Supporting Information

Spectral Signature of a Ru(II, III, IV) Complex: A Combined Experimental and Theoretical Investigation

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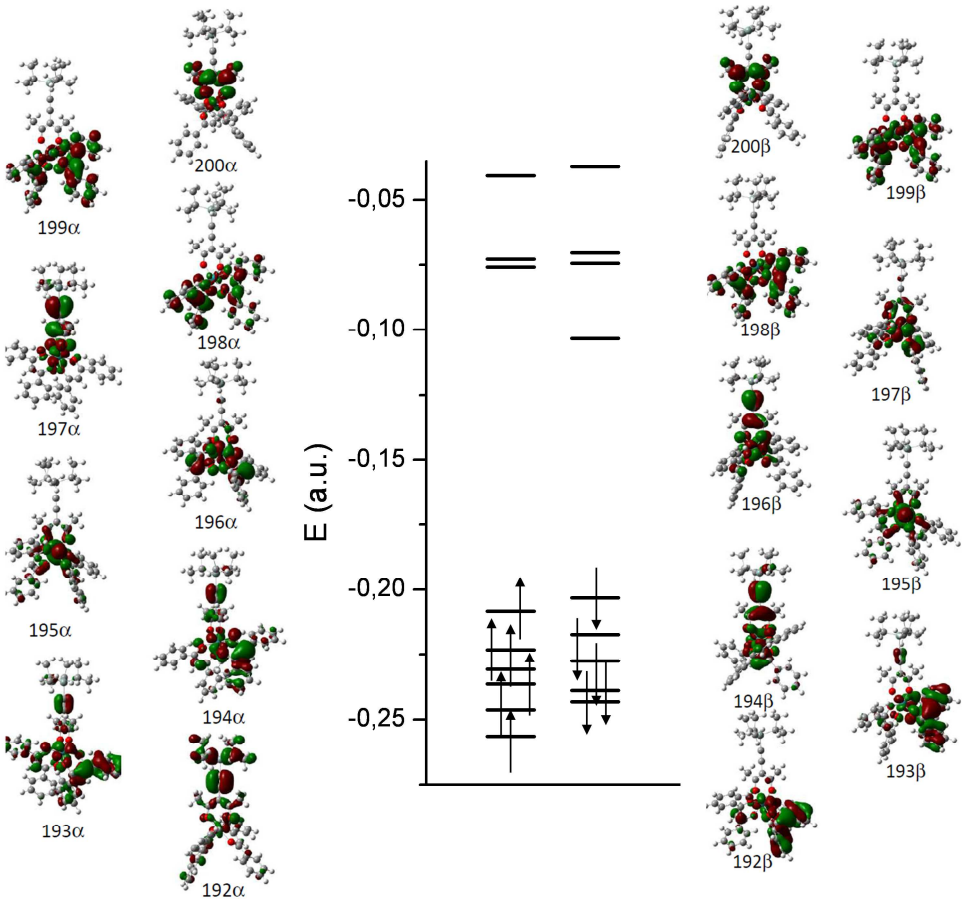


Figure SI.1 Orbital energies (in a.u., orbitals from 192 to 200) and isodensity plots of relevant MOs (contour value 0.025 a.u.) computed for the native $[Ru(III)(dbm)_2(acac\text{-}TIPSA)]^0$ species.

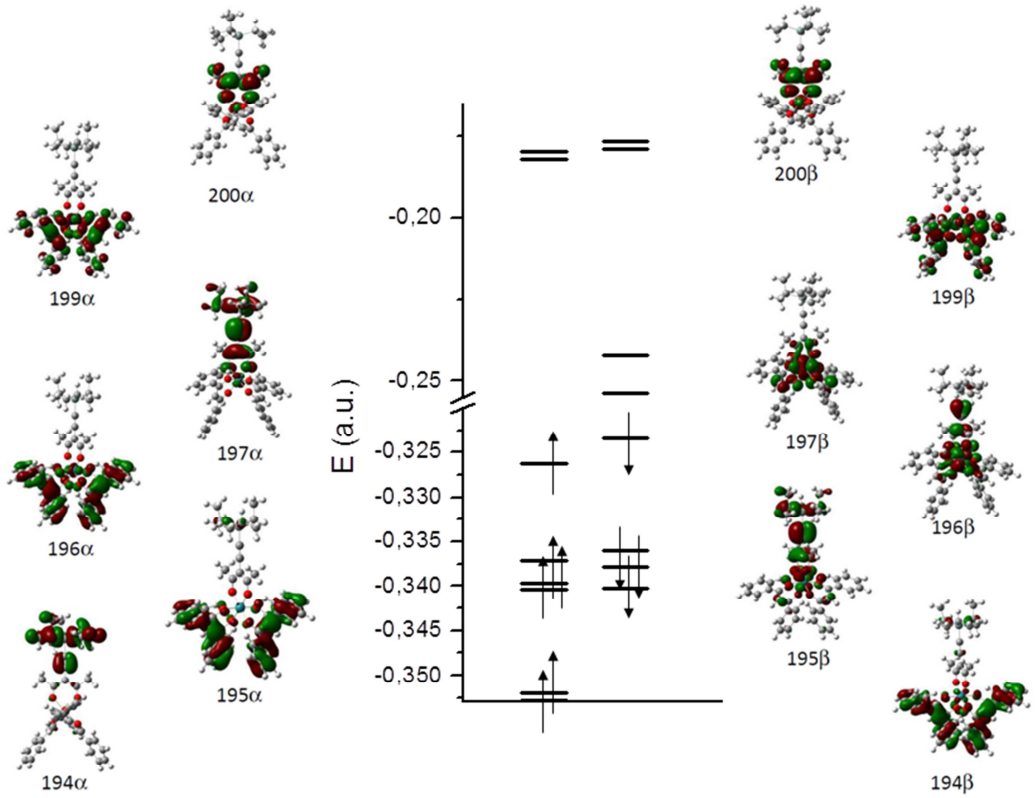
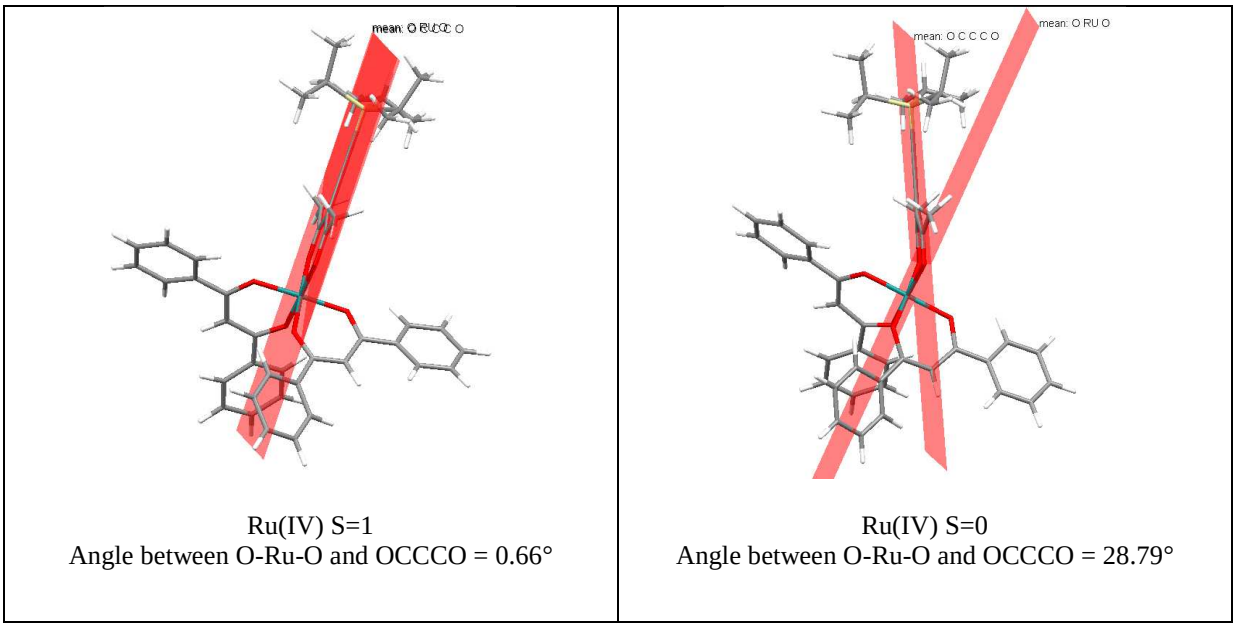


Figure SI.2 Orbital energies (in a.u., orbitals from 192 to 200) and isodensity plots of relevant MOs (contour value 0.025 a.u.) computed for the triplet (S=1) state of the oxidized $[Ru(IV)(dbm)_2(acac\text{-}TIPSA)]^{+1}$ species.



Ru(IV) S=1
Angle between O-Ru-O and OCCCO = 0.66°

Ru(IV) S=0
Angle between O-Ru-O and OCCCO = 28.79°

Figure SI.3 Optimized structure for the triplet (most stable, left) and the singlet state of the oxidized (Ru(IV)) $[Ru(IV)(dbm)_2(acac\text{-}TIPSA)]^{+1}$ complex.

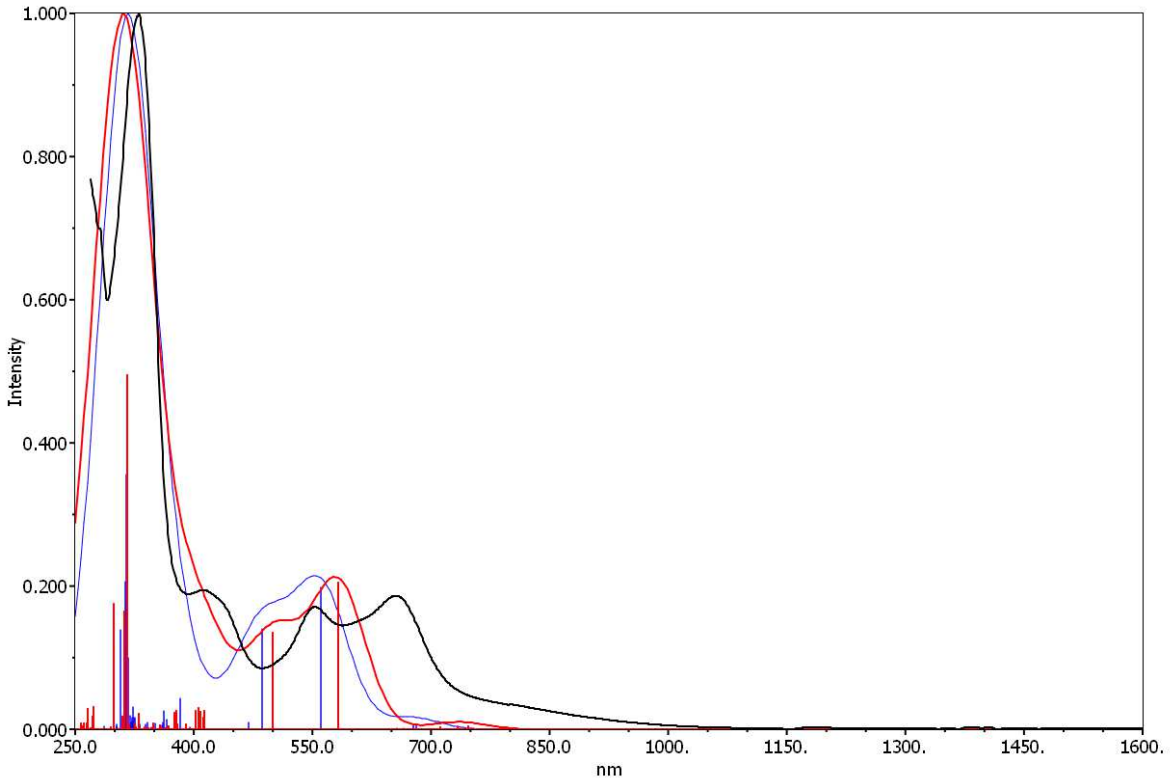


Figure SI.4: Experimental normalized absorption spectra of reduced $[Ru(II)(dbm)_2(acac\text{-}TIPSA)]^{-1}$ form (black line) together with the corresponding computed transition energies in gas phase (red line) and in DCM (blue line)

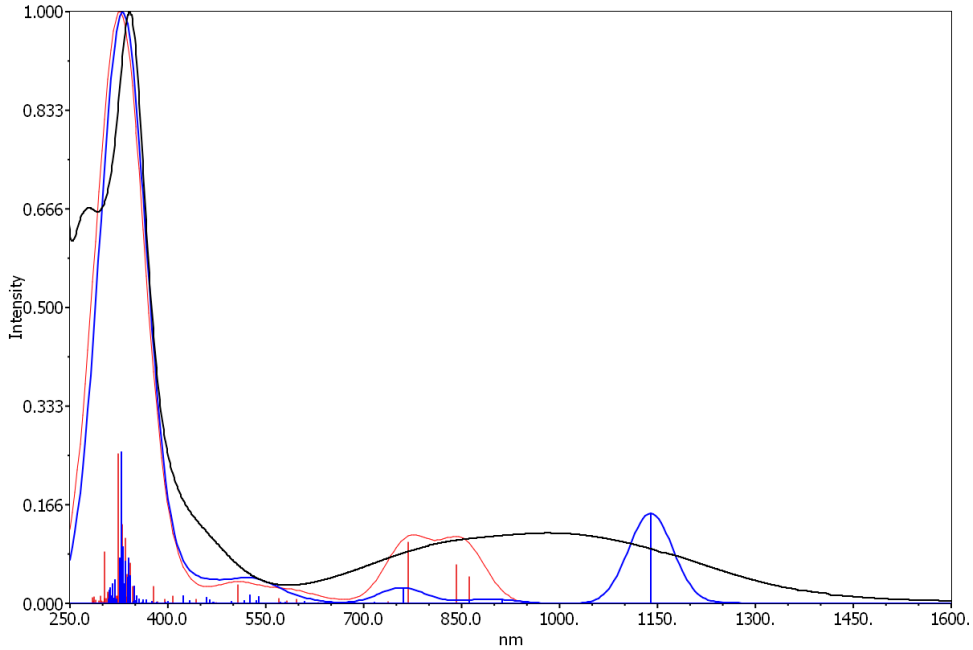


Figure SI.5 Experimental normalized absorption spectra of oxidized $[Ru(IV)(dbm)_2(acac\text{-}TIPSA)]^{+1}$ form (black line) together with the corresponding computed transition energies of $[Ru(IV)(dbm)_2(acac\text{-}TIPSA)]^{+1}{}_{S=0}$ (red) and $[Ru(IV)(dbm)_2(acac\text{-}TIPSA)]^{+}{}_{S=1}$ (blue).

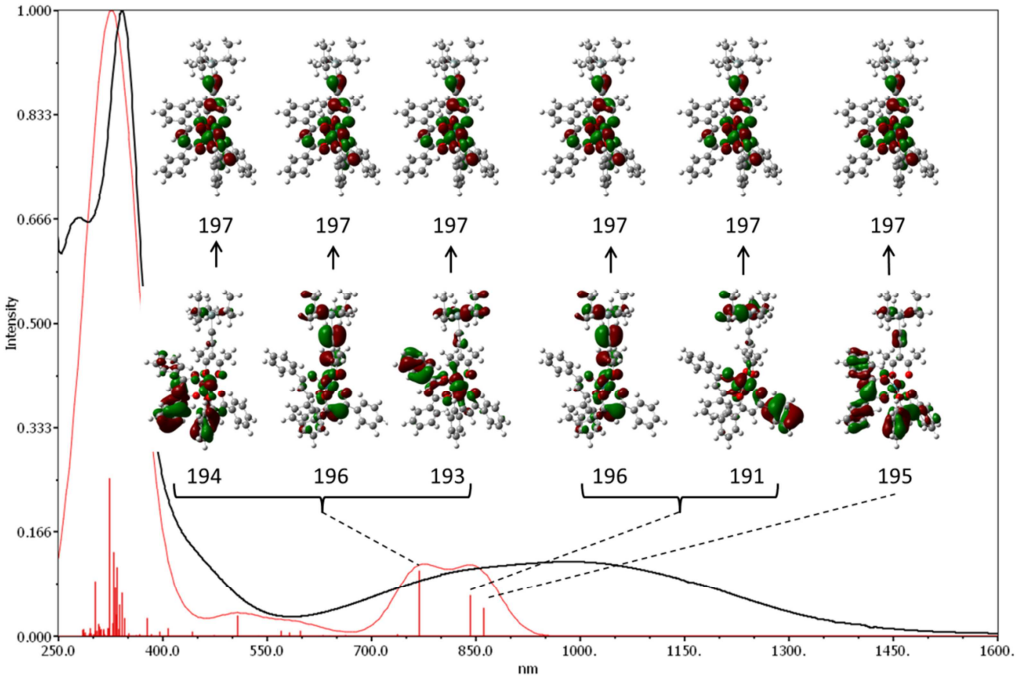


Figure SI.6 Experimental (black line, in DCM) absorption spectra of the oxidized (Ru(IV)) $[Ru(IV)(dbm)_2(acac\text{-}TIPSA)]^{+1}$ complex together with the corresponding computed vertical transition energies and simulated spectra for RuIV S=0 (red line)