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Electronic Supplementary Information

Non-fused molecular photovoltaic acceptor with a planar core structure enabled by bulky and embracing type side chains[†]

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1. Materials and Instruments

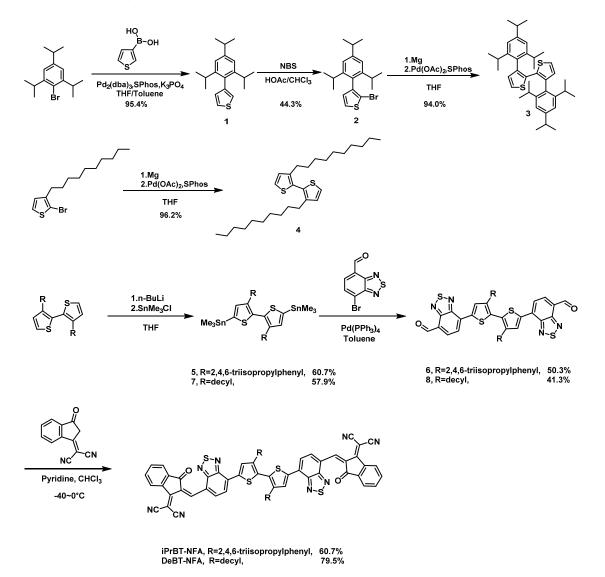
Unless otherwise noted, all chemicals were purchased form Aldrich, Acros, TCI or Bide Pharmatech Ltd. and used without further purification. Unless otherwise noted, all reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica plates. Column chromatography was carried out with 300-400 mesh silica gel. ¹H and ¹³C NMR spectra were recorded on Bruker DRX 400, Bruker DRX 500, or Varian Mercury 300 (400 MHz) nuclear magnetic resonance (NMR) spectrometers. Mass spectra were measured on Agilent Technologies 5973N, Shimadzu Biotech Axima Performance, Thermo Fisher Scientific LTO FT Ultra or Shimadzu Biotech Axima MALD mass spectrometers. Elemental analyses were performed on an Elementar Vario EL III analyzer. Ultraviolet-visible (UV-Vis) spectra were taken on a Hitachi U-3310 spectrophotometer. Cyclic voltammetry (CV) was done on a CHI610D electrochemical workstation with a Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO₃ reference electrode in a 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) CH₃CN solution. The experiments were calibrated with standard ferrocene/ferrocenium (Fc/Fc⁺) redox system having an energy level of 4.8 eV below vacuum. GIWAXS measurements were performed in a Xeuss SAXS/WAXS system (Xeuss 3.0) with a wavelength of $\lambda = 1.3414$ Å. Multimode atomic force microscopy (AFM) was performed using a Nanonavi E-Sweep instrument operating in the tapping mode. The thicknesses of the blend films were determined by a Veeco Dektak 150 surface profilometer.

2. Organic Solar Cells Fabrication and Characterization

Organic solar cells were fabricated with a device configuration of ITO/PEDOT:PSS/active layer /PFN-Br/Al. The conductivity of ITO is 20 Ω . A mixture of **PM6** and acceptor molecule (**iPrBT-NFA** or **DeBT-NFA**) in chloroform was stirred at 50 °C three hours to ensure sufficient dissolution and then spin-coated onto PEDOT:PSS layer to form active layer. On one substrate, five cells with an effective area of 0.04 cm² for each were fabricated. Current-voltage characteristics were recorded using Keithley 2420 (Enli Technology Ltd., Taiwan) under an AM 1.5G AAA class solar simulator with an intensity of 100 mW cm⁻² as the white light source and

the intensity was calibrated with a standard single crystal Si photovoltaic cell. The temperature while measuring the J-V curves was approximately 25 °C. The EQE measurements of OSCs were performed by the solar cell spectral response measurement system 74125 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

3. Material Synthesis



Scheme S1. Synthetic routes of iPrBT-NFA and DeBT-NFA.

Compound 1: 3-(2,4,6-triisopropylphenyl)thiophene

A mixture of 2-bromo-1,3,5-triisopropylbenzene (14.16 g, 50 mmol), thiophen-3-ylboronic acid (12.80 g, 100 mmol), K₃PO₄ (21.23 g, 100 mmol), SPhos (821 mg, 2 mmol), anhydrous toluene (100 mL) and anhydrous THF (100 mL) was carefully degassed, then Pd₂(dba)₃ (458 mg, 0.5 mmol) was added. The mixture was stirred and refluxed 16h, then extracted with DCM. The organic phase was dried over anhydrous Na₂SO₄ and filtered. After the solvent had been removed from the filtrate, the residue was purified by chromatography using PE as eluent, yielding compound **1** as white solid (14.10 g, 95.4 %). ¹H NMR (400 MHz, CDCl₃) δ : 7.35 (dd, *J*₁=2.9 Hz, *J*₂=4.8 Hz, 1H), 7.04 (s, 2H), 7.01 (dd, *J*₁=1.2 Hz, *J*₂=2.9 Hz, 1H), 6.94 (dd, *J*₁=1.2 Hz, *J*₂=4.8 Hz, 1H), 2.92 (m, *J*=6.8 Hz, 1H), 2.66 (m, *J*=6.8 Hz, 2H), 1.29 (d, *J*=6.8 Hz, 6H), 1.09 (d, *J*=6.8 Hz, 6H). MS (EI) m/z: 286 (M⁺).

Compound 2: 2-bromo-3-(2,4,6-triisopropylphenyl)thiophene

To a three-necked round-bottomed flask, compound **1** (13.28 g, 46.4 mmol) was dissolved in chloroform (30 mL) and acetic acid (30 mL). The solution was stirred at room temperature and NBS (8.66 g, 48.7 mmol) was added slowly to this solution. After the mixture became clear, it was neutralized with NaOH, then extracted with DCM. The organic phase was dried over anhydrous Na₂SO₄ and filtered. After the solvent had been removed from the filtrate, the residue was purified by chromatography using PE as eluent, yielding compound **2** as white solid (7.51 g, 44.3 %). ¹H NMR (400 MHz, CDCl₃) δ : 7.30 (d, *J*=5.4 Hz, 1H), 7.04 (s, 2H), 6.78 (d, *J*=5.4 Hz, 1H), 2.93 (m, *J*=6.9 Hz, 1H), 2.56 (m, *J*=6.9 Hz, 2H), 1.29 (d, *J*=6.9 Hz, 6H), 1.16 (d, *J*=6.9 Hz, 6H), 1.05 (d, *J*=6.9 Hz, 6H). MS (EI) m/z: 364 (M⁺).

Compound 3: 3,3'-bis(2,4,6-triisopropylphenyl)-2,2'-bithiophene

To a mixture of magnesium turning (237 mg, 9.75 mmol), 4 mL anhydrous THF and a grain of iodine, a solution of compound **2** (3.56 g, 9.75 mmol) in 8 mL anhydrous THF was slowly added. The mixture was stirred and refluxed under nitrogen till the magnesium was exhausted. The prepared grignard reagent was added to a mixture of compound **2** (2.37 g, 6.5 mmol), $Pd(OAc)_2$ (22.5 mg, 0.10 mmol), SPhos (160.1 mg, 0.39 mmol) and 16 mL anhydrous THF. The mixture was stirred and refluxed overnight. Water (20 mL) was added and the mixture was

extracted with DCM. The organic phase was dried over anhydrous Na₂SO₄ and filtered. After the solvent had been removed from the filtrate, the residue was purified by chromatography using PE as eluent, yielding compound **3** as white solid (3.49 g, 94.0 %). ¹H NMR (400 MHz, CDCl₃) δ : 7.08 (s, 2H), 6.98 (d, *J*=5.0 Hz, 1H), 6.67 (d, *J*=5.0 Hz, 1H), 2.98 (m, *J*=6.9 Hz, 1H), 2.62 (m, *J*=6.9 Hz, 2H), 1.33 (d, *J*=6.9 Hz, 6H), 1.06 (d, *J*=6.9 Hz, 6H), 1.02 (d, *J*=6.9 Hz, 6H). MS (EI) m/z: 571.3(M⁺).

Compound 5: (3,3'-bis(2,4,6-triisopropylphenyl)-[2,2'-bithiophene]-5,5'-diyl)bis (trimethylstannane)

To a three-necked round-bottomed flask, compound **3** (3.40 g, 5.96 mmol) was dissolved in anhydrous THF (80 mL). A solution of n-butyllithium (2.5 M in hexane, 8.4 mL, 20.9 mmol) was added dropwise at room temperature. After 1h of stirring, a solution of SnMe₃Cl (1 M, 14.4 mL, 14.4 mmol) was added to this solution. Water (50 mL) was added after stirring overnight, and the mixture was extracted with DCM. The organic phase was dried over anhydrous Na₂SO₄ and filtered. After the solvent had been removed from the filtrate, the residue was recrystallized from ethanol, yielding compound **5** as yellow solid (3.24 g, 60.7 %). ¹H NMR (400 MHz, CDCl₃) δ : 7.06 (s, 2H), 2.96 (m, *J*=7.0 Hz, 1H), 2.56 (m, *J*=7.0 Hz, 2H), 1.32 (d, *J*=7.0 Hz, 6H), 1.01 (d, *J*=7.0 Hz, 6H), 1.00 (d, *J*=7.0 Hz, 6H), 1.84 (s, 6H), 0.17 (s, 9H). MS (EI) m/z: 897.3(M⁺).

Compound 6: 7,7'-(3,3'-bis(2,4,6-triisopropylphenyl)-[2,2'-bithiophene]-5,5'-diyl) bis(benzo[c][1,2,5]thiadiazole-4-carbaldehyde)

A mixture of compound **5** (1.62 g, 1.81 mmol), 7-bromobenzo[c][1,2,5]thiadiazole -4carbaldehyde (1.10 g, 4.53 mmol) and anhydrous toluene (20 mL) was carefully degassed, then Pd(PPh₃)₄ (41.8 mg, 0.04 mmol) was added. The mixture was stirred and refluxed 16h, then extracted with DCM. The organic phase was dried over anhydrous Na₂SO₄ and filtered. After the solvent had been removed from the filtrate, the residue was purified by chromatography using DCM as eluent, yielding compound **6** as dark red solid (859 mg, 53.0 %). ¹H NMR (400 MHz, CDCl₃) δ : 10.67 (s, 1H), 8.24 (s, 1H), 8.11 (d, *J*=7.5 Hz, 1H), 7.61 (d, *J*=7.5 Hz, 1H), 7.25(s,2H), 3.10 (m, *J*=6.9 Hz, 1H), 2.77 (m, *J*=6.9 Hz, 2H), 1.44 (d, *J*=6.9 Hz, 6H), 1.17 (d, *J*=6.9 Hz, 6H),

Compound iPrBT-NFA:

To a flask were added compound 6 (357.7 mg, 0.40 mmol), chloroform (40 mL) and pyridine (2.4 mL). 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (310.7 mg, 1.60 mmol) was slowly added to the mixture at -40 °C. After 10 min, the mixture was allowed to warm to -15 °C and stirred 4h. The mixture was poured into methanol (150 mL) and filtered. The residue was successively washed by methanol, hexane and acetone, then purified by column chromatography using chloroform as eluent, yielding **iPrBT-NFA** as dark blue solid (302.5 mg, 60.7 %). ¹H NMR (400 MHz, CDCl₃) δ : 9.51 (s, 1H), 9.09-9.07 (m, 1H), 8.73 (d, *J*=8.2 Hz, 1H), 8.21 (s, 1H), 7.96-7.94 (m,1H), 7.86-7.77 (m, 2H), 7.67 (d, *J*=8.2 Hz, 1H), 7.26(s, 2H), 3.11 (m, *J*=6.9 Hz, 1H), 2.77 (m, *J*=6.9 Hz, 2H), 1.44 (d, *J*=6.9 Hz, 6H), 1.18 (d, *J*=6.9 Hz, 6H), 1.14 (d, *J*=6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 187.34, 161.58, 155.92, 151.38, 150.65, 147.95, 140.90, 140.37, 139.96, 137.91, 137.46, 137.15, 136.28, 135.86, 135.05, 134.05, 132.37, 130.65, 130.58, 125.47, 124.48, 123.96, 123.30, 121.94, 114.27, 113.83, 35.69, 31.76, 26.21, 24.57, 23.95. HRMS (MALDI) m/z: 1246.4(M⁺). Element anal. calcd. for C₇₆H₆₂N₈O₂S₄: C 73.2%, H 5.10%, N 8.98%, found C 72.6%, H 5.26%, N 8.77%.

Compound 4: 3,3'-didecyl-2,2'-bithiophene

To a mixture of magnesium turning (219 mg, 9 mmol), 4 mL anhydrous THF and a grain of iodine, a solution of 2-bromo-3-decylthiophene (2.73 g, 9 mmol) in 8 mL anhydrous THF was slowly added. The mixture was stirred and refluxed under nitrogen till the magnesium was exhausted. The prepared grignard reagent was added to a mixture of 2-bromo-3-decylthiophene (1.82 g, 6 mmol), Pd(OAc)₂ (20.2 mg, 0.09 mmol), SPhos (147.8 g, 0.36 mmol) and 15 mL anhydrous THF. The mixture was stirred and refluxed overnight. Water (20 mL) was added and the mixture was extracted with DCM. The organic phase was dried over anhydrous Na₂SO₄ and filtered. After the solvent had been removed from the filtrate, the residue was purified by chromatography using PE as eluent, yielding compound **4** as yellow oil (2.58 g, 96.2 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 5.2 Hz, 1H), 6.95 (d, *J* = 5.2 Hz, 1H), 2.48 (t, *J* = 7.9 Hz,

Compound 7: (3,3'-didecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane)

To a three-necked round-bottomed flask, compound 4 (3.23g, 7.22 mmol) was dissolved in anhydrous THF (100 mL). A solution of n-butyllithium (2.5 M in hexane, 10.1 mL, 25.3 mmol) was added dropwise at room temperature. After 1h of stirring, a solution of SnMe₃Cl (1 M, 17.4 mL, 17.4 mmol) was added to this solution. Water (50 mL) was added after stirring overnight, and the mixture was extracted with DCM. The organic phase was dried over anhydrous Na₂SO₄ and filtered. After the solvent had been removed from the filtrate, the residue was recrystallized from ethanol, yielding compound 7 as yellow solid (4.01 g , 79.6 %) . ¹H NMR (400 MHz, Chloroform-*d*) δ 7.01 (s, 1H), 2.49 (t, *J* = 7.9 Hz, 2H), 1.30-1.17 (m, 16H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.35 (s, 9H). MS (EI) m/z: 772.2(M⁺).

Compound 8: 7,7'-(3,3'-didecyl-[2,2'-bithiophene]-5,5'-diyl)bis(benzo[c][1,2,5]thiadiazole -4carbaldehyde)

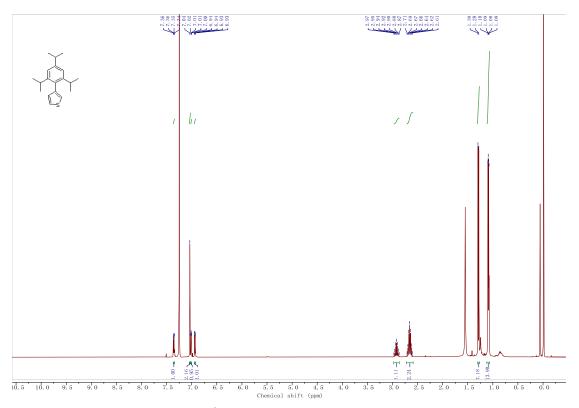
A mixture of compound 7 (1.40 g, 1.81 mmol), 7-bromobenzo[c][1,2,5]thiadiazole-4carbaldehyde (1.10 g, 4.53 mmol) and anhydrous toluene (20 mL) was carefully degassed, then Pd(PPh₃)₄ (41.8 mg, 0.04 mmol) was added. The mixture was stirred and refluxed 16h, then extracted with DCM. The organic phase was dried over anhydrous Na₂SO₄ and filtered. After the solvent had been removed from the filtrate, the residue was purified by chromatography using DCM as eluent, yielding compound **8** as dark red solid (576 mg, 41.2 %). ¹H NMR (400 MHz, CDCl₃) δ 10.73 (s, 1H), 8.24 (d, *J* = 7.5 Hz, 1H), 8.24 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 2.70 (t, *J* = 7.9 Hz,2H), 1.33-1.18 (m, 16H), 0.81 (d, *J* = 7.1 Hz, 3H). MS (EI) m/z: 771.2(M⁺).

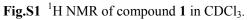
Compound DeBT-NFA:

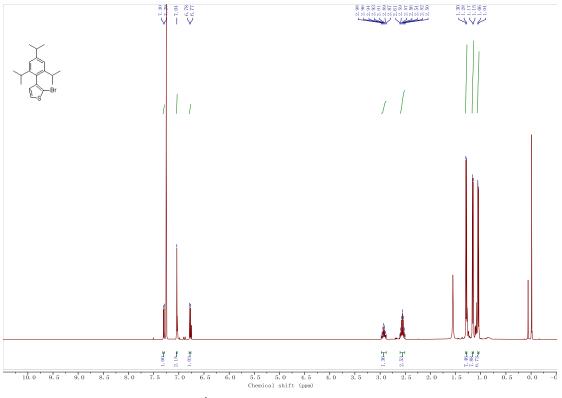
To a flask were added compound **8** (385.2 mg, 0.50 mmol), chloroform (40 mL) and pyridine (2.4 mL). 2-(3- ∞ -2,3-dihydro-1H-inden-1-ylidene)malononitrile (388.1 mg, 2.0 mmol) was slowly added to the mixture at -40 °C. 10 min later the mixture was allowed to warm to -15 °C and stirred 4 h. The mixture was poured into methanol (150 mL) and filtered. The residue was

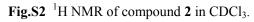
successively washed by methanol, hexane and acetone, then purified by column chromatography using chloroform as eluent, yielding **DeBT-NFA** as dark blue solid (305 mg, 51.2 %). ¹H NMR (400 MHz, CDCl₃) δ 9.58 (s, 1H), 9.23 (d, *J* = 7.7 Hz, 1H), 8.75 (d, *J* = 7.3 Hz, 1H), 8.32 (s, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 6.9 Hz, 1H), 7.85 (m, 2H), 2.73 (t, *J* = 7.9 Hz, 3H), 1.33-1.17 (m, 16H), 0.83 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 186.47, 161.41, 155.94, 151.62, 144.74, 140.10, 139.09, 137.68, 136.19, 135.88, 135.10, 133.77, 132.60, 132.21, 131.27, 125.39, 124.61, 123.82, 120.54, 114.26, 113.87, 31.92, 30.67, 29.68, 29.56, 29.51, 29.49, 29.34, 22.68, 22.61, 14.07. HRMS (MALDI) m/z: 1122.3 (M⁺). Element anal. calcd. for C₆₆H₅₈N₈O₂S₄ :C 70.2%, H 5.20%, N 9.97%, found C 69.9%, H 5.39%, N 9.77%.

4. Supporting Figures and Tables









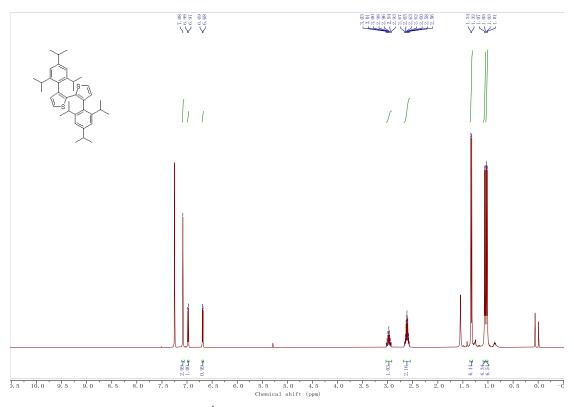


Fig.S3 ¹H NMR of compound **3** in CDCl₃.

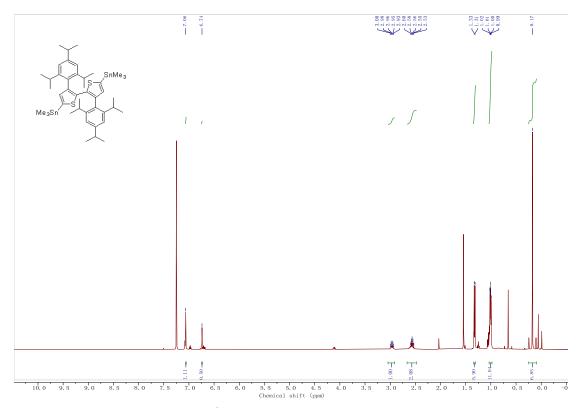


Fig.S4 ¹H NMR of compound **5** in CDCl₃.

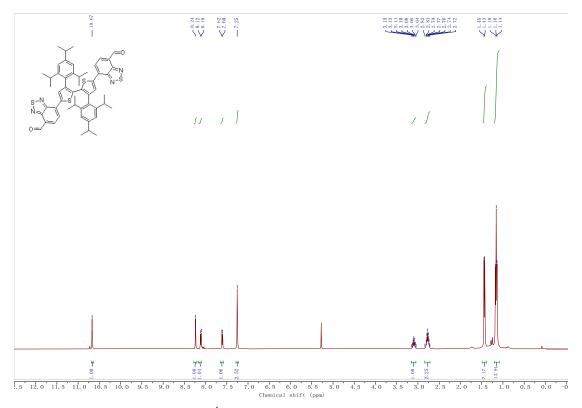


Fig.S5 ¹H NMR of compound **6** in CDCl₃.

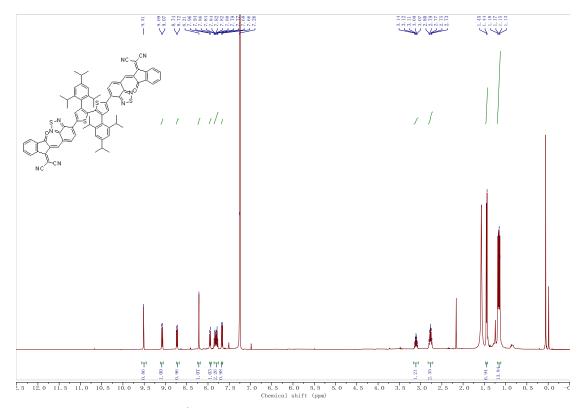
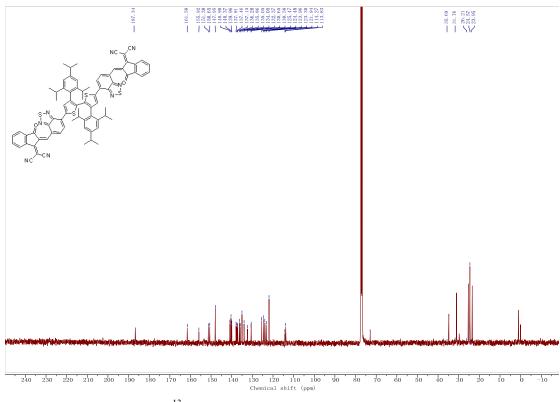
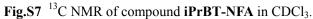


Fig.S6¹H NMR of compound iPrBT-NFA in CDCl₃.





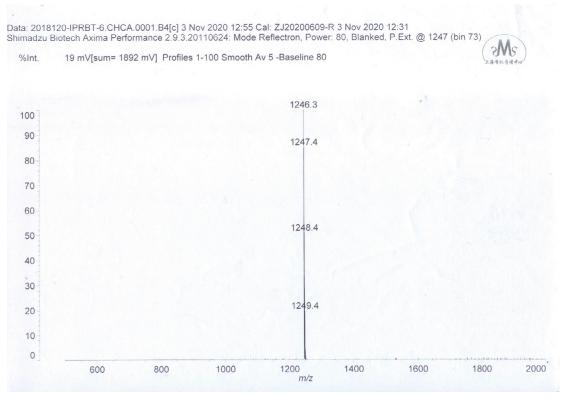


Fig.S8 MALDI-TOF-MS spectrum of compound iPrBT-NFA.

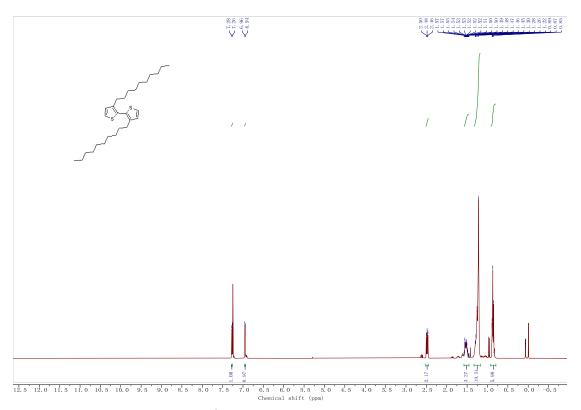


Fig.S9 ¹H NMR of compound **4** in CDCl₃.

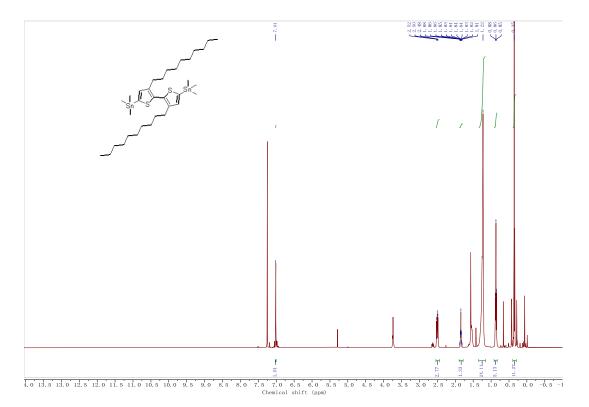
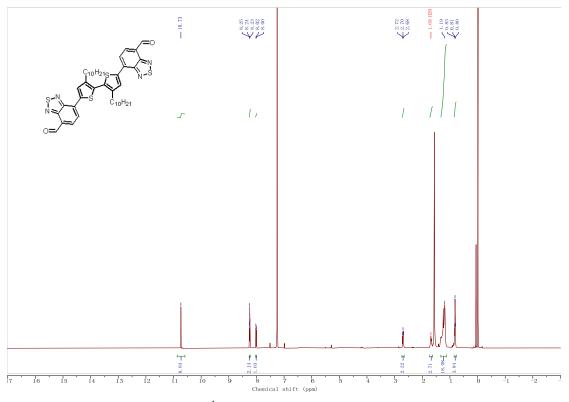
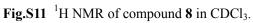


Fig.S10 ¹H NMR of compound **7** in CDCl₃.





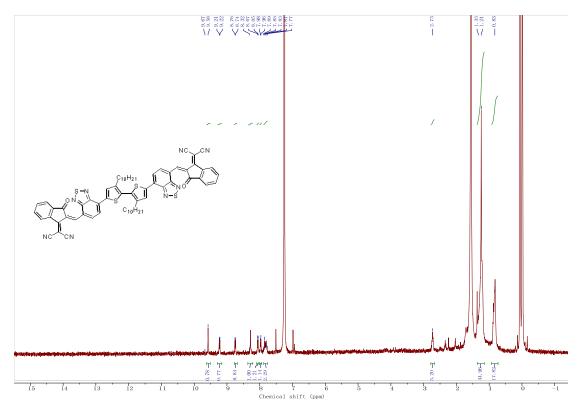


Fig.S12 ¹H NMR of compound DeBT-NFA in CDCl₃.

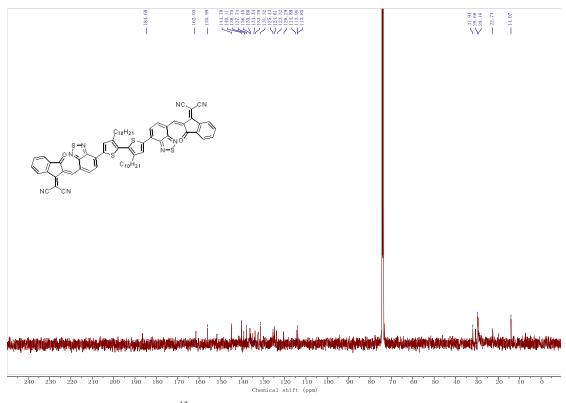


Fig.S13¹³C NMR of compound DeBT-NFA in CDCl₃.

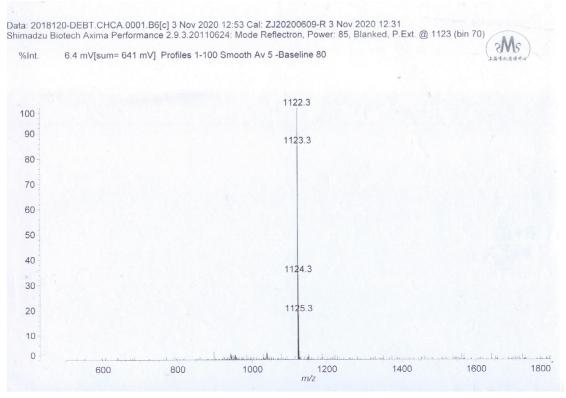


Fig.S14 MALDI-TOF-MS spectrum of compound DeBT-NFA.

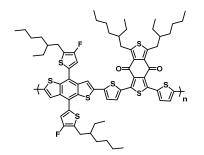


Fig. S15 The chemical structure of PM6

Table S1. The photovoltaic performance of iPrBT-NFA based devices with different D:A ratios.

D/A Ratio	V _{OC} (V)	$J_{\rm SC}$ (mA/cm ²)	Fill Factor (%)	PCE (%)
1:1	0.79	12.30	44.15	4.29
1:1.5	0.76	12.39	45.94	4.34
1:2	0.76	11.42	45.99	3.95

(Chloroform as solvent, no additive, spin-coating speed = 3000 rpm, no annealing treatment).

Additive	V _{OC} (V)	$J_{\rm SC}$ (mA/cm ²)	Fill Factor (%)	PCE (%)
0.25% DIO	0.77	14.71	60.34	6.79
0.5% DIO	0.75	15.99	59.18	7.06
0.75% DIO	0.73	16.32	60.80	7.29
1% DIO	0.72	16.67	57.52	6.93
0.25% CN	0.77	12.99	43.96	4.40
0.5% CN	0.79	13.24	45.77	4.78
1% CN	0.73	14.47	52.57	5.57

 Table S2. The photovoltaic performance of iPrBT-NFA based devices with different additives.

(D:A ratios =1:1.5, annealing at 100 °C for 10 min).

Solvent	V _{OC} (V)	J _{SC} (mA/cm ²)	Fill Factor (%)	PCE (%)
CF	0.74	15.66	57.88	6.73
СВ	0.73	4.96	55.69	1.98
Toluene	0.72	5.03	49.03	1.64

Table S3. The photovoltaic performance of iPrBT-NFA based devices with different solvent.

(D:A ratios =1:1.5, 0.75% DIO as additive, annealing at 100 °C for 10 min).

Table S4. The photovoltaic performance of **iPrBT-NFA** based devices with different spin-coating rotationl speed.

rpm	V _{OC} (V)	$J_{\rm SC}$ (mA/cm ²)	Fill Factor (%)	PCE (%)
3100	0.72	15.61	60.55	6.85
3400	0.73	15.30	60.56	6.80
3700	0.73	16.32	60.80	7.29
4000	0.73	15.70	61.66	7.08
4300	0.74	14.59	63.09	6.80
4600	0.74	14.33	62.28	6.59
4900	0.74	14.09	63.83	6.63

(D:A ratios =1:1.5, 0.75% DIO as additive, annealing at 100 °C for 10 min).

Temperature (°C)	Time (min)	Voc (V)	Jsc (mA/cm ²)	Fill Factor (%)	PCE (%)
	5	0.74	16.12	59.68	7.09
80	10	0.74	15.98	61.46	7.31
	15	0.75	15.75	62.24	7.32
	5	0.74	16.30	61.41	7.42
100	10	0.74	15.76	60.97	7.13
	15	0.73	15.42	62.48	7.08
	5	0.74	15.58	62.06	7.15
120	10	0.74	15.73	61.95	7.20
	15	0.73	16.12	58.78	6.95

 Table S5. The photovoltaic performance of iPrBT-NFA based devices with different annealing conditions.

(D:A ratios =1:1.5, 0.75% DIO as additive, spin-coating speed = 3700 rpm,).

D/A Ratio	V _{oc} (V)	J_{SC} (mA/cm ²)	Fill Factor (%)	PCE (%)
1:1.2	0.74	15.44	62.89	7.16
1:1.4	0.73	16.24	61.46	7.30
1:1.6	0.74	16.32	62.92	7.57
1:1.8	0.74	16.31	59.78	7.24

Table S6. The photovoltaic performance of iPrBT-NFA based devices with different D:A ratios.

(D:A ratios =1:1.5, 0.75% DIO as additive, spin-coating speed = 3700 rpm, annealing at 100 °C for 5 min).