

Asymmetric Acceptors with Benzotriazine Central Core Achieving 19.63% Efficiency in Organic Solar Cells

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Decreasing the symmetry of acceptors can enhance the molecular dipole moment, influence intermolecular packing and has been proven to be an efficient strategy to improve device performance. This study presents a new asymmetric design strategy to develop acceptors beyond conventional end group or side chain engineering. Specifically, an asymmetric unit, 1,2,4-benzotriazine, is introduced as the central core in Y-series acceptors. Additionally, monophenyl with and without fluorine, are substituted on the asymmetric core. This combination yields two asymmetric acceptors, H-1 and H-2F, both of which exhibit large dipole moments and strong packing interactions. Consequently, organic solar cells (OSCs) based on D18:H-1 and D18:H-2F achieved a high power conversion efficiencies (PCEs) of 18.56% and 18.85%, respectively. By incorporating BO-4Cl into the D18:H-2F blend, the ternary device achieved a remarkable efficiency of 19.63% due to the extended absorption and improved morphology. This work establishes a new asymmetric and easily modifiable central unit, highlights the advantages of asymmetric acceptors, and demonstrates their potential in OSCs.

1. Introduction

Organic solar cells (OSCs) offer advantages such as lightweight, flexibility, solution processing manufacture,^[1] demonstrating significantly potential applications for wearable electronics, building integrated photovoltaics and etc.^[2] To date, OSCs have achieved power conversion efficiencies (PCEs) $\approx 20\%$,^[3] primarily attributed to the development of non-fullerene acceptors (NFAs), particularly, those NFAs featuring A-D-A architecture,^[4] like ITIC, Y6, and their derivatives.^[5] Among these, Y-series NFAs strike a balance between short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}), resulting in the best device performance reported to date.^[6] To further improve OSCs performance, it is still essential to design new active layer materials and subtly tune molecular electronic properties and aggregation.

In the past few years, various molecular design strategies have been proposed to further improve device efficiency.^[7] Among

these strategies, asymmetric molecule design has been proven to be a promising approach since asymmetric molecules can increase molecular dipoles, enhance intermolecular forces, regulate intermolecular interactions, and demonstrate significant potential to further improve device efficiencies.^[8] Among various asymmetric strategies for Y-series acceptors, most research focused on the asymmetry of end groups and alkyl chains,^[9] while less attention was paid to the asymmetry of central unit.^[10] In fact, the central unit has a significant impact on various properties of Y-series molecules, including absorption, energy levels, stacking, and other properties, as confirmed by recent work from our group and others.^[11] For instance, we have developed a series of acceptors with extended conjugated central cores, exhibiting strong intermolecular interactions and crystallinity, low reorganization energy, high carrier transport properties, and remarkable efficiencies.^[12] Given the advantages of asymmetric molecules and the critical role of the central unit in Y-series acceptors, it is essential to design acceptors with a focus on the central unit. With this in mind, in this study, we introduce 3-phenyl-1,2,4-benzotriazine as the central core, integrating an asymmetric 1,2,4-triazine unit into the molecular skeleton to create two novel asymmetric acceptors: H-1 and H-2F. H-1 uses a 3-phenyl-1,2,4-benzotriazine core, while H-2F adds fluorination to the

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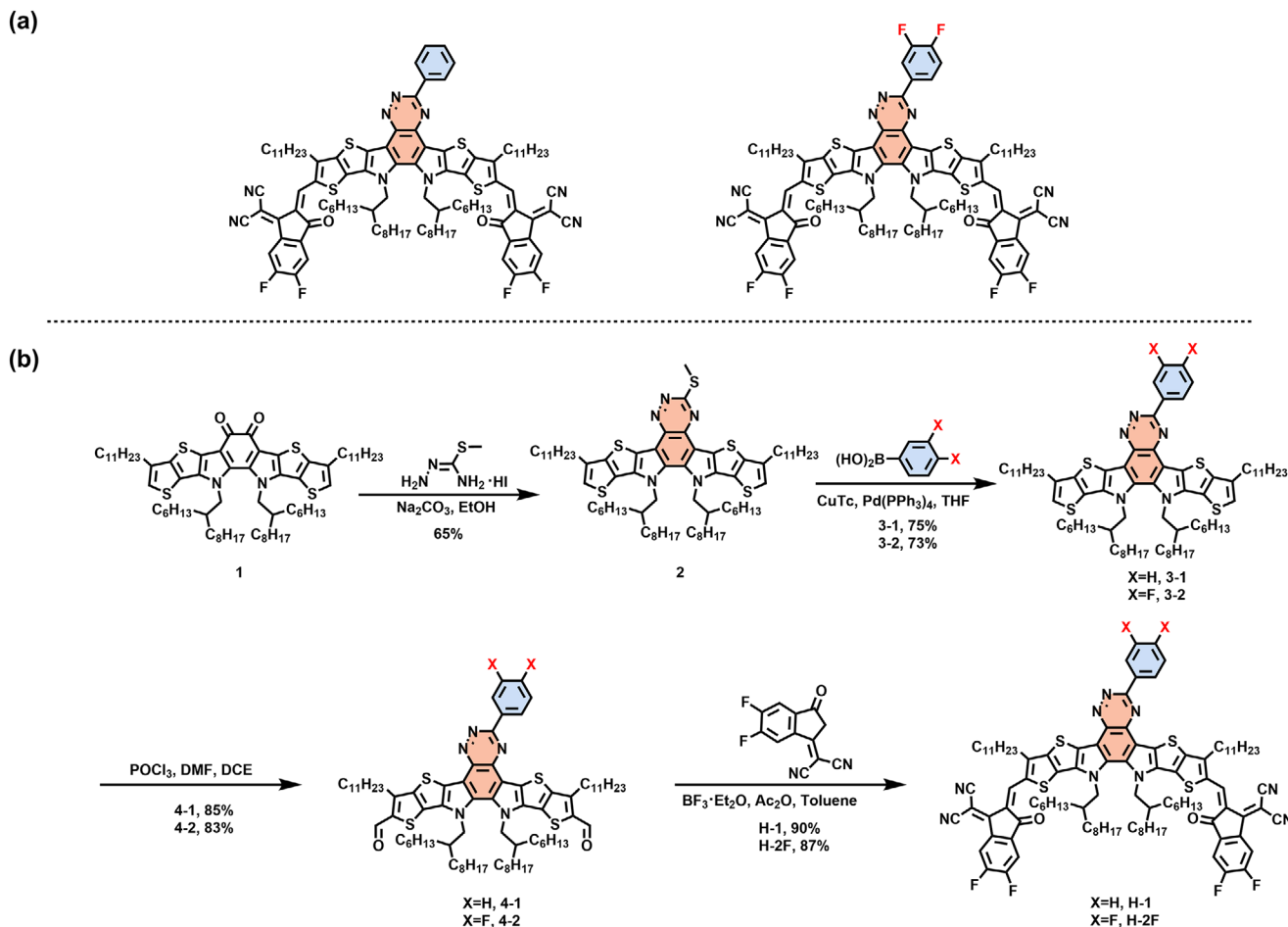


Figure 1. a) chemical structure of H-1 and H-2F. b) The synthetic routes of H-1 and H-2F.

phenyl group, further increasing asymmetry. OSCs based on D18: H-2F achieved a PCE of 18.85%, with a V_{oc} of 0.917 V, a J_{sc} of 26.16 mA cm^{-2} , and a fill factor (FF) of 78.6%. In comparison, D18:H-1 OSCs showed a slightly lower PCE of 18.56%, with a V_{oc} of 0.927 V, a J_{sc} of 25.76 mA cm^{-2} , and an FF of 77.8%. Moreover, by incorporating BO-4Cl, which has a redshifted absorption range compared to H-2F, into H-2F-based OSCs, the PCE was further boosted to 19.63%, with a J_{sc} increase from 26.16 to 27.96 mA cm^{-2} . Our work demonstrates the advantages of using an asymmetric central unit in molecular design, providing a feasible strategy for improving efficiencies in organic solar cells.

2. Results and Discussion

The molecular structures of H-1 and H-2F are shown in **Figure 1a**, and the detailed synthetic route to these two asymmetric molecules are displayed in **Figure 1b**. First, diketone compound 1 and S-Methylthiosemicarbazide hydrogen iodide undergo a condensation reaction to obtain compound 2. Then, compound 3 was synthesized from compound 2 through palladium-catalyzed 3-thiomethyltriazine-boronic acid coupling under mild conditions.^[13] It is worthy to note that other functional groups can be connected in this way on the 3-position of 1,2,4-benzotriazine. Subsequently, formylation and the Knoevenagel condensa-

tion reaction were conducted, yielding the two target molecules H-1 and H-2F.

The two asymmetric molecular geometries were first studied by density functional theory (DFT) calculations. As illustrated in **Figure S1** (Supporting Information), the two asymmetric molecules both displayed a planar geometry. Particularly, the benzene units linked on the central cores of H-1 and H-2F are nearly in the same plane with the triazine units, with the dihedral angles 1.54° and 1.50° , respectively, indicating that the grafted benzene units on the central 1,2,4-benzotriazine do not influence the overall molecular planarity. The electrostatic potential (ESP) distributions and dipoles of the two acceptors were calculated with density functional theory (DFT) at the B3LYP/6-31G(d,p) level. As shown in **Figure 2a** and **Figure S2** (Supporting Information), the ESP maps indicate that positive ESP values are distributed on the two molecular backbones. In particular, higher negative ESP values are observed not only on the cyano and carbonyl in the end groups, but also on the N = N in the triazine units. H-2F showed a slightly larger average ESP value of $5.28 \text{ Kcal mol}^{-1}$ compared to H-1 with value of $4.52 \text{ Kcal mol}^{-1}$ due to the additional F atoms on the grafted benzene on the central units of H-2F. Moreover, H-1 and H-2F exhibited large dipole moments with values of 2.06 and 4.80 Debye respectively, indicating that they can have a strong interaction with the donor.^[14]

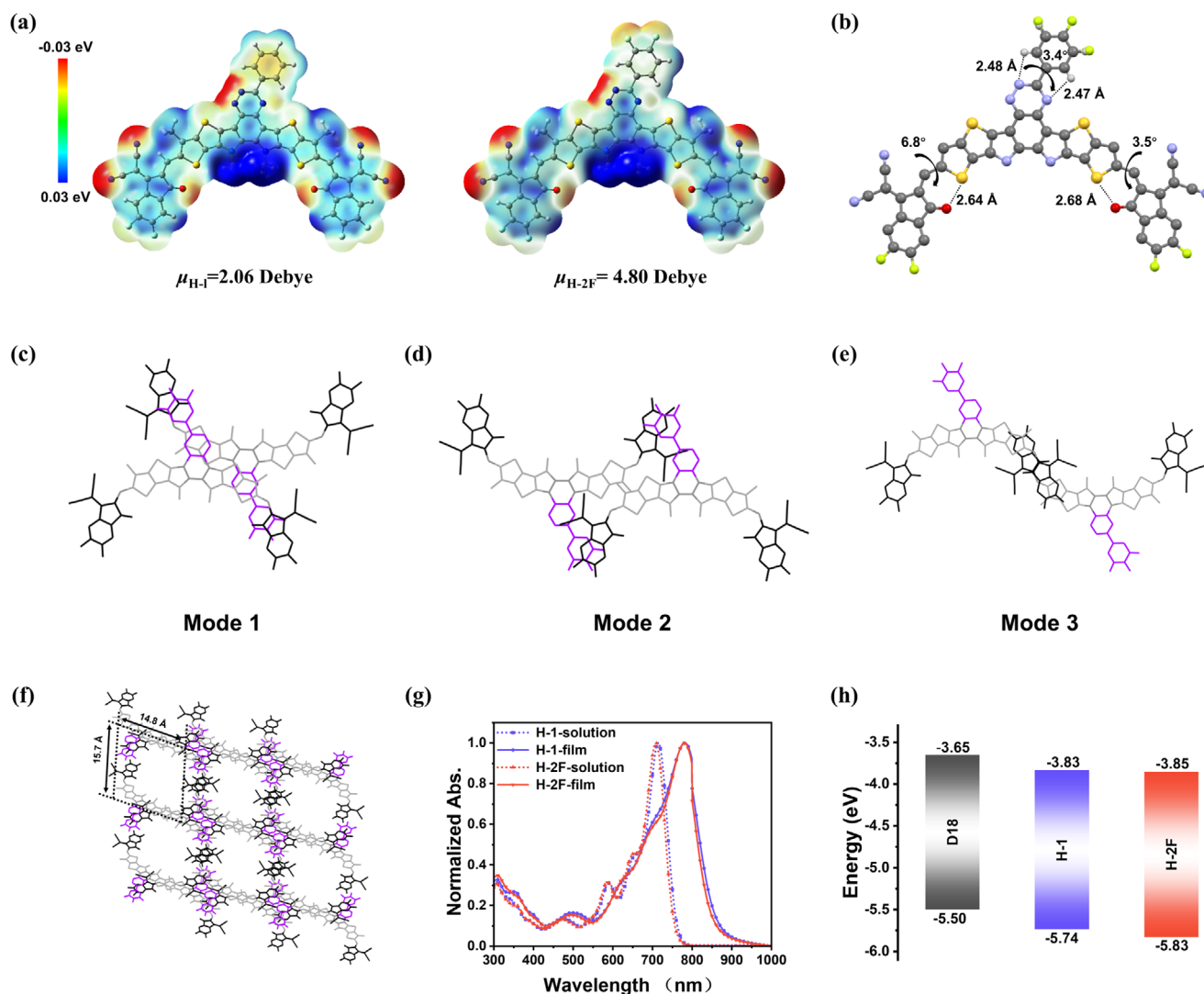


Figure 2. a) Electrostatic surface potential (ESP) maps with dipole moment values of H-1 and H-2F. b) Single crystal structure of H-2F. c–e) the three types of intermolecular packing modes in the single crystal of H-2F. f) Single-crystal packing topological structures of H-2F on the top view. g) Normalized absorption spectra. h) Energy level diagram of D18, H-1 and H-2F derived from CVs.

The single crystal of H-2F was obtained by diffusing methanol into the chloroform solution of H-2F. The related parameters of H-2F X-ray data is listed in Table S1 (Supporting Information). As depicted in Figure 2b and H-2F exhibits a planar-lock skeleton due to the strong intramolecular S...O interaction between the terminal thiophene of the molecular backbone and end group. Particularly, a strong intramolecular N...H interactions can be observed between phenyl and triazine units, resulting in the grafted benzene unit on the triazine core align nearly in the same plane with the adjacent pyrazine unit with the dihedral angles of 3.4°, indicating that the grafted benzene unit has no negative effect on the overall planarity of H-2F, which is consistent with the above calculation results. The stacking of H-2F can be observed in Figure 2c–e, three main packing modes can be found, including dual central unit to the thieno[3,2-b]thiophene unit mode (Mode 1), dual end group to central unit (Mode 2), and dual end group to the thieno[3,2-

b]thiophene unit mode (Mode 3), where the distances of three stacking modes are 3.41, 3.36, and 3.34 Å, respectively. The 3D packing network of H-2F could be found in Figure 2f, and the size of voids for H-2F is $\approx 14.8 \times 15.7$ Å. The crystal analysis results demonstrate that H-2F with the asymmetric central core and grafted benzene unit can preserve the planar skeleton and form intense intermolecular interaction with 3D packing network, facilitating the charge transport same to those symmetric acceptors.^[15]

The two molecules demonstrate high thermal stability, with a decomposition temperature (T_d) of 307 and 322 °C, respectively (Figure S3a, Supporting Information). The H-1 and H-2F exhibit exothermal peaks at 287 and 285 °C, respectively, corresponding to a melting enthalpy (ΔH_m) of 22.98 for H-1, and 24.57 J g⁻¹ for H-2F. The larger ΔH_m of H-2F than that of H-1 suggests its stronger molecular interactions (Figure S3b, Supporting Information). The UV/vis absorption spectra of H-1 and H-2F in dilute

Table 1. Photovoltaic parameters of the optimized devices.

Active layer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	J_{sc}^a [mA cm^{-2}]	FF [%]	PCE b) [%]
D18:H-1	0.927 (0.921 ± 0.004)	25.76 (25.99 ± 0.26)	24.65	77.79 (76.36 ± 0.98)	18.56 (18.27 ± 0.15)
D18:H-2F	0.917 (0.911 ± 0.004)	26.16 (26.21 ± 0.18)	25.34	78.63 (77.95 ± 0.33)	18.85 (18.62 ± 0.16)
D18:H-2F:BO-4Cl (1:1:0.4)	0.899 (0.898 ± 0.005)	27.96 (27.78 ± 0.18)	26.65	78.12 (77.34 ± 0.35)	19.63 (19.27 ± 0.19)

^a) Current densities by integrating EQE plots; ^b) Average parameters derived from 15 independent OSCs.

chloroform solution and film states are depicted in Figure 2g. In CF solution, H-1 and H-2F exhibited maximum absorption (λ_{max}) peaks at 715 and 708 nm, respectively. In film states, their absorptions were all red-shifted with λ_{max} peaks at 781 and 779 nm, respectively. Compared to H-1, the slight, blue-shifted absorptions of H-2F are caused by the stronger electron withdrawing effect of the two F substituted phenyl, which will slightly decrease the overall donor ability of the central units and thus reduce the intramolecular charge transfer effects between the end groups and central units. These phenomena have also been found in other central unit modified Y-series acceptors.^[16] The energy levels of H-1 and H-2F were estimated using electrochemical cyclic voltammetry (CV). From the Figure 2h and Figure S4 (Supporting Information), the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels of H-1 and H-2F were estimated to be $-3.83/-5.74$, and $-3.85/-5.83$ eV, respectively, which approximately con-

sistent with the calculated results (Figure S5, Supporting Information).

The intermolecular packing morphology and crystallinity of the H-1 and H-2F neat films were studied using grazing incidence wide-angle X-ray scattering (GIWAXS). As shown in Figure S6 and Table S3 (Supporting Information), all neat films exhibits strong π - π stacking (010) diffraction peaks in the out-of-plane (OOP) and have same d-spacing in the OOP direction. The results indicate that they all have ordered molecular packing. It is worth noting that H-2F has larger coherence length (CCL) in the OOP direction which proved that H-2F has stronger crystallinity.

OSCs with a conventional device structure of ITO/2PACz/BHJ layer/PNDIT-F3N/Ag were fabricated to investigate the photovoltaic properties of the two acceptors. Polymeric donor D18 with matched energy levels was chosen to blend with H-1 and H-2F.^[17] The relevant photovoltaic parameters and the best current density-voltage ($J-V$) curves were shown in Table 1 and Figure 3a.

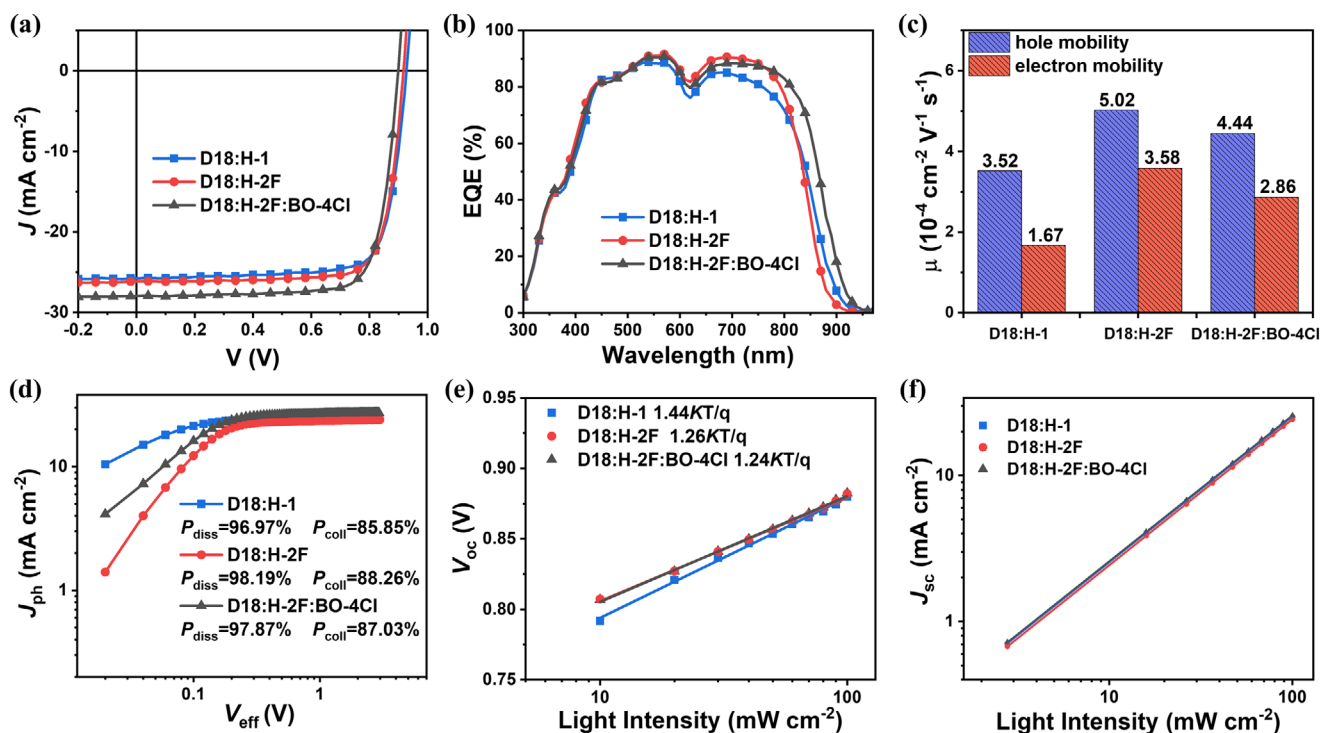


Figure 3. a) $J-V$ curves for OSCs. b) EQE plots and integrated J_{sc} curves. c) Histograms of the hole and electron mobility of blended films. d) J_{ph} versus V_{eff} curves indicating P_{diss} and P_{coll} . e) Light intensity (P_{light}) dependence of V_{oc} . f) Dependence of current density (J_{sc}) on light of optimized OSCs.

The H-1-based OSCs exhibited a high PCE of 18.56%, with a V_{oc} of 0.927 V, a J_{sc} of 25.76 mA cm⁻², and an FF of 77.79%. A better PCE of 18.85% was achieved for D18:H-2F based devices, along with a V_{oc} of 0.917 V, a J_{sc} of 26.16 mA cm⁻², and an impressed FF of 78.63%. Moreover, after adding BO-4Cl (the HOMO is -5.66 eV and the LUMO is -4.09 eV) with a redshifted absorption range into D18:H-2F system, the ternary device demonstrated a PCE of 19.63%, with an increase in J_{sc} from 26.16 to 27.96 mA cm⁻². The structure of BO-4Cl shown in Figure S7 (Supporting Information). The external quantum efficiencies (EQEs) were measured and displayed in Figure 3b. The integrated J_{sc} of H-1-, H-2F-, H-2F:BO-4Cl-based OSCs are 24.65, 25.34, and 26.65 mA cm⁻², respectively, aligning well with those measured in the J - V curves.

To reveal the reasons for the performance differences among the three OSCs, some measurements about the charge generation, transport and recombination have been conducted. First, as shown in Figure 3c and Figure S8 (Supporting Information), the hole only mobility and electron-only mobility were measured to be $3.52 \times 10^{-4}/1.67 \times 10^{-4}$, $5.02 \times 10^{-4}/3.58 \times 10^{-4}$, and $4.44 \times 10^{-4}/2.86 \times 10^{-4}$ cm² V⁻¹ s⁻¹ for D18:H-1, D18:H-2F, and D18:H-2F:BO-4Cl blend films, respectively. Among them, D18:H-2F showed increased and more balanced μ_e/μ_h , which is consistent with its higher J_{sc} and FF compared to D18:H-1. However, after incorporating BO-4Cl into the D18:H-2F blend, the μ_e , μ_h and μ_e/μ_h exhibited a little decrease, which should be aroused by the reduced crystallinity in the ternary system (as discussed below). Subsequently, the exciton dissociation efficiency (P_{diss}) and charge collection efficiency (P_{coll}) were further evaluated by plots of photocurrent density (J_{ph}) versus effective voltage (V_{eff}) (Figure 3d). The slight improvement of P_{diss} and P_{coll} can be observed, which varied from 96.97% and 85.85% for D18:H-1 based devices to 98.19% and 88.26% for D18:H-2F based devices respectively, indicating D18:H-2F-based OSCs possesses more efficient exciton dissociation and charge extraction properties, which contribute to the high J_{sc} and FF of the H-2F based device. Similar to the mobilities values, D18:H-2F:BO-4Cl showed a slight decrease in P_{diss} and P_{coll} compared to D18:H-2F. The results are the main reasons for the slight decrease in FF of the ternary system. In addition, the dependence of V_{oc} and J_{sc} on light intensity was determined and depicted in Figure 3e,f. The value of $S/(kT/q)$ for D18: H-1-, D18:H-2F-, D18:H-2F:BO-4Cl-based OSCs were provided as 1.44, 1.26 and 1.24, respectively, implying gradually suppressed trap-assisted charge recombination.^[18] Furthermore, the very similar and close to 1 of α values were observed for all three OSCs, indicating the few bimolecular recombination.^[19] Then, a detailed energy loss (E_{loss}) analysis was conducted following the established method and the results are summarized in Table S4 (Supporting Information). The overall E_{loss} are 0.531, 0.556, 0.525 eV, respectively. Particularly, nonradiative recombination energy loss (ΔE_{nr}) values were calculated to be 0.221, 0.244 and 0.202 eV for D18:H-1, D18:H-2F and D18:H-2F:BO-4Cl, respectively. This shows that the introduction of BO-4Cl can significantly reduce ΔE_{nr} . Besides, as shown in Figures S11 and S12 (Supporting Information), the Stokes shift values of H-1 and H-2F neat film are 193 and 196 nm, respectively, and the Urbach energy are 20.6 meV for D18:H-1 and 22.16 meV for D18:H-2F. This results are consistent with the above E_{loss} results.

To investigate the influence of morphology on the performance of the three OSCs, GIWAXS measurements were

performed to reveal the molecular packing and orientations (Figure 4a). All the blended films showed an evident (010) diffraction peak in OOP directions, and a (100) diffraction peak in in-plane (IP) direction. As displayed in Figure S13 and Table S5 (Supporting Information), the (010) diffraction peak in OOP direction for D18:H-2F blend locates at 1.73 Å⁻¹ with a smaller π - π packing distance of 3.63 Å compared to that of 3.67 Å with a diffraction peak of 1.71 Å⁻¹ for D18:H-1 blend. Meanwhile, the enlarged CCL of 33.26 Å for D18:H-2F with respect to that of 25.70 Å for D18:H-1, suggested more ordered molecular packings and stronger crystallinity for D18:H-2F blend. Besides, the D18:H-2F:BO-4Cl blend exhibited a slightly larger π - π packing distance and a relatively smaller CCL than that of D18:H-2F, indicating a weaker crystallinity of the ternary system.

To reveal the interaction between donor and acceptor of the three systems, we simulated the packing arrangements of the two acceptors using a molecular dynamics (MD) approach. The interaction energy between donor and acceptor were listed in Table S6 (Supporting Information). The electrostatic and van der Waals interactions between D18 and H-2F have increased compared to those between D18 and H-1, perhaps mainly due to the enlargement of the dipole moment of H-2F. Meanwhile, the total interaction of the ternary system is further increased compared to the interaction between D18 and H-2F. The gradually increasing total interaction is conducive to causing tighter stacking between the donor and acceptor. Afterwards, the packing between donor and acceptor was simulated (Figure 4b; Figure S14, Supporting Information), the acceptors are divided into three segments, labeled A, D, and A', while D18 is divided into two segments, labeled C and E, resulting in six possible packing configurations (Table S7, Supporting Information). As summarized in Table S7 (Supporting Information), the total stacking count per unit volume for H-2F is 112.27, higher than the 91.98 count for H-1. The increased stacking count of H-2F with D18 enhances their interaction, promotes appropriate phase separation, thus facilitates charge generation and transfer. Furthermore, the stacking count for the D18:H-2F:BO-4Cl system is significantly higher than that for D18:H-2F, which may be the reason for the slight decrease in crystallinity of the ternary system, and suggesting the potential for improved morphology that contributes to achieving a higher PCE.

The nanoscale morphology was investigated by atomic force microscopy (AFM) (Figure 4d; Figures S15–S17, Supporting Information). All three blend films had the relatively smooth surface, and the root-mean square (RMS) roughness of 1.07 nm for D18:H-2F blend film increased compared to 0.91 nm for D18:H-1 blend film, probably due to its strong crystallinity. Additionally, the D18:H-2F:BO-4Cl blend achieved a smoother surface with a reduced RMS of 1.03 nm, due to the stronger interaction between donor and acceptors. Meanwhile, the fiber sizes of D18:H-1, D18:H-2F and D18:H-2F:BO-4Cl blend films, are 12.4, 15.0 and 13.5 nm, respectively, which are consistent with their RMS roughness. Afterwards, AFM-IR was used to further characterize these results, as shown in Figure 4c (blue and red represent donors and acceptors). All three blends exhibited continuous phase separation, D18:H-1 blend showing more pronounced acceptor aggregation compared to D18:H-2F blend, which is consistent with the result of MD approach. This also proves that H-2F has a stronger intermolecular interaction with D18 compared

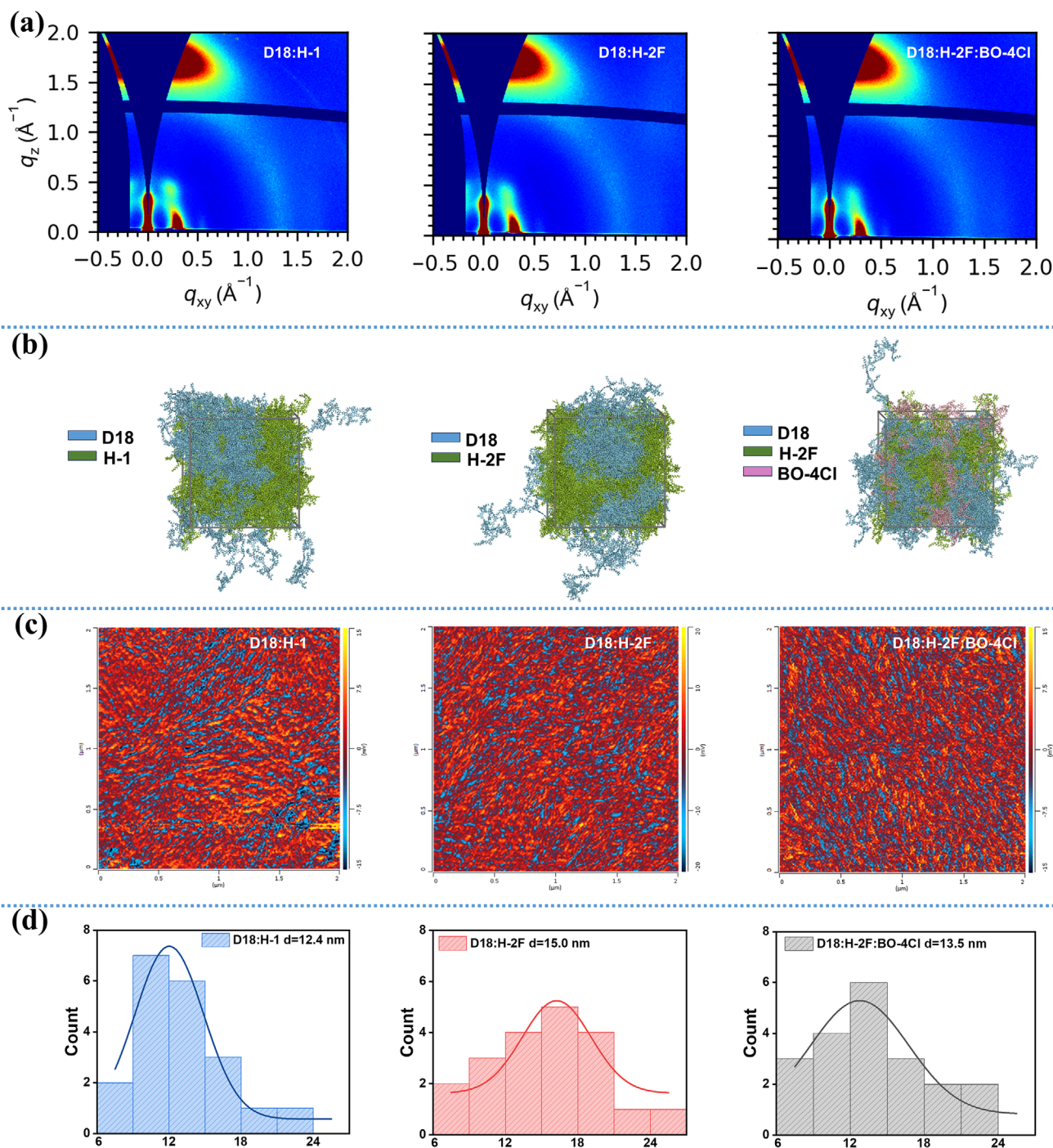


Figure 4. a) 2D GIWAXS patterns of D18:H-1, D18:H-2F, D18:H-2F:BO-4Cl blend films. b) MD simulation of the blend film situation of D18:H-1, D18:H-2F and D18:H-2F:BO-4Cl. c) AFM-IR images of D18:H-1, D18:H-2F, D18:H-2F:BO-4Cl blend films. d) Statistical distribution of fibril diameters.

with the molecular interaction between D18 and H-1. Besides, due to the reduced crystallinity and enhanced interactions between donor and acceptor, D18:H-2F:BO-4Cl blend improved the aggregation of acceptors, forming appropriate phase separation and more donor-acceptor interfaces, which is conducive to the exciton dissociation and charge transfer, and achieving a higher PCE.

3. Conclusion

In this work, we designed two acceptors, H-1 and H-2F, incorporating an asymmetric 1,2,4-benzotriazine central core. The asymmetry in these structures results in large dipole moments, enhancing intermolecular interactions and facilitating charge transport. The crystal analysis results demonstrate that H-2F has a

planar skeleton, strong intermolecular interaction with a 3D packing structure, facilitating the charge transport same to those symmetric acceptors. Binary OSC devices based on H-1 and H-2F with D18 as the donor were fabricated. The H-2F-based device demonstrated a PCE of 18.85%, higher than that of the H-1-based device, due to its more efficient charge transport and suppressed charge recombination, which primarily result from the larger dipole moment and stronger intermolecular interactions. Additionally, by incorporating BO-4Cl with a redshifted absorption into the H-2F-based OSC, the ternary device achieved a high PCE of 19.63%, attributed to an improved active layer morphology and enhanced J_{sc} . Our work highlights the impact of molecular asymmetry on OSC performance and provides a straightforward approach for synthesizing asymmetric acceptors featuring the 1,2,4- benzotriazine unit.

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.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

asymmetric structure, electron acceptor, organic photovoltaics

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