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Central unit hetero-di-halogenation of acceptors enables organic solar cells with 19% efficiency*

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Although peripheral hetero-di-halogenation of non-fullerene acceptors (NFAs) would allow more precise optimization of molecular properties by providing the complementary advantages of two different halogens, thus enabling further improvements of organic solar cells (OSCs), heterodi-halogenated NFAs are seldom prepared due to the challenging construction of building blocks with two adjacent hetero-halogens. Herein, three CH-series acceptors with hetero-di-halogenated central units, named CH-FC, CH-FB and CH-CB, are constructed successfully. PM6:D18:CH-FB-based OSCs afforded an attractive PCE of 19.0% due to tighter intermolecular packing at both the single-crystal and blendedfilm levels, more efficient charge transfer/dissociation, and superior film morphology compared to those of PM6:D18:CH-FC (PCE 18.41%) and PM6:D18:CH-CB (PCE 18.21%). Our work highlights the effectiveness of such a CH-series molecular platform in conducting heterodi-halogenation and achieving high-performance OSCs, and will stimulate further exploration of hetero-substitution-based acceptors.

Considering the continuously increasing power conversion efficiencies (PCEs) of organic solar cells $(OSCs)^{1,2}$ and their intrinsic merits, including tunable flexibility and transparency, low cost, and solution processability, the status of OSCs as a significant solar energy conversion technology is drastically growing.³ Every upgrade of OSCs should lead to an improvement in balancing the three pivotal parameters, namely short-circuit current density (I_{SC}), open-circuit voltage (V_{OC}), and fill

factor (FF), through increased charge transfer/transport and suppressed charge recombination.^{4–6} One of the crucial reasons is the extensive development of novel active layer materials, especially non-fullerene acceptors (NFAs), which have afforded attractive PCEs of over 19% in OSCs.³

A dramatic improvement could be achieved for OSCs based on halogenated NFAs, although with minor changes in molecular structure.⁷ The great effectiveness of halogenation in upgrading OSCs could come down to the relatively high electronegativity of halogen atoms and simultaneously small steric hindrance, which would bring the following effects: (1) tuning of the photophysical properties and donor-acceptor features of light-harvesting molecules;⁸ (2) enhancement of the molecular packing and improvement of the morphology.⁹ As a result, facilitated exciton dissociation and charge transport, and suppressed charge recombination in corresponding blend films can be achieved, providing higher PCEs of OSCs when all the above factors are taken into consideration.^{10,11}

Fluorination is the most extensively studied among all halogenations.7 OSCs based on NFAs with fluorination on the peripheral units, such as typical NFAs like ITIC,¹² F,¹³ and Y6-series analogs,^{14,15} mostly display improved photovoltaic performance. The main reason is that the above-mentioned effects can be fully reflected in fluorinated NFAs.¹⁶ Compared to fluorination, chlorination of NFAs¹⁷ can provide various features, such as improved optical absorption coefficient/range, and enhanced crystallinity caused by the atomic differences between fluorine and chlorine atoms.18 Furthermore, although brominated NFAs are seldom explored in OSCs due to their challenging construction, the increased polarizability of the bromine atom could enhance their σ-hole interactions significantly, thus enhancing intermolecular interactions and crystallinity.¹⁹ However, most studies on halogenation of NFAs only focus on a single type of halogenated peripheral unit, which gives the limited merits of one type of halogenation.²⁰ Therefore, more combined advantages could be provided if two or more different halogenations are performed on one lightharvesting molecule, thus affording a further increase in the photovoltaic performance of OSCs immediately.21,22

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Fig. 1 (a) Chemical structures of the three acceptors. (b) Normalized absorption spectra of D18, PM6, CH-FC, CH-FB and CH-CB in films. (c) Energy level diagram.

Bearing the above considerations in mind, three CH-series acceptors with hetero-di-halogenation on the central unit, named CH-FC (fluorination and chlorination), CH-FB (fluorination and bromination) and CH-CB (chlorination and bromination) (Fig. 1a), were synthesized. Only one atomic alteration is found when any two of these acceptors are compared, allowing precise regulation at the level of individual atoms. Similar photophysical properties of the three hetero-di-halogenation acceptors could be observed, as predicted. Nevertheless, an attractive PCE of 18.97% based on CH-FB was afforded, attributed to the enhanced charge transfer/dissociation caused by enhanced intermolecular packing, which was observed at both the single-crystal and blended-film levels. Therefore, our work provides a significant platform for the construction of heterodi-halogenated materials to further upgrade OSCs.

The three hetero-di-halogenated molecules, CH-FC, CH-FB and CH-CB, were successfully synthesized in 82%, 86% and 82% yields, respectively (see ESI⁺). As displayed in Fig. S1 (ESI⁺), thermogravimetric analysis results show that the decomposition temperatures of CH-FC, CH-FB and CH-CB are all over 300 °C, indicating all three acceptors meet the needs of thermal stability for OSC fabrication. The photophysical properties of the three acceptors were investigated via UV-vis absorption spectroscopy. As presented in Fig. 1b and Fig. S2 (ESI⁺), the maximum absorption peaks (λ_{max}) of CH-FC, CH-FB and CH-CB are at 742, 742 and 740 nm, respectively, in diluted chloroform solutions, compared to 801, 801 and 804 nm in thin films, exhibiting an ~ 60 nm red-shift from solutions to thin films. The experimental HOMO and LUMO energy levels of the three acceptors were derived from cyclic voltammetry (CV) measurements. The upshifted LUMO for CH-CB, as displayed in Fig. 1c, is beneficial for a higher V_{OC}, which is consistent with the highest V_{OC} being obtained for the CH-CB-based device in comparison to CH-FC and CH-FB-based devices (vide infra).

Single crystals of the three acceptors were grown through solvent diffusion (see ESI[†]). The molecular torsion angles between the two planes formed from the two end units of CH-FC, CH-FB and CH-CB are 14.4, 13.4 and 14.5, respectively



Fig. 2 (a) Top and side-views of single-crystal structures of CH-FC, CH-FB and CH-CB, which have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with numbers 2291654, 2291653 and 2291652, respectively.† (b) Overview of single-crystal packing.

(Fig. 2a). Note that the smallest torsion angle for CH-FB would contribute to the tightest molecular packing. Furthermore, **CH-CB** possesses rectangle-shaped voids of $\sim 22.27 \times$ 15.47 Å, larger than those of $\sim 21.09 \times 15.16$ Å for CH-FC and $\sim 20.81 \times 15.08$ Å for CH-FB (Fig. 2b), probably because of the larger bromine atom on the central units. Note that the diverse intermolecular packing modes may cause significant variation in the molecular packing networks. CH-FC, CH-FB and CH-CB with different hetero-di-halogenated central units all possess three main packing modes, namely the "E/E" mode, "E/C" mode and "dual C/b" mode (Fig. 3a).⁹ The statistical results showed that CH-FB exhibits shorter average π - π distances in the E/E mode, E/C mode and dual C/b mode (3.392 Å, 3.337 Å and 3.369 Å) than those exhibited by CH-FC (3.398 Å, 3.338 Å and 3.372 Å) and CH-CB (3.397 Å, 3.338 Å and 3.368 Å) (Fig. 3b). Furthermore, the packing distance for the dual C/b and E/C modes is obviously smaller than that for E/E mode, in which only the end units participate. This phenomenon again demonstrates the importance of the central unit's involvement in stacking for CH-series acceptors. The shortest π - π distance of the three modes for **CH-FB** and the tightest molecular packing in CH-FB are conducive to more efficient



Fig. 3 (a) Molecular packing modes in single-crystal states. (b) Statistical distributions of π - π interlayer distances between acceptor molecular layers.



Fig. 4 (a) Device architecture of the OSCs. (b) J-V curves of OSCs. (c) EQE plots of OSCs. (d) Hole and electron mobilities according to space-charge-limited current (SCLC) measurements.

charge separation and transport properties in multiple directions in thin films.

To investigate the photovoltaic properties, a conventional device architecture with PM6 as a donor was fabricated (Fig. 4a). The OSC employing PM6:CH-CB achieved the lowest PCE of 17.93% with a $V_{\rm OC}$ of 0.897 V, a $J_{\rm SC}$ of 25.78 mA cm⁻² and an FF of 77.56%. PM6:CH-FC reached a PCE of 18.10% with a $V_{\rm OC}$ of 0.886 V, a $J_{\rm SC}$ of 26.31 mA cm⁻² and an FF of 77.66% (see Table 1). Notably, the PM6:CH-FB based OSC rendered the highest PCE of 18.26% among the three acceptors, with a $V_{\rm OC}$ of 0.889 V, a J_{SC} of 26.38 mA cm⁻² and an FF of 77.86%. When matched with D18 as a donor (Table S1, ESI[†]), the D18:CH-FBbased OSC achieved the highest efficiency of 18.33% compared to those of D18:CH-FC (18.12%) and D18:CH-CB (17.99%). In order to improve the crystallinity and optimize the morphology of the blended films for further enhancing the efficiency, D18 was further screened as the third component in fabricating ternary devices. As expected, the PM6:D18:CH-FB-based device obtained a champion PCE of 18.97% with a J_{SC} of 26.69 mA cm⁻², a V_{OC} of 0.888 V, and an impressive FF of 80.03% among the three acceptor-based devices (Fig. 4b and Table 1; the detailed optimization processes are listed in Tables S2-S5, ESI[†]). For the PM6:D18:CH-FC ternary OSC, a PCE of 18.41% with a $V_{\rm OC}$ of 0.885 V, a $J_{\rm SC}$ of 26.51 mA cm⁻² and an FF of 78.46% are delivered. Due to the loose molecular packing of **CH-CB**, with large steric hindrance from chlorine and bromine, the device based on PM6:D18:**CH-CB** has a relatively poor PCE of 18.21% with a V_{OC} of 0.901 V, a J_{SC} of 26.22 mA cm⁻² and an FF of 77.07%. The integrated current densities derived from external quantum efficiency (EQE) spectra of **CH-FC**, **CH-FB** and **CH-CB**-based ternary devices are 25.84 mA cm⁻², 26.09 mA cm⁻² and 25.63 mA cm⁻², respectively (Fig. 4c), close to those derived from the J-V curves (within 3% error). Among the three photovoltaic parameters, the significantly improved FF of the **CH-FB**-based ternary OSCs drives an increase in efficiency, mainly determined by the superior charge transfer/ transport properties due to the more compact molecular packing of **CH-FB**.

As shown in Fig. 4d, the electron/hole mobilities (μ_e/μ_h) of the PM6:D18:CH-FC, PM6:D18:CH-FB and PM6:D18:CH-CB based devices can be calculated to be 5.24/3.10, 5.56/3.34 and 5.10/2.87 \times 10⁻⁴ cm² V⁻¹ s⁻¹, and the corresponding μ_e/μ_h ratios are 1.69, 1.66 and 1.78 respectively. Moreover, measurements under varying light intensity were performed to investigate the charge recombination. The slope of V_{OC} versus $\ln P_{light}$ values for the PM6:D18:CH-FC, PM6:D18:CH-FB and PM6:D18:CH-CB-based devices are 1.10, 1.07 and 1.13 kT/q (where k is Boltzmann's constant, T is absolute temperature and q is elementary charge), respectively, and the corresponding α values (where α is the exponential factor of the equation $J_{\rm SC} \propto P_{\rm light}^{\alpha}$ are 0.981, 0.989 and 0.985 (see Fig. S4 and S5, ESI[†]). This indicates that the charge recombination process was effectively suppressed in the CH-FB-based OSCs, which is consistent with the corresponding device performance.

As displayed in Fig. 5a, the values of the root-mean square (RMS) roughness of the CH-FC, CH-FB and CH-CB-based ternary films are 0.82, 0.89 and 0.90 nm, respectively, as observed using atomic force microscopy (AFM). The PM6:D18:CH-FB and PM6:D18:CH-CB blends present more clear fiber-like surface features than the PM6:D18:CH-FC blend, attributed to the enhanced molecular crystallinity induced by the bromine atom. The 2D grazing-incidence wide-angle X-ray (GIWAXS) images and corresponding in-plane (IP) and out-of-plane (OOP) extracted line-cut profiles of the three blended films are presented in Fig. 5b, and Fig. S6 and Table S6 (ESI[†]). The neat CH-FC, CH-FB and CH-CB films exhibit pronounced (010) diffraction peaks at *ca.* 1.74, 1.77 and 1.76 $Å^{-1}$ in the OOP direction with π - π stacking distances of *ca.* 3.62, 3.54 and 3.57 Å, respectively, and (100) diffraction peaks at ca. 0.28, 0.29 and 0.29 \AA^{-1} in the IP direction with π - π stacking

Table 1	Summary	of device	e parameters	for	optimized	OSCs
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Devices	$V_{ m OC}$ [V]	$J_{\rm SC} [{ m mA} { m cm}^{-2}]$	$J_{\rm SC}^{b}$ (EQE _{cal}) [mA cm ⁻²]	FF [%]	PCE [%]
PM6:CH-FC PM6:D18:CH-FC PM6:CH-FB PM6:D18:CH-FB PM6:CH-CB PM6:D18:CH-CB	$\begin{array}{c} 0.886 \ (0.883 \pm 0.004) \\ 0.885 \ (0.880 \pm 0.002) \\ 0.889 \ (0.885 \pm 0.004) \\ 0.888 \ (0.886 \pm 0.004) \\ 0.897 \ (0.895 \pm 0.002) \\ 0.901 \ (0.900 \pm 0.003) \end{array}$	$\begin{array}{c} 26.31 \ (26.21 \pm 0.28) \\ 26.51 \ (26.51 \pm 0.16) \\ 26.38 \ (26.25 \pm 0.15) \\ 26.69 \ (26.64 \pm 0.15) \\ 25.78 \ (25.59 \pm 0.44) \\ 26.22 \ (26.02 \pm 0.23) \end{array}$	25.33 25.84 25.28 26.09 25.10 25.63	77.66 (77.52 ± 0.69) 78.46 (78.12 ± 0.58) 77.86 (77.61 ± 0.61) 80.03 (79.31 ± 0.69) 77.56 (75.52 ± 0.68) 77.07 (77.08 ± 0.52)	$\begin{array}{c} 18.10 \ (17.90 \pm 0.23) \\ 18.41 \ (18.31 \pm 0.16) \\ 18.26 \ (18.11 \pm 0.18) \\ 18.97 \ (18.65 \pm 0.13) \\ 17.93 \ (17.80 \pm 0.19) \\ 18.21 \ (18.01 \pm 0.18) \\ \end{array}$

^{*a*} The average parameters in parentheses were derived from 10 devices. ^{*b*} The J_{SC} (EQE_{cal}) is obtained by integrating the EQE plots.



Fig. 5 (a) AFM height/phase images. (b) The corresponding in-plane (IP) and out-of-plane (OOP) extracted line-cut profiles from 2D GIWAXS with D18, PM6, **CH-FC, CH-FB** and **CH-CB**-based neat and blended ternary films.

distances of *ca.* 20.05, 19.45 and 21.97 Å. It turns out that all three acceptors display face-on molecular packing patterns. The tighter π - π stacking and slightly larger crystal coherence length (CCL) of **CH-FB** indicate higher crystallinity and better molecular packing ordering, which is in accordance with the trend of the single crystals. Moreover, in their blended films (Fig. 5b), strong (010) and (100) diffraction peaks can be still observed in the OOP and IP directions, respectively. The PM6:D18:**CH-FB** film exhibited the smallest π - π stacking distance of 3.61 Å and largest CCL of 23.56 Å compared with those of the PM6:D18:**CH-FC** film (3.63 Å π - π stacking distance; 22.99 Å CCL) and the PM6:D18:**CH-CB** film (3.62 Å π - π stacking distance; 23.27 Å CCL).

In summary, three CH-series acceptors with hetero-dihalogenation, named **CH-FC** (fluorination and chlorination on the central unit), **CH-FB** (fluorination and bromination on the central unit) and **CH-CB** (chlorination and bromination on the central unit), were constructed. Based on single-crystal X-ray analysis, **CH-FB** shows the shortest π - π distance for the "E/E" mode and tightest molecular packing compared with **CH-FC** and **CH-CB**, and thus is favourable for more efficient charge separation and transport properties in multiple directions. Moreover, **CH-FB**-based blended films present superior morphological features, which effectively promotes charge transport dynamics. As a result, an attractive PCE of 18.97% was afforded by **CH-FB**-based OSCs. Our work provides significant insight into hetero-di-halogenation on the central units of CH-series acceptors to further upgrade OSCs and will stimulate further exploration of hetero-substitution-based acceptors.

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Conflicts of interest

There are no conflicts to declare.

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