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Efficient Modulation of End Groups for the Asymmetric Small Molecule Acceptors Enabling Organic Solar Cells with over 15% Efficiency

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Non-fullerene organic solar cells (OSCs) have attracted tremendous interest and made an impressive breakthrough, largely due to advances in high-performance small molecule acceptors (SMAs). The relationship between short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) is usually shown as one falls and another rises. Controlling the trade-off between J_{sc} and V_{oc} to harvest high power conversion efficiencies (PCEs) still remains as a challenge. Herein, dithieno[3,2-b:2',3'-d]pyrrole (DTP) based asymmetric SMAs with different chlorinated dicyanoindanone-based end groups, named TPIC, TPIC-2Cl and TPIC-4Cl, are designed and synthesized. These asymmetric acceptors exhibit remarkable red-shifted absorption profile, while energy levels are simultaneously down-shifted when the numbers of chlorine atoms alter from 0, 1 to 2, due to the gradually improved electronegativity. As a result, PM7: TPIC-4Cl based OSCs achieved a champion PCE of 15.31%, which is the highest PCEs for non-fullerene binary OSCs based on asymmetric SMAs. The superiority of PM7: TPIC-4Cl system consists of the balanced charge transport, favorable phase separation, efficient exciton dissociation and extraction, coupled with remarkable π - π stacking and crystallinity of the SMAs. Our results highlight the important strategy of asymmetric molecular design to optimize the trade-off between V_{oc} and J_{sc} , reaching a high PCE.

1. Introduction

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Organic solar cells (OSCs) deliver the promising alternatives to conventional Si-based inorganic analogue owing to their advantages, such as low-cost, light-weight, and transparency.^[1-5] Generally, active layers of OSCs consist electron-donors and deficient electron-acceptors. Compared to versatile and highly efficient donors, cost-effective acceptors are still scarce thanks to synthetic challenge and photovoltaic characteristics optimization. Fullerene derivatives such as [6,6]-phenyl- C_{61}/C_{71} -butyric acid methyl ester (PC₆₁BM/PC₇₁BM) and

indene- C_{60}/C_{70} bisadducts (ICBAs) have played a dominant role as high-efficient electron acceptors ^[6-11] in the past two decades due to their excellent charge transport performance. However, the intrinsic defects of fullerene acceptors, such as high cost, narrow and weak absorption in visible region, limited tunability of energy levels, and poor flexibility seriously hindered further development.^[12-21] Therefore, much effort has been devoted to non-fullerene acceptors (NFAs) to overcome abovementioned defects of fullerene molecules. ^[22-24]

The pioneering research of fused-ring acceptor-donoracceptor (A-D-A) NFA, 3,9-bis(2-methylene-(3-(1,1dicyanomethylene)-indanone))-5,5,11,11-tetrakis (4hexylphenyl)-dithieno[2,3-d:2',3'-d']-sindaceno[1,2-b:5,6b ']-dithiophene (ITIC) of Zhan's group challenged the fullerene-based devices, yielded a PCE of up to 6.8% in 2015.^[25] Power conversion efficiencies (PCEs) of NFA based OSCs have been significantly improved and surpassed 16% within four years.^[24, 26-32] ITIC-like acceptors are comprised of ladder-type fused-ring cores (D) peripherally connected with aryl or alkyl side chains, and strong electron-accepting groups (A) endcapped on both sides. The ladder-type fused-ring core plays a crucial role for the delocalization of $\pi\text{-}electrons,^{[33-37]}$ and central cores mainly include IDT,^[38] IDTT^[39] and DTP.^[40] At present, most fused-ring cores are synthesized by symmetric regulation from both sides,^[41-43] which restricts precise tuning of spectral absorption range, molecular packing and orientation. Nevertheless, the asymmetric molecular core can

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Fig. 1 Donor and acceptor materials and their optical properties. (a) Donor PM7 molecular structures; Acceptors TPIC, TPIC-2CI and TPIC-4CI molecular structures. (b) Absorption spectra of TPIC, TPIC-2CI and TPIC-4CI in dichloromethane solutions. (c) Solid-state absorptions for TPIC, TPIC-2CI and TPIC-4CI.

increase the molecular dipole moment and dielectric constant, reducing the exciton binding energy, which is greatly beneficial to exciton dissociation and charge transportation.[44-52]

Meanwhile, end group also matters a lot in burgeoning efficient SMAs. Firstly, end groups can interact with donor cores to reduce the bandgap, leading absorption spectra to near-infrared region.^[53-55] Secondly, close π - π stacking of the end groups can achieve high electron mobility and fill factor (FF).[56-58] Finally, end groups have great influence on the LUMO levels of A-D-A acceptors and the resultant open-circuit voltage (V_{OC}) of the devices.^[59-61] With the increase of electron-withdrawing properties of end groups, a distinct nearinfrared absorption and π - π interaction of the neighboring molecular can be enhanced and thereby the J_{sc} and FF, but the $V_{\rm OC}$ will drop due to the downshifted LUMO energy levels of SMAs.^[62] So how to better harmonize the V_{OC} and J_{SC} to yield a high PCE still remains a big challenge.

Based on the abovementioned considerations, herein we developed three electron acceptors, with an asymmetric dithieno[3,2-b:2',3'-d]pyrrole-like core and end-capped with three different chlorinated dicyanoindanone terminal groups, named TPIC, TPIC-2Cl and TPIC-4Cl with 0, 1, and 2 chlorine atom(s). The photoelectrical properties and OSCs performance of these three SMAs were measured. They exhibited broad absorption ranging from 600 to 900 nm with ultralow bandgap of 1.50, 1.45, and 1.40 eV, respectively. Their HOMOs and LUMOs descended when chlorine atom(s) were changed from 0, 1 to 2. When paired with polymeric donor PM7, PM7: TPIC-4Cl based OSCs achieved a champion PCE of 15.31% with J_{sc} of 23.03 mA cm⁻², a V_{oc} of 0.881 V and FF of 75.5%, outperforming PM7: TPIC (13.33%) and PM7: TPIC-2Cl counterparts (14.53%). The 15.31% PCE is the highest value among binary OSCs with asymmetrical fused core functionalized SMAs. The superiority of PM7: TPIC-4Cl system consists of the more balanced and higher hole and electron mobilities, favorable phase separation, more efficient exciton dissociation, charge transport, and extraction, coupled with remarkable π - π stacking and crystallinity of the SMAs.

2. Results and Discussion

2.1 Material synthesis and characterization

The structures of TPIC, TPIC-2Cl and TPIC-4Cl are shown in Fig. 1a, and the synthetic routes are displayed in Scheme 1. Compound 1 was obtained through the Negishi coupling reaction between 2,5-dibromo-terephthalic acid diethyl ester and thiophen-2-ylzinc chloride (II). Then another Negishi coupling reaction was conducted and compound 2 was synthesized through 1 and N-(2-ethylhexyl)dithieno[3,2-b:2',3'd]pyrrole-2-ylzinc chloride (II). Afterwards, double nucleophilic addition reaction was implemented to convert the ester groups into hydroxyls which were subjected to an acidmediated Friedel-Crafts reaction to yield fused compound 3.

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Without further purification, the crude 3 was converted to the important intermediate 4 by Vilsmeier-Haack reaction using dry DMF and POCl₃, which followed the end-capping by the Knoevenagel condensation with 2-(5,6-dichloro-3-oxo-2,3dihydro-1H-inden-1-ylidene)malononitrile (IC-2Cl) afforded the target product TPIC-4Cl in high yields. The other two asymmetrical analogues (TPIC and TPIC-2CI) were also synthesized according to the similar method. The detailed synthesis procedure is provided in the Supporting Information. The molecular structures of three molecules were characterized by ¹H NMR, ¹³C NMR, and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF). Due to the sp³ carbon linked hexylphenyl side chains and the branched 2-ethylhexyl groups, TPIC, TPIC-2Cl and TPIC-4Cl were readily soluble in common organic solvents, such as dichloromethane (DCM), chloroform (CF) and odichlorobenzene (o-DCB) at room temperature. Furthermore, thermogravimetric analysis indicated that TPIC, TPIC-2Cl and TPIC-4Cl also exhibited excellent thermal stability with decomposition temperature (T_d, 5% weight loss) exceeding 300 °C in the nitrogen atmosphere (Fig. S8).

2.2 Optical properties

UV-Vis absorption spectra of the three SMAs are shown in Fig. 1b and 1c. In dichloromethane solutions, all three acceptors exhibit strong and broad absorption (molar extinction coefficient >10⁵ M⁻¹cm⁻¹) ranging from 600 to 800 nm. The dichlorinated and tetrachlorinated TPIC-2Cl and TPIC-4Cl displayed remarkable and red-shifted intramolecular chargetransfer absorption (ICT) relative to TPIC owing to highly electronegative chlorine atoms. The maximal peaks of TPIC, TPIC-2Cl and TPIC-4Cl are located at 711, 725 and 738 nm, respectively (Table 1). In solid-state films (Fig. 1c), these three asymmetrical SMAs displayed broad and structured vibration shoulder peaks ranging from 600 to 900 nm. Considerable redshifts of 41 (TPIC), 57 (TPIC-2CI) and 66 nm (TPIC-4CI) are observed upon moving from solution to the film state, which demonstrated close π - π stacking interactions could be formed in the films. Furthermore, the optical bandgaps of TPIC, TPIC-2Cl and TPIC-4Cl calculated from solid-state absorption edges are 1.50, 1.45, and 1.40 eV, which

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Fig. 2 (a) J-V curves of PM7: TPIC, PM7: TPIC-2CI and PM7: TPIC-4CI-based devices. (b) EQE curves of the devices. (c) Dark current density-voltage characteristics for electron-only devices with optimized PM7: TPIC, PM7: TPIC-2CI and PM7: TPIC-4CI BHJ films. (d) J_{ph} versus V_{eff} of the optimized devices.

Table 1 Basic Prope	erties of three	SMAs							
Acceptors	λ _{max} ^{a)} (nm)	ε _{max} ^{a)} (M ⁻¹ cm ⁻¹)	λ _{onset} ^{a)} (nm)	λ ^{film} max ^{b)} (nm)	λ ^{film} onset ^{b)} (nm)	E _g ^{opt c)} (eV)	HOMO (eV)	LUMO ^{d)} (eV)	μ _e ^{e)} (cm² V ⁻¹ s ⁻¹)
TPIC	711	2.05 × 10⁵	768	752	826	1.50	-5.30	-3.85	3.66×10 ⁻⁴
TPIC-2CI	725	2.07 × 10 ⁵	780	782	855	1.45	-5.36	-3.92	4.45×10 ⁻⁴
TPIC-4CI	738	2.19 × 10⁵	794	804	885	1.40	-5.35	-3.97	5.15×10-4

^{a)} In a dichloromethane solution. ^{b)} In a neat film. ^{c)} Calculated from empirical the formula: $E_g^{opt} = 1240 / \lambda^{film}_{onset}$. ^{d)} Cyclic voltammetry (CV) method by measuring in dichloromethane. ^{e)} Measured by the space charge limited current (SCLC) method.

Active lever	Annealing	Voc	J _{sc}	calc. J _{sc} ^{b)}	FF	PCE a)
Active layer	(°C)	(V)	(mA cm ⁻²)	(mA cm ⁻²)	(%)	(%)
PM7:TPIC	100°C	1.002 (0.994±0.005)	18.77 (18.59±0.265)	18.50	70.9 (70.8±0.3)	13.33 (13.07±0.159)
PM7:TPIC-2CI	100 °C	0.941 (0.942±0.005)	21.37 (20.85±0.225)	21.10	72.2 (0.725±0.008)	14.53 (14.24±0.216)
PM7:TPIC-4CI	100 °C	0.881 (0.880±0.003)	23.03 (23.02±0.179)	22.81	75.5 (74.0±0.9)	15.31 (14.99±0.162)

^{a)} Mean and mean error values are obtained from 20 devices for each. ^{b)} Values of integration based on IPCE spectra.

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show the gradually decreased trend with the increase of chlorine atoms.

2.3 Electrochemical properties

The electrochemical properties of these three asymmetric SMAs were evaluated by cyclic voltammetry (CV) measurement in anhydrous dichloromethane solution with Ag/AgCl as reference electrodes, the corresponding data are summarized in Table 1. As shown in Fig. S3, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels were estimated through the onset reduction and oxidation potentials according to the equation: $E_{LUMO/HOMO} = - (E_{red/ox} - E_{Fc/Fc^{+}} + 4.8)$ (eV),^[63] assuming the Fc/Fc⁺ to be -4.8 eV.^[64] Thus the LUMO / HOMO of TPIC, TPIC-2Cl and TPIC-4Cl was determined to be -3.85 /- 5.30 eV, - 3.92 / - 5.36 eV and - 3.97 / - 5.35 eV, respectively. These results demonstrated that both the LUMO and HOMO energy levels of chlorinated NFAs (TPIC-2Cl and TPIC-4Cl) are downshifted compared with the nonhalogenated counterpart (TPIC), which could be explained by the electron-withdrawing effect of chlorine atoms. In addition, the molecular energy levels are consistent with the trend of the DFT calculations [65] (Table S1).

2.4 Photovoltaic Properties

The as-synthesized molecules were applied as electronacceptors partnering with the medium bandgap polymer PM7 as electron-donor for complementary absorption and matched energy levels. The traditional device architecture of ITO PEDOT:PSS (indium tin oxide)/ (poly(3,4ethylenedioxythiophene):poly sulfonate))/ (stvrene PM7:acceptor/ PNDIT-F3N (poly[(9,9-bis(3 -(N,Ndimethylamino)propyl)-2,7- fluorene)-alt-5,5 ['] -bis(2,2 thiophene)-2,6-naphthalene-1,4,5,8- tetracaboxylic-N,N di(2-ethylhexyl)imide)/ Ag were fabricated to check the device performance of three acceptors, where PNDIT-F3N was used as the cathode interfacial layer. The corresponding devicefabrication conditions including the donor/acceptor weight ratios, blend-film thickness, and thermal annealing in the active layer were carefully optimized (the detailed optimization process is shown in supporting information). The photovoltaic parameters of the optimized OSCs are summarized in Table 2 with corresponding current densityvoltage (J-V) curves are depicted in Fig. 2a. The optimized PM7: TPIC based OSCs achieved a PCE of 13.33% with a short circuit J_{SC} of 18.77 mAcm⁻², a V_{OC} of 1.002V, and a FF of 70.9%. Interestingly, when using dichlorinated analogue TPIC-2Cl as electron acceptors, the PCE was improved to 14.53%, with a J_{SC} of 21.37 mAcm⁻², a $V_{\rm OC}$ of 0.941 V and FF of 72.2%. The higher

 $J_{\rm SC}$ of the TPIC-Cl-based solar cell than the TPIC-based counterpart is mainly due to its broader absorption. When changed to TPIC-4Cl, the PCE of PM7:TPIC-4Cl is further improved to a champion value of 15.31%, with a $J_{\rm SC}$ of 23.03 mA cm⁻², a $V_{\rm OC}$ of 0.881 V and a *FF* of 75.5%, which is the highest PCE among binary OSCs with asymmetric non-fullerene SMAs. Although $V_{\rm OC}$ is reduced gradually due to the deeper LUMO energy level triggered by electron-withdrawing effect of chlorine atoms, smaller bandgap and broader absorption notably enhanced the corresponding $J_{\rm SC}$. Finally, TPIC-4Cl balanced the level between $V_{\rm OC}$ and $J_{\rm SC}$ best among all three NFAs.

The external quantum efficiency (EQE) measurement of the photovoltaic devices based on TPIC, TPIC-2CI and TPIC-4CI were carried out to exploring the J_{SC} distinction. As shown in Fig. 2b, with the increase of chlorine atoms from TPIC, TPIC-2CI to TPIC-4CI, PM7: acceptor based devices gradually ascend the photoresponse region, which is consistent with the absorption range for the three SMAs. PM7: TPIC-4CI obtained the highest EQE, which is credited to the higher electron mobility.^[66] Furthermore, the integrated J_{SC} of PM7: TPIC, PM7: TPIC-2CI, and PM7: TPIC-4CI from EQE are 18.501, 21.907, 22.809, mA cm⁻², respectively, which exhibited good match with the measured J_{SC} from the J-V curves within 5% error (Table 2).

2.5 Active Layer Charge Transport

Charge transport properties were probed using the SCLC (space charge limited current) method. Single-charge carrier diodes of ITO/MoO_x/organics/MoO_x/Ag structure for hole-only and of ITO/ZnO/organics/PNDIT-F3N/Ag for electron-only devices were evaluated and shown in Fig. 2c, S4 and S5. The extracted mobilities data demonstrated in Table S2. With regard to neat TPIC, TPIC-2Cl and TPIC-4Cl films, the electron mobilities (μ_e s) upward from 6.66 × 10 ⁻⁴, 7.53 × 10 ⁻⁴ to 8.78 × 10 ⁻⁴ cm ² V ⁻¹ s ⁻¹, illustrating the μ_e values of the pristine TPIC films ascend with increasing number of chlorine atoms. This trend was maintained in blend films. The $\mu_e s$ of the corresponding PM7 based blend films were 3.66×10^{-4} , $4.45 \times$ 10^{-4} , and 5.15×10^{-4} cm²V⁻¹s⁻¹. The corresponding μ_{h} s were 6.97×10^{-4} , 7.96 × 10⁻⁴, and 8.49 ×10⁻⁴ cm²V⁻¹s⁻¹. The μ_h/μ_e of TPIC, TPIC-2Cl and TPIC-4Cl blend films were 1.90, 1.78 and 1.64, respectively. It is obviously illustrated that PM7: TPIC-4Cl blend film displayed simultaneously balanced and higher hole and electron mobilities, which is beneficial to the charge transport and thereby higher J_{SC} and FF.^[67]

2.6 Exciton dissociation and charge extraction

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Fig. 3. Film morphology images, AFM height (a, c, e) and phase (b, d, f) images of blend films. a, b) PM7: TPIC, RMS = 0.818 nm; c, d) PM7: TPIC-2CI, RMS = 1.05 nm; e, f) PM7: TPIC-4CI, RMS = 1.17 nm.



Fig. 4 2D GIWAXS patterns of (a) TPIC; (b) TPIC-2CI; (c) TPIC-4CI and (d) PM7: TPIC; (e) PM7: TPIC-2CI; (f) PM7: TPIC-4CI blend films.

To evaluate the exciton dissociation and charge extraction processes, the dependence of photocurrent density (J_{ph}) on the effective voltage (V_{eff}) was measured (Fig. 2d and Table S3). Where $J_{ph} = J_L - J_D$, J_L and J_D represent the photocurrent

density under light and dark conditions. $V_{eff} = V_0 - V_{app}$, where V_0 is the voltage when $J_{ph} = 0$ and V_{app} is the applied external voltage. The saturated photocurrent (J_{sat}) is defined by $J_{sat} = qG_{max}L$, where q means the electric charge, L reflects the

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thickness of the active layer and G_{max} represents the maximum generation rate of excitons dominated in principle by optical absorption. The optimized PM7: TPIC-4Cl achieved a J_{sat} of 23.032 mA cm⁻², obviously higher than PM7: TPIC (18.776 mA



Fig. 5 In-plane (black dotted lines) and out-of-plane (red lines) line-cut profiles of the GIWAXD results.

PM7: TPIC, PM7: TPIC-2Cl, and PM7: TPIC-4Cl based OSCs can be derived by J_{ph} / J_{sat} under short current and maximal power output conditions with the following equations: $\eta_{diss} = J_{sc}$ / J_{sat} and $\eta_{coll} = J_{max}/J_{sat}$.^[65] Consequently, PM7: TPIC-4Cl based OSC devices delivered the maximal values of $\eta_{diss} = 94.9\%$ and $\eta_{coll} =$ 85.1%, obviously exceeded the other two OSCs. Therefore, the efficient exciton dissociation and charge extraction process in PM7: TPIC-4Cl based device contributes to its high J_{sc} and FF.^[68]

2.7 Morphology characterization

The surface morphology of blend film is closely related with photovoltaic performance, so atomic force microscope (AFM) measurements were carried out and presented in Fig. 3 and S6. AFM height images showed that all of blend films displayed clear phase separation, and exhibited root-mean-square roughness (RMS) value of 0.818 nm (PM7: TPIC), 1.05 nm (PM7: TPIC-CI), 1.17 nm (PM7: TPIC-2CI), indicative of their smooth and uniform surface morphology favorable for interface contact. Whereas AFM phase images of the blend films, PM7: TPIC-4CI exhibited relatively bicontinuous interpenetrating network morphology in relative to PM7: TPIC and PM7: TPIC-2CI, which is favorable to exciton dissociation and charge transfer and thus results in high FF.^[69, 70]

2.8 Grazing Incidence Wide-Angle X-ray Scattering (GI-WAXS)

To reveal the intermolecular packing morphology and orientation characteristics of neat and blend films, grazing incidence wide-angle X-ray scattering (GI-WAXS) measurements are performed. Fig. 4 presented the twodimensional (2D) GI-WAXS patterns of three SMAs based neat and blend films and the corresponding cut-line profiles along the in-plane and out-of-plane directions were shown in Fig. 5, the calculated parameters listed in Table S4. The individual components of TPIC, TPIC-2CI and TPIC-4CI displayed similar crystallinity in the horizontal (100) lamellar scattering, and they showed more discernible (010) out-of-plane diffraction peak considering preferential face-on orientation, so as polymer donor PM7 (Fig. S7). With regards to the three blended PM7: SMAs films along the in-plane (IP) direction, PM7: TPIC, PM7: TPIC-2Cl and PM7: TPIC-4Cl showed strong and similar (100) lamellar peaks at $q \approx 0.30$ Å⁻¹ (d ≈ 20.9 Å) with crystalline coherent length (CCL) of 77.02, 82.42 and 83.34 nm. Along the out-of-plane (OOP) direction, all three blend films displayed strong π - π stacking with strong (010) diffraction peak in its q_z direction. The CCL calculated from outof-plane cut-line profiles is 20.56 nm for PM7: TPIC, 21.22 nm for PM7: TPIC-2Cl and 23.89 nm for PM7: TPIC-4Cl systems. The obviously larger coherence length in PM7: TPIC-4Cl blend film indicated the stronger crystallinity than that of the TPIC and TPIC-2Cl-based films, contributing to the charge transport and photovoltaic performance in devices. [68]

cm⁻²) and PM7: TPIC-2Cl (21.371 mA cm⁻²). So we can infer

that G_{max} for PM7: TPIC-4Cl system is significantly higher than

PM7: TPIC-2Cl and PM7: TPIC systems. The probabilities of

exciton dissociation (η_{diss}) and the charge collection (η_{coll}) of

3. Conclusions

In conclusion, dithieno[3,2-b:2',3'-d]pyrrole based asymmetric small molecule acceptors with different chlorinated dicyanoindanone-based end groups, named TPIC, TPIC-2Cl and TPIC-4Cl, are synthesized and characterized. These materials exhibit strong and broad absorption from 600 to 900 nm and optical bandgaps of below 1.50 eV in films. With the increase of chlorine atoms, the absorption edge of the SMAs show significantly red-shifted and gradually decreased optical bandgap, although they also simultaneously cause downshifted LUMO energy levels and notably enhanced electron mobility. When combined with polymer donor PM7, PM7:TPIC-4Cl based OSCs delivered a champion PCE of 15.31% with a relatively low Voc of 0.881 V, significantly enhanced Jsc of 23.03 mA cm⁻² and FF of 75.5%, surpassing the TPIC (PCE = 13.33%) and TPIC-2Cl (PCE = 14.53%) based OSCs. The photovoltaic efficiency of 15.31% is the highest value among binary OSCs based on asymmetric acceptors eve reported.

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These results demonstrate that dithieno[3,2-b:2',3'-d]pyrrolecontaining fused-ring as asymmetric donor core, together with electron-withdrawing chlorinated dicyanoindanone as terminal unit is a successful and expanded strategy to construct highperformance NF-SMAs.

Conflicts of interest

There are no conflicts to declare.

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Three asymmetric SMAs based on dithieno[3,2-b:2',3'-d]pyrrole that exhibit a high efficiency of 15.31%, which is the highest value in asymmetric acceptor-based binary organic solar cells.