

Theoretical study on photoelectric property of ruthenium complex dye-sensitizer

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DFT and TD-DFT calculations were performed on the modified polypyridyl ruthenium complexes. Influences of substituent groups on the electronic structures, optoelectronic properties and charge redistributions were probed. The results show that the E_{LUMO} levels of all the modified dyes are between -1.01 to 0.19 eV, endowing sufficient thermodynamic driving force for charge injection to the TiO_2 conduction band (-4.0 eV). The E_{HOMO} energy level of the dyes are in the narrow range of -4.77 to -4.15 , ensuring an efficiently regeneration of dyes through the recapture of the injected electrons Γ^- to the oxidized sensitizers. This driving force is efficiently improved in **8** in comparison with the prototype cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) (**N3**). The attachment of amino group to the thiophene ring in **10** not only dramatically increases the adsorption strength but also causes a large red-shift. It is expected that the modified complexes have higher light harvesting efficiency than the prototype **N3**.

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1. Introduction

An increasing demanding for renewable energy sources in recent decades promotes the development of dye sensitized solar cells (DSSCs). The sensitized dyes are important mediums in optoelectronics as well as the most key component in DSSCs [1-3], which plays an important role in lots of aspects such as hole or electron injection, charge redistribution and photochemical reaction. The photon harvesting efficiency of the dye is a prerequisite for its use in DSSCs. Polypyridyl complexes of the d^6 transition metals of Ru(II), Os(II), and Re(I) are widely known as DSSCs dyes since they have a rich photochemistry due to their long-lived metal to ligand charge transfer (MLCT) excited states [4-5]. Among different metal complexes used in DSSCs, ruthenium complexes were observed to be the most efficient ones [5].

Di-tetrabutylammonium cis-bis(isothio- cyanato) bis(2,2'-bipyridyl-4,4'- dicarboxylato) ruthenium (II) (also named as **N719**) and cis-bis (isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) (**N3**) showed the best efficiency among the ruthenium sensitizers [6-7]. Therefore, attempts have been made to design new molecular structures for efficient sensitizers in DSSC by modifying the reference dyes with a red-shifted absorption band to cover all visible region, increasing the molar absorption coefficient and

improving the long-term stability [8]. By doing so, Ru complexes would be much more promising for developing panchromatic sensitizers. It is anticipated that perturbing the potential energy levels of the Ru dye by changing substituents may induce a substantial effect on the efficiency of devices [9].

When the n -type dyes are excited by photons, the electron leaps from the donor that is far away from the anode to the acceptor that is close to the anode. The carboxyl as an anchoring group is able to adsorb on the semiconductors firmly. An optimal anchoring group for the n -type dye should have strong electron withdrawing abilities, under the premise of strong adsorption on the semiconductor, which will enhance the charge separation and, consequently, the power conversion efficiencies. To realize this goal, strong electron donating groups on the opposite end of the molecules will facilitate the charge separation further. Consequently, one of the best strategies of extending the absorption band to near infrared region and increasing the sunlight absorbance is to replace the anchoring ligand of dicarboxyl group in **N3** champion dye with highly conjugated ancillary ligands [10]. With this aim, various electron donating groups such as methyl and thiophene-based linkage/fuse rings were attached to the pyridyl moiety. The modified dyes (Fig. 1) were investigated by DFT and TD-DFT methods. Influences of substituent groups on the electronic structures, optoelectronic properties and charge redistributions were probed.

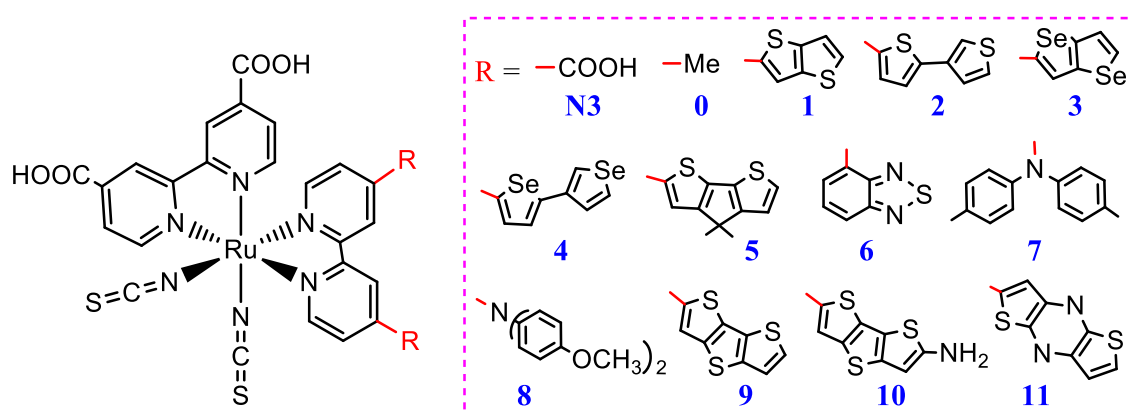


Fig. 1. Molecular structures and numbering of ruthenium complexes (color online)

2. Computational method

All the calculations were performed in Gaussian 09W package [11]. Geometrical optimizations were done at the B3LYP/LanL2MB level. On the basis of optimized geometrical structures, the excited states of all the complexes were calculated by the TD-DFT method at the CAM-B3LYP/LanL2MB level combined with polarized continuum model in solvent DMF. Previous studies showed that the results from range-separated functional of CAM-B3LYP approach to the experimental values [12-13].

3. Results and discussion

3.1. Electronic structures

The electronic distribution of HOMO and LUMO for the optimized prototype **N3** and its modified dyes were displayed in Fig. 2. The E_{LUMO} levels of all the dyes are between -1.01 to 0.19 eV. These values may vary depending on factors such as the semiconductor material chosen and the electrolyte system utilized in the DSSC. On the other hand, the semiconductors in DSSCs are usually oxides of transition metals, which have very low conduction band due to strong withdrawing ability of oxygen atoms. Consequently, the E_{LUMO} levels of all the dyes are larger than the lowest conduction band of TiO_2 (-4.0 eV) as an example, indicating that there is sufficient thermodynamic driving force for charge injection from the excited sensitizer molecule to the TiO_2 conduction band. The E_{HOMO} energy level of the dyes are in the narrow range of -4.77 to -4.15 . These values are lower than the electrolyte oxidation potential (I^-/I_3^- : -4.8 eV), ensuring that the driving forces are large enough to efficiently regenerate dyes through the recapture of the injected electrons I^- to the oxidized sensitizers. This driving force is efficiently improved in **8** in comparison

with the prototype **N3**.

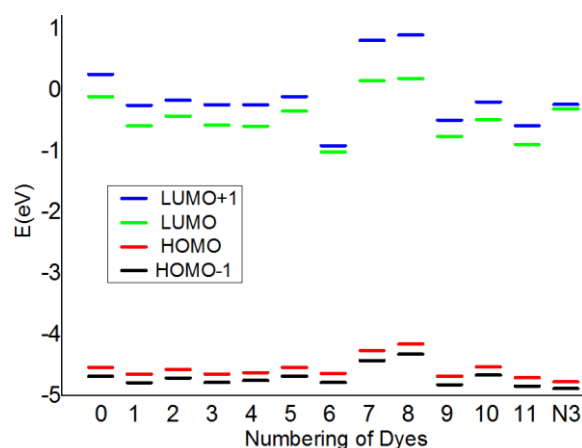


Fig. 2. The frontier molecular orbital energy levels for studied dyes in DMF solvent at Cam-B3LYP/LanL2MB level with PCM model (color online)

As can be seen from Fig. 3, the electron distributions of HOMO in all complexes are on the isothiocyanato group which is rich of π -electron with the cumulative double bond. Whereas the contours of LUMOs distribute on the polypyridyl moiety with an exception of **N3**. That the HOMO and LUMO delocalize on different regions of molecular skeletons is beneficial for the charge separation upon light excitation, which can reduce the charge recombination. The modified complexes are more in favor of electron injection than prototype **N3** since the HOMOs and LUMOs of these modified complexes hardly overlap with each other, and therefore a rapid electron injection and low charge recombination are guaranteed [13].

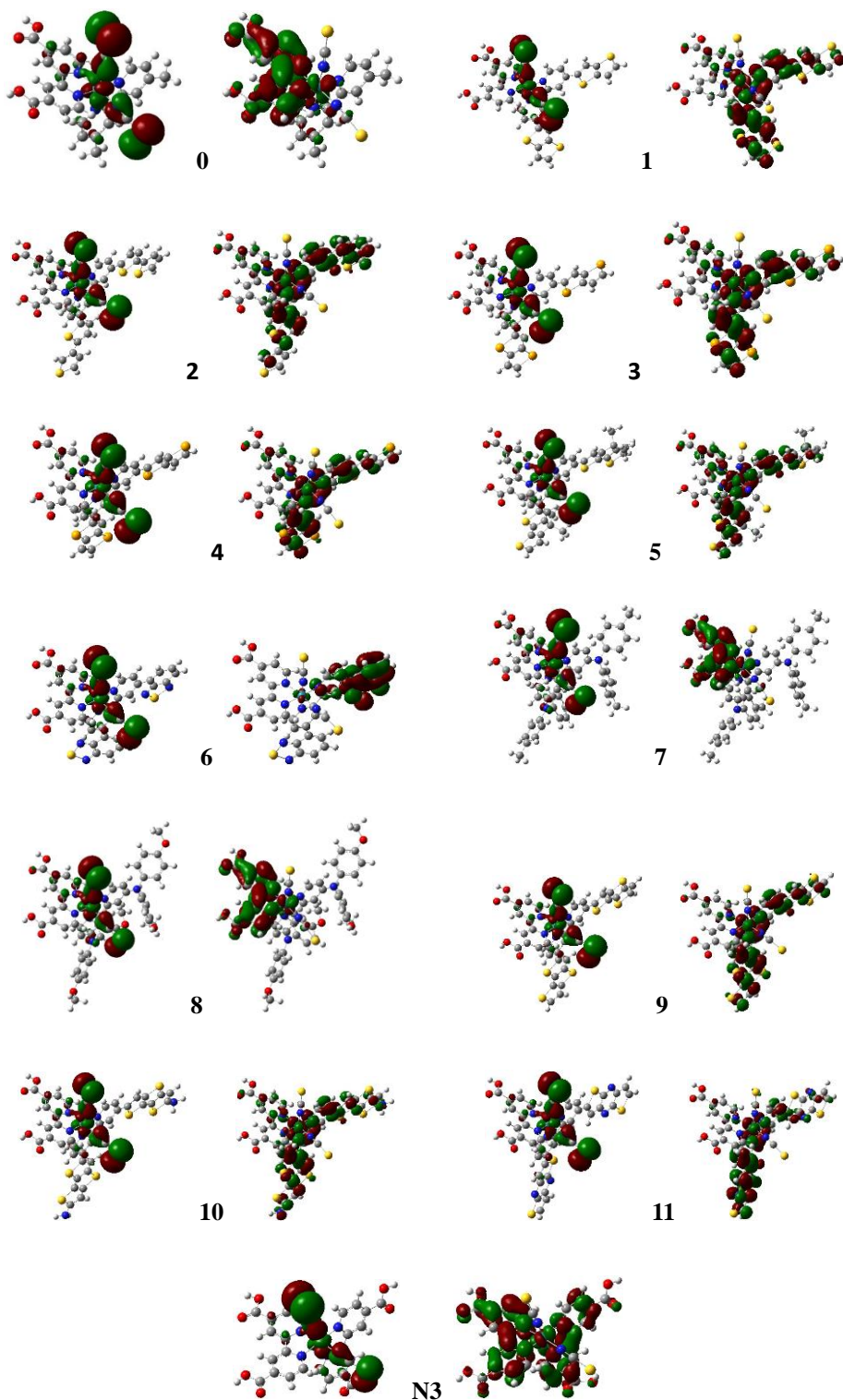


Fig. 3. HOMO (left) and LUMO (right) of N3 and its modified dyes (color online)

3.2. UV-Vis absorption spectra

The absorption spectrum of a sensitizer is a key parameter for evaluating its light-harvesting ability. In order to evaluate the designed complexes, the excited states of all the complexes were calculated at the CAM-B3LYP/LanL2MB level combined with polarized

continuum model in solvent DMF. The calculated excitation energy (E), maximum absorption wavelength (λ_{\max}), oscillator strength f , and transition properties were listed in Table 1.

As can be seen in Table 1, the order of the dye excitation energy is **7** (4.26 eV) > **0** (4.05 eV) ~ **9** (4.02 eV) ~ **N3** (4.03 eV), while excitation energy of all the

other complexes are lower than that of **N3**. Compared to two experimental adsorption peaks of **N3** at 385 nm and 530 nm, the calculated value of 308 nm is blue shifted [14]. The inclusion of long-range Hartree-Fock exchange in CAM-B3LYP functional into TD-DFT overestimates the energy gap between the occupied and virtual orbitals. This type of sensitivity with respect to treatment of exact exchange seems to play a more important role in systems with transition metals rather than in organic molecules [15]. The maximum absorption wavelength (λ_{max} /nm) is in the order of **10** (361 nm) > **6** (343 nm) > **5** (333 nm), while the maximum absorption wavelength of other complexes are similar or slightly red-shifted to that of **N3** with an exception of **7**. Apart from **0**, the absorption peaks of all other complexes are much wider and stronger in the visible region than that of **N3**, which is beneficial for the light harvesting of the sensitized solar cell dyes. The oscillator strengths of all modified complexes are at least two times larger than that of the prototype **N3**. Since the f value is positively correlated with light harvesting efficiency, it is expected that the modified complexes have higher light harvesting efficiency than the prototype **N3**. Furthermore, the electron transition configurations are not from HOMO to LUMO since the molecules are non-coplanar and lack of large π conjugated features.

It can be seen from Fig. 4 that the absorption peak areas of the dyes are larger or much larger than that of **N3** in the visible region, that is, the absorbency is improved greatly. **N3** has two absorption peaks at 300 nm and 450 nm, both are less than experiment values by 80 nm [14]. The absorption peak of **10** has the maximum red-shift and molar absorption coefficient, endowing it the largest light harvest efficiency. In comparison with **9**, the attachment of amino group to the thiophene ring in **10** not only increases the adsorption strength dramatically but also causes a large red-shift. However, due to the complexes being non-coplanar, the introduction of phenylamine group do not cause a large red-shift in visible light as compared to **N3**. It should be pointed out that there is a considerable difference between UV-Vis spectra for the free and the adsorbed dye systems on electrode materials. For instance, when **N3** dye adsorbs on (110) ZnTiO₃ surface, there is a red shift about 80 nm in absorption spectra [16]. In order to verify this red shift, we performed the calculation of **10** on the surface of (TiO₂)₂₈ clusters, the maximum wavelength becomes 394 nm which is red-shifted by 34 nm compared to unadsorbed **10**. Considering another fact that the calculated peaks are less the experiment values by 80 nm, the adsorption peaks in Fig. 4 are expected to be shifted actually much more than 80 nm when the dyes adsorb on electrode materials. This means all the modified dyes are expect to have absorption peaks around 500 nm. Although the absorptions in 600-700 nm are weak, this disadvantage could be overcome by using composite dyes with complementary absorptions.

Table 1. Computed maximum absorption wavelengths (λ_{max} /nm), oscillator strengths (f) and transition configurations

No.	E (eV)	λ_{max} (nm)	f	Configurations ^a
0	4.05	306	0.12	H-6→L (38%) H-4→L (19%)
1	3.89	319	0.25	H-6→L+1 (33%) H-4→L (14%)
2	3.76	330	0.26	H→L+5 (30%) H-4→L (20%) H-5→L (11%)
3	3.90	318	0.23	H-6→L (36%) H-4→L (13%)
4	3.89	319	0.20	H-6→L (29%) H-6→L+2 (15%) H-4→L (10%)
5	3.73	333	0.30	H-5→L (22%) H-2→L+3 (29%)
6	3.62	343	0.22	H-10→L (25%) H-5→L+3 (41%)
7	4.26	291	0.19	H-5→L+1 (60%)
8	3.79	327	0.14	H-3→L+1 (56%) H-3→L+2 (14%)
9	4.02	308	0.27	H-8→L (11%) H-3→L+3 (13%) H-3→L+3 (17%) H→L+5 (18%)
10	3.44	361	0.27	H-5→L (14%) H-3→L+1 (47%) H-3→L+2 (17%)
11	3.82	325	0.38	H-6→L (16%) H-5→L+3 (15%) H-4→L+3 (20%)
N3	4.03	308	0.06	H-4→L (21%) H-3→L+3 (11%) H→L+5 (14%)

^aOnly the main configurations of electron transitions were listed. H, H-4, L and L+5 denote HOMO, HOMO-4, LUMO and LUMO+5, respectively, and so on

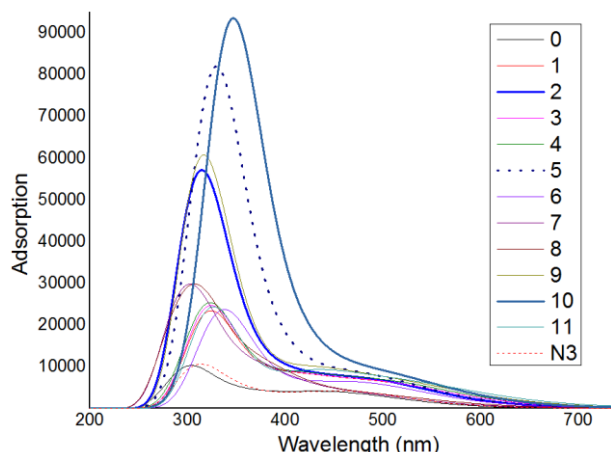


Fig. 4 Absorption spectra of **N3** and its modified dyes (color online)

4. Conclusions

By attaching electron donating groups to the cyclometalated Ru(II) complex **N3**, the modified dyes have enough driving forces for both charge injection and dye regeneration. The modified complexes are more in favor of electron injection than prototype **N3** due to their low charge recombinations. The absorption peaks of almost all complexes are much wider and stronger in the visible region than that of **N3**, and the oscillator strengths of them are at least two times larger than that of the prototype **N3**. The attachment of amino group in **10** not only dramatically increases the adsorption strength but also causes a large red-shift. However, due to the complexes being non-coplanar, the introduction of phenylamine group do not cause a red-shift in visible light as compared to **N3**. Therefore, the combination of fused thiophene and electron lone pair group of amine as an extended electron donor is highly efficient strategy for light harvesting.

Acknowledgements

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