

## **Supporting Information**

### **Theoretical insight into photophysical properties of long lifetime Ir(III) and Rh(III) complexes for two-photon photodynamic therapy**

Xue Yin, Xiao-Yong Lai, Xin Wang\*, Ying-Tao Liu\*

State key laboratory of High-efficiency coal utilization and Green Chemical Engineering,  
College of Chemistry Chemical Engineering, Ningxia University,  
Yinchuan 750021, China,

(Dated: March 8 2019)

Table S-1 The one-photon maximum absorption wavelengths, strongest absorption wavelengths, transition energy, oscillator strength ( $f$ ) and the experimental values of complex  $[\text{Ir}(\text{N}^{\wedge}\text{C})_2(\text{N}^{\wedge}\text{N})]^+$  in  $\text{CH}_2\text{Cl}_2$  solvent by Gaussian 16 program.

| Functional        | Wavelength (nm) | $f$    | Excitation energy (eV) |
|-------------------|-----------------|--------|------------------------|
| TPSSh             | 534.5           | 0.0002 | 2.32                   |
|                   | 337.3           | 0.5730 | 3.68                   |
| B3LYP             | 486.6           | 0.0003 | 2.55                   |
|                   | 328.5           | 0.5324 | 3.77                   |
| M06               | 466.8           | 0.0003 | 2.66                   |
|                   | 330.2           | 0.5372 | 3.76                   |
| PBE0              | 452.5           | 0.0005 | 2.74                   |
|                   | 258.2           | 0.3306 | 4.80                   |
| M06-2X            | 335.9           | 0.0060 | 3.69                   |
|                   | 311.7           | 0.6746 | 3.98                   |
| Exp. <sup>1</sup> | 468.0           | -      | 2.65                   |
|                   | 260.0           | -      | 4.77                   |

1. L. K. McKenzie, I. V. Sazanovich, E. Baggaley, M. Bonneau, V. Guerchais, J. A. G. Williams, J. A. Weinstein and H. E. Bryant, *Chemistry-a European Journal*, 2017, **23**, 234-238.

Table S-2 The maximum absorption wavelengths transition energy and oscillator strength ( $f$ ) of complex  $[\text{Rh}(\text{N}^{\wedge}\text{C})_2(\text{N}^{\wedge}\text{N})]^+$  in  $\text{CH}_2\text{Cl}_2$  solvent by Gaussian 16 program. (Here, the experimental value of maximum absorption wavelength is complex  $[\text{Rh}(\text{phpy})_2(\text{CN}_2)]^-$ , which has the similar structure to complex  $[\text{Rh}(\text{N}^{\wedge}\text{C})_2(\text{N}^{\wedge}\text{N})]^+$ ).

| Functional        | Wavelength (nm) | $f$    | Excitation energy (eV) |
|-------------------|-----------------|--------|------------------------|
| TPSSh             | 471             | 0.0003 | 2.63                   |
| B3LYP             | 426             | 0.0004 | 2.91                   |
| M06               | 416.2           | 0.0001 | 2.98                   |
| PBE0              | 397.8           | 0.0007 | 3.12                   |
| M06-2X            | 327.1           |        | 3.79                   |
| Exp. <sup>2</sup> | 363.0           |        | 3.41                   |

[2] H. Kunkely and A. Vogler, *Chemical Physics Letters*, 2000, **319**, 486-488.

Table S-3 Partial molecular orbital (MO) energy ( $E$  in eV) and compositions (%) in  $S_0$  state of complexes

$[\text{Ir}(\text{N}^{\wedge}\text{C})_2(\text{N}^{\wedge}\text{N})]^+$  and  $[\text{Rh}(\text{N}^{\wedge}\text{C})_2(\text{N}^{\wedge}\text{N})]^+$  in  $\text{CH}_2\text{Cl}_2$  solution.

|   | State | MO     | $E$ (eV) | Main Contribution (%) |                             |                             | Assignment   |
|---|-------|--------|----------|-----------------------|-----------------------------|-----------------------------|--|
|   |       |        |          | M                     | $\text{N}^{\wedge}\text{C}$ | $\text{N}^{\wedge}\text{N}$ |  |
| $[\text{Ir}(\text{N}^{\wedge}\text{C})_2(\text{N}^{\wedge}\text{N})]^+$ | $S_0$ | LUMO+4 | -1.11    | 7                     | 91                          |                             | $d(\text{Ir})+\pi^*(\text{N}^{\wedge}\text{C})$                              |
|   |       | LUMO+1 | -1.78    | 6                     | 91                          |                             | $d(\text{Ir})+\pi^*(\text{N}^{\wedge}\text{C})$                              |
|   |       | LUMO   | -2.44    |                       |                             | 95                          | $\pi^*(\text{N}^{\wedge}\text{N})$   |
|   |       | HOMO   | -6.03    | 47                    | 50                          |                             | $d(\text{Ir})+\pi(\text{N}^{\wedge}\text{C})$                                |
|   |       | HOMO-1 | -6.69    | 15                    | 80                          |                             | $d(\text{Ir})+\pi(\text{N}^{\wedge}\text{C})$                                |
|   |       | HOMO-2 | -6.69    | 45                    | 12                          | 44                          | $d(\text{Ir})+\pi(\text{N}^{\wedge}\text{C})+\pi(\text{N}^{\wedge}\text{N})$ |
|   |       | HOMO-3 | -6.85    | 50                    | 28                          | 22                          | $d(\text{Ir})+\pi(\text{N}^{\wedge}\text{C})+\pi(\text{N}^{\wedge}\text{N})$ |
|   |       | HOMO-6 | -7.12    | 26                    | 17                          | 57                          | $d(\text{Ir})+\pi(\text{N}^{\wedge}\text{C})+\pi(\text{N}^{\wedge}\text{N})$ |
| $[\text{Rh}(\text{N}^{\wedge}\text{C})_2(\text{N}^{\wedge}\text{N})]^+$ | $S_0$ | LUMO+1 | -1.78    | 6                     | 92                          |                             | $d(\text{Ir})+\pi^*(\text{N}^{\wedge}\text{C})$                              |
|   |       | LUMO   | -2.37    |                       |                             | 96                          | $\pi^*(\text{N}^{\wedge}\text{N})$   |

|        |       |    |    |    |                    |
|--------|-------|----|----|----|--------------------|
| HOMO   | -6.31 | 44 | 53 |    | d(Rh)+ $\pi$ (N^N) |
| HOMO-1 | -6.72 |    | 93 |    | $\pi$ (N^C)        |
| HOMO-2 | -6.79 | 14 |    | 84 | d(Ir)+ $\pi$ (N^N) |

Table S-4 Partial molecular orbital (MO) energy ( $E$  in eV) and compositions (%) in  $T_1$  states of complexes  $[\text{Ir}(\text{N}^{\text{C}})_2(\text{N}^{\text{N}})]^+$  and  $[\text{Rh}(\text{N}^{\text{C}})_2(\text{N}^{\text{N}})]^+$  in  $\text{CH}_2\text{Cl}_2$  solution.

|   | State | MO     | $E$ (eV) | Main Contribution (%) |     |     | Assignment                      |
|---|-------|--------|----------|-----------------------|-----|-----|---------------------------------|
|   |       |        |          | M                     | N^C | N^N |                                 |
| $[\text{Ir}(\text{N}^{\text{C}})_2(\text{N}^{\text{N}})]^+$ | $T_1$ | LUMO   | -2.89    |                       |     | 95  | $\pi^*(\text{N}^{\text{N}})$    |
|   |       | HOMO   | -6.06    | 47                    | 49  |     | d(Ir)+ $\pi$ (N^C)              |
|   |       | HOMO-1 | -6.55    | 27                    | 7   | 66  | d(Ir)+ $\pi$ (N^C)+ $\pi$ (N^N) |
| $[\text{Rh}(\text{N}^{\text{C}})_2(\text{N}^{\text{N}})]^+$ | $T_1$ | LUMO   | -2.84    |                       |     | 96  | $\pi^*(\text{N}^{\text{N}})$    |
|   |       | HOMO   | -6.33    | 43                    | 52  |     | $\pi$ (N^C)+ $\pi$ (N^N)        |
|   |       | HOMO-1 | -6.46    | 10                    |     | 86  | d(Rh)+ $\pi$ (N^N)              |

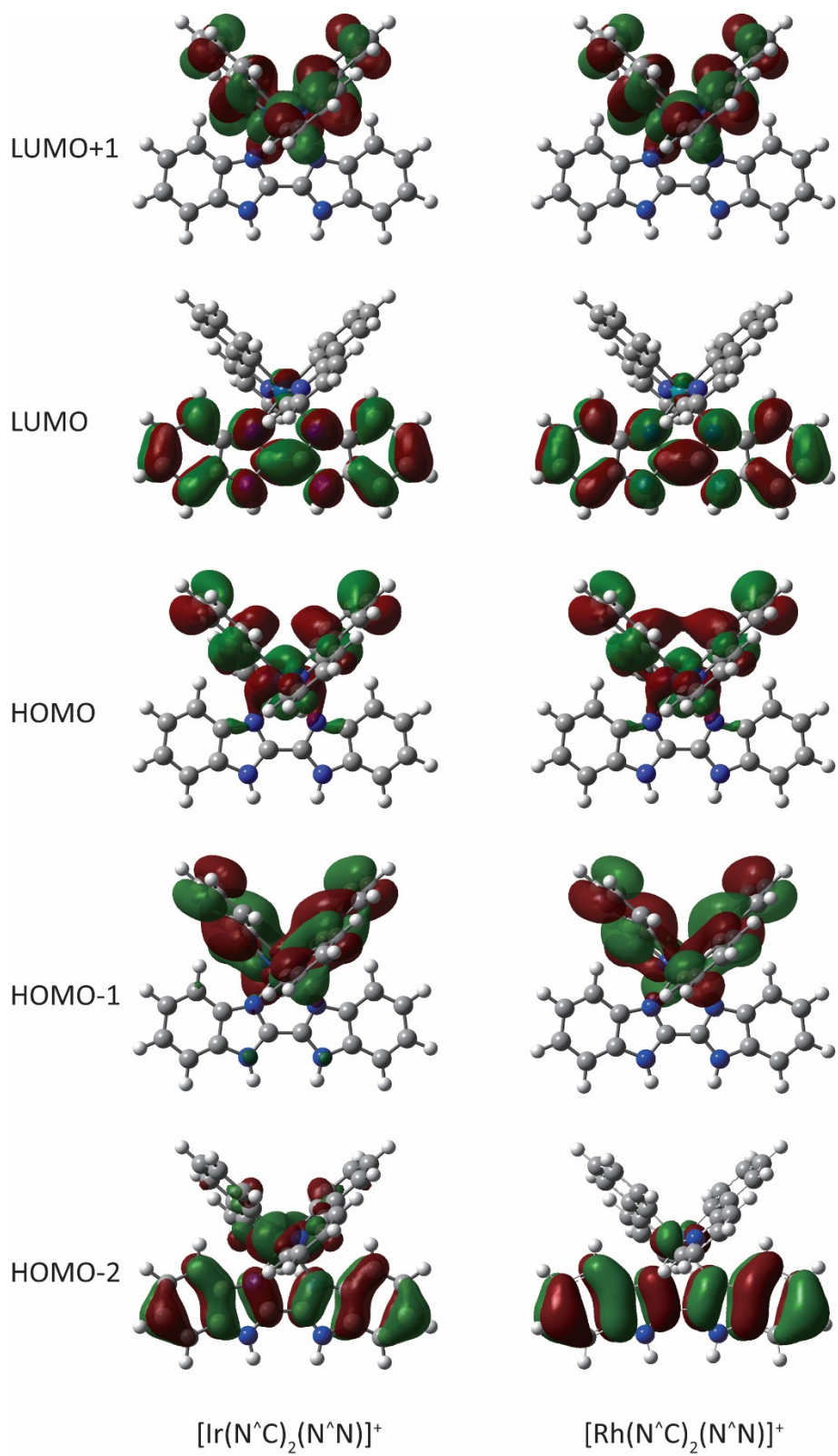


Fig. S-1 The frontier molecular orbital maps of two complexes in  $S_0$  state.