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The effect of relative position of the π-spacer center between donor and acceptor on the overall performance of D-π-A dye: a theoretical study with organic dye

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ABSTRACT

The influence of the relative position of π-spacer center between donor and acceptor on the dye-sensitized solar cell (DSSC) performance is expounded by analyzing the geometry, electronic structure, optical absorption property, and intramolecular charge transfer, as well as reorganization energy by means of density functional theory (DFT) and time-dependent DFT (TD-DFT) approaches. The results based on electronic structure and absorption property indicate that the dyes with introduction of building blocks to *p*1 position will generate more efficient charge separated states and present red-shifted in spectra. According to the analysis of intramolecular charge transfer, the results show that although introducing building blocks to *p*1 position can not make all structures to reduce orbital overlap, all the dyes with relatively small distance between donor and π-spacer center can enhance the amount of q_{CT} and D_{CT}. Additionally, the dyes with building blocks are introduced to *p*1 position that give better charge transfer balance performance due to their smaller Λ_h and Λ_e values. That is to say, the dye with a rigidified-aromatic as π-spacer, properly adjusting the position of π-spacer center is a valid approach for achieving great performance of DSSC.

1. Introduction

In the past decades, due to the demand of pollution-free and renewable energy resource, dye-sensitized solar cell (DSSC) has aroused widely interest in both scientist and sociologist. And plenty attempts have been devoted in pursuing highly efficient DSSC device since the seminal work first proposed by O'Regan and Grätzel in 1991 [1]. Until now, Ru(II)-based chromophores [2–4] and Zn(II) porphyrin complexes [5–7] have achieved high efficiency, and as promising sensitizers are widely applied in DSSC field. However, in regard to the cost-effective, environmentally friendly, and low synthetic yield, these aspects may restrain the potentially large-scale application of these complexes. Therefore, the abundance of metal-free organic dyes have attracted many attentions, due to they exhibit many advantages, such as higher molar extinction coefficient, lower cost and more facile in molecular design. Hitherto, because of these merits, organic dyes have been made great achievement in DSSC field [8–10], providing an alternative option for highly efficient DSSC.

In general, typical organic sensitizers contain an electron donor group (D), in conjunction with an electron acceptor group (A) by a conjugated linker (π), it shows apparent push-pull character. This configuration is in favor of the effective charge separation and photoexcited electrons inject into the conduction band of the semiconductor, as well as the regeneration of oxidized dyes. DSSC performance is improved dramatically with such organic sensitizers through sensible modification on donor [11–13,8], π-spacer [14–21], and acceptor [22–26] subunits.

The π-spacer, it is crucial in possessing the slow charge recombination, the fast electron injection process, and the large light absorption range [27]. In fact, the appropriate molecular modifications on π-spacer have been investigated widely not only in experiment but also in theory [17–19,28]. Yang et al.[29] have screened and designed novel triphenylamine-based organic dyes by means of theoretical calculation. In their works, they have designed a series of dyes with different π-spacer groups to explore highly efficient sensitizers. Chen et al.[30] have synthesized a series of new organic dyes with coplanar indacenodithiophene as π-spacer. The results emphasize that the importance of coplanarity for π-spacer. Moreover, a series of sensitizers with rigidified-aromatics as the conjugated spacers for application in DSSC have been reported by Sumit et al.[31], this review summarizes the

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significance of rigidified aromatic systems as conjugated spacers. Recently, Ni et al.[32] have synthesized an organic dye named as BZTP-1, which with dithieno[3,2-b]pyrrolobenzotriazole entity comprising fused electron rich and electron deficient entities as the conjugated spacer. In addition, the π-spacer in BZTP-1 dye possesses obvious symmetry. The results reveal that the dye with a fused aromatic segment in the π-conjugated spacer is beneficial to red-shifting and intensifying the absorption spectra of the dye. In regard to above references, it is apparent that these works focus on using many kinds of rigidified-aromatics as π-spacer. This configuration not only improves the coplanarity of dyes, but is helpful in the delocalization of π-electrons and electron transfer from the donor to the acceptor. Although the sensitizers with a rigidified-aromatic as π-spacer have reached high efficiency significantly, the main reason of the rigid spacer on electronic structure properties and whether the symmetry of π-spacer plays a key role in regulating the efficiency of DSSC are unclear and need to be processed urgently. With this in mind, we are set to design a series of unsymmetrical π-spacer and further investigate the influence of relative conjugate center of π-spacer between donor and acceptor on DSSC performance.

In current content, we take the BZTP-1 [32] as prototype, due to donor, π-spacer and acceptor subunits play a vital role in adjusting the properties of HOMO-LUMO gap, absorption spectrum, intramolecular charge transfer and so on, therefore, the rigid π-spacer is divided into three types to investigate the effect of relative conjugate center of π-spacer on the performance of DSSC. As shown in Fig. 1, we have calculated the relative distance between donor and π centers. Based on the calculated values, taking the value of t-btz-t dye as comparison, we define that the building blocks are introduced to *p*1 position, the center is closer to the donor portion, and similarly, the building blocks are introduced to *p*2 position, the center is farther to the donor portion. While the center distance locates in the middle of the above two cases when introducing building blocks to *p*3 position.

In addition, with the purpose of further demonstrates the optimal relative position of π-spacer center, a series of electron-withdrawing building blocks are introduced to the *p*1, *p*2, and *p*3 positions, respectively. These electron-withdrawing groups can significantly extend and red shift the absorption spectra of dyes, all the detailed informations are depicted in Fig. 2. Through the detailed calculation, we expect that the gist, which how relative position of π-spacer center affects DSSC performance can be presented, and look forward to screening out the optimized relative center position, which can provide a commendable option for further optimization of sensitizers' design.

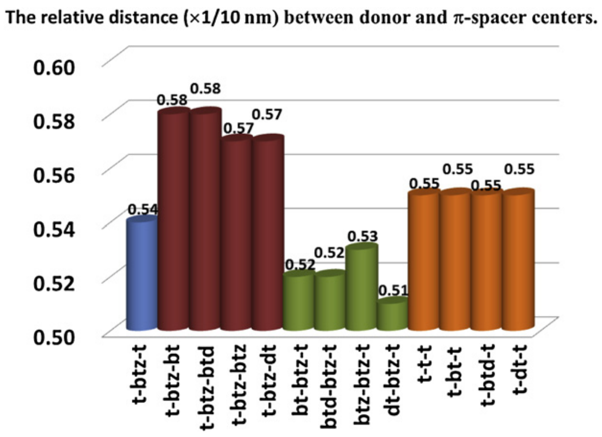

Fig. 1. The relative distance ($\times$1/10 nm) between donor and π-spacer center.

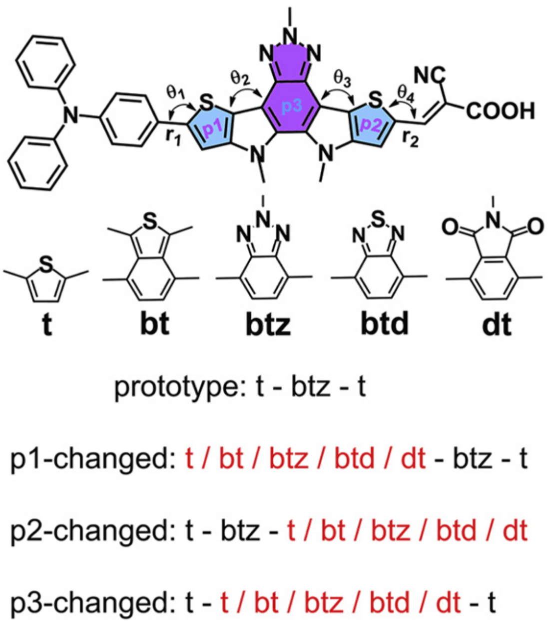

Fig. 2. Molecular geometries of the dyes and a series of introduced groups.

2. Computational details

In current work, all the calculations are carried out by using the Gaussian 09 package [33]. The ground state geometric optimizations for all organic dyes in their neutral and cationic states in gas phase are performed by using density functional theory (DFT) method at B3LYP/6-31G(d) level of theory. This level of theory for DFT calculation has been applied widely in many relevant works that are based on organic dyes [34–37]. The frequency calculations are performed in order to confirm the stationary nature of the optimized geometries at energy minimum with the same level of theory. In order to reduce the calculation cost, the hydrocarbon chains at the triazole moiety are replaced by methyl groups for geometry optimization. The excited state properties of these D-π-A dyes are calculated by using time-dependent density functional theory (TD-DFT) method in conjunction with B3LYP exchange correlation functional and 6-31G(d) basis set in tetrahydrofuran (THF) solvent. The TD-DFT computational level has been used in many relevant works [32,38,39]. Solvent effects are considered by using the Polarizable Continuum Model (PCM)[40] of SCRF procedure in THF for forecasting optic properties of the dyes. Additionally, Multiwfn program [41] is applied to plot the absorption spectra of the dyes, using gaussian function with full width at half maximum (FWHM) of 0.3 eV.

3. Results and discussion

3.1. Molecular geometry and electronic structure of the dye

In order to investigate the influence of relative position of π-spacer center on DSSC performance, the rigid π-spacer that has a symmetry is divided into three special positions, that are *p*1, *p*2, and *p*3. Actually, the original conjugate bridge has three-fragment structural feature. And we used the label *p*1, *p*2 and *p*3 to denote the relative site of these fragments. Then we constructed new π-spacers by replacing these fragments with building blocks based on thiophene or benzotriazole groups. As illustrated in Fig. 2, we show the schematic diagram for the molecular geometries and list corresponding name of each dye. As collected in Table 1, we list the main bond lengths and dihedral angles. It is clear that the