

Supplementary Information

Redox-triggered Switch Based on Platinum(II) Acetylacetonate Complexes Bearing the Isomeric Donor–Acceptor Conjugation Ligand Showing High Second-Order Nonlinear Optical Response

Yuan Zhang, Hongqiang Wang, Jinting Ye, Yongqing Qiu *

Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal
University, Changchun 130024, People's Republic of China

* Corresponding Author. Fax: +86 431 85098768.
E-mail addresses: qiuyq466@nenu.edu.cn (Y. Q. Qiu).

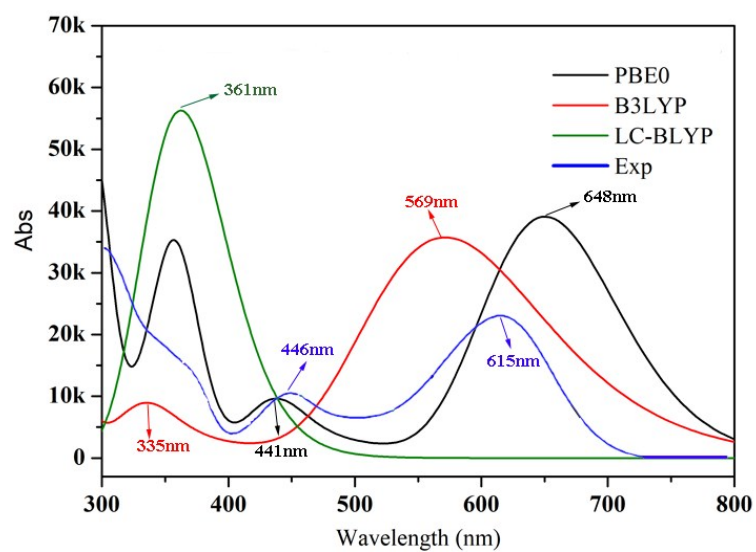


Figure S1. Simulated absorption spectrum of complex **2** at various levels of theory and experiment.

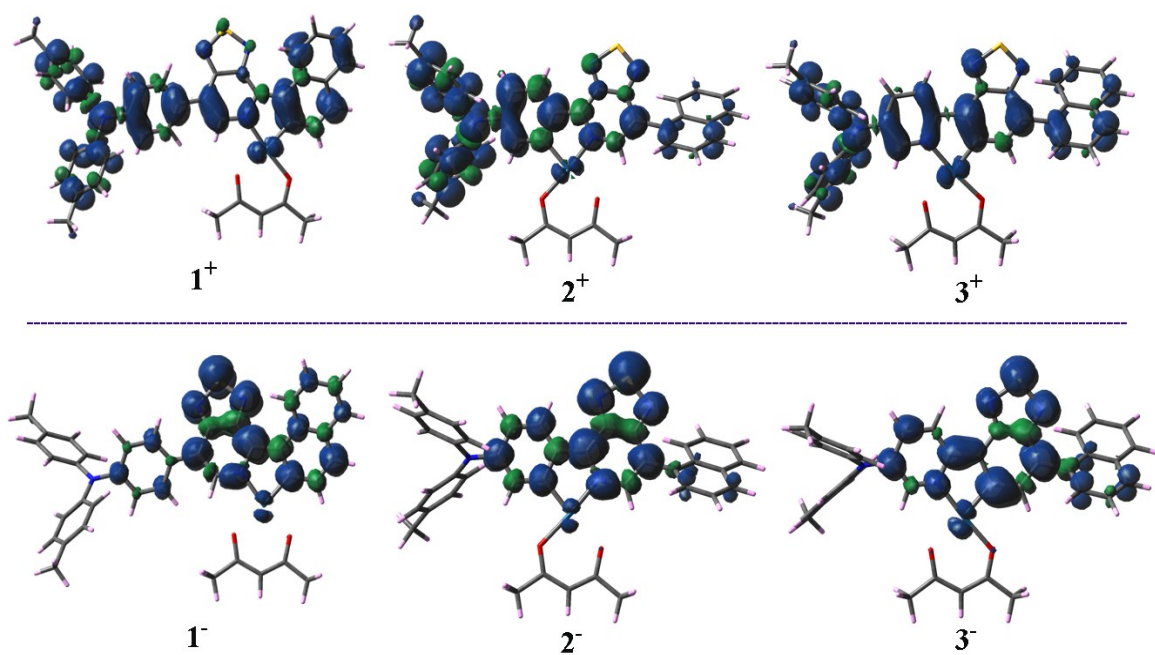


Figure S2. Mulliken spin populations of redox species.

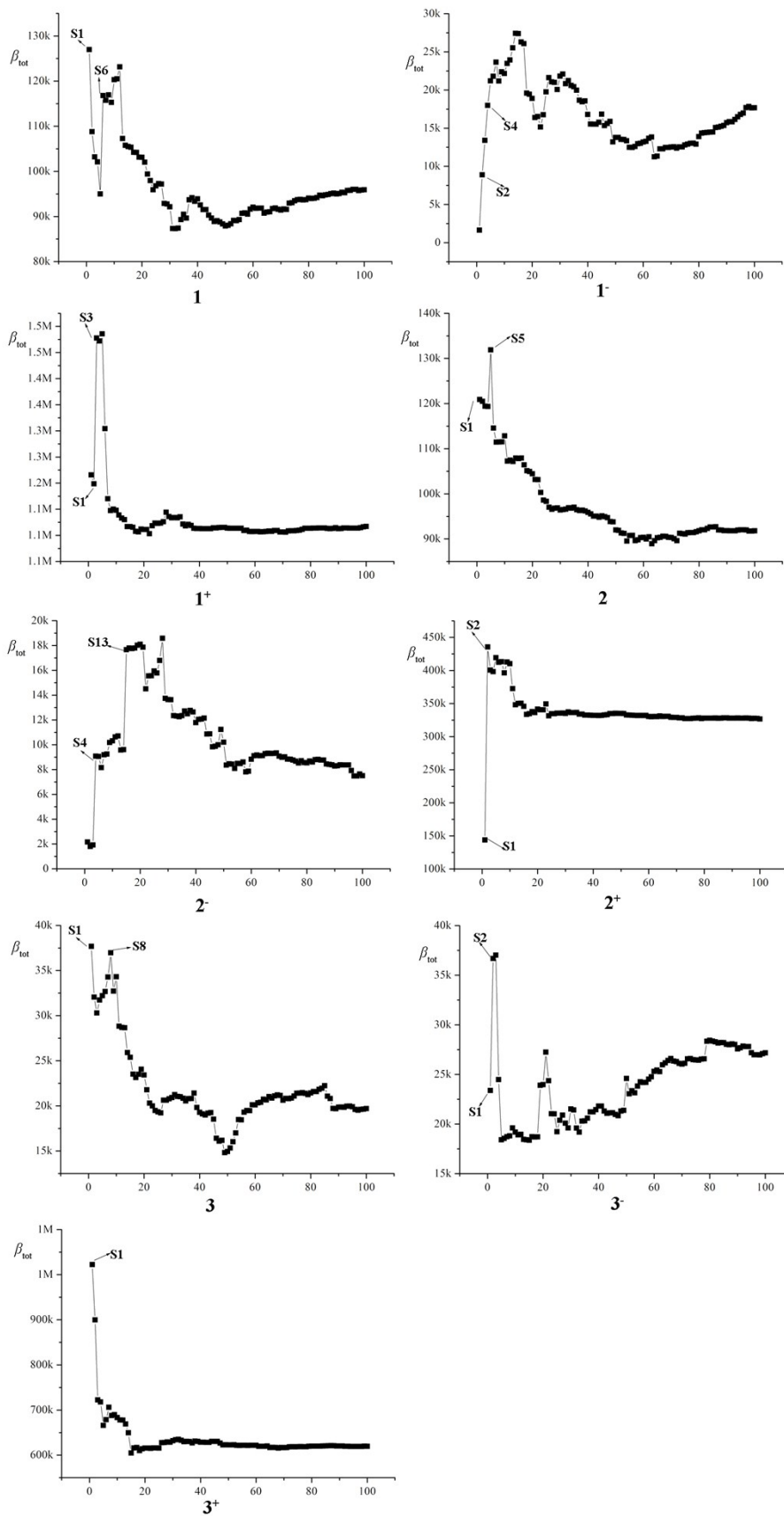


Figure S3. Convergent behavior of β_{tot} value of all complexes dependent on the 100 states.

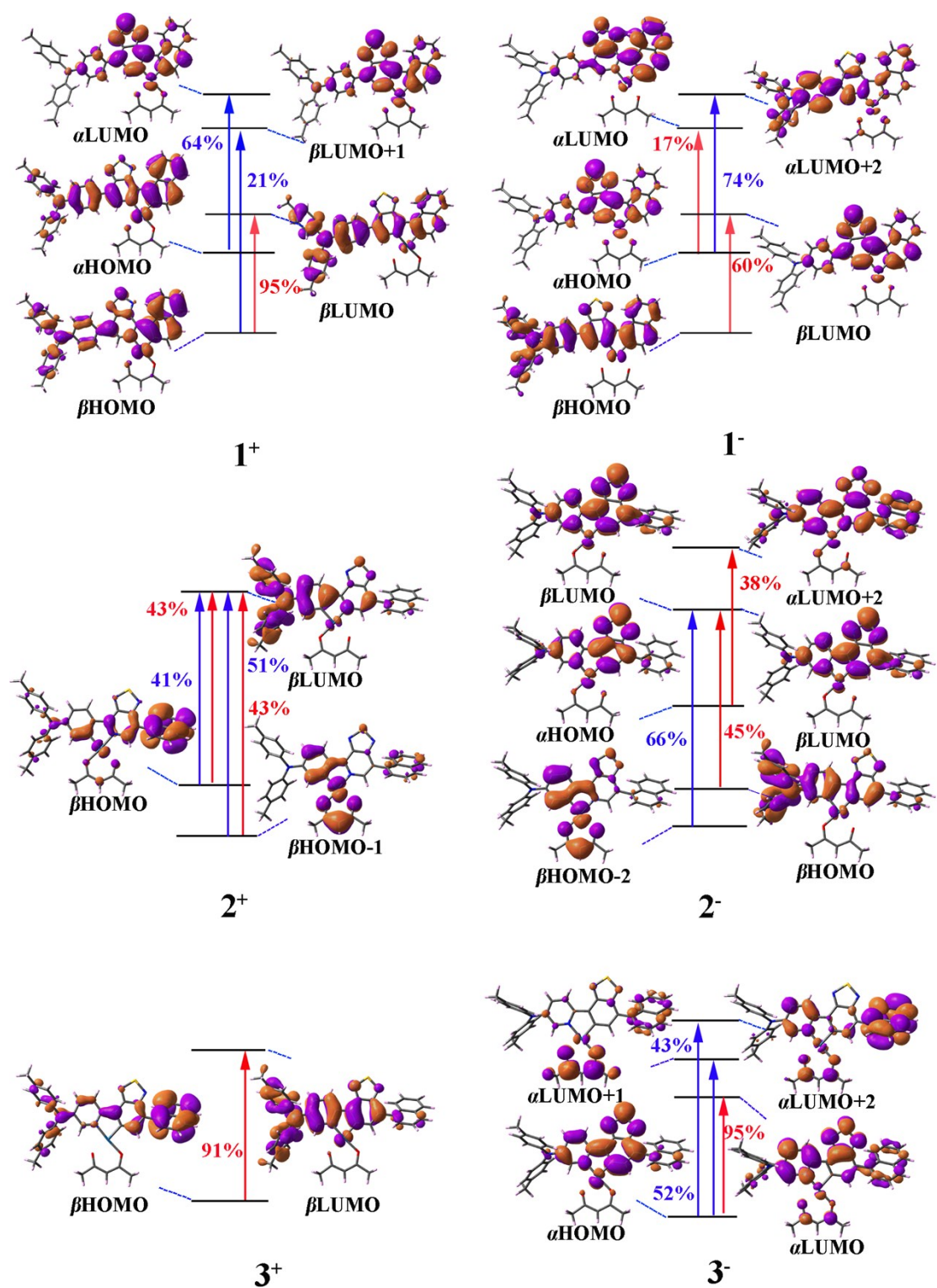


Figure S4. The molecular orbitals involved in the main excited states that contribute to the β_{tot} values for both reduced and oxide species.

Table S1. The calculated square of total spin and relative eigenvalue for all of oxidized and reduced complexes.

| Complex | charge | Spin multiplicity | $\langle S^2 \rangle$ | eigenvalue |
|----------|--------|-------------------|-----------------------|------------|
| 1 | 1 | 2 | 0.765 | 0.75 |
| | -1 | 2 | 0.768 | 0.75 |
| 2 | 1 | 2 | 0.774 | 0.75 |
| | -1 | 2 | 0.765 | 0.75 |
| 3 | 1 | 2 | 0.760 | 0.75 |
| | -1 | 2 | 0.761 | 0.75 |

Table S2. Tensorial components of α (10^{-24} esu), the electronic spatial extent $\langle R^2 \rangle$ (10^3 a.u.) and total first hyperpolarizability (10^{-29} esu) of complex **1-3** calculated by the 6-31+G(d) basis set using various functionals.

| Complex | functional | β_{tot} | α_{xx} | α_{yy} | α_{zz} | α | $\langle R^2 \rangle$ |
|----------|----------------|----------------------|---------------|---------------|---------------|----------|-----------------------|
| 1 | ω B97XD | 14.5 | 68.8 | 171.5 | 140.6 | 127.1 | 47.3 |
| | LC-BLYP | 7.4 | 66.8 | 157.2 | 132.2 | 118.7 | |
| | BHandHLYP | 22.5 | 67.6 | 174.1 | 136.8 | 126.2 | |
| 2 | ω B97XD | 32.9 | 85.8 | 168.6 | 123.5 | 126.0 | 42.0 |
| | LC-BLYP | 24.5 | 83.1 | 155.7 | 115.6 | 118.1 | |
| | BHandHLYP | 40.8 | 84.7 | 170.1 | 120.5 | 125.1 | |
| 3 | ω B97XD | 5.5 | 87.1 | 149.7 | 122.5 | 119.8 | 41.2 |
| | LC-BLYP | 3.4 | 84.2 | 139.2 | 115.7 | 113.1 | |
| | BHandHLYP | 6.9 | 85.8 | 148.3 | 119.3 | 117.8 | |

Table S3. The first hyperpolarizability (10^{-29} esu) of all neutral complexes computed by ω B97XD functional with various basis sets.

| basis set | 1 | 2 | 3 |
|------------|----------|----------|----------|
| 6-31G(d) | 13.9 | 32.1 | 4.7 |
| 6-31+G(d) | 14.5 | 32.9 | 5.5 |
| 6-311+G(d) | 14.2 | 32.5 | 5.3 |
| 6-311G(d) | 13.7 | 31.4 | 4.8 |