Single-Crystalline Structure Assisted Revealing the Critical Factors for the Properties of All-Small-Molecule Organic Solar Cells

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All-small-molecule organic solar cells have attracted great interests due to their well-defined molecular structures and suitability for investigating the relationship between the structure and properties. Herein, two small-molecule donors (SMDs) based on DTBDT core with chlorine atoms and alkylsilyl side chains, namely, ZR-Si3 and ZR-Si4, are synthesized and their respective photovoltaic properties by blending them with IDIC-4Cl and Y6 are studied. The power conversion efficiency (PCE) based on IDIC-4Cl is higher than that of Y6 systems due to low driving force between the donors and Y6. Although the two IDIC-4Cl systems have similar morphology, the PCE of 10.10% is attained based on ZR-Si4, which is higher than that of ZR-Si3-based devices (8.12%). To obtain an in-depth insight into the structure and performance relationship, single crystals of two SMDs and acceptors are obtained successfully. The shortest π−π stacking distance of 3.43 Å and a transport channel between the layers are observed for ZR-Si4, which is beneficial for getting better performance.

1. Introduction

Recently, the organic bulk heterojunction (BHJ) solar cells were rapidly developed due to the extensive research on organic photovoltaic materials. With the emergence of a new nonfullerene acceptor (NFA) Y6 and its various derivatives, the power conversion efficiencies (PCE) of polymer solar cells (PSCs) have reached beyond 18%. Likewise, the PCEs of the organic solar cells (OSCs) based on all-small-molecule (ASM) systems have reached an efficiency of 15%. Although the performance is lower than their polymer counterpart, a lot of research is still focused on the ASM solar cells because of their various advantages, such as being able to efficiently control the absorbance and the energy levels, synthesizing molecules with clear structure without a batch-to-batch difference, as well as ensuring good processability. At present, designing new small-molecule donors (SMDs) and small-molecule acceptors is still a conservative strategy to improve the PCE of ASM OSCs due to the limited availability of methods for controlling the morphology. In this regard, a large number of SMDs reported generally have an A−π−D−π−A architecture, whereas benzodithiophene (BDT), naphth[1,2-b:5,6-b′]dithiophene (NDT), and dithieno[2,3-d:2′,3′-d′]benzo[1,2-b:4,5-b′]dithiophene (DTBDT) are commonly used donor units for such SMDs. Interestingly, the extended conjugation plane of DTBDT can effectively improve the packing structure of SMDs and reduce the conformational disorder of the backbone, which can effectively improve the photovoltaic characteristics. Our group designed a series of SMDs ZR1, ZR1-Cl, and ZR1-S-Cl based on DTBDT unit, all of which produced good PCEs with Y6 and IDIC-4Cl acceptors. In most of such reports, the open-circuit voltage (VOC) appeared to be the PCE-limiting parameter in the ASM devices. Therefore, a key strategy for increasing the VOC is to design new ASM systems that demonstrate low driving force and low energy losses. Accordingly, it has been observed that the introduction of alkylsilyl on the base of the central donor unit can downshift the highest occupied molecular orbital (HOMO) energy level and red shift the absorption spectrum, thereby enabling high PCEs with lower energy losses. Moreover, the alkylsilyl side chain can proficiently affect the photovoltaic properties by influencing the molecular packing structure, absorption coefficient, and charge carrier mobility. The influence of different molecular structures on the phase separation and morphology of the active layer has been intensively investigated by the transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements.
and grazing-incidence wide-angle X-ray scattering (GIWAXS). However, the stacking motif and explicit stacking structures of different molecules are worthy of further study, and the single-crystal structures of molecules can clearly establish the relationship between molecular design, stacking structure, and device performance. For instance, our group reported a strong crystalline donor ZR1, which produced a high PCE of 14.34%, by optimizing hierarchical morphology when blended with Y6.\(^{[24]}\) The single crystal of ZR1 was obtained, and the formed nanocrystal structures played an important role for obtaining optimal hierarchical phase separation of active layer. In contrast, a rising trend has been observed for the research on the NFA single-crystal structures, which has enabled a better understanding of the stacking motif of the acceptors.\(^{[6,32–36]}\) Cao and coworkers reported the distinctive $\pi-\pi$ molecular packing of Y6, and the 3D molecular arrangement makes Y6 an ambipolar material with low voltage loss and high charge generation efficiency, which also provided new design strategies for excellent performance acceptors.\(^{[37]}\) However, the structure of donor single crystals has not been discussed extensively,\(^{[18,19]}\) and it generally becomes quite difficult to obtain a high-quality single crystal.

Herein, we designed and synthesized two SMDs based on the DTBDT unit, named as ZR-Si3 and ZR-Si4, and their molecular structures are shown in Figure 1a. In contrast to the reported ZR1 donor, the introduction of chlorine to form ZR-Si3 down-shifted the HOMO energy level and thus, regulated the aggregation behaviors of the molecule, which significantly increased the open-circuit voltage ($V_{OC}$) of the devices with IDIC-4Cl and Y6. Similarly, for the ZR–Si4 molecule, the changing side chain has been used to fine tune the stacking behavior of molecules in the films, which enabled the corresponding devices to realize a simultaneous increase in the $V_{OC}$, the short circuit current density ($J_{SC}$), and the fill factor (FF), ultimately, achieving optimal efficiency of 10.10% with IDIC–4Cl. Furthermore, the single-crystal structures of two donors demonstrate strong $\pi-\pi$ interaction between donor molecules and short contact between adjacent layers for extending the charge transport channel. In addition, Y6 exhibits a unique 3-D stacking structure superior to that of IDIC-4Cl, and a further investigation indicates that small driving force prevents Y6-based systems from exhibiting excellent photovoltaic performance.

2. Results and Discussion

The detailed SMD synthesis method has been provided in the Supporting Information, whereas the synthetic routes of the two donor molecules are shown in Figure S1, Supporting Information. The cyclic voltammetry measurements were used to measure the energy levels of the two SMDs, where the HOMO and lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the onset oxidation and reduction potentials, and the two donors have the same HOMO and LUMO energy levels, which were calculated to be at $-5.60$ and $-3.61$ eV (Figure 1b). The two SMDs indicate a well-matched energy-level configuration with IDIC-4Cl; however, the HOMO energy-level difference between the donors and Y6 is too small, which is unfavorable for efficient excitons’ dissociation.

The normalized absorption spectrum of donors and acceptors in dilute chloroform solution and thin films is shown in Figure 2a and Figure S2, Supporting Information, which reveal the maximum absorption peak near 523 nm, and the absorption edge is at 608 nm for all donors in the solution form, whereas an absorption edge at around 669 nm, indicating a red shift of about 146 nm, has been observed for the thin films. Furthermore, ZR-Si4 revealed a more ordered structure and stronger $\pi-\pi$ stacking, as evident from the change in the absorption peak at 602 nm, which is beneficial for hole mobility and thus, the photovoltaic performance. The presence of the strong shoulder peaks of ZR-Si3 and ZR-Si4 may be due to the introduction of Cl atoms, which can enhance the intermolecular interaction.

Conventional devices with an ITO/PEDOT:PSS/active layer/ PDINO/Al architecture were fabricated to investigate the photovoltaic performance of two SMDs with IDIC-4Cl and Y6, respectively. An optimized donor: acceptor weight ratio of 1:0.7 has been used for IDIC–4Cl, with a total concentration of 17 mg ml$^{-1}$ in chloroform solution to form the active layers. For Y6-based devices, the optimized donor: acceptor weight ratio and total concentration are 1:0.5 and 15 mg ml$^{-1}$ (as shown in Table S1–S4, Supporting Information). Furthermore, thermal annealing treatment was used to improve the morphology of active layers at 120 °C for 10 min. Figure 2b shows the current density–voltage ($J–V$) curves tested under the illumination of AM1.5 G, 100 mW cm$^{-2}$, whereas the optimized device performance and
the corresponding parameters are shown in Table 1. Eventually, the PCE of ZR-Si3: IDIC-4Cl blends was 8.12% with a $V_{OC}$ of 0.82 V, $J_{SC}$ of 16.01 mA cm$^{-2}$, and FF of 61.66%, respectively. The devices based on ZR-Si4:IDIC-4Cl blends achieved the best PCE of 10.10%, with a $V_{OC}$ of 0.89 V, $J_{SC}$ of 16.40 mA cm$^{-2}$, and FF of 68.93%, indicating that the change of side chain plays a crucial role in regulating photovoltaic characteristics. However, the PCE of the devices is quite low after the two donors blended with Y6, showing relatively poor FF and $J_{SC}$. Similarly, the external quantum efficiency (EQE) curves of all the devices are shown in Figure 2c. Obviously, the EQE curve for ZR-Si4:IDIC-4Cl blends exhibited significantly improved EQE from 300 to 720 nm; as a result, the highest $J_{SC}$ has been calculated from the corresponding EQE curves. The corresponding $J_{SC}$ values calculated from the EQE curves turned out to be 16.59, 17.15, and 16.01 mA cm$^{-2}$ for ZR-Si3: IDIC-4Cl, ZR-Si4:IDIC-4Cl, ZR-Si3:Y6, and ZR-Si4:Y6-based devices, respectively. Consequently, all the $J_{SC}$ values calculated by the EQE curves were in good agreement with the $J_{SC}$ values obtained by the $J-V$ test. The inferior EQE of Y6-based systems could be due to the small HOMO energy-level difference between the donors and Y6.

Accordingly, the space–charge-limited-current (SCLC) method has been used to measure the corresponding hole and electron mobility, using an ITO/PEDOT:PSS/active layer/MnO$_2$/Ag and ITO/ZnO/active layer/Al architecture respectively. As a result, the corresponding hole mobility of ZR-Si3: IDIC-4Cl and ZR-Si4:IDIC-4Cl blends came out to be $2.05 \times 10^{-3}$ and $3.96 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, whereas the electron mobility turned out to be $3.17 \times 10^{-4}$ and $6.74 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. For ZR-Si3:Y6- and ZR-Si4:Y6-based devices, the corresponding hole mobility and electron mobility turned out to be $6.73 \times 10^{-3}$, $2.33 \times 10^{-3}$, $3.25 \times 10^{-3}$, and $4.53 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively.

To obtain an in-depth insight into the relationship of the charge transport and corresponding stacking tendencies, the diffusion method has been used to cultivate the single crystals of ZR-Si3, ZR-Si4 donors, IDIC-4Cl, and Y6 acceptors, which have been effectively characterized by single-crystal diffraction. Figure 3a, therefore, shows the intermolecular interactions and packing motif of ZR-Si3 donor, which revealed a triclinic unit cell with corresponding parameters as $a = 11.51 \text{Å}$, $b = 13.78 \text{Å}$, $c = 16.29 \text{Å}$, $\alpha = 82.40^\circ$, $\beta = 80.08^\circ$, and $\gamma = 85.95^\circ$. The backbone of the molecule likewise revealed a good coplanar structure, as well as an alkylsilyl-influenced large steric hindrance. However, no obvious overlap of the central DTBDT core was observed as it revealed a large accumulation distance of 4.01 Å is thus attained. It can be seen from the side view of the molecular conformation that the alkylsilyl side chain and the octane side chain are located on both sides of the molecular skeleton, which makes it difficult to stack the DTBDT core between adjacent molecules. Furthermore, short contact has been observed from the accumulation of the crystal structure between the molecular end groups of adjacent transport layers with a distance of 3.38 Å, indicating the system to exhibit appropriate intermolecular $\pi-\pi$ interaction, beneficial for effective hole transportation. For the ZR-Si4 crystal structure (Figure 3b), again, a triclinic unit cell with corresponding parameters as $a = 8.45 \text{Å}$, $b = 15.65 \text{Å}$, $c = 20.21 \text{Å}$, $\alpha = 78.78^\circ$, $\beta = 84.22^\circ$, and $\gamma = 76.38^\circ$ have been obtained. Interestingly, from the side view of the molecular conformation, the alkylsilyl side chain and the octyl side chain are located on the same side of the molecular skeleton, and a $\pi-\pi$ stacking distance of 4.10 Å has been observed between the DTBDT cores. Furthermore, a slightly twisted backbone with about a 13.31° torsion angle between the two $\pi$-bridge thiophene rings has been observed.

### Table 1. Photovoltaic performance of devices.

| D:A          | $V_{OC}$ [V] | $J_{SC}$ [mA cm$^{-2}$] | FF [%] | PCE [%] | $\mu_h$ [cm$^2$ V$^{-1}$ s$^{-1}$] | $\mu_e$ [cm$^2$ V$^{-1}$ s$^{-1}$] |
|--------------|-------------|-------------------------|--------|---------|----------------------------------|----------------------------------|
| ZR-Si3:Y6   | 0.91        | 14.27                   | 53.19  | 6.96    | $6.73 \times 10^{-3}$            | $3.25 \times 10^{-3}$            |
| ZR-Si4:Y6   | 0.91        | 12.08                   | 51.99  | 5.74    | $2.33 \times 10^{-3}$            | $4.53 \times 10^{-3}$            |
| ZR-Si3:IDIC-4Cl | 0.82     | 16.01                   | 61.66  | 8.12    | $2.05 \times 10^{-3}$            | $3.17 \times 10^{-4}$            |
| ZR-Si4:IDIC-4Cl | 0.89     | 16.40                   | 68.93  | 10.10   | $3.96 \times 10^{-3}$            | $6.74 \times 10^{-4}$            |

![Figure 2](image-url) a) UV absorption spectra of donor and acceptor thin films. b) $J-V$ curves and c) EQE spectra of devices.
in the crystal. Hence, this slight twist allowed the distance between the π-bridge thiophene and the DTBDT core to be shortened to 3.43 Å, which effectively improved the intermolecular hole transport capability. More interestingly, the same short contact with a distance of 3.18 Å exists between the π-bridge thiophene of the adjacent molecules, which indicated the possibility of hole transportation between different layers. Thus, in terms of the molecular interactions at the atomic level, the ZR-Si4 has better charge transport ability than ZR-Si3. It is in accordance with the results based on IDIC-4Cl systems. However, the hole mobility of ZR-Si4:Y6 is lower than that of ZR-Si3:Y6. It must be pointed out that the comparison with two IDIC-4Cl systems is reasonable due to similar morphology (discussed in the following section).

In the crystal structure of IDIC-4Cl (Figure 3c), the molecules revealed a monoclinic unit cell with corresponding parameters as \( a = 10.30 \text{ Å}, b = 20.71 \text{ Å}, c = 32.24 \text{ Å}, \alpha = 90^\circ, \beta = 96.33^\circ, \text{and } \gamma = 90^\circ \). From the top and side view of the molecular structure, IDIC-4Cl molecule possess an S-shaped conformation and the octyl side chain stretches out from the conjugated molecular skeleton. In addition, the adjacent molecules are closely packed through the overlap between the end groups, with a distance of 3.44 Å. Due to the orientation of the alkyl chain, the distance between adjacent transmission layers is relatively large, reaching a distance of 6.21 Å, which makes the transmission channels in the crystal limited. For Y6, a triclinic unit cell with corresponding parameters as \( a = 14.53 \text{ Å}, b = 19.80 \text{ Å}, c = 28.53 \text{ Å}, \alpha = 95.14^\circ, \beta = 101.46^\circ, \text{and } \gamma = 107.36^\circ \) have been obtained, similar to the previously reported continuous and regular 3D crystal structure.\(^{[37]}\) In the cell of Y6, there are two conformations of molecules, and the unique molecular conformation makes the stacking of Y6 molecules exceptionally unique. In the crystal, not only the π–π interaction between the end groups with distances of 3.36, 3.43, and 3.57 Å, but also the overlapping between the cores with a distance of 3.42 Å occur; such abundant accumulation pairs could form 3D charge transport channels. Thus, for the acceptors, Y6 has better charge transport ability than IDIC-4Cl.

To further study the relationship between structure and performance, we are concerned about whether or not the donors and acceptors in the active layer have similar stacking structures to that in the single crystal. GIWAXS was used to investigate the stacking behavior of the molecules in thin films. As shown in Figure 4a, ZR-Si3 donor showed good crystallinity as strong first-, second-, and third-order diffraction peaks in the out-of-plane (OOP) direction have been observed, located at 0.33, 0.67, and 0.98 Å\(^{-1}\), indicating the corresponding stacking distances to be 19.04, 9.38, and 6.41 Å, and the distance is consistent with the distance 19.18 Å obtained from the crystal structure shown in Figure S3, Supporting Information. In the in-plane (IP) direction, the diffraction peak at 0.79 Å\(^{-1}\) \( (d = 7.95 \text{ Å}) \) can be attributed to the (111) crystal plane \( (d_{111} = 8.60 \text{ Å}) \).
Furthermore, another diffraction peak at 1.68 Å (d = 3.74 Å) in the IP direction is generally attributed to the π–π stacking peak, which is close to the packing distance of the molecular skeleton (d = 4.01 Å) in the single crystal. For ZR-Si4, in Figure 4b, the diffraction peaks at 0.35, 0.71, and 1.05 Å, corresponding to the (001), (002), and (003) planes. The 0.49 Å−1 diffraction peak (d = 12.82 Å) in the IP direction corresponds to the (011) plane (d_{011} = 13.11 Å) in the crystal. Another two peaks at 1.58 Å−1 and 1.74 Å−1 with distances of 3.98 Å and 3.61 Å are similar to the π–π stacking distance in the single crystal. Moreover, from the GIWAXS image of Y6 (Figure 4c), it exists a visible π–π stacking peak at 1.74 Å−1 with a distance of 3.61 Å, corresponding to the π–π stacking distance in the crystal. In the IP direction, in addition to the strongest diffraction peaks at 0.28 Å−1 Y6 presented another peak at 0.23 Å−1, 0.34 Å−1, and 0.39 Å−1 which are similar to the (001), (010), and (01-1) plane distance (d_{001} = 27.61 Å, d_{010} = 18.66 Å, d_{01-1} = 16.75 Å). Furthermore, it has been reported that the peak at 0.42 Å−1 in the IP direction also belongs to the corresponding lamellar diffraction peak in the single crystal. As shown in Figure 4d, the strong lamellar stacking peak at 0.38 Å−1 in IDIC-4Cl scattering patterns in the IP direction correspond to a stacking distance of about 16.53 Å, which is similar to the corresponding value of the (011) plane (d_{011} = 17.39 Å) in the single crystal. From the peak at 1.82 Å−1 in the OOP direction, the distance is consistent with the end-group π–π stacking distance 3.44 Å measured from the crystal structure. As for the slight lack of coincidence between the plane distance of crystal and film, it is due to the difference in the driving force of accumulation during crystal growth and spin-coating process. However, the similar stacking distance can be reasonably inferred to the fact that the molecular packing structure of the film is generally consistent with the single crystal.

Figure 4. GIWAXS images of a–d) as-cast pure donors and acceptors and e–h) blend films’ thermal annealing at 120 °C. i–l) Corresponding line cuts of the GIWAXS images of pure donors and acceptors.
In the ZR-Si3: Y6 blend film (Figure S4, Supporting Information), the diffraction peaks located at 0.31 Å\(^{1}\), 0.98 Å\(^{1}\) in the OOP direction, and 0.32 Å\(^{1}\), 1.68 Å\(^{1}\) in the IP direction were from ZR-Si3 donor, and other peaks at 0.27, 0.29, 0.34, 1.73 Å\(^{1}\) in the OOP direction matched well with the scattering patterns of pure Y6. For ZR-Si4: Y6 blend film, similar to the result of the ZR-Si3: Y6 blend film, donor and acceptor maintained the same ordered packing structure to their pure films. What’s more, it is worth noting that the diffraction peaks of Y6 became more obvious and sharper, which may be due to the significant phase separation caused by poor compatibility between donors and Y6. From the GIWAXS images of ZR-Si3: IDIC-4Cl blends, it can be seen that upon IDIC-4Cl addition, the diffraction peaks in the OOP direction did not move obviously, compared with pure films. However, the diffraction peaks of ZR-Si4 significantly shifted from 0.35 to 0.31 Å\(^{1}\), 0.71 to 0.62 Å\(^{1}\), and 1.05 to 0.93 Å\(^{1}\), in the OOP direction before and after blending with IDIC-4Cl. Ultimately, the corresponding stacking distances of 20.26, 10.13, and 6.75 Å have been attained, which matched well with the values of the bulk crystal (\(d_{001} = 19.79\) Å, \(d_{002} = 9.89\) Å, \(d_{003} = 6.59\) Å), respectively. These mean that the donors and acceptors in the active layer have similar stacking structures to that in the crystal.

Similarly, the TEM and AFM measurements have been utilized to better understand the relationship between the structure and the performance of the involved species. As shown in Figure 5, large phase separation was observed in the active layer of Y6-based films, especially some large-sized rod-shaped structures in the film of ZR-Si4: Y6 system. The large phase-separation domains reduce the interfacial area between the donor and acceptor, resulting in low \(J_{SC}\). What’s more, the AFM images of ZR-Si4: Y6 systems confirmed the same structure in the active layer with a root-mean-square (RMS) roughness of 3.06 nm. Furthermore, an appropriate phase separation has been observed in the TEM images of IDIC-4Cl-based blend films. In contrast, the remaining two blend films revealed obvious fiber-like structures. Hence, the as-cast blend films based on ZR-Si3 and ZR-Si4 donors with IDIC-4Cl revealed relatively smooth surfaces with the RMS roughness values of 2.49 and 2.02 nm, respectively. As discussed previously, both ZR-Si3 and ZR-Si4 systems have similar morphology but different device performance. It means the molecular stacking plays the crucial role with the device performance.

3. Conclusion

In summary, two SMDs based on DTBDT units with alkylsilyl-thienyl-conjugated side chains have been synthesized, named as ZR-Si3 and ZR-Si4. Compared with ZR-Si3, the single-crystal analysis for ZR-Si4 donor showed that the \(\pi-\pi\) stacking distance has been reduced to 3.43 Å due to a slight twisting of the molecular skeleton, which enabled the charge transfer between different layers possible. Combining the analysis of single-crystal structures with GIWAXS results can scientifically infer the stacking motif of donors and acceptors in the active layers. As a consequence, although the two systems based on IDIC-4Cl have similar morphology, a PCE of 10.10% has been achieved for ZR-Si4, which is higher than that of ZR-Si3 (8.12%). Although Y6 shows 3D transport ability, the PCE is low due to low energy offset of the HOMO between the donors and Y6. Thus, the single-crystal results can aid in extracting important information for investigating the relationship between the structure and the performance of the involved systems, especially when the systems show similar morphology.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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Research data are not shared.

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