Electronic Supporting Information

Preparing Non-fullerene Acceptors with Multi-asymmetric Configuration in One-pot Reaction for Organic Solar Cells

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General Procedure:

All reactions were carried out under argon using solvents and reagents as commercially supplied, unless otherwise stated. Compound 1, compound 2 and compound 3 were synthesized by the reported method.[1] ^{1}H NMR and ^{13}C NMR spectra were collected on a Bruker AV-400 (400 MHz) or a Bruker Advanced III (500 MHz) spectrometers and are given in ppm, the residual solvent resonance of $CDCl_3$ was used as an internal reference. UV-vis absorption spectra were measured by a PerkinElmer Lambda 750S recording spectrophotometer. Cyclic voltammetry (CV) measurements of the target products were conducted on a CHI660D voltammetric analyzer in dichloromethane solution with 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) as supporting electrolyte at room temperature via conventional three-electrode configuration consisting of a platinum working electrode, a platinum wire counter electrode and an Ag/AgCl wire reference electrode. Grazing-incidence wide-angle x-ray scattering (GIWAXS) was carried out at beamline 7.3.3 Lawrence Berkeley National Lab (LBNL). The sample was put inside a helium chamber, and Pilatus 2M detector was used to collect the signal.

Device Fabrication and Measurement:

Device Fabrication

The patterned indium tin oxide glass (ITO) glass substrates with sheet resistance of 15 Ω sq^{-1} were used. They were cleaned with deionized water, acetone, chloroform, acetone, and isopropanol sequentially by ultra-sonic bath for 15 min each and then dried by N_2 gas. Then, 10 min UV-Ozone treatment was applied before use. The PEDOT-PSS solution was spin-coated onto the cleaned ITO glass substrate at 3000 rpm of 30s followed by annealing at 150 ℃ of 15 min in air. Then the PEDOT-PSS coated substrates were transferred into a nitrogen-filled glove box. PM6:acceptors blends were dissolved in chlorobenzene: CN (99.5: 0.5, v/v) at 60 ℃ and stirred overnight in a nitrogen-filled glove box. The active layers with optimized thicknesses were obtained by spin-coating the blend solution at room temperature with polymer concentrations of 10 mg mL^{-1}. Then, a 10 mg mL^{-1} ZnO nanoparticle solution was spin-coated onto the active layer at 3000 rpm for 40 s. Finally, the anode, 100 nm Al was deposited at a speed of 0.3 nm/s through a shadow mask by

thermal evaporation in a vacuum chamber of under 3×10^{-6} Torr to complete the device fabrication. Each device's active area was 3.64 mm^2.

OPV device characterization:
The device J-V characteristics were recorded by a Keithley 2420 Source Meter unit in forward direction under AM 1.5G 1 sun irradiance (100 mW cm^{-2}) as generated by a 300W Xe lamp solar simulator (Enlitech SS-F5-3A) at room temperature. Standard Si diode with KG-5 filter was used to calibrate the light intensity. Enlitech EQE system (Enlitech QE-M110) with a Si diode as reference cell was used to characterize the EQE spectra. Monochromatic light was generated from an Enlitech lamp source with a monochromator.

Electron and hole mobility measurement:
Hole-only diode configuration: ITO/PEDOT-PSS/blend films/MoO_3/Al. PEDOT-PSS was firstly spin-coated onto the ITO-glass substrate. Then the following layer were deposited by the same procedure as OPV devices. Electron-only diode configuration: ITO/ZnO/blend films/ZnO/Al.
The mobility in blend films were determined by fitting the dark current hole/electron-only diodes to the space-charge limited current (SCLC) model. The mobility was determined by the equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0 V^2}{8L^3}$$

where J is current density, μ_0 is the hole or electron mobility, ε_0 is the dielectric permittivity of the active layer (generally taken to be about 3 for organic materials), ε_0 is the dielectric permittivity of free space, L is the film thickness, and V is the voltage, which is defined as $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, V_{bi} is the built-in voltage which is related to the difference in the work function of the electrodes.

Synthesis:
The synthesis of compound **3**
In a dry flask, compound **1** (320 mg, 0.30 mmol) and compound **2** (150 mg, 0.35 mmol) were added, then $Pd(PPh_3)_4$ (17 mg, 5% mol) was added under argon atmosphere, followed by the addition of anhydrous toluene (10 mL). After being stirred at 110 °C overnight, the mixture was cooled to room temperature and extracted by ethyl acetate. The organic phase was dried over Na_2SO_4 and then the solvent was removed with rotary evaporator. The crude product was purified by column chromatography on silica gel with dichloromethane: hexane (v/v, 1/1) as eluent to afford compound **3** (260 mg, 0.23 mmol, 75% yield) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.59 (s, 1H), 7.43 - 7.08 (m, 5H), 6.98 (m, 1H), 4.29 (m, 2H), 2.07 - 1.94 (m, 4H), 1.88 (m, 4H), 1.73 (m, 1H), 1.51 - 1.30 (m, 8H), 1.30 - 1.00 (m, 36H), 1.00 - 0.70 (m, 26H) ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$), δ 178.66, 161.04, 156.88, 156.21, 154.02, 153.97, 151.83, 149.00, 147.32, 142.54, 141.36, 137.81, 134.21, 133.99, 129.12, 128.91, 127.53, 124.87, 124.77, 122.49, 121.84, 114.21, 113.31, 68.14, 54.55, 53.89, 39.17, 38.94, 31.91, 31.88, 30.53, 30.08, 30.04, 29.40, 29.37, 29.32, 29.05, 24.35, 24.27, 23.98, 23.07, 22.71, 14.18, 14.15, 11.17.
MS (MALDI-TOF) *m/z*: Calculated for [M^+] 1054.58; found: 1054.52.

The synthesis of compound **4**

Phosphoryl chloride (0.19 mL, 2.0 mmol) was added dropwise into DMF (0.23 mL, 3.0 mmol) at 0 ^{o}C and stirred for 30 minutes to prepare Vilsmeier reagent. Compound **3** (220 mg, 0.19 mmol) was dissolved in 10 mL dichloromethane, then the fresh-made Vilsmeier reagent (0.40 mmol) was added dropwise into the mixture. After being stirred at room temperature for 2 h, the mixture was poured into ice water (50 mL) and neutralized with CH_3COONa, and then extracted with dichloromethane (3×50 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4. After removal of solvent, it was purified by column chromatography on silica gel using a mixture of dichloromethane: hexane (v/v, 1/1) as eluent to afford compound **4** (164 mg, 0.14 mol, 74%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 9.85 (s, 1H), 7.62 (m, 2H), 7.45 (s, 1H), 7.38 (s, 1H), 4.29 (m, 2H), 2.10 - 1.84 (m, 8H), 1.72 (m, 1H), 1.51 - 1.31 (m, 8H), 1.28 - 1.11 (m, 40H), 1.00 - 0.73 (m, 26H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.90, 178.70, 160.89, 157.89, 155.74, 155.23, 154.30, 151.77, 148.75, 146.03, 145.28, 141.67, 136.92, 135.64, 135.27, 130.44, 129.48, 129.27, 124.61, 124.51, 123.04, 115.00, 114.18, 68.14, 54.65, 54.21, 38.97, 38.94, 38.84, 31.77, 31.76, 30.43, 29.90, 29.88, 29.26, 29.18, 28.95, 24.28, 23.88, 22.97, 22.60, 18.58, 14.07, 14.04, 11.07.
MS (MALDI-TOF) *m/z*: Calculated for [M^+] 1082.58; found: 1082.59.

The synthesis of **2FIFIC** and **ICIF2F**
Compound **4** (300 mg, 0.28 mmol), 2FIC (126 mg, 0.55 mmol) and IC (107 mg, 0.55 mmol) were added in *n*-butanol (20 ml). Then the mixture was heated to 100 ^{o}C and kept stirring overnight. After cooling to room temperature, the solvent was removed. The crude product was purified by silica-gel column chromatography, and eluted with dichloromethane: hexane (2/1, v/v) to afford compound **2FIFIC** (110mg, 0.0748 mmol, 27%) and **ICIF2F** (100mg, 0.068 mmol, 24%) as a dark-green solid, with 2FIF2F (50 mg, 0.033 mmol, 11.8%) and ICIFIC (30 mg, 0.021 mmol, 7.5%) as the byproducts.
2FIFIC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.86 (s, 1H), 8.71 (m, 1H), 8.56 (m, 1H), 7.97 - 7.92 (m, 1H), 7.82 - 7.67 (m, 5H), 7.60 (s, 1H), 7.44 (s, 1H), 4.31 (m, 2H), 2.16 - 1.90 (m, 8H), 1.76 (m, 1H), 1.50 - 1.32 (m, 8H), 1.27 - 1.06 (m, 40H), 0.96 (m, 8H), 0.80 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.24, 186.09, 162.59, 160.44, 159.48, 159.11, 158.71, 157.36, 157.13, 155.84, 155.73, 155.38, 153.26, 153.12, 152.75, 152.68, 151.48, 149.15, 148.65, 146.97, 140.63, 140.24, 138.91, 138.79, 138.65, 136.96, 136.71, 136.21, 135.35, 134.64, 134.38, 130.72, 128.97, 128.76, 125.76, 125.69, 125.39, 123.67, 122.37, 120.75, 120.57, 117.01, 116.90, 116.28, 115.16, 114.97, 114.88, 114.77, 114.61, 112.75, 112.57, 69.24, 68.97, 68.64, 54.82, 54.50, 39.20, 39.14, 38.94, 31.90, 30.56, 30.03, 29.41, 29.35, 29.04, 24.54, 24.49, 24.02, 23.11, 22.73, 14.23, 14.19, 11.20.
MS (MALDI-TOF) *m/z*: Calculated for [M^+] 1470.63; found: 1470.39.
ICIF2F: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.83 (s, 1H), 8.73 - 8.69 (m, 1H), 8.54 (m, 1H), 7.97 - 7.92 (m, 1H), 7.80 (s, 1H), 7.77 (m, 2H), 7.72 (s, 1H), 7.68 (m, 1H), 7.59 (s, 1H), 7.44 (s, 1H), 4.31 (m, 2H), 2.08 (m, 4H), 2.01 - 1.90 (m, 4H), 1.76 (m, 1H), 1.50 - 1.34 (m, 8H), 1.15 (m, 40H), 1.00 - 0.92 (m, 8H), 0.80 (m, 18H).^{13}C NMR (101 MHz, $CDCl_3$) δ 188.44, 186.73, 161.07, 160.77, 160.28, 159.53, 157.21, 156.89, 156.84, 155.90, 155.76, 155.49, 153.57, 153.49, 153.31, 153.17, 153.07, 152.93, 151.40, 150.36, 148.57, 148.34, 140.91, 140.05, 138.61, 138.20, 138.06, 137.02, 136.80, 136.51, 135.12, 134.48, 134.21, 130.44, 128.92, 128.71, 126.37, 126.29, 125.36, 123.77, 122.01, 121.71, 119.41, 117.19, 117.07, 116.11, 115.06, 115.00, 114.91, 114.74, 114.41,

112.60, 112.42, 69.33, 68.72, 54.83, 54.49, 39.20, 39.11, 38.93, 31.89, 30.55, 30.03, 29.40, 29.34, 29.02, 24.53, 24.49, 24.01, 23.09, 22.72, 14.21, 14.18, 11.18.

MS (MALDI-TOF) *m/z*: Calculated for [M^+] 1470.63; found: 1470.41.

ICIFIC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.87 (s, 1H), 8.71 (m, 2H), 7.94 (m, 2H), 7.87 - 7.68 (m, 6H), 7.59 (s, 1H), 7.43 (s, 1H), 4.31 (m, 2H), 2.01 (m, 8H), 1.81 - 1.72 (m, 1H), 1.55 - 1.30 (m, 10H), 1.15 (m, 36H), 0.89 (m, 28H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.95, 188.31, 161.25, 160.64, 160.25, 159.29, 158.56, 157.04, 156.79, 155.28, 152.69, 149.49, 147.13, 140.75, 140.03, 138.50, 137.99, 136.92, 136.60, 136.44, 135.02, 134.34, 134.07, 130.27, 125.84, 125.20, 123.63, 123.46, 122.15, 121.48, 120.36, 116.03, 114.90, 114.62, 69.02, 68.51, 54.71, 54.67, 54.37, 39.08, 38.83, 31.79, 30.46, 29.96, 29.30, 29.23, 28.94, 24.43, 23.92, 23.00, 22.62, 14.10, 14.06, 11.08.

MS (MALDI-TOF) *m/z*: Calculated for [M^+] 1434.65; found: 1434.57.

2FIF2F: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.71 (s, 1H), 8.56 (m, 1H), 8.47 (m, 1H), 7.85 (s, 1H), 7.76 (s, 1H), 7.71 (m, 1H), 7.64 (m, 2H), 7.51 (s, 1H), 4.34 (m, 2H), 2.21 - 1.90 (m, 8H), 1.84 - 1.74 (m, 1H), 1.53 - 1.34 (m, 8H), 1.31 - 1.08 (m, 40H), 0.91 (m, 26H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.72, 186.06, 162.35, 160.26, 159.73, 158.62, 157.49, 157.16, 156.74, 155.77, 155.59, 151.35, 150.13, 148.17, 140.74, 138.76, 138.65, 136.74, 136.53, 134.67, 134.20, 130.40, 130.39, 129.69, 128.96, 128.75, 126.27, 122.08, 120.68, 119.51, 117.30, 117.17, 116.31, 115.11, 114.70, 114.55, 114.37, 112.78, 112.58, 112.42, 110.25, 100.10, 93.65, 69.47, 69.11, 68.75, 54.89, 54.52, 39.19, 39.11, 38.94, 31.89, 30.56, 30.03, 30.01, 29.40, 29.35, 29.33, 29.03, 24.54, 24.50, 24.02, 23.09, 22.72, 14.21, 14.17, 11.18.

MS (MALDI-TOF) *m/z*: Calculated for [M^+] 1506.62; found: 1506.72.

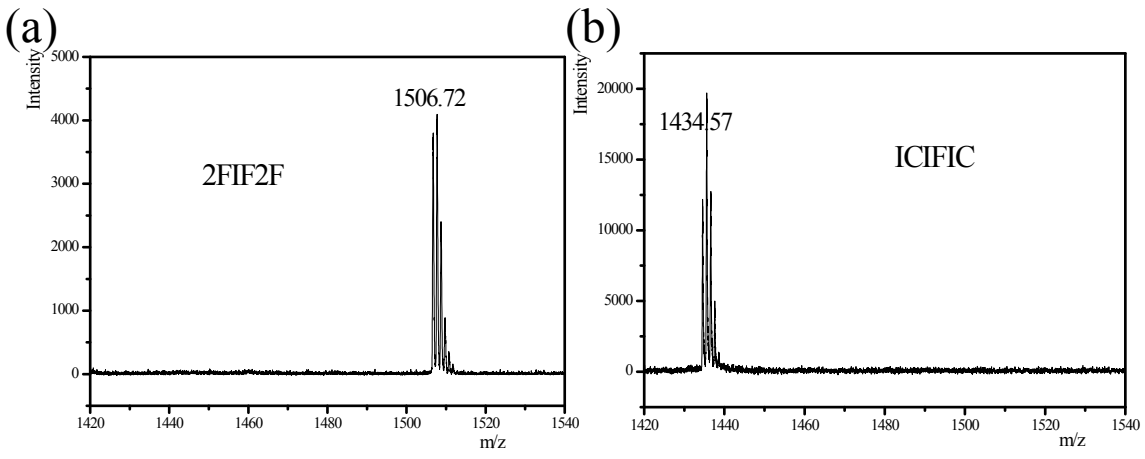

Fig. S1. The Mass spectra of (a) 2FIF2F and (b) ICIFIC.

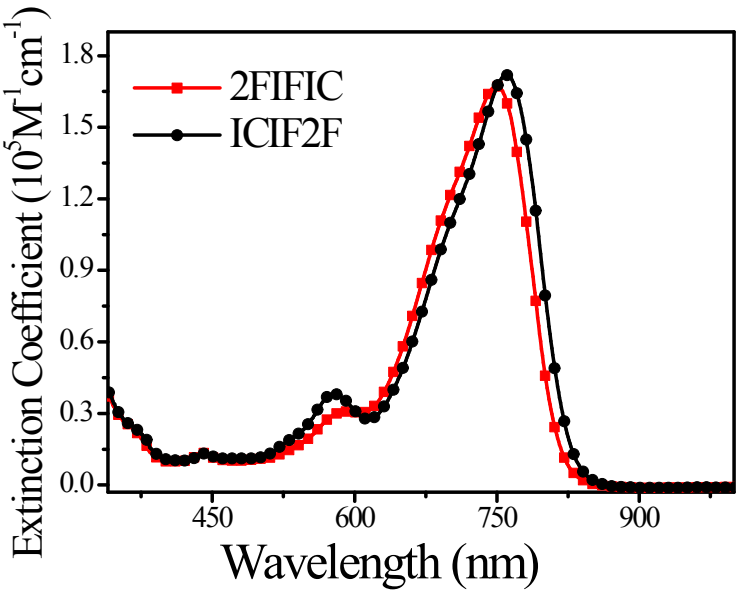

Fig. S2. The absorption spectra of the acceptors in dilute chloroform solution.

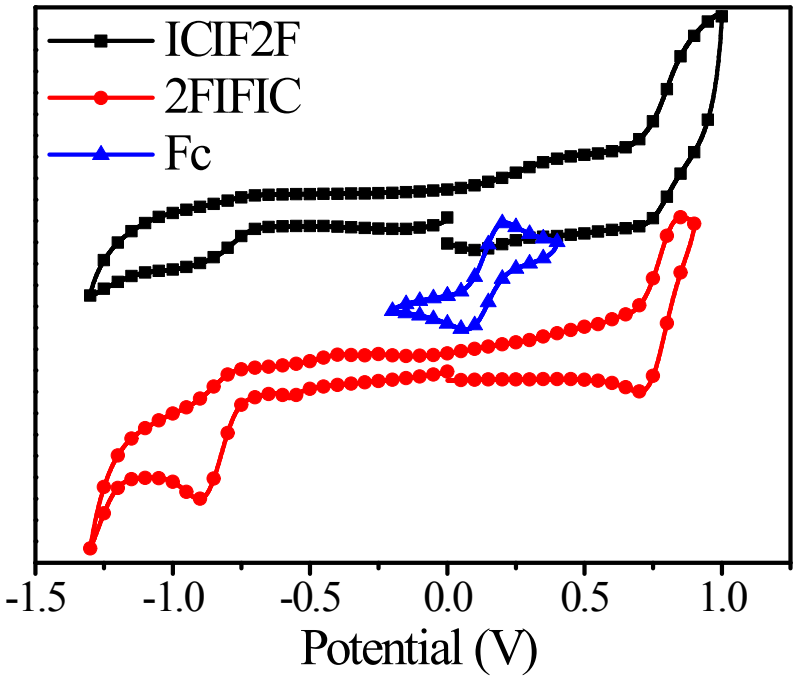

Fig. S3. Cyclic voltammetry curves of **2FIFIC** and **ICIF2F**.

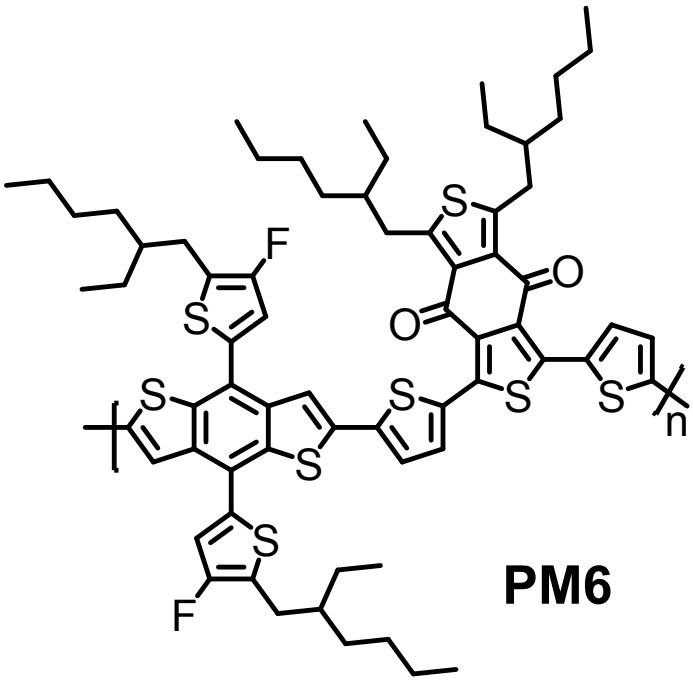

Fig. S4. Chemical structure of **PM6**.

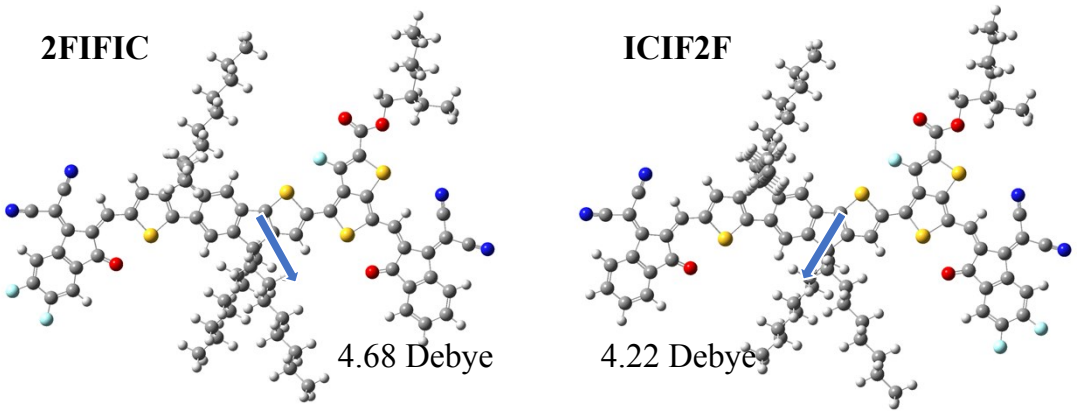

Fig. S5. The dipole moments of optimized geometries **2FIFIC** and **ICIF2F**. The simulations were performed by density functional theory (DFT) at B3LYP/6-31G level.

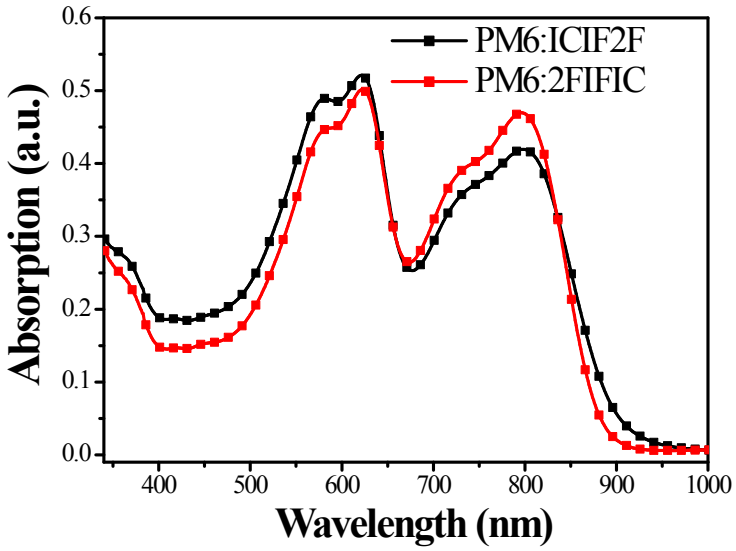

Fig. S6. The absorption spectra of the optimized blend film of **PM6**:acceptors.

Table S1. Photovoltaic parameters of OSCs based on **PM6**:acceptors with different D:A weight under the illumination of AM1.5G, 100 mW/cm2. The devices were in a conventional architecture ITO/PEDOT:PSS/**PM6**:acceptors/ZnO/Al.

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Active Layer	D:A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PM6:2FIFIC	1:0.8	0.86	18.36	51.4	8.12
	1:1	0.85	18.47	53.8	8.45
	1:1.2	0.84	19.31	53.3	8.65
	1:1.4	0.84	19.47	54.5	8.91
	1:1.6	0.83	19.66	52.3	8.53
PM6:ICIF2F	1:0.8	0.83	15.28	46.2	5.86
	1:1	0.83	15.45	48.3	6.19
	1:1.2	0.83	15.55	48.1	6.21
	1:1.4	0.82	15.87	47.9	6.23
	1:1.6	0.82	15.91	47.1	6.14

Table S2. Photovoltaic parameters of OSCs based on **PM6**:acceptors(1: 1.4, w/w) with

different additives under the illumination of AM1.5G, 100 mW/cm2. The devices were in a conventional architecture ITO/PEDOT:PSS/**PM6**:acceptors/ZnO/Al.

Active Layer	Additive	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PM6:2FIFIC	As-cast	0.84	19.73	50.4	8.35
	0.5% CN	0.82	20.80	61.4	10.47
	1.0% CN	0.83	20.80	60.0	10.36
	0.5% DIO	0.82	21.45	58.9	10.36
	1.0% DIO	0.82	20.17	62.7	10.37
PM6:ICIF2F	As-cast	0.82	15.89	48.0	6.25
	0.5% CN	0.80	18.16	62.4	9.07
	1.0% CN	0.80	18.45	61.2	9.03
	0.5% DIO	0.81	18.23	58.4	8.62
	1.0% DIO	0.81	18.37	56.7	8.44

Table S3. Photovoltaic parameters of OSCs with PM6: acceptors (1: 1.4, w/w) at different thermal annealing temperatures for 5 min under the illumination of AM1.5G, 100 mW/cm2. The devices were in a conventional architecture ITO/PEDOT:PSS/**PM6**:acceptors/ZnO/Al.

Active Layer	Additive	Thermal Annealing	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PM6:2FIFIC	0.5% CN	w/o	0.83	20.87	63.4	10.98
		90^{o}C	0.81	21.01	64.9	11.04
		100^{o}C	0.80	21.60	63.2	10.92
		110^{o}C	0.80	22.80	62.2	11.34
		120^{o}C	0.80	22.04	62.5	11.02
PM6:ICIF2F	0.5% CN	w/o	0.80	18.23	62.3	9.09
		90^{o}C	0.79	19.25	61.9	9.41
		100^{o}C	0.79	19.34	62.3	9.52
		110^{o}C	0.79	19.61	62.0	9.60
		120^{o}C	0.79	19.62	61.5	9.53

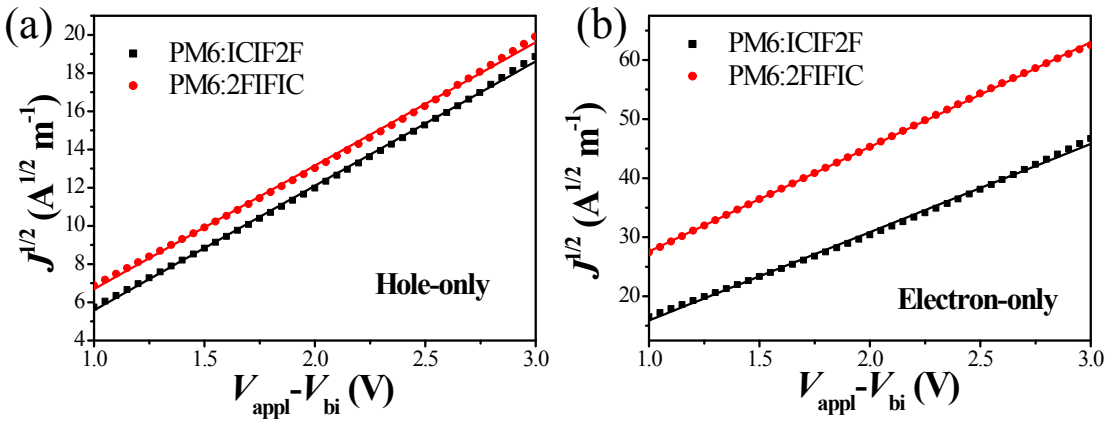

Fig. S7. (a) The $J^{1/2}$-V curves of the hole-only devices; (b) The $J^{1/2}$-V curves of the electron-only devices.

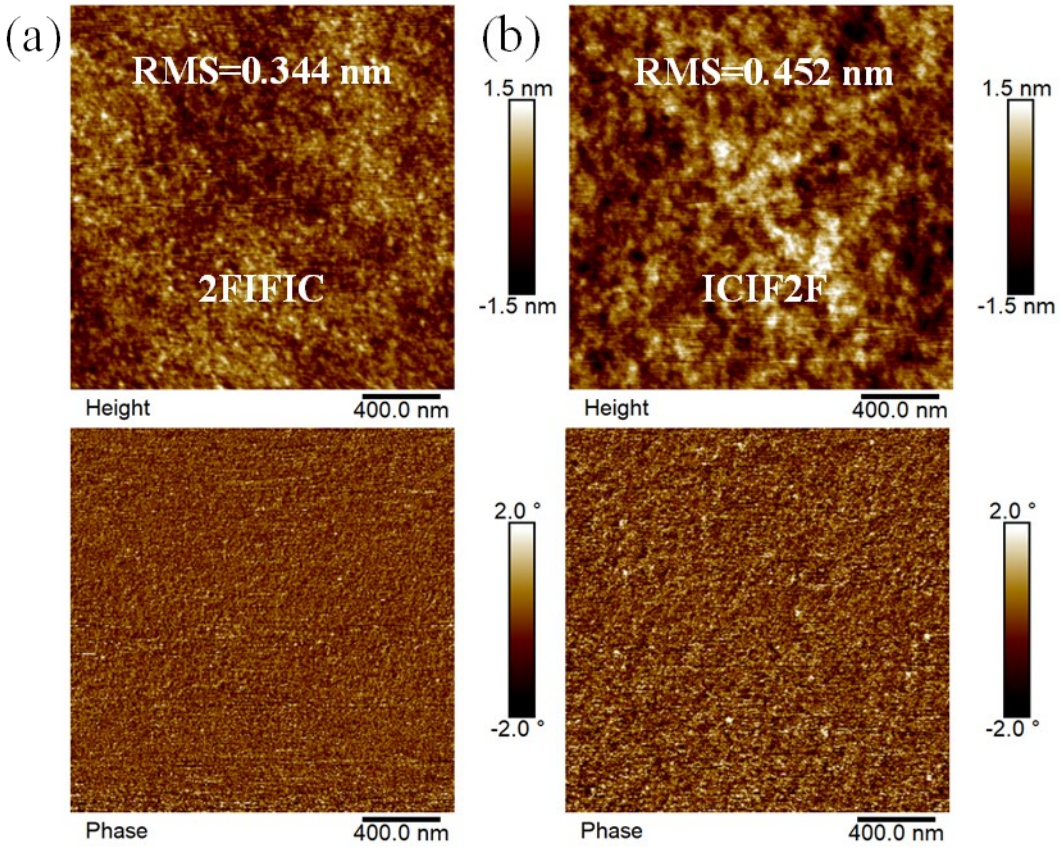

Fig. S8. AFM height (up) and phase images (down) of (a) **2FIFIC** neat film and (b) **ICIF2F** neat film.

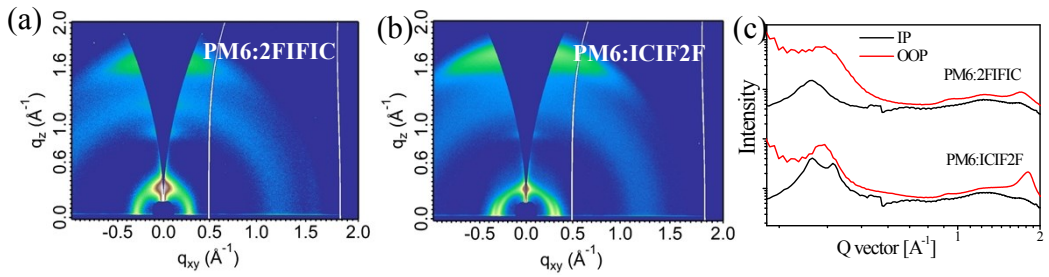

Fig. S9. GIWAXS patterns of the optimized blend films based on (a) **PM6**:**2FIFIC** blend films and (b) **PM6**:**ICIF2F** and (c) corresponding 1D line cut profiles.

Table S4 Contact angle of water and diiodomethane (DIM), surface tension of **PM6**, **ICIF2F**, and **2FIFIC**, Flory-Huggins interaction parameter χ of two blends.

Film	θ_{water} [°]	θ_{DIM} [°]	Y_s [mN m^{-1}]	χ [PM6, i]
PM6	**98.2**	**62.4**	**28.75**	**-**
ICIF2F	**96.1**	**36.0**	**41.57**	**1.18**
2FIFIC	**90.9**	**32.0**	**43.71**	**1.57**

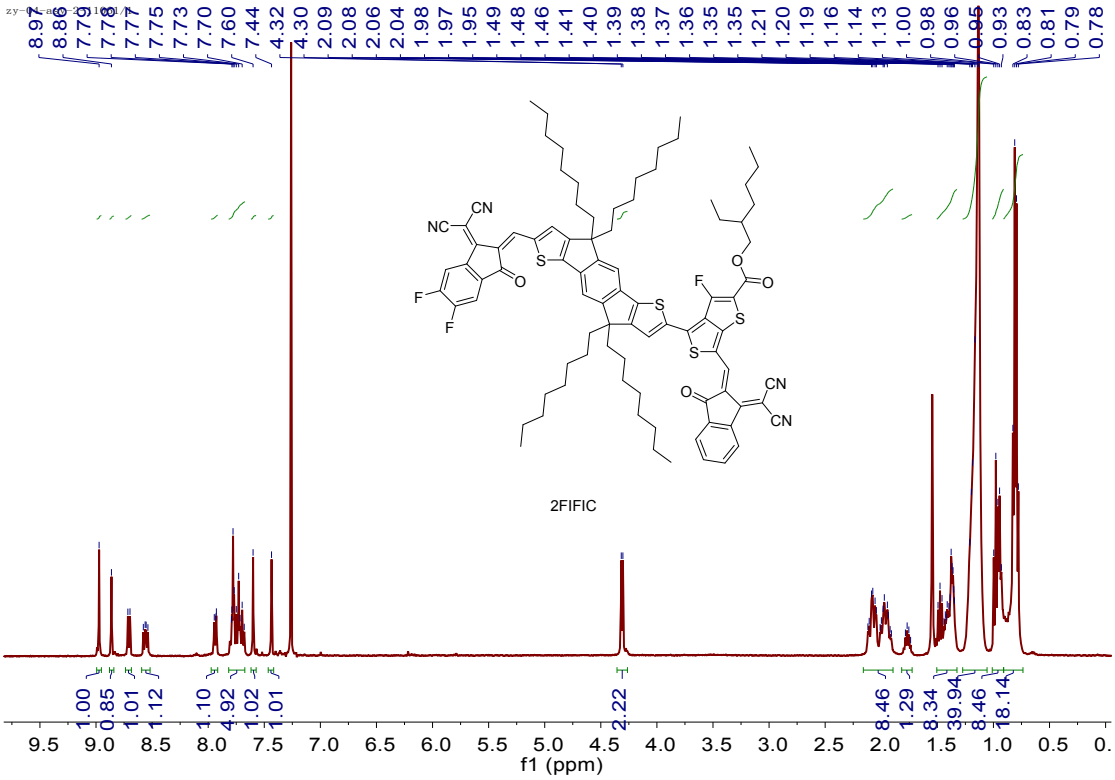

Fig. S10. ^{1}H NMR spectra of **2FIFIC**.

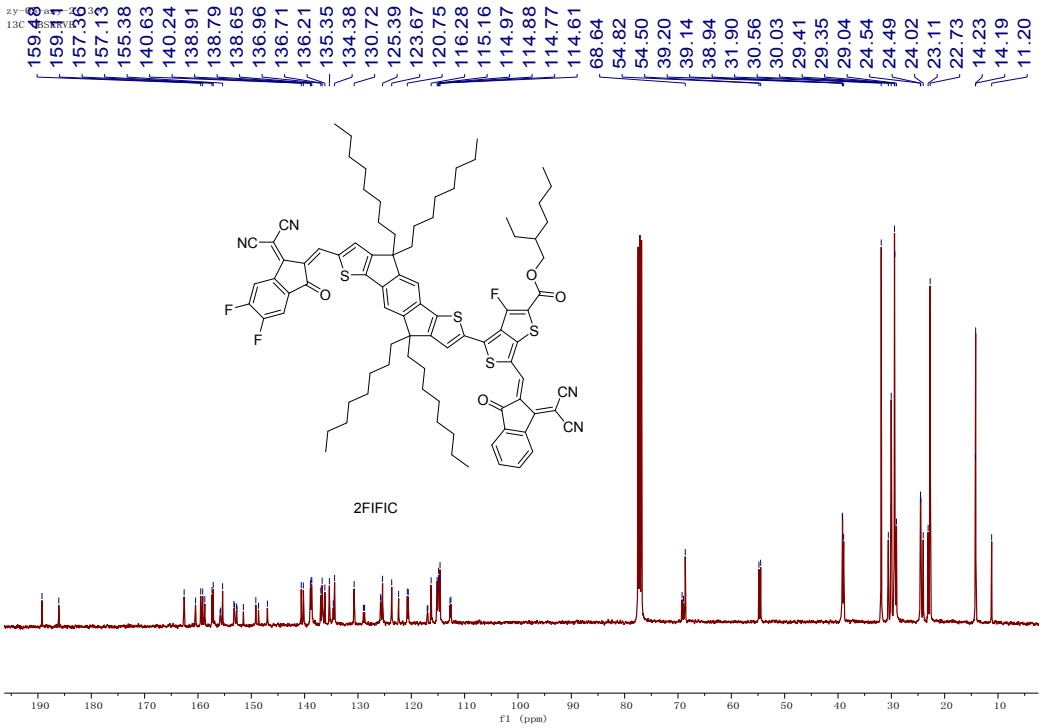

Fig. S11. ^{13}C NMR spectra of **2FIFIC**.

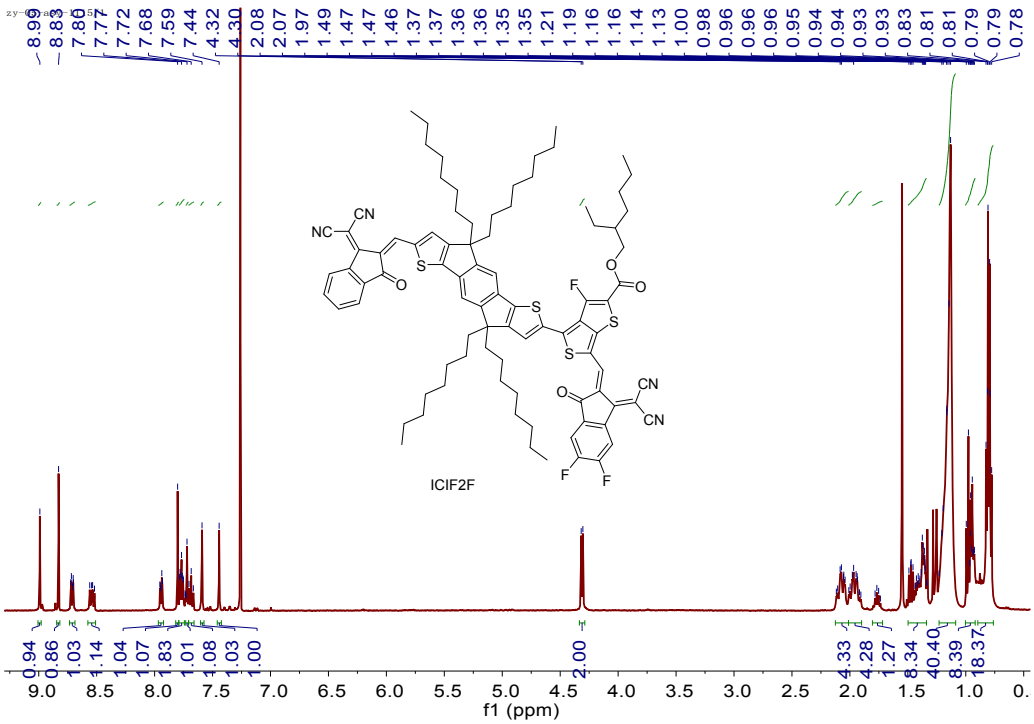

Fig. S12. ^{1}H NMR spectra of **ICIF2F**.

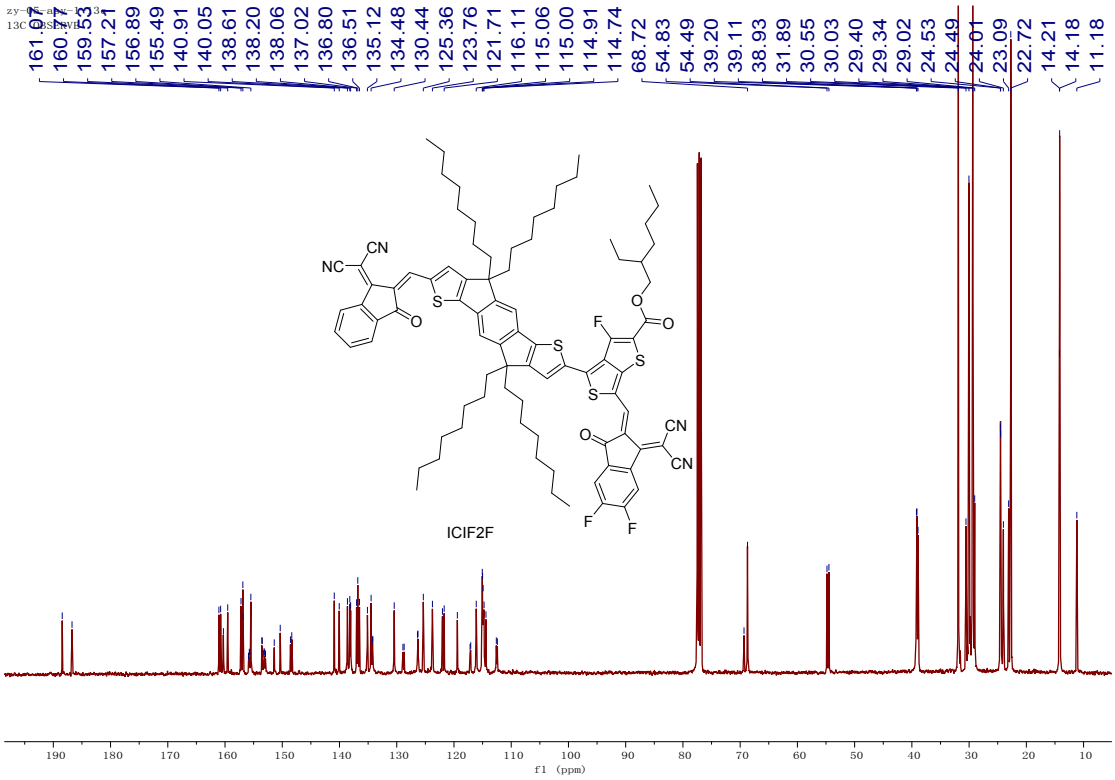

Fig. S13. ^{13}C NMR spectra of **ICIF2F**.

References :

1. F. X. Chen, J. Q. Xu, Z. X. Liu, M. Chen, R. Xia, Y. Yang, T. K. Lau, Y. Zhang, X. Lu, H. L. Yip, A. K. Jen, H. Chen and C. Z. Li, *Adv. Mater.*, 2018, **30**, 1803769.