Electronic Supplementary Information

Polymer Donor Based on Difluoro-quinoxaline with Naphthalimide Substituent Unit Exhibits Low-lying HOMO Level for Efficient Non-fullerene Polymer Solar Cells

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Experimental Section

Materials: All solvents and reagents were purchased from commercial sources and used without further purification unless stated otherwise. The materials of M4, M7, M8 were purchased from Derthon OPV Co Ltd. Monomer M1 and M2 were prepared according to the previously reported literature.[1, 2]

Measurements: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ^{1}H NMR and ^{13}C NMR spectra were referenced to tetramethylsilane (0 ppm) for CDCl$_3$. The molecular mass was confirmed using an Autoflex III matrix-assisted laser desorption ionization mass spectrometer (MALDI-TOF-MS). Molecular weights of the copolymers were determined using an Agilent Technologies PL-GPC 220 high-temperature chromatograph in 150 °C and 1,2,4-trichlorobenzene using a calibration curve of polystyrene standards. Elemental analysis was performed on an instrument of Flash EA1112. Thermogravimetric (TGA) measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Cyclic voltammetry (CV) was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV s^{-1} against a platinum wire and saturated calomel electrodes (SCE) as reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The ferrocene/ferrocene (Fc/Fc$^+$) pair was used as an internal reference and the potential was calculated to be 0.38 V. The corresponding HOMO values were estimated from the formula $E_{HOMO} = -e (E_{ox} + 4.80 - E_{Fc/Fc^+})$. The deposition of a copolymer on the electrode was done by the evaporation of a chloroform solution. Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system (Digital Instrument). Transmission electron microscopy (TEM) images were obtained using a JEM-2100F instrument.

DFT Calculations. The geometry was optimized with Density Functional Theory (DFT) using B3LYP hybrid functional with basis set 6-31g*. Quantum-chemical calculation was performed with the Spartan 10 software. All of the alkyl side chains were replaced with

methyl groups to simplify the calculation.

Charge Carrier Mobility Measurements. The hole-only and electron-only devices were measured with device structures of ITO/PEDOT:PSS/copolymer:Y6/MoO$_3$/Al and ITO/ZnO/copolymer:Y6/PFN-Br/Al, respectively. The mobility was determined by fitting the dark current to the model of a single-carrier SCLC, which is described by the following equation:

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

where J is the current, μ_0 is the carrier mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), i.e., $V = V_{appl} - V_{bi} - V_s$. The carrier mobility can be calculated from the slope of the $J^{1/2}$–V curves.

Fabrication of Non-fullerene Polymer Solar Cells and Characterization: The indium tin oxide (ITO) glass substrates were cleaned sequentially under sonication for 30 min with acetone, detergent, deionized water and isopropyl alcohol and then dried at 80 °C in baking oven overnight, followed by a plasma treatment for 4 min. The pre-cleaned ITO substrate were coated with PEDOT:PSS (filtered through a 0.45 μm PES filter) by spin-coating (3000 rpm. for 30 s, thickness of ~40 nm) and then baked at 150 °C for 15 min in air. Then, the substrates were transferred into a nitrogen (N$_2$) protected glovebox. The device configuration was ITO/PEDOT:PSS/copolymer:Y6/PFN-Br/Al, and the active layers were spin coated from CF solution containing copolymer:Y6 (weight ratio 1:1.2). Thermal annealing of the blend films was carried out by placing them onto a hot plate in a nitrogen atmosphere. A 5 nm PFN-Br layer was then spin-coated from methanol solution onto the active layer. The thin films were transferred into a vacuum evaporator connected to the glove box, and Al (90 nm) was deposited sequentially through a shadow mask under 10^{-7} Pa, with an active area of the cells of 0.04 cm^2.

The current–voltage (J–V) curves were measured on a computer-controlled Keithley 2400

sourcemeter under 1 sun, AM 1.5 G spectra from a class solar simulator (Taiwan, Enlitech), and the light intensity was 100 mW cm^{-2} as calibrated by a China General Certification Center certified reference monocrystal silicon cell (Enlitech). Before the *J–V* test, a physical mask of an aperture with a precise area of 0.04 cm^2 was used to define the device area. The EQE data were recorded with a QE-R3011 test system from Enli technology company (Taiwan).

Synthesis of the monomers and polymers

7, 10 – dibromo – 2 - (2 - decyltetradecyl) - 8, 9 – difluoro - 1H - pyrido[3', 4', 5' : 5, 6] acenaphtho [1,2-b] quinoxaline - 1,3(2H) - dione (M3)

Compound M1 (1.52 g, 5 mmol) and Compound M2 (2.94 g, 5 mmol) were dissolved in acetic acid (200 mL), the mixture was refluxed overnight. The reaction mixture was cooled to the room temperature and poured into water, and extracted with dichloromethane for three times. After removal of the solvent by vacuum evaporation, the residue was purified by column chromatography on silica gel (PE : CH$_2$Cl$_2$ = 3:1), followed by re-crystallization from ethanol to give product as pea green solid (2.9 g, yield 68%). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.70 (d, *J* = 7.3 Hz, 2H), 8.58 (d, *J* = 7.3 Hz, 2H), 4.15 (d, *J* = 7.3 Hz, 2H), 1.99 (d, *J* = 5.7 Hz, 1H), 1.35 – 1.13 (m, 40H), 0.86 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$), δ (ppm): 163.45, 154.99, 151.70, 149.64, 149.48, 136.99, 135.31, 132.51, 111.21, 44.85, 36.85, 31.93, 31.72, 29., 29.70, 29.66, 29.65, 29.37, 22.69, 14.12.

2-(2-decyltetradecyl)-7,10-bis(4-(2-ethylhexyl)thiophen-2-yl)-8,9-difluoro-1H-pyrido[3',4',5':5,6]acenaphtho[1,2-b]quinoxaline-1,3(2H)-dione (M5)

Compound M3 (1.71 g, 2 mmol), Compound M4 (2.91 g, 6 mmol), and Pd(pph$_3$)$_4$ (92.74 mg) were put into 100 mL three-neck flask and then purged with nitrogen. Subsequently, anhydrous DMF (50 mL) was added. The mixture was heated to reflux overnight. Then the solvent was removed and the residue was purified by column chromatography on silica gel (PE : CH$_2$Cl$_2$ = 3:1) to afford the product as red solid (1.52 g, yield 70%). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.61 (d, *J* = 7.3 Hz, 2H), 8.38 (d, *J* = 7.3 Hz, 2H), 7.81 (s, 2H), 7.27 (s, 2H), 4.14 (d, *J* = 7.3 Hz, 2H), 2.70 (d, *J* = 6.8 Hz, 4H), 1.99 (s, 1H), 1.69 (s, 2H), 1.44 – 1.21 (m, 56H), 0.98 – 0.84 (m, 18H).^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 163.70, 152.17, 141.56,

136.43, 134.56, 133.32, 132.42, 129.98, 126.55, 125.18, 124.53, 123.37, 119.45, 40.50, 32.58, 31.93, 31.76, 30.07, 29.70, 29.66, 29.36, 29.00, 26.56, 25.69, 23.12, 22.69, 14.21, 14.12, 10.96.

7,10-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-2-(2-decyltetradecyl)-8,9-difluoro-1H-pyrido[3',4',5':5,6]acenaphtho[1,2-b]quinoxaline-1,3(2H)-dione (M6)

N-Bromosuccinimide (352.40 mg, 1.98 mmol) was added to a mixture of compound M5 (1.12 g, 0.9 mmol) in 30mL THF at 0°C. The reaction mixture was warmed to r.t. and stirred overnight. 50 mL water was added and the mixture was extracted with dichloromethane for three times. The organic phase was dried with Mg_2SO_4 and the solvent was evaporated. The residue was purified with flash column chromatography (PE : CH_2Cl_2 = 3:1) to afford the product as dark red solid (1.42 g, yield 80%). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.24 (d, J = 7.1 Hz, 2H), 7.62 (d, J = 7.1 Hz, 2H), 7.32 (s, 2H), 4.10 (d, J = 6.8 Hz, 2H), 2.51 – 2.38 (m, 4H), 1.98 (s, 1H), 1.63 (d, J = 5.8 Hz, 2H), 1.37- 1.24 (m, 56H), 0.98 – 0.85 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm): 163.03, 150.58, 140.48, 134.62, 133.71, 133.21, 132.32, 131.80, 129.90, 124.40, 122.97, 118.17, 117.35, 40.03, 37.11, 33.71, 32.60, 31.99, 31.78, 30.26, 29.78, 29.42, 28.89, 26.58, 25.75, 23.19, 22.72, 14.25, 14.14, 10.91. MS (MALDI-TOF): Calculated for $C_{68}H_{89}Br_2F_2N_3O_2S_2$: 1242.40. Found: 1242.19.

PDNB: To a mixture of compound M6 (124.24 mg, 0.1 mmol), compound M7 (90.46 mg, 0.1 mmol) and 2 mL chlorobenzene were added to a 35 mL flask protected with N_2. The mixture was purged with argon for 15 min. Then catalyst $Pd_2(dba)_3$ (2.5 mg) and P(o-tol)$_3$ (5 mg) was quickly added under a stream of argon, and the mixture was purged with argon for another 15 min. Subsequently, the reaction mixture was then sealed and heated at 160 °C for 2 days. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol (100 mL), the solid was collected by filtration and loaded into an extraction thimble and washed successively with methanol, acetone, dichloromethane, and chloroform. The chloroform solution was then concentrated by evaporation, precipitated into methanol. The solid was collected by filtration and dried in vacuo to get the polymer as a black solid (150 mg, 89%). M_n = 35.99 kDa, M_w = 87.62 kDa, PDI = 2.43. Anal. Calcd for $C_{104}H_{135}F_2N_3O_2S_6$: C, 73.93; H, 8.05; N, 2.49. Found: C, 73.41; H, 8.03; N, 2.38.

PDNB-2F: PDNB-2F was synthesized according to the similar procedures for PDNB. Compound M6 (124.24 mg, 0.1 mmol), compound M8 (94.05 mg, 0.1 mmol) and 2 mL chlorobenzene were added to a 35 mL flask protected with N_2. The mixture was purged with argon for 15 min. Then catalyst $Pd_2(dba)_3$ (2.5 mg) and $P(o\text{-tol})_3$ (5 mg) was quickly added under a stream of argon, and the mixture was purged with argon for another 15 min. Subsequently, the reaction mixture was then sealed and heated at 160 °C for 2 days. Finally, the polymer as a black solid (146 mg, 85%). M_n = 39.31 kDa, M_w = 106.43 kDa, PDI= 2.71. Anal. Calcd for $C_{104}H_{133}F_4N_3O_2S_6$: C, 72.39; H, 7.77; N, 2.44. Found: C, 72.18; H, 7.68; N, 2.36.
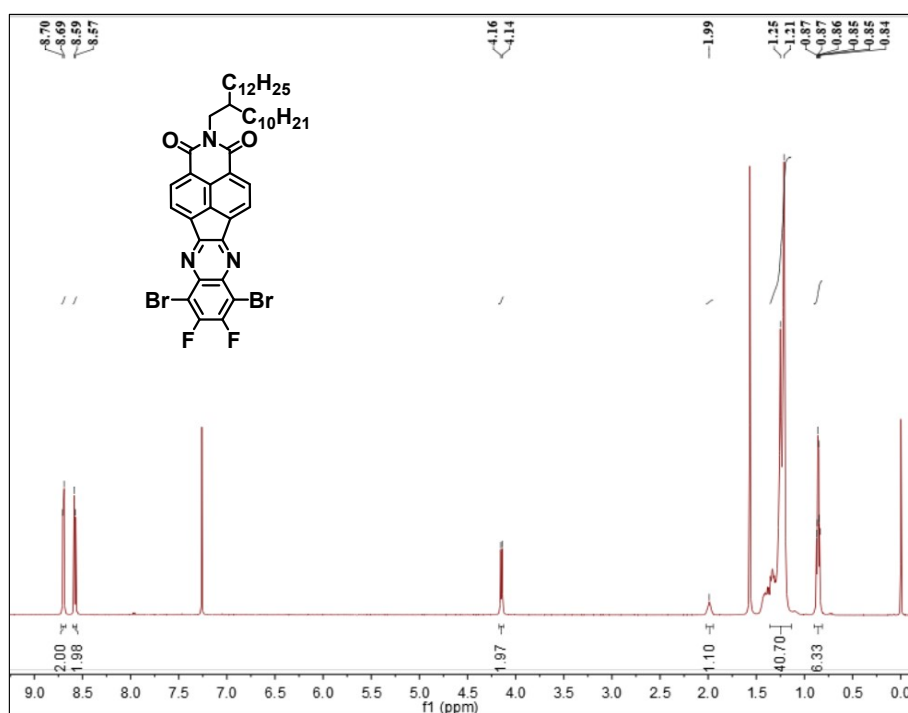
Fig. S1 ^{1}H NMR spectrum of compound M3.
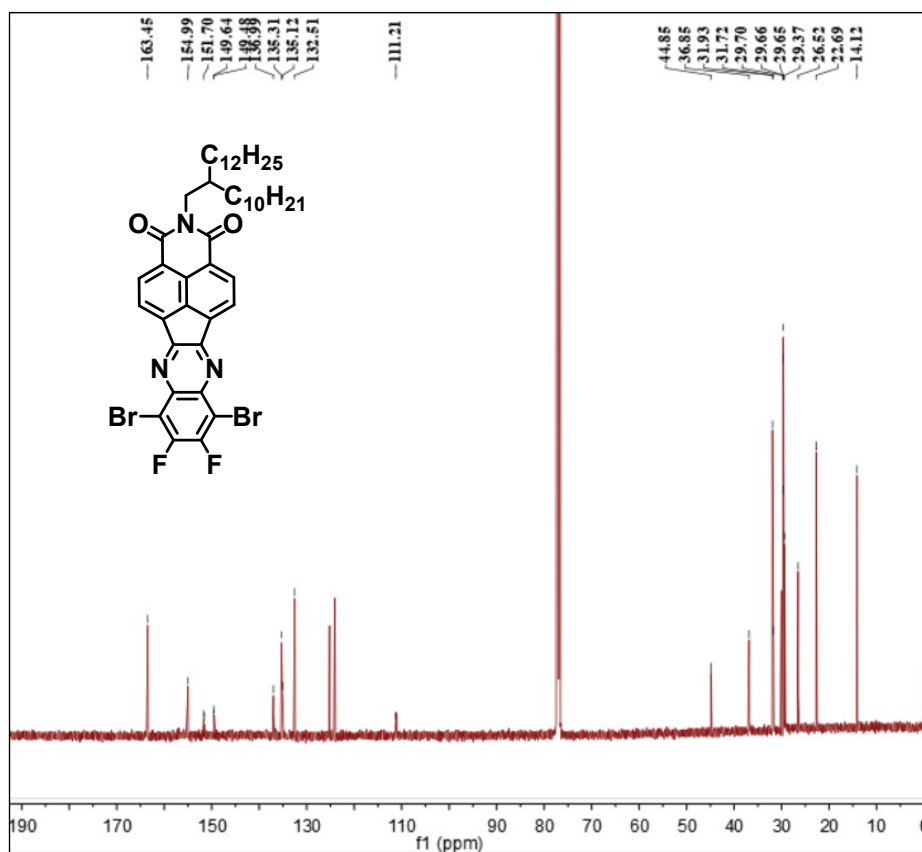
Fig. S2 ^{13}C NMR spectrum of compound M3.
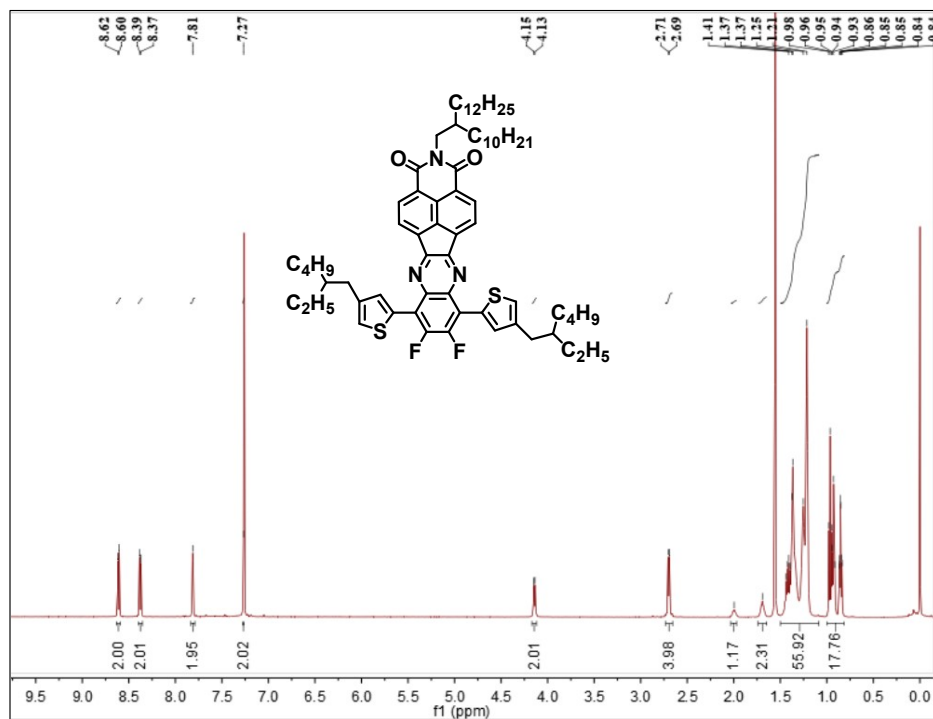
Fig. S3 ^{1}H NMR spectrum of compound M5.
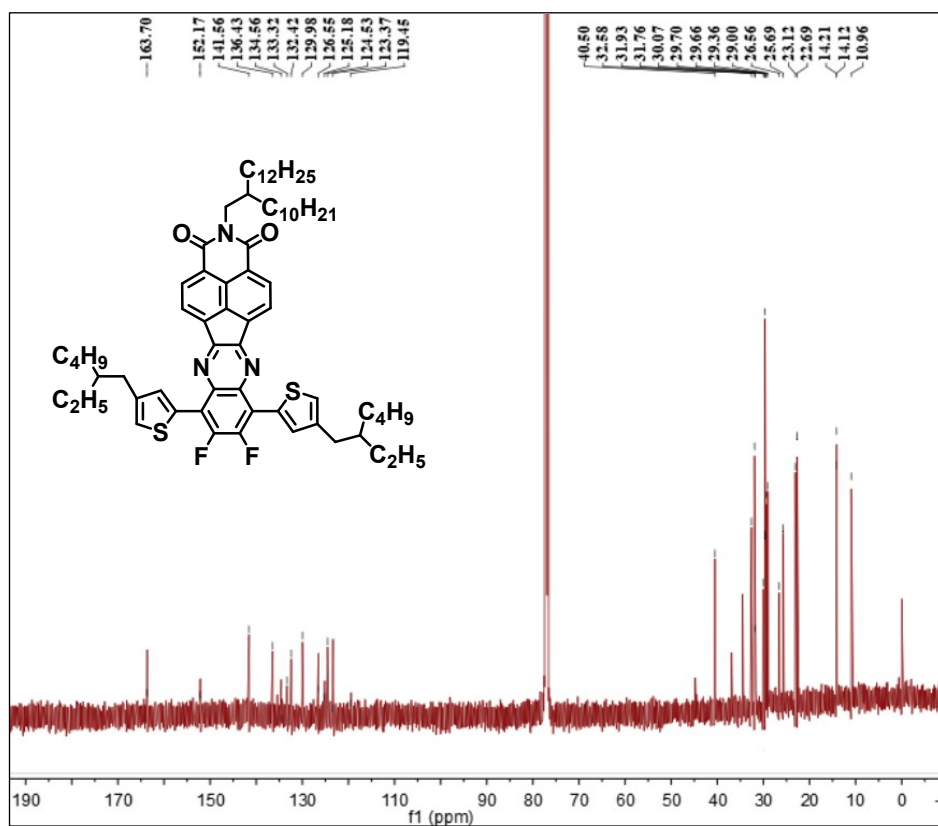
Fig. S4 ^{13}C NMR spectrum of compound M5.

Fig. S5 ^{1}H NMR spectrum of compound M6.

Fig. S6 ^{13}C NMR spectrum of compound M6.
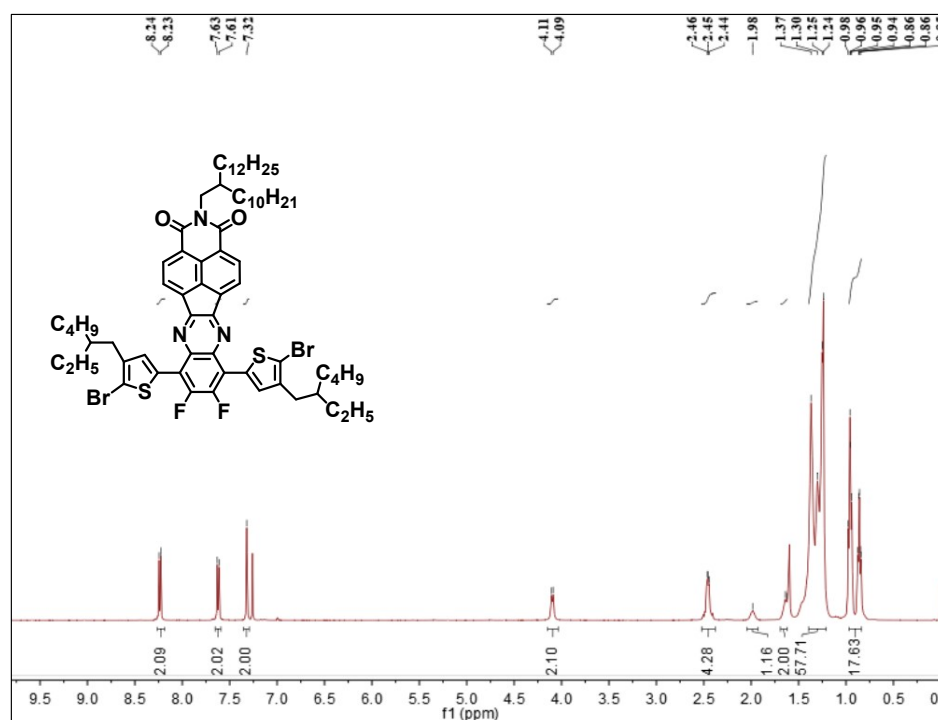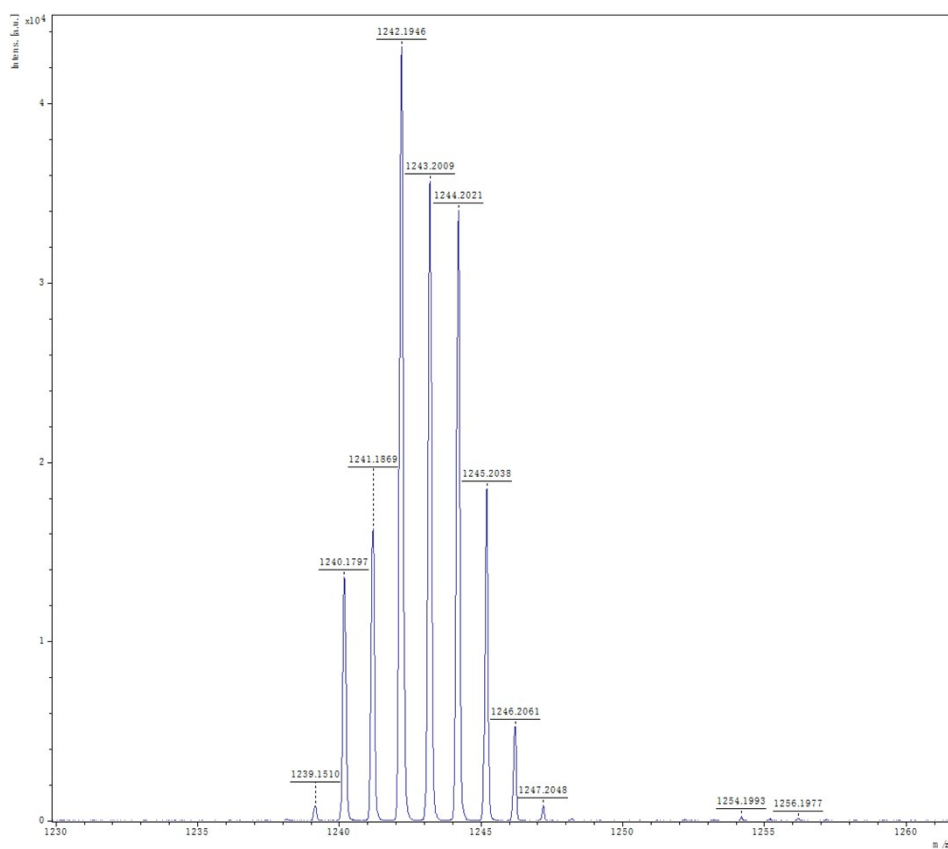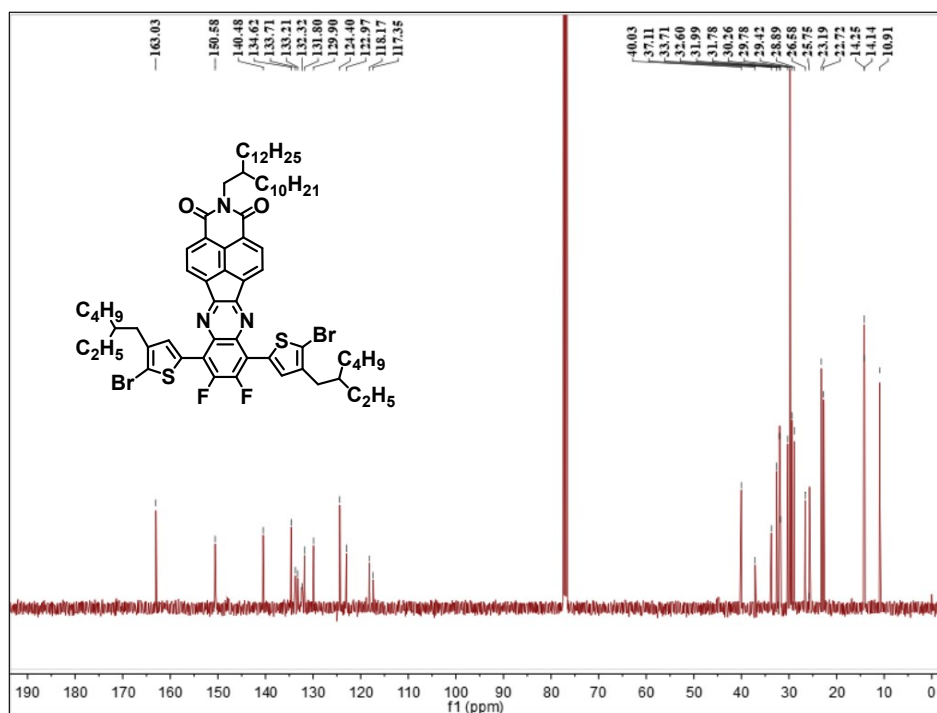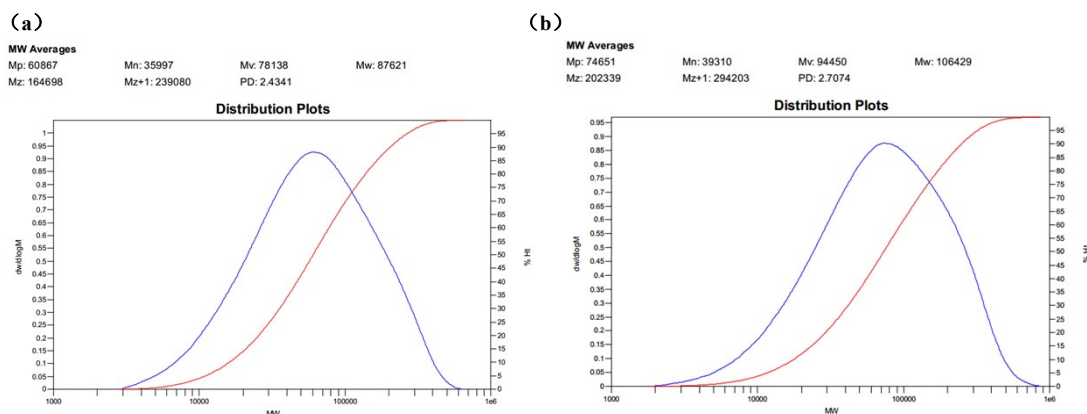

Fig. S7 MS spectrum of compound M6.

Fig. S8 GPC chart relates to the molecular weight of (a) PDNB and (b) PDNB-2F.
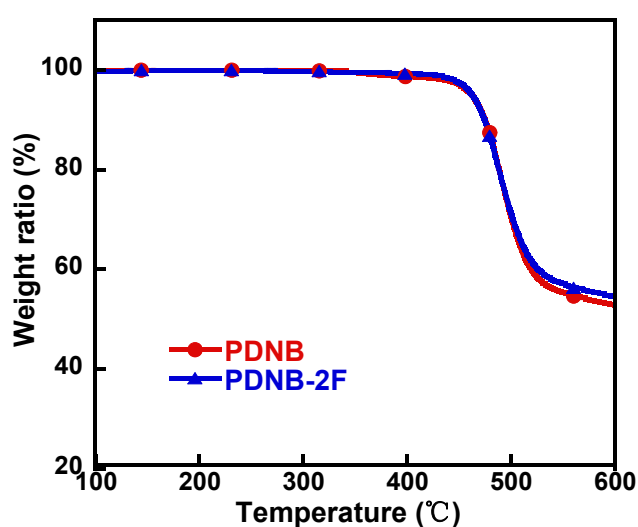
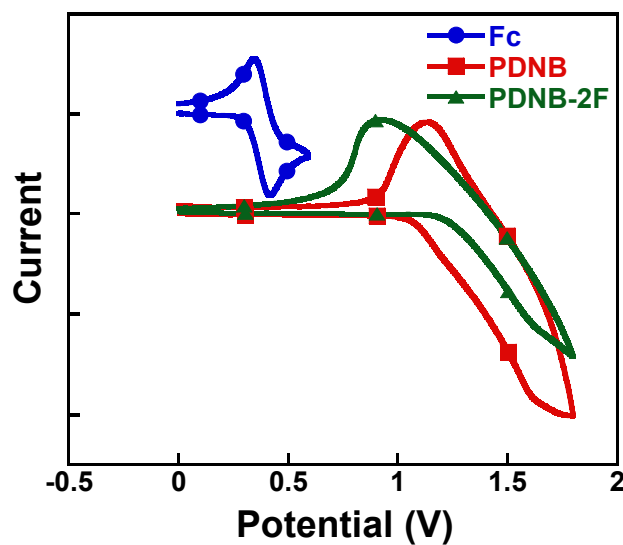**Fig. S9** TGA plot of copolymers at a heating rate of 20 °C/min under a nitrogen atmosphere.

Fig.S10 CV curves of copolymers with Fc/Fc$^+$ as the reference, using platinum electrodes as

the working electrode, platinum wire as the counter electrode and SCE as the reference

electrode, scan one cycle at the potential scanning rate of 50 mV•s^{-1} in 0.1 M

tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) acetonitrile solution.
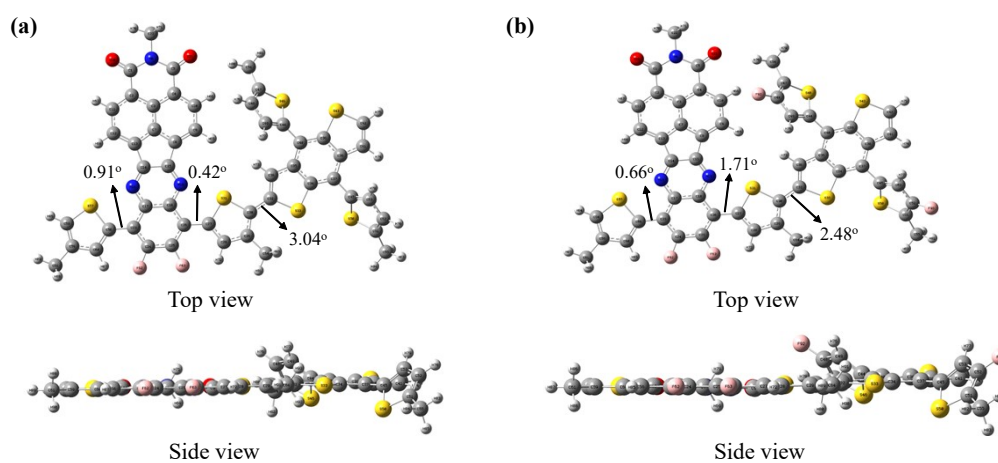

Fig. S11 The top and side view of molecular configuration of PDNB (a) and PDNB-2F (b) calculated by DFT.
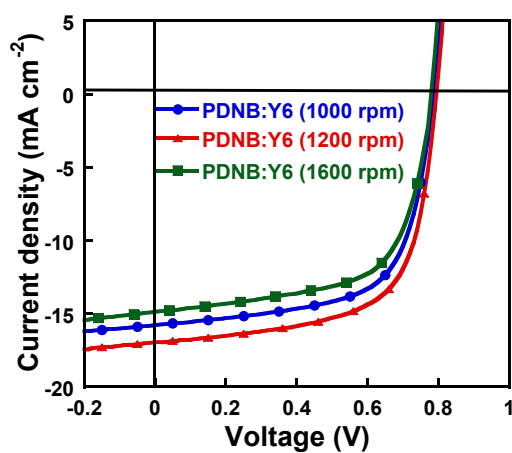

Fig. S12 *J–V curves of NF-PSCs under AM1.5 Illumination at 100 mW cm^{-2} with different spin coating speed of PDNB:Y6.*
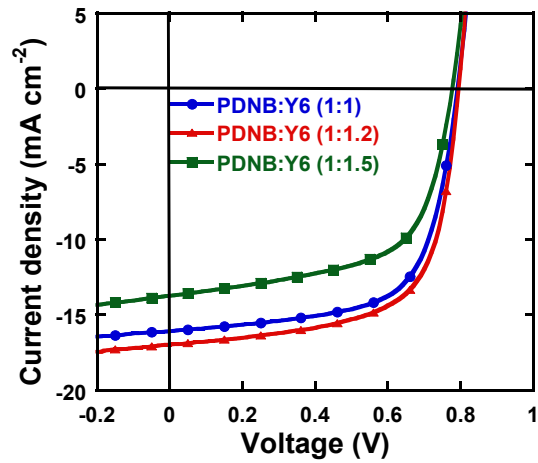
Fig. S13 *J–V curves of NF-PSCs under AM1.5 Illumination at 100 mW cm⁻² with different D/A ratios of PDNB:Y6.*
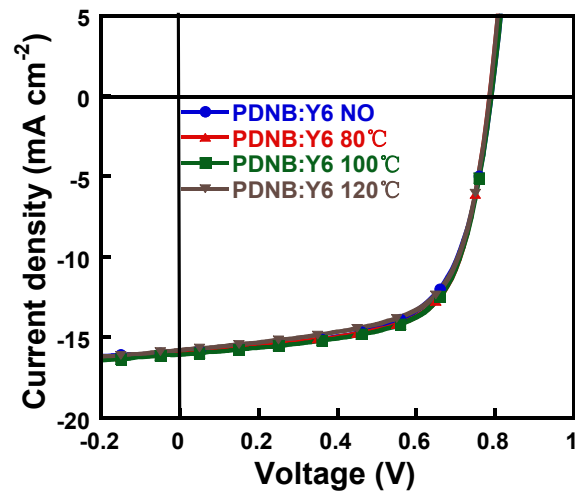

Fig. S14 *J–V curves of NF-PSCs under AM1.5 Illumination at 100 mW cm⁻² with different thermal annealing temperature of PDNB:Y6.*
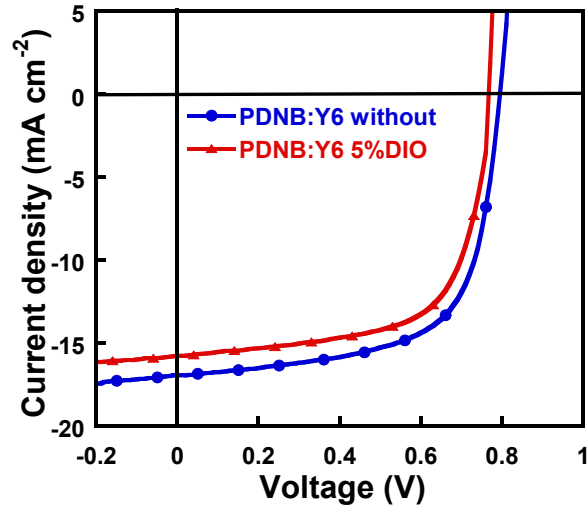
Fig. S15 *J–V curves of NF-PSCs under AM1.5 Illumination at 100 mW cm^{-2} with different*
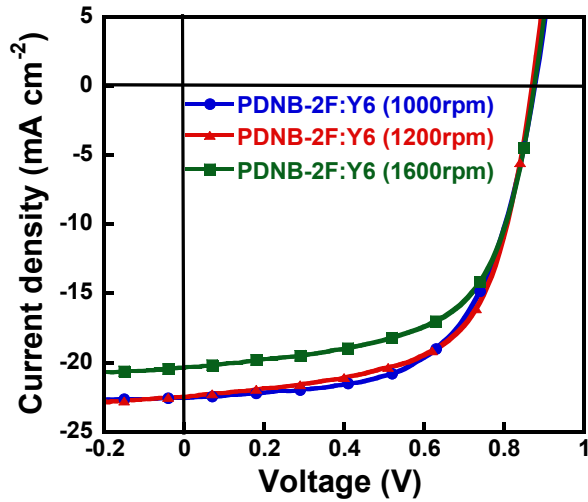
with or without additive of PDNB:Y6.

Fig. S16 *J–V curves of NF-PSCs under AM1.5 Illumination at 100 mW cm^{-2} with different*
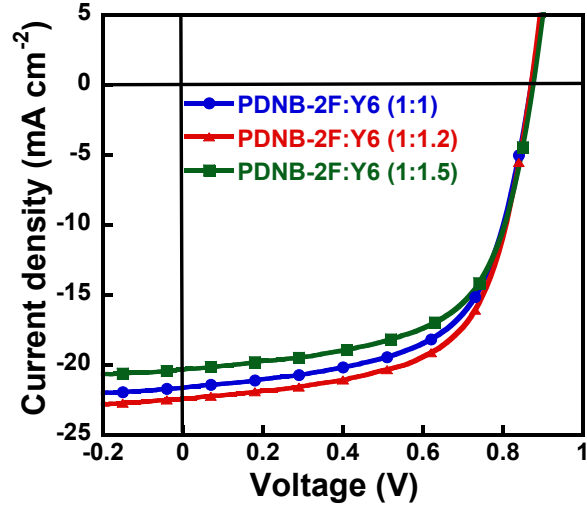
spin coating speed of PDNB-2F:Y6.

Fig. S17 *J–V curves of NF-PSCs under AM1.5 Illumination at 100 mW cm^{-2} with different D/A ratios of PDNB-2F:Y6.*
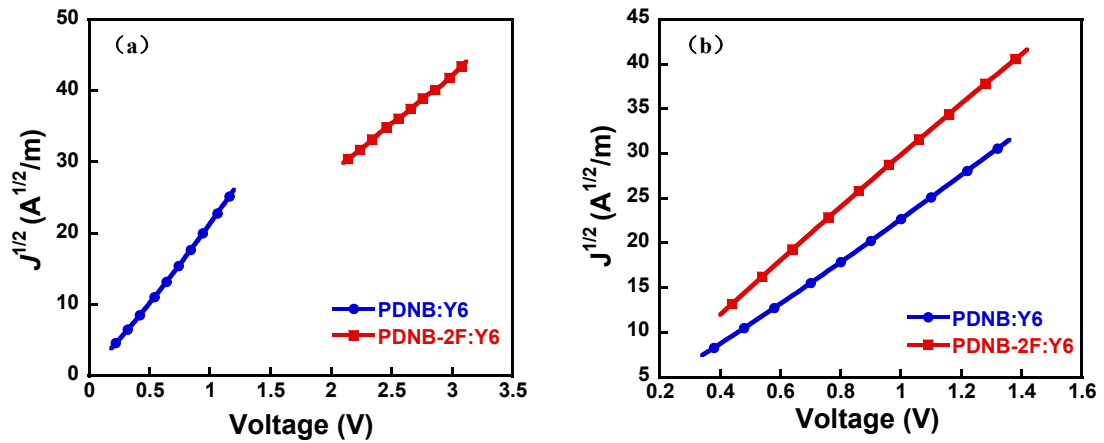

Fig. S18 $J^{1/2} \sim (V_{appl}\text{-}V_{bi}\text{-}V_s)$ characteristics of hole-only (a) and electron-only (b) devices.
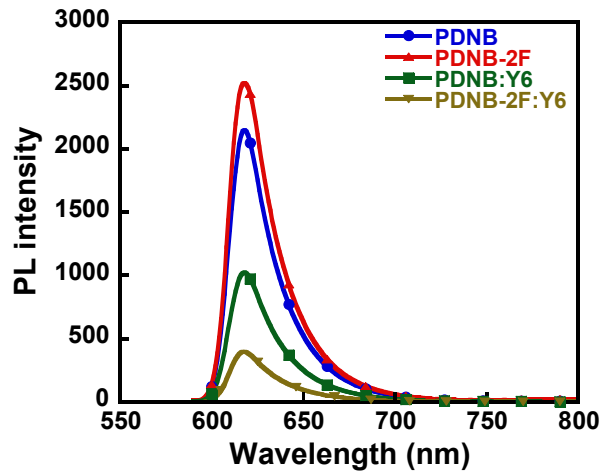

Fig. S19 Photoluminescence spectra of PDNB, PDNB-2F and corresponding blended films,.

Table S1 Device performance of the NF-PSCs based on PDNB: Y6 with different spin coating speed under AM1.5 Illumination at 100 mW cm^{-2}.

Blend film [a]	Speed (rpm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
	1000	0.779	14.88	64.01	7.42
PDNB: Y6	1200	0.791	15.91	64.03	8.06
	1600	0.786	13.95	64.99	7.13

[a] All of the blend films are processed by CF with Donor : Acceptor =1:1.2.

Table S2 Device performance of the NF-PSCs based on PDNB: Y6 with different D/A ratios under AM1.5 Illumination at 100 mW cm^{-2}.

Blend film [a]	D/A (wt/wt)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
	1:1	0.784	15.12	65.28	7.75
PDNB: Y6	1:1.2	0.791	15.91	64.03	8.06
	1:1.5	0.776	13.73	61.04	6.51

[a] All of the blend films are processed by CF, spin coating speed = 1200 rpm.

Table S3 Device performance of the NF-PSCs based on PDNB: Y6 with different thermal annealing under AM1.5 Illumination at 100 mW cm^{-2}.

Blend film [a]	Thermal annealing	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
	No	0.791	15.91	64.03	8.06
PDNB: Y6	80°C	0.786	15.99	66.34	8.34
	100°C	0.795	16.97	65.47	8.83
	120°C	0.786	15.78	65.04	8.07

[a] All of the blend films are processed by CF with Donor : Acceptor =1:1.2, spin coating speed = 1200 rpm.

Table S4 Device performance of the NF-PSCs based on PDNB: Y6 with or without additive under AM1.5 Illumination at 100 mW cm^{-2}.

Blend film [a]	Additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PDNB: Y6	without	0.795	16.97	65.47	8.83
	0.5% DIO	0.767	15.79	66.26	8.07

Table S5 Device performance of the NF-PSCs based on PDNB-2F: Y6 with different spin coating speed under AM1.5 Illumination at 100 mW cm^{-2}.

Blend film [a]	Speed (rpm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PDNB-2F: Y6	1000	0.878	22.55	60.76	12.02
	1200	0.870	22.45	62.37	12.18
	1600	0.882	21.65	63.02	12.03

[a] All of the blend films are processed by CF with Donor : Acceptor =1:1.2.

Table S6 Device performance of the NF-PSCs based on PDNB-2F: Y6 with different D/A ratios under AM1.5 Illumination at 100 mW cm^{-2}.

Blend film [a]	D/A (wt/wt)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PDNB-2F: Y6	1:1	0.870	21.64	61.14	11.52
	1:1.2	0.870	22.45	62.37	12.18
	1:1.5	0.876	20.35	61.30	10.93

[a] All of the blend films are processed by CF, spin coating speed = 1200 rpm.

Table S7 Relevant parameters obtained from J_{ph}–V_{eff} curves.

Blend films [a]	J_{ph} [b] (mA cm^{-2})	J_{sat} (mA cm^{-2})	P (E,T) [b]	L (nm)

PDNB: Y6	16.39	17.53	93.5%	102
PDNB-2F: Y6	21.34	22.61	94.4%	102

[a] Donor : Acceptor =1:1.2; all of the blend films are processed by CF with thermal annealing at 100 °C. [b] At the condition of $V_{eff} = V_0 \square V_{appl}$ ($V_{appl} = 0$, under short-circuit condition).

Reference

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2 H. Li, F. S. Kim, G. Ren, E. C. Hollenbeck, S. Subramaniyan and S. A. Jenekhe, *Angew. Chem. Int. Ed.*, 2013, **52**, 5513 – 5517.