



First principles study of thieno[2,3-*b*]indole-based organic dyes for dye-sensitized solar cells: Screen novel π -linkers and explore the interface between photosensitizers and TiO₂



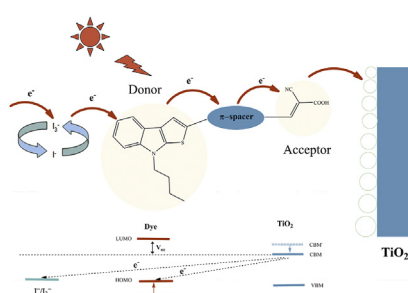
Yaping Wen, Wenpeng Wu, Yuanyuan Li, Weiyi Zhang, Zhaoyang Zeng, Li Wang^{**}, Jinglai Zhang^{*}

Institute of Environmental and Analytical Sciences, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China

HIGHLIGHTS

- Explore the influence of π -linker on overall conversion efficiency.
- The interfacial properties of dyes adsorbed on TiO₂ surface are investigated.
- The change of the performance before and after adsorbed is compared.

GRAPHICAL ABSTRACT



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ABSTRACT

Four organic compounds with different π -linkers are theoretically explored as potential photosensitizers for application in dye-sensitized solar cells (DSSCs). Besides the isolated dyes, the interfacial properties of dyes adsorbed on TiO₂ anatase (101) surface are theoretically investigated. The overall conversion efficiency (η) of DSSCs is evaluated by the following items on the basis of the isolated dyes, including structures, absorption spectrum, energy gap, open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and reorganization energies (λ_{total}). After adsorbed on the TiO₂ surface, the electron would be efficiently injected from dye into the TiO₂ surface because of the increased of the lowest unoccupied molecular orbital (LUMO) energy level of the dyes, the decreased of the conduction band of TiO₂ surface, and the narrowed band gaps for both dye and TiO₂. Moreover, the injection times are in a reasonable range indicating that they are ideal dyes. Combination of all items, the performance of **THI-2T-C** (See Scheme 1, the sketch structures of all the investigated isolated dyes) stands out from the rest investigated dyes from the theoretical viewpoint. Only enlargement of the π -linker extent is not a smart choice, since the nature of π -linker plays a more important role in affecting the performance of DSSCs.

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1. Introduction

Searching for the alternative energy supplies has attracted tremendous attentions from both academic and industrial communities because of the increasing demand for energy and the

* Corresponding author.

** Corresponding author.

E-mail addresses: chemwangl@henu.edu.cn (L. Wang), zhangjinglai@henu.edu.cn (J. Zhang).

continuous depleting fossil fuels together with the serious environmental issues [1]. Undoubtedly solar energy is the most promising renewable energy with the advantages of clear, inexhaustible, and abundant. The dye-sensitized solar cells (DSSCs) are regarded as one of the attractive photovoltaic methodologies owing to the low cost, acceptable power conversion efficiency (PCE), and facile fabrication [2], which is even regarded as a potential alternative for the conventional silicon solar cells [3].

The main components of DSSCs include the dye/sensitizer, counter electrode, electrolyte, and semiconductor. Among them, the dye is a vital element to control the overall conversion efficiency (η) and the stability of cell [4]. Until now, the ruthenium sensitizers and zinc–porphyrin dyes stand out due to the high efficiency with the PCE over 11% and 13%, respectively [5,6]. However, their large scale applications are plagued by the high cost and scarcity for ruthenium resources as well as the tedious synthetic procedure and the low yield of zinc–porphyrin. In contrast, the organic dyes could be easily prepared from the commercial available raw materials and simply purified, which are regarded as an effective alternative to metal dyes. Also, they have the higher molar extinction coefficients than ruthenium-based dyes and the broader absorption in longer wavelength by facilely structural modification [7]. To facilitate the intramolecular charge transfer (ICT) upon excitation, most of dyes are constructed by a D– π –A structure, where D/A stands for donor/acceptor and π is the conjugated linker between D and A. The aggressive investigations are performed to design and synthesize the three parts. As compared with the popular donors, such as, carbazole [8], triphenylamine [9], and phenothiazine [10], the thieno[2,3-*b*]indole is rarely taken as the donor.

Recently, Irgashev et al. [11] have synthesized two novel organic dyes 3-(5-(8-ethyl-8*H*-thieno[2,3-*b*]indole-2-yl) thiophen-2-yl)-2-cyanoacrylic acid and 3-(5-(8-butyl-8*H*-thieno[2,3-*b*]indole-2-yl) thiophen-2-yl)-2-cyanoacrylic acid (**THI-T**) by a convenient approach, wherein thieno[2,3-*b*]indole, thiophene, and cyanoacrylic acid are taken as the donor, π -linker, and acceptor, respectively. However, their conversion efficiency is not satisfactory. Except for employing different donors, the variation of the π -linker has much greater influence on the overall conversion efficiency [12], which would affect not only the absorption region but also the degree of electron injection from excited dyes to the conduction band (CB) of TiO₂ [13]. Besides the dye **THI-T** synthesized in experiment, three novel dyes are theoretically designed by insertion of dithiophene (**THI-Di**), thienothiophene (**THI-2T**), and cyclopentadithiophene (**THI-2T-C**) as the conjugation linker. It is expected that a tiny variation would induce a substantial effect on the PCE. In this work, the PCE of solar cells based on above-mentioned dyes are qualitatively estimated by theoretical method. In the past decade, numerous research endeavors have been implemented to study an isolated dye or a dye adsorbed on a small TiO₂ cluster [14,15]. However, limited theoretical investigations have been performed on the microscopic interfacial property between the dye and the TiO₂ photoanodes.

Herein, the properties of four organic dyes adsorbed before/after on the TiO₂ anatase (101) surface are investigated by the density functional theory (DFT) and time-dependent DFT (TD-DFT) method [16]. The crucial parameters related with the open-circuit voltage (V_{oc}), the short-circuit current density (J_{sc}), and in turn the PCE are theoretically evaluated including absorption spectrum, light harvesting efficiency (*LHE*), electron injection efficiency (Φ_{inject}), anchoring state, electronic redistribution, charge transfer, injection time (τ_{inj}), variation of the band gap, and others. One of our goals is to screen out the suitable π -conjugation linker with D– π –A structure for the dye based on the thieno[2,3-*b*]indole as the donor and cyanoacrylic acid as the acceptor. The other one is that the

theoretical study would play a more important role in developing novel dyes with increased conversion efficiency [17].

2. Computational details

The ground-state geometries of a free dye as well as the cation and anion were optimized by the restricted and unrestricted hybrid Perdew–Burke–Ernzerhof exchange correlation functional (PBE0) [18] with the 6-31G(d,p) basis set, which is one of the most popular and reliable methods to study the geometries of free dyes [19]. At the same level, the frequency was calculated to confirm each stationary point to be an energy minimum. On the basis of the optimized geometries, the absorption spectrum of **THI-T** was simulated by four different methods, i.e., CAM-B3LYP [20], LC-BLYP [21,22], M06-2X [23], and PBE0 methods with the 6-31G(d,p) basis set. The simulated absorption curves are plotted in Fig. S1 of the Supporting information together with the experimental curve. Both the simulated absorption shape and the absorption bands simulated at the PBE0 method reproduce well the experimental result. Consequently, the TD-PBE0 functional was employed to study the absorption spectrum for other dyes. The solvent effect was taken into consideration by the polarized continuum model (PCM) [24,25] in chloroform solvent. Abovementioned electronic calculations were performed by the Gaussian 09 program [26].

To study the interaction between dye and TiO₂, a 4 × 5 × 6 TiO₂ anatase (101) supercell was taken as the adsorption surface, since the thermodynamically stable (101) facet has been testified to be the most favorable surface in TiO₂ anatase crystals [27–29]. The bottom three layers were fixed to simulate the bulk geometry. A vacuum buffer space of 22, 19, and 54 Å was added in x-, y-, and z-direction, respectively. The isolated TiO₂ and dye-TiO₂ were optimized by means of projector-augmented wave methods with the generalized gradient approximation (GGA) using Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional implemented in VASP (Vienna ab initio simulation package) program [30–32]. The energy cutoff was set to be 400 eV and the optimization would stop when the force on each atom was smaller than 0.1 eV Å⁻¹.

3. Results and discussion

The following discussed items could not be directly compared with the value of PCE measured in experiment. They are only employed to qualitatively determine the performance of a series of similar dyes. The performance of three newly designed dyes is compared with that of the experimental reported dye **THI-T** [11].

Table 1

Selected dihedral angles (in degree) for all the isolated dyes calculated at the PBE0/6-31G(d,p) level of theory.

Dye	Dihedral angle (ϕ)	
	D– π	π –A
THI-T	–173.70	179.78
THI-Di	–164.72	–179.75
THI-2T	165.46	179.90
THI-2T-C	161.60	179.89

Note:

1. D is donor, π is π -linker, and A is acceptor.

2. The definition of dihedral angle is “Taking the π -linker as the datum plane and putting the donor moiety in the far away, clockwise direction is positive and counter-clockwise direction is negative”.

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