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Short Communication

Over 15.5% efficiency organic solar cells with triple sidechain engineered ITIC

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Bulk-heterojunction (BHJ) organic solar cells (OSCs) showcase great advantages in device fabrication via low-cost and convenient solution-processing techniques for diverse applications (e.g., flexible and semitransparent devices) [1,2]. Over the past few years, great research efforts have been made for photovoltaic material development and device optimization, pushing rapidly improved power conversion efficiencies (PCEs) for OSCs. The main driving force lies in the innovation of non-fullerene acceptors (NFAs) [3], especially fused-ring electron acceptors (FREAs) featuring acceptor-donor-acceptor (A-D-A) architecture. Classic FREAs are ITIC [4], INPIC-4F [5], COi8DFIC [6] and Y6 [7]. Nowadays, 15% efficiency for binary OSCs seems to be a key hurdle for newly designed acceptors. FREAs contributing high performance (PCE > 15%) are still limited, most of which belong to the "Y" family (e.g. Y6, Y11 and BTP-4Cl) [8]. In contrast, the OSCs based on classic ITIC series acceptors gradually lag behind in performance. However, the ITIC series FREAs boast their distinct strength in: (i) facile and mature syntheses; (ii) versatile structure modification; (iii) systematic researches on the structure-property relationship. Thus, in order to develop higher performance NFAs, molecular engineering on ITIC is in great demanding.

Our group has devoted significant efforts to modify ITIC via sidechain engineering (Fig. 1a). Sidechains were firstly introduced onto both ends of indacenodithieno[3,2-*b*]thiophene (IT) core to address conformation change due to the rotation of IC moiety along the C–C bond. A conformation locked FREA (called ITC6-IC) was thus designed with an up-shifted lowest unoccupied molecular orbital (LUMO) level, which contributes improved open-circuit voltage (V_{OC}) and fill factor (FF) in OSCs [9]. Large area devices with over 10% PCE were fabricated via layer-by-layer blade-coating J71 and ITC6-IC, outperforming the traditional BHJ counterparts [10]. Secondly, fluorination on IC group of ITC6-IC endows ITC6-4F with broadened absorption and enhanced crystallinity [11]. The optimized morphology of active layer rendered PM7/ITC6-4F with a boosted PCE to 14.47%. Thirdly, electron-donating groups (methyl or methoxy) were introduced into central benzene ring of IT core to develop new FREAs (IM-4F and IOM-4F) with up-shifted energy levels, narrower optical bandgap and enhanced crystallinity [12]. Significantly improved PCEs have been achieved by reducing energy loss from both radiative and nonradiative recombination. In continuing our study, we report herein our exploration of triple sidechain engineering on ITIC (Fig. 1a) to develop low-cost and efficient acceptors for OSCs. The as-designed IMC6-4F contributes a maximum PCE of 15.57% with a FF up to 77.59% by blending with PM6, which is by far the highest efficiency for ITIC-like NFAs based OSCs to date. As shown in Fig. 1a, IMC6-4F can rival Y6 [7], while outperforms less sidechain engineered ITIC analogues such as ITIC [13], ITC6-IC [9], and ITC6-4F [11].

The synthetic routes for IMC6-4F are shown in Schemes S1 and S2 (online). The key intermediate, ethyl-2-chloro-6-hexyl-5-(trimethylsilyl)thieno[3,2-b]thiophene-3- carboxylate [11], was specially developed to couple with 2,2′-(2,5-dimethyl-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). Subsequent ring-closure and deprotection reactions afforded double sidechain engineered IT core (IMC6) in 55% yield. The Vilsmeier-Haack reaction further generated the aldehyde (IMC6-CHO) in high yields (>80%). IMC6-4F was then prepared with Knoevenagel condensation between IMC6-CHO and (2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)) malononitrile[14] in good yields (~75%). IMC6-4F was structurally characterized using ^{1}H NMR, ^{13}C NMR and ^{19}F NMR (Figs. S1–S3 online). IMC6-4F exhibits good solubility in common solvents (e.g., dichloromethane, chloroform, and

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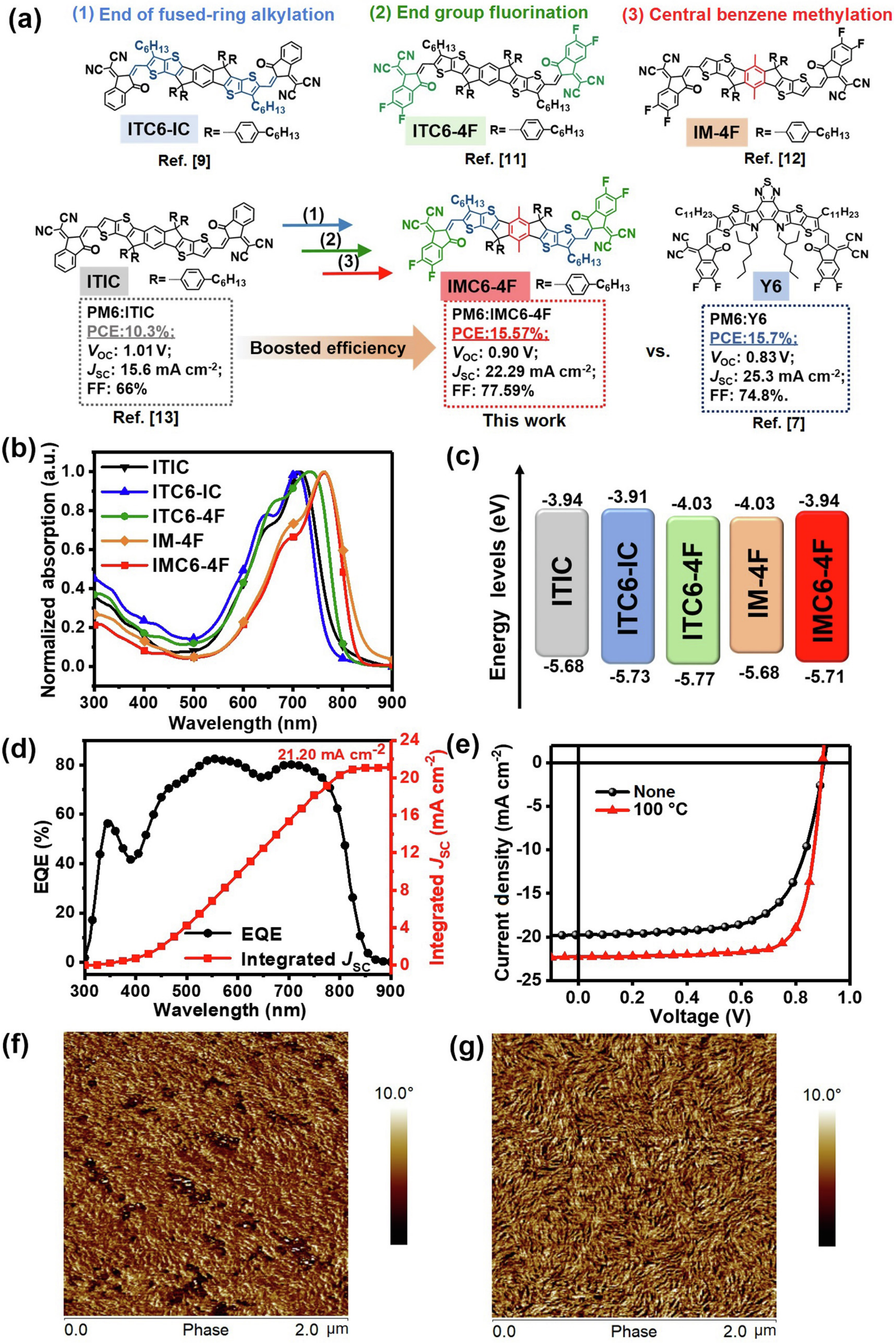

Fig. 1. (Color online) Structure design, optoelectronic properties and morphology characterization. (a) Level-increasing sidechain engineering on classic ITIC explored in our group and the best-performing PM6 OSCs with different FREAs in literature. (b) Absorption spectra and (c) energy levels alignments of ITIC, ITC6-IC, ITC6-4F IM-4F and IMC6-4F neat films. (d) EQE spectrum and integrated J_{SC} for PM6:IMC6-4F optimized OSCs. (e) *J-V* curves for PM6:IMC6-4F devices with or without TA; AFM phase images for the blend films (f) without or (g) with TA.

chlorobenzene). The absorption spectra for neat films of ITIC, ITC6-IC, ITC6-4F, IM-4F and IMC6-4F are compared in Fig. 1b. Alkylation on both ends of IT core leads to blue-shifted absorption for ITIC, while the fluorination on accepting ends and methylation on IT center offset this effect. IMC6-4F shows the widest absorption spectrum peaking at 762 nm (~60 nm red-shifted than ITIC). The E_g^{opt} of 1.49 eV is calculated for IMC6-4F with the absorption onset (830 nm). The LUMO and the highest occupied molecular orbital (HOMO) levels obtained by cyclic voltammetry (Fig. S4 online) are compared in Fig. 1c. Dual sidechain engineering on IT core can effectively compensate the drop in energy levels due to accepting end fluorination. IMC6-4F thus shows a similar LUMO (3.94 eV) to ITIC, which is beneficial to realize a high V_{OC}.

The OSCs were fabricated with a structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS)/PM6: IMC6-4F/PDINO/Al. The device fabrication details and optimization processes are elaborated in the Supplementary materials (Tables S1–S3 and Fig. S5 online). The optimized PM6:IMC6-4F (1:1, w:w) blend film was spin-coated from their mixture solution in chloroform (20 mg mL^{-1}) with DIO (5 vol%) as the processing additive. By thermal annealing (TA) at 100 °C for 5 min, PM6:IMC6-4F devices exhibit a highest PCE of 15.57%, with a V_{OC} of 0.90 V, a J_{SC} of 22.29 mA cm^{-2} and a FF of 77.59% (Fig. 1d, e) [15]. To the best of our knowledge, this performance is among the best values for binary OSCs, and IMC6-4F is one of the few NFAs to contribute PCE over 15.5% [8]. The PM6:IMC6-4F devices deliver external quantum efficiency (EQE) over 70% in the range of 460–780 nm and peaking 82% at 550 nm, suggesting efficient photocurrent generation. The J_{SC} (21.20 mA cm^{-2}) calculated from integration of EQE spectrum with AM 1.5G falls within 5% mismatch to the one measured from *J-V* curve (Fig. 1e). The device presents a high exciton dissociation (P_{diss}) of 98.4% (Fig. S6 online). Measured the hole and electron mobilities (μ_h and μ_e) using space charge limited current (SCLC) method (Fig. S7 online), PM6:IMC6-4F blend film exhibits high μ_h (5.57×10^{-4} cm^2 V^{-1} s^{-1}) and μ_e (5.26×10^{-4} cm^2 V^{-1} s^{-1}). The balanced charge carrier transport (μ_h/μ_e = 1.06) accounts for high FFs (ca. 77.59%) in OSCs.

The charge recombination behavior was investigated by plotting J_{SC} against light intensity (P) according to the formula $J_{SC} \propto P^{\alpha}$ (Fig. S8 online). The fitted slope (α = 0.986) close to 1 indicates the negligible bimolecular recombination in PM6:IMC6-4F active layers. The surface morphology for PM6:IMC6-4F blend films with or without TA were studied utilizing atomic force microscope (AFM) (Fig. S9 online). PM6:IMC6-4F blend films show quite similar root mean square roughness (RMS) without TA (1.35 nm) or with TA (1.44 nm). However, the TA treated blend film presents highly ordered nanofibers in morphology, indicating the positive effect of TA in promoting aggregation to form well-defined phase separation (Fig. 1f, g) [16,17]. This nanostructure facilitates efficient charge transport and reduces charge recombination, resulting in greatly improved J_{SC} and FF.

In conclusion, a new FREA (IMC6-4F) has been developed through triple sidechain engineering on ITIC. IMC6-4F has a high LUMO level of −3.94 eV and a narrow E_g^{opt} of 1.49 eV to extend the absorption beyond 830 nm. IMC6-4F blend with PM6 contributes a maximum PCE of 15.57% in OSCs, rivaling Y6 while outperforming all reported ITIC-like NFAs to date. Thermal annealing fine-tunes the aggregation in IMC6-4F blend films to afford much enhanced J_{SC} and FF in devices. Our molecular engineering strategy demonstrates as the golden touch for classic ITIC to develop more low-cost and efficient NFAs for OSCs.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Zhuohan Zhang and Shun Guang contributed equally for this work, who completed the material synthesis, device fabrication and characterization. Hongtao Wang, Jinru Cao, Fuqiang Du and Xinlei Wang helped in experiment and discussed the results. Zhuohan Zhang and Weihua Tang wrote the paper. Jiangsheng Yu and Weihua Tang directed the project.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2020.05.022.

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