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Theoretical study on a high-efficient porphyrin-sensitizer in a local electric field: How does the local electric field affects the performance of dye-sensitized solar cells?

Miao Xie [a], Jian Wang [a], Jie Ren [a], Li Hao [a], Fu-Quan Bai [a,*], Qing-Jiang Pan [b,*], Hong-Xing Zhang [a,*]

[a] Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China
[b] Key Laboratory of Functional Inorganic Material Chemistry of Education Ministry, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China

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ABSTRACT

The local electric field formed between dye sensitizers and semiconductor interface is one of key factors to determine the overall performance of dye-sensitized solar cells (DSSCs). Herein, a strategy has been proposed to explore the influence of the local electric field on the functionality of DSSCs of YD2-O-C8 dye via calculating the relevant properties in various electric field strengths. The YD2-O-C8 dye has been systemically studied with density functional theory (DFT) and time-dependent DFT (TD-DFT) for its electronic structure and optical properties in tetrahydrofuran (THF) solution. The absorption spectra are gradually narrowing and blue-shifting while increasing the electric field strength. Two key parameters of the light harvesting efficiency (LHE) and the TiO_2 conduction band shift (ΔE_{cb}) have been examined for the YD2-O-C8 sensitized TiO_2 system. It is found that it is of great importance to reduce the charge accumulation on the TiO_2 film, which lowers the electric field strength and shows the best performance of DSSCs. This study is expected to deepen our understanding of the function of local electric field and the operational principles of the DSSCs for further optimization.

1. Introduction

The energy and environmental crisis have been stimulating the rapid design and development of renewable energy sources over the past few decades. Many newly emerging solar-energy-based renewable energy sources are extensively investigated to relieve the pressure of the shortage of fossil fuels in the near feature [1–3]. Among these solar-energy-based renewable energy sources, the dye-sensitized solar cells (DSSCs) are one of the most promising technologies in the field. DSSCs have gained widespread attention because of their low production costs, simplicity of fabrication and tunable optical properties [4–6]. Recently, the cobalt redox-based DSSCs allow the record conversion efficiency to exceed 12% (12.3% with YD2-O-C8 dye [7] and 13% with SM315 dye [8]), thus promoting the further development of the photovoltaic devices of this kind.

The typical DSSC are constructed with four major parts: an anchored molecular sensitizer [7–13], a wide band gap semiconductor (typically the wide band gap semiconductor is TiO_2) [14,15], and a redox electrolyte (usually the redox couple) [16,17] as well as counter electrode [18]. The photo-to-current conversion mechanism of DSSC can be described as follow [19–21]: the photo absorptions of sensitizers result in electron injection from the excited dyes to the conduction band of the oxide semiconductor film. Then, the oxidized dye is reduced back to its neutral state by redox mediator which is usually an organic solvent containing a redox system, such as the iodide/triiodide couple or cobalt (III/II) polypyridyl complexes. Finally, the remaining conducting electrons flow into the external circuit, and the redox mediator can be regenerated at the counter electrode. Unfortunately, there are undesirable side processes: (1) the injected electron can recombine with the oxidized sensitizer dyes or with redox mediator at the TiO_2 surface (Recombination); (2) the radioless relaxation of the photo-excited dye, resulting in lower photovoltaic performances of DSSCs.

However, the detailed operating principle of DSSCs is still extensively required to identify the processes that actually limit their performance. In fact, when the DSSCs work, the electron-injection process occurs, thereby causing a lot of electron accumulation in semiconductor. As a consequence, the local

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* Corresponding authors.
E-mail addresses: baifq@jlu.edu.cn (F.-Q. Bai), panqjitc@163.com (Q.-J. Pan), zhanghx@mail.jlu.edu.cn (H.-X. Zhang).

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electric field is inevitably created between dye and semiconductor through charge separation, which influence on the behavior of dyes during the operation of DSSCs, further determining the overall performance of solar cells to some extent. In the previous article, several cases were reported that the change of absorption spectra is due to accumulation of electrons in the TiO_2 or local electric fields [22,23]. For TiO_2 films dyed in ID28, Boschloo et al. observed blue-shifts in the absorption spectra of attached dyes on account of electrons accumulation in the TiO_2 [24]. In addition, they published a paper reporting the occurrence of Stark shifts in D149 and P1 sensitizer molecules in DSSCs under the electrical field across the dye changes upon illumination [25]. They interpreted that this appearance could be caused by a band edge shift of the TiO_2 semiconductor in these devices and/or a shift of the redox potential of the electrolyte.

Thus in this paper, we questioned whether local electric fields acting on ground-state dye molecules can provide a better explanation for the observed appearance. Herein, we constructed a model containing TiO_2 substrate and planar YD2-O-C8 dye (Fig. 1) with high symmetry. This investigation aims at finding how the local electric field of TiO_2 surface affects the absorption spectra and the dipole moment of the YD2-O-C8 dye, revealing the property of short-circuit photocurrent density and open-circuit photo-voltage under different electric field strengths, and thus providing an effective method to modulate the efficiency of DSSCs by adjusting a local electric field.

2. Method

2.1. Density functional theory calculations

A crucial step in density functional theory (DFT) is the choice of an appropriate exchange–correlation (xc) functional and a reasonable basis sets. It is important to investigate their applicability to study porphyrin and identify low-cost alternative methods. In this respect, the well-established hybrid xc functional B3LYP (Becke's three parameter functional and the Lee–Yang–Parr functional) [26] was chosen. The calculated values are reasonable and acceptable while comparing with the experimentally known values [7].

All calculations have been performed with the Gaussian09 suite of program [27] (Revision D.01) with a tight self-consistent filed convergence threshold (10^{-8} a.u.) in this work. All molecules were fully optimized using DFT with the B3LYP functional. On the basis of such calculations, spectroscopic absorptions of dyes with films were obtained by time-dependent density functional theory (TD-DFT) [28–30]. The polarizable continuum model (PCM) [31–33] was employed to simulate the solvent effects of dichloromethane.

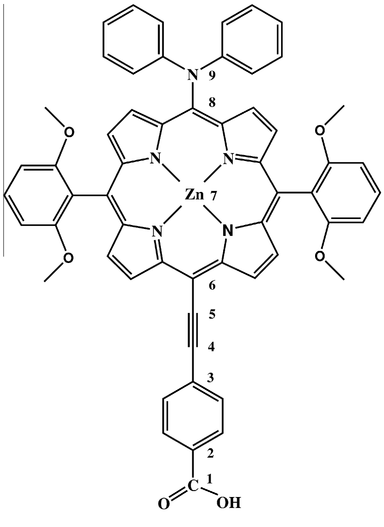

Fig. 1. Molecular structures and numbering atoms of YD2-O-C8 dye.

In the calculations, quasi-relativistic pseudopotential of Ti and Zn atoms were carried out with LanL2DZ basis sets. The split valence basis set 6-31G(d) were used for other atoms. Therefore, the optimized ground state geometry and UV/Vis spectra were obtained by the use of the DFT and TD-DFT with the B3LYP functional and LanL2DZ/6-31G(d) basis sets. All UV/Vis spectra of the current system were simulated with Gaussian curves under full-width at half-maximum (FWHM) of 0.10 eV. The natural bond orbital (NBO) charges analysis at the same level of theory were performed using the program packages of NBO 3.1 under a series of electric fields. Five different electric fields of 5, 10, 15, 20 and 25×10^{-4} a.u. (electric field strength, 1 a.u. = 5.142×10^{9} V/cm) paralleled to x-axis (normal to the TiO_2 surface) were applied on the dye and dye-TiO_2 system.

2.2. Theoretical background

As we have known, the overall efficiency (η) of the DSSCs is defined as the ratio of the maximum output electrical power of the DSSC to the energy of incident sunlight (P_{in}) and is therefore determined by the short-circuit current density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (ff) and P_{in} (generally AM 1.5, 100 mW cm^{-2}). It can be expressed by the following equation [34]:

$$\eta = \frac{J_{sc} V_{oc} ff}{P_{in}} \tag{1}$$

2.2.1. Short-circuit current density Jsc

Correspondingly, the J_{sc} value is the photocurrent per unit area (mA cm^{-2}) when a DSSC under irradiation is short-circuited. It is related to the interaction between TiO_2 and dye as well as the absorption coefficient of the dye. The J_{sc} in DSSCs can be expressed as [35]:

$$J_{sc} = \int_{\lambda} \mathrm{LHE}(\lambda)\phi_{inject}\eta_{collect} d\lambda \tag{2}$$

where LHE(λ) is the light harvesting efficiency at a given wavelength, ϕ_{inject} denotes the electron injection efficiency, and $\eta_{collect}$ is the charge collection efficiency. First, based on Eq. (2), to obtain a high J_{sc}, the efficient dyes used in DSSCs should have a large LHE, which is described by:

$$\mathrm{LHE}_{\lambda} = 1 - 10^{-A} = 1 - 10^{-f} \tag{3}$$

where A (f) is the absorption (oscillator strength) of the dye; the larger A (f) could fulfill a better light capturing.

2.2.2. Open circuit photovoltage V_{oc}

V_{oc} is defined as the voltage difference between the electrolyte redox potential (E_{redox}/q) and the quasi-Fermi potential of electrons ($E_{F,n}/q$) in the TiO_2 semiconductor. As for V_{oc} in DSSCs, it could be described by [36]:

$$V_{OC} = \frac{E_{CB} + \Delta CB}{q} + \frac{k_b T}{q} \ln\left(\frac{n_c}{N_{cb}}\right) - \frac{E_{redox}}{q} \tag{4}$$

where E_{CB} is the conduction band edge of the semiconductor, E_{redox} is the electrolyte Fermi level, k_b is the Boltzmann constant, T is the absolute temperature, q is the unit charge, n_c is the number of electron in the conduction band, and N_{CB} is the accessible density of conduction band (CB) states. ΔCB is the shift of E_{CB} when the dyes