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# **Metrohm**



### Molecular Packing and Dielectric Property Optimization through Peripheral Halogen Swapping Enables Binary Organic Solar Cells with an Efficiency of 18.77%

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Peripheral halogen regulations can endow non-fullerene acceptors (NFAs) with enhanced features as organic semi-conductors and further boost efficient organic solar cells (OSCs). Herein, based on a remarkable molecular platform of CH14 with more than six halogenation positions, a preferred NFA of CH23 is constructed by synergetic halogen swapping on both central and end units, rendering the overall enlarged molecular dipole moment, packing density and thus relative dielectric constant. Consequently, the CH23-based binary OSC reaches an excellent efficiency of 18.77% due to its improved charge transfer/transport dynamics, much better than that of 17.81% for the control OSC of CH14. This work demonstrates the great potential for further achieving state-of-the-art OSCs by delicately regulating the halogen formula on these newly explored CH-series NFAs.

#### 1. Introduction

Organic solar cell (OSC) has been regarded as one of the most attractive technologies for renewable energy applications, due to its complementary advantages to silicon solar cells in solution processing, low cost, light-weight, flexibility, semitransparency, etc.<sup>[1–7]</sup> Recently, over 19% power conversion efficiencies (PCEs) of OSCs have been achieved,<sup>[8–17]</sup> narrowing the PCE gap with other inorganic solar cells greatly. These encouraging advances of OSCs are mainly caused by the rapid development of non-fullerene acceptors (NFAs), which have caused the overall improvements of three tangling photovoltaic

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parameters of OSCs including the open circuit voltage (V<sub>OC</sub>), short-circuit current density (I<sub>SC</sub>), and fill factor (FF).<sup>[18-20]</sup> In such a complicated system like OSCs, the ultimate output should be determined by diverse components. Among them, it is beyond doubt that organic active layers play a dominant role in the competitive multi-channel charge transfer/transport dynamics, such as the light harvesting, exciton separation, charge transport, and recombination.<sup>[21,22]</sup> However, with respect to that of inorganic light absorption semiconductors of silicon or perovskite crystals with much larger relative dielectric constants ( $\varepsilon_r$ ) of  $\approx 12$  and  $\approx 20$ , respectively,<sup>[23-25]</sup> organic molecules in OSCs

usually are hindered by their inherently low dielectric constants ( $\varepsilon_r < 6$ ).<sup>[23,26]</sup> As it has been already demonstrated in high-performance OSCs systems,<sup>[27]</sup> the increased dielectric property of organic semiconductors is expected to contribute to more efficient charge generations and transports in corresponding OSCs, thus resulting in a high FF and partly dependent  $J_{SC}$ . It is well known that the relative dielectric constants of organic semi-conductors can be affected intrinsically by a series of structurally determining factors, including dipole moment, chromophore conjugation length, packing orientation, and molecular packing density, etc.<sup>[28–30]</sup> Fortunately, despite the huge gap of  $\varepsilon_r$  between organic and inorganic materials, great

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Figure 1. a) Molecular structures of CH14 and CH23. b) Energy level diagram of PM6, CH14 and CH23 neat films derived from CVs. c) Normalized absorption spectra of two NFAs in solutions and neat films. d) DSC curves of CH14 and CH23. e)  $\varepsilon_r$  as a function of frequency measured by impedance spectroscopy.

potentials for improving dielectric properties to further evaluate the FF and  $J_{SC}$  of OSCs have been attached by the remarkable structural diversity of organic molecules.<sup>[26,31]</sup>

Recently, a series of high-performance CH-series NFAs featuring with conjugation-extended phenazine central units have been constructed by our group.<sup>[32–34]</sup> The conjugation-extended central unit of CH-series NFAs not only renders the superior molecular packing modes, but also affords sufficient modification sites on molecular skeletons with more structural optimization possibilities. It has been proven that the superior three-dimensionally molecular packing networks in CH-series NFAs are established by three essentially important peripheral units (two electron-deficient end units and a conjugation-extended central unit).<sup>[32]</sup> Therefore, even a minor structural

modification, such as halogenation alternations, on both central and end units of CH-series NFAs could bring forth a dramatical change of molecular packings and also final photovoltaic performances.<sup>[33]</sup> After a synergetic halogenation engineering on such an excellent molecular platform, the superior molecular packing and film morphologies were achieved by CH14 (also named as CH-4Cl, **Figure 1**a), which has rendered the best binary and ternary OSCs based on CH-series NFAs with PCEs of 17.72% and 18.22%, respectively.<sup>[34]</sup> In spite of the great success achieved by CH14, the FF of CH14-based OSC is only  $\approx$ 76%, still lagging far behind that of perovskite solar cells (PSCs)<sup>[35]</sup> and also some other high-performance OSCs,<sup>[8,36]</sup> which has limited its potential for reaching the level of the state-of-the-art OSCs. For example, over 19% or approaching



20% PCEs could be achieved immediately if improving the FF of CH14-based OSCs to the similar values with PSCs, such as 82%. When taking the relatively satisfactory film morphology but quite negligible dipole moment of CH14 (0.12 Debye) into considerations, one of the reasons for inferior FFs of CH14-based OSCs might be the relatively low dielectric property of active layers according to the discussions above. Therefore, we believe that there are still great potentials for further maximizing the PCEs of CH-series NFAs-based OSCs through improving their dielectric properties.<sup>[27]</sup> For example, operating the precise peripheral halogen regulations to control the dipole moment and molecular packing density of NFAs, which are closely related to the relative dielectric constant of organic molecules.<sup>[28,37]</sup>

Bearing these thoughts in mind, a preferred NFA of CH23 is constructed only by halogen swapping between fluorinated central unit and chlorinated end units of CH14 (Figure 1a). Due to the larger electronegativity of fluorine atom than chlorine (4.0 for Fluorine and 3.0 for Chlorine), a greatly increased dipole moment of 2.48 Debye with a direction from central unit to end groups is afforded by CH23 than that of 0.12 Debye for CH14. Simultaneously, benefitting from the slightly less steric hindrance of fluorine than chlorine caused by their different atom radius (0.071 for Fluorine and 0.099 nm for Chlorine), the molecular packing mode of end unit to end unit ("E/E" mode) in CH23 is enhanced significantly, resulting in a more compact molecular packing network with a larger molecular packing density of 65.8% compared to that of 59.9% for CH14. The larger dipole moment and enhanced molecular interaction of CH23 contribute to an increased  $\varepsilon_r$  of 3.10, 3.68 than that of 2.58, 3.42 for CH14-based neat and blended films, respectively. As a result, the facilitated charge generation/ transport dynamics can be achieved by CH23-based OSCs, rendering a much better PCE of 18.77% with an excellent FF of 80.5% compared to that of 17.81% for CH14-based OSCs with an FF of 77.8%. These results demonstrate that precise halogenation swapping on central and end units of CH-series NFAs still have huge potentials to improve the PCEs of resulting OSCs via tuning the dielectric properties and molecular packings of NFAs.

#### 2. Results and Discussion

#### 2.1. Physicochemical Properties

The successful synthesis route through one-step Knoevenagel condensation reaction to afford CH23 with an excellent yield of 86% is presented in Scheme S1 (Supporting Information). The detailed procedures and characterizations (Figures S1–S3, Supporting Information) were described in Synthetic Section of Supporting Information. After altering the fluorine atoms from central unit to end units, a greatly increased dipole moment of 2.48 Debye with the direction from central to end units for CH23 is afforded compared to that 0.12 Debye for CH14, which should be ascribed to the larger electronegativity of fluorine than that of chlorine (Figure S4, Supporting Information). Moreover, a clear acceptor-donor-acceptor (A-D-A) feature for both CH14 and CH23 can be indicated by the peak-valley-peak

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plots of frontier orbital charge density differences ( $\Delta$ Q) at the longest direction of molecular skeletons (Figure S4, Supporting Information).<sup>[38]</sup> As it has been proven that such an obvious A-D-A character could endow NFAs with enhanced light harvesting, facilitated charge generation/transport, suppressed charge recombination, and thus improved photovoltaic performance with respect to other types of molecules.<sup>[18,39–42]</sup>

The experimental HOMO and LUMO energy levels of CH23 derived from cyclic voltammetry (CV) measurements can be estimated to be -5.74 and -3.82 eV, respectively, compared to those of -5.75 and -3.85 eV for CH14 (Figure 1b; Figure S5, Supporting Information). As it can be observed that both HOMO and LUMO energy levels of CH23 upshift by 10 and 30 meV, respectively, giving rise to a larger bandgap of 1.92 eV than that of 1.90 eV for CH14. In theory, the upshifted LUMO energy level of CH23 is conducive to achieving a larger  $V_{OC}$ if the same electron donor PM6<sup>[43]</sup> (Figure S6, Supporting Information) is applied in OSCs. Please note that the relative alignments of both HOMO and LUMO energy levels are in good accordance with the results predicted by the density functional theory (DFT) calculations (Figure S7, Supporting Information). As shown in Figure 1c, the maximum absorption peak  $(\lambda_{max})$  of CH23 in dilute chloroform solution locates at 729 nm, slightly blue-shifting by 15 nm compared to that of 744 nm for CH14. And the corresponding molar extinction coefficients of CH14 and CH23 are estimated, which are  $2.20 \times 10^5$  and  $2.08 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup>, respectively (Figure S8a, Supporting Information). Meanwhile, the  $\lambda_{max}$  of CH23 and CH14 in solid states locate at 811 and 821 nm, respectively, maintaining a similar variation tendency with that in solutions. Furthermore, the optical bandgaps ( $E_o^{opt}$ ) of CH23 and CH14 could be derived from their thin-film absorption edges ( $\lambda_{onset}$ ), being 1.39 and 1.37 eV, respectively. The enlarged  $E_{\sigma}^{opt}$  for CH23 comparing to that of CH14 is consistent with the tendency of energy gaps obtained from CVs. The variation of energy levels and absorption spectra for CH23 after peripheral halogen swapping should be caused by the quite different p- $\pi$  conjugation and electronegativity of fluorine and chlorine. More interestingly, a slightly enlarged redshift  $(\Delta \lambda)$  from solutions to films for CH23 (≈82 nm) can be observed with respect to that of CH14 (≈77 nm), suggesting the potentially stronger molecular interactions in CH23 films.<sup>[44,45]</sup> Based on the differential scanning calorimetry (DSC) curves in Figure 1d, CH14 and CH23 present the exothermal peaks at 281.6 and 274.8 °C and their corresponding melting enthalpy  $(\Delta H_m)$  are integrated to be 11.64 and 17.83 J g<sup>-1</sup>, respectively. The larger  $\Delta H_{\rm m}$  of CH23 compared to that of CH14 also indicates the stronger molecular interactions,<sup>[46,47]</sup> which may result in a larger molecular packing density, and hence leading to the improved dielectric properties. In order to verify the improved dielectric properties of CH23, the relative dielectric constant ( $\varepsilon_r$ ) was further measured. As shown in Figure le and Figure S9 (Supporting Information), CH23 shows a larger average  $\varepsilon_r$  of 3.10 than that of 2.58 for CH14 in their neat films, in good accordance with the enlarged dipole moment and stronger intermolecular interaction of CH23. Furthermore, the relatively larger  $\varepsilon_r$  of 3.68 for CH23 can be also observed in its blended films with PM6 comparing to that of 3.42 for CH14 blended film. The enlarged  $\varepsilon_r$ could contribute to an improved charge generation/transport



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dynamic in theory<sup>[26,28]</sup> and thus enable CH23-based OSCs to afford a better FF and  $I_{SC}$ , which will be discussed in detail below. As displayed in Figure S10 (Supporting Information), both CH14 and CH23 possess a good thermal stability with a large decomposition temperature >320 °C, meeting the basic stability criterion as light harvesting materials. The corresponding physicochemical data of CH14 and CH23 have been summarized in Tables S1 and S2 (Supporting Information) for a clear comparison. To sum up, a clear change of fundamental physicochemical properties at both levels of single molecule and aggregations has been observed for CH23 after halogen swapping between fluorinated central unit and chlorinated end units. Among them, an exciting improvement of dielectric property of CH23 comparing to that of CH14, caused by its greatly enlarged dipole moment and enhanced intermolecular interaction, is expected to result in a better OSC with the enlarged FF and even  $I_{SC}$ .

#### 2.2. Molecular Packing in Single Crystals

As it was mentioned above, peripheral halogen regulation on CH-series NFAs could cause a dramatic change in molecular packings,<sup>[32,34]</sup> and it is indeed that CH23 has demonstrated stronger intermolecular actions indicated by its enlarged  $\Delta\lambda$ and  $\Delta H_{\rm m}$  after halogen swapping on the already outstanding CH14 platform. Therefore, it is essential to have their singlecrystal structures for a more accurate analysis. Herein, needlelike crystals with a beautiful metallic luster were grown through a slow solvent diffusion method (the detail in Supporting Information) and measured by X-Ray diffractions (Table S3, Supporting Information; CCDC: 2 233 780). The related X-Ray parameters of CH23 are listed in Table 1 and those of CH14 were obtained from our previous literature.<sup>[34]</sup> From the top view of single-crystal packing diagrams in Figure 2a,b, both the central and end units of CH14 and CH23 are fully involved in molecular packing network through  $\pi$ - $\pi$  stacking, which is one of the main superiorities of CH-series acceptors than other type of molecules.<sup>[32,34]</sup> Meanwhile, both CH14 and CH23 construct a circle-shaped void with a diameter of  $\approx 20.0$  Å and a rectangle-shaped void with a size of  $\approx 18.6 \times 12.1$  Å, respectively. The smaller void of CH23 is expected to contribute to a more compact molecular packing network than that of CH14, which is further proven by the larger molecular packing density (MPD)<sup>[28]</sup> of 65.8% for CH23 compared to that of 59.9% for CH14. Note that the larger MPD of CH23 comparing to that of CH14 should be beneficial for its improved dielectric properties (Figure 1e).

Intrinsically, the significant difference of 3D molecular packing networks between CH23 and CH14 should be determined by their different intermolecular interaction. Therefore, the molecular packing modes with over 70 kJ mol<sup>-1</sup> of intermolecular potential were extracted from CH14 and CH23 single crystals (Figure 2c) and a detailed comparison was conducted in Table 1. Three packing modes for CH23 and two packing modes for CH14 can be observed. Among them, Mode 1 is the molecular packing only involving the "end unit to end unit" ("E/E") interaction, existing in both CH23 and CH14 crystals and also playing a dominant role in some other high-performance A-D-A type acceptors.<sup>[39,45,48–52]</sup> Note that after substituting chlorine atoms on end units with fluorine, the "E/E" mode of CH23 affords an obviously decreased  $\pi$ - $\pi$  packing distance of 3.274-3.346 Å with respect to that of 3.297-3.467 Å for CH14 (Figure 2d and Table 1), which should be mainly caused by the smaller steric hindrance of fluorine atoms than chlorine. Together with the obviously enlarged overlapping area of end units, a much larger intermolecular potential of 130.1 kJ mol<sup>-1</sup> is afforded by the "E/E" mode of CH23 compared with that of 77.6 kJ mol<sup>-1</sup> for CH14. More importantly, the greatly increased electron and hole transfer integrals of 38.75 and 39.48 meV, respectively, can be also observed for the "E/E" mode in CH23, which are much larger than those of 20.25 and 5.09 meV in CH14. The enhanced intermolecular packing and charge transfer integrals for the "E/E" mode in CH23 could facilitate the charge transfer/transport dynamics effectively in its resulting OSCs. The Mode 2 in CH14 single crystals is actually a dual (two-way) packing between the end and central units ("dual E/C" mode), with an intermolecular potential of 207.7 kJ mol<sup>-1</sup>. This is also the quite unique packing mode observed only in CH-series NFAs thus far and plays an important role in forming the 3D packing network.<sup>[32,34]</sup> As shown in Mode 2 of CH23, the similar molecular packing mode of "dual E/b" could be also observed with a comparable intermolecular potential of 194.3 kJ mol<sup>-1</sup>, indicating the strong dual-path intermolecular interaction between end units and bridged thiophene groups. Moreover, a specific packing mode of "E/C" is also been afforded by CH23, featuring with the interaction between a central unit and an end unit of two adjacent molecules and possessing a relatively small packing distance of 3.319-3.474 Å and intermolecular potential of 75.2 kJ mol<sup>-1</sup>. This unique

Compound	Void sizes (shape)	Packing modes	$d_{\pi-\pi}^{b)}$ [Å]	Intermolecular potentials [kJ mol <sup>-1</sup> ]	V <sub>H</sub> <sup>c)</sup> [meV]	V <sub>E</sub> <sup>d)</sup> [meV]
CH14 <sup>a)</sup>	20.0 Å (circle)	Mode 1 (E/E)	3.297-3.467	77.6	5.09	20.25
		Mode 2 (Dual E/C)	3.226-3.347	207.7	52.88	34.34
CH23	18.6 $ imes$ 12.1 Å (rectangle)	Mode 1 (E/E)	3.274-3.346	130.1	39.48	38.75
		Mode 2 (Dual C/b)	3.245-3.429	194.3	1.93	5.27
		Mode 3 (E/C)	3.319-3.474	75.2	5.63	8.34

**Table 1.** Crystallographic and  $\pi$ - $\pi$  interaction parameters of CH14 and CH23.

<sup>a)</sup>Crystal structure of CH14 was obtained from previously reported work;<sup>[34]</sup> <sup>b)</sup>d<sub> $\pi-\pi$ </sub> is the  $\pi-\pi$  interlayer distance including the main types of intermolecular packing modes of CH14 and CH23, which is consistent with that of Figure 2c; <sup>c)</sup>V<sub>E</sub> and; <sup>d)</sup>V<sub>H</sub> are the electron and hole transfer integrals of the corresponding packing modes.

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**Figure 2.** a,b) Single-crystal packing diagrams from the top view of CH14 and CH23, respectively. Red: end groups (E); grey: bridge unit (b); blue: central unit (C). c) Different intermolecular packing modes of CH14 and CH23. d) Interlayer  $\pi$ - $\pi$  stacking distances including all the corresponding intermolecular packing modes of CH14 and CH23.

packing mode of "E/C" in CH23 single crystal should partly account for its enlarged molecular packing density compared to that of CH14. In brief, the effective intermolecular packing modes in CH23 single crystals, especially the greatly enhanced "E/E" and the unique "E/C" modes, have enabled a more compact molecular packing network for CH23 indicated by the larger molecular packing density. This is in good agreement with the enlarged  $\Delta\lambda$  and  $\Delta H_{\rm m}$  of CH23 comparing to those of

CH14, and further contributing to the enlarged dielectric constant of CH23 as discussed above.

#### 2.3. Photovoltaic Performances

To further investigate the influences of enlarged molecular packing density and  $\varepsilon_r$  on device performances, binary OSCs

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**Figure 3.** a) Current density–voltage curves of PM6:CH14 and PM6:CH23 based OSCs; the inset shows the histogram of PCEs fitted with Gaussian distributions (solid lines). b) EQE spectra and integral  $J_{SC}$  values. c) Histograms of the electron and hole mobility of blended films. d)  $J_{ph}$  versus  $V_{eff}$  curves.

based on CH14 and CH23 with a conventional structure of ITO/PEDOT:PSS/BHJ layer/PNDIT-F3N/Ag were fabricated, where PM6 was selected as the polymeric donor due to its suitable energy levels and complementary absorption.<sup>[43]</sup> The detailed experimental conditions are described in Supporting Information and the data of device optimizations are presented in Tables S9–S11 (Supporting Information). The optimal current density–voltage (J–V) characteristics are shown in **Figure 3**a and summarized in **Table 2**.

The champion PCE of 18.77% is achieved by CH23-based OSCs along with a  $V_{\rm OC}$  of 0.876 V, a  $J_{\rm SC}$  of 26.64 mA cm<sup>-2</sup>, and an impressive FF of 80.45%, much better than that of 17.81% for its counterpart of CH14 that affords a slightly smaller  $V_{\rm OC}$  of 0.869 V and  $J_{\rm SC}$  of 26.35 mA cm<sup>-2</sup> but dramatically inferior FF of 77.79%. The efficiency distribution histogram for 15 independently measured OSCs (see the detailed device parameters in Tables S12 and S13, Supporting Information) is inset in Figure 3a, exhibiting the evidently higher average PCEs for CH23-based OSCs comparing to that of CH14. The

slightly higher  $V_{OC}$  of CH23-based OSCs is consisted with the upshifted LUMO energy level of CH23 with respect to that of CH14. The corresponding integrated current densities derived from the external quantum efficiency (EQE) curves (Figure 3b) are 26.05 mA m<sup>-2</sup> for CH23- and 25.65 mA cm<sup>-2</sup> for CH14-based OSCs, which match well with the  $J_{SC}$  afforded by J-V tests (within the 3% error range). As it is well known that the polymeric donor D18 possesses a lower-lying HOMO than PM6, which is conducive to obtain a larger  $V_{OC}$ . As it can be expected, the higher  $V_{OC}$  of 0.881 and 0.893 V for CH14 and CH23-based OSCs can be afforded (Figure S11 and Table S4, Supporting Information). However, the inferior  $J_{SC}$  and FF lead to slightly lower PCEs compared to those of PM6-based OSCs.

The PM6:CH14 and PM6:CH23 OSCs show the strong photoresponse during 450–850 nm, which matches well with the light absorption range of the blended films (Figure S8b, Supporting Information) and agrees well to the light harvesting efficiencies at the corresponding wavelength ( $\mathcal{O}_{lh}$ , Figure S12, Supporting Information). The higher photocurrent response in

Table 2. Summary of device	e parameters for	optimized OSCs.
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Active layers <sup>a)</sup>	V <sub>OC</sub> [V]	J <sub>SC</sub> [mA cm <sup>-2</sup> ]	Cal. J <sub>SC</sub> <sup>b)</sup> [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
PM6:CH14	0.869 (0.868 ± 0.005)	26.35 (26.27 ± 0.15)	25.65	77.79 (77.60 ± 0.21)	17.81 (17.69 ± 0.11)
PM6:CH23	0.876 (0.877 ± 0.004)	26.64 (26.54 ± 0.11)	26.05	80.45 (80.22 ± 0.16)	18.77 (18.67 ± 0.09)

<sup>a)</sup>The average photovoltaic parameters calculated from 15 independent devices; <sup>b)</sup>Current densities calculated from EQE curves.

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the most of wavelength range for CH23-based OSCs should be attributed to the facilitated exciton dissociation, charge transport and collection, which will be further discussed below. Note that the greatly improved PCE for CH23-based OSCs mainly benefits from the significantly enlarged FF, which could be determined by the charge transport property of blended films at vertical directions. Furthermore, as we have discussed above, the enhanced molecular packing and relatively larger  $\varepsilon_r$  of CH23 film are expected to facilitate the charge transfer/transport dynamics and thus contribute to an improved FF. Therefore, the electron/hole mobilities  $(\mu_e/\mu_h)$  of PM6:CH14 and PM6:CH23 were measured by using the space-charge limited current (SCLC) method, being  $5.12 \times 10^{-4}/2.89 \times 10^{-4}$  and  $6.21 \times 10^{-4}/4.00 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , corresponding to the  $\mu_e/\mu_h$ ratios of 1.77 and 1.55, respectively (Figure 3c; Figure S13, Supporting Information). The increased and balanced hole and electron mobilities of CH23-based devices should account for its higher FF to some extent comparing to that of CH14 counterpart.

#### 2.4. Charge Dynamics Analysis

The variation of photovoltaic parameters of OSCs should be determined by several multi-channel charge competitive dynamics, that is, exciton dissociation, charge transport, collection and recombination. Therefore, the exciton dissociation efficiency  $(P_{diss})$  and charge collection efficiency  $(P_{coll})$  were first evaluated to unveil the better photovoltaic performance of CH23-based OSCs with respect to that of CH14-based ones. As displayed in Figure 3d, the  $P_{diss}$  and  $P_{coll}$  for CH23-based OSCs can be calculated to be 98.12% and 89.18%, respectively, both higher than that of 97.51% and 86.86% for CH14-based ones. The larger P<sub>diss</sub> and P<sub>coll</sub> of CH23-based OSCs should partially account for their higher photocurrent response observed from the EQE spectra (Figure 3b). Simultaneously, the larger  $P_{diss}$ of CH23-based device is also well consisted with its relatively higher photoluminescence quenching yield of 97.59% compared to that of 96.60% for CH14 (Figure 4a). As shown in Figure 4b, the device based on CH23 shows a faster charge extraction time (0.34 µs) than that of CH14 (0.39 µs) by fitting the transient photocurrent (TPC) decay curves, suggesting the more efficient charge extraction. Meanwhile, a longer charge lifetime of 58.21 µs in CH23-based device than that of 48.88 µs in CH14-based one can be observed by fitting the transient photovoltage (TPV) decay curves in Figure 4c, indicating the slightly suppressed charge recombination in CH23 system. Moreover, by analyzing the dependence of  $J_{SC}$  and  $V_{OC}$  on light intensity in Figure S14 (Supporting Information), S/(kT/q) values for CH23 and CH14-based OSCs are 1.11 and 1.14, respectively, and the  $\alpha$ for CH23 and CH14-based OSCs are 0.99 and 0.98, respectively. The comparable but slightly superior S/(kT/q) and  $\alpha$  values for CH23 system also indicate the suppressed charge recombination comparing to that of CH14,<sup>[53]</sup> which is in good agreement



**Figure 4.** a) Photoluminescence spectra of neat and blend films. b) Transient photocurrent (TPC) and c) transient photovoltage (TPV) measurements of the devices based on PM6:CH14 and PM6:CH23. d) Statistical diagram of detailed  $E_{loss}$  of CH14 and CH23 based devices.

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Figure 5. a,b) AFM height images and c,d) phase images of PM6:CH14 and PM6:CH23 blended films. e,f) The statistical distribution of the fibril diameter for PM6:CH14- and PM6:CH23-based blended films (see Figure S20, Supporting Information, for the details).

with the TPV results. The detailed photodynamic parameters have been summarized in Table S5 (Supporting Information).

#### 2.5. Energy Losses and Morphology Analysis

A detailed analysis of energy losses ( $E_{\rm loss}$ ) based on the detailed balance theory<sup>[54–57]</sup> has been displayed in Figure 4d and

Table S6 (Supporting Information). The detailed information for calculating the  $E_{\rm loss}$  is described in Supporting Information. First, the optical bandgaps ( $E_{\rm g}$ s) of blended films were estimated to be 1.414 and 1.407 eV for CH23 and CH14, respectively (Figure S15, Supporting Information).<sup>[54,58]</sup> Therefore, the overall  $E_{\rm loss}$  for CH23 and CH14-based OSCs could be calculated as 0.537 and 0.538 eV, respectively, indicating no significant influences on overall  $E_{\rm loss}$  after halogen swapping. Due

to the quite similar  $E_{\rm g}$ s, CH23 and CH14-based OSCs afford almost the same radiative recombination energy losses above the bandgap ( $\Delta E_1$ ) of 0.265 and 0.264 eV, respectively. Note that CH23-based OSC shows a slightly lower radiative recombination energy loss below the bandgap ( $\Delta E_2$ ) of 0.035 eV compared to that of 0.048 eV for CH14. This is generally related to the more ordered molecular packing of CH23, which was indicated by the slightly smaller Urbach energy ( $E_{\rm U}$ ) of 19.83 meV for CH23 than that of 20.45 meV for CH14. (Figures S16

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for CH23 than that of 20.45 meV for CH14 (Figures S16 and S17, Supporting Information).<sup>[59]</sup> Lastly, the comparable non-radiative recombination energy losses ( $\Delta E_3$ ) for OSCs based on CH23 and CH14 have been determined to be 0.237 and 0.226 eV, respectively, ranking among the smallest values in high-performance OSCs.<sup>[20,33,60,61]</sup>

To further explore the effects of peripheral halogen swapping on morphologies of blended films, grazing-incidence wideangle X-ray scattering (GIWAXS) measurement and atomic force microscopy (AFM) were performed to unveil the molecular packing orientations and aggregation properties. Note that a favorable face-on orientation of molecular packing can be achieved by both CH14 and CH23-based films, indicated by the strong (010) and (100) diffraction peaks in out-of-plane (OOP) and in-plane (IP) directions, respectively (Figure S18 and Table S7, Supporting Information). The face-on orientation of molecular packing will be in favor of the efficient charge transport in such a vertical structure of OSCs.<sup>[62]</sup> Note the corresponding strong peaks of GIWAXS data in the CH23 film match well with that of X-ray diffraction pattern generated from the single crystal structure, respectively, indicating that the packing modes of CH23 in single crystals can be largely preserved in the spincoated films (Figure S19, Supporting Information).<sup>[32,34]</sup> As shown in Figure 5a,b, both PM6:CH14 and PM6:CH23 blended films exhibit a uniform and relative smooth surface morphology by AFM analysis, where the root-mean-square (RMS) of PM6:CH23 and PM6:CH14 are 1.06 and 1.11 nm, respectively. In addition, the phase images (Figure 5c,d) of the blended films present the clearly bundle-like fibers for both PM6:CH23 and PM6:CH14, which has been regarded as the preferred morphology features for the high-performance OSCs.<sup>[63]</sup> Simultaneously, a statistical size analysis of bundle-like nanofibers has been conducted and displayed in Figure 5e,f and Figure S20 (Supporting Information), showing a slightly smaller size of 12.1 nm for CH23 comparing to that of 13.2 nm for CH14. Note that the reduced size of nanofibers for CH23 may be caused by the increased miscibility when blending with the polymeric donor of PM6, which can be indicated by its slightly smaller Flory-Huggins interaction parameter  $\chi$  (0.660 for CH23 and 0.756 for CH14; Figure S21 and Table S8, Supporting Information).<sup>[64,65]</sup> The better miscibility between CH23 and PM6 should be ascribed to the reduced crystallinity induced by the decreased numbers of chlorination after peripheral halogen swapping.<sup>[66]</sup>

#### 3. Conclusion

A high performance NFA of CH23 is constructed successfully just by peripheral halogen swapping on the high-performance molecular platform of CH14 to further enhance its dielectric feature and intermolecular interaction. As a result, CH23 possesses both a larger dipole moment of 2.48 Debye and molecular packing density of 65.8% compared to that of 0.12 Debye and 59.9% for CH14, thus rendering an increased relative dielectric constant for CH23-based films. Furthermore, the enhanced molecular packing density and dielectric property of CH23 also contribute to the facilitated charge separation/transport and suppressed charge recombination in resulting OSCs. Therefore, CH23-based binary OSCs achieved an excellent PCE of 18.77% along with an impressive FF of 80.5%, which are both the best values for OSCs employing newly explored CH-series NFAs. Our work paves a new avenue to improve dielectric properties of organic semi-conductors, like NFAs, through synergetic peripheral halogenation regulations and also demonstrates huge potentials for achieving recordbreaking OSCs based on the excellent molecular platforms of CH-series NFAs.

#### **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 from the corresponding author upon reasonable request.

#### **Keywords**

dielectric constant, halogen regulation, molecular packing, non-fullerene acceptors, organic solar cells

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