Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Information for

The effect from embedded o-carborane ligand to the photophysical property of a cyclometalated Pt(II) complex: a theoretical investigation

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Table S1 The singlet ground state geometries of complex 1 analogue optimized by different functionals together with experimental values.

	Exp[32].	B3P86	B3LYP	PBE0	M06-2X
Bond length[Å]					
Pt-N	2.064	2.067	2.090	2.063	2.094
Pt-C1	2.089	2.096	2.121	2.093	2.116
Pt-C4	2.062	2.064	2.084	2.060	2.053
C1-C2	1.726	1.700	1.719	1.693	1.691
C2-C3	1.501	1.503	1.511	1.503	1.510
C3-N	1.355	1.355	1.360	1.353	1.348
Bond angle[deg.]					
C1-Pt-N	82.54	82.22	81.95	82.22	81.63
N-Pt-C4	81.28	81.16	80.96	81.22	81.03

Table S2 The geometry parameters for **2**-**5** in the optimized ground state and lowest lying triplet excited state. (The number below C-B, Pt-C1-B and B-B represents the atomic serial number in the molecule.)

2			3			4			5		
C-B	S_0	T_1	C-B	S_0	T_1	C-B	S_0	T_1	C-B	S_0	T_1
	Bond length[Å]			Bond length[Å]			Bond length[Å]			Bond length[Å]	
55-58	1.620	1.621	37-39	1.710	1.711	55-58	1.853	1.970	54-55	1.722	1.724
55-59	1.600	1.600	37-45	1.709	1.710	55-59	1.601	1.595	54-56	1.649	1.646
55-60	1.608	1.611	37-47	1.707	1.707	55-60	1.793	1.777	54-58	1.662	1.669
54-59	1.801	1.800	37-55	1.706	1.707	54-56	1.597	1.635	54-59	1.849	1.859
54-60	1.792	1.790	38-39	1.716	1.715	54-57	1.827	1.727	57-55	1.653	1.652
54-56	1.711	1.712	38-45	1.716	1.717	54-58	1.833	1.891	57-58	1.708	1.703
54-57	1.713	1.714	38-41	1.695	1.695				57-62	1.926	1.986
			38-43	1.695	1.696				57-65	1.656	1.658
Pt-C1-B	S_0	T_1	Pt-C1-B	S_0	T_1	Pt-C1-B	S_0	T_1	Pt-C1-B	S_0	T_1
	Bond angle[deg]			Bond angle[deg]			Bond angle[deg]			Bond angle[deg]	
38-54-59	127.1	127.1	59-38-39	113.6	113.4	38-54-56	119.4	118.2	38-54-55	115.1	115.7
38-54-60	121.9	121.9	59-38-45	113.9	114.2	38-54-57	128.8	123.4	38-54-56	123.2	122.6
38-54-56	128.4	128.4	59-38-41	129.4	129.3	38-54-58	127.3	129.4	38-54-58	107.3	108.3
38-54-57	124.5	124.5	59-38-43	129.7	129.9				38-54-59	134.4	133.9
B-B	S_0	T_1	B-B	S_0	T_1	B-B	S_0	T_1	B-B	S_0	T_1
	Bond length[Å]			Bond length[Å]			Bond length[Å]			Bond length[Å]	
56-57	1.813	1.814	39-41	1.759	1.758	56-57	1.799	1.806	55-56	1.773	1.779
56-59	1.793	1.791	39-47	1.777	1.775	56-58	1.929	1.844	55-60	1.727	1.731
56-61	1.698	1.697	39-49	1.766	1.767	56-61	1.786	1.758	55-62	1.910	1.914
56-62	1.848	1.847	41-43	1.758	1.758	56-62	1.747	1.758	56-59	1.881	1.881
57-61	1.697	1.697	41-49	1.774	1.773	57-60	1.936	1.961	56-60	1.774	1.777
57-64	1.844	1.843	41-51	1.775	1.775	57-62	1.794	1.789	56-63	1.739	1.738
57-60	1.790	1.788	43-45	1.759	1.757	57-64	1.738	1.761	59-58	1.888	1.888
60-64	1.775	1.755	43-51	1.776	1.775	60-59	1.817	1.866	59-63	1.892	1.889
60-58	1.823	1.820	43-53	1.774	1.775	60-64	1.751	1.765	59-66	1.894	1.890
58-64	1.796	1.793	45-53	1.766	1.765	60-68	1.805	1.800	59-68	1.906	1.905
58-62	1.800	1.800	45-55	1.778	1.778	59-58	1.933	1.951	58-65	1.785	1.786
58-59	1.834	1.836	53-51	1.780	1.780	59-66	1.775	1.754	58-66	1.724	1.720
59-62	1.774	1.774	53-55	1.770	1.770	59-68	1.735	1.759	65-62	1.906	1.907
62-64	1.836	1.836	53-57	1.782	1.781	58-61	1.860	1.828	65-66	1.765	1.772
62-61	1.705	1.704	51-49	1.780	1.779	58-66	1.842	1.828	65-72	1.736	1.741
61-64	1.705	1.705	51-57	1.775	1.776	61-62	1.761	1.771	62-60	1.873	1.852
			49-47	1.770	1.769	61-66	1.731	1.749	62-70	1.903	1.893
			49-57	1.782	1.781	61-71	1.768	1.767	62-72	1.861	1.843
			47-55	1.773	1.773	62-64	1.780	1.774	60-63	1.762	1.764
			47-57	1.770	1.769	62-71	1.765	1.765	60-70	1.745	1.746
			55-57	1.770	1.771	64-68	1.786	1.773	63-68	1.748	1.751
						64-71	1.789	1.784	63-70	1.749	1.748
						68-66	1.778	1.785	68-66	1.737	1.736
						68-71	1.761	1.766	68-70	1.748	1.747
						66-71	1.765	1.766	68-72	1.762	1.763
									66-72	1.773	1.775
									72-70	1.744	1.745
average	1.783	1.781	average	1.772	1.772	average	1.797	1.797	average	1.804	1.803

Table S3 The frontier molecular orbitals energy level and detailed distribution of complexes **1**-**5**.

			MO composition (%)			
Complexes	Orbital	Energy(eV)	Pt	CB	CN	CNC
	L+1	-1.43	1	18	82	0
	LUMO	-1.94	10	17	68	7
	HOMO	-5.71	13	16	70	0
1	H-1	-6.39	13	39	47	2
	H-2	-6.43	8	41	45	6
	H-3	-6.55	2	13	85	0
	H-4	-6.88	8	44	48	1
	L+1	-1.56	0	18	82	0
	LUMO	-2.12	8	13	73	6
	HOMO	-6.11	6	1	94	0
2	H-1	-6.61	4	2	94	0
	H-2	-6.93	22	6	72	0
	H-3	-7.02	10	49	35	6
	H-4	-7.16	84	1	7	9
	L+1	-1.49	0	10	90	0
	LUMO	-2.1	7	6	81	5
	HOMO	-6.19	8	1	91	0
3	H-1	-6.57	0	1	99	0
	H-2	-6.93	24	4	71	0
	H-3	-7.07	23	53	19	6
	H-4	-7.17	69	1	24	7
	L+1	-1.96	4	7	86	3
	LUMO	-3.03	4	64	31	2
	HOMO	-6.2	6	2	93	0
4	H-1	-6.59	2	4	94	0
	H-2	-6.89	6	57	32	4
	H-3	-7.07	21	5	73	0
	H-4	-7.3	87	3	3	8
	L+1	-1.76	1	43	56	1
	LUMO	-2.23	7	25	62	5
	HOMO	-6.2	7	1	91	0
5	H-1	-6.6	1	2	96	0
	H-2	-6.91	21	62	15	4
	H-3	-6.96	24	7	69	0
	H-4	-7.23	68	3	23	7

Table S4 The SOC integral $\langle S_n|H_{soc}|T_m\rangle$ (n = 1-10, and m = 1-5) between different singlet and triplet state combinations.

Complexes	$<S_n\|H_{soc}\|T_m>$	T_1	T_2	T_3	T_4	T_5
1	S_1	1.94	55.39	162.22	165.67	185.22
	S_2	33.51	0.42	2.72	1.13	2.20
	S_3	155.90	1.20	105.13	211.98	31.00
	S_4	44.28	1.19	96.96	137.20	202.54
	S_5	263.69	2.39	115.16	272.23	115.98
	S_6	704.34	12.34	782.28	973.41	318.64
	S_7	188.17	6.27	243.10	273.81	175.89
	S_8	2.26	137.58	1.39	13.68	39.40
	S_9	4.44	34.57	23.66	78.95	7.42
	S_{10}	1.25	174.82	19.96	10.42	1.91
2	S_1	0.58	27.29	134.36	160.67	820.72
	S_2	77.64	0.41	15.50	186.68	653.11
	S_3	21.02	0.04	4.92	2.46	26.63
	S_4	177.19	0.34	217.86	257.10	128.96
	S_5	671.38	0.72	959.43	1037.20	21.83
	S_6	154.66	2.23	26.63	77.15	1084.34
	S_7	7.07	54.77	113.52	37.35	44.14
	S_8	248.76	8.72	371.89	476.70	1441.13
	S_9	35.83	0.67	70.75	81.30	238.44
	S_{10}	4.22	158.23	5.11	8.45	7.30
3	S_1	0.63	34.83	159.76	177.56	1125.28
	S_2	42.80	0.05	3.03	91.12	85.00
	S_3	42.74	0.19	47.68	9.42	403.42
	S_4	752.62	0.46	486.92	1294.87	33.25
	S_5	241.95	0.08	331.27	767.28	40.71
	S_6	168.85	1.86	93.57	11.89	766.92
	S_7	0.07	24.08	24.27	2.87	0.41
	S_8	168.88	1.14	177.54	363.08	1057.04
	S_9	298.47	6.79	306.61	629.92	1818.73
	S_{10}	72.58	105.69	25.86	103.68	143.74
4	S_1	0.75	148.72	78.69	73.94	854.08
	S_2	179.04	1.72	80.46	1.01	158.55
	S_3	91.82	2.05	0.41	0.01	426.89
	S_4	838.10	187.57	483.82	0.38	3.52
	S_5	176.52	111.63	153.75	0.71	1474.03
	S_6	170.32	124.08	124.99	0.17	463.49
	S_7	270.00	82.60	53.16	0.22	412.41
	S_8	53.65	73.70	55.17	0.04	348.51
	S_9	356.89	321.84	201.29	0.03	1485.64
	S_{10}	77.46	153.30	61.09	0.22	476.79
5	S_1	3.47	51.32	314.06	487.27	273.39
	S_2	102.45	5.90	13.33	249.72	62.06
	S_3	34.80	6.47	3.03	8.00	2.98
	S_4	394.26	19.26	247.45	28.14	590.37
	S_5	511.12	23.53	372.68	816.11	720.26
	S_6	174.07	5.94	444.03	353.70	154.21
	S_7	6.75	74.22	63.89	9.87	13.71
	S_8	35.64	123.07	6.03	19.89	7.38
	S_9	92.92	105.45	8.11	54.68	8.45
	S_{10}	79.98	7.02	4.37	7.21	5.75

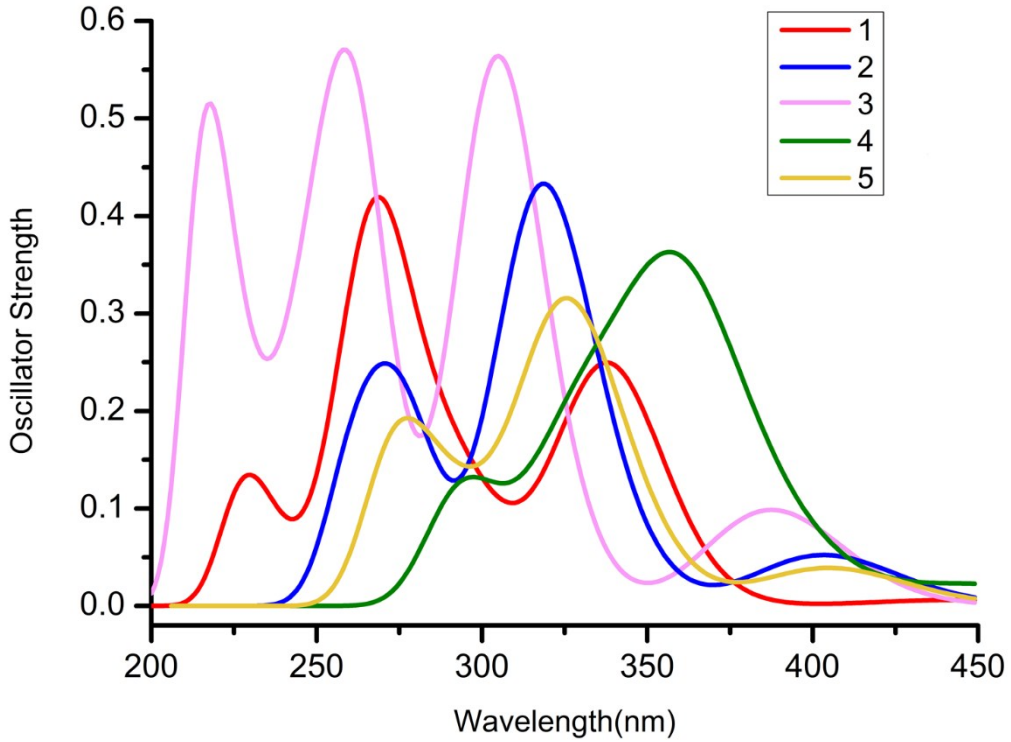

Fig. S1 The absorption spectra of complexes **1**-**5** in 2-MeTHF media.

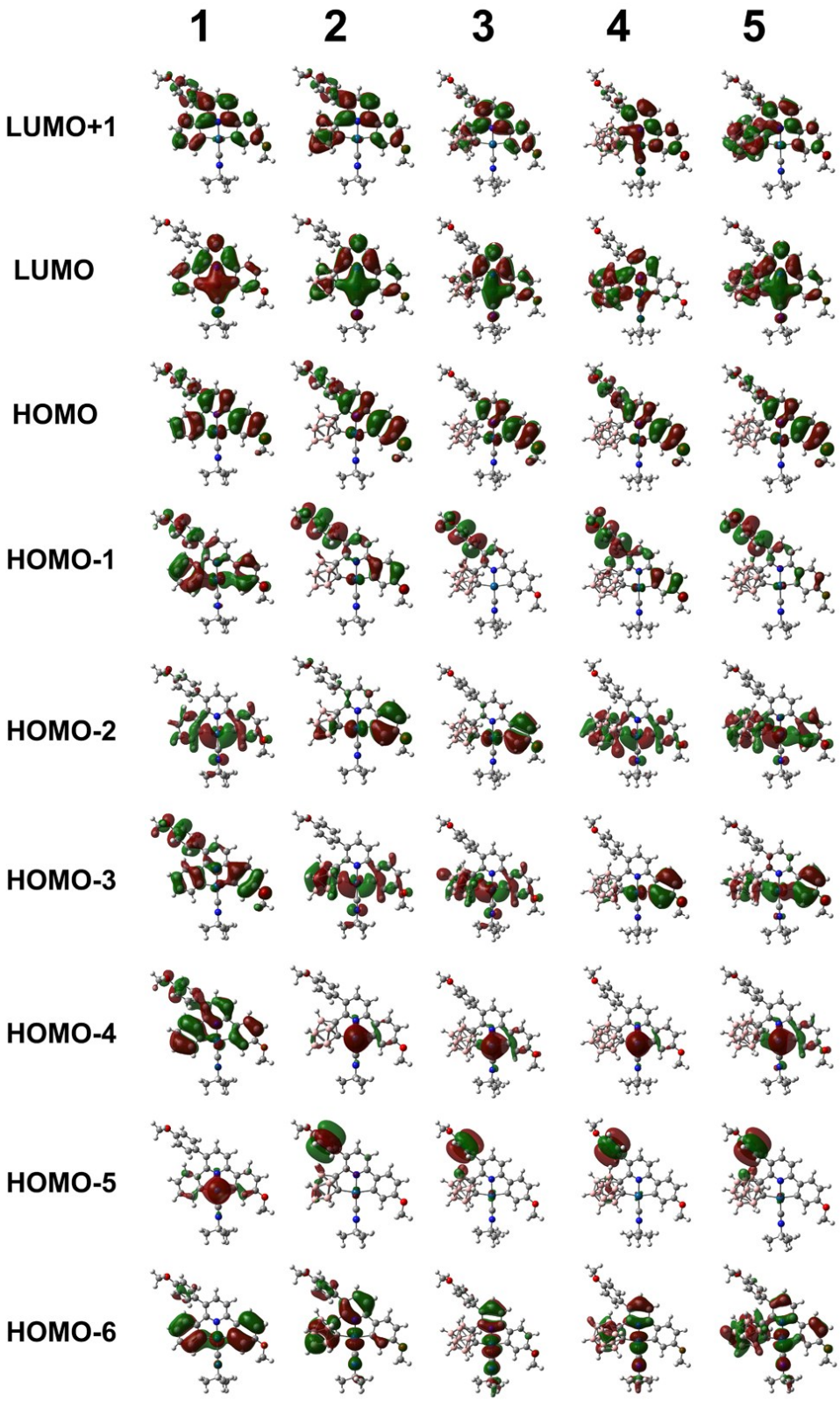

Fig S2 Corresponding frontier molecular orbitals distribution for **1**-**5** at their optimized S_0 geometries

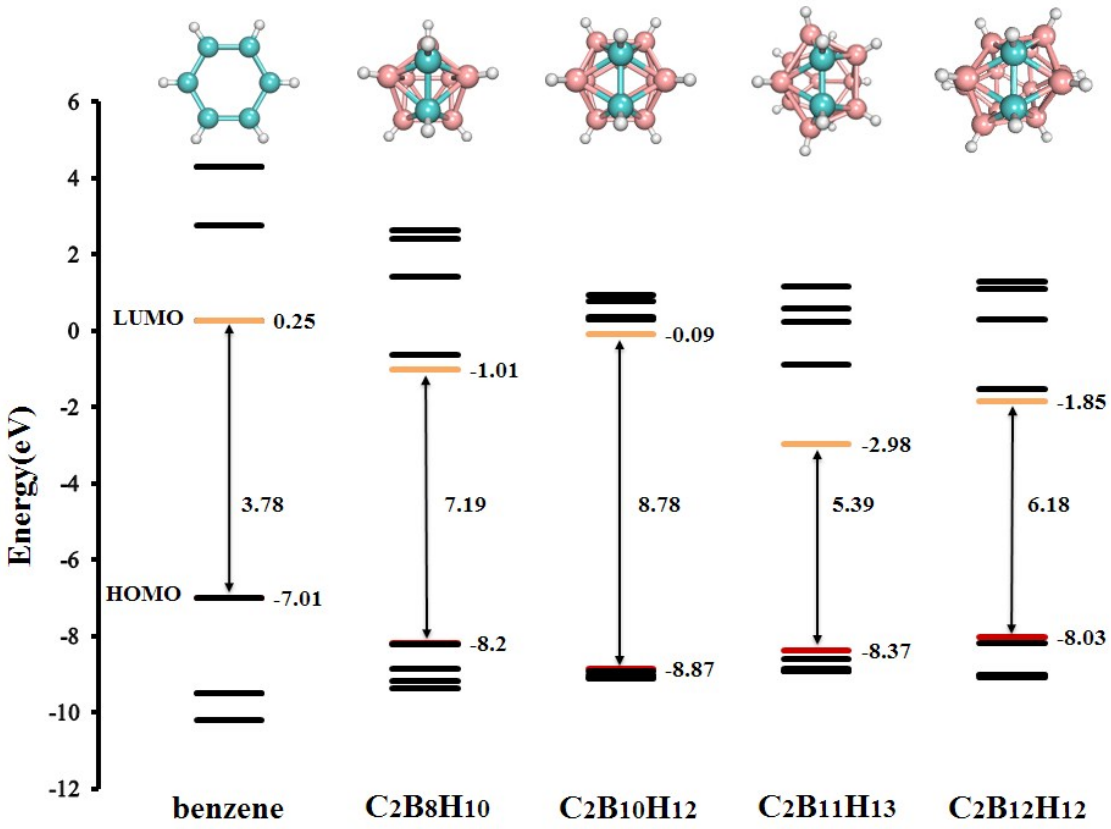

Fig S3 The energy levels and energy gaps of the HOMO and LUMO for benzene and four o-carboranes ($C_2B_8H_{10}$, $C_2B_{10}H_{12}$, $C_2B_{11}H_{13}$, $C_2B_{12}H_{14}$) at their optimized S_0 states.

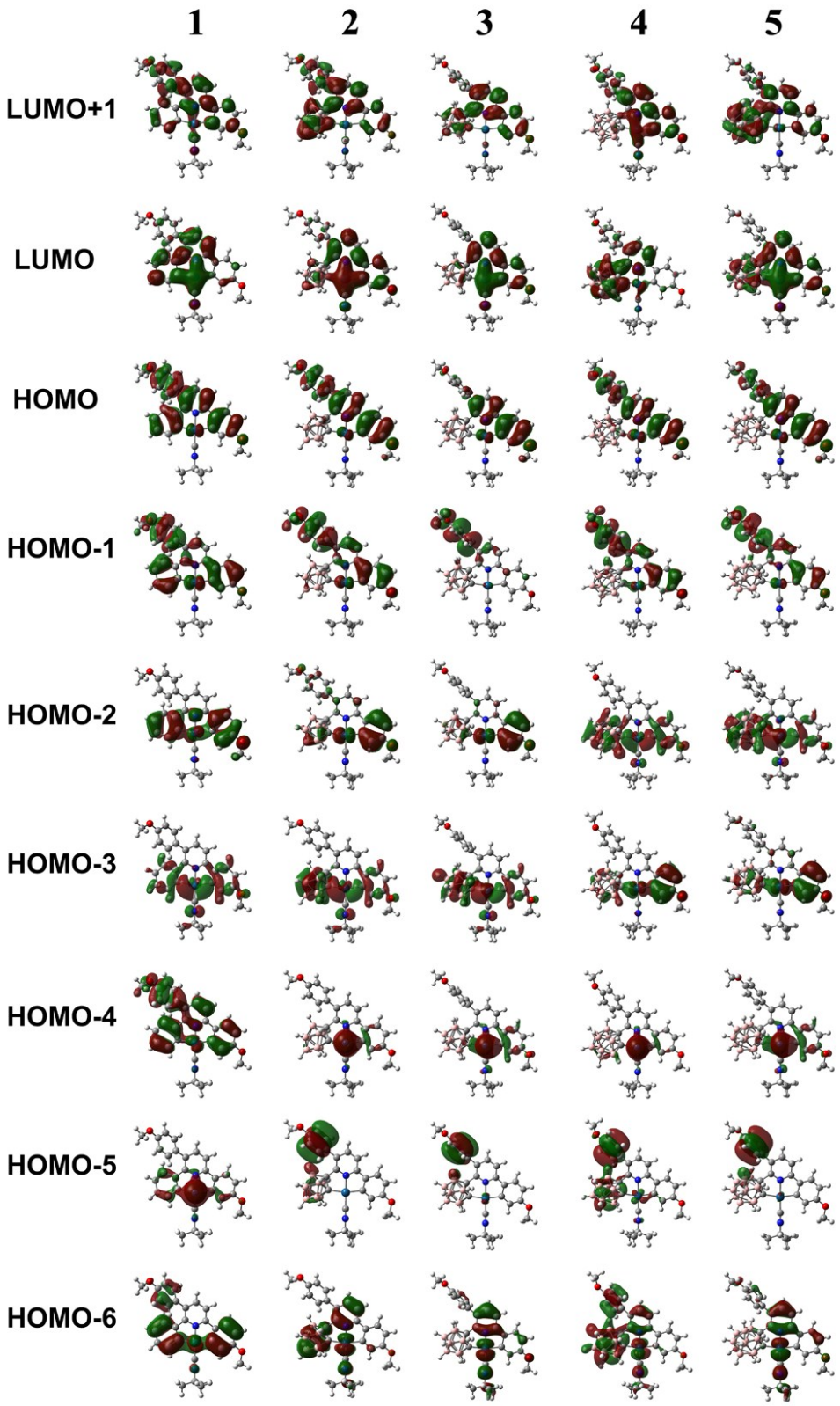

Fig S4 Corresponding frontier molecular orbitals distribution for **1**-**5** at their optimized T_1 geometries

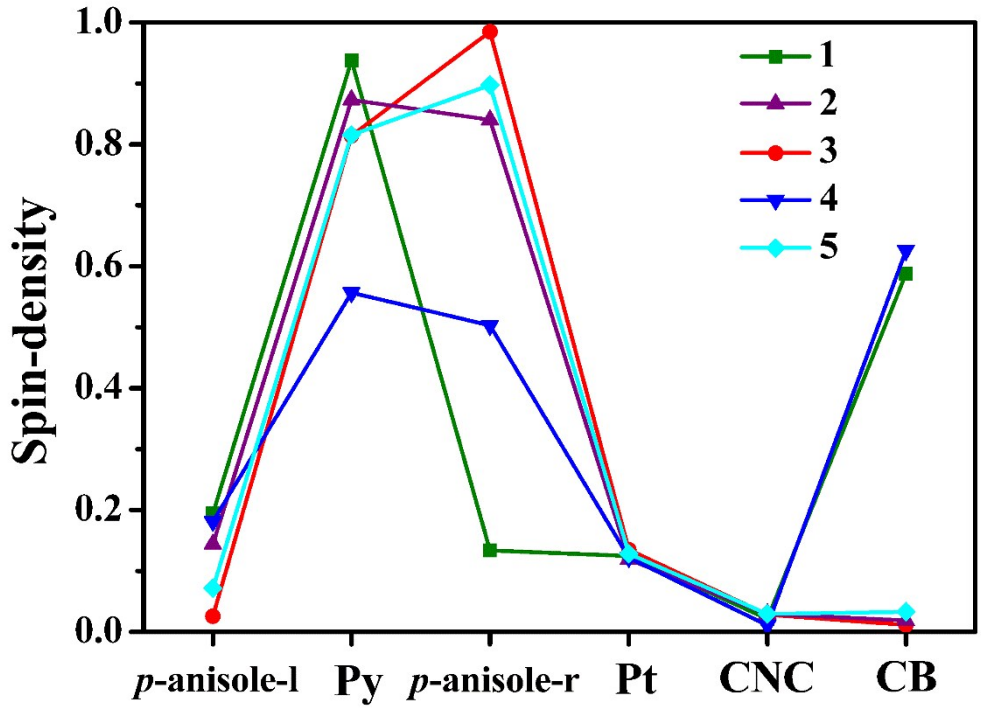

Fig S5 The spin population for each part in **1**-**5.**

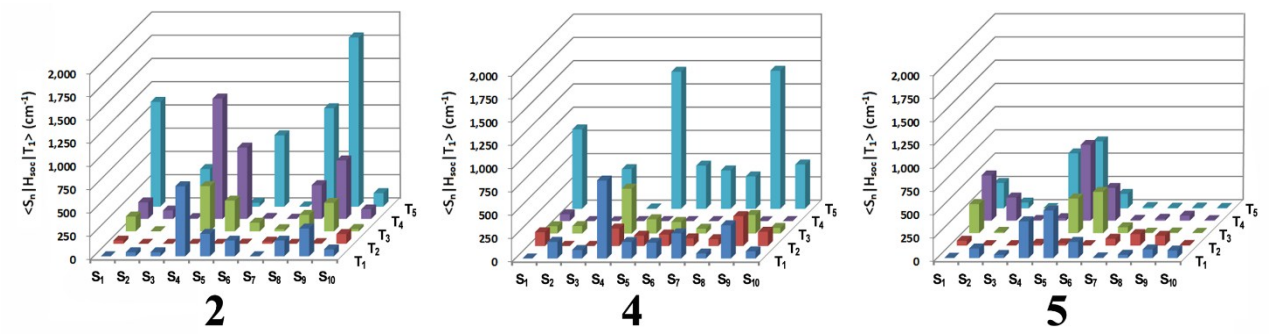

Fig S6 The SOC integrals (cm^{-1}) for complexes **2**, **4** and **5** between S_n(n=10) and T_m(n=5) states.

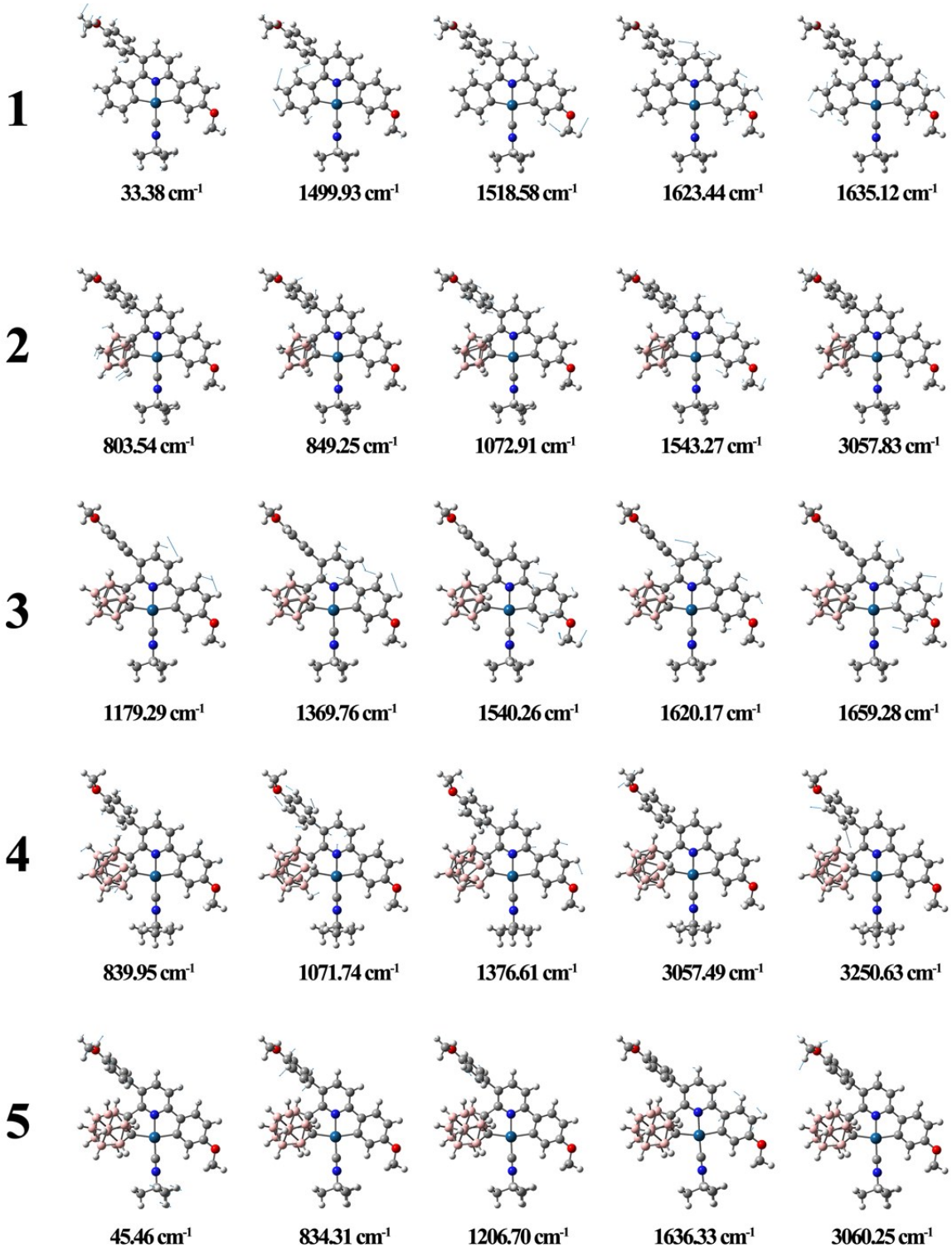

Fig S7 The top five normal mode displacement vectors for the corresponding vibrations at the reorganization energy contribution of complexes **1**-**5**.