Synthetic Metals 237 (2018) 1–9

Contents lists available at ScienceDirect

Synthetic Metals

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

Rational tailoring of C275 towards promising organic dyes: Enhancing light absorption and charge separation

Zhu-Zhu Sun[a,*], Xiao-Ju Geng[a], Wei-Lu Ding[b], Shuai Feng[c,*], Yu-Lin Xu[a], Yan-Lei Li[a], Zhen-Yu Xiao[a], Shu-Jie Sun[a], Zhi-Qiang Zhao[a], Jiang-Feng Liu[a]

[a] *Energy-Saving Building Materials Innovative Collaboration Center of Henan Province, Xinyang Normal University, Xinyang, 464000, China*

[b] *Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry, Beijing Institute of Technology, Beijing, 100081, China*

[c] *College of Chemistry and Chemical Engineering, Taishan University, Taian, 271021, China*

ARTICLE INFO

Keywords:
Dye-sensitized solar cells
Organic dyes
Light absorption
Charge transfer
Density functional theory

ABSTRACT

Designed with electron-donating and electron-withdrawing moieties as donors and acceptors, respectively, a series of novel organic dyes for dye-sensitized solar cells (DSCs) are simulated using density functional theory (DFT) and time-dependent DFT (TD-DFT) methods The interacting dye/TiO_2 systems are also studied to further explore the interfacial injection process of photo-excited electron. The model dye C275 is featured with donor/acceptor (D/A) molecular architecture, which is primary to achieve the easy charge-transfer excitation and suitable energy levels alignment. To date, considerable efforts are devoted to the design and synthesis of D/A type organic dyes, and the initial configurations are typically comprised of N-annulated perylene donor, porphyrin linker, and carboxylic acid acceptor. Our results show that, the electronic levels and optical absorption properties can be tuned gradually by introducing auxiliary donor units or electron-deficient spacer in acceptor groups. Moreover, the designed dyes also exhibit good performance in terms of photoinduced charge transfer, electron injection, and dye regeneration, *etc.* Through structural modification of donor moieties, the new tailored dyes provide appropriate energy levels, strong light-harvesting and easy charge separation. Meanwhile, the distinct red-shift of optical absorption and large amount of transferred charges are also obtained by structural tailoring of acceptor groups, whereas the large values of injection time may be harmful for the interfacial photoelectron injection. Therefore, comparing with donor modification, it should be more carefully to choose appropriate acceptor group with the balance of various energetic and kinetic factors for the rational design of high-efficient organic dyes.

1. Introduction

Dye-sensitized solar cells (DSCs) have been extensively investigated due to their comparable efficiency and cost-effectiveness since the breakthrough by O'Regan and Grätzel in 1991 [1]. As the heart of DSCs, the dye is responsible for light-harvesting, charge separation at dye/semiconductor interface, and dye regeneration, *etc*. To improve the power conversion efficiency (PCE) of DSCs, substantial efforts have been devoted to design and synthesis of high effective dyes through reducing molecular energy gap and enhancing optical absorption. To date, some cells made of ruthenium polypyridine and zinc porphyrin complexes exhibit excellent performance in the aspects of cell stability and efficiency [2–5]. Meanwhile, the metal-free organic dyes have also attracted considerable research interests due to the abundance of raw materials, the flexibility of molecular design, and the cheerful vision effects [6,7].

The metal-free organic dyes are commonly characterized by the donor-π-acceptor (D-π-A) configuration, featuring with an effective intramolecular charge-transfer excitation. The most representative donor moieties include triphenylamine, carbazole, and indoline, which can notably affect the photovoltaic performance of DSCs through the electron-donating ability and the steric architecture. In 2014, Yang et al. reported two molecularly engineered organic dyes (YA421 and YA422) by adding auxiliary electron-donating moieties based on the typical IQ4 dye ($\eta = 9.24\%$), consequently, the new designed dye YA422 obtained a higher PCE of 10.65%, which benefits from the increased steric hindrance and the widened absorption spectra [8]. Particularly, even a minor modification of donor moiety may also lead to prominent changes in cell performance. Thus, it is essential to choose appropriate donors with matched energy levels, strong light absorption, and easy

---

* Corresponding authors.
E-mail addresses: zhuzhusun@xynu.edu.cn (Z.-Z. Sun), hffsh.1982@163.com (S. Feng).

https://doi.org/10.1016/j.synthmet.2018.01.004
Received 13 October 2017; Received in revised form 14 December 2017; Accepted 10 January 2018

charge separation. Apart from the donor moiety, cell performance can also be significantly influenced by the nature of π-conjugated linker, and the acceptor group. The π-conjugated linker is imperative to facilitate the effective light-induced charge transfer, and to regulate the molecular energy levels. Meanwhile, the acceptor group plays an important role for the interfacial photoelectron injection.

In the past decade, considerable efforts have been made on the exploration of superb electron-donating moieties. Perylene and its derivatives have also been employed as the building blocks of organic and metal-organic dyes [9–11]. Among the various building blocks, N-annulated perylene (NP), in which the nitrogen atom is annulated at the bay region of perylene, has been demonstrated to be an ideal candidate as donor moiety due to its intrinsic electron-rich nature [12–23]. As a coplanar electronic skeleton, the NP unit initially used by Wu and coworkers as an electron-donating moiety of zinc-porphyrin dye, and achieved an encouraging PCE of 10.5% [12]. Subsequently, Wang et al. employed a modified Phenyl-functionalized N-annulated perylene (PNP) as electron-donor, and conjugated it with the electron-acceptor ethynylbenzothiadiazole-benzoic acid (EBTBA) to prepare a structurally simple perylene dye C272, exhibiting an equal PCE of 10.4% [24]. By further rigidifying the aromatic units of donor part (N-annulated indenoperylene, NIP), the new designed indenoperylene dye C275 achieves a higher PCE of 12.5% [25], and recently, the cell efficiency has upgraded of 13% [26], setting a benchmark for the coadsorbate-free organic DSCs.

Inspired by the successful utilization of perylene dyes in the prepared device, in this manuscript, the C275 dye was judiciously tailored to further explore the clues that guide the rational design of organic dyes and to scrutinize the promising dyes used in DSCs. By replacing the three parts of alkoxyphenyl, ethynylene, and benzothiadiazolylbenzoic acid (BTBA), twelve new dyes were designed based on the model dye C275. As displayed in Fig. 1, the replaced parts of C275 dye were denoted as R1, R2 and R3, and the segments employed to build new dyes were listed below. The electronic and optical properties and the photoelectron injection process have been studied for all considered dyes using density functional theory (DFT) and time-dependent DFT (TD-DFT) approaches. Through systemic investigations, several dyes were proposed as potential candidates toward more efficient DSCs.

2. Computational details

The ground-state geometries of investigated dyes were optimized using DFT with the hybrid functional B3LYP, coupled with the 6–31G* basis set [27,28]. Based on the optimized geometries, the UV–vis spectra were obtained by performing single-point TD-DFT calculations with the hybrid functional MPW1 K and 6–31G* basis set [29,30]. In order to consider the solvent effects, the tetrahydrofuran (THF) solvent was employed during the ground-state optimizations and the TD-DFT calculations with the C-PCM method [31]. Frequency calculations were performed at the same theoretical level as the ground-state optimizations to confirm the nature of the minima. The geometry optimizations of the first exited singlet electronic state were carried out using the CAM-B3LYP/6-31G* method in THF solution [32]. To get the vertical emission energies, single-point TD-DFT calculations were implemented based on the optimized excited-state geometries, where the hybrid functional MPW1 K and 6–31G* basis set were used. The light-harvesting efficiencies (LHE) were assessed according to: $LHE = 1 - 10^{-f}$, where f is the oscillator strength of dye [33]. The exited-state lifetimes (τ) were evaluated by applying the definition $\tau = 1.499/(fE^2)$, where f and E are the oscillator strength and the excitation energy of different electronic states, respectively [34,35]. Moreover, the amount of transferred charges (q_{CT}) and the charge-transfer distances (d_{CT}) were calculated with the method reported by Ciofini et al. [36,37]. It should be also noted that the photochemically idle alkyl chains of dyes were omitted in this work to minimize the amount of calculations. All the calculations above were performed with the Gaussian 09 program package [38].

The full geometry optimizations of dye/$(TiO_2)_{38}$ complexes were carried out using spin-unrestricted DFT with the PBE functional and double-numeric quality basis set with polarization functions (DNP) in vacuum [39], and performed with the DMol^3 package in Materials Studio [40,41]. Based on the optimized dye/$(TiO_2)_{38}$ geometries, single-point DFT and TD-DFT calculations in THF solution were performed with Gaussian 09 to gain the electronic and optical properties of dye adsorbed systems at the same level of theory as that for the free dyes. The injection times of photo-excited electron were estimated according to the Newns-Anderson model $\tau(fs) = 658/\hbar\Gamma(meV)$, where $\hbar\Gamma$ is the LUMO broadening width [42,43]. Herein, the $(TiO_2)_{38}$ cluster was obtained by appropriately cutting an anatase slab with the (101) surface exposed, which was believed to be reliable to simulate the effects of the semiconductor surface (displayed in Fig. S2) [44,45]. The carboxylate groups are working as anchors for the organic dyes to coordinate with the Ti atoms on the TiO_2 surface, and the bidentate-bridging architecture is energetic favorable [46]. Therefore, the interacting dye/$(TiO_2)_{38}$ complexes with bidentate-bridging configuration was employed in the following investigations.

3. Results and discussions

3.1. Modification and improvement of donor moiety

Benefiting from the development of DFT and TD-TDF approaches, computational simulations have played an important role for designing new dyes with great light-harvesting capacity and appreciate energy levels. It is well known that the electron-donating capacity of donor moiety puts remarkable impacts on the energy level of the highest occupied molecular orbital (HOMO), which further affects the absorption spectra of dye and the interfacial charge transfer such as dye regeneration and charge recombination. Thus, we firstly modified the donor part of C275 dye by replacing the alkoxyphenyl group with four segments denoted as R1-1, R1-2, R1-3 and R1-4, (see Fig. 1 for more details), to regulate the electron-donating capacity of donor moiety. Notably, the R2 and R3 parts of C275 were unaltered when the alkoxyphenyl group (R1) was replaced.

The calculated absorption maximum of C275 is found to locate at 543 nm (2.28 eV), which is in good agreement with the experimental value of 536 nm in THF solution [25]. This maximal absorption is mainly contributed by the transition from the HOMO to the lowest unoccupied molecular orbital (LUMO) (88%, as listed in Table 1). Comparing the HOMO and the LUMO energies of −5.06 and −2.99 eV with the data derived from experimental results (-5.05 eV for the HOMO and −3.29 eV for the LUMO) [25], we found that an accurate description for the HOMO energy level was given by the calibration of B3LYP/6-311G** method, whereas the LUMO was slightly destabilized. Based on the discussion above, we believe that the method used here is suitable for considering the effect of dye tailoring.

The electronic and optical properties of the C275 and the designed dyes are summarized in Table 1. The HOMOs of the R1-1, R1-2, R1-3, and R1-4 dyes are −5.02, −4.88, −4.84, and −4.77 eV, respectively, which exhibit an ascending trend with the enhancing of the electron-donating capacity of donor moieties, whereas the LUMOs (from −3.0 eV to −2.97 eV) are less influenced by these changes in donor. The energetic up-shift of the HOMOs and the stable LUMOs result in gradually reduced molecular energy gaps ($\triangle E_{HL}$) from 2.07 eV (R1-1) to 1.81 eV (R1-4), as illustrated in Fig. 2a. Meanwhile, the absorption spectra exhibit obvious red-shift from R1-1 (548 nm), R1-2 (556 nm), R1-3 (569 nm), to R1-4 (577 nm) (see Fig. 2b), following the decreased energy gaps. The lowest excitation energies ($\triangle E_{EX}$) and corresponding oscillator strength (f), as well as the light-harvesting efficiencies (LHE) are listed in Table 1. As the case of C275, the maximum optical absorption of the R1-series dyes is mainly composed of the transition from the HOMO to the LUMO. Particularly, the proportion of the HOMO-1 to