

## Theoretical Studies on the Excited-state Properties of Ru(II) Polypyridyl Complexes (Postprint)

**Authors:** ZHANG Jian-Fu, MIAO Ti-Fang, ZHANG Zhi-Qiang, LI Shuang, LUO Yao

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### Abstract

Using DFT/TDDFT methods, the excited-state lifetimes of Ru(II) polypyridyl complexes were accurately computed, and the origin of the long excited-state lifetimes in these complexes was elucidated through electron-transfer distances and HOMO-LUMO gaps. Furthermore, the photovoltaic conversion efficiencies of these complexes were predicted using DFT and docking methods. This study provides methodologies for predicting the excited-state lifetimes and photovoltaic conversion efficiencies of Ru(II) polypyridyl complexes.

### Full Text

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**ZHANG Jian-Fu<sup>1</sup>, MIAO Ti-Fang<sup>2</sup>, ZHANG Zhi-Qiang<sup>3</sup>, LI Shuang<sup>2</sup>, LUO Yao<sup>2</sup>**

<sup>1</sup>School of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou 466001, China

<sup>2</sup>School of Chemistry and Materials Science, Huaibei Normal University, Huaibei 235000, China

<sup>3</sup>Department of Material and Chemical Engineering, Zhengzhou Institute of Light Industry, Zhengzhou 450002, China

### ABSTRACT

Using DFT/TDDFT methods, the excited-state lifetimes of Ru(II) polypyridyl complexes were computed accurately, and the origin of their long excited-state lifetimes was explained through electron-transfer distances and HOMO-LUMO gaps. Finally, the photovoltaic conversion efficiencies of the complexes were

predicted using DFT and docking methods. This work provides methods for predicting the excited-state lifetimes and photovoltaic conversion efficiencies of Ru(II) polypyridyl complexes.

**Keywords:** Ru(II) complexes; excited-state lifetimes; DFT; docking model

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## 1. INTRODUCTION

Owing to their excellent photophysical and photochemical properties, Ru(II) polypyridyl complexes have attracted considerable attention for important applications such as photochemical conversion of solar energy, DNA photocleavage reagents, and molecular “light switches” [1–4]. For example, Ru(II) polypyridyl complexes can effectively cleave DNA under light irradiation, with the DNA damage attributed to the generation of singlet oxygen ( $^1\text{O}$ ) [5], which is usually related to the quantum yield [6, 7]. Additionally, many Ru(II) polypyridyl complexes emit strong fluorescence, where their excited-state lifetimes play a crucial role in determining the quantum yield. Consequently, studies on excited-state lifetimes have become a hot topic and are widely explored experimentally. Research results [8–10] show that emission intensity relates to the excited-state lifetimes of complexes, which are typically dominated by metal-centered (MC) states and metal-to-ligand charge transfer (MLCT) states. However, these states are difficult to determine experimentally. If MC and MLCT states of complexes can be obtained theoretically, the results would be of great significance for predicting emission intensity and guiding the design of novel luminescent complexes.

In this work, we selected five experimentally reported Ru(II) polypyridyl complexes [11] (1–5), namely  $[\text{Ru}(\text{tpy}-\text{PhCH})]^{2+}$ ,  $[\text{Ru}(\text{tpy})]^{2+}$ ,  $[\text{Ru}(\text{H pbbzim})]^{2+}$ ,  $[\text{Ru}(\text{tpy}-\text{HImzphen})]^{2+}$ , and  $[(\text{tpy}-\text{PhCH})\text{Ru}(\text{tpy}-\text{HImzphen})]^{2+}$  (structural diagrams are shown in Fig. 1 [Figure 1: see original paper]), to perform a theoretical study using density functional theory (DFT) and time-dependent DFT (TDDFT) methods [12–15]. Additionally, as is well known, many Ru(II) polypyridyl complexes can be widely used in dye-sensitized solar cells (DSSCs). To predict the photovoltaic conversion properties of these complexes, their excited-state properties were also explored [16, 17]. We hope that this work lays a theoretical foundation for designing and synthesizing novel complexes with improved luminescence properties.

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(No. 201510373083). Corresponding author. E-mail: miaotifang@163.com (T. F. Miao)

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## 2. THEORY AND COMPUTATIONAL METHODS

### 2.1 Computations of the Excited-state Lifetimes

Full geometry optimization of complexes 1-5 in the ground state was carried out using the restricted B3LYP method with the LanL2DZ basis set [18, 19] for the Ru atom and the 6-31G(d) basis set for all other atoms. For the obtained structures, frequency calculations were also performed using the same method to verify that the optimized structures correspond to energy minima. To obtain energies of MLCT and MC states, 240 singlet-excited-state energies of these complexes were calculated based on the optimized ground-state geometries using the TDDFT method at the same level of theory.

Many Ru(II) complexes can be excited under light irradiation, and their excited-state lifetimes are governed by the nonradiative decay rate constant  $k$ , given by [8, 9]:

$$k_{nr} = k_{nr} + k'_{nr} \quad (1)$$

where the overall radiationless decay  $k$  is the sum of  $k$  and  $k'$ . Specifically,  $k$  leads directly from the MLCT state to the ground state, whereas  $k'$  is related to a thermally activated process that involves surface-crossing to a low-lying metal-centered (MC) level, and thus depends on the energy gap  $\Delta E$  between MLCT and MC states.

The excited-state lifetimes ( $\tau$ ) of complexes can be obtained from the reciprocal of Eq. 1, expressed as:

$$\tau = 1/(k_{nr} + k'_{nr}) \quad (2)$$

The rate constant  $k$  ( $k$  and  $k'$ ) can be obtained by Eq. 3, where  $A$  is the frequency factor,  $T$  is the temperature, and  $E$  is the free activation energy. The frequency factor  $A$  can be obtained by the following equation, where  $d$  is the diameter of the complex,  $L$  is the Avogadro constant,  $T$  is the temperature, and  $M$  is the molar mass of the complex. The excited-state lifetimes were obtained via Eqs. 2-4.

### 2.2 Computations of Photovoltaic Conversion Properties

The optimized structures of these complexes were docked with two TiO molecules using the Dock6.0 program [20]. The box size, grid space, energy cutoff distance, and maximum orientation were set to 20, 0.3, 9999 Å, and

200,000, respectively, while all other parameters used default values. Two distinct docking approaches exist: rigid docking and flexible docking. In rigid docking, which is based on receptor spheres generated by the SPHGEN module as well as the heavy atom centers of the ligand, the ligand is docked rigidly to the receptor. In flexible docking, which employs an anchor-and-growing algorithm, the ligand is docked flexibly to the receptor. Here, using the rigid docking method, the docking models (complex-TiO) were obtained. To accurately compute the electron-transfer properties between the Ru(II) complexes and TiO, further optimization of the obtained docking models in the ground state was carried out using the CAM-B3LYP method with the LanL2DZ basis set [18, 19] for the Ru atom and the 6-31G(d) basis set for all other atoms. The optimized results are shown in Fig. 2 [Figure 2: see original paper]. Frequency calculations were also performed to verify that the optimized docking models correspond to energy minima. Additionally, to obtain the excited-state properties of the docking models, optimization of the docking models in the lowest triplet/singlet states was also performed at the same level of theory.

All calculations were performed using the Gaussian09 program package [21].

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### 3. RESULTS AND DISCUSSION

#### 3.1 Evaluation of Computational Accuracy

Complex 4 was selected for optimization at the B3LYP/LanL2DZ + 6-31G(d) level, as its crystal structure has been determined experimentally. The calculated results for complex 4 and the corresponding X-ray data are listed in Table 1. Comparison of the calculated geometrical parameters of complex 4 with the corresponding X-ray data shows that the DFT method results are in satisfying agreement with the experimental data [11].

Additionally, complexes 4 and 5 were selected for electronic absorption spectra calculations, as their electronic absorption spectra have been determined experimentally. The computed electronic absorption spectra of 4 and 5 are shown in Fig. 3 [Figure 3: see original paper]. The computed maximum absorption bands for complexes 4 and 5 appear at 498.2 nm ( $f = 0.617$ ) and 502.8 nm ( $f = 0.759$ ), respectively, which are in good accordance with the experimental results [11] of 492 and 502 nm. Fig. 3 also shows that the simulated absorption spectra of 4 and 5 agree well with experimental results in terms of both spectral shapes and band positions, further demonstrating the reliability of the DFT method.

#### 3.2 Excited-state Lifetimes of Complexes

The energies of MLCT and MC states in Ru(II) polypyridyl complexes play an important role in determining excited-state lifetimes. To obtain these lifetimes, absorption spectra of complexes 1–5 were computed using the TDDFT method.

The computed energies of MLCT and MC states are given in Table 2, and the excited-state lifetimes calculated via Eqs. 2-4 along with corresponding experimental results are presented in Table 3. The computed values for complexes 1-5 are 4599216.6, 6368.4, 202.6, 66222084.1, and 8752385.3 ns, respectively, which deviate significantly from experimental results. Nevertheless, the general trends are consistent with experimental data [11], i.e.,  $(4) > (5) > (1) > (2) > (3)$ . The main source of error may be that the rate constant  $k$  in Eq. 3 was obtained from classical collision theory without accounting for light irradiation. Based on this consideration, Eq. 3 was revised as follows:

Complex 1 was selected as an example. The experimental value of 5.0 ns was substituted into Eq. 2, yielding  $A' = 920037.6$  via Eqs. 1-5. Using this obtained  $A'$ , the revised values for complexes 2-5 were computed to be 0.07, 0, 71.9, and 9.5 ns, respectively, which are much closer to the experimental results [11] of 0.25, 0, 55.5, and 10.2 ns. Therefore, the frequency factor  $A' = 920037.6$  may be used for computations of excited-state Ru(II) polypyridyl complexes, enabling accurate prediction of their excited-state lifetimes.

### 3.3 Molecular Orbital Analysis

Frontier molecular orbitals play an important role in exploring the relationship between molecular structure and excited-state lifetimes, making it necessary to analyze and discuss their energies and compositions. The highest occupied molecular orbitals (HOMO), lowest unoccupied molecular orbitals (LUMO), and HOMO-LUMO gaps were computed and are listed in Table 4, with corresponding stereocontour plots shown in Fig. 4 [Figure 4: see original paper].

Fig. 4 reveals that the "electron cloud" of the HOMO in the ground state is mainly distributed at the end of one ligand, while that of the LUMO is located on another ligand for complexes 4 and 5. This indicates that electrons transfer from the end of one ligand to another ligand upon excitation, resulting in long electron-transfer distances. In contrast, for complexes 1-3, electrons transfer from one ligand to another or from the Ru atom to the ligands upon excitation, leading to relatively short electron-transfer distances. Additionally, Table 4 shows that the computed HOMO-LUMO gaps for complexes 1-5 are 3.222, 3.603, 3.094, 1.087, and 1.190 eV, respectively, indicating that complexes 4 and 5 have smaller HOMO-LUMO gaps compared to complexes 1-3 and can be excited more easily.

From this analysis, complexes 4 and 5 exhibit two characteristics that contribute to their long excited-state lifetimes: (1) smaller HOMO-LUMO gaps and (2) long electron-transfer distances. These two features may explain why the excited-state lifetimes of complexes 4 and 5 are longer than those of complexes 1-3.

### 3.4 Photovoltaic Conversion Property

The calculated net charges of two TiO<sub>2</sub> molecules in the docking models of complexes 1-5 in the ground state and lowest triplet states are listed in Table 5. Since the photovoltaic conversion efficiencies of complexes 1-5 were not determined experimentally, complexes 3a and 3b [22] with known experimental photovoltaic conversion efficiencies were also computed for comparison. The computed net charges of two TiO<sub>2</sub> molecules in their docking models in the ground state and lowest triplet/singlet states are also listed in Table 5.

For complexes 3a and 3b, the calculated net charges of two TiO<sub>2</sub> molecules in the docking models in the ground state are -0.3079 and -0.2098 |e|, respectively, while those in the lowest singlet states are -0.3356 and -0.2305 |e|. Their gaps ( $\Delta$ ) are 0.0277 and 0.0207 |e|, suggesting greater charge transfer from complex 3a to TiO<sub>2</sub> molecules compared to complex 3b, which would predict better photovoltaic conversion efficiency for 3a—contradicting the experimental result [22]. Conversely, the calculated gaps of net charges on two TiO<sub>2</sub> molecules in docking models between the ground state and lowest triplet states for 3a and 3b are 0.0217 and 0.0499 |e|, respectively, indicating less charge transfer from complex 3a to TiO<sub>2</sub> molecules compared to complex 3b and predicting better photovoltaic conversion efficiency for 3b, which is consistent with the experimental result [22]. Therefore, the net charges in the docking models of complexes 1-5 in the lowest triplet states were computed for further analysis.

Table 5 shows that the gaps ( $\Delta$ ) of net charges on two TiO<sub>2</sub> molecules in docking models between the ground state and lowest triplet states are 0.0127, 0.0237, 0.1256, 0.0022, and 0.0287 |e| for complexes 1-5, respectively. Based on these results, we predict that the order of photovoltaic conversion efficiencies for complexes 1-5 should be  $3 > 5 > 2 > 1 > 4$ . This result is inconsistent with the excited-state lifetimes of complexes 1-5, further demonstrating that the photovoltaic conversion efficiencies of these complexes are not related to their excited-state lifetimes [22].

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## 4. CONCLUSION

Theoretical studies on the excited-state lifetimes and photovoltaic conversion efficiencies of Ru(II) polypyridyl complexes 1-5 have been carried out using DFT/TDDFT and docking methods, leading to the following conclusions: (1) A computational method for excited-state lifetimes of Ru(II) polypyridyl complexes 1-5 was developed, enabling accurate prediction of their excited-state lifetimes. (2) The reason for the longer excited-state lifetimes of complexes 4 and 5 compared to complexes 1-3 was explained by electron-transfer distances and HOMO-LUMO gaps. (3) The photovoltaic conversion efficiencies of complexes 1-5 were predicted.

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**Fig. 1.** Structural diagrams of complexes 1–5 and atom labels.

**Fig. 2.** Optimized docking models of complexes 1–5 with two TiO<sub>2</sub> molecules.

**Fig. 3.** Simulated absorption spectra of complexes 4 and 5.

**Fig. 4.** Molecular orbitals of complexes 1–5 in the ground states.

**Table 1.** Computed Selective Bond Lengths (Å) and Bond Angles (°) of Complex 4 and Corresponding Experimental Data [11]

**Table 2.** Calculated Related Excitation Energies ( $\Delta E/eV$ ), Oscillator Strengths and Main Orbital Transition Contributions of Complexes 1–5 Using the TDDFT Method

**Table 3.** Calculated Excited-state Lifetimes ( $\tau$ , ns), Corrected Excited-state Lifetimes ( $\tau_{cp}$ , ns) and the Experimental Values [11] of Complexes 1–5

**Table 4.** Computed Energies (eV) of HOMO, LUMO and HOMO-LUMO Gaps ( $E_{gap}$ )

**Table 5.** Computed Net Charges ( $|e|$ ) of Two TiO<sub>2</sub> in Docking Models in the Ground States and in the Lowest Singlet/Triplet States and Gaps ( $E_{gap}$ ) for Complexes 1–5, 3a and 3b

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