Cyclometalated Ruthenium (II) Electronic Structure Influence on dye-sensitized solar cell performance: A Density Functional Theory

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Abstract

According to problems originating from the use of fossil fuels to generate electricity, solar energy has been considered. One method that can be used for this issue is dye-sensitized solar cell technology. There are several ways to increase the efficiency of a cell which one of them is choosing appropriate dye molecules. In this paper, the FT dyes series were selected and the effect of electronegative group as well as alkyl chain length is examined. All DFT computations were performed with plane-wave basis set. According to the results, substituting an electronegative group leads to reducing the difference between HOMO energy and potential energy of I^-/I_3^- in order to facilitate electron transfer from I^-/I_3^- to the stable energy. Energy difference between LUMO of dye sensitizer and conduction band of semiconductor TiO_2 decreases as the substitution takes place on the anchoring bidentate ligand of Ru(II) complex. Whatever the difference is less; dye regeneration will be favored and cell efficiency improves. In addition, FT57 dye is the most efficient during the considered dyes because of its appropriate electronic and quantum properties.

Keywords: Cyclometalated Ruthenium (II) Sensitizer; Dye Sensitized Solar Cell; Efficiency; Conduction band (CB) of TiO_2; Oxidized state

Introduction

One of the greatest challenges facing humanity in the present day is replacing fossil fuels with renewable energy sources [1] because of rising prices of oil and other fossil fuels such as gas and coal as well as greenhouse effect. One solution is nuclear power which is ignored for enormous expense of nuclear power plants and taking a long time to be built; in addition, the disposal and storage of radioactive waste is a serious problem [2]. As a result, clean energy sources such as solar energy for generating electricity have expanded after 1970. Photovoltaic technology (PV) is the most direct way which converts solar energy into electricity without producing carbon dioxide and other greenhouse gases [3]. In other words, sun as a source of clean and inexpensive energy will play a strategic role in the future. Solar cell (SC) is a device that converts the sun's energy by photovoltaic effect to electricity [4]. Some applications for SC include airport landing lights, preventing the pumping of water for irrigation, energy source for homes and commercial buildings, perimeter alarm transmitter, fence (wall) border, electronic highway signs, electronic surveillance systems unmanned, railways, earthquake warning systems, satellite communications, space surveillance systems, and identification of space missiles [2].

Today, three generations of solar cells exist; the first generation technology is based on silicon wafers with high efficiency as a benefit and not being economically viable as a disadvantage. The second generation technology is called thin film SC which is based on semiconductor deposition on a suitable substrate. This generation is not economically effective that means extensive research on SCs has taken place leading to the introduction of third generation with low conversion efficiency as a shortcoming and low cost as a remarkable advantage [5]. Dye sensitized solar cell (DSSC) is known as third-generation technology [5a] and a real solution to trap the sun's energy and convert into electrical energy with conversion efficiency of 11%. Among the different types of DSSCs one made of TiO_2 is a cheaper. In fact, TiO_2 is a semiconductor selected due to low cost, non-toxicity, and availability.

The first time, in 1991, Gratzel and O'Regan's introduced [6] DSSC photovoltaics with low production cost and easy make as a means of appropriate and applicable technology. The other advantages are transparency, flexibility, low weight, the availability of raw materials for manufacturing, better performance at high temperatures, and suitable for internal applications [5a, 7]. Similar to the photosynthetic process in plants where chlorophyll absorbs photons but does not participate in charge transfer, the photoreceptor and charge carrier are implemented by different components in DSSCs. This is contrary to conventional PV cells where a semiconductor assumes both functions. This separation of functions leads to lower purity demands on raw materials and consequently makes DSSCs a low-cost alternative. Because of the low cost, easy preparation, good performance, and environmentally benign compared with traditional PV devices [8], DSSCs have aroused intense interest and been regarded as one of the most prospective SCs among the third-generation PVs. Although the power conversion efficiencies of DSSCs are lower than first and second-generation PV cells [8], there still is a high potential for improvement in their efficiency [8].

The typical basic configuration of the device contains mesoporous oxide layer composed of a network of TiO_2 nanoparticles as heart of the device to establish electronic conduction. A deposited mesoporous layer on a glass or plastic substrate is also observed. The other part is organic solvent containing the iodide/triiodide redox system and the next is cathode coated with a thin layer of platinum catalyst [1a, 3-5, 6b, 9]. From the other side of view, operating principles of DSSC are absorption of a photon by the sensitizer to be excited, injecting the excited state electron to semiconductor TiO_2, flowing electron through the semiconductor network to arrive at the counter electrode

(at this stage the electricity is generated) and reduce the redox mediator, and finally regenerating the sensitizer [1, 3, 6, 9]. However, some undesirable reactions lose cell efficiency, which are the recombination of the injected electrons either with oxidized sensitizer or with the oxidized redox couple at the TiO_2 surface [9]. In order to overcome these difficulties, it is important to introduce dyes which bind appropriately to the nanoparticles. As it can be realized from the account, photosensitizer dye plays a key role in DSSC technology [1a, 3-4]. As a crucial component of a DSSC, when using TiO_2 and iodine/iodide, the dye sensitizer should fulfill the following characteristics. (i) It should absorb spectrum spanning the entire visible region and ideally the part of the near-infrared (IR) region. (ii) It should strongly bind to the TiO_2 surface for electron injection and cell stability. For this feature, anchoring groups such as carboxyl groups should be present. (iii) The excited state energy level (LUMO level) should be more positive than the conduction band (CB) edge of TiO_2. (iv) The energy difference between LUMO level of dye and CB edge of TiO_2 should allow for an efficient electron transfer process between the excited state of dye and TiO_2 CB. (v) The oxidized state (E_{ox}, HOMO level) should be more negative than the iodine/iodide redox potential of the electrolyte, and their energy difference should allow for efficient dye regeneration by I^-. (vi) The dye must avoid unfavorable aggregation on the TiO_2 surface which fulfills if the structure is optimized. (vii) The sensitizer should be stable thermally, electro-, and photo-chemically [1b, 9b].

Currently, considerable synthetic works is devoted to the chemical modification of dye molecules in order to use more sunlight [6b, 10]. In general, there are two main strategies to design the molecules for use as efficient sensitizers; the first one is modifying dye with highly conjugated groups. Other strategy adopted is to enhance the electron-withdrawing ability to facilitate electron injection from dye molecule into CB of semiconductor [6a].

Up to now, Ru(II) complexes, such as tetraprotonated Ru (4,40-dicarboxy- 2,20-bipyridine)2(NCS)2 complex (N3) and its doubly protonated analog (N719) are still the most widely used sensitizers in current DSSCs devices [1, 4-5, 5c, 6a]. This is due to the above mentioned and conversion efficiency (about 10-11%) [1a, 5b,c, 11].

In molecular and material science, modeling and computer simulation have gained a central role thanks to the exponential growth of computing power delivered by modern computers paralleled by similarly significant advances in theoretical methods and algorithms. Therefore, computational methods are currently employed at molecular level in order to identify and rationalize the fundamental chemical processes which mimic complex environments such as surfaces and hetero interfaces, guide the synthesis and production of new materials via molecular design, and design and optimize nanosystems for a variety of applications ranging from electronics to energy conversion and storage to the development of materials with specific target properties. In line with these important points, the current study has carried out a computational

investigation to shed light on electronic and structural properties of some selected dyes applied in DSSCs. Due to the simple chemical structure and excellent performance of N3 dye, we choose it as ideal dye to do our comparison. But the drawbacks to instability of dye, because the bond between ruthenium and NCS is a weak link [9], low efficiency [5b], lack of absorption in the red colors of the visible spectrum [5a], and weak binding to the film surface has necessitated us to replace one ambidentate ligand thiocyanate (–NCS) group with a tridentate group. The role of the carboxylate groups is to allow immobilization of sensitizer to the film surface via the formation of bidentate coordination and ester linkages [5a,b, 6a, 12]. Therefore, the goal of the present investigation is to study the dyes that a bidentate ligand instead of two NCS ligands is present. In addition, the effects of withdrawing electron groups on anchoring bidentate ligand besides alkyl chain variation are considered. Furthermore, to enhance DSSC performance and to overcome the limitations of the N749 dye, terpyridyl Ru(II) complexes Ru(H3tcterpy)L(NCS), where L is 4-trifluoromethylphenyl pyrimidinato ligand, were selected.

In this article, we report the results of density functional theory (DFT) on the series of 4-trifluoromethylphenyl pyrimidinato derivatives (Figure 1), where CF_3, H, and F are substituted in the phenyl ring. The study concentrates on the applications of DFT which allows a reliable interpretation, a better understanding, and (to some extent) the prediction of the properties of dyes in DSSCs. Owing to their environmentally friendly nature, ruthenium dyes are expected to replace organic exerting an adverse effect on the environment.

Quantum Chemical Calculations

DFT with generalized gradient approximation (GGA) and hybrid approximation [13] for the exchange-correlation energy represents the primary theoretical framework for our study. All DFT computations were performed using the Quantum ESPRESSO software package [14], which performs an iterative solution of Kohn-Sham equations in a plane-wave basis set. The geometry optimization in the gas phase was carried out using DFT calculations employing the PBE exchange-correlation functional at BYLP (Becke, Lee-Yang-Parr) level with a DZP (C, F, H, O, N)/DZ (Ru) basis set, along with a double-ζ plus polarization (DZ) basis set. The force field and wavenumber calculations were also performed at the same level of theory. The absence of imaginary wavenumbers (negative values of Hessian matrix) confirmed that the stationary points found correspond to real minima, instead of being saddle points. The computed values of bond length, angle, HOMO energy, LUMO energy, and their gap were compared with Gaussian basis sets [15] in order to be sure on the accuracy and the precision of the computational level used.

Results and discussion

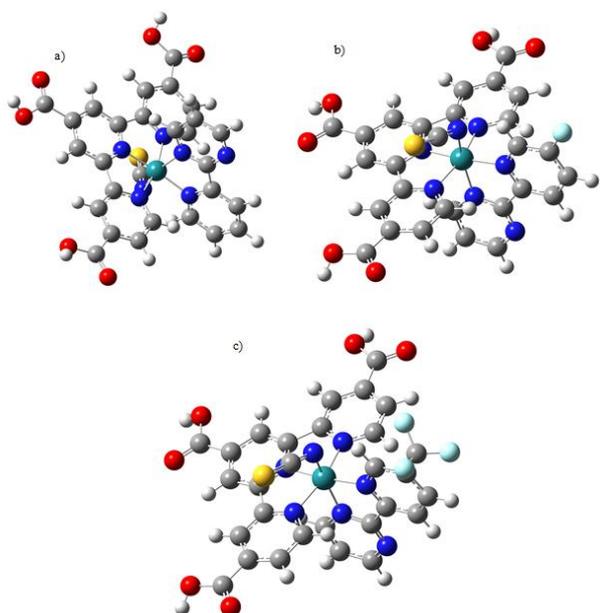Figure 1 illustrates the structure of optimized dyes with their common name.

Figure 1. The optimized structure of dyes under consideration a) FT67, b) FT10, and c) FT57

Table 1 shows HOMO energy (ε_{HOMO}), LUMO energy (ε_{LUMO}), and their gap (g_{HL}) in eV for each complex studied as well as the values of CB of TiO$_2$ and redox potential energy (E_{red}) of I$^-$/I$_3^-$. Energy difference between LUMO of each dye sensitizer and CB$_{TiO2}$, where CB is equal to -6.55 eV [11], and difference between HOMO energy level of the dye and E$_{red}$ of I$^-$/I$_3^-$, E$_{red}$ (I$^-$/I$_3^-$ = -4.9 eV [16]), are also reported in Table 1.

Table 1. The values of ε_{HOMO}, ε_{LUMO}, g_{HL}, ε_{HOMO}-E$_{red}$, and ε_{LUMO}-CB$_{TiO2}$ for each target dye.

Dye	ε_{HOMO} (eV)	ε_{HOMO}-E$_{red}$ (eV)	E$_{LUMO}$ (eV)	ε_{LUMO}-CB$_{TiO2}$ (eV)	g_{HL} (eV)
FT67	-4.882	0.018	-4.256	2.294	-0.626
FT10	-4.970	-0.070	-4.351	2.199	-0.619
FT57	-5.175	-0.275	-4.379	2.171	-0.796
N3	-4.924	-0.024	-4.384	2.166	-0.540

Altering one of the hydrogen atoms on the cyclometalating2-phenylpyrimidinato ligand with CF$_3$ leads to reducing g_{HL}; as a result, electrons with less energy excite and electron injection and cell efficiency increase.

In addition, our calculations claim that the π electron-rich ligand may increase the energies of occupied orbitals and reduce the energy gap of the HOMO-LUMO in these ruthenium based complexes as the results of Wang et al. [17] supports this observation.

Altering one of the hydrogen atoms on the cyclometalating2-phenylpyrimidinato ligand with fluorine leads to reducing the difference between HOMO energy and potential energy of I$^-$/I$_3^-$. From the other side of view, if H atom is replaced with an electronegative atom such as F, energy difference between LUMO of dye sensitizer and CB$_{TiO2}$ decreases. Whatever the difference is less, dye regeneration will be favored; in addition, the electron transfer from the dye to the semiconductor increases and the efficiency improves. It is interesting to know that the lowest difference between LUMO of dye sensitized and TiO$_2$ conducting band is for a strongly electron-withdrawing trifluoromethyl (CF$_3$) group on the strong σ-donating cyclometalating2-phenylpyrimidinato ligand that is numerically very similar to the difference between LUMO of N3 and TiO$_2$ conducting band as it can be seen in the table.

HOMO Energy of dye sensitizer should be lower than redox potential energy I$^-$/I$_3^-$; as a result, electrons can be transferred from I$^-$/I$_3^-$ to the stable energy that dyes with electron-withdrawing substitutes demonstrate this feature. However, LUMO of sensitizer should be more positive than CB of TiO$_2$, in this case if the electron is transferred from LUMO to TiO$_2$ CB, it would be more stable. Noticeably, all dyes selected show this character; besides, HOMO energy level of dye sensitizer should be lower than E$_{red}$ of I$^-$/I$_3^-$ in order to electron transfer from I$^-$/I$_3^-$ to the stable energy that all dye sensitizers studied follow this feature. All these observations are in agreement with Kusama et al. study [15].

Another important point for mention is that HOMO of dye should be between HOMO and LUMO of TiO$_2$ semiconductor. In this condition, electron injection process from the excited dye to the semiconductor is performed properly as revealed by Zhang et al. [11]. In semiconductor (TiO$_2$)$_{38}$ nanostructure, HOMO, LUMO, and band gap are -6.55 eV, -2.77 eV, and 3.78 eV, respectively [11]. In fact, HOMO of all target dyes is in this range.

Compared to N3 dyes, FT57 improves the short-circuit photocurrent density by tuning of the HOMO energy level and its difference from E$_{red}$ with strongly electron-withdrawing CF$_3$ group on the strong donating cyclometalating2-phenylpyrimidinato ligand. Consequently, a DSSC sensitized with FT57 induces a higher performance than N749 benchmark under same cell fabrication conditions.

Conclusions

Modern quantum chemical calculations, such as DFT, provide the theoretical/computational framework to understand and predict the desired properties of individual dyes, such as HOMO, LUMO, HOMO-LUMO gap, and adsorption spectrum and may save substantial experimental time and resources. Present work considers geometry and electronic structures of some sensitizers.

In order to improve efficiency of N749 and eliminate its difficulties, dyes of FT series were used that among these dyes FT67, FT57, and FT10 were investigated. According to the energy levels of HOMO, LUMO, CB$_{TiO2}$, and E$_{red}$, it can be concluded that the substituting an electronegative atom to dye may improve electron injection to semiconductor and dye regeneration; as a result, efficiency enhances.

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