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Theoretical investigation of phenothiazine–triphenylamine-based organic dyes with different π spacers for dye-sensitized solar cells

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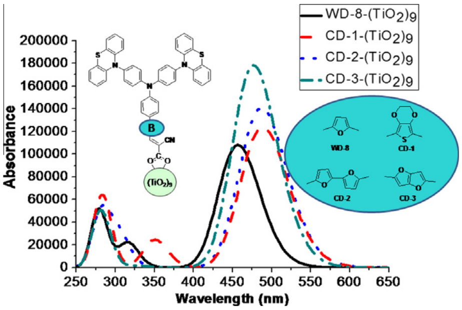
HIGHLIGHTS

- Three novel phenothiazine–triphenylamine-based organic dyes are designed.
- The dyes contain different aromatic groups as conjugated spacers.
- The dyes before and after binding to TiO_2 are studied by DFT and TD-DFT.
- The simulated spectra of **CD-1**~**3** show better absorption than that of **WD-8**.
- The dyes could be used as potential sensitizers for DSSCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Three phenothiazine–triphenylamine-based organic dyes (**CD-1**, **CD-2** and **CD-3**) are designed based on the dye **WD-8**. The geometries, electronic structures, and electronic absorption spectra of these dyes before and after binding to TiO_2 are studied by density functional theory (DFT) and time-dependent density functional theory (TD-DFT). The calculated geometries indicate that these dyes show good steric hindrance effect which is advantage to inhibit the close intermolecular π–π aggregation effectively. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of these dyes could ensure positive effect on the process of electron injection and dye regeneration. The simulated spectra of **CD-1**~**3** show better absorption than that of **WD-8** in the low energy zone. All the calculated results demonstrate that these dyes could be used as potential sensitizers for DSSCs and show better performances than **WD-8**.

Introduction

Dye-sensitized solar cells (DSSCs) have attracted the considerable attention of many research groups owing to their high efficiencies and low costs, since the seminal work was reported in 1991 by Grätzel and O'Regan [1–3]. Up to now, DSSCs based on ruthenium and porphyrin dyes have shown very impressive solar to electric power conversion efficiencies. The DSSC based on black dye with donor–acceptor type coadsorbent has reached an overall solar energy conversion efficiency (η) of 11.4% [4], and the DSSC based on porphyrin with cobalt (II/III)–based redox electrolyte has obtained a new record efficiency of more than 12% [5]. Although ruthenium and porphyrin dyes have high efficiencies, the large-scale application of them is limited due to practical issues. For example, the synthesis and purification of ruthenium and por-

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phyrin dyes are very difficult, especially the ruthenium dyes need noble metal Ru which is scarce and disadvantage to environmental protection.

Fortunately, metal-free organic dyes are various alternatives to ruthenium and porphyrin dyes due to their high molecular extinction coefficients, simple preparations, low costs, and environment friendly [6,7]. At present, lots of efforts have been dedicated to the development of metal-free organic dyes. Coumarin [8–10], squaraine [11,12], indoline [13–15], phenothiazine [16–19], triphenylamine [20–22], fluorene [15,23,24], carbazole [25–27] and tetrahydroquinoline [28] based organic dyes have been developed and shown good performances. In particular, it encourages to note that a promising overall solar energy conversion efficiency (η) up to 10.3% has been demonstrated by Wang et al. [29].

Most organic dyes are composed by electron donor, π spacer and acceptor moieties and usually have a rod-like configuration. However, the rod-like molecules are elongated, which may facilitate the recombination of electrons with the triiodide and the formation of aggregates between the neighbor molecules [30]. Therefore, organic dyes with a starburst conformation were designed and synthesized by introducing additional electron donor groups into the D–π–A molecule to form the starburst 2D–D–π–A structure [31–33], which avoids the charge recombination process of injected electrons with the triiodide in the electrolyte and the formation of aggregates between dye molecules. Recently, we reported a novel organic dye **WD-8** [34] and the η of 6.79% was obtained based on the corresponding DSSC. Compared with the reported **WD-1** [35] by our group, the conversion efficiency of DSSC based on the dye **WD-8** has increased by 2.25% (that of **WD-1** is 4.54%). This work suggested that optimizing the phenothiazine–triphenylamine-based organic dyes by introducing furan groups as π configuration spacer between electron donors and electron acceptor is a promising way for improving optical absorption, charge transfer and photovoltaic performance.

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 [36–41]. In this paper, this theoretical computation method is used to find more promising π configuration spacers for phenothiazine–triphenylamine-based organic dyes. With this purpose, we designed three new starburst 2D-D-π-A organic dyes (**CD-1**, **CD-2,** and **CD-3**) with different conjugated spacer groups (Fig. 1). These organic dyes are comprised by phenothiazine–triphenylamine unit as a starburst electron donor, 2-cyanoacetic acid as an electron acceptor, and the different aromatic groups as conjugated spacers, i.e., EDOT, 2-(furan-2-yl)furan, and furo[3,2-b]furan. The effects of the different conjugated spacers on the geometries, electronic structures and simulated absorption spectra properties of these organic dyes were studied to compare with the dye **WD-8**. Besides, a simple dye–titanium dioxide $(TiO_2)_9$ model [42] was chosen to simulate the electron transfer between the dyes and TiO_2, and the effects of the dyes adsorbed to TiO_2 film on the simulated absorption spectra were further studied.

Computational methods

Technical details

The phenothiazine–triphenylamine-based dyes **WD-8** and **CD-1∼3** before and after binding to TiO_2 in vacuum are calculated at density functional B3LYP [43] level using the 6-31G* for C, H, O, N, S atoms and effective core potential (ECP) LANL2DZ and its accompanying basis set for Ti atom for both geometry optimizations and frequency calculations. None of the frequency calculations generated imaginary frequencies, indicating that the optimized geometries are true energy minima. Electronic populations of the HOMO and LUMO are calculated to show the position of the localization of electron populations along with the calculated molecular orbital energy diagram. As for the absorption, coulomb-attenuating method CAM-B3LYP [44] functional was chosen to calculate the vertical excitation energies and the oscillator strengths [45] within the framework of TD-DFT. The solvent effect of acetonitrile (the solvent used to record the experimental spectra) on the absorption spectra, was considered using non-equilibrium implementation of the conductor-like polarizable continuum model (CPCM), which returns valid solvent effects when there are no specific interactions between the solute and the solvent molecules [46]. All calculations have been performed with the Gaussian 09 packages [47].

Models

The similar computational methodology has been applied to four dyes (**WD-8**, **CD-1**, **CD-2** and **CD-3**) and each dye adsorbed onto a $(TiO_2)_9$ cluster. The starting geometry for **WD-8** was taken from the literature [34], and the starting geometry for $(TiO_2)_9$ cluster was taken from the literature [42]. This cluster was obtained via geometry optimization of the originally spherical shape resulting in a compact structure with only 4-fold coordinated Ti-atoms and with one terminal Ti–O bond. The modeling of $(TiO_2)_9$ cluster has been proved that it is enough to reproduce adequately the electronic absorption spectra of dye-TiO_2 systems by Sanchez-de-Armas and his group [48,49].

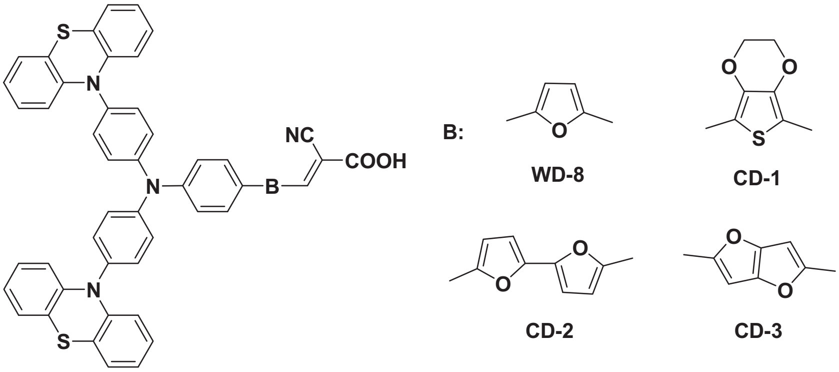

Fig. 1. Molecular structures of **WD-8** and **CD-1∼3**.