Non-Fullerene Small Molecular Acceptors Based on Dithienocyclopentafluorene and Dithienocyclopentacarbazole Cores for Polymer Solar Cells

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Abstract: Recently, acceptor-donor-acceptor (A-D-A) type of small molecules based on indacenodithieno[3,2-b]thiophene (**IDTT**) or indacenodithiophene (**IDT**) as the electron-donating cores were very promising non-fullerene (NF) acceptors to overcome the energy levels and absorption drawbacks of the fullerene-based acceptors in polymer solar cells (PSCs). However, few attempts have been done to develop novel electron-donating cores to construct highly efficient A-D-A acceptors in PSCs. We design and prepare two novel non-fullerene small molecular acceptors (**DTF-IC** and **DTC-IC**) based on dithienocyclopentafluorene and dithienocyclopentacarbazole as the electron-donating cores sealed with 2-(3-oxo-indane-1-

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ylidene)-malononitrile as the electron-withdrawing groups. The two molecules exhibit relatively high lowest unoccupied molecular orbital (LUMO) energy levels and strong absorption in the region from 550 to 740 nm. Relative to the molecule **DTF-IC** possessing dithienocyclopentafluorene core, the dithienocyclopentacarbazole based acceptor **DTC-IC** shows slightly red-shifted absorption spectrum, enhanced extinction coefficients, better crystallinity and improved electron mobility. The polymer solar cells based on these two NF acceptors exhibit power conversion efficiencies of 7% when blended with the narrow bandgap polymer poly({4,8-bis[(5-(2-ethylhexyl)-2-thienyl]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl}) (**PTB7-Th**) in inverted solar cells.

Keywords: Polymer solar cells, Dithienocyclopentafluorene, Dithienocyclopentacarbazole, Non-fullerene small molecular acceptors.

1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs), with a bicontinuous network by blending a p-type conjugated polymer as donor and an n-type fullerene derivative as acceptor in the active layer, have been intensively investigated for their advantages, such as light weight, flexibility, low cost, and suitability for large-scale fabrication.^[1-3] Up till now, state-of-the-art PSCs have already achieved power conversion efficiencies (PCEs) above 11%.^[4-7] However, the intrinsic drawbacks of the fullerene-based acceptors, such as weak absorption in the visible spectral region, restricted energy level variability, and inherent tendency of aggregation in the blend film, make it difficult to further increase the photovoltaic performance of this type of

P S C s .

To overcome those drawbacks of fullerene-based acceptors, non-fullerene (NF) acceptors were developed in the past few years.^[8] At present, PSCs based on NF acceptors have been accomplished great progress, resulting in the realization of remarkable PCEs above 11%^[9-10] by blending acceptor-donor-acceptor (A-D-A) small molecular acceptors with suitable donor polymers, which can be compared with fullerene-based devices. A successful A-D-A type NF small molecular (**ITIC**) used indacenodithieno[3,2-b]thiophene (**IDTT**) as electron-donating core sealed with strong electron-withdrawing groups 2-(3-oxo-indane-1-ylidene)-malononitrile (**INCN**) developed by Zhan and co-workers is more attractive,^[11] for their strong absorptive properties in the range of 600-800 nm as well as adjustable energy levels to achieve complementary absorption with medium bandgap donor polymers to harvest the light in high energy region. Many A-D-A type NF acceptors based on **IDTT** and its derivatives as the electron-donating cores have been designed and achieved promising performances in the PSCs. For instances, through structural modification either in the side-chain of the **IDTT** core or in the end group, several novel **ITIC**-based NF small molecules with tuneable energy levels, carrier mobilities and absorption behaviours have been synthesized to promote the photovoltaic performances.^[12-15] However, few attempts have been done to develop novel electron-donating cores based A-D-A type NF small molecular acceptors with promising performance in PSCs.^[16]

To investigate the influences of electron-donating cores on the performances of the A-D-A type NF acceptors and eventually obtain alternative novel acceptors, herein, we synthesize two small molecular electron acceptors (**DTF-IC** and **DTC-IC**, **Scheme 1**) based on dithienocyclopentafluorene (**DTF**) and dithienocyclopentacarbazole (**DTC**) as electron-donating units end-capped with **INCN**. **DTF-IC** and **DTC-IC** exhibit strong absorption in 550-740 nm, relative high lowest unoccupied molecular orbital (LUMO) energy levels, and good miscibility

with polymer donors. PSCs fabricated by blending the promising narrow bandgap polymer based on benzodithiophene and thieno[3,4-b]thiophene units (**PTB7-Th**^[17]) as donor with **DTF-IC**/**DTC-IC** as acceptors exhibited PCEs up to 7.0%, indicating the promising performances of **DTF** and **DTC** based A-D-A types of small molecular NF acceptors.

2. Experimental Section

2.1 Materials

Unless noted, all the reactions were carried out under a nitrogen or argon atmosphere. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (THF), and freshly distilled prior to use. Other materials were purchased from commercial resources and used without further purification. **DTC-IC** and **DTF-IC** were prepared according to the routes in **Scheme 1**.

Scheme 1. Chemical structures and synthetic route of **DTF-IC** and **DTC-IC**.

Synthesis of compound 3a

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-octyl-9H-carbazole (**1a**) (6.57 g, 10 mmol), methyl 2-bromothiophene-3-carboxylate (**2**) (5.4 g, 24 mmol), K_2CO_3 (8.2 g, 60 mmol), Aliquant 336 (1.2 g, 3.0 mmol), and $Pd(PPh_3)_4$ (1.15 g, 1 mmol) were dissolved in deoxygenated toluene/ H_2O (90 mL, 5:1, v/v). The reaction mixture was refluxed at 120 °C for 72 h and then extracted with diethyl ether (100 mL $\times$ 3) and water (150 mL). The collected organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/dichloromethane, v/v, 20/1) to give a yellow liquid product **3a** (3.8 g, 56%). 1H NMR ($CDCl_3$, 500 MHz) δ 8.15 – 8.05 (2H, m), 7.76 (1H, s), 7.55 (3H, d, J = 5.4 Hz), 7.36 (2H, m), 7.28 (2H, d, J = 5.4 Hz), 4.58 – 4.52 (1H, m), 3.72 (6H, s), 2.28 (2H, m), 1.93 (2H, m), 1.27 – 1.09 (24H, m), 0.81 (6H, t, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 164.01, 152.23, 142.11, 130.16, 124.03, 120.90, 113.27, 110.45, 56.74, 51.55, 33.78, 31.75, 29.41, 29.34, 29.19, 26.94, 22.58, 14.04.

Synthesis of compound 4a

To a solution of **3a** (3.57 g, 7.8 mmol) in dry THF (100 mL) was added dropwise (4-hexylphenyl)lithium which was freshly prepared by reacting 1-bromo-4-hexylbenzene (11.3 g, 46 mmol) with 2 M n-butyllithium (23.4 mL, 46.8 mmol) at -78 °C. The reaction mixture was warmed at room temperature and stirred for 12 h. Then the mixture was quenched with water, followed by extraction with diethyl ether (50 mL $\times$ 3) and water (100 mL). The collected organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ dichloromethane, v/v, 10/1) to give a yellow liquid product **4a** (3.9 g, 60%). 1H NMR ($CDCl_3$, 500 MHz) δ 7.86 (1H, s), 7.82 (1H, s), 7.52 (1H, s), 7.38 (1H, s), 7.27 (2H, d, J = 4.8 Hz), 7.25 (2H, s), 7.18 (8H, d, J = 7.8 Hz),

7.03 – 7.01 (10H, m), 4.64 – 4.49 (1H, m), 2.56 – 2.50 (8H, m), 2.36 – 2.24 (2H, m), 2.03 – 1.92 (2H, m), 1.65 – 1.49 (16H, m), 1.35 – 1.12 (41H, m), 0.86 (12H, t, $J = 6.6$ Hz), 0.79 (6H, t, $J = 6.7$ Hz). ^{13}C NMR (CDCl_3 , 126 MHz) δ 156.38, 144.97, 141.06, 128.18, 127.91, 127.15, 123.35, 62.21, 56.80, 35.57, 33.79, 31.76, 31.73, 31.33, 29.50, 29.33, 29.20, 29.17, 27.00, 22.60, 14.09, 14.04.

Synthesis of compound 5a

To a solution of **4a** (3.9 g, 1.2 mmol) in dichloromethane (150 mL) was added boron trifluoridediethyl etherate (15 mL). The reaction mixture was refluxed at 80 °C for 12 h and then was extracted with dichloromethane (50 mL $\times$ 4) and water (100 mL). The collected organic layer was dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **5a** as a yellow solid (3.2 g, 83%). ^1H NMR (CDCl_3 , 500 MHz) δ 7.86 (1H, s), 7.83 (1H, s), 7.52 (1H, s), 7.38 (1H, s), 7.27 (1H, s), 7.26 (1H, s), 7.18 (8H, d, $J = 8.3$ Hz), 7.06 – 7.00 (10H, m), 4.63 – 4.49 (1H, m), 2.57 – 2.48 (8H, m), 2.41 – 2.23 (2H, m), 2.00 – 1.94 (2H, m), 1.62 – 1.47 (11H, m), 1.39 – 1.09 (46H, m), 0.86 (12H, t, $J = 6.9$ Hz), 0.79 (6H, t, $J = 6.9$ Hz). ^{13}C NMR (CDCl_3 , 126 MHz) δ 156.39, 144.98, 143.08, 143.04, 141.08, 135.11, 134.66, 128.20, 127.93, 127.18, 123.36, 102.15, 99.54, 62.20, 56.81, 35.59, 33.81, 31.78, 31.74, 31.36, 29.73, 29.51, 29.35, 29.22, 29.19, 27.02, 22.62, 14.11, 14.07.

Synthesis of compound 6a

N-bromosuccinimide (0.91 g, 5.7 mmol) was added in one portion to a solution of **5a** (3.2 g, 2.59 mmol) in THF (60 mL). The reaction was stirred under darkness for 12 h at room temperature. The mixture solution was extracted with diethyl ether (60 mL $\times$ 3) and water (60 mL). The combined organic layer was dried over MgSO_4 . After removal of the solvent under

reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **6a** as a yellow solid (2.5 g, 83%). ^1H NMR (CDCl_3 , 500 MHz) δ 7.83 (1H, s), 7.79 (1H, s), 7.43 (1H, s), 7.29 (1H, s), 7.14 (8H, d, $J = 8.3$ Hz), 7.03 (8H, d, $J = 8.3$ Hz), 7.02 (2H, s), 4.69 – 4.33 (1H, m), 2.64 – 2.45 (8H, m), 2.35 – 2.22 (2H, m), 1.96 (2H, m), 1.60 – 1.52 (13H, m), 1.29 – 1.25 (44H, m), 0.86 (12H, t, $J = 6.9$ Hz), 0.79 (6H, t, $J = 7.0$ Hz). ^{13}C NMR (CDCl_3 , 126 MHz) δ 155.19, 143.86, 142.36, 141.36, 128.30, 127.82, 126.33, 117.84, 113.18, 102.07, 62.97, 56.88, 35.56, 33.77, 31.76, 31.72, 31.31, 29.46, 29.31, 29.18, 29.16, 26.96, 22.59, 14.08, 14.04.

Synthesis of compound **7a**

In a dry round-bottomed flask, compound **6a** (970 mg, 0.70 mmol) was dissolved in THF (50 mL) and placed under a nitrogen atmosphere. The solution was cooled to -78°C and stirred while 2.0 M n-butyllithium in hexane (0.91 mL, 1.82 mmol) was added dropwise. The mixture was stirred for 1 h at -78°C , and then anhydrous DMF (1.32 g, 18.15 mmol) was added dropwise. The reactant was warmed to room temperature and stirred overnight. Thereafter, brine was added and extracted with dichloromethane. The resulting crude compound was purified by silica gel chromatography (hexane/dichloromethane, v/v, 20/1) to give **7a** as a yellow solid (550 mg, 61%). ^1H NMR (CDCl_3 , 500 MHz) δ 9.84 (2H, s), 7.93 (1H, s), 7.89 (1H, s), 7.67 (3H, s), 7.54 (1H, s), 7.17 (8H, d, $J = 8.3$ Hz), 7.05 (8H, d, $J = 8.3$ Hz), 4.80 – 4.49 (1H, m), 2.58 – 2.50 (8H, m), 2.34–2.28 (2H, m), 2.06–1.99 (2H, m), 1.63 – 1.51 (16H, m), 1.39 – 1.09 (41H, m), 0.86 (12H, t, $J = 6.9$ Hz), 0.77 (6H, t, $J = 6.9$ Hz). ^{13}C NMR (CDCl_3 , 126 MHz) δ 182.84, 156.90, 146.03, 145.59, 141.73, 132.22, 128.46, 127.73, 110.03, 103.95, 62.39, 62.36, 57.55, 35.54, 33.77, 31.73, 31.70, 31.31, 29.71, 29.41, 29.29, 29.13, 26.95, 22.58, 22.56, 14.07, 14.02.

Synthesis of compound **9a** (DTC-IC)

1,1-Dicyanamethylene-3-indanone (**8**) (30 mg, 0.154 mmol) was added into the mixture of compound **7a** (50 mg, 0.039 mmol) in chloroform (10 mL) with pyridine (0.2 mL), the reactant was deoxygenated with nitrogen for 30 min and then refluxed for 12 h. After cooling to room temperature, the reaction was poured into water and then extracted with chloroform. The crude product was purified by silica gel column (chloroform) to give **9a** as a purple solid (52 mg, 82%). ¹H NMR (CDCl₃, 500 MHz) δ 8.93 (1H, s), 8.92 (1H, s), 8.70 (1H, s), 8.69 (1H, s), 7.99 – 7.86 (4H, m), 7.84 (1H, s), 7.80 – 7.68 (7H, m), 7.17 (8H, d, J = 8.3 Hz), 7.07 (8H, d, J = 8.3 Hz), 4.62 – 4.59 (1H, m), 2.61 – 2.51 (8H, m), 2.32 – 2.27 (2H, m), 2.11 – 2.05 (2H, m), 1.58 – 1.55 (14H, m), 1.41 – 1.11 (43H, m), 0.86 (12H, t, J = 6.9 Hz), 0.78 (6H, t, J = 6.9 Hz). ¹³C NMR (CDCl₃, 126 MHz) δ 188.75, 147.25, 141.92, 141.54, 140.68, 134.35, 128.57, 127.76, 125.42, 123.66, 114.78, 102.45, 101.18, 62.35, 57.53, 35.55, 31.74, 31.70, 31.29, 29.38, 29.32, 29.12, 27.11, 22.57, 14.06, 14.03.

Synthesis of compound **3b**

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-9H-fluorene (**1b**) (8.9 g, 13.9 mmol), methyl 2-bromothiophene-3-carboxylate (**2**) (7.7 g, 34.7 mmol), K₂CO₃ (11.5 g, 83.2 mmol), Aliquant 336 (1.5 g, 3.8 mmol), and Pd(PPh₃)₄ (1.6 g, 1.39 mmol) were dissolved in deoxygenated toluene/H₂O (120 mL, 5:1, v/v). The reaction mixture was refluxed at 120 °C for 72 h and then extracted with diethyl ether (100 mL $\times$ 3) and water (150 mL). The collected organic layer was dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/dichloromethane, v/v, 20/1) to give a yellow liquid product (**3b**) (6.4 g, 55%). ¹H NMR (CDCl₃, 500 MHz) δ 7.74 – 7.73 (1H, m), 7.73 – 7.72 (1H, m), 7.54 (1H, s), 7.53 (1H, s), 7.49 (1H, d, J = 1.6 Hz), 7.48 (1H, d, J = 1.6 Hz), 7.46 (2H, d, J = 1.1 Hz), 7.25 (1H, s), 7.24 (1H, s), 3.71 (6H, s), 2.08 – 1.90 (4H,

m), 1.23 – 1.04 (24H, m), 0.80 (6H, t, $J = 5.9$ Hz). ^{13}C NMR (CDCl_3 , 201 MHz) δ 163.94, 151.48, 150.80, 140.94, 132.29, 130.18, 128.61, 127.87, 124.53, 123.93, 119.44, 55.28, 51.44, 40.28, 31.76, 30.08, 29.25, 29.23, 23.81, 22.57, 14.06.

Synthesis of compound 4b

To a solution of **3b** (6.4 g, 9.5 mmol) in dry THF (100 mL) was added dropwise (4-hexylphenyl)lithium which was freshly prepared by reacting 1-bromo-4-hexylbenzene (18 g, 73 mmol) with 2 M n-butyllithium (38 mL, 76 mmol) at -78°C . The reaction mixture was warmed at room temperature and stirred for 12 h. Then the mixture was quenched with water, followed by extraction with diethyl ether (50 mL $\times$ 3) and water (100 mL). The collected organic layer was dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ dichloromethane, v/v, 10/1) to give a yellow liquid product (**4b**)(8.5 g, 57%). ^1H NMR (CDCl_3 , 500 MHz) δ 7.51 (1H, s), 7.50 (1H, s), 7.23 (1H, d, $J = 1.5$ Hz), 7.22 (1H, d, $J = 1.5$ Hz), 7.16 (8H, d, $J = 8.3$ Hz), 7.12 – 7.02 (10H, m), 6.93 (2H, d, $J = 1.2$ Hz), 6.44 (1H, s), 6.42 (1H, s), 2.64 – 2.58 (8H, m), 1.67 – 1.58 (4H, m), 1.48 – 1.41 (9H, m), 1.39 – 1.27 (26H, m), 1.25 – 0.93 (22H, m), 0.93 – 0.87 (12H, m), 0.80 (6H, t, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 126 MHz) δ 151.04, 145.56, 144.16, 141.90, 140.30, 139.24, 133.54, 131.53, 129.09, 127.94, 127.59, 124.00, 122.39, 119.79, 80.78, 54.98, 39.56, 35.64, 31.84, 31.78, 31.70, 31.55, 29.96, 29.35, 29.28, 29.11, 23.69, 22.66, 22.66, 14.14, 14.09.

Synthesis of compound 5b

To a solution of **4b** (8.5 g, 6.8 mmol) in dichloromethane (300 mL) was added boron trifluoridediethyl etherate (35 mL). The reaction mixture was refluxed at 80°C for 12 h and then was extracted with dichloromethane (80 mL $\times$ 4) and water (100 mL). The collected organic layer was dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue

was purified by column chromatography on silica gel (hexane) to give **5b** as a yellow solid (4.4 g, 67%). ¹H NMR (CDCl₃, 500 MHz) δ 7.51 (2H, s), 7.36 (2H, s), 7.25 (2H, d, *J* = 4.9 Hz), 7.14 (8H, d, *J* = 8.2 Hz), 7.04 (8H, d, *J* = 8.2 Hz), 6.99 (2H, d, *J* = 4.9 Hz), 2.57 - 2.50 (8H, m), 2.00 - 1.95 (4H, m), 1.61 - 1.49 (10H, m), 1.41 - 1.23 (46H, m), 0.86 (12H, t, *J* = 6.8 Hz), 0.79 (6H, t, *J* = 7.0 Hz). ¹³C NMR (CDCl₃, 126 MHz) δ 156.18, 152.83, 151.04, 142.39, 141.42, 141.18, 139.23, 136.24, 128.26, 128.01, 127.21, 123.25, 117.49, 113.76, 62.69, 54.46, 40.65, 35.59, 31.84, 31.75, 31.30, 30.14, 29.29, 29.25, 29.21, 23.97, 22.63, 22.62, 14.15, 14.10.

Synthesis of compound **6b**

N-bromosuccinimide (1.4 g, 7.8 mmol) was added in one portion to a solution of **5b** (4.4 g, 3.6 mmol) in THF (100 mL). The reaction was stirred under darkness for 12 h at room temperature. The mixture solution was extracted with diethyl ether (60 mL × 3) and water (60 mL). The combined organic layer was dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **6b** as a yellow solid (3.5 g, 71%). ¹H NMR (CDCl₃, 500 MHz) δ 7.47 (2H, s), 7.28 (2H, s), 7.10 (8H, d, *J* = 8.3 Hz), 7.04 (8H, d, *J* = 8.3 Hz), 6.99 (2H, s), 2.59-2.51 (8H, m), 2.01 - 1.91 (4H, m), 1.57 - 1.55 (10H, m), 1.38 - 1.04 (46H, m), 0.87 (12H, t, *J* = 6.9 Hz), 0.80 (6H, t, *J* = 7.1 Hz). ¹³C NMR (CDCl₃, 126 MHz) δ 154.95, 151.73, 151.25, 141.68, 141.48, 139.35, 135.93, 128.36, 127.88, 126.18, 117.46, 113.65, 113.27, 63.45, 54.51, 40.52, 35.57, 31.81, 31.72, 31.27, 30.06, 29.24, 29.21, 29.18, 23.93, 22.61, 22.59, 14.08.

Synthesis of compound **7b**

In a dry round-bottomed flask, compound **6b** (0.93g, 0.68 mmol) was dissolved in THF (50 mL) and placed under a nitrogen atmosphere. The solution was cooled to -78 °C and stirred while 2.0 M n-butyllithium in hexane (0.88 mL, 1.76 mmol) was added dropwise. The mixture

was stirred for 1 h at -78 °C, and then anhydrous DMF (1.32 g, 18.2 mmol) was added dropwise. The reactant was warmed to room temperature and stirred overnight. Thereafter, brine was added and extracted with dichloromethane. The resulting crude compound was purified by silica gel chromatography (hexane/dichloromethane, v/v, 20/1) to give a yellow solid (**7b**) (0.50g, 58%). ¹H NMR (CDCl₃, 500 MHz) δ 9.76 (2H, s), 7.57 (2H, s), 7.50 (2H, s), 7.45 (2H, s), 7.05 (8H, d, *J* = 8.3 Hz), 6.99 (8H, d, *J* = 8.3 Hz), 2.51 – 2.45 (8H, m), 2.02 – 1.92 (4H, m), 1.56 – 1.46 (10H, m), 1.31 – 0.98 (46H, m), 0.79 (12H, t, *J* = 6.9 Hz), 0.71 (6H, t, *J* = 7.0 Hz). ¹³C NMR (CDCl₃, 126 MHz) δ 182.81, 156.69, 154.25, 152.05, 151.28, 145.65, 141.85, 141.18, 141.14, 135.32, 132.16, 128.53, 127.79, 118.04, 115.59, 62.90, 54.79, 40.43, 35.54, 31.77, 31.69, 31.24, 29.96, 29.70, 29.18, 29.13, 23.98, 22.57, 14.05.

Synthesis of compound **9b** (DTF-IC)

1,1-Dicyanamethylene-3-indanone (**8**) (0.091 g, 0.154 mmol) was added into the mixture of compound **7b** (0.15 g, 0.039 mmol) in chloroform (30 mL) with pyridine (0.62 mL), the reactant was deoxygenated with nitrogen for 30 min and then refluxed for 12 h. After cooling to room temperature, the reaction was poured into water and then extracted with chloroform. The crude product was purified by silica gel column (chloroform) to give a purple solid (**9b**) (0.095 g, 50%). ¹H NMR (CDCl₃, 500 MHz) δ 8.90 (2H, s), 8.73 – 8.67 (2H, m), 7.93 – 7.90 (2H, m), 7.79 – 7.72 (4H, m), 7.69 (2H, s), 7.68 (2H, s), 7.61 (2H, s), 7.13 (8H, d, *J* = 8.4 Hz), 7.09 (8H, d, *J* = 8.4 Hz), 2.62 – 2.52 (8H, m), 2.05 – 2.03 (4H, m), 1.58 (10H, m), 1.38 – 1.10 (46H, m), 0.87 (12H, t, *J* = 6.9 Hz), 0.80 (6H, t, *J* = 7.0 Hz). ¹³C NMR (CDCl₃, 126 MHz) δ 188.40, 160.58, 160.30, 157.79, 155.52, 152.88, 142.44, 142.06, 140.80, 140.70, 139.99, 139.64, 138.62, 136.95, 135.79, 135.05, 134.39, 128.65, 127.83, 125.30, 123.72, 121.74, 118.47, 116.52, 114.75, 68.78,

62.92, 54.66, 40.32, 35.56, 31.78, 31.70, 31.26, 30.03, 29.25, 29.20, 29.13, 24.17, 22.61, 22.58, 14.07.

2.2 Measurements

All compounds were characterized by nuclear magnetic resonance spectra (NMR) recorded on a Bruker AV 500 or 800 spectrometer in CDCl_3 at room temperature using tetramethylsilane (TMS) as an internal reference at room temperature. The chemical shifts were accounted in ppm related to the singlet of CDCl_3 at 7.26 ppm and 77 ppm for ^1H and ^{13}C NMR, respectively. The absorption spectra were measured using a PerkinElmer Lambda 750 UV/Vis/NIR Spectrometer. Thermogravimetric analysis (TGA) was performed on a Universal V2.6D TA instrument. Photoluminescence spectra of the pure and blend films were measured on a fluorospectrophotometer (Edinburgh Instruments, FLSPP20). The electrochemical cyclic voltammetry was conducted on a CHI 660D Electrochemical Workstation equipped with glassy carbon, Pt wire, and Ag/Ag^+ as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. Atomic force microscopy (AFM) measurement of the surface morphology of samples was conducted in air under ambient conditions using the DI MultiMode Nanoscope IIIa (Veeco). The thickness of the active layer of the device was measured using Bruker Dektak-XT surface profiler.

2.3 Fabrication and characterization of OSCs

The inverted device structure of the OSCs was ITO/ZnO (40 nm)/poly[(9,9-dioctyl-2,7-fluorene)-alt-(9,9-bis(3-N,N-dimethylamino)propyl)-2,7-fluorene] (PFN, 10 nm)/PTB7-Th:acceptors(80-90 nm)/ MoO_3 (10 nm)/Al(100nm). The ITO glass was ultrasonically cleaned with detergent, distilled water, acetone, isopropyl alcohol, and then treated with ultraviolet-ozone (Ming Heng, PDC-MG) for 20 min. Zinc acetate dihydrate dissolved in 2-methoxyethanol and a

small amount of ethanolamine was spin-cast on ITO substrates and baked at 200 °C for 30 minutes in the air to form a ZnO layer with a thickness of 40 nm. The substrates were transferred into a nitrogen filled glove box, then the PFN (0.5 mg ml⁻¹) methanol solution was spin-coated the on the top of ZnO layer at 2000 rpm for 20 sec. The photoactive layer (80-90nm) was then prepared by spin-coating a blend solution of the acceptors and **PTB7-Th** in ortho-dichlorobenzene (**oDCB**) on the top of ITO/ZnO/PFN substrate. The weight ratios of PTB7-Th and acceptors were varied from 1:1 to 1:1.5 to optimize the device performances. The total concentration was fixed at 25 mg ml⁻¹ for all blend solutions. Finally, the films were transferred into a vacuum evaporator and MoO₃ (10 nm) and Al (120 nm) were evaporated through a shadow mask (0.16 cm²) under vacuum onto the active layer. The current density -voltage (*J-V*) curves of devices were measured by using a Keithley 2400 source meter. The PCE was tested under Air Mass 1.5 Global (AM 1.5G) illumination of 100 mW cm⁻² (Newport Solar Simulator 94021A). A monocrystal silicon cell (VLSI Standards Inc.) calibrated by the National Renewable Energy Laboratory (NREL) was used as a reference. The external quantum efficiency (EQE) spectra of the devices were measured on a hypermonolight system (QTEST 1000 AD, Crowntech Inc.).

2.4 Mobility measurement

Space-charge limited current (SCLC) method was used to measure the hole and electron mobilities with a hole-only devices structure of ITO/PEDOT:PSS/active layer/MoO₃/Al and and an electron-only device architecture of ITO/ZnO/PFN/active layer/PFN/Al, by taking the dark current density in the range of 0-8 V and fitting the results to a space charge limited form. SCLC is described by the equation: $J = 9\varepsilon_0\varepsilon_r\mu_0V^2/8L^3$, where J is the current density, ε_0 is the permittivity of free space, ε_r is the relative dielectric constant of the transport medium, μ_0 is the

hole or electron mobility, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The hole-mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

2.5 Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) Characterization

GIWAXS measurements were performed at beamline 7.3.3^[18] at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12° - 0.16° , selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector.

3. Results and discussion

3.1 Materials design and synthesis

Figure 1. Optimized geometries (side view) of **DTF-IC** and **DTC-IC**

Density functional theory calculations by the DFT (B3LYP/6-31G* level) method were performed to investigate the molecular geometries and frontier orbitals of **DTF-IC** and **DTC-IC**. The detailed frontier orbitals are described in the ESI (**Table S1**). The space distances between the oxygen atoms of carbonyl groups and the hydrogen atoms of the adjacent thiophene rings on the same side are only 2.04 angstrom, indicating the O-H hydrogen-bond interactions, which facilitate the nearly flat backbone configurations of the two acceptors (**Figure 1**).

The synthetic routines of **DTF-IC** and **DTC-IC** are provided in **Scheme 1**. The *para*-hexylphenyl substituted **DTF** and **DTC** bromides (**6a** and **6b**) were synthesized according to the literature.^[19] The aldehydes **7a** and **7b** were prepared by lithiation with n-butyllithium followed by quenching with dimethylformamide (DMF). Subsequent Knoevenagel condensation between **7a/7b** and **INCN** afforded the two molecules. All the intermediates, as well as the **DTF-IC** and **DTC-IC**, were fully characterized by ¹H-NMR and ¹³C-NMR spectra (**Figure S1-S16**, ESI). The two acceptors exhibit good solubility in common organic solvents, such as chloroform, toluene and *ortho*-dichlorobenzene at room temperature.

3.2 Properties of the acceptors

The thermal properties of two acceptors were investigated by thermogravimetric analysis (TGA) and showed in **Figure S17** (ESI). The corresponding 5% weight-loss temperature (*T_d*) are 338 °C for **DTF-IC** and 344 °C for **DTC-IC**, separately, indicating their good thermal stabilities.

Table 1 Optical and electrochemical properties of **DTF-IC** and **DTC-IC**

Acceptor	$\lambda_{\max}$ solution [nm]	$\lambda_{\max}$ film [nm]	λ_{onset} [nm]	E_g ^[a] [eV]	E_{LUMO} ^[b] [eV]	E_{HOMO} ^[b] [eV]
DTF-IC	653	663	725	1.71	-3.80	-5.40
DTC-IC	671	679	738	1.68	-3.81	-5.41

^[a] estimated from the onset of electronic absorption of the acceptors films ($E_g=1240/\lambda_{\text{onset}}$ (nm)). ^[b] cyclic voltammetry results.

The chloroform solutions of the two acceptors show strong and narrow absorption in the region of 550-700 nm with maximum extinction coefficient of $2.02 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 653 nm for **DTF-IC** and $2.22 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 671 nm for **DTC-IC** (**Figure 2a**). From **Figure 2b**, the thin films of **DTF-IC** exhibit strong absorption in the region from 550 to 700 nm with absorption onset of 725 nm corresponding to an optical bandgap of 1.71 eV. In contrast, the absorption edge of **DTC-IC** film shows significant redshift of 13 nm (738 nm), which provide a relative small

Figure 2. (a) Absorption spectra of **DTF-IC** and **DTC-IC** in CHCl₃; (b) Absorption spectra of **DTF-IC**, **DTC-IC** and **PTB7-Th** films; (c) Cyclic voltammograms of **DTF-IC** and **DTC-IC** measured in 0.1 mol/L Bu₄NPF₆ solutions at a scan rate of 50 mV/s; (d) schematic illustration of relative positions of HOMO/LUMO energy levels of **DTF-IC**, **DTC-IC**, **PTB7-Th** and PC₇₁BM.

optical bandgap of 1.68 eV. Obviously, the reduced bandgap of **DTC-IC** can be ascribed to the relatively strong electron-donating property of the carbazole unit.^[20] **PTB7-Th**, a promising narrow bandgap donor polymer reported by Chen^[17], was chosen as the donor material to blend with **DTF-IC** and **DTC-IC** in this study. The normalized absorption spectrum of **PTB7-Th** film is also given in **Figure 2b**. It should be pointed out that the absorption spectrum of **PTB7-Th** showed strong overlapping with **DTF-IC** and **DTC-IC** in the region of 500-740 nm, indicating somewhat mismatching absorption of **PTB7-Th** with these two acceptors. The absorption data of **DTF-IC** and **DTC-IC** are summarized in **Table 1**.

The electrochemical behaviours of **DTF-IC** and **DTC-IC** were investigated by cyclic voltammetry (CV) (**Figure 2c**). From the onset reduction potential (E_{red}), the lowest unoccupied molecular orbital (LUMO) energy levels (E_{LUMO}) are determined according to the equation $E_{\text{LUMO}} = -e(E_{\text{red}} + 4.71)$ (eV)^[21] (redox potential of Fc/Fc^+ is 0.09 V vs Ag/AgCl in our CV measurement system). From **Figure 2c**, the oxidation/reduction potentials are measured as 0.70/0.91 V for **DTF-IC** and 0.71/0.90 V for **DTC-IC**, corresponding to the E_{HOMO} and E_{LUMO} values of -5.41/-3.80 eV (**DTF-IC**) and -5.42/-3.81 eV (**DTC-IC**), respectively. The CV data of **DTF-IC** and **DTC-IC** are presented in **Table 1**. We also estimated the energy levels of **PTB7-Th** by CV. Notably, the E_{LUMO} (-3.67 eV) and E_{HOMO} (-5.26 eV) of **PTB7-Th** are only 0.13/0.14 eV and 0.15/0.16 eV higher than those of **DTF-IC** and **DTC-IC**, respectively, which are smaller than the empirical threshold of 0.3 eV for effective exciton dissociation to overcome the binding energy of the excitons. However, highly effective photo-induced charge transfer are occurred between **PTB7-Th** and the two acceptors in the blended films, which can be confirmed by the photoluminescence (PL) quenching measurement as described in ESI (**Figure S18**). When excited at a wavelength of 706 nm, the PL spectrum of **PTB7-Th** ranged from 720 to 850 nm

with a peak value of 795 nm. However, the PL spectra were almost totally quenched when blended with **DTF-IC** or **DTC-IC**. To make a clear comparison, the energy levels diagrams of the used materials in the PSCs and fullerene-based acceptor [6,6]-phenyl-C71 butyric acid methyl ester (PC₇₁BM) are summarized in **Figure 2d**. Obviously, the two acceptors possessed similar E_{LUMO} values, about 0.1 eV higher than that of PC₇₁BM (-3.91eV),^[22] which facilitate high open-circuit voltage (V_{oc}) in PSCs.

3.3 Characteristics of Photovoltaic Devices

PSCs were fabricated using inverted device structure of indium tin oxide (ITO)/Zinc oxide (ZnO)/poly[(9,9-dioctyl-2,7-fluorene)-*alt*-(9,9-bis(3-N,N-dimethylamino)propyl)-2,7-fluorene] (**PFN**)/active layer/Al. **PFN** was used as cathode interlayer to modify the work function of the electrode, improve the charge extraction efficiency and reduce the recombination losses.^[23] Detailed device data are listed in the ESI (**Tables S2** and **Figure S19-20**). The optimized device performance data are summarized in **Table 2**, and the corresponding *J*-*V* characteristics are shown in **Figure 3a**. Under their optimal conditions, the **PTB7-Th:DTF-IC** (1:1.3,w/w) blend film displays a high open-circuit voltage (V_{oc}) of 0.88 V, 0.01 V bigger than that of the **PTB7-Th:DTC-IC** (1:1.3,w/w) based device and is coincided with its higher LUMO energy level. Both two acceptors-based devices exhibit highly similar short-circuit current density (J_{sc}) over 14 mA cm⁻², indicating weak effects of their absorption differences on the photo-to-current conversion process, which might be the result of the absorption overlapping of **PTB7-Th** with **DTF-IC/DTC-IC**. Relative to **DTF-IC**, the **DTC-IC** based device exhibits a slightly higher fill factor (FF), due to its better solubility from the longer alkyl side-chain.

Table 2. Device performance parameters of PSCs based on **PTB7-Th** and two acceptors

Acceptor	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	PCE ^[a,b] [%]
DTF-IC	0.87±0.01	14.35±0.25	53.9±0.9	6.70±0.27(6.92)

DTC-IC	0.86±0.01	14.12±0.09	55.7±0.6	6.80±0.16(7.02)
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^[a] Average values from 10 devices. ^[b] The best PCEs are provided in parentheses.

Under their optimal conditions, both two acceptors-based devices show similar photo-to-current response from 450 to 800 nm (**Figure 3b**) with a maximum value of 64% at 577nm for **DTF-IC** and 63% at 651nm for **DTC-IC**, respectively. Noticeably, EQE values of the two NF acceptors-based films exhibit over 50% only across a limited range of 522–705 nm (**Figure 3b**). If a more complementary absorption wide-bandgap donor polymer (like **J51**^[24], **J61**^[14] or **PBDB-T**^[13]) is used to blend with these two acceptors, enhanced PCEs can be anticipated, especially for the **DTC-IC**-based devices due to its narrow bandgap.

Figure 3. (a) The *J-V* curves of PSCs based on **PTB7-Th:DTF-IC** (1:1.3, w/w) and **PTB7-Th:DTC-IC**(1:1.3, w/w) under the illumination of AM 1.5G, 100 mW cm⁻²; (b) the corresponding EQE curves of **DTF-IC** and **DTC-IC** devices.

3.4 Charge transport and morphology properties

The morphology of the blend films with a weight ratio (polymer/acceptor) of 1:1.3 was investigated by atomic force microscopy (AFM). Both two acceptors-based films are very smooth with a root-mean-square (RMS) roughness of 1.16 nm for **PTB7-Th:DTF-IC** and slightly bigger RMS of 1.23 nm for **PTB7-Th:DTC-IC**, respectively (**Figure 4a, 4b**). As for the

phase images (**Figure 4c, 4d**), clear phase separation with domain size of 5-10 nm are observed, which facilitate the effectively exciton dissociation and high FF.

To characterize molecular packing as well as crystallinity, grazing incidence wide angle X-ray scattering (GIWAXS) was used to detect pure films of two acceptors and their blend films. **PTB7-Th** pure film exhibits broad scattering pattern in out of plane direction corresponding to π - π stacking peak ($q \approx 1.61 \text{ \AA}^{-1}$) in 1D line-cut, and also show face-on orientation relative to substrate(**Figure S21**, ESI). Pure **DTC-IC** film (**Figure 5b**) exhibits sharper scattering peaks than pure **DTF-IC** film (**Figure 5a**), which means **DTC-IC** adopted a more ordered packing and thus has better crystallinity than **DTF-IC**. The different crystallinities of two small molecules are remained when blending with **PTB7-Th**. While (100) peak disappears in **PTB7-Th:DTF-IC** blend film, the (100) peak in out-of-plane direction in **PTB7-Th:DTC-IC** blend film is remained at $q \approx 0.49 \text{ \AA}^{-1}$, indicating an ordered lamellar stacking. Meanwhile, double-peak fitting

Figure 4. (a) AFM height images for **PTB7-Th:DTF-IC** (1:1.3) and (c) the corresponding phase images ($4\ \mu\text{m} \times 4\ \mu\text{m}$); (b) AFM height images for **PTB7-Th:DTC-IC** (1:1.3) and (d) the corresponding phase images ($4\ \mu\text{m} \times 4\ \mu\text{m}$).

is applied to determine the (010) peaks relating to π - π stacking in the out-of-plane line-cuts of two blends, because the (010) peaks of donor and acceptor are too close to recognize. The fitting result shows that both π - π stacking peaks of **DTF-IC** and **DTC-IC** are located at $q \approx 1.54\ \text{\AA}^{-1}$ in the blend film, while the scattering peaks at $q \approx 1.62\ \text{\AA}^{-1}$ are attributed to **PTB7-Th** π - π stacking. According to the Scherrer equation,^[25] the information of crystalline size is related to the width of the diffraction peaks as coherence length ($CL = \frac{2\pi K}{FWHM}$, where $K=0.9$ is a shape factor (typically 0.8–1) and FWHM is the full width at half-maximum of a diffraction peak^[26]). CL values of donor and acceptor in the blend system are calculated and listed in **Table 3**. CL of **DTC-IC** (010) peak in **PTB7-Th:DTC-IC** ($51.4\ \text{\AA}$) is much greater than that of **DTF-IC** in **PTB7-Th:DTF-IC** ($12.4\ \text{\AA}$). The different crystallinity of acceptors also influences the degree of order of **PTB7-Th**, which shows larger CL in **PTB7-Th:DTC-IC** ($39.6\ \text{\AA}$) than in **PTB7-Th:DTF-IC** ($13.3\ \text{\AA}$). Better crystallinity leads to better charge transport which improves the mobility of both holes and electrons as discussed below. Thus a higher FF is obtained in **PTB7-Th:DTC-IC** than in **PTB7-Th:DTF-IC**.

Figure 5. GIWAXS 2D patterns for (a) pure **DTF-IC**, (b) pure **DTC-IC**, (c) **PTB7-Th:DTF-IC** blend, (d) **PTB7-Th:DTC-IC** blend and (e) 1D line-cuts.

Table 3. Coherence length of GIWAXS for two blend films

Sample	Coherence Length [$\text{\AA}$]	
	acceptor	donor
PTB7-Th:DTF-IC	12.36	13.32
PTB7-Th:DTC-IC	51.39	39.57

The bulk charge mobility properties of the optimized **PTB7-Th:DTF-IC** and **PTB7-Th:DTC-IC** blend films were investigated by the space-charge limited current (SCLC) method. The hole and electron mobilities were measured with device structures of ITO/poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS)/active layer/ (MoO_3)/Al and ITO/ZnO/PFN/active layer/PFN/Al, respectively. As shown in **Figure S21** (ESI), the **PTB7-Th:DTF-IC** blend films exhibit hole mobility of $2.31 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobility of $1.37 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. For the **DTC-IC** based films, the hole mobility is increased to $2.82 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as well as an improved electron mobility of $2.67 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The enhanced and

more balanced electron and hole mobility of **DTC-IC**-based device are contributed to the slightly higher FF value. To further investigate the performances of the two acceptors with wide bandgap polymers, J52 ^[27] was used as the donor materials blended with **DTC-IC** and **DTF-IC**, an improved PCE of 8.06% was achieved for the J52:**DTC-IC** (1:1, w/w) based device for the complementary absorption between J52 and **DTC-IC**, indicating the potential application of **DTC-IC** in highly efficient PSCs. Detailed results will be reported in our further paper.

When we prepare this manuscript, a novel A-D-A non-fullerene small molecule (**FDICTF**) based on dithienocyclopentafluorene core with four octyl side-chains was reported by Chen and co-workers ^[28], 10% PCE was achieved when blended **FDICTF** with a wide bandgap polymer (**PBDB-T**), indicating the effectiveness and bright future of these two electron-donating cores based NF acceptors.

4. Conclusion

In summary, we have prepared two novel A-D-A types of non-fullerene acceptors (**DTF-IC** and **DTC-IC**) based on dithienocyclopentafluorene and dithienocyclopentacarbazole as the electron-rich cores. Benefit from its strong electron-donating property, film absorption of **DTC-IC** shows 13 nm red-shifts comparing to that of **DTF-IC**. Under their optimal donor/acceptor weight ratios, inverted heterojunction solar cells fabricated with these two analogy molecules as acceptors and **PTB7-Th** as donor realized moderate PCEs of 6.92% for **DTF-IC** and 7.02% for **DTC-IC**, respectively. Considering the potential wide structure varieties and the absorption mismatch of these two acceptors with **PTB7-Th**, it is believed that enhanced PCE could be realized through adopting a wide bandgap polymer with complementary absorption or structural modification to red-shift the absorption spectra of the acceptors. We believe that these results can promote the design and synthesis of novel NF acceptors for high-performance PSCs.

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