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

Supporting Information

of

Aerobic photolysis of methylcobalamin: unraveling the photoreaction mechanism

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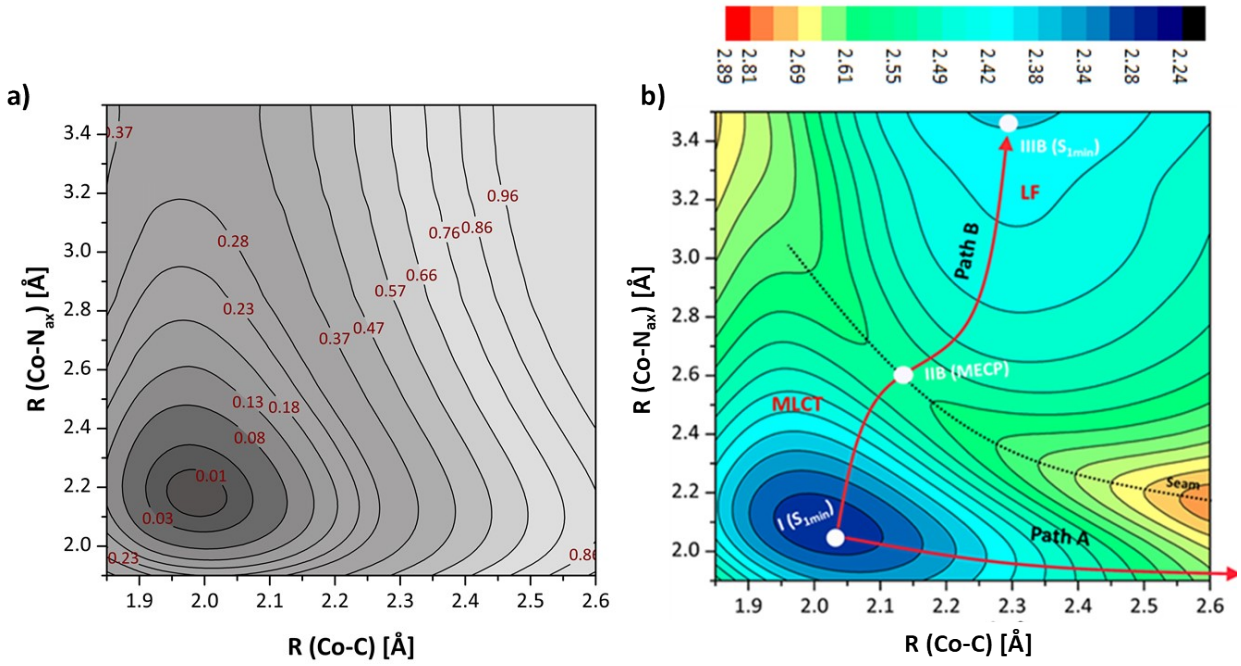

Figure S1. Potential energy surfaces Im−[Co^{III}(corrin)]−Me^{+} base-on model complex for the S_0 and S_1 state plotted as functions of axial bond lengths along **(a)** Ground state of MeCbl **(b)** Scheme of photoreaction on the S_1 PES with minima regions, separated by a seam, where MLCT minimum is denoted as I (S_{1min}) and LF minimum is denoted IIIB (S_{1min}).

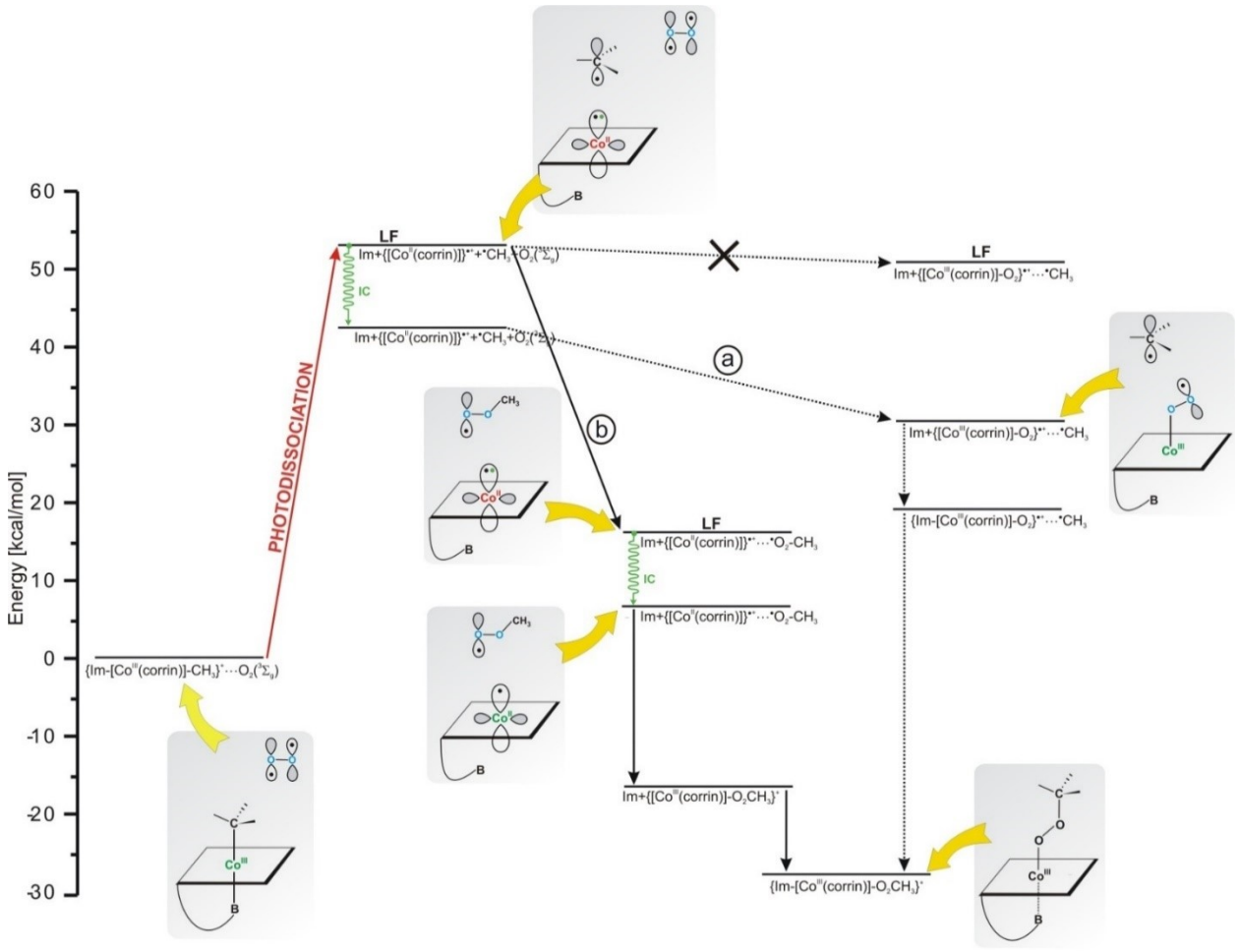

Figure S2. Energy diagram of photolytic reaction along paths a and b (path a, b of Scheme 2) showing the involvement of electronically excited states in MeCbl photoreaction in the presence of oxygen and the formation of $\{Im\text{-}[Co^{III}(corrin)]\text{-}OO\text{-}CH_3\}^+$) complex.

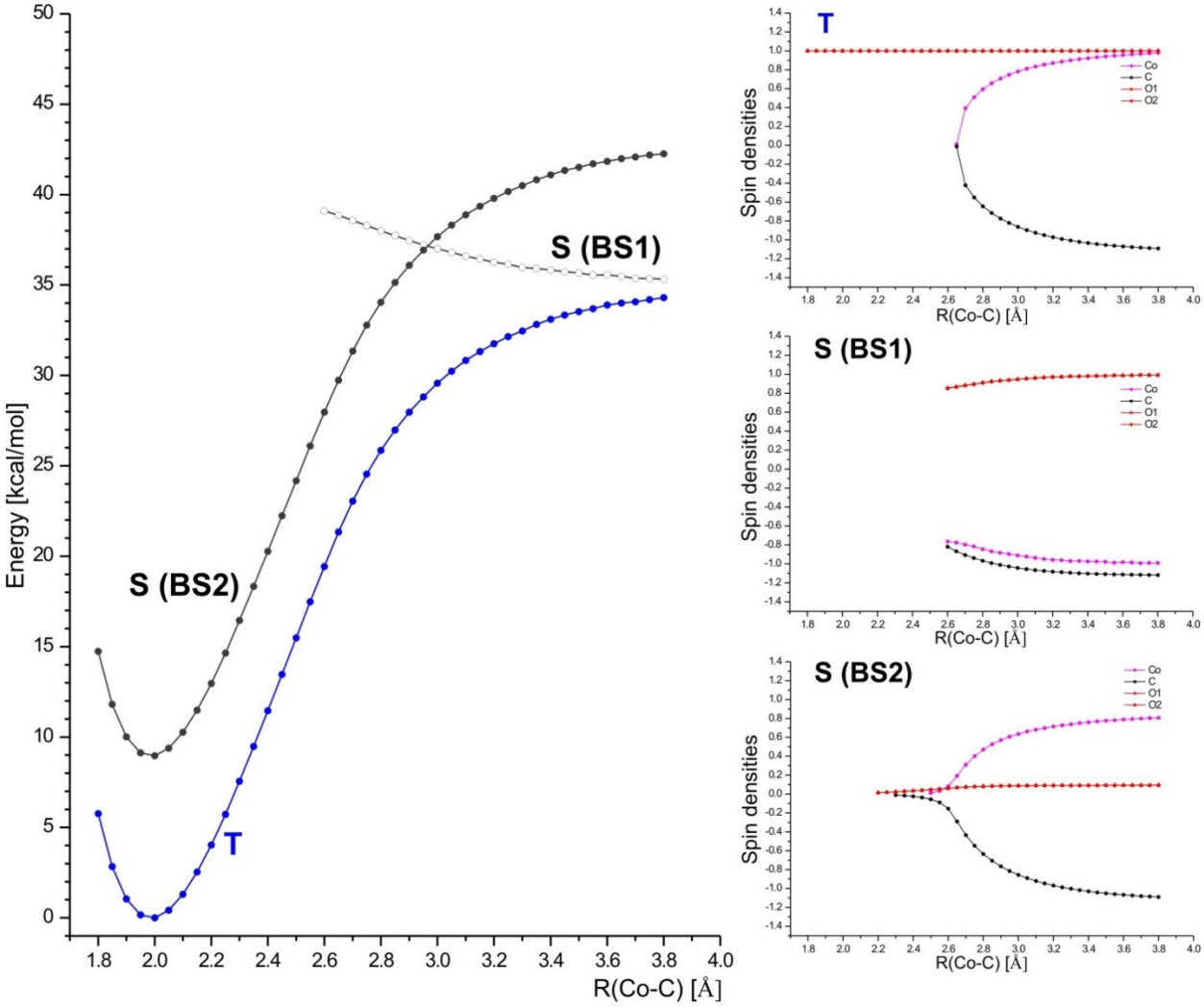

Figure S3. Potential energy curves along reaction path for {Im-[Co^{III}(corrin)]- CH_3}$^+$ + O_2 → {Im-[Co^{II}(corrin)]}$^{+\bullet}$ + $^\bullet OO\text{-}CH_3$ model reaction. Based on the UDFT/BP86 level of theory, the three electronic states were considered, namely the triplet state (T) and two singlet states with broken symmetry wave function (S(BS1), S(BS2)). The distribution of spin in the reaction system schematically can be presented as follows: ↑Co □ C↓□↑O-O↑ for T, ↓Co □ C↓□↑O-O↑ or ↑Co □ C↑□↓O-O↓ for S(BS1), and ↑Co □ C↓□↑O-O↓ for S(BS2). Mülliken spin densities on cobalt, carbon, and oxygen atoms, directly involved in the reaction are also shown.

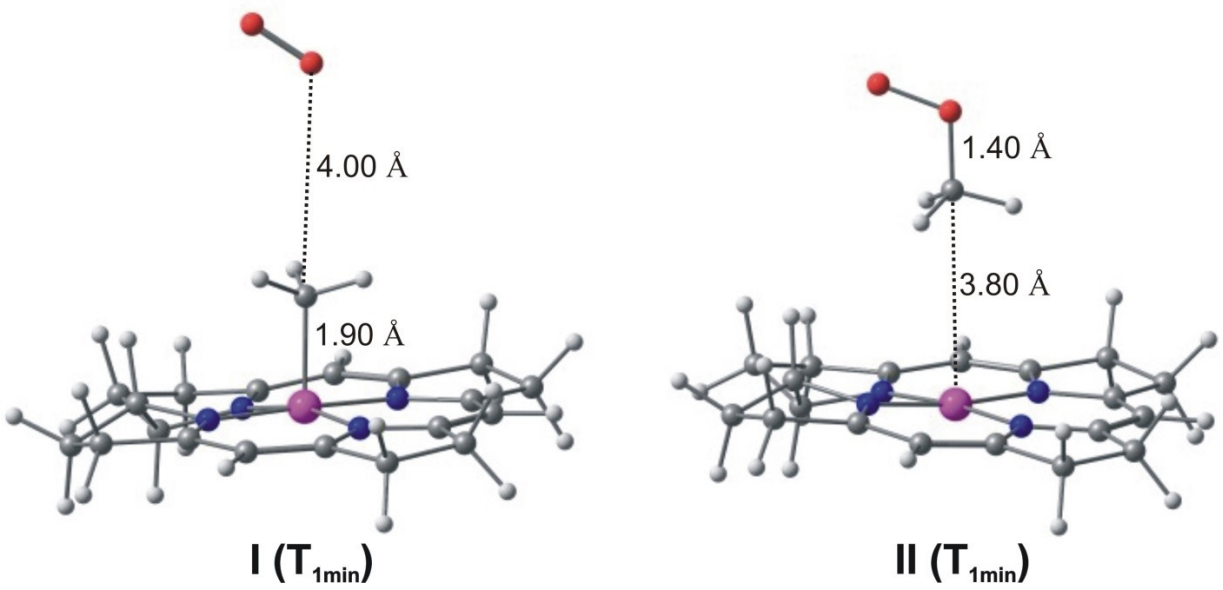

Figure S4. Corresponding optimized geometries of the I (T_{1min}) and II (T_{1min}) on the PES (Figures 4a and 4b).

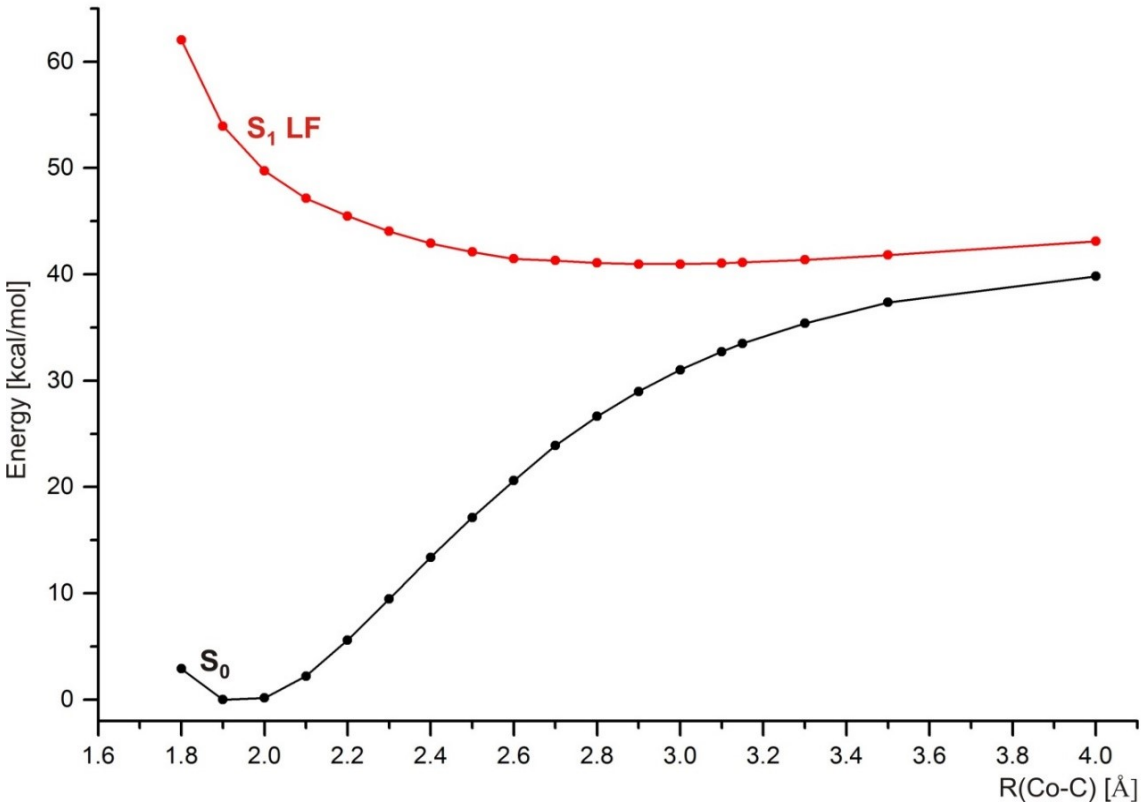

Figure S5. Potential energy curves of S_0 ground state and S_1 singlet state for $\{[Co^{III}(corrin)]–CH_3\}^+$ model complex as function Co-C axial bond length, obtained on the basis of calculation

results using the MS CAS/CASPT2 method. The CAS active space used in this calculation contains occupied d orbitals of cobalt: $3d_{xz}$, $3d_{yz}$, $3d_{x2-y2}$, $3d_{xv}$ + n, a pair of sigma, sigma * orbitals of Co-C bond, and five unoccupied orbitals: $3d_{xy}$-n, $4d_{xz}$, $4d_{yz}$, 4_{dx2-y2}, $4d_{z}^{2}$.