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Design of acceptors with high mobility via substitutions on dimeric perylene diimide for organic solar cells: A theoretical study

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ABSTRACT

The aim of this work is to provide an in-depth study of the optical, electronic, and charge transfer properties for substituent effects on the dimeric perylene diimide (**PPDI**). The ground state geometry and relevant electronic properties of investigated molecules for photovoltaic applications were evaluated by the CAM-B3LYP/6–31G (d,p) method. The absorption spectra simulated at the TD-B3LYP/6–31 + G (d,p) level. The results reveal that different positions and amount of substituents significantly affect on the distributions of frontier molecular orbitals for **PPDI**. The different positions of the same substituent group affect the frontier molecular orbital energy and energy gap of **PPDI** slightly. The different positions and amount of substituents affect the absorption spectra of **PPDI** slightly. The calculated reorganization energies of electrons and holes for **PPDI** and its derivatives implied that their charge transfer rates are higher than that of the typical electron and hole transport materials, respectively. Moreover, we have also predicted the mobility of designed molecules with better performances.

1. Introduction

It is a challenge to achieve the high power conversion efficiency (PCE) of the organic solar cell (OSC). The PCE of the optimal perovskite solar cell has achieved a certified value of 20.1% [1]. It is approximately two times higher than that of the traditional OSC [2,3]. Now the fullerene and its derivatives, typically, [6,6]-phenyl-C61(or C71)-butyric acid methyl ester (PC61BM or PC71BM), are mainly as the electron acceptor materials for the traditional OSCs [4–7]. They are excellent electron acceptors and transporting materials for OSCs. However, it is not only difficult to chemically modify the backbone of fullerene and its derivatives, but also difficult to readily tune their absorption region and the frontier molecular orbital (FMO) energy levels [8]. Lately, more and more researchers found that organic small molecules as the acceptors materials of OSCs have more potential than the fullerene and its derivatives. It is because that the organic small molecules have easily modified the molecular structures, easily tunable FMO energy levels and absorption spectra region, low cost, and light weight [9]. Many organic small molecule acceptors for OSCs have been synthetised, diketopyrrolopyrrole derivatives [10,11], 9,9′-bifluorenylidene [12,13], electron-deficient pentacenes [14], dicyan substituted quinacridone [15], naphthalene diimides [16,17], vinazene [18,19], perylene diimides (PDIs) [20–23], fluoranthene-fused imide [24,25], and so on. Recently, PDI and its derivatives attract more and more attentions among the organic small molecule acceptors. It is because that they own easily tunable FMO energies and absorption spectra properties. Moreover, the most remarkable aspect of PDI and its derivatives is that their short-circuit current density (J_{sc}) ranging from 8 to 12 mA/cm^2 is good [26–29]. Frank Würthner et al. found that there are a remarkably small Stokes′ shift and intense fluorescence in the solid state when the PDI owned diphenylphenoxy groups [30]. Thuc−Quyen Nguyen et al. obtained the bulk heterojunction solar cell based on the PDI molecule, and its exciton dissociation efficiency had a significant improvement [31]. Jingping Zhang et al. [32,33] and Shanshan Tang et al. [34,35] thought that the PDI and its derivatives as acceptors are suitable and recommended for high performance solar cell devices via the simulating their properties. Jiannian Yao et al. prepared the solar cells device with the PCE of 4.34% on the basis of the PDI molecule [23].

Jianhui Hou et al. designed, synthesized, and characterized a new nonfullerene small molecule **PPDI** with fine-tailored alkyl chains. The PCE of the solar cell with the **PPDI** molecule as the

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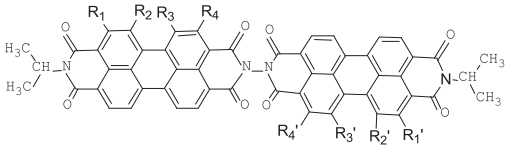

Molecules	R-groups	Molecules	R-groups
PPDI	Rn = H	**PPDI12**	R_1 = -CN $R_{1'}$ = -CN
PPDI1	R_1 = -CH_3	**PPDI13**	R_2 = -CN $R_{2'}$ = -CN
PPDI2	R_2 = -CH_3	**PPDI14**	R_3 = -CN $R_{3'}$ = -CN
PPDI3	R_3 = -CH_3	**PPDI15**	R_4 = -CN $R_{4'}$ = -CN
PPDI4	R_4 = -CH_3	**PPDI16**	R_1 = -CH_3 $R_{4'}$ = -CH_3
PPDI5	R_1 = -CN	**PPDI17**	R_1 = -CH_3 $R_{3'}$ = -CH_3
PPDI6	R_2 = -CN	**PPDI18**	R_1 = -CH_3 $R_{2'}$ = -CH_3
PPDI7	R_3 = -CN	**PPDI19**	R_1 = -CH_3 $R_{1'}$ = -CH_3
PPDI8	R_4 = -CN	**PPDI20**	R_2 = -CH_3 $R_{2'}$ = -CH_3
PPDI9	R_1 = -CN $R_{4'}$= -CN	**PPDI21**	R_3 = -CH_3 $R_{3'}$ = -CH_3
PPDI10	R_1 = -CN $R_{3'}$= -CN	**PPDI22**	R_4 = -CH_3 $R_{4'}$ = -CH_3
PPDI11	R_1 = -CN $R_{2'}$ = -CN	**PPDI23**	R_1 = -CN $R_{1'}$ = -CH_3

Fig. 1. Chemical Structures of **PPDI** derivatives.

electron acceptor is 5.40% which is higher than the others under the same experiment condition [36]. Here, to improve the performances of molecule **PPDI**, we designed three groups of **PPDI** derivatives (see Fig. 1). The first group is the derivatives (**PPDI1-4**) with -CH_3 group. The second group is the molecules (**PPDI5-8**) with -CN group. The third group is derivatives (**PPDI9-15**) with di-CN groups. The four group is molecules (**PPDI16-22**) with di-CH_3 groups. The five group is derivative (**PPDI23**) with -CN and -CH_3 groups. The density function theory (DFT) has been used to simulate the ground-states of the designed molecules owing to its remarkably successful in accurately evaluating the similar systems. The time-dependent DFT approach was employed to calculate the optical properties of the designed molecules. The FMOs (the highest occupied molecular orbital, HOMO and the lowest unoccupied molecular orbital, LUMO) energies (E_{HOMO} and E_{LUMO}), the HOMO–LUMO gaps (E_g), and the absorption spectra of the designed molecules were predicted.

On the basis of the Marcus model [37–39], we simulated the reorganization energies of all designed molecules. The mobility properties of the molecules with better performances as the representative have been calculated to study their charge transport properties.

2. Computational details

It is because that the CAM-B3LYP/6–31G (d,p) method was reasonable for optimization of PDI and its derivatives [34,35], and the TD-B3LYP/6–31 + G (d,p) was reliable for optical property simulation. Here, all the geometry including neutral, cation, and anion of **PPDI** and its derivatives were optimized by the CAM-B3LYP/6–31G(d,p) method. The TD-B3LYP/6–31 + G(d,p) method was employed to simulate the absorption spectra of **PPDI** and its derivatives. In the organic solid, usually, the charge transport could be thought as a hopping process. It could be evaluated by the Marcus model. On the basis of the Einstein relation, the carrier mobility can be obtained according to the following equation:

$$\mu = \frac{e}{\kappa_B T} D \tag{1}$$

where D is the diffusion constant. The diffusion constant can be evaluated as Eq. (2), if the charge transfer is considered as a homogeneous random walk [40].

$$D = \lim_{i\to\infty} \frac{1}{2n} \frac{< x(t)^2 >}{t} \approx \frac{1}{2n} \sum_i d_i^2 k_i p_i = \frac{1}{2n} \frac{\Sigma_i d_i^2 k_i^2}{\Sigma_i k_i} \tag{2}$$

where $n = 3$ represents the spatial dimension of the crystal and d means the center-to-center distance between adjacent molecules. The inverse of the rate constant $1/k$ is to the hopping time between adjacent molecules. $P_i = k_i/\Sigma_i k_i$ corresponds a probable specific hopping route. Namely, it is a three-dimension averaged diffusion process. One can clearly see that the mobility is linearly proportional to the electron transfer rate. It could infer that the localized electron is only hopping between the adjacent molecules utilizing this mechanism. Here, the charge transfer reaction is the self-exchange reaction. In other words, the free energy difference ($\Delta G°$) of the transfer process could be approximately considered as zero. Thus, the charge transfer rate could be calculated following

$$\kappa = \frac{V^2}{\hbar} \sqrt{\frac{\pi}{\lambda \kappa_B T}} \exp\left(-\frac{\lambda}{4\kappa_B T}\right) \tag{3}$$

where V means the electronic coupling matrix element (transfer integral) between the two adjacent species, λ corresponds to the

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