Full Length Article

Inclusion of aggregation effect to evaluate the performance of organic dyes in dye-sensitized solar cells

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ABSTRACT

Two new indoline-based D-A-π-A dyes, **D3F** and **D3F2** (see Scheme 1), are developed on the basis of the reported **D3** by insertion of one or two F atoms on benzothiadiazole group. Our central aim is to explore high-efficiency organic dyes applied in dye-sensitized solar cells by inclusion of a simple group rather than by employment of new complicated groups. The performance of two new designed organic dyes, **D3F** and **D3F2**, is compared with that of **D3** from various aspects including absorption spectrum, light harvesting efficiency, driving force, and open-circuit voltage. Besides the isolated dye, the interfacial property between dye and TiO$_2$ surface is studied. **D3F** and **D3F2** do not show absolute superiority than **D3** not only for the isolated dyes but also for the monomeric adsorption system. However, **D3F** and **D3F2** would effectively reduce the influence of aggregation resulting in the much smaller intermolecular electronic coupling. Although the aggregation has attracted much attention recently, it is studied alone in most of studies. To comprehensively evaluate the performance of dye-sensitized solar cells, it is necessary to consider aggregation along with electron injection time from dye into TiO$_2$ rather than only static items, such as, band gap and absorption region.

1. Introduction

The utilization of renewable and pollution-free energy has been the global motif because of the rapid depletion of fossil fuels and more severe environmental issue. Photovoltaic technology has aroused tremendous attention since it would directly convert abundant and clean solar energy to electricity. Since the seminal report by Grätzel [1], dye-sensitized solar cells (DSSCs) are regarded as one of the most promising alternatives to silicon-based solar cells due to its relative reasonable power conversion efficiency (PCE), easy of fabrication, tunable optical properties, and low cost [2–5]. As the vital component of DSSCs, dye sensitizer governs the photon harvest and charge generation and separation [6]. Although the metal sensitizers, Ru-complexes and Zn-porphyrins, have achieved the remarkable PCE so far, their large scale applications are still limited because of the scarcity, complicated synthetic process, tedious purification, and environmental issue [5]. In contrast, organic sensitizers as the other major category are fascinating due to their versatile molecular engineering, high molar extinction coefficients, and abundant raw material [7].

D-π-A configuration is the most classical structure for organic dyes, which ensures the effective intramolecular charge transfer [8]. In 2011, Zhu et al. proposed a new D-A-π-A model by incorporation of an auxiliary acceptor into π bridge to further broaden the spectral response and improve the dye stability [9]. Recently, several kinds of electron-withdrawing groups have been developed to be auxiliary acceptor for D-A-π-A motif, including benzothiadiazole (BTD) [10], benzotriazole (BTZ) [11], and diketopyrrolopyrrole (DPP) [12]. Last year, Song et al. have synthesized a novel indoline-based D-A-π-A dye (**D1**) with BTD as auxiliary acceptor and benzoic acid as anchoring group. On the basis of **D1**, another organic dye (**D3**) is explored by inclusion of an ethynyl unit between BTD and benzoic acid [13] (see Scheme 1). Correspondingly, the PCE is improved from 6.12% (**D1**) to 7.13% (**D3**). The ultimate goal to design a new dye is that the PCE would be greatly improved by insertion of a simple group or by a slight variation in configuration. Serials of organic dyes have been synthesized by insertion of F atom in different positions of π group to refine the performance of DSSCs [14–18]. Moreover, the F atom (s) has also been substituted on BTD group to develop D-A-π-A dyes [19]. Inspired by previous research, two novel D-A-π-A dyes (**D3F** and **D3F2**) are designed by inclusion of one or two F atoms in BTD on the basis of **D3** with the aim to explore the influence of F atoms (see Scheme 1).

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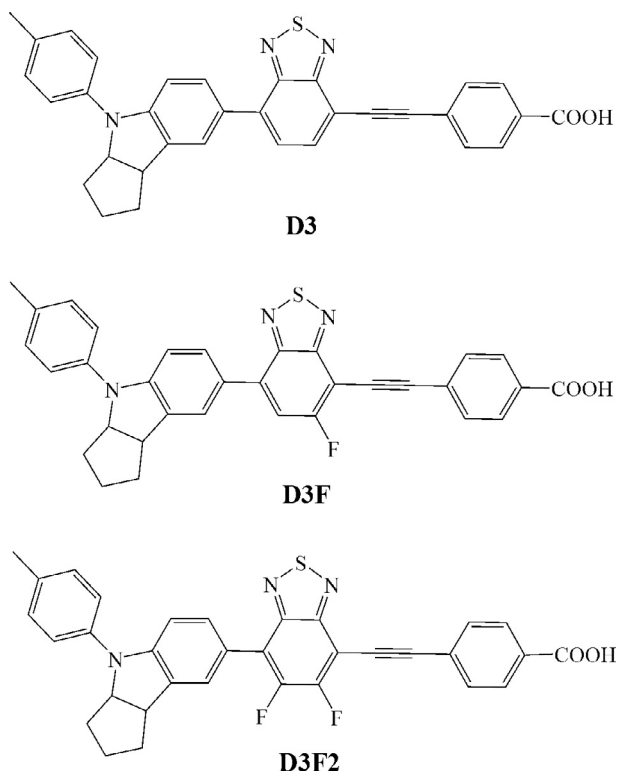
Scheme 1. The sketch structures of all the investigated dyes.

It is well known that the PCE of DSSCs is greatly affected by the molecular structure of organic dyes. Numerous investigations have been reported to develop various organic dyes with different motif, individual groups, and combination of them [20–23]. Besides the experimental studies, extensive theoretical studies have also been carried out to elucidate the structure-activity relationship [24,25]. It is beneficial to develop novel high-efficiency organic dyes with the desired goals. However, there are two common shortcomings in almost all studies. The photoinduced electron injection in DSSCs takes place in the femtosecond time scale, which is required to be analyzed to explain the deviations among different solar cells. In contrast, only the static items associated with the PCE, such as, band gap, absorption region, and injection free energy, are reported in previous reports [26]. Additionally, there are a number of deactivation pathways that could compete with the electron injection, which is neglected in development of new dyes. The aggregation is one of the most common and well known deactivation pathways, which is related with the sensitizing dye orientation and molecular packing on the semiconductor surfaces. It is a difficult and almost impossible task for experiment to analyze the aggregation. In contrast, the computational modeling is a powerful tool to study it.

In this work, three D-A-π-A configuration dyes are investigated with the goal to explore more efficient organic dyes. Besides the properties, such as, frontier molecular orbitals, absorption spectrum, and injection free energy, related with the free dyes, the interfacial properties between dyes and TiO$_2$ surface is explored. The electron injection time is estimated to evaluate the performance of dyes from the kinetic viewpoint. Finally, the influence of aggregation of dyes on performance of DSSCs is carried out. The great challenge of DSSCs is the purposeful design of novel organic dyes. We expect that this work would shed light on the numerous factors contributing to the cell performance rather than take PCE alone.

2. Computational details

The ground-state geometries of isolated dyes were optimized by the three- parameter functional of Becke and the correlation functional of Lee et al. (B3LYP) [27,28] with a standard 6-31G(d, p) basis set on all atoms. The nature of optimized structures is confirmed by the frequency calculations at the same level. Based on the optimized ground-state geometries, the absorption spectra were simulated by LC-BLYP method [29,30] with the polarized continuum model (PCM) in dichloromethane [31,32]. Abovementioned electronic calculations were performed by the Gaussian 09 program [33].

The following calculations were completed in VASP (Vienna ab initio simulation package) program [34,35]. To study the interaction between dye and TiO$_2$, a $6 \times 7 \times 4$ TiO$_2$ anatase (1 0 1) supercell was taken as the adsorption surface, since the thermodynamically stable (1 0 1) facet has been testified to be the most favorable surface in TiO$_2$ anatase crystals [36]. A vacuum buffer space of 30 Å was added in z direction. The isolated dye, bare TiO$_2$ surface, and dye-TiO$_2$ system were optimized by means of projector-augmented wave methods with the generalized gradient approximation (GGA) using Perdewe-Burkee-Ernzerhof (PBE) exchange-correlation functional implemented [37,38]. Grimme D2 dispersion correction was added to the functional to take into account dispersion effects [39]. 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}. Furthermore, the densities of states (DOS) and projected density of states (PDOS) were calculated at the same level to deeply analyze the adsorption properties.

3. Results and discussion

3.1. Frontier molecular orbitals

On the basis of working principle of DSSCs, the lowest unoccupied molecular orbital (LUMO) energy level of dye should be higher than the conduction band (CB) of TiO$_2$ to ensure that electrons from photo-excited sensitizer would be efficiently injected into the TiO$_2$. At the same time, the highest occupied molecular orbital (HOMO) energy level of dye should be lower than the redox couple iodine/triiodide electrolytes to ensure that the oxidized sensitizer would accept the electron from redox couple back to the ground state by electron transfer [6]. Three investigated dyes are all satisfied for the basic requirement to be a sensitizer in DSSCs (see Fig. 1).
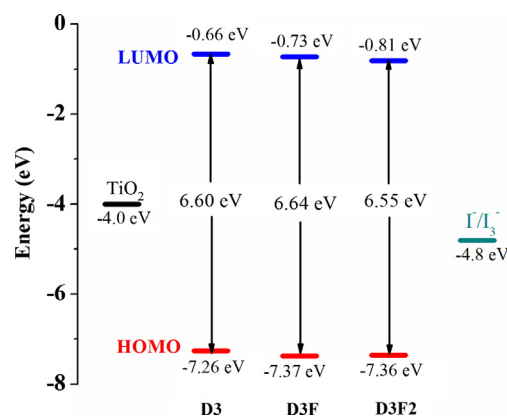

Fig. 1. Molecular orbital energy levels of all the investigated dyes along with the energy levels of TiO$_2$ and the electrolyte.