Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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

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Contents

1 Experimental Section

1.1 Materials and instruments

All reagents were purchased from Inno-chem, *J&K*, Sigma-Aldrich, Acros, Alfa Aesar or TCI, unless specified and used as received. The polymer PM6 (M_n = 22.4 kDa, PDI = 2.15) was purchased from Solarmer Company. TEM measurements were performed on a JEM-1400 transmission electron microscope operated at 80 kV. UPS experiments were performed on a Thermo Scientific ESCALab 250Xi spectrometer. The 500 μm X-ray spot was used for XPS analysis using 200 W monochromatized Al Kα radiation. The base pressure in the analysis chamber was about 3E-10 mbar. Typically, the hydrocarbon C 1s line at 284.8 eV from adventitious carbon was used for energy referencing. The gas discharge lamp was used for UPS, with helium gas admitted and the He I (21.22eV) emission line employed. The helium pressure in the analysis chamber during analysis was about 2E-8 mbar. The data were acquired with −10V bias. Absorption spectra were measured on an Agilent Cary 5000 UV−vis-NIR spectrophotometer. The thickness of the solid films was measured using a Dektak 150 Profilometer. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer with $CDCl_3$ or CD_2Cl_2 as a solvent and tetramethylsilane as an internal reference. MALDI-TOF mass spectra were recorded by a Bruker Autoflex III TOF/TOF. Gel permeation chromatography (GPC) was performed to provide the molecular weight and the polydispersity (PDI) by using chloroform as eluent on a Waters 1525 GPC instrument and polystyrene as a standard.

1.2 Solar cell device fabrications and measurements

The photovoltaic devices were fabricated with a structure of glass/ITO/ZnO/PFN-Br/PM6:**TITI-4F**/MoO_x/Ag. The ITO coated glass substrates were cleaned by detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and dried by a nitrogen blow. The sol-gel ZnO were spin-coated on the substrates and annealed at 200 °C for 1 hour in the air. The PFN-Br layer was then deposited on top of ZnO films by spin-coating. Then ITO substrates coated with ZnO layer and PFN-Br layer were transferred into a high purity nitrogen-filled glovebox. The mixed PM6: TTCn-4F was respectively dissolved in chlorobenzene (w/o or with 1% 1-chloronaphthalene) to prepare 20 mg/ml blend solutions. The mixed solutions were spin coated onto the ITO/ZnO substrates at 100 °C and annealed at 100 °C for 10 minutes to prepare the active layers. A thin molybdenum trioxide (MoO_x) layer (10 nm) and a silver (Ag) layer (80 nm) were sequentially deposited by thermal evaporation.

The current density-voltage (*J-V*) characteristics of photovoltaic devices were obtained using a Keithley 2400 source-measure unit. The photocurrent was measured under illumination simulated 100 mW cm^{-2} AM1.5G irradiation using a xenon-lamp-based solar simulator (Oriel 96000) in an argon filled glove box. Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was set using a certified silicon diode. External quantum efficiency (EQE) values of the devices were measured using Stanford Research Systems SR810 lock-in amplifier.

1.3 Sample preparations and characterizations

For UV-vis measurement, the neat and blend films were all prepared on quartz substrate. For UPS, the neat films was prepared on the ITO substrate. The specimen for TEM measurement was prepared by spin casting the blend solution on ITO/PEDOT:PSS substrate, then floating the film on a water surface, and transferring to TEM grids.

1.4 Quantum chemical calculations

Density functional theory (DFT) calculations were performed using the Gaussian 16 program with the B3LYP exchange-correlation functional.[1] All-electron triple-ξ valence basis sets with polarization functions (6-31G) are used for all atoms. Geometry optimizations were performed with full relaxation of all atoms. Calculations were performed in gas phase without solvent effects. Vibrational frequency calculations were performed to check that the stable structures had no imaginary frequency.

1.5 Measurements of the hole and electron mobility by the space-charge limited current (SCLC) method

The hole and electron mobility were measured using the space charge limited current (SCLC) method, employing a diode configuration of ITO/PEDOT:PSS/active layer/Au for hole and glass/Al/active layer/Al for electron by taking the dark current density in the range of 0 – 10 V. The hole and electron mobility was extracted by fitting the current density–voltage curves using the Mott–Gurney law[2], Equation (1)

$$J_{\mathrm{SCL}} = 9\varepsilon\varepsilon_0\mu V^2/(8L^3) \tag{1}$$

where ε is the dielectric constant of the active layer, ε_0 is the permittivity of the vacuum (8.85419×10^{-12} CV^{-1}m^{-1}), μ is the zero-field mobility, J is the current density, L is the thickness of the active layer, and $V = V_{\mathrm{appl}} - V_{\mathrm{bi}}$, here V_{appl} is the applied potential, and V_{bi} the built-in potential which results from the difference in the work function of the anode and the cathode. The hole and electron mobility of the solar cell blend are deduced from the intercept value of $9\varepsilon\varepsilon_0\mu/(8L^3)$ by linearly plotting ln(J) *vs*. ln(V) (the slope of ln(J) vs. ln(V) is ≈ 2).

2 Synthetic Section

Compounds **2** and heptadecan-9-yl 4-methylbenzenesulfonate were synthesized following reported literatures[3, 4].

2,2'-(1,5-dinitronaphthalene-2,6-diyl)dithiophene (3)

A mixture of compound **2** (376.0 mg, 1.0 mmol), tributyl(thiophen-2-yl)stannane (1.12 g, 3.0 mmol), and $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol) in dry toluene (30 mL) was stirred at 110 °C under argon for 24 h. After cooling to room temperature, the mixture was poured into a solution of KF and extracted with DCM (50 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified via column chromatography on silica gel (petroleum ether/CH_2Cl_2, 1:2) to afford compound **3** (324.7 mg, 0.85 mmol, yield = 84.9%) as a yellow solid. ^{1}H NMR (400MHz, $CDCl_3$, δ): 7.83 (s, 4H), 7.54 (d, J = 5.0 Hz, 2H), 7.33 (d, J = 3.4 Hz, 2H), 7.19–7.13 (m, 2H).

6,12-dihydrothieno[3',2':2,3]indolo[7,6-*g*]thieno[3,2-*b*]indole (4)

Compound **3** (305.9 mg, 0.80 mmol) in triethyl phosphite (40.0 ml) and 1,2-dichrolobenzene (20.0 ml) was heated at reflux for 2 days under argon. The reaction mixture was cooled and concentrated under reduced pressure. The residual was used without further purification.

6,12-di(heptadecan-9-yl)-6,12-dihydrothieno[3',2':2,3]indolo[7,6-*g*]thieno[3,2-*b*]indole (5, TITI)

To a suspension solution of crude material 4 (0.80 mmol), and heptadecan-9-yl 4-methylbenzenesulfonate (1.64 g, 4.0 mmol) in DMSO (40 mL) was added potassium hydroxide (673.3 mg, 12 mmol) in one portion at room temperature. The resulting solution was stirred at room temperature for 12 h. The reaction mixture was then extracted with DCM (200 mL × 3) and water (100 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified via column chromatography on silica gel (petroleum ether/CH_2Cl_2, 5:1) to afford compound **5** (293.3 mg, 0.37 mmol, yield = 46.1%) as an off-white solid. ^{1}H NMR (4 00MHz, CD_2Cl_2, δ): 8.15 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.34 (d, J = 5.1 Hz, 2H), 7.29 (d, J = 5.1 Hz, 2H), 5.41–5.32 (m, 2H), 2.26–2.14 (m, 4H), 2.07–1.96 (m, 4H), 1.34–1.01 (m, 48H), 0.83 (t, J = 7.1 Hz, 12H); ^{13}C NMR (100MHz, $CDCl_3$, δ): 143.19, 139.71, 124.72, 121.14, 119.93, 117.36, 117.20, 115.05, 114.14, 59.67, 35.22, 31.90, 29.54, 29.36, 29.25, 26.44, 22.76, 14.22; HR-MS (MALDI-TOF): *m/z* calcd. for $C_{52}H_{78}N_2S_2$: 794.5606; found: 794.5637.

6,12-di(heptadecan-9-yl)-6,12-dihydrothieno[3',2':2,3]indolo[7,6-*g*]thieno[3,2-*b*]indole-4,10-dicarbaldehyde (6)

To a solution of compound **5** (0.50 mmol) in anhydrous THF (30 mL), *n*-BuLi (2.5 M in hexane, 0.48 mL, 1.20

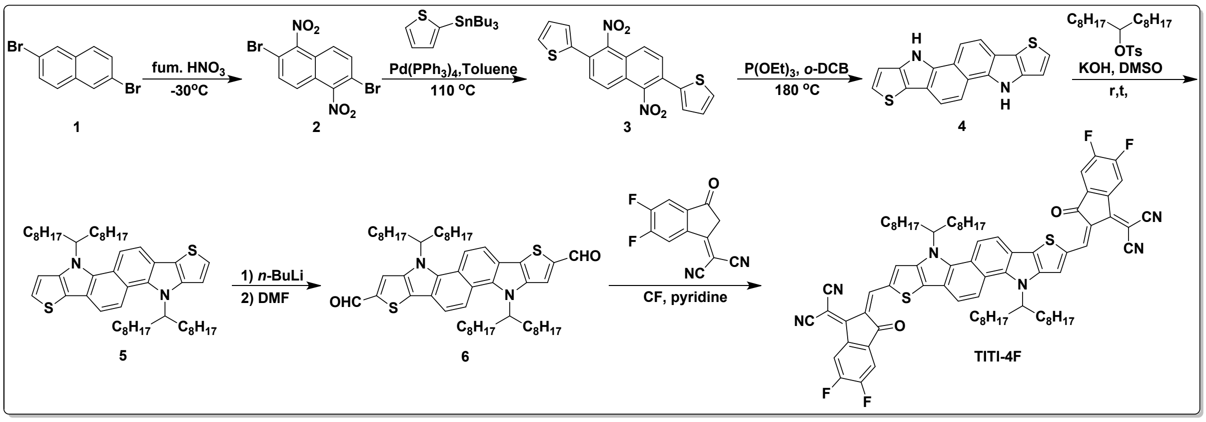
mmol) was added dropwise under the protection of argon at –78 °C. After the mixture was stirred at –78 °C for 1 h, 0.8 mL DMF was added. Then the mixture was warmed to room temperature and stirred overnight. The mixture was poured into water and extracted with DCM (50 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified via column chromatography on silica gel (petroleum ether/CH_2Cl_2, 1:2) to afford compound **6** (348.72 mg, 0.41 mmol, yield = 81.9%) as an orange solid. ^{1}H NMR (400MHz, $CDCl_3$, δ): 9.98 (s, 2H), 8.20 (d, *J* = 8.9 Hz, 2H), 7.96 (s, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 5.41–5.32 (m, 2H), 2.28–2.14 (m, 4H), 2.12–1.99 (m, 4H), 1.24–0.97 (m, 48H), 0.79 (t, *J* = 7.1 Hz, 12H); ^{13}C NMR (100MHz, $CDCl_3$, δ): 183.33, 142.87, 142.45, 142.37, 127.56, 122.68, 122.00, 118.12, 117.64, 116.28, 60.22, 35.15, 31.81, 29.31, 29.28, 29.14, 26.33, 22.70, 13.92; HR-MS (MALDI-TOF): *m/z* calcd. for $C_{54}H_{78}N_2O_2S_2$: 850.5505; found: 850.5567.

2,2'-((6,12-di(heptadecan-9-yl)-6,12-dihydrothieno[3',2':2,3]indolo[7,6-*g*]thieno[3,2-*b*]indole-4,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (TITI-4F)

To a solution of compound **6** (85.1 mg, 0.10 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (115.1 mg, 0.50 mmol) and pyridine (0.5 mL) in $CHCl_3$ (50 mL) was heated at 60 °C overnight. After cooling to room temperature, the mixture was concentrated to 5 mL and poured into methanol (50 mL) and then filtered. The residue was purified via column chromatography on silica gel (petroleum ether/CH_2Cl_2, 1:2) to afford compound **TITI-4F** (107.5 mg, 0.084 mmol, yield = 84.3%) as a deep purple solid with metallic luster. ^{1}H NMR (400MHz, $CDCl_3$, δ): 8.88 (s, 2H), 8.48 (dd, *J* = 9.9, 6.5 Hz, 2H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.97 (s, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.72 (t, *J* = 7.5 Hz, 2H), 5.28-5.08 (m, 2H), 2.27–2.15 (m, 4H), 2.15–2.02 (m, 4H), 1.29–0.94 (m, 48H), 0.81 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (100MHz, $CDCl_3$, δ): 185.69, 158.08, 155.85, 153.26, 144.88, 144.04, 138.55, 138.10, 137.95, 136.43, 134.59, 128.00, 122.38, 121.02, 119.04, 118.29, 117.02, 115.05, 114.83, 114.56, 114.47, 112.75, 112.56, 69.20, 60.82, 34.85, 31.91, 29.42, 29.32, 29.23, 26.46, 22.76, 14.22; HR-MS (MALDI-TOF): *m/z* calcd. for $C_{78}H_{82}F_4N_6O_2S_2$: 1274.5877; found: 1274.5903.

3 Supporting Scheme

Scheme S1. Synthetic Route to **TITI-4F**.



4 Supporting Figures

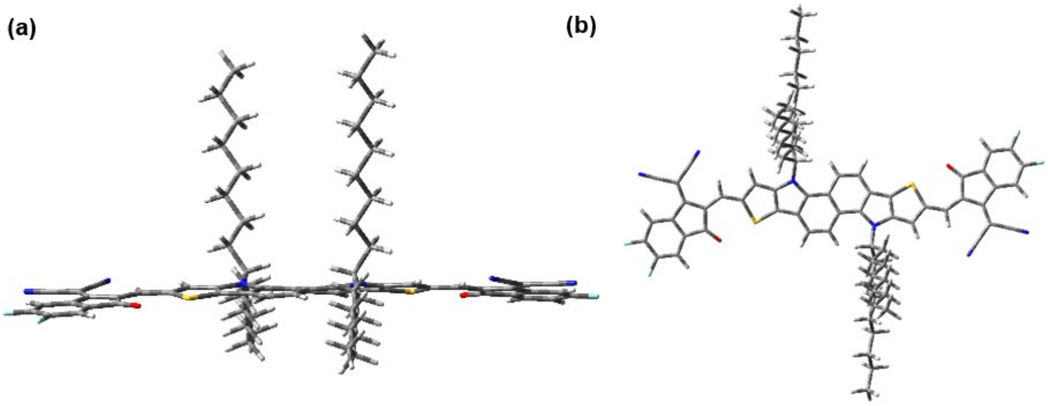


Fig. S1. (a) Side-view and (b) top-view of optimized conformation of **TITI-4F** by DFT calculation.

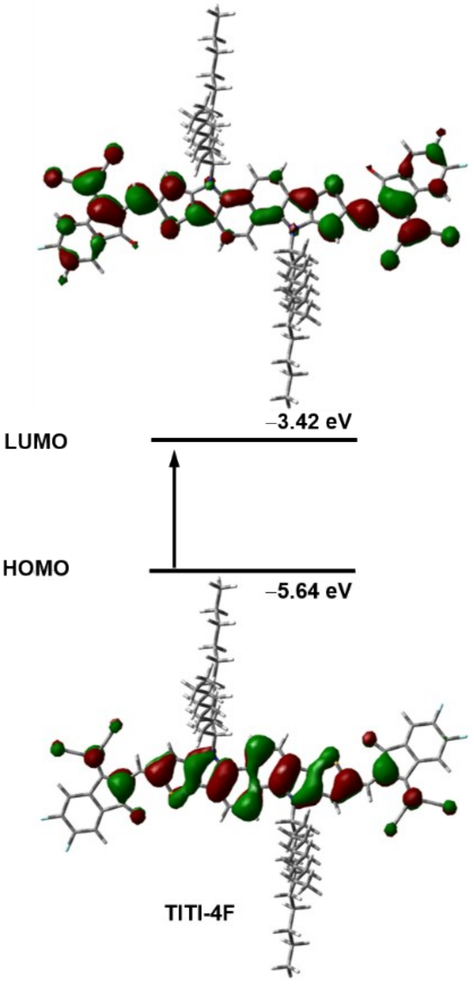


Fig. S2. FMOs distributions, calculated energy levels for **TITI-4F** by DFT calculation.

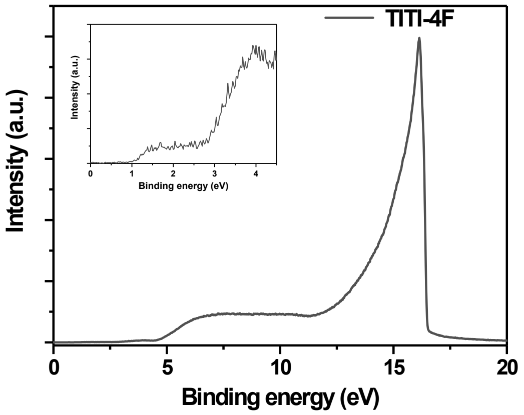


Fig. S3. UPS spectra of the onset (inset) and the secondary edge region of **TITI-4F**.

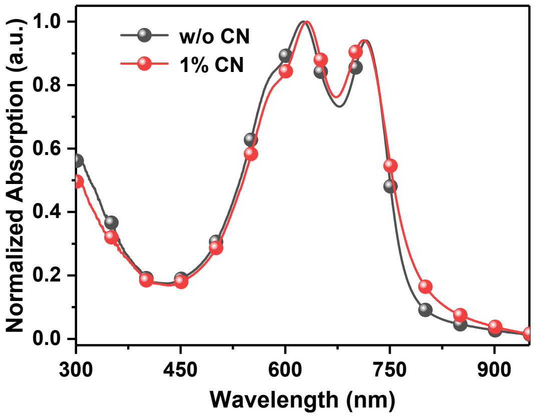


Fig. S4. Normalized UV−vis spectra of PM6:**TITI-4F** blend films w/o or with 1% CN.

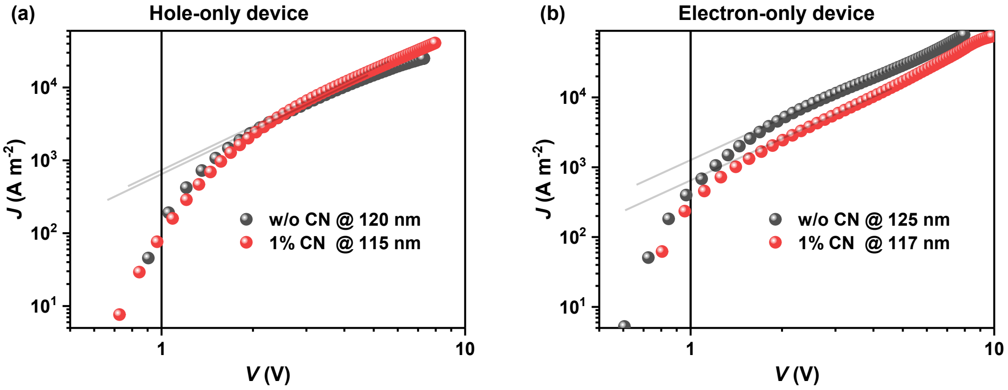


Fig. S5. Plots of *J*–*V* obtained from the hole-only (a) and electron-only (b) device w/o or with 1% CN based on SCLC method. Grey lines represent fits of the curves using the Mott–Gurney relationship.

5 Device Optimization Section

Photovoltaic performance of OSCs based on the PM6:**TITI-4F** with different processing temperatures for the blend solution, with the structure of ITO/ZnO/PFN-Br/PM6:**TITI-4F** (D:A = 1:1, w/w)/MoO_X/Ag, under AM 1.5G, 100 mW cm^{-2} illumination.

Processing temperatures [°C]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
ambient temperature	0.90	0.99	0.29	0.26
50	0.95	11.65	0.57	6.31
100	0.98	11.84	0.66	7.66

Photovoltaic performance of OSCs based on the PM6:**TITI-4F** with different D:A ratios (w/w), with the structure of ITO/ZnO/PFN-Br/PM6:**TITI-4F** (casted from hot CB solution at 100 °C/MoO_X/Ag, under AM 1.5G, 100 mW cm^{-2} illumination.

D:A [w/w]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
1:0.5	0.99	10.04	0.69	6.86
1:0.8	0.98	10.62	0.68	7.08
1:1	0.98	11.84	0.66	7.66
1:1.2	0.97	12.39	0.62	7.45
1:1.5	0.96	12.52	0.56	6.73

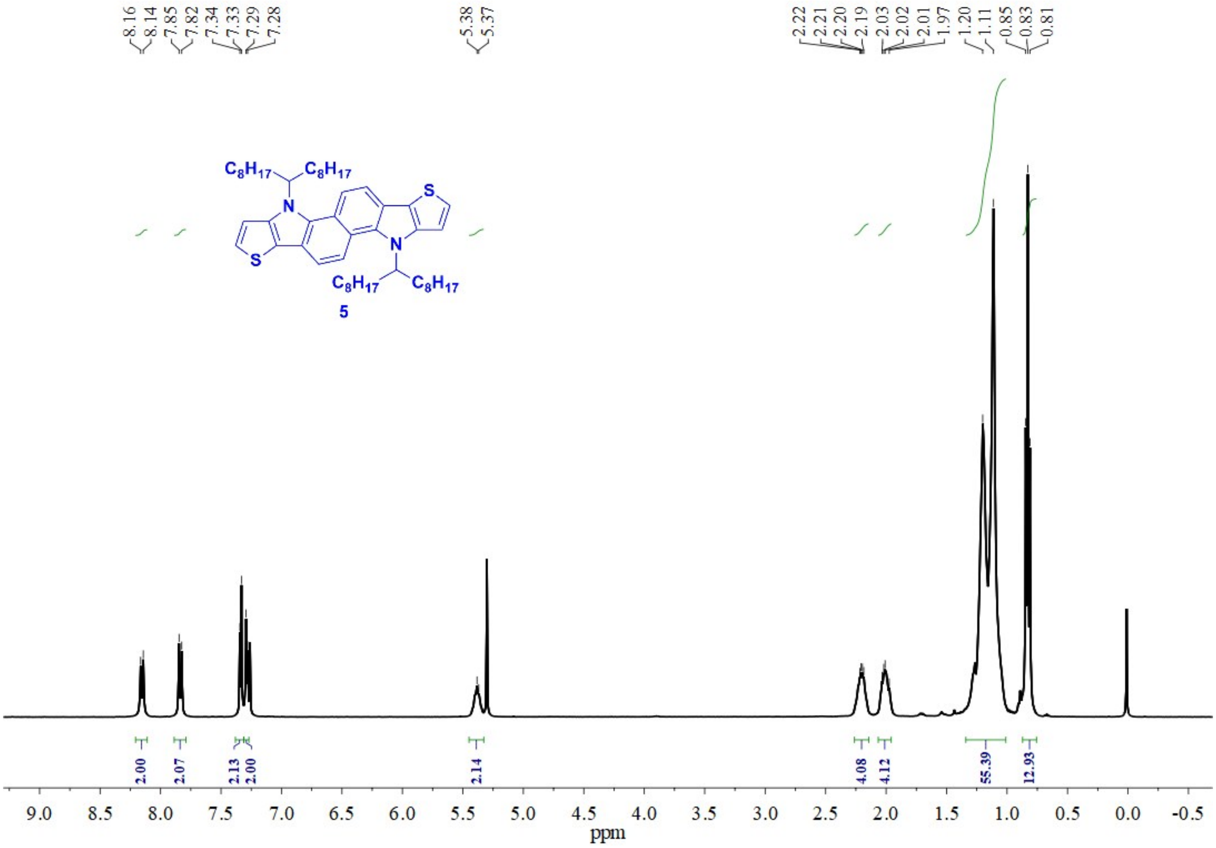
Photovoltaic performance of OSCs based on the PM6:**TITI-4F** with different thermal annealing (TA) temperatures, with the structure of ITO/ZnO/PFN-Br/PM6:**TITI-4F** (casted from hot CB solution at 100 °C, D:A = 1:1, w/w)/MoO_X/Ag, under AM 1.5G, 100 mW cm^{-2} illumination.

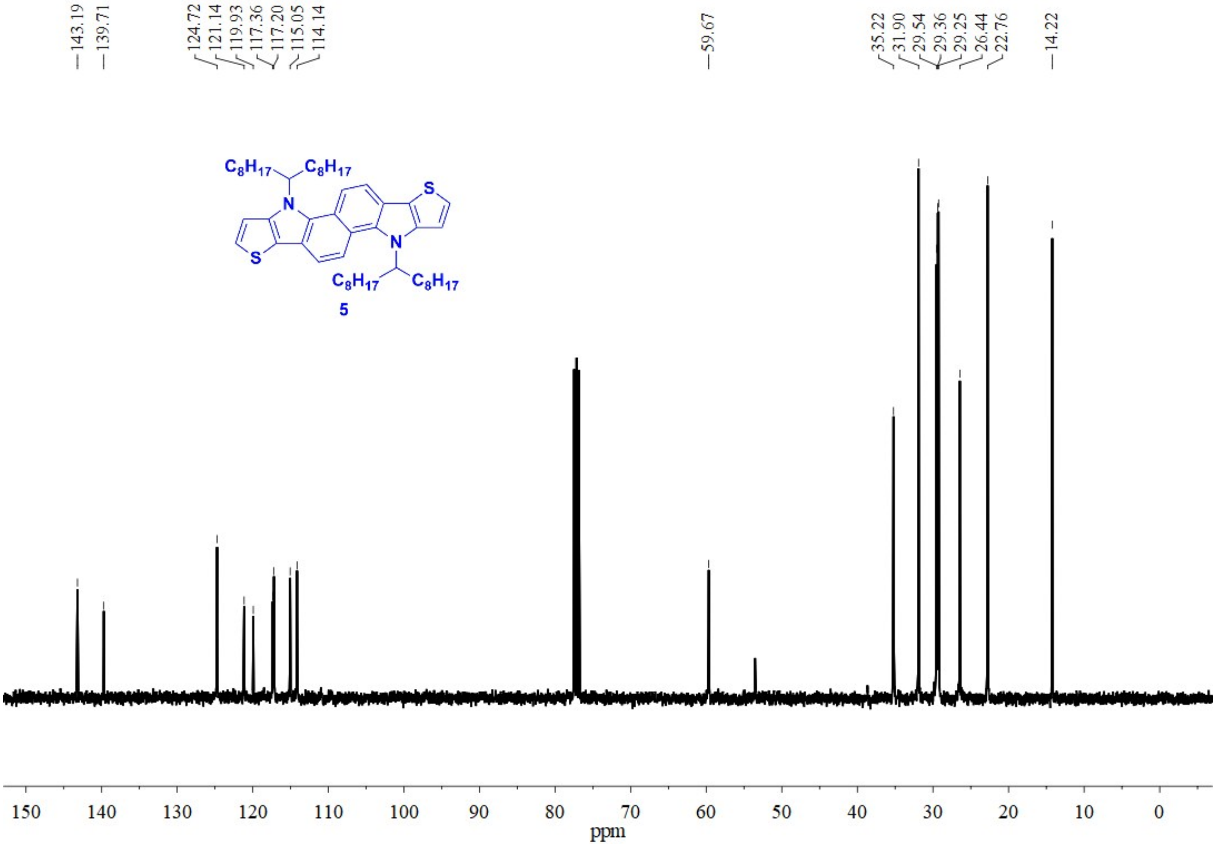
Thermal annealing [°C]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
w/o	0.98	11.84	0.66	7.66
80	0.98	12.31	0.67	8.08
100	0.98	12.86	0.66	8.32
120	0.97	13.05	0.62	7.85
140	0.97	12.36	0.61	7.31

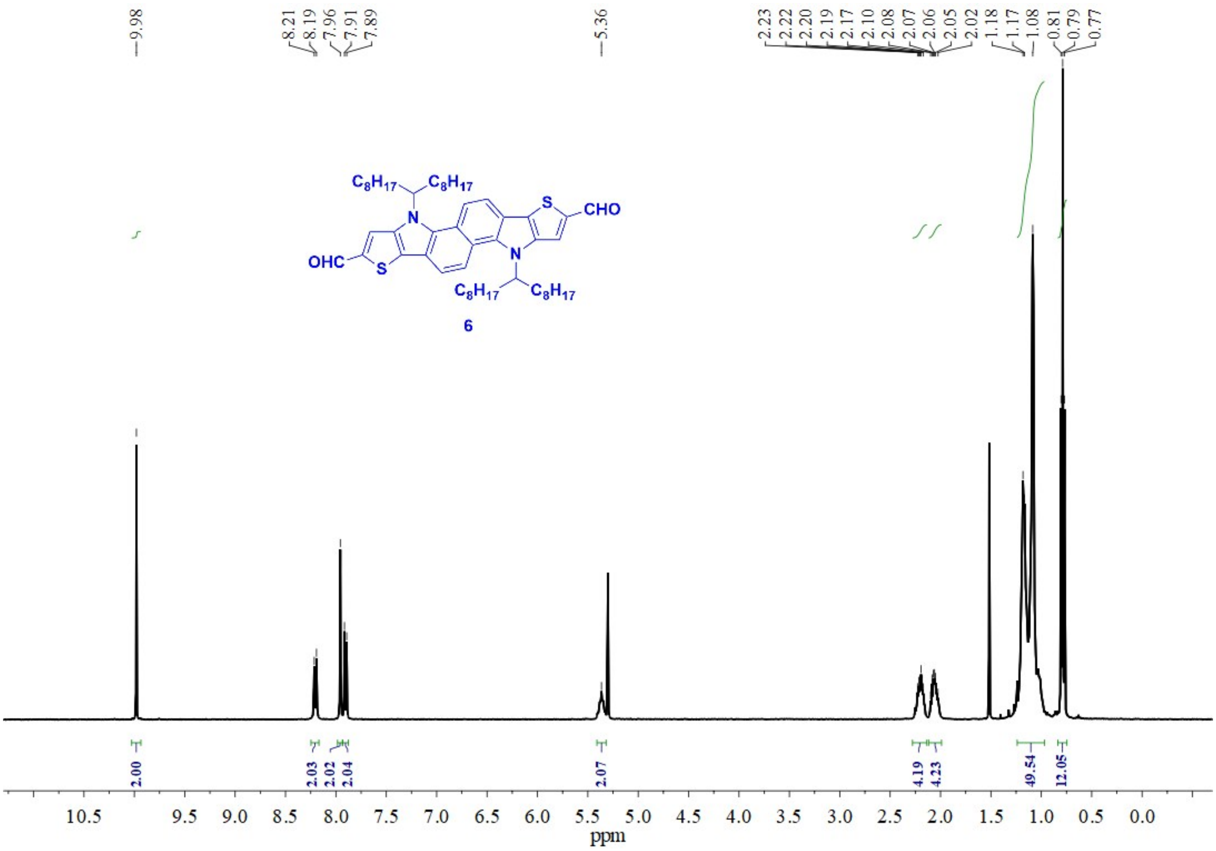
Photovoltaic performance of OSCs based on the PM6:**TITI-4F** with different contents of CN, with the structure of ITO/ZnO/PFN-Br/PM6:**TITI-4F** (casted from hot CB solution at 100 °C, D:A (w/w) = 1:1, TA at 100 °C)/MoO_X/Ag, under AM 1.5G, 100 mW cm^{-2} illumination.

CN [v/v]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
w/o	0.98	12.86	0.66	8.32
0.3%	0.95	13.87	0.72	9.49
0.5%	0.94	14.51	0.72	9.82
0.7%	0.93	14.91	0.74	10.26
1.0%	0.91	15.96	0.75	10.89
1.3%	0.90	15.27	0.73	10.03
1.5%	0.88	13.46	0.71	8.41

6 ^{1}H and ^{13}C NMR Spectra of the Key Intermediates and Final Products



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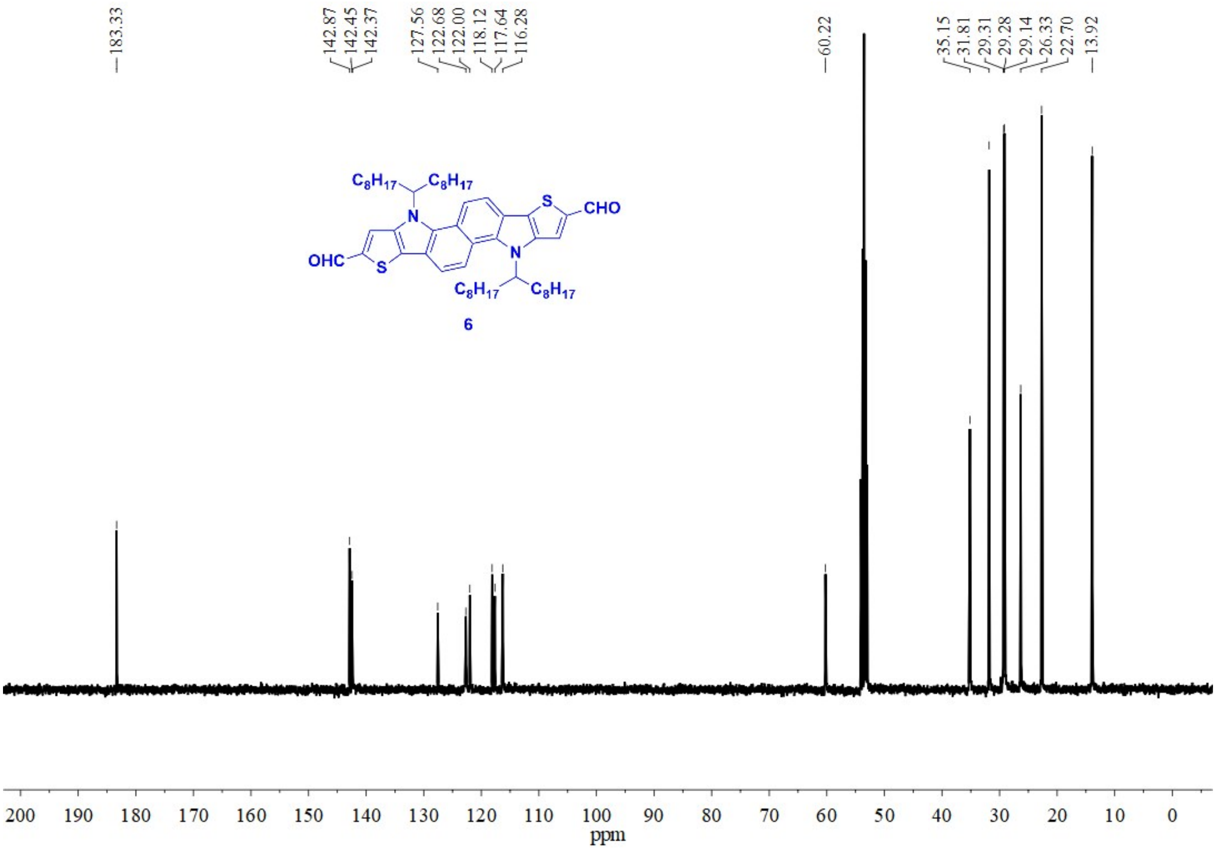
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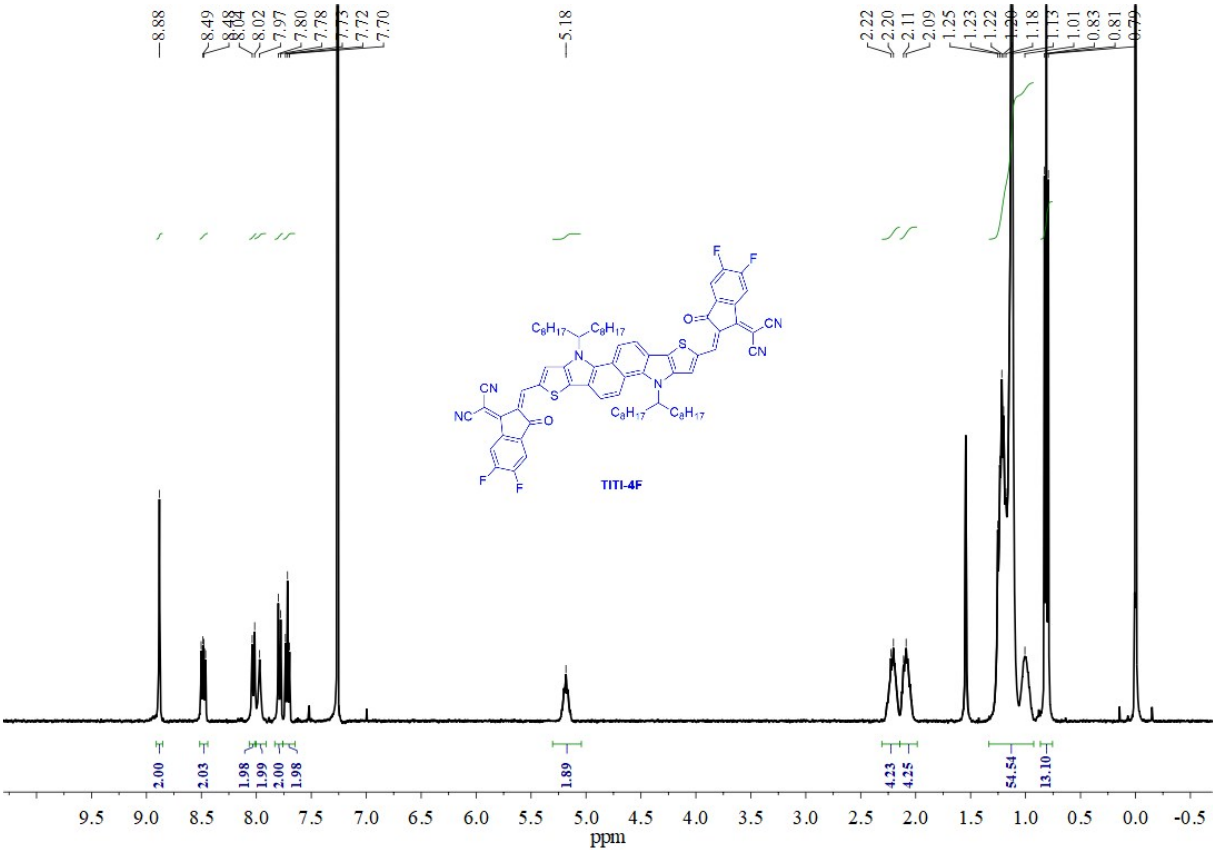

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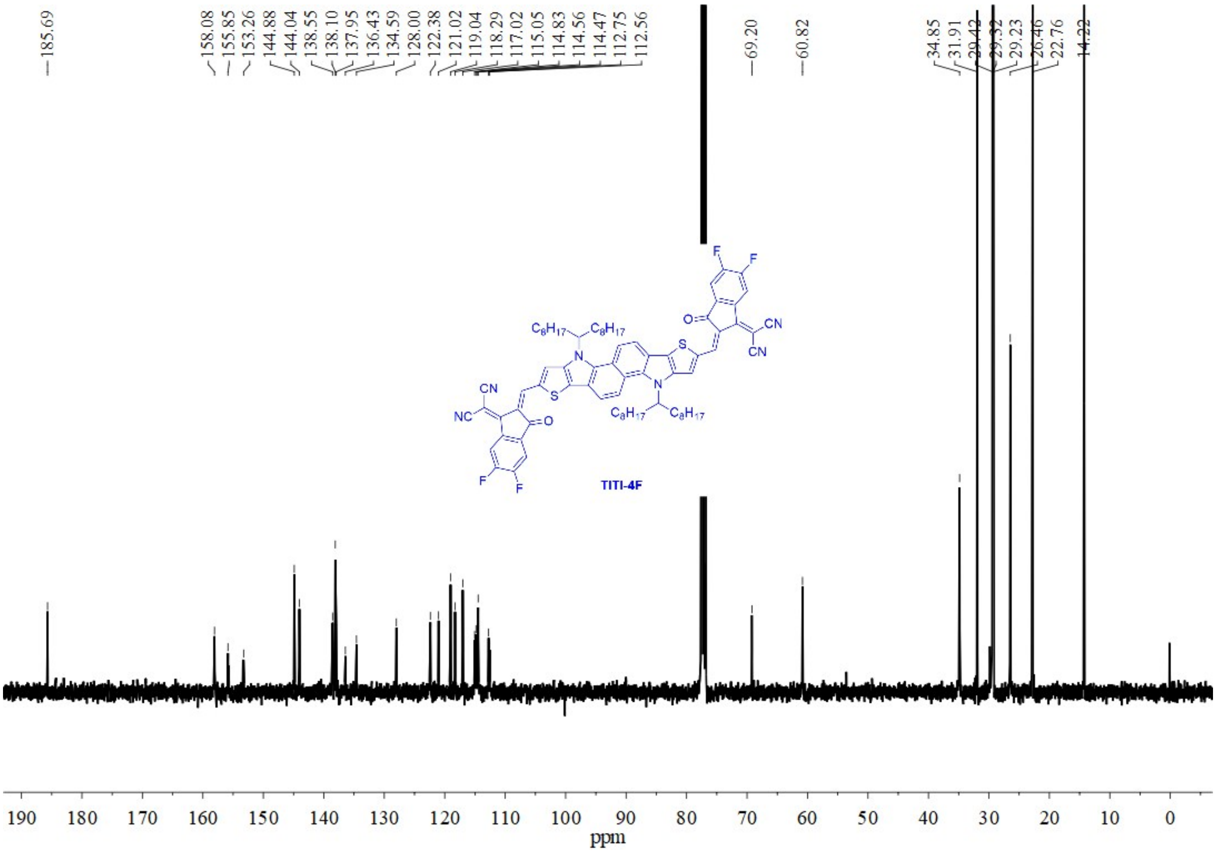

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TITI-4F

References

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