Interfacial properties of high-order aggregation of organic dyes: A combination of static and dynamic properties

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ABSTRACT

Aggregation is inevitable for the organic dyes, and it is difficult to evaluate its effects due to its complexity. Herein, we combine first principles and molecular dynamics (MD) simulations to explore the influence of aggregation on the optical and electronic properties for **THI-BTZ-2T-C**. If only the static properties are considered, the configuration of dye is not varied greatly when the adsorbed dyes are increased from monomer to hexamer. However, the absorption spectrum varies regularly with the increased aggregation order. In addition, the contribution of different orbitals of various atoms to density of states (DOS) gradually increases with the aggregation order increasing. When dynamics simulation is performed, the torsion between different components of dye is enlarged. Meanwhile, the perpendicular model is altered during the dynamics simulations, the dye would like to bend towards the TiO$_2$ surface. Moreover, the electronic coupling is greatly improved during the molecular dynamics simulations especially for the H-aggregation. The dye aggregation mainly affects the electrons injection process resulting in the reduction of the photoelectric conversion efficiency for dye sensitized solar cells (DSSCs). Reduction of perfect face to face stacking would be an efficient pathway to weaken the aggregation.

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1. Introduction

Since the seminal report by O'Regan and Grätzel in 1991 [1], dye sensitized solar cells (DSSCs) utilizing nanoporous TiO$_2$ electrode has aroused considerable attentions from both academic and engineering community. There are many prominent advantages for DSSCs including low cost, facile fabrication, and acceptable photovoltaic conversion efficiency [2—4]. Sensitizes are responsible for the light harvesting and charge separation, which is one of the most vital components to determine the overall performance of DSSCs [5]. Although the DSSCs based on metal sensitizers have achieved remarkable power conversion efficiency (PCE) so far, their applications have been limited due to the rare materials, tedious synthetic process, and low yields [6]. In contrast, organic sensitizers are promising alternative because of adjustable molecular design, abundant raw materials, and low environmental pollution [7,8].

The relative low PCE is one of the largest obstacles for the large scale application of DSSCs based on organic dyes. Variation of the configuration and/or incorporation of new groups are the powerful pathways to improve the performance of organic dyes, which has been widely investigated in previous literature [9,10]. Alternatively, reduction of the negative effects is also a pathway to enhance the overall performance. Aggregation is inevitable for organic dyes due to the strong attractive force between organic dyes resulting in a reduced electron injection efficiency and lowered conversion efficiency [11,12]. Meanwhile, the aggregation would increase the dye loading on the TiO$_2$ surface leading to an improved amount of light harvesting. Consequently, the recombination of the injected electrons would be effectively inhibited owing to the blocking layer formed by aggregated dyes [13]. In general, dye aggregation dictates structural and optoelectronic properties of photoelectrodes in DSSCs, thereby playing an essential role in their photovoltaic performance. Therefore, it is important to deeply understand dye aggregation with the aim to suitably control the performance of DSSCs. However, it is difficult or almost impossible to study it by experimental method. The theoretical method has been testified to be a powerful tool to understand the aggregation behavior. If the aggregation effect is clearly elucidated, it is not only beneficial to reduce the negative effects but also helpful to enlarge the positive influence by the variation of dye configuration.

Pastore and De Angelis firstly reported the aggregation effect of indoline **D102** and **D149** dyes on TiO$_2$ surface providing the

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possibility to calculate the various aggregation modes for screening and predicting the corresponding optical response [14]. Later, Zhang et al. have studied the adsorption properties of high-order aggregates (from monomeric to pentameric aggregates) on TiO₂ anatase (101) surface via density functional theory (DFT) [15]. In previous studies, the organic dyes are perpendicular to the TiO₂ surface, which is far from the real situation in DSSCs. The bent of organic dyes would result in the different electron coupling between two dyes, diverse possibility of electron recombination, and other properties. It is necessary to investigate the dynamic behaviors of organic dyes rather than only the static properties. Li and coworkers reported the dynamic effect on the dimeric aggregates by joint of first-principle calculations and molecular dynamics (MD) simulations [16]. However, the high-order aggregation of organic dyes has never been studied by MD method to our best knowledge.

In this work, the monomeric, dimeric, trimeric, tetrameric, pentameric, and hexameric aggregates of **THI-BTZ-2T-C** (See Scheme 1), are investigated by both first principles calculations and MD simulations. **THI-BTZ-2T-C** is D-A-π-A configuration dye, which has been designed in our previous work [17]. As compared with **IK-2** (See Scheme 1) reported by Irgashev et al. [18], it presents more potential applications in DSSCs with stronger light harvesting due to the involvement of electron-withdrawing group in π group. However, the aggregation effect is not considered in our previous work. Here, the variation of band gap, coverage value of dyes, electron injection time, and others are compared for different order of aggregation. Moreover, the variation of aggregation is inspected as a function of time. The deep understanding of the dye aggregation effects would not only throw light on the complex factors related with the DSSCs performance but also pave a way to rationally design high-efficiency sensitizers.

2. Computational details

In order to analyze the high-order dye aggregation, a $4 \times 8 \times 6$ TiO₂ anatase (101) supercell was applied as the adsorption surface since most of the available TiO₂ anatase crystals are mainly based on thermodynamically stable (101) surface [19]. In Fig. 1, there are six dye-TiO₂ adsorption sites on the five-coordinated unsaturated titanium atoms of the (101) surface of anatase unit cells, named a, b, c, d, e, and f, respectively. Based on these six adsorption sites, six configurations ("monomer", "dimer", "trimer", "tetramer", "pentamer", and "hexamer") were evaluated in the study to explore the aggregation effects, apart from the isolated dyes and the clean TiO₂. "monomer" refers to the monomeric adsorption configuration of the dye at site a; "dimer" refers to dimeric adsorption configuration of the dye at both a and b sites; similarly, "trimer" is the trimeric adsorption configuration of the dye at a, b, and c sites; "tetramer" is the tetrameric adsorption of the dye at a, b, c, and d sites; "pentamer" is the pentameric adsorption configuration of the dye at a, b, c, d, and e sites; and "hexamer" refers to hexameric adsorption configuration in which the dye occupies all available sites (a, b, c, d, e, and f). A vacuum buffer space of at least 10 Å was set for slabs with adsorbed atoms. In order to reduce the computational cost,
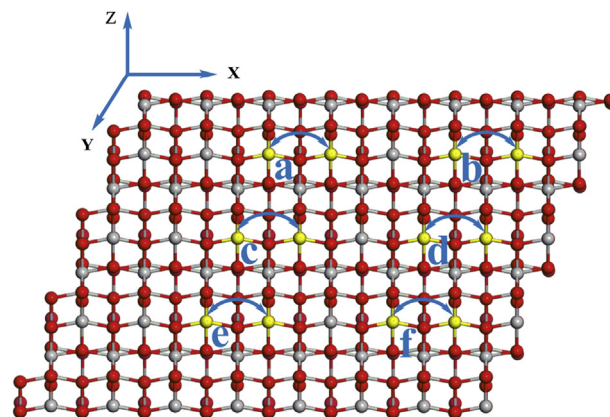

Fig. 1. Top view of the unit cell with the TiO₂ anatase (101) surface exposed. Six adsorption sites on the TiO₂ anatase (101) surface are labeled as a, b, c, d, e, and f, respectively.

the bottom three layers were fixed. The bidentate bridging anchoring mode was utilized for the carboxylic acid anchoring group on anatase (101) surface which is proposed in previous study [20]. The above configurations are geometrically optimized in VASP (Vienna ab initio simulation package) [21,22] using projector-augmented wave methods with PBE [23] generalized gradient approximation (GGA) [24] exchange correlation. Dispersion corrections of noncovalent interactions, such as electrostatic interactions, π-effects, and Van der Waals interactions by the Grimme D2 [25] method can improve the accuracy of theoretical simulations for systems. An energy cutoff of 400 eV was used and the optimization would stop when the force on each atom was smaller than 0.1 eV Å⁻¹. Furthermore, the densities of states (DOS) and projected density of states (PDOS) were calculated at the same level to deeply analyze the adsorption properties.

After geometry optimization, TD-DFT calculations were performed at TD-PBE0 level to simulate the UV—vis spectra of the monomer and other aggregates in chloroform by removing the TiO₂. Polarizable continuum model of solvation (PCM) [26,27] was used to consider solvent effects in the Gaussian 09 program [28].

The intermolecular electron coupling V_{12} can be estimated by the calculation of the overlap of the frontier orbitals between stacking dyes of position ab and ac in all aggregates. Direct method defined as follows was employed to calculate the V_{12} [29,30]:

$$V_{12} = \left\langle \varphi^1_{FMO} | F | \varphi^2_{FMO} \right\rangle \tag{1}$$

where φ^1_{FMO} and φ^2_{FMO} are frontier molecular orbitals (FMO) of two adjacent molecules 1 and 2; F is the Fock operator and its density matrix is constructed from noninteracting molecular orbitals.

The molecular dynamics simulations of dyes adsorbed on the TiO₂ surface (from monomer to hexamer) were performed by the DFTB method. The DFTB method can be used to achieve the

IK-2
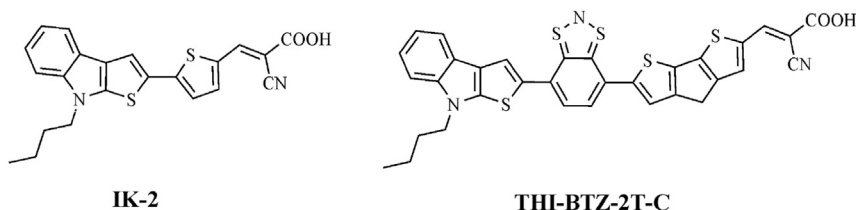
THI-BTZ-2T-C

Scheme 1. Molecular structures of **IK-2** and **THI-BTZ-2T-C**.