Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information for

Incorporating silicon bridging atom to construct small-molecule acceptor for efficient nonfullerene polymer solar cells

Guang Zeng, [abc] *Jinyang Ouyang,* [abc] *Yue Xin,* [abd] *Xiaoli Zhao** [ab] *and Xiaoniu Yang** [ab]

[a]State Key Laboratory of Polymer Physics and Chemistry Changchun Institute of Applied Chemistry, Chinese Academy of Sciences Renmin Str. 5625, Changchun 130022, P. R. China. *E-mail: zhaoxiaoli@ciac.ac.cn (X. Zhao), xnyang@ciac.ac.cn (X. Yang)

[b]Polymer Composites Engineering Laboratory Changchun Institute of Applied Chemistry, Chinese Academy of Sciences Renmin Str. 5625, Changchun 130022, P. R. China

[c]University of Chinese Academy of Sciences Beijing 100049, P. R. China

[d]University of Science and Technology of China, Hefei 230026, P. R. China

S1. Experimental Section

1. Materials

1-CN (95%) was purchased from Energy Chemical without any treatment. Poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS, Clevios PVP Al4083) were acquired from HC Starck, Inc. Chlorobenzene(CB) was acquired from Sigma-Aldrich and used without further purification.

2. Synthesis

All chemicals and most solvents purchased from commercial sources were used without any further purification. Anhydrous THF and diethyl ether were purified by the distillation from Na and benzophenone solution. Anhydrous N,N-Dimethylformamide was stirred with Calcium hydride to be anhydrated for two days. Most of reactions were carried out under argon atmosphere.

Synthesis of 3,6-Dibromo-2,5-bis(3-bromothiophen-2-yl)thieno[3,2-b]thiophene (1).

2, 3-dibromothiophene (4.24 g, 17.5 mmol) dissolved in 40 ml ethyl ether under argon. *n*-butyl lithium (1.6 M in hexane, 11.08 ml, 17.7 mmol) was added dropwise to the system at -78 °C and the mixture was stirred at -78 °C for 1 hour. Then, a solution of $ZnCl_2$ in THF (0.125 g/ml, 19.6 ml, 18.0 mmol) was added dropwise and the solution was warmed slowly to 0 °C. After stirring at 0 °C for 1 hour, Pd(dppf)Cl_2 (250 mg, 0.34 mmol) and 2,3,5,6-tetrabro-mothieno[3,2-b]thiophene (2 g, 4.39 mmol) were added to the solution and the mixture was heated to 50 °C for 24 hours. Then, 100 ml water was added and the solid was filtered off. The insoluble solid was washed with ethyl ether and acetone and compound 1 was obtained as an insoluble yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.48 (d, 2H), 7.12 (d, 2H). There was no ^{13}C NMR spectroscopy because of the poor solubility of compound 1.

Synthesis of 4,4,9,9 tetrahexyl-bis-silolo[2’,3’-d’:4’’, 5’’-b’’]thieno[4,5-b’:2’’,3’’-d] thieno[3,2-b]thiophene (2).

Compound 1 (1 g, 1.61 mmol) was stirred in 40 ml dry THF under -78 °C. After 15 min, n-butyl lithium (1.6 M in hexane, 4.2 mL, 6.72 mmol) was added dropwise to the solution and the mixture was warmed slowly to 0 °C. Then, dichlorodi-n-hexylsilane (0.95 mg, 3.54 mmol) was added dropwise at -78 °C, and the reactant was stirred at room temperature overnight. The reaction was quenched with water (20 ml) and extracted with diethyl ether for twice. After removing the solvent under vacuum, the crude product was purified with silica gel chromatography (eluent: hexane) and compound 2 was obtained as a yellow crystalline material (235 mg, 21%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.22 (d, 2H), 7.09 (d, 2H), 1.52 (m, 8H), 1.35 (m, 24H), 1.01(t, 8H), 0.87 (t, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm): 149.64, 148.92, 143.34, 139.84, 132.80, 129.15, 124.30, 32.43, 30.91, 23.71, 22.06, 13.57, 11.24. HRMS (MALDI-TOF): *m/z* calcd. for $C_{38}H_{56}S_4Si_2$ (M+) 696.28; found 696.30.

Synthesis of 4,4,9,9 tetrahexyl(2,7-bis-carbaldehyde)bis-silolo[2',3'-d':4'',5''-b'']thieno[4,5-b':2'',3''-d] thieno[3,2-b]thiophene (3).

$POCl_3$ (0.17 ml) was added dropwise to dry DMF (2.4 ml) at 0 °C. After being stirred at low temperature for 15 min, a solution of compound 2 (245 mg, 0.35 mmol) in 1,2-dichloroethane (20 ml) was added. Then the reactant was stirred at 60 °C for 2 hours. After the reaction finished, saturated sodium carbonate solution (15 ml) was added at room temperature, and the solution was stirred for 5 hours. Then the mixture was extracted by dichloromethane for several times. After removing the solvent, the crude product was purified by silica gel chromatography (eluent: hexane/ dichloromethane 1:2) and compound 3 was obtained as a red solid (195 mg, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm): 9.89 (s, 1H), 7.73 (s, 1H), 1.49 (m, 8H), 1.32 (m,24H), 1.05 (t, 8H), 0.86 (t, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm): 181.96, 158.38, 149.67, 145.87, 144.27, 141.33, 138.85, 137.53, 32.31, 30.80, 23.59, 21.98, 13.51, 10.94. HRMS (MALDI-TOF): *m/z* calcd. for $C_{40}H_{56}O_2S_4Si_2$ (M+) 752.27; found 752.30.

Synthesis of Si4TIC-F.

Compound 3 (171 mg, 0.23 mmol) and INCN-F (145 mg, 0.69 mmol) were dissolved in chloroform (30 ml) and 0.8 ml pyridine was added to the mixture. Then, the reactant was heated to 70 °C and stirred for 24 hours. The solvent was removed directly under reduced pressure and the crude product was purified by silica gel chromatography (eluent: dichloromethane). Si4TIC-F was obtained as a dark red solid (158 mg, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm): 8.94 (s, 2H), 8.73 (q, 0.58H), 8.40 (d, 1.5H), 7.94 (q, 1.54H), 7.84 (d, 2H), 7.56 (d, 0.58H), 7.44 (t, 2H), 1.51 (m, 8H), 1.36 (m, 24H), 1.10 (m, 8H), 0.88 (t, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm): 188.46, 166.83, 160.36, 152.05, 148.70, 148.37, 143.54, 139.99, 136.85, 135.03, 134.33, 125.23, 123.58, 120.93, 114.85, 114.78, 68.53, 32.93, 31.34, 24.15, 22.54, 14.05, 11.51.HRMS (MALDI-TOF): *m/z* calcd. for $C_{64}H_{62}F_2N_4O_2S_4Si_2$ (M+) 1140.33; found 1140.30. Elemental analysis: calcd for $C_{64}H_{62}F_2N_4O_2S_4Si_2$, C: 67.33, H: 5.47, N: 4.91, S: 11.23; found: C: 66.05, H: 5.78, N: 4.59, S: 10.63.

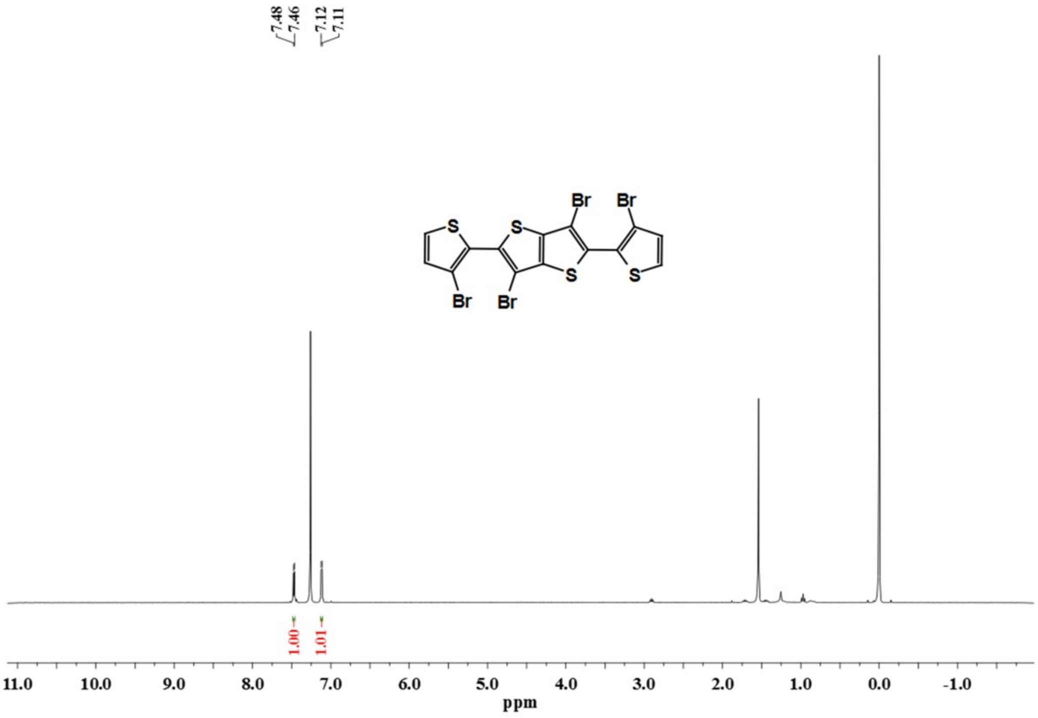

Figure S1. ^{1}H NMR spectrum of compound 1.

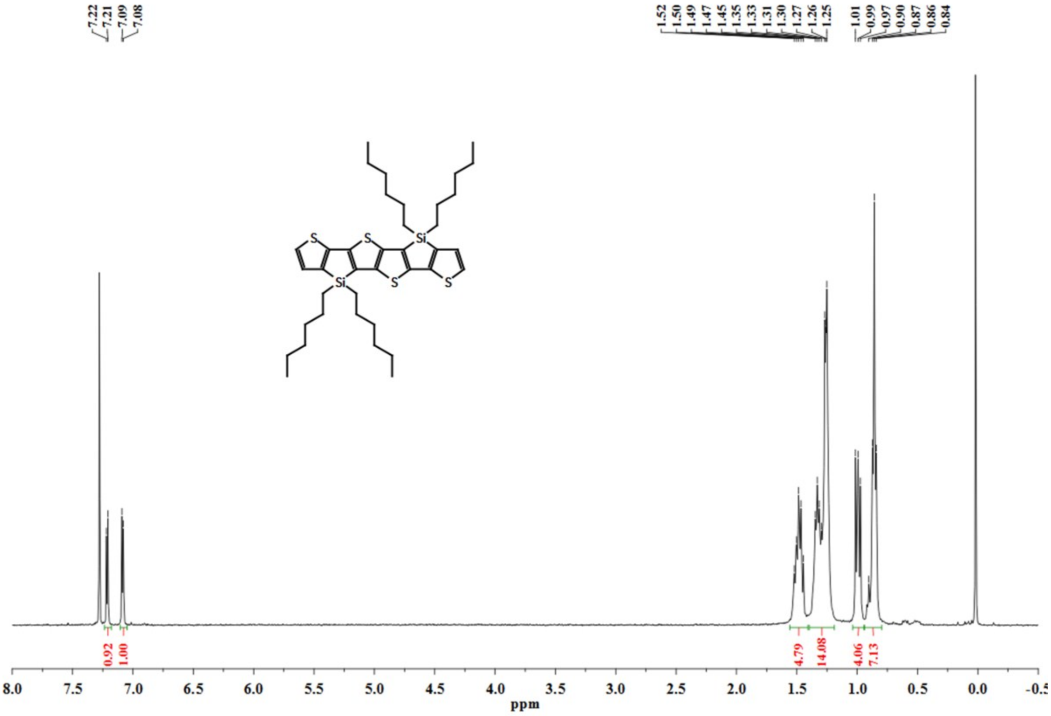

Figure S2. ^{1}H NMR spectrum of compound 2.

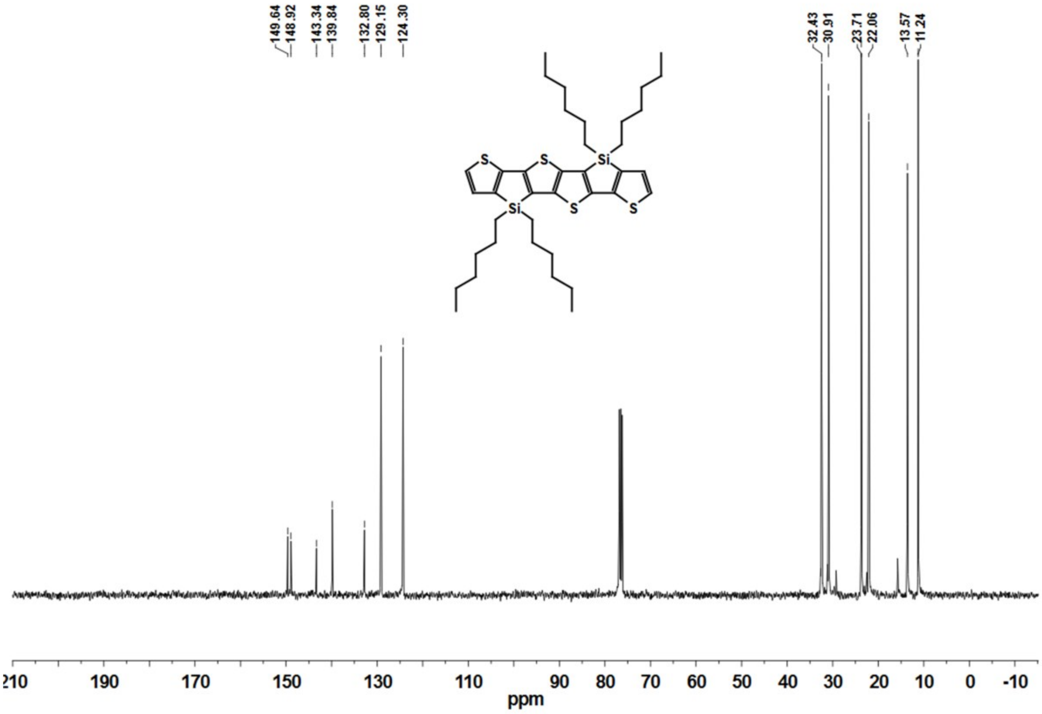

Figure S3. ^{13}C NMR spectrum of compound 2.

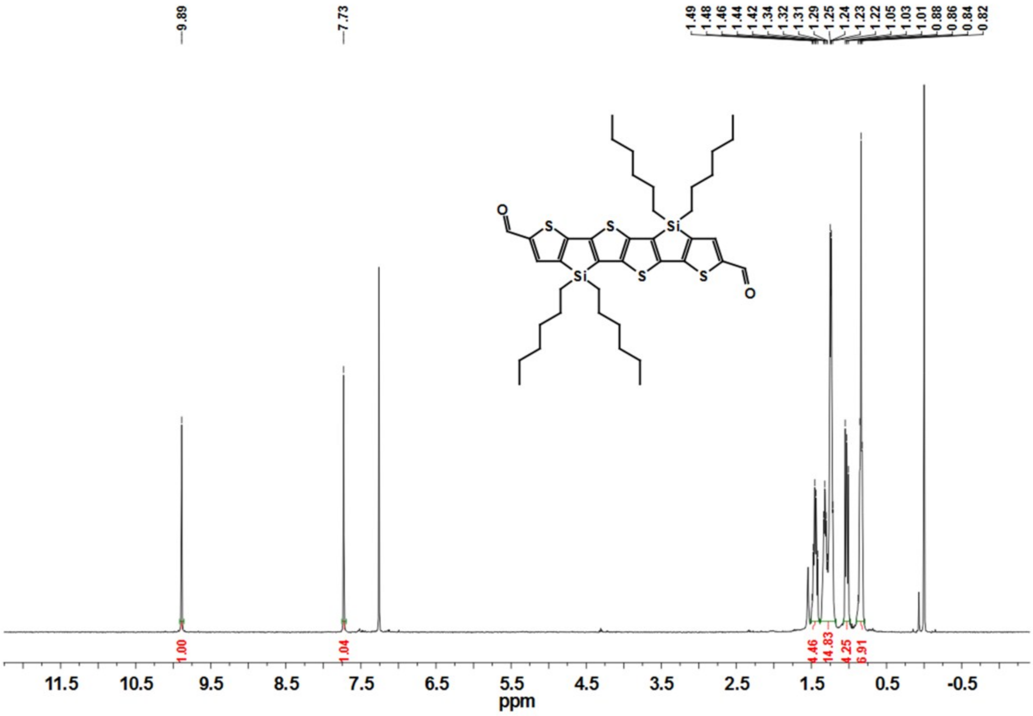

Figure S4. ^{1}H NMR spectrum of compound 3.

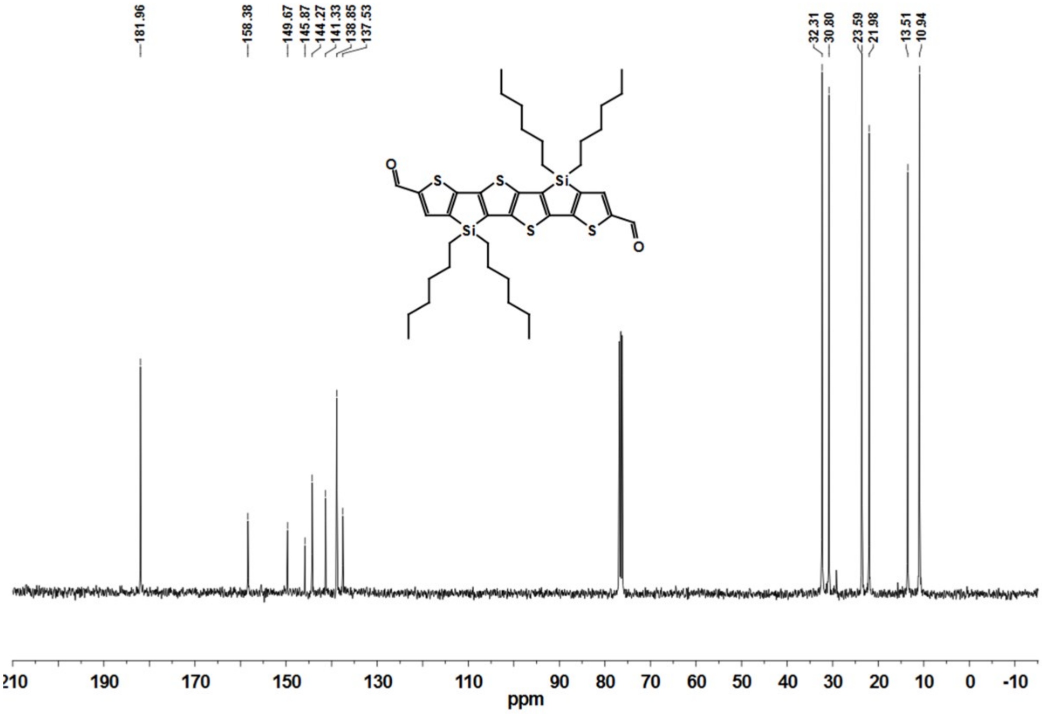

Figure S5. ^{13}C NMR spectrum of compound 3

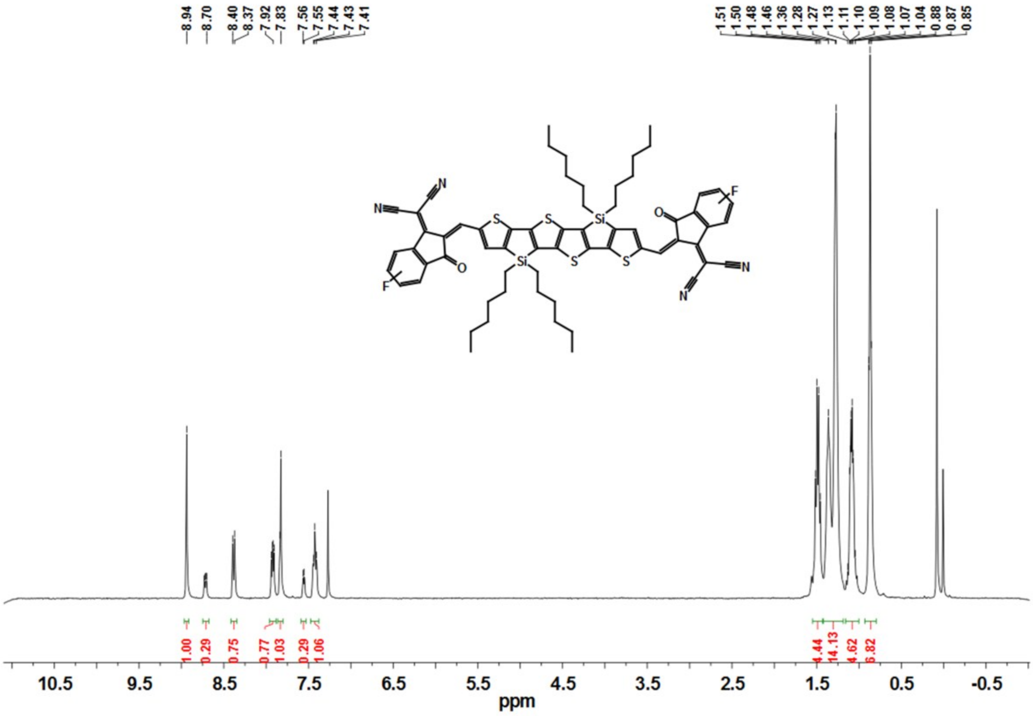

Figure S6. ^{1}H NMR spectrum of compound Si4TIC-F.

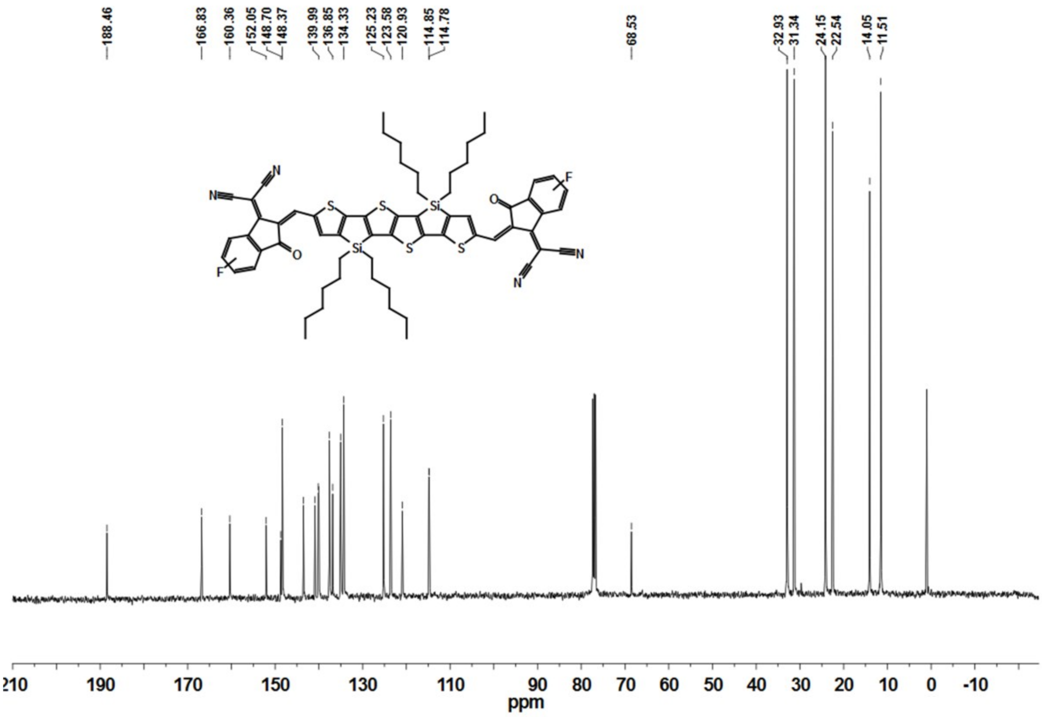

Figure S7. ^{13}C NMR spectrum of compound Si4TIC-F.

3. General measurements

MALDI measurements were performed on MALDI-TOF MS BrukerAutoflex III instruments. TGA was carried out on a METTLER TOLEDO TGA/DSC1/1100 LF apparatus operated at a heating rate of 10 °C min^{-1} under N_2 atmosphere.

4. Cyclic voltammetry (CV) measurements

The electrochemical property of PBTIBDTT and Si4TIC-F films were performed on a CHI600D electrochemical instrument in anhydrous acetonitrile. Tetrakis-(n-butyl) ammonium hexafluorophosphate (Bu_4NPF_6) of 0.1 M in anhydrous acetonitrile was used as the electrolyte. Glassy carbon electrode, $Ag/AgNO_3$ electrode, and Pt wire were used as the working electrode, reference and counter electrode, respectively. The films were drop-coated onto the glassy carbon working electrode from CB solution. The potential of $Ag/AgNO_3$ reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+). The electrochemical onsets were estimated at the position where the current starts to leave the baseline quickly. The HOMO energy levels were calculated according to the equation: $E_{HOMO} =- (E_{ox} - E_{Ferrocene} + 4.80)(eV)$. The LUMO energy values were calculated by $E_{LUMO} = E_{HOMO} + E_g$ (where E_g was determined from the UV–vis-NIR spectra).

5. *J–V* measurements

The *J–V* characteristics of OSCs were measured in nitrogen atmosphere using a Keithley-2400 source meter and a solar simulator (SAN-EI, XES-70S1, San-Ei. Electric Co. Ltd., Osaka, Japan) at AM 1.5 G illumination of 100 mW cm^{-2} with a standard silicon solar cell as a reference to adjust the light intensity. The EQE spectra of devices were tested using chopped monochromatic light from a xenon lamp under ambient conditions. A standard silicon solar cell was used as a reference to determine the light intensity at each wavelength. The thicknesses of the films were acquired on a KLA-Tencor D-100 surface profiler.

6. Space charge limited current (SCLC) measurement

The carrier mobilities were measured by the space charge limited current (SCLC) method with hole-only devices (ITO/PEDOT:PSS/active layer/Au) and electron only devices (ITO/ZnO/active layer/PDIN/Al). The measurements of the *I-V* curves were carried out in dark on a computer-controlled Keithley 2400 source-measure unit. The hole and electron mobility was estimated by fitting the *I-V* curves with SCLC model and the Mott-Gurney law: $\ln\left(I/V^2\right) = 0.89\beta(V/L)^{1/2} + \ln\left(9\mu\varepsilon_0\varepsilon S/\left(8L^3\right)\right)$. Where I is the current, V is the applied voltage, β is the field activation factor, L is the thickness of films, μ is the mobility, ε_0 is the permittivity of free space, ε is the relative permittivity, and S is the area of films.

7. UV-vis absorption

UV-vis absorption spectra were gained on a Perkin-Elmer UV-vis Lambda 750 spectrophotometer (Wellesley, MA).

8. Transmission electron microscopy (TEM)

The TEM images were obtained with a Tecnai G2 F20 high resolution transmission electron microscope operated at an acceleration voltage of 200 KV.

9. Atomic force microscopy (AFM)

AFM measurements were performed on a SPA300HV instrument with an SPI 3800 controller (Seiko Instruments).

10. Grazing incidence wide angle X-ray scattering (GIWAXS)

GIWAXS patterns were obtained at BL14B1 at Shanghai Synchrotron Radiation Facility (SSRF) (λ = 0.69 Å). Samples for GIWAXS were all prepared on top of Si (100) substrates.

11. Device fabrication

Indium tin oxide (ITO) substrates were cleaned by detergent solution, deionized water, isopropanol and acetone in sequence with ultrasonication, and then treated with UVozone for 15 min for further application. Photovoltaic devices were fabricated in traditional structure of ITO/PEDOT:PSS/active layer/PDIN/Al. PEDOT:PSS was spin-coated on the ITO substrates at 3000 rpm for 30 s to form 30 nm thick films and then baked on a heating equipment at 150 °C for 30 min in air. The active layers were spin-coated from chlorobenzene (CB) solution (with polymer concentration of 5 mg mL^{-1}) added with or without 1-CN at 1000-3000 rpm for 2 min to obtain conceivable films in nitrogen atmosphere, and then treated by spin-coating PDIN from the methanol solution (2 mg mL^{-1}) at 4000 rpm for 30 s. Finally, Al was used as cathodes by vapor deposition techniques. The active area of 9 mm^2 and 4 mm^2 was defined by the overlapping of patterned anode and cathode.

S2. TGA curve and Electrochemical voltammetry

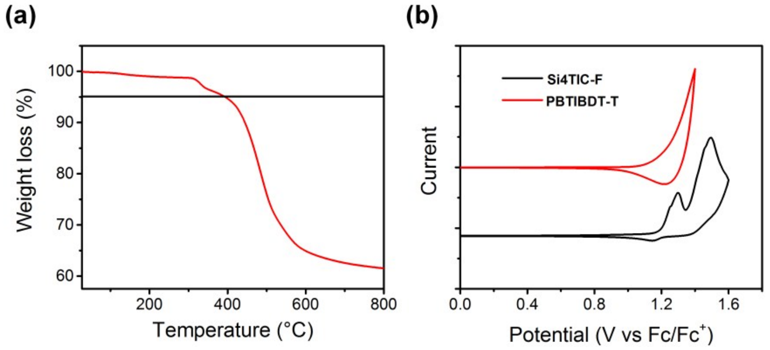

Figure S8. (a) TGA curve of Si4TIC-F. (b) Electrochemical voltammetry of Si4TIC-F and PBTIBDTT.

S3. Optimization of organic photovoltaic devices

Table S1. The photovoltaic parameters of the devices based on PBTIBDTT:Si4TIC-F with different D:A ratio under illumination of AM 1.5 G, 100 mW cm^{-2}.

D:A(w/w)	V_{OC}(V)	J_{SC}(mA cm^{-2})	FF(%)	PCE [a] (%)
1:0.7	0.79	13.07	56.8	5.86(5.42)
1:1	0.79	14.93	63.9	7.53(7.32)
1:1.5	0.79	16.32	58.8	7.59(7.38)
1:2	0.78	16.29	57.4	7.29(6.80)

[a] Values in the parentheses are average values obtained from more than 8 devices.

Table S2. The photovoltaic parameters of the PBTIBDTT:Si4TIC-F devices processed by CB and varied amount of CN under illumination of AM 1.5 G, 100 mW cm^{-2}.

CN(v/v)	V_{OC}(V)	J_{SC}(mA cm^{-2})	FF(%)	PCE [a] (%)
0	0.79	16.32	58.8	7.59(7.38)
0.3%	0.78	17.19	63.1	8.46(7.77)
0.5%	0.78	18.84	69.4	10.20(9.86)
1%	0.77	17.90	62.3	8.59(8.25)

[a] Values in the parentheses are average values obtained from more than 8 devices.

S4. Frontier molecular orbitals

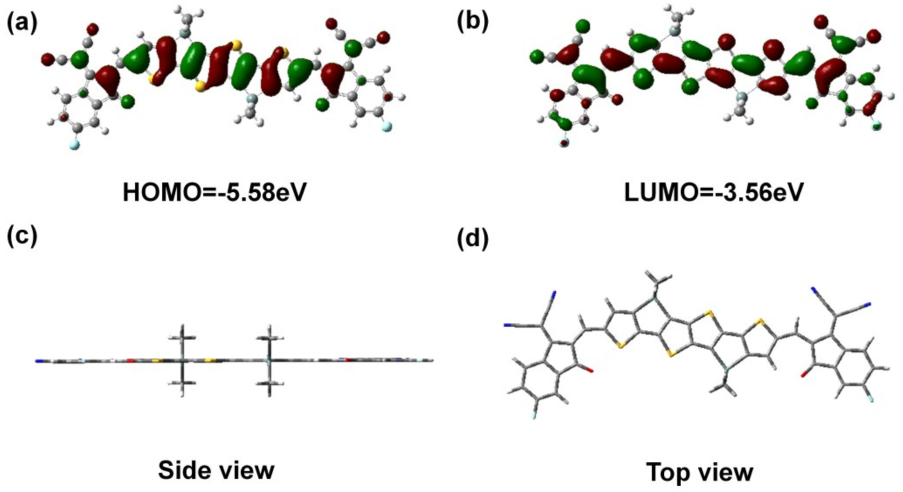

Figure S9. (a), (b)Frontier molecular orbitals (HOMO/LUMO) of Si4TIC-F. Side view (c) and (d) top view of the optimized geometry of Si4TIC-F calculated by DFT/B3LYP/6-31G.

S5. SCLC

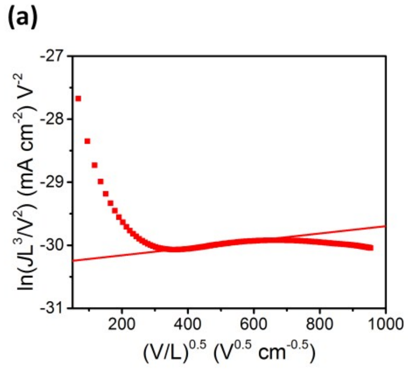

Figure S10. (a) J–V characteristics in the dark for electron-only device based on Si4TIC-F.

S6. GIWAXS

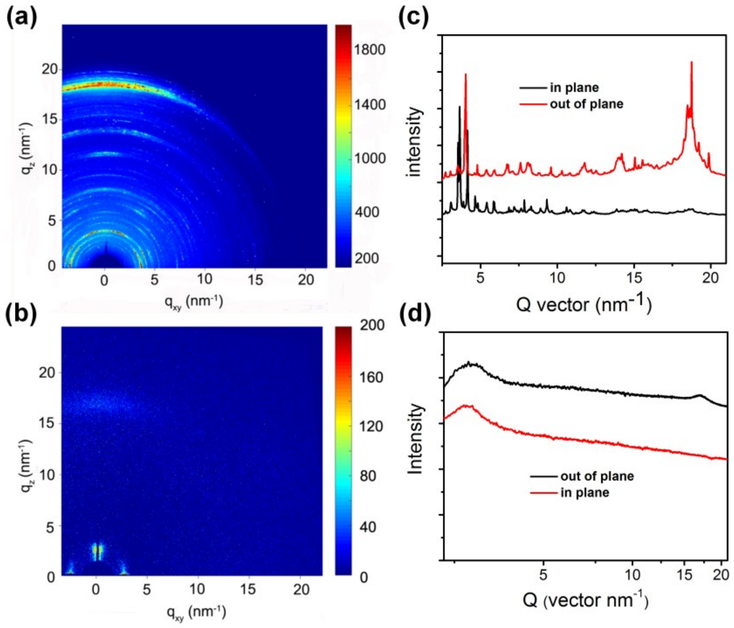

Figure S11. 2D-GIWAXS diffraction (a) Si4TIC-F and (b) PBTIBDTT pure films. (c) and (d) Corresponding line-cuts of these pattern.