Supporting Information

Naphthalene Core-Based Noncovalently Fused-ring Electron Acceptors: Effect of Linkage Positions on Photovoltaic Performances

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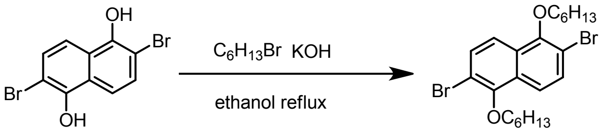
1. Experimental section:

Materials and synthesis

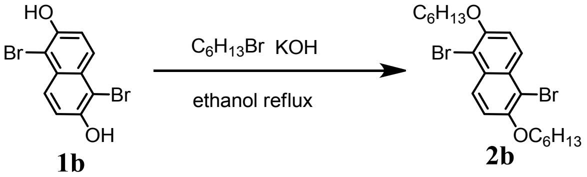
Unless specifically stated, all chemicals were purchased from Aldrich or Acros and used without further purification. The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature and stored in a Schlenk tube under nitrogen atmosphere. Unless specifically stated, all reactions were carried out under the protection of nitrogen and monitored by thin layer chromatography (TLC) on silica gel. Column chromatography was performed on silica gel (200-300 mesh).



1a **2a**

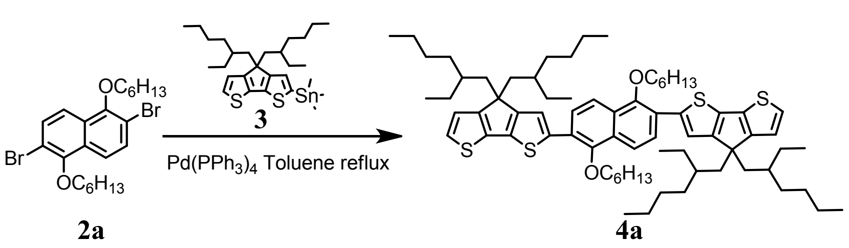
2a) 2,6-dibromo-1,5-bis(hexyloxy)naphthalene

Dissolved 2,6-dibromonaphthalene-1,5-diol (370 mg, 1.16 mmol) and 1-bromohexane (574 mg, 3.48 mmol) in anhydrous ethanol (20 mL),degassed carefully and added KOH (195 mg, 3.48 mmol) to the mixture. The mixture was refluxed overnight. After the reaction, the mixture was extracted with DCM and H_2O for three times. The combined organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified using silica gel chromatography with an eluent of DCM/petroleum ether (1:5, v/v), yielding a yellow solid (413 mg, yield: 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (d, J = 8.88 Hz, 2H), 7.61 (d, J = 8.84 Hz, 2H), 4.07 (t, J = 6.68 Hz, 4H), 1.91-1.98 (m, 4H), 1.54-1.62 (m, 4H), 1.36-1.44 (m, 8H), 0.93 (t, J = 7.16 Hz, 6H).



2b) 1,5-dibromo-2,6-bis(hexyloxy)naphthalene

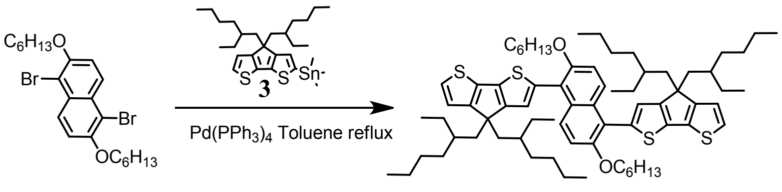
Dissolved 1,5-dibromonaphthalene-2,6-diol (300 mg, 0.94 mmol) and 1-Bromohexane (460 mg, 2.79 mmol) in anhydrous ethanol (20 mL),degassed carefully and added KOH (157 mg, 2.79 mmol) to the mixture. The mixture was refluxed overnight. After the reaction, the mixture was extracted with DCM and H_2O for three times. The combined organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified using silica gel chromatography with an eluent of DCM/petroleum ether (1:5, v/v), yielding a yellow solid (352 mg, yield: 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm):8.21 (d, J = 9.24 Hz, 2H), 7.32 (d, J = 9.18 Hz, 2H), 4.17 (t, J = 6.54 Hz, 4H), 1.87 (m, 4H), 1.55 (m, 4H), 1.37 (m, 4H), 0.918 (t, J = 7.02 Hz, 6H).



4a)2,2'-(1,5-bis(hexyloxy)naphthalene-2,6-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclo-penta[1,2-b:5,4-b']dithiophene)

To a solution of compound **2a** (413 mg, 0.85 mmol) and compound **3** (1.2 g, 2.13 mmol) in toluene (30 mL) was added $Pd(PPh_3)_4$ (98 mg, 0.085 mmol) under nitrogen. The mixture was refluxed for 48 h. After the reaction, the mixture was extracted with

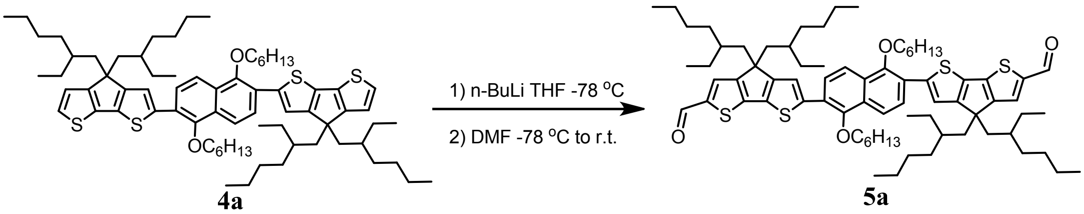
DCM and H_2O for three times. The combined organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified using silica gel chromatography with an eluent of DCM/petroleum ether (1:5, v/v), yielding an orange oil (906 mg, yield: 95%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90 (d, J = 9.24 Hz, 2H), 7.78 (m, 2H), 7.47 (t, J = 4.96 Hz, 2H), 7.16 (d, J = 4.92 Hz, 2H), 6.96 (m, 2H), 3.96 (m, 4H), 1.95-2.08 (m, 12H), 1.56-1.62 (m, 4H), 1.38-1.46 (m, 8H), 0.94-1.06 (m, 38H), 0.73-0.78 (m, 16H), 0.62-0.69 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 182.49, 161.83, 157.61, 151.53, 148.35, 143.91, 137.37, 130.67, 129.57, 126.30, 123.96, 120.86, 119.21, 74.61, 53.97, 43.32, 35.34, 34.20, 31.76, 30.50, 29.71, 28.57, 27.40, 25.79, 22.77, 14.08, 10.72.



2b **4b**

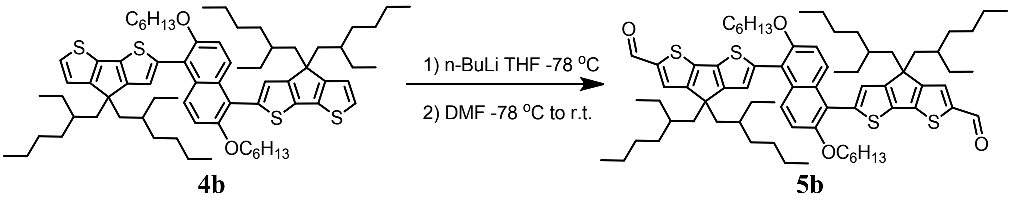
4b)2,2'-(2,6-bis(hexyloxy)naphthalene-1,5-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene)

To a solution of compound **2b** (160 mg, 0.33 mmol) and compound **3** (465 mg, 0.83 mmol) in toluene (20 mL) was added $Pd(PPh_3)_4$ (38 mg, 0.033 mmol) under nitrogen. The mixture was refluxed for 48 h. After the reaction, the mixture was extracted with DCM and H_2O for three times. The combined organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified using silica gel chromatography with an eluent of DCM/petroleum ether (1:6, v/v), yielding an orange oil (320 mg, yield: 96%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 (m, 2H), 7.32 (d, J = 9.44 Hz, 2H), 7.14 (d, J = 4.84 Hz, 2H), 6.97 (d, J = 4.84 Hz, 2H), 6.92 (m, 2H), 3.99 (t, J = 6.54 Hz, 4H), 1.88-1.98 (m, 8H), 1.65 (m, 4H), 1.24-1.37 (m, 12H), 0.94-1.15 (m, 32H), 0.77-0.89 (m, 22H), 0.63-0.71 (m, 12H).



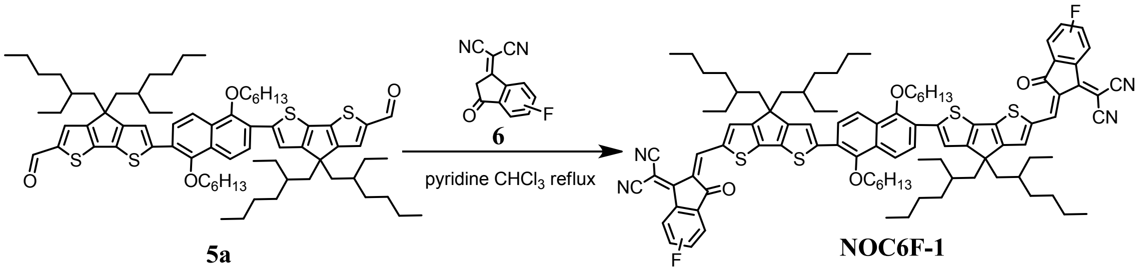
5a)6,6'-(1,5-bis(pentyloxy)naphthalene-2,6-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2-carbaldehyde)

To a solution of compound **4a** (906 mg, 0.80 mmol) in THF (30 mL) was added n-BuLi (2.0 mL, 2.4M, 4.8 mmol) dropwise slowly under nitrogen at -78 °C. The mixture was stirred for 2 h and then the dry DMF (2 mL) was added at -78 °C. The mixture was allowed to warm to room temperature and stirred overnight. After the reaction, the mixture was poured into water and extracted with DCM for three times. The combined organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified using silica gel chromatography with an eluent of ethyl acetate/petroleum ether (1:10, v/v), yielding an orange oil (855 mg, yield: 90%). ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.85 (s, 2H), 7.94 (d, *J* = 8.64 Hz, 2H), 7.78 (m, 2H), 7.59 (m, 2H), 7.53 (t, *J* = 8.22 Hz, 2H), 3.96 (m, 4H), 1.93-2.03 (m, 12H), 1.57 (m, 4H), 1.35-1.47 (m, 8H), 0.89-1.09 (m, 38H), 0.79-0.60 (m, 28H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm):182.56, 161.79, 157.61, 151.53, 148.35, 143.91, 143.08, 137.37, 130.67, 129.57, 126.30, 123.93, 120.86, 119.21, 74.61, 53.97, 43.32, 35.34, 34.20, 31.76, 30.50, 29.71, 28.57, 27.40, 25.79, 22.77, 14.08, 10.72.



5b)6,6'-(2,6-bis(hexyloxy)naphthalene-1,5-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2-carbaldehyde)

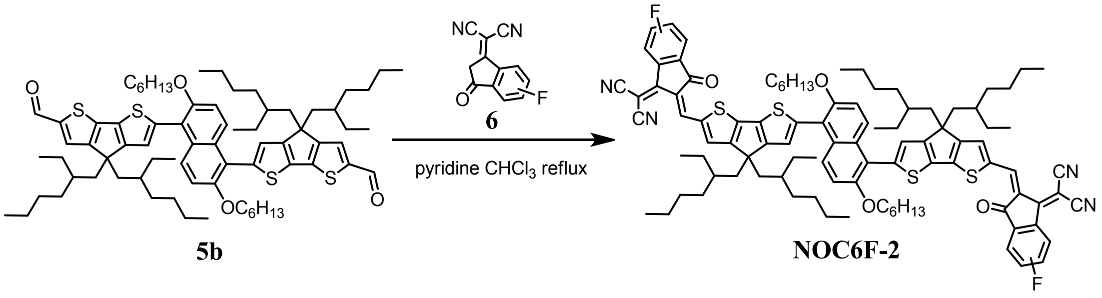
To a solution of compound **4b** (320 mg, 0.28 mmol) in THF (30 mL) was added n-BuLi (0.7 mL, 2.4M, 1.7 mmol) dropwise slowly under nitrogen at -78 °C. The mixture was stirred for 2 h and then the dry DMF (1 mL) was added at -78 °C. The mixture was allowed to warm to room temperature and stirred overnight. After the reaction, the mixture was poured into water and extracted with DCM for three times. The combined organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified using silica gel chromatography with an eluent of ethyl acetate/petroleum ether (1:10, v/v), yielding an orange oil (290 mg, yield: 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.86 (s, 2H), 7.83 (m, 2H), 7.61 (m, 2H), 7.22 (d, *J* = 9.48 Hz, 2H), 4.02 (t, *J* = 6.48 Hz, 4H), 1.99 (m, 8H), 1.65 (m, 4H), 0.96-1.06 (m, 16H), 0.94-1.15 (m, 32H), 0.65-0.88 (m, 30H).



5a **NOC6F-1**

6a) NOC6F-1

To a solution of compound **5a** (285 mg, 0.24 mmol) and compound **6** (306 mg, 1.44 mmol) in $CHCl_3$ (30 mL) was added pyridine (1 mL) under nitrogen and the mixture was stirred overnight. After the reaction, the mixture was concentrated under reduced pressure. The residue was purified using silica gel chromatography with an eluent of DCM/petroleum ether (2:1, v/v), yielding a dark purple solid (223 mg, yield: 59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.93 (s, 2H), 8.69 (m, 1H), 8.36 (d, *J* =8.52 Hz, 1H), 7.97 (d, *J* = 8.82 Hz, 2H), 7.90 (m, 1H), 7.86 (m, 2H), 7.66 (s, 2H), 7.60 (m, 2H), 7.55 (m, 1H), 7.40 (m, 2H), 3.99 (m, 4H), 1.97-2.09 (m, 12H), 1.57-1.63 (m, 4H), 1.39-1.48 (m, 8H), 0.91-1.07 (m, 38H), 0.73-0.789 (m, 12H), 0.62-0.70 (m, 16H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 187.23, 167.60, 165.25, 152.04, 147.92, 142.37, 139.99, 138.14, 135.82, 133.05, 129.81, 127.54, 126.04, 125.38, 123.98, 121.03, 119.53, 114.79, 112.80, 110.47, 75.10, 67.88, 67.06, 53.91, 43.39, 35.57, 34.16, 31.80, 30.54, 29.71, 28.48, 27.38, 25.80, 22.80, 14.09, 10.74, 1.03. MS (MALDI-TOF): calculated for $C_{98}H_{110}F_2N_4O_4S_4$ (M^+): 1572.74, Found: 1573.51.



6b) NOC6F-2

To a solution of compound **5b** (145 mg, 0.12 mmol) and compound **6** (153mg, 0.72 mmol) in $CHCl_3$ (30 mL) was added pyridine (1 mL) under nitrogen and the mixture was stirred overnight. After the reaction, the mixture was concentrated under reduced pressure. The residue was purified using silica gel chromatography with an eluent of DCM/petroleum ether (2:1, v/v), yielding a dark purple solid (106 mg, 55%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.97 (s, 2H), 8.71 (m, 1H), 8.38 (d, *J* = 9.12 Hz, 1H), 7.91 (m, 1.5H), 7.86 (d, *J* = 9.42 Hz, 1H), 7.82 (d, *J* = 9.42 Hz, 0.5H), 7.72 (m, 2H), 7.54 (m, 1H), 7.41 (m, 2H), 7.24 (d, *J* = 9.66 Hz, 2H), 7.08 (m, *J* = 7.32 Hz, 2H), 4.07 (m, *J* = 6.42 Hz, 4H), 1.98-2.05 (m, 8H), 1.67-1.72 (m, 4H), 1.37 (m, 4H), 1.27 (m, 8H), 0.99-1.15 (m, 32H), 0.86 (m, 8H),0.77-0.81 (m, 14H), 0.67-0.73 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 187.32, 167.70, 167.32, 165.66, 165.26, 159.54, 153.47, 146.46, 142.47, 140.21, 138.63, 137.74, 135.92, 133.20, 129.56, 127.77, 125.59, 125.04, 121.82, 121.41, 119.72, 117.34, 115.64, 112.92, 110.73, 69.79, 67.93, 67.16, 54.19, 43.45, 35.64, 34.37, 31.55, 29.39, 28.63, 27.53, 25.68, 22.97, 22.69, 14.26, 10.96. MS (MALDI-TOF): calculated for $C_{98}H_{110}F_2N_4O_4S_4$ (M^+): 1572.74, Found: 1573.48.

Measurements and Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 or 600 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Thermal gravimetric analysis (TGA) measurements were performed on TA2100 at a heating rate of 10 °C/min from 40 °C to 600 °C. Differential scanning calorimetry (DSC) measurements were tested on Perkin-Elmer Diamond DSC instrument, under a nitrogen atmosphere at a heating rate and cool rate of 10 °C/min from 50 °C to 300 °C. The electrochemical behavior of the small molecules was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6 solution in CH_3CN at room temperature under an atmosphere of nitrogen with a scanning rate of 100 mV/s. A Pt plate working electrode, a Pt wire counter electrode, and an $Ag/AgCl/Cl^-$ reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum. MS (MALDI-TOF) measurements were performed with an Autoflex III instrument. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai TF20 transmission electron microscopy. The thickness of the blend films was determined by a Dektak 6 M surface profilometer.

Hole/electron devices with a structure of ITO/PEDOT:PSS (30 nm)/active layer (80 nm)/Au and ITO/ZnO (30 nm)/active layer/Ag (100 nm) are fabricated. Hole and electron mobilities of devices are calculated according to the Mott-Gurney equation $J = 9\varepsilon_o\varepsilon_r\mu V^2/8d^3$ where J is the space charge limited current, ε_o is the vacuum permittivity ($\varepsilon_o = 8.85\times10^{-12}$ F/m), ε_r is the permittivity of the active layer ($\varepsilon_r = 3$), μ is mobility, and d is the thickness of the active layer.[S1, S2]

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) measurements were performed at beamline 7.3.3 at the Advanced Light Source.[S3] Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector.

Solar Cells Fabrication and Characterization

OSCs were fabricated with the device configuration of ITO/ZnO (30 nm)/active layer (100 nm)/MoO_3 (8.5 nm)/Ag (100 nm). ITO glasses with a conductivity of 15 Ω/square were cleaned according to the standard procedures before use. Precleaned ITO substrates were treated by UV-ozone for 20 min. A thin layer of ZnO was spin-coated on top of a cleaned ITO substrate at 3500 rpm for 40 s and annealed subsequently at 200 °C for 20 min on a hotplate before being transferred into a glove box. All the solutions (with 4 mg mL^{-1} concentration) were heated at 110 °C for at least 30 min and then spin-coated on the ZnO layer. The top electrode was thermally evaporated, with an 8.5 nm MoO_3 layer, followed by a 100 nm Ag layer at a base pressure below 10^{-7} Torr. Six cells were fabricated on one substrate with an effective area of 0.04 cm^2. The measurement of the devices was conducted in a glove box without encapsulation. The temperature while measuring the J-V curves was approximately 25 °C.

2. Tables and Figures

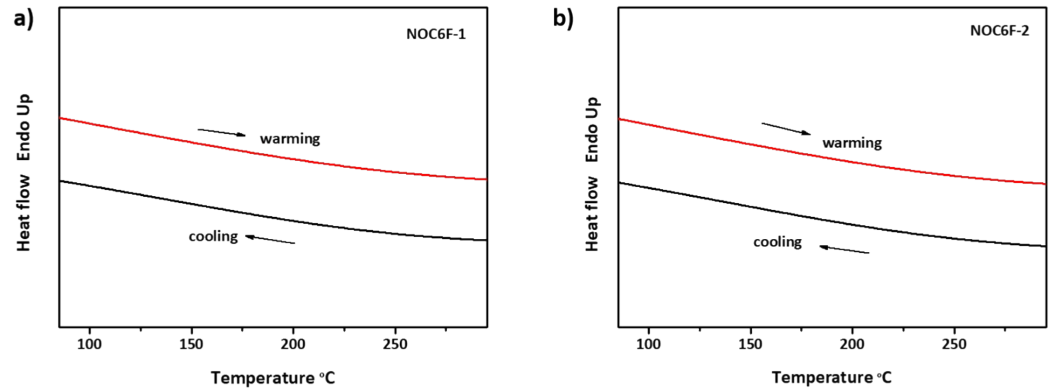


Fig. S1. DSC curves of a) **NOC6F-1** and b) **NOC6F-2** under nitrogen atmosphere.

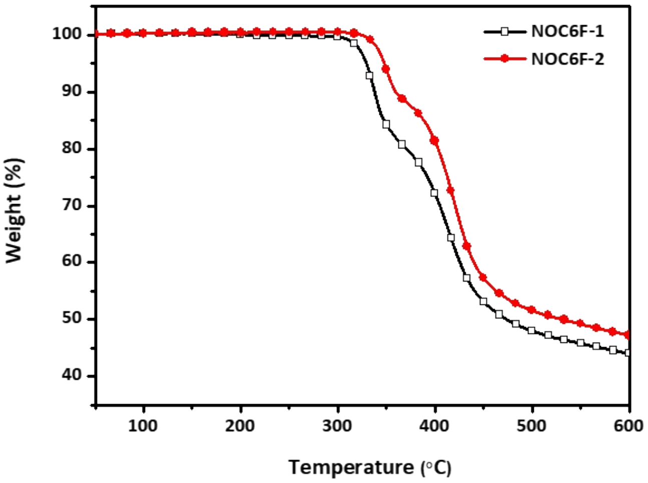


Fig. S2. TGA curves of **NOC6F-1** and **NOC6F-2** under nitrogen atmosphere.

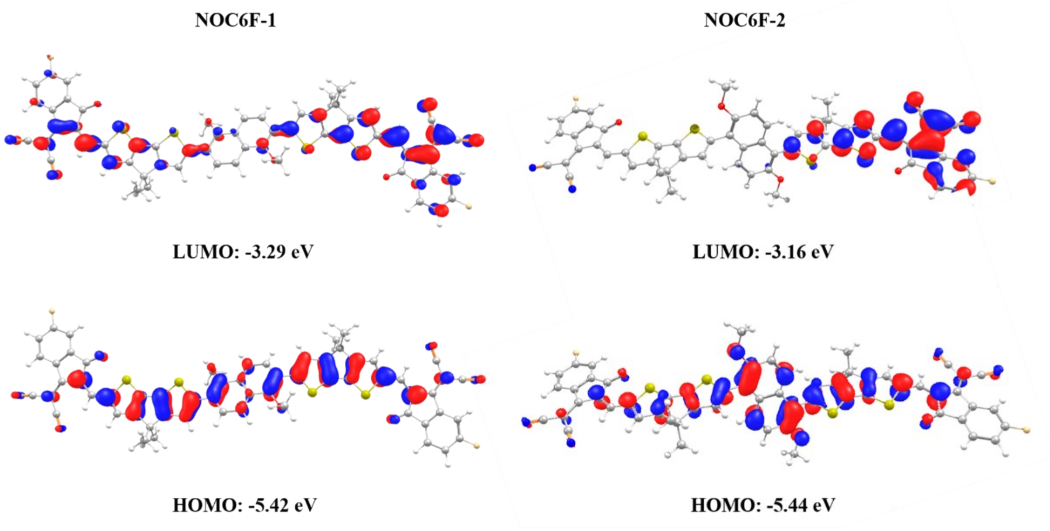


Fig. S3. Frontier molecular orbitals calculated by density functional theory.

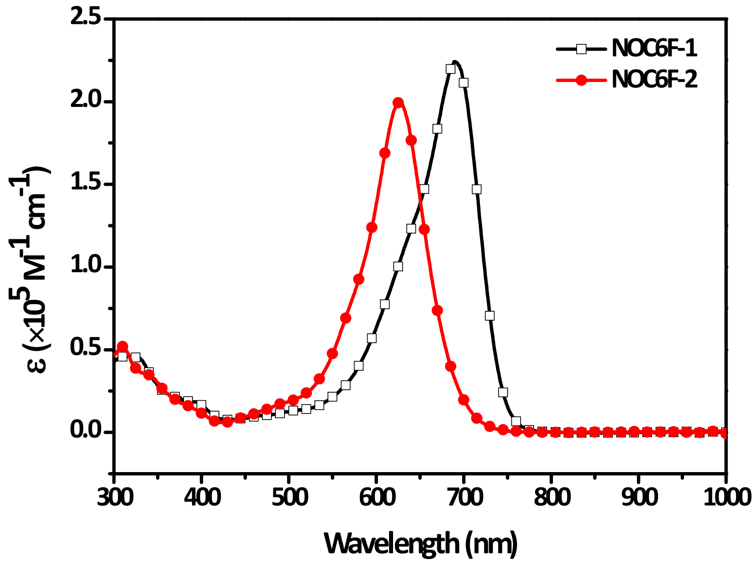


Fig. S4. Molar extinction coefficient of **NOC6F-1** and **NOC6F-2** in CF solutions.

Table S1. Photovoltaic performance of devices fabricated with PBDB-T and **NOC6F-1** with various D:A ratios.

Active layer (D:A ratio)	Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PBDB-T:**NOC6F-1**=1:0.8	90-100	0.94	16.14	62.50	9.48
PBDB-T:**NOC6F-1**=1:1		0.94	15.37	67.62	9.78
PBDB-T:**NOC6F-1**=1:1.2		0.95	17.08	65.79	10.62
PBDB-T:**NOC6F-1**=1:1.5		0.94	16.03	63.30	9.52

Table S2. Photovoltaic performance of devices fabricated with PBDB-T and **NOC6F-1** **(**1:1.2) at different annealing temperatures.

Active layer (D:A ratio)	Annealing (℃)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PBDB-T:**NOC6F-1**	-	0.95	17.08	65.79	10.62
PBDB-T:**NOC6F-1**	130	0.91	13.29	65.57	7.95
PBDB-T:**NOC6F-1**	150	0.86	9.64	50.26	4.18

Table S3. Photovoltaic performance of devices fabricated with PBDB-T and **NOC6F-1** **(**1:1.2) with CN as the additive.

Active layer (D:A ratio)	Additive (wt%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PBDB-T:**NOC6F-1**	-	0.95	17.08	65.79	10.62
PBDB-T:**NOC6F-1**	0.5%CN	0.93	13.29	65.57	7.95
PBDB-T:**NOC6F-1**	0.75%CN	0.92	9.64	50.26	4.18

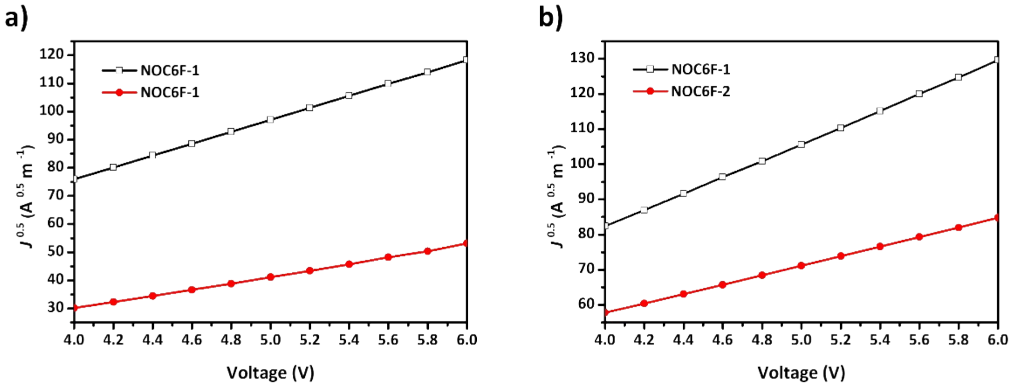


Fig. S5. a) The electron mobility and b) hole mobility of PBDB-T:**NOC6F-1** and PBDB-T:**NOC6F-2** blend film.

Table S4. The electron mobility and hole mobility of PBDB-T:**NOC6F-1** and PBDB-T:**NOC6F-2** blend film.

System	μ_e (cm^2 V^{-1} S^{-1})	μ_h (cm^2 V^{-1} S^{-1})
PBDB-T:**NOC6F-1**	2.07×10^{-3}	2.56×10^{-3}
PBDB-T:**NOC6F-2**	6.02×10^{-4}	8.39×10^{-4}

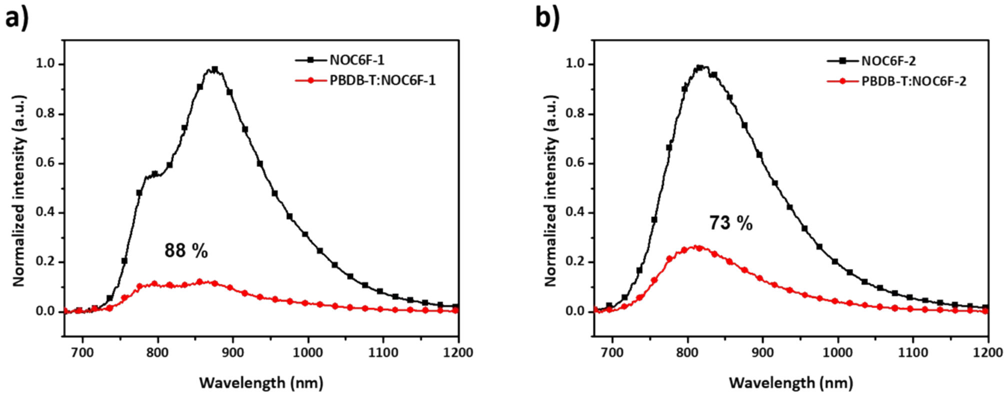


Fig. S6. Photoluminescence spectra of a) **NOC6F-1** pure film and PBDB-T: **NOC6F-1** blend film as well as b) **NOC6F-2** pure film and PBDB-T: **NOC6F-2** blend film (excited at 650 nm).

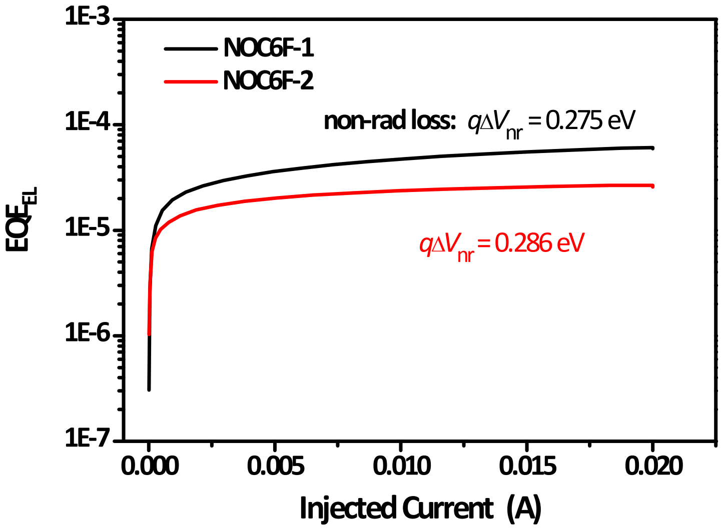


Fig. S7. EQE_{EL} of OSCs based on **NOC6F-1** and **NOC6F-2**.

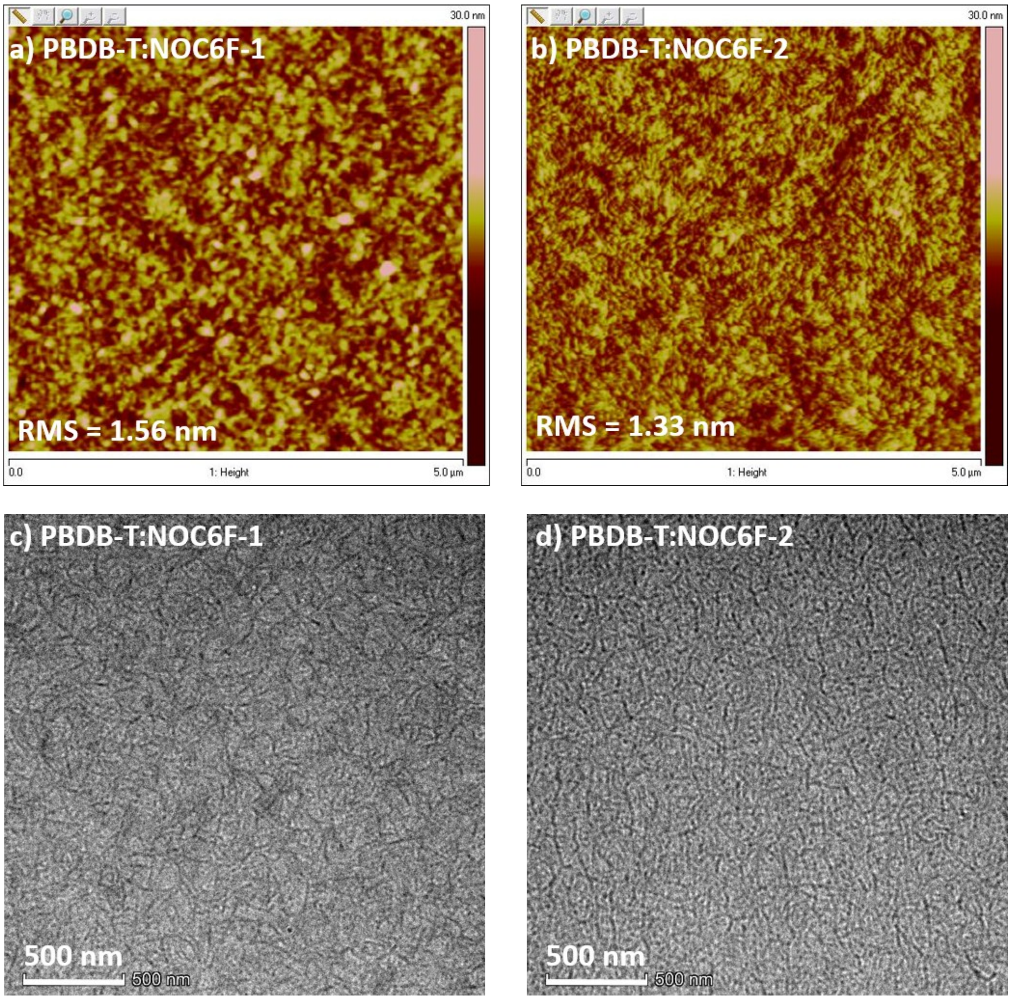


Fig. S8. AFM images of a) PBDB-T:**NOC6F-1** and b) PBDB-T:**NOC6F-2** blend films (5 × 5 µm); TEM images of c) PBDB-T:**NOC6F-1** and d) PBDB-T:**NOC6F-2** blend films.

Table S5. Structural parameters obtained by fitting the out-of-plane profiles from GIWAXS.

System	D-spacing (Å)	C.L. (Å)
PBDB-T	3.76	22.10
PBDB-T:**NOC6F-1**	3.80	35.56
PBDB-T:**NOC6F-2**	3.82	18.32

Table S6. Structural parameters obtained by fitting the in-plane profiles from GIWAXS.

System	D-spacing (Å)	C.L. (Å)
PBDB-T	21.69	91.50
PBDB-T:**NOC6F-1**	21.03	86.98
PBDB-T:**NOC6F-2**	21.14	82.42

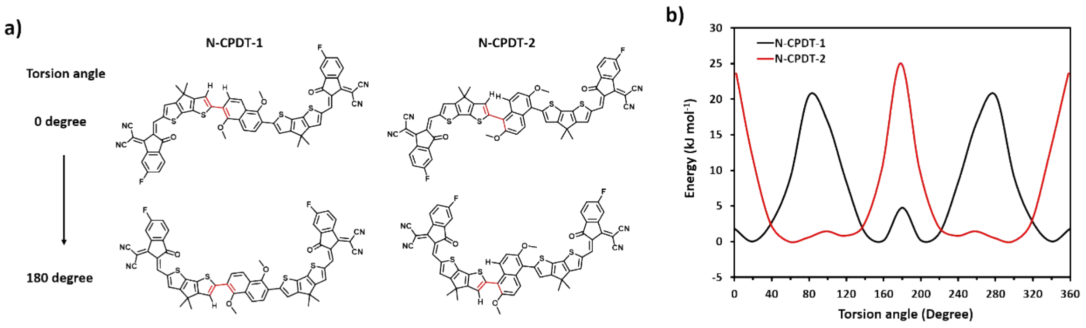


Fig. S9. a) Possible rotamers N-CPDT-1 in **NOC6F-1** and N-CPDT-2 in **NOC6F-2**. b) Potential energy surface scan of N-CPDT-1 and N-CPDT-2.

Table S7. Photovoltaic performance of devices based on PTB7-Th:**NOC6F-1** and PTB7-Th:**NOC6F-2**.

Active layer	D:A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PTB7-Th:**NOC6F-1**	1:1	0.85	10.52	34.91	3.14
PTB7-Th:**NOC6F-2**		0.88	8.33	38.88	2.83

References

[S1] C. Goh, R. J. Kline, M. D. McGehee, E. N. Kadnikova and J. M. J. Fréchet, *Appl. Phys. Lett.*, 2005, **86**, 122110-122113.

[S2] M. Koppe, H.-J. Egelhaaf, G. Dennler, M. C. Scharber, C. J. Brabec, P. Schilinsky and C. N. Hoth, *Adv. Funct. Mater.*, 2010, **20**, 338-346.

[S3] A. Hexemer, W. Bras, J. Glossinger, E. Schaible, E. Gann, R. Kirian, A. MacDowell, M. Church, B. Rude and H. Padmore, *J. Phys. Confer. Ser.*, 2010, **247**, 012007.