Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

Photodissociation of EtPhCbl Antivitamin B_{12}

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Table S1. TD-DFT excitation energies, oscillator strengths, Λ parameters, composition and characters of ten low-lying, singlet electronic transitions for the Im-[Co^{III}(corrin)]-$EtPh^+$ model complex based on the BP86/TZVPP calculations with use PCM solvent model.

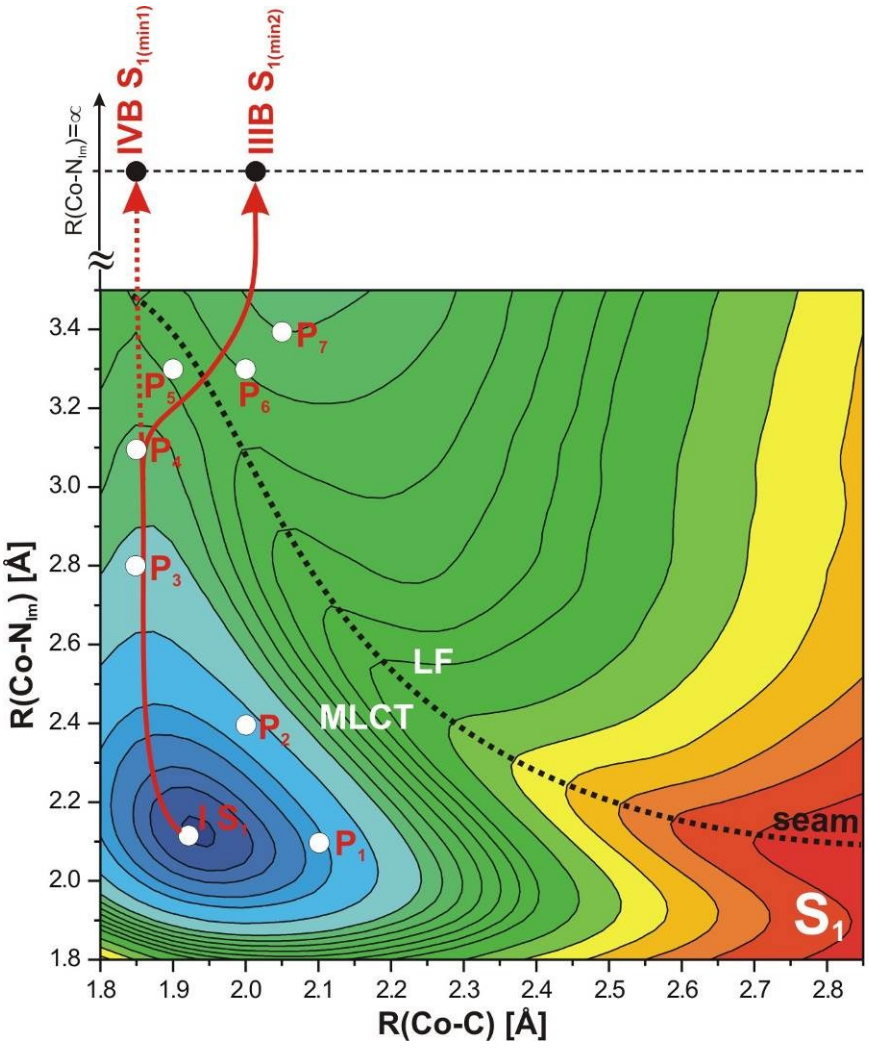
	E(eV)	λ(nm)	*f*	Λ	%	character		
S_1	2.24	552.8	0.001	0.541	51	140 → 142	H-1 → L	$\pi + d_{xz} \rightarrow \pi^*$
					47	139 → 142	H-2 → L	$d_{xz} + \pi_{Ph} \rightarrow \pi^*$
S_2	2.44	508.2	0.048	0.712	75	141 → 142	H → L	$d_{yz} + \pi \rightarrow \pi^*$
					11	140 → 142	H-1 → L	$\pi + d_{xz} \rightarrow \pi^*$
S_3	2.47	501.6	0.072	0.550	47	139 → 142	H-2 → L	$d_{xz} + \pi_{Ph} \rightarrow \pi^*$
					36	140 → 142	H-1 → L	$\pi + d_{xz} \rightarrow \pi^*$
					11	141 → 142	H → L	$d_{yz} + \pi \rightarrow \pi^*$
S_4	2.66	466.2	0.001	0.302	97	138 → 142	H-3 → L	$d_{x^2-y^2} \rightarrow \pi^*$
S_5	2.91	426.4	0.001	0.581	57	141 → 143	H → L+1	$d_{yz} + \pi \rightarrow d_{xy}$ - n
					17	137 → 142	H-4 → L	$\pi_{Ph} + d_{xz} \rightarrow \pi^*$
					12	139 → 143	H-2 → L+1	$d_{xz} + \pi_{Ph} \rightarrow d_{xy}$ - n
					12	141 → 144	H → L+2	$d_{yz} + \pi \rightarrow d_{xy}$ - n + π^*
S_6	2.94	422.5	0.005	0.607	77	140 → 143	H-1 → L+1	$\pi + d_{xz} \rightarrow d_{xy}$ - n
					13	140 → 144	H-1 → L+2	$\pi + d_{xz} \rightarrow d_{xy}$ - n + π^*
S_7	2.99	414.7	0.009	0.515	51	137 → 142	H-4 → L	$\pi_{Ph} + d_{xz} \rightarrow \pi^*$
					16	139 → 143	H-2 → L+1	$d_{xz} + \pi_{Ph} \rightarrow d_{xy}$ - n
					10	141 → 144	H → L+2	$d_{yz} + \pi \rightarrow d_{xy}$ - n + π^*
S_8	3.05	407.0	0.005	0.610	35	141 → 144	H → L+2	$d_{yz} + \pi \rightarrow d_{xy}$ - n + π^*
					32	141 → 145	H → L+3	$d_{yz} + \pi \rightarrow \sigma^*(d_z^2)$ - n
S_9	3.07	404.2	0.001	0.314	76	136 → 142	H-5 → L	$\pi_{Ph} + \pi_{Im} \rightarrow \pi^*$
					10	141 → 145	H → L+3	$d_{yz} + \pi \rightarrow \sigma^*(d_z^2)$ - n
S_{10}	3.11	398.2	0.007	0.248	69	135 → 142	H-6 → L	$\pi_{Ph} + \pi_{Im} \rightarrow \pi^*$

Table S2. TD-DFT excitation energies, oscillator strengths, Λ parameters, composition and characters of ten low-lying, singlet electronic transitions for the [Co^{III}(corrin)]-$EtPh^+$ model complex (*base-off* form of Im-[Co^{III}(corrin)]-$EtPh^+$) based on the BP86/TZVPP calculations with use PCM solvent model.

	E(eV)	λ(nm)	*f*	Λ	%	character		
S_1	2.19	565.7	0.000	0.506	50	122 → 124	H-1 → L	$\pi_{Ph}+d_{xz} \rightarrow \pi^*$
					42	123 → 125	H → L+1	$d_{yz}+\pi \rightarrow \sigma^*(d_z^2)-n$
S_2	2.22	559.8	0.011	0.532	46	122 → 124	H-1 → L	$\pi_{Ph}+d_{xz} \rightarrow \pi^*$
					36	123 → 125	H → L+1	$d_{yz}+\pi \rightarrow \sigma^*(d_z^2)-n$
					12	123 → 124	H → L	$d_{yz}+\pi \rightarrow \pi^*$
S_3	2.33	531.5	0.007	0.567	85	122 → 125	H-1 → L+1	$\pi_{Ph}+d_{xz} \rightarrow \sigma^*(d_z^2)-n$
S_4	2.41	515.2	0.045	0.698	68	123 → 124	H → L	$d_{yz}+\pi \rightarrow \pi^*$
					13	123 → 125	H → L+1	$d_{yz}+\pi \rightarrow \sigma^*(d_z^2)-n$
S_5	2.69	461.3	0.001	0.428	88	121 → 124	H-2 → L	$d_{x^2-y^2} \rightarrow \pi^*$
S_6	2.93	423.2	0.013	0.571	37	121 → 125	H-2 → L+1	$d_{x^2-y^2} \rightarrow \sigma^*(d_z^2)-n$
					27	120 → 125	H-3 → L+1	$\pi+d_{yz} \rightarrow \sigma^*(d_z^2)-n$
					15	122 → 127	H-1 → L+3	$\pi_{Ph}+d_{xz} \rightarrow \pi^*+d_{xz}$
S_7	2.97	416.9	0.012	0.620	27	123 → 126	H → L+2	$d_{yz}+\pi \rightarrow d_{xy}-n$
					23	123 → 127	H → L+3	$d_{yz}+\pi \rightarrow \pi^*+d_{xz}$
					23	120 → 124	H-3 → L	$\pi+d_{yz} \rightarrow \pi^*$
					11	122 → 126	H-1 → L+2	$\pi_{Ph}+d_{xz} \rightarrow d_{xy}-n$
S_8	3.01	412.2	0.051	0.611	40	120 → 124	H-3 → L	$\pi+d_{yz} \rightarrow \pi^*$
					16	119 → 124	H-4 → L	$\pi_{Ph}+d_{xz} \rightarrow \pi^*$
					13	121 → 125	H-2 → L+1	$d_{x^2-y^2} \rightarrow \sigma^*(d_z^2)-n$
					10	123 → 127	H → L+3	$d_{yz}+\pi \rightarrow \pi^*+d_{xz}$
S_9	3.03	408.8	0.019	0.603	23	123 → 127	H → L+3	$d_{yz}+\pi \rightarrow \pi^*+d_{xz}$
					21	120 → 125	H-3 → L+1	$\pi+d_{yz} \rightarrow \sigma^*(d_z^2)-n$
					15	123 → 126	H → L+2	$d_{yz}+\pi \rightarrow d_{xy}-n$
					14	121 → 125	H-2 → L+1	$d_{x^2-y^2} \rightarrow \sigma^*(d_z^2)-n$
S_{10}	3.10	400.3	0.009	0.399	45	118 → 124	H-5 → L	$\pi_{Ph} \rightarrow \pi^*$
					19	119 → 124	H-4 → L	$\pi_{Ph}+d_{xz} \rightarrow \pi^*$
					10	123 → 126	H → L+2	$d_{yz}+\pi \rightarrow d_{xy}-n$

Table S3. TD-DFT excitation energies, oscillator strengths, Λ parameters, composition and characters of transitions for optimized geometry of the S_1 singlet excited state of Im-[Co^{III}(corrin)]-$EtPh^+$ model complex at selected points on the S_1 PES. Location of selected points on the S_1 surface shown below table. Results based on the BP86/TZVPP calculations with use PCM solvent model.

	R_{Co-C} (Å)	R_{Co-N} (Å)	E(eV)	λ(nm)	*f*	Λ	%	character	
I S_1	1.927	2.107	1.74	714.3	0.0026	0.490	97	H → L	$d_{xz} + \pi + \pi_{Ph} \rightarrow \pi^*$
IVB $S_{1(min1)}$	1.852		1.66	748.4	0.0039	0.482	91	H → L	$(d_{xz}+d_{yz}) + \pi_{Ph} \rightarrow \pi^*$
IIIB $S_{1(min2)}$	2.016		1.39	891.7	0.0020	0.612	99	H → L	$(d_{xz}+d_{yz}) + \pi_{Ph} \rightarrow \sigma^*(d_{z2})$ - n + π^*
P_1	2.100	2.100	1.74	711.1	0.0060	0.547	97	H → L	$d_{xz} + \pi + \pi_{Ph} \rightarrow \pi^*$
P_2	2.000	2.400	1.88	659.8	0.0013	0.581	81	H → L	$(d_{xz}+d_{yz}) + \pi + \pi_{Ph} \rightarrow \pi^*$
							15	H-1 → L	$(d_{xz}-d_{yz}) + \pi \rightarrow \pi^*$
P_3	1.850	2.800	1.86	671.9	0.0007	0.443	85	H → L	$(d_{xz}+d_{yz})$ - n + $\pi_{Ph} \rightarrow \pi^*$
							11	H-1 → L	$(d_{xz}-d_{yz}) + \pi + \pi_{Ph} \rightarrow \pi^*$
P_4	1.850	3.100	1.83	677.9	0.0016	0.499	82	H → L	$(d_{xz}+d_{yz})$ - n + $\pi_{Ph} \rightarrow \pi^*$
P_5	1.900	3.300	1.85	670.6	0.0026	0.578	64	H → L	$(d_{xz}+d_{yz})$ - n + $\pi_{Ph} \rightarrow \pi^*$
							35	H-1 → L	$(d_{xz}-d_{yz}) + \pi + \pi_{Ph} \rightarrow \pi^*$
P_6	2.000	3.300	1.57	787.9	0.0023	0.635	99	H → L	$(d_{xz}+d_{yz})$ - n + $\pi_{Ph} \rightarrow \sigma^*(d_{z2})$-n + π^*
P_7	2.050	3.400	1.57	790.0	0.0025	0.662	99	H → L	$(d_{xz}+d_{yz})$ - n + $\pi_{Ph} \rightarrow \sigma^*(d_{z2})$-n



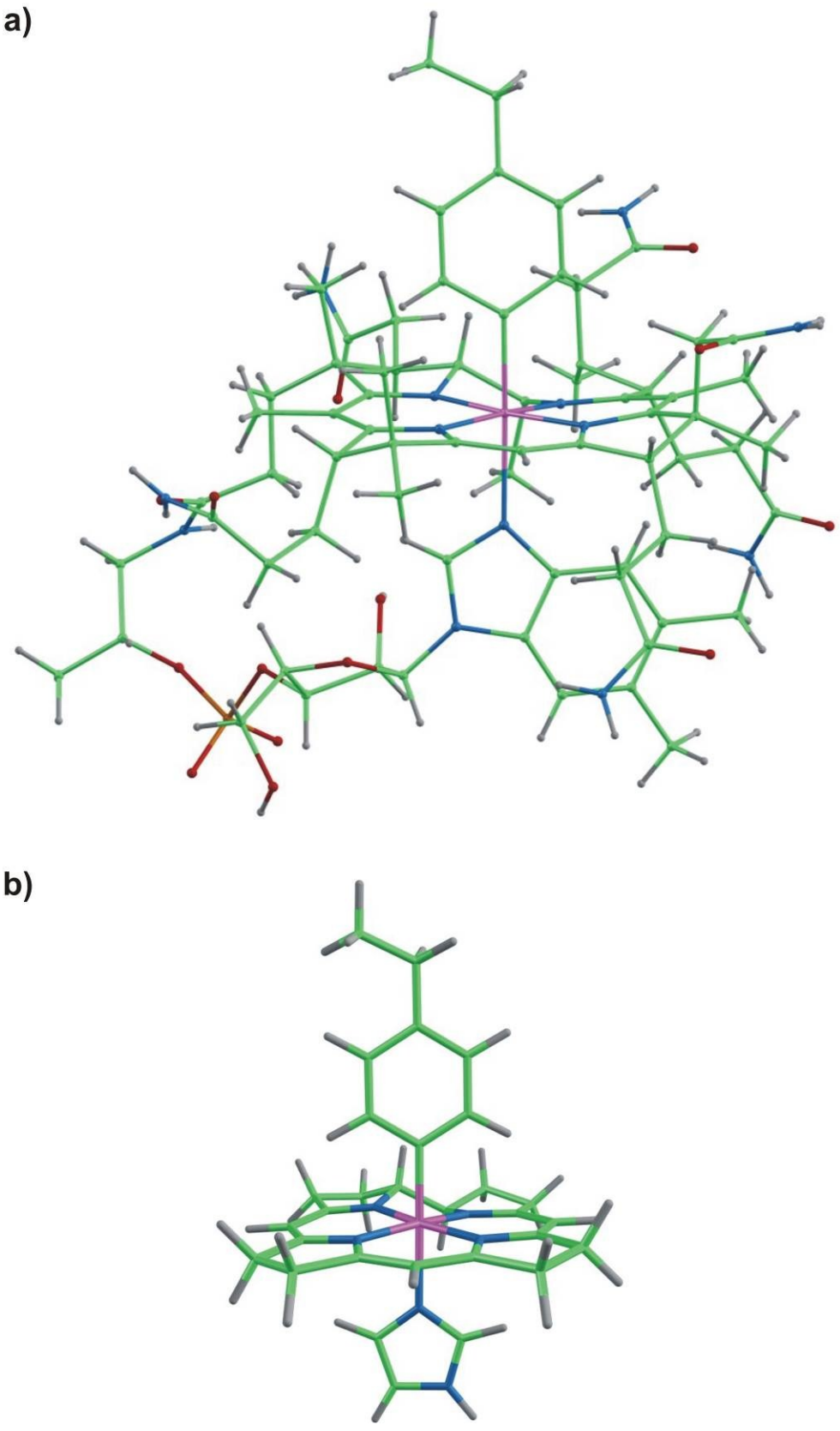


Figure S1. (a) Molecular structure of antivitamin B_{12}, 4-ethylphenylcobalamin (EtPhCbl) and (b) structure of model complex used in calculations. The full structure of EtPhCbl is drawn based on the crystallographic structure from M. Ruetz, C. Gherasim, K. Gruber, S. Fedosov, R. Banerjee, B. Kräutler, Access to Organometallic Arylcobaltcorrins through Radical Synthesis: 4-Ethylphenylcobalamin, a Potential "Antivitamin B_{12}", *Angew. Chem. Int. Ed.* 2013, **52**, 2606 – 2610, and CCDC 848663 data obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif .

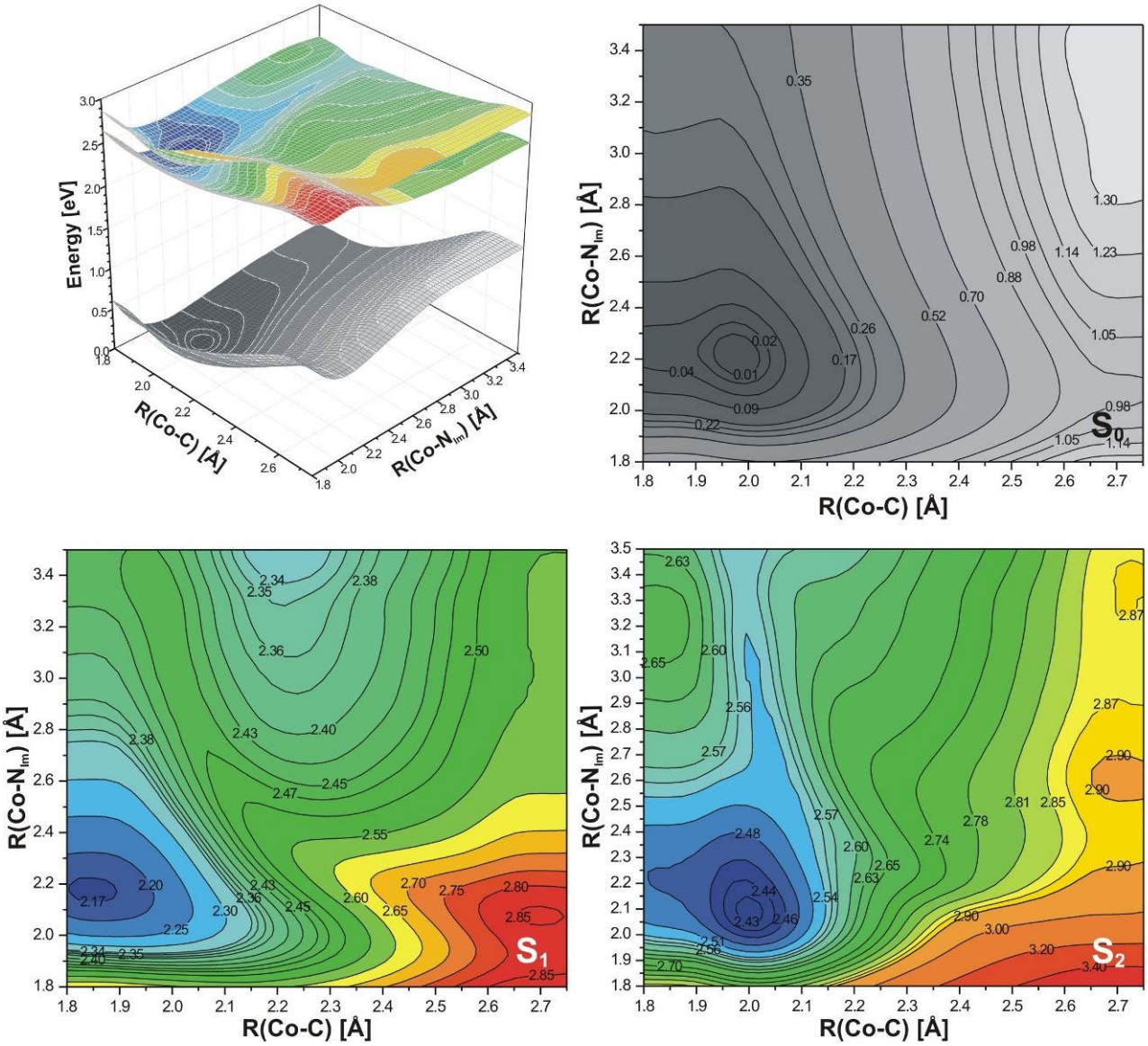


Figure S2. Potential energy surfaces (PESs) for ground state and two lowest excited states of Im-[Co^{III}(corrin)]-EtPh$^+$ model complex together with vertical projections of PES for S_0, S_1 and S_2 electronic states, plotted as a function of axial bond lengths calculated in water solution (COSMO) at BP86/TZVPP level of theory. The vertical projections plots have separate color scales.

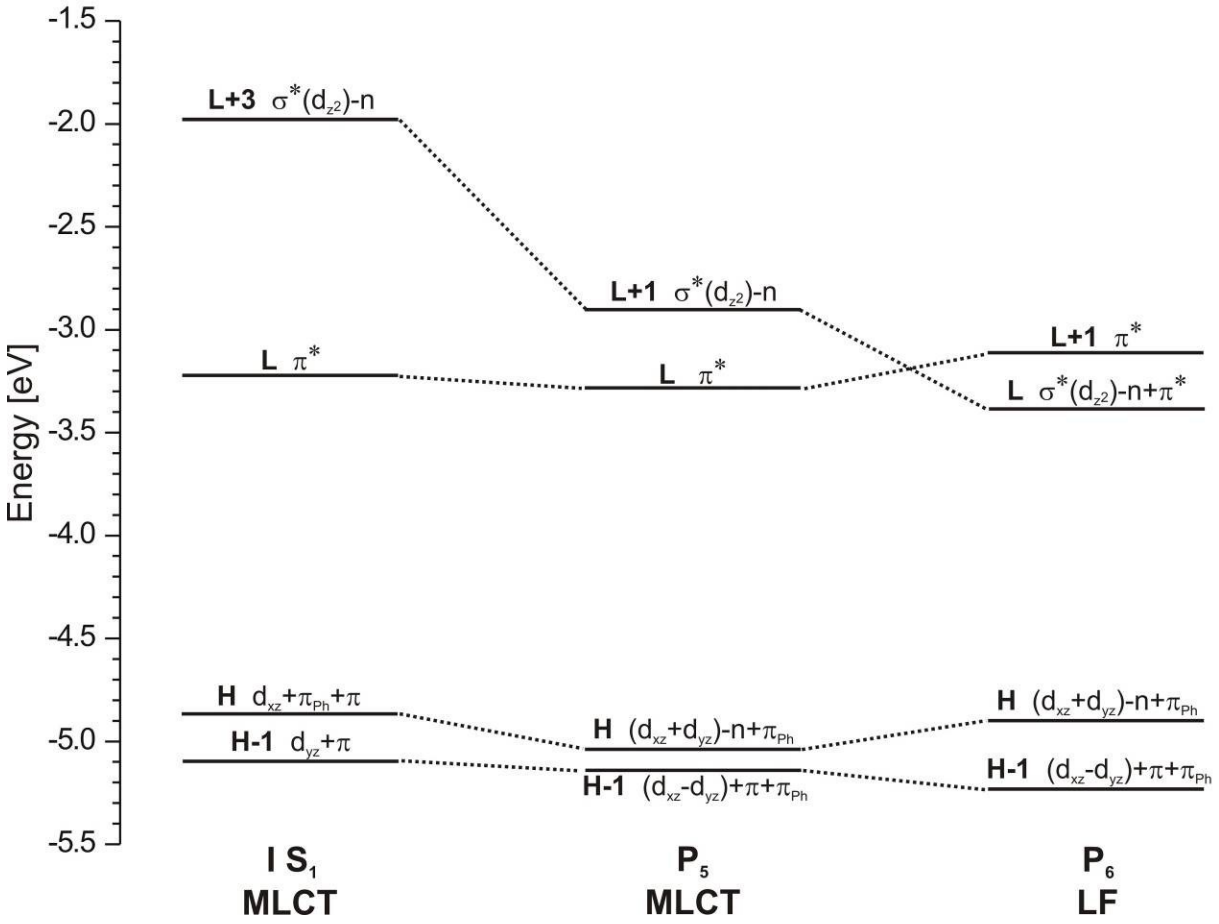


Figure S3. Energy diagram of molecular orbitals involved in electronic excitations to S_1 and S_2 excited states for optimized S_1 geometries of Im-[Co^{III}(corrin)]-$EtPh^+$ model complex at minimum energy and two points of S_1 PES located near the S_1/S_2 intersection. P_5 and P_6 refer to selected points on S_1 PES shown in Table S3.

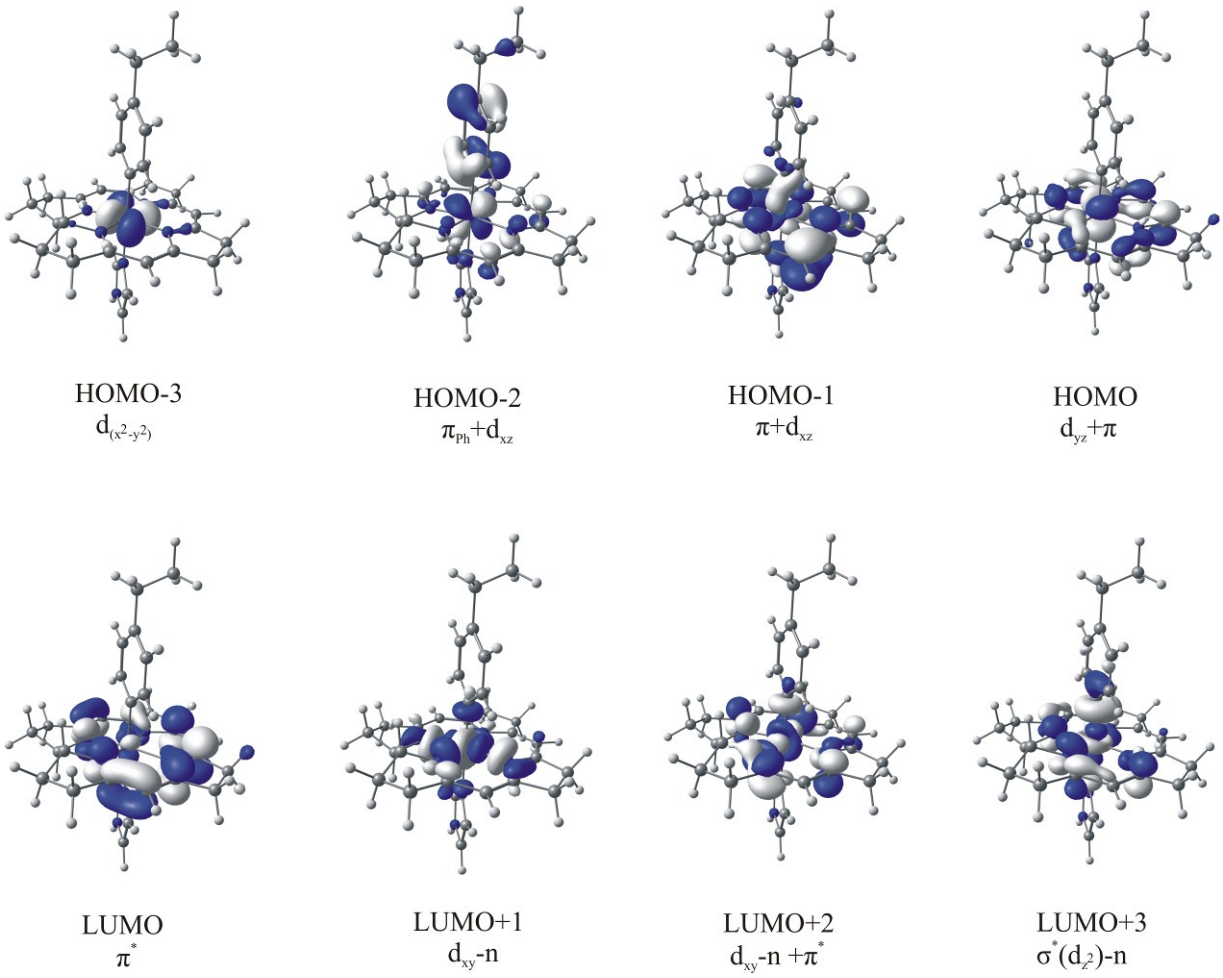


Figure S4. Selected molecular orbitals involved in vertical electronic excitations for the Im-[Co^{III}corr]-$EtPh^+$ model complex in the ground state S_0, obtained from DFT/BP86 level of theory.

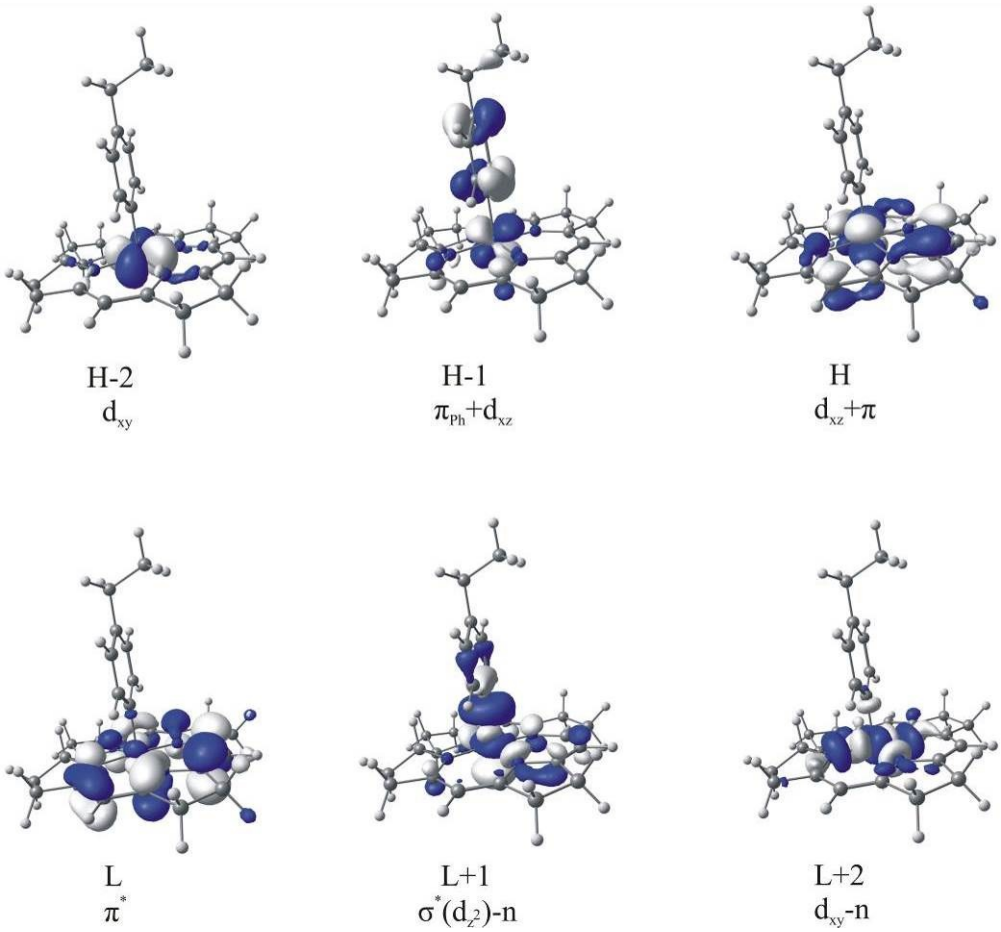


Figure S5. Selected molecular orbitals involved in vertical electronic excitations for the [Co^{III}(corrin)]-$EtPh^+$ model complex (*base-off* form of Im-[Co^{III}(corrin)]-$EtPh^+$) in the ground state S_0, obtained from DFT/BP86 level of theory.