

Theoretical Prediction of the Photovoltaic Properties of BFBPD-PC61BM System as a Promising Organic Solar Cell (Postprint)

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Abstract

In this work, the photovoltaic properties of the BFBPD-PC61BM system as a promising high-performance organic solar cell (OSC) were theoretically investigated by means of quantum chemistry and molecular dynamics calculations coupled with the incoherent charge-hopping model. Moreover, the hole carrier mobility of the BFBPD thin film was also estimated using an amorphous cell containing 100 BFBPD molecules. The results revealed that the BFBPD-PC61BM system possesses a moderate open-circuit voltage of 0.70 V, a large short-circuit current density of $17.26 \text{ mA} \cdot \text{cm}^{-2}$, a high fill factor of 0.846, and a power conversion efficiency of 10%. Using the Marcus model, the exciton-dissociation rate, k_{dis} , at the BFBPD-PC61BM interface was predicted to be $2.684 \times 10^{13} \text{ s}^{-1}$, which is 3-5 orders of magnitude larger than the decay (radiative and non-radiative) rate (10^{-10} s^{-1}), indicating a high exciton-dissociation efficiency of 100% at the BFBPD-PC61BM interface. Furthermore, through molecular dynamics simulation, the hole mobility of the BFBPD thin film was predicted to be as high as $1.265 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which can be attributed to its dense packing in the solid state.

Full Text

Theoretical Prediction of the Photovoltaic Properties of BFBPD-PC61BM System as a Promising Organic Solar Cell

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ABSTRACT

In this work, the photovoltaic properties of the BFBDP-PC61BM system as a promising high-performance organic solar cell (OSC) were theoretically investigated by means of quantum chemistry and molecular dynamics calculations coupled with the incoherent charge-hopping model. Moreover, the hole carrier mobility of BFBDP thin-film was also estimated with the aid of an amorphous cell including 100 BFBDP molecules. Results revealed that the BFBDP-PC61BM system possesses a moderate open-circuit voltage of 0.70 V, large short-circuit current density of $17.26 \text{ mA} \cdot \text{cm}^{-2}$, high fill factor of 0.846, and power conversion efficiency of 10%. With the Marcus model, in the BFBDP-PC61BM interface, the exciton-dissociation rate, k_{dis} , was predicted to be $2.684 \times 10^{13} \text{ s}^{-1}$, which is 3–5 orders of magnitude larger than the decay (radiative and non-radiative) rate (10^{-10} s^{-1}), indicating a high exciton-dissociation efficiency of 100% in the BFBDP-PC61BM interface. Furthermore, by molecular dynamics simulation, the hole mobility of BFBDP thin-film was predicted to be as high as $1.265 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which can be attributed to its dense packing in the solid state.

Keywords: photovoltaic performances; theoretical prediction; carrier mobility; hopping mechanism

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1 INTRODUCTION

With the global fossil energy crisis intensifying, the development of clean and renewable energy sources has gained widespread attention [1-3]. As a clean, stable, and renewable energy source, solar energy represents an ideal alternative. Over the past two decades, organic solar cells (OSCs) have attracted intense interest due to their specific advantages compared to traditional photovoltaic technology, such as low cost, solution processability, light weight, and the ability to fabricate flexible large-area devices [4-6]. Since the invention of OSCs in 1991, tremendous efforts have been made to improve their performance. Nowadays, the power conversion efficiency (PCE) of OSC devices has been increased to 10%-12% or even higher [7], which demonstrates their broad application prospects in the near future.

In OSC devices, the active layer is one of the most critical components and

plays a very important role. It is generally a blend composed of an electron donor material and an electron acceptor material. The electron donors mainly include organic small molecules and polymers with strong optical absorption, while the electron acceptor materials are usually fullerene derivatives, such as [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) and [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) [8, 9]. Although PC61BM/PC71BM has several distinct disadvantages (such as low solubility in organic solvents, poor film-forming properties, and weak light-harvesting capability) compared to non-fullerene acceptors, their high electron affinity and electron mobility still make them preferred electron acceptors in the development of high-performance OSC devices.

Recently, Cai et al. synthesized a novel small molecule material (BFBPD) with donor-acceptor (D-A) character and found that the BFBPD thin-film exhibits high hole mobility as well as prominent capture of solar radiation [10]. From the perspective of molecular properties, BFBPD is likely to be an excellent electron donor material. In this work, to explore a novel OSC system, we carried out a computational investigation on the photovoltaic performance of the BFBPD-PC61BM system based on density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations coupled with the incoherent charge-hopping transfer model. The main objectives of this work were to explore the possibility of the BFBPD-PC61BM system as a potential high-performance OSC device by estimating properties related to PCE, such as open-circuit voltage, short-circuit current density, fill factor, exciton-dissociation/charge recombination rate, hole mobility, and so on. Results showed that, as expected, the BFBPD-PC61BM system is a promising OSC candidate, and its PCE was predicted to be as high as 10%.

2 COMPUTATIONAL DETAILS

All calculations were performed with density functional theory (DFT) and time-dependent density functional theory (TD-DFT) using the Gaussian 09 package [11]. The ground-state geometries were fully optimized without any symmetry constraints using the hybrid B3LYP functional [12] combined with the 6-31G(d) basis set. Local minima were identified by frequency analysis at the same theoretical level. The absorption spectrum at the optimized ground-state geometry was calculated using the TD-MPW1PW91 method [13] and the 6-31G(d) basis set.

To search for the most reasonable geometry of the BFBPD-PC61BM complex, a detailed potential-energy surface scan was carried out between BFBPD and PC61BM with the CAM-B3LYP-D3(BJ)/6-311G(d,p) scheme [14, 15]. As seen in Fig. S1, the BFBPD-PC61BM complex was found to be most stable when the centroids distance of BFBPD and PC61BM is equal to 7.9 Å, which is in good agreement with recent studies [16, 17]. Therefore, in subsequent calculations,

the centroids distance of the donor-acceptor complex was invariably fixed at 7.9 Å. In addition, we also considered the influence of molecular orientation on the geometry of the donor-acceptor complex. As shown in Fig. S2, molecular orientation has only a minor effect on the studied complex.

The inner reorganization energy in the electron transfer process was estimated by the classical adiabatic potential energy surface method [18, 19], which has been verified to be accurate and has been widely used in numerous theoretical studies [20-24]. Meanwhile, the influence of solid stacking on the inner reorganization energy was also considered using the conductor-like polarizable continuum model (C-PCM) [25]. The effective electron coupling (VDA) in the Marcus model was calculated using the PW91PW91/6-31G(d) scheme [26, 27], which has been demonstrated to provide the most accurate VDA value at the DFT level [28, 29].

3 RESULTS AND DISCUSSION

The molecular structures and abbreviated notations for the studied compounds are depicted in Fig. 1 [Figure 1: see original paper].

Fig. 1. Structures and abbreviated notations of studied compounds in this work.

3.1 Molecular Geometries, Electronic Properties, and Open-Circuit Voltage

As seen in Fig. S3, our optimization revealed that the BFBPD molecule maintains good planar geometry, with the dihedral angle between diketopyrrolopyrrole (DPP) and thiophene units being about 19.5°, which remarkably reduces to 1.5° between benzofuran and thiophene, indicating that BFBPD has good electronic delocalization. Fig. 2 [Figure 2: see original paper] shows the HOMO and LUMO for BFBPD, PC61BM, and BFBPD-PC61BM complexes.

Fig. 2. HOMO and LUMO of BFBPD, PC61BM, and BFBPD-PC61BM complex.

As seen, in the BFBPD molecule both the HOMO and LUMO mainly distribute over the molecular core, with small contribution from the benzofuran unit, indicating that the frontier molecular orbitals are mainly determined by the core rather than the benzofuran unit. In addition, it can be noted that the CH₃ group located in the DPP unit contributes nothing to both HOMO and LUMO, denoting that CH₃ has no influence on the frontier molecular orbitals and electronic properties of BFBPD, verifying that it is very rational to replace 2-ethylhexyl with CH₃ in this work. Similarly, the methyl-4-phenylbutanoate contributes only slightly to both HOMO and LUMO in PC61BM, meaning the substituent only enhances C solubility and has no influence on its electronic properties, which is in good agreement with previous experimental studies [30, 31]. As for

the BFBPD-PC61BM complex, the HOMO and LUMO exhibit obvious separation characteristics, with the HOMO completely localized on BFBPD while the LUMO mainly centers on PC61BM, which suggests easy formation of the BFBPD • -PC61BM • charge-separated state.

According to previous studies, the open-circuit voltage (V_{oc}) for OSCs can be estimated with [32]:

$$V_{oc} = \frac{1}{e} (|E_{HOMO}(D)| - |E_{LUMO}(A)|) - 0.3 \quad (1)$$

where $E_{HOMO}(D)/E_{LUMO}(A)$ is the HOMO/LUMO level of donor/acceptor, e is the electron charge, and the value of 0.3 is an empirical factor. Based on the experimental HOMO (-5.0 eV [10]) for BFBPD and LUMO (-4.0 eV [33, 34]) for PC61BM, the V_{oc} was estimated to be 0.70 V for the BFBPD-PC61BM system. Moreover, we also estimated the PCE for the BFBPD-PC61BM system using the Scharber diagram. As shown in Fig. 3 [Figure 3: see original paper], the PCE of the BFBPD-PC61BM system was predicted to be 10%, which indicates its excellent photovoltaic performance.

Fig. 3. Predicted PCE for BFBPD-PC61BM cell with the Scharber diagram.

3.2 Exciton Binding Energy and Optical Absorption Properties

As is well known, the exciton binding energy (E_b) is one of the most important parameters, which is directly related to exciton-separation efficiency. Usually, E_b is taken as the difference between the transport gap (E_t) and the optical band gap (E_{opt}). The former is the difference between the adiabatic ionization potential (EAIP) and electron affinity (EAEA) of the donor in the solid state, while the latter is the first-singlet emission energy (E_m). Then, E_b can be calculated using the following expression [35]:

$$E_b = E_{AIP} - E_{AEA} - E_m \quad (2)$$

where E_{AIP} and E_{AEA} are the adiabatic ionization potential (AIP) and adiabatic electron affinity (AEA) of the donor material, and E_m is the lowest-singlet emission energy. As seen in Eq. (2), to calculate E_b , the EAIP and EAEA of the donor in the solid state must first be calculated. In this work, the EAIP/EAEA of solid BFBPD was estimated via the method reported by Schwenn et al. [36], which has been verified to be a good scheme for estimating the electronic properties of organic materials in the solid state.

Table 1 . Calculated EAIP, EAEA, and E_b values in gas/solid state for BFBPD with two different DFT methods (eV)

Method	Gas state	Solid state
B3LYP/6-311G(d,p)
CAM-B3LYP/6-311G(d,p)

Table 1 lists the EAIP/EAEA values for BFBPD in gas/solid state calculated with two different DFT methods. It can be noted that E_b was estimated to be 2.139/2.207 eV in the gas phase, which is unusually larger than the measured values of 0.2-1.0 eV in numerous organic materials [37], indicating that solid stacking may have a quite strong influence on the electronic properties of organic materials. Calculated cation/anion polarization energy (P/P) verifies this speculation. As seen, the P/P is as high as 0.744/0.984 eV, indicating that it is essential to consider the solid stacking effect for accurately estimating E_b in theoretical studies. Comparing the EAIP/EAEA values in the gas phase to those in the solid state, it can be noticed that in the gas phase the EAIP is larger, while the EAEA is smaller, which is similar to measured and theoretical results in acenes [38]. According to the calculated EAIP, EAEA, and E_m for solid BFBPD, E_b was estimated to be about 0.427 eV. Previous studies showed that the exciton is unstable if $E_b < kBT$, which amounts to 0.025 eV at room temperature [39]. According to the calculated E_b for BFBPD solid, it can be deduced that the photo-induced exciton in BFBPD is relatively stable and can be efficiently transported to the BFBPD-PC61BM interface without rapidly decaying in transit.

As we know, strong harvesting of solar radiation is very important for high-performance donor materials, as it directly determines the short-circuit current density. To explore reliable TD-DFT methods for estimating optical absorption properties of BFBPD, a set of popular DFT methods were tested. As seen in Table S1, compared with the experimental value, the TD-MPW1PW91/6-31G(d) [40] scheme can accurately estimate the excited energy of BFBPD, with a deviation between theoretical and experimental values of only about 1.0 nm (approximately 2.0×10^{-2} eV). Moreover, the full absorption spectrum of BFBPD was also simulated. As seen in Fig. S4, in the UV-vis region the simulated spectrum for BFBPD is in excellent agreement with the experimental one, indicating that the TD-MPW1PW91/6-31G(d) scheme is reliable for estimating light absorption and subsequent short-circuit current density. In addition, it can be noticed in Table S2 that the strongest absorption for the BFBPD molecule can be assigned to the $\pi \rightarrow \pi^*$ type, dominated completely by the electron transition of HOMO \rightarrow LUMO (~100%).

3.3 Short-Circuit Current Density J_{sc} , Fill Factor FF, and PCE

The short-circuit current density, J_{sc} , is another key parameter that determines the PCE of OSC devices, which can be expressed as [41, 42]:

$$J_{sc} = q \int_0^{\infty} S(\lambda) \eta_{IQE}(\lambda) d\lambda \quad (3)$$

where $S(\lambda)$ is the incident photon-to-current conversion efficiency at a fixed wavelength, q is the unit charge, and $\eta_{IQE}(\lambda)$ is the internal quantum efficiency. The $\eta_{IQE}(\lambda)$ term can be described as the product of η_{λ} (light-harvesting efficiency), η_{CT} (charge transfer efficiency), and η_{coll} (charge collection efficiency):

$$\eta_{IQE} = \eta_{\lambda} \eta_{CT} \eta_{coll} \quad (4)$$

The η_{λ} can be calculated by $\eta_{\lambda} = 1 - 10^{-f}$, where f is the oscillator strength. To estimate the maximum Jsc, we set $\eta_{CT} = 1.0$ and $\eta_{coll} = 1.0$. Our calculation showed that f is about 1.4692 at the lowest-excited singlet state for BFBPD, yielding $\eta_{\lambda} = 0.770$. Fig. 4 [Figure 4: see original paper] shows the simulated $\eta_{IQE}(\lambda)$ and Jsc with the above-mentioned parameters. As seen, the Jsc for the BFBPD-PC61BM system was predicted to be as high as $17.26 \text{ mA} \cdot \text{cm}^{-2}$, which can be attributed to BFBPD's strong spectral response. In addition, it can be noticed that $\eta_{IQE}(\lambda)$ is as large as 81.7% in the visible region. Relatively, BFBPD exhibits weak capture for ultraviolet radiation ($\eta_{IQE}(\lambda) \approx 57\%$).

For the FF calculation, an approximate scheme can be expressed as [43, 44]:

$$FF = \frac{\nu_{oc} - \ln(\nu_{oc} + 0.72)}{\nu_{oc} + 1} \quad (5)$$

where ν_{oc} is the dimensionless voltage, which can be estimated with the Voc [45, 46]:

$$\nu_{oc} = \frac{qV_{oc}}{nk_B T} \quad (6)$$

where k_B , T , and q are the Boltzmann constant, temperature (here, we set $T = 300 \text{ K}$), and elementary charge, respectively, and n is an ideality factor relating to an ideal ($n = 1$) or non-ideal ($n > 1$) diode [47]. Organic solar cells typically have ideality factors in the range of 1.5-2.0 due to their inherent disorder in the solid state [48].

According to the calculated Voc (0.70 V) for the BFBPD-PC61BM system, ν_{oc} was estimated to be 27.08 at $n = 1.0$ and 13.54 at $n = 2$. Then, the FF for BFBPD-PC61BM was predicted to be as high as 0.748 ($n = 2.0$) and 0.846 ($n = 1.0$), in excellent agreement with measured values in most OSC devices. According to previous studies, the PCE (η) of OSC devices can be estimated with the following equation [49, 50]:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{V_{oc}J_{sc}FF}{P_{in}} \quad (7)$$

where P_{max} and P_{in} ($= 100 \text{ mW} \cdot \text{cm}^{-2}$) are the maximum and incident power, respectively. With the calculated Voc, Jsc, and FF, the PCE of the BFBDP-PC61BM system was predicted to be 9.23% ($n = 2.0$) and 10.22% ($n = 1.0$), which is in excellent agreement with the estimated value ($\sim 10\%$) obtained using the Scharber diagram.

Fig. 4. Simulated $\eta_{IQE}(\lambda)$ and Jsc for the BFBDP-PC61BM system.

3.4 Gibbs Free Energies and Reorganization Energies in Exciton-Dissociation and Charge-Recombination

The change in Gibbs free energy (ΔG) in the charge transfer process can be estimated as the energy difference between the final and initial states, accounting for the Coulombic attraction between two opposite charges in the charge-separated state. Thus, for exciton-dissociation, ΔG (ΔG_{dis}) can be written as [51]:

$$\Delta G_{dis} = [E_D^*(Q^*) + E_A^-(Q^-)] - [E_D^+(Q^+) + E_A^0(Q^0)] + \Delta E_{coul} \quad (8)$$

where $E_D^*(Q^*)/E_D^+(Q^+)$ is the total energy of isolated donor in its equilibrium geometry of the lowest singlet-excited/cationic state, $E_A^-(Q^-)/E_A^0(Q^0)$ is the total energy of isolated acceptor in its equilibrium geometry of anionic/neutral state, and ΔE_{coul} is the Coulombic attraction between donor and acceptor in the charge-separated state, which can be estimated with the following equation:

$$\Delta E_{coul} = \frac{1}{4\pi\epsilon_0\epsilon_s} \sum_{i,j} \frac{q_D^i q_A^j}{r_{ij}} \quad (9)$$

where q_D^i and q_A^j are the atomic charges on donor and acceptor in their relevant states with a separation distance r_{ij} . ϵ_0 is the vacuum dielectric constant ($8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$), and ϵ_s is the static dielectric constant of the medium. Similarly, the Gibbs free energy change (ΔG_{rec}) in charge recombination can also be estimated with an expression similar to Eqs. (8) and (9). Here, ϵ_s was estimated with the Clausius-Mossotti equation [52]:

$$\epsilon_s = \frac{1 + \frac{8\pi\bar{\alpha}}{3V}}{1 - \frac{4\pi\bar{\alpha}}{3V}} \quad (10)$$

where V is the Connolly molecular volume, $\bar{\alpha}$ is the isotropic component of molecular polarizability ($\bar{\alpha} = \frac{1}{3} \sum_i \alpha_{ii}$), and α_{ii} is the diagonal matrix elements of the first-order polarizability tensor. Calculations showed that ϵ_s is 3.653 for BFBDP, which is in good accordance with measured values (ranging from 2.0

to 5.0 [53, 54]) in most organic materials. As for PC61BM, the experimental ε_s value of 3.9 [55] was used in this work. The total ε_s of the FBPD-PC61BM system was taken as an average of their respective contributions. Our calculation showed that ΔG_{dis} is about -0.476 eV, while ΔG_{rec} decreases to -0.720 eV. Obviously, both ΔG_{dis} and ΔG_{rec} are negative, denoting that exciton-dissociation and charge-recombination are thermodynamically favorable. In addition, the smaller ΔG_{rec} indicates a larger driving force in the charge-recombination process.

Generally, in organic solids the total reorganization energy (λ) of electron transfer can be divided into two components, namely the internal reorganization energy (λ_{int}) and the external one (λ_{ext}). In the case of charge dissociation, λ_{int} is taken as an average of the following λ_1 and λ_2 [56]:

$$\lambda_{int} = \frac{\lambda_1 + \lambda_2}{2} \quad (11)$$

where $\lambda_1 = [E_D^*(Q^+) + E_A^0(Q^-)] - [E_D^*(Q^*) + E_A^0(Q^0)]$ and $\lambda_2 = [E_D^+(Q^*) + E_A^-(Q^0)] - [E_D^+(Q^+) + E_A^-(Q^-)]$. Our calculation showed that λ_{int} (λ_{dis}) is 0.119 eV in the charge-dissociation process for FBPD-PC61BM, which remarkably increases to 0.189 eV in the case of charge recombination. Compared to λ_{int} , λ_{ext} is difficult to calculate accurately. Here, we used the classical dielectric continuum model initially developed by Marcus for electron-transfer reactions between spherical ions in solution to estimate λ_{ext} . According to this model, the λ_{ext} term is given by [57]:

$$\lambda_{ext} = \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{R_D} + \frac{1}{R_A} - \frac{2}{r_{DA}} \right) \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right) \quad (12)$$

where ε_{op} is the optical dielectric constant of the medium, R_D ($= 6.30 \text{ \AA}$ for FBPD) and R_A ($= 6.50 \text{ \AA}$ for PC61BM) are the effective radii of donor and acceptor estimated as the radius of a sphere having the same surface area as the surface-accessible area of the molecule. The q_D and q_A denote the atomic charges on the ions. ε_{op} can be estimated with the Lorentz-Lorenz equation [58, 59]:

$$\varepsilon_{op} = \frac{2\bar{n}^2 + 1}{\bar{n}^2 + 2} \quad (13)$$

where n is the refractive index, V_m is the molar volume ($V_m = M/\rho$, where M is the molar mass and ρ is the density of the material), and R is the molar refraction. Here, ρ was estimated with the molecular dynamics method, and the simulation details are shown in the supporting information. Our results showed that ε_{op} and ρ for FBPD are 1.523 and $1.334 \text{ g} \cdot \text{cm}^{-3}$, respectively. As for PC61BM, the experimental refractive index ($n = 1.866$) was used to estimate

ε_{op} , which equals 3.482 according to our calculation. With the above-mentioned parameters, λ_{ext} was estimated to be 0.239 eV. In summary, $\lambda = 0.512$ eV in the charge-dissociation process for the BFBPD-PC61BM system, which remarkably increases to 0.582 eV for the charge-recombination process.

3.5 Electron Couplings and Exciton-Dissociation/Charge-Recombination Rates

The VDA is an important parameter that determines the charge transfer rate constant (kDA). In this work, the direct-coupling (DC) method was used to estimate VDA [60, 61]. In terms of this scheme, VDA can be calculated by the following expression [62, 63]:

$$V_{DA} = \frac{T_{DA} - 0.5S_{DA}(e_D + e_A)}{1 - S_{DA}^2} \quad (14)$$

where $T_{D(i)A(j)}$ is the electron coupling of the i th molecular orbital of donor and the j th molecular orbital of acceptor, $S_{D(i)A(j)}$ is the spatial overlap integral, and $e_{D(i)}/e_{A(j)}$ is the site energy. $T_{D(i)A(j)}$, $S_{D(i)A(j)}$, and $e_{D(i)}/e_{A(j)}$ can be obtained from $T_{D(i)A(j)} = \langle \psi_{D(i)} | F_{KS} | \psi_{A(j)} \rangle$, $S_{D(i)A(j)} = \langle \psi_{D(i)} | \psi_{A(j)} \rangle$, and $e_{D(i)}/e_{A(j)} = \langle \psi_{D(i)} / \psi_{A(j)} | F_{KS} | \psi_{D(i)} / \psi_{A(j)} \rangle$. Among them, $\psi_{D(i)}$ is the HOMO (for charge-recombination) or LUMO (for charge-dissociation) of the donor, $\psi_{A(j)}$ is the LUMO of the acceptor, and F_{KS} is the Kohn-Sham matrix of the donor-acceptor system.

$$V_{DA} = \frac{C_D^T F_{KS} C_A - S C_D^T \varepsilon C_A}{1 - S^2} \quad (15)$$

where S is the intermolecular overlap matrix, C is the molecular orbital coefficient matrix from the isolated monomer, and ε is the orbital energy from one-step diagonalization without iteration.

Generally, VDA in the exciton-dissociation process is taken as the coupling between the LUMO of donor and acceptor. However, since the LUMO+1 and LUMO+2 in PC61BM are energetically degenerate with its LUMO [64], the VDA between the LUMO of BFBPD and LUMO+1/LUMO+2 of PC61BM was also computed. Finally, the average VDA was used to calculate kDA. The same treatment was applied for charge-recombination. Our results showed that VDA is about 0.034 eV in exciton dissociation, which decreases to 0.026 eV in charge recombination.

At high temperature and weak coupling limits, charge transfer in organic materials involves a thermally activated hopping mechanism. According to Marcus theory [65, 66], kDA can be expressed as:

$$k_{DA} = \frac{V_{DA}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right) \quad (16)$$

where λ is the total reorganization energy, V_{DA} is the effective electron coupling, T is the temperature, \hbar and k_B are the reduced Planck and Boltzmann constants, respectively, and ΔG is the change in Gibbs free energy between the final and initial states. Based on the calculated λ and V_{DA} , the exciton-dissociation (k_{dis}) and charge-recombination (k_{rec}) rate constants were estimated to be as high as 2.684×10^{13} and $1.108 \times 10^{13} \text{ s}^{-1}$, respectively, at the BFBPD-PC61BM interface. Recent studies have illustrated that the decay rate constant (k_d) of excited organic molecules typically ranges from 1.0×10^8 to $1.0 \times 10^{11} \text{ s}^{-1}$ [67]. Our results showed that k_{dis} is 3-5 orders of magnitude larger than k_d , which indicates very high exciton-dissociation efficiency ($\sim 100\%$) at the BFBPD-PC61BM interface. In addition, although k_{rec} is relatively large, the charge-recombination efficiency is still very low. According to previous studies, the electron transferred onto PC61BM can be rapidly converted from the singlet state to the triplet state [68, 69], which remarkably hinders recombination of free carriers.

3.6 Hole Transfer Rate and Hole Mobility in BFBPD Thin-Film

As is well known, the charge transport ability of the donor remarkably affects solar cell performance. Thus, it is essential to estimate the charge transport properties of BFBPD thin-film. The charge transport ability in organic materials can be characterized by its carrier mobility (μ), which can be calculated using the Einstein-Smoluchowski equation [70, 71]:

$$\mu = \frac{eD}{k_B T} \quad (17)$$

where D is the diffusion coefficient, e is the elementary charge, k_B is the Boltzmann constant, and T is the temperature, respectively. D can be estimated using the following appropriate relation [72, 73]:

$$D = \frac{1}{2n} \sum_i d_i^2 k_i P_i \quad (18)$$

where n is the spatial dimensionality (which is 3 for organic solids), d_i is the centroids distance of the i th hopping dimer, k_i is the charge transfer rate constant, and P_i ($P_i = k_i / \sum_i k_i$) is the hopping probability. In this work, the charge mobility of BFBPD thin-film was evaluated using an amorphous cell with 100 BFBPD molecules built by molecular dynamics simulation. As seen in Fig. 5 [Figure 5: see original paper], our result showed that BFBPD molecules in the solid state exhibit a close-packed pattern, which is favorable for hole-carrier transfer.

Fig. 5. Optimized amorphous cell with 100 BFBPD molecules.

Table 2 . Calculated λ_{int} for BFBPD with two different DFT methods (eV)

Method	Gas state	Solid state
B3LYP/6-311G(d,p)
CAM-B3LYP/6-311G(d,p)

Table 2 shows the calculated λ_{int} term for BFBPD in hole transfer with two different DFT methods. As seen, the CAM-B3LYP/6-311G(d) scheme presented quite large λ_{int} values due to considering the long-range correlation effect. In addition, it can be noticed that λ_{int} in the solid state is obviously smaller than that in the gas phase, denoting that solid stacking, to some extent, limits the structural relaxation of the BFBPD molecule in the charge transfer process. Since donor materials in OSC devices usually remain in the solid state under operating conditions, the λ_{int} estimated using the solid-state model is more reasonable and reliable.

To explore possible charge transfer dimers, 20 molecular pairs with relatively large V_{DA} values were abstracted from the optimized amorphous cell, and their geometries, centroids distances, and estimated V_{DA} values are shown in Table S3. Based on λ_{int} in the solid state and V_{DA} values, the hole carrier mobility (μ_h) of solid BFBPD thin-film was estimated to be as high as $1.265 \times 10^2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which is in excellent agreement with the measured value of $3.7 \times 10^3 - 9.0 \times 10^2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [10]. According to previous investigations, for high-performance electron donor materials, μ_h should be not less than $10^3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [32]. Our result showed that as a potential donor material, BFBPD can satisfy the requirement for rapid hole transport.

4 CONCLUSION

In this work, the photovoltaic properties of the BFBPD-PC61BM system were theoretically investigated using DFT/TD-DFT calculations. Results revealed that the BFBPD-PC61BM system possesses a moderate open-circuit voltage of 0.70 V, large short-circuit current density of $17.26 \text{ mA} \cdot \text{cm}^{-2}$, high fill factor of 0.846, and power conversion efficiency of 10%. Based on the Marcus charge transfer model, k_{dis} ($2.684 \times 10^{13} \text{ s}^{-1}$) was estimated to be 3-5 orders of magnitude larger than k_d (1.0×10^0 to $1.0 \times 10^1 \text{ s}^{-1}$), which indicates very high exciton-dissociation efficiency (~100%) at the BFBPD-PC61BM interface. Moreover, using an amorphous cell optimized by molecular dynamics, the hole carrier mobility for BFBPD thin-film was predicted to be as high as $1.265 \times 10^2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at room temperature. In brief, our calculations showed that BFBPD is an excellent electron donor material, and the BFBPD-PC61BM system is a promising OSC candidate. However, these results need to be confirmed experimentally.

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