Photovoltaic Performance of 4,8-Bis(2′-ethylhexylthiophene)thieno[2,3-f]benzofuran-Based Dyes Fabricated with Different Donors in Dye-Sensitized Solar Cells

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ABSTRACT: Thieno[2,3-f]benzofuran (BDF) has the advantages of a highly planarized structure, strong electron-donating ability, high hole mobility, good conjugation, and a wide spectral response range. In recent years, BDF has been widely used in organic solar cells, especially in bulk-heterojunction (BHJ) organic solar cells. In this work, a model molecule PSB-1 was synthesized based on this highly planar fragment and used as a photosensitizer in dye-sensitized solar cells (DSCs), then different aromatic amine donors such as triphenylamine (TPA), carbazole (CZ), and phenothiazine (PTZ) were introduced to the end of PSB-1, and a series of dyes PSB-2, PSB-3, and PSB-4 were designed and synthesized. After that, the relationship among the molecular structure, energy level, and photovoltaic performance of the benzo-[1,2-b:4,5-b′]dithiophene (BDT) dye was studied by theoretical calculations, photophysics, electrochemistry, and photovoltaic properties. The results show that the introduction of a strong donor can effectively improve the energy level, absorption spectrum, and photovoltaic performance of PSB-1. Through the preliminary test, we found that the energy conversion efficiency (photovoltaic conversion efficiency—PCE) of PSB-4 is up to 5.5%, which is nearly 90% higher than that of PSB-1 (PCE = 2.9%), while the introduction of a weak donor greatly weakens the efficiency, in which the PCE of PSB-3 is 3.5%, which is only 20% higher than that of the model molecule. By an analysis of the molecular frontier orbital distribution using theoretical calculations, we found that the electron cloud of the highest occupied molecular orbital—HOMO) of PSB-3 is mainly distributed on the BDF group so that the electron transfer of excited-state molecules mainly occurs from the BDF to the receptor (CA).

1. INTRODUCTION

Despite the decreased research interest in recent years as a photo-electric conversion device, owing to their simple structure, high photovoltaic conversion efficiency (PCE), and long cycle life, dye-sensitized solar cells (DSCs) have still attracted unremitting research efforts of many research groups. The performance of DSCs depends on many factors, such as light absorption capacity, energy level, interface performance, electron-transfer ability, and so on, all of which are related to photosensitizing organic structures chemically anchored on the surface of a nanocrystalline titanium dioxide semiconductor. Thus, in this photovoltaic device, the dye has been anchored on the surface of a nanocrystalline titanium dioxide semiconductor. So far, some metal complex sensitizers, such as ruthenium polypyrpyridine, and zinc porphyrin complexes, have been reported as the best-performing DSC dyes for their high PCE. However, the development of metal complex dyes has to suffer some defects that cannot be ignored, for instance, the synthesis of ruthenium dye has to bear the defect of resource scarcity and heavy-metal toxicity and a high-performance zinc porphyrin dye suffers from low synthetic yield and the use of highly toxic raw materials such as CSCl2, DDQ, and heptachloroheptane (HCl). Therefore, the development of pure organic dyes with donor–π–acceptor (D–π–A) structures has attracted the interest of many groups owing to their abundant raw materials, adjustable structures, and flexible molecular designs. Inspired by the highly planarized structure and strong electronic properties of metal complex dyes, more attention has been paid to the design and synthesis of pure organic dyes with high planarization, small dihedral angle, and strong electron-donating capacity. In this regard, some organic small molecules with highly coplanar structures are constantly reported, such as perylene, benzo-[1,2-b:4,5-b′]dithiophene (BDT), bidithieno[3,2-b:2′,3′-d]pyrrole, thiophene fluorene, isoindigo, coumarin, and indacenodithiophene (IDT) and its derivatives. In addition, it has been found that arylamine...
and its derivatives have strong an electron-pushing ability and are often designed as donors of organic dyes, such as triphenylamine, tetrahydroquinoline, phenothiazine, indole, carbazole, phenoxazine, and their derivatives. The dyes based on the donor of arylamine and its derivatives almost cover more than 90% of the reported pure organic dyes and have achieved very good results. Benzo aromatic heterocyclic compounds such as benzodithiophene and thiene benzofuran (BDF) have been actively pursued as a polycyclic aromatic hydrocarbon (PAH) module for many photovoltaic materials for OPVs, but they are rarely used in DSCs.

Herein, a series of small molecular dyes PSB-1, PSB-2, PSB-3, and PSB-4 on the basis of highly planarized BDF are designed, synthesized, and characterized. As shown in Figure 1.

Figure 1. Structures of BDF-based dyes PSB-1, PSB-2, PSB-3, and PSB-4.

PSB-1 is used as a model molecule and compared with PSB-2, PSB-3, and PSB-4 by introducing different aromatic amine donors to its end, and then the changes in the energy level and photovoltaic properties of the dyes are preliminarily studied. It is found that BDF can be used in DSCs, and the energy conversion efficiency of the model molecule is 2.9%, while the energy conversion efficiencies of PSB-2, PSB-3, and PSB-4 are greatly improved after the introduction of aromatic amine donors, which are 4.7, 3.5, and 5.5%, respectively. Note that the increase in the energy conversion efficiency of PSB-3 is much smaller than that of PSB-2 and PSB-4. Upon an analysis from the theoretical calculation and absorption spectrum performance, we found that when a strong donor (TPA or PTZ) is added to BDF, the dye’s energy level, absorption spectrum, and photovoltaic characteristics can be effectively improved, while the effect will be greatly weakened when a weak donor (CZ) is added because intramolecular electron transfer reduces the potential energy. Therefore, the photovoltaic properties can be effectively improved only by fully considering the push–pull electronic ability of each molecular segment and assembling in a certain order.

2. RESULT AND DISCUSSION

2.1. Materials and Synthesis. The intermediate and reagents were purchased from a commercial corporation or synthesized as described. The important intermediate 1 was purchased from the commercial corporation, and 5, 6, and 7 were synthesized according to our research group’s previous work. Ultradry solvents involved in the synthesis process such as tetrahydrofuran (THF), N,N-dimethyl formamide (DMF), toluene, CH2Cl2, CHCl3, and acetonitrile (AN) were purchased from Saan Chemical (Shanghai) Co., Ltd. Reagents Pd catalysts Pd(PPh3)4 and Pd2(dba)2, POCl3, and piperidine were purchased from Sigma-Aldrich Co., Ltd. Other reagents and solvents were purchased according to the National Drug Standards. All of the structures of intermediate products were verified by 1H NMR recorded on a Bruker Avance400 II and mass spectra from the college. The dye structure was verified by 1H NMR, 13C NMR, and mass spectra. Scheme 1 shows the synthetic route of the intermediate compounds and dyes. Compounds 2, 3, 4, 8, 9, and 10 and dyes PSB-1, PSB-2, PSB-3, and PSB-4 were synthesized as described in the following synthetic procedures. All intermediates and dyes were prepared with high yield (60–95%) by the classical organic synthesis method, according to the previous methods of our group. Among them, compound 2 was synthesized by the Stille coupling method, and compounds 3 and 4 were prepared by the Vilsmeier–Haack formylation reaction and bromine substitution reaction, respectively. Important intermediates 8–10 were synthesized by the Suzuki coupling reaction. Finally, the dye was obtained by Knoevenagel condensation. The detailed synthesis procedures are described in the following.

2.1.1. Synthesis of Compound 2. For the classical Stille coupling reaction, refer to our previous work. Under nitrogen, compound 1 (5.150 g, 1 equiv), 2-bromothiophene (4.080 g, 2.5 equiv), and Pd2(dba)2 (0.120 g, 1%) were mixed in dry toluene and refluxed for 24 h. After postprocessing, the residue was purified by column chromatography (ethyl acetate/petroleum ether, 1:20, v/v, 60–90 °C) on silica gel to yield a yellow-green solid compound 2 (4.44 g, yield 80%). ESI-MS: m/z = 554.1. 1H NMR (400 MHz, CDCl3, ppm): 7.88 (s, 1H), 7.69–7.73 (d, J = 11.3 Hz, 4H), 7.35 (s, 1H), 7.18–7.25 (t, 2H), 6.98–7.12 (d, J = 11.3 Hz, 4H), 3.85–3.88 (d, J = 11.0 Hz, 4H), 1.78–1.90 (m, 2H), 1.56–1.85 (m, 16H), 0.80–0.85 (t, J = 6.8 Hz, 12H).

2.1.2. Synthesis of Compound 3. Classical Vilsmeier–Haack reaction is given in our previous work. Under nitrogen, dry DMF (1.72 mL, 2.8 equiv), compound 2 (4.400 g, 1 equiv), and POCl3 (0.89 mL, 1.2 equiv) were mixed in dry C6H5Cl2 (80 mL), and the mixture was heated to 80 °C and stirred for 4 h. After postprocessing, the residue was purified by column chromatography (DCM/petroleum ether, 1:3, v/v, 60–90 °C) on silica gel to yield a yellow solid compound 3 (4.39 g, yield 95%). ESI-MS: m/z = 582.1. 1H NMR (400 MHz, CDCl3, ppm): 9.98 (s, 1H), 8.15 (d, J = 9.3 Hz, 1H), 7.98 (s, 1H), 7.78–7.86 (d, J = 3.3 Hz, 2H), 7.65–7.74 (d, J = 9.5 Hz, 2H), 7.31 (s, 1H), 6.89–7.21 (d, J = 11.0 Hz, 4H), 4.05–4.12 (d, J = 11.3 Hz, 4H), 1.88–1.95 (m, 2H), 1.52–1.88 (m, 16H), 0.80–0.88 (t, J = 6.8 Hz, 12H).

2.1.3. Synthesis of Compound 4. Bromine substitution reaction is also given in our previous work. Under nitrogen, compound 3 (1.510 g, 1 equiv) and NBS (0.427 g, 1.2 equiv) were mixed in dry THF (30 mL) and stirred overnight at room temperature. After postprocessing, the residue was purified by column chromatography (DCM/petroleum ether, 1:3, v/v, 60–90 °C) on silica gel to yield a red solid compound 8 (1.500 g, yield 89%). ESI-MS: m/z = 662.1. 1H NMR (400 MHz, CDCl3, ppm): 9.95 (s, 1H), 8.10 (d, J = 9.5 Hz, 1H), 7.99 (s, 1H), 7.83 (d, J = 9.5 Hz, 1H), 7.46–7.55 (t, J = 9.8 Hz, 3H), 6.88–7.06 (d, J = 11.8, 8.2 Hz, 4H), 3.98–4.02 (d, J = 11.5 Hz, 4H), 1.85–1.92 (m, 2H), 1.50–1.91 (m, 16H), 0.81–0.87 (t, J = 6.8 Hz, 12H).

2.1.4. Synthesis of Compound 8. For the classical Suzuki coupling reaction, refer to the literature. Under nitrogen, compound 4 (0.417 g, 0.5 mmol), compound 5 (0.377 g, 1.2
equiv), SPhos (20 mg, 3% equiv), Pd(OAc)$_2$ (16 mg, 3% equiv), and K$_2$PO$_4$ (1.06 g, 10 equiv) were mixed in dioxane/H$_2$O (5:1, v/v) and stirred overnight at room temperature. After postprocessing, the residue was purified by column chromatography (DCM/petroleum ether, 1:3, v/v, 60−90 °C) on silica gel to yield a red powder as the desired product 8 (0.41 g, 76% yield). ESI-MS: $m/z = 1081.5$. 1H NMR (400 MHz, DMSO, ppm): 9.85 (s, 1H), 8.15 (d, $J = 9.3$ Hz, 1H), 7.87 (s, 1H), 7.71−7.75 (d, $J = 9.0$ Hz, 1H), 7.55−7.60 (d, $J = 11.5$ Hz, 2H), 7.43 (s, 1H), 7.15−7.38 (d, $J = 8.0$, 6H), 6.95−7.10 (d, $J = 8.0$ Hz, 6H), 6.68−6.83 (dd, $J = 11.5, 8.6$ Hz, 4H), 3.58−4.02 (dd, $J = 11.3, 11.8$ Hz, 4H), 1.83−1.92 (m, 6H), 1.45−1.90 (m, 32H), 0.85−0.90 (t, $J = 6.8$ Hz, 12H), 0.66−0.70 (t, $J = 6.8$ Hz, 12H).

2.1.5. Synthesis of Compound 9. The synthesis of compound 9 followed the same procedure as that for compound 8, yielding a red powder as the desired product 9 (0.32 g, 78% yield). ESI-MS: $m/z = 859.3$. 1H NMR (400 MHz, DMSO, ppm): 9.98 (s, 1H), 8.23 (d, $J = 9.9$ Hz, 1H), 7.86 (s, 1H), 7.73−7.78 (d, $J = 9.3$ Hz, 1H), 7.70−7.76 (m, 4H), 7.51−7.59 (d, $J = 11.3$ Hz, 2H), 7.36 (s, 1H), 7.10−7.35 (m, 3H), 6.55−6.78 (dd, $J = 11.5, 8.2$ Hz, 4H), 3.56−4.00 (dd, $J = 11.3, 11.8$ Hz, 4H), 1.80−1.93 (m, 6H), 1.25−1.85 (m, 24H), 0.80−0.86 (t, $J = 6.8$ Hz, 12H), 0.66−0.70 (t, $J = 6.8$ Hz, 6H).

2.1.6. Synthesis of Compound 10. The synthesis of compound 10 followed the same procedure as that for compound 8, yielding a red powder as the desired product 10 (0.33 g, 75% yield). ESI-MS: $m/z = 891.3$. 1H NMR (400 MHz, DMSO, ppm): 9.84 (s, 1H), 8.17 (d, $J = 9.5$ Hz, 1H), 7.88 (s, 1H), 7.71−7.75 (d, $J = 9.8$ Hz, 1H), 7.50−7.56 (d, $J = 11.3$ Hz, 2H), 7.36 (s, 1H), 7.00−7.28 (m, 7H), 6.51−6.75 (dd, $J = 11.9, 8.6$ Hz, 4H), 3.52−3.88 (dd, $J = 11.5, 8.2$ Hz, 4H), 1.81−1.92 (m, 6H), 1.23−1.76 (m, 24H), 0.79−0.87 (t, $J = 6.8$ Hz, 12H), 0.63−0.68 (t, $J = 6.8$ Hz, 6H).

2.1.7. Synthesis of Dye PSB-1. For the classical Knoevenagel condensation reaction, refer to our previous work. Under nitrogen, aldehyde 3 (0.378 g, 0.5 mmol), cyanoacetic acid (0.255 g, 6 equiv), and piperidine (0.65 mL, 14 equiv) were mixed in chloroform (15 mL) and refluxed for 12 h. After postprocessing, the residue was purified by column chromatography (chloroform/methanol, 10:1, v/v) on silica gel to yield a dark red powder as the desired product PSD-09 (0.370 g, 90% yield). ESI-MS: $m/z$ calcd. for C$_{46}$H$_{47}$NO$_3$S$_5$: 822.19. Found: 821.22 ([M−H]$^+$). Anal. calcd. for C$_{46}$H$_{47}$NO$_3$S$_5$: C, 67.16; H, 5.74; N, 1.70. Found: C, 67.01; H, 5.79; N, 1.72. 1H NMR (400 MHz, DMSO ppm): 12.98−13.10 (s, 2H), 10.68−10.80 (s, 1H), 9.58−9.70 (s, 1H), 8.23−8.35 (m, 4H), 7.70−7.80 (d, $J = 9.3$ Hz, 1H), 7.60−7.76 (d, $J = 9.9$ Hz, 1H), 7.20−7.35 (d, $J = 11.3$ Hz, 2H), 7.00−7.10 (s, 1H), 6.55−6.78 (dd, $J = 11.5, 8.2$ Hz, 4H), 3.56−4.00 (dd, $J = 11.3, 11.8$ Hz, 4H), 1.80−1.93 (m, 6H), 1.25−1.85 (m, 24H), 0.80−0.86 (t, $J = 6.8$ Hz, 12H), 0.66−0.70 (t, $J = 6.8$ Hz, 6H).

Scheme 1. Synthetic Route for Organic Dyes PSB-1, PSB-2, PSB-3, and PSB-4
2.1.8. Synthesis of Dye PSB-2. The synthesis of dye PSB-2 followed the same procedure as that for PSB-1, yielding a dark red powder as the desired product PSB-2 (0.35 g, 82% yield). HR-MS (ESI): m/z calcd. for C_{80}H_{92}N_{2}O_{5}S_{5}: 1121.4912. Found: 1122.4856 ([M − H]^+). Anal. calcd. for C_{80}H_{92}N_{2}O_{5}S_{5}: C, 72.69; H, 7.01; N, 2.12. Found: C, 72.56; H, 7.08; N, 2.18. \(^1\)H NMR (400 MHz, DMSO, ppm): 13.25 (s, 1H), 8.75 (s, 1H), 8.25 (d, \(J = 9.3\) Hz, 1H), 8.01−8.11 (d, \(J =

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Figure 2. Electron cloud distribution of dyes and corresponding optimized structures performed at the B3LYP/6-31G(d,p) level with Gaussian 09.
The synthesis of dye PSB-3 followed the same procedure as that for PSB-1, yielding a dark red powder as the desired product PSB-3 (0.33 g, 85% yield). ESI-MS: m/z calc. for C_{26}H_{26}N_{10}O_{11}S_{6}: 1099.4434. Found: 1098.4389 ([M – H]). Anal. calc. for C_{26}H_{26}N_{10}O_{11}S_{6}: C, 72.12; H, 6.43; N, 3.08. Found: C, 72.23; H, 6.46; N, 3.11. ^1H NMR (500 MHz, DMSO, ppm): 13.15 (s, 1H), 8.53 (s, 1H), 8.15 (d, J = 9.5 Hz, 1H), 7.78 (s, 1H), 7.73–7.78 (d, J = 9.8 Hz, 1H), 7.60–7.67 (m, 4H), 7.51–7.59 (d, J = 11.3 Hz, 2H), 7.33 (s, 1H), 7.08–7.16 (m, 3H), 6.55–6.78 (dd, J = 11.5, 8.2 Hz, 4H), 5.32–3.86 (dd, J = 11.3, 6.8 Hz, 4H), 1.80–1.98 (m, 4H), 1.23–1.78 (m, 24H), 0.78–0.85 (t, J = 6.8 Hz, 12H), 0.66–0.70 (t, J = 6.8 Hz, 6H). ^13C NMR (100 MHz, DMSO): δ = 161.33, 159.63, 148.7, 147.76, 145.47, 140.81, 139.57, 138.84, 137.62, 135.58, 130.73, 129.47, 127.33, 126.46, 125.75, 124.72, 124.45, 120.81, 120.42, 118.47, 117.52, 117.62, 115.02, 111.05, 110.63, 107.87, 102.91, 95.86, 92.74, 63.18, 38.68, 35.73, 34.83, 31.65, 30.39, 27.38, 25.73, 23.75, 22.73, 14.12, 11.66.

Theoretical Analysis of Frontier Orbital Distribution and Electron-Donating Ability. Density functional theory (DFT) calculations performed at the B3LYP/6-31G(d,p) level with Gaussian 09 were used to evaluate the dyes at a theoretical level. Figure 2 shows the optimized structures and electronic cloud distribution of dyes PSB-1, PSB-2, PSB-3, and PSB-4. Because the long alkyl chain has a little effect on the electronic cloud of the molecule, it was intentionally removed to save the calculation time. According to the optimized molecular ball-and-stick model, BDF has a highly planar molecular structure. When thiophene groups were introduced at both ends of BDF, the dihedral angle between the thiophene and BDF was about 8°, while the dihedral angle between the benzene and thiophene was about 24–28° when different arylamines were introduced. It can be seen from the electron cloud distribution diagram of the dyes that the electron cloud distribution at the highest occupied molecular orbital (HOMO) level has a good overlap with the lowest occupied molecular orbital (LUMO) level, speculating that the intramolecular electron-transfer efficiency will be high. Among them, the electron cloud of PSB-1 at the HOMO level was mainly distributed on the BDT unit and partly on thiophene, and the electron cloud at the LUMO level was mainly distributed on the CA unit. After introducing a strong electron donor unit at the end of PSB-1, the electron clouds of PSB-2 and PSB-4 were mainly distributed on TPA and PTZ units at the HOMO level and partly on thiophene and BDF units close to the donor, and the electron clouds at the LUMO level were mainly distributed on the CA unit and partly on thiophene and BDF units close to the CA. However, PSB-3 was quite different; the electron cloud at the HOMO level was mainly distributed on the BDF unit and some on CZ and thiophene close to the donor (CZ), and the electron cloud at the LUMO level was mainly distributed on CA unit and some on thiophene and BDF near CA. By comparing the dihedral angles, it is found that there was little difference (25° for PSB-2, 28.7° for PSB-3, and 24.6° for PSB-4) between the donor and π-bridge unit in the twist angles for PSB-2, PSB-3, and PSB-4. It can be basically ruled out that the large twist angle affected the electron cloud distribution at the HOMO level of PSB-3.

The theoretical energy levels and band gaps of each fragment and dye can be obtained by converting the energy calculated by Gauss 09 according to formula 1. The relevant results are listed in Table 1. It can be seen from Table 1 that the HOMO energy levels of each molecular fragment increase in the order CZ, BDF, TPA, and PTZ; the LUMO energy levels decrease in the order PTZ, TPA, CZ, and BDF; and the band gap (E_{0,0}) narrows in the order CZ, PTZ, TPA, and BDF. After these fragments were assembled into dyes, the HOMO energy levels increased in the order PSB-1, PSB-3, PSB-2, and PSB-4; the LUMO energy levels decreased in the order PSB-4, PSB-3 = PSB-2, and PSB-1; and E_{0,0} narrowed in the order PSB-1, PSB-3, PSB-2, and PSB-4.

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E_{0,0} = \text{band gap} = \text{HOMO} - \text{LUMO}
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The HOMO energy levels of the dyes increased with the introduction of different donors; in addition, the LUMO energy level decreased obviously and the band gap narrowed, which were caused by the introduction of a strong acceptor CA. Compared with those of PSB-1, it can be seen that the
theoretical HOMO levels of PSB-2, PSB-3, and PSB-4 have increased, the LUMO levels have decreased, and the band gaps have narrowed, indicating that the absorption spectrum of the dye has also broadened and enhanced. From the quantum chemical calculation, we noted that the molecular design strategy based on BDF can effectively improve the dye energy level and reduce the band gap. The HOMO and LUMO energy levels of the dye vary with each structural unit, so it is difficult to directly infer the electron-donating ability of each structural unit (Figure 3A,B) from the energy level data of dye. It is necessary to indirectly determine the electron feeding property of each structural unit by calculating the $D_A$ value of the electron feeding capacity parameter.

To intuitively compare the electron-donating properties of the donor or organic fragment and verify the particularity of the ground-state electron cloud distribution of PSB-3 in the above electron cloud distribution diagram, the electron-donating capacity parameters ($D_A$) of each unit and dye was calculated with reference to the previous work of our research group, and the results are listed in Table 1. The $D_A$ trend of each donor and dye is shown in Figure 3C. It can be seen that the $D_A$ value of the fragments increased in the order CZ < BDF < TPA < PTZ. It can explain the changes of HOMO and LUMO energy levels of each dye more intuitively: the model dye PSB-1 has the lowest HOMO energy level, which was because its donor (thiophene) was weaker than the other three dyes. After introducing different aromatic amine donors into PSB-1, the HOMO energy levels of PSB-2, PSB-3, and PSB-4 were increased, LUMO levels were decreased, the band gaps were narrowed, and the electron-donating abilities of the dyes were increased in the order PSB-1, PSB-3, PSB-2, and PSB-4. In addition, the electron-donating ability of the CZ unit was lower than that of BDF, which may be the reason why the electron cloud at the HOMO level of PSB-3 was mainly distributed in the BDF unit.

Figure 3. (A) Molecular fragments and dye structures for theoretical calculation, (B) theoretical HOMO and LUMO levels of molecular fragments and dyes, and (C) $D_A$ values of molecular fragments and dyes.

Figure 4. (A) UV–vis absorption spectra on a UV-2600 spectrometer of 30 μg L$^{-1}$ dyes in THF and (B) fluorescence spectra recorded with a PerkinElmer LS55 luminescence spectrometer of 30 μg L$^{-1}$ dyes in THF.
Table 2. Photophysical and Electrochemical Energy Level Parameters of Dyes PSB-1, PSB-2, PSB-3, and PSB-4

| dye   | \( \lambda_{\text{abs}}^{\text{max}} \) (nm) | \( \varepsilon_{\text{max}}^{\text{abs}} \) \((10^4 \text{ M}^{-1} \text{ cm}^{-1})\) | \( \lambda_{\text{abs}}^{\text{max}} \) (nm) | \( E_{\text{onset}}^{\text{abs}} \) (eV) | HOMO\(^{\text{d}}\) (eV) | LUMO\(^{f}\) (eV) | D\(_\Lambda\) |
|-------|---------------------------------------------|-----------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------|
| PSB-1 | 435                                        | 4.4                               | 583                                         | 0.69                                        | −5.49                                       | 2.42                                         | −3.07   |
| PSB-2 | 510                                        | 5.2                               | 623                                         | 0.31                                        | −5.11                                       | 2.25                                         | −2.86   |
| PSB-3 | 484                                        | 4.8                               | 615                                         | 0.45                                        | −5.25                                       | 2.30                                         | −2.95   |
| PSB-4 | 518                                        | 5.1                               | 629                                         | 0.27                                        | −5.07                                       | 2.19                                         | −2.88   |

“Derived from the extremum of intramolecular electron transfer (ICT) peaks. \(^{4}\)In THF, the maximum absorption wavelength was used as the excitation wavelength. \(^{5}\)\( E_{\text{onset}}^{\text{abs}} \) was obtained using \( F_{0}/F_{0}^{*} \) (\( E_{\text{ox}} = 0.46 \text{ V} \)) as an internal label. \(^{6}\)Determined by cyclic voltammetry, \( F_{0}/F_{0}^{*} \), as an internal standard, HOMO = −(\( E_{\text{onset}}^{\text{abs}} + 4.8 \)) eV. \(^{7}\)Optical band gap, calculated from the normalized UV−vis absorption and emission spectra. \(^{8}\)LUMO = HOMO − \( E_{0,0} \).

2.3. Analysis of Photophysical and Electrochemical Properties. By measuring the UV−vis absorption spectra of the dyes in THF, the influence of the introduction of donors on the light capture ability of dyes can be investigated. The results are shown in Figure 4, and the relevant photophysical data are listed in Table 2. It can be seen from Figure 4A that when the aromatic amine structural units, such as triphenylamine (TPA), carbazole (CZ), and phenothiazine (PTZ), were added at the end of model dye PSB-1, the absorption spectrum of the dye red-shifted and the molar extinction coefficient increased. It is shown that the absorption spectrum can be improved by enhancing the electron-donating ability of the model BDF dye (PSB-1), which was in accordance with the theoretical analysis.

In detail, the absorption spectrum of model dye PSB-1 appeared at 300−550 nm in the visible light range, the maximum absorption wavelength appeared at 435 nm, and the maximum molar extinction coefficient (\( \varepsilon_{\text{max}}^{\text{abs}} \)) was 4.4 × 10^4 m^{-1} cm^{-1}. When TPA, CZ, or PTZ was added to the end of PSB-1, the absorption spectra of the dyes PSB-2, PSB-3, and PSB-4 showed a large red shift and two relatively independent absorption peaks, which were the characteristic absorption peaks of aromatic amine dyes. The absorption peak in the range of 300−400 nm belonged to the \( \pi−\pi^* \) transition absorption peak of aromatic amine dyes, while the stronger absorption peak in the range of 450−600 nm was the intramolecular electron transfer (ICT) characteristic absorption peak. Compared with that of the model dye, the maximum absorption wavelength of dye PSB-2 was shifted by 75 nm, which appeared at 510 nm, while those of dyes PSB-3 and PSB-4 were red-shifted by 49 and 83 nm, which were 584 and 518 nm, respectively. At the same time, the \( \varepsilon_{\text{max}}^{\text{abs}} \) values of dyes PSB-2, PSB-3, and PSB-4 also increased significantly, which were 5.2 × 10^4, 4.8 × 10^4, and 5.1 × 10^4 m^{-1} cm^{-1}, respectively, and was consistent with the electron-donating difference of TPA, CZ, and PTZ and the dispersed state of the dyes in THF.

Figure 4B shows the fluorescence emission spectra of four dyes in THF. Note that the maximum emission wavelength of the model dye PSB-1 appeared at 583 nm, while those of dyes PSB-2, PSB-3, and PSB-4 showed a red shift, which appeared in the range of 615−629 nm, and the fluorescence intensities were also enhanced compared with that of PSB-1.

For investigating the effect of energy level when introducing different aromatic amines at the end of PSB-1, the electrochemical cyclic voltammetry curves of the dyes were measured and the initial oxidation potentials of the dyes were obtained, as shown in Figure 5B. Combined with the optical band gap (\( E_{\text{g}} \)) of the dye and formula (2), the electrochemical energy level and the electron-donating capacity (\( D_\Lambda \)) were calculated. The detailed parameters are listed in Table 2. According to the normalized UV−vis absorption spectrum and fluorescence spectrum shown in Figure 5A, the \( E_{\text{g}} \) values of dyes PSB-1, PSB-2, PSB-3, and PSB-4 were calculated as 2.42, 2.25, 2.30,
Energy levels were obtained as the difference in the HOMO energy levels of the dyes were −0.45, and 0.27 V, respectively, using the tangent method, and the oxidation potentials (E_{ox}^{ onset}) of PSB-1, PSB-2, PSB-3, and PSB-4 vs F/F^− (E_{ox} = 0.46 V) were calculated as 0.69, 0.31, 0.45, and 0.27 V, respectively, using the tangent method, and the HOMO energy levels of the dyes were −5.49, −5.11, −5.25, and −5.07 V, respectively, calculated by formula 2.

\[ E_{HOMO} = -e\left(E_{ox}^{ onset} + 4.8\right) \text{ (eV)} \]  

Based on the energy level, the \( D_A \) values of the dyes were obtained as 1.22, 1.51, 1.40, and 1.53 eV, respectively, referring to the method in our previous work. Due to the introduction of receptor CA, the \( D_A \) values of the dyes were smaller than that of the aromatic amine donor. Although it is of little practical significance to study the difference of the electron-donating ability of a dye, the intramolecular electron-transfer dynamics can be predicted by it; the latter was of a great significance to study the absorption spectrum and electron injection efficiency. As shown in Table 2, note that after the introduction of an electron donor group, the electron-donating ability of dyes increases in the order \( D_A \) (PSB-1) < \( D_A \) (PSB-3) < \( D_A \) (PSB-2) < \( D_A \) (PSB-4). Because the dyes have the same \( \pi \)-bridge (BDF) and receptor (CA), the change is mainly caused by the introduction of the aromatic amine donor, so it can be inferred that dyes PSB-2, PSB-3, and PSB-4 have stronger intramolecular electron-transfer potential energy, which can be verified by the fact that the three dyes have red absorption spectra and stronger ICT absorption peaks compared with those of PSB-1, which shows that the design strategy here can effectively regulate the energy levels and band gaps and improve the absorption spectra of BDF dyes.

2.4. Photovoltaic Performance of DSCs. A TiO2 nanocrystalline photoanode was prepared according to our previous work. After activation at 500 °C on a hot air gun, a photoanode (cylindrical TiO2 electrode ~0.28 cm2) was stained by immersing in the dye (PSB-1, PSB-2, PSB-3 and PSB-4) solution (200 µg L\(^{-1}\)) in THF/AN (1:4, v/v) for 12 h. After being washed with acetonitrile and dried by airflow, the photoanode of the BDF dye-based DSCs was obtained. Then, the sensitized TiO2 photoanode was placed upward on the hot press platform; a 30 µm thick Surlyn ring was covered around the TiO2 film with the hot platinum counter electrode; the appropriate temperature, pressure, and time were adjusted for hot pressing; and then it was blown to cool immediately by an air gun. One drop of \( I^{+}/I^{−} \) electrolyte was dropped into the hole of the counter electrode, a diaphragm pump was used to vacuum for a few seconds, and the vacuum backfill principle was used to inject the electrolyte into the battery cavity through the hole. The remaining electrolyte around the electrode hole was wiped, and a Bynel disk and coverglass were placed on the hole in turn to heat seal it. Finally, the electrode of the cell was coated with a uniform solder by an ultrasonic welding gun to enhance its conductivity.

To detect the relationship between the dye/device and photovoltaic performance, the determination of incident photon-to-current conversion efficiency (IPCE) and current–voltage (\( J-V \)) characteristic curve was necessary. Figure 6A illustrates the IPCE spectrum based on the devices above, measured on a Zolix DCS300PA data system and a Zolix SCS100-Omni-λ3007 monochromator equipped with a 300 W xenon lamp. Note that the IPCE response range of model dye PSB-1 was between 350 and 650 nm and the maximum monochromatic light conversion efficiency was 45%. The initial response wavelengths of PSB-2, PSB-3, and PSB-4 were the same as that of PSB-1, while the response sideband shifts to about 700 nm. Also, the maximum monochromatic optical conversion efficiency (IPCE\(_{max}\)) was also higher than that of PSB-1, and the IPCE\(_{max}\) values are 65, 73, and 76% for PSB-2, PSB-3, and PSB-4, respectively. The reason was that the introduction of TPA, CZ, and PTZ increased the potential energy of intramolecular electron transfer, which was consistent with the above-mentioned UV–vis absorption spectrum.
Figure 6B illustrates the J−V curves of DSCs devices based on PSB-1, PSB-2, PSB-3, and PSB-4, measured on a Keithley 2450 source meter and a Zolix SS150 solar simulator under a simulated solar irradiation condition of AM 1.5G (100 mW cm−2). The measurements were fully automated using the software from Zolix Instruments Co. Ltd. The detailed parameters are listed in Table 3; note that the short-circuit current ($J_{sc}$) and open-circuit voltage ($V_{oc}$) of dyes PSB-2, PSB-3, and PSB-4 are higher than those of the model PSB-1. The $V_{oc}$, $J_{sc}$, and fill factor (FF) of PSB-1 were 0.61 $V$, 6.80 mA cm$^{-2}$, and 0.70, respectively, and the photoelectric conversion efficiency (PCE) is 2.9%, however, the $V_{oc}$, $J_{sc}$, and FF of the other three dyes have significant increasing: 0.70 $V$, 9.66 mA cm$^{-2}$ and 0.70 for PSB-2, 0.67 $V$, 7.80 mA cm$^{-2}$ and 0.68 for PSB-3, 0.72 $V$, 10.26 mA cm$^{-2}$ and 0.72 for PSB-4, and the PCE were 4.7, 3.5, and 5.5% respectively, which are 62, 20, and 90% higher than PSB-1, which was because the introduction of the aromatic amine donor makes the former dyes to have a better energy level and absorption spectrum.

To investigate whether the adsorption capacity of dyes has a great impact on the photovoltaic data, under the same conditions, we prepared 100 $\mu$m dye solutions with THF and AN/THF with a mass ratio of 4:1 as a solvent. Then, a 0.7 $\mu$m thick transparent titanium dioxide electrode was immersed in the above dye solution for 16 h to ensure that the dye molecules reach the adsorption–desorption equilibrium on the surface of titanium dioxide. Combined with the UV−vis absorption spectrum method, the dye molecular loading was examined. The results show that the loading capacity of the four dyes remains at the same order of magnitude and it was very close (Table 2), which shows that the adsorption capacity has a little effect on the photovoltaic data between the dyes.

By comparing the photovoltaic data of dyes PSB-2, PSB-3, and PSB-4, we noted that PSB-4 obtained the highest $V_{oc}$, $J_{sc}$, and PCE. This may be because the stronger donor of PSB-4 has a narrower band gap and wider absorption spectrum, which effectively improved the short-circuit current. Another reason may be that the unique butterfly structure of PTZ can effectively suppress the dark current caused by the interface charge recombination, thereby increasing the open-circuit voltage. At the same time, PSB-3 has the lowest $V_{oc}$, $J_{sc}$, and PCE, which was mainly due to CZ’s lower electron-donating ability than BDT. When the dye molecule absorbs photons, the intramolecular electron transition mainly occurs from the BDT unit to the LUMO level. It was also found in Table 3 that the open-circuit voltage of PSB-3 is lower than those of PSB-2 and PSB-4 but higher than that of PSB-1. The former may be due to the weaker donor CZ affected the electron density of the semiconductor surface, while the latter may be because the introduction of CZ increases the volume of PSB-3, more effectively suppresses the dark current at the interface than PSB-1, and improves the electronic density of the TiO$_2$ surface relative to PSB-1.

3. CONCLUSIONS

In this work, a model dye PSB-1 was first synthesized based on thiene[2,3-f]benzofuran (BDF), by the introduction of several strong donors TPA, CZ, and PTZ at the end of PSB-1, and a series of BDF-based dyes PSB-2, PSB-3, and PSB-4 were synthesized and characterized. Then, density functional theory (DFT) calculations performed at the B3LYP/6-31G(d,p) level with Gaussian 09 were used to optimize the structures and observe the trend of frontier orbital energy and electronic cloud distribution of the sensitizers. We found that the introduction of aromatic amines can improve the energy level of dyes and increase the potential energy difference of intramolecular electron transfer. In addition, the energy level of dyes can be effectively improved only when the molecule fragment is arranged in a descending order of the $D_0$ value. The results of UV−vis absorption spectra, cyclic voltammetry curves, IPCE, and J−V characteristic curves revealed that adding an electron donor group to the donor end of PSB-1, as predicted by theoretical calculations, can effectively improve the energy level of the dyes, broaden the absorption spectrum, and improve the photovoltaic performance of DSCs. Among the dyes, PSB-4 has the highest $V_{oc}$, $J_{sc}$, and PCE (5.5%) because PTZ has the strongest electron-donating property, which increases the potential energy difference within the molecule and improves the absorption spectrum of the dye. In particular, PSB-3 has a relatively lower $V_{oc}$, $J_{sc}$, and PCE (3.5%) because CZ has a weaker electron-donating property than BDF, and when the molecule is excited, the electron transition mainly occurs from the BDF to the receptor (CA).

In conclusion, we conclude that when a strong donor is added to the BDF dye, its energy level, absorption spectrum, and photovoltaic characteristics can be effectively improved, but when a donor weaker than BDF is used, this effect will be greatly weakened. To improve the photovoltaic properties of new sensitizers, we need to fully consider the push−pull electronic ability of each molecular segment and assemble them in a certain order.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The work was supported by the National Natural Science Foundation of China (51703062), the Natural Science Foundation of Hunan Province (2019JJ50408 and 2018JJ3370), and the Huxiang Youth Talent Support Program (2018RS1417).

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