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Theoretical design of thiazolothiazole-based organic dyes with different electron donors for dye-sensitized solar cells

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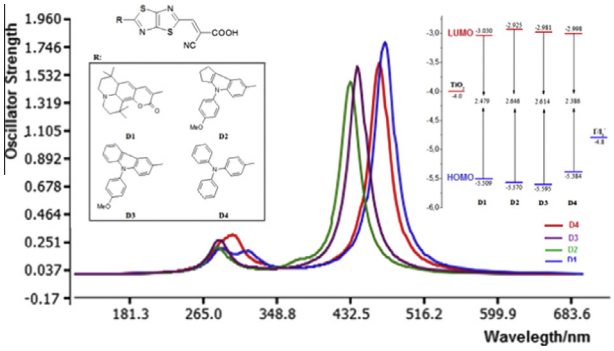
HIGHLIGHTS

- Four novel thiazolothiazole-based dyes are designed by modifying electron donor.
- The absorption shift to lower energies favors the light harvesting process.
- The better *Jsc* of D2 with indoline donor can be ascribed to enhanced LHE and $\Delta G^{inject.}$.
- The dyes could be used as potential sensitizers for DSSCs.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we have designed four novel organic donor–π–acceptor dyes (D1, D2, D3, D4), used for dye sensitized solar cells (DSSCs). The electron acceptor (anchoring) group was 2-cyanoacrylic for all dyes whereas the electron donor unit varied (coumarin, indoline, carbazole, triphenylamine) and the influence was investigated. These dyes, based on thiazolothiazole as π-spacer, were studied by density functional theory (DFT) and its extensible time dependant DFT (TDDFT) approaches to shed light on how the π-conjugation order influence the performance of the dyes in the DSSCs. The theoretical results have shown that the LUMO and HOMO energy levels of these dyes can be ensuring positive effect on the process of electron injection and dye regeneration. The trend of the calculated HOMO–LUMO gaps nicely compares with the spectral data. Key parameters in close connection with the short-circuit current density (*Jsc*), including light harvesting efficiency (LHE), injection driving force ($\Delta G^{inject.}$) and total reorganization energy (λ_{total}), were discussed. The calculated results of these dyes reveal that dye D2, with indoline as electron donor group, can be used as a potential sensitizer for TiO_2 nanocrystalline solar cells due to its best electronic and optical properties and good photovoltaic parameters.

Introduction

The constant growth in global energy demand, coupled with the environmental and economic concerns, has led to an intense research in the field of renewable energy resources, among which

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solar energy is widely seen as particularly promising. In this context, dye sensitized solar cells (DSSCs) certainly appear one of the most important devices for converting the solar energy to the electricity. DSSCs have attracted significant attention in scientific research and in practical applications due to their high efficiencies and low costs, since the first report by O'Regan and Grätzel in 1991 [1–3]. Up to now, DSSCs based on ruthenium and porphyrin dyes have shown very impressive solar to electric power conversion efficiencies. The PCE of Zn–porphyrin based DSSCs is up to 12% at the AM 1.5G condition using Cobalt (II/III) as redox electrolyte [4]. Although ruthenium and porphyrin dyes have high efficiencies, the large scale application of them is limited due to practical issues. For example, the difficulty of synthesis and purification of ruthenium and porphyrin dyes, and especially the limited availability and environment issues of the noble-metal ruthenium. Fortunately, metal-free organic dyes have been intensively investigated as alternatives owing to their high molecular extinction coefficients, simple preparations, low costs, various structures, unlimited resources, and environment friendly [5,6]. At present, lots of efforts have been dedicated to the development of metal-free organic dyes. Squaraine [7,8], coumarin [9,10], indoline [11], phenothiazine [12–15], triphenylamine [16–20], fluorene [21,22], thienopyrazine [23], carbazole [24–26] and tetrahydroquinoline [27] based organic dyes have been developed and exhibited satisfactory performance (up to 10.3% of PCE).

A typical DSSC based on organic dyes is constructed with a wide band gap semi-conductor (typically TiO_2) sensitized with molecular dyes, able to capture light in the visible region of the spectrum, electrolyte containing Iodide/triiodide (I^-/I_3^-) redox couple, and a platinum counter electrode [28–32]. In these cells, the sensitizers play an important role of capturing solar energy and generating electric charges. The most extensively studied organic dyes usually adopt the donor–π spacer–acceptor (D–π–A) structural motif in order to improve the efficiency of the UV/Visible (UV/Vis) photoinduced intramolecular charge transfer (ICT) [33]. In this structure, the ICT from D to A at the photoexcitation will inject the photoelectron into the conduction band of the semiconductor through the electron accepting group at the anchoring unit. Commonly, in order to obtain better performance of DSSCs, the following four factors are needed: good conjugation between the donor and acceptor through π-spacer; a strong absorption band which could cover almost all visible and near-infrared light region; proper redox potential of dye in the ground state and oxidization potential of dye in the excited state to facilitate dye regeneration and electron injection, respectively; strong electronic coupling between dye and conduction band of TiO_2 to speed up charge-transfer from dye to TiO_2 [34].

As we know, thiazolothiazole is rigid, coplanar and electron-accepting fused heterocycle due to the electron-withdrawing nitrogen of imine (C=N) and giving rise to a highly extended π-electron system [35]. Recently, thiazolothiazole frameworks have aroused interest as semiconducting materials with high carrier mobility, in organic electronics, in photovoltaics, as fluorescent sensors, as components of high performance polymer solar cells with the power conversion efficiency (PCE) up to 5–6% [36–39]. Despite the large body of work outlined above, to the best of our knowledge, the employment of thiazolothiazole as photosensitizers for DSSCs remains rare [40–43]. In our recent work, we have reported a theoretical study on a series of molecules with thiazolothiazole as π-spacer, some different heteroaromatic rings acting as donor groups, and linked to cyanoacrylic acid acting as acceptor/anchoring group forming D–π–A architecture, as photoactive components in DSSCs [44]. Considering lots of advantages of the thiazolothiazole as π-spacer together the most commonly used cyanoacrylic acid acceptor, and the excellent electron donating ability of coumarin, indoline, carbazole and triphenylamine, we decided in this work to design new four organic D1, D2, D3 and D4 thiazolothiazole-based dyes (Fig. 1).

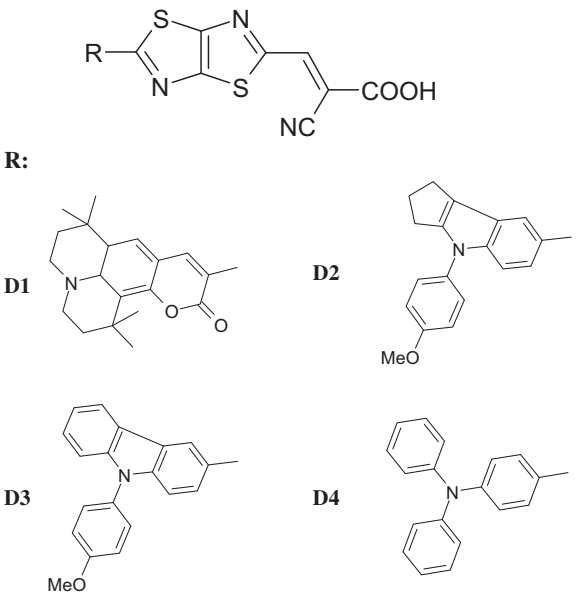

Fig. 1. Sketch map of dyes structure.

In current contribution, the density functional theory (DFT) and its extension, time-dependent DFT (TD-DFT), have been proved to be the promising methods in the obtaining of accurate results of dye sensitizers in DSSCs system, not incurring high computational cost and being reasonable to experiment results [45–49]. In the present work, this theoretical computation method is used to analyze the role of different electron donor groups on the geometries, electronic structures and simulated absorption spectra properties. Also, the injection driving force ($\Delta G^{\text{inject.}}$), light harvesting efficiency (LHE), and total reorganization energy (λ_{total}) have been investigated to see the sensitizer donor effects on the short-circuit current density (*Jsc*) with the goal of finding potential sensitizers for use in DSSCs. We hope our work could facilitate the future experimental studies to design and fast screen new efficient organic dyes.

Methods

Theoretical background

Generally, the short-circuit current density *Jsc* in DSSCs is determined as:

$$J_{sc} = \int_{\lambda} LHE(\lambda)\Phi_{\text{inject}}\eta_{\text{collect}}d\lambda \quad (1)$$

where $LHE(\lambda)$ is the light harvesting efficiency, Φ_{inject} is the electron injection efficiency, and η_{collect} is the charge collection efficiency. For the same DSSCs with only different dyes, it is reasonable to assume that the η_{collect} is a constant.

As a result, to shed light onto the relationship between the *Jsc* and η theoretically, we investigated the *LHE*, Φ_{inject} and total reorganization energy (λ_{total}). From Eq. (1), to obtain a high *Jsc*, the efficient sensitizers applied in DSSCs should have a large *LHE*, which can be expressed as [50]:

$$LHE = 1 - 10^{-f} \quad (2)$$

where f is the oscillator strength of the dye associate to the wavelength $\lambda_{\max}$. We noticed that the larger f obtained, the higher *LHE*