Supporting Information

An A-D-D-A-type non-fullerene small-molecule acceptor with strong near-infrared absorption for high performance polymer solar cells

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Content

1. General experimental information on materials and characterizations.

All manipulations were performed under dry nitrogen flow. All reagents were obtained from Aldrich and directly used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 spectrometer using tetramethylsilane as a reference in deuterated chloroform solution at 298 K. UV-Vis absorption spectra were recorded on a HP-8453 UV visible system. MALDI-TOF mass spectrometric measurements were performed on Bruker Bifiex III MALDI-TOF. TGA was tested with a TA Q600 thermogravimetric analyzer. Differential scanning calorimeter (DSC) was measured on a TA Q200 Instrument. Cyclic voltammetry was carried out on a CHI660A electro-chemical work station in a three-electrode cell dipped in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution calibrated with a ferrocene/ferrocenyl couple (Fc/Fc^+) under nitrogen protection at a scan rate of 100 mV s^{-1} and room temperature (RT). In this three-electrode cell, a platinum rod, platinum wire and Ag/AgCl were used as a working electrode, counter electrode and reference electrode, respectively. Surface morphologies were recorded by transmission electron microscopy (TEM), which was carried out on a FEI Tecnai T20 with LaB_6 operated at 200 kV.

Synthesis of IDT2-CHO

The compound Br-IDT-CHO (300 mg, 0.30 mmol) and Bu_6Sn_2 (79 mg, 0.14 mmol) were dissolved in toluene (15 mL). $Pd_2(dba)_3$ (30 mg) was added as a catalyst and $P(o\text{-}tol)_3$ (40 mg) was refluxed for 24 hours at 110 °C under N_2 atmosphere. After cooling to room temperature and vacuum to remove the solvent, the crude product was

purified by silica gel using a mixture of hexane/dichloromethane as the eluent to give an orange solid (227 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm), 9.80 (s, 2H), 7.63 (s, 2H), 7.52 (s, 2H), 7.39 (s, 2H), 7.14-7.12 (m, 16H), 7.09-7.07 (m, 18H), 2.58-2.55 (m, 16H), 1.60-1.54 (m, 16H), 1.33-1.30 (m, 48H), 0.89-0.86 (m, 24H).

Synthesis of IDT2-DFIC

The compound IDT2-CHO (260 mg, 0.14 mmol) and DFIC (170 mg, 0.70 mmol) were dissolved in THF (15 mL) and pyridine (1 mL). The reaction was stirred at 50 °C for 12 h to precipitate crude product into methanol, vacuum filter after 3h. Then, the product was purified by silica gel using a mixture of hexane/dichloromethane as the eluent to give a black solid (266 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm), ^{1}H NRM (400 MHz, $CDCl_3$), δ / ppm), δ 8.87 (s, 2H), 8.55-8.51 (m, 2H), 7.69-7.63 (m, 6H), 7.41 (s, 2H), 7.17-7.09 (m, 34H), 2.59-2.56 (m, 16H), 1.59-1.57 (m, 16H), 1.40-1.30 (m, 48H), 0.89-0.86 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.09, 162.09, 158.86, 158.44, 157.46, 156.64, 154.29, 142.69, 142.25, 142.03, 140.90, 140.52, 140.27, 139.83, 139.45, 138.71, 133.46, 128.66, 127.75, 120.29, 119.81, 117.47, 114.44, 68.82, 63.09, 62.87, 35.59, 31.73, 31.34, 29.13, 22.61, 14.12. MS (MALDI-TOF) of $C_{154}H_{150}F_4N_4O_2S_4$ for [M]+: calcd. 2292.06; found: 2292.14.

2. Devices Fabrication and Characterizations

Bulk heterojunction solar cells were fabricated with the following conventional structure: ITO/ZnO/active layer/MoO_3/Ag. ITO substrates were cleaned and then dried in an oven at 85℃ for 12 hours. The ZnO precursor was spin-coated at 3000 r.p.m. onto the ITO surface and thermal annealed (200 °C) for 60 min in air, and the thickness of ZnO films are about 30 nm. Then the ZnO-coated substrates were transferred into a nitrogen-filled glove box. A 22 mg mL^{-1} chlorobenzene solution of PBDB-T: IDT2-DFIC and PBDB-T: IDIC-4F (1:1.2 weight ratio) was spin-coated at 3000 r.p.m. upon ZnO layer. The active layer thermal annealed (110 °C for PBDB-T:IDT2-DFIC and 150℃ for PBDB-T: IDIC-4F) for 10 min. Then evaporated 10 nm thick MoO_3 and 100 nm thick Ag on the active layer. The current density-voltage (*J-V*) characteristics of the devices under illumination of AM 1.5 G solar simulator (Newport, 100 mW cm^{-2}, calibrated by a silicon reference cell) were measured on a computer-controlled Keithley 2420 Source Measure Unit. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system (Model 66902). The hole mobilities of blend films were investigated by employing the hole-only devices with a structure of ITO/PEDOT:PSS/active layer/MnO_3/Al. The electron mobilities of blend films were performed in the electron-only devices with a structure of ITO/ZnO/active layer/Ca/Al.

3. Supplementary figures and tables

Figure S1

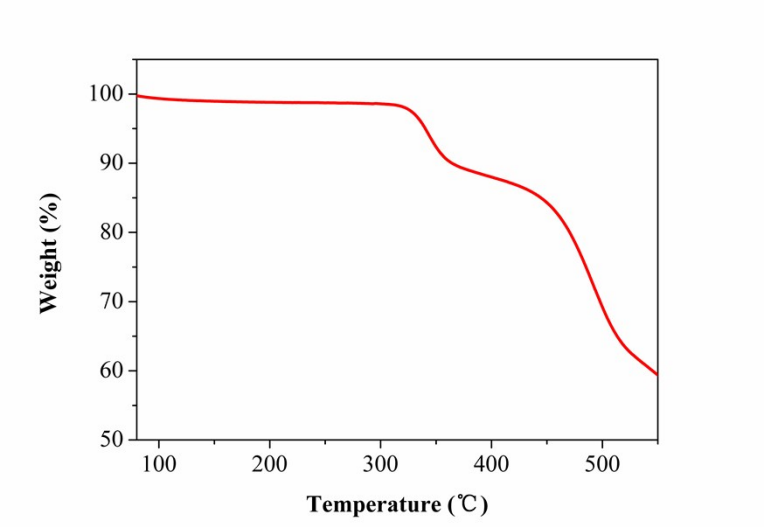


Figure S2

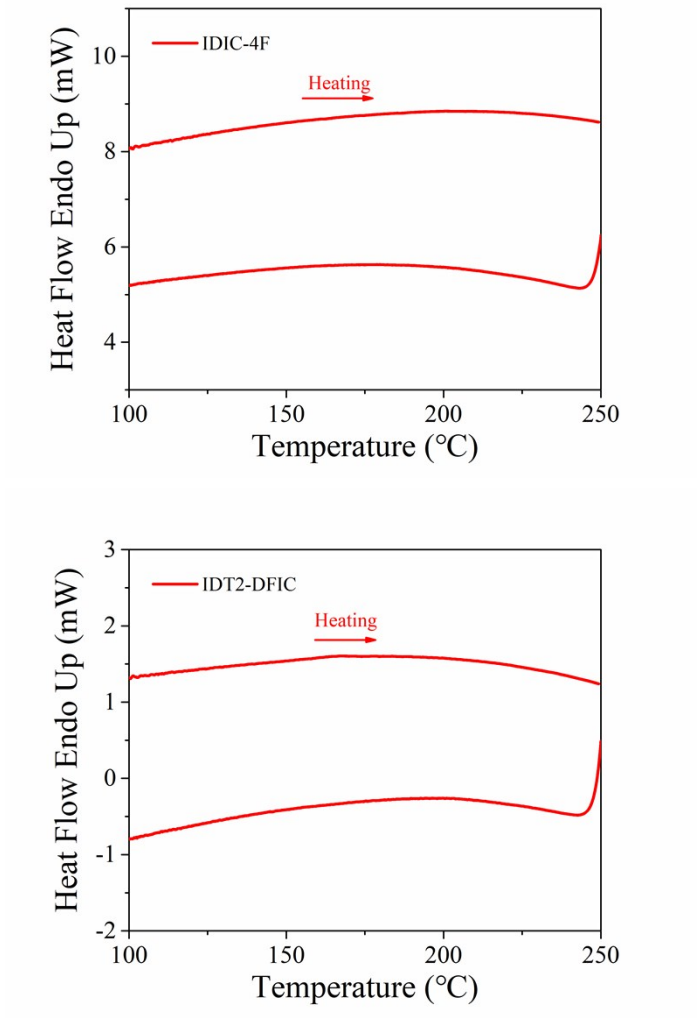


Figure S3

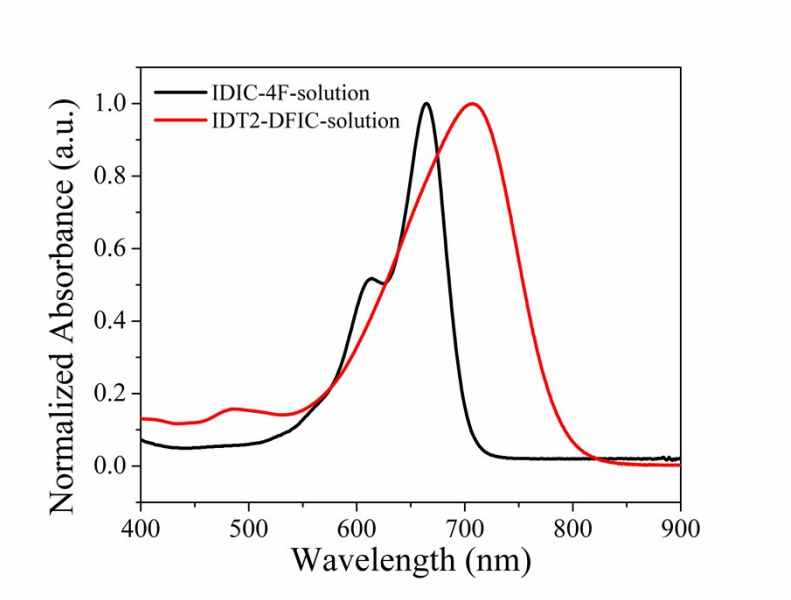

IDIC-4F-solution
IDT2-DFIC-solution
Normalized Absorbance (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800
900
Wavelength (nm)

Figure S4

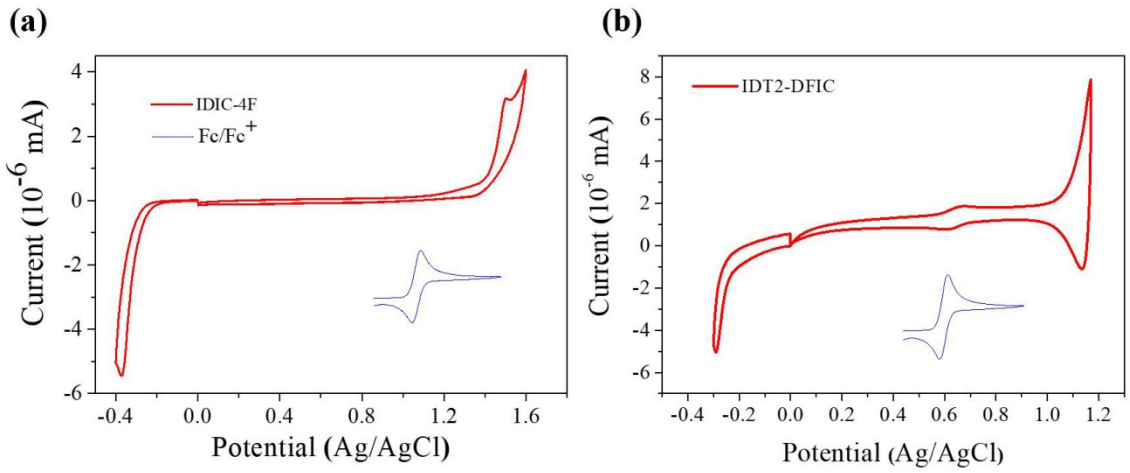

(a)
IDIC-4F
Fc/Fc+
Current (10-6 mA)
Potential (Ag/AgCl)
(b)
IDT2-DFIC
Current (10-6 mA)
Potential (Ag/AgCl)

Figure S5

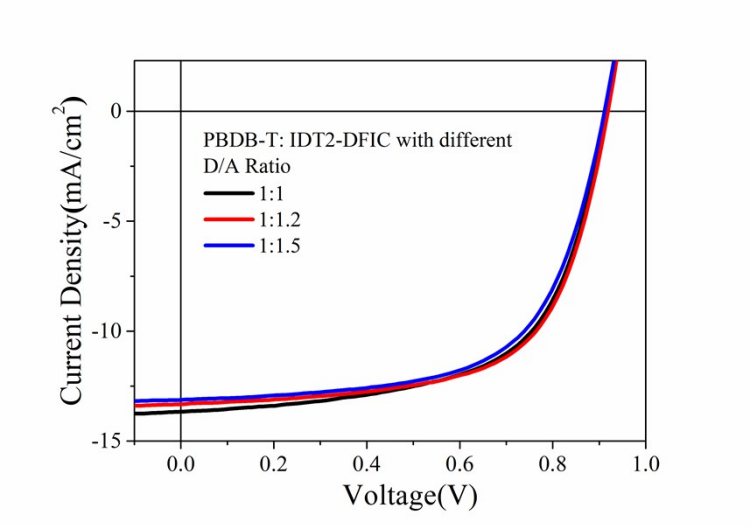


Table S1. Photovoltaic properties of the PSCs based on PBDB-T: IDT2-DFIC with different D/A Ratio.

		Voc [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%] [a]
D/A	1:1	0.91	13.65	61.81	7.71 (7.65)
	1:1.2	0.92	13.63	62.48	7.83 (7.79)
	1:1.5	0.91	13.11	62.82	7.51 (7.45)

[a] The average PCE in parentheses were obtained from 10 devices.

Figure S6

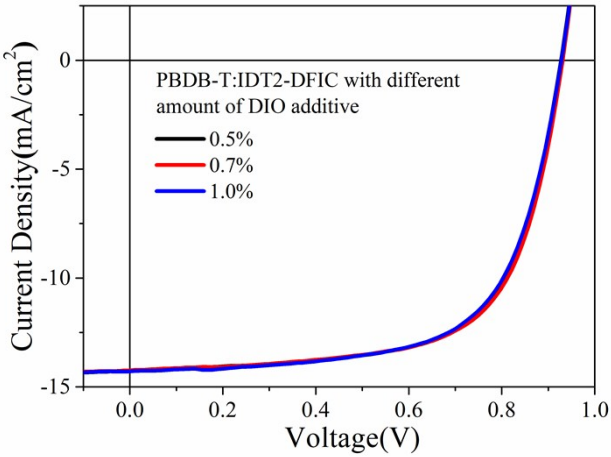


Table S2. Photovoltaic properties of the PSCs based on PBDB-T: IDT2-DFIC with different amount of DIO additive.

		Voc [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%] [a]
DIO	0.5%	0.93	14.25	65.37	8.77 (8.67)
	0.75%	0.93	14.23	66.43	8.80 (8.69)
	1.0%	0.93	14.28	65.42	8.66 (8.56)

Figure S7

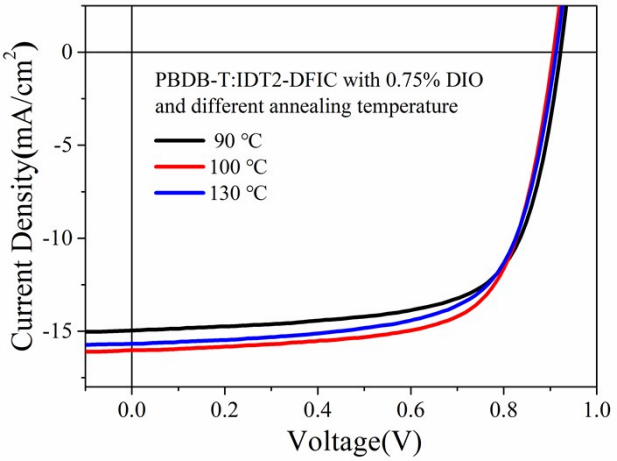


Table S3. Photovoltaic properties of the PSCs based on PBDB-T: IDT2-DFIC with different annealing temperature.

		Voc [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%] [a]
TA	90℃	0.92	15.48	66.18	9.44 (9.38)
	110℃	0.91	16.00	69.22	10.06(10.00)
	130℃	0.91	15.67	67.55	9.66 (9.61)

Figure S8

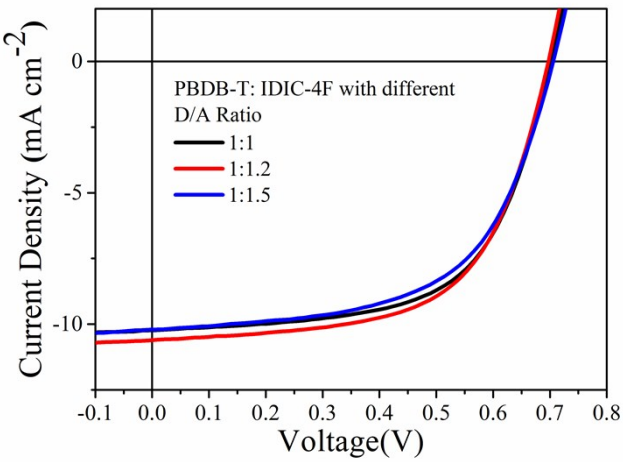


Table S4. Photovoltaic properties of the PSCs based on PBDB-T: IDIC-4F with different D/A Ratio.

		Voc [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%] [a]
D/A	1:1	0.70	10.21	61.50	4.40 (4.22)
	1:1.2	0.70	10.58	60.97	4.50 (4.41)
	1:1.5	0.71	10.19	58.61	4.21 (4.14)

Figure S9

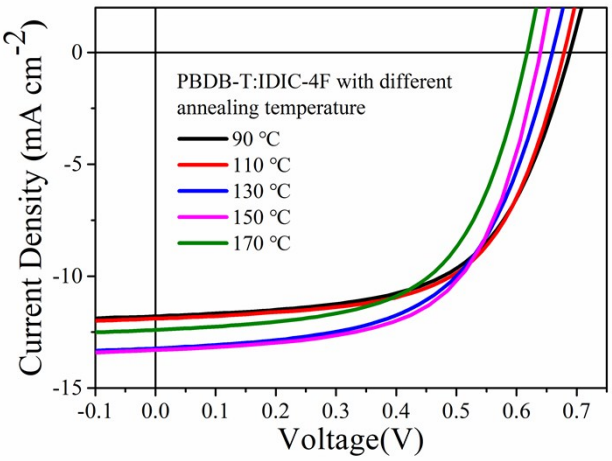


Table S5. Photovoltaic properties of the PSCs based on PBDB-T: IDTC-4F with different annealing temperature.

		Voc [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%] [a]
TA	90℃	0.69	11.82	59.66	4.84 (4.83)
	110℃	0.68	11.88	61.24	4.93 (4.83)
	130℃	0.66	13.08	58.42	5.04 (4.97)
	150℃	0.64	13.28	60.92	5.17 (5.15)
	170℃	0.62	12.37	59.57	4.55 (4.52)

Figure S10

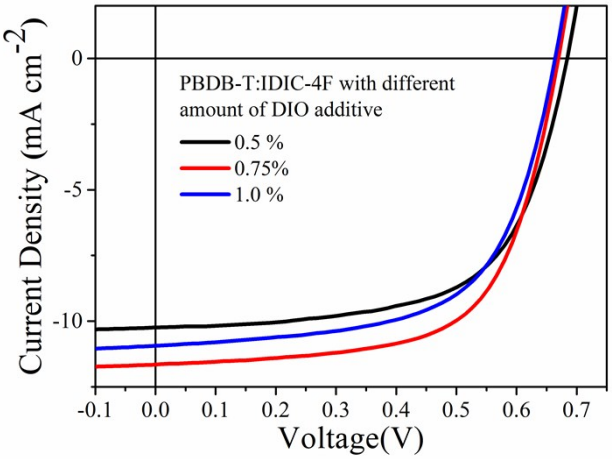
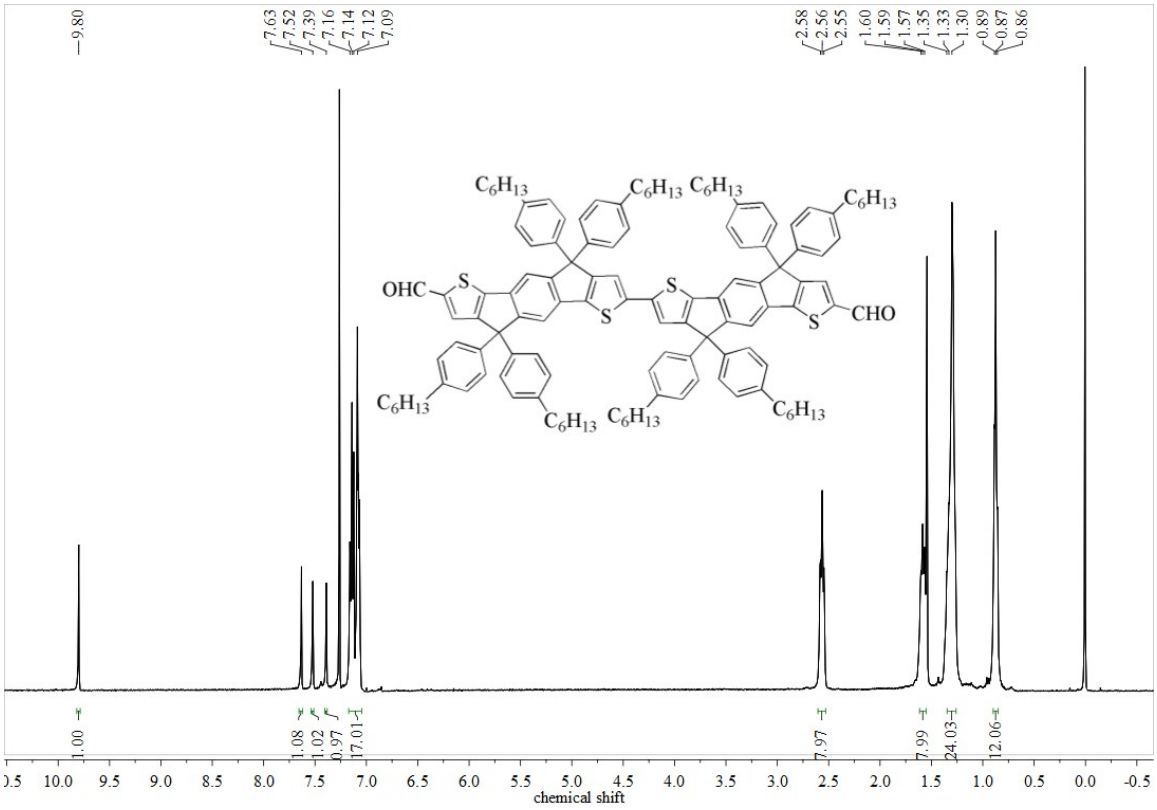
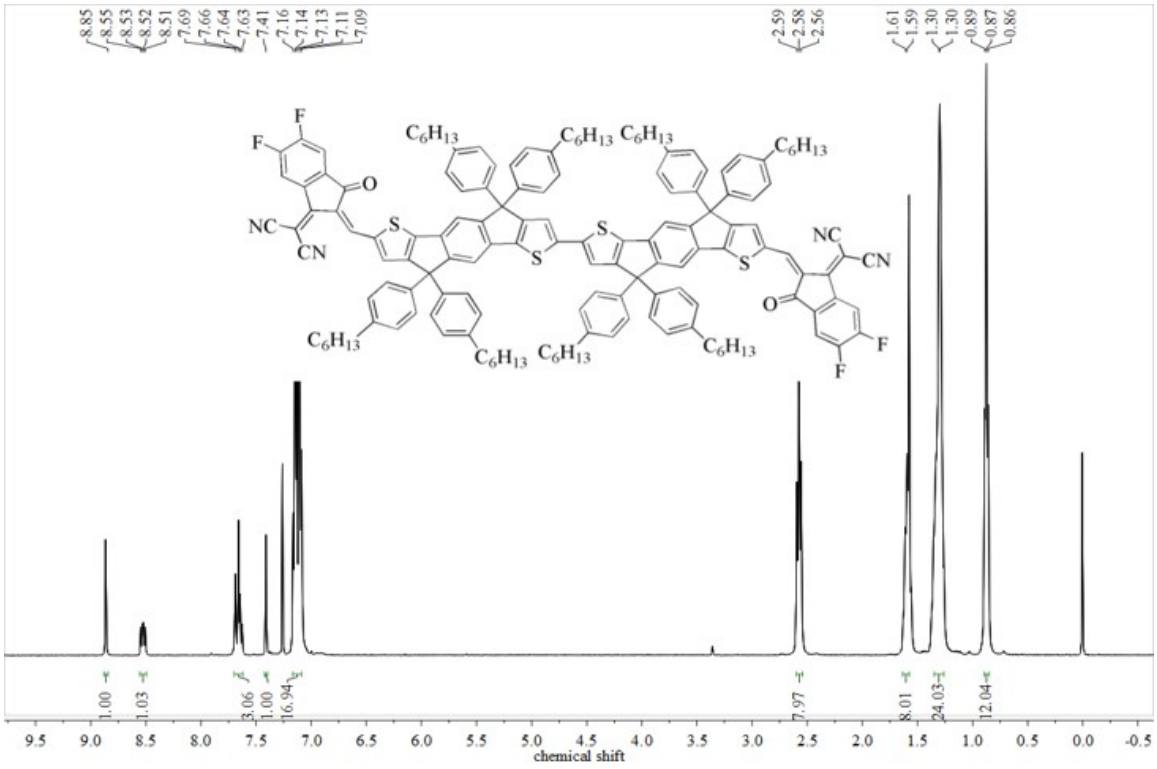


Table S6. Photovoltaic properties of the PSCs based on PBDB-T: IDIC-4F with different amount of DIO additive.

		Voc [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
DIO	0.5%	0.69	10.23	62.81	4.39
	0.5% [a]	0.64	11.12	61.17	4.22
	0.75%	0.67	11.63	64.32	5.01
	0.75% [a]	0.65	11.40	65.11	4.82
	1.0%	0.66	10.91	62.03	4.50
	1.0% [a]	0.64	10.80	62.22	4.28

Figure S11


9.80
7.63
7.52
7.39
7.16
7.14
7.12
7.09
2.58
2.56
2.55
1.60
1.59
1.57
1.35
1.33
1.30
0.89
0.87
0.86
OHC
CHO
S
C6H13
1.00
1.08
1.02
0.97
17.01
7.97
7.99
24.03
12.06
chemical shift


8.85
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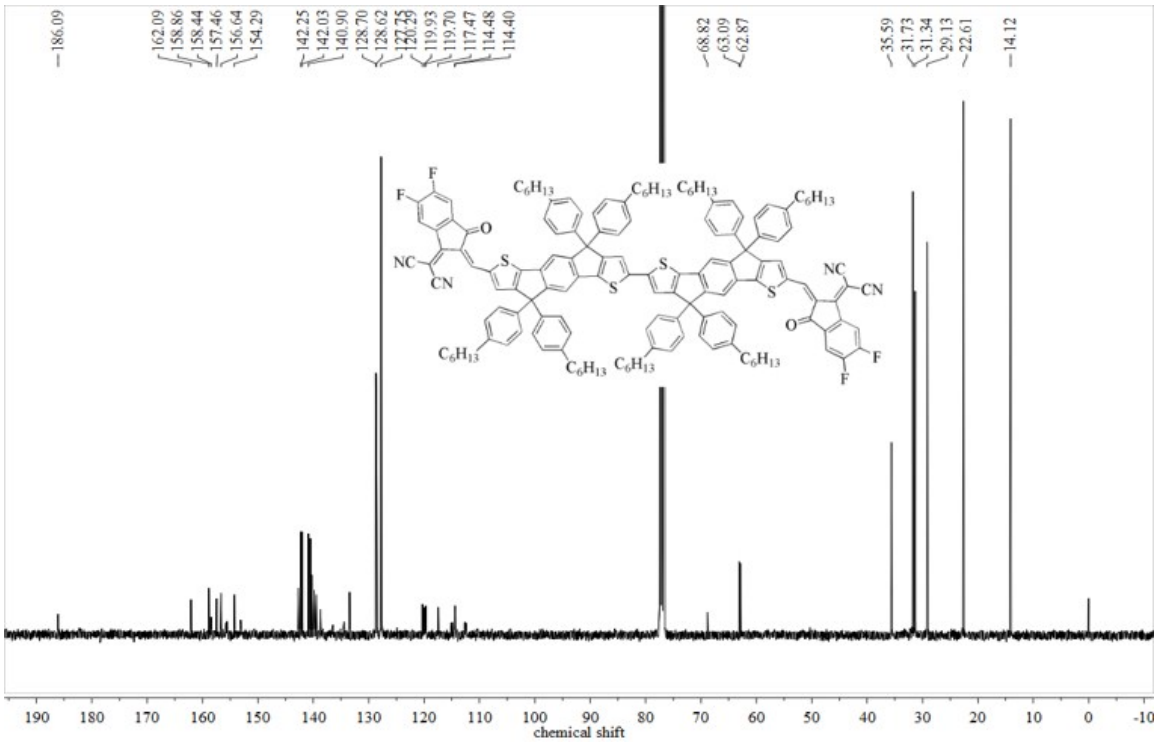
8.53
8.52
8.51
7.69
7.66
7.64
7.63
7.41
7.16
7.14
7.13
7.11
7.09
2.59
2.58
2.56
1.61
1.59
1.30
1.30
0.89
0.87
0.86
F
O
NC
CN
S
C6H13
1.00
1.03
3.06
1.00
16.94
7.97
8.01
24.03
12.04
chemical shift


186.09
162.09
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158.44
157.46
156.64
154.29
142.25
142.03
140.90
128.70
128.62
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119.70
117.47
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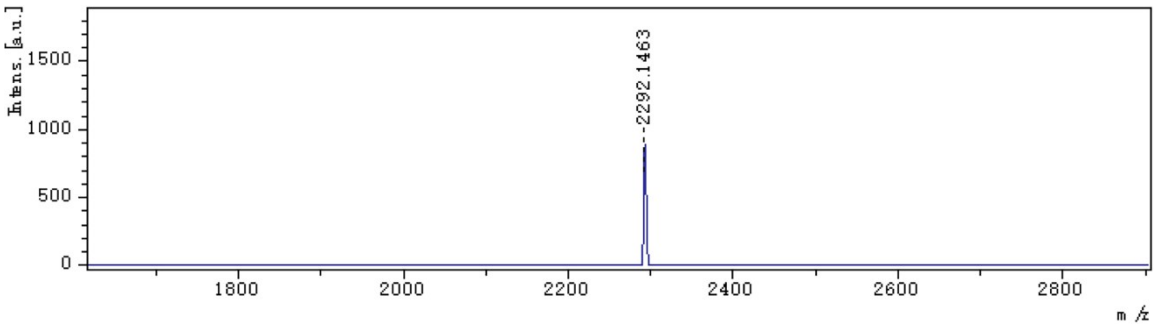
31.73
31.34
29.13
22.61
14.12
chemical shift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m/z