Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Enhanced intramolecular charge transfer of unfused electron acceptors for efficient organic solar cells

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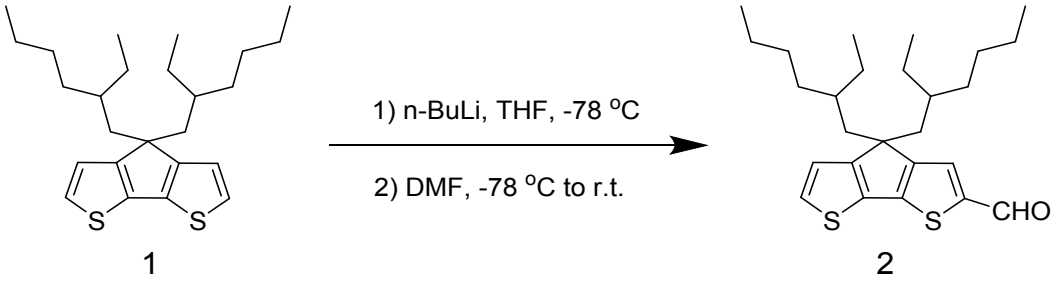
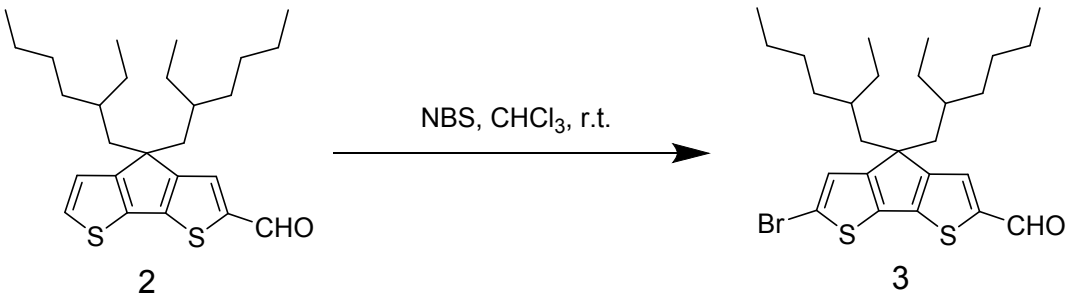
Synthesis of DF-TCIC and HF-TCIC



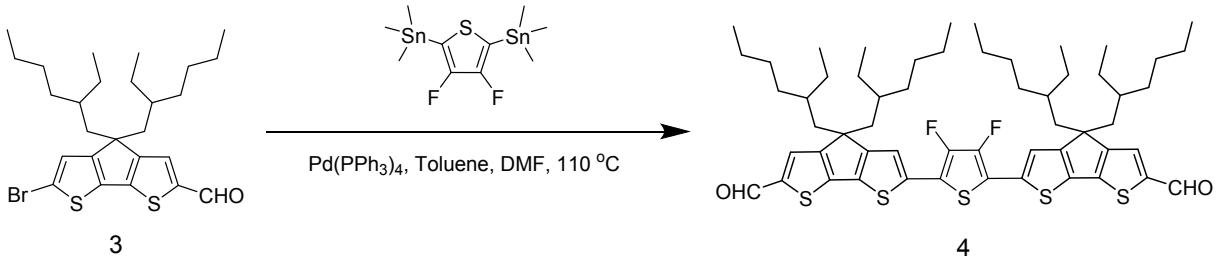
4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (2).

To a solution of **1** (2.01 g, 5.00 mmol) in 30 mL THF under the protection of nitrogen, n-BuLi (2.4 mL, 2.5 M, 6.0 mmol) was added dropwise at -78 °C. After stirring at -78 °C for 1.5 h, 1.0 mL DMF was added and continued to stir for 0.5 h. Then the mixture was warmed to room temperature and stirred overnight. The reaction was quenched by water, and then the mixture was extracted by dichloromethane. The organic layer was washed with water and then dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation and the obtained product was purified by column chromatography on silica gel with the mixture of hexane/dichloromethane (2:1). Yellow liquid. (1.09 g, 50.6%) ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.83(s, 1H), 7.57(s, 1H), 7.38 (d, J = 4.9 Hz, 1H), 6.99 (d, J = 4.9 Hz, 1H), 2.01-1.84 (m, 4H), 1.07-0.86(m, 16H), 0.79-0.71(m, 6H), 0.69-0.58 (m, 8H).



6-bromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (3).

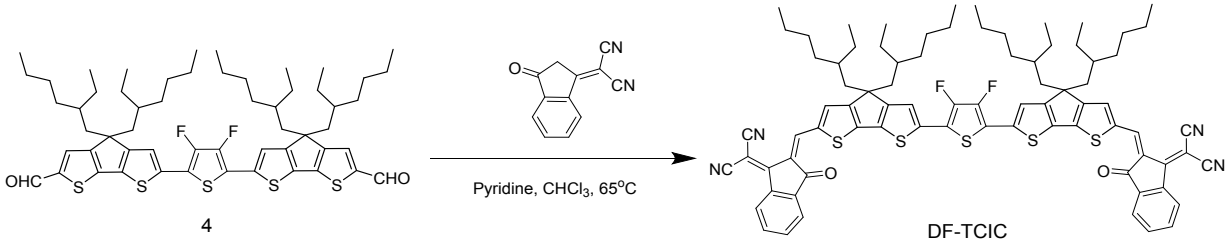
To a solution of **2** (1.09 g, 2.53 mmol) in 30 mL THF was added N-bromosuccinimide (NBS, 0.68 g, 3.79 mmol) at room temperature. The mixture was stirred for 4 h. Then the reaction mixture was extracted with chloroform and the organic phase was washed with water, dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation and the obtained product was purified by column chromatography on silica gel with the mixture of hexane/dichloromethane (2:1). Yellow liquid. (0.86 g, 66.7%) ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.83(s, 1H), 7.56 (t, J = 3.9 Hz, 1H), 7.03 (t, J = 3.8 Hz, 1H), 1.98-1.81 (m, 4H), 1.10-0.82(m, 16H), 0.81-0.71(m, 6H), 0.69-0.56 (m, 8H).



6,6'-(3,4-difluorothiophene-2,5-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde) (4).

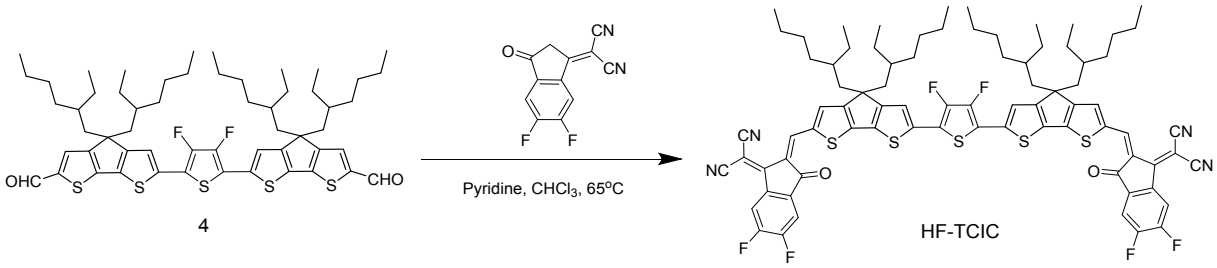
$Pd(PPh_3)_4$ was added to a degassed solution of **3** and **4** in toluene and DMF. The mixture was stirred at 110 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane and the organic phase was washed with water, dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation and the obtained product was purified by column chromatography on silica gel with the mixture of hexane/dichloromethane (1:2). Red solid. (0.46 g, 91.2%) ^{1}H NMR (400 MHz, $CDCl_3$): δ=

9.86(s, 2H), 7.58 (t, J = 3.6 Hz, 2H), 7.18 (t, J = 2.6 Hz, 2H), 2.03 – 1.87 (m, 8H), 1.09 – 0.83 (m, 32H), 0.79-0.71(m, 12H), 0.68-0.57 (m, 16H).



2,2'-((2Z,2'Z)-(((3,4-difluorothiophene-2,5-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (DF-TCIC)

To a solution of **5** (0.13 g, 0.13mmol) and 6 (0.13 g, 0.65 mmol) in dried $CHCl_3$ (30 mL), pyridine (1 mL) was added under the protection of nitrogen. The mixture was stirred at 65 °C for 12 h. After cooling to room temperature, the mixture was extracted with chloroform and the organic phase was washed with water, dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation and the obtained product was purified by column chromatography on silica gel with the mixture of hexane/dichloromethane (1:2). brown solid. (0.11 g, 60.4%) ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.88(s, 2H), 8.64 (d, J = 6.6 Hz, 2H), 7.94 – 7.86 (m, 2H), 7.75 (p, J = 7.1 Hz, 2H), 7.64 (s, 1H), 7.23 (s, 1H), 2.05 – 1.92 (m, 16H), 1.12 – 0.88 (m, 32H), 0.83-0.69(m, 16H), 0.69-0.60(m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 189.50, 188.77, 143.84, 142.36, 140.48, 139.78, 138.07, 137.99, 137.79, 137.73, 136.80, 135.14, 135.04, 134.41, 134.34, 134.28, 125.10, 123.46, 114.97, 114.94, 114.89, 114.86, 114.81, 54.12, 53.45, 43.15, 43.06, 35.43, 35.40, 34.28, 34.06, 28.50, 28.43, 27.48, 27.32, 22.91, 14.15, 14.08, 10.57, 10.53. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -130.95. MS (MALDI-TOF): Calcd for $C_{80}H_{82}F_2N_4O_2S_5$ (M+): 1329.86, Found: 1329.41.

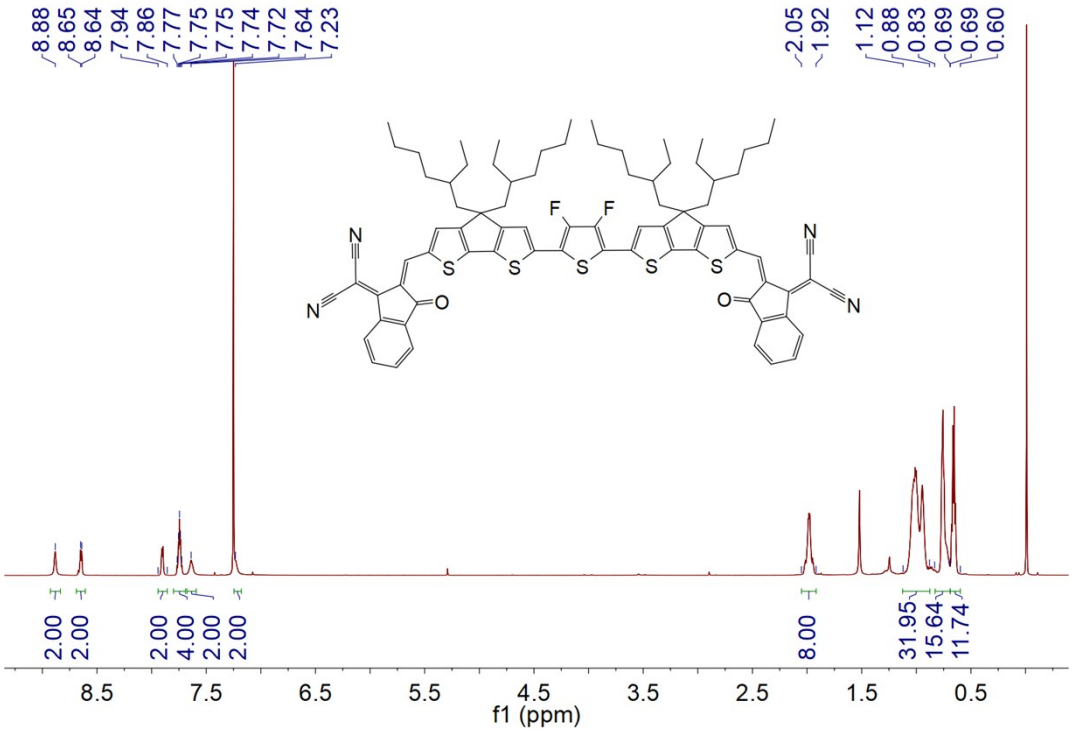


2,2'-((2Z,2'Z)-(((3,4-difluorothiophene-2,5-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (HF-TCIC)

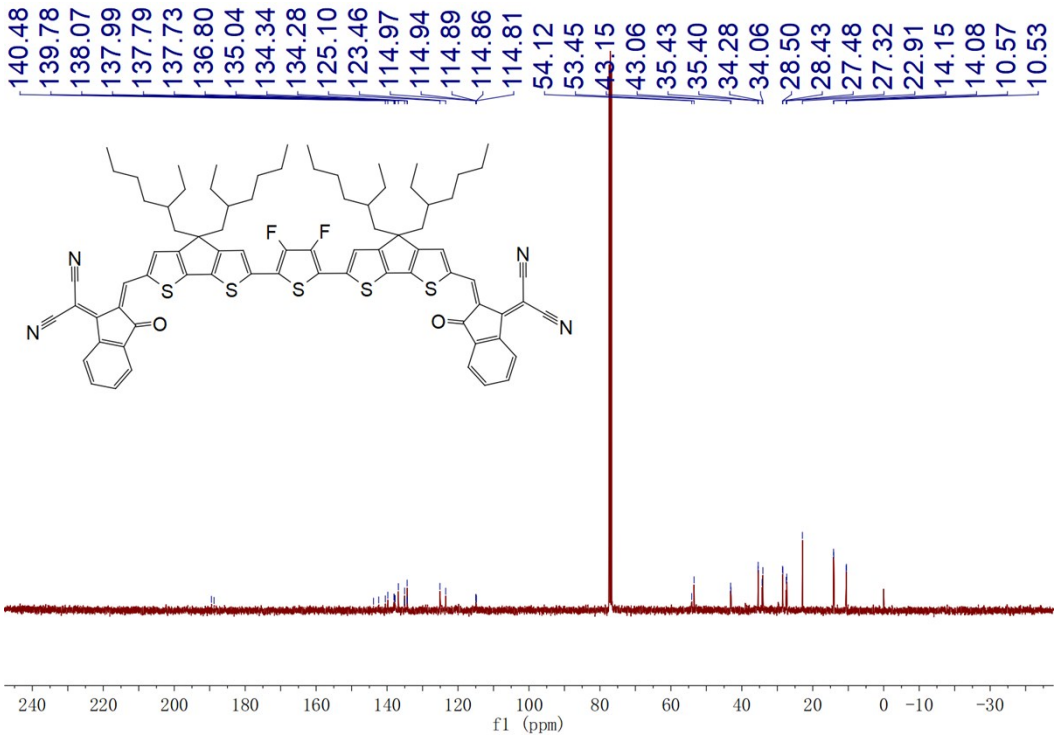
To a solution of **5** (0.13 g, 0.13mmol) and **7** (0.13 g, 0.65 mmol) in dried $CHCl_3$ (30 mL), pyridine (1 mL) was added under the protection of nitrogen. The mixture was stirred at 65 °C for 12 h. After cooling to room temperature, the mixture was extracted with chloroform and the organic phase was washed with water, dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation and the obtained product was purified by column chromatography on silica gel with the mixture of hexane/dichloromethane (1:2). brown solid. (0.11 g, 60.4%) ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.90(s, 2H), 8.53 (dd, J = 9.9, 6.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 4H), 7.25(s, 2H), 2.06 – 1.91 (m, 8H), 1.10 – 0.89 (m, 32H), 0.80 – 0.73 (m, 12H), 0.70 – 0.57 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.90, 186.14, 165.63, 165.57, 159.70, 158.42, 155.68, 152.95, 139.35, 138.21, 138.12, 137.49, 136.54, 134.47, 119.91, 119.89, 115.04, 114.81, 114.56, 114.07, 112.59, 112.39, 100.00, 68.45, 54.20, 53.45, 43.19, 43.11, 35.52, 35.47, 34.25, 34.01, 29.71, 28.48, 27.50, 27.28, 22.81, 14.09, 14.03, 10.60. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -123.25, -124.34, 130.77. MS (MALDI-TOF): Calcd for $C_{80}H_{82}F_2N_4O_2S_5$ (M+): 1401.82, Found: 1401.50.

NMR Spectra

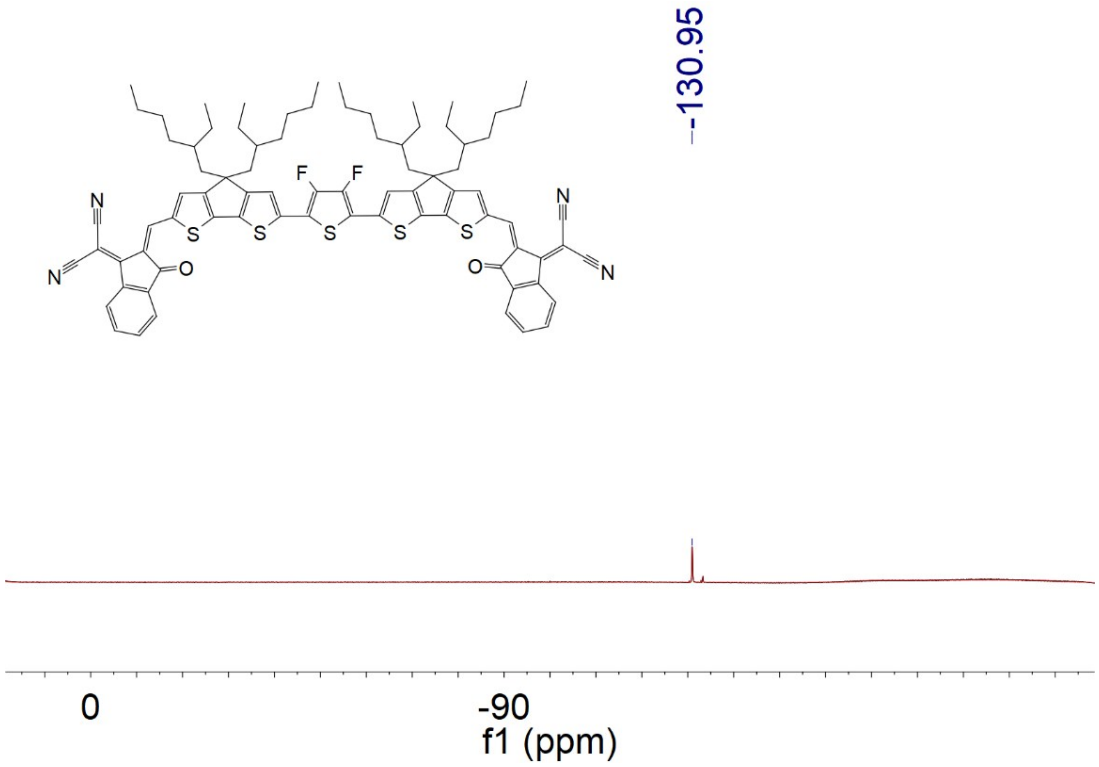
^{1}H NMR Spectrum of DF-TCIC



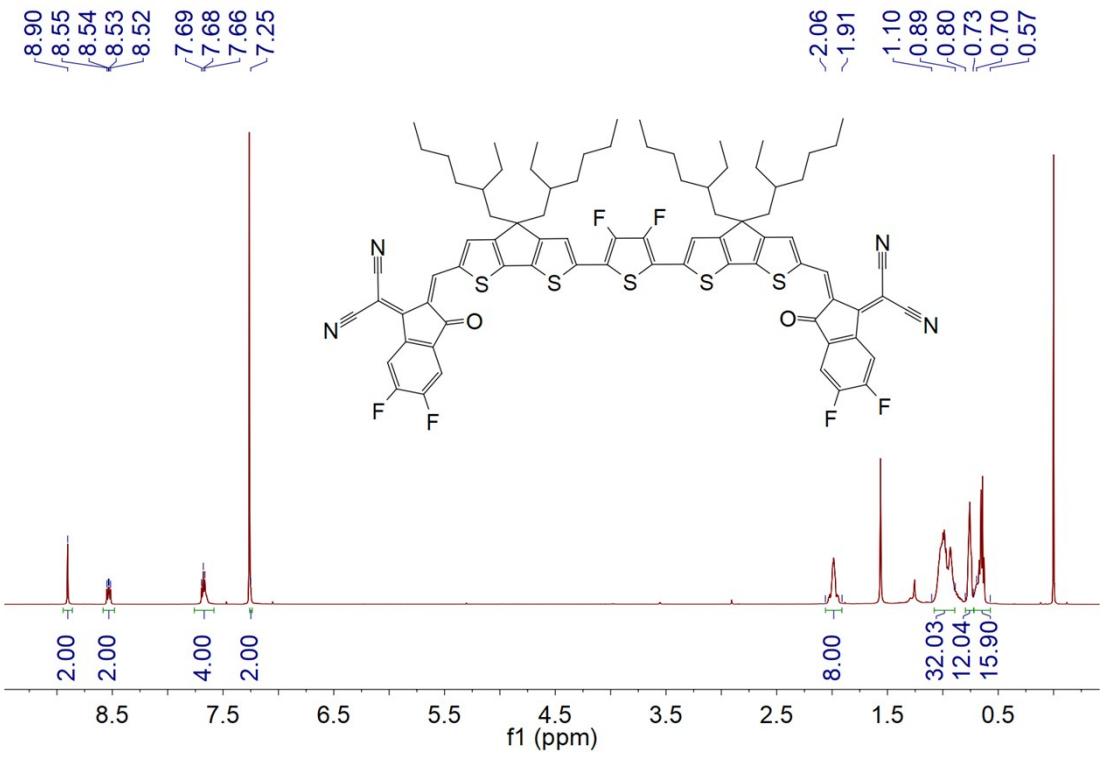
^{13}C NMR Spectrum of DF-TCIC



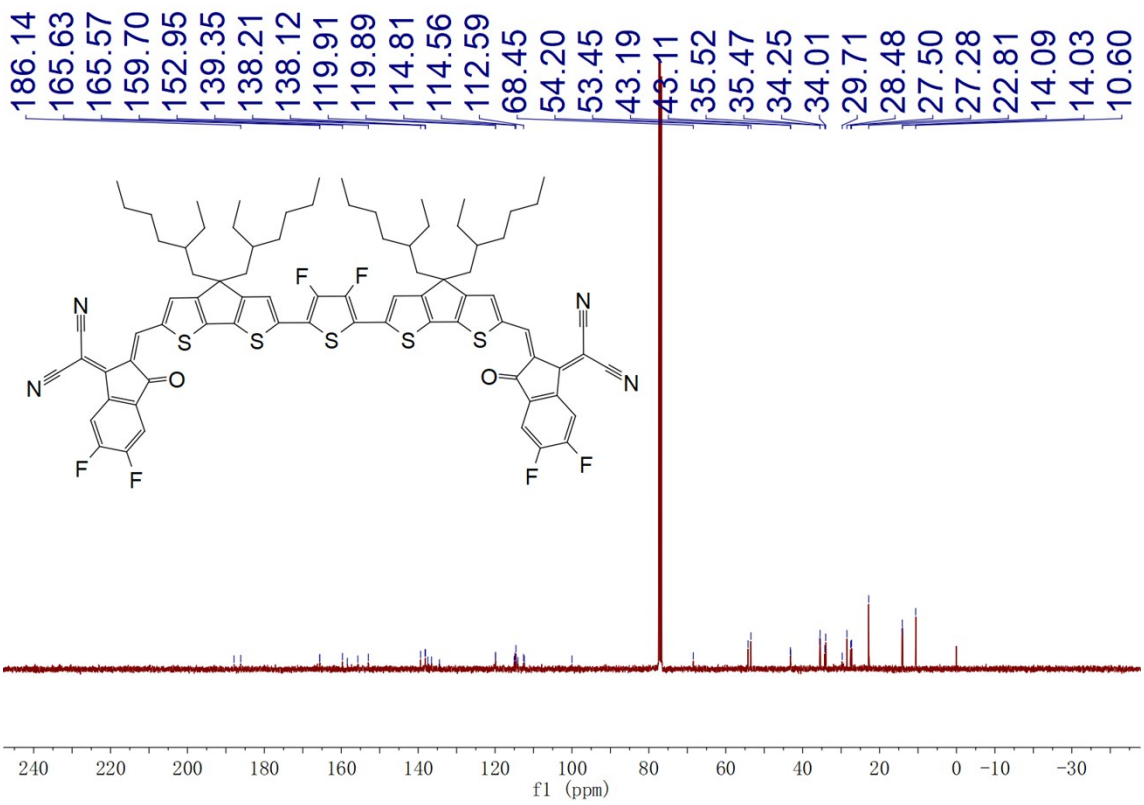
^{19}F NMR Spectrum of DF-TCIC



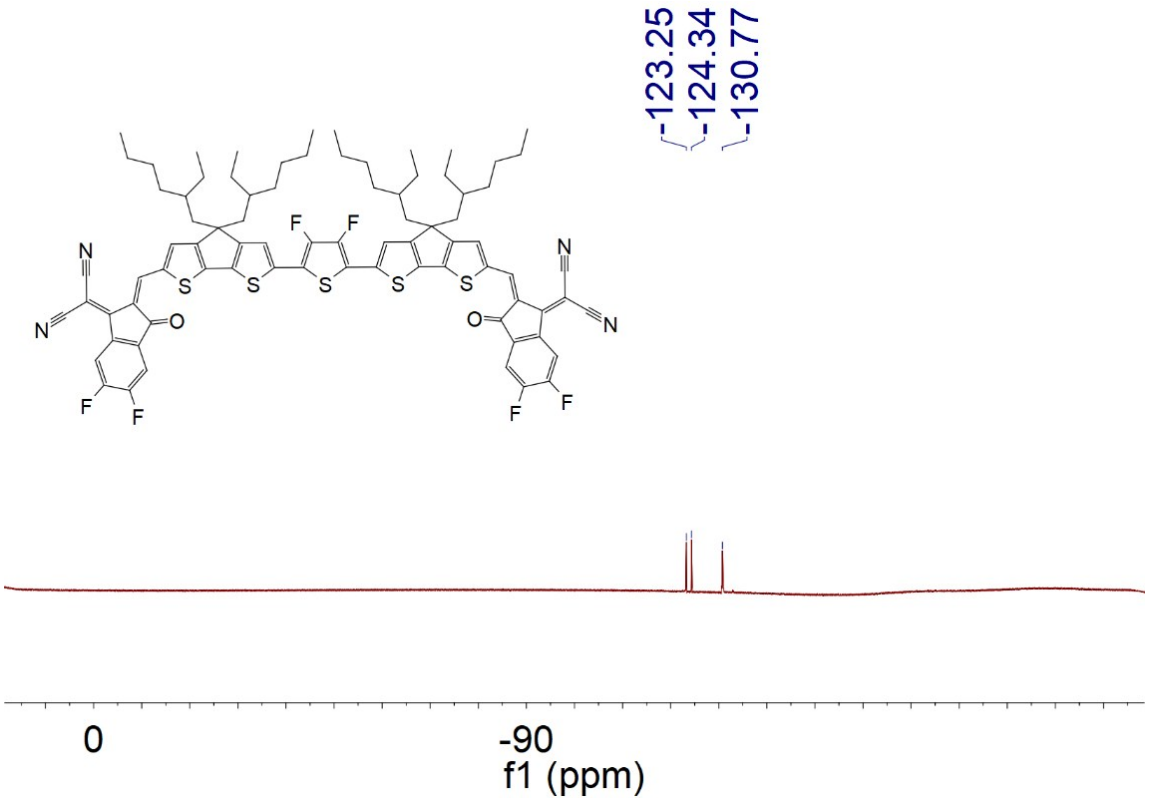
^{1}H NMR Spectrum of HF-TCIC



^{13}C NMR Spectrum of HF-TCIC



^{19}F NMR Spectrum of HF-TCIC



Supporting Figures and Tables

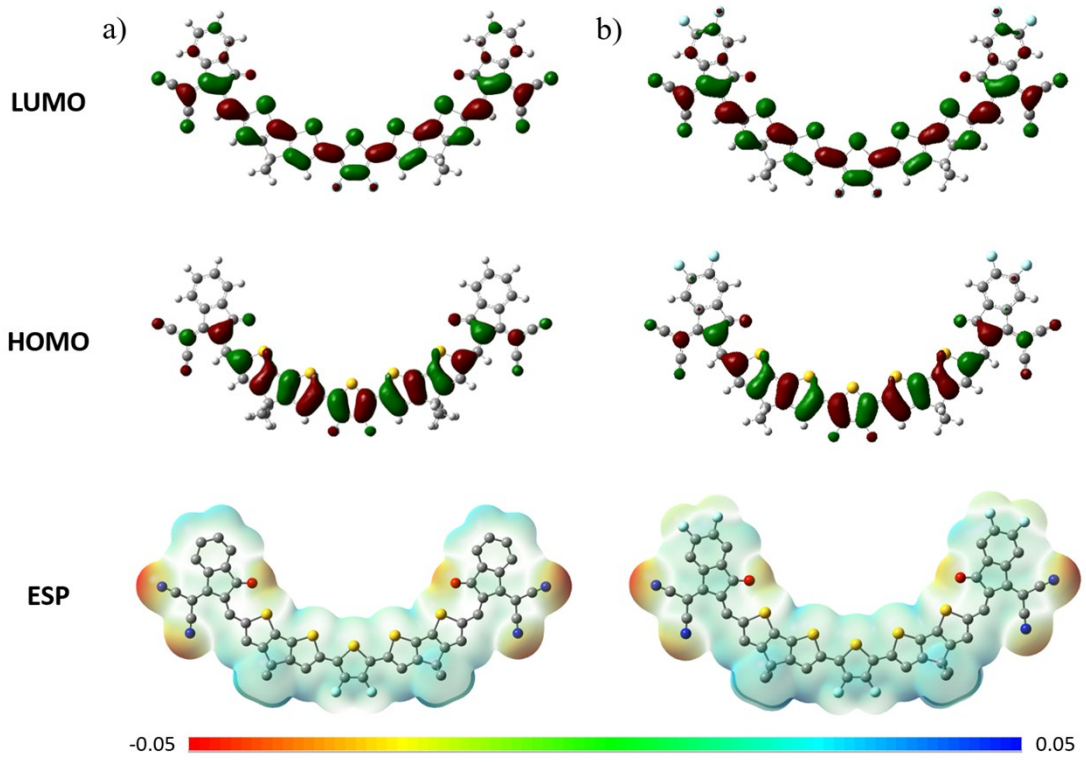


Figure S1. HOMO/LUMO frontier molecular orbitals and molecular electrostatic potential (ESP) map of a) DF-TCIC and b) HF-TCIC.

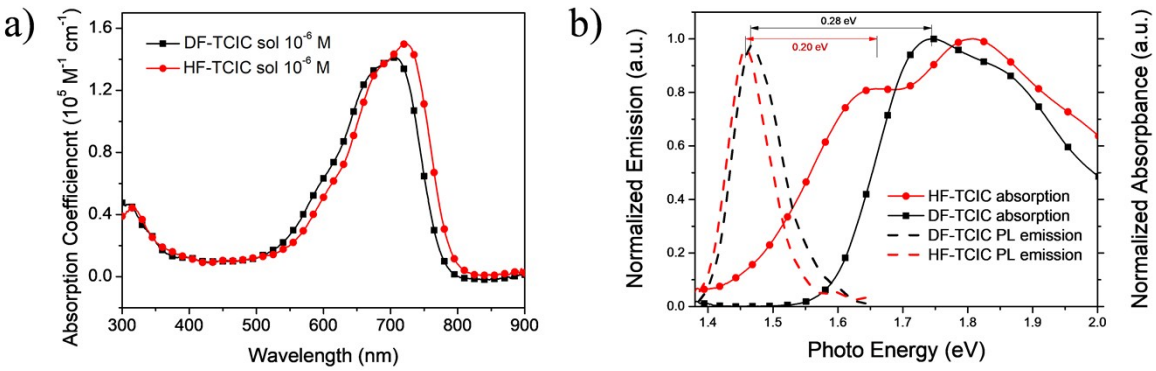


Figure S2. a) The absorption spectra of DF-TCIC and HF-TCIC in chloroform. b) PL emission and UV−vis absorption spectra of DF-TCIC and HF-TCIC films.

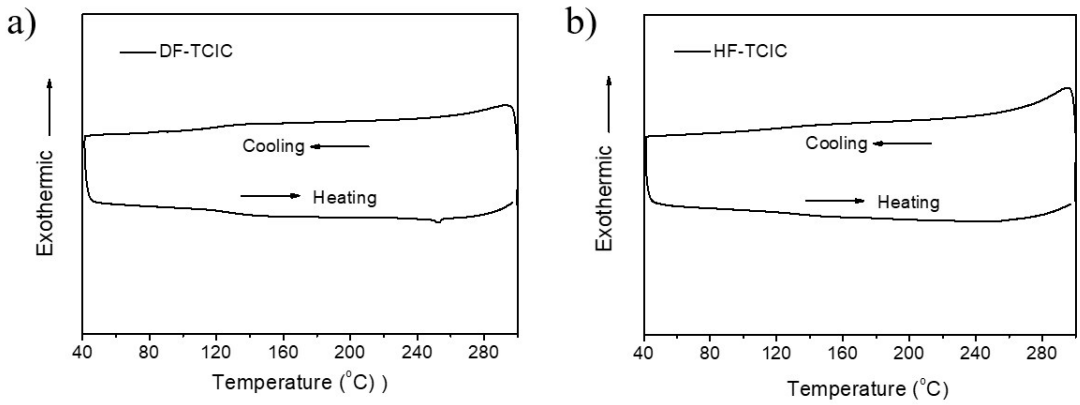


Figure S3. DSC curves of a) DF-TCIC and b) HF-TCIC.

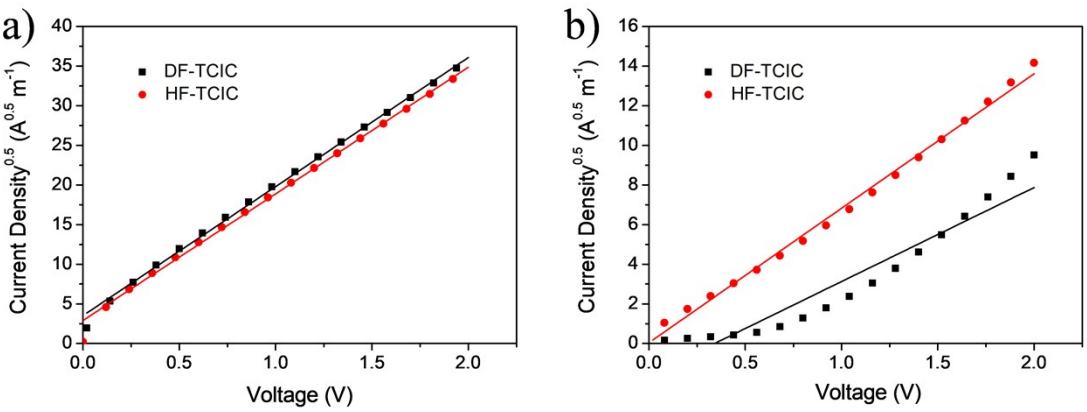


Figure S4. a) $J^{0.5}$-V curves of the hole-only devices based on PBDB-T:DF-TCIC and PBDB-T: HF-TCIC films. b) $J^{0.5}$-V curves of the electron-only devices based on PBDB-T:DF-TCIC and PBDB-T: HF-TCIC films.

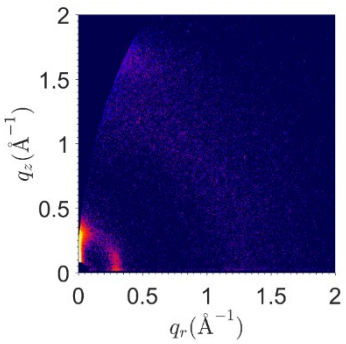


Figure S5. 2D GIWAXS pattern of PBDB-T

Table S1. GISAXS fitted parameters.

Active layer	Amorphous intermixing phase (nm)	Acceptor Domain size $2R_g$ (nm)
PBDB-T: DF-TCIC	42	9.8
PBDB-T: HF-TCIC	54	10