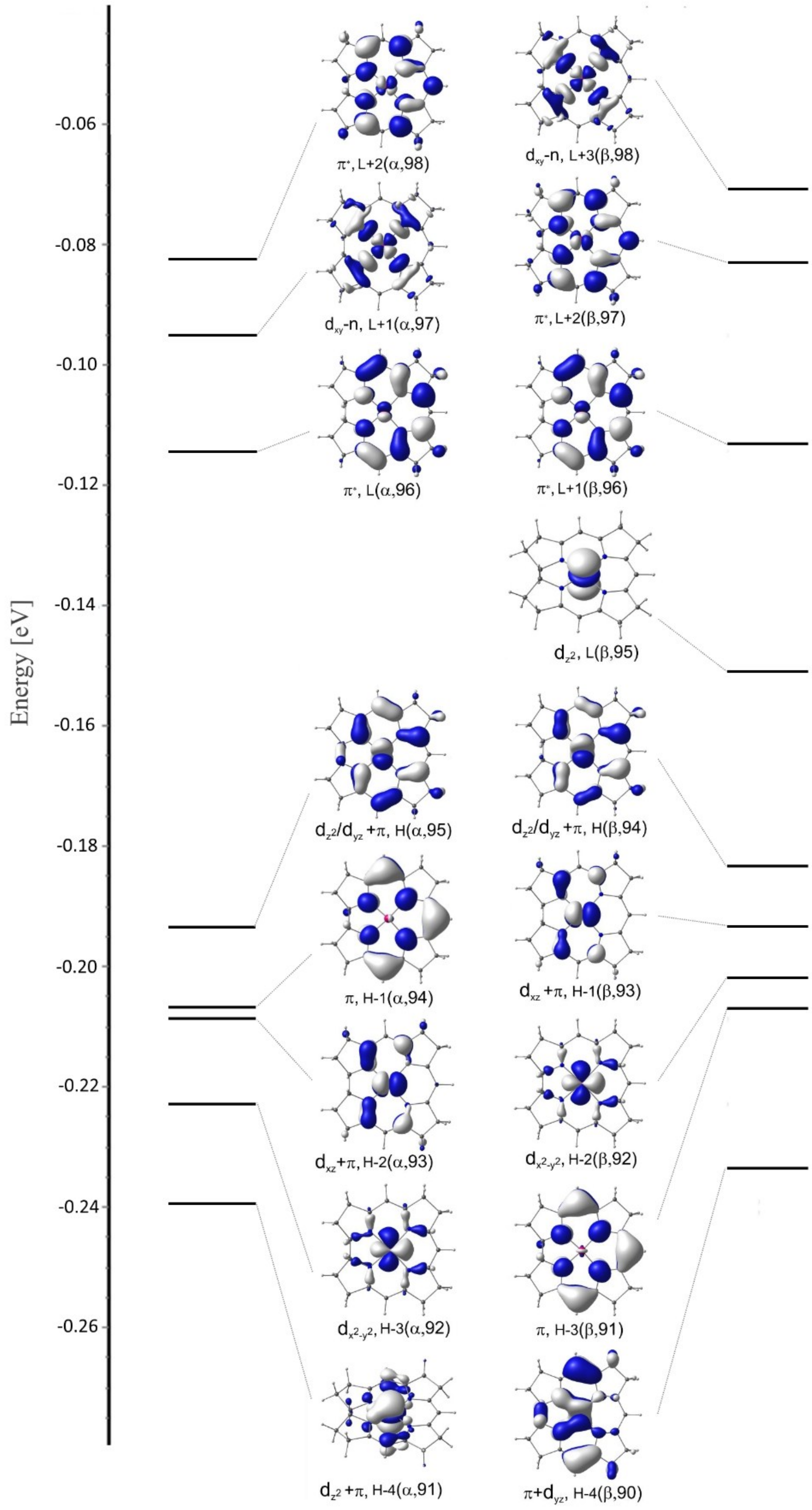


Figure S1. Isosurface plots of selected frontier MOs for $[Co^{II}(corrin)]^+$ based on uBP86/6-311G(d,p) TD-DFT calculations.

Table S1. The 10 lowest excited states of $[Co^{II}(corrin)]^+$, obtained from TD-DFT/BP86/6-311G(d,p) calculations.

	E(eV)	λ(nm)	*f*	Coeff.	Character		
D_1	0.45	2767.4	0.0000	100	94(β) → 95(β)	H(β) → L(β)	$d_{yz} + \pi \rightarrow d_{z^2}$
D_2	0.68	1834.9	0.0000	100	93(β) → 95(β)	H-1(β) → L(β)	$d_{xz} + \pi \rightarrow d_{z^2}$
D_3	1.38	898.9	0.0007	99	92(β) → 95(β)	H-2(β) → L(β)	$d_{x^2-y^2} \rightarrow d_{z^2}$
D_4	1.52	816.6	0.0003	99	91(β) → 95(β)	H-3(β) → L(β)	$\pi \rightarrow d_{z^2}$
D_5	1.73	716.0	0.0005	39	95(α) → 96(α)	H(α) → L(α)	$d_{yz} + \pi \rightarrow \pi^*$
				61	94(β) → 96(β)	H(β) → L+1(β)	$d_{yz} + \pi \rightarrow \pi^*$
D_6	2.13	583.3	0.0002	99	90(β) → 95(β)	H-4(β) → L(β)	$\pi + d_{yz} \rightarrow d_{z^2}$
D_7	2.13	582.2	0.0034	8	93(β) → 96(β)	H-1(β) → L+1(β)	$d_{xz}+\pi \rightarrow \pi^*$
				92	94(α) → 96(α)	H-1(α) → L(α)	$d_{xz}+\pi \rightarrow \pi^*$
D_8	2.34	529.2	0.0002	37	95(α) → 97(α)	H(α) → L+1(α)	$\pi \rightarrow \pi^*$
				15	95(α) → 97(α)	H(α) → L+1(α)	$d_{yz}+\pi \rightarrow d_{xy}$-n
				38	94(β) → 98(β)	H(β) → L+3(β)	$\pi \rightarrow \pi^*$
				11	94(β) → 98(β)	H(β) → L+3(β)	$d_{yz} +\pi \rightarrow d_{xy}$-n
D_9	2.37	523.9	0.0000	47	95(α) → 97(α)	H(α) → L+1(α)	$d_{yz}+\pi \rightarrow d_{xy}$-n
				12	95(α) → 97(α)	H(α) → L+1(α)	$\pi \rightarrow \pi^*$
				26	94(β) → 98(β)	H(β) → L+3(β)	$d_{yz}+\pi \rightarrow d_{xy}$-n
				15	94(β) → 98(β)	H(β) → L+3(β)	$\pi \rightarrow \pi^*$
D_{10}	2.38	520.8	0.0006	4	95(α) → 96(α)	H(α) → L(α)	$d_{z^2}/d_{yz} + \pi \rightarrow \pi^*$
				96	93(β) → 97(β)	H-1(β) → L+2(β)	$d_{x^2-y^2} \rightarrow \pi^*$

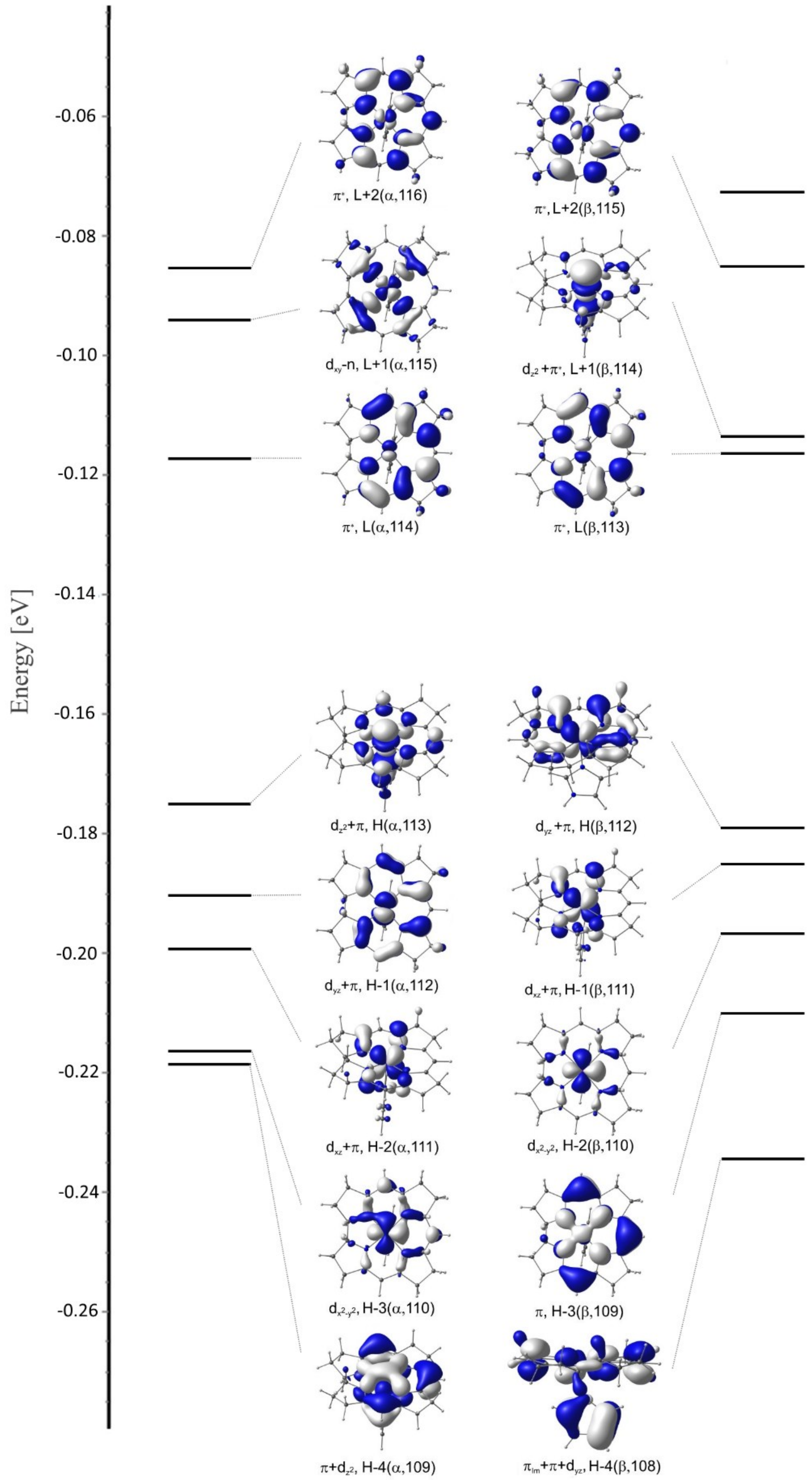


Figure S2. Isosurface plots of selected frontier MOs for $[Im\text{-}Co^{II}(corrin)]^+$ based on uBP86/6-311G(d,p) calculations .

Table S2 The 10 lowest excited states of $[\text{Im-Co}^{II}(\text{corrin})]^{+}{}_{(2.13\ \text{Å}\ \text{min})}$ obtained from TDDFT/BP86/6-311G(d,p) calculations.

	E(eV)	λ(nm)	*f*	NTO Coeff.	TDDFT Character		
D_1	1.40	884.9	0.0001	31	$113(\alpha) \rightarrow 114(\alpha)$	$H(\alpha) \rightarrow L(\alpha)$	$d_{z}{}^{2} + \pi_{Im} \rightarrow \pi^*$
				69	$112(\beta) \rightarrow 114(\beta)$	$H(\beta) \rightarrow L+1(\beta)$	$d_{yz} + \pi \rightarrow d_{z}{}^{2} + \pi_{Im}{}^*$
D_2	1.50	826.3	0.0008	36	$112(\alpha) \rightarrow 114(\alpha)$	$H\text{-}1(\alpha) \rightarrow L(\alpha)$	$d_{yz} + \pi \rightarrow \pi^*$
				64	$112(\beta) \rightarrow 113(\beta)$	$H(\beta) \rightarrow L(\beta)$	$d_{yz} + \pi \rightarrow \pi^*$
D_3	1.59	779.5	0.0010	17	$113(\alpha) \rightarrow 114(\alpha)$	$H\ (\alpha) \rightarrow L(\alpha)$	$d_{z}{}^{2} + \pi_{Im} \rightarrow \pi^*$
				83	$111(\beta) \rightarrow 113(\beta)$	$H\text{-}1(\beta) \rightarrow L+1(\beta)$	$d_{xz}+\pi \rightarrow d_{z}{}^{2} + \pi_{Im}{}^*$
D_4	1.65	752.0	0.0026	52	$113(\alpha) \rightarrow 114(\alpha)$	$H\ (\alpha) \rightarrow L(\alpha)$	$d_{z}{}^{2} + \pi_{Im} \rightarrow \pi^*$
				48	$112(\beta) \rightarrow 114(\beta)$	$H(\beta) \rightarrow L+1(\beta)$	$d_{yz} + \pi \rightarrow d_{z}{}^{2} + \pi_{Im}{}^*$
D_5	1.81	683.3	0.0028	8	$111(\alpha) \rightarrow 114(\alpha)$	$H\text{-}2(\alpha) \rightarrow L(\alpha)$	$d_{xz} + \pi_{Im} \rightarrow \pi^*$
				92	$111(\beta) \rightarrow 113(\beta)$	$H\text{-}1(\beta) \rightarrow L+1(\beta)$	$d_{xz} + \pi_{Im} \rightarrow \pi^*$
D_6	2.13	583.6	0.0094	25	$112(\alpha) \rightarrow 114(\alpha)$	$H\text{-}1(\alpha) \rightarrow L(\alpha)$	$d_{yz} + \pi \rightarrow \pi^*$
				75	$110(\beta) \rightarrow 113(\beta)$	$H\text{-}2(\beta) \rightarrow L+1(\beta)$	$d_{x}{}^{2}{}_{-y}{}^{2} + \pi \rightarrow d_{z}{}^{2} + \pi_{Im}{}^*$
D_7	2.15	576.8	0.0045	57	$113(\alpha) \rightarrow 115(\alpha)$	$H\ (\alpha) \rightarrow L+1(\alpha)$	$d_{z2} + \pi_{Im} \rightarrow d_{xy}\text{-n}$
				34	$111(\alpha) \rightarrow 114(\alpha)$	$H\text{-}2(\alpha) \rightarrow L(\alpha)$	$d_{xz}+\pi \rightarrow \pi^*$
				8	$110(\beta) \rightarrow 113(\beta)$	$H\text{-}2(\beta) \rightarrow L(\beta)$	$d_{x}{}^{2}{}_{-y}{}^{2} \rightarrow \pi^*$
D_8	2.17	570.5	0.0062	14	$112(\alpha) \rightarrow 114(\alpha)$	$H\text{-}2(\alpha) \rightarrow L(\alpha)$	$d_{yz} + \pi \rightarrow \pi^*$
				86	$110(\beta) \rightarrow 113(\beta)$	$H\text{-}2(\beta) \rightarrow L(\beta)$	$d_{x}{}^{2}{}_{-y}{}^{2} + \pi \rightarrow \pi^*$
D_9	2.22	557.6	0.0004	62	$112(\alpha) \rightarrow 115(\alpha)$	$H\text{-}1(\alpha) \rightarrow L+1(\alpha)$	$d_{yz} + \pi \rightarrow d_{xy}\text{-n}$
				38	$112(\beta) \rightarrow 116(\beta)$	$H(\beta) \rightarrow L+3(\beta)$	$d_{yz} + \pi \rightarrow d_{xy}\text{-n}$
D_{10}	2.28	543.5	0.0026	54	$111(\alpha) \rightarrow 114(\alpha)$	$H\text{-}2(\alpha) \rightarrow L(\alpha)$	$d_{xz} + \pi \rightarrow \pi^*$
				33	$111(\alpha) \rightarrow 115(\alpha)$	$H\text{-}2(\alpha) \rightarrow L+1(\alpha)$	$d_{xz} + \pi \rightarrow d_{xy}\text{-n}$
				14	$112(\beta) \rightarrow 114(\beta)$	$H(\beta) \rightarrow L+1(\beta)$	$d_{yz} + \pi \rightarrow d_{z}{}^{2} + \pi^*$

Table S3. Comparison of Co 3d→$3d_{z^2}$ transition energies of $Co^{II}(corrin)^+$ obtained from experimental and computed results through MCD spectrum, TDDFT, CASSCF/MC-XQDPT2 and SORCI approaches.

	donor MO		
	$3d_{yz}$	$3d_{xz}$	$3d_{x^2-y^2}$
MCD expt [a]	< 1.16 eV (9000cm^{-1})	< 1.16 eV (9000cm^{-1})	1.68 eV (16500 cm^{-1})
TDDFT(4coord)	0.45 eV	0.68 eV	1.38 eV
$TDDFT_{(LF\ 5\text{-}coord)}$	0.72 eV	0.91 eV	1.55 eV
CASSCF/ MC-XQDPT2	0.01 eV	0.01eV	1.35 eV
SORCI [a]	0.03 eV (256 cm^{-1})	0.26 eV (2154 cm^{-1})	1.16 eV (9389 cm^{-1})

[a] Data from ref. 12.

Table S4. Comparison of Co 3d → $3d_{z^2}$ transition energies of Im-$[Co^{II}(corrin)]^+$ obtained from experimental and computed results through MCD spectrum, TDDFT, CASSCF/XMCQDPT2 and SORCI approaches.

	donor MO		
	$3d_{yz}$	$3d_{xz}$	$3d_{x^2-y^2}$
MCD expt [a]	1.79 eV (14470cm^{-1})	1.79 eV (14470cm^{-1})	2.19 eV (17700 cm^{-1})
$TDDFT_{(trunc.)}$	1.40 eV	1.59 eV	2.13 eV
$TDDFT_{(full)}$	1.27 eV	1.42 eV	2.08 eV
$TDDFT_{(LF)}$	0.72 eV	0.91 eV	1.55 eV
CASSCF/ XMCQDPT2	0.90 eV	0.90 eV	2.09 eV

[a] read from ref. 24.

Table S5. The 10 lowest excited states $[Im\text{-}Co^{II}(corrin)]^{+}_{(1.85\ Å)}$ obtained from TDDFT/BP86/6-311G(d,p) calculations.

	E(eV)	λ(nm)	*f*	Coeff.	TDDFT Character		
D_1	0.83	1495.1	0.0007	99	112(α) → 113(α)	H-2(α) → L(α)	$d_{z^2} + \pi_{Im} \rightarrow \pi^*$
				1	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{yz} + \pi \rightarrow d_{z^2} + \pi_{Im}^*$
D_2	1.50	829.3	0.0004	34	93(α) → 96(α)	H-2(α) → L(α)	$\pi \rightarrow \pi^*$
				66	91(β) → 96(β)	H-3(β) → L+1(β)	$\pi \rightarrow \pi^*$
D_3	1.54	805.7	0.0016	92	93(α) → 96(α)	H-2(α) → L(α)	$d_{z^2} + \pi_{Im} \rightarrow d_{xy}$-n
				8	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{yx} + \pi \rightarrow \pi^*$
D_4	1.69	731.9	0.0005	92	93(α) → 96(α)	H-2(α) → L(α)	$d_{z^2} + \pi_{Im} \rightarrow \pi^*$
				8	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{yz} + \pi + \pi_{Im} \rightarrow d_{z^2} + \pi$
D_5	1.77	699.3	0.0018	11	93(α) → 96(α)	H-2(α) → L(α)	$d_{xz} + \pi + \pi_{Im} \rightarrow \pi^*$
				89	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{xz} + \pi + \pi_{Im} \rightarrow \pi^*$
D_6	2.04	608.1	0.0007	6	93(α) → 96(α)	H-2(α) → L(α)	$d_{xz} + \pi + \pi_{Im} \rightarrow \pi^*$
				94	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{yx} + \pi \rightarrow d_{z^2} + \pi$
D_7	2.14	578.6	0.0041	60	93(α) → 96(α)	H-2(α) → L(α)	$d_{xz} + \pi + \pi_{Im} \rightarrow \pi^*$
				40	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{z^2}/d_{yz} + \pi + \pi_{Im} \rightarrow d_{z^2} + \pi$
D_8	2.16	574.9	0.0031	28	93(α) → 96(α)	H-2(α) → L(α)	$d_{xz} + \pi + \pi_{Im} \rightarrow \pi^*$
				72	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{x^2-y^2} \rightarrow \pi^*$
D_9	2.18	568.7	0.0061	8	93(α) → 96(α)	H-2(α) → L(α)	$d_{yx} + \pi \rightarrow \pi^*$
				68	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{yx} + \pi \rightarrow d_{z^2} + \pi_{Im}$
				24	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{x^2-y^2} \rightarrow \pi^*$
D_{10}	2.24	553.0	0.0044	61	93(α) → 96(α)	H-2(α) → L(α)	$d_{yx} + \pi \rightarrow d_{xy}$-n
				39	91(β) → 96(β)	H-3(β) → L+1(β)	$d_{yx} + \pi \rightarrow d_{xy}$-n

Figure S3. NTOs for $[Im\text{-}Co^{II}(corrin)]^{+}$ (1.85 A)

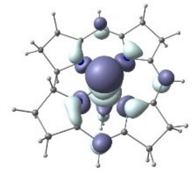
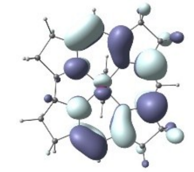
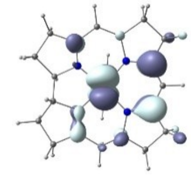
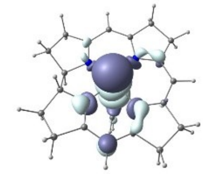
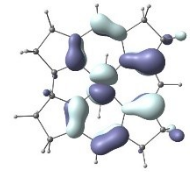
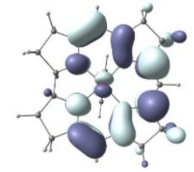
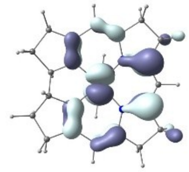
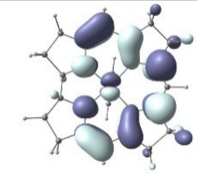
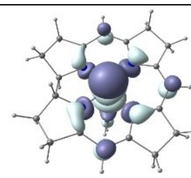
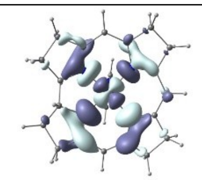
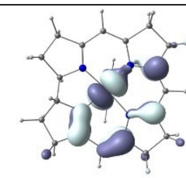
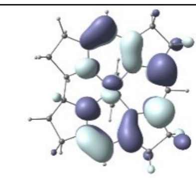
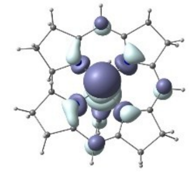
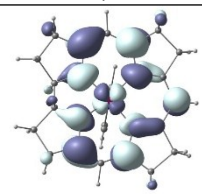
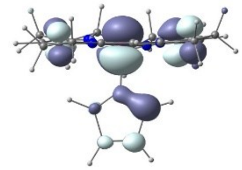
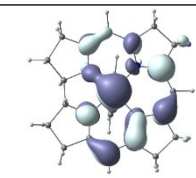
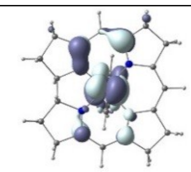
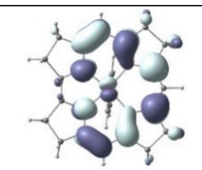
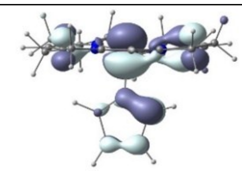
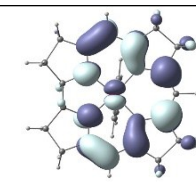
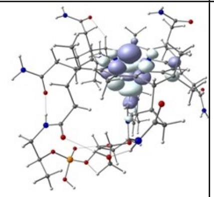
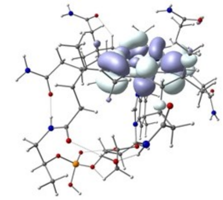
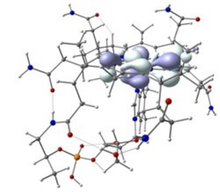
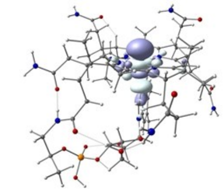
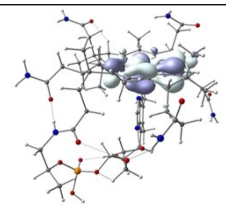
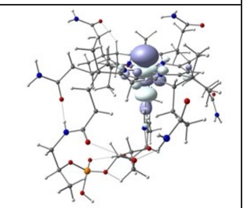
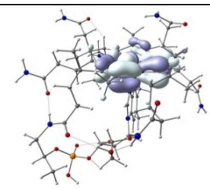
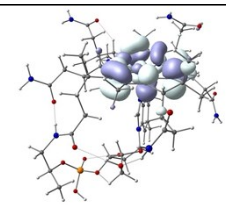
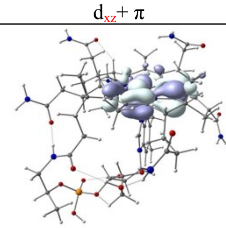
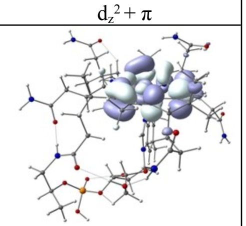
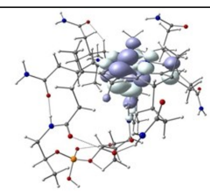
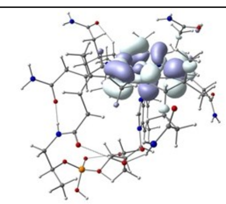
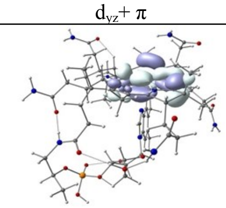
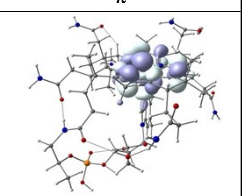
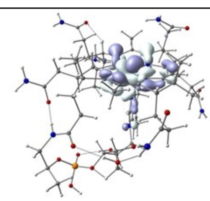
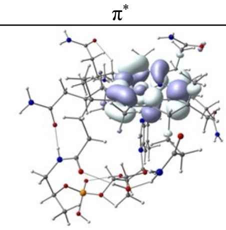
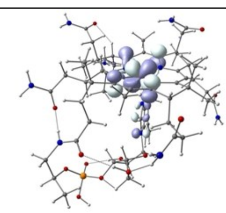
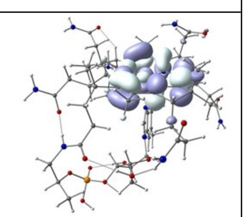
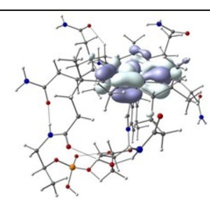
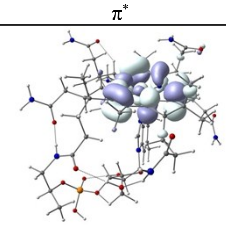
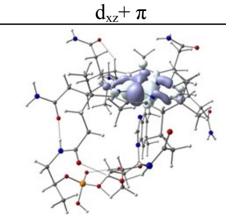
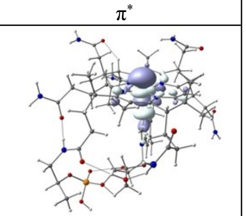
NTO	E(eV)	NTO Coeff	f	α hole	α particle	β hole	β particle
D_1	0.83	99 (α) 1 (β)	0.0007	 $d_{z^2} + \pi_{Im}$	 π*	 $d_{yz} + \pi$	 $d_{z^2} + \pi_{Im}^{*}$
D_2	1.50	34 (α) 66 (β)	0.0004	 π	 π*	 π	 π*
D_3	1.54	92 (α) 8 (β)	0.0016	 $d_{z^2} + \pi_{Im}$	 d_{xy}-n	 $d_{yx} + \pi$	 π*
D_4	1.69	92 (α) 8 (β)	0.0005	 $d_{z^2} + \pi_{Im}^{*\backslash}$	 π*	 $d_{yz} + \pi + \pi_{Im}$	 $d_{z^2} {}_{+} \pi_{Im}^{*}$
D_5	1.77	11 (α) 89 (β)	0.0018	 $d_{xz} + \pi + \pi_{Im}$	 π*	 $d_{xz} + \pi + \pi_{Im}$	 π*

Figure S4. NTOs of the first 10 TDDFT excited states of the $[Im\text{-}Co^{II}(corrin)]^{+}$ full structure at the BP86/6-311G (d,p) level of theory.

NTO	eV	NTO Coeff. & TDDFT Character	*f*	α hole	α particle	β hole	β particle
D_1	1.27	6%(α) H → L 94 %(β) H → L	0.0001	 $d_{z^2} + \pi_{Im}$	 π^*	 $d_{yz} + \pi$	 $d_{z^2} + \pi$
D_2	1.42	100 %(β) H-1 → L	0.0001			 $d_{xz} + \pi$	 $d_{z^2} + \pi$
D_3	1.48	37% (α)H-1→ L 63% (β) H→ L+1	0.0005	 $d_{yz} + \pi_{Im}$	 π^*	 $d_{yz} + \pi$	 π^*
D_4	1.72	91% (α) H → L 8% (β)	0.0074	 $d_{z^2} + \pi_{Im}$	 π^*	 $d_{yz} + \pi$	 $d_{z^2} + \pi^*$
D_5	1.78	14 % (α)H-2→L 85 % (β)H-2→L+1	0.0023	 $d_{xz} + \pi$	 π^*	 $d_{xz} + \pi$	 π^*
D_6	2.00	14% (α)H-1→L 86 % (β)H-2→L	0.0079	 $d_{yz} + \pi$	 π^*	 $d_{x^2-y^2}$	 d_{z^2}

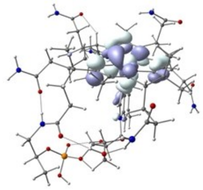
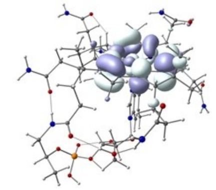
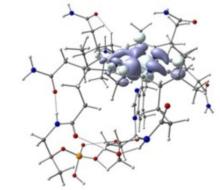
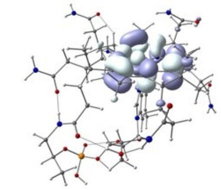
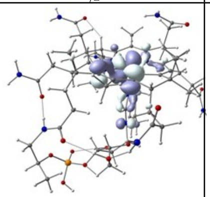
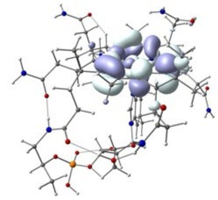
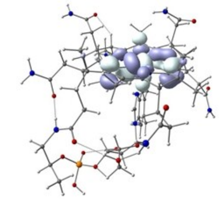
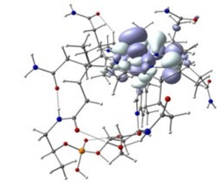
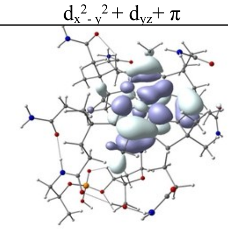
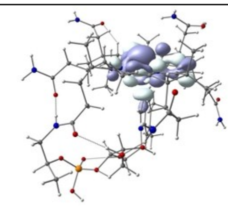
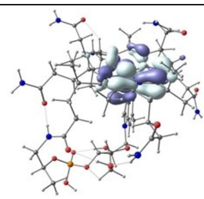
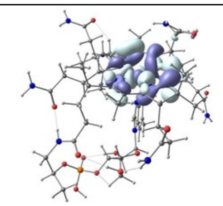
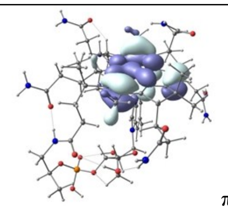
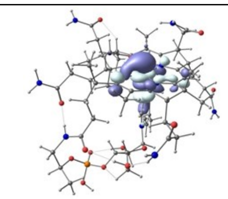
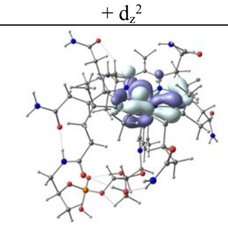
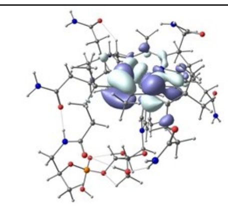
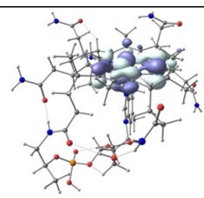
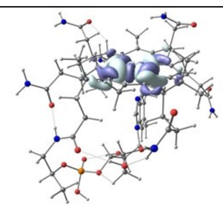
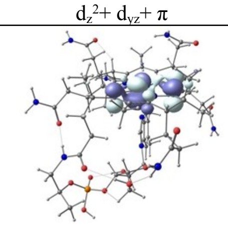
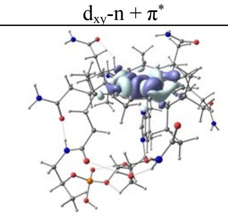
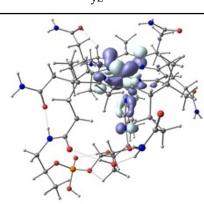
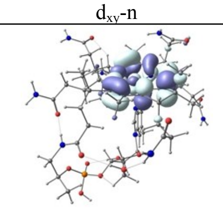
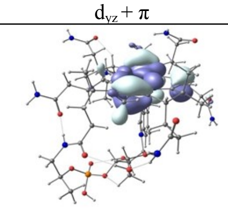
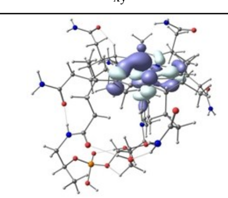
D_7	2.08	11% (α) H-3→L 89 % (β)H-2 → L+1 *H-3= π + d_z^2	0.0027	 $d_{yz} + \pi$	 π^*	 $d_{x^2-y^2} + \pi$	 $\pi^* + d_z^2$
D_8	2.15	60% (α)H-2→L 25% (β1) 16% (β2)	0.0080	 $d_{xz} + \pi$	 π^*	 $d_{x^2-y^2} + d_{yz} + \pi$	 $d_z^2 + \pi^*$
						 π	 d_z^2
D_9	2.18	40% (α)H-1→L+1 35 % (β1)H-3→L 24% (β2)	0.0064	 $d_{yz} + \pi$	 d_{xy}-n	 π + d_z^2	 d_z^2
						 $d_z^2 + d_{yz} + \pi$	 d_{xy}-n + π^*
D_{10}	2.23	36% (α1)H-1→L+1 26% (α2)H-2→L 22 % (β1)H→L+4 14% (β2)H-3→L	0.0018	 $d_{yz} + \pi$	 d_{xy}-n	 $d_{yz} + \pi$	 d_{xy}-n
				 $d_{yz} + \pi$	 π^*	 π + d_z^2	 d_z^2

Figure S5. Frontier orbitals of the cob(II)alamin full structure at the BP86/6-311G(d,p) level (left panel), and the BP86/SDD level (right panel).

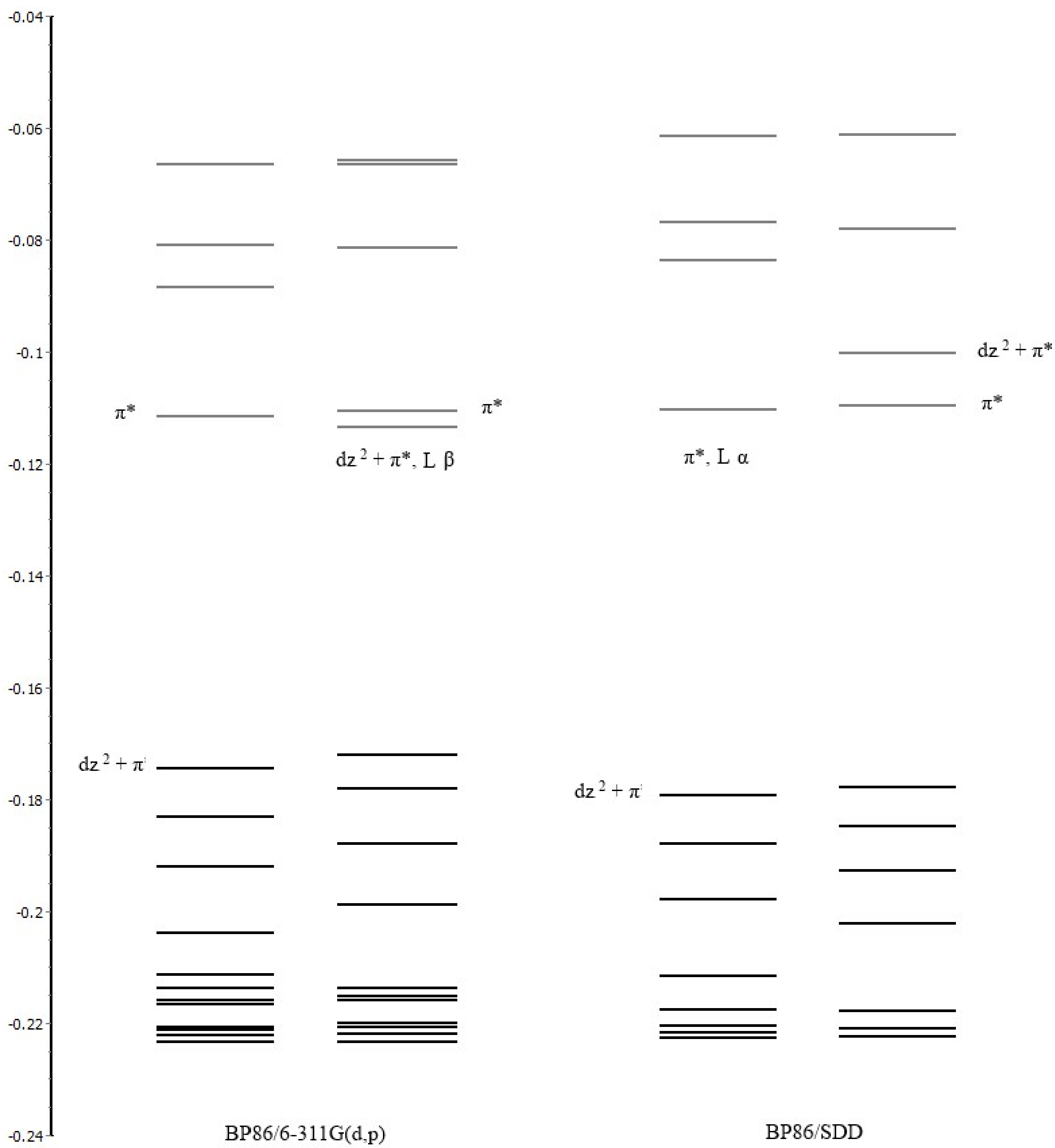


Figure S6. Frontier orbitals of the cob(II)alamin full structure at the BP86/SDD level of theory.

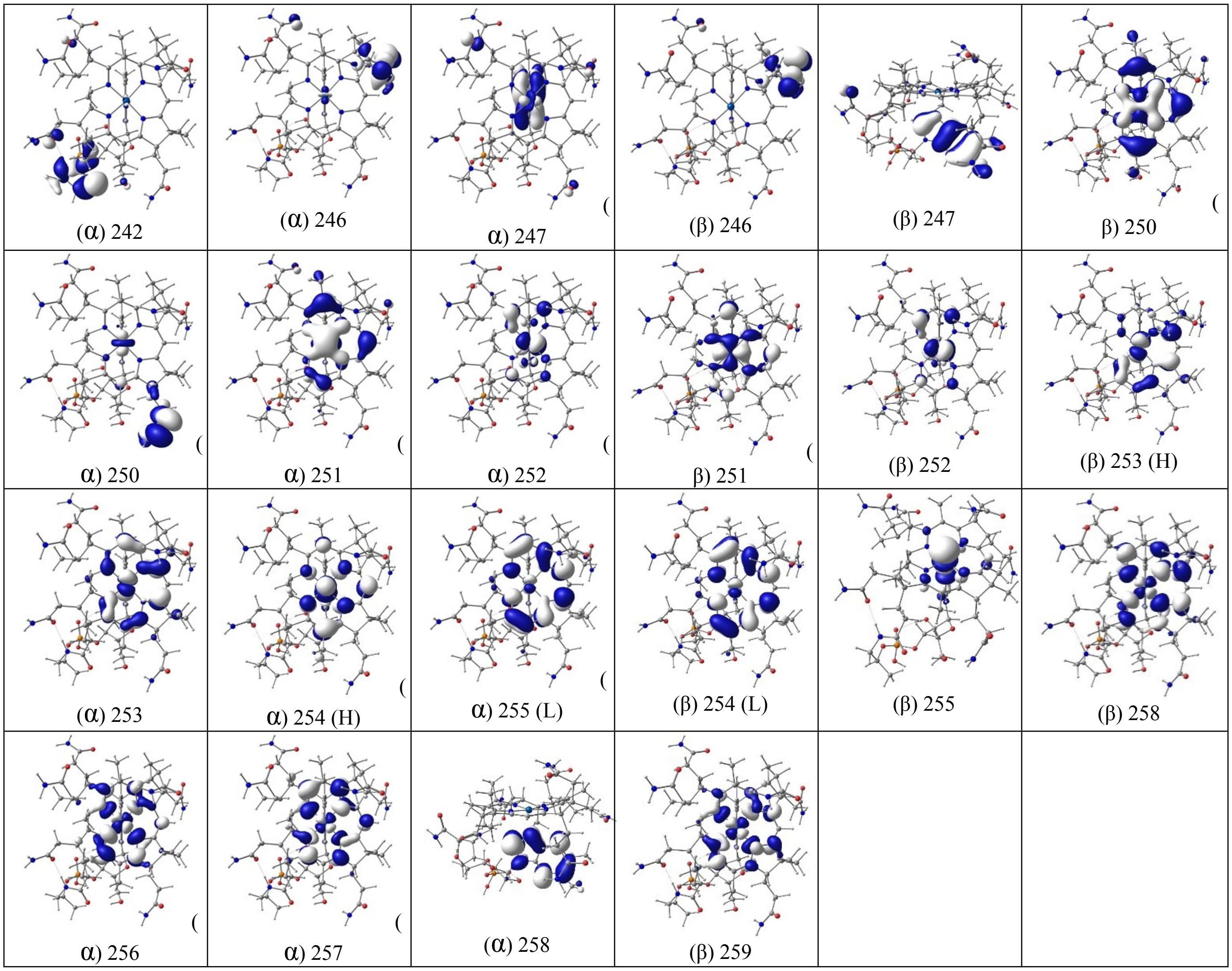


Figure S7. NTOs of the first 5 TDDFT excited states of cob(II)alamin at the BP86/SDD level of theory.

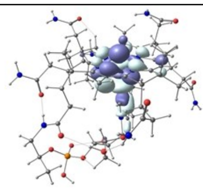
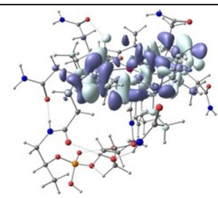
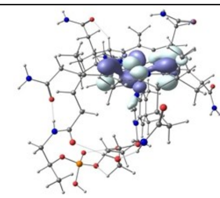
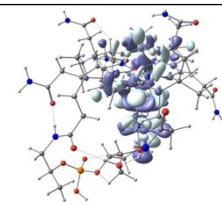
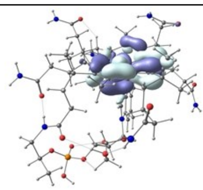
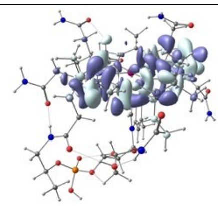
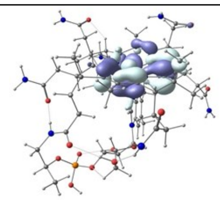
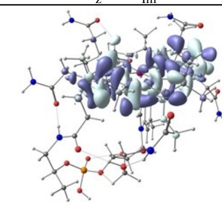
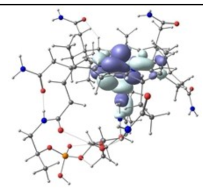
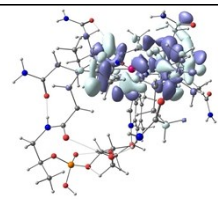
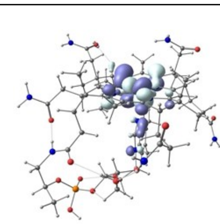
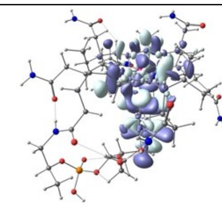
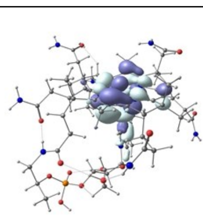
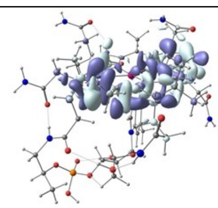
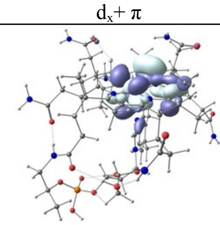
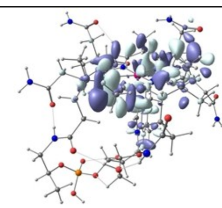
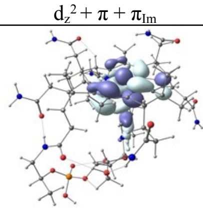
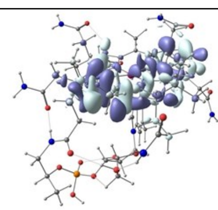
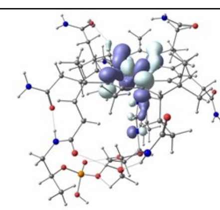
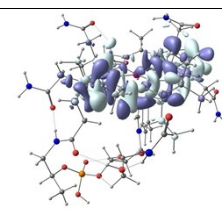
NTO	eV	NTO Coeff	*f*	α hole	α particle	β hole	β particle
D_1	1.37	93% (β) 7% (α)	0.0001	 $d_{z^2} + \pi_{Im}$	 π^*	 $d_{yz} + \pi$	 $d_{z^2} + \pi_{Im}$
D_2	1.46	62% (β) 38% (α)	0.0001	 $d_{yz} + \pi$	 π^*	 $d_{yz} + \pi$	 π^*
D_3	1.53	96% (β) 4% (α)	0.0005	 $d_{z^2} + \pi_{Im}$	 π^*	 $d_x + \pi$	 $d_{z^2} + \pi^*$
D_4	1.76	80%(α) 20%(β)	0.0074	 $d_{z^2} + \pi + \pi_{Im}$	 π^*	 $d_{xz} + \pi$	 π_{Im}^*
D_5	1.84	80%(α) 20%(β)	0.0023	 $d_{z^2} + d_{xz} + \pi_{Im}$	 π^*	 $d_{xz} + \pi$	 π^*

Figure S8. NTOs of selected TDDFT excited states of the cob(II)alamin full structure at the BP86/SDD (d,p) level of theory.

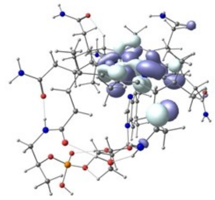
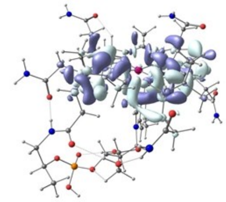
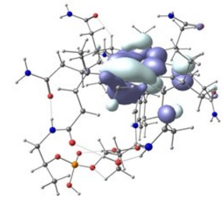
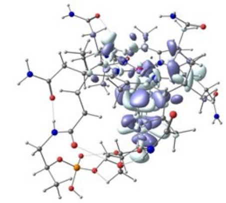
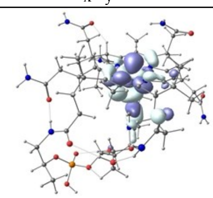
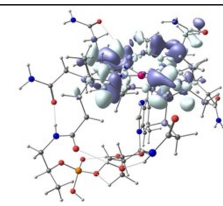
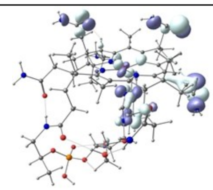
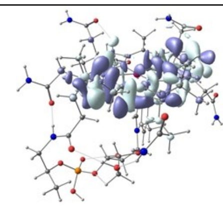
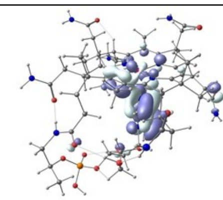
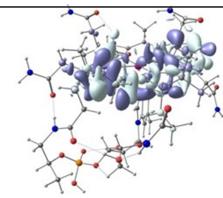
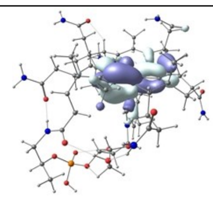
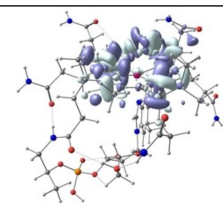
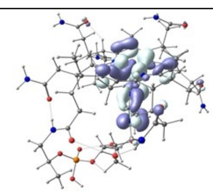
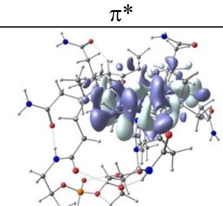
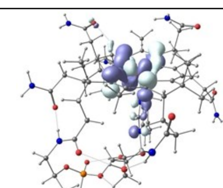
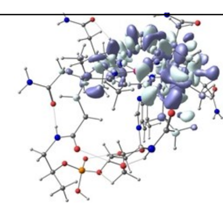
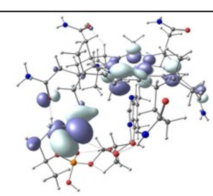
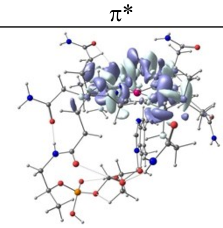
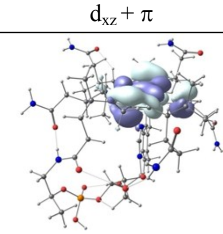
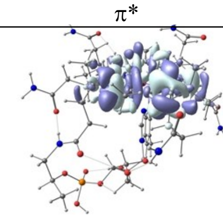
NTO	eV	NTO Coeff.	*f*	α hole	α particle	β hole	β particle
D_{19}	2.71	46% (α,1) 29 % (β,1)	0.0276	 $d_{x^2-y^2} + \pi$	 π *	 $d_{x2-y2} + \pi$	 $d_{z2} + \pi_{Im}*$
		25% (α,2)		 $d_{z^2} + \pi$	 $\pi*$		
D_{29}	2.93	63% (α,1) 19% (β,1)	0.0377	 π_{Im} + p	 $\pi*$	 π_{Im}	 $\pi*$
		19% (α,2)		 $\pi + d_{z^2}$	 $\pi*$		
D_{61}	3.39	78 % (β) 22 % (α)	0.0263	 $d_{xz} + \pi_{Im}$	 $\pi*$	 $d_{xz} + \pi$	 $\pi*$
D_{144}	3.95	60 % (β) 40 % (α)	0.0923	 π_p	 $\pi*$	 $d_{x^2-y^2} + \pi$	 d_{xy}-n

Figure S9. NTOs of selected TDDFT excited states of the $[Im\text{-}Co^{II}(corrin)]^{+}_{(min,\ 2.13\ Å)}$ model at the BP86/6-311g (d,p) level of theory.

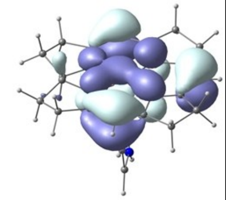
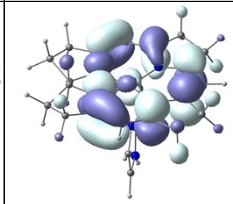
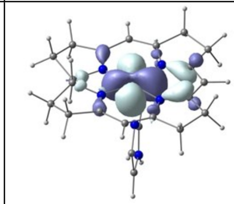
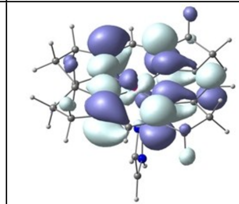
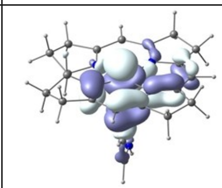
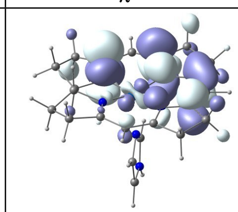
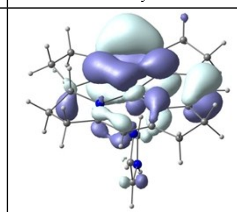
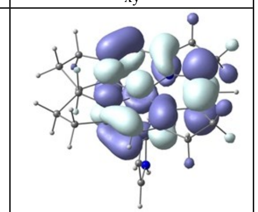
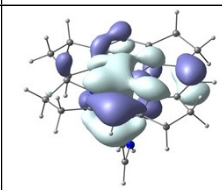
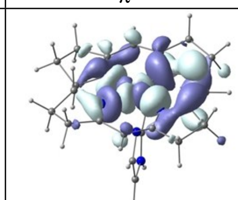
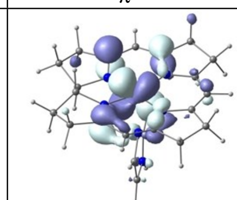
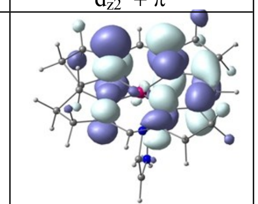
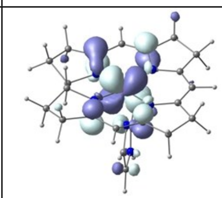
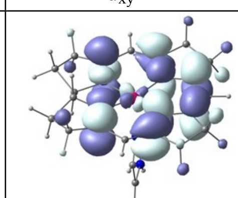
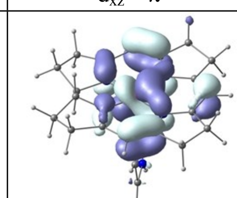
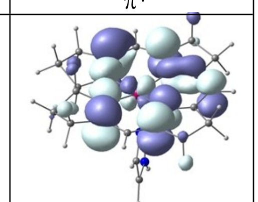
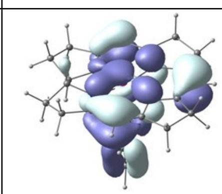
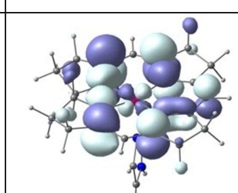
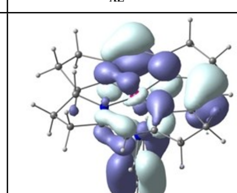
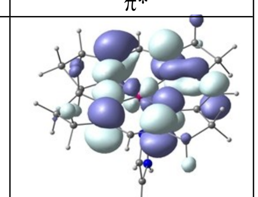
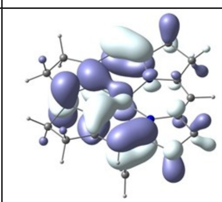
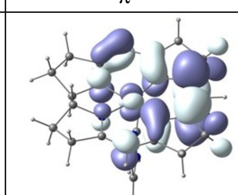
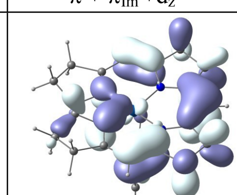
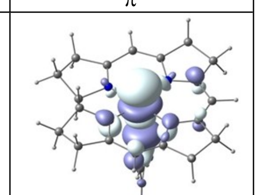
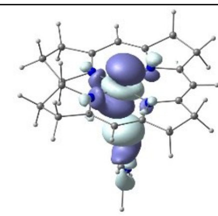
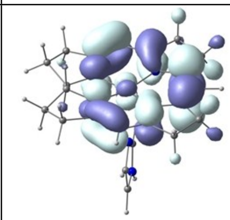
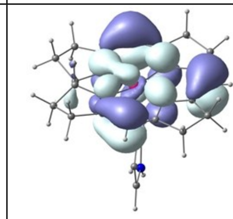
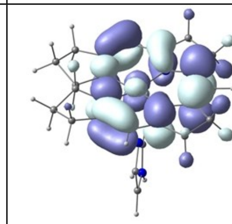
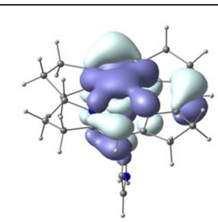
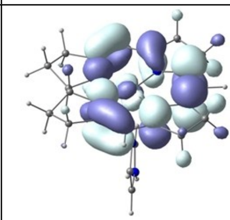
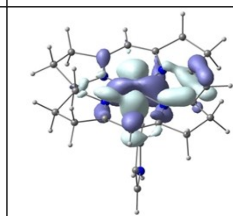
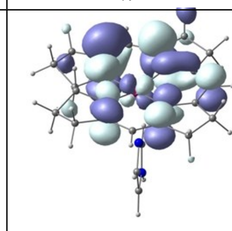
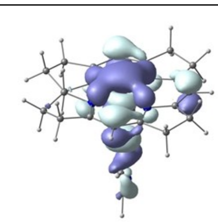
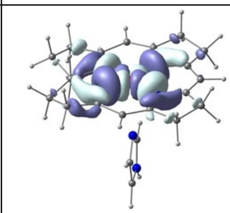
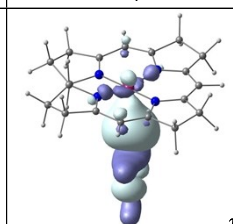
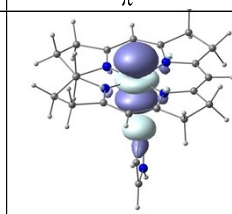
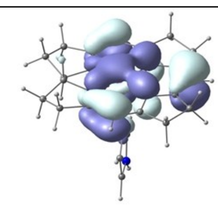
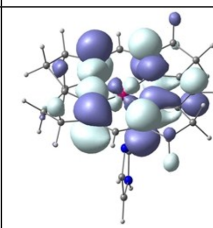
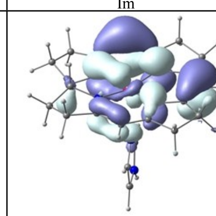
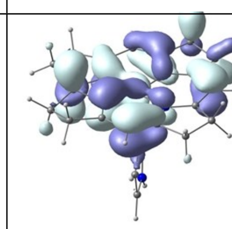
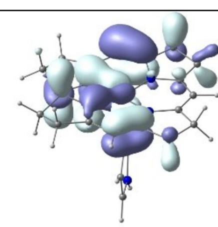
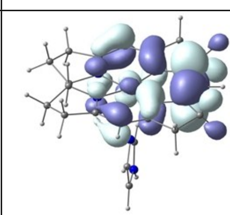
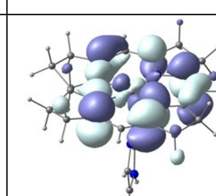
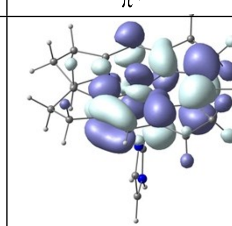
NTO	eV	NTO Coeff.	*f*	α hole	α particle	β hole	β particle
D_{23}	3.00	32 % (α,1) 30 % (β,1)	0.0160	 $\pi + d_{z}^{2}$	 π*	 $d_{x^2-y^2}$	 d_{xy}-n
		17 % (α,2) 30 % (β,2)		 $d_{z}^{2} + \pi$	 π*	 π	 $d_{z2} + \pi^*$
D_{33}	3.38	75 % (β) 25 % (α)	0.0500	 $d_{x^2-y^2}$	 d_{xy}-n	 $d_{xz} + \pi$	 π*
D_{45}	3.80	89 % (α) 11 % (β)	0.0689	 $d_{xz} + \pi + \pi_{Im}$	 π*	 $d_{xz} + \pi$	 π*
D_{56}	4.09	37 % (α,1) 33 % (β,1)	0.2433	 $\pi + \pi_{Im} + d_{z}^{2}$	 π*	 $\pi + \pi_{Im} + d_{z}^{2}$	 π*
		13 % (α,2) 18 % (β,2)		 π	 π*	 π	 d_{z}^{2}

Figure S10. NTOs of selected TDDFT excited states of the [Im- - - Co^{II}(corrin)]$^{+}_{(LF,\ 2.80\ Å)}$ model at the BP86/6-311g (d,p) level of theory.

NTO	eV	NTO Coeff.	*f*	α hole	α particle	β hole	β particle
D_{17}	2.73	58 % (α) 42 % (β)	0.0455	 $d_{z^2} + \pi$	 π*	 $d_{z^2} + \pi$	 π*
D_{26}	3.09	66 % (α) 34 % (β)	0.0953	 $\pi + d_{z^2}$	 π*	 $d_{x^2-y^2}$	 π*
D_{33}	3.44	74 % (β) 26 % (α)	0.0520	 $\pi + d_{z^2}$	 d_{xy}-n	 π_{Im}	 $d_{z^2} + \pi_{Im}$ *
D_{54}	4.06	40 % (α,1) 33 % (β,1)	0.2472	 $\pi + d_{z^2}$	 π*	 $\pi + d_{z^2}$	 π*
		15 % (α,2) 12 % (β,2)		 $\pi + d_{yz}$	 π*	 π	 $d_{yz} + \pi$*