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A novel acceptor with a *N*,*N*-dialkyl thieno[3',2':2,3]indolo[7,6-*g*]thieno[3,2-*b*]indole (TITI) core for organic solar cells with a high fill factor of 0.75⁺

A novel non-fullerene small molecule acceptor, TITI-4F, containing a *N*,*N*-dialkyl thieno[3',2':2,3]indolo[7,6-*g*]thieno[3,2-*b*]indole (TITI) core, was designed and synthesized. Photovoltaic devices based on PM6:TITI-4F can realize a high FF of 0.75, and a PCE of 10.89%. Our work demonstrates that TITI is a promising fused core for high quality acceptors.

As a promising energy source, solution-processed organic solar cells (OSCs) with a bulk-heterojunction (BHJ) structure have been deeply studied in the last few decades.^{1,2} One of the great advances in OSCs comes with the recent significant development of A-D-A type non-fullerene small molecular acceptors (NF-SMAs).³⁻⁵ Power conversion efficiencies (PCEs) exceeding 16% have been achieved in single-junction OSCs^{6,7} and 17% for tandem cells.⁸ To date, almost all such high performance NF-SMAs adopt an A-D-A architecture, which contains a conjugated ladder core as the electron-donating (D) unit sitting in the middle of two electron-accepting (A) units. Among the reported NF-SMAs, lots of efforts have been devoted to modifying the structure of fused π -conjugated D units to modulate photovoltaic performance.^{3,9–13} As it is known, such fused ladder cores originated from the early studies on polymer donors in the fullerene era.14-19 Those hardwon research results have become a valuable asset for OSCs and enable this field to move forward with a big leap. Now the phenomenon of knowledge flow and boundary crossing is very common, and has given rise to a large number of unexpected results. Is it possible to find or design a new type of fused core for NF-SMAs by learning from other fields? Motivated by this, we have recently thought about the 3,8-dihydroindolo[7,6-g]indole fused ring (Fig. 1), of which derivations and isomers were previously found to possess germicidal activity in the 1990s,^{20,21}

and it was thought that the bulky substituted amine group might work as the sp³ carbon bridge in the widely used fused core system. Although little attention has been paid to this structure since then, we believe that this coplanar fused structure with artful chemical modifications might have some potential to be applied for high performance OSCs.

In this communication, we present a new acceptor **TITI-4F** based on a ladder core, *N*,*N*-dialkyl thieno[3',2':2,3]indolo[7,6-g]-thieno[3,2-b]indole (TITI), by fusing 3,8-dihydroindolo[7,6-g]-indole with two adjacent thiophene units and linking with two alkyl substitutions on the sp²-hybridized nitrogen positions. The device based on the widely used polymer donor PM6²² and the new acceptor **TITI-4F** exhibits a fill factor (FF) of 0.75, which provides a new choice for molecular design with high FFs.

The synthetic approach to **TITI-4F** is shown in Scheme S1 (ESI[†]). Firstly, commercial reagent 2,6-dibromonaphthalene **1** was nitrated at low temperature to obtain 1,5-dinitro-2,6-dibromonaphthalene **2**, which then was reacted with 2-tribuylstannyl thiophene by the palladium-catalyzed Stille cross-coupling reaction to give intermediate product **3** in 85% yield. Furthermore, intra-molecular Cadogan reductive cyclization of **3** in the presence of triethyl phosphate gave the intermediate product **4** at high reaction temperature. *N*-Alkylation of **4** was performed with an excess amount of heptadecan-9-yl 4-methylbenzenesulfonate in the presence of potassium hydroxide to afford the fused core **5**, TITI, which was then lithiated with *n*-butyllithium (*n*-BuLi),



Fig. 1 Design origination and chemical structure of TITI-4F.

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and quenched with *N*,*N*-dimethylformamide (DMF) to yield compound **6**. The Knoevenagel condensation between **6** and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malono-nitrile (DFIC) affords the target compound **TTTI-4F** in 84% yield. The final product was fully characterized by ¹H and ¹³C NMR and high-resolution mass spectrometry (see the ESI†). To our knowledge, this is the first work to synthesize and utilize the fused core TITI for organic solar cells.

Density functional theory (DFT) calculations are performed to evaluate the configuration and energy levels. As presented in Fig. S1 (ESI[†]), the acceptor **TITI-4F** shows good coplanarity, which is favorable for efficient intermolecular π - π stacking and intramolecular charge transfer (ICT). The calculated energy levels and distributions of the frontier molecular orbitals (FMOs) are shown in Fig. S2 (ESI[†]). For **TITI-4F**, the highest occupied molecular orbital (HOMO) is well delocalized along the π -conjugated backbone, while the lowest unoccupied molecular orbital (LUMO) involves a strong contribution from the electronaccepting DFIC unit. The calculated HOMO and LUMO levels are -5.64 and -3.42 eV, respectively.

As depicted in Fig. 2a, molecular aggregation for **TITI-4F** was studied by temperature dependent UV-vis absorption in dilute chlorobenzene (CB) solution under different temperatures. These spectra revealed slight blueshift and declined absorption intensity as the solution temperature increased, indicating dissociation of aggregated **TITI-4F**. The optical absorption spectra of **TITI-4F** and PM6 recorded in a thin film are shown in Fig. 2b. Compared with that in solution, UV-vis absorption of **TITI-4F** in the film was further red-shifted from 680 to 726 nm, with the absorption edge at 795 nm. Hence, the optical bandgap estimated from the onsets of the absorption spectrum in the film is 1.56 eV for **TITI-4F**. The absorption spectrum of PM6 is complementary to that of the neat **TITI-4F** film, benefiting the solar energy utilization.

Ultraviolet photoelectron spectroscopy (UPS) is an effective tool to estimate the energy levels of photovoltaic materials. The HOMO energy level of **TITI-4F** determined by UPS was -5.81 eV (Fig. S3, ESI[†]), and the LUMO energy level was -4.25 eV calculated using the HOMO energy level and the optical bandgap. The HOMO and LUMO energy levels of **TITI-4F** match well with those of PM6, thus ensuring the driving force for efficient exciton dissociation.

To demonstrate potential applications of **TITI-4F** in OSCs, we fabricated BHJ OSCs with an inverted configuration of ITO/ ZnO/PFN-Br/PM6:**TITI-4F**/MoO_{*X*}/Ag, where ITO is indium tin oxide, and PFN-Br is a conjugated polyelectrolyte interfacial layer of poly[(9,9-bis(3-((*N*,*N*-dimethyl)-*N*-ethylammonium)-propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)]dibromide. The current density–voltage (*J*–*V*) curves of the representative devices are shown in Fig. 3a, and the detailed photovoltaic parameters are summarized in Table 1. We first tried to prepare the as-cast



Fig. 2 (a) Temperature-dependent UV-vis spectra of TITI-4F in CB solution (10^{-5} mol L⁻¹). (b) Normalized UV-vis spectra of TITI-4F and PM6 in a thin film on quartz at ambient temperature.



Fig. 3 J-V curves (a) and EQE responses (b) of devices based on PM6:TITI-4F w/o or with 1% CN after thermal annealing.

Table 1 Photovoltaic performance of PM6:TITI-4F-based devices

Additive [v/v]	$V_{\rm oc} \left[V \right]$	$J_{ m sc} \ [m mA~cm^{-2}]$	FF	PCE^{a} [%]	$\begin{bmatrix} \mu_{\rm h} / \mu_{\rm e} \\ 10^{-4} \ {\rm cm}^2 \ {\rm V}^{-1} \ {\rm s}^{-1} \end{bmatrix}$
w/o ^b	0.90	0.99	0.29	0.26 (0.23)	_
w/o^c	0.98	11.84	0.66	7.66 (7.39)	—
$w/o^{c,d}$	0.98	12.86	0.66	8.32 (8.08)	3.9/7.1
$1\% \text{ CN}^{c,d}$	0.91	15.96	0.75	10.89 (10.55)	3.7/3.5

 a The values in parentheses stand for the average PCEs from over 20 devices. b The solution of the active layer is kept at ambient temperature. c The solution of the active layer is kept at 100 °C. d Thermal annealing at 100 °C for 10 min.



Fig. 4 TEM images of the thin films of PM6:TITI-4F (a) w/o CN and (b) with 1% CN after thermal annealing.

devices where the PM6:TTTI-4F films were cast from CB solutions at ambient temperature. Unfortunately, a very poor PCE of 0.26% was obtained with a low quality short circuit current (J_{sc}) and FF. At an elevated temperature of 100 °C, the device performance was significantly improved, with a PCE of 7.66%, indicating that TITI-4F was disaggregated and could be well dissolved in CB at a concentration of 9 mg mL $^{-1}$. This is consistent with the result of the temperature dependent optical absorption of TITI-4F as mentioned above. Furthermore, thermal annealing (TA) was found to be beneficial for this system to achieve a higher PCE of 8.32%. After introducing 1% (v/v) 1-chloronaphthalene (CN) as the solvent additive, PM6:TITI-4F achieved a high PCE of 10.89% with a $V_{\rm oc}$ of 0.91 V, a $J_{\rm sc}$ of 15.96 mA cm⁻² and a FF of 0.75. Fig. 3b exhibits the external quantum efficiency (EQE) responses, which are consistent with the blend absorption spectra (Fig. S4, ESI⁺). The current densities integrated from the EQE spectra are 12.36 and 15.35 mA cm^{-2} for the devices w/o or with 1% CN after thermal annealing, respectively, which are comparable to those measured from the corresponding J-V curves within 5% error.

Hole (μ_h) and electron (μ_e) mobilities of PM6:**TITI-4F** w/o or with 1% CN after thermal annealing were measured by using the space charge-limited current (SCLC) method as shown in Fig. S5 (ESI[†]), and the corresponding data are listed in Table 1. For PM6:**TITI-4F** w/o CN, the μ_h and μ_e values are 3.9×10^{-4} and 7.1×10^{-4} cm² V⁻¹ s⁻¹, respectively. After adding 1% CN, μ_h is almost the same, while μ_e is reduced by half. At this time, a relatively balanced carrier mobility ($\mu_h/\mu_e = 1.1$) is obtained, which is consistent with the FF value as high as 0.75.

To find more straightforward clues about the additive effect on the active layer and the resulting device performance, the morphology of PM6:**TITI-4F** blend films w/o and with 1% CN after thermal annealing was investigated by transmission electron microscopy (TEM). As shown in Fig. 4a, the TEM image of the blend film w/o CN shows nanowire structures of ~ 200 nm, which is consistent with strong aggregation of **TITI-4F** and higher μ_e . In comparison, with addition of 1% CN, the PM6:**TITI-4F** blend film shows a favourable morphology, resulting in balanced carrier mobility, and thus a high FF and PCE (Fig. 4b).

In conclusion, a novel electron-rich fused core TITI and a derivative, **TITI-4F**, as an acceptor for OSCs have been synthesized. The current results demonstrate that TITI is a candidate for constructing efficient OSCs with a high FF of 0.75.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 L. Dou, Y. Liu, Z. Hong, G. Li and Y. Yang, Chem. Rev., 2015, 115, 12633.
- A. Wadsworth, M. Moser, A. Marks, M. S. Little, N. Gasparini, C. J. Brabec, D. Baran and I. McCulloch, *Chem. Soc. Rev.*, 2019, 48, 1596.
- J. Braber, D. Baran and T. McCuntori, *Chan. Soc. Rev.*, 2015, 40, 1350.
 Y. Lin, J. Wang, Z.-G. Zhang, H. Bai, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2015, 27, 1170.
- 4 B. Kan, H. Feng, H. Yao, M. Chang, X. Wan, C. Li, J. Hou and Y. Chen, *Sci. China: Chem.*, 2018, **61**, 1307.
- 5 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.
- 6 Q. An, X. Ma, J. Gao and F. Zhang, Sci. Bull., 2019, 64, 504.
- 7 Y. Cui, H. Yao, J. Zhang, T. Zhang, Y. Wang, L. Hong, K. Xian, B. Xu, S. Zhang, J. Peng, Z. Wei, F. Gao and J. Hou, *Nat. Commun.*, 2019, 10, 2515.
- 8 L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao and Y. Chen, *Science*, 2018, 361, 1094.
- 9 Y. Lin, Q. He, F. Zhao, L. Huo, J. Mai, X. Lu, C.-J. Su, T. Li, J. Wang, J. Zhu, Y. Sun, C. Wang and X. Zhan, *J. Am. Chem. Soc.*, 2016, **138**, 2973.
- 10 N. Qiu, H. Zhang, X. Wan, C. Li, X. Ke, H. Feng, B. Kan, H. Zhang, Q. Zhang, Y. Lu and Y. Chen, *Adv. Mater.*, 2017, 29, 1604964.
- 11 B. Kan, H. Feng, X. Wan, F. Liu, X. Ke, Y. Wang, Y. Wang, H. Zhang, C. Li, J. Hou and Y. Chen, *J. Am. Chem. Soc.*, 2017, **139**, 4929.
- 12 H.-H. Gao, Y. Sun, X. Wan, B. Kan, X. Ke, H. Zhang, C. Li and Y. Chen, *Sci. China Mater.*, 2017, **60**, 819.
- 13 B. Fan, D. Zhang, M. Li, W. Zhong, Z. Zeng, L. Ying, F. Huang and Y. Cao, *Sci. China: Chem.*, 2019, **62**, 746.
- 14 Y.-X. Xu, C.-C. Chueh, H.-L. Yip, F.-Z. Ding, Y.-X. Li, C.-Z. Li, X. Li, W.-C. Chen and A. K. Y. Jen, *Adv. Mater.*, 2012, **24**, 6356.
- 15 M. Zhang, X. Guo, X. Wang, H. Wang and Y. Li, *Chem. Mater.*, 2011, 23, 4264.
- 16 C.-Y. Chang, Y.-J. Cheng, S.-H. Hung, J.-S. Wu, W.-S. Kao, C.-H. Lee and C.-S. Hsu, *Adv. Mater.*, 2012, 24, 549.
- 17 Y.-L. Chen, C.-Y. Chang, Y.-J. Cheng and C.-S. Hsu, Chem. Mater., 2012, 24, 3964.
- 18 Y.-J. Cheng, C.-H. Chen, T.-Y. Lin and C.-S. Hsu, Chem. Asian J., 2012, 7, 818.
- 19 Y.-J. Cheng, Y.-J. Ho, C.-H. Chen, W.-S. Kao, C.-E. Wu, S.-L. Hsu and C.-S. Hsu, *Macromolecules*, 2012, **45**, 2690.
- 20 S. A. Samsoniya, N. A. Ésakiya, S. V. Dolidze, M. V. Trapaidze, Z. S. Lomtatidze and N. N. Suvorov, *Pharm. Chem. J.*, 1991, 25, 638.
- 21 S. A. Samsoniya and M. V. Trapaidze, Russ. Chem. Rev., 2007, 76, 313.
- 22 M. Zhang, X. Guo, W. Ma, H. Ade and J. Hou, *Adv. Mater.*, 2015, 27, 4655.