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Broader context

Fine-tuning central extended unit symmetry via atom-level asymmetric molecular design enables efficient binary organic solar cells[†]

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The central unit plays a significant role in Y-type acceptor-based organic solar cells (OSCs). However, acceptors featuring an asymmetric central unit are rare, and their structural properties as well as interactions with donors remain unclear. In this work, we propose an atom-level asymmetric molecular design strategy to develop and synthesize two asymmetric acceptors, **CH-Bzq** and **CH-Bzq-Br**, alongside a control acceptor, **CH-PHE**, which has a symmetric structure. Theoretical calculations and experimental results demonstrate that subtle variations in the atom-level chemical structure effectively regulate molecular dipole moments, packing behavior, and active layer morphology, ultimately influencing device performance. Notably, due to favorable phase separation, improved charge carrier dynamics, and superior morphology, the PM6:**CH-Bzq-Br**-based binary device achieves an impressive power conversion efficiency (PCE) of 19.42%. Remarkably, when the green solvent *ortho*-xylene (*o*-xy) was used for processing, an outstanding PCE of 16.08% was achieved in a module. Our work highlights the significant potential of atom-level asymmetric molecular design for fine-tuning active layer nanomorphology, a crucial factor in the development of high performance OSCs.

The molecular symmetry of Y-type acceptors significantly influences photovoltaic performance. Currently, most studies on asymmetric acceptors primarily focus on terminal groups and alkyl side chains. However, asymmetric unit molecules at the central core remain rare, and their interactions with donors and structural properties are not well understood. In this work, we designed two asymmetric acceptors, **CH-Bzq** and **CH-Bzq-Br**, using an atomic-level asymmetric molecular design strategy. Compared to the symmetric control acceptor **CH-PHE**, subtle modifications in the central core effectively regulate the molecular dipole moment, packing behavior, and active layer morphology, ultimately impacting device performance. As a result, the **CH-Bzq-Br**-based binary device processed with chloroform achieved an efficiency of 19.42%. Furthermore, when the non-halogenated solvent *ortho*-xylene was used to process both a smallarea device and a large-area module (13.5 cm²), efficiencies of 18.89% and 16.08% were obtained, respectively. This work presents a promising approach for designing high-performance acceptors with asymmetric structures.

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Introduction

Solution-processed organic solar cells (OSCs) have attracted considerable attention from both academia and industry due to their advantages including light weight, low cost, flexibility and semitransparency.^{1–3} In recent years, OSCs have made significant advancements, achieving power conversion efficiencies (PCEs) of around 20%, thanks to rapid developments in active layer material design, particularly non-fullerene acceptors, nanomorphology regulation and device engineering.^{4–10} Currently, most high-efficiency acceptors focus on highly symmetrical Y-series acceptors with an A–D–A-type structure.^{11–13} To further improve the device performance, asymmetric structure acceptors may be promising

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compared to their symmetric acceptor counterparts. Recently, asymmetric acceptors have attracted considerable interest due to their unique properties arising from the destruction of molecular symmetry, particularly molecular dipole moment. Generally, asymmetric acceptors feature larger dipole moments, resulting in stronger intermolecular interactions that influence packing behavior, photoelectric properties and device performances.^{14–20} However, most asymmetric molecular design strategies mainly focus on terminal groups^{21–26} and side chains,^{27–30} and few research studies on modifying central units have been reported,^{31–34} leaving a gap in understanding the relationship between the device performance and central core symmetry. Therefore, it is essential to develop a simple yet efficient molecular design strategy to reveal how asymmetric central units affect solar cell performance.

In this work, we propose an atomic-level asymmetric molecular design strategy to investigate the relationship between central unit asymmetry and device performance. Specifically, we designed and synthesized two asymmetric acceptors, namely CH-Bzq and CH-Bzq-Br, with similar backbones but different core symmetries by introducing N and Br atoms on the central unit. Herein, bromine was introduced in CH-Bzq-Br based on the rationale as follows. (1) Bromine has lower electronegativity and a larger atomic radius than fluorine and chlorine, which may enhance intermolecular interactions through π /p-electron orbital overlap.³⁵ (2) Brominated compounds generally demonstrate stronger crystallinity compared to their fluorinated and chlorinated counterparts, promoting better molecular crystalline ordering.³⁶ (3) Brominated compounds are easier to synthesize in the benzo[h]quinoline unit than other halogenated derivatives.³⁷ Additionally, a symmetric structure acceptor named CH-PHE was synthesized as the control molecule. It has been found that the variations in the atom-level chemical structure effectively regulated the molecular dipole moments and packing behavior of the acceptors, as demonstrated by theoretical calculations and experimental results. Among the three acceptors, CH-Bzq-Br with the largest dipole moment exhibited enhanced intermolecular interaction, improved carrier dynamics and optimized blend morphology. Consequently, the PM6:CH-Bzq-Br-based device achieved an efficiency of 19.42%. Moreover, CH-Bzq-Br demonstrated good solubility in the green solvent ortho-xylene (o-xy) due to the presence of long-branched alkyl chains and maintained the favourable morphology in the o-xy, allowing the o-xy processed large-area module to reach a PCE of 16.08%. By showcasing high-performance acceptors via atomic-level asymmetric molecular design strategy, our work paves the way for designing new asymmetric acceptors for organic photovoltaics, which is crucial for the development of high performance OSCs.

Results and discussion

The chemical structures of **CH-PHE**, **CH-Bzq** and **CH-Bzq-Br** are illustrated in Fig. 1a, and the corresponding synthetic routes are provided in the ESI[†] (Schemes S1–S3). The three molecular backbones were obtained through a reduction reaction with

lithium aluminium hydride, followed by a ketoamine condensation reaction. Then, the two acceptors were synthesized by the Vilsmeier–Haack reaction, followed by the Knoevenagel condensation reaction. All new intermediates and the three acceptors were characterized by ¹H NMR, ¹³C NMR and highresolution mass spectrometry (HRMS), as shown in the ESI[†] (Fig. S1–S26). It is worth noting that the incorporation of 11-methyltricosane alkyl chains on the pyrrole N atom ensures sufficient solubility in conventional organic solvents, such as chloroform (CF), toluene, *ortho*-xylene (*o*-xy), chlorobenzene (CB), and o-dichlorobenzene (*o*-DCB), making them suitable for large-area modules. Thermogravimetric analysis (TGA) measurement showed that the decomposition temperature (*T*_d, 5% weight loss) of the three acceptors exceeded 320 °C, demonstrating their good thermal stability (Fig. S27, ESI[†]).

Density functional theory (DFT) calculation at the B3LYP/6-31G* level was conducted to elucidate the differences in the dipole moments of molecular orbitals among the three acceptors resulting from the atom-level asymmetric molecular design strategy. As illustrated in Fig. S28 (ESI⁺), the ground-state molecular dipole moments (μ_{α}) of the three acceptors were calculated as 2.24 Debye for CH-PHE, 0.61 Debye for CH-Bzq and 2.68 Debye for CH-Bzq-Br, accompanied by a clear change in the dipole moment direction. Note that CH-Bzq-Br exhibits the largest μ_{g} value with a nearly vertical orientation to the molecular skeleton among the three acceptors, due to its largest asymmetry arising from the atom-level chemical structure variation. The largest μ_g value of CH-Bzq-Br can reinforce the intermolecular interaction and J-aggregation behavior, consistent with ultraviolet-visible (UV-vis) absorption results discussed below. In Fig. S29 and Tables S1-S3 (ESI⁺), time-dependent DFT (TD-DFT) was carried out to evaluate the excited-state dipole moment (μ_e) and the difference between μ_g and μ_e ($\Delta\mu_{ge}$). $\Delta\mu_{ge}$ is closely related to the degree of photoinduced intramolecular charge transfer^{38,39} and can be calculated using the margin of ground-state and excited-state dipole moments along each axis, yielding values of 0.13 Debye for CH-Bzq and 0.18 Debye for **CH-Bzq-Br.** The larger $\Delta \mu_{ge}$ means a stronger intermolecular interaction and lower coulombic binding energy of exciton, as reported in previous report.40 This results in a more efficient separation efficiency of the electron-hole pair and charge transfer rate for CH-Bzq-Br, contributing to improved photovoltaic performance.41

The single crystals of **CH-Bzq** and **CH-Bzq-Br** were obtained *via* a slow solvent diffusion method, using chloroform as a good solvent and methanol as a poor solvent. Unfortunately, the single crystals of **CH-PHE** were not obtained using many methods. Their detailed X-ray parameters and structural output results for **CH-Bzq** and **CH-Bzq-Br** are provided in Tables S4 and S5 and Fig. S30 and S31 (ESI†). The monomolecular geometry in single crystals of **CH-Bzq** and **CH-Bzq-Br** are shown in Fig. 1b, with all the alkyl chains omitted for clarity. Both acceptors exhibit a similar banana-curved and helical conformation with a relatively planar conjugated skeleton caused by the effective intramolecular S···O interactions between the end unit and adjacent bridged thiophene.^{2,42} Note that the distances of S···N between the



Fig. 1 (a) Chemical structures of CH-PHE, CH-Bzq and CH-Bzq-Br. (b) The single crystal structures of CH-Bzq and CH-Bzq-Br from the top view. The distances between the atoms are marked in red and purple colours, and the unit is A°. (c) Different intermolecular packing modes in single crystals of CH-Bzq and CH-Bzq-Br. Herein, red, green and blue colors highlight the central unit (C), bridge unit (B) and end groups (E), respectively. Normalized UV-vis absorption spectra of diluted chloroform solution (d) and neat film (e) for PM6, CH-PHE, CH-Bzq and CH-Bzq-Br. (f) Energy level diagram of PM6, CH-PHE, CH-Bzq and CH-Bzq-Br neat film derived from CV.

nitrogen on phenazine and the sulfur on adjacent bridged thiophene range from 3.2 to 3.4 Å, slightly smaller than the sum of van der Waals radii (\sim 3.55 Å) of S and N atoms, indicating the possible noncovalent interactions between S and N in the two acceptors.⁴³ These two noncovalent interactions contributed to the planarity of the conjugate skeleton and are beneficial for the formation of favorable intermolecular packing, generating efficient charge transport channels. According to the molecular single-crystal packing patterns in Fig. S32 (ESI†), both acceptors show two-dimensional packing, rather than the three-dimensional packing of conventional Y-series acceptors.⁴⁴

Specifically, three packing modes were identified in both **CH-Bzq** and **CH-Bzq-Br** single crystals, including one type of end-to-end units (mode 1, "E/E" mode) and two types of dual end to central units (mode 2 and mode 3, "dual E/C-1" and dual E/C-2" modes) with $\pi \cdots \pi$ stacking distances of 3.437/3.381/

3.403 Å for **CH-Bzq** and 3.447/3.359/3.382 Å for **CH-Bzq-Br**, respectively (Fig. S33 (ESI[†]) and Fig. 1c). It is obvious that **CH-Bzq-Br** shows a smaller $\pi \cdots \pi$ packing distance for the dual end group to the central unit with higher intermolecular potentials, while **CH-Bzq** exhibits more compact packing in the end group to end group. All three packing modes synergistically improved intermolecular packing, thus enhancing charge carrier transport. Overall, the atom-level chemical structure variation in the central unit preserves molecular planarity and balances diverse packing modes, ultimately enhancing molecular packing and improving device performance in the resulting OSCs.

The normalized ultraviolet-visible (UV-vis) absorption spectra of PM6 and the three acceptors in chloroform solution and films are depicted in Fig. 1d and e and Fig. S34–S36 (ESI†), with the corresponding data summarized in Table 1. The maximum absorption peak (λ_{max}) of **CH-PHE** in diluted chloroform

solution is at 750 nm. In contrast, after the asymmetric atomiclevel core vibration, the absorbance of CH-Bzq and CH-Bzq-Br in diluted solution showed a slight blue shift, with the λ_{max} values located at 744 and 740 nm, respectively. This blue shift can be attributed to the reduced intramolecular charge transfer (ICT) effect. In addition, clearly significant red shifts of λ_{max} are observed from solutions to neat thin films for all three acceptors. The extent of this red shift is closely related to the molecular packing and aggregation behavior within the thin films. In particular, CH-PHE, CH-Bzq and CH-Bzq-Br showed λ_{max} values of 790, 795 and 799 nm, resulting in red shifts of 41, 51 and 59 nm. The largest red shift observed for CH-Bzq-Br indicates enhanced π - π stacking behavior compared to CH-PHE and CH-Bzq, contributing to enhancing its device performance.^{45,46} The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of PM6 and the three acceptors in solid films were investigated by cyclic voltammetry (CV) measurements, as depicted in Fig. S37 (ESI⁺). The energy level diagrams of PM6 and the three acceptors are illustrated in Fig. 1f, with HOMO/LUMO energy levels of CH-PHE, CH-Bzq and CH-Bzq-Br at -5.63/-3.70, -5.67/-3.74 and -5.71/-3.79 eV. Note that the relative alignment of energy levels derived from CV was in accordance with the results from theoretical calculations (Fig. S38, ESI[†]). Compared to CH-PHE, the energy levels of CH-Bzq and CH-Bzq-Br are slightly downshifted, which can be ascribed to their different packing behavior in the solid films. The atom-level variation in the central core leads to a lower HOMO energy level, thereby increasing the HOMO offset with the donor and providing a greater driving force for exciton dissociation, which is consistent with the fluorescence quenching efficiency results (Fig. S39, ESI⁺).

To investigate the photovoltaic device performance of the three acceptors, OSCs were fabricated using a conventional device architecture of ITO/2PACz/PM6:acceptors/PNDIT-F3N/Ag. Chloroform was used as the processing solvent and the detailed device fabrication, optimization process and characterization procedures are summarized in the ESI† (Tables S6–S8). The current density–voltage (J–V) curves of the optimized devices are shown in Fig. 2a, and the corresponding photovoltaic parameters are listed in Table 2. For the three acceptors blended with the polymer donor PM6, all binary systems can achieve high V_{oc} values exceeding 0.9 V. The device of PM6:CH-PHE exhibited a PCE of 15.20% with a V_{oc} value of 0.944 V, a J_{sc} value of 21.91 mA cm⁻² and an FF of 73.52%. When the symmetry of the central core was broken, the two asymmetric acceptor-based devices demonstrated significant enhancement of PCEs. Specifically, PM6:CH-BZq

exhibited a higher PCE of 16.71% with a V_{oc} value of 0.957 V, a J_{sc} value of 25.06 mA cm⁻² and an FF of 69.70%. Impressively, the PM6:**CH-Bzq-Br** device achieved a high PCE of 19.42%, with an enhanced J_{sc} value of 26.95 mA cm⁻² and an improved FF of 77.26%, and nearly maintained a high V_{oc} value of 0.933 V. The efficiency distribution box plots for 20 independent devices (see the detailed device parameters in Tables S9–S12, ESI†) are displayed in Fig. 2b. It is clear that **CH-Bzq-Br**-based devices exhibit a narrower efficiency distribution compared to **CH-PHE**- and **CH-Bzq**-based devices. The average PCEs also follow the same trend.

Currently, the majority of high-performance OSCs are fabricated with the halogenated solvent CF, due to its excellent solubility for active layer materials. However, CF presents serious challenges for large-scale organic photovoltaic module fabrication due to its low boiling point and high toxicity.^{47,48} Thus, utilizing green solvents with higher boiling points is essential for developing efficient large-area modules, significantly impacting the commercial application of OSCs in the future.^{49,50} Considering the high efficiency of the PM6:CH-Bzq-Br blend and its good solubility in the non-halogen green solvent o-xy, we fabricate OSCs using o-xy as a processed solvent. As shown in Fig. 2a, the o-xy-processed device achieved a PCE of 18.89% with a J_{sc} value of 27.04 mA cm⁻², a V_{oc} value of 0.920 V and an FF of 75.94%. Fig. 2c shows a comparison of our result with other reported non-halogenated solvent-processed binary devices, demonstrating competitive performance (Table S13, ESI⁺).

External quantum efficiency (EQE) spectra of optimal devices are shown in Fig. 2d. Among these devices, PM6:CH-PHE shows the lowest EQE response and narrowest range. In contrast, PM6:CH-Bzq exhibits an obviously enhanced EQE response in the range of 450-850 nm, with the EQE curve edge at 882 nm. With further increased core asymmetry, the PM6:CH-Bzq-Br-based device demonstrates the highest EQE response over 80% in the range of 500-820 nm, with the highest value of 92.9% at 600 nm, and the EQE curve edge red-shifted to 902 nm. The higher EQE response in the range of 500-850 nm and a broader EQE range of CH-Bzq-Br-based OSCs are attributed to the improved exciton kinetics behavior and reduced recombination as discussed below, leading to the highest Jsc value. The integrated Jsc values derived from EQE curves were 21.19, 24.14, 26.36 and 25.97 mA cm⁻² for CH-PHE-, CH-Bzq-, CH-Bzq-Br- and CH-Bzq-Br in o-xy-based devices, respectively, matching well with the *I*_{sc} values obtained from the *I*–*V* curves within 4% mismatch.

Building on the excellent performance of the **CH-Bzq-Br**based small area device, we further fabricated a large-area module processed with *o*-xy *via* blade-coating. The detailed

| Table 1 The optical and electrochemical properties of CH-PHE, CH-Bzq and CH-Bzq-Br | | | | | | | | | | | |
|--|-----------------------------|---|----------------------|--|------------------------------------|---|----------------------------|--|--|--|--|
| Acceptors | λ_{\max}^{sol} (nm) | $\lambda_{\max}^{\mathrm{film}}\left(\mathrm{nm} ight)$ | $\Delta\lambda$ (nm) | $\lambda_{\mathrm{onset}}^{\mathrm{film}}\left(\mathrm{nm}\right)$ | $E_{g}^{\operatorname{opt}a}$ (eV) | $E_{\rm HOMO}^{b}$ (eV) | E_{LUMO}^{b} (eV) | | | | |
| CH-PHE | 750 | 791 | 41 | 879 | 1.41 | -5.63 | -3.70 | | | | |
| CH-Bzq CH-Bzq-B | 744 sr 740 | 795 799 | 51 59 | 881 875 | 1.40 1.41 | $\begin{array}{c} -5.67 \\ -5.71 \end{array}$ | $-3.74 \\ -3.79$ | | | | |

^{*a*} Optical band gap was calculated using 1240/ $\lambda_{\text{onset}}^{\text{film}}$. ^{*b*} The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the onset oxidation potential and the onset reduction potential using the equations: $E_{\text{HOMO}} = -(4.80 + E_{\text{ox}}^{\text{onset}}) \text{ eV}$ and $E_{\text{LUMO}} = -(4.80 + E_{\text{ox}}^{\text{onset}}) \text{ eV}$.



Fig. 2 (a) J-V curves of the optimal device based on PM6:acceptors. (b) Box plots of the PCE distribution for devices under corresponding conditions of AM 1.5G and 100 mA cm⁻². (c) Plots of PCE *versus* V_{oc} for the binary OSCs fabricated with *o*-xy with a PCE of over 16% reported in the literature and this work. (d) EQE curves of the optimal device based on PM6:acceptors. (e) The corresponding J-V curve of the PM6:**CH-Bzq-Br**-based large-area OSC modules. (f) The photograph of the blade-coated large-area OSC modules processed with *o*-xy on 5.2×5.5 cm² substrate (effective area = 13.5 cm²). (g) Plots of the PCE *versus* area for the OSC modules with an effective area over 10 cm² reported in the literature and this work. (h) Statistical diagram of detailed energy loss for the optimized device, where ΔE_3^a was obtained using $\Delta E_3^a = E_{loss} - \Delta E_1 - \Delta E_2$, and ΔE_3^b was obtained using the equation $\Delta E_3 = -kT \ln(\text{EQE}_{\text{EL}})$. (i) Plots of the asymmetrical acceptor materials reported in the literature and this work.

preparation process is provided in the ESI[†] and the module schematic diagram is shown in Fig. S40 and S41 (ESI[†]). After initial optimization, an impressive PCE of 16.08% with a $V_{\rm oc}$ value of 5.42 V, a $J_{\rm sc}$ value of 4.09 mA cm⁻², and an FF of 72.60% (Fig. 2e) was achieved for the module. The photograph of the modules, consisting of six sub-cells connected in series with an

effective area of 13.5 cm² is displayed in Fig. 2f. Fig. 2g illustrates the development of large-area modules by plotting PCE against the area, with our work ranking among the highest (Table S14, ESI[†]), providing an effective approach to achieving high-performance large-area modules processed with green solvents through straightforward molecular design.

| Table 2 Summary of device parameters for optimized OSCs ^a | | | | | | | | | | | |
|--|---|---|--|--|---|--|--|--|--|--|--|
| Active layers | $V_{\rm oc}$ (V) | $J_{\rm sc} ({ m mA}{ m cm}^{-2})$ | Cal. $J_{\rm sc}^{\ b}$ (mA cm ⁻²) | FF (%) | PCE (%) | | | | | | |
| PM6:C H-PHE PM6:C H-Bzq PM6:C H-Bzq-Br PM6:C H-Bzq-Br in <i>o</i> -xy | $\begin{array}{c} 0.944 \; (0.949 \pm 0.004) \\ 0.957 \; (0.955 \pm 0.003) \\ 0.933 \; (0.928 \pm 0.002) \\ 0.920 \; (0.915 \pm 0.004) \end{array}$ | $\begin{array}{c} 21.91 \ (21.61 \pm 0.22) \\ 25.06 \ (24.41 \pm 0.28) \\ 26.95 \ (27.09 \pm 0.19) \\ 27.04 \ (26.97 \pm 0.27) \end{array}$ | 21.19 24.14 26.36 25.97 | $\begin{array}{c} 73.52 \ (71.61 \pm 1.61) \\ 69.70 \ (70.29 \pm 0.79) \\ 77.26 \ (76.32 \pm 0.53) \\ 75.94 \end{array}$ | $\begin{array}{c} 15.20 \; (14.71 \pm 0.36) \\ 16.71 \; (16.41 \pm 0.21) \\ 19.42 \; (19.21 \pm 0.10) \\ 18.89 \; (18.67 \pm 0.13) \end{array}$ | | | | | | |

^a The average parameters afforded by 20 independent devices and the device area is 0.04 cm². ^b Current densities calculated from EQE curves.

The three acceptor-based devices all showed a high $V_{\rm oc}$ value exceeding 0.9 V. In order to investigate the influence of the atom-level chemical structure variation on V_{oc} , the energy loss (E_{loss}) analysis was conducted following the established method.⁵¹ E_{loss} can be divided into three components: E_{loss} = $E_{\rm g} - qV_{\rm oc} = (E_{\rm g} - qV_{\rm oc}^{\rm SQ}) + (qV_{\rm oc}^{\rm SQ} - qV_{\rm oc}^{\rm rad}) + (qV_{\rm oc}^{\rm SQ} - qV_{\rm oc}) = (E_{\rm g} - qV_{\rm oc}^{\rm SQ}) + (qV_{\rm oc}^{\rm rad-below \, gap}) + qV_{\rm oc}^{\rm non-rad} = \Delta E_1 + \Delta E_2 + \Delta E_3$, where $E_{\rm g}$ is the band gap, $V_{\rm oc}^{\rm SQ}$ is the maximum $V_{\rm oc}$ according to Shockley-Queisser (SQ) theory, and $V_{\rm oc}^{\rm rad}$ is the $V_{\rm oc}$ considering only radiative recombination. Each term represents a distinct energy loss mechanism. ΔE_1 is the radiative loss above the bandgap. It is unavoidable for any type of solar cell under standard conditions but can be minimized with strict light management strategies.⁵² ΔE_2 is the sub-bandgap radiative loss. In OSCs, charge transfer (CT) states contribute to a larger ΔE_2 compared to inorganic solar cells, as CT states typically lie at lower energies than the bandgap. Additionally, the reorganization energy and energetic disorder of the active layer films influence ΔE_2 by affecting band tail absorption. Reducing CT states and minimizing the energy difference between the singlet exciton on the donor and/or acceptor can help decrease ΔE_2 .⁵³ ΔE_3 is also referred to as nonradiative recombination energy loss $(\Delta E_{\rm nr})$. It is the dominant loss factor in OSCs and arises from the non-radiative decay of charge transfer states and the recombination of free charges. ΔE_3 can be determined from the electroluminescence external quantum efficiency (EQE_{EL}) using the equation: $\Delta E_3 = -kT \ln(\text{EQE}_{\text{EL}})$, where k is the Boltzmann constant and T is the Kelvin temperature.^{54–58} The detailed analysis data of the three acceptor-based devices are summarized in Table S15 (ESI^{\dagger}). The E_g values of all the blend films were estimated via the derivatives of the sensitive EQE (EQE_{PV}) spectra, as plotted in Fig. S42 (ESI[†]). The E_{σ} values of PM6:CH-PHE, PM6:CH-Bzq PM6:CH-Bzq-Br and PM6:CH-Bzq-Br in o-xy systems are 1.478, 1.486, 1.432 and 1.431 eV, resulting in the overall E_{loss} values of 0.534, 0.529, 0.499 and 0.511 eV, respectively. A detailed comparison of E_{loss} parameters is depicted in Fig. 2h. All devices show similar ΔE_1 values of 0.270, 0.270, 0.266 and 0.266 eV. Note that the CH-PHE-based device shows the largest ΔE_2 of 0.094 eV compared to other devices, correlating with the most unordered molecular packing of CH-PHE, as supported by its maximum Urbach energy $(E_{\rm u})$ of 25.46 meV, larger than those of CH-Bzq (22.74 meV), CH-Bzq-Br (21.54 meV) and CH-Bzq-Br in o-xy (22.25 meV) (Fig. S43, ESI[†]). These results were further confirmed by its Stokes shifts as provided in Fig. S44 (ESI[†]). As shown in Fig. S45 (ESI[†]), CH-PHE-, CH-Bzq-, CH-Bzq-Br and CH-Bzq-Br in o-xy-based devices exhibit EQE_{EL} values of 6.94 \times 10⁻⁴, 5.36 \times 10⁻⁴, 5.68 \times 10⁻⁴ and 4.07 \times 10⁻⁴, corresponding to ΔE_3 values of 0.188, 0.195, 0.193 and 0.202 eV, respectively, following the equation of $\Delta E_3 = -kT \ln(\text{EQE}_{\text{EL}})$. According to the above analysis, CH-**Bzq-Br**-based device balances J_{sc} and V_{oc} with minimal E_{loss} , which highlights the potential of asymmetric acceptors in reducing E_{loss} and is essential for achieving high efficiency (Fig. 2i and Table S16, ESI[†]).

The properties of the charge recombination, exciton dissociation and charge transport of the three devices were investigated via a series of tests. To investigate the charge recombination characteristics for the three acceptor-based devices, the current density-voltage curves at varying light intensities (Plight) were obtained. The relationship between V_{oc} and P_{light} can be described as $V_{\rm oc} \propto (nkT/q)\ln(P_{\rm light})$, where k is the Boltzmann constant, T is the absolute temperature and q is the elemental charge. With regard to the relationship between P_{light} and V_{oc} , the slopes are fitted to be 1.432kT/q for PM6:CH-PHE, 1.107kT/qfor PM6:CH-Bzq- and 1.104kT/q for the PM6:CH-Bzq-Br-based device (Table S17, ESI⁺). The smaller slope close to 1 in the PM6:CH-Bzq-Br device indicates well-suppressed trap-assisted recombination, compared with PM6:CH-Bzq-based devices, contributing to high J_{sc} and FF. To study the behavior of charge recombination of the three devices, the plots of light-intensity dependence (P) of J_{sc} ($J_{sc} \propto P^{\alpha}$), where the exponent of α being close to 1 reflects a weak bimolecular recombination, were measured (Fig. S46, ESI^{\dagger}). The J_{sc} values of all the devices were highly linearly correlated with P, with the α values approaching 1, illustrating that these devices showed efficient charge dissociation and less bimolecular recombination.59,60 Charge transport properties in blend films were characterized using the spacecharge-limited current (SCLC) method, yielding the hole mobility ($\mu_{\rm h}$) and electron mobility ($\mu_{\rm e}$). (Fig. S47, ESI[†]). The calculated values of $\mu_{\rm h}/\mu_{\rm e}$ are 2.73/1.57, 2.96/1.88 and 3.28/2.73 \times 10⁻⁴ cm² V⁻¹ s⁻¹ for CH-PHE-, CH-Bzq- and CH-Bzq-Br-based blends. The highest charge mobilities in CH-Bzq-Br-based blend support its superior charge transport, in comparison to CH-PHEand **CH-Bzq**-based blends. Additionally, a more balanced $\mu_{\rm b}/\mu_{\rm e}$ ratio (1.20) for the PM6:CH-Bzq-Br blend was obtained compared to those of PM6:CH-PHE (1.74) and PM6:CH-Bzq (1.57) blends. The enhanced charge mobilities and well balanced $\mu_{\rm b}/\mu_{\rm e}$ ratio in the CH-Bzq-Br-based blend contributed to the improved FF and Jsc. 61,62

Grazing-incidence wide angle X-ray scattering (GIWAXS) measurement was employed to investigate the effect of the atom-level asymmetric molecular design strategy on molecular packing and orientation in neat and blend films. The 2D GIWAXS patterns and line-cut profiles of the two acceptor-based neat films and blend films are shown in Fig. 3, and the detailed parameters are summarized in Tables S18 and S19 (ESI⁺). All three acceptors show preferential face-on orientation, characterized by pronounced π - π packing (010) peaks in the out-of-plane (OOP) direction at 1.673, 1.685 and 1.690 \AA^{-1} and sharp lamellar (100) peaks at 0.280, 0.275 and 0.277 \AA^{-1} in the in-plane (IP) direction for CH-PHE, CH-Bzq and CH-Bzq-Br. Although the three acceptors showed similar *d*-spacing distances, CH-Bzq-Br displayed the largest crystal coherence length (CCL) of 23.75 Å compared to 20.86 Å for CH-PHE and 22.16 Å for CH-Bzq in the OOP direction, indicating the enhanced π - π packing ordering. Upon blending with PM6, the three blends can still maintain a face-on orientation. The π - π packing (010) peaks in the OOP direction for the three blend films are located at 1.660, 1.732 and 1.723 \AA^{-1} , corresponding to the π - π stacking distances of 3.78, 3.62 and 3.64 Å, respectively. In the OOP direction, crystal coherence length (CCL) values were 22.52 Å for PM6:CH-PHE, 23.85 Å for PM6:CH-Bzq and 24.68 Å for PM6:CH-Bzq-Br. These results are consistent



Fig. 3 2D GIWAXS patterns of (a) CH-PHE, CH-Bzq and CH-Bzq-Br pristine films and (b) optimized PM6:CH-PHE, PM6:CH-Bzq and PM6:CH-Bzq-Br blend films. (c) The corresponding in-plane (IP) and out-of-plane (OOP) extracted line-cut profiles of CH-PHE, CH-Bzq and CH-Bzq-Br-based pristine and blend films.

with the charge mobilities of the blend films. The largest CCL value in the (010) direction in the **CH-Bzq-Br**-based blend was beneficial for improving charge transport and suppressing charge recombination. Such a pronounced face-on orientation with enhanced crystallinity for **CH-Bzq-Br** could be responsible for improved charge transport properties and suppressed bimolecular charge recombination,⁶³ leading to the improved J_{sc} and FF in comparison with PM6:**CH-PHE** and PM6:**CH-Bzq** based devices.

The morphology of blend films in OSCs plays an essential role in photovoltaic performance.^{23,64} The miscibility between PM6 and acceptors was correlated with the phase separation of blends, as assessed by contact angle tests (Fig. S48, ESI[†]), and the relevant data are summarized in Table S20 (ESI[†]). Among the three acceptors, CH-Bzq-Br exhibits clearly reduced surface energies (γ) of 31.82 mN m⁻¹, compared to CH-PHE $(34.22 \text{ mN m}^{-1})$ and CH-Bzq $(33.66 \text{ mN m}^{-1})$. The miscibility between the donor and acceptors can be evaluated using the Flory-Huggins interaction parameter (χ), which is calculated using the equation $\chi_{D:A} = K(\sqrt{\gamma_D} - \sqrt{\gamma_A})^2$. The χ values are 0.33 K for PM6:CH-PHE, 0.28 K for PM6:CH-Bzq and 0.13 K for PM6:CH-Bzq-Br. The lower γ value in PM6:CH-Bzq-Br implies favorable miscibility between PM6 and CH-Bzq-Br, which is beneficial for forming more donor/acceptor interfaces, favoring charge separation and producing high J_{sc} . Atomic force microscopy (AFM) was used to analyse morphologies of the three blend films, as displayed in Fig. 4. The PM6:CH-Bzq-Br blend film showed minimum root-mean-square surface roughness (R_{α}) with a value of 1.68 nm compared with PM6:CH-PHE (2.10 nm) and PM6:CH-Bzq (1.89 nm), which should be attributed to good miscibility between PM6 and CH-Bzq-Br. According to the phase images, PM6:CH-Bzq-Br shows a clear interpenetrating structure. This result was further confirmed by atomic force microscopy-based infrared spectroscopy (AFM-IR) measurement, using a specific IR absorption at 2216 cm^{-1} of the CN groups on the three acceptors. As shown in Fig. 4c, compared to the clear and obvious separation in the blend film of PM6:CH-PHE and PM6:CH-Bzq, the PM6:CH-Bzq-Br blend film showed an interpenetrating structure with proper phase separation, which is consistent with the above miscibility results. The favorable morphology and optimal phase separation formed in the PM6:CH-Bzq-Br-based device were consistent with their better miscibility, improved charge transport and a high J_{sc} and FF.

Conclusions

In this work, we propose a novel atom-level asymmetric molecular design strategy to design and synthesize two asymmetric

Energy & Environmental Science



Fig. 4 (a) AFM height, (b) phase images and (c) tapping AFM-IR images at a wavenumber of 2216 cm⁻¹ for optimized PM6:**CH-PHE**, PM6:**CH-Bzq** and PM6:**CH-Bzq-Br** blend films (2 μ m × 2 μ m), where the blue part represents the donor domain, and red and yellow parts represent the domain containing acceptors.

acceptors, CH-Bzq and CH-Bzq-Br. Compared to the control molecule CH-PHE, even a minor variation in the central core asymmetry led to significant changes in the molecular packing behavior, donor-acceptor interactions and active layer morphology, thus influencing carrier dynamics and overall device performance. As a result, a high PCE of 19.42% was achieved for PM6:CH-Bzq-Br-based binary OSCs due to the improved carrier dynamics and superior active layer morphology. This represents one of the highest PCE values reported for asymmetric acceptor-based binary systems to date. Remarkably, when the green solvent o-xy was used as the processing solvent, an impressive PCE of 16.08% was obtained in a 13.5 cm² module, highlighting the scalability and practical applicability of our approach. Our work not only introduces an effective molecular design strategy for constructing highly efficient acceptors but also paves a promising pathway for advancing the development of green solvent processed OSCs. This strategy is expected to play a crucial role in further enhancing the performance and commercial viability of organic photovoltaics in the future.

Author contributions

The synthesis studies were carried out by J. L., and three acceptors were characterized by J. L., and R. W. carried out most of the device fabrication and measurements. L. L. performed the large-area module experiments and analysed the data. W. Z. and G. L. carried out the theoretical computation of the three acceptors. Z. S. performed the contact angle tests and analysed the data. W. S. performed the GIWAXS characterization and analysed the data. X. W. and Y. C. supervised and directed this project. J. L., X. W. and Y. C. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789–1791.
- 2 H. Chen, Y. Zou, H. Liang, T. He, X. Xu, Y. Zhang, Z. Ma, J. Wang, M. Zhang, Q. Li, C. Li, G. Long, X. Wan, Z. Yao and Y. Chen, *Sci. China: Chem.*, 2022, **65**, 1362–1373.
- 3 G. Wang, M. A. Adil, J. Zhang and Z. Wei, *Adv. Mater.*, 2019, **31**, 1805089.
- 4 C. Chen, L. Wang, W. Xia, K. Qiu, C. Guo, Z. Gan, J. Zhou,
 Y. Sun, D. Liu, W. Li and T. Wang, *Nat. Commun.*, 2024,
 15, 6865.
- 5 Z. Chen, J. Ge, W. Song, X. Tong, H. Liu, X. Yu, J. Li, J. Shi, L. Xie, C. Han, Q. Liu and Z. Ge, *Adv. Mater.*, 2024, 36, 2406690.
- 6 S. Guan, Y. Li, C. Xu, N. Yin, C. Xu, C. Wang, M. Wang, Y. Xu, Q. Chen, D. Wang, L. Zuo and H. Chen, *Adv. Mater.*, 2024, **36**, 2400342.
- 7 Y. Jiang, S. Sun, R. Xu, F. Liu, X. Miao, G. Ran, K. Liu, Y. Yi,
 W. Zhang and X. Zhu, *Nat. Energy*, 2024, 9, 975–986.
- 8 C. Li, G. Yao, X. Gu, J. Lv, Y. Hou, Q. Lin, N. Yu, M. S. Abbasi, X. Zhang, J. Zhang, Z. Tang, Q. Peng, C. Zhang, Y. Cai and H. Huang, *Nat. Commun.*, 2024, **15**, 8872.
- 9 N. Wei, J. Chen, Y. Cheng, Z. Bian, W. Liu, H. Song, Y. Guo,
 W. Zhang, Y. Liu, H. Lu, J. Zhou and Z. Bo, *Adv. Mater.*, 2024,
 36, 2408934.
- L. Zhu, M. Zhang, G. Zhou, Z. Wang, W. Zhong, J. Zhuang, Z. Zhou, X. Gao, L. Kan, B. Hao, F. Han, R. Zeng, X. Xue, S. Xu, H. Jing, B. Xiao, H. Zhu, Y. Zhang and F. Liu, *Joule*, 2024, 8, 3153–3168.
- 11 B. Kan, M. Li, Q. Zhang, F. Liu, X. Wan, Y. Wang, W. Ni,
 G. Long, X. Yang, H. Feng, Y. Zuo, M. Zhang, F. Huang,
 Y. Cao, T. P. Russell and Y. Chen, *J. Am. Chem. Soc.*, 2015,
 137, 3886–3893.
- 12 J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li and Y. Zou, *Joule*, 2019, 3, 1140–1151.
- 13 Y. Shi, Y. Chang, K. Lu, Z. Chen, J. Zhang, Y. Yan, D. Qiu, Y. Liu, M. A. Adil, W. Ma, X. Hao, L. Zhu and Z. Wei, *Nat. Commun.*, 2022, **13**, 3256.

- 14 W. Gao, T. Liu, R. Sun, G. Zhang, Y. Xiao, R. Ma, C. Zhong, X. Lu, J. Min, H. Yan and C. Yang, *Adv. Sci.*, 2020, 7, 1902657.
- 15 W. Gao, T. Liu, C. Zhong, G. Zhang, Y. Zhang, R. Ming, L. Zhang, J. Xin, K. Wu, Y. Guo, W. Ma, H. Yan, Y. Liu and C. Yang, ACS Energy Lett., 2018, 3, 1760–1768.
- 16 W. Gao, M. Zhang, T. Liu, R. Ming, Q. An, K. Wu, D. Xie, Z. Luo, C. Zhong, F. Liu, F. Zhang, H. Yan and C. Yang, *Adv. Mater.*, 2018, **30**, 1800052.
- 17 M. Li, Y. Zhou, J. Zhang, J. Song and Z. Bo, *J. Mater. Chem. A*, 2019, 7, 8889–8896.
- 18 X. Li, C. Li, L. Ye, K. Weng, H. Fu, H. S. Ryu, D. Wei, X. Sun, H. Y. Woo and Y. Sun, *J. Mater. Chem. A*, 2019, 7, 19348–19354.
- 19 J. Song, C. Li, L. Ye, C. Koh, Y. Cai, D. Wei, H. Y. Woo and Y. Sun, *J. Mater. Chem. A*, 2018, **6**, 18847–18852.
- 20 J. Zhang, W. Liu, S. Chen, S. Xu, C. Yang and X. Zhu, J. Mater. Chem. A, 2018, 6, 22519–22525.
- 21 C. He, Z. Chen, T. Wang, Z. Shen, Y. Li, J. Zhou, J. Yu, H. Fang, Y. Li, S. Li, X. Lu, W. Ma, F. Gao, Z. Xie, V. Coropceanu, H. Zhu, J.-L. Bredas, L. Zuo and H. Chen, *Nat. Commun.*, 2022, **13**, 2598.
- 22 S. Li, L. Zhan, Y. Jin, G. Zhou, T.-K. Lau, R. Qin, M. Shi, C.-Z. Li, H. Zhu, X. Lu, F. Zhang and H. Chen, *Adv. Mater.*, 2020, **32**, 2001160.
- 23 S. Li, L. Zhan, N. Yao, X. Xia, Z. Chen, W. Yang, C. He, L. Zuo, M. Shi, H. Zhu, X. Lu, F. Zhang and H. Chen, *Nat. Commun.*, 2021, **12**, 4627.
- 24 Z. Luo, R. Ma, T. Liu, J. Yu, Y. Xiao, R. Sun, G. Xie, J. Yuan, Y. Chen, K. Chen, G. Chai, H. Sun, J. Min, J. Zhang, Y. Zou, C. Yang, X. Lu, F. Gao and H. Yan, *Joule*, 2020, 4, 1236–1247.
- 25 R. Sun, Y. Wu, X. Yang, Y. Gao, Z. Chen, K. Li, J. Qiao, T. Wang, J. Guo, C. Liu, X. Hao, H. Zhu and J. Min, *Adv. Mater.*, 2022, **34**, 2110147.
- 26 L. Zhan, S. Li, Y. Li, R. Sun, J. Min, Z. Bi, W. Ma, Z. Chen, G. Zhou, H. Zhu, M. Shi, L. Zuo and H. Chen, *Joule*, 2022, 6, 662–675.
- 27 S. Chen, S. Zhu, L. Hong, W. Deng, Y. Zhang, Y. Fu, Z. Zhong, M. Dong, C. Liu, X. Lu, K. Zhang and F. Huang, *Angew. Chem., Int. Ed.*, 2024, **63**, e202318756.
- 28 C. Kim, S. Chen, J. S. Park, G.-U. Kim, H. Kang, S. Lee, T. N.-L. Phan, S.-K. Kwon, Y.-H. Kim and B. J. Kim, *J. Mater. Chem. A*, 2021, **9**, 24622–24630.
- 29 Y.-J. Su, H. Nie, C.-F. Chang, S.-C. Huang, Y.-H. Huang, T.-W. Chen, K.-K. Hsu, T.-Y. Lee, H.-M. Shih, C.-W. Ko, J.-T. Chen and C.-S. Hsu, ACS Appl. Mater. Interfaces, 2021, 13, 59043–59050.
- 30 T. Li, K. Wang, G. Cai, Y. Li, H. Liu, Y. Jia, Z. Zhang, X. Lu,
 Y. Yang and Y. Lin, *JACS Au*, 2021, 1, 1733–1742.
- 31 W. Gao, H. Fu, Y. Li, F. Lin, R. Sun, Z. Wu, X. Wu, C. Zhong, J. Min, J. Luo, H. Y. Woo, Z. Zhu and A. K. Y. Jen, *Adv. Energy Mater.*, 2021, **11**, 2003177.
- 32 X. Si, W. Shi, R. Wang, W. Zhao, Z. Suo, Z. Fu, G. Long, X. Hao, Z. Yao, X. Wan, C. Li and Y. Chen, *Nano Energy*, 2024, **131**, 110204.
- J. Wang, H. Chen, X. Xu, Z. Ma, Z. Zhang, C. Li, Y. Yang,
 J. Wang, Y. Zhao, M. Zhang, X. Wan, Y. Lu and Y. Chen, *J. Mater. Chem. A*, 2022, **10**, 16714–16721.

- 34 C. Yang, Q. An, H.-R. Bai, H.-F. Zhi, H. S. Ryu, A. Mahmood,
 X. Zhao, S. Zhang, H. Y. Woo and J.-L. Wang, *Angew. Chem.*,
 Int. Ed., 2021, **60**, 19241–19252.
- 35 J. Qu, D. Li, H. Wang, J. Zhou, N. Zheng, H. Lai, T. Liu, Z. Xie and F. He, *Chem. Mater.*, 2019, **31**, 8044–8051.
- 36 C. Zhang, T. Liu, J.-L. Wang, K.-K. Liu, C. Yang, H.-J. Zhang, R. Ma and H. Yan, *Sol. RRL*, 2020, 4, 2000212.
- 37 H. Liang, X. Bi, H. Chen, T. He, Y. Lin, Y. Zhang, K. Ma,
 W. Feng, Z. Ma, G. Long, C. Li, B. Kan, H. Zhang,
 O. A. Rakitin, X. Wan, Z. Yao and Y. Chen, *Nat. Commun.*, 2023, 14, 4707.
- 38 M. P. De Haas and J. M. Warman, *Chem. Phys.*, 1982, 73, 35–53.
- 39 C. Dehu, F. Meyers and J. L. Bredas, J. Am. Chem. Soc., 1993, 115, 6198–6206.
- 40 Y. Cai, C. Xie, Q. Li, C. Liu, J. Gao, M. H. Jee, J. Qiao, Y. Li, J. Song, X. Hao, H. Y. Woo, Z. Tang, Y. Zhou, C. Zhang, H. Huang and Y. Sun, *Adv. Mater.*, 2023, 35, 2208165.
- 41 W. Liu, S. Sun, L. Zhou, Y. Cui, W. Zhang, J. Hou, F. Liu, S. Xu and X. Zhu, *Angew. Chem., Int. Ed.*, 2022, 61, e202116111.
- 42 Y. Zou, H. Chen, X. Bi, X. Xu, H. Wang, M. Lin, Z. Ma, M. Zhang, C. Li, X. Wan, G. Long, Y. Zhaoyang and Y. Chen, *Energy Environ. Sci.*, 2022, 15, 4000.
- 43 P. Politzer and J. S. Murray, Struct. Chem., 2021, 32, 623-629.
- 44 T. Duan, J. Wang, X. Zuo, X. Bi, C. Zhong, Y. Li, Y. Long, K. Tu, W. Zhang, K. Yang, H. Zhou, X. Wan, Y. Zhao, B. Kan and Y. Chen, *Mater. Horiz.*, 2024, **11**, 4413–4423.
- 45 C. He, Z. Bi, Z. Chen, J. Guo, X. Xia, X. Lu, J. Min, H. Zhu,
 W. Ma, L. Zuo and H. Chen, *Adv. Funct. Mater.*, 2022,
 32, 2112511.
- 46 Y. Gong, T. Zou, X. Li, S. Qin, G. Sun, T. Liang, R. Zhou, J. Zhang, J. Zhang, L. Meng, Z. Wei and Y. Li, *Energy Environ. Sci.*, 2024, 17, 6844–6855.
- 47 X. Fang, S. Park, T. Saito, R. Tunnicliffe, A. L. Ganesan, M. Rigby, S. Li, Y. Yokouchi, P. J. Fraser, C. M. Harth, P. B. Krummel, J. Mühle, S. O'Doherty, P. K. Salameh, P. G. Simmonds, R. F. Weiss, D. Young, M. F. Lunt, A. J. Manning, A. Gressent and R. G. Prinn, *Nat. Geosci.*, 2019, **12**, 89–93.
- 48 A. J. Zuckerman, J. Clin. Pathol., 1995, 48, 691.

- 49 X. Dong, Y. Jiang, L. Sun, F. Qin, X. Zhou, X. Lu, W. Wang and Y. Zhou, *Adv. Funct. Mater.*, 2022, 32, 2110209.
- 50 S. Yoon, S. Park, S. H. Park, S. Nah, S. Lee, J.-W. Lee, H. Ahn, H. Yu, E.-Y. Shin, B. J. Kim, B. K. Min, J. H. Noh and H. J. Son, *Joule*, 2022, 6, 2406–2422.
- 51 J. Yao, T. Kirchartz, M. S. Vezie, M. A. Faist, W. Gong, Z. He, H. Wu, J. Troughton, T. Watson, D. Bryant and J. Nelson, *Phys. Rev. Appl.*, 2015, 4, 014020.
- 52 U. Rau, U. W. Paetzold and T. Kirchartz, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, **90**, 035211.
- 53 J. Liu, S. Chen, D. Qian, B. Gautam, G. Yang, J. Zhao, J. Bergqvist, F. Zhang, W. Ma, H. Ade, O. Inganäs, K. Gundogdu, F. Gao and H. Yan, *Nat. Energy*, 2016, 1, 16089.
- 54 T. Kirchartz, U. Rau, M. Kurth, J. Mattheis and J. H. Werner, *Thin Solid Films*, 2007, **515**, 6238–6242.
- 55 R. T. Ross, J. Chem. Phys., 1967, 46, 4590-4593.
- 56 G. Smestad and H. Ries, Sol. Energy Mater. Sol. Cells, 1992, 25, 51–71.
- 57 K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs and J. V. Manca, *Nat. Mater.*, 2009, 8, 904–909.
- 58 U. Rau, Phys. Rev. B: Condens. Matter Mater. Phys., 2007, 76, 085303.
- P. Hartnagel and T. Kirchartz, *Adv. Theory Simul.*, 2020, 3, 2000116.
- 60 U. Würfel, L. Perdigón-Toro, J. Kurpiers, C. M. Wolff, P. Caprioglio, J. J. Rech, J. Zhu, X. Zhan, W. You, S. Shoaee, D. Neher and M. Stolterfoht, *J. Phys. Chem. Lett.*, 2019, **10**, 3473–3480.
- 61 H. Liang, H. Chen, P. Wang, Y. Zhu, Y. Zhang, W. Feng, K. Ma, Y. Lin, Z. Ma, G. Long, C. Li, B. Kan, Z. Yao, H. Zhang, X. Wan and Y. Chen, *Adv. Funct. Mater.*, 2023, 33, 2301573.
- 62 C. M. Proctor, J. A. Love and T.-Q. Nguyen, *Adv. Mater.*, 2014, 26, 5957–5961.
- 63 H. Tang, H. Chen, C. Yan, J. Huang, P. W. K. Fong, J. Lv, D. Hu, R. Singh, M. Kumar, Z. Xiao, Z. Kan, S. Lu and G. Li, *Adv. Energy Mater.*, 2020, **10**, 2001076.
- 64 L. Zhu, M. Zhang, J. Xu, C. Li, J. Yan, G. Zhou, W. Zhong, T. Hao, J. Song, X. Xue, Z. Zhou, R. Zeng, H. Zhu, C.-C. Chen, R. C. I. MacKenzie, Y. Zou, J. Nelson, Y. Zhang, Y. Sun and F. Liu, *Nat. Mater.*, 2022, **21**, 656–663.