Supporting Information

Substituent and redox effects on the second-order NLO response of Ru(II) complexes with polypyridine ligands: A theoretical study

Yingying Wang, Yu Chen, Yuanyuan Zhao,*and Yongqing Qiu*

Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, China

*Corresponding Author. Fax: +86043185099291
E-mail addresses: yuanyuan-zhao@outlook.com (Y. Y. Zhao)
*Corresponding Author. Fax: +86043185098768.
E-mail addresses: qiuyq466@nenu.edu.cn (Y. Q. Qiu)

General Comments

Table S1 Electronic Energy (kJ/mol) calculated in two spin states of complexes 1-4 at the B3LYP/6-31G(d)/LANL2DZ level of theory.

Table S2 Total first hyperpolarizabilities β_{tot} (a.u.) of all studied complexes calculated with two methods.

Fig.S1 Spin density diagrams for one-electron reduced and oxidized species of complexes 1-4.

Fig.S2 Simulated absorption spectra of complex 1 in acetonitrile solution by four functionals.

Fig.S3 Molecular orbitals involved in crucial electronic transitions of complexes 1, 1^{+} and 1^{-}.

Fig.S4 Molecular orbitals involved in crucial electronic transitions of complexes 2, 2^{+} and 2^{-}.

Fig.S5 Molecular orbitals involved in crucial electronic transitions of complexes 3, 3^{+} and 3^{-}.

Fig.S6 Molecular orbitals involved in crucial electronic transitions of complexes 4, 4^{+} and 4^{-}.

Table S1 Electronic Energy (kJ/mol) calculated in two spin states of complexes 1-4 at the B3LYP/6-31G(d)/LANL2DZ level of theory.

Single electron	**1**	**2**	**3**	**4**
S=0	0.0	0.0	0.0	0.0
S=4	427.0	488.2	437.8	1001.3

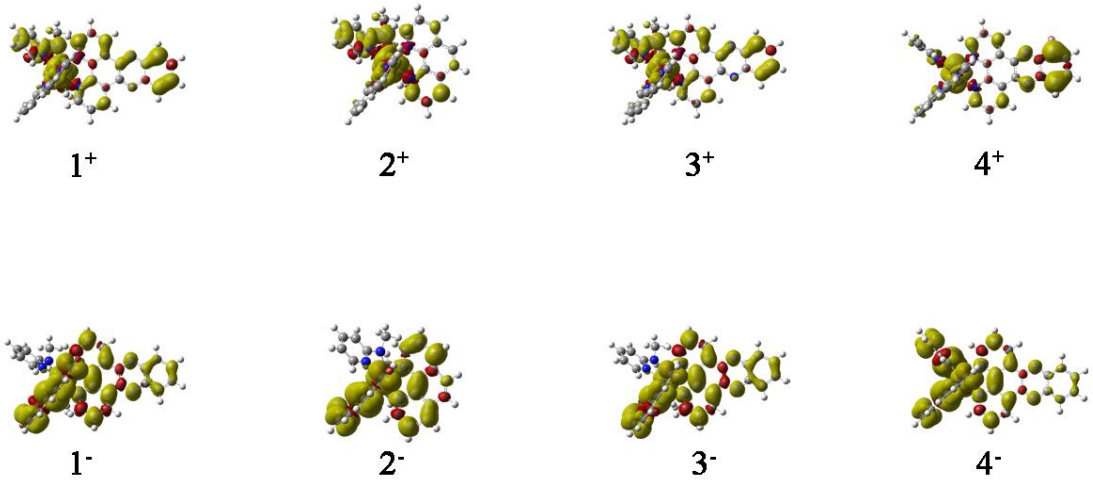

Fig.S1 Spin density diagrams for one-electron reduced and oxidized species of complexes 1–4.

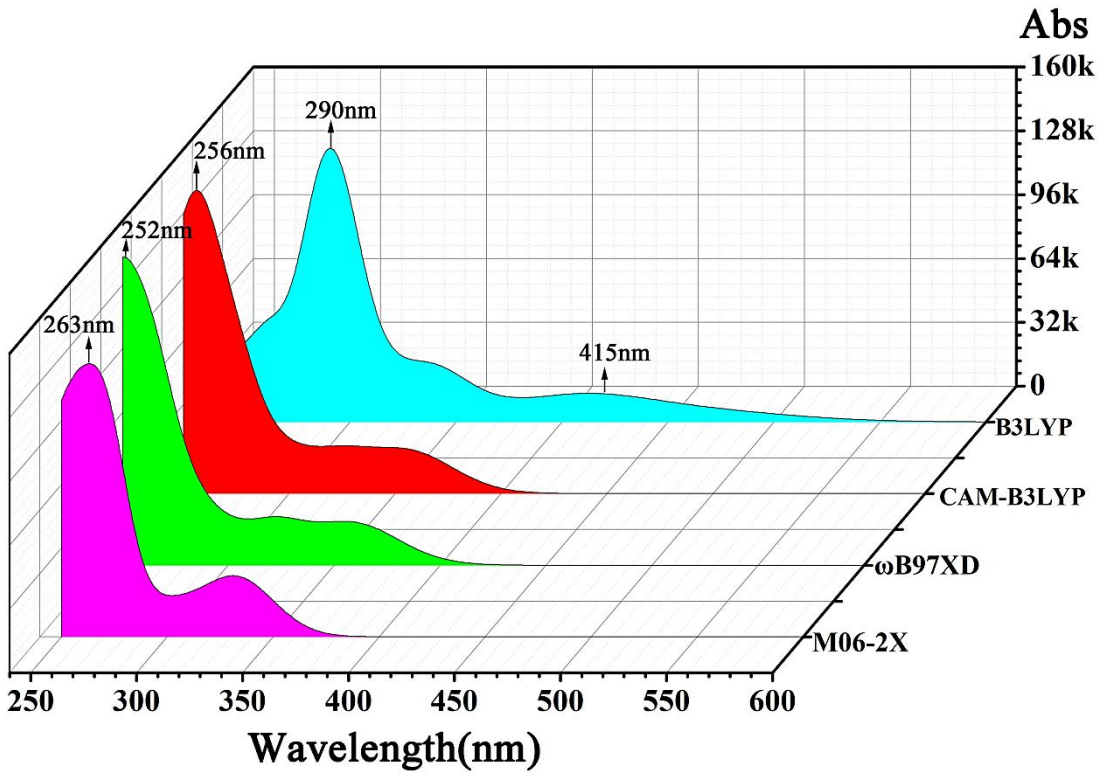

Fig.S2 Simulated absorption spectra of complex 1 in acetonitrile solution by four functionals.

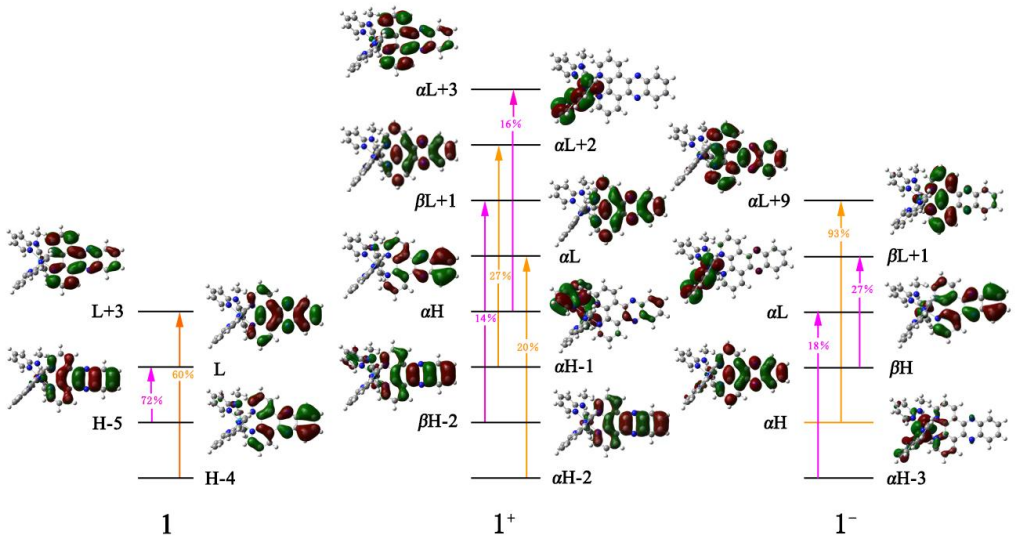

Fig.S3 Molecular orbitals involved in crucial electronic transitions of complexes 1, 1^{+}, and 1^{-}.

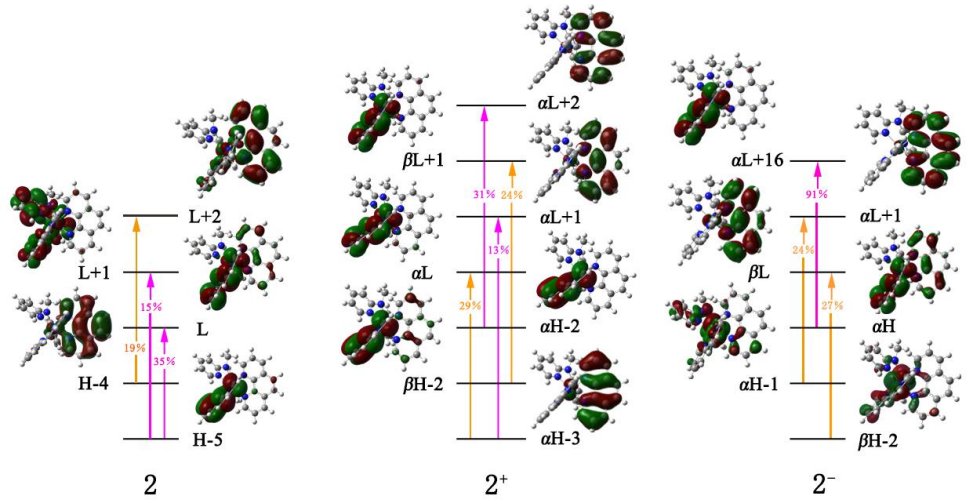

Fig.S4 Molecular orbitals involved in crucial electronic transitions of complexes 2, 2^{+}, and 2^{-}.

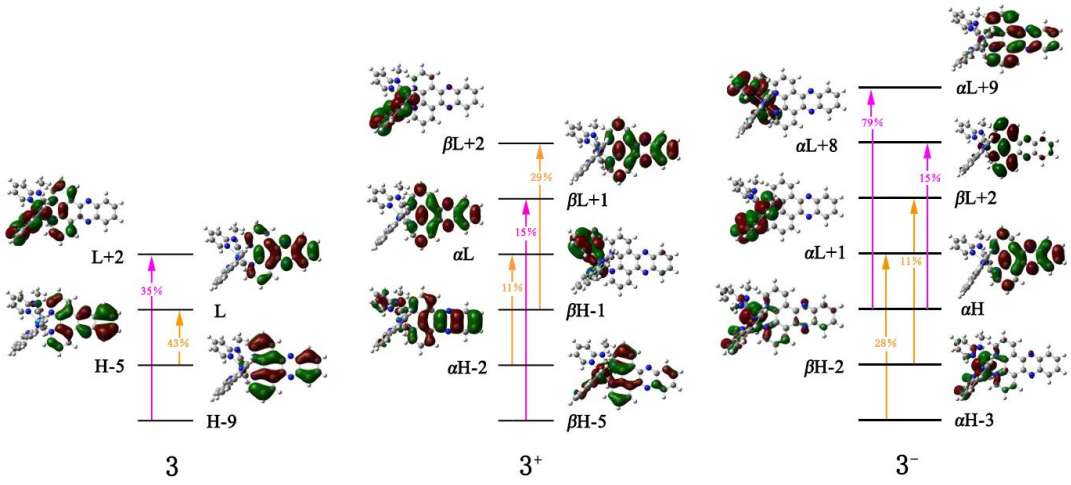

Fig.S5 Molecular orbitals involved in crucial electronic transitions of complexes 3, 3^{+}, and 3^{-}.

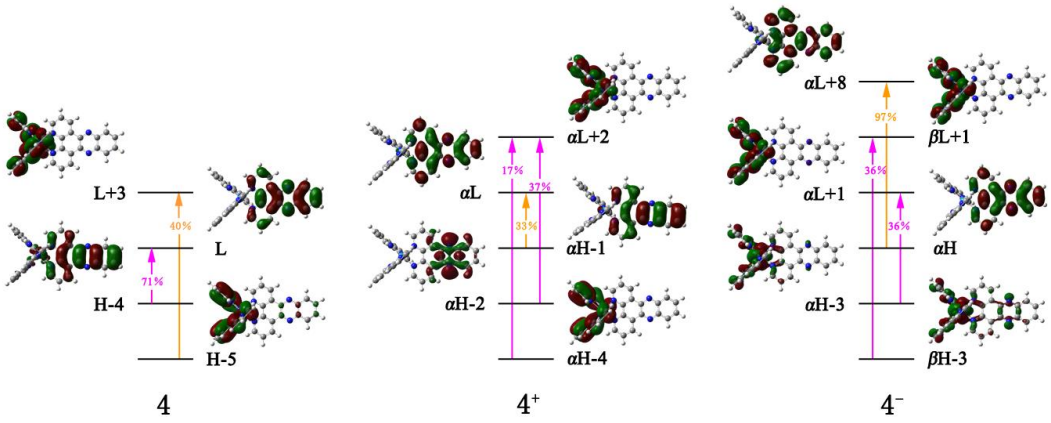

Fig.S6 Molecular orbitals involved in crucial electronic transitions of complexes 4, 4^{+}, and 4^{-}.

Table S2 Total first hyperpolarizabilities β_{tot} (a.u.) of all studied complexes calculated with two methods.

Complex	method	β_{tot}	Complex	method	β_{tot}
$\mathbf{1}^{+}$	CAM-B3LYP	6.24×10^{3}	$\mathbf{3}^{+}$	CAM-B3LYP	4.36×10^{3}
	ωB97XD	6.83×10^{3}		ωB97XD	6.18×10^{3}
1	CAM-B3LYP	1.79×10^{3}	**3**	CAM-B3LYP	1.67×10^{3}
	ωB97XD	1.76×10^{3}		ωB97XD	1.65×10^{3}
$\mathbf{1}^{-}$	CAM-B3LYP	1.44×10^{5}	$\mathbf{3}^{-}$	CAM-B3LYP	1.89×10^{5}
	ωB97XD	1.09×10^{5}		ωB97XD	1.58×10^{5}
$\mathbf{2}^{+}$	CAM-B3LYP	4.75×10^{3}	$\mathbf{4}^{+}$	CAM-B3LYP	3.12×10^{3}
	ωB97XD	5.54×10^{3}		ωB97XD	2.92×10^{3}
2	CAM-B3LYP	1.53×10^{3}	**4**	CAM-B3LYP	1.02×10^{3}
	ωB97XD	1.57×10^{3}		ωB97XD	8.36×10^{2}
$\mathbf{2}^{-}$	CAM-B3LYP	9.15×10^{3}	$\mathbf{4}^{-}$	CAM-B3LYP	5.36×10^{5}
	ωB97XD	6.52×10^{3}		ωB97XD	1.05×10^{5}