Comparison of p-type sensitizers with different electron-induced effects in dye-sensitized solar cells: A theoretical investigation

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ABSTRACT

Two classical p-type photosensitizers with modified conjugation spacers by the electron-rich unit (thiophene) and electron-deficient unit (pyrimidine) are calculated and investigated using density functional theory (DFT) and time-dependent DFT (TD-DFT). Creatively, regeneration reactions between reduced sensitizers and I_3^- as well as I_2^- are explored theoretically, reappearing the regeneration process that electrons are transferred from reduced dyes to I_3^- or I_2^- in p-type dye-sensitized solar cells (p-type DSSCs) intuitively, and uncovering the difference of π-spacers with different electron-induced effects in the process of dye regeneration. Besides, calculation also indicates that thiophene-based dye (P_S) has better light capture efficiency but unfavorable performance of charge transfer when compared with the pyrimidine-based dye (P_N). From another perspective, both sensitizers have efficient driving forces of injection. In addition, dyes absorbing on the $(NiO)_9$ semiconductor are also considered. Our comparison discussion of two sensitizers with different π-spacers provides great assistance for deeply investigating p-type photosensitizes with higher efficiencies and their regeneration processes, contributing to the potential tandem DSSCs.

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1. Introduction

Enormous efforts have been devoted to dye sensitized solar cells (DSSCs) owing to their great potential of environment-friendly and low-cost, since crucial contributions were made by Grätzel and co-workers in 1991 [1]. It's worth noting that more attention is gained for classical n-type DSSCs, while, comparatively little work is paid on the p-type DSSCs, their highest power conversion efficiency (PCE) is only 2.51% [2], far below 13% realized in a zinc-porphyrin sensitized n-type DSSC [3]. Fundamentally and practically, one type of promising tandem devices, pn-type DSSCs, are confined by the p-type DSSCs with low-efficiency, upgrading the efficiency of p-type DSSCs is becoming a crucial task in the development of solar cells [4].

Although two types of mechanisms have be conceived for the hole and electron transfer process in p-type DSSCs [5], the primary one is that one electron is transferred from the valence band (VB) of mesoporous nickel oxide (NiO) to dye* as soon as the sensitizer is triggered by the photoexcitation, subsequently, the reduced dye transfers one of its electrons to the oxidized regenerator (typically the iodide/triiodide in electrolyte) [5–8]. Apparently, the photosensitizer plays an irreplaceable role in the photoelectric conversion process, and it exerts great influence on the optical performance and power conversion efficiency of the cell device. It is necessary to deeply explore the effect of architectural difference of p-type dyes on PCEs.

In n-type sensitizers, π-spacers with different electron-induced effects, typically the electron-rich units [9–12] (benzene, thiophene and furan, etc.) and the electron-deficient units [13–15] (pyridine, pyrrole and pyrimidine, etc.), are explored and reported in some degrees. Besides, the pivotal dye regeneration processes, especially for the Ru-based sensitizers N3 [16–21], N719 [22–24] and their analogues [25–27], are widely explored involving both experiment and theory. On the contrary, there is a little comparative calculation investigation on the π-spacers of p-type sensitizers [11,28], especially for their different electron-induced effects. Importantly, differing from the process of dye regeneration in n-type DSSCs, there are some difficulties to explore the regeneration process of p-type DSSCs on account of the involved excited state of dye [5]. Thus, it's meaningful to investigate the p-type dyes with different electron-induced effects theoretically. What's more, their interactions with redox couple in electrolyte also should be taken into account intuitively.

In previous work, actually, we have explored the effect of different linker moieties on the performance of p-type dye-sensitized

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solar cells (DSSCs) on the basis of the electron-rich unit (thiophene) and the electron-deficient unit (pyrimidine) with different lengths in two special bridge-sites of sensitizers [29]. Here, our study is mainly focused on the regeneration process of p-type photosensitizer for investigating the effect of conjugation bridges with different electron-induced effects on regeneration process. Based on the classical sensitizer with "push-pull" configuration: 4-(Bis-{4-[5-(2,2-dicyano-vinyl)-thiophene-2-yl]-phenyl}-amino)-benzoic acid (P1, also be named P_S), which had captured much attention since it was came up by Peng and co-workers in 2008 [30–32], the electron-deficient unit pyrimidine is introduced and replaced the thiophene unit with electron-rich property as the π-spacer, being named P_N. To investigate how the π-spacers with different electron-induced effects affect the performance of appliances, some important parameters, such as electronic property, optical property, charge transfer property, as well as the driving forces of hole injection, dye regeneration and charge recombination, are systematically surveyed for the two typical sensitizers P_S and P_N. Interestingly, in the second part of our discussion, interactions between reduced dyes and redox couples in electrolyte are introduced and discussed, describing two kinds of dye regeneration processes vividly. We believe that these good comprehension of the difference between thiophene-based bridge and pyrimidine-based bridge could provide some important guidance for the further research of p-type sensitizers with higher PCEs, additionally, this exploration of interactions between dyes and triiodide (I_3^-) as well as diiodide (I_2^-) clearly presents the way of regeneration and their interplays.

2. Computational details

It is reliable to obtain the ground state structures of sensitizers with B3LYP based on a great number of literature researches [33–35], moreover, some studies have applied this functional to investigate our target molecule P_S successfully [5,36–38]. Where, the ground-state geometries of all the studied dyes, regardless of the isolated dyes or dyes binding with $(NiO)_9$ cluster, are fully optimized at the calculated level of density functional theory (DFT) using B3LYP functional combined with 6-311G(d,p) basis set for light atoms (C, H, O, N, S) and LanL2DZ with corresponding pseudopotential for heavy atom (Ni), as presented in Fig. S1. To simulate the photoexcitation characters of sensitizes more accurately, four vital functionals generally applying for properties of excited states (B3LYP, PBE0, wB97XD and CAM-B3LYP) are carried out on the basis of time-dependent density functional theory (TD-DFT) [5], which is slightly different with our previous study [29]. As shown in Table S1, the hybrid functional CAM-B3LYP together with 6-311G(d,p) basis set is selected as the most suitable calculation method for optical parameters. Besides, solvent effects are investigated by using acetonitrile as the solvent in the whole computation, and the polarized continuum model (PCM) is taken throughout. Additionally, frequency calculations are put into effect in the geometry optimizations for avoiding the occurrence of imaginary. All the calculations are gained by the Gaussian 09 program [39].

What's more, the results of electron-hole separation induced by light are obtained by Multwfn 2.5 [40]. Some properties of charge transfer, such as the electron transfer distance, the fraction of charge exchange and overlaps between the regions of density depletion and increment, are computed by *DctViaCube* [41].

3. Results and discussion

3.1. Geometries and electronic properties

Generally, structures of photosensitizers are bound up closely with their important performance parameters, it is quite important for us to discuss their geometries. As shown in Fig. 1, there are two target dyes containing different π-spacers, electron-rich thiophene (P_S) and electronic-deficient pyrimidin (P_N), making them possess different electron-induced effects.

From these optimized geometries, it can be easily found that there is a certain degree of deflection with angle of $-20.3°$ for P_S between the donor (triphenylamine, TPA) and π-bridge (thiophene), but for P_N, there is almost a very small dihedral angle between the phenyl and pyrimidine moiety. This discrepancy of geometries for P_S and P_N is ascribed to the slight steric hindrance of H atoms in P_S which lead to the twist in structure. This structural discrepancy indicates that the fine planarity realized in P_N can induce a better electron delocalization. Inversely, the sufficient separation between hole and electron pairs is presented in P_S due to its unfavorable conjugation, leading to the decrease of radiative and non-radiative recombination [42].

Interestingly, the electronic properties and energy levels of P_S and P_N are analyzed and presented in Fig. 2, which shows unambiguously that there are sufficient driving forces for hole injection and dye regeneration on account of the higher energies of the lowest unoccupied molecular orbital (LUMO) than that of valence band of NiO (-5.04 eV [36]), the lower energies of the highest occupied molecular orbital (HOMO) than the redox potential of I_2/I_3^- (-4.15 eV [36]). Besides, according to the diagram of frontier molecular orbitals (FMOs), HOMOs distribute dominantly on the anchoring groups (COOH), donor groups (TPA), linker bridges (thiophene or pyrimidine) and their surroundings. As for LUMOs, they delocalize over the acceptor moieties (malononitrile) and π-linkers (thiophene or pyrimidine). Those characteristics of FMOs demonstrate that the favorable electron transfer process can be achieved in both P_S and P_N. Further exploration of electron transfer is presented and discussed in next discussion.

3.2. Properties of photoexcitation

To insight into the optical performance of P_S and P_N meticulously, Fig. 3 collects their absorption spectra in acetonitrile simulated as the experiment, which are executed to be one kind of powerful parameter in evaluating the abilities of light-harvesting for dyes. In addition, the practical situation of photosensitizer
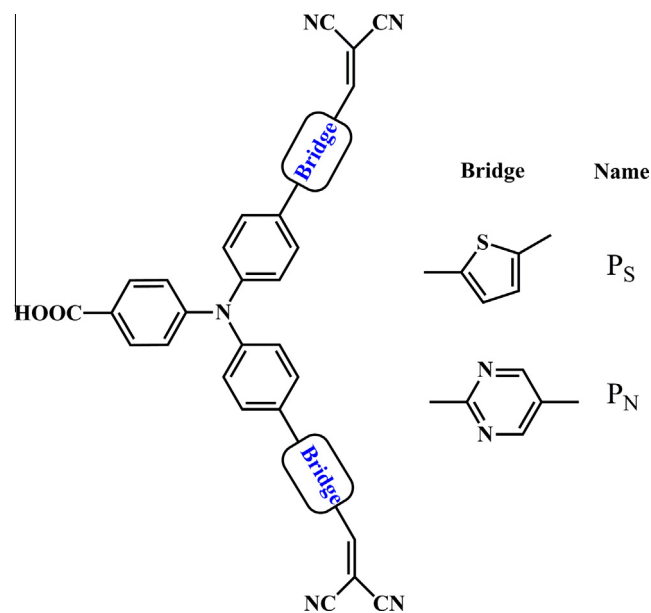

Fig. 1. The structures of objective dyes.