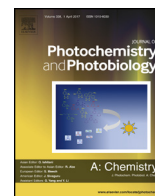




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Full length article

Molecular engineering of bithiazole-based organic dyes with different electron-rich linkers toward highly efficient dye-sensitized solar cells

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ARTICLE INFO

Article history:

Received 16 June 2017

Received in revised form 29 August 2017

Accepted 1 September 2017

Available online 4 September 2017

Keywords:

Dye-sensitized solar cells

Bithiazole-based organic dyes

Electron-rich π -spacer

Charge transfer

Absorption spectrum

ABSTRACT

A series of bithiazole-based dye sensitizers have been designed by employing various electron-rich moieties as π -spacer, which are based on the reported experimentally synthesized dye T-BT, to shed a light on the impact of both the nature and position of electron-rich moiety on the efficiency of dyes in DSSCs.

To evaluate the efficiency of these dyes, various key parameters associated with overall conversion efficiency (η), including electronic and optical properties of free dyes are calculated, based on the computational methods. Besides, the dye/TiO₂ structures have been taken into account to investigate the interfacial features of the dye sensitizers adsorbed on TiO₂ semiconductor and explore the plausible mechanism of the electron injection. The results show that, compared with the reference dye, T-BT, the newly designed dyes with electron-rich moiety close to the donor group show a better efficiency for using in the DSSCs. Our calculations show that this result is valid for other electron-withdrawing auxiliary acceptor in the range of moderate to strong. Also, we found that the incorporation of pyrrolo [3,2 -b] pyrrole (PP) unit in the π -spacer would be more favorable to enhance the efficiency of DSSCs, compared to other electron-rich groups. This computational study is expected to be a helpful guidance for the rational modification of organic dyes in future.

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1. Introduction

Due to increasing energy consumption and rapid depletion of natural fuel sources such as oil, gas, and coal together with serious ecological problems, the renewable energy sources in the future are considered as an alternative to fossil fuel sources. Indeed, since the received energy from the sun by the earth in one hour is more than the annual energy consumption of the entire world, so solar energy is one of the best candidates for solving energy problem with its advantages of non-polluting, reliable, and abundant supply. Dye-sensitized solar cells (DSSCs) are considered as an appealing photovoltaic methodologies for the conversion of sunlight into electrical energy, since the pioneering research by Grätzel et al. [1].

The efficiency of a DSSC depends on several factors such as photoanode, dye-sensitizer, counter electrode and electrolyte. Among them, the dye has a key role in the efficient conversion of

solar energy to electric power. Over the past years, a large number of dyes have been synthesized for using in the DSSCs. Among them, until now, organic dyes have received a remarkable attention owing to their low cost, tunable structures, high molar extinction coefficients and an easy preparation process [2–7]. An organic dye sensitizer consists of three units with the D- π -A configuration. Although the variation of each unit in the configuration has impact on the efficiency, however, the modification of π -spacer is more significant due to the fact that it can both tune the absorption region and also facilitate the injection of the excited electrons into the conduction band of TiO₂ semiconductor [8,9]. One of the successful strategies for the molecular engineering of organic dyes is to incorporate one additional acceptor as D-A- π -A motif that was proposed by Zhu et al. in 2011. They achieved improved photostability, broad spectral response and consequently a higher DSSCs performance with such a configuration [10].

As we know, bithiazole, is a good electron deficient unit due to the presence of C=N bonds. In 2011, Tian et al. investigated the influence of bithiazole moiety in the π -spacer on the efficiency of DSSCs [11]. They showed that these dyes have high open-circuit photovoltage (V_{OC}) due to the long alkyl chains of bithiazole moieties and consequently the reduction in charge recombination

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and inducing the conduction band edge shift. However, the reported short-circuit photocurrent density (J_{SC}) for these dyes is lower than that of the metal-based dyes and even some other metal-free organic dyes owing to their narrow spectral response. In recent years, considerable efforts have been made to improve the efficiency of these dyes by using different donor groups, inserting thiophene and cyano moieties as the π -spacer to increase light harvesting efficiency [12–14]. However, since experimental studies of the novel dye sensitizers design are based on trial and error approach, they are costly and time consuming. Therefore, theoretical methods based on density functional theory (DFT) and time-dependent DFT (TD-DFT) are considered as powerful guidelines for screening new efficient dye sensitizers. The recently experimentally synthesized dye **T-BT**, a bithiazole based dye (Starting at triphenylamine as a donor group, linked by thiophene as π -spacer and bithiazole unit as auxiliary acceptor and ending up with the cyanoacrylic acid as the electron-accepting unit), has a high V_{OC} but its J_{SC} is not satisfactory [12]. Thus, we have chosen **T-BT** as a reference dye for the computational design of novel dyes in this work.

To investigate the relationship between the structure and performance, the modification of thiophene group near the donor group in dye **T-BT** has been done. It has been shown that the existence of electron-rich π -spacer group is beneficial to enhance the intramolecular charge transfer (ICT) process owing to their ability to reduce the energy gap of the organic dye sensitizers, and consequently capturing more sunlight [15,16].

However, the influence of different electron-rich groups and their relative positions with respect to the bithiazole unit, auxiliary acceptor, in the π -spacer have not been studied to our knowledge. The structure of the investigated dyes are depicted in Fig. 1. It can be seen that the thiophene moiety near the donor group in the reference dye, **T-BT**, was substituted by a set of electron-rich moieties including 3,4-ethylenedioxythiophene (EDOT) [17], 3,4-ethylenedioxypyrrole (EDOP) [18], thieno [3,2-*b*] thiophene (TT) [19], pyrrolo [3,2-*b*] pyrrole (PP) [20], and thieno [3,2-*b*] pyrrole (TP) [21] on the left side of bithiazole unit (near the donor) from now on will be referred to as group 1, including **EDOT-BT**, **EDOP-BT**, **TT-BT**, **PP-BT**, and **TP-BT** respectively and on the right side of bithiazole unit (near the anchoring group) for dyes which will be referred to as group 2, including **BT-EDOT**, **BT-EDOP**, **BT-TT**, **BT-PP**, and **BT-TP**, respectively. Also, since the microscopic interfacial interaction between dyes and TiO_2 semiconductor has a vital effect on the efficiency of electron injection and consequently, the performance of the cell, the effect of TiO_2 semiconductor is considered in our theoretical modeling.

In this paper, the properties of ten pure organic dyes before and after adsorption on the TiO_2 nanoparticles are studied. Our first aim in this study is to shed light on how different electron-rich moieties affect on the performance of bithiazole-based dyes. The second aim is to investigate the effect of the relative position of electron-rich moieties with respect to the bithiazole unit on the efficiency of these dyes. We have found that the incorporation of electron-rich moiety as π -spacer near the donor group in bithiazole-based dyes is a valuable strategy to improve the efficiency of the dyes for using in the DSSCs.

2. Computational details

All the free organic dyes in neutral and ionic states (cationic and anionic) were optimized at the B3LYP/6-31G (d, p) [22] level of theory in the gas phase. To confirm the nature of each stationary point, vibrational analysis was performed at the same level. The results show that all the optimized structures correspond to an energy minimum with no imaginary frequency. Besides, since recent studies have shown that the replacement of long alkyl

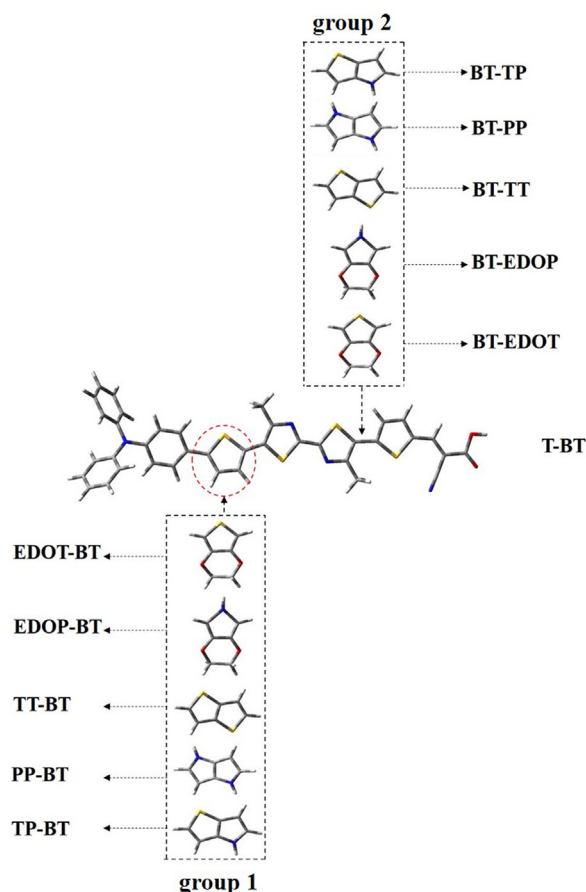


Fig. 1. Molecular structures of bithiazole-based dyes. The newly dyes are designed by substituting the thiophene unit near the donor group (as depicted in the red dashed circle) with a set of electron-rich moieties. The color-coding is as follows: blue (Nitrogen), gray (Carbon), white (Hydrogen), and yellow (Sulfur). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

chains on the bithiazole moiety by methyl groups does not have any significant influence on the electronic properties of the dyes, this replacement is done to reduce the computational costs [23,24]. To simulate optical absorption spectra of all dyes in their optimized geometries, the TD-DFT method was used for 30 lowest singlet–singlet excitations. The WB97X-D functional [25] at 6-311G (d, p) level has been chosen to obtain excited energies as we have reported in our recent work that this level leads to a better compatibility with experimental values for a series of bithiazole-based dyes [26]. To investigate the effect of solvent environmental (CH_2Cl_2), the conductor-like polarized continuum model (C-PCM) was employed [27,28]. All of these calculations were performed using GAMESS [29] program package. To analyze charge transfer phenomenon during electron transition process, the charge transfer parameters were calculated at the WB97X-D/6-311G (d, p) level using a method developed by Ciofini et al. [30,31] which was implemented in MULTIWFN 3.3.8 code [32].

To gain an insight into the electron injection properties at the interface of dye/ TiO_2 , the adsorption of the dyes on $(TiO_2)_9$ cluster was investigated with DFT calculations using SIESTA code [33–35]. Sanches et al. reported that $(TiO_2)_9$ cluster is large enough to replicate the electronic properties of dye/ TiO_2 systems [36]. For all dyes, the dye/ $(TiO_2)_9$ system was optimized by employing a double- ξ polarized basis set with a density mesh cutoff of 300Ry, norm-conserving pseudopotentials [37], and PBE generalized gradient approach [38] for all atoms in the system until the forces

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