Supporting Information for:

Identifying Charge-Transfer and Trip-Multiplet States in Co(I), Co(II), and Co(III) phthalocyanines using (magneto)optical spectroscopy and (TD)DFT calculations.

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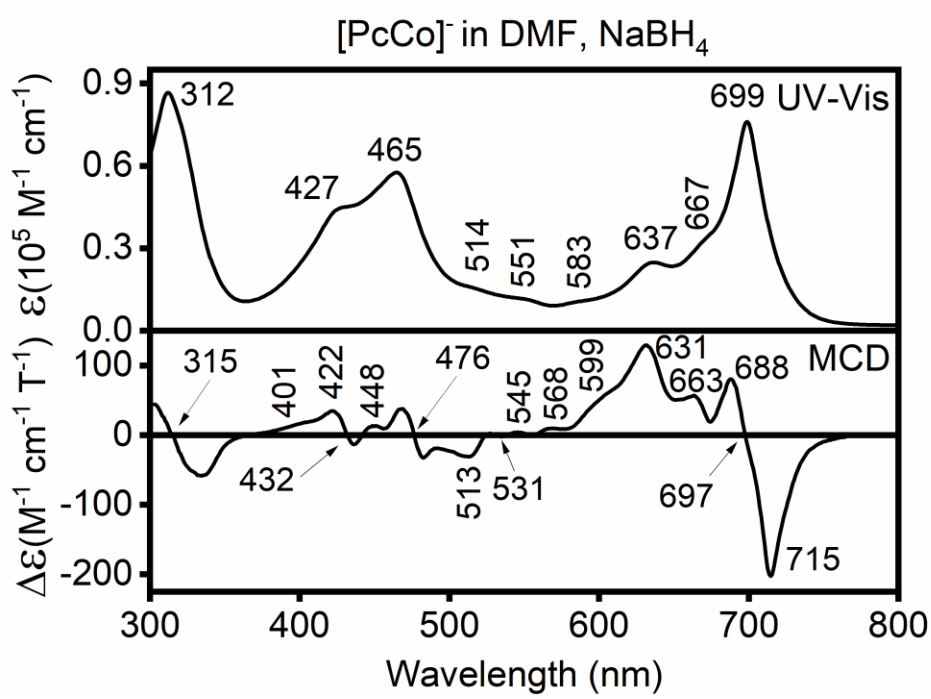

Figure S1. UV-Vis and MCD spectra of $[Pc(2-)Co^{I}]^{-}$ in DMF.

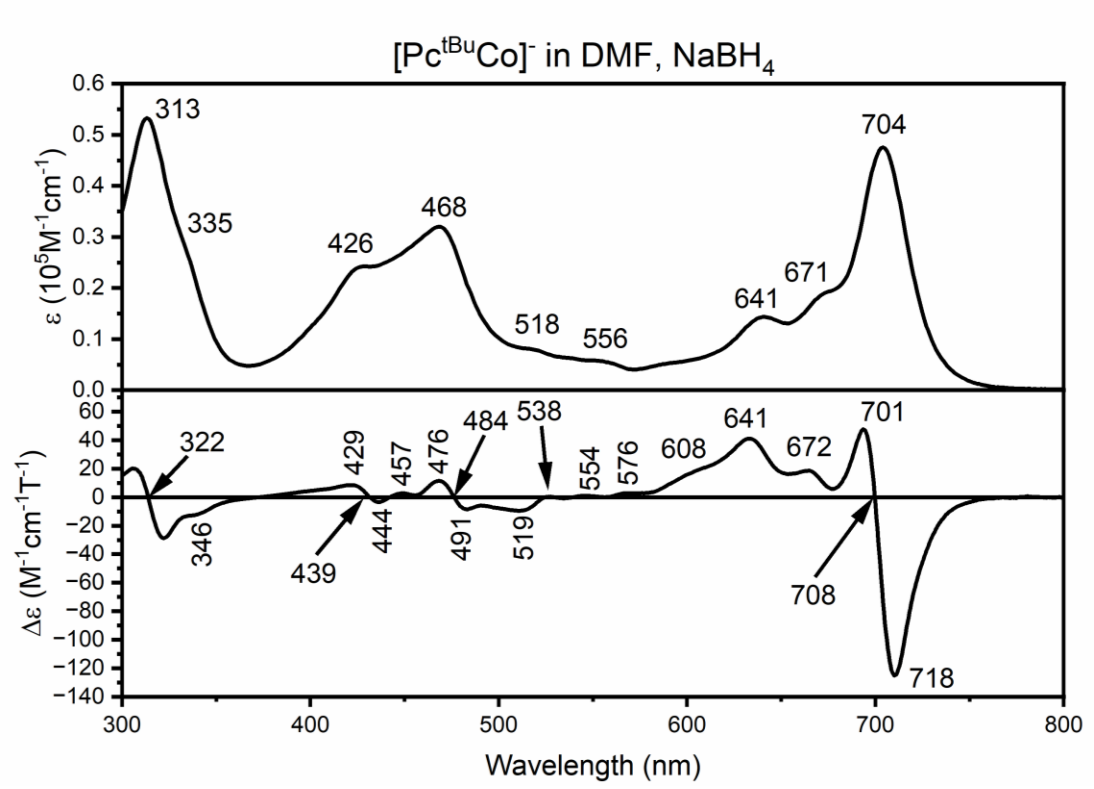

Figure S2. UV-Vis and MCD spectra of $[Pc^{tBu}(2-)Co^{I}]^{-}$ in DMF.

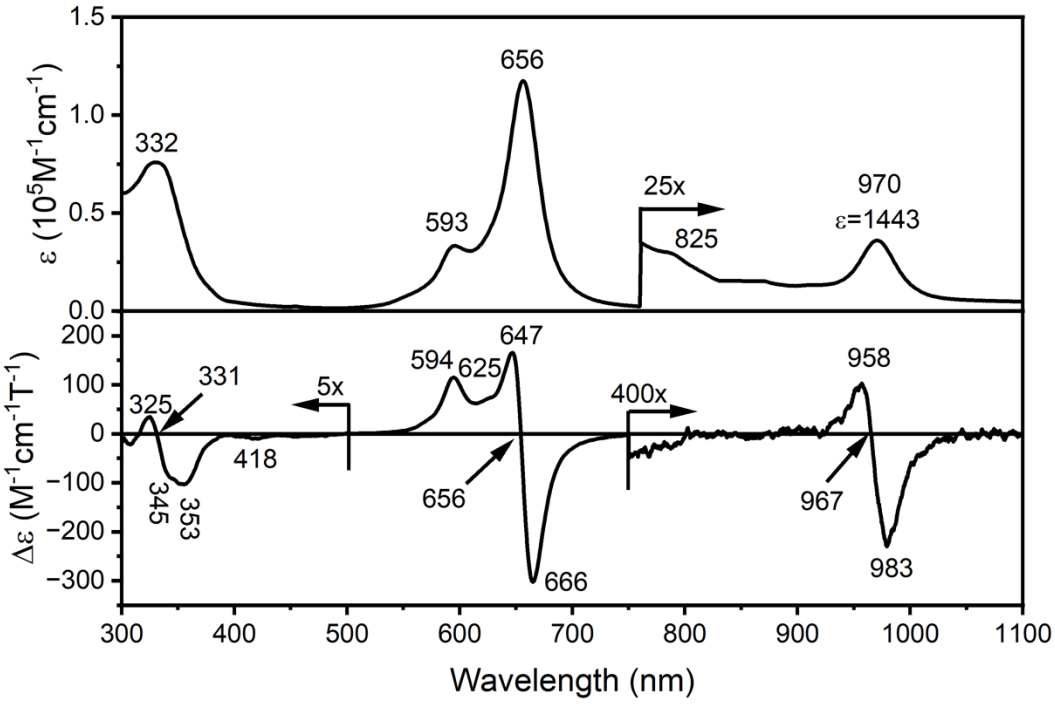

Figure S3. UV-Vis and MCD spectra of Pc(2-)$Co^{II}Py_2$ in pyridine.

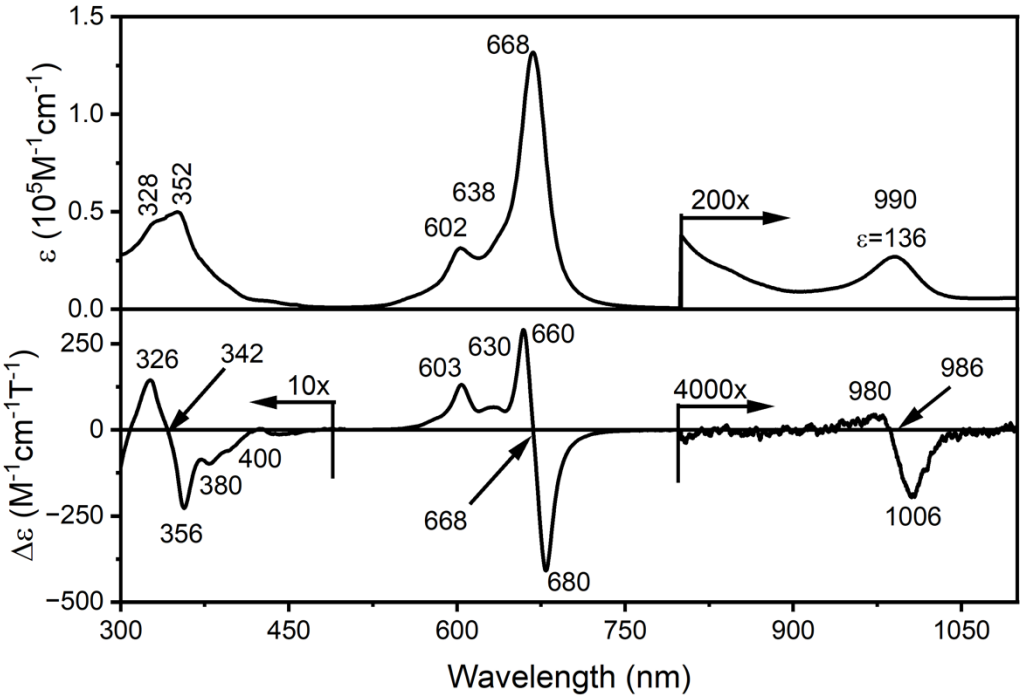

Figure S4. UV-Vis and MCD spectra of Pc(2-)Co^{II}(*n*$BuNH_2$)$_2$ in DMF/*n*$BuNH_2$ (97.5/2.5% v/v).

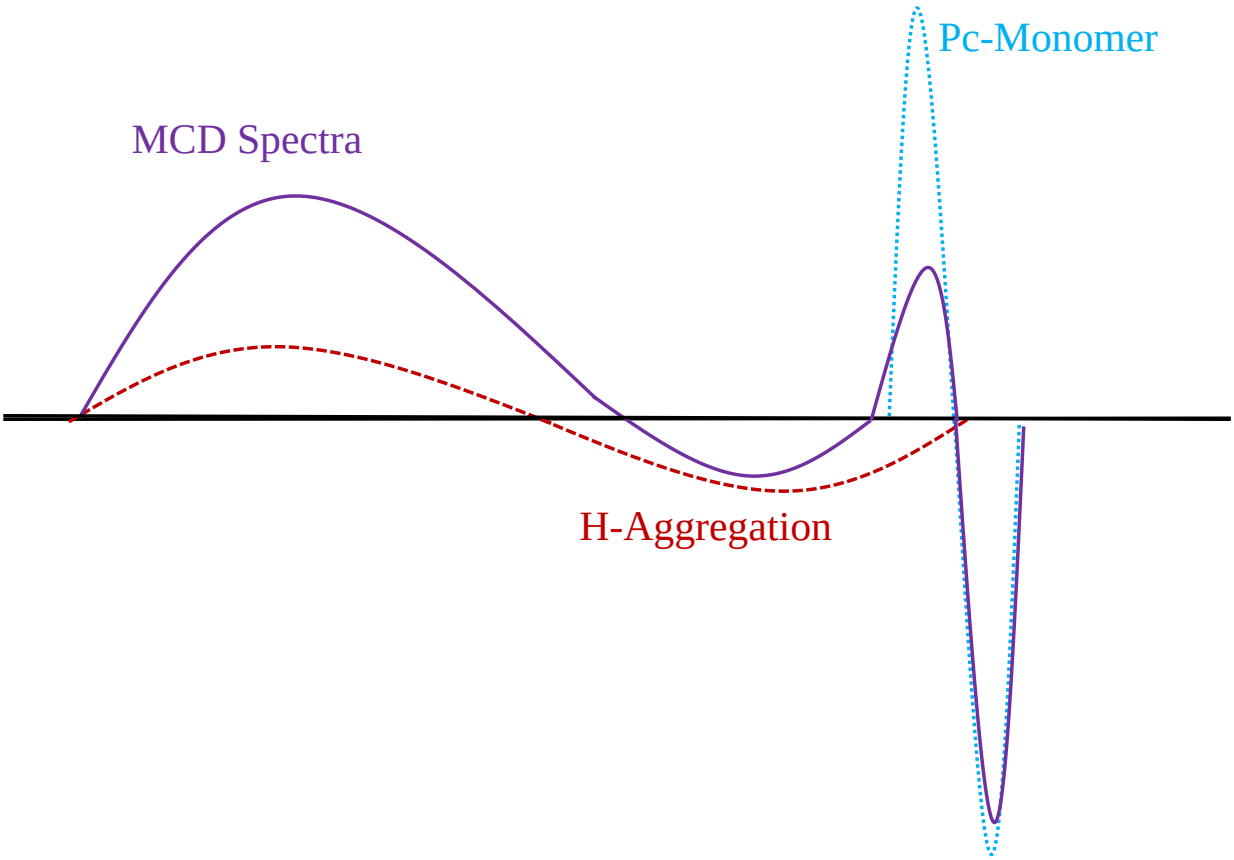

Figure S5. Possible overlap between MCD spectra of $Q_{0\text{-}0}$-band of monomeric $[Pc(2\text{-})Co^{I}]^{-}$ (blue) and its H-aggregate (red). The grey oval is the area of destructive interference between the H-aggregate's negative component and the monomer's positive component.

$[PcCo(Br)_2]^-$

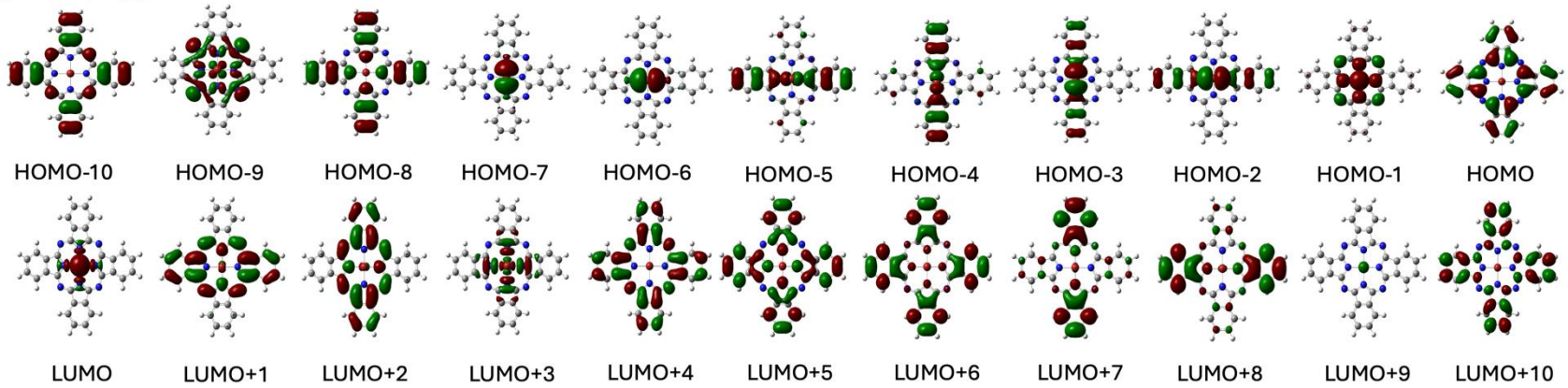

Figure S6. DFT-predicted frontier orbitals of $[Pc(2-)Co^{III}Br_2]^-$.

$[PcCo(CN)_2]^-$

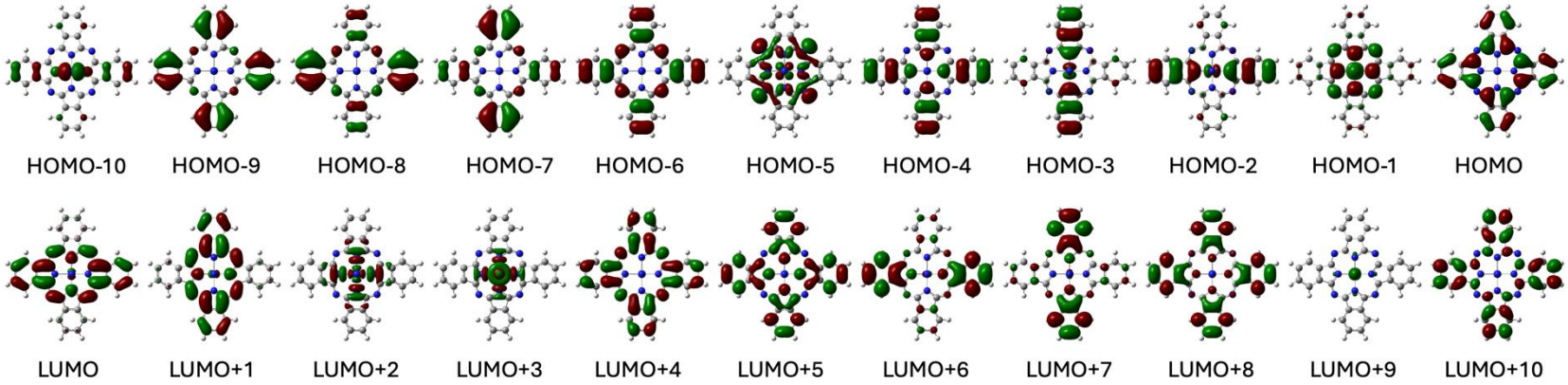

Figure S7. DFT-predicted frontier orbitals of $[Pc(2-)Co^{III}(CN)_2]^-$.

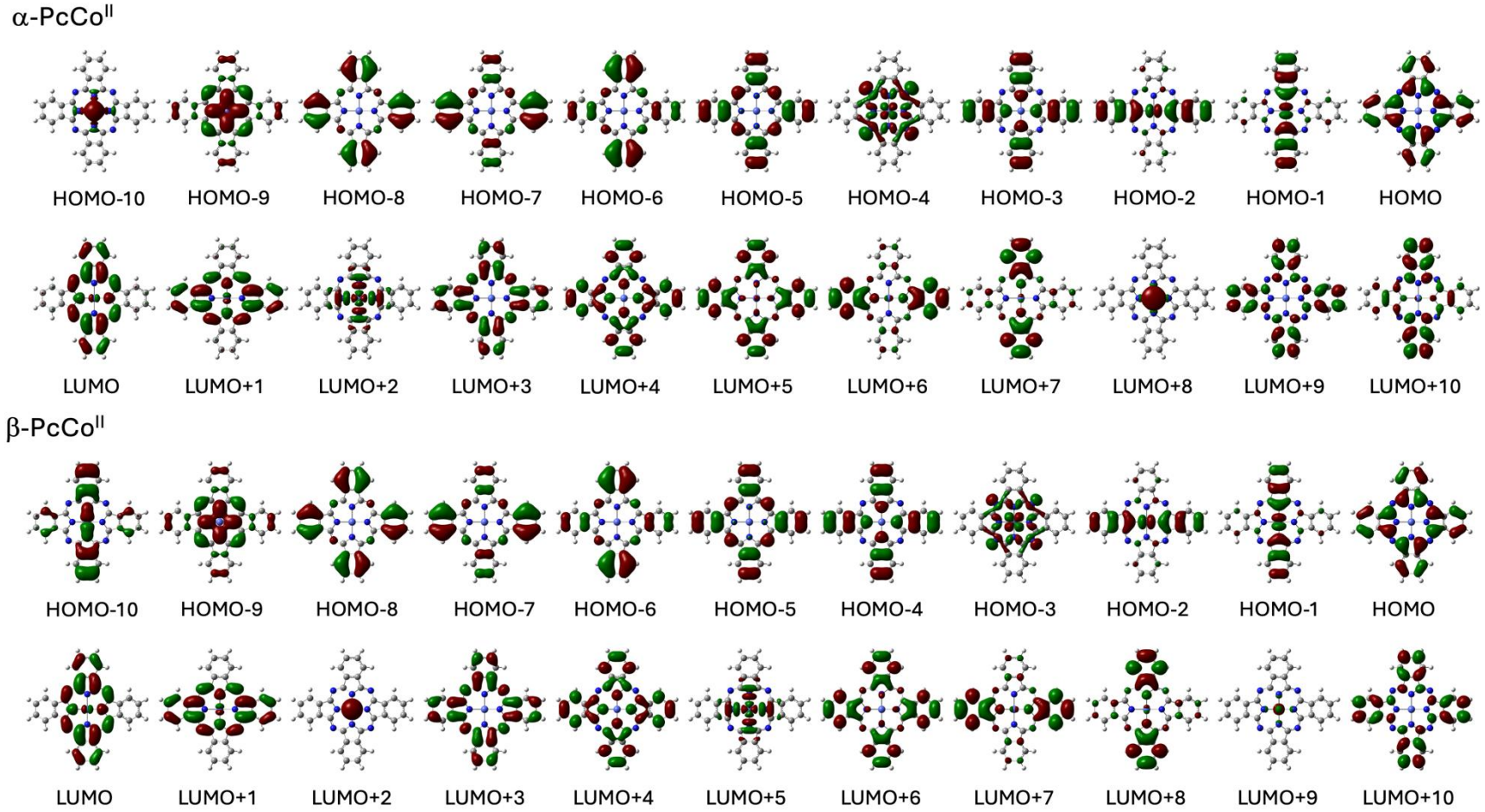

Figure S8. α- and β-sets of the DFT-predicted frontier orbitals of Pc(2-)Co^{II}.

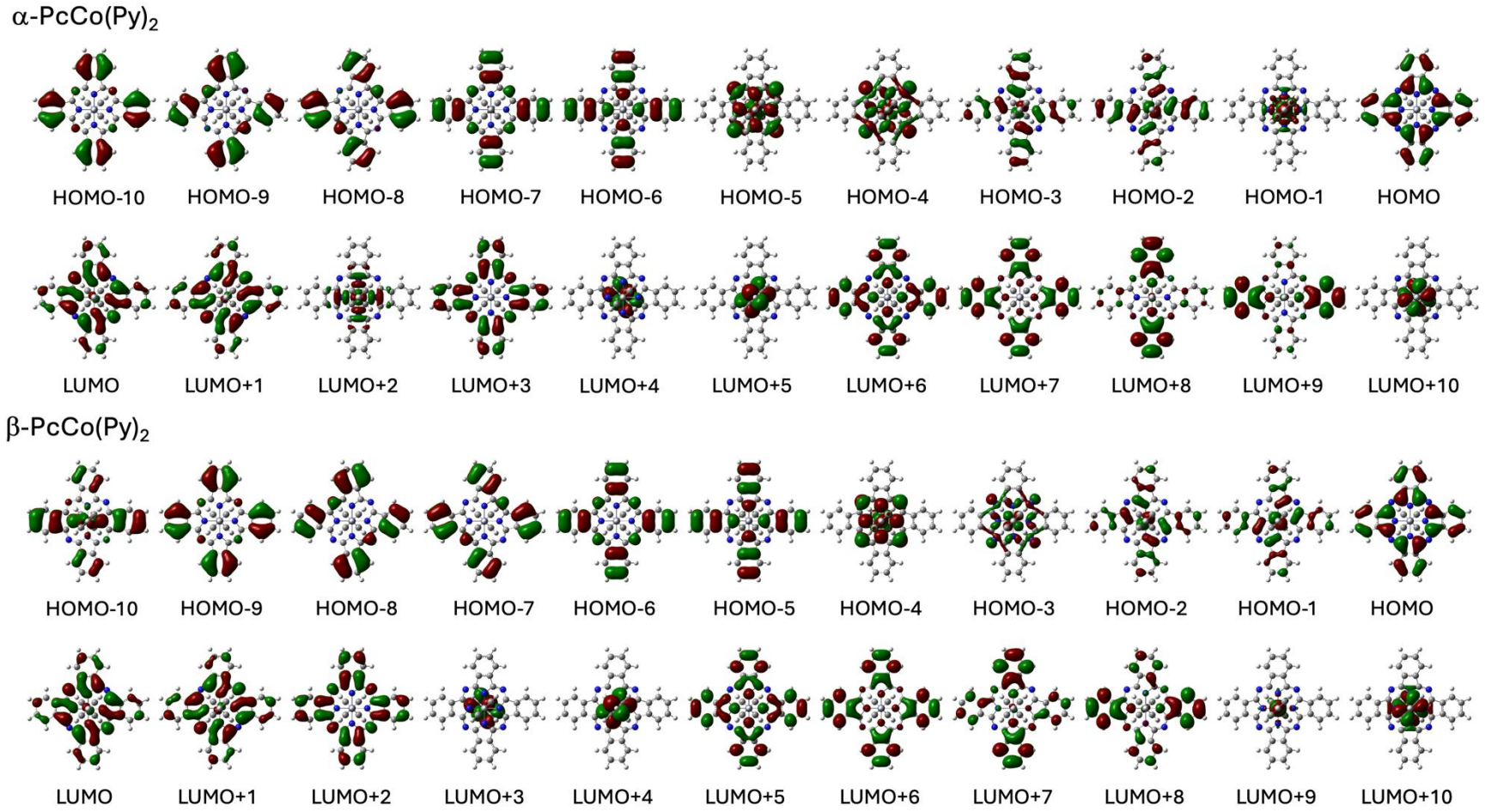

Figure S9. α- and β-sets of the DFT-predicted frontier orbitals of Pc(2-)$Co^{II}Py_2$.

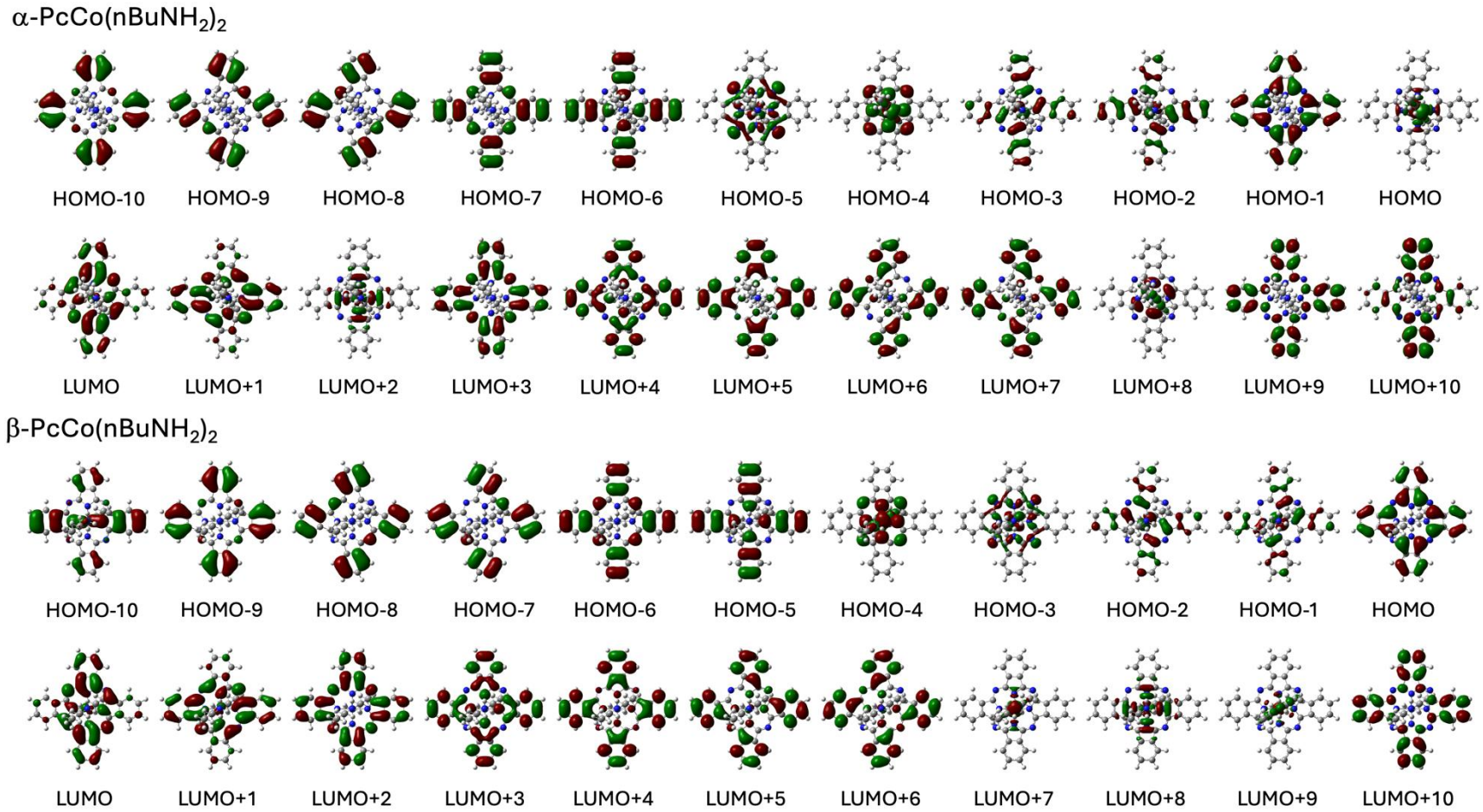

Figure S10. α- and β-sets of the DFT-predicted frontier orbitals of Pc(2-)$Co^{II}(nBuNH_2)_2$.

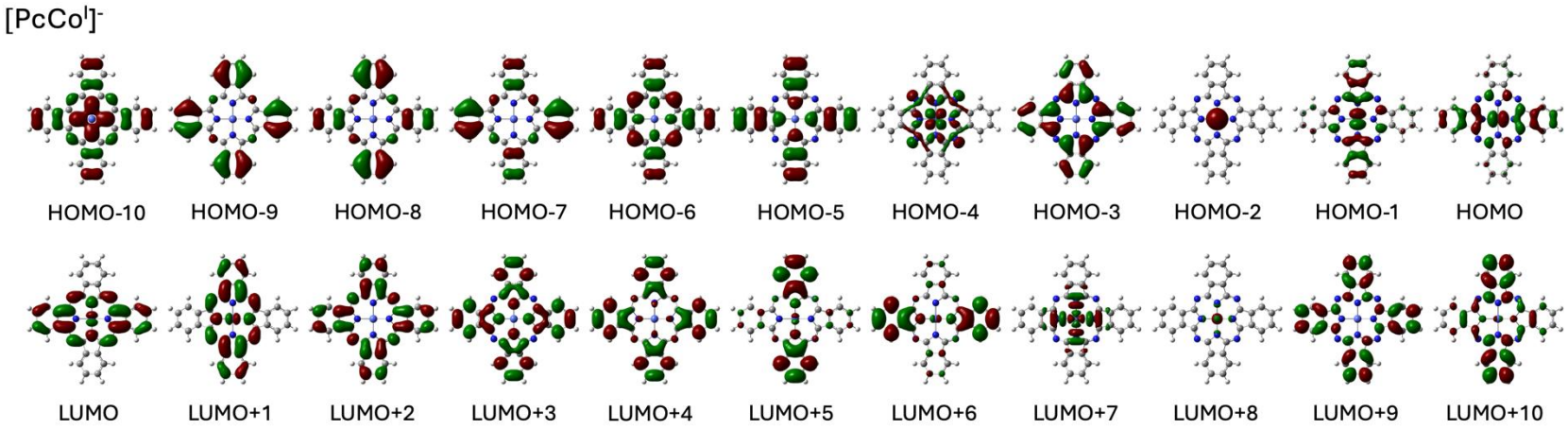

Figure S11. DFT-predicted frontier orbitals of [Pc(2-)Co^{I}]$^{-}$.

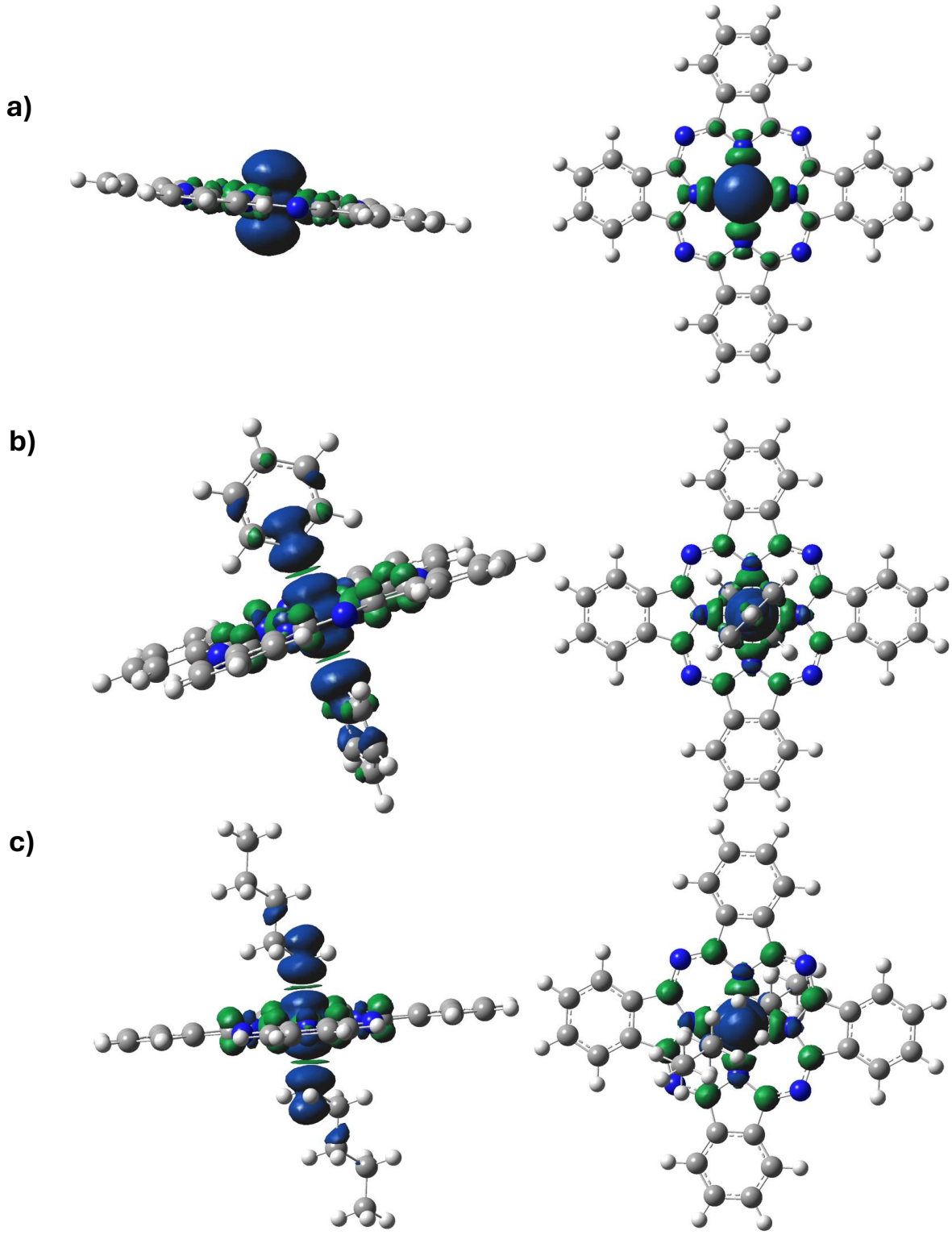

Figure S12. DFT-predicted total spin densities in Pc(2-)Co^{II} (a), Pc(2-)$Co^{II}Py_2$ (b), and Pc(2-)Co^{II}(*n*$BuNH_2)_2$ (c).

Table S1. TDDFT predicted energies, oscillator strengths, and contributions for the major excited states of cobalt(III) complexes.[a]

Excited State	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Band Assignment	Contributions[b]
				$[Pc(2-)Co^{III}(Br)_2]^-$	
4, 5	15100	662	0.8010	Q	88.3% HOMO → L+1; 88.3% HOMO → L+2
9	20954	477	0.1570	LMCT	95.6% H-1 → LUMO
11, 12	22454	445	0.0462	LMCT	49.8% H-7 → LUMO, 40.2% H-1 → L+2; 49.8% H-6 → LUMO, 40.2% H-1 → L+1
18, 19	23030	434	0.1020	B1/LMCT	29.8% H-1 → L+1, 26.7% H-6 → LUMO, 20.5% H-1 → L+2, 18.4% H-7 → LUMO; 29.8% H-1 → L+2, 26.7% H-7 → LUMO, 20.5% H-1 → L+1, 18.4% H-6 → LUMO
30	25356	394	0.0211	ILCT	46.0% H-6 → L+1, 46.0% H-7 → L+2
31	25762	388	0.0123	LMCT	93.3% H-10 → LUMO
35, 36	26706	374	0.0098	B2	91.5% H-8 → L+2
42, 43	28065	356	0.8220	$\pi \rightarrow \pi^*$	73.2% H-10 → L+1, 12.4% H-10 → L+2; 73.2% H-10 → L+2, 12.4% H-10 → L+1
45, 46	28664	349	0.0032	B3	74.9% H-13 → L+1, 12.1% HOMO → L+8; 74.9% H-13 → L+2, 12.1% HOMO → L+7
51, 52	29416	340	0.0379	L	79.3% HOMO → L+7; 79.3% HOMO → L+8
56, 57	30432	329	0.0201	LMCT	51.4% H-15 → LUMO, 47.3% H-16 → LUMO; 51.4% H-16 → LUMO, 47.3% H-15 → LUMO
61, 62	31685	316	0.0479	LMCT	95.5% H-6 → L+3; 95.5% H-7 → L+3
66	32032	312	0.0034	$\pi \rightarrow \pi^*$	49.3% H-15 → L+2, 49.3% H-16 → L+1

67, 68	33008	303	0.0373	π → π*	52.1% H-14 → L+1, 40.3% H-14 → L+2; 52.1% H-14 → L+2, 40.3% H-14 → L+1
80, 81	35646	281	0.0310	MLCT1	40.3% H-5 → L+4, 36.6% H-4 → L+4, 10.5% H-2 → L+4; 40.3% H-4 → L+4, 36.6% H-5 → L+4, 10.5% H-3 → L+4
86	36119	277	0.7680	LMCT	95.5% H-20 → LUMO
87, 88	36340	275	0.1060	ILCT	51.2% H-2 → L+5, 30.7% H-20 → L+1, 15.7% H-5 → L+5; 51.2% H-3 → L+5, 30.7% H-20 → L+2, 15.7% H-4 → L+5
89, 90	36387	275	0.2580	π → π*	45.7% H-20 → L+1, 16.5% H-5 → L+5, 13.4% H-20 → L+2, 11.3% H-2 → L+5, 4.82% H-4 → L+5, 3.32% H-3 → L+5, 45.7% H-20 → L+2, 16.5% H-4 → L+5, 13.4% H-20 → L+1, 11.3% H-3 → L+5, 4.82% H-5 → L+5, 3.32% H-2 → L+5
92, 93	37132	269	0.3030	MLCT2	58.4% H-4 → L+5, 31.6% H-3 → L+5, 2.62% HOMO → L+11, 58.4% H-5 → L+5, 31.6% H-2 → L+5, 2.62% HOMO → L+12
100	38348	261	0.0021	π → π*	98.5% H-9 → L+4
				$[Pc(2-)Co^{III}(CN)_2]^-$	
1, 2	14899	671	0.788	Q	97.4% HOMO → LUMO; 97.4% HOMO → L+1
4, 5	22553	443	0.1644	B_1	93.8% H-1 → L+1; 93.8% H-1 → LUMO
17, 18	26352	379	0.0104	B2	96.5% H-4 → L+1; 96.5% H-4 → LUMO
22, 23	27682	361	0.8872	π–π*	83.6% H-6 → L+1, 13.4% H-9 → LUMO; 83.6% H-6 → LUMO, 13.4% H-9 → L+1
25, 26	28283	354	0.0012	B3	81.3% H-9 → LUMO, 11.2% H-6 → L+1; 81.3% H-9 → L+1, 11.2% H-6 → LUMO
35, 36	29540	339	0.0406	L	94.2% HOMO → L+7; 94.2% HOMO → L+6
41	31369	319	0.0017	π–π*	48.2% H-13 → L+1, 48.2% H-14 → LUMO

42	32161	311	0.0228	LMCT	70.1% H-4 → L+2, 28.2% H-1 → L+3
43	32222	310	0.059	LMCT	66.2% H-1 → L+3, 29.4% H-4 → L+2
44, 45	32674	306	0.033	π–π*	95.0% H-12 → LUMO, 95.0% H-12 → L+1
56	34465	290	0.0084	π–π*	48.7% H-15 → L+1, 48.7% H-16 → LUMO
60, 61	35851	279	0.0352	MLCT1	97.8% H-3 → L+4; 97.8% H-2 → L+4
65, 66	36920	271	0.0243	π–π*	85.0% H-18 → L+1, 12.6% H-13 → L+2; 85.0% H-18 → LUMO, 12.6% H-14 → L+2
67, 68	37260	268	0.5824	MLCT2	83.0% H-2 → L+5, 10.6% H-13 → L+2; 83.0% H-3 → L+5, 10.6% H-14 → L+2
72	37671	265	0.0012	π–π*	99.5% H-6 → L+3
76,77	37892	264	0.1257	LMCT	67.7% H-13 → L+2, 10.1% H-2 → L+5; 67.7% H-14 → L+2, 10.1% H-3 → L+5
81,82	38487	260	0.0676	π–π*	88.9% H-1 → L+6; 88.9% H-1 → L+7
83	38665	259	0.0021	MLCT	98.4% H-5 → L+4
91,92	39781	251	0.0318	MLCT3	52.4% H-2 → L+8, 20.1% H-8 → L+4, 17.1% HOMO → L+12; 52.4% H-3 → L+8, 20.1% H-7 → L+4, 17.1% HOMO → L+11
96,97	39991	250	0.0449	LMCT	93.2% H-15 → L+2; 93.2% H-16 → L+2
100	40363	248	0.0244	π–π*	50.2% HOMO → L+12, 44.3% H-8 → L+4

[a] Only major excited states with relatively high oscillator strengths are shown. [b] Only contributions with more than 10% are shown.

Table S2. TDDFT predicted energies, oscillator strengths, and contributions for the excited states of cobalt(II) complexes.[a]

Excited State	Energy (cm^{-1})	Wavelength (nm)	$<S^2>$	Osc. Strength	Band Assignment	Contributions[b]
					Pc(2-)Co^{II}	
3, 4	9967	1003	2.756	0.0004	*t-m*	52.2% HOMO(α) → L+1(α), 47.8% HOMO(β) → L+1(β); 52.2% HOMO(α) → LUMO(α), 47.8% HOMO(β) → LUMO(β)
6, 7	15116	662	0.759	0.8380	Q	51.6% HOMO(β) → L+1(β), 47.2% HOMO(α) → L+1(α); 51.6% HOMO(β) → LUMO(β), 47.2% HOMO(α) → LUMO(α)
37, 38	26372	379	0.775	0.0203	B2	54.1% H-4(β) → L+1(β), 42.5% H-3(α) → L+1(α); 54.1% H-4(β) → LUMO(β), 42.5% H-3(α) → LUMO(α)
48, 49	27285	367	2.746	0.0026	B3	31.7% H-8(α) → L+1(α), 23.9% H-8(β) → L+1(β), 16.2% HOMO(α) → L+7(α), 14.1% HOMO(β) → L+8(β); 31.7% H-8(α) → LUMO(α), 23.9% H-8(β) → LUMO(β), 16.2% HOMO(α) → L+6(α), 14.1% HOMO(β) → L+7(β)
50, 51	27787	360	0.768	0.6320	B1	46.7% H-5(β) → LUMO(β), 39.9% H-5(α) → LUMO(α); 46.7% H-5(β) → L+1(β), 39.9% H-5(α) → L+1(α)

55, 56	28318	353	0.763	0.0691	B3	47.9% H-8(β) → L+1(β), 39.4% H-8(α) → L+1(α); 47.9% H-8(β) → LUMO(β), 39.4% H-8(α) → LUMO(α)
67, 68	29616	338	0.762	0.0454	L	47.7% HOMO(β) → L+8(β), 46.7% HOMO(α) → L+7(α); 47.7% HOMO(β) → L+7(β), 46.7% HOMO(α) → L+6(α)
73, 74	30309	330	0.790	0.2970	π–π*	40.8% H-9(α) → LUMO(α), 36.0% H-9(β) → LUMO(β); 40.8% H-9(α) → L+1(α), 36.0% H-9(β) → L+1(β)
75	30405	329	792	0.0024	LMCT	65.6% H-5(β) → L+2(β), 34.4% H-9(β) → L+2(β)
76, 77	30731	325	2.745	0.0034	π–π*	43.1% H-13(α) → L+1(α), 41.6% H-13(β) → L+1(β); 43.1% H-13(α) → LUMO(α), 41.6% H-13(β) → LUMO(β)
80, 81	30956	323	2.106	0.0531	MLCT1	85.6% H-2(β) → L+3(β); 85.6% H-1(β) → L+3(β)
89	31620	316	0.793	0.0037	LMCT	65.3% H-9(β) → L+2(β), 34.4% H-5(β) → L+2(β)
91, 92	31682	316	2.345	0.1370	MLCT2	78.9% H-2(β) → L+4(β); 78.9% H-1(β) → L+4(β)
93	31735	315	0.762	0.0042	π–π*	24.6% H-14(β) → L+1(β), 24.6% H-15(β) → LUMO(β), 24.2% H-14(α) → L+1(α), 24.2% H-15(α) → LUMO(α)
98, 99	32961	303	1.310	0.0115	MLCT + π–π*	46.1% H-2(α) → L+3(α), 18.4% H-13(α) → LUMO(α), 12.4% H-13(β) → LUMO(β);

100, 101	33088	302	1.033	0.2160	π–π* + MLCT	46.1% H-1(α) → L+3(α), 18.4% H-13(α) → L+1(α), 12.4% H-13(β) → L+1(β) 32.7% H-13(β) → L+1(β), 25.1% H-1(α) → L+3(α), 23.0% H-13(α) → L+1(α); 32.7% H-13(β) → L(β), 25.1% H-2(α) → L+3(α), 23.0% H-13(α) → L(α)
					Pc(2-)$Co^{II}Py_2$	
1, 2	10443	958	2.755	0.0013	*t-m*	53.9% HOMO(α) → LUMO(α), 45.9% HOMO(β) → LUMO(β); 53.9% HOMO(α) → L+1(α), 45.9% HOMO(β) → L+1(β)
13, 14	15405	649	0.765	0.7900	Q	53.1% HOMO(β) → LUMO(β), 45.0% HOMO(α) → LUMO(α); 53.1% HOMO(β) → L+1(β), 45.0% HOMO(α) → L+1(α)
39, 40	25727	389	0.839	0.0094	MLCT (Pc, Py)	25.9% H-2(α) → L+2(α), 25.9% H-1(β) → L+12(β), 16.3% H-1(β) → L+10(β); 25.9% H-3(α) → L+2(α), 25.9% H-2(β) → L+12(β), 16.3% H-2(β) → L+10(β)
42, 43	25943	385	1.115	0.0901	B1 + B3	25.0% H-6(α) → L+1(α), 22.4% H-5(α) → LUMO(α), 18.6% H-4(β) → LUMO(β), 14.6% HOMO(β) → L+3(β); 25.0% H-6(α) → LUMO(α), 22.4% H-5(α) → L+1(α), 18.6% H-4(β) → L+1(β), 14.6% HOMO(β) → L+4(β)
45, 46	26068	384	1.314	0.0542	ILCT	58.3% HOMO(β) → L+3(β), 11.2% H-5(β) → L+1(β);

						58.3% HOMO(β) → L+4(β), 11.2% H-5(β) → LUMO(β)
55, 56	27042	370	0.772	0.0218	B2	37.3% H-5(β) → LUMO(β), 29.7% H-6(α) → LUMO(α), 10.9% H-4(β) → L+1(β), 10.1% H-5(α) → L+1(α); 37.3% H-5(β) → L+1(β), 29.7% H-6(α) → L+1(α), 10.9% H-4(β) → LUMO(β), 10.1% H-5(α) → LUMO(α)
62, 63	27923	358	1.879	0.0192	MLCT1	87.4% H-1(β) → L+2(β); 87.4% H-2(β) → L+2(β)
67, 68	28367	353	0.927	0.5490	π–π*	39.4% H-6(β) → LUMO(β), 29.4% H-7(α) → LUMO(α); 39.4% H-6(β) → L+1(β), 29.4% H-7(α) → L+1(α)
69	28422	352	1.974	0.0196	MLCT (Py)	44.2% H-1(β) → L+4(β), 44.2% H-2(β) → L+3(β)
78, 79	28992	345	1.84	0.3070	MLCT2	67.2% H-1(β) → L+5(β); 67.2% H-2(β) → L+5(β)
81, 82	29025	345	0.899	0.0361	B3	37.3% H-9(β) → L+1(β), 21.6% H-10(α) → L+1(α), 11.2% HOMO(β) → L+7(β); 37.3% H-9(β) → LUMO(β), 21.6% H-10(α) → LUMO(α), 11.2% HOMO(β) → L+8(β)
85, 86	29480	339	2.247	0.0300	π–π*	78.6% H-14(β) → L+1(β), 10.2% H-18(α) → L+1(α); 78.6% H-14(β) → LUMO(β), 10.2% H-18(α) → LUMO(α)
88, 89	29555	338	0.904	0.0279	L	39.4% HOMO(β) → L+7(β), 23.7% HOMO(α) → L+8(α);

						39.4% HOMO(β) → L+8(β), 23.7% HOMO(α) → L+9(α)
92	29771	336	0.881	0.0038	MLCT	85.8% H-1(α) → L+7(α)
					$Pc(2-)Co^{II}(n BuNH_2)_2$	
3, 4	10549	948	2.754	0.0017	*t-m*	53.8% H-1(α) → LUMO(α), 45.2% HOMO(β) → LUMO(β);
	10572	946	2.755	0.0017		53.8% H-1(α) → L+1(α), 45.1% HOMO(β) → L+1(β)
13, 14	15455	647	0.767	0.7920	Q	37.8% HOMO(β) → LUMO(β), 33.1% H-1(α) → LUMO(α), 15.7% HOMO(β) → L+1(β), 11.3% H-1(α) → L+1(α);
	15471	646	0.767	0.7910		37.8% HOMO(β) → L+1(β), 33.1% H-1(α) → L+1(α), 15.7% HOMO(β) → LUMO(β), 11.3% H-1(α) → LUMO(α)
23, 24	21274	470	2.733	0.0014	B1	51.4% H-4(β) → L+1(β), 33.3% H-4(α) → L+1(α);
	21288	470	2.732	0.0015		51.6% H-4(β) → LUMO(β), 33.1% H-4(α) → LUMO(α)
35, 36	24182	414	0.811	0.1490	B1	55.1% H-4(α) → LUMO(α), 35.9% H-4(β) → LUMO(β);
	24232	413	0.808	0.1450		54.8% H-4(α) → L+1(α), 36.2% H-4(β) → L+1(β)
52, 53	26965	371	1.292	0.0124	B2 + MLCT1	30.8% H-1(β) → L+2(β), 27.2% H-5(β) → L+1(β), 21.5% H-6(α) → L+1(α);
	26987	371	1.255	0.0131		

						30.7% H-5(β) → LUMO(β), 23.7% H-6(α) → LUMO(α), 20.0% H-2(β) → L+2(β), 12.7% H-1(β) → L+2(β)
54, 55	27082	369	1.320	0.0310	B2 + MLCT1	40.0% H-1(β) → L+2(β), 27.1% H-5(β) → L+1(β), 17.4% H-6(α) → L+1(α);
	27103	369	1.562	0.0394		58.4% H-2(β) → L+2(β), 18.3% H-5(β) → LUMO(β), 11.6% H-6(α) → LUMO(α)
65, 67	28680	349	0.950	0.7950	π–π*	38.3% H-7(α) → LUMO(α), 36.4% H-6(β) → LUMO(β);
	28699	348	0.931	0.8000		38.6% H-7(α) → L+1(α), 37.3% H-6(β) → L+1(β)
78, 79	29536	339	0.811	0.0247	B3	25.6% H-9(β) → LUMO(β), 20.7% H-10(α) → LUMO(α);
	29543	338	0.813	0.0250		25.9% H-9(β) → L+1(β), 20.9% H-10(α) → L+1(α)
85, 86	29994	333	1.667	0.0851	MLCT1	88.1% H-2(α) → L+3(α);
	30030	333	1.667	0.0860		88.0% H-3(α) → L+3(α)
99, 100	31223	320	1.684	0.4502	MLCT2	63.1% H-2(α)→ L+4(α), 16.8% H-2(β)→ L+4(β);
	31239	320	1.718	0.4309		61.1% H-3(α)→ L+4(α), 13.7% H-1(β)→ L+4(β)

[a)] Only major excited states with relatively high oscillator strengths are shown. [b)] Only contributions with more than 10% are shown.

Table S3. TDDFT predicted energies, oscillator strengths, and contributions for the excited states of $[Pc(2-)Co^{I}]^{-}$.[a]

Excited State	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Band Assignment	Contributions[b]
6, 7	16004	625	0.6870	Q	97.8% H-3 → L+1; 97.8% H-3 → LUMO
12, 13	22880	437	0.0655	MLCT1	90.9% H-1 → L+2; 90.9% HOMO → L+2
18, 19	23825	420	0.4970	MLCT2	89.1% HOMO → L+3; 89.1% H-1 → L+3
21	25253	396	0.0121	MLCT	99.5% H-2 → L+4
22, 23	25581	391	0.2780	MLCT3	97.7% HOMO → L+4; 97.7% H-1 → L+4
33, 34	28116	356	0.0091	B2	86.5% H-5 → L+1; 86.5% H-5 → LUMO
35, 36	28697	348	0.0702	L	89.0% H-3 → L+5; 89.0% H-3 → L+6
37, 38	29972	334	0.7640	B1	76.8% H-6 → L+1, 13.0% H-10 → L+1; 76.8% H-6 → LUMO, 13.0% H-10 → LUMO
45, 46	30815	325	0.2750	B3	75.0% H-9 → LUMO, 22.6% H-10 → L+1; 75.0% H-9 → L+1, 22.6% H-10 → LUMO
49	31188	321	0.0011	MLCT	95.1% H-4 → L+2
50, 51	31350	319	0.2500	π–π*	59.4% H-10 → L+1, 17.6% H-9 → LUMO, 14.0% H-6 → L+1; 59.4% H-10 → LUMO, 17.6% H-9 → L+1, 14.0% H-6 → LUMO
59	32915	304	0.0033	π–π*	47.4% H-14 → L+1, 47.4% H-15 → LUMO

63, 64	34853	287	0.0543	π–π*	93.2% H-16 → LUMO; 93.2% H-16 → L+1
70, 71	37289	268	0.0029	π–π*	96.7% H-1 → L+9; 96.7% HOMO → L+9
80	39420	254	0.2450	$d_{z2} \rightarrow 4p_z$	99.0% H-2 → L+13
83, 84	39741	252	0.0076	π–π*	78.6% H-3 → L+11; 78.6% H-3 → L+10
88, 89	40644	246	0.0098	π–π*	71.5% H-8 → L+2; 71.5% H-7 → L+2
94, 95	41522	241	0.0048	π–π*	73.9% HOMO → L+13, 19.2% HOMO → L+12; 73.9% H-1 → L+13, 19.2% H-1 → L+12
96, 97	41611	240	0.0344	π–π*	83.9% H-12 → L+2; 83.9% H-11 → L+2
98, 99	41716	240	0.4100	MLCT	62.4% HOMO → L+12, 17.0% HOMO → L+13; 62.4% H-1 → L+12, 17.0% H-1 → L+13

[a)] Only major excited states with relatively high oscillator strengths are shown. [b)] Only contributions with more than 10% are shown.

The DFT-predicted EPR parameters for cobalt(II) phthalocyanines are shown in **Tables 1** and S4. TPSSh, BP86, TPSS, wB97XD, and CAM-B3LYP exchange-correlation functionals give correct trends in $g_{\perp}$ and $A_{\perp}$ values. Although errors in DFT-predicted *g*-values are relatively small (except in some cases of M06 and MN12L), it seems that standard DFT protocols have trouble predicting the trends in $g_{\parallel}$ values going from Pc(2-)Co^{II} to Pc(2)$Co^{II}Py_2$ and Pc(2-)$Co^{II}(n BuNH_2)^2$. When using the same exchange-correlation functional, it seems that a large basis set dependence is present for hyperfine values, while the influence of the basis set on the predicted *g*-values is smaller (Table S4). Overall, it seems that we need to develop a different computational protocol to accurately predict both *g*- and *A*-values observed in the EPR spectra of cobalt(II) phthalocyanines.

Table S4. DFT-predicted EPR spectra of cobalt(II) systems.

Compound, ECF	Basis set	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$, cm^{-1}	$A_{\perp}$, cm^{-1}
Pc(2-)Co^{II}					
Experiment		1.945	2.677	150	190
TPSSh	Wf/6-311G(d)[a]	2.004	2.314	195	31
BP86	Wf/6-311G(d)[a]	1.999	2.395	225	55
TPSS	Wf/6-311G(d)[a]	2.002	2.286	215	51
wB97XD	Wf/6-311G(d)[a]	2.008	2.593	178	1
CAM-B3LYP	Wf/6-311G(d)[a]	2.007	2.567	188	14
LC-wHPBE	Wf/6-311G(d)[a]	2.004	2.447	195	24
wB97[b]	Wf/6-311G(d)[a]	2.004	2.836, 2.763	178	1, 2
MN12L	Wf/6-311G(d)[a]	2.012	2.278	14	169
M06	Wf/6-311G(d)[a]	1.997	0.855	283	98
TPSSh	def2-TZVP	2.004	2.307	303	127
TPSSh	def2-TZVPP	2.004	2.302	305	128
TPSSh	DGDZVP	2.010	2.310	280	100
TPSSh	cc-pVTZ	2.004	2.306	307	129
Pc(2-)$Co^{II}Py_2$[c]					
Experiment		2.013	2.250	85	

TPSSh	Wf/6-311G(d)[a]	1.994	2.155	113	61
BP86	Wf/6-311G(d)[a]	1.987	2.140	115	60
TPSS	Wf/6-311G(d)[a]	1.992	2.124	119	54
wB97XD	Wf/6-311G(d)[a]	2.000	2.253	107	84
CAM-B3LYP	Wf/6-311G(d)[a]	2.000	2.236	117	72
LC-wHPBE	Wf/6-311G(d)[a]	1.998	2.184	122	63
wB97	Wf/6-311G(d)[a]	1.996	2.228	109	78
MN12L	Wf/6-311G(d)[a]	2.009	2.132	228	60
M06	Wf/6-311G(d)[a]	1.982	2.546	206	11
Pc(2-)Co^{II}(nBuNH$_2$)$_2$[d]					
Experiment		2.01	2.18		53
TPSSh	Wf/6-311G(d)[a]	1.991	2.136, 2.135	102	76, 76
BP86	Wf/6-311G(d)[a]	1.983	2.110, 2.109	101	73, 72
TPSS	Wf/6-311G(d)[a]	1.989	2.100, 2.099	106	66, 65
wB97XD	Wf/6-311G(d)[a]	1.999	2.221, 2.222	93	98, 100
CAM-B3LYP	Wf/6-311G(d)[a]	1.999	2.209, 2.208	103	86, 85
LC-wHPBE	Wf/6-311G(d)[a]	1.998	2.182, 2.187	109	78, 75
wB97	Wf/6-311G(d)[a]	1.998	2.206, 2.201	96	90, 92
MN12L	Wf/6-311G(d)[a]	2.008	2.106, 2.105	63	230, 229
M06	Wf/6-311G(d)[a]	1.980	2.484, 2.483	196	1, 0

[a)] Wachter's full-electron basis set for cobalt and 6-311G(d) basis set for all other atoms. [b)] Wave function converged to Abelian symmetry (D_{2h}). [c)] D_{2d} point group was used for DFT calculations. [d)] Since this complex has C_i point group in DFT calculations, the DFT-predicted $g_\perp$ and $A_\perp$ split into two slightly non-equivalent components.

Optimized coordinates for $[Pc(2-)Co^{III}Br_2]^-$:

N	-1.3741	-1.3741	0.
N	1.3741	-1.3741	0.
N	1.3741	1.3741	0.
C	-1.16	2.7386	0.
C	-3.43955	2.44196	0.
C	-2.7386	1.16	0.
C	-2.7386	-1.16	0.
C	-3.43955	-2.44196	0.
C	-2.44196	-3.43955	0.
C	-1.16	-2.7386	0.
C	1.16	-2.7386	0.
C	2.44196	-3.43955	0.
C	3.43955	-2.44196	0.
C	2.7386	-1.16	0.
C	2.7386	1.16	0.
C	3.43955	2.44196	0.
C	2.44196	3.43955	0.
C	1.16	2.7386	0.
C	-2.44196	3.43955	0.
N	-1.3741	1.3741	0.
N	0.	3.38494	0.
N	-3.38494	0.	0.
N	0.	-3.38494	0.
N	3.38494	0.	0.
C	4.80023	2.77563	0.
C	5.13559	4.13651	0.
H	6.1886	4.43308	0.
C	4.13651	5.13559	0.
H	4.43308	6.1886	0.
C	2.77563	4.80023	0.
H	5.57146	2.00065	0.
H	2.00065	5.57146	0.
C	-2.77563	4.80023	0.
C	-4.13651	5.13559	0.
H	-4.43308	6.1886	0.
C	-4.80023	2.77563	0.
C	-5.13559	4.13651	0.
H	-6.1886	4.43308	0.
C	-4.80023	-2.77563	0.
C	-5.13559	-4.13651	0.
H	-6.1886	-4.43308	0.
C	-4.13651	-5.13559	0.
H	-4.43308	-6.1886	0.
C	-2.77563	-4.80023	0.

H	-2.00065	-5.57146	0.
H	-5.57146	-2.00065	0.
H	-5.57146	2.00065	0.
H	-2.00065	5.57146	0.
C	2.77563	-4.80023	0.
C	4.13651	-5.13559	0.
H	4.43308	-6.1886	0.
C	5.13559	-4.13651	0.
H	6.1886	-4.43308	0.
C	4.80023	-2.77563	0.
H	5.57146	-2.00065	0.
H	2.00065	-5.57146	0.
Co	0.	0.	0.
Br	0.	0.	-2.47908
Br	0.	0.	2.47908

Optimized coordinates for $[Pc(2-)Co^{III}(CN)_2]^-$:

N	-1.38161	-1.38161	0.
N	1.38161	-1.38161	0.
N	1.38161	1.38161	0.
C	-1.16257	2.74376	0.
C	-3.44374	2.44528	0.
C	-2.74376	1.16257	0.
C	-2.74376	-1.16257	0.
C	-3.44374	-2.44528	0.
C	-2.44528	-3.44374	0.
C	-1.16257	-2.74376	0.
C	1.16257	-2.74376	0.
C	2.44528	-3.44374	0.
C	3.44374	-2.44528	0.
C	2.74376	-1.16257	0.
C	2.74376	1.16257	0.
C	3.44374	2.44528	0.
C	2.44528	3.44374	0.
C	1.16257	2.74376	0.
C	-2.44528	3.44374	0.
N	-1.38161	1.38161	0.
N	0.	3.38827	0.
N	-3.38827	0.	0.
N	0.	-3.38827	0.
N	3.38827	0.	0.
C	4.80425	2.77923	0.
C	5.13921	4.14013	0.
H	6.19224	4.43673	0.
C	4.14013	5.13921	0.

H	4.43673	6.19224	0.
C	2.77923	4.80425	0.
H	5.57521	2.00376	0.
H	2.00376	5.57521	0.
C	-2.77923	4.80425	0.
C	-4.14013	5.13921	0.
H	-4.43673	6.19224	0.
C	-4.80425	2.77923	0.
C	-5.13921	4.14013	0.
H	-6.19224	4.43673	0.
C	-4.80425	-2.77923	0.
C	-5.13921	-4.14013	0.
H	-6.19224	-4.43673	0.
C	-4.14013	-5.13921	0.
H	-4.43673	-6.19224	0.
C	-2.77923	-4.80425	0.
H	-2.00376	-5.57521	0.
H	-5.57521	-2.00376	0.
H	-5.57521	2.00376	0.
H	-2.00376	5.57521	0.
C	2.77923	-4.80425	0.
C	4.14013	-5.13921	0.
H	4.43673	-6.19224	0.
C	5.13921	-4.14013	0.
H	6.19224	-4.43673	0.
C	4.80425	-2.77923	0.
H	5.57521	-2.00376	0.
H	2.00376	-5.57521	0.
N	0.	0.	3.10709
N	0.	0.	-3.10709
C	0.	0.	1.93071
C	0.	0.	-1.93071
Co	0.	0.	0.

Optimized coordinates for Pc(2-)Co^{II}:

N	0.	1.93189	0.
N	1.93189	0.	0.
N	0.	-1.93189	0.
C	-2.75658	-1.1173	0.
C	-4.15527	0.70534	0.
C	-2.75658	1.1173	0.
C	-1.1173	2.75658	0.
C	-0.70534	4.15527	0.
C	0.70534	4.15527	0.
C	1.1173	2.75658	0.

C	2.75658	1.1173	0.
C	4.15527	0.70534	0.
C	4.15527	-0.70534	0.
C	2.75658	-1.1173	0.
C	1.1173	-2.75658	0.
C	0.70534	-4.15527	0.
C	-0.70534	-4.15527	0.
C	-1.1173	-2.75658	0.
C	-4.15527	-0.70534	0.
N	-1.93189	0.	0.
N	-2.39338	-2.39338	0.
N	-2.39338	2.39338	0.
N	2.39338	2.39338	0.
N	2.39338	-2.39338	0.
C	1.4319	-5.35404	0.
C	0.70675	-6.55256	0.
H	1.24124	-7.50694	0.
C	-0.70675	-6.55256	0.
H	-1.24124	-7.50694	0.
C	-1.4319	-5.35404	0.
H	2.52509	-5.35123	0.
H	-2.52509	-5.35123	0.
C	-5.35404	-1.4319	0.
C	-6.55256	-0.70675	0.
H	-7.50694	-1.24124	0.
C	-5.35404	1.4319	0.
C	-6.55256	0.70675	0.
H	-7.50694	1.24124	0.
C	-1.4319	5.35404	0.
C	-0.70675	6.55256	0.
H	-1.24124	7.50694	0.
C	0.70675	6.55256	0.
H	1.24124	7.50694	0.
C	1.4319	5.35404	0.
H	2.52509	5.35123	0.
H	-2.52509	5.35123	0.
H	-5.35123	2.52509	0.
H	-5.35123	-2.52509	0.
C	5.35404	1.4319	0.
C	6.55256	0.70675	0.
H	7.50694	1.24124	0.
C	6.55256	-0.70675	0.
H	7.50694	-1.24124	0.
C	5.35404	-1.4319	0.
H	5.35123	-2.52509	0.
H	5.35123	2.52509	0.

Co	0.	0.	0.

Optimized coordinates for [Pc(2-)Co^{I}]$^{-}$:

N	0.	1.91276	0.
N	1.91276	0.	0.
N	0.	-1.91276	0.
C	-2.74971	-1.11553	0.
C	-4.14846	0.70565	0.
C	-2.74971	1.11553	0.
C	-1.11553	2.74971	0.
C	-0.70565	4.14846	0.
C	0.70565	4.14846	0.
C	1.11553	2.74971	0.
C	2.74971	1.11553	0.
C	4.14846	0.70565	0.
C	4.14846	-0.70565	0.
C	2.74971	-1.11553	0.
C	1.11553	-2.74971	0.
C	0.70565	-4.14846	0.
C	-0.70565	-4.14846	0.
C	-1.11553	-2.74971	0.
C	-4.14846	-0.70565	0.
N	-1.91276	0.	0.
N	-2.39284	-2.39284	0.
N	-2.39284	2.39284	0.
N	2.39284	2.39284	0.
N	2.39284	-2.39284	0.
C	1.42996	-5.34992	0.
C	0.70694	-6.55047	0.
H	1.24283	-7.50473	0.
C	-0.70694	-6.55047	0.
H	-1.24283	-7.50473	0.
C	-1.42996	-5.34992	0.
H	2.52392	-5.34787	0.
H	-2.52392	-5.34787	0.
C	-5.34992	-1.42996	0.
C	-6.55047	-0.70694	0.
H	-7.50473	-1.24283	0.
C	-5.34992	1.42996	0.
C	-6.55047	0.70694	0.
H	-7.50473	1.24283	0.
C	-1.42996	5.34992	0.
C	-0.70694	6.55047	0.
H	-1.24283	7.50473	0.
C	0.70694	6.55047	0.

H	1.24283	7.50473	0.
C	1.42996	5.34992	0.
H	2.52392	5.34787	0.
H	-2.52392	5.34787	0.
H	-5.34787	2.52392	0.
H	-5.34787	-2.52392	0.
C	5.34992	1.42996	0.
C	6.55047	0.70694	0.
H	7.50473	1.24283	0.
C	6.55047	-0.70694	0.
H	7.50473	-1.24283	0.
C	5.34992	-1.42996	0.
H	5.34787	-2.52392	0.
H	5.34787	2.52392	0.
Co	0.	0.	0.

Optimized coordinates for Pc(2-)Co^{II}(*n*BuNH$_2$)$_2$:

N	1.9344	0.16301	0.04944
N	0.06352	-0.15807	-1.93391
N	-1.9344	-0.16301	-0.04944
C	-1.20206	0.12426	2.72269
C	0.56867	0.39322	4.16552
C	1.02249	0.3171	2.77873
C	2.71428	0.32376	1.18283
C	4.12428	0.4137	0.8093
C	4.1694	0.30494	-0.59803
C	2.78619	0.14969	-1.0427
C	1.20206	-0.12426	-2.72269
C	0.83775	-0.27038	-4.13038
C	-0.56867	-0.39322	-4.16552
C	-1.02249	-0.3171	-2.77873
C	-2.71428	-0.32376	-1.18283
C	-4.12428	-0.4137	-0.8093
C	-4.1694	-0.30494	0.59803
C	-2.78619	-0.14969	1.0427
C	-0.83775	0.27038	4.13038
N	-0.06352	0.15807	1.93391
N	-2.46302	-0.01954	2.32585
N	2.30773	0.39556	2.44689
N	2.46302	0.01954	-2.32585
N	-2.30773	-0.39556	-2.44689
C	-5.29612	-0.57554	-1.5611
C	-6.5143	-0.62502	-0.86943
H	-7.4474	-0.75028	-1.42685
C	-6.55935	-0.51584	0.53855

H	-7.52661	-0.55834	1.04812
C	-5.38723	-0.35443	1.29006
H	-5.25981	-0.6601	-2.65078
H	-5.41948	-0.2697	2.37989
C	-1.59707	0.3022	5.30813
C	-0.91376	0.46048	6.52174
H	-1.47716	0.48961	7.45919
C	1.25241	0.55103	5.37874
C	0.49337	0.58344	6.55671
H	0.99628	0.70574	7.52066
C	5.29612	0.57554	1.5611
C	6.5143	0.62502	0.86943
H	7.4474	0.75028	1.42685
C	6.55935	0.51584	-0.53855
H	7.52661	0.55834	-1.04812
C	5.38723	0.35443	-1.29006
H	5.41948	0.2697	-2.37989
H	5.25981	0.6601	2.65078
H	2.34165	0.64551	5.40318
H	-2.68608	0.20678	5.27962
C	1.59707	-0.3022	-5.30813
C	0.91376	-0.46048	-6.52174
H	1.47716	-0.48961	-7.45919
C	-0.49337	-0.58344	-6.55671
H	-0.99628	-0.70574	-7.52066
C	-1.25241	-0.55103	-5.37874
H	-2.34165	-0.64551	-5.40318
H	2.68608	-0.20678	-5.27962
H	0.80068	2.66772	0.10005
H	-0.10295	2.49285	-1.25093
H	0.10295	-2.49285	1.25093
H	-0.80068	-2.66772	-0.10005
N	0.10617	-2.32692	0.23819
N	-0.10617	2.32692	-0.23819
C	-1.19454	3.11205	0.38847
H	-2.14927	2.71663	0.00356
H	-1.17434	2.89689	1.47005
C	1.19454	-3.11205	-0.38847
H	1.17434	-2.89689	-1.47005
H	2.14927	-2.71663	-0.00356
C	-1.11835	4.62828	0.15141
H	-0.15088	5.00821	0.53235
H	-1.12275	4.82679	-0.93767
C	1.11835	-4.62828	-0.15141
H	1.12275	-4.82679	0.93767
H	0.15088	-5.00821	-0.53235

C	-2.27059	5.39782	0.81809
H	-3.23485	5.01064	0.4393
H	-2.26592	5.19218	1.90478
C	2.27059	-5.39782	-0.81809
H	3.23485	-5.01064	-0.4393
H	2.26592	-5.19218	-1.90478
C	2.19785	-6.91246	-0.5824
H	3.03499	-7.43785	-1.07062
H	2.23657	-7.1527	0.4938
H	1.26074	-7.33558	-0.98264
C	-2.19785	6.91246	0.5824
H	-3.03499	7.43785	1.07062
H	-1.26074	7.33558	0.98264
H	-2.23657	7.1527	-0.4938
Co	0.	0.	0.

Optimized coordinates for Pc(2-)Co^{II}Py$_2$:

N	1.37213	1.37213	0.
N	-1.37213	1.37213	0.
N	-1.37213	-1.37213	0.
C	1.16274	-2.73977	0.06064
C	3.44108	-2.44457	-0.04292
C	2.73977	-1.16274	-0.06064
C	2.73977	1.16274	-0.06064
C	3.44108	2.44457	-0.04292
C	2.44457	3.44108	0.04292
C	1.16274	2.73977	0.06064
C	-1.16274	2.73977	0.06064
C	-2.44457	3.44108	0.04292
C	-3.44108	2.44457	-0.04292
C	-2.73977	1.16274	-0.06064
C	-2.73977	-1.16274	-0.06064
C	-3.44108	-2.44457	-0.04292
C	-2.44457	-3.44108	0.04292
C	-1.16274	-2.73977	0.06064
C	2.44457	-3.44108	0.04292
N	1.37213	-1.37213	0.
N	0.	-3.38381	0.10239
N	3.38381	0.	-0.10239
N	0.	3.38381	0.10239
N	-3.38381	0.	-0.10239
N	0.	0.	-2.35236
C	0.	-1.15467	-3.05045
C	0.	1.15467	-3.05045
C	0.	-1.20334	-4.44845

H	0.	-2.07503	-2.45981
C	0.	1.20334	-4.44845
H	0.	2.07503	-2.45981
C	0.	0.	-5.16376
H	0.	-2.16923	-4.95983
H	0.	2.16923	-4.95983
H	0.	0.	-6.25725
N	0.	0.	2.35236
C	1.15467	0.	3.05045
C	-1.15467	0.	3.05045
C	1.20334	0.	4.44845
H	2.07503	0.	2.45981
C	-1.20334	0.	4.44845
H	-2.07503	0.	2.45981
C	0.	0.	5.16376
H	2.16923	0.	4.95983
H	-2.16923	0.	4.95983
H	0.	0.	6.25725
C	-4.80101	-2.7811	-0.08645
C	-5.13817	-4.1409	-0.04324
H	-6.19065	-4.43783	-0.07607
C	-4.1409	-5.13817	0.04324
H	-4.43783	-6.19065	0.07607
C	-2.7811	-4.80101	0.08645
H	-5.57134	-2.00786	-0.15274
H	-2.00786	-5.57134	0.15274
C	2.7811	-4.80101	0.08645
C	4.1409	-5.13817	0.04324
H	4.43783	-6.19065	0.07607
C	4.80101	-2.7811	-0.08645
C	5.13817	-4.1409	-0.04324
H	6.19065	-4.43783	-0.07607
C	4.80101	2.7811	-0.08645
C	5.13817	4.1409	-0.04324
H	6.19065	4.43783	-0.07607
C	4.1409	5.13817	0.04324
H	4.43783	6.19065	0.07607
C	2.7811	4.80101	0.08645
H	2.00786	5.57134	0.15274
H	5.57134	2.00786	-0.15274
H	5.57134	-2.00786	-0.15274
H	2.00786	-5.57134	0.15274
C	-2.7811	4.80101	0.08645
C	-4.1409	5.13817	0.04324
H	-4.43783	6.19065	0.07607
C	-5.13817	4.1409	-0.04324

H	-6.19065	4.43783	-0.07607
C	-4.80101	2.7811	-0.08645
H	-5.57134	2.00786	-0.15274
H	-2.00786	5.57134	0.15274
Co	0.	0.	0.