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

Supporting Information

for

Regulating Ancillary Ligands of Ru(II) Complex with Square-Planar Quadridentate Ligand for More Efficient Sensitizers in Dye-sensitized Solar Cells: Insights from Theoretical Investigations

Teng-Fei Lu, Wei Li, Jie Chen*, Fu-Quan Bai, Jian Wang, Ling-Jun He, Hong-Xing Zhang*

International Joint Research Laboratory of Nano-Micro Architecture Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun, 130023, People's Republic of China

*Corresponding author, email:

zhanghx@jlu.edu.cn (Hong-Xing ZHANG)

drjchen09@gmail.com (Jie CHEN)

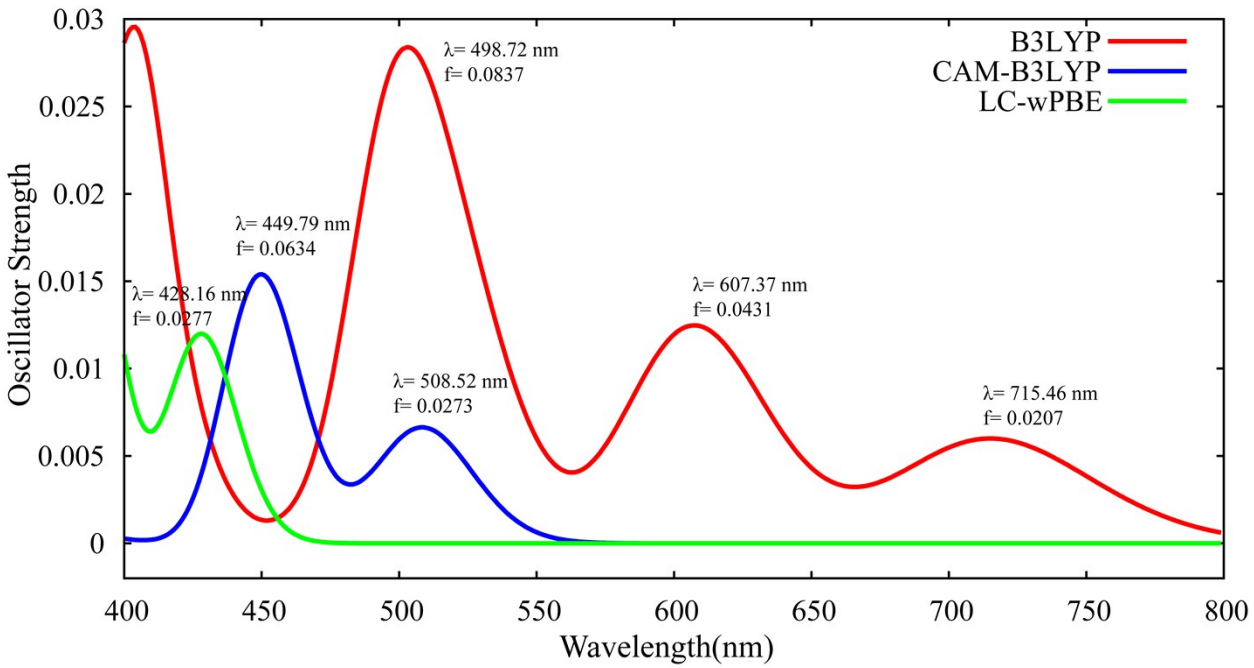

Figure S1. Calculated absorption spectra for dye **K1** using different functionals dissolved in DMF solvent.

Table S1. Comparisons of the geometrical parameters between dyes **K1**, **Ru1**, **Ru2**, and **Ru3**. Bond lengths are in angstrom (Å), and angles are in degree (°).

	K1	**Ru1**	**Ru2**	**Ru3**
dRu-N_1	2.129	2.162	2.188	2.068
dRu-N_2	2.129	2.153	2.188	2.068
dRu-N_3	2.041	2.058	1.982	2.032
dRu-N_4	2.041	2.063	1.982	2.032
θRu-N_5-S_1	170. 8	169.2	163.3	167.4
θRu-N_6-S_2	170. 9	171.2	163.3	167.4
θN_1-Ru-N_2	99.8	96.6	108.1	97.7
θN_2-Ru-N_3	89.7	91.9	86.2	90.3
θN_3-Ru-N_4	82.1	80.6	79.9	83.0
θN_1-Ru-N_4	89.7	92.3	86.2	90.3
θN_1-N_2-N_3-N_4	12.6	13.9	7.8	13.0

Theoretical backgrounds for quantum dynamics simulation

Below we briefly summarized the implementation of quantum dynamics. The more detailed description can be found in (*Modelling Electron Quantum Dynamics in Large Molecular Systems*; RSC Publishing: London, 2013.)

The procedure for quantum propagation of the photo-excited electron: the time-evolved wave function $|\phi_i\rangle$ can be written as a liner combination of atomic orbitals:

$$|\phi(t)\rangle = \sum_{i,\alpha} B_{i,\alpha}(t)|i,\alpha\rangle \qquad (1)$$

where $|i,\alpha\rangle$ represents the atomic orbital α of atom *i*. The expansion coefficients $|B_{i,\alpha}(t)\rangle$, introduced in eq 5, are computed according to:

$$B_{i,\alpha}(t) = \sum_q Q^q_{i,\alpha} C_q \exp\left(-\frac{i}{\hbar} E_q t\right) \qquad (2)$$

after solving the generalized eigenvalue equation,

$$HQ^q = E_q S Q^q \qquad (3)$$

Where *H* is the EH matrix and *S* is the overlap matrix in the atomic orbital basis. The coefficients C_q, introduced in eq 6, are defined by the expansion of the initial state in the orthonormal basis set of eigenvectors $|q\rangle$,

$$|\phi(0)\rangle = \sum_q C_q |q\rangle \qquad (4)$$

The coefficients $Q^q_{i,\alpha}$, introduced in eq 6, are defined according to the expansion of the eigenvectors $|q\rangle$ as a linear combination of atomic orbitals,

$$|q\rangle = \sum_{i,\alpha} Q^q_{i,\alpha} |i,\alpha\rangle \qquad (5)$$

The projection of the time-evolved electronic wave function onto the atomic orbitals of the molecular adsorbate is, therefore, obtained according to the equation,

$$P(t) = \left| \sum_{i,\alpha}^{MOL} \sum_{i,\beta} B^*_{i,\alpha}(t) B_{j,\beta}(t) S^{i,j}_{\alpha,\beta} \right| \qquad (6)$$

Here $S^{i,j}_{\alpha,\beta} = \langle i,\alpha | j,\beta \rangle$, where the indices α and β label specific orbitals in atoms *i* and *j*, respectively. Note that the sum over *j* includes all of the atoms in the nanostructure, whereas the sum over *i* includes only atoms in the initially excited molecular adsorbate. Population is the survival probability of photo-excited electron is still in the adsorbate molecule at time *t* after the excitation of the system.