+11 (15%) |
| 77 | 39723 | 251.74 | 0.05 | H-11→L+2 (36%), H-10→L+2 (28%), H-3→L+6 (11%) |
| 80 | 39983 | 250.11 | 0.05 | H-13→L+1 (70%), H-2→L+6 (18%) |

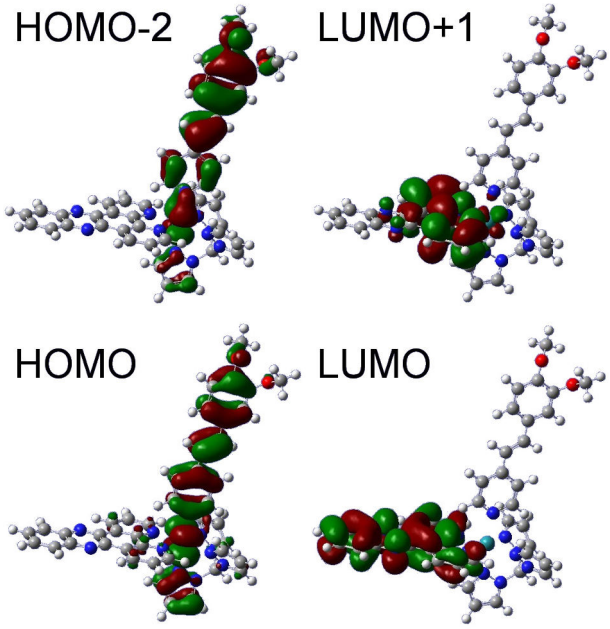
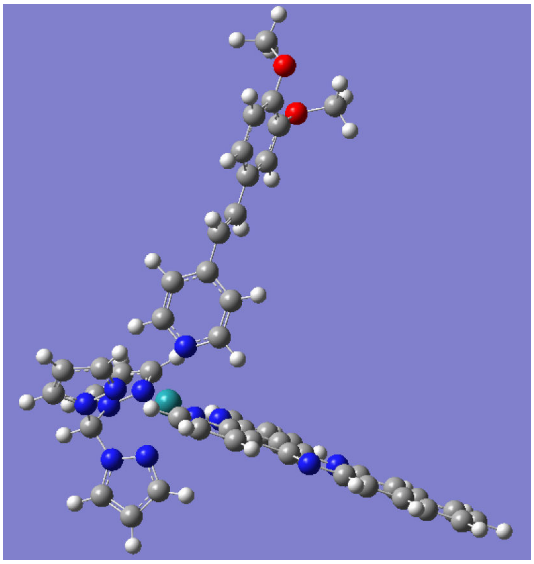



FIG. S11. Frontier orbitals involved in the $S_0 \longrightarrow S_1$ and $S_0 \longrightarrow S_2$ transitions at the $S_0$ geometry.

### S4.4. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ ($S_0$) (90° degree rotation)



| | | |
|---|---|---|
| Route | : # opt=qst3 freq b3lyp/genecp scrf=(solvent=water) geom=connectivity int=ultrafine pop=regular scf=tight | |
| SMILES | : COc1ccc(cc1OC)C=Cc2cc[n+](cc2)[Ru]345([n+]6cccc7c6c8[n+]3cccc8c9c7nc1cc2ccccc2cc1n9)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 | |
| Formula | : $C_{47}H_{37}N_{11}O_2Ru^{2+}$ | |
| Charge | : 2 | |
| Multiplicity | : 1 | |
| Energy | : -2661.32208568 | a.u. |
| Gibbs Energy | : -2660.64432600 | a.u. |
| Number of imaginary frequencies | : 1 | |

#### *S4.4.1. Cartesian Co-ordinates (XYZ format)*

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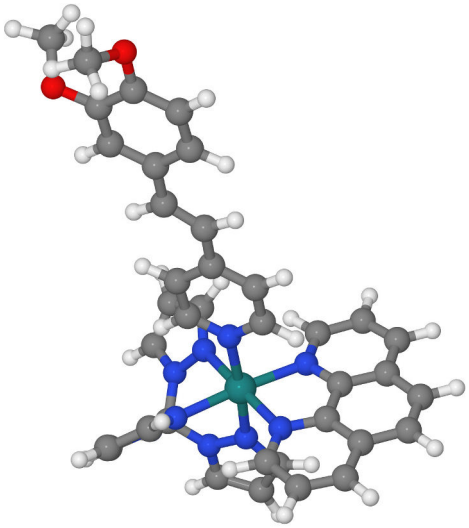
| | | | |
|---|---|---|---|
| Ru | -0.61645401 | -2.55070901 | 0.01953500 |
| N | -1.37750006 | -1.08990800 | 1.32129502 |
| N | -4.17681408 | 2.82792711 | 1.38741505 |
| N | -4.61153221 | 2.50287795 | -1.38328898 |
| N | -1.78455901 | -1.39349604 | -1.28536201 |
| N | 0.00577800 | -4.04986477 | -1.34193003 |
| N | -0.13681100 | -5.34539318 | -0.94755697 |
| N | 0.43997100 | -3.72839308 | 1.42907298 |
| N | 0.23430499 | -5.07369423 | 1.39159095 |
| N | -2.24858904 | -3.82122397 | 0.42184901 |
| N | -1.99623001 | -5.15226889 | 0.53929698 |
| C | -1.18584597 | -1.00178599 | 2.64283705 |
| H | -0.56654000 | -1.76337099 | 3.09339094 |
| C | -0.64139003 | -5.63916397 | 0.38169399 |
| H | -0.65202397 | -6.71683121 | 0.51061600 |
| C | -1.75361300 | 0.01002200 | 3.41675591 |
| H | -1.55940497 | 0.03245700 | 4.48068190 |
| C | -2.55274105 | 0.96372497 | 2.81307507 |
| H | -3.00828290 | 1.76439798 | 3.37962389 |
| C | -2.78320503 | 0.88168401 | 1.43350005 |

| | | | |
|---|---|---|---|
| C | -3.63151193 | 1.83734906 | 0.71673602 |
| C | -4.96226311 | 3.70299697 | 0.70519102 |
| C | -5.56095886 | 4.77353382 | 1.37795997 |
| H | -5.38217115 | 4.88134623 | 2.44135690 |
| C | -6.37067318 | 5.68380594 | 0.69613302 |
| C | -6.99278498 | 6.78637505 | 1.36207294 |
| H | -6.82524014 | 6.91065598 | 2.42592812 |
| C | -7.78065491 | 7.66394997 | 0.67308700 |
| H | -8.24692822 | 8.49578762 | 1.18786097 |
| C | -8.00038242 | 7.49940586 | -0.72738498 |
| H | -8.62963200 | 8.20919609 | -1.25141501 |
| C | -7.42686605 | 6.46128416 | -1.40482903 |
| H | -7.59312296 | 6.33553886 | -2.46871805 |
| C | -6.59391594 | 5.51667404 | -0.72656697 |
| C | -5.99630308 | 4.44757414 | -1.39651704 |
| H | -6.15087605 | 4.30533123 | -2.45967603 |
| C | -5.18472815 | 3.53660297 | -0.71203500 |
| C | -3.85422111 | 1.67094505 | -0.70311499 |
| C | -3.22844291 | 0.54952002 | -1.40809202 |
| C | -3.42728901 | 0.31189799 | -2.77449894 |
| H | -4.06093597 | 0.98014599 | -3.34155393 |
| C | -2.81254196 | -0.77919698 | -3.36106300 |
| H | -2.94791794 | -1.00246096 | -4.41083717 |
| C | -2.00204492 | -1.61016500 | -2.58796906 |
| H | -1.51909697 | -2.47325802 | -3.02189589 |
| C | -2.40104389 | -0.33138600 | -0.69781202 |
| C | -2.17865801 | -0.16542301 | 0.72402102 |
| C | 0.54938102 | -4.10487700 | -2.55883288 |
| H | 0.77831799 | -3.19686389 | -3.09267902 |
| C | 0.75444001 | -5.43888521 | -2.95410204 |
| H | 1.17191505 | -5.78881693 | -3.88260889 |
| C | 0.30987099 | -6.20654392 | -1.90202796 |
| H | 0.27278399 | -7.27364302 | -1.75644898 |
| C | 0.98506999 | -5.71710110 | 2.32661605 |
| H | 0.94672602 | -6.78845882 | 2.43541193 |
| C | 1.69925797 | -4.75060701 | 2.99720502 |
| H | 2.39387012 | -4.89994097 | 3.80595207 |
| C | 1.33100104 | -3.53070092 | 2.40209508 |
| H | 1.67611301 | -2.53468394 | 2.62772989 |
| C | -3.13563204 | -5.85228109 | 0.79519302 |
| H | -3.12079811 | -6.92276812 | 0.91709399 |
| C | -4.16085386 | -4.93591404 | 0.84551901 |
| H | -5.20251894 | -5.13660812 | 1.02877104 |
| C | -3.56109405 | -3.68560910 | 0.60720497 |
| H | -4.02085304 | -2.71202302 | 0.56337702 |
| N | 1.13310695 | -1.39759302 | -0.38846201 |
| C | 1.10705996 | -0.05866200 | -0.54840797 |
| C | 2.33532691 | -2.00333190 | -0.49514401 |
| C | 2.23961306 | 0.69635201 | -0.80825800 |
| H | 0.14656800 | 0.42692900 | -0.46389899 |
| C | 3.50998092 | -1.31465197 | -0.75217700 |
| H | 2.34803700 | -3.07542300 | -0.36579499 |
| C | 3.48706198 | 0.07396700 | -0.91075599 |
| H | 2.14263511 | 1.76816499 | -0.92363399 |
| H | 4.43866682 | -1.86615002 | -0.82253599 |
| C | 4.72349024 | 0.84803301 | -1.19199896 |
| H | 4.96625423 | 0.98106998 | -2.24343300 |
| C | 5.50122023 | 1.36043203 | -0.23066200 |
| H | 5.20498896 | 1.20128703 | 0.80369198 |
| C | 6.73817682 | 2.13604808 | -0.40455499 |
| C | 7.37646914 | 2.64056897 | 0.73823500 |
| C | 7.31400490 | 2.41107512 | -1.65567005 |
| C | 8.54986763 | 3.38443089 | 0.65472198 |
| H | 6.96037579 | 2.46165895 | 1.72367203 |

| | | | |
|---|---|---|---|
| C | 8.49089241 | 3.14161801 | -1.74643505 |
| H | 6.85520697 | 2.04350209 | -2.56532192 |
| C | 9.12641430 | 3.62955809 | -0.60271698 |
| H | 8.94550323 | 3.34548211 | -2.70893097 |
| O | 10.27322388 | 4.37178612 | -0.74576002 |
| O | 9.13715839 | 3.82635808 | 1.81808901 |
| C | 9.09361362 | 5.25140619 | 2.02077508 |
| H | 8.05659199 | 5.59722281 | 2.06672096 |
| H | 9.58113480 | 5.43670893 | 2.97669506 |
| H | 9.62489319 | 5.77834320 | 1.22575903 |
| C | 11.47398472 | 3.76001692 | -0.23600000 |
| H | 12.28011322 | 4.46392679 | -0.43669999 |
| H | 11.39811897 | 3.57821393 | 0.83747798 |
| H | 11.67134571 | 2.81975102 | -0.75931400 |

### S4.5. $[Ru(tpm)(DMSP)(phen)]^{2+}$ ($S_0$)



| | | |
|---|---|---|
| SMILES | : | [Ru]123(n4cccc5ccc6cccn1c6c45)(N1N([C@@H](N4N2C=CC4)N2N3C=CC2)CC=C1)N1C=C[C@@H](C=C1)/C=C/c1cc(c(cc1)OC)OC |
| Formula | : | $C_{37}H_{33}N_9O_2Ru^{2+,3}$ |
| Charge | : | 2 |
| Multiplicity | : | 3 |
| Energy | : | -2168.22139967 a.u. |
| Number of imaginary frequencies | : | 0 |

#### *S4.5.1. Cartesian Co-ordinates (XYZ format)*

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| | | | |
|---|---|---|---|
| Ru | 2.36117 | -0.30567 | 0.01307 |
| N | 2.76435 | 1.22689 | -1.36799 |
| N | 2.76112 | 1.30816 | 1.29977 |
| N | 2.09325 | -1.81730 | 1.47134 |
| N | 2.76459 | -2.98727 | 1.28448 |
| N | 2.09264 | -1.90013 | -1.35257 |
| N | 2.76540 | -3.05682 | -1.09936 |
| N | 4.38819 | -0.87708 | 0.03049 |
| N | 4.66767 | -2.20726 | 0.06968 |
| C | 2.80158 | 1.15236 | -2.69766 |
| H | 2.58712 | 0.18883 | -3.13708 |
| C | 3.58112 | -3.16523 | 0.09722 |
| H | 4.01081 | -4.16248 | 0.12668 |
| C | 3.10709 | 2.25405 | -3.50960 |
| H | 3.11555 | 2.12604 | -4.58377 |
| C | 3.38908 | 3.47280 | -2.93130 |
| H | 3.62559 | 4.33776 | -3.53913 |
| C | 3.37575 | 3.58509 | -1.52585 |
| C | 3.67377 | 4.79830 | -0.82134 |
| C | 3.67140 | 4.83987 | 0.53871 |
| C | 3.37079 | 3.67210 | 1.31522 |
| C | 3.37823 | 3.64627 | 2.72498 |
| H | 3.61151 | 4.54698 | 3.27997 |
| C | 3.09409 | 2.46509 | 3.37574 |

| | | | |
|---|---|---|---|
| H | 3.09774 | 2.40317 | 4.45577 |
| C | 2.79263 | 1.31538 | 2.63160 |
| H | 2.57620 | 0.38061 | 3.12853 |
| C | 3.05743 | 2.47072 | 0.64420 |
| C | 3.05939 | 2.42714 | -0.78365 |
| C | 1.39492 | -1.98161 | 2.59562 |
| H | 0.76090 | -1.18980 | 2.96034 |
| C | 1.61786 | -3.25942 | 3.13953 |
| H | 1.19350 | -3.67013 | 4.03959 |
| C | 2.49361 | -3.87830 | 2.27713 |
| H | 2.93916 | -4.85919 | 2.28761 |
| C | 2.49441 | -4.00332 | -2.03939 |
| H | 2.94015 | -4.98314 | -1.99422 |
| C | 1.61715 | -3.43583 | -2.93484 |
| H | 1.19241 | -3.89783 | -3.80950 |
| C | 1.39327 | -2.12931 | -2.46476 |
| H | 0.75784 | -1.36054 | -2.87360 |
| C | 6.01067 | -2.43114 | 0.07784 |
| H | 6.41266 | -3.43008 | 0.10790 |
| C | 6.61869 | -1.19723 | 0.04212 |
| H | 7.67598 | -0.99457 | 0.03724 |
| C | 5.56903 | -0.26050 | 0.01342 |
| H | 5.62044 | 0.81543 | -0.01846 |
| N | 0.27437 | 0.11571 | -0.00067 |
| C | -0.22431 | 1.36906 | -0.03641 |
| C | -0.62809 | -0.89371 | 0.02774 |
| C | -1.57910 | 1.64582 | -0.04446 |
| H | 0.48941 | 2.17913 | -0.05941 |
| C | -1.99411 | -0.69632 | 0.02174 |
| H | -0.22449 | -1.89507 | 0.05606 |
| C | -2.52335 | 0.60628 | -0.01536 |
| H | -1.89997 | 2.67992 | -0.07378 |
| H | -2.63326 | -1.56860 | 0.04661 |
| C | -3.94630 | 0.92437 | -0.02485 |
| H | -4.17086 | 1.98594 | -0.05206 |
| C | -4.95505 | 0.03026 | -0.00394 |
| H | -4.71522 | -1.02900 | 0.02066 |
| C | -6.38765 | 0.31907 | -0.01099 |
| C | -7.28638 | -0.76121 | -0.00652 |
| C | -6.92266 | 1.62003 | -0.03382 |
| C | -8.66346 | -0.56981 | -0.01089 |
| H | -6.91775 | -1.78101 | -0.00330 |
| C | -8.29502 | 1.81842 | -0.02596 |
| H | -6.27019 | 2.48396 | -0.04392 |
| C | -9.18085 | 0.73771 | -0.00486 |
| H | -8.71215 | 2.81856 | -0.03069 |
| O | -10.52817 | 0.98981 | -0.02693 |
| O | -9.48533 | -1.67237 | 0.01750 |
| C | -10.22516 | -1.91265 | -1.19496 |
| H | -9.53974 | -2.07976 | -2.03106 |
| H | -10.81084 | -2.81350 | -1.01888 |
| H | -10.89021 | -1.07713 | -1.42238 |
| C | -11.25930 | 0.59625 | 1.15197 |
| H | -12.29542 | 0.87636 | 0.96989 |
| H | -11.18787 | -0.47945 | 1.31948 |
| H | -10.88287 | 1.13527 | 2.02613 |
| H | 3.90418 | 5.75958 | 1.06169 |
| H | 3.90830 | 5.68436 | -1.39893 |

*S4.5.2. TD-DFT Results*

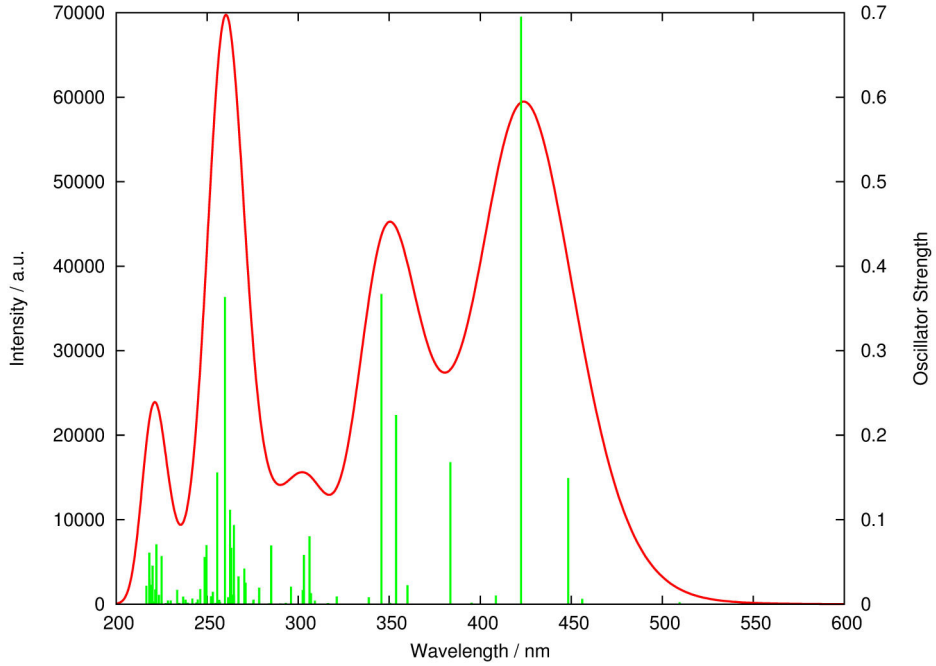
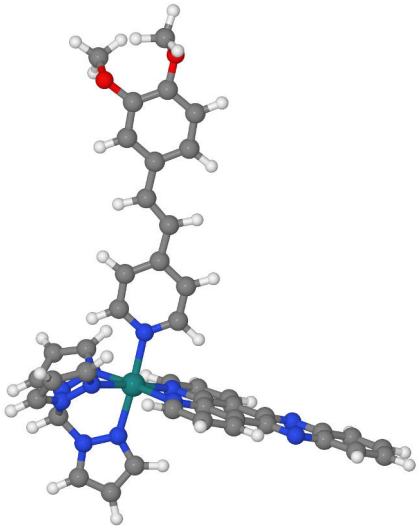



FIG. S12. Absorption Spectrum for $[Ru(tpm)(DMSP)(phen)]^{2+}$ in water.

TABLE S2: Major transitions ($f > 0.04$) for $[Ru(tpm)(DMSP)(phen)]^{2+}$ in water. Additionally, the transitions to $S_1$ and $S_2$ are included.

| No. | Energy ($cm^{-1}$) | Wave length (nm) | Osc. Strength | Major contribs |
|---|---|---|---|---|
| 1 | 19624 | 509.57 | 0.00 | HOMO→LUMO (93%) |
| 2 | 21928 | 456.04 | 0.01 | H-1→LUMO (59%), HOMO→L+1 (23%), HOMO→L+2 (13%) |
| 3 | 22306 | 448.31 | 0.15 | H-1→LUMO (30%), HOMO→L+1 (58%) |
| 4 | 23671 | 422.46 | 0.70 | H-3→LUMO (12%), HOMO→L+1 (15%), HOMO→L+2 (69%) |
| 7 | 26067 | 383.62 | 0.17 | H-3→LUMO (76%), HOMO→L+2 (10%) |
| 10 | 28268 | 353.76 | 0.22 | H-2→L+1 (95%) |
| 13 | 28927 | 345.69 | 0.37 | H-2→L+2 (96%) |
| 21 | 32658 | 306.20 | 0.08 | H-4→L+1 (47%), H-4→L+2 (41%) |
| 22 | 32984 | 303.17 | 0.06 | H-5→LUMO (15%), H-1→L+3 (34%), H-1→L+11 (20%), HOMO→L+12 (11%) |
| 29 | 35071 | 285.14 | 0.07 | H-1→L+3 (11%), H-1→L+5 (32%), H-1→L+11 (11%), HOMO→L+4 (14%) |
| 39 | 36983 | 270.39 | 0.04 | H-7→L+1 (16%), H-3→L+5 (35%) |
| 42 | 37778 | 264.71 | 0.09 | H-6→LUMO (46%), H-2→L+5 (14%) |
| 45 | 37991 | 263.22 | 0.07 | H-7→L+1 (27%), H-3→L+5 (11%), H-2→L+4 (11%), HOMO→L+9 (13%) |
| 46 | 38093 | 262.52 | 0.11 | H-2→L+5 (34%), H-1→L+7 (33%), H-1→L+8 (12%) |
| 49 | 38499 | 259.75 | 0.36 | H-7→LUMO (24%), H-2→L+5 (40%) |
| 54 | 39136 | 255.52 | 0.16 | H-10→L+1 (17%), H-10→L+2 (10%), HOMO→L+9 (16%), HOMO→L+10 (24%) |
| 59 | 40058 | 249.64 | 0.07 | H-9→L+2 (69%), H-2→L+6 (12%) |
| 60 | 40231 | 248.56 | 0.06 | H-11→LUMO (91%) |
| 84 | 44449 | 224.98 | 0.06 | H-5→L+3 (89%) |
| 90 | 45021 | 222.12 | 0.07 | H-16→LUMO (26%), H-15→L+1 (14%), H-5→L+5 (35%) |
| 94 | 45460 | 219.97 | 0.05 | H-16→LUMO (57%), H-5→L+5 (11%), H-4→L+6 (10%) |
| 99 | 45833 | 218.18 | 0.06 | H-15→L+1 (38%), H-14→L+2 (17%), H-5→L+5 (13%) |

## S4.6. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ ($T_1$)



| | | |
|---|---|---|
| SMILES | : | COc1ccc(cc1OC)C=Cc2cc[n+](cc2)[Ru]345([n+]6cccc7=c8c(=c9ccc[n+]3c9=c76)nc1ccccc1n8)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 |
| Formula | : | $C_{43}H_{35}N_{11}O_2Ru^{2+,3}$ |
| Charge | : | 2 |
| Multiplicity | : | 3 |
| Energy | : | -2507.58955395 a.u. |
| Number of imaginary frequencies | : | 0 |

### *S4.6.1. Cartesian Co-ordinates (XYZ format)*

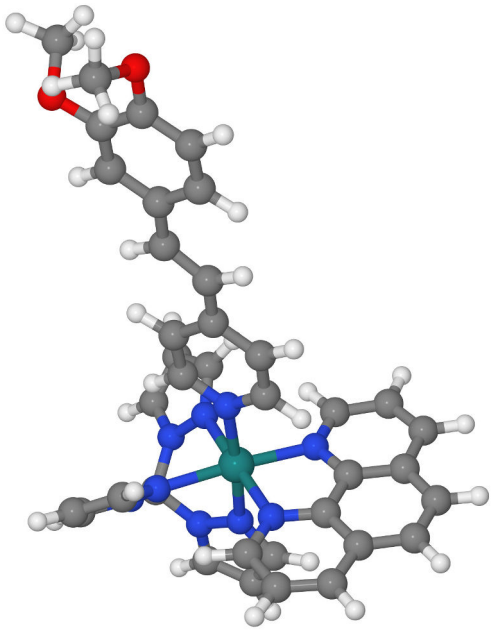
92

| | | | |
|---|---|---|---|
| Ru | 1.38069046 | -1.69220829 | 0.02030331 |
| N | 2.18250632 | -0.32709068 | -1.32682765 |
| N | 4.61558056 | 3.87487602 | -1.44636917 |
| N | 4.60454941 | 3.90879750 | 1.37750995 |
| N | 2.17250180 | -0.29516178 | 1.33978474 |
| N | 0.72473961 | -3.14272499 | 1.45174718 |
| N | 1.09825480 | -4.43498039 | 1.24607229 |
| N | 0.73637474 | -3.18031788 | -1.37795925 |
| N | 1.10731792 | -4.46682739 | -1.13425195 |
| N | 3.18576574 | -2.74268651 | 0.03918300 |
| N | 3.14356232 | -4.10428572 | 0.05906929 |
| C | 2.20354533 | -0.39616105 | -2.66149235 |
| H | 1.73920691 | -1.26258767 | -3.11054730 |
| C | 1.86131990 | -4.78434896 | 0.06325231 |
| H | 2.04414368 | -5.85395336 | 0.07858773 |
| C | 2.79595852 | 0.58175415 | -3.45462775 |
| H | 2.77969360 | 0.47227770 | -4.52994823 |
| C | 3.40241456 | 1.68461049 | -2.84322715 |
| H | 3.86934233 | 2.46151519 | -3.43472362 |
| C | 3.41969180 | 1.79122710 | -1.45926225 |
| C | 4.04695082 | 2.90252066 | -0.74805284 |
| C | 5.19672537 | 4.89491653 | -0.75957280 |
| C | 5.81657505 | 5.95561218 | -1.46072650 |
| H | 5.81052923 | 5.92456341 | -2.54401541 |

| | | | |
|---|---|---|---|
| C | 6.40805721 | 6.99324226 | -0.77109009 |
| C | 6.40257311 | 7.01021576 | 0.64147234 |
| C | 5.80565214 | 5.98940039 | 1.35123014 |
| H | 5.79121447 | 5.98443842 | 2.43487597 |
| C | 5.19114828 | 4.91211128 | 0.67097151 |
| C | 4.04135132 | 2.91988325 | 0.69831216 |
| C | 3.40869999 | 1.82576239 | 1.43103600 |
| C | 3.38126826 | 1.75192738 | 2.81695938 |
| H | 3.84397936 | 2.54264164 | 3.39326763 |
| C | 2.77033877 | 0.66374886 | 3.44990897 |
| H | 2.74630618 | 0.57977754 | 4.52737284 |
| C | 2.18374443 | -0.33274344 | 2.67587972 |
| H | 1.71616328 | -1.18839586 | 3.14182711 |
| C | 2.79293990 | 0.76757044 | 0.69264579 |
| C | 2.79821014 | 0.75086844 | -0.70057398 |
| C | 0.00164255 | -3.14913845 | 2.57408786 |
| H | -0.42597327 | -2.23502016 | 2.95316911 |
| C | -0.09152531 | -4.44919443 | 3.09410620 |
| H | -0.60791570 | -4.75981808 | 3.98590922 |
| C | 0.61783540 | -5.24683571 | 2.22354388 |
| H | 0.81885248 | -6.30569601 | 2.22020340 |
| C | 0.63230681 | -5.30483007 | -2.09213829 |
| H | 0.83178490 | -6.36337900 | -2.05816126 |
| C | -0.07018941 | -4.53089428 | -2.98918796 |
| H | -0.58080548 | -4.86559725 | -3.87558341 |
| C | 0.02095537 | -3.21711349 | -2.50458121 |
| H | -0.40298766 | -2.31337094 | -2.91155910 |
| C | 4.39326668 | -4.62607670 | 0.07083309 |
| H | 4.55761051 | -5.69092846 | 0.08695251 |
| C | 5.27676821 | -3.56381941 | 0.05805541 |
| H | 6.35175610 | -3.61662078 | 0.06233922 |
| C | 4.48226833 | -2.41299510 | 0.03847763 |
| H | 4.77852631 | -1.37694800 | 0.02406607 |
| N | -0.47701097 | -0.73835862 | 0.00159277 |
| C | -0.59929371 | 0.61131603 | -0.01595630 |
| C | -1.62415695 | -1.46793699 | 0.00753966 |
| C | -1.82027948 | 1.24641430 | -0.02751551 |
| H | 0.31544292 | 1.18447399 | -0.02052031 |
| C | -2.87541318 | -0.89921963 | -0.00312392 |
| H | -1.51126385 | -2.54149294 | 0.02142534 |
| C | -3.01939869 | 0.50466818 | -0.02091034 |
| H | -1.84482563 | 2.32864451 | -0.04110794 |
| H | -3.73218513 | -1.55847025 | 0.00193556 |
| C | -4.28730536 | 1.20291114 | -0.03242456 |
| H | -4.21222973 | 2.28464794 | -0.05350051 |
| C | -5.50722313 | 0.61554176 | -0.01631982 |
| H | -5.56389618 | -0.46854660 | 0.00755591 |
| C | -6.79898405 | 1.28201115 | -0.02411775 |
| C | -7.95967770 | 0.48692536 | -0.00460648 |
| C | -6.95574808 | 2.68165207 | -0.06320129 |
| C | -9.23021793 | 1.04695487 | -0.00605302 |
| H | -7.88283253 | -0.59451312 | 0.00650382 |
| C | -8.21935749 | 3.24690652 | -0.05208974 |
| H | -6.09144211 | 3.33282351 | -0.08794165 |
| C | -9.36829662 | 2.44886518 | -0.00943589 |
| H | -8.34876347 | 4.32241344 | -0.06723102 |
| O | -10.58617496 | 3.06663251 | -0.02467695 |
| O | -10.32199669 | 0.21345587 | 0.02873440 |
| C | -11.09462547 | 0.17127831 | -1.18758118 |
| H | -10.47708225 | -0.18652162 | -2.01629972 |
| H | -11.90533066 | -0.53226399 | -1.00621867 |
| H | -11.50429916 | 1.15442562 | -1.42835128 |
| C | -11.43315506 | 2.84938502 | 1.12453032 |
| H | -12.33801651 | 3.42469025 | 0.93876410 |

| | | | |
|---|---|---|---|
| H | -11.67734814 | 1.79345906 | 1.24254441 |
| H | -10.94017506 | 3.22186446 | 2.02652597 |
| H | 6.88150072 | 7.80322886 | -1.31364465 |
| H | 6.87187576 | 7.83304262 | 1.16806960 |

## S4.7. $[Ru(tpm)(DMSP)(phen)]^{2+}$ ($T_1$)



| | | |
|---|---|---|
| SMILES | : | [Ru]123(n4cccc5ccc6cccn1c6c45)(N1N([C@@H](N4N2C=CC4)N2N3C=CC2)CC=C1)N1C=C[C@@H](C=C1)/C=C/c1cc(c(cc1)OC)OC |
| Formula | : | $C_{37}H_{33}N_9O_2Ru^{2+,3}$ |
| Charge | : | 2 |
| Multiplicity | : | 3 |
| Energy | : | -2168.14884057 a.u. |
| Number of imaginary frequencies | : | 0 |

### *S4.7.1. Cartesian Co-ordinates (XYZ format)*

82

| | | | |
|---|---|---|---|
| Ru | -2.33252 | -0.30336 | -0.01194 |
| N | -2.75109 | 1.22970 | 1.36613 |
| N | -2.74135 | 1.30724 | -1.30222 |
| N | -2.07180 | -1.82234 | -1.46649 |
| N | -2.74821 | -2.98921 | -1.28061 |
| N | -2.07785 | -1.90157 | 1.35492 |
| N | -2.75510 | -3.05555 | 1.10278 |
| N | -4.37105 | -0.87390 | -0.03338 |
| N | -4.65277 | -2.20377 | -0.07185 |
| C | -2.78662 | 1.15581 | 2.69546 |
| H | -2.55788 | 0.19653 | 3.13674 |
| C | -3.56815 | -3.16451 | -0.09544 |
| H | -3.99992 | -4.16086 | -0.12457 |
| C | -3.10839 | 2.25459 | 3.50503 |
| H | -3.11472 | 2.12876 | 4.57939 |
| C | -3.40861 | 3.46754 | 2.92395 |
| H | -3.65802 | 4.32993 | 3.53025 |
| C | -3.39656 | 3.57805 | 1.51827 |
| C | -3.71120 | 4.78550 | 0.81136 |
| C | -3.70540 | 4.82519 | -0.54877 |
| C | -3.38449 | 3.66112 | -1.32243 |

| | | | |
|---|---|---|---|
| C | -3.38359 | 3.63321 | -2.73226 |
| H | -3.62671 | 4.52986 | -3.28956 |
| C | -3.07836 | 2.45609 | -3.38060 |
| H | -3.07455 | 2.39333 | -4.46051 |
| C | -2.76466 | 1.31140 | -2.63382 |
| H | -2.53184 | 0.37955 | -3.12856 |
| C | -3.05718 | 2.46525 | -0.64870 |
| C | -3.06269 | 2.42367 | 0.77860 |
| C | -1.37146 | -1.98831 | -2.58911 |
| H | -0.73219 | -1.19937 | -2.95082 |
| C | -1.59814 | -3.26470 | -3.13332 |
| H | -1.17317 | -3.67703 | -4.03231 |
| C | -2.47826 | -3.88041 | -2.27277 |
| H | -2.92758 | -4.85957 | -2.28474 |
| C | -2.49041 | -3.99967 | 2.04634 |
| H | -2.94030 | -4.97770 | 2.00331 |
| C | -1.61292 | -3.43321 | 2.94256 |
| H | -1.19224 | -3.89451 | 3.81949 |
| C | -1.38213 | -2.12959 | 2.46948 |
| H | -0.74302 | -1.36279 | 2.87619 |
| C | -5.99494 | -2.42472 | -0.08290 |
| H | -6.39909 | -3.42283 | -0.11280 |
| C | -6.60181 | -1.18928 | -0.04988 |
| H | -7.65881 | -0.98533 | -0.04770 |
| C | -5.55165 | -0.25516 | -0.01971 |
| H | -5.60213 | 0.82085 | 0.01100 |
| N | -0.29360 | 0.10773 | 0.00558 |
| C | 0.21625 | 1.38333 | 0.04184 |
| C | 0.62648 | -0.90678 | -0.02089 |
| C | 1.55133 | 1.66316 | 0.05047 |
| H | -0.50330 | 2.18747 | 0.06398 |
| C | 1.97988 | -0.71390 | -0.01443 |
| H | 0.22237 | -1.90797 | -0.04804 |
| C | 2.53359 | 0.61430 | 0.02163 |
| H | 1.86954 | 2.69855 | 0.07942 |
| H | 2.61862 | -1.58607 | -0.03701 |
| C | 3.89169 | 0.90565 | 0.02884 |
| H | 4.15210 | 1.95790 | 0.05742 |
| C | 4.96609 | -0.05626 | -0.00078 |
| H | 4.70920 | -1.10842 | -0.03656 |
| C | 6.33327 | 0.25397 | 0.01234 |
| C | 7.29660 | -0.80764 | -0.00785 |
| C | 6.85252 | 1.59180 | 0.06420 |
| C | 8.65039 | -0.56875 | -0.00561 |
| H | 6.95918 | -1.83785 | -0.01665 |
| C | 8.21056 | 1.82481 | 0.05498 |
| H | 6.17792 | 2.43656 | 0.09541 |
| C | 9.13524 | 0.76994 | -0.00019 |
| H | 8.60024 | 2.83590 | 0.07739 |
| O | 10.46526 | 1.07060 | 0.00844 |
| O | 9.51798 | -1.63498 | -0.03886 |
| C | 10.24645 | -1.86241 | 1.18347 |
| H | 9.55355 | -2.07289 | 2.00326 |
| H | 10.87470 | -2.73327 | 1.00405 |
| H | 10.87009 | -1.00252 | 1.43730 |
| C | 11.24153 | 0.63978 | -1.13149 |
| H | 12.26066 | 0.96848 | -0.93728 |
| H | 11.21071 | -0.44377 | -1.24471 |
| H | 10.86657 | 1.12157 | -2.03851 |
| H | -3.95014 | 5.74052 | -1.07385 |
| H | -3.96048 | 5.66869 | 1.38704 |

### S4.8. Cis-trans isomerisation of DMSP

From the literature it is clear[1–3] that the DMSP ligand can isomerize from the *trans* to the *cis* form, which will lead to triplet emission at a smaller wavelength than the $T_1$ to $S_0$ emission. This process was investigated as well. On the triplet surface two alternative configurations for the DMSP ligand were found, one with the top part of the ligand at 90 with respect to the pyridine part of the ligand (intermediate cis isomer), as shown in Figure S13(a) and one purely cis as shown in Figure S13(b). According to ref. 23b emission should happen to the corresponding geometry in its singlet ground state. For the purely cis isomer, this would lead to an emission at 654 nm. The second isomer does not have an equivalent on the ground state surface. If it is assumed that emission will go back to the trans-isomer of the DMSP ligand, then emission will occur at 652 nm. Emission to the cis isomer of the DMSP ligand would occur at 726 nm. For completeness, emission from the the cis-isomer to the trans-isomer would occur at 570 nm. Ignoring the zero-point energies will shift all wavelengths by approximately 25 nm to the blue. However, it is clear from these calculations that trans-cis isomerization cannot explain the occurrence of the peak at 550 nm, unless it is from the cis-isomer to the trans-isomer, which is unlikely.

### S4.9. References Cis-trans isomerisation of DMSP


1. Whitten, D. G., & McCall, M. T. (1969). Radiationless processes in the photochemistry of stilbazoles and 1,2-bispyridylethylenes. Journal of the American Chemical Society, 91(18), 50975103.

2. Vedernikov, A. I., Gromov, S. P., Lobova, N. A., Kuz'mina, L. G., Strelenko, Y. A., Howard, J., & Alfimov, M. V. (2005). Stereospecific solid-state [2+2] autophotocycloaddition of a styryl dye containing a 18-crown-6 fragment. Russian Chemical Bulletin, 54(8), 19541966.

3. Vedernikov, A. I., Sazonov, S. K., Loginov, P. S., Lobova, N. A., Alfimov, M. V., & Gromov, S. P. (2007). Hydrogen bonding- and stacking-induced stereospecific [2 + 2]-photocycloaddition within a pseudodimeric complex of two styryl dyes. Mendeleev Communications, 17(1), 2931.

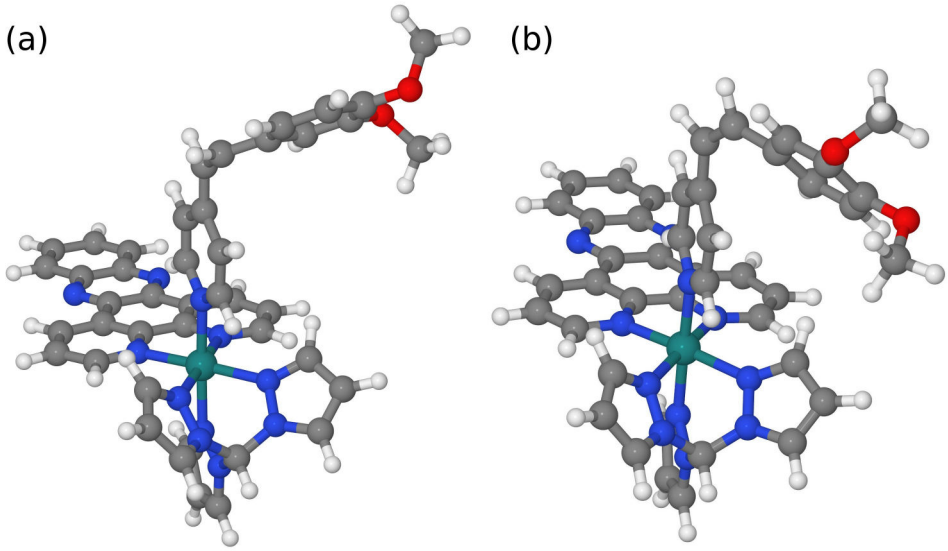
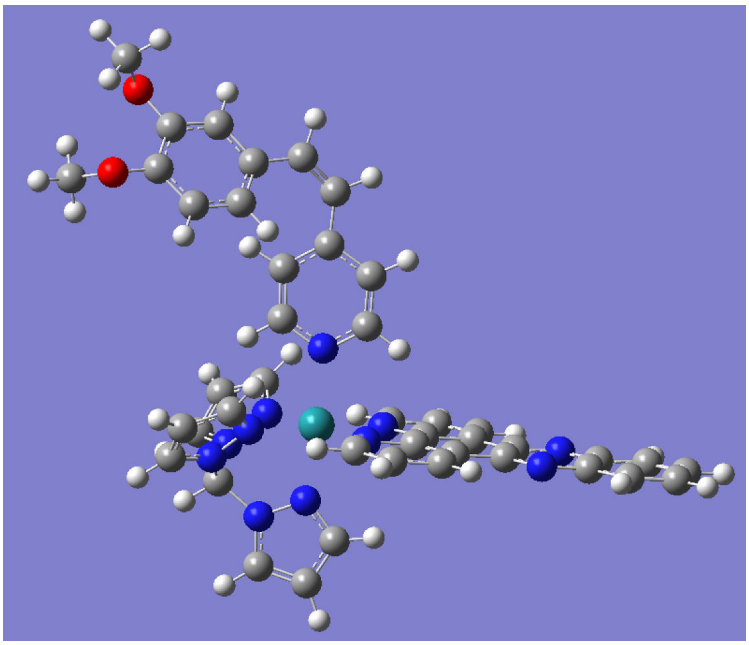




FIG. S13. Two alternative configurations for the DMSP ligand for complex **1**. Panel (a): Intermediate cis-isomer. Panel (b): Full cis isomer.

## S4.10. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ (full cis isomer)($T_1$)



| | | |
|---|---|---|
| Route | : # opt freq b3lyp/genecp scrf=(solvent=water) geom=connectivity int=ultrafine | |
| SMILES | : COc1ccc(cc1OC)C=Cc2cc[n+](cc2)[Ru]345([n+]6cccc7c6c8[n+]3cccc8c9c7nc1ccccc1n9)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 | |
| Formula | : $C_{43}H_{35}N_{11}O_2Ru^{2+,3}$ | |
| Charge | : 2 | |
| Multiplicity | : 3 | |
| Energy | : -2507.57875746 | a.u. |
| Gibbs Energy | : -2506.94703400 | a.u. |
| Number of imaginary frequencies | : 0 | |

### *S4.10.1. Cartesian Co-ordinates (XYZ format)*

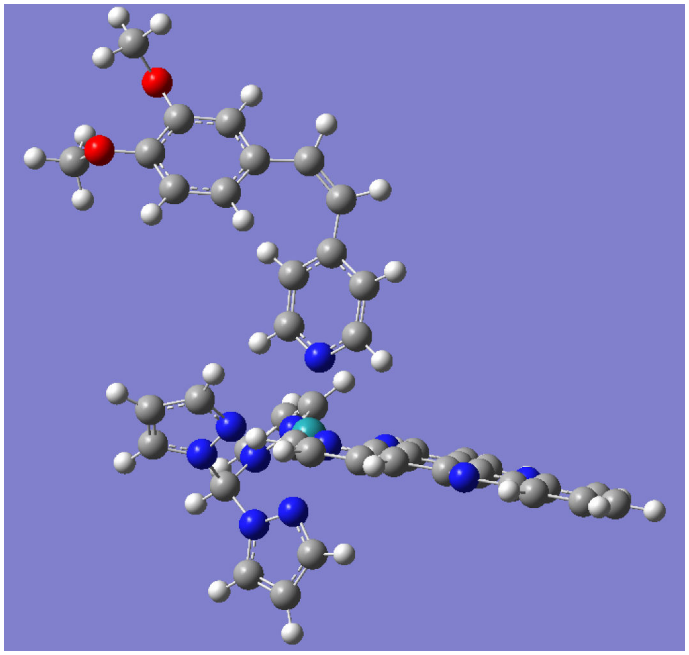
92

| | | | |
|---|---|---|---|
| Ru | 0.53718501 | 1.44465196 | 0.09787200 |
| N | 2.08442903 | 0.77066803 | 1.30991101 |
| N | 6.06552982 | -2.00784302 | 1.15277100 |
| N | 5.58193493 | -2.46631503 | -1.58961594 |
| N | 1.62964106 | 0.34050700 | -1.28157198 |
| N | -0.93608999 | 2.24509597 | -1.23324704 |
| N | -1.16627800 | 3.58527994 | -1.17634201 |
| N | -0.46494001 | 2.68527198 | 1.52241898 |
| N | -0.77079499 | 3.95555711 | 1.14227402 |
| N | 1.63156903 | 3.15681601 | -0.36835399 |
| N | 0.97330499 | 4.34851122 | -0.44072500 |
| C | 2.31178308 | 1.05146205 | 2.59852004 |
| H | 1.60487795 | 1.70917201 | 3.08426189 |
| C | -0.45925301 | 4.39663792 | -0.20381400 |
| H | -0.78768402 | 5.42551088 | -0.31297499 |
| C | 3.39916801 | 0.54082400 | 3.29750395 |
| H | 3.52899003 | 0.80178303 | 4.33844519 |

| | | | |
|---|---|---|---|
| C | 4.30403614 | -0.30168501 | 2.63833904 |
| H | 5.15664721 | -0.71823198 | 3.15884399 |
| C | 4.12006187 | -0.60565197 | 1.29789996 |
| C | 5.02687311 | -1.46324396 | 0.53700298 |
| C | 6.89579487 | -2.79826903 | 0.42249599 |
| C | 8.01779842 | -3.40282702 | 1.03721094 |
| H | 8.18639183 | -3.21478009 | 2.09108090 |
| C | 8.86292267 | -4.20612907 | 0.30205101 |
| C | 8.62067986 | -4.43574190 | -1.07151997 |
| C | 7.53560305 | -3.85984111 | -1.69676900 |
| H | 7.33263683 | -4.02368402 | -2.74862194 |
| C | 6.65062380 | -3.03068304 | -0.96772599 |
| C | 4.77894592 | -1.69831598 | -0.86852902 |
| C | 3.62424111 | -1.07577002 | -1.51336300 |
| C | 3.33357310 | -1.22212100 | -2.86138105 |
| H | 3.98514199 | -1.82952297 | -3.47607803 |
| C | 2.21595192 | -0.58126801 | -3.41191411 |
| H | 1.97688198 | -0.67021000 | -4.46237278 |
| C | 1.39832103 | 0.18597899 | -2.59052205 |
| H | 0.53644502 | 0.69721800 | -2.99495101 |
| C | 2.75062299 | -0.26574799 | -0.72268403 |
| C | 2.98888302 | -0.04007000 | 0.63064498 |
| C | -1.75529099 | 1.77621496 | -2.17761898 |
| H | -1.77439499 | 0.72423297 | -2.41173291 |
| C | -2.51587510 | 2.81673598 | -2.73199701 |
| H | -3.25563097 | 2.74143004 | -3.51016998 |
| C | -2.11704206 | 3.95805502 | -2.07193494 |
| H | -2.42562509 | 4.98618221 | -2.16636205 |
| C | -1.40751803 | 4.62484503 | 2.13820910 |
| H | -1.72481000 | 5.64706087 | 2.01433396 |
| C | -1.51571596 | 3.75535989 | 3.20095396 |
| H | -1.96538699 | 3.95323896 | 4.15858698 |
| C | -0.91671598 | 2.56125307 | 2.77255893 |
| H | -0.80359799 | 1.63033295 | 3.30409408 |
| C | 1.82904398 | 5.35345793 | -0.74450201 |
| H | 1.48795497 | 6.37115002 | -0.84421200 |
| C | 3.08555794 | 4.79283619 | -0.87350100 |
| H | 4.00129986 | 5.30603504 | -1.11115098 |
| C | 2.91548705 | 3.42630696 | -0.63130701 |
| H | 3.64616394 | 2.63414788 | -0.63364297 |
| N | -0.66630298 | -0.20664801 | 0.57947302 |
| C | -0.16475999 | -1.45580602 | 0.71883100 |
| C | -2.00004506 | -0.04287600 | 0.76930201 |
| C | -0.95426399 | -2.54168797 | 1.03213894 |
| H | 0.89854598 | -1.57437801 | 0.57505101 |
| C | -2.84781694 | -1.08598399 | 1.06799400 |
| H | -2.38031197 | 0.96355599 | 0.68015701 |
| C | -2.34384394 | -2.39377689 | 1.19518602 |
| H | -0.48735401 | -3.51230788 | 1.13993001 |
| H | -3.89596105 | -0.87278998 | 1.21938503 |
| C | -3.14739704 | -3.55280304 | 1.57397497 |
| H | -2.58911800 | -4.30910110 | 2.11819196 |
| C | -4.45872784 | -3.81118393 | 1.37516797 |
| H | -4.83475018 | -4.70022917 | 1.87574100 |
| C | -5.46353579 | -3.11428595 | 0.56536502 |
| C | -6.80383110 | -3.14734793 | 0.98594201 |
| C | -5.16829681 | -2.48954296 | -0.65734500 |
| C | -7.81095314 | -2.52463889 | 0.25868899 |
| H | -7.08100986 | -3.65963697 | 1.90043294 |
| C | -6.16954899 | -1.86827302 | -1.39122903 |
| H | -4.15738106 | -2.50083709 | -1.04387403 |
| C | -7.49034786 | -1.85624099 | -0.93889600 |
| H | -5.94832087 | -1.38224995 | -2.33403206 |
| O | -8.44346333 | -1.24985099 | -1.71301305 |

| | | | |
|---|---|---|---|
| O | -9.09599400 | -2.55790496 | 0.74507600 |
| C | -10.01444054 | -3.37314796 | -0.00939000 |
| H | -9.67824554 | -4.41397905 | -0.01764800 |
| H | -10.97196579 | -3.30356312 | 0.50402701 |
| H | -10.11537647 | -3.00786805 | -1.03328896 |
| C | -9.09749985 | -0.10530300 | -1.12734604 |
| H | -9.80471897 | 0.24981000 | -1.87472904 |
| H | -9.62607193 | -0.37751001 | -0.21287000 |
| H | -8.36469364 | 0.67832601 | -0.91516602 |
| H | 9.72084141 | -4.66720200 | 0.77736402 |
| H | 9.29556561 | -5.07028294 | -1.63402402 |

### S4.11. [Ru(tpm)(DMSP)(dppz)]$^{2+}$ (full cis isomer)($S_0$)



| | | |
|---|---|---|
| Route | : # opt freq b3lyp/genecp scrf=(solvent=water) geom=connectivity int=ultrafine | |
| SMILES | : COc1ccc(cc1OC)C=Cc2cc[n+](cc2)[Ru]345([n+]6cccc7c6c8[n+]3cccc8c9c7nc1ccccc1n9)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 | |
| Formula | : $C_{43}H_{35}N_{11}O_2Ru^{2+}$ | |
| Charge | : 2 | |
| Multiplicity | : 1 | |
| Energy | : -2507.65154229 | a.u. |
| Gibbs Energy | : -2507.01565500 | a.u. |
| Number of imaginary frequencies | : 0 | |

#### *S4.11.1. Cartesian Co-ordinates (XYZ format)*

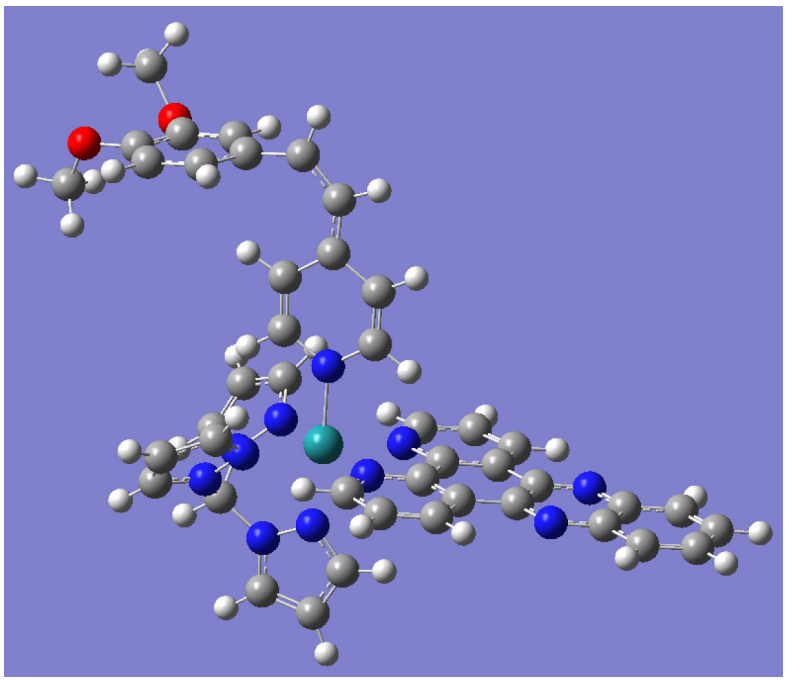
92

| | | | |
|---|---|---|---|
| Ru | 0.54699701 | 1.45065105 | 0.09901700 |
| N | 2.12827802 | 0.76423699 | 1.29839396 |
| N | 6.08653784 | -1.98299003 | 1.13069701 |
| N | 5.57759523 | -2.46892095 | -1.59476101 |
| N | 1.65029395 | 0.30915901 | -1.27549601 |
| N | -0.93942600 | 2.19602299 | -1.21308804 |
| N | -1.19257498 | 3.53335500 | -1.16971600 |
| N | -0.43678600 | 2.66801190 | 1.52426696 |
| N | -0.76717198 | 3.93244791 | 1.14208496 |
| N | 1.62701297 | 3.18928003 | -0.40257099 |
| N | 0.93841898 | 4.35988522 | -0.47470400 |
| C | 2.36282611 | 1.05900300 | 2.58175802 |
| H | 1.65761304 | 1.72059202 | 3.06298089 |
| C | -0.48680300 | 4.36795807 | -0.21412300 |
| H | -0.84579003 | 5.38673210 | -0.32478401 |
| C | 3.45978189 | 0.55269402 | 3.28013110 |

| | | | |
|---|---|---|---|
| H | 3.59383607 | 0.82333201 | 4.31885481 |
| C | 4.35250998 | -0.28315800 | 2.63571310 |
| H | 5.21239805 | -0.69710702 | 3.14443111 |
| C | 4.13866282 | -0.59210199 | 1.28525901 |
| C | 5.04044914 | -1.45189095 | 0.51877302 |
| C | 6.90684319 | -2.77152491 | 0.40620801 |
| C | 8.04192924 | -3.36612010 | 1.01874995 |
| H | 8.22082233 | -3.16727996 | 2.06825209 |
| C | 8.87420273 | -4.16693115 | 0.28011999 |
| C | 8.61698914 | -4.41250706 | -1.09668601 |
| C | 7.53043509 | -3.85437107 | -1.71913099 |
| H | 7.31743002 | -4.02931881 | -2.76652002 |
| C | 6.64712811 | -3.01948309 | -0.98441303 |
| C | 4.78097010 | -1.69962001 | -0.87064302 |
| C | 3.61653590 | -1.09043205 | -1.51331997 |
| C | 3.32518005 | -1.26367104 | -2.87342191 |
| H | 3.97637105 | -1.87707198 | -3.48106503 |
| C | 2.21431994 | -0.63558298 | -3.40485191 |
| H | 1.96016002 | -0.73546600 | -4.45157194 |
| C | 1.40266800 | 0.14371499 | -2.57939792 |
| H | 0.53566998 | 0.65162200 | -2.97546911 |
| C | 2.75374389 | -0.29153401 | -0.74916703 |
| C | 3.01468801 | -0.04277400 | 0.65153199 |
| C | -1.77631402 | 1.70357502 | -2.12759495 |
| H | -1.78347898 | 0.64757597 | -2.34350300 |
| C | -2.56950808 | 2.72515607 | -2.67990208 |
| H | -3.32669306 | 2.62696600 | -3.43877697 |
| C | -2.17546606 | 3.88054204 | -2.04464293 |
| H | -2.50532103 | 4.90176010 | -2.14129710 |
| C | -1.40637195 | 4.60074091 | 2.14044690 |
| H | -1.74185205 | 5.61643791 | 2.01184607 |
| C | -1.48900497 | 3.73714089 | 3.20866990 |
| H | -1.93103898 | 3.93408108 | 4.17025995 |
| C | -0.87692797 | 2.54677296 | 2.77757812 |
| H | -0.74756199 | 1.61882198 | 3.31051302 |
| C | 1.75776100 | 5.39708614 | -0.80159402 |
| H | 1.37939203 | 6.40092802 | -0.90190202 |
| C | 3.02212000 | 4.87357807 | -0.94561702 |
| H | 3.92064500 | 5.40827799 | -1.20191503 |
| C | 2.89167500 | 3.49656391 | -0.68774903 |
| H | 3.64991903 | 2.73080397 | -0.69757497 |
| N | -0.68310601 | -0.21126300 | 0.61656898 |
| C | -0.20519200 | -1.46398699 | 0.76513201 |
| C | -2.00919104 | -0.03922400 | 0.82348001 |
| C | -1.00135398 | -2.54348302 | 1.10449803 |
| H | 0.85380101 | -1.60653198 | 0.61062300 |
| C | -2.86833405 | -1.07021594 | 1.15357006 |
| H | -2.38327098 | 0.96882099 | 0.72315699 |
| C | -2.38141108 | -2.37883806 | 1.29278398 |
| H | -0.54091901 | -3.51736593 | 1.21579099 |
| H | -3.91246104 | -0.84235901 | 1.31585705 |
| C | -3.20127296 | -3.52585602 | 1.70315599 |
| H | -2.66006589 | -4.25620413 | 2.29860210 |
| C | -4.50111914 | -3.79342103 | 1.47239304 |
| H | -4.89489412 | -4.66950417 | 1.98232400 |
| C | -5.48317719 | -3.10865402 | 0.61612898 |
| C | -6.82996321 | -3.09722590 | 1.01259601 |
| C | -5.15470791 | -2.53778911 | -0.62291402 |
| C | -7.81287098 | -2.48907709 | 0.23930000 |
| H | -7.13363695 | -3.56339908 | 1.94340706 |
| C | -6.13119793 | -1.92867398 | -1.40152705 |
| H | -4.13549185 | -2.57697201 | -0.98535901 |
| C | -7.45965385 | -1.87899196 | -0.97822303 |
| H | -5.88227081 | -1.48319101 | -2.35759401 |

| | | | |
|---|---|---|---|
| O | -8.39345074 | -1.28979397 | -1.79353094 |
| O | -9.10723305 | -2.47525191 | 0.70470101 |
| C | -10.03038597 | -3.30032301 | -0.03161400 |
| H | -9.71770000 | -4.34796715 | 0.00776700 |
| H | -10.99487305 | -3.18992209 | 0.46154699 |
| H | -10.10623837 | -2.97493696 | -1.07100296 |
| C | -8.99898434 | -0.08825700 | -1.27719498 |
| H | -9.69716740 | 0.24956700 | -2.04128194 |
| H | -9.53316593 | -0.28489000 | -0.34617400 |
| H | -8.23650932 | 0.67903501 | -1.11388803 |
| H | 9.74075127 | -4.62180614 | 0.74482697 |
| H | 9.29246044 | -5.04978800 | -1.65467894 |

### S4.12. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ (TS between full and intermediate cis isomer)($T_1$)



| | | |
|---|---|---|
| Route | : # opt=qst3 freq b3lyp/genecp scrf=(solvent=water) geom=connectivity int=ultrafine | |
| SMILES | : COc1ccc(cc1OC)[CH][CH]c2cc[n+](cc2)[Ru]345([n+]6cccc7c6c8[n+]3cccc8c9c7nc1ccccc1n9)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 | |
| Formula | : $C_{43}H_{35}N_{11}O_2Ru^{2+,3}$ | |
| Charge | : 2 | |
| Multiplicity | : 3 | |
| Energy | : -2507.56164476 | a.u. |
| Gibbs Energy | : -2506.93005000 | a.u. |
| Number of imaginary frequencies | : 1 | |

#### *S4.12.1. Cartesian Co-ordinates (XYZ format)*

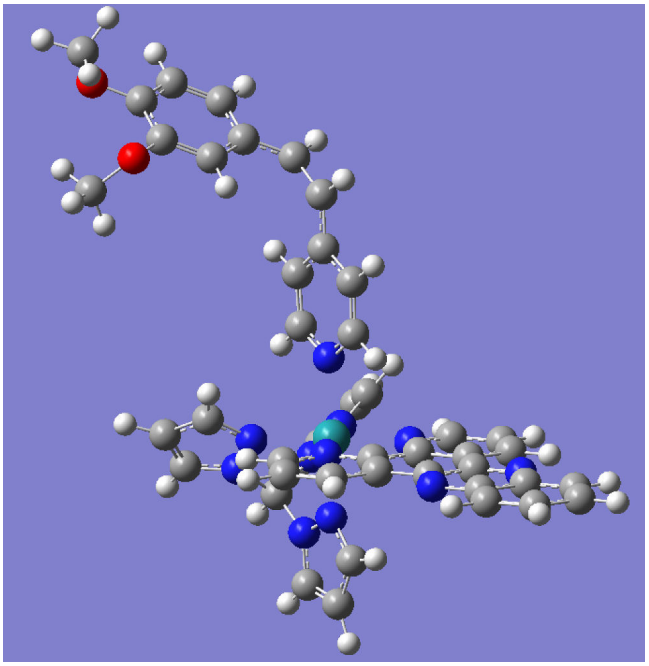
92

| | | | |
|---|---|---|---|
| Ru | 0.35881099 | 1.23584104 | -0.02939300 |
| N | 1.72334898 | 0.38520601 | 1.32659805 |
| N | 6.00226688 | -1.81951904 | 1.50150502 |
| N | 6.17288589 | -1.61031199 | -1.30116701 |
| N | 1.88250196 | 0.57850599 | -1.32035899 |
| N | -0.87569302 | 2.22663808 | -1.44604194 |
| N | -1.26823497 | 3.49835896 | -1.16252601 |
| N | -1.04432499 | 2.02713394 | 1.35587800 |
| N | -1.41369295 | 3.32862401 | 1.20773304 |
| N | 1.33183599 | 3.11973310 | 0.16618900 |
| N | 0.55145699 | 4.23401690 | 0.19772300 |
| C | 1.61560905 | 0.34105700 | 2.65787911 |
| H | 0.72819299 | 0.77868199 | 3.09021211 |
| C | -0.88881898 | 4.10483599 | 0.09976700 |
| H | -1.32118797 | 5.09971905 | 0.14374200 |

| | | | |
|---|---|---|---|
| C | 2.59741592 | -0.23419000 | 3.46566510 |
| H | 2.45599389 | -0.24684501 | 4.53778696 |
| C | 3.72896194 | -0.77430499 | 2.88415408 |
| H | 4.51010418 | -1.22876704 | 3.47835207 |
| C | 3.86979294 | -0.72380900 | 1.49000299 |
| C | 5.04016781 | -1.25359201 | 0.79123503 |
| C | 7.07466316 | -2.29799604 | 0.83866602 |
| C | 8.13371658 | -2.91494799 | 1.55615103 |
| H | 8.04957581 | -2.98594093 | 2.63350701 |
| C | 9.22297192 | -3.39971709 | 0.87972999 |
| C | 9.30927181 | -3.29385996 | -0.53595001 |
| C | 8.30533314 | -2.70443892 | -1.25963998 |
| H | 8.35265636 | -2.61431599 | -2.33780503 |
| C | 7.16180992 | -2.19108009 | -0.59191197 |
| C | 5.12697077 | -1.14715505 | -0.63634700 |
| C | 4.04417610 | -0.51053798 | -1.38527703 |
| C | 4.07205296 | -0.35532999 | -2.77855110 |
| H | 4.92339993 | -0.72368300 | -3.33468795 |
| C | 3.01273108 | 0.27217001 | -3.40645599 |
| H | 3.00079012 | 0.41744900 | -4.47805882 |
| C | 1.93520296 | 0.72984999 | -2.64699888 |
| H | 1.10142303 | 1.23214495 | -3.11426091 |
| C | 2.92758489 | -0.02542400 | -0.69139099 |
| C | 2.84074903 | -0.13139100 | 0.74592900 |
| C | -1.43067706 | 1.92985201 | -2.62239790 |
| H | -1.28299201 | 0.95788300 | -3.06429601 |
| C | -2.18162203 | 3.01500392 | -3.10243297 |
| H | -2.73716688 | 3.06812906 | -4.02280903 |
| C | -2.06105399 | 3.99877906 | -2.14641094 |
| H | -2.46432304 | 4.99633789 | -2.08730006 |
| C | -2.32586598 | 3.69025898 | 2.14824796 |
| H | -2.73143792 | 4.68809700 | 2.17906499 |
| C | -2.55006194 | 2.58288407 | 2.93536592 |
| H | -3.21389294 | 2.50954795 | 3.77947092 |
| C | -1.73406100 | 1.57166004 | 2.40299511 |
| H | -1.63119400 | 0.54582000 | 2.71736097 |
| C | 1.30254495 | 5.35666990 | 0.32899100 |
| H | 0.84806699 | 6.33293104 | 0.37161899 |
| C | 2.62010908 | 4.95355988 | 0.38360599 |
| H | 3.48733401 | 5.58297014 | 0.48518899 |
| C | 2.58926296 | 3.55562091 | 0.27877799 |
| H | 3.41203809 | 2.85978508 | 0.28021199 |
| N | -0.68809801 | -0.48892799 | -0.21997701 |
| C | -0.09010400 | -1.75149202 | -0.27764899 |
| C | -2.07989812 | -0.48580500 | -0.28722799 |
| C | -0.78868598 | -2.90446997 | -0.38186401 |
| H | 0.98753899 | -1.77193105 | -0.23528001 |
| C | -2.84040189 | -1.60121298 | -0.39143601 |
| H | -2.54526496 | 0.48778901 | -0.25020599 |
| C | -2.23870611 | -2.92648697 | -0.44364601 |
| H | -0.24142200 | -3.83965993 | -0.41961101 |
| H | -3.91284490 | -1.48401999 | -0.43593299 |
| C | -2.91464996 | -4.14375591 | -0.54330301 |
| H | -2.26486993 | -5.01609087 | -0.57076401 |
| C | -4.28192711 | -4.44278193 | -0.61235398 |
| H | -4.53792000 | -5.49664116 | -0.68330699 |
| C | -5.42844820 | -3.49907088 | -0.59593397 |
| C | -6.04740381 | -3.14709091 | 0.61151898 |
| C | -5.96056414 | -2.98457193 | -1.78582096 |
| C | -7.14626217 | -2.29098296 | 0.64358300 |
| H | -5.67844391 | -3.53650808 | 1.55354500 |
| C | -7.05143404 | -2.11839890 | -1.76119196 |
| H | -5.50947523 | -3.25180602 | -2.73441911 |
| C | -7.64867687 | -1.75722504 | -0.55565000 |

| | | | |
|---|---|---|---|
| H | -7.45748091 | -1.70758402 | -2.67856002 |
| O | -8.74505901 | -0.92497897 | -0.57306099 |
| O | -7.68817282 | -1.95443201 | 1.86389697 |
| C | -8.99719620 | -2.49567795 | 2.12067103 |
| H | -8.96601963 | -3.58942103 | 2.10760188 |
| H | -9.27796745 | -2.15254903 | 3.11542010 |
| H | -9.72175312 | -2.13685799 | 1.38704801 |
| C | -8.52260399 | 0.38991499 | -0.03189900 |
| H | -9.46840763 | 0.92160898 | -0.12626199 |
| H | -8.23026085 | 0.33844599 | 1.01877105 |
| H | -7.75171280 | 0.91256499 | -0.60659999 |
| H | 10.03255844 | -3.87075710 | 1.42409003 |
| H | 10.18288708 | -3.68635798 | -1.04228497 |

### S4.13. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ (Intermediate cis isomer)($T_1$)



| | | |
|---|---|---|
| Route | : # opt freq b3lyp/genecp scrf=(solvent=water) geom=connectivity int=ultrafine | |
| SMILES | : COc1ccc(cc1OC)[CH][CH]c2cc[n+](cc2)[Ru]345([n+]6cccc7c6c8[n+]3cccc8c9c7nc1ccccc1n9)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 | |
| Formula | : $C_{43}H_{35}N_{11}O_2Ru^{2+,3}$ | |
| Charge | : 2 | |
| Multiplicity | : 3 | |
| Energy | : -2507.58785844 | a.u. |
| Gibbs Energy | : -2506.95729700 | a.u. |
| Number of imaginary frequencies | : 0 | |

#### *S4.13.1. Cartesian Co-ordinates (XYZ format)*

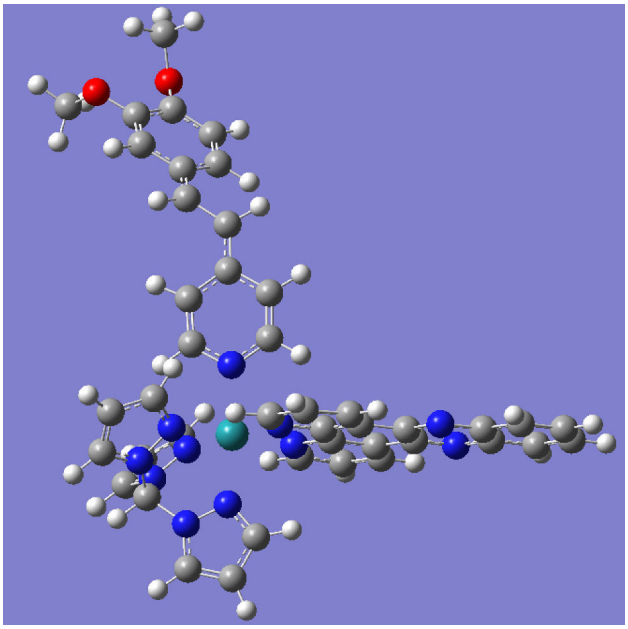
92

| | | | |
|---|---|---|---|
| Ru | 0.78974700 | 1.63873804 | 0.00464100 |
| N | 2.26204491 | 0.77133501 | 1.22475803 |
| N | 5.62098312 | -2.68645597 | 1.22404599 |
| N | 4.88440609 | -3.33773708 | -1.41354299 |
| N | 1.56879604 | 0.15903200 | -1.26624203 |
| N | -0.57722199 | 2.54101992 | -1.34234905 |
| N | -0.53987700 | 3.89799690 | -1.44928396 |
| N | 0.15106900 | 3.18468094 | 1.30773401 |
| N | 0.07032000 | 4.44100094 | 0.78917599 |
| N | 2.18166399 | 3.04939508 | -0.72122401 |
| N | 1.74756098 | 4.32425022 | -0.90770698 |
| C | 2.61116910 | 1.13908195 | 2.46214890 |
| H | 2.06927609 | 1.96909595 | 2.89113903 |
| C | 0.36975399 | 4.66033506 | -0.61393100 |
| H | 0.22599900 | 5.71450996 | -0.82981902 |
| C | 3.62613797 | 0.50066102 | 3.17631888 |

| | | | |
|---|---|---|---|
| H | 3.86098194 | 0.84008998 | 4.17622280 |
| C | 4.31173897 | -0.55013603 | 2.59621000 |
| H | 5.10282898 | -1.07019901 | 3.11897206 |
| C | 3.97565508 | -0.94291002 | 1.29325700 |
| C | 4.65957785 | -2.03080606 | 0.59428102 |
| C | 6.24143982 | -3.68419099 | 0.56149000 |
| C | 7.27928686 | -4.41775179 | 1.19537199 |
| H | 7.54832697 | -4.15180588 | 2.21020198 |
| C | 7.90882301 | -5.43102598 | 0.51973498 |
| C | 7.53640079 | -5.76040316 | -0.81255001 |
| C | 6.53889990 | -5.07260418 | -1.45401895 |
| H | 6.24102592 | -5.30821705 | -2.46828699 |
| C | 5.86548901 | -4.01665115 | -0.78423899 |
| C | 4.28423786 | -2.36262798 | -0.75034201 |
| C | 3.22019196 | -1.61049604 | -1.41524601 |
| C | 2.82464290 | -1.86393404 | -2.73593998 |
| H | 3.31410098 | -2.65031695 | -3.29410601 |
| C | 1.82143104 | -1.09358704 | -3.29355693 |
| H | 1.49297404 | -1.25132406 | -4.31206703 |
| C | 1.21858299 | -0.09126200 | -2.53232694 |
| H | 0.43944901 | 0.52891898 | -2.95052195 |
| C | 2.56706810 | -0.58581501 | -0.71524698 |
| C | 2.94466710 | -0.25223699 | 0.64036500 |
| C | -1.54810905 | 2.14480209 | -2.16680098 |
| H | -1.78984797 | 1.09825802 | -2.25717592 |
| C | -2.13771605 | 3.24751091 | -2.81025410 |
| H | -2.93932700 | 3.23328996 | -3.52862811 |
| C | -1.47492099 | 4.35256290 | -2.32702804 |
| H | -1.58706295 | 5.40459299 | -2.53133011 |
| C | -0.37732100 | 5.33218384 | 1.71469998 |
| H | -0.50473303 | 6.37433290 | 1.47232401 |
| C | -0.58779001 | 4.62662077 | 2.87742305 |
| H | -0.93870300 | 5.01455402 | 3.81828094 |
| C | -0.24981600 | 3.29539895 | 2.57529712 |
| H | -0.29024899 | 2.42503190 | 3.21001291 |
| C | 2.74663401 | 5.12556982 | -1.36846399 |
| H | 2.57890391 | 6.17055798 | -1.57040405 |
| C | 3.86752200 | 4.33550215 | -1.48387897 |
| H | 4.84396410 | 4.63915014 | -1.82047498 |
| C | 3.46772790 | 3.05185890 | -1.07002103 |
| H | 4.05046606 | 2.14732409 | -1.01164198 |
| N | -0.70850903 | 0.34134799 | 0.73891300 |
| C | -0.48268199 | -0.97059202 | 1.01058495 |
| C | -1.96684599 | 0.80272198 | 0.96824700 |
| C | -1.44681799 | -1.82269502 | 1.49429595 |
| H | 0.51585901 | -1.33871400 | 0.83006299 |
| C | -2.98927212 | 0.01893400 | 1.44978905 |
| H | -2.13755107 | 1.84642899 | 0.75002098 |
| C | -2.76655889 | -1.35451102 | 1.73925602 |
| H | -1.18778706 | -2.85635209 | 1.68767095 |
| H | -3.96472692 | 0.46083900 | 1.60650396 |
| C | -3.76924396 | -2.20997810 | 2.23825693 |
| H | -3.48071289 | -3.24232793 | 2.43567395 |
| C | -5.13999510 | -1.80416000 | 2.55777597 |
| H | -5.33089495 | -1.44758201 | 3.56872702 |
| C | -6.24421215 | -1.90919805 | 1.68215096 |
| C | -6.11234903 | -2.37974405 | 0.34520999 |
| C | -7.54700184 | -1.52955699 | 2.11480498 |
| C | -7.20460606 | -2.48385191 | -0.49649799 |
| H | -5.14116621 | -2.66565108 | -0.04134100 |
| C | -8.63650608 | -1.64467704 | 1.27285504 |
| H | -7.68088293 | -1.15887797 | 3.12468600 |
| C | -8.49252605 | -2.13015294 | -0.03301500 |
| H | -9.63015938 | -1.36794806 | 1.60598099 |

| | | | |
|---|---|---|---|
| O | -9.60007095 | -2.20236802 | -0.83762997 |
| O | -7.01692295 | -2.97261810 | -1.76983702 |
| C | -7.17542791 | -2.00317788 | -2.82245302 |
| H | -6.44626188 | -1.19546294 | -2.70782495 |
| H | -6.98673296 | -2.53361297 | -3.75457001 |
| H | -8.18657207 | -1.59108198 | -2.82968092 |
| C | -10.01325798 | -3.52996492 | -1.21974194 |
| H | -10.89857483 | -3.40249801 | -1.84055603 |
| H | -9.23105145 | -4.03776503 | -1.78594899 |
| H | -10.27020836 | -4.11482811 | -0.33179301 |
| H | 8.70098972 | -5.99207020 | 1.00082695 |
| H | 8.05185318 | -6.56624222 | -1.32116401 |

### S4.14. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ (TS Intermediate cis → trans isomer)($T_1$)



| | | |
|---|---|---|
| Route | : # opt=qst3 freq b3lyp/genecp scrf=(solvent=water) geom=connectivity int=ultrafine | |
| SMILES | : COc1ccc(cc1OC)[CH][CH]c2cc[n+](cc2)[Ru]345([n+]6cccc7c6c8[n+]3cccc8c9c7nc1ccccc1n9)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 | |
| Formula | : $C_{43}H_{35}N_{11}O_2Ru^{2+,3}$ | |
| Charge | : 2 | |
| Multiplicity | : 3 | |
| Energy | : -2507.58706058 | a.u. |
| Gibbs Energy | : -2506.95402900 | a.u. |
| Number of imaginary frequencies | : 1 | |

#### *S4.14.1. Cartesian Co-ordinates (XYZ format)*

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| | | | |
|---|---|---|---|
| Ru | 1.20241499 | -1.67160201 | -0.01670100 |
| N | 1.96901405 | -0.21964900 | -1.32669199 |
| N | 4.78597593 | 3.69165111 | -1.40841401 |
| N | 5.20189285 | 3.39251494 | 1.35950398 |
| N | 2.35909510 | -0.49954301 | 1.28679097 |
| N | 0.58345699 | -3.16760492 | 1.35066402 |
| N | 0.74018902 | -4.46512318 | 0.96868002 |
| N | 0.16909000 | -2.87239408 | -1.42490804 |
| N | 0.38617700 | -4.21543789 | -1.37545002 |
| N | 2.85212898 | -2.93712306 | -0.39649799 |
| N | 2.61038804 | -4.27087021 | -0.50439799 |
| C | 1.78368604 | -0.13987200 | -2.64858603 |
| H | 1.16416395 | -0.90227002 | -3.09749389 |
| C | 1.25763905 | -4.76637220 | -0.35398701 |
| H | 1.27762306 | -5.84493208 | -0.47422299 |
| C | 2.35845709 | 0.86553901 | -3.42727590 |
| H | 2.16864991 | 0.88094801 | -4.49209118 |

| | | | |
|---|---|---|---|
| C | 3.15773296 | 1.82052195 | -2.82728791 |
| H | 3.61837602 | 2.61562490 | -3.39753699 |
| C | 3.38150501 | 1.74756205 | -1.44539106 |
| C | 4.22759199 | 2.70253801 | -0.72968799 |
| C | 5.56441307 | 4.55997086 | -0.73044097 |
| C | 6.18453312 | 5.63927603 | -1.41433406 |
| H | 6.01258898 | 5.73763800 | -2.47909498 |
| C | 6.97542191 | 6.52020216 | -0.72296399 |
| C | 7.18556309 | 6.36895084 | 0.67527199 |
| C | 6.60234308 | 5.33845186 | 1.36619496 |
| H | 6.75005102 | 5.20615292 | 2.43092990 |
| C | 5.77671003 | 4.40725517 | 0.68185300 |
| C | 4.43954182 | 2.55019999 | 0.68125600 |
| C | 3.80781603 | 1.44159603 | 1.39653397 |
| C | 3.99623990 | 1.21934903 | 2.76770592 |
| H | 4.62777519 | 1.89223802 | 3.33161712 |
| C | 3.37388206 | 0.13757300 | 3.36201310 |
| H | 3.50042796 | -0.07385100 | 4.41530514 |
| C | 2.56613111 | -0.70084703 | 2.59248400 |
| H | 2.07776403 | -1.55712497 | 3.03382111 |
| C | 2.98260593 | 0.55444801 | 0.69077402 |
| C | 2.76980090 | 0.70726597 | -0.73139602 |
| C | 0.03063900 | -3.21600294 | 2.56351590 |
| H | -0.21134000 | -2.30496502 | 3.08633304 |
| C | -0.16619700 | -4.54798603 | 2.96904492 |
| H | -0.58822799 | -4.89320421 | 3.89724398 |
| C | 0.29321000 | -5.32123089 | 1.92738497 |
| H | 0.34031400 | -6.38926888 | 1.79184997 |
| C | -0.35195500 | -4.87194204 | -2.31129408 |
| H | -0.30456299 | -5.94379187 | -2.41117311 |
| C | -1.06894696 | -3.91653800 | -2.99478507 |
| H | -1.75608397 | -4.07784224 | -3.80759192 |
| C | -0.71580899 | -2.68925405 | -2.40609503 |
| H | -1.06844902 | -1.69793701 | -2.64053297 |
| C | 3.75696301 | -4.96486998 | -0.74153697 |
| H | 3.75118399 | -6.03654623 | -0.85351002 |
| C | 4.77658415 | -4.04170322 | -0.79019302 |
| H | 5.82137585 | -4.23690987 | -0.96107501 |
| C | 4.16574287 | -2.79401112 | -0.56984502 |
| H | 4.61814594 | -1.81677401 | -0.53059900 |
| N | -0.53250003 | -0.54143500 | 0.36199000 |
| C | -0.51897103 | 0.81321400 | 0.51444900 |
| C | -1.74610996 | -1.15183198 | 0.46903399 |
| C | -1.64189196 | 1.55999005 | 0.76207697 |
| H | 0.44064099 | 1.30016804 | 0.43075600 |
| C | -2.91822791 | -0.48128200 | 0.71666902 |
| H | -1.74984705 | -2.22480512 | 0.34678900 |
| C | -2.92112494 | 0.93729699 | 0.87570298 |
| H | -1.54704797 | 2.63347507 | 0.87090302 |
| H | -3.83891797 | -1.04579306 | 0.78438097 |
| C | -4.07552290 | 1.68521297 | 1.13056505 |
| H | -3.95233107 | 2.76256895 | 1.22088099 |
| C | -5.41447687 | 1.12469006 | 1.32874095 |
| H | -5.52284384 | 0.31160000 | 2.04169607 |
| C | -6.57231522 | 1.58830595 | 0.68318099 |
| C | -7.84069586 | 0.99290800 | 0.96395600 |
| C | -6.54882097 | 2.64121604 | -0.28319100 |
| C | -8.99873543 | 1.42680204 | 0.35523701 |
| H | -7.90859413 | 0.17382701 | 1.67095900 |
| C | -7.71358490 | 3.07695508 | -0.88292497 |
| H | -5.60793591 | 3.11238194 | -0.53923798 |
| C | -8.95240021 | 2.50018501 | -0.57129103 |
| H | -7.69925594 | 3.88651800 | -1.60350204 |
| O | -10.07008934 | 2.96268296 | -1.20938599 |

| | | | |
|---|---|---|---|
| O | -10.19230747 | 0.82751101 | 0.68716103 |
| C | -10.77041435 | 0.01181200 | -0.34954199 |
| H | -10.09220695 | -0.80554497 | -0.61194903 |
| H | -11.69064426 | -0.39743799 | 0.06431500 |
| H | -10.99645233 | 0.60514802 | -1.23804498 |
| C | -11.07615566 | 3.57505703 | -0.37519300 |
| H | -11.87565613 | 3.88139796 | -1.04744005 |
| H | -11.45816326 | 2.87023497 | 0.36403999 |
| H | -10.66178513 | 4.45425081 | 0.12615100 |
| H | 7.44961405 | 7.34441805 | -1.24212801 |
| H | 7.81582117 | 7.08083200 | 1.19462395 |

### S4.15. Electrostatic potentials for triplet states of 1 at different geometries

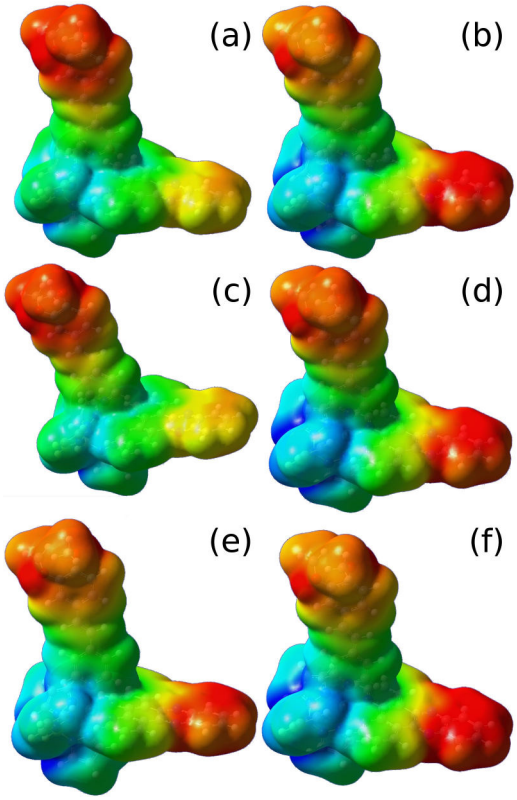
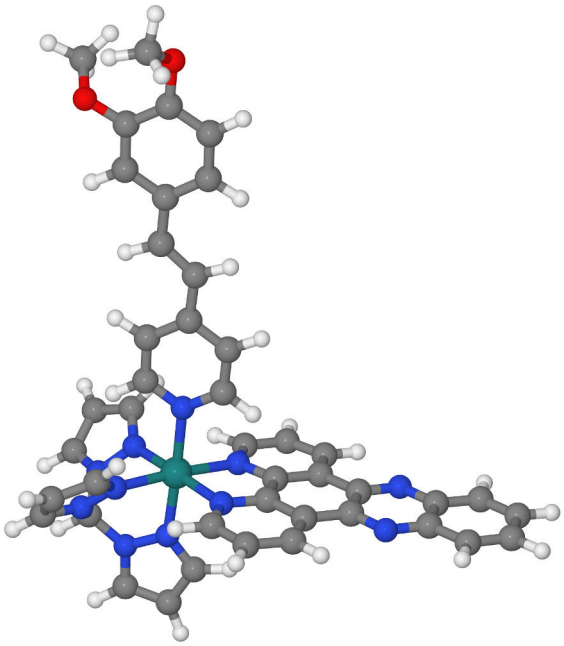



FIG. S14. Electrostatic potential for **1** for 6 electronic state and geometry combinations. Panel (a): $S_0$ (optimized geometry); Panel (b): $T_1$ ($S_0$ geometry); Panel (c): $T_2$ ($S_0$ geometry); Panel (d): $T_1$ (optimized geometry); Panel (e): $T_2$ ($T_1$ geometry); Panel (f): $T_3$ ($T_1$ geometry). Because the overall charge on the molecule is 2+, the scale has been shifted such that red corresponds to a charge of +0.075e and blue to a charge of +0.25.

## S4.16. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ ($T_2$)



SMILES : [Ru]123(n4cccc5c6nc7ccccc7nc6c6cccn1c6c45)(N1N([C@@H](N4N2C=CC4)N2N3C=CC2)CC=C1)N1C=C[C@@H](C=C1)/C=C/c1cc(c(cc1)OC)OC

Formula : $C_{43}H_{35}N_{11}O_2Ru^{2+,3}$

Charge : 2

Multiplicity : 3

Energy : -2507.57720907 a.u.

### *S4.16.1. Cartesian Co-ordinates (XYZ format)*

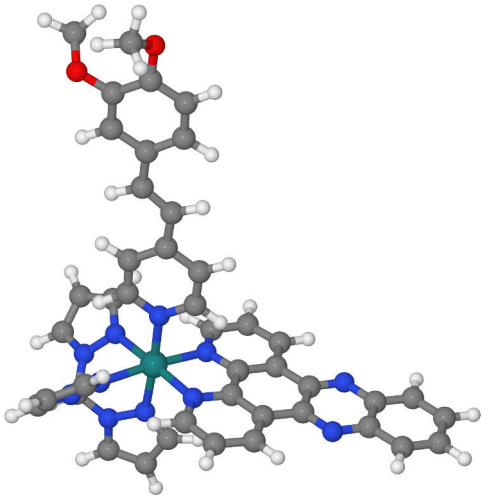
92

| | | | |
|---|---|---|---|
| Ru | 1.50196 | -1.72362 | 0.01393 |
| N | 2.25530 | -0.30821 | -1.33456 |
| N | 4.32103 | 4.08035 | -1.44123 |
| N | 4.30278 | 4.11071 | 1.38029 |
| N | 2.23888 | -0.27980 | 1.34132 |
| N | 0.89623 | -3.14328 | 1.42761 |
| N | 1.31474 | -4.42928 | 1.23720 |
| N | 0.91330 | -3.17537 | -1.37449 |
| N | 1.32833 | -4.45694 | -1.14894 |
| N | 3.36095 | -2.72052 | 0.03435 |
| N | 3.35424 | -4.07730 | 0.05158 |
| C | 2.31276 | -0.38670 | -2.66925 |
| H | 1.93501 | -1.29336 | -3.12019 |
| C | 2.08798 | -4.77099 | 0.05230 |
| H | 2.27663 | -5.83950 | 0.06622 |
| C | 2.82999 | 0.63357 | -3.45907 |
| H | 2.84360 | 0.51560 | -4.53344 |
| C | 3.32681 | 1.78872 | -2.84414 |
| H | 3.73663 | 2.60042 | -3.43106 |
| C | 3.31254 | 1.90012 | -1.46037 |
| C | 3.83827 | 3.06175 | -0.74564 |

| | | | |
|---|---|---|---|
| C | 4.80901 | 5.14604 | -0.75410 |
| C | 5.33478 | 6.25789 | -1.45430 |
| H | 5.33315 | 6.22725 | -2.53754 |
| C | 5.83121 | 7.34147 | -0.76257 |
| C | 5.82190 | 7.35677 | 0.65123 |
| C | 5.31632 | 6.28829 | 1.35963 |
| H | 5.30048 | 6.28102 | 2.44315 |
| C | 4.79967 | 5.16147 | 0.67676 |
| C | 3.82899 | 3.07728 | 0.70059 |
| C | 3.29435 | 1.93102 | 1.43329 |
| C | 3.29144 | 1.84910 | 2.81917 |
| H | 3.69387 | 2.67323 | 3.39375 |
| C | 2.78722 | 0.70707 | 3.45229 |
| H | 2.78762 | 0.61188 | 4.52900 |
| C | 2.27992 | -0.32994 | 2.67798 |
| H | 1.89685 | -1.22694 | 3.14347 |
| C | 2.76201 | 0.83219 | 0.69290 |
| C | 2.77069 | 0.81732 | -0.70347 |
| C | 0.13772 | -3.16670 | 2.53328 |
| H | -0.32605 | -2.26284 | 2.89365 |
| C | 0.07524 | -4.46087 | 3.05669 |
| H | -0.45263 | -4.78516 | 3.93675 |
| C | 0.82716 | -5.24445 | 2.20203 |
| H | 1.04377 | -6.30053 | 2.20528 |
| C | 0.84964 | -5.29437 | -2.09911 |
| H | 1.06440 | -6.35050 | -2.07466 |
| C | 0.10806 | -4.53068 | -2.98032 |
| H | -0.41073 | -4.87548 | -3.85798 |
| C | 0.16672 | -3.22445 | -2.48737 |
| H | -0.29176 | -2.32884 | -2.87417 |
| C | 4.62101 | -4.57298 | 0.06369 |
| H | 4.80812 | -5.63387 | 0.07770 |
| C | 5.47079 | -3.49008 | 0.05392 |
| H | 6.54692 | -3.51057 | 0.05920 |
| C | 4.64150 | -2.35524 | 0.03560 |
| H | 4.91225 | -1.31211 | 0.02345 |
| N | -0.41339 | -0.79410 | -0.00626 |
| C | -0.56485 | 0.54650 | -0.02093 |
| C | -1.54139 | -1.54414 | -0.00326 |
| C | -1.80339 | 1.15806 | -0.03180 |
| H | 0.33514 | 1.14220 | -0.02367 |
| C | -2.80868 | -1.00150 | -0.01343 |
| H | -1.41268 | -2.61662 | 0.00795 |
| C | -2.98337 | 0.39491 | -0.02741 |
| H | -1.84744 | 2.23992 | -0.04291 |
| H | -3.65015 | -1.68058 | -0.01069 |
| C | -4.27405 | 1.06841 | -0.03689 |
| H | -4.21862 | 2.15179 | -0.05600 |
| C | -5.47830 | 0.46083 | -0.02102 |
| H | -5.51671 | -0.62449 | 0.00034 |
| C | -6.78781 | 1.10594 | -0.02597 |
| C | -7.93294 | 0.29132 | -0.00866 |
| C | -6.97070 | 2.50072 | -0.05858 |
| C | -9.21472 | 0.82907 | -0.00758 |
| H | -7.83748 | -0.78877 | 0.00090 |
| C | -8.24586 | 3.04399 | -0.04551 |
| H | -6.11843 | 3.16799 | -0.08087 |
| C | -9.37900 | 2.22613 | -0.00898 |
| H | -8.39336 | 4.11741 | -0.05729 |
| O | -10.61486 | 2.81634 | -0.02449 |
| O | -10.29121 | -0.02541 | 0.03263 |
| C | -11.07665 | -0.07419 | -1.17436 |
| H | -10.46260 | -0.41519 | -2.01297 |
| H | -11.87199 | -0.79422 | -0.98886 |

| | | | |
|---|---|---|---|
| H | -11.50733 | 0.90258 | -1.40358 |
| C | -11.42115 | 2.62148 | 1.15563 |
| H | -12.34932 | 3.16120 | 0.97637 |
| H | -11.63027 | 1.56364 | 1.32040 |
| H | -10.91588 | 3.04223 | 2.02958 |
| H | 6.23284 | 8.19071 | -1.30292 |
| H | 6.21650 | 8.21755 | 1.17832 |

## S4.17. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ ($S_1$)



| | | |
|---|---|---|
| SMILES | : | COc1ccc(cc1OC)C=Cc2cc[n+](cc2)[Ru]345([n+]6cccc7=c8c(=c9ccc[n+]3c9=c76)nc1ccccc1n8)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 |
| Formula | : | $C_{43}H_{35}N_{11}O_2Ru^{2+}$ |
| Charge | : | 2 |
| Multiplicity | : | 1 |
| Energy | : | -2507.65495232 a.u. |

### *S4.17.1. Cartesian Co-ordinates (XYZ format)*

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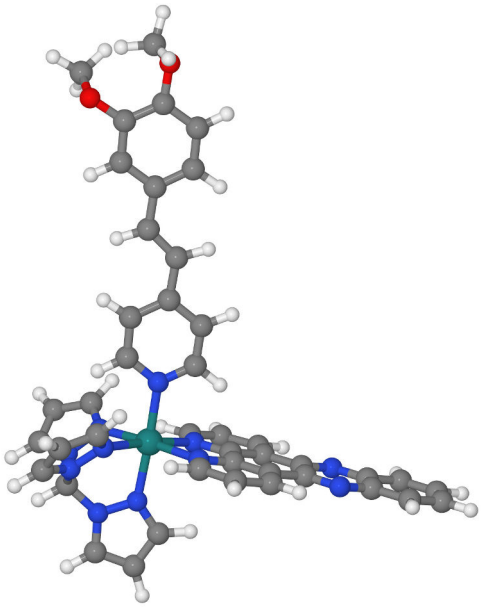
| | | | |
|---|---|---|---|
| Ru | 1.36971414 | -1.69933200 | 0.02200346 |
| N | 2.17380929 | -0.31977248 | -1.33311176 |
| N | 4.61918354 | 3.86987591 | -1.44863415 |
| N | 4.61311245 | 3.90242791 | 1.37770045 |
| N | 2.16785455 | -0.28862256 | 1.34804797 |
| N | 0.71910346 | -3.14517856 | 1.45002019 |
| N | 1.09904528 | -4.43553543 | 1.24606109 |
| N | 0.72614658 | -3.18044448 | -1.37299836 |
| N | 1.10433185 | -4.46546030 | -1.13444126 |
| N | 3.17591500 | -2.73426533 | 0.03770361 |
| N | 3.14103746 | -4.09605646 | 0.05592349 |
| C | 2.18809581 | -0.38227838 | -2.66322660 |
| H | 1.71766531 | -1.24464571 | -3.11426568 |
| C | 1.86137235 | -4.78136158 | 0.06164914 |
| H | 2.04842091 | -5.85024500 | 0.07575650 |
| C | 2.78232574 | 0.59805149 | -3.45839977 |
| H | 2.76095700 | 0.49367461 | -4.53398514 |
| C | 3.39349151 | 1.69020462 | -2.84369636 |
| H | 3.86231542 | 2.46963167 | -3.43048000 |
| C | 3.41562462 | 1.79039478 | -1.45586836 |
| C | 4.04861021 | 2.89864683 | -0.74804634 |
| C | 5.20486593 | 4.88819933 | -0.76106018 |
| C | 5.82651424 | 5.94733572 | -1.46188283 |
| H | 5.81850386 | 5.91699123 | -2.54519415 |
| C | 6.42291832 | 6.98401213 | -0.77314919 |
| C | 6.42005110 | 7.00019932 | 0.63830668 |

| | | | |
|---|---|---|---|
| C | 5.82076693 | 5.97959518 | 1.34822440 |
| H | 5.80834627 | 5.97420835 | 2.43190742 |
| C | 5.20186663 | 4.90464449 | 0.66937649 |
| C | 4.04548311 | 2.91531157 | 0.69718987 |
| C | 3.40935040 | 1.82365763 | 1.42755544 |
| C | 3.38137150 | 1.75530910 | 2.81722498 |
| H | 3.84796238 | 2.54794145 | 3.38787603 |
| C | 2.76747084 | 0.67760956 | 3.45427871 |
| H | 2.74161434 | 0.59795046 | 4.53187609 |
| C | 2.17646980 | -0.32069615 | 2.67929602 |
| H | 1.70409691 | -1.17255235 | 3.14789295 |
| C | 2.78905821 | 0.76494706 | 0.69616461 |
| C | 2.79215741 | 0.74871182 | -0.70300901 |
| C | -0.00133681 | -3.15343404 | 2.57310629 |
| H | -0.43307769 | -2.24069452 | 2.95074487 |
| C | -0.08688909 | -4.45341301 | 3.09615183 |
| H | -0.60001183 | -4.76517582 | 3.98942423 |
| C | 0.62462145 | -5.24881744 | 2.22557473 |
| H | 0.83075291 | -6.30664539 | 2.22317457 |
| C | 0.63292921 | -5.30324364 | -2.09459877 |
| H | 0.83787721 | -6.36081171 | -2.06408405 |
| C | -0.07431926 | -4.52996635 | -2.98822808 |
| H | -0.58405358 | -4.86426401 | -3.87526608 |
| C | 0.01030505 | -3.21706080 | -2.49841332 |
| H | -0.41896892 | -2.31389880 | -2.90102553 |
| C | 4.39279890 | -4.61282301 | 0.06522983 |
| H | 4.56187725 | -5.67690611 | 0.07978297 |
| C | 5.27161980 | -3.54646063 | 0.05251639 |
| H | 6.34678459 | -3.59450364 | 0.05517355 |
| C | 4.47132778 | -2.39953470 | 0.03556806 |
| H | 4.76295805 | -1.36233187 | 0.02205827 |
| N | -0.47854730 | -0.74794370 | 0.00646264 |
| C | -0.60039598 | 0.60257852 | -0.01092808 |
| C | -1.62850606 | -1.47468710 | 0.01326303 |
| C | -1.81943429 | 1.24030805 | -0.02191856 |
| H | 0.31481826 | 1.17420423 | -0.01600173 |
| C | -2.87861371 | -0.90509623 | 0.00336709 |
| H | -1.51672924 | -2.54826927 | 0.02698047 |
| C | -3.02020550 | 0.50009972 | -0.01472262 |
| H | -1.84271538 | 2.32246661 | -0.03559432 |
| H | -3.73650384 | -1.56274760 | 0.00880645 |
| C | -4.28399944 | 1.19958198 | -0.02640987 |
| H | -4.20834303 | 2.28103471 | -0.04911033 |
| C | -5.50713778 | 0.61255938 | -0.00837992 |
| H | -5.56442499 | -0.47120351 | 0.01811456 |
| C | -6.79386711 | 1.28048110 | -0.01701907 |
| C | -7.95739603 | 0.48773295 | 0.00667699 |
| C | -6.94699955 | 2.68193197 | -0.06256156 |
| C | -9.22558880 | 1.05009639 | 0.00455283 |
| H | -7.88266468 | -0.59372425 | 0.01959733 |
| C | -8.20776367 | 3.24970484 | -0.05179732 |
| H | -6.08107710 | 3.33052325 | -0.09124997 |
| C | -9.35991859 | 2.45420051 | -0.00121008 |
| H | -8.33544159 | 4.32519674 | -0.07045414 |
| O | -10.56965923 | 3.08022928 | -0.01400683 |
| O | -10.31929874 | 0.22022532 | 0.03597888 |
| C | -11.07925701 | 0.17053917 | -1.18864536 |
| H | -10.45371532 | -0.19553953 | -2.00746870 |
| H | -11.89404488 | -0.52880490 | -1.01004255 |
| H | -11.48335361 | 1.15302086 | -1.44192517 |
| C | -11.45024204 | 2.83320165 | 1.10503078 |
| H | -12.33989811 | 3.43031883 | 0.91617793 |
| H | -11.71282387 | 1.77829444 | 1.17907012 |
| H | -10.97391796 | 3.16574788 | 2.03091979 |

| | | | |
|---|---|---|---|
| H | 6.89753437 | 7.79250097 | -1.31687474 |
| H | 6.89251232 | 7.82095480 | 1.16527283 |

## S4.18. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ ($S_2$)



SMILES : COc1ccc(cc1OC)C=Cc2cc[n+](cc2)[Ru]345([n+]6cccc7=c8c(=c9ccc[n+]3c9=c76)nc1ccccc1n8)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1
Formula : $C_{43}H_{35}N_{11}O_2Ru^{2+}$
Charge : 2
Multiplicity : 1
Energy : -2507.65720683 a.u.

### *S4.18.1. Cartesian Co-ordinates (XYZ format)*

92

| | | | |
|---|---|---|---|
| Ru | 1.38370156 | -1.68645179 | 0.01731653 |
| N | 2.19110394 | -0.29240340 | -1.32217693 |
| N | 4.61796665 | 3.86726928 | -1.45557308 |
| N | 4.61997509 | 3.89315820 | 1.38364577 |
| N | 2.19287229 | -0.26796451 | 1.32945549 |
| N | 0.73443663 | -3.13484716 | 1.44226825 |
| N | 1.11060679 | -4.42590046 | 1.23604310 |
| N | 0.73327202 | -3.16409802 | -1.37739193 |
| N | 1.10904419 | -4.45071602 | -1.14393520 |
| N | 3.18925047 | -2.72677684 | 0.02552728 |
| N | 3.14991093 | -4.08860111 | 0.04101874 |
| C | 2.19358182 | -0.36455533 | -2.67746329 |
| H | 1.72460151 | -1.23083138 | -3.11788964 |
| C | 1.86862636 | -4.77099943 | 0.04902460 |
| H | 2.05344343 | -5.84031057 | 0.06007526 |
| C | 2.77784681 | 0.61335105 | -3.46007490 |
| H | 2.75064993 | 0.50889981 | -4.53687620 |
| C | 3.39513445 | 1.71504378 | -2.86000443 |
| H | 3.85955071 | 2.49629140 | -3.44386506 |
| C | 3.41678572 | 1.79645920 | -1.46047020 |
| C | 4.04903364 | 2.89605641 | -0.73840559 |
| C | 5.20147276 | 4.87974310 | -0.76353174 |
| C | 5.82247972 | 5.94423532 | -1.46186113 |

| | | | |
|---|---|---|---|
| H | 5.81176233 | 5.91702557 | -2.54518628 |
| C | 6.41914225 | 6.97771168 | -0.77240545 |
| C | 6.42025232 | 6.99057722 | 0.64115083 |
| C | 5.82466364 | 5.96985006 | 1.35026002 |
| H | 5.81566811 | 5.96246815 | 2.43391895 |
| C | 5.20253563 | 4.89283228 | 0.67242187 |
| C | 4.05004644 | 2.90905833 | 0.68508822 |
| C | 3.41882181 | 1.82282567 | 1.42793429 |
| C | 3.39921784 | 1.76683056 | 2.82872868 |
| H | 3.86464286 | 2.55854225 | 3.39751482 |
| C | 2.78280616 | 0.67625594 | 3.44968009 |
| H | 2.75730181 | 0.59139699 | 4.52824211 |
| C | 2.19735289 | -0.31568551 | 2.68583488 |
| H | 1.72918284 | -1.17395163 | 3.14243078 |
| C | 2.80749035 | 0.78366619 | 0.71290970 |
| C | 2.80651140 | 0.77044284 | -0.72580749 |
| C | 0.01933332 | -3.14216495 | 2.56884027 |
| H | -0.40740976 | -2.22834539 | 2.94954205 |
| C | -0.06738269 | -4.44239521 | 3.09108591 |
| H | -0.57730281 | -4.75353384 | 3.98641777 |
| C | 0.63836706 | -5.23895550 | 2.21685863 |
| H | 0.84209073 | -6.29723883 | 2.21290112 |
| C | 0.63554001 | -5.28429365 | -2.10673332 |
| H | 0.83875883 | -6.34230852 | -2.08011603 |
| C | -0.07062154 | -4.50632954 | -2.99718285 |
| H | -0.58146966 | -4.83634710 | -3.88519239 |
| C | 0.01721149 | -3.19528508 | -2.50293946 |
| H | -0.40943015 | -2.28959513 | -2.90268135 |
| C | 4.39981318 | -4.61010456 | 0.04534006 |
| H | 4.56487465 | -5.67482090 | 0.05711073 |
| C | 5.28238964 | -3.54715180 | 0.03219736 |
| H | 6.35738420 | -3.59882355 | 0.03144344 |
| C | 4.48603201 | -2.39739203 | 0.02013771 |
| H | 4.78532314 | -1.36259043 | 0.00793981 |
| N | -0.46642029 | -0.73514313 | 0.00917830 |
| C | -0.59633285 | 0.61459929 | -0.00344780 |
| C | -1.61350667 | -1.46692455 | 0.01670304 |
| C | -1.81822467 | 1.24673867 | -0.00890722 |
| H | 0.31305513 | 1.19410384 | -0.00923521 |
| C | -2.86650920 | -0.90373588 | 0.01180797 |
| H | -1.49676991 | -2.53989220 | 0.02714590 |
| C | -3.01545644 | 0.50076967 | -0.00147238 |
| H | -1.84647655 | 2.32879543 | -0.01902237 |
| H | -3.72091866 | -1.56588817 | 0.01849226 |
| C | -4.28208113 | 1.19407403 | -0.00770056 |
| H | -4.21163368 | 2.27602029 | -0.01890764 |
| C | -5.50308037 | 0.60100824 | -0.00023363 |
| H | -5.55543947 | -0.48323867 | 0.01088670 |
| C | -6.79172707 | 1.26340806 | -0.00422613 |
| C | -7.95242691 | 0.46572456 | -0.00660016 |
| C | -6.95035601 | 2.66537237 | -0.02088335 |
| C | -9.22264194 | 1.02275825 | -0.00736621 |
| H | -7.87331533 | -0.61541796 | -0.01699660 |
| C | -8.21306705 | 3.22764564 | -0.00774795 |
| H | -6.08692074 | 3.31779623 | -0.02755540 |
| C | -9.36278725 | 2.42662072 | 0.01702198 |
| H | -8.34522152 | 4.30270958 | -0.00339396 |
| O | -10.57282639 | 3.04996061 | 0.00920101 |
| O | -10.31299210 | 0.18817189 | -0.00579010 |
| C | -11.05755901 | 0.16056247 | -1.24065804 |
| H | -10.42012691 | -0.18539505 | -2.05900168 |
| H | -11.87115574 | -0.54596007 | -1.08674419 |
| H | -11.46321964 | 1.14630568 | -1.47854066 |
| C | -11.47315788 | 2.76308751 | 1.10312295 |

| | | | |
|---|---|---|---|
| H | -12.35733414 | 3.37045979 | 0.92178810 |
| H | -11.73993397 | 1.70723951 | 1.13302946 |
| H | -11.01129723 | 3.05875349 | 2.04854846 |
| H | 6.89208555 | 7.78823996 | -1.31453419 |
| H | 6.89405060 | 7.81082344 | 1.16769290 |

### S4.19. Differential density maps of 1 for different excited singlet states

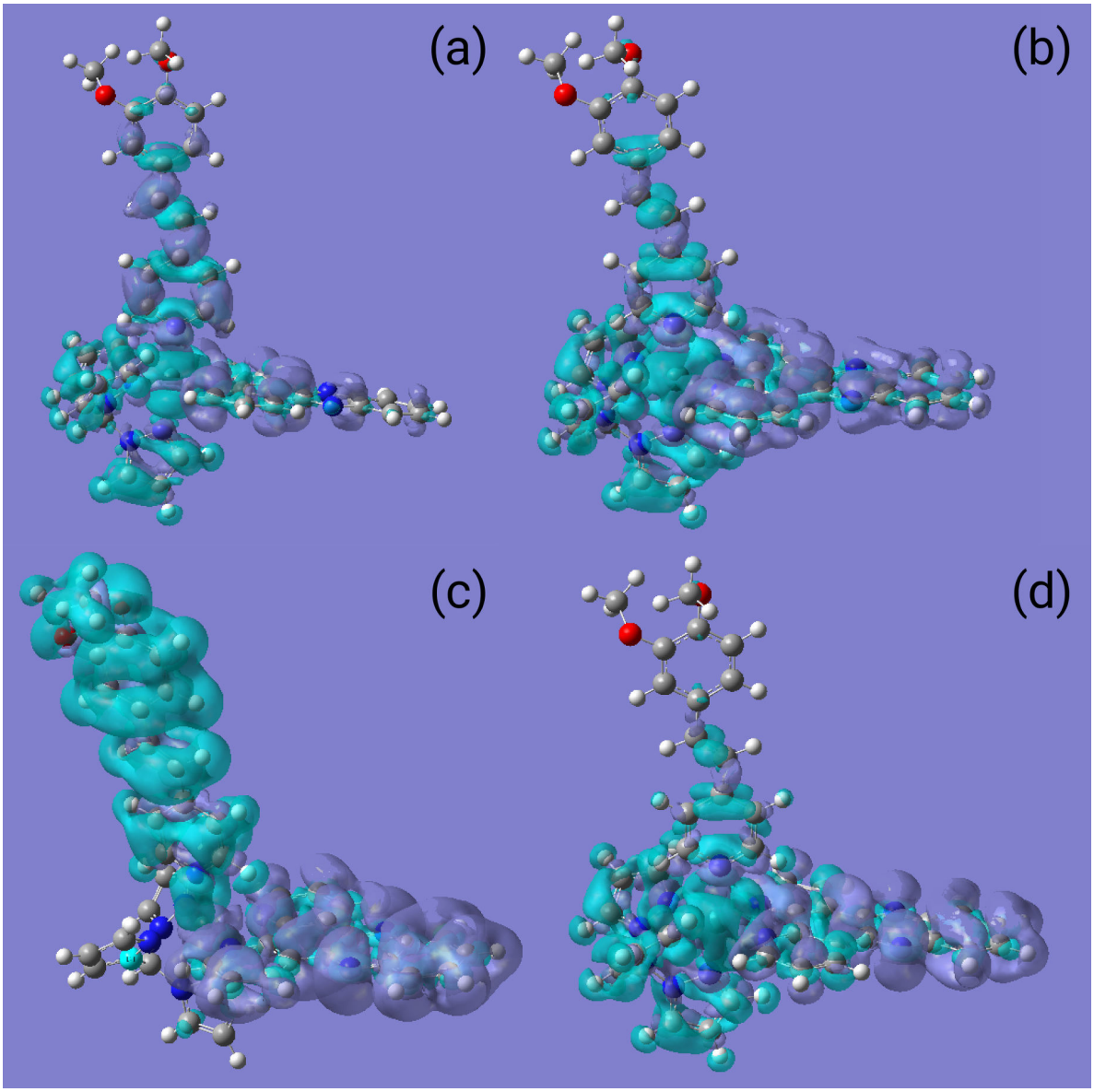
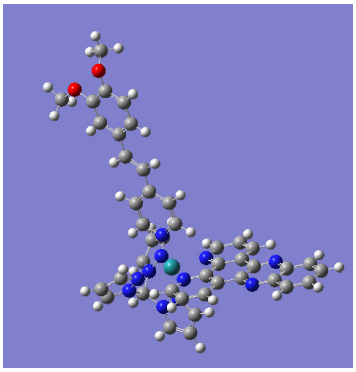



FIG. S15. Differential Density maps for **1** for 4 transition on the singlet manifold, all originating from and at the geometry of $S_0$. Panel (a): Transition to $S_5$; Panel (b): Transition to $S_6$. Panel (c): Transition to $S_7$. Panel (d): Transition to $S_8$. In all maps green indicates a decrease in electron density, whereas blue indicates an increase.

### S4.20. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ ($S_0$); alternative isomer



| | | |
|---|---|---|
| Route | : # opt freq b3lyp/genecp scrf=(solvent=water) geom=connectivity int=ultrafine pop=regular scf=tight | |
| SMILES | : COc1ccc(cc1OC)C=Cc2cc[n+](cc2)[Ru]345([n+]6cccc7c6c8[n+]3cccc8c9c7nc1ccccc1n9)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 | |
| Formula | : $C_{43}H_{35}N_{11}O_2Ru^{2+}$ | |
| Charge | : 2 | |
| Multiplicity | : 1 | |
| Energy | : -2507.66396831 | a.u. |
| Gibbs Energy | : -2507.02787500 | a.u. |
| Number of imaginary frequencies | : 0 | |

#### *S4.20.1. Cartesian Co-ordinates (XYZ format)*

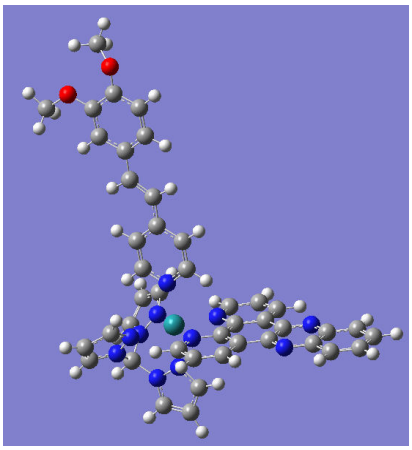
92

| | | | |
|---|---|---|---|
| Ru | -1.37717903 | -1.69129205 | -0.00069900 |
| N | -2.16916895 | -0.27689201 | 1.33404601 |
| N | -4.64246082 | 3.86050701 | 1.43340802 |
| N | -4.73431015 | 3.81923294 | -1.37965000 |
| N | -2.25619197 | -0.31572199 | -1.32070100 |
| N | -0.72028601 | -3.12526298 | -1.41580701 |
| N | -1.03067696 | -4.42803717 | -1.16963696 |
| N | -0.62580103 | -3.08822107 | 1.40583396 |
| N | -0.94644600 | -4.39725018 | 1.21205294 |
| N | -3.15719604 | -2.81778193 | 0.07492900 |
| N | -3.04386497 | -4.17256403 | 0.09097500 |
| C | -2.14125800 | -0.31562400 | 2.67056704 |
| H | -1.64762604 | -1.16498601 | 3.11943698 |
| C | -1.73040795 | -4.78072977 | 0.05213700 |
| H | -1.85767102 | -5.85837793 | 0.07096800 |
| C | -2.72051597 | 0.67643201 | 3.46289301 |
| H | -2.66181898 | 0.59210199 | 4.53974104 |
| C | -3.35804009 | 1.74509096 | 2.86082792 |
| H | -3.81767607 | 2.53315806 | 3.44155693 |
| C | -3.41520596 | 1.79995406 | 1.46131396 |
| C | -4.08534002 | 2.88144398 | 0.73923898 |
| C | -5.25905180 | 4.84609699 | 0.74930799 |
| C | -5.87125111 | 5.91930103 | 1.44973505 |
| H | -5.82531691 | 5.91728306 | 2.53179598 |
| C | -6.49781513 | 6.91952181 | 0.75221002 |
| C | -6.54413509 | 6.89871693 | -0.66886997 |

| | | | |
|---|---|---|---|
| C | -5.96333694 | 5.87793922 | -1.37616003 |
| H | -5.98790121 | 5.84422684 | -2.45839691 |
| C | -5.30584288 | 4.82508087 | -0.68598700 |
| C | -4.13235283 | 2.86032295 | -0.69487602 |
| C | -3.51024389 | 1.75728798 | -1.42717302 |
| C | -3.54540896 | 1.66085196 | -2.82516289 |
| H | -4.04327488 | 2.43171811 | -3.39742589 |
| C | -2.94779611 | 0.57416499 | -3.43592000 |
| H | -2.96013093 | 0.45778799 | -4.51132488 |
| C | -2.31634212 | -0.39431900 | -2.65441489 |
| H | -1.85246503 | -1.25723398 | -3.10900092 |
| C | -2.85648704 | 0.74415100 | -0.71116698 |
| C | -2.80901289 | 0.76534599 | 0.73413998 |
| C | -0.02528900 | -3.13319707 | -2.55438590 |
| H | 0.35311601 | -2.21143103 | -2.96573591 |
| C | 0.11087200 | -4.44346523 | -3.04717898 |
| H | 0.61653101 | -4.75478888 | -3.94509292 |
| C | -0.53787303 | -5.24749279 | -2.13805294 |
| H | -0.68804502 | -6.31394100 | -2.09982300 |
| C | -0.38759699 | -5.19195700 | 2.16496992 |
| H | -0.53745699 | -6.25904179 | 2.16233301 |
| C | 0.31731999 | -4.36489916 | 3.00928807 |
| H | 0.88296402 | -4.65329123 | 3.87861705 |
| C | 0.14342700 | -3.06726694 | 2.49549699 |
| H | 0.54590398 | -2.13528895 | 2.85784888 |
| C | -4.26479197 | -4.77191782 | 0.14978901 |
| H | -4.36196280 | -5.84471178 | 0.17185000 |
| C | -5.20060587 | -3.76334500 | 0.17090200 |
| H | -6.27077818 | -3.87152100 | 0.21505199 |
| C | -4.46457005 | -2.56511807 | 0.12272100 |
| H | -4.82398510 | -1.54927003 | 0.12166700 |
| N | 0.50240302 | -0.69202101 | -0.07224700 |
| C | 0.62154400 | 0.65188801 | -0.09528100 |
| C | 1.65591502 | -1.40152895 | -0.09484100 |
| C | 1.83943903 | 1.30479896 | -0.13781001 |
| H | -0.29316199 | 1.22536600 | -0.07879600 |
| C | 2.90759897 | -0.82146603 | -0.13634799 |
| H | 1.55672705 | -2.47684693 | -0.07973400 |
| C | 3.04185796 | 0.57865298 | -0.15686700 |
| H | 1.85033202 | 2.38770700 | -0.15309800 |
| H | 3.76967502 | -1.47458994 | -0.15701699 |
| C | 4.31347084 | 1.28994799 | -0.19707701 |
| H | 4.22556496 | 2.36980510 | -0.26249000 |
| C | 5.53569412 | 0.72243500 | -0.14845100 |
| H | 5.60514879 | -0.35854799 | -0.06489100 |
| C | 6.82669306 | 1.40653896 | -0.18446200 |
| C | 7.99138880 | 0.62429202 | -0.05143700 |
| C | 6.96585417 | 2.79233694 | -0.35156000 |
| C | 9.26071072 | 1.19711304 | -0.07683100 |
| H | 7.88558578 | -0.44611701 | 0.06485200 |
| C | 8.22989655 | 3.36873698 | -0.36552501 |
| H | 6.09680891 | 3.42718792 | -0.46721399 |
| C | 9.38056946 | 2.59656811 | -0.22864300 |
| H | 8.35163403 | 4.43790579 | -0.49379200 |
| O | 10.60303593 | 3.20892596 | -0.31513000 |
| O | 10.42572212 | 0.50154501 | 0.01813000 |
| C | 10.36353111 | -0.91922402 | 0.16493300 |
| H | 9.87263966 | -1.38419902 | -0.69483900 |
| H | 11.39712334 | -1.25431895 | 0.21703100 |
| H | 9.84185505 | -1.20046401 | 1.08430898 |
| C | 11.40013790 | 3.21159410 | 0.88432997 |
| H | 12.30216217 | 3.77192402 | 0.64292300 |
| H | 10.86493015 | 3.71433401 | 1.69562602 |
| H | 11.66444111 | 2.19691896 | 1.18431401 |

| | | | |
|---|---|---|---|
| H | -6.96570683 | 7.73932123 | 1.28394306 |
| H | -7.04641819 | 7.70307684 | -1.19275498 |

## S4.21. $[Ru(tpm)(DMSP)(dppz)]^{2+}$ ($T_1$); alternative isomer



| | | |
|---|---|---|
| Route | : # opt freq b3lyp/genecp scrf=(solvent=water) geom=connectivity int=ultrafine pop=regular scf=tight | |
| SMILES | : COc1ccc(cc1OC)C=Cc2cc[n+](cc2)[Ru]345([n+]6cccc7c6c8[n+]3cccc8c9c7nc1ccccc1n9)[n+]1cccn1C(n1[n+]4ccc1)n1[n+]5ccc1 | |
| Formula | : $C_{43}H_{35}N_{11}O_2Ru^{2+,3}$ | |
| Charge | : 2 | |
| Multiplicity | : 3 | |
| Energy | : -2507.59273562 | a.u. |
| Gibbs Energy | : -2506.96277300 | a.u. |
| Number of imaginary frequencies | : 0 | |

### *S4.21.1. Cartesian Co-ordinates (XYZ format)*

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| | | | |
|---|---|---|---|
| Ru | -1.33238101 | -1.68442798 | 0.00838800 |
| N | -2.15081191 | -0.30814999 | 1.33864403 |
| N | -4.68695688 | 3.83312011 | 1.40669000 |
| N | -4.69687891 | 3.81920004 | -1.42050505 |
| N | -2.16038704 | -0.32134300 | -1.32963395 |
| N | -0.66593599 | -3.15165210 | -1.40107095 |
| N | -1.01924396 | -4.44514608 | -1.16815996 |
| N | -0.65391397 | -3.13610291 | 1.42790699 |
| N | -1.00925195 | -4.43199396 | 1.21242404 |
| N | -3.12387896 | -2.76401806 | 0.02055400 |
| N | -3.06038189 | -4.12453985 | 0.02899500 |
| C | -2.15720797 | -0.35261601 | 2.67251110 |
| H | -1.66735899 | -1.19858801 | 3.13329101 |
| C | -1.76761496 | -4.78367710 | 0.02719600 |
| H | -1.93341696 | -5.85610819 | 0.03397000 |
| C | -2.76726794 | 0.62689102 | 3.45423794 |
| H | -2.73795295 | 0.53793901 | 4.53121519 |
| C | -3.40537000 | 1.70014405 | 2.82923603 |
| H | -3.88706207 | 2.47625208 | 3.40990090 |
| C | -3.43719292 | 1.78155601 | 1.44156396 |
| C | -4.09790707 | 2.86373901 | 0.71877700 |
| C | -5.30030012 | 4.82619715 | 0.70564902 |
| C | -5.94325399 | 5.88152409 | 1.39240205 |
| H | -5.92894411 | 5.86922121 | 2.47609496 |

| | | | |
|---|---|---|---|
| C | -6.56800890 | 6.89252377 | 0.69019598 |
| C | -6.57294512 | 6.88556194 | -0.72112101 |
| C | -5.95307684 | 5.86765623 | -1.41764796 |
| H | -5.94631481 | 5.84459686 | -2.50123906 |
| C | -5.30531311 | 4.81914806 | -0.72500300 |
| C | -4.10296392 | 2.85663509 | -0.72724003 |
| C | -3.44723201 | 1.76744401 | -1.44400096 |
| C | -3.42486095 | 1.67264402 | -2.83101392 |
| H | -3.91033411 | 2.44321990 | -3.41588211 |
| C | -2.79115891 | 0.59329897 | -3.44993806 |
| H | -2.76917005 | 0.49391899 | -4.52617884 |
| C | -2.17595792 | -0.37872899 | -2.66293311 |
| H | -1.68953097 | -1.22931695 | -3.11881900 |
| C | -2.80057311 | 0.73533899 | -0.69577599 |
| C | -2.79565692 | 0.74220300 | 0.69895899 |
| C | 0.05066900 | -3.16993093 | -2.52732611 |
| H | 0.46235099 | -2.25728297 | -2.92697597 |
| C | 0.16007601 | -4.47850418 | -3.02264190 |
| H | 0.67575002 | -4.79892206 | -3.91139793 |
| C | -0.53208202 | -5.26913023 | -2.13226390 |
| H | -0.71667302 | -6.33064222 | -2.10653496 |
| C | -0.51554501 | -5.24511290 | 2.18236208 |
| H | -0.70110601 | -6.30672312 | 2.17032290 |
| C | 0.18361400 | -4.44464684 | 3.05840111 |
| H | 0.70577699 | -4.75506878 | 3.94691706 |
| C | 0.07109700 | -3.14177108 | 2.54892492 |
| H | 0.48610601 | -2.22481203 | 2.93506789 |
| C | -4.30177593 | -4.66684723 | 0.03791300 |
| H | -4.44844484 | -5.73428106 | 0.04558800 |
| C | -5.20175695 | -3.61897993 | 0.03493400 |
| H | -6.27579021 | -3.68864703 | 0.03997200 |
| C | -4.42510796 | -2.45526505 | 0.02405800 |
| H | -4.73798084 | -1.42401195 | 0.01866400 |
| N | 0.50133598 | -0.70237201 | -0.00310100 |
| C | 0.59867901 | 0.65094602 | -0.00860400 |
| C | 1.66457200 | -1.40866697 | -0.00666500 |
| C | 1.80568397 | 1.30952597 | -0.01891400 |
| H | -0.32685000 | 1.20639300 | -0.00481500 |
| C | 2.90364194 | -0.81581903 | -0.01743600 |
| H | 1.57291901 | -2.48440695 | -0.00053100 |
| C | 3.02135992 | 0.59225398 | -0.02531500 |
| H | 1.80877602 | 2.39206409 | -0.02277600 |
| H | 3.77305794 | -1.45840597 | -0.01935600 |
| C | 4.27045679 | 1.31496203 | -0.03955700 |
| H | 4.17393780 | 2.39518499 | -0.04101000 |
| C | 5.50617599 | 0.75273103 | -0.05364000 |
| H | 5.58302879 | -0.33047101 | -0.05430800 |
| C | 6.77815104 | 1.44493997 | -0.06892800 |
| C | 7.95681715 | 0.66919601 | -0.09368500 |
| C | 6.90057516 | 2.84718108 | -0.06887200 |
| C | 9.21866608 | 1.25171602 | -0.11698700 |
| H | 7.86457205 | -0.40825099 | -0.11599500 |
| C | 8.15307045 | 3.43341708 | -0.06989500 |
| H | 6.02380323 | 3.48114109 | -0.05263300 |
| C | 9.32330608 | 2.66610003 | -0.08116700 |
| H | 8.26453209 | 4.51072407 | -0.05627400 |
| O | 10.49272060 | 3.34964800 | -0.12486700 |
| O | 10.38296127 | 0.55705100 | -0.19933200 |
| C | 10.33148956 | -0.87225997 | -0.21491900 |
| H | 9.78343105 | -1.23735094 | -1.08807099 |
| H | 11.36653233 | -1.20130503 | -0.27209800 |
| H | 9.87395000 | -1.26074505 | 0.69928801 |
| C | 11.62123299 | 2.92487907 | 0.66851997 |
| H | 12.26632404 | 3.79937792 | 0.73489499 |

| | | | |
|---|---|---|---|
| H | 11.29738045 | 2.63233399 | 1.66975904 |
| H | 12.14956570 | 2.10046506 | 0.19457200 |
| H | -7.05896997 | 7.69829321 | 1.22349799 |
| H | -7.06764412 | 7.68604708 | -1.25890803 |

## S5. ADDITIONAL EXPERIMENTAL DATA II

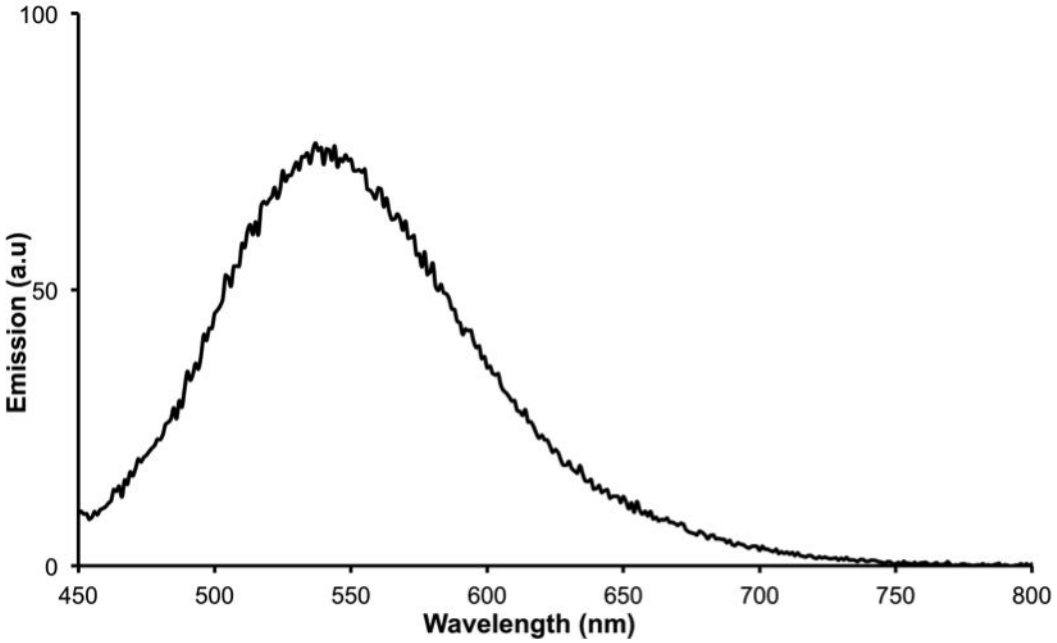


FIG. S16. Emission spectrum of [**1**]$Cl_2$ in water

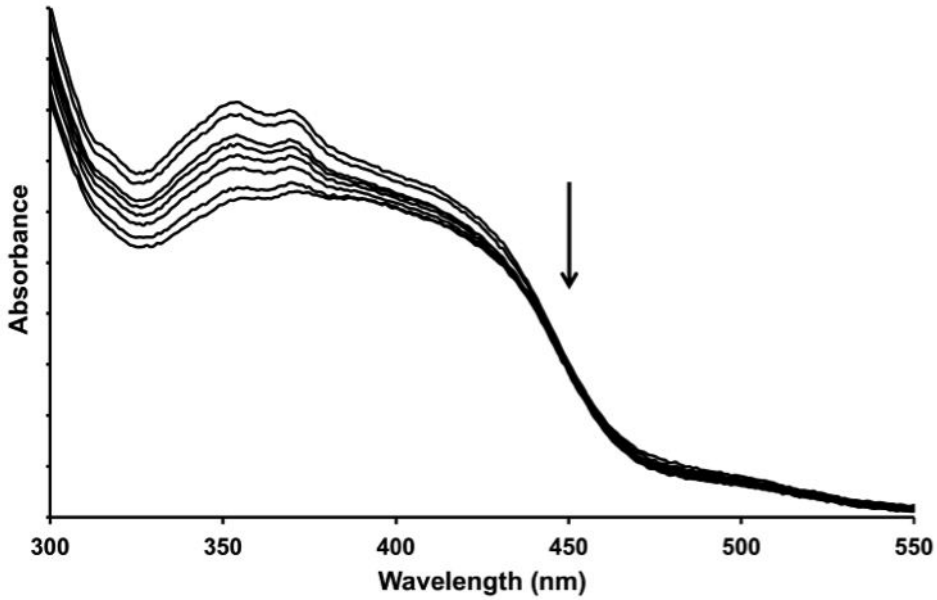


FIG. S17. Details of changes in the absorption spectrum of complex [**1**]$Cl_2$ on progressive addition of CT-DNA. Conditions: 5mM Tris, 25 mM NaCl, pH 7.4 at 25°C.

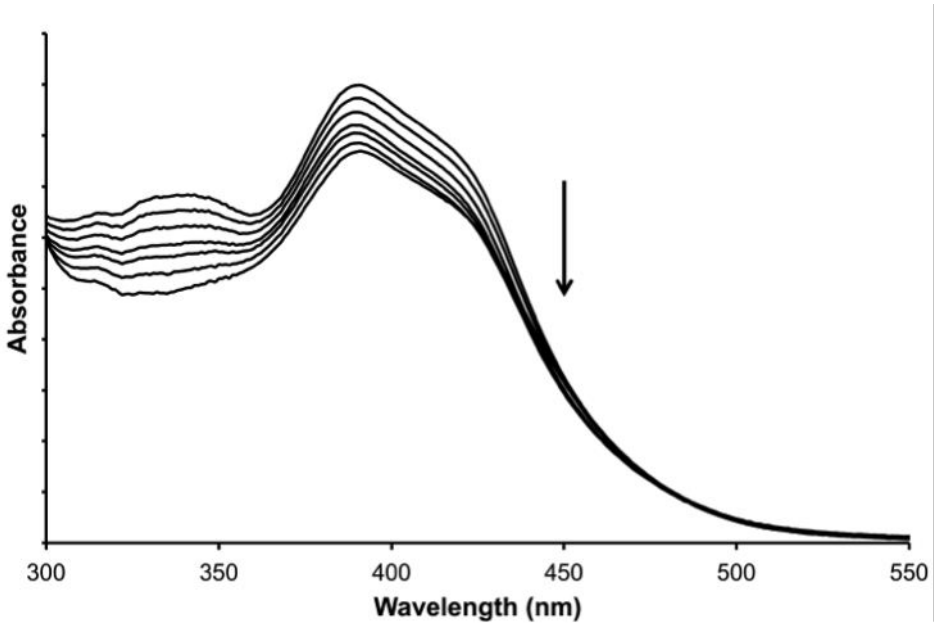


FIG. S18. Details of changes in the absorption spectrum of complex [**2**]$Cl_2$ on progressive addition of CT-DNA. Conditions: 5mM Tris, 25 mM NaCl, pH 7.4 at 25°C.

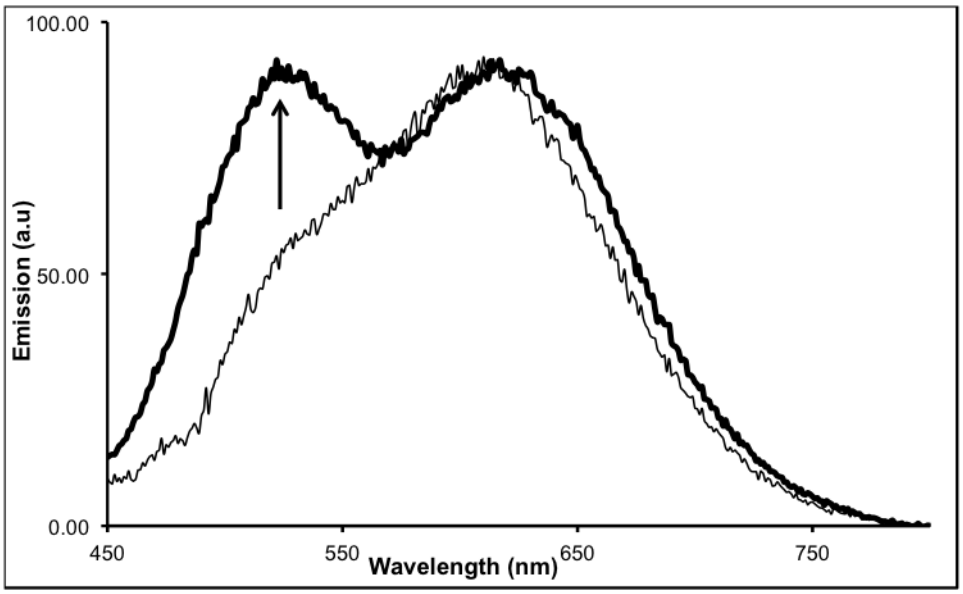


FIG. S19. Changes in the emission of complex [**2**] on the addition of excess CT-DNA. Conditions: 5mM Tris, 25 mM NaCl, pH 7.4 at 25°C.

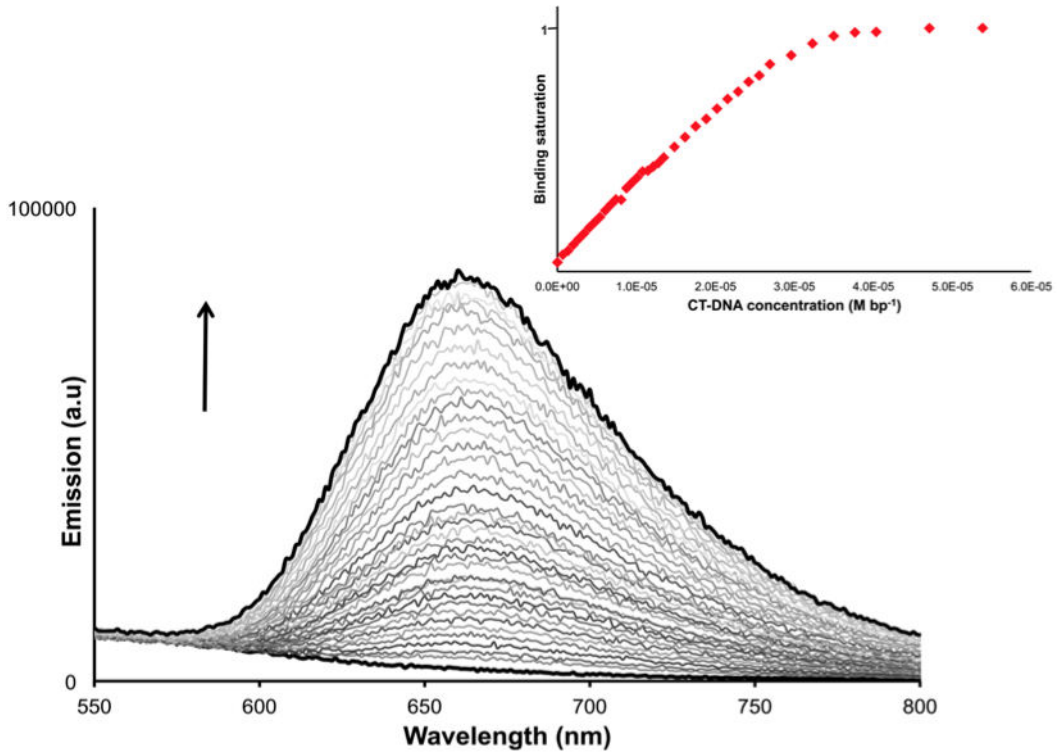


FIG. S20. Details of changes in low-energy steady-state emission of buffered aqueous solution of complex $[1]Cl_2$ on addition of CT-DNA. Inset: saturation binding curved derived from this change of intensity. Conditions: 5 mMTris, 25 mMNaCl, pH 7.4 at 25°C.

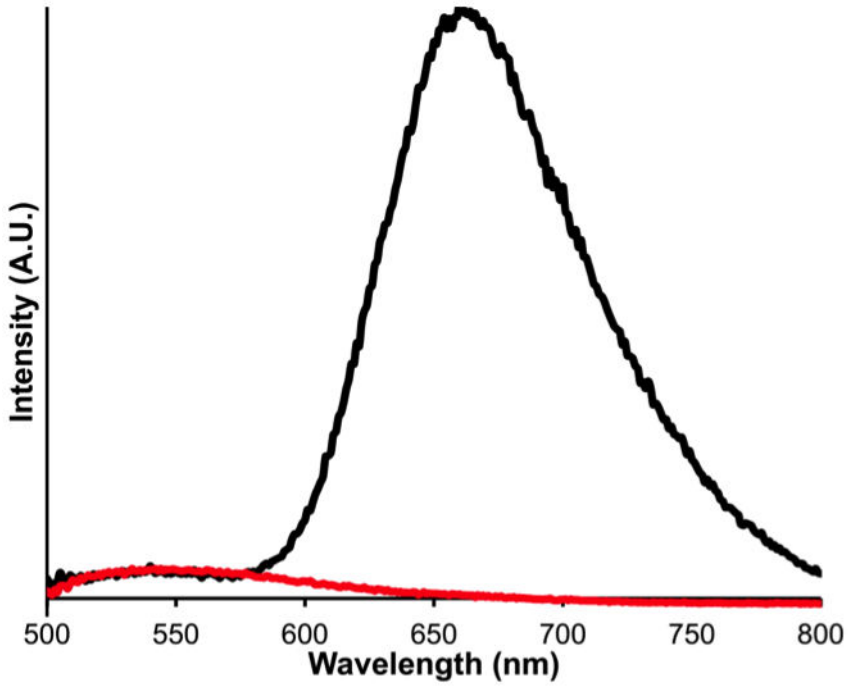


FIG. S21. Comparison of the total change in the emission of complex [**1**]. (—) = before DNA addition, (—) = after DNA addition