Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

for

Aerobic photolysis of MeCbl: structural and electronic properties of Cbl-O-O-CH_3 intermediate

Arghya Pratim Ghosh,[1] Piotr Lodowski,[2] Aida Bazarganpour,[1] Marzena Leks,[2] and Pawel M. Kozlowski[1,*]

[1] Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, United States

[2] Institute of Chemistry, University of Silesia in Katowice, Szkolna 9, PL-40 006 Katowice, Poland

Table S1. Selected structural parameters for singlet and triplet states of {Im-[Co^{III}(corrin)]-O-O-CH_3}$^+$ model complex.

Table S2. The ten lowest vertical singlet and five lowest vertical triplet electronic transitions for Im-[Co^{III}(corrin)]-O_2Me^+ model complex based on the TD-DFT/BP86/TZVPP calculations.

Table S3. The ten lowest vertical singlet and five lowest vertical triplet electronic transitions for Im-[Co^{III}(corrin)]-O_2Me^+ model complex based on the TD-DFT/ωB97x/TZVPP calculations.

Table S4. The ten lowest, vertical singlet and triplet electronic transitions for Im-[Co^{III}(corrin)]-O_2Me^+ model complex based on the TD-DFT/LB94/TZ2P calculations (geometry of complex was optimized at DFT/BP86/TZVPP level).

Figure S1. Molecular geometry of {Im-[Co^{III}(corrin)]-O-O-CH_3}$^+$ model complex.

Figure S2. Optimized geometries of {[Co^{III}(corrin)]-O-O-CH_3}$^+$ model complex at frozen Co-O distance equal to 2.30 Å for a) ground state S_0 (calculations with broken symmetry UHF wave function), b) lowest triplet state T_1, c) superimpose of geometries S_0 and T_1 (black - S_0 geometry, blue - T_1 geometry).

Figure S3. Composition of two lowest occupied molecular orbitals H and H-1 (in %) of the {Im-[CoIII(corrin)]-O-O-CH3}$^+$ complex at BP86/TZVPP level of theory.

Figure S4. Key low-energy singlet (S1, S2, S3) and triplet (T1, T2) vertical excitations of {Im-[CoIII(corrin)]-O-O-CH3}+ model complex calculated using TD-DFT/LB94/TZ2P level of theory (ground state geometry of complex was optimized at DFT/BP86/TZVPP level).

Figure S5. Bond dissociation curves for the {Im-[Co^{III}(corrin)]-O-O-CH_3}$^+$ complex computed at BP86/TZVPP level of theory by systematically stretching Co-O and O-O bond. a) along Co-O bond b) along O-O bond.

Table S1. Selected structural parameters for singlet and triplet states of {Im-[Co^{III}(corrin)]-O-O-CH_3}$^+$ model complex.

	S_0	S_1	T_1
	Bond Distances, Å		
Co-O	1.929	1.971	2.001
Co-N_{Im}	2.033	1.901	2.529
Co-N_{21}	1.889	1.904	1.889
Co-N_{22}	1.945	1.952	1.939
Co-N_{23}	1.944	1.961	1.950
Co-N_{24}	1.885	1.907	1.886
O-O	1.441	1.351	1.403
O-C_{CH3}	1.426	1.451	1.434
	Bond Angles, deg		
N_{Im}-Co-O	174.1	175.2	179.2
Co-O-O	114.9	116.3	116.1
O-O-C_{CH3}	108.1	109.3	108.1
N_{21}-Co-N_{23}	173.1	172.7	169.1
N_{22}-Co-N_{24}	172.3	172.6	173.4
	Torsion Angles, deg		
N_{21}-N_{22}-N_{23}-N_{24}	-4.5	-3.1	-5.3
N_{21}-N_{22}-N_{23}-Co	-1.3	-1.2	-6.2
C_{10}-Co-O-O	-22.8	-44.8	4.1
Co-O-O-C_{CH3}	-107.2	178.3	-178.6

Table S2. The ten lowest vertical singlet and five lowest vertical triplet electronic transitions for Im-[Co^{III}(corrin)]-O_2Me^+ model complex based on the TD-DFT/BP86/TZVPP calculations.

	E(eV)	λ(nm)	*f*	%	Character		
				Singlet states			
S_1	1.89	655.9	0.0040	94	125 → 126	H → L	$p_O+d_{yz} \rightarrow \pi^*$
S_2	2.14	578.0	0.0017	91	125 → 127	H → L+1	$p_O+d_{yz} \rightarrow \sigma^*(d_{z2})$
S_3	2.37	522.7	0.0291	81	124 → 126	H-1 → L	$\pi+d_{yz}+p_O \rightarrow \pi^*$
				13	122 → 126	H-3 → L	$p_O+ d_{xz}+\pi \rightarrow \pi^*$
S_4	2.47	501.8	0.0102	68	124 → 127	H-1 → L+1	$\pi+d_{yz}+p_O \rightarrow \sigma^*(d_{z2})$
				12	123 → 127	H-2 → L+1	$\pi+[d_{xz}+d_{yz}] +p_O \rightarrow \sigma^*(d_{z2})$
				10	125 → 128	H → L+2	$p_O+d_{yz} \rightarrow d_{xy}$-n
S_5	2.53	489.6	0.0007	76	125 → 128	H → L+2	$p_O+d_{yz} \rightarrow d_{xy}$-n
				12	122 → 127	H-3 → L+1	$p_O+ d_{xz}+\pi \rightarrow \sigma^*(d_{z2})$
S_6	2.62	473.5	0.0188	61	123 → 126	H-2 → L	$\pi+[d_{xz}+d_{yz}] +p_O \rightarrow \pi^*$
S_7	2.65	467.4	0.0066	63	123 → 127	H-2 → L+1	$\pi+[d_{xz}+d_{yz}] +p_O \rightarrow \sigma^*(d_{z2})$
				12	125 → 129	H → L+3	$p_O+d_{yz} \rightarrow \pi^*$
S_8	2.70	458.5	0.0107	49	125 → 129	H → L+3	$p_O+d_{yz} \rightarrow \pi^*$
				15	121 → 126	H-4 → L	$p_O+[d_{x2-y2}+d_{yz}]+\pi \rightarrow \pi^*$
S_9	2.74	451.7	0.0105	52	121 → 126	H-4 → L	$p_O+[d_{x2-y2}+d_{yz}]+\pi \rightarrow \pi^*$
				23	125 → 129	H → L+3	$p_O+d_{yz} \rightarrow \pi^*$
S_{10}	2.79	444.9	0.0613	37	122 → 126	H-3 → L	$p_O+ d_{xz}+\pi \rightarrow \pi^*$
				32	124 → 128	H-1 → L+2	$\pi+d_{yz}+p_O \rightarrow d_{xy}$-n
				Triplet states			
T_1	1.45	857.1		49	125 → 127	H → L+1	$p_O+d_{yz} \rightarrow \sigma^*(d_{z2})$
T_2	1.70	727.9		47	125 → 126	H → L	$p_O+d_{yz} \rightarrow \pi^*$
T_3	1.98	625.1		22	124 → 127	H-1 → L+1	$\pi+d_{yz}+p_O \rightarrow \sigma^*(d_{z2})$
				15	125 → 128	H → L+2	$p_O+d_{yz} \rightarrow d_{xy}$-n
T_4	2.00	621.2		25	125 → 128	H → L+2	$p_O+d_{yz} \rightarrow d_{xy}$-n
				12	124 → 127	H-1 → L+1	$\pi+d_{yz}+p_O \rightarrow \sigma^*(d_{z2})$
T_5	2.03	611.4		46	124 → 126	H-1 → L	$\pi+d_{yz}+p_O \rightarrow \pi^*$

Table S3. The ten lowest vertical singlet and five lowest vertical triplet electronic transitions for Im-[Co^{III}(corrin)]-O_2Me^+ model complex based on the TD-DFT/ωB97x/TZVPP calculations.

	E(eV)	λ(nm)	*f*	%	Character		
				Singlet states			
S_1	2.32	533.3	0.0001	32	124 → 128	H-1 → L+2	$[p_O+d_{yz}]+\pi \rightarrow \sigma^*(d_{z2})$
				17	122 → 128	H-3 → L+2	$p_O+d_{yz} \rightarrow \sigma^*(d_{z2})$
S_2	2.62	473.1	0.0000	26	119 → 128	H-6 → L+2	$d_{xz}+\pi_{Im} \rightarrow \sigma^*(d_{z2})$
				17	120 → 128	H-5 → L+2	$\pi+[p_O+d_{xz}] \rightarrow \sigma^*(d_{z2})$
S_3	3.11	399.3	0.0116	37	116 → 129	H-9 → L+3	d_{x2-y2}+corr → d_{xy}-n
				22	118 → 129	H-7 → L+3	d_{x2-y2}+n → d_{xy}-n
				10	117 → 129	H-8 → L+3	corr+ $d_{x2-y2}+\pi \rightarrow d_{xy}$-n
S_4	3.19	388.9	0.1484	79	125 → 126	H → L	$\pi \rightarrow \pi^*$
S_5	3.41	364.1	0.0004	27	124 → 129	H-1 → L+3	$[d_{yz}+p_O]+\pi \rightarrow d_{xy}$-n
				13	122 → 129	H-3 → L+3	$p_O+d_{yz} \rightarrow d_{xy}$-n
S_6	3.69	335.6	0.0006	31	119 → 129	H-6 → L+3	$d_{xz}+\pi_{Im} \rightarrow d_{xy}$-n
				21	120 → 129	H-5 → L+3	$\pi+[p_O+d_{xz}] \rightarrow d_{xy}$-n
S_7	3.74	331.1	0.0011	40	116 → 128	H-9 → L+2	d_{x2-y2}+corr → $\sigma^*(d_{z2})$
				21	118 → 128	H-7 → L+2	d_{x2-y2}+n → $\sigma^*(d_{z2})$
				10	117 → 128	H-8 → L+2	corr+ $d_{x2-y2}+\pi \rightarrow \sigma^*(d_{z2})$
S_8	4.16	298.0	0.0440	75	125 → 128	H → L+2	$\pi \rightarrow \sigma^*(d_{z2})$
S_9	4.24	292.7	0.2061	40	124 → 126	H-1 → L	$[d_{yz}+p_O]+\pi \rightarrow \pi^*$
				28	125 → 129	H → L+3	$\pi \rightarrow d_{xy}$-n
				18	125 → 127	H → L+1	$\pi \rightarrow \pi^*$
S_{10}	4.31	288.0	0.0566	49	125 → 129	H → L+3	$\pi \rightarrow d_{xy}$-n
				18	124 → 126	H-1 → L	$[d_{yz}+p_O]+\pi \rightarrow \pi^*$
				Triplet states			
T_1	1.46	849.3		16	124 → 128	H-1 → L+2	$[p_O+d_{yz}]+\pi \rightarrow \sigma^*(d_{z2})$
				8	122 → 128	H-3 → L+2	$p_O+d_{yz} \rightarrow \sigma^*(d_{z2})$
T_2	1.80	687.0		13	119 → 128	H-6 → L+2	$d_{xz}+\pi_{Im} \rightarrow \sigma^*(d_{z2})$
				8	120 → 128	H-5 → L+2	$\pi+[p_O+d_{xz}] \rightarrow \sigma^*(d_{z2})$
T_3	2.04	608.7		10	124 → 129	H-1 → L+3	$[p_O+d_{yz}]+\pi \rightarrow d_{xy}$-n
T_4	2.23	556.1		17	116 → 128	H-9 → L+2	d_{x2-y2}+corr → $\sigma^*(d_{z2})$
				8	118 → 128	H-7 → L+2	d_{x2-y2}+n → $\sigma^*(d_{z2})$
T_5	2.29	541.6		39	125 → 126	H → L	$\pi \rightarrow \pi^*$

Table S4. The ten lowest, vertical singlet and triplet electronic transitions for Im-[Co^{III}(corrin)]-O_2Me^+ model complex based on the TD-DFT/LB94/TZ2P calculations (geometry of complex was optimized at DFT/BP86/TZVPP level).

	E(eV)	**λ(nm)**	***f***	**%**	**Character**		
				Singlet states			
S_1	1.96	632.9	0.0005	75	125 → 126	H → L	$p_O+d_{yz} \rightarrow \sigma^*(d_{z2})$
				20	124 → 126	H-1 → L	$\pi \rightarrow \sigma^*(d_{z2})$
S_2	2.01	618.2	0.0093	73	124 → 126	H-1 → L	$\pi \rightarrow \sigma^*(d_{z2})$
				16	125 → 126	H → L	$p_O+d_{yz} \rightarrow \sigma^*(d_{z2})$
S_3	2.10	590.1	0.0156	85	125 → 127	H → L+1	$p_O+d_{yz} \rightarrow \pi^*$
S_4	2.35	528.1	0.0162	80	123 → 126	H-2 → L	$\pi+[d_{xz}+p_O] \rightarrow \sigma^*(d_{z2})$
S_5	2.36	524.3	0.1264	82	124 → 127	H-1 → L+1	$\pi \rightarrow \pi^*$
S_6	2.51	493.2	0.0018	71	125 → 128	H → L+2	$p_O+d_{yz} \rightarrow d_{xy}$-n
				22	122 → 126	H-3 → L	$[d_{xz}+p_O]+\pi \rightarrow \sigma^*(d_{z2})$
S_7	2.52	491.3	0.0038	93	124 → 128	H-1 → L+2	$\pi \rightarrow d_{xy}$-n
S_8	2.59	478.9	0.0690	78	123 → 127	H-2 → L+1	$\pi+[d_{xz}+p_O] \rightarrow \pi^*$
S_9	2.69	461.2	0.0057	50	122 → 126	H-3 → L	$[d_{xz}+p_O]+\pi \rightarrow \sigma^*(d_{z2})$
				16	122 → 127	H-3 → L+1	$[d_{xz}+p_O]+\pi \rightarrow \pi^*$
S_{10}	2.73	454.0	0.0387	59	122 → 127	H-3 → L+1	$[d_{xz}+p_O]+\pi \rightarrow \pi^*$
				13	122 → 126	H-3 → L	$[d_{xz}+p_O]+\pi \rightarrow \sigma^*(d_{z2})$
				Triplet states			
T_1	1.49	830.5		98	125 → 126	H → L	$p_O+d_{yz} \rightarrow \sigma^*(d_{z2})$
T_2	1.82	683.1		77	124 → 126	H-1 → L	$\pi \rightarrow \sigma^*(d_{z2})$
				14	125 → 127	H → L+1	$p_O+d_{yz} \rightarrow \pi^*$
T_3	1.87	664.0		81	125 → 127	H → L+1	$p_O+d_{yz} \rightarrow \pi^*$
				15	124 → 126	H-1 → L	$\pi \rightarrow \sigma^*(d_{z2})$
T_4	1.99	622.7		96	124 → 127	H-1 → L+1	$\pi \rightarrow \pi^*$
T_5	2.01	618.3		82	123 → 126	H-2 → L	$\pi+[d_{xz}+p_O] \rightarrow \sigma^*(d_{z2})$

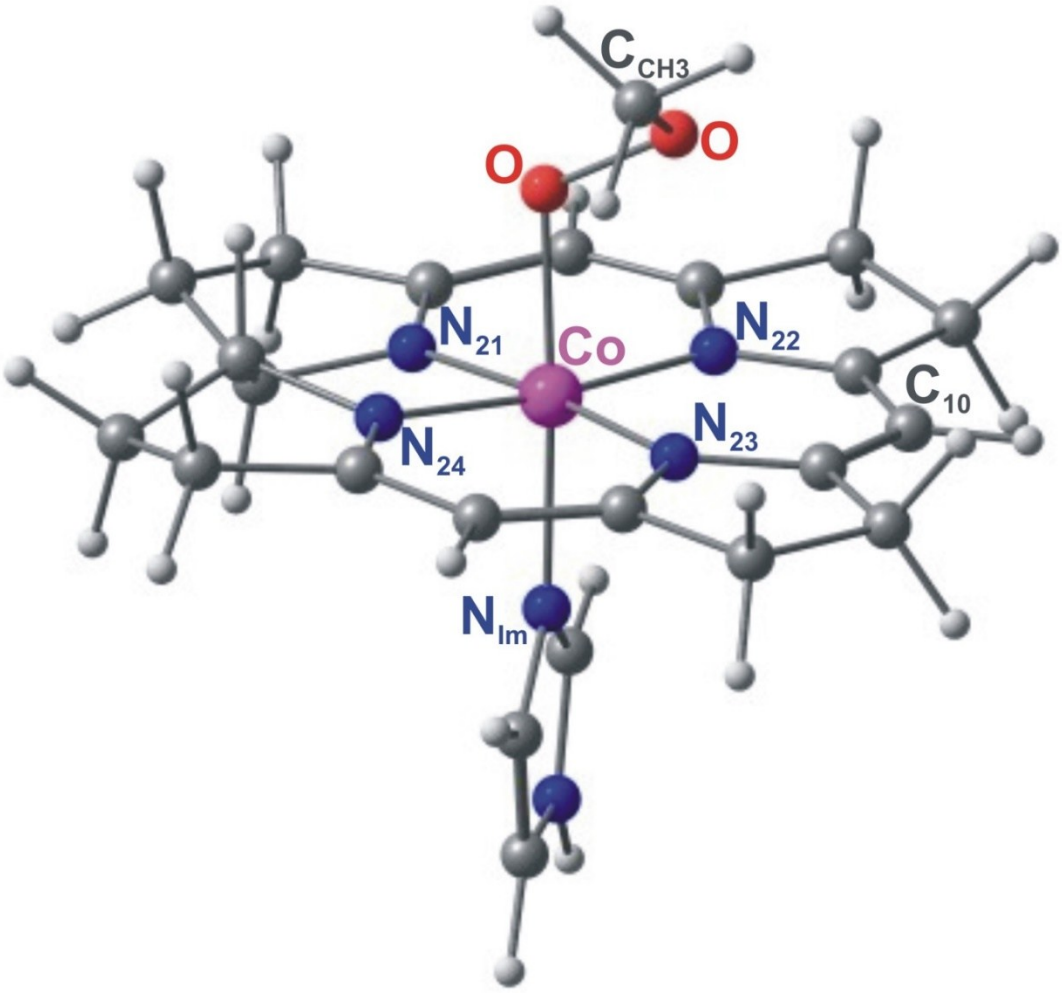

Figure S1. Molecular geometry of $\{Im\text{-}[Co^{III}(corrin)]\text{-}O\text{-}O\text{-}CH_3\}^+$ model complex.

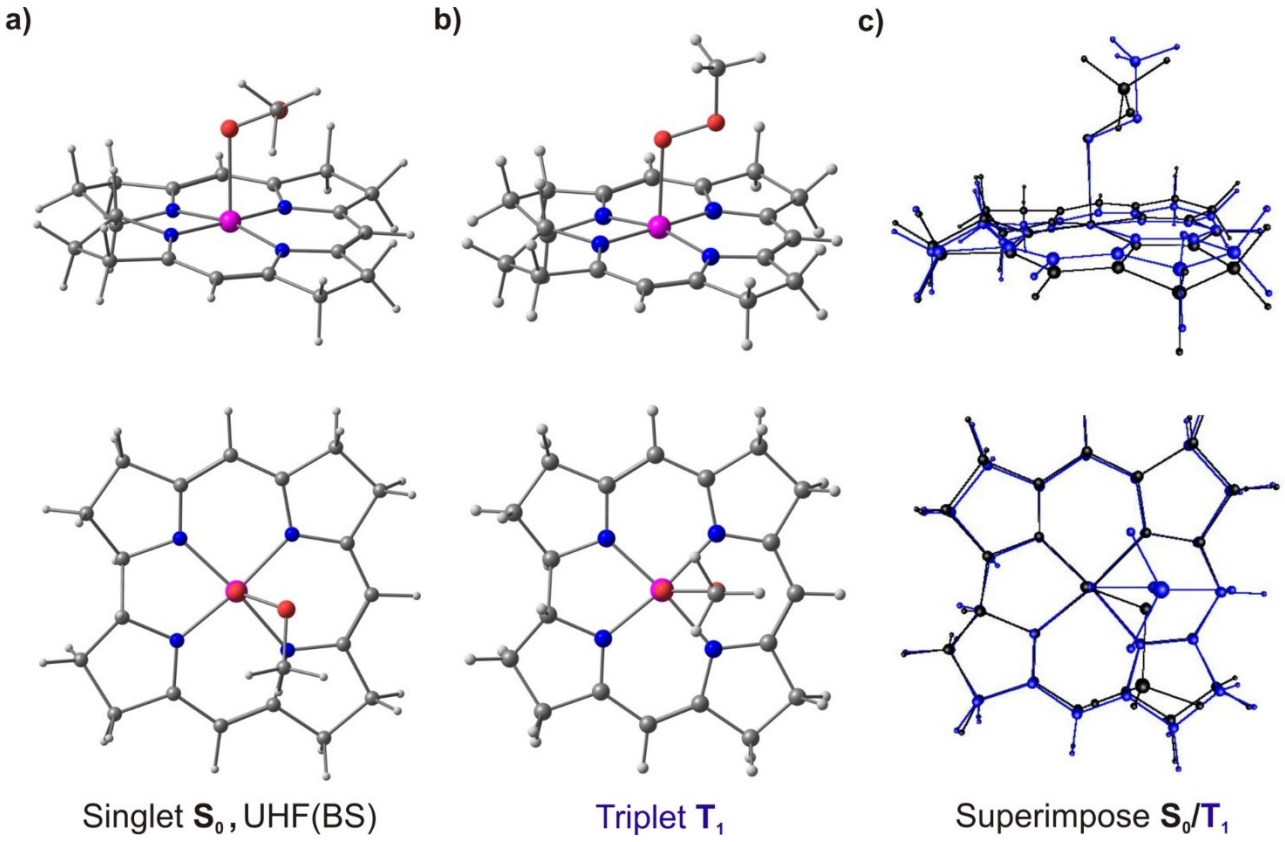

Figure S2. Optimized geometries of $\{[Co^{III}(corrin)]\text{-}O\text{-}O\text{-}CH_3\}^+$ model complex at frozen Co-O distance equal to 2.30 Å for a) ground state S_0 (calculations with broken symmetry UHF wave function), b) lowest triplet state T_1, c) superimpose of geometries S_0 and T_1 (black - S_0 geometry, blue - T_1 geometry).

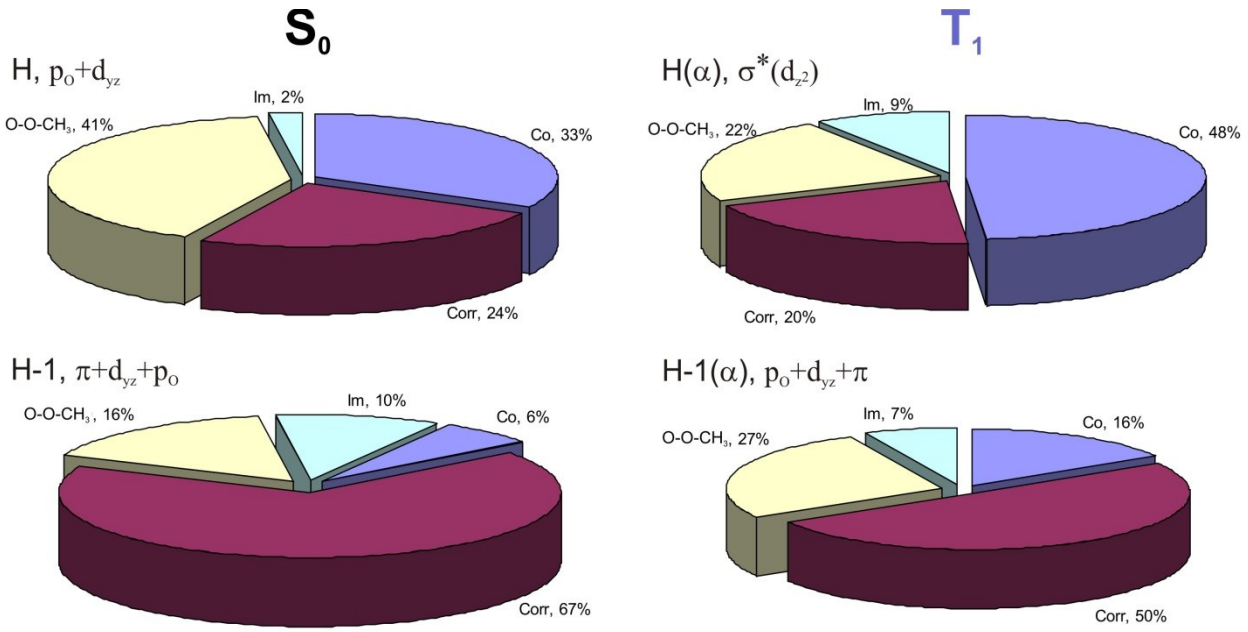

Figure S3. Composition of two lowest occupied molecular orbitals H and H-1 (in %) of the {Im-[Co^{III}(corrin)]-O-O-CH_3}$^+$ complex at BP86/TZVPP level of theory.

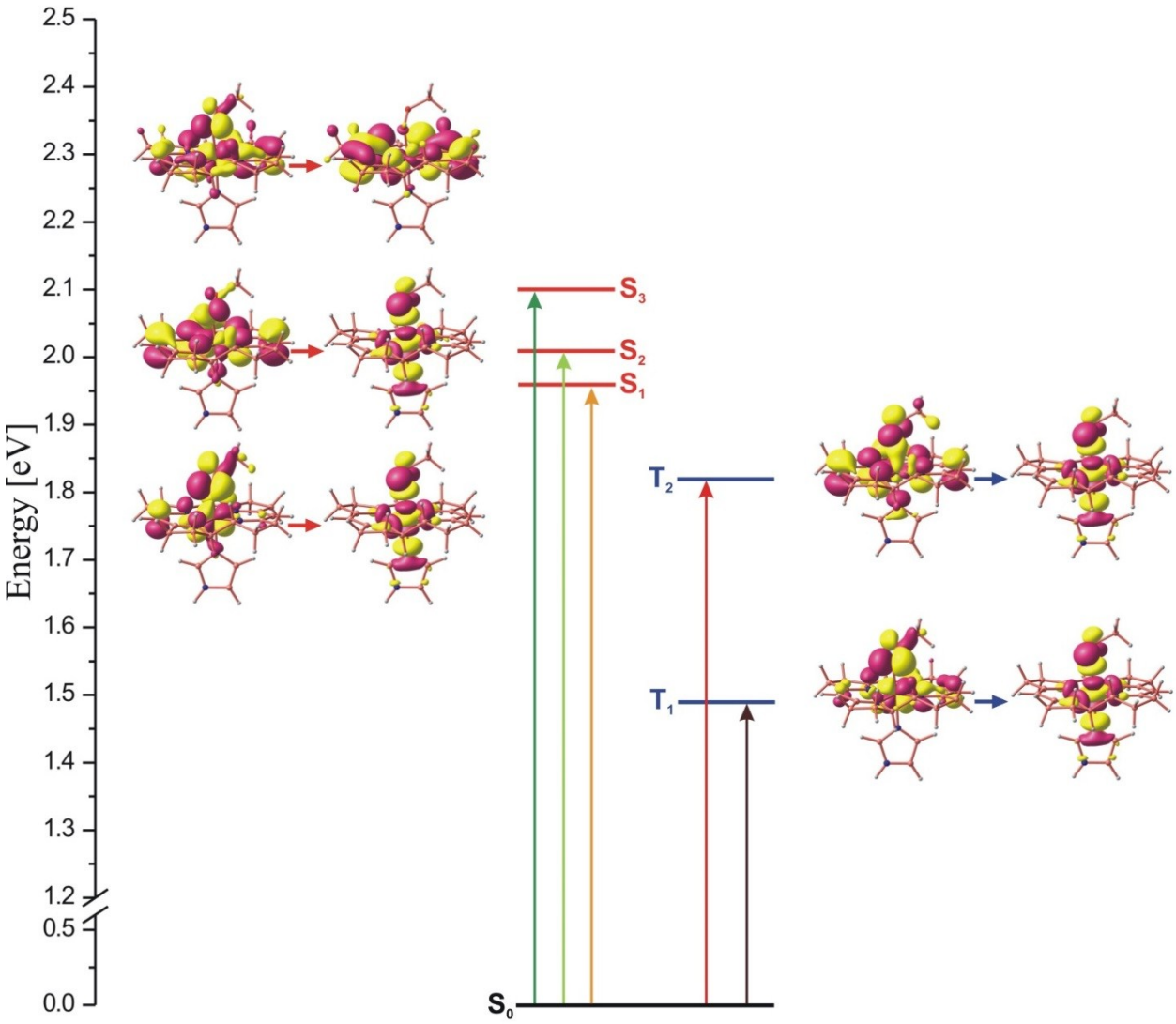

Figure S4. Key low-energy singlet (S1, S2, S3) and triplet (T1, T2) vertical excitations of {Im-[CoIII(corrin)]-O-O-CH3}+ model complex calculated using TD-DFT/LB94/TZ2P level of theory (ground state geometry of complex was optimized at DFT/BP86/TZVPP level).

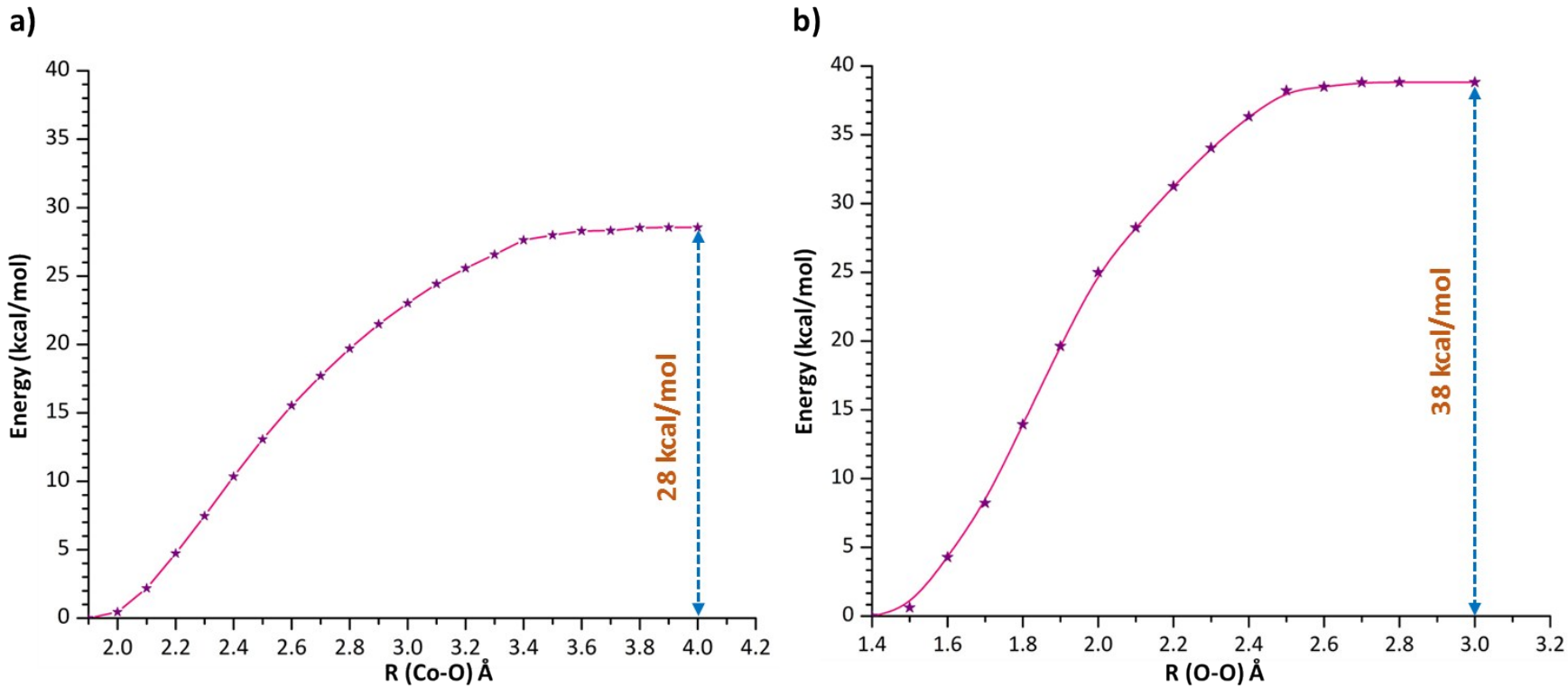

Figure S5. Bond dissociation curves for the $\{Im\text{-}[Co^{III}(corrin)]\text{-}O\text{-}O\text{-}CH_3\}^+$ complex computed at BP86/TZVPP level of theory by systematically stretching Co-O and O-O bond. a) along Co-O bond b) along O-O bond