Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A DFT study on second-order nonlinear optical properties of Ru (II) polypyridine complexes

Yu Chen, Yuan Zhang, Yang Shen, Yuanyuan Zhao,[1] and Yong-Qing Qiu[2]

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

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

General Comments

Fig. S1. Polarizabilities α (a.u.) of all studied complexes calculated by four functionals with 6-31+G(d) basis set.

Fig. S2. Total first hyperpolarizabilities β_{tot} (a.u.) of all studied complexes calculated by four functionals with 6-31+G(d) basis set.

Fig. S3. Plots of $-y\rho_{yy}^{(2)}$ for the neutral complexes **1-10** (yellow color represents positive value, pink color represents negative value, respectively).

Fig. S4. Natural transition orbitals diagrams of complexes 1-10 obtained at the B3LYP/6-31+G(d) level of theory. Red and blue parts correspond to electron depletion and accumulation, respectively.

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

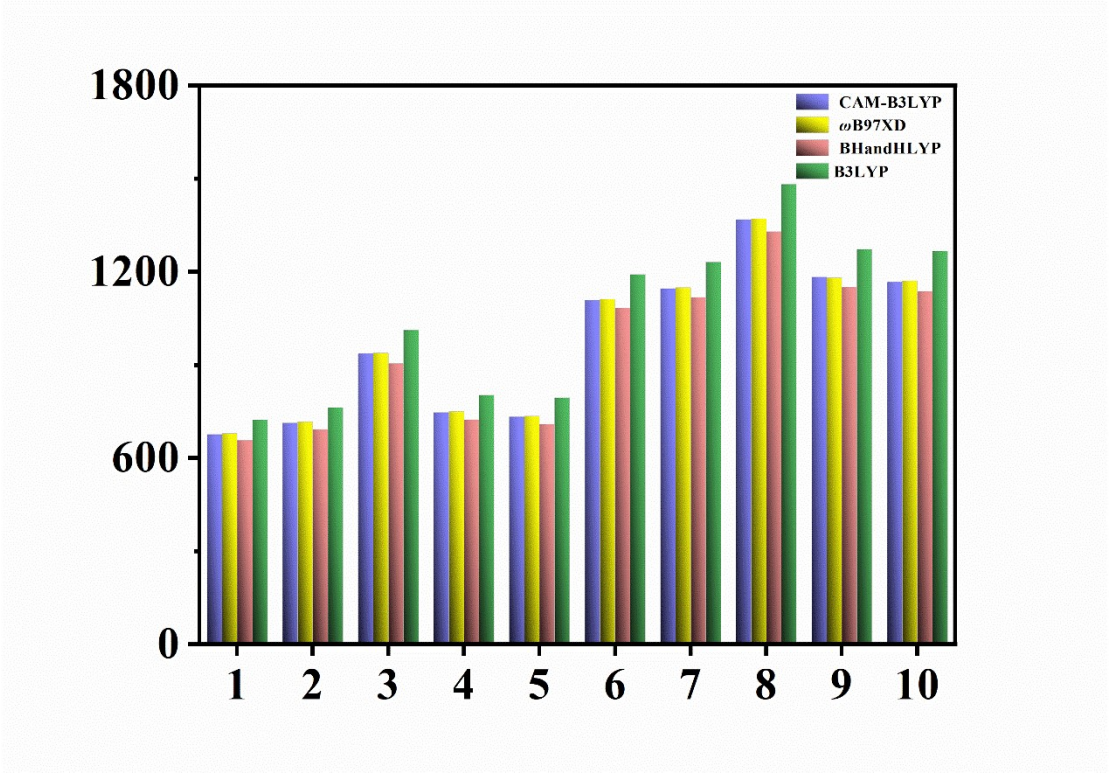


Fig. S1 Polarizabilities α (a.u.) of all studied complexes calculated by four functionals with 6-31+G(d) basis set

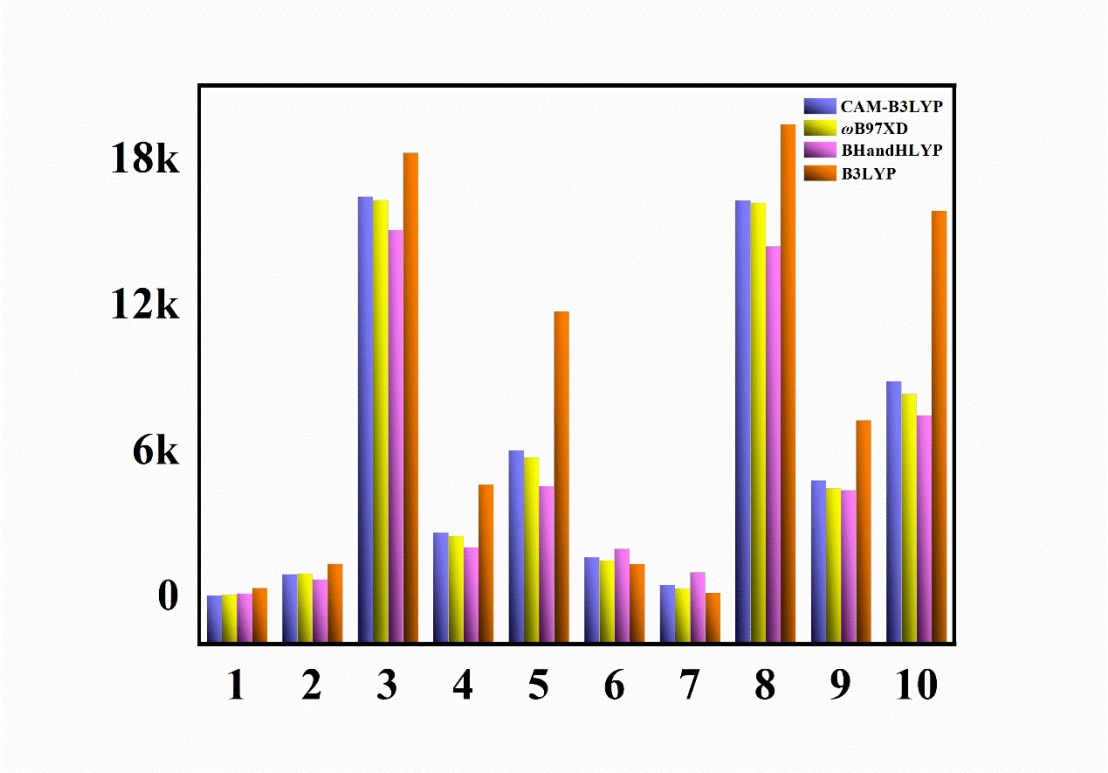


Fig. S2 Total first hyperpolarizabilities β_{tot} (a.u.) of all studied complexes calculated by four functionals with 6-31+G(d) basis set

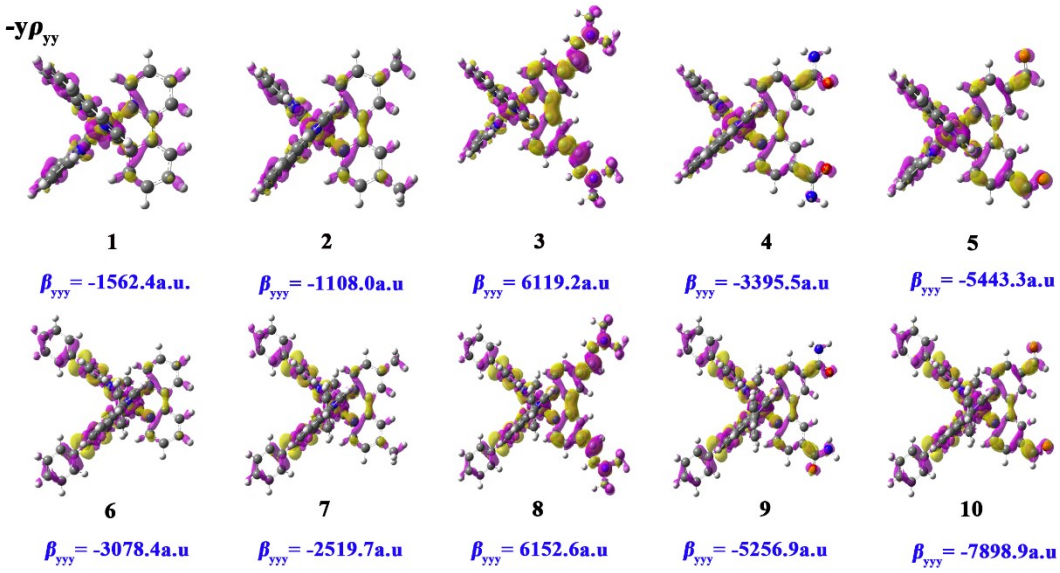
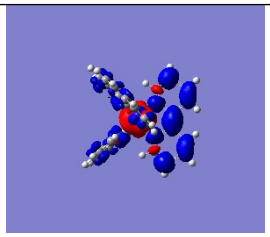
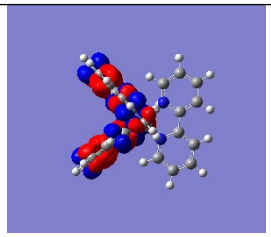
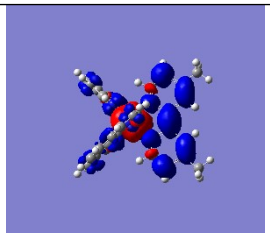
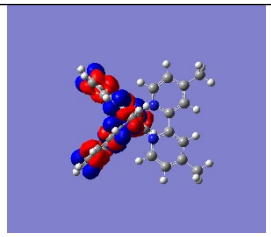
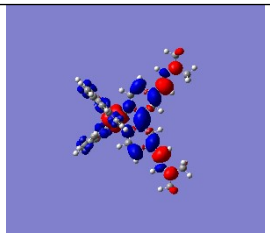
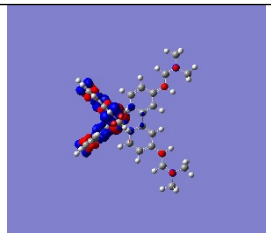
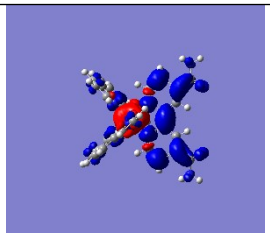
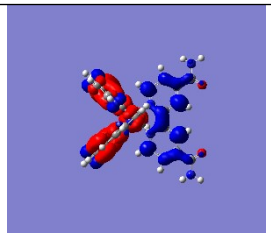
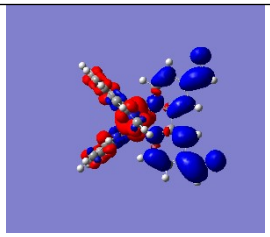
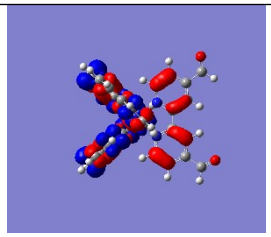
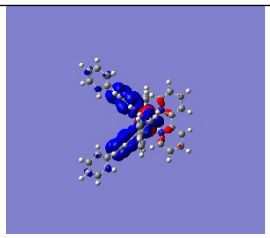
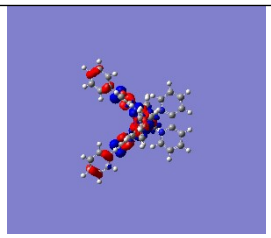
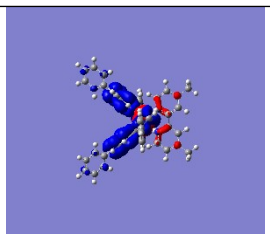
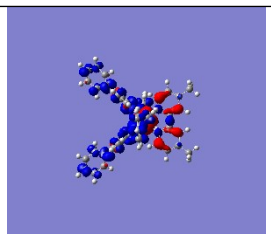


Figure S3 Plots of $-y\rho_{yy}^{(2)}$ for the neutral complexes **1-10** (yellow color represents positive value, pink color represents negative value, respectively).

Transition 1		Transition 2	
1 Weight: L′=0.101 Ru=0.737 L=0.162		Weight: L′=0.023 Ru=0.061 L=0.917	
2 Weight: L′=0.110 Ru=0.729 L=0.161		Weight: L′=0.021 Ru=0.132 L=0.846	
3 Weight: L′=0.615 Ru=0.321 L=0.065		Weight: L′=0.072 Ru=0.264 L=0.663	
4 Weight: L′=0.124 Ru=0.730 L=0.146		Weight: L′=0.065 Ru=0.085 L=0.850	
5 Weight: L′=0.057 Ru=0.688 L=0.255		Weight: L′=0.197 Ru=0.102 L=0.702	
6 Weight: L′=0.063 Ru=0.759 L=0.178		Weight: L′=0.034 Ru=0.028 L=0.945	
7 Weight: L′=0.076 Ru=0.750 L=0.174		Weight: L′=0.212 Ru=0.499 L=0.288	

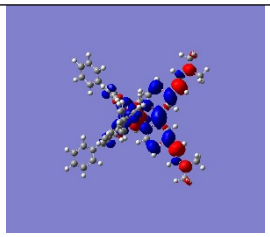
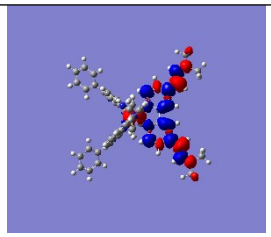
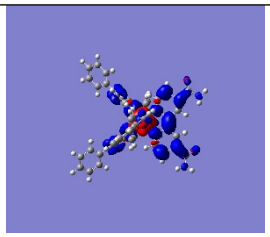
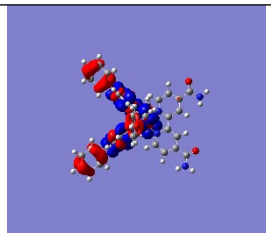
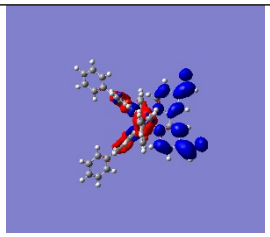
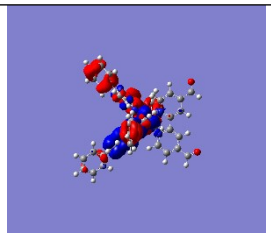
8 Weight: L′=0.504 Ru=0.388 L=0.107		Weight: L′=0.704 Ru=0.252 L=0.044	
9 Weight: L′=0.096 Ru=0.682 L=0.223		Weight: L′=0.020 Ru=0.105 L=0.876	
10 Weight: L′=0.059 Ru=0.606 L=0.335		Weight: L′=0.025 Ru=0.218 L=0.757	

Fig. S4. Natural transition orbitals diagrams of complexes 1-10 obtained at the B3LYP/6-31+G(d) level of theory. Red and blue parts correspond to electron depletion and accumulation, respectively.

Computational detail:

"The magnitude of charge transfer(q^{CT}) is calculated as,

$$q^{CT} = \int \rho_{+}(r)dr = \int \rho_{-}(r)dr$$

Where ρ_{+} and ρ_{-} represent an increase and a decrease of the density in space resulting from the electronic transition.

And the length of charge shift (d^{CT}) is thus defined as the distance separating between the starting and ending points of transfer,

$$d^{CT} = \left| r_{+} - r_{-} \right|$$

where r_{+} and r_{-} are defined as

$$r_{+} = (x_{+}, y_{+}, z_{+}) = \frac{1}{q^{CT}} \int r \rho_{+}(r)dr$$

$$r_{-} = (x_{-}, y_{-}, z_{-}) = \frac{1}{q^{CT}} \int r \rho_{-}(r)dr$$

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

Complex	Ru-N_1	Ru-N_2	Ru-N_3	Ru-N_4	Ru-N_5	Ru-N_6	∠N_5-Ru-N_6	∠N_3-Ru-N_4	$\Delta r_{Ru\text{-}N}$
1[a]	2.071	2.054	2.073	2.069	2.065	2.058	78.6	80.0	
1^{PBE1PBE}	2.086	2.082	2.086	2.083	2.073	2.073	78.4	79.3	0.013
1^{B3LYP}	2.115	2.111	2.115	2.115	2.101	2.101	78.8	78.8	0.023
1$^{\omega B97XD}$	2.107	2.100	2.107	2.100	2.090	2.090	78.2	79.0	0.034
2[a]	2.072	2.070	2.060	2.078	2.062	2.058	78.8	79.5	
2	2.082	2.085	2.085	2.081	2.074	2.074	78.2	79.3	
3	2.075	2.084	2.084	2.075	2.074	2.074	78.0	79.3	
4	2.073	2.073	2.077	2.077	2.077	2.077	78.6	79.2	
5	2.086	2.088	2.087	2.085	2.067	2.068	79.2	78.7	
6	2.075	2.075	2.071	2.076	2.076	2.071	78.4	78.8	
7	2.078	2.079	2.071	2.071	2.079	2.078	78.1	78.8	
8	2.083	2.086	2.086	2.083	2.071	2.072	78.8	78.8	
9	2.068	2.068	2.078	2.078	2.078	2.080	78.5	78.7	
10	2.081	2.080	2.080	2.080	2.063	2.064	78.7	78.7	

Note: The a denotes as the experimental values that are from Ref. 42.