Theoretical studies of fluorine substituent effect on organic photo-sensitizers in dye sensitized solar cells

Li Hao, Jian Wang, Fu-Quan Bai *, Miao Xie, Hong-Xing Zhang *

International Joint Research Laboratory of Nano-Micro Architecture Chemistry, Institute of Theoretical Chemistry, Jilin University, 130023 Changchun, China

ABSTRACT

Based on titanium dioxide model and LJBs sensitizers (triphenylamine as the donor, 3,4-ethylene dioxy thiophene plus various functionalized phenylenes as the π-spacer, and cyanoacrylic acid as the anchoring group) with different connection types on TiO_2 substrate, the reasonable dye-TiO_2 connection has been located. The results show that the dissociative adsorption of LJBs is more thermodynamically favorable than the neutral molecule bound configurations. LJBs adsorb onto TiO_2 via interaction between 3d orbital of surface Ti atom and 2p orbital of N/O atoms in the acceptors. This result is confirmed in both neutral and dissociation forms of LJBs molecules. According to our calculations, adding a meta-fluorine substituent to the phenyl group of cyanoacrylic acid (LJB-Fm) may damage the planarity and conjugation. Consequently, the light harvesting efficiency decreased, and that is particularly unfavorable for the DSSCs application. The Ortho F-substituted dye (LJB-Fo), however, exhibited enhanced light absorption and more efficient intra-molecular charge transport. The bigger J_{sc}, V_{oc} values of LJB-Fo system predicts its superior DSSC performance. Additionally, LJBs anchored on TiO_2 surface via group –COO (LJB-H and LJB-Fo) lead to an indirect mechanism for electron injection. While LJB-Fm preferred to direct electron injection mechanism due to the strong orbital-coupling between sensitizer and the TiO_2 substrate.

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1. Introduction

Since invented by Grätzel [1] in 1991, Dye-Sensitized Solar Cells (DSSCs) have attracted considerable attention as currently one of the most efficient third-generation solar technologies [2–4]. In recent years, metal-free dyes, commonly constructed with donor-π bridge-acceptor (D-π-A) structure, are attracting more and more attentions due to the high molar extinction coefficients, low manufacturing cost and simple fabrication process. Tremendous efforts have been devoted to design organic sensitizers for more efficient dye sensitized solar cells [5–14]. For example, several researchers have incorporated fluorine atom into the π bridge of organic sensitizers [15–18]. It is found that the electron-withdrawing effects of the halogen atom influence the properties of fluorinated sensitizers, such as changing the molecular energy levels, the charge-transfer absorption band, the charge distribution and the electron mobility.

Recently, Chou et al. [17] reported a series of simple D-π-A organic sensitizers with high molar absorption coefficient, and found that the ortho-fluorine substituted LJB (LJB-Fo) can enhance

DSSC performance and show a higher photo-electrical conversion efficiency with respect to meta-fluorine (LJB-Fm) and fluorine-free (LJB-H) dyes. As far as we know, the mechanism of the fluorine substitution acting as a key component remains to be studied. For gaining more insight into fluorine substitution effect, a question pertaining to the electron transport mechanisms is the binding configuration as dyes attached onto the TiO_2 surface. The role of the anchor group is not only to bind onto these semiconductor surfaces, but also to pump the electrons from the sensitizer molecule to the conduction band of the metal oxide semiconductor. Different binding configurations or the orientation of the sensitizer onto the TiO_2 surface would influence the overall performance of dye-sensitized solar cells.

In this paper, we have performed theoretical calculations based on the density functional theory as considering different fluorine substitutions (ortho-, meta-substituted and fluorine-free) as shown in Scheme 1. The influence of different fluorine substituent on the geometries, electronic structures and intra-molecular charge transport properties has been investigated in detail. Furthermore, the interaction between dyes and the TiO_2 plays a crucial role in electron injection process. The dye-TiO_2 complex systems are built up to understand the behavior of the interfacial charge transfer from LJBs dyes to TiO_2. Four different adsorbed configurations binding onto the TiO_2 substrate have been investigated.

* Corresponding authors.
E-mail addresses: baifq@jlu.edu.cn (F.-Q. Bai), zhanghx@mail.jlu.edu.cn (H.-X. Zhang).
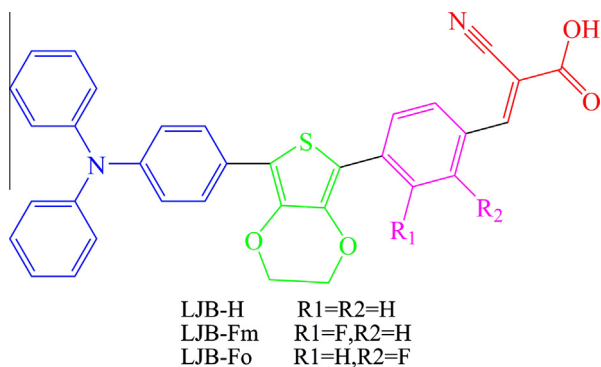
Scheme 1. Molecular structures of the LJBs dyes.

2. Computational modeling and details

In general, anatase nano-TiO$_2$ is more photo-catalytic than the rutile form, and nanoscale rutile less photoreactive than anatase. Moreover, titanium dioxide (1 0 1) surfaces, most thermodynamically stable in nanocrystal, dominated the majority of the external surface of TiO$_2$ (more than 94% percent) [19]. Taking into account of computational cost and accuracy, a TiO$_2$ substrate was set up with five titanium atoms [20]. In this model, oxygen atoms of coordination bond were saturated with two hydrogen bonds rather than oxygen atoms of covalent bond with one, as shown in Fig. 1. Saturating H atoms were maintained along the direction of the anatase lattice with 0.958 Å, which avoided the chaos of charge and multiplicity in the whole system. Adopting this model, reasonable and reliable results had been obtained in our previous work [21].

Nowadays, Density functional theory (DFT) is probably the most widely used and versatile method in computational chemistry, yielding an accurate prediction of several ground and excited state properties. Due to the exact functional for exchange and correlation remains unknown and must be approximated we have tested series of DFT methods such as PBE [22], B3LYP (Becke, three-parameter, Lee–Yang–Parr) [23–25], M06 and M062X [26] for optimizing and simulating absorption spectra of LJB-H (as shown in Scheme 1) in combination with the 6-31G (d) basis set. The excitation energies using M06-2X (423 nm) were closer to the experimental absorption data (420 nm) than other DFT methods, such as PBE (563 nm), B3LYP (606 nm) and M06 (549 nm). Therefore, full ground state (S$_0$) and the first excited singlet state (S$_1$) geometry optimization of LJBs dyes was carried out using M06-2X functional with 6-31G (d) (6-311G (d) for fluorine). On the basis of such calculations, ultraviolet–visible spectra and spectroscopic properties related to the absorption were obtained by time-dependent density functional theory (TD-DFT) [31–33]. At the same time, we performed calculations using the polarizable continuum model (PCM) [34,35] account for the solvent effect of DMF, which was used in the experiment by Chou et al. [17].

After dye LJBs binding to the TiO$_2$ substrate, we have used both CAM-B3LYP [27] and LC-wPBE functional [28–30] to describe the through-interfacial electron-transfer and electronic structures of the complexes as considering long-range correlation correction. It is found that the LC-wPBE gave a better agreement with the observed properties of the complexes. Thus, LC-wPBE functional has been adopted in both geometry optimization and ultraviolet–visible spectra for adsorbed systems with 6-31G (d) [36–38]. All UV/Vis absorption spectral curves and data were simulated based on a 0.333 eV peak half-width at half-height. All calculations were performed within the Gaussian 09 program package (Revision D.01) [39].

3. Results and discussion

3.1. Organic dye sensitizer binding onto TiO$_2$

As we all know, dyes are mainly connected onto the surface of nanometer-size TiO$_2$ in a DSSC [40–42]. The adsorption way of the dye on the TiO$_2$ is important to the electron injection process. Meng et al. investigated three possible dye-TiO$_2$ adsorption models [43]. Moreover, Pastore, Meng and Duncan have also reported that dyes could bind on TiO$_2$ through two O–Ti bonds (bidentate chelation) [44–46]. In this paper, we have investigated the performance of dye-TiO$_2$ complexes with four different binding geometries as shown in Fig. 2. Configuration (a) is a case where binds through both of –CN and –CO (H) groups to the 5-fold Ti on the TiO$_2$. The –COH unit can be easily exchanged location as binding onto TiO$_2$, forming configuration (b). Moreover, the H atom of –COH unit can be removed in dye's dissociated form, resulting in configuration (c). Configuration (d) is a case where dyes bind through or two –O–Ti bonds to the same surface atom.

All adsorbed configurations were optimized utilizing LC-wPBE method with 6-31G (d) basis sets. The synthesized dyes by Chou et al. [17] were adopted in the adsorbed systems as shown in Fig. 3. It is interesting to find that the angle between plane Ti1–Ti2–N1–O3 (or Ti1–Ti2–O3–O4) and planeTi1–Ti2–Ti3–Ti4 is about 72–75°, which is close to the angle between plane O1–O2–Ti3–Ti4 and Ti1–Ti2–Ti3–Ti4 (78°) (labeled in Figs. 1 and 2). That can be seen dyes would prefer to connect onto semiconductor surface along the direction of the anatase lattice. Compared with configurations (a) and (b), configuration (c) had the shorter O–Ti and N–Ti distances between dye and the TiO$_2$ as shown in Table 1. In addition, the BSSE corrected binding energy has been obtained (shown in Table 1s), reflecting quite a strong interaction between the dye and the surface for all configurations. It can be seen that the binding energies for configurations (c) and (d) were significantly larger than that of the configurations (a) and (b) for all LJBs dyes. The results showed that dissociative adsorption is more thermodynamically favorable than the natural form.

3.2. Fluorine modified sensitizers

3.2.1. Effect of F-modified on geometry and electronic structures

In DSSC, the conjugation degree between the donor and acceptor, which could be related to the extent of intra-molecular charge transfer, is an important factor influencing the performance of the dyes. The strong orbital mixing between donor and acceptor units will result in relative small energy gap (hence red shift of light absorptions) and high absorption coefficient, which promote the photovoltaic performance to some degree. The fluoride-modified π-conjugation (substituent effect) would change the molecular structure: the bond length, angle and dihedral angle. The torsion angles between the various parts of the dye molecules can qualitatively reflect the extension of the conjugation. Therefore, we analyzed molecular structures of dyes in the ground states (S$_0$) and the first excited states (S$_1$) by checking out the change of torsion angles between thienyl and adjacent phenyl rings in the organic molecules (as shown in Table 2).

In battery device, besides the neutral forms, the dye molecules will dissociate and adsorb on the semiconductor surface. Dissociative adsorption is more thermodynamically favorable than neutral molecular adsorption because it saturates a larger number of surface dangling bonds [46]. Therefore, we have carefully analyzed torsion angles for both neutral and dissociative forms (0H). It was found that the dihedrals between thienyl (π$_1$) and adjacent phenyl (π$_2$) rings of dissociated LJBs dyes were bigger than these of neutral forms. For the meta-fluorine substitution system, the