

P-10-4

Theoretical Study on the Photophysical Properties of an Efficient Sensitizer for Nanocrystalline TiO₂-Based Solar Cells

Agalya Govindasamy¹, Chen Lv¹, Hideyuki Tsuboi¹, Michihisa Koyama¹, Akira Endou¹, Hinomitsu Takaba¹, Carlos A. Del Carpio¹, Momoji Kubo^{1,2}, Akira Miyamoto^{1,3}

¹Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-11-132, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
Phone: +81-22-795-7237 E-mail: miyamoto@aki.che.tohoku.ac.jp

²JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

³New Industry Creation Hatchery Center, Tohoku University, 6-6-11, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

1. Introduction

Dye-sensitized solar cells (DYSC) have attracted considerable interest over the last 10 years due to high efficiency in conversion of sunlight into electricity. DYSC are rather less expensive alternative device compared to the conventional solid-state photovoltaic devices. The sensitizer is one of the critical components in nanocrystalline DYSC for high power conversion efficiency. The ideal sensitizer for DYSC should be stable and absorb visible light in all colors, must be firmly grafted to the semiconductor surface and inject electrons in to the conduction band of the semiconductor. In the attempt to find dyes satisfying these requirements, several different molecules have been synthesized and investigated. The cell shows excellent stability when ruthenium complexes are employed as sensitizers, making practical applications feasible. The most successful charge transfer sensitizer employed so far is cis-dithiocyanato-bis(4-4'-dicarboxy-2-2'-bipyridine)ruthenium(II) complex, known as N3 dye [1]. Using N3 as a charge-transfer sensitizer the incident photon-to-current conversion efficiencies (IPCE) was reported as 80-85% [2]. The main drawback of this sensitizer is the lack of absorption in the red region of the visible spectrum. The black dye (BD), tris-thiocyanato(4,4',4''-tricarboxy-2,2':6',2''-terpyridine)ruthenium (II) complex have been synthesized by Nazeeruddin et al. in the search of panchromatic sensitizer that can absorb visible light of all colors [3]. BD exhibits better near-IR photoresponse than N3 dye and meets most of the demanding requirements of an efficient sensitizer. It shows absorption close to 920nm, near the optimal threshold for a single junction converter. Despite the large number of experimental studies performed on BD, only a few theoretical investigations have been reported, which is generally limited to gas-phase and based on semi-empirical approaches. In the present study, we have theoretically investigated the effect of deprotonation of the terminal carboxylic groups on the electronic structure and optical properties of BD to simulate the influence of different pH values.

2. Computational Methods

All the calculations reported in this article have been carried out using Gaussian03 program package. Geometry optimizations were performed by means of DFT method in vacuo. The inclusion of solvation effects has shown to be crucial when describing electronic structure and the

absorption spectra of ruthenium polypyridyl complexes. The electronic structure and the excitation energies of the complexes in ethanol solution were computed taking in to account solvation effects by means of conductor-like polarizable continuum model (C-PCM). All the calculations have been performed using the B3LYP exchange-correlation functionals and LanL2DZ basis set. In the calculation of absorption spectra, the 60 lowest spin-allowed singlet-singlet transitions were taken in to account.

3. Results and Discussion

The optimized structure of protonated (P-BD) and deprotonated BD (D-BD) is shown in Figure.1. A schematic representation of the molecular orbital energy levels for protonated and deprotonated BD (D-BD) obtained in ethanol solution is given in Figure. 2. The H, H-1 and H-2 (H-HOMO, L-LUMO) of the P-BD are almost degenerate and have anti-bonding nature between ruthenium t_{2g} and NCS ligand orbitals. The set of orbitals from H-3 to H-5 corresponds to the non-bonding combination of p-orbital of nitrogen and lone pair on the sulphur from NCS ligand. The H-6 to H-8 represents the bonding nature of Ru-t_{2g} and π-orbitals of NCS ligand. The six lowest occupied orbitals for the D-BD have the same character as that of P-BD. The H and L diagrams of P-BD are given in Figure. 3. The H-6/H-8 set of D-BD has contributions mainly from COO⁻ ligands. The H-9 and low-lying orbitals is the bonding counterpart of H to H-2. The deprotonation of the carboxylic groups leads to increase in the H - L energy gap and first excitation energy. The L of the P-BD is in perfect alignment with the edge of the conduction band of the TiO₂. The L of the D-BD lays 0.62 eV above the TiO₂ conduction band edge. The deprotonation of the terminal COOH groups destabilized the occupied and unoccupied orbitals.

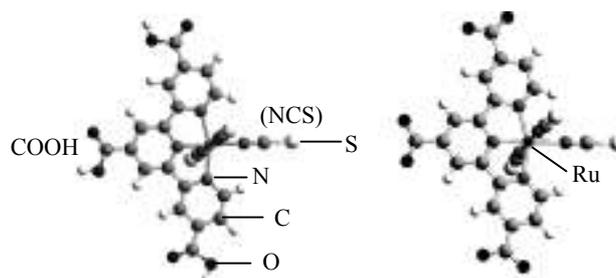


Figure. 1. Optimized structure of P-BD (right) and D- BD (left)

The L orbitals are the π^* orbitals delocalized in the terpyridine ligand.

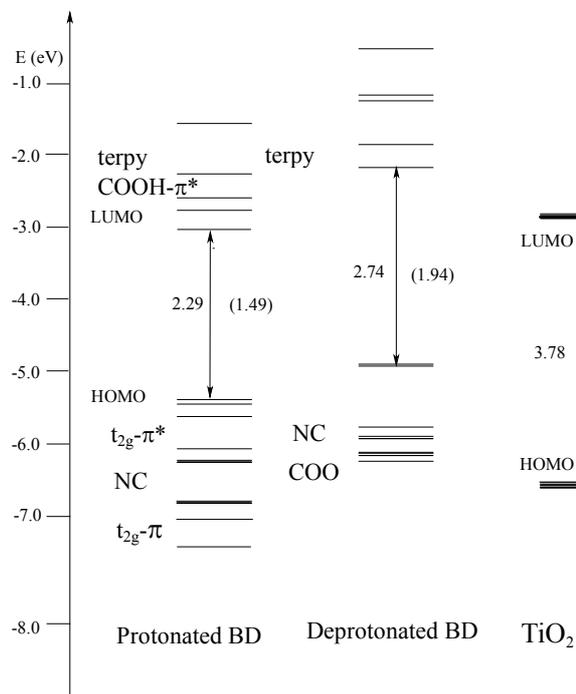


Figure 2. Orbital energy levels, HOMO-LUMO energy gap and the lowest singlet-singlet excitation energy indicated in parentheses.

The calculated absorption spectra of protonated and deprotonated BD in ethanol solution using TDDFT is given in Figure 4. We have observed blue shift in the absorption spectrum with the deprotonation of the $-\text{COOH}$ ligands. The first intense band for fully protonated and fully deprotonated complex is located at 617 nm and 582 nm respectively. We observed that this band is due to mixed MLCT (Metal to ligand charge transfer) and LLCT (Ligand to ligand charge transfer) from Ru metal and NCS ligand to π^* orbitals in terpyridine ligand. The 35 nm red shift of the longer wavelength band in fully protonated complex was observed, which is in exact agreement with the experimental result [3]. This red shift is due to the stronger electron-withdrawing nature of the COOH compare to the COO^- groups. The second band is also due to mixed ruthenium-NCS to terpyridine- π^* transitions. The third band is due to the intraligand $\pi-\pi^*$ transition in terpyridine ligand.

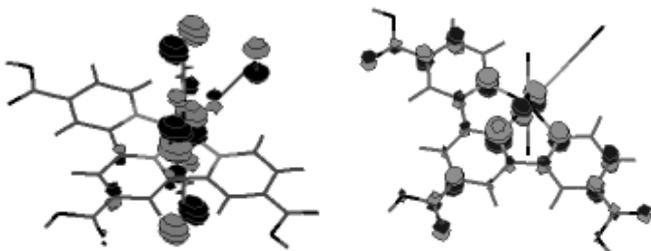


Figure 3 The HOMO (left) and LUMO (right) diagram of protonated BD

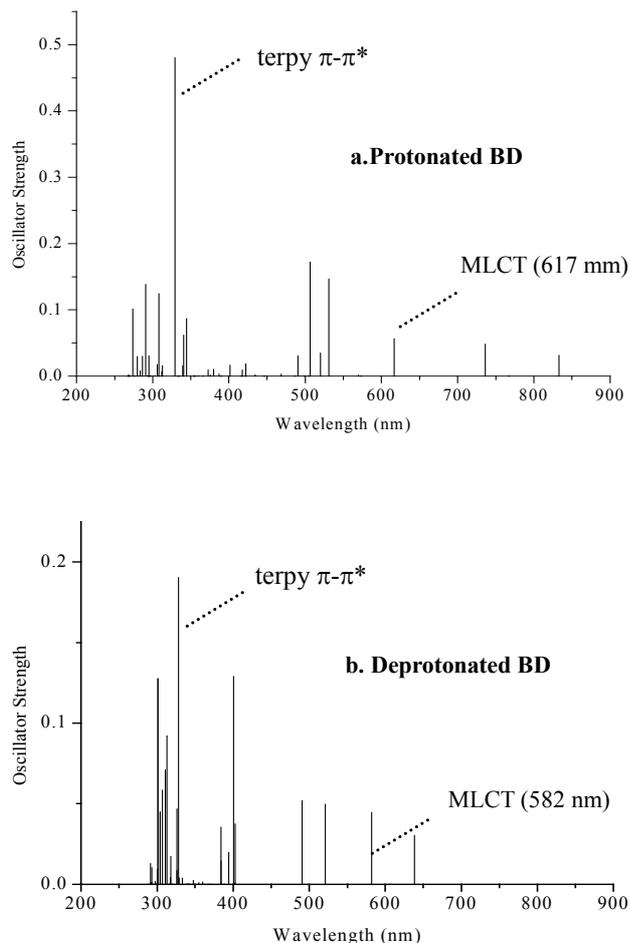


Figure 4. Calculated absorption spectra of (a.) protonated and (b.) deprotonated black dye.

4. Conclusions

The effect of pH on the electronic and optical properties of black dye was simulated by deprotonation of the carboxylic acid groups attached to the terpyridine ligand using TDDFT method. The orbital levels are destabilized in the deprotonated complex, which lead to blue shift in the absorption spectra. This blue shift upon deprotonation, which was observed experimentally, was well reproduced by our calculation. This study shows that TDDFT calculation in solution is an effective tool for the prediction of electronic and optical properties of BD, thus will help to design an efficient solar cell sensitizers with slight modifications in the acceptor and donor ligands of the dye.

References

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