Supporting Information

A Computational Study on Second-Order Nonlinear Optical Properties Based on Bis-Cyclometalated Ir(Ⅲ) Complexes: Redox and Substituent Effects

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General Comments

Table S1 Selected bond lengths (Å) and bond angles (º) of all studied complexes obtained at the PBE1PBE//6-31G(d)/SDD level.

Fig. S1 Comparison of the absorption spectra of complex **2** computed by four various functions of theory.

Fig. S2 Molecular orbitals related to the dominant electron transitions of all studied complexes.

Fig. S3 The β_{tot} values of all studied complexes by using the CAM-B3LYP and ωB97XD functionals with 6-31+G(d) basis set.

Table S1. Selected bond lengths (Å) and bond angles (º) of all studied complexes obtained at the PBE1PBE//6-31G(d)/SDD level.

Complex	Ir-N_1	Ir-C_2	Ir-N_3	Ir-C_4	Ir-C_5	Ir-C_6	$\angle N_3$-Ir-C_6	$\angle N_1$-Ir-C_2
1	2.062	2.059	2.069	2.087	2.069	2.107	95.4	80.4
1$^+$	2.072	2.005	2.076	2.064	2.156	2.118	95.7	81.3
1$^-$	2.069	2.060	2.068	2.089	2.046	2.107	96.3	80.2
2[a]	2.059	2.059	2.061	2.073	2.054	2.086	97.3	80.1
2	2.065	2.060	2.071	2.083	2.066	2.105	96.0	80.4
2$^+$	2.075	2.005	2.077	2.057	2.143	2.124	95.9	81.3
2$^-$	2.068	2.060	2.066	2.087	2.052	2.110	95.0	80.1
3	2.063	2.058	2.070	2.087	2.071	2.107	95.0	80.3
3$^+$	2.072	2.062	2.077	2.082	2.057	2.084	97.2	80.4
3$^-$	2.069	2.059	2.068	2.088	2.049	2.107	96.0	80.1
4	2.064	2.059	2.070	2.087	2.061	2.107	95.7	80.3
4$^+$	2.075	2.004	2.076	2.064	2.151	2.120	95.7	81.3
4$^-$	2.063	2.058	2.060	2.088	2.075	2.107	94.7	80.2
5	2.062	2.057	2.068	2.086	2.073	2.107	95.3	80.3
5$^+$	2.073	2.008	2.073	2.064	2.156	2.119	95.8	81.3
5$^-$	2.069	2.058	2.068	2.087	2.049	2.107	96.4	80.1

[a] Experimental values from X-ray data in ref [54]

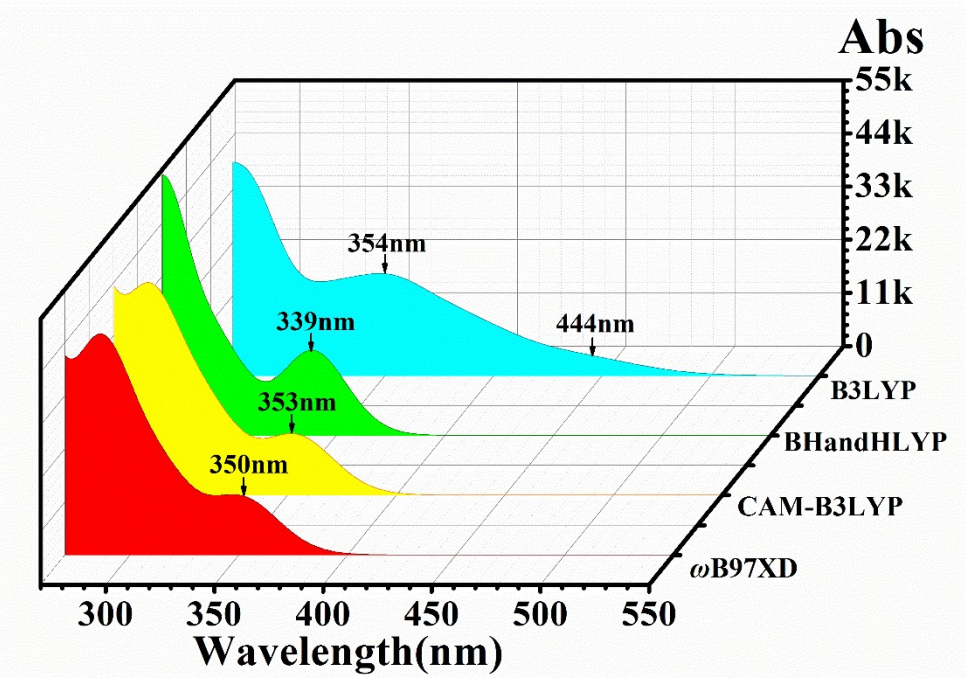

Fig. S1 Comparison of the absorption spectra of complex **1** computed by four various functions of theory.

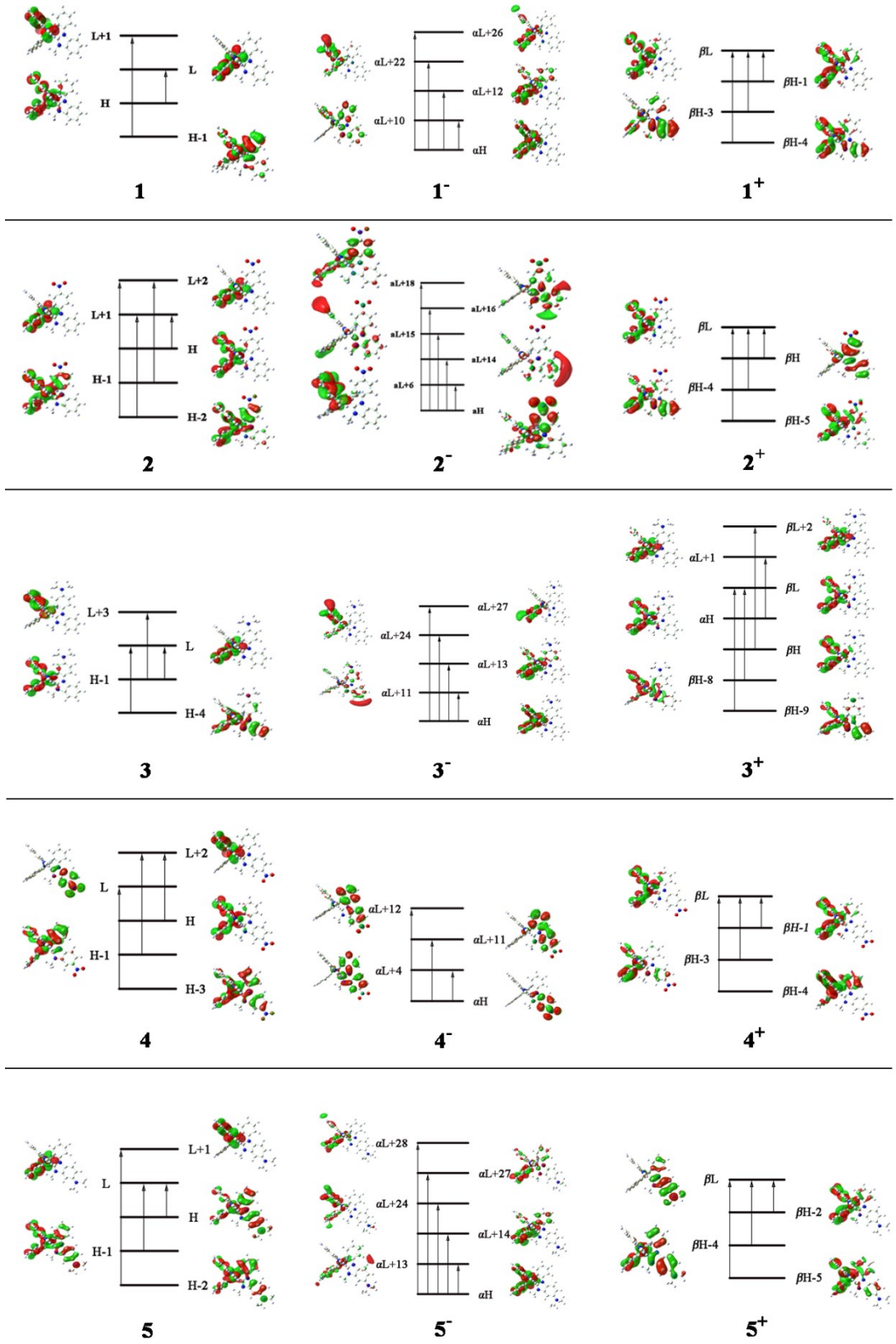

Fig. S2 Molecular orbitals related to the main excited states for all studied complexes.

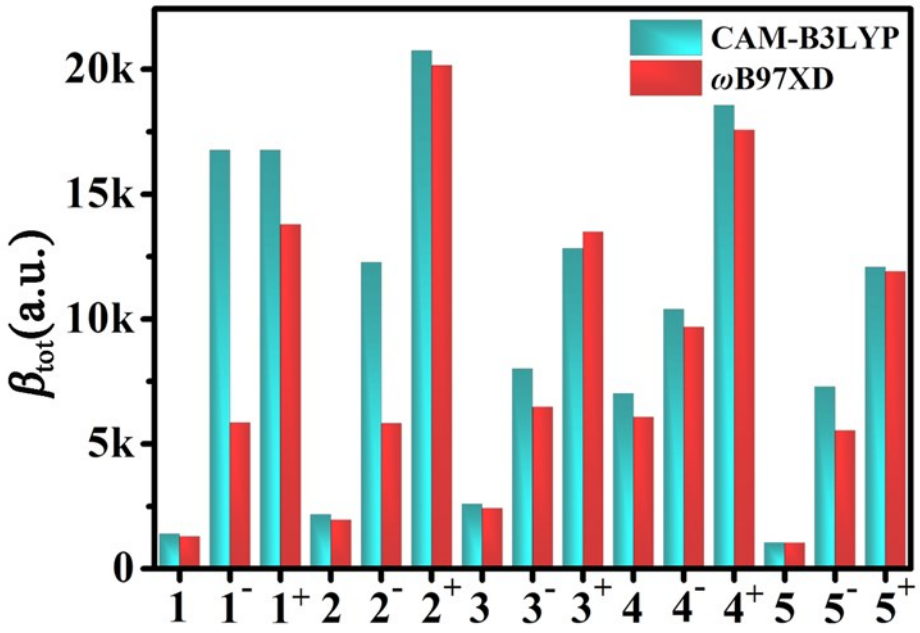

Fig. S3 The β_{tot} values of all studied complexes by using the CAM-B3LYP and ωB97XD functionals with 6-31+G(d) basis set.