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Research paper

# Computational study of interfacial charge transfer complexes of 2-anthroic acid adsorbed on a titania nanocluster for direct injection solar cells

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ABSTRACT

Adsorption and light absorption properties of interfacial charge transfer complexes of 2-anthroic acid and titania, promising for direct-injection solar cells, are studied ab initio. The formation of interfacial charge transfer bands is observed. The intensity of visible absorption is relatively low, highlighting a key challenge facing direct injection cells. We show that the popular strategy of using a lower level of theory for geometry optimization followed by single point calculations of adsorption or optical properties introduces significant errors which have been underappreciated: by up to 3 eV in adsorption energies, by up to 5 times in light absorption intensity.



## 1. Introduction

Solar cells operating by interfacial charge transfer bands, or so-called direct injection, are a type of dye-sensitized solar cells (DSSC) [1,2] which are promising as they offer several advantages over conventional DSSC. In a conventional DSSC [2], solar radiation is absorbed by a dye molecule which is itself adsorbed on a surface of a semiconductor (typically oxide); electrons are excited from the ground state of the *dye* to an excited state of the *dye*. The molecular ground state energy level is inside the semiconductor's band gap, and the excited state is inside the conduction band (CB) of the semiconductor. Following the excitation, the electron transfers (is 'injected') into the CB, quickly relaxes to the CB minimum, and is collected at the negative electrode. While there is some hybridization between the molecular and oxide states, molecular excited states preserve their identity and the absorption spectrum is relatively little modified by the oxide. In contrast, in cells with direct injection, the electron is excited from the ground state of the *dye* (which is in the band gap) directly into a state localized on the semiconductor (whose energy is in the CB). As a result, a band is formed in the absorption spectrum of the surface complex which is not present in the molecule or in the oxide individually; this is the so-called interfacial charge transfer band, ICTB. This is advantageous, because the excitation step is combined with 'injection'; the localization of the excited state in the CB allows achieving very high injection yields. Also, the light absorption spectrum is then determined by the energy of the *dye's* HOMO (highest occupied molecular orbital) with respect to the CB rather than the molecular HOMO-LUMO gap; the energy of the molecular LUMO (lowest unoccupied molecular orbital) becomes little relevant. While extended π conjugation, i.e. a relatively larger molecule, is required to obtain a HOMO-LUMO gap suitable for visible absorption in conventional DSSCs, with direct injection, it is possible to achieve visible absorption with very small molecules adsorbed on $TiO_2$, for example, TCNE/TCNQ/TCNAQ [4,5] or catechol-containing *dyes* [3,6–11].

Fujisawa and Nagata [12] reported the formation of interfacial charge transfer bands in surface complexed of 2-anthroic acid (AT-COOH) with titania. While the molecule exhibited an absorption peak maximum below 400 nm, the surface complex AT-COOH-$TiO_2$ exhibited onset of absorption near 600 nm [12]. Fujisawa and Nagata [12] fabricated a photovoltaic cell with a solar-to-electricity conversion efficiency of 2.2%, a short-circuit current density $J_{SC}$ = 6.6 mA/cm$^2$, an open-circuit voltage $V_{OC}$ = 0.50 V, and a fill factor FF = 0.66. The incident photon-to-current conversion efficiency (IPCE) exceeded 85%. Considering that this kind of cell has not yet benefitted from an extensive experimental optimization from which conventional DSSCs benefitted, these results appear impressive. To guide such optimization, understanding of elementary processing through modeling is helpful.

In Refs. [12,13] the AT-COOH–titania complex was also studied using DFT (density functional theory) [14,15] and a simplified, single Ti atom model of titania. In Ref. [16], we performed a comparative DFT and density functional tight binding (DFTB) [17] study of 2-anthroic acid adsorption on the anatase (1 0 1) surface of titania.

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In that work, a slab model of the surface was used, and electronic structure was computed with the PBE functional [18]. The study confirmed at the DFT level the band alignment between the molecule and the interface which is favorable for a DSSC, namely, that the molecular HOMO is in the titania bandgap, while the LUMO is inside the CB. However, as the study used the PBE functional, the computed band alignment was qualitatively but not quantitatively accurate, as GGA functionals significantly underestimate the band gap. Also, in the periodic DFT study of Ref. [16], no light absorption properties were computed. A calculation of the absorption spectrum is needed to directly confirm the formation of an interfacial charge transfer band.

Here, we present the modeling of the adsorption of 2-anthroic acid on a nanocluster $TiO_2$ using a hybrid functional to compute with quantitative accuracy the band structure as well as light absorption properties, and to directly confirm the interfacial charge transfer band observed in Ref. [12]. We use a titania cluster exhibiting a (1 0 1)-like facet on which we identify bidentate and monodentate adsorption modes which are similar to those studied in Ref. [16]. We compare adsorption properties obtained with the hybrid B3LYP functional (with which a quantitative accuracy is expected) and the computationally more efficient GGA functional PBE (as GGA functionals are still the most widely used for the studies of interfaces that provide the functionality of electrochemical energy conversion and storage technologies, including DSSC [19–30] and also test a popular strategy of using a more computationally efficient DFT functional or even DFTB for structure optimization followed by higher-accuracy single point calculations [20,21,25,26,29–34]. Optimization with the PBE functional followed by B3LYP spectral calculations were reported in a preliminary study of a single monodentate adsorption configuration in Ref. [35]. Here, we study four adsorption configurations, bidentate and monodentate, perform calculations with a hybrid and a GGA functional, and compare them. We test the approach of optimization with a less expensive GGA functional followed by property calculations at the hybrid level in that the titania cluster and the adsorbate systems are relaxed and adsorption energies computed using either the PBE functional followed by single point B3LYP calculations of the band alignment and absorption spectra or by using the B3LYP functional throughout, and show that it leads to substantial errors.

## 2. Methods

Structures and electronic structures were optimized with DFT. Light absorption properties were computed with Time-Dependent DFT (TD-DFT) [36–38] using 12 lowest excited states. The calculations were done in Gaussian 09 [39]. The LANL2DZ [40,41] basis set was used. We previously showed that this basis is suitable for modeling of direct injection [3,4]. Specifically, with the LANL2DZ basis set, the absorption spectra due to charge transfer between a molecule and a simplified model of titania did not appreciably change compared to 6-31g(d,p), 6-31g+(d,p) or 6-31g +(2d,2p) basis [3]. The relatively small size of LANL2DZ is expected to give rise to a BSSE affecting $E_{ads}$; however, in Ref. [16] we showed that relative changes in adsorption energies (which are important here) of anthroic acid on $TiO_2$ are remarkably stable with respect to changes in a double-ζ basis. For the calculation of the optical properties, the B3LYP [42,43] exchange-correlation functional was used, as it resulted in a good match of the absorption spectrum of AT-COOH with the experiment [12]: the computed absorption peak maximum is at about 408 nm (3.04 eV) vs. the experimental peak around 400 nm (3.1 eV) [12]. In contrast, the use of a range-separated hybrid functional WB97XD [44] resulted in the peak at about 360 nm (3.44 eV). With B3LYP, we also obtain the onset of $TiO_2$ absorption (optical gap) near 400 nm (3.1 eV) (see below), in agreement with experiment [12], although the electronic bandgap of the titania cluster is overestimated, at 4.18 eV vs. known experimental values around 3.2 eV, possibly due to nano-confinement. SCF convergence setting Conver = 5 was used (i.e. by change in the density matrix, similar to typical periodic calculations).

The calculations were performed in vacuum. We have confirmed that the spectrum of AT-COOH is not very different in vacuum and in acetonitrile (peak shift by only 4 nm or 0.03 eV). A cluster model of a nanoparticle of $TiO_2$ was used. The cluster $(TiO_2)_{38}$ was taken from Ref. [45], it exhibits (1 0 1)-like interfaces which allow molecular adsorption in similar configurations as that in a slab model, i.e. a bidentate bridging (BB), bidentate chelating (BC), and two monodentate configurations M1 and M2, similar to those studied in Ref. [16]. The cluster and the adsorbate systems were relaxed and adsorption energies as well as band alignment were computed by (i) using the (more computationally efficient) PBE functional; (ii) using the B3LYP functional; (iii) using PBE-optimized geometries followed by single point B3LYP calculations. The adsorption energies were computed as

$$E_{ads} = E_{titania} + E_{molecule} - E_{complex}, \quad (1)$$

where $E_{titania}$, $E_{molecule}$, and $E_{complex}$ are the energies of a free titania cluster, free molecule, and the adsorbate complex, respectively. Thus a positive value of $E_{ads}$ corresponds to favored adsorption. The absorption spectra were computed with B3LYP for cases (ii) and (iii).

## 3. Results and discussion

### 3.1. Adsorption properties

The optimized structure of AT-COOH is shown in Fig. 1 together with the HOMO and LUMO orbitals. The absorption spectrum of isolated AT-COOH is shown in Fig. 3. The HOMO and LUMO energies and optical transition data are listed in Table 1, for the molecule, the titania cluster, and the adsorbate systems. Fig. 2 shows the adsorption geometries of AT-COOH on the nanocluster: two bidentate bridging configurations (BB1 and BB2) and two monodentate configurations (M1 and M2). BB1, M1, and M2 configurations correspond to those studied in Ref. [16] on a periodic slab model of the $TiO_2$ (1 0 1) surface. The BB2 configuration was formed

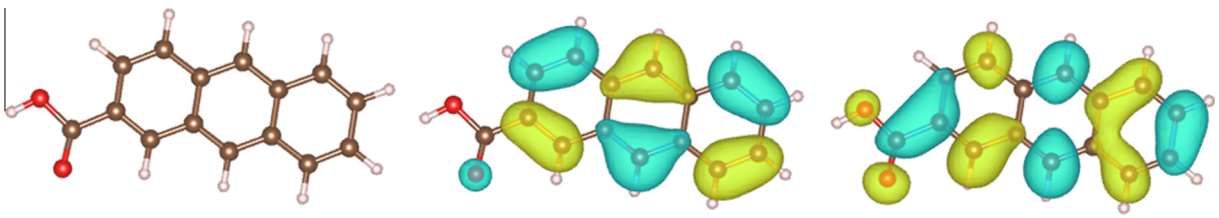

**Fig. 1.** Structure (left), HOMO (middle) and LUMO (right) orbitals of 2-anthroic acid. Atom color scheme here and elsewhere: C – brown, O – red, H – pink, Ti – blue. Visualization here and elsewhere by VESTA [46]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)