Wide Band-gap Two-dimension Conjugated Polymer Donors with Different Amounts of Chlorine Substitution on Alkoxyphenyl Conjugated Side Chains for Non-fullerene Polymer Solar Cells

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INTRODUCTION

Polymer solar cells (PSCs) consist of a p-type conjugated polymer donor and an n-type organic semiconductor (including fullerene derivatives and non-fullerene organic semiconductors)\textsuperscript{[1−32]}. For the past few years, PSCs have been developed rapidly, exhibiting outstanding advantages such as simple device structure, low cost, lightweight, flexibility, and semitransparency.\textsuperscript{[33−36]} Now, it has become a global frontier and hot spot in organic photovoltaic research, which mainly focuses on improving power conversion efficiency (PCE) and stability, reducing the cost of photovoltaic materials and device preparation, and subsequent industrialization and practical application.\textsuperscript{[37]} PCEs of the single-junction solar cells have been over 16% according to reported studies so far.\textsuperscript{[38−43]} Currently, typical polymer donors are mainly D-A type copolymers PBDB-T,\textsuperscript{[44]} PM6,\textsuperscript{[45]} P3HT,\textsuperscript{[46]} J91,\textsuperscript{[47]} P2F-EHp,\textsuperscript{[48]} and 2D conjugated side chains, and 2D polymer donors have more advantages such as extensive intramolecular conjugation, facilitated intermolecular interaction and π-π overlap, compared with 1D conjugated polymer donors. Meanwhile, acceptors are mainly n-type organic semiconductors. With regard to fullerene and its derivatives as acceptors for PSCs, fused-ring acceptors (some typical ones such as ITIC, Y6) feature good stability, easily tailored synthesis methods, strong absorption in the visible light region, and tunable energy levels, thus becoming more and more dominant in PSC research community. Excellent polymer donors usually contain complementary absorption spectra with above-mentioned acceptors, which is very important to build...
highly efficient organic photovoltaics. \cite{48,49}

It is well known that donor materials need to match the energy level of the acceptors to obtain increased open-circuit voltages (V_{OC}), and have a relatively strong absorption spectrum and morphological compatibility with the acceptors to increase short-circuit current densities (J_{SC}) and fill factors (FFs) for PSCs. Benzodithiophene (BDT) is an excellent electron-donating donor unit with a large planar structure and outstanding crystallinity. Highly efficient PSCs generally include BDT units for D-A copolymer donors as electron-rich segments and A-D-A type small molecule donors or acceptors as conjugated core to build two-dimension (2D) excellent molecular systems.\cite{30-33} In general, BDT unit based 2D conjugated photoelectronic materials show excellent photovoltaic performance in nonfullerene PSCs (NF-PSCs).\cite{54} BDT unit with 2D conjugated side chains is adopted most widely by phenyl and thiophene substitution to tune energy levels and improve geomorphology of active layers.\cite{51,55,56} In order to further improve the photovoltaic properties of PSCs, halogen atoms are introduced into 2D conjugated side chains to regulate molecular energy levels, charge transfer, and the compatibility of donor and acceptor, since halogenation is a very effective method for increasing the corresponding parameters of organic semiconductors. In recent years, fluorinated and chlorinated substituted photoactive materials (including donors and acceptors) have shown great potential in achieving highly efficient PSCs.\cite{37-41} Hou’s group studied systematically the effects of fluorinated and chlorinated donors and acceptors on the performance, and the results indicated that chlorination was more effective than fluorination in reducing molecular energy levels and broadening absorption spectra.\cite{62,63} Zhang et al. introduced a fluorine atom into the thienyl conjugated side chain to synthesize the polymer donor PM6, which was measured with deeper HOMO levels and higher PCE.\cite{61} Recently, Yan’s group used polymer donor PM7 with chlorine atoms to replace fluorine atoms on thienyl side chains, which resulted in enhanced V_{OC} when coping with acceptor Y6 achieving a PCE as much as 17% efficiency.

PSCs based on BDT unit with conjugate side chains on phenyl group using chlorine substitution also obtain the excellent performance in reported literatures, and chlorinated polymer acquired the lower HOMO energy level as well as high V_{OC} and PCE.\cite{64} Huang’s group synthesized PF-Elp by introducing two chlorine atoms on phenyl substituted side chains and it was applied in PSCs, which achieved higher V_{OC} and PCE.\cite{65} These results imply that chlorination may have greater potential for large-scale applications as it is more attractive to design low-cost photovoltaic materials.

In this study, we designed and synthesized WBG 2D copolymers DZ1, DZ2, and DZ3 with different degrees of chlorine substitution by using difluorobenzotriazole (FBTZ) through Stille coupling polymerization (Scheme 1 and Scheme S1 in the electronic supplementary information, ESI). Three polymer donors DZ1, DZ2, and DZ3 displayed broad absorption in the ultraviolet-visible light region of 300−700 nm with optional band-gap (E_{g opt}) of 1.84, 1.92, and 1.97 eV, respectively. HOMO energy level of polymer donors DZ2 and DZ3 by introducing chlorine into the alkoxylphenyl group is deeper than that of reported DZ1 without chlorine substitution, which can increase V_{OC} of PSCs, correlative charge carrier, compatibility of donor and acceptor, and photovoltaic performance.\cite{66} Non-fullerene PSCs based on DZ2 as the donor and MeIC as the acceptor demonstrates a relatively high PCE of 10.22% with a V_{OC} of 0.88 V, a J_{SC} of 17.62 mA/cm², and a FF of 68%, compared with PSCs based on DZ1:MeIC (a PCE of 8.26%) and DZ3:MeIC (a PCE of 6.28%). The results suggest that introducing different numbers of chlorine atoms on alkoxylphenyl conjugated side chains based on BDT polymer donors is a vigorous strategy to synthesize electron-rich building block for high performance of PSCs.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization**

The molecular structures of polymer donors DZ1, DZ2, DZ3, and acceptor MeIC are shown in Figs. 1(a) and 1(b). Three

![Scheme 1 Chemical structures and synthetic routes of DZ1, DZ2, and DZ3.](https://doi.org/10.1007/s10118-020-2435-5)
polymer donors were synthesized through the Stille coupling reaction using Pd(PPh3)4 as a catalyst and toluene as a reactive solvent. The detailed synthetic procedures and characterization methods of monomers and polymers are displayed in ESI. The high-temperature gel permeation chromatography was used to test the number-average molecular weight (Mn) and polydispersity index (PDI) of polymers DZ1, DZ2, and DZ3. M, of polymer donors DZ1, DZ2, and DZ3 was 15.3, 19.6, and 9.04 kDa with a PDI of 2.06, 2.20, and 3.10, respectively. The data were tested at 160 °C using polystyrene as a reference and 1,2,4-trichlorobenzene as the eluent. Three polymers showed good solubility in normal organic solvents, such as toluene, o-dichlorobenzene, chlorobenzene, and chloroform. Thermodynamic stability of the three polymers was measured by TGA in a nitrogen atmosphere at a rate of 10 °C/min. The decomposition temperatures (defined as the temperature of 5% weight loss) of polymers DZ1, DZ2, and DZ3 were 359, 352, and 400 °C, respectively (Fig. S1a, in ESI). Fig. S1b (in ESI) shows differential scanning calorimetry (DSC) thermograms of three polymers DZ1, DZ2, and DZ3, which suggest no obvious crystalline peaks from 50 °C to 300 °C.

**Optical and Electrochemical Properties**

Fig. 1 and Fig. S2 (in ESI) show the UV-visible absorption spectra of three polymers in chloroform solution and as film, respectively. In solution, the absorption spectra of polymers DZ2 and DZ3 were slightly red-shifted, and displayed the strong n–n stacking. And three polymers showed a similar intramolecular charge transfer (ICT) peak at around 532 nm. In the solid film, by comparison with polymer DZ1, the absorption spectra of DZ2 and DZ3 were slightly blue-shifted and narrow (Fig. 1c). And the absorption maxima of all polymers were at 538, 540, and 542 nm, respectively. The absorption edges of the three donors were at 647, 629, and 640 nm with the corresponding optical bandgap (Eg) of 1.84, 1.92, and 1.97 eV, respectively (Table 1). Such a blueshift phenomenon expended the main absorption region, which would enable the greater complementary light-harvesting spectrum to produce higher Jsc and PCE values. The absorption maximum and absorption edge of the acceptor MeIC were 718 and 795 nm, respectively. The UV-visible absorption spectra of three polymer blends with acceptor MeIC are shown in Fig. 1(d). The blend film absorption intensity (ε) exhibited the following order: DZ2:MeIC (5.30 × 10^4 cm\(^{-1}\)) > DZ1:MeIC (4.50 × 10^4 cm\(^{-1}\)) > DZ3:MeIC (2.95 × 10^4 cm\(^{-1}\)), as outlined in Table 1. It was obvious that DZ2:MeIC obtained the strongest absorption coefficient among the three blends. The result is consistent with the Jsc discussed below. The hole mobilities of three polymers were measured by using space charge limited current (SCLC) method, as shown in Fig.

**Table 1** Optical properties, electronic levels and hole mobilities of DZ1, DZ2, and DZ3.

| Donor | Tg (°C) | Emax<sup>1</sup> (nm) | λmax<sup>2</sup> (nm) | ε<sub>0</sub> (eV) | ε<sub>0</sub> × 10<sup>-4</sup> (cm<sup>-1</sup>) | HOMO<sup>4</sup> (eV) | LUMO<sup>4</sup> (eV) | μh (cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) |
|-------|---------|-----------------|-----------------|---------|-----------------|-----------------|-----------------|-----------------|
| DZ1   | 359     | 535             | 538             | 1.84    | 4.50            | −5.26           | −3.05           | 7.56 × 10<sup>−4</sup> |
| DZ2   | 352     | 531             | 540             | 1.92    | 5.30            | −5.32           | −3.13           | 8.43 × 10<sup>−4</sup> |
| DZ3   | 400     | 533             | 542             | 1.97    | 5.40            | −5.40           | −3.17           | 9.64 × 10<sup>−4</sup> |

<sup>1</sup> Estimated from the absorption edge in film; <sup>2</sup> Molar absorptivity at λmax in blended films; <sup>4</sup> Measured from the cyclic voltammograms.
S3 (in ESI). Polymer donors DZ2 and DZ3 exhibited higher hole mobility (8.43 × 10^{-4} and 9.64 × 10^{-4} cm^{2}V^{-1}s^{-1}) than DZ1 (7.56 × 10^{-4} cm^{2}V^{-1}s^{-1}) (Table 1). Such high mobility of neat films may be ascribed to the introduction of chlorine atoms, which resulted in the stronger molecular interaction to improve more effective charge transport.

The electrochemical properties of three polymer donors were measured by cyclic voltammetry (CV) using the standard three electrode electrochemical cell. The energy level diagram and the CV curves of the three polymers are shown in Fig. 1(e) and Fig. S4 (in ESI). According to the formula: \( E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.71) \) (eV) and \( E_{\text{LUMO}} = -e(E_{\text{red}} + 4.71) \) (eV), the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) were calculated, respectively. The HOMO energy levels of the three polymer donors were measured as −5.26, −5.32, and −5.40 eV, respectively. The HOMOs and LUMOs of polymers DZ1, DZ2, and DZ3 were consistent with the results of DFT calculation with the HOMO/LUMO of −4.86/−2.78 eV for DZ1, −5.05/−2.94 eV for DZ2, and −5.19/−3.05 eV for DZ3 (Fig. S5, in ESI). Obviously, the HOMO energy level of polymer DZ3 with four chlorinated substitutions was deeper than those of polymers DZ1 without chlorinated substitution and DZ2 with two chlorinated substitutions, which was beneficial to obtaining a high \( V_{\text{OC}} \) value. Besides, the strategy demonstrated that chlorine atom was a stronger electron-withdrawing group, generating the deeper HOMO energy levels. And the trend is similar to the reported literature with fluorinated and trifluoromethyl substitution on phenyl conjugated side chains. These results implied that chlorinated substitution is a promising approach of achieving deeper HOMO energy levels to increase \( V_{\text{OC}} \) for efficient NF-PSCs.

**Theoretical Calculations**

Theoretical calculations were performed by adopting density functional theory (DFT) with the B3LYP/6-31G (d, p) basis set. To simplify the calculation procedure, long alkyl chains were changed to methyl groups. As shown in Fig. S5 (in ESI), HOMO surface of the polymers was delocalized on both BDT and FBTZ segments. Nevertheless, LUMO surface of the polymers was more localized on the acceptor units, demonstrating that FBTZ unit displayed strong electron-withdrawing character. In addition, three polymeric skeletons exhibited good planar and linear construction, as well as a predominant homogeneous dispersion of positive electrostatic potential (ESP), which is beneficial to obtaining high charge carrier mobilities (Fig. 2). As illustrated in Fig. 2, the optimal molecular configuration of polymer DZ2 is that the asymmetrical side chains with two chlorine substitutions on phenyl groups were located on the two sides of the molecule plane, which is different from polymers DZ1 and DZ3 without and with the symmetrical chlorine substitution conjugated side chains, generating the different molecular arrangement and dipole moments. Polymer DZ2 with two chlorine substitutions on the phenyl conjugated side chains obtained the dipole moment value of 8.81 D, being superior to that of DZ1 (5.43 D) and DZ3 (3.15 D). The result indicates that the orientation of the dipole moment would force polymer DZ2 to enlarge the accumulation area and intensity.\(^{[66–68]}\)

**Photovoltaic Properties**

The photovoltaic performance of polymer donors DZ1, DZ2, and DZ3 was studied by fabricating NF-PSCs with MelC as an acceptor and DZ1 or DZ2 or DZ3 as a donor with the conventional device architecture of ITO/PEDOT:PSS/photo-voltaic active layer/Zracac/Al, where ITO is indium tin oxide, PEDOT is poly(3,4-ethylenedioxythiophene), and Zracac is zirconium(IV) acetylaceton. Fig. 3(a) depicts the current density-voltage (\( J-V \)) plots of the devices with the best performance. The corresponding device parameters with \( J_{\text{SC}}, V_{\text{OC}}, \) FF, and PCE are outlined in Table 2. The PSC based on DZ1:MelC obtained a PCE of 8.262%, a \( V_{\text{OC}} \) of 0.814, a FF of 0.667, and a \( J_{\text{SC}} \) of 15.237 mA·cm\(^{-2}\), PCE of 10.215% based on DZ2:MelC blend with \( V_{\text{OC}} \) of 0.877, FF of 0.684, and \( J_{\text{SC}} \) of

![Fig. 2](https://doi.org/10.1007/s10118-020-2435-5)  

**Fig. 2** Optimized geometries of polymers DZ1, DZ2, and DZ3 by DFT at the B3LYP/6-31G (d, p) level. (a, c, e) Side view and (b, d, f) map of the DFT electrostatic potential (ESP) surface of DZ1, DZ2, and DZ3, respectively. Cyan color indicates greater negative charge, while yellow and red colors indicate positive charges.
17.061 mA·cm$^{-2}$ is higher than that of DZ3:MeIC (PCE of 5.966%, $V_{OC}$ of 1.000, FF of 0.609, and $J_{SC}$ of 10.311 mA·cm$^{-2}$). It is obvious that $V_{OC}$ of the DZ3:MeIC-based PSC was the highest due to the deeper HOMO energy level of polymer DZ3. Furthermore, a device based on DZ2:MeIC achieved the optimized efficiency of photovoltaic performance, which was attributed to the balanced charge transport below discussed mobiles. The result suggested that introducing suitable chlorine amount on phenyl conjugated side chains could obtain the increments of $J_{SC}$, $V_{OC}$, FF, and PCE.

### Charge Carrier Mobilities

In order to better understand the effect of internal charge carriers on the photovoltaic properties of NF-PSCs, the charge mobility measurements of the neat polymer donors DZ1, DZ2, and DZ3, and the polymer blends of DZ1:MeIC, DZ2:MeIC, and DZ3:MeIC were carried out by adopting the space-charge-limited current (SCLC) method with a device structure of ITO/PEDOT:PSS/active layer/MoO$_3$/Al for the hole mobility ($\mu_h$) and ITO/ZnO/active layer/Zracac/Al for the electron mobility ($\mu_e$). The current-voltage curves of mobilities are exhibited in Fig. 4. It can be seen from Table 2 that the hole mobilities of DZ1:MeIC, DZ2:MeIC, and DZ3:MeIC blends were $6.12 \times 10^{-4}$, $6.78 \times 10^{-4}$, and $7.36 \times 10^{-4}$ cm$^2$·V$^{-1}$·s$^{-1}$, respectively. The electron mobility of DZ2:MeIC blend ($3.74 \times 10^{-4}$ cm$^2$·V$^{-1}$·s$^{-1}$) was higher than those of DZ1:MeIC ($3.02 \times 10^{-4}$ cm$^2$·V$^{-1}$·s$^{-1}$), and DZ3:MeIC blends ($3.34 \times 10^{-4}$ cm$^2$·V$^{-1}$·s$^{-1}$). And the specific value of hole and electron mobility of DZ2:MeIC blend ($\mu_h/\mu_e = 1.81$) was more balanced than that of DZ1:MeIC ($\mu_h/\mu_e = 2.00$) and DZ3:MeIC blends ($\mu_h/\mu_e = 2.20$) (Table 2). The result demonstrates

![Graph](image)

**Fig. 4** $J-V$ ($V = V_{appl} - V_b - V_c$) characteristics of (a) the hole-only devices (ITO/PEDOT:PSS/active layer/MoO$_3$/Al) and (b) the electron-only devices (ITO/ZnO/active layer/Zracac/Al).

### Table 2 Photovoltaic data of the donors:MeIC (1:1, W/W)-based OSCs.

| Donor | $V_{OC}$ (V) | $J_{SC}$ (mA·cm$^{-2}$) | Calc. $J_{SC}$ (mA·cm$^{-2}$) | FF (%) | PCE (%) | $\mu_h \times 10^4$ (cm$^2$·V$^{-1}$·s$^{-1}$) | $\mu_e \times 10^4$ (cm$^2$·V$^{-1}$·s$^{-1}$) | $\mu_h/\mu_e$ |
|-------|-------------|--------------------------|------------------------------|--------|---------|---------------------------------|---------------------------------|-------------|
| DZ1   | 0.810 ± 0.010 (0.814) | 15.010 ± 0.211 (15.237) | 14.530 ± 0.000 (0.667) | 7.939 ± 0.19 (8.262) | 6.12 ± 3.02 | 1.000 ± 0.011 (1.000) | 9.997 ± 0.230 (10.311) | 7.36 ± 3.34 |
| DZ2   | 0.872 ± 0.008 (0.877) | 16.911 ± 0.231 (17.061) | 16.688 ± 0.010 (0.684) | 9.983 ± 0.20 (10.215) | 6.78 ± 3.74 | 1.000 ± 0.011 (1.000) | 9.977 ± 0.231 (10.311) | 7.36 ± 3.34 |
| DZ3   | 0.998 ± 0.011 (1.000) | 9.997 ± 0.228 (10.311) | 9.763 ± 0.006 (0.609) | 5.77 ± 0.56 (5.966) | 7.36 ± 3.34 | 1.000 ± 0.011 (1.000) | 9.977 ± 0.238 (10.311) | 7.36 ± 3.34 |

* Average values and standard deviation are calculated from 20 devices. The values in parentheses belong to the best device.
that a better balance charge mobility was achieved by DZ2 based system, which could contribute to its higher FF value.

**Morphology Study**

The optimized geomorphology is important to enhance the photovoltaic performance of PSCs. To further gain insight into the morphology of the photovoltaic layers, atomic force microscopy (AFM) was implemented. As shown in Fig. S6 (in ESI), the AFM images of neat DZ1, DZ2, and DZ3 films revealed that the root mean square (RMS) values of neat DZ1, DZ2, and DZ3 films were 1.00, 1.10, and 1.32 nm, respectively. Fig. 5 shows the AFM images of DZ1:MeIC, DZ2:MeIC, and DZ3:MeIC blends. The arranged order of surface roughness of blends was DZ1:MeIC < DZ2:MeIC < DZ3:MeIC, and the corresponding RMS values were 1.34, 2.10, and 2.89 nm, respectively. The result implied that the suitable surface roughness was crucial to enhancing the efficiency of PSCs.

**CONCLUSIONS**

In summary, we have successfully designed and synthesized new WBG 2D copolymer donors DZ1, DZ2, and DZ3 without and with different degrees of chlorination for application in NF-PSCs. These 2D conjugated polymer donors exhibited the broad absorption spectra in the UV-visible light region and its absorption spectra were well complementary with that of acceptor MeIC. Polymers DZ2 and DZ3 displayed deeper HOMO energy levels, compared with polymer DZ1, and generated the higher V<sub>OC</sub> value. The NF-PSCs based on DZ2:MeIC with two chlorinated substitutions achieved an optimized PCE of 10.215% with V<sub>OC</sub> of 0.877, FF of 0.684, and J<sub>SC</sub> of 17.061 mA·cm<sup>-2</sup>, which was superior to those of DZ1:MeIC (PCE = 8.262%) and DZ3:MeIC (PCE = 5.966%). More balanced charge carrier mobilities and suitable surface roughness are consistent with the best device condition of NF-PSCs based on DZ2:MeIC. Obviously, these BDT unit-based-chlorinated polymers significantly enhanced the photovoltaic performance of NF-PSCs. In addition, we revealed the close-knit relationship between the molecular structure with chlorinated substitution and device properties. This study implies that appropriately introducing chlorine atoms on alkoxyphenyl side chains based on BDT polymer donors was a feasible strategy for efficient NF-PSCs.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2435-5.

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