

# Effects of carboxylic acid and phosphonic acid anchoring groups on the efficiency of dye sensitized solar cells: A computational study



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## ARTICLE INFO

### Article history:

Received 7 January 2016

Received in revised form

10 March 2016

Accepted 11 March 2016

Available online 26 March 2016

### Keywords:

Dye sensitized solar cell

Axially coordinated binding

Anatase TiO<sub>2</sub>

Surface modification

## ABSTRACT

In axially coordinated DSSCs the dye is attached to the surface via linker and the linker play a role of a conductor of electron and a bridge to the surface which has a very important effect on the efficiency of the cell. It has been shown that using one particular dye with different linkers could result in different efficiencies. In this paper, using density functional theory, different carboxylic acid (CA) linkers, and different phosphonic acid (PA) linkers are studied and their effects on the electronic structure of the surface and changes in the HOMO and LUMO of the linkers due to adsorption on the surface are investigated. For each family of linkers, based on calculations, the best one to be used in axially coordinated DSSCs is suggested. Comparing these two families, carboxylic acid linkers show superior properties in terms of cell efficiencies. Phosphonic acid linkers, however, are shown to strongly bond to surface while resulting in lower conversion efficiencies compared to the carboxylic acid linkers the reason of which is still a question. Based on calculation of the changes in properties of the surface and properties of phosphonic acid linkers some reasons behind their low performances are suggested.

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## 1. Introduction

The solar energy is a promising solution to the sustainable energy supply and the relevant environmental concerns [1]. Production of the traditional types of solar cells is expensive and this fact makes the application of this kind of solar cells limited (e.g., satellites) [2,3]. So, there has been a lot of effort and interest to produce inexpensive and efficient solar cells such as dye-sensitized solar cells (DSSCs) [4]. Since the introduction of DSSCs by O'Regan and Gratzel in 1991 [5], many works have been done to improve the conversion efficiency of DSSCs [6–8].

Attachment of the molecules on the surface of metal oxides could modify the surface and make the surface of the metal oxide suitable for potential practical applications [9–11]. One of the application of molecule attachment on the surface of metal oxides is for DSSCs [5,12]. In Dye Sensitized Solar Cells, electron injection from the photoexcited dye molecule to the surface of a wide band gap metal oxide takes place and because of the attachment of dye molecules on the surface of the metal oxide there is a current flow

through an external circuit. The characteristics of dye-semiconductor interface could deeply influence parameters such as photoinduced electron transfer, stability of attachment, charge recombination, electron transfer to and from redox and the degree of dye aggregation which can greatly affect the performance of the DSSC.

Photoexcitation of dye molecule leads to electron-hole separation and consequently electron injection from dye molecule to the semiconductor surface [12]. The effort in DSSCs is to enhance the photoconversion efficiency. In this work we focus on the characteristics of molecular linkers and on their importance in electron injection. By the means of anchoring groups of the linkers that coordinate to the metal center in the axial position, metal porphyrins can bind directly to the semiconductor surface [13–16]. Direct binding to the semiconductor surface via anchoring groups at beta and meso-positions have been investigated broadly. Axial binding, on the other hand, have been less investigated. In axial binding anchoring group play a vital role both in stability and electron injection process from the dye molecule to the surface of the wide band gap semiconductor [13,16]. Previously, it has been shown that cells with carboxylic acid anchoring group compared with the cells with phosphonic acid anchoring group resulted in

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better performance. On the other hand, cells that were made using phosphonic acid linkers, show better stability than the cells with carboxylic acid anchoring groups. To the best of our knowledge and based on the references, until today there is no scientific reason for this behavior [17–21].

In this work our aim is to study the effect of different linker molecules with carboxylic acids and phosphonic acids as the most extensively studied anchoring groups to modify anatase TiO<sub>2</sub> surface. For this purpose, we considered five linkers (L1– L5) with carboxylic acid anchoring group and five linkers (M1– M5) with phosphonic acid anchoring group (Fig. 1).

## 2. Computational method

Using density functional theory (DFT) with the SIESTA package [22] we studied the modification of anatase TiO<sub>2</sub> surface by the attachment of different linkers on the anatase TiO<sub>2</sub> surface. For this purpose, five different structures (Bridge + acceptor) with two most common anchoring groups, carboxylic acid and phosphonic acid, were studied and compared. For Linker/TiO<sub>2</sub> system a two dimensional slab of anatase (101) surface similar to that of in previous studies have been considered [23,24]. The surface area of the periodic system is 10.490 Å × 11.567 Å with the vacuum layer of 20 Å to minimize the interactions between different slabs. The thickness of each slab is 6.189 Å. Because the geometrical optimization of large systems is time consuming, all the calculations have been done at the  $\Gamma$ -point. Anatase TiO<sub>2</sub> (101) surface modeled by a three atomic layer periodic slab and the bottom slab of the surface has been constrained and other layers and linkers have been allowed to relax throughout our simulations. The generalized gradient approximation (GGA) with the Perdew–Becke–Erzenhof (PBE) [25] function was chosen for exchange correlation (XC) functional. We used a double zeta polarization (DZP) basis set for all atoms. Optimization was carried out with a force tolerance of 0.04 eV Å<sup>-1</sup>. Also, a 200 Ry mesh cutoff for the geometrical optimization of the system was used. Moreover, we used a confinement radius corresponding to an energy shift of 0.01 eV for all studied systems.

To study the adsorption energy of linkers on the surface the following formula is used [26,27]:

$$E_{\text{ads}} = E(\text{linker/slab}) - (E(\text{slab}) + E(\text{linker})) \quad (1)$$

In this formula  $E(\text{linker/slab})$  is the energy of the system composed of linker adsorbed on the surface and  $E(\text{linker})$  is the energy of the linker far from the surface while  $E(\text{slab})$  is indicative of the energy of the surface in the absence of the linker. To find the binding mode of anchor groups on TiO<sub>2</sub> surface, the minimum energy for monodendate and bidendate modes has been calculated

and compared.

## 3. Result and discussion

### 3.1. Adsorption modes of different linkers

The linkers studied in this paper are shown in Fig. 1 the first groups of linkers studied are linkers with different bridges and carboxylic acid, COOH, (CA) as their anchor (Fig. 1 (a)). Two different modes of adsorption studied, namely, monodendate and bidendate. Calculating adsorption energy using formula 1, the monodendate adsorption mode found to be energetically more favorable than bidendate mode (Fig. 2), which is in accordance with the literature [28,29]. To further investigate the effect of bridge of the linkers on adsorption energy in most stable mode, monodendate mode, adsorption energies of the linkers are compared. There is little difference between the adsorption energy of linkers with different bridges with carboxylic acid anchor (Fig. 3). Changing the bridges in this family of linkers affects adsorption energy by less than 0.16 eV. In this family of linkers the most stable linker is L5 while the least stable linker is L2.

The other family of linkers studied is linkers with phosphonic acid (PA) as their anchor which are shown in Fig. 1 (b). PA family of linkers shows more sensitive behavior by changing its adsorption energy by 0.33 eV, when the bridges are changed, (Fig. 3). For this group of linkers the most stable linker is M3 and the least stable one is M4.

Among these two different families which studied, from the stability point of view, PA show stronger bonding to the surface and more stable energetically by about 0.6 eV and they seem to form stronger bonding with surface compared to CA linkers. This result is in accordance agreement with other reports [17–21].

Another property of linkers that is investigated is their bond length with surface, i.e. Ti<sub>surf</sub>–O<sub>lin</sub> bond shown in Fig. 2. The calculated bond lengths are shown in Fig. 3. For all the linkers (CA and PA) bond lengths found to be between 2.07 and 2.22 Å. In Fig. 3(a) correlation between bond length and stability can be found in both of the groups of the linkers, so that the shortest bond belongs to the most stable linker.

### 3.2. Effects of linkers on electronic structure of TiO<sub>2</sub> surface

The electronic structure of the surface is an important factor in determining performance of DSSCs. Among these properties Fermi

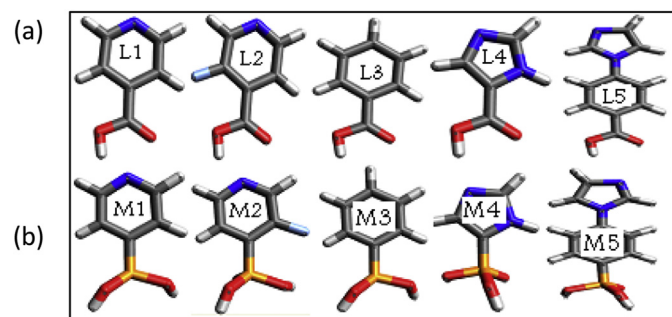


Fig. 1. Two different families of linkers all labeled for further references (a) Carboxylic acids, (b) Phosphonic acids.

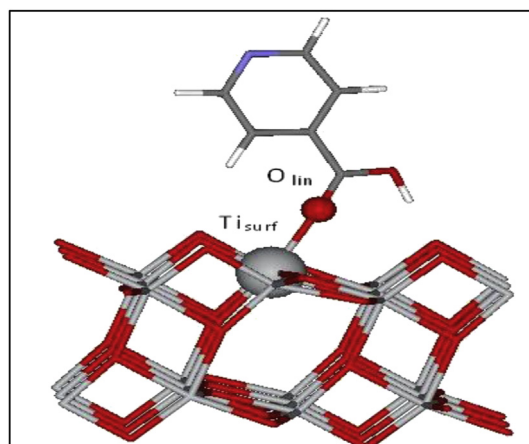


Fig. 2. Schematic view of bonding between linker's Oxygen atom (O<sub>lin</sub>) and Ti atom of the surface (Ti<sub>surf</sub>).

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