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)\textsubscript{2}(acac-TIPSA)]\textsuperscript{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)\textsubscript{2}(acac-TIPSA)]\textsuperscript{+1} species.
- **Figure SI.3** Optimized structure for the triplet (most stable, left) and the singlet state of the oxidized (Ru(IV)) [Ru(IV)(dbm)\textsubscript{2}(acac-TIPSA)]\textsuperscript{+1} complex.
- **Figure SI.4**: Experimental normalized absorption spectra of reduced [Ru(II)(dbm)\textsubscript{2}(acac-TIPSA)]\textsuperscript{1}\textsuperscript{-} 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)\textsubscript{2}(acac-TIPSA)]\textsuperscript{+1} form (black line) together with the corresponding computed transition energies of [Ru(IV)(dbm)\textsubscript{2}(acac-TIPSA)]\textsuperscript{1}\textsubscript{S=0} (red) and [Ru(IV)(dbm)\textsubscript{2}(acac-TIPSA)]\textsuperscript{1}\textsubscript{S=1} (blue).
- **Figure SI.6** Experimental (black line, in DCM) absorption spectra of the oxidized (Ru(IV)) [Ru(IV)(dbm)\textsubscript{2}(acac-TIPSA)]\textsuperscript{+1} complex together with the corresponding computed vertical transition energies and simulated spectra for RuIV S=0 (red line)
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)₃(acac-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-TIPSA)]$^{1+}$ species.
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-TIPSA)]⁺¹ complex.
Figure SI.4: Experimental normalized absorption spectra of reduced [Ru(II)(dbm)$_2$(acac-TIPSA)]$^{1-}$ form (black line) together with the corresponding computed transition energies in gas phase (red line) and in DCM (blue line)
Figure S1.5 Experimental normalized absorption spectra of oxidized [Ru(IV)(dbm)$_2$(acac-TIPSA)]$^+$ form (black line) together with the corresponding computed transition energies of [Ru(IV)(dbm)$_2$(acac-TIPSA)]$^{1+}_{S=0}$ (red) and [Ru(IV)(dbm)$_2$(acac-TIPSA)]$^+_S$ (blue).
Figure SI.6 Experimental (black line, in DCM) absorption spectra of the oxidized (Ru(IV)) [Ru(IV)(dbm)$_2$(acac-TIPSA)]$^{1+}$ complex together with the corresponding computed vertical transition energies and simulated spectra for RuIV S=0 (red line)