

Supporting Information

Design and synthesis of non-fused non-fullerene acceptors containing naphthobisthiadiazole for organic solar cells

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Experimental Section

Measurements and characterization.

^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ^1H NMR and ^{13}C NMR spectra were referenced to tetramethylsilane (0 ppm) for CDCl_3 . Single crystals were grown by liquid-liquid diffusion with ethanol into chloroform. Olex2 was used to solve the structure with the ShelXT structure solution program by inner Phasing, and the structure was solved with the ShelXL refinement package, by least squares minimization.¹ Cyclic voltammetry was carried out on a CHI660A Electrochemical Workstation with three electrodes configuration, using $\text{Hg}/\text{Hg}_2\text{Cl}_2$ as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. 0.1 mol/L tetrabutylammonium hexafluorophosphate in acetonitrile was used as the supporting electrolyte. Potentials were referenced to the ferrocenium/ferrocene couple by using ferrocene as external standards in acetonitrile solutions. Differential scanning calorimetry (DSC) were recorded on a DSC214 at a heating rate of $15\text{ }^\circ\text{C min}^{-1}$ under a nitrogen flow rate of 20 mL min^{-1} . The absorption spectra of materials were achieved via UV-Vis spectrometer (HP 8453, photodiode array type). Photoluminescence (PL) spectra were measured on a Horiba Fluoromax-4 spectrofluorometer. Electroluminescence (EL) spectra were recorded by optical analyzer Photo Research PR745, and EQE_{EL} were measured by setting external current source equivalent to short-circuit current under AM 1.5G. Films for Grazing-incidence wide-angle X-ray scattering (GIWAXS) were prepared by spin-coating active layers on $\text{SiO}_2/\text{PEDOT:PSS}$ substrates and was performed on a Xenocs Xeuss 2.0 system with an Excillum MetalJet-D2 X-ray source. All the samples were prepared under the optimized photovoltaic device processing conditions.

Device fabrication and characterization.

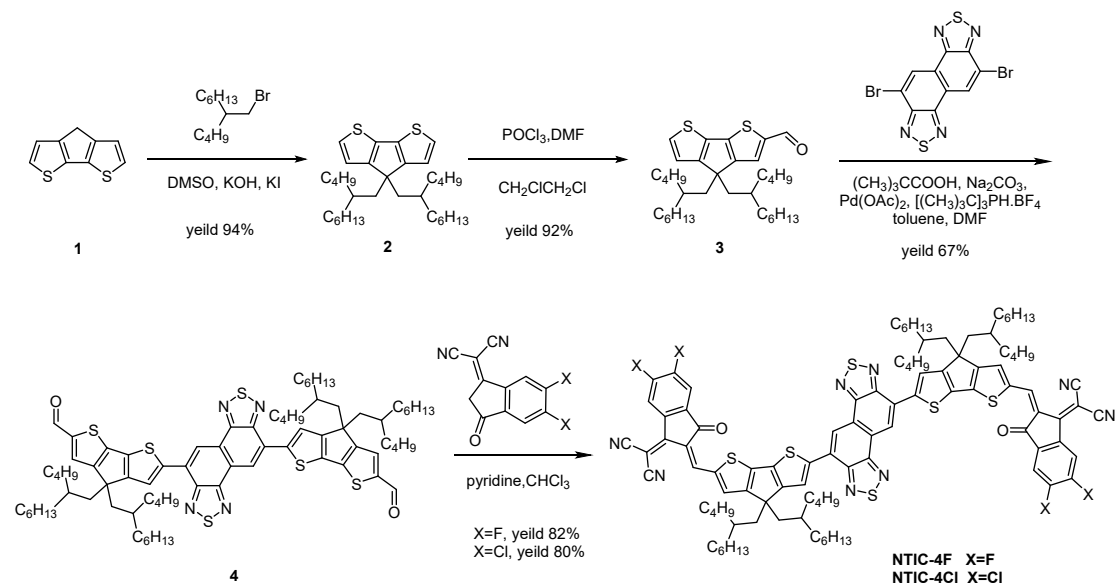
The device structure of organic solar cells was ITO/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, P VP Al 4083)/Active

layer/PFN-Br/Ag. Pre-cleaned ITO glass substrates were treated with plasma for 2 min, and PEDOT:PSS was spin-coated on the substrates at 3000 r.p.m. After thermal annealing for 150 °C/10 min, all the substrates were transferred to N₂ glovebox. Solutions for active layers were prepared by dissolving PTzBI-dF:acceptors (1:1, wt:wt) blend in chloroform, and the concentrations were 11 mg/mL in total. The solutions were preheated on 50 °C hotplate for one night, and CN was added in the solutions 10 min before used. 100 nm-thickness active layers were achieved by spin-coating (800 r.p.m.) on PEDOT:PSS, and then thermal annealed at hotplate for 110 °C/10 min. 0.5 mg/mL PFN-Br methanol solution was spin-coated (2000 r.p.m.) on the active layer before the evaporation of Ag at 1×10^{-6} mbar N₂ pressure. *J-V* measurements were conducted on Keithley 2400 source meter under 1 sun, and AM 1.5G spectrum provided by a class solar simulator (Enlitech Taiwan SS-F5) was calibrated by a Si solar cell in N₂ glovebox. Active layer area was redefined by a mask of 0.04 cm². The hole-only and electron-only devices were measured in dark using the same system and fitted with single-carrier SCLC model. EQE profiles were measured on Enlitech Taiwan QE-R3011 with a standard single-crystal Si solar cell.

Materials and Synthesis

Two end groups (2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (IC-2F) or (2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile(IC-2Cl) were purchased from SunaTech Inc.. And the polymer donor PTzBI-dF were synthesized according to our previous report.¹ Additionally, all the solvents and organic reagents were got from commercial sources and used without further purification.

5,10-dibromonaphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole),² PTzBI-dF,³ PFN-Br⁴ were synthesized according to methods in previous reports. Other raw materials and reactants were obtained from commercial sources without further purification.



Scheme S1. Synthesis of aceptors NTIC-4F and NTIC-4Cl.

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

Weighed 4H-cyclopenta[2,1-b:3,4-b']dithiophene(1) 2.00 g (11.22 mmol), potassium hydroxide 2.52 g (44.88 mmol), potassium iodide 190 mg (1.12 mmol) and dissolve them in 40 ml dimethyl sulfoxide in 100 ml flask under nitro protection. Stir the mixture at 25 degrees Celsius, away from light for 30 minutes. Then the 5-(bromomethyl)undecane 6.43 g (25.80 mmol) was measured and dropped into the flask. Next, the reaction system was stirred at 25 °C for 8 hours. After the reaction, methylene chloride was used to extract the reaction solution with deionized water for three times. The organic phase was dried with anhydrous sodium sulfate, and the solvent was removed by vacuum distillation after filtration. Finally, the crude product was purified by column chromatography and petroleum ether was used as eluent to afford 4,4-bis(2-butyldecyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene(2) 5.42 g (10.53 mmol), colorless oily liquid. Yield 94%. ¹H NMR (400 MHz, CDCl₃) δ 7.10 (dt, *J* = 4.8, 0.7 Hz, 2H), 6.91 (d, *J* = 4.9 Hz, 2H), 1.86 (d, *J* = 5.2 Hz, 4H), 1.25 – 1.18 (m, 4H), 1.14 – 1.07 (m, 4H), 1.01 – 0.83 (m, 30H), 0.75 (t, *J* = 6.9 Hz, 6H), 0.62 (dt, *J* = 10.9, 5.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 157.73, 136.96, 124.08, 122.48, 53.41, 44.00, 35.15, 34.88, 33.68, 32.00, 29.55, 28.75, 26.44, 22.92, 22.82, 14.28, 14.24.

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

N,N-dimethylformamide (DMF) 1.64 g (10.68 mmol) was cooled down to 0 °C, then dropped phosphorus oxychloride 0.85 g (11.65 mmol) into the DMF step by step to hold the low temperature, followed by stirred continuously at 0 °C for 45 minutes. After that, warmed it to room temperature for another 15 minutes in order to prepare the Vilsmeier-Haack (V-H) reagent. Next, dropped the V-H reagent into the 1,2-dichloroethane (100 ml) solution of the compound 2 5.00 g (9.71 mmol) under nitrogen for 15 minutes. Heated the system to 120 °C to reflux the solvent for 4 hours. Returned the reaction to room temperature and extracted the solution with methylene chloride and deionized water for three times. The organic phase was then evaporated by rotary evaporator, followed by column chromatography and petroleum ether was used as eluent. Ended up with the 4.87 g (8.97 mmol) 4,4-bis(2-butyloctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde(3), pale green viscous liquid. Yield 92%. ¹H NMR (400 MHz, CDCl₃) δ 9.82 (s, 1H), 7.56 (s, 1H), 7.36 (d, *J* = 4.9 Hz, 1H), 6.98 (d, *J* = 4.9 Hz, 1H), 1.97 – 1.87 (m, 4H), 1.22 – 0.81 (m, 38H), 0.74 (t, *J* = 6.9 Hz, 6H), 0.63 – 0.55 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 182.64, 182.61, 182.58, 162.14, 162.13, 162.11, 157.87, 148.13, 142.98, 136.11, 131.07, 129.23, 122.76, 53.94, 43.84, 35.24, 35.10, 34.97, 34.84, 33.95, 33.83, 31.96, 31.92, 29.51, 29.46, 28.69, 28.68, 26.39, 22.87, 22.84, 22.77, 22.63, 14.24, 14.23, 14.19, 14.18.

6,6'-(naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)-5,10-diyl)bis(4,4-bis(2-butyloctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde) (4)

In a nitrogen environment, 5,10-dibromonaphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) 1.30 g (3.23 mmol), compound 3 4.04 g (7.44 mmol), pivalic acid 0.83 g (8.10 mmol), sodium carbonate 1.71 g (16.17 mmol), palladium (II) acetate 73 mg (0.32 mmol) and tri-tert-butylphosphine tetrafluoroborate 94 mg (0.32 mmol) were weighted in turn and dissolved in the mixture of 50 ml toluene and 50 ml DMF. The reaction system was heated to 140 °C and refluxed for 12 hours. Afterward, returned the reaction to room temperature and extracted the solution with methylene chloride and deionized water for three times. The organic phase was then evaporated by rotary evaporator, followed by column chromatography. A mixture of petroleum

ether to methylene chloride with a volume ratio of 3 to 1 was used as eluent. At last, dark violet solid 6,6'-(naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)-5,10-diyl)bis(4,4-bis(2-butyloctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde)(4) 2.87 g was obtained. Yield 67%. ¹H NMR (400 MHz, CDCl₃) δ 9.83 (s, 1H), 7.56 (s, 1H), 7.37 (d, *J* = 4.8 Hz, 1H), 6.99 (d, *J* = 4.9 Hz, 1H), 1.92 (d, *J* = 5.0 Hz, 4H), 1.23 – 0.84 (m, 40H), 0.75 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 182.77, 162.83, 158.61, 153.65, 152.35, 147.61, 144.20, 143.33, 138.68, 130.80, 127.08, 125.08, 123.63, 123.49, 122.04, 54.50, 43.36, 43.25, 35.56, 35.52, 34.45, 34.29, 28.74, 28.64, 27.72, 27.51, 22.92, 14.22, 14.16, 10.90, 10.78.

2,2'-((2Z,2'Z)-((naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)-5,10-diyl)bis(4,4-bis(2-butyloctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (NTIC-4F)

Chloroform solution (50 ml) of compound 4 150 mg(0.11 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile 156.2 mg (0.68 mmol) and pyridine 0.6 ml was blended away from light for 15 min, then heated to 80 °C to reflux 8 hours. The reaction mixture was precipitated in absolute methanol, followed by filtration. The crude product was purified by column chromatography with chloroform as eluent to afford the product 2,2'-((2Z,2'Z)-((naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)-5,10-diyl)bis(4,4-bis(2-butyloctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2, 3-dihydro-1H-indene-2,1-diylidene)) dimalononitrile (NTIC-4F) 144 mg, a dark blue solid. Yield 82%. ¹H NMR (400 MHz, CDCl₃) δ 9.20 (s, 2H), 8.93 (s, 2H), 8.54 (dd, *J* = 10.0, 6.5 Hz, 2H), 8.44 – 8.39 (m, 2H), 7.71 (dd, *J* = 15.9, 8.2 Hz, 4H), 2.19 – 2.03 (m, 8H), 1.23 – 0.61 (m, 80H), 0.61 (dd, *J* = 50.1, 5.9 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 186.00, 166.27, 158.49, 155.44, 153.49, 152.08, 147.11, 139.81, 139.33, 138.60, 138.12, 136.55, 134.53, 126.97, 125.25, 124.39, 122.53, 119.80, 114.92, 114.64, 112.60, 112.46, 68.27, 54.52, 43.90, 35.41, 35.17, 34.90, 34.30, 32.02, 31.97, 29.71, 28.66, 26.45, 23.04, 22.84, 22.71, 14.29, 14.21, 13.99. MALDI-TOF:1749.5.

2,2'-((2Z,2'Z)-((naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)-5,10-diyl)bis(4,4-bis(2-

butyloctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methaneylylidene))bis(5,6-dichloro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile(NTIC-4Cl)

Chloroform solution (50 ml) of compound 4 150 mg (0.11 mmol), 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile 178.5 mg (0.68 mmol) and pyridine 0.6 ml was blended away from light for 15 min, then heated to 80 °C to reflux 8 hours. The reaction mixture was precipitated in absolute methanol, followed by filtration. The crude product was purified by column chromatography with chloroform as eluent to afford the product 2,2'-((2Z,2'Z)-((naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)-5,10-diylbis(4,4-bis(2-butylloctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methaneylylidene))bis(5,6-dichloro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (NTIC-4Cl) 147 mg, a dark blue solid. Yield 80%. ¹H NMR (400 MHz, CDCl₃) δ 9.06 (s, 2H), 8.91 (s, 2H), 8.75 – 8.68 (m, 2H), 8.44 (s, 2H), 7.92 (s, 2H), 7.74 (s, 2H), 2.22 – 2.05 (m, 8H), 1.21 – 0.50 (m, 92H). MALDI-TOF:1816.5.

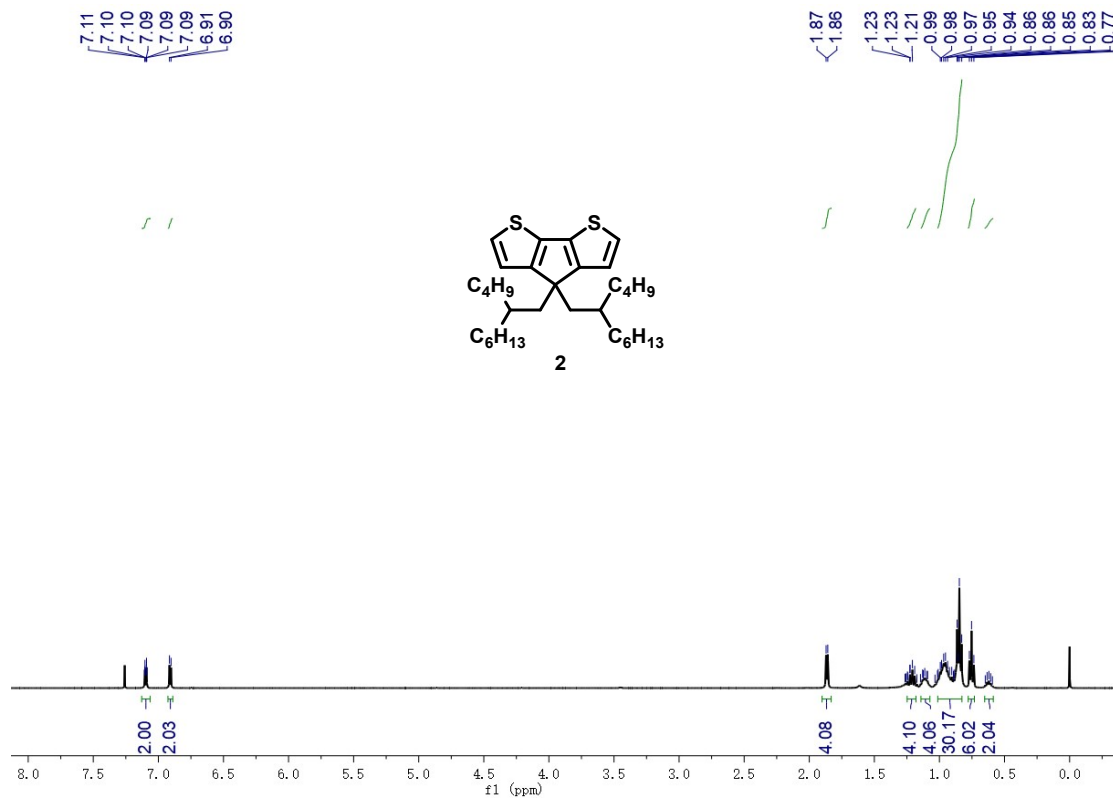


Fig. S1 Detailed ¹H NMR spectra in CDCl₃ for compound 2.

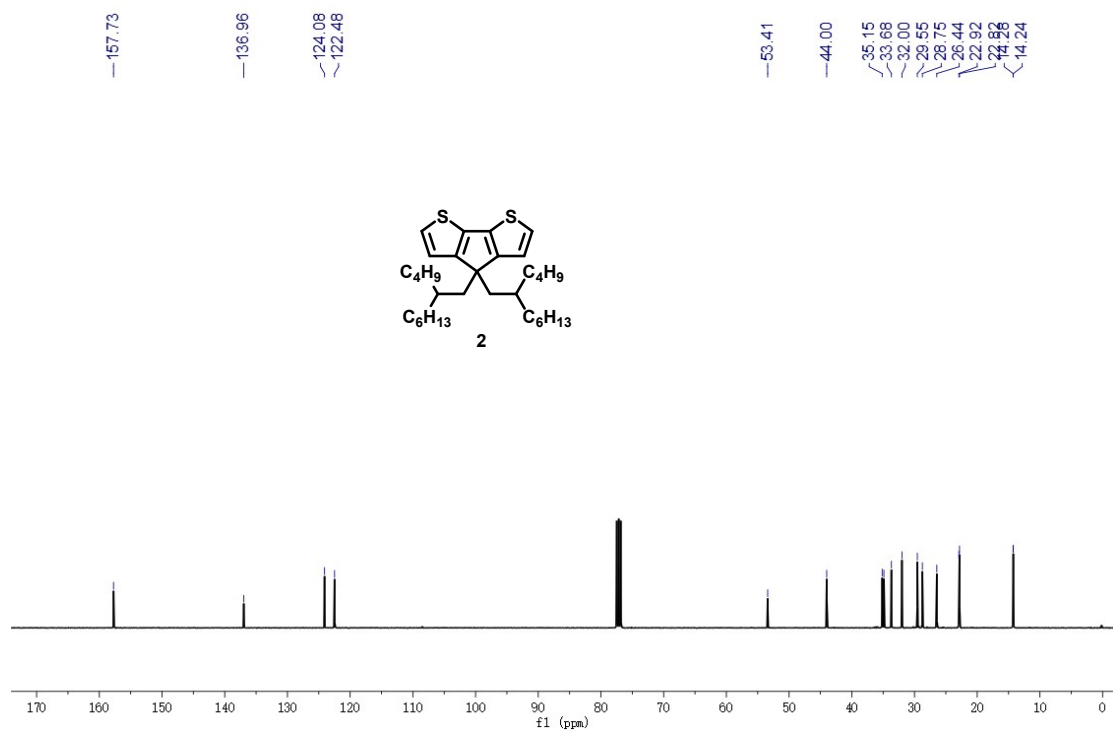


Fig. S2 Detailed ¹³C NMR spectra in CDCl₃ for compound 2.

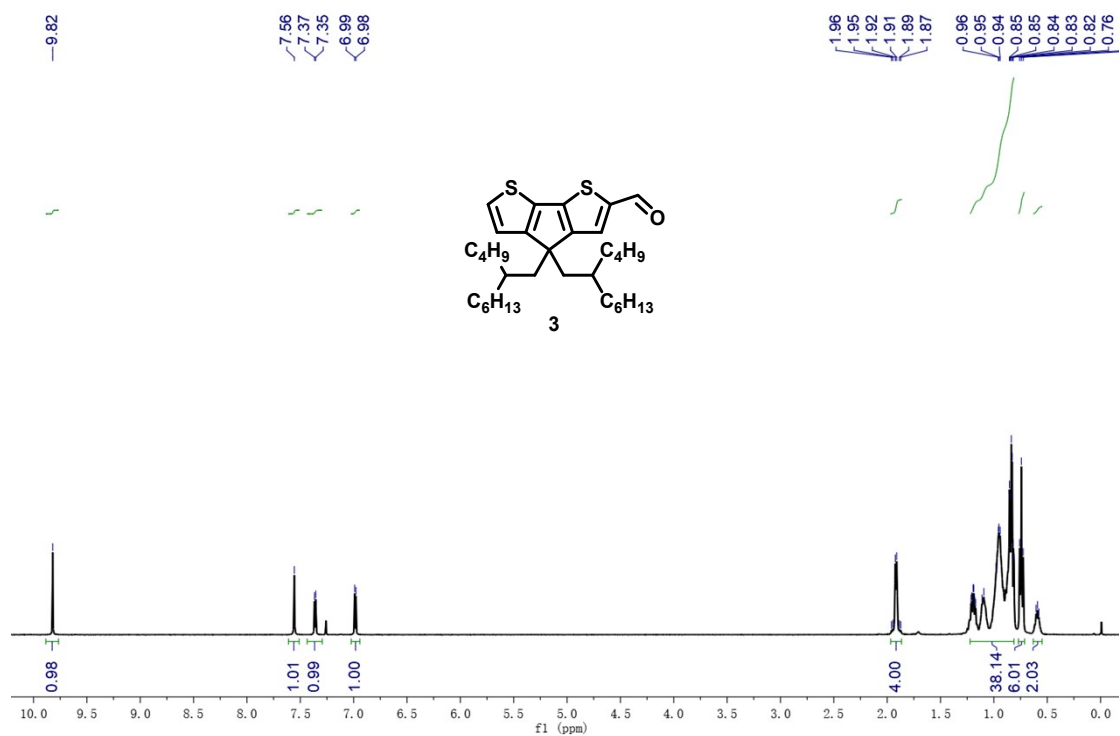


Fig. S3 Detailed ¹H NMR spectra in CDCl₃ for compound 3.

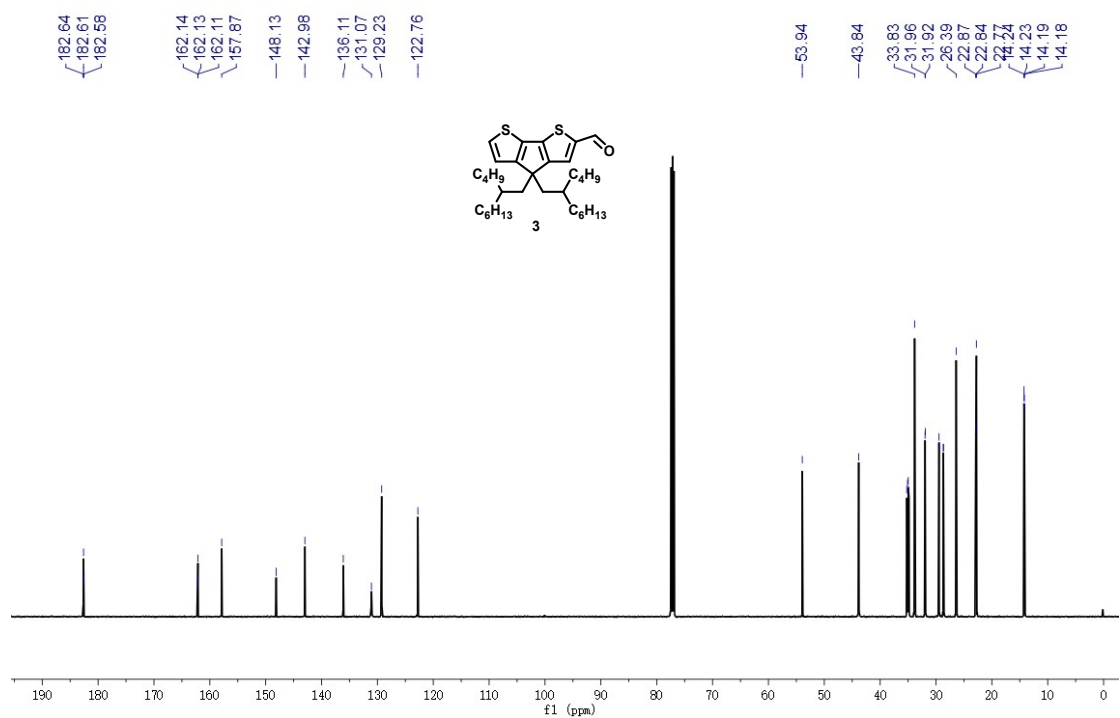


Fig. S4 Detailed ¹³C NMR spectra in CDCl₃ for compound 3.

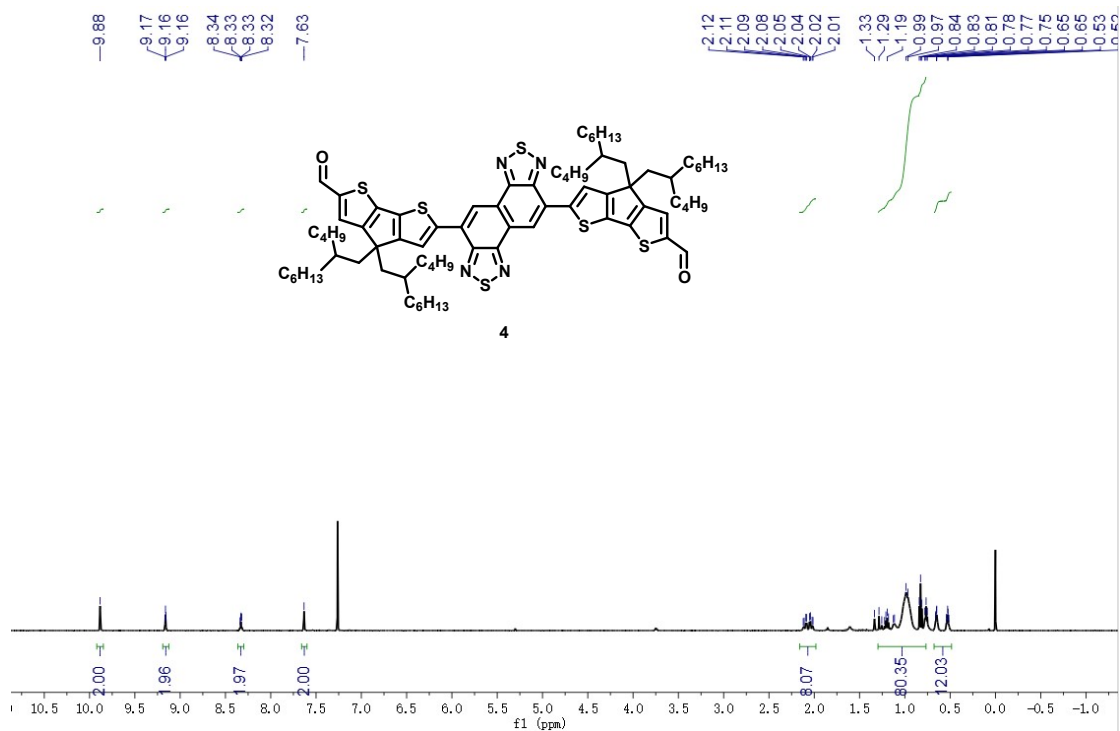


Fig. S5 Detailed ^1H NMR spectra in CDCl_3 for compound 4.

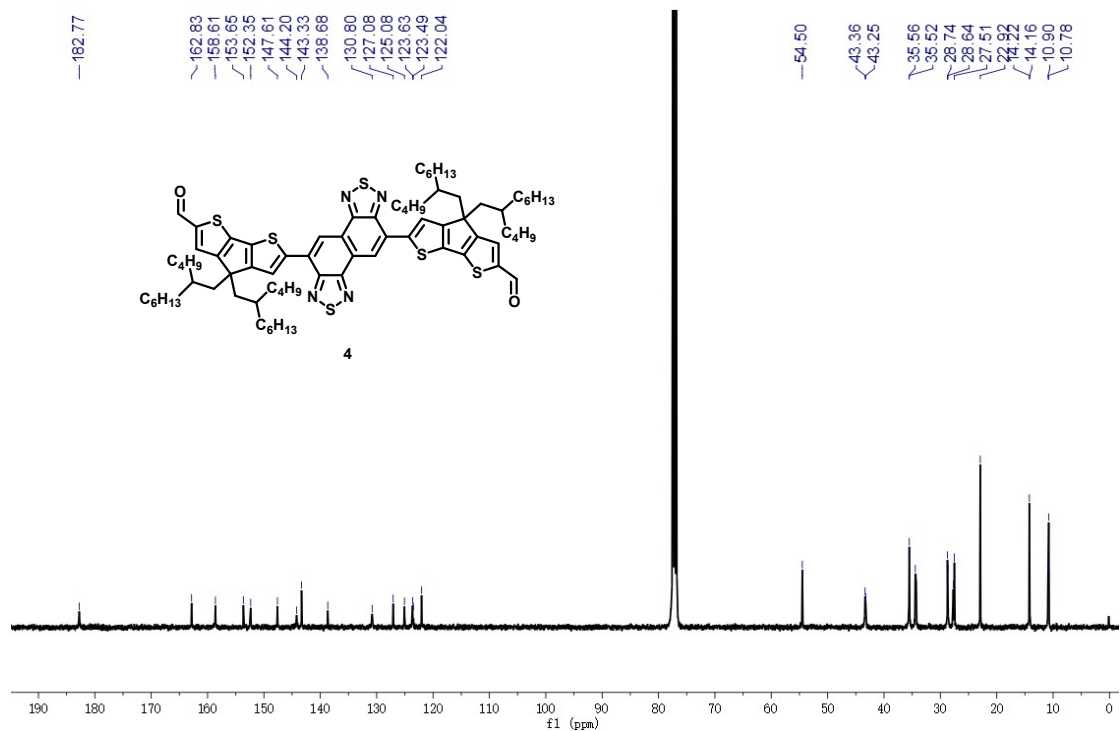


Fig. S6 Detailed ^{13}C NMR spectra in CDCl_3 for compound 4.

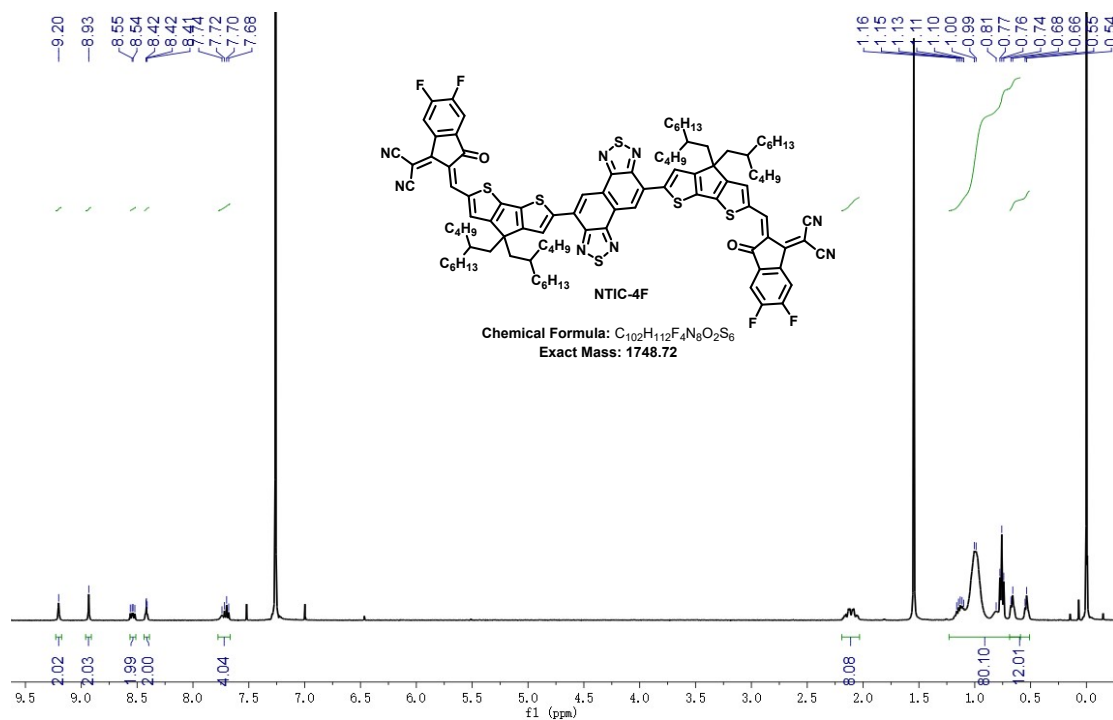


Fig. S7 Detailed 1H NMR spectra in $CDCl_3$ for compound NTIC-4F.

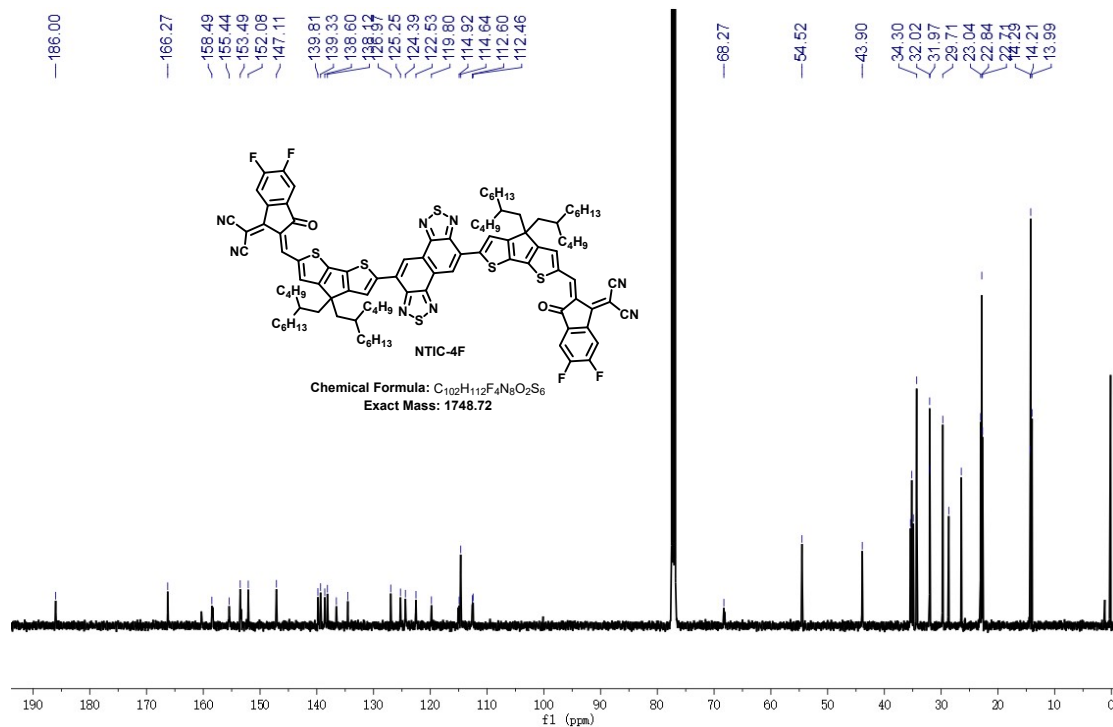


Fig. S8 Detailed ^{13}C NMR spectra in $CDCl_3$ for compound NTIC-4F.

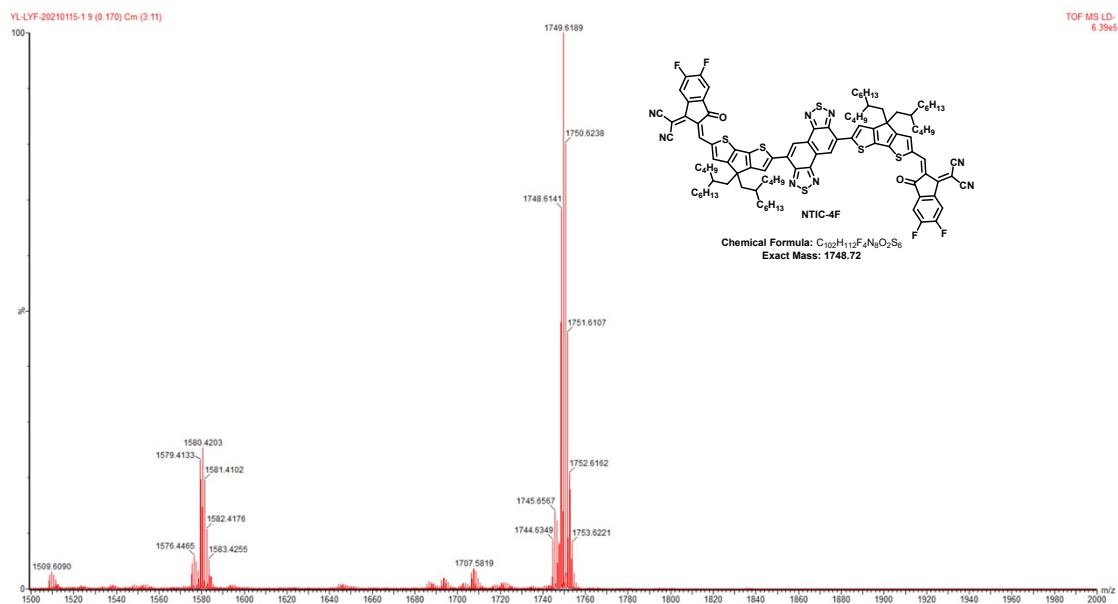


Fig. S9 MALDI-TOF spectra for NTIC-4F.

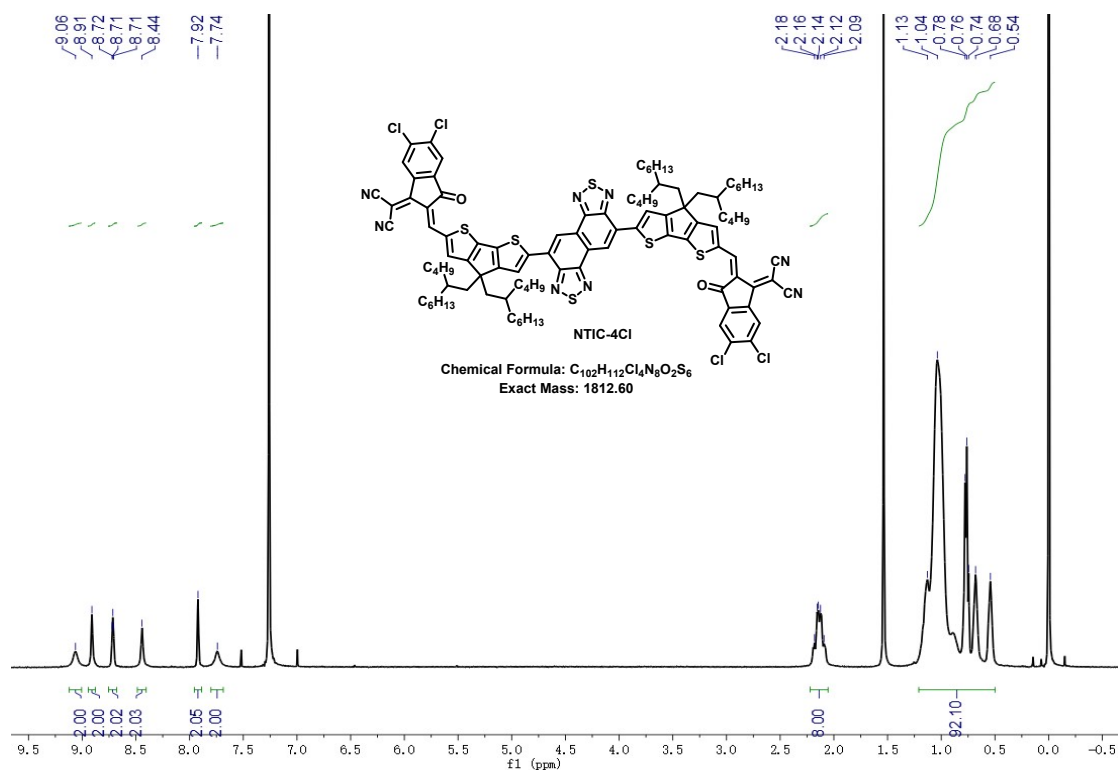


Fig. S10 Detailed 1H NMR spectra in $CDCl_3$ for compound NTIC-4Cl.

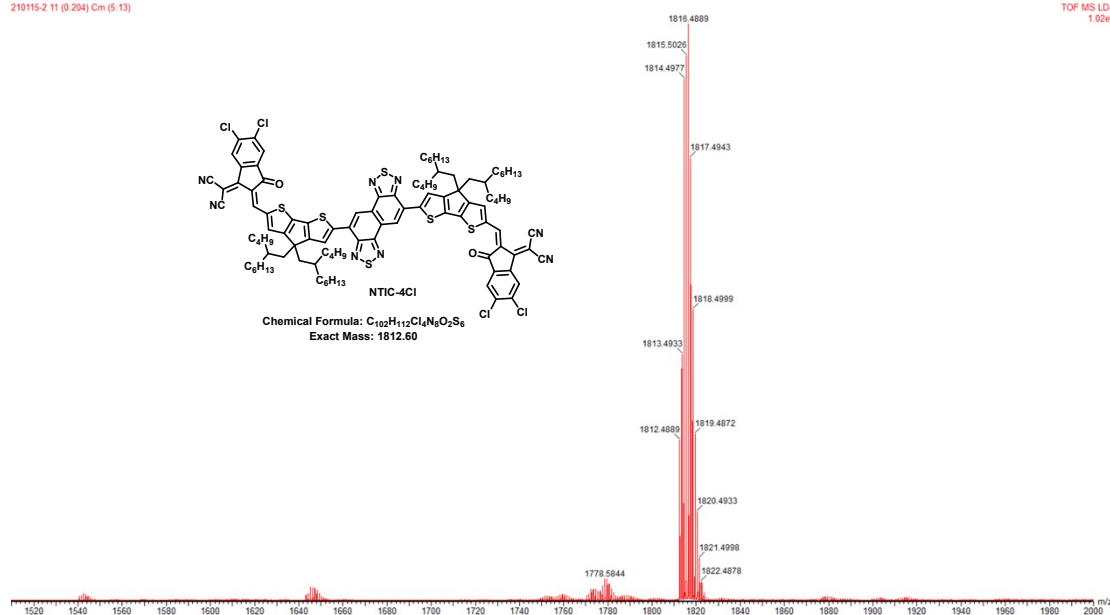


Fig. S11 MALDI-TOF spectra for NTIC-4Cl.

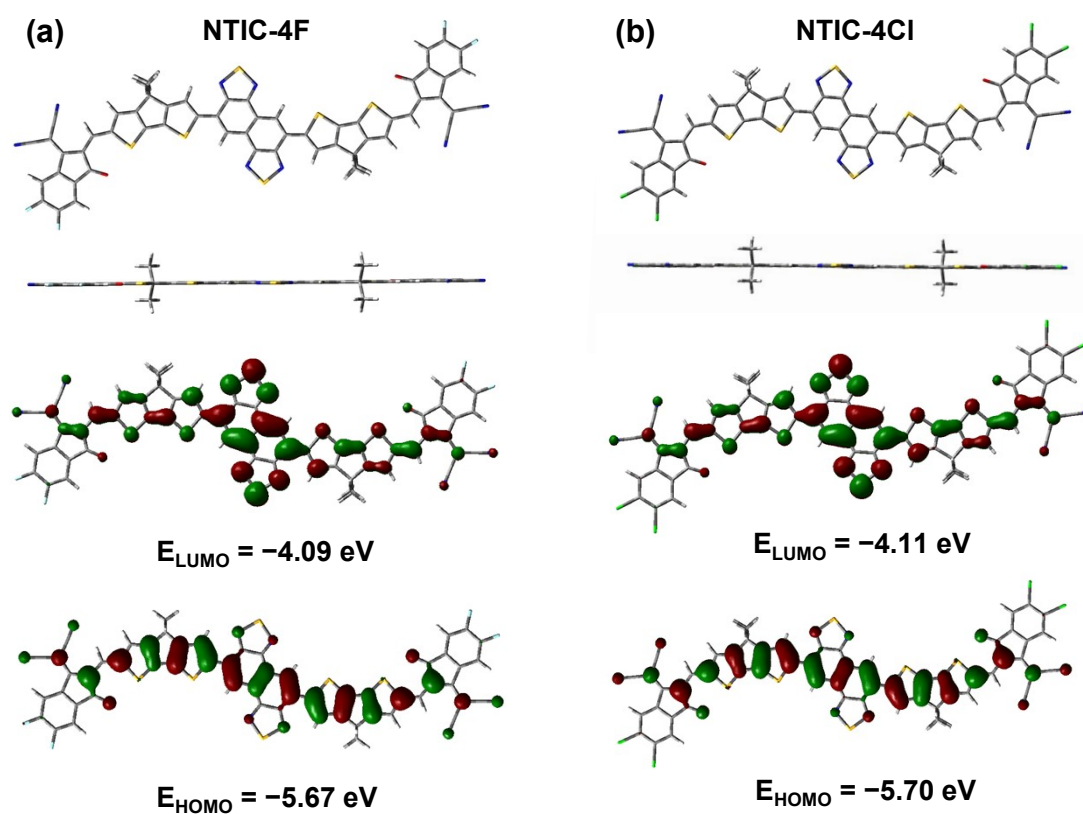


Fig. S12 The chemical geometry and frontier molecular orbitals of NTIC-4F and NTIC-4Cl calculated by DFT at the B3LYP/6-31G(d) level.

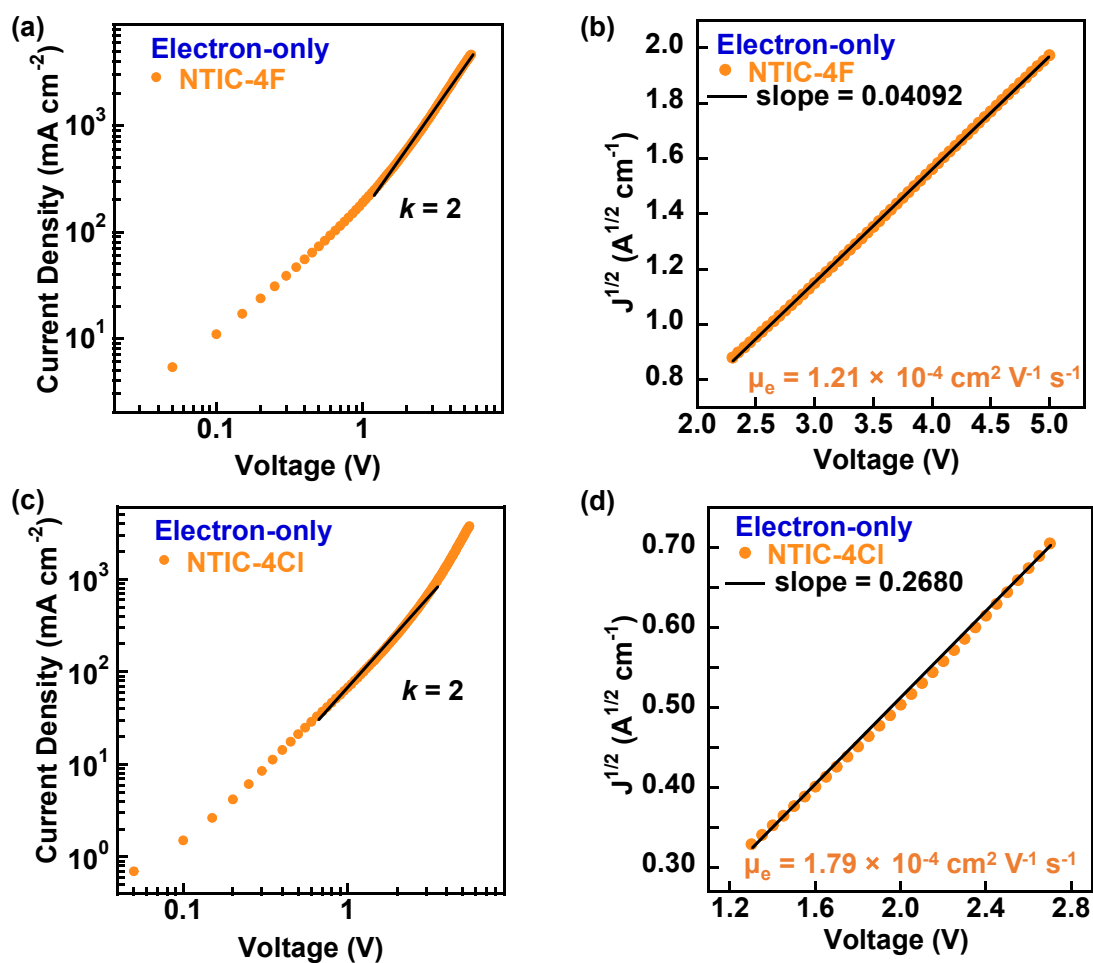


Fig. S13 Dark J - V (a, c) and $J^{1/2}$ - V (b, d) characteristics for electron-only devices based on neat NTIC-4F (a, b) and NTIC-4Cl (c, d) films, with the device structure of ITO/ZnO/active layer/PFN-Br/Ag.

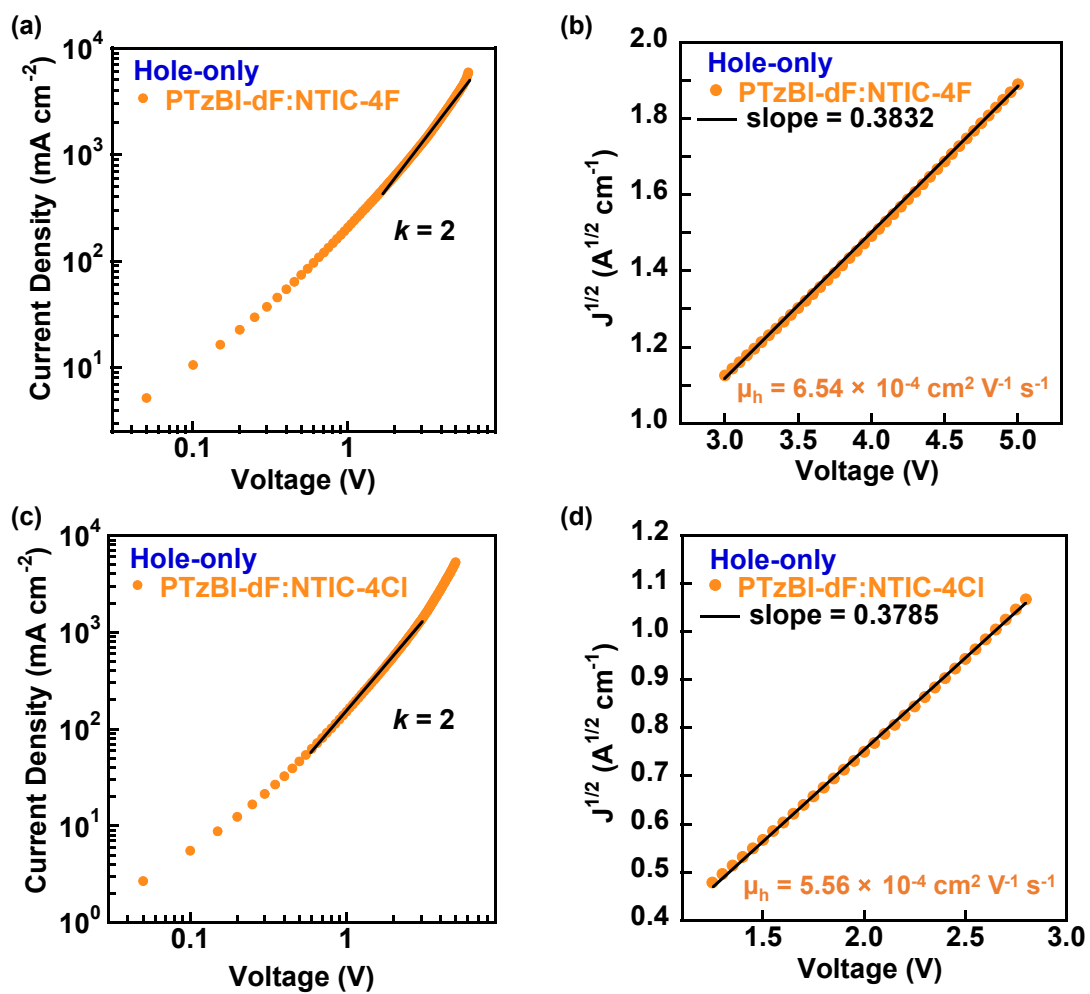


Fig. S14 Dark J - V (a, c) and $J^{1/2}$ - V (b, d) characteristics for electron-only devices based on PTzBI-dF:NTIC-4F (a, b) and PTzBI-dF:NTIC-4Cl (c, d) blend films, with the device structure of ITO/ZnO/active layer/PFN-Br/Ag.

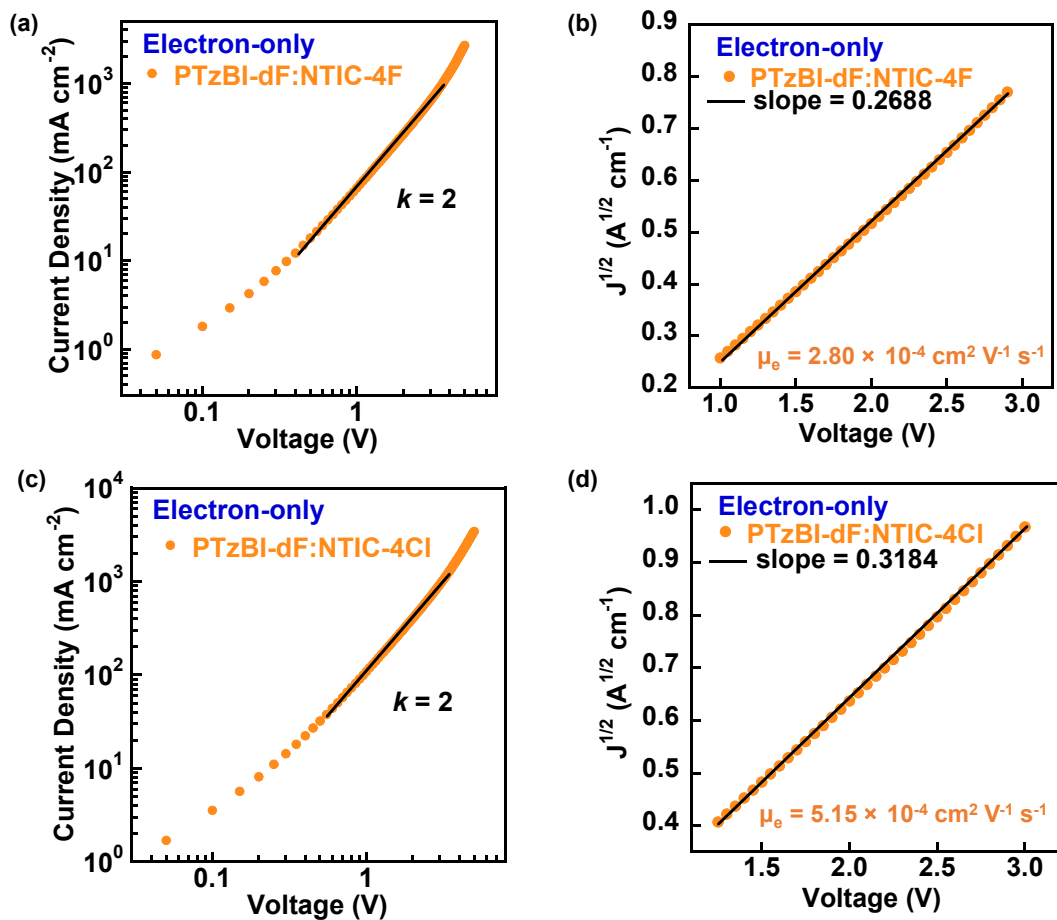


Fig. S15 Dark J - V (a, c) and $J^{1/2}$ - V (b, d) characteristics for hole-only devices based on PTzBI-dF:NTIC-4F (a, b) and PTzBI-dF:NTIC-4Cl (c, d) blend films, with the device structure of ITO/PEDOT:PSS/active layer/MoO₃/Ag.

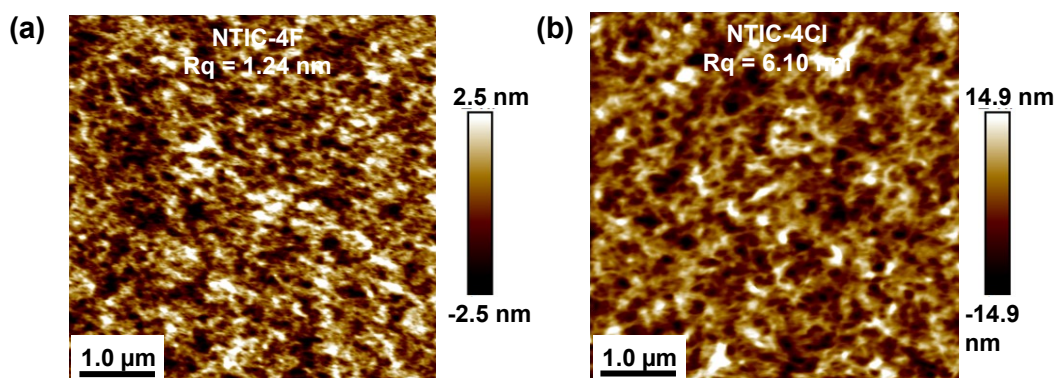


Fig. S16 AFM images of pure NTIC-4F (a) and NTIC-4Cl (b) films.

References

- 1 N. Tang, J. Zhou, L. Wang, M. Stolte, G. Xie, X. Wen, L. Liu, F. Wurthner, J. Gierschner and Z. Xie, *Nat. Commun.*, 2023, **14**, 1922-1931.
- 2 M. Wang, X. Hu, P. Liu, W. Li, X. Gong, F. Huang and Y. Cao, *J. Am. Chem. Soc.*, 2011, **133**, 9638-9641.
- 3 B. Fan, M. Li, D. Zhang, W. Zhong, L. Ying, Z. Zeng, K. An, Z. Huang, L. Shi, G. C. Bazan, F. Huang and Y. Cao, *ACS Energy Lett.*, 2020, **5**, 2087-2094.
- 4 F. Huang, L. Hou, H. Wu, X. Wang, H. Shen, W. Cao, W. Yang and Y. Cao, *J. Am. Chem. Soc.*, 2004, **126**, 9845-9853.