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Supporting Information

Cathode Interfacial Layer-Free All Small-Molecule Solar Cells with Efficiency over 12%

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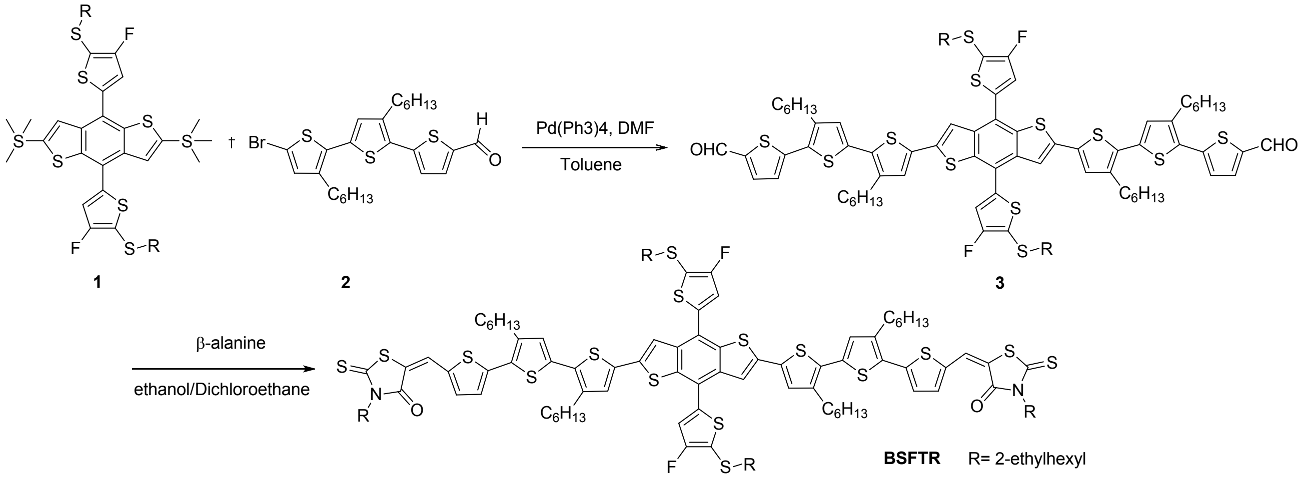
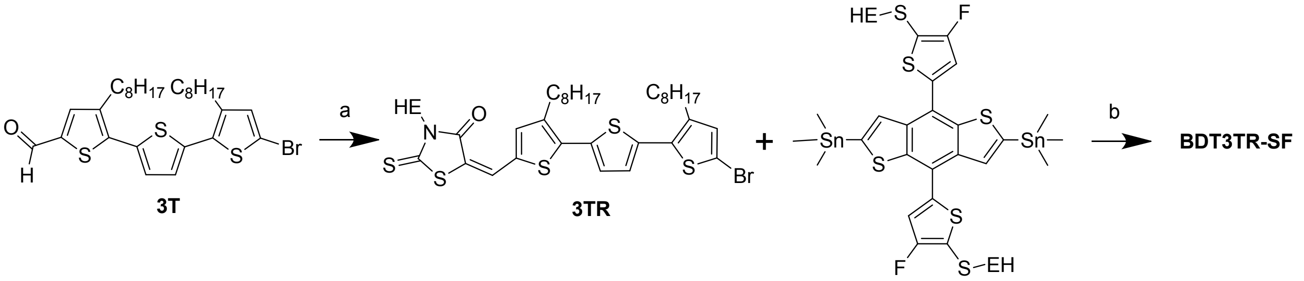
Materials

Unless otherwise stated, all starting materials were purchased from Innochem or Energy Chemicals, which were used without further purification. The reactions referred to air- or moisture-sensitive compounds were carried out in a dry reaction vessel under N_2. Molecular donor BDT3TR-SF,[1] molecular acceptor NBDTP-F_{out}[1]and the related intermediates[2] for BSFTR (see Scheme S1), were synthesized according to the reported procedures.



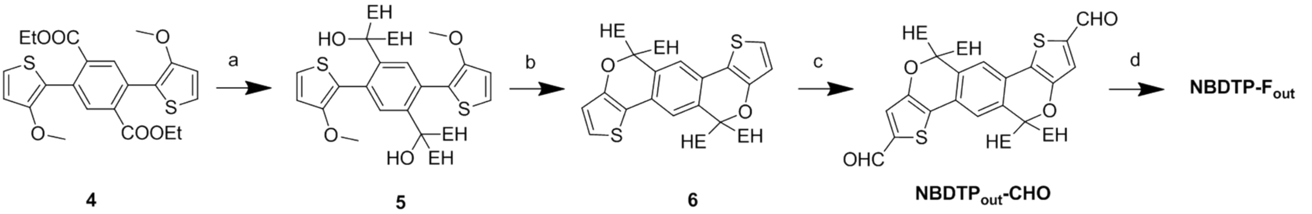
Scheme 1. Synthesis of molecular donor BSFTR.

***Compound BSFTR*:** Compound 3 (100mg, 0.062 mmol) were dissolved in $CH_2CH_2Cl_2$:ethanol (6 mL:3mL) and 15 mg *β*-alanine was added to was added to start the reaction. The reaction was carried out for 36 h at 75 ºC. The mixture was quenched with water and then extracted by $CHCl_3$. The compound BSFTR was obtained as a solid (113mg, 90%) after being concentrated under reduced pressure and purified by silica-gel column chromatography with using $CHCl_3$ as the eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.79 (s, 2H), 7.516 (s, 2H), 7.32 (d, J=4Hz, 2H), 7.22 (m, 4H),7.18 (d, J=4Hz,2H), 7.09(s, 2H), 7.00(s, 2H) 4.01(d, J=7.2, 4H), 2.95 (d, J=6.0Hz, 4H), 2.82-2.74 (m, 8H), 2.08-2.05 (m, 2H), 1.71-0.917 (m, 100H). ^{13}C NMR (151 MHz, CDCl3) δ 192.50, 167.96, 159.62, 157.88, 144.12, 141.89, 140.99, 139.17, 139.11, 138.44, 138.37, 137.12, 137.06, 135.32, 134.58, 134.54, 131.24, 129.96, 129.12, 128.78, 126.46, 124.87, 122.34, 120.11, 117.95, 115.15, 115.01, 48.74, 42.83, 39.41, 37.02, 32.03, 31.74, 31.70, 30.53, 30.31, 29.93, 29.79, 29.73, 29.40, 29.37, 28.80, 28.48, 25.34, 23.94, 23.02, 22.99, 22.71, 22.67, 14.21, 14.18, 14.09, 10.95, 10.57, 0.02. HRMS (MALDI-TOF) Calcd for $C_{106}H_{134}F_2N_2O_2S_{16}$ $[M]^+$: 2016.5925; Found: 2016.5939.



Scheme 2. Synthesis of molecular donor BDT3TR-SF.[1] Reagents and conditions: (a) 3-(2-ethylhexyl)-2-thioxothiazolidin-4-one, *β*-alanine ethanol/ dichloroethane; (b) $Pd(PPh_3)_4$, Toluene/DMF.

***Compound BDT3TR-SF*:** To the mixture of compound 3TR (5-((5''-bromo-3,3''-dioctyl-[2,2':5',2''-terthiophen]-5-yl)methylene)-3-(2-ethylhexyl)-2-thioxothiazolidin-4-one) (185 mg, 0.229 mmol) and (4,8-bis(5-((2-ethylhexyl)thio)-4-fluorothiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (0.1 g, 0.0995 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in toluene (4 mL) and DMF (1ml) was added in nitrogen, which was deoxidized by bubbling with nitrogen for 15 min. The solution was refluxed for 24 h. After quenching the reaction with water, the product was extracted with $CHCl_3$. The $CHCl_3$ solution was then washed with KF (aq.), condensed under the reduced pressure, and purified by silica-gel column chromatography using $CHCl_3$ as an eluent to afford BDT3TR-SF as a black solid (90 mg, 43%).^{1}H NMR(300MHz, $CDCl_3$): δ 7.76 (s, 2H), 7.56 (s, 2H), 7.23 (s, 6H), 7.15-7,14 (m, 4H), 4.02 (d, J=7.1Hz, 4H), 2.94 (d, J=6.1Hz, 4H), 2.88-2.64 (m, 8H), 2.08-1.97 (m, 4H), 1.71-1.64 (m, 8H), 1.43-0.82 (m, 108H).



Scheme 3. Synthesis of molecular acceptor NBDTP-F_{out}.[1] Reagents and conditions: (a) 2-ethylhexyllithium, THF; (b) TsOH, THF/H_2O; (c) $POCl_3$, DMF; (d) 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile, Piperidine, $CHCl_3$

Compound NBDTP-F_{out}: Compound $NBDTP_{out}$-CHO (70 mg, 0.0872 mmol) and 2-(5-fluoro-3-oxo-2,3-dihydro-1*H*-inden-1*B*-ylidene) malononitrile (93 mg, 0.436 mmol) were dissolved in $CHCl_3$ (6 mL) and pyridine (0.1 ml). The reaction was carried out under N_2 atmosphere at room temperature for 12 h. The mixture was precipitated with water and then extracted with $CHCl_3$. The organic phase was concentrated under reduced pressure and purified on a silica-gel column chromatography with using $CHCl_3$ as the eluent, which produced 70 mg NBDTP-F_{out} (blue solid, yield: 70%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.75-8.71 (m, 2.5H),8.4-8.37 (m, 1.5H),7.96-7.92 (m, 1.5H), 7.58 (m, 0.5H), 7.45-7.40 (m; 4H), 7.15(s, 2H), 2.00-1.92 (m, 8H), 1.54-1.50 (m, 4H), 1.25-0.81 (m, 56H).

Instruments

BRUKER Avance III 400 or 300 HD spectrometer was employed to measure ^1H NMR and ^{13}C NMR spectra. MALDI-TOF measurements were performed on an Applied Biosystems 4700 Proteomics Analyzer. UV-vis spectra were recorded by a JASCO V-570 spectrometer. Cyclic voltammetry (CV) measurements calibrated under N_2 with ferrocene/ferrocenium (F_c/F_c+) were carried out in an anhydrous CH_3CN solution with 0.1 M tetrabutylammonium perchlorate (TBAP) supporting electrolyte utilizing a CHI640C analyzer with a scan rate of 100 mV/s, which uses glassy-carbon as the working electrode, platinum-wire as the counter electrode, and Ag/Ag+ as the reference electrode.. The HOMO/LUMO was calculated by equation: $E_{HOMO/LUMO} = -(4.8 + E_{ox/red} - E_{Fc/Fc+})$ eV. Thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG 60 instrument at a heating rate of 10 °C min^{-1} under a N_2 atmosphere recording from 30°C to 450 °C.

Device Fabrication and Characterization

Organic photovoltaic devices were fabricated with a conventional structure of ITO/PEDOT:PSS/active layer/PDINO/Al. ITO-coated glass substrates (15 Ω sq^{-1}) were cleaned by sequential ultrasonication in soap deionized water, deionized water, acetone, and isopropanol. The washed substrates were further treated with oxygen plasma for 20 min to eliminate any remaining organic component. A thin layer (ca. 30 nm) of PEDOT:PSS was first spin-coated on the ITO substrates at 4000 rpm and baked at 150 °C for 30 min in air. The substrates were then transferred into a nitrogen-filled glovebox. Subsequently, the active layer was spin-coated on the PEDOT:PSS layer from a chloroform solution with 11.25 mg ml^{-1} BSFTR (or BDT3TR-SF) and 9 mg ml^{-1} BODT-Fout at various spin rates. The resulting film thickness was measured via a surface profilometer (Dektak XT, Bruker). Here, solvent vapor annealing (SVA) was used to optimize the blend morphology and promote device performance. Then, 1 mg ml^{-1} PDINO in methanol was spin-coated on the active layer at 3000 rpm. At the final stage, aluminum (100 nm) was thermally evaporated onto the active layer as the top electrode. Shadow masks were used to define the OSC active area (0.05 cm^2) of the devices. The current density–voltage (*J–V*) characteristics of photovoltaic devices were measured under N2 using a Keithley 2400 source meter. A 300 W xenon arc solar simulator (Oriel) with an AM 1.5 global filter operated at 100 mW cm^{-2} was used to simulate the AM 1.5G solar irradiation. The illumination intensity was corrected by using a silicon photodiode with a protective KG5 filter calibrated by the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) was performed using certified IPCE equipment from Enlitech, Taiwan.

AFM and TEM

Atomic force microscopy (AFM) were performed on a NanoscopeIIIa AFM (Digital Instruments) operating in tapping mode. Transmission electron microscopy (TEM) images of the thin films was obtained using a JEOL 2200FS instrument at 160 kV accelerating voltage.

GIWAXS

PLS-II 9A USAXS beam line was employed to perform Grazing incidence X-ray scattering (GIWAXS) characterization of the thin films. X-rays coming from the in-vacuum undulator (IVU) were monochromated (wavelength λ = 1.109 94 Å) using a double crystal monochromator and focused both horizontally and vertically (450 (H) × 60 (V) μm^2 in fwhm at sample position) using K-B type mirrors. GIWAXS patterns were recorded with a 2D CCD detector (Rayonix SX165), and X-ray irradiation time was 6-9 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (monoclinic, P21, a = 10.8631 Å, b = 8.7044 Å, c = 7.7624 Å, β = 102.938 Å) and the sample-to-detector distance was ~231 mm.

TPC and TPV Measurment

Transient photocurrent (TPC) and photovoltage (TPV) were measured by applying a 488 nm solid state laser (Coherent OBIS CORE 488LS) with a pulse width of ~30 ns. The current traces were recorded using a mixed domain oscilloscope (Tektronix MDO3032) by measuring the voltage drop across a 2 Ω resistor load connected in series with the solar cell. TPV measurements were performed by using the same laser pulse as for TPC at open-circuit condition. The photovoltage traces were recorded by the oscilloscope with an external 10 MΩ resistor in series.

Charge Carrier Mobility

Space charge-limited currents were tested in electron-only devices with a configuration of ITO/ZnO/active layer/PFN/Al and hole-only devices with a configuration of ITO/PEDOT:PSS/active layer/Au. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC current with field dependent mobility, which is described as:

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

where J is the current, μ_0 is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, V is the effective voltage, and L is the thickness of the active layer. From the plots of $J^{0.5}$ vs V, hole and electron mobilities can be deduced.

Table S1. Physical, Electronic, and Optical Properties of BSFTR and NBDTP-F_{out}

Materials	**λ_{sol}^{max} [nm]**	**λ_{film}^{max} [nm]**	**ε^{max} [M^{-1} cm^{-1}]**	**E_g^{opt} [eV]^a**	**E_{HOMO} [eV]**	**E_{LUMO} [eV]**	**E_g^{cv} [eV]^b**
NBDTP-F_{out}	720	802	2.5×10^5	1.41	-5.45	-4.00	1.45
BSFTR	516	570	1.8×10^5	1.83	-5.28	-3.19	2.09

$^{a)}E_g^{opt} = 1240/\lambda_{abs}^{onset}$. $^{b)}$ $E_g^{cv} = E_{LUMO} - E_{HOMO}$.

Table S2. The photovoltaic parameters for devices based on BSFTR:NBDTP-F_{out} with different D:A ratios, measured under AM 1.5G, 100 mW cm^{-2}.

D:A	**V_{oc} [V]**	**J_{sc} [mA cm^{-2}]**	**FF [%]**	**PCE [%]**
1:0.8	0.796	21.00	71.62	11.97 (11.74±0.17)
1:1	0.798	20.69	70.33	11.61 (11.49±0.15)
1:1.2	0.795	19.24	69.96	10.71(10.60±0.13)

Table S3. The photovoltaic parameters for devices based on BSFTR:NBDTP-F_{out} of 1:0.8 weight ratio with different SVA time, measured under AM 1.5G, 100 mW cm^{-2}.

SVA Time	**V_{oc} [V]**	**J_{sc} [mA cm^{-2}]**	**FF [%]**	**PCE [%]**
CF 0s	0.863	9.58	42.40	3.51 (3.38±0.17)
CF 20s	0.828	19.08	62.12	9.81 (9.67±0.12)
CF 40s	0.810	20.73	68.60	11.52 (11.41±0.13)
CF 60s	0.796	21.00	71.62	11.97 (11.74±0.17)
CF 80s	0.780	21.60	69.53	11.70 (11.59±0.11)

Table S4. The photovoltaic parameters for BSFTR:NBDTP-F_{out} devices of different active layer thicknesses, measured under AM 1.5G, 100 mW cm^{-2}.

Thickness [nm]	**V_{oc} [V]**	**J_{sc} [mA cm^{-2}]**	**FF [%]**	**PCE [%]**
95	0.797	20.85	71.30	11.84 (11.69±0.10)
120	0.796	21.00	71.62	11.97 (11.74±0.17)
150	0.792	22.02	68.09	11.88 (11.67±0.15)

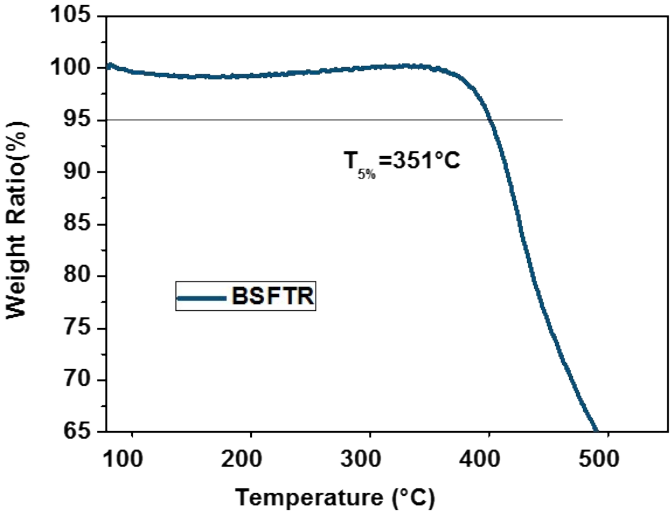


Figure S1 Thermal gravimetric analysis (TGA) curve of BSFTR.

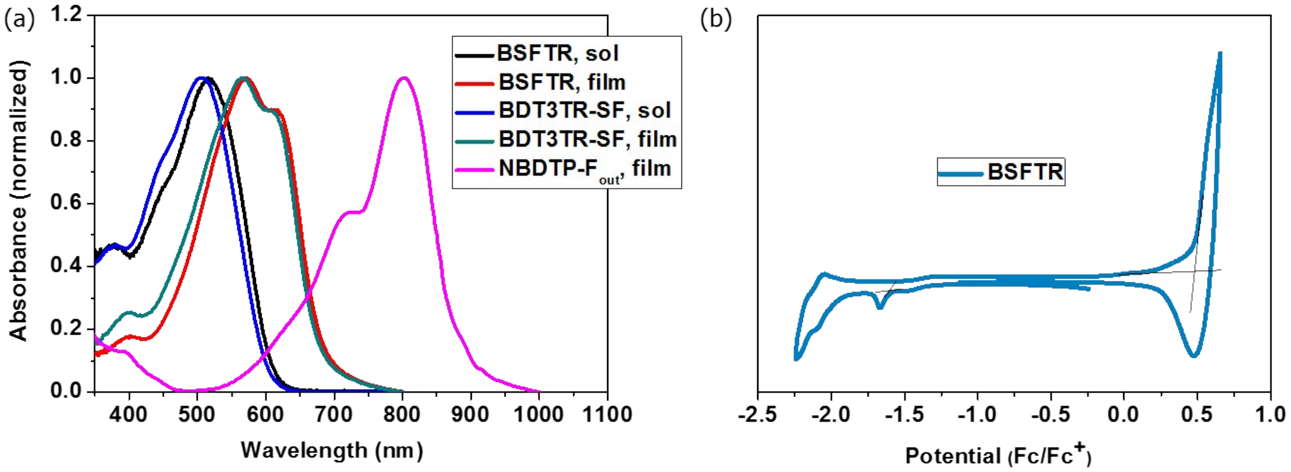


Figure S2 a) Absorption spectrum of BSFTR, BDT3TR-SF, and NBDTP-F_{out} in solution and film states. b) Cyclic voltammetry curve of BSFTR.

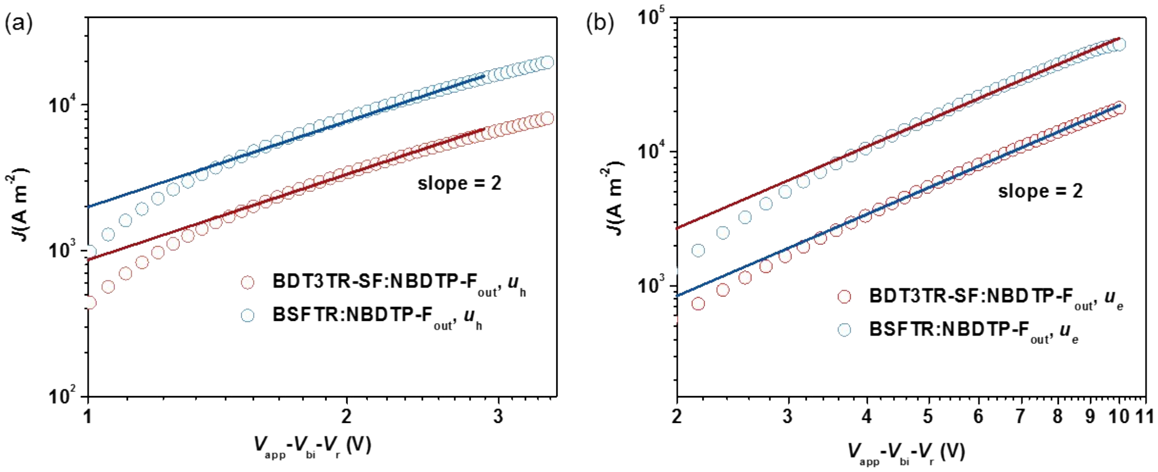


Figure S3 SCLC mobility of BDT3TR-SF:NBDTP-F_{out} and BSFTR:NBDTP-F_{out} film.

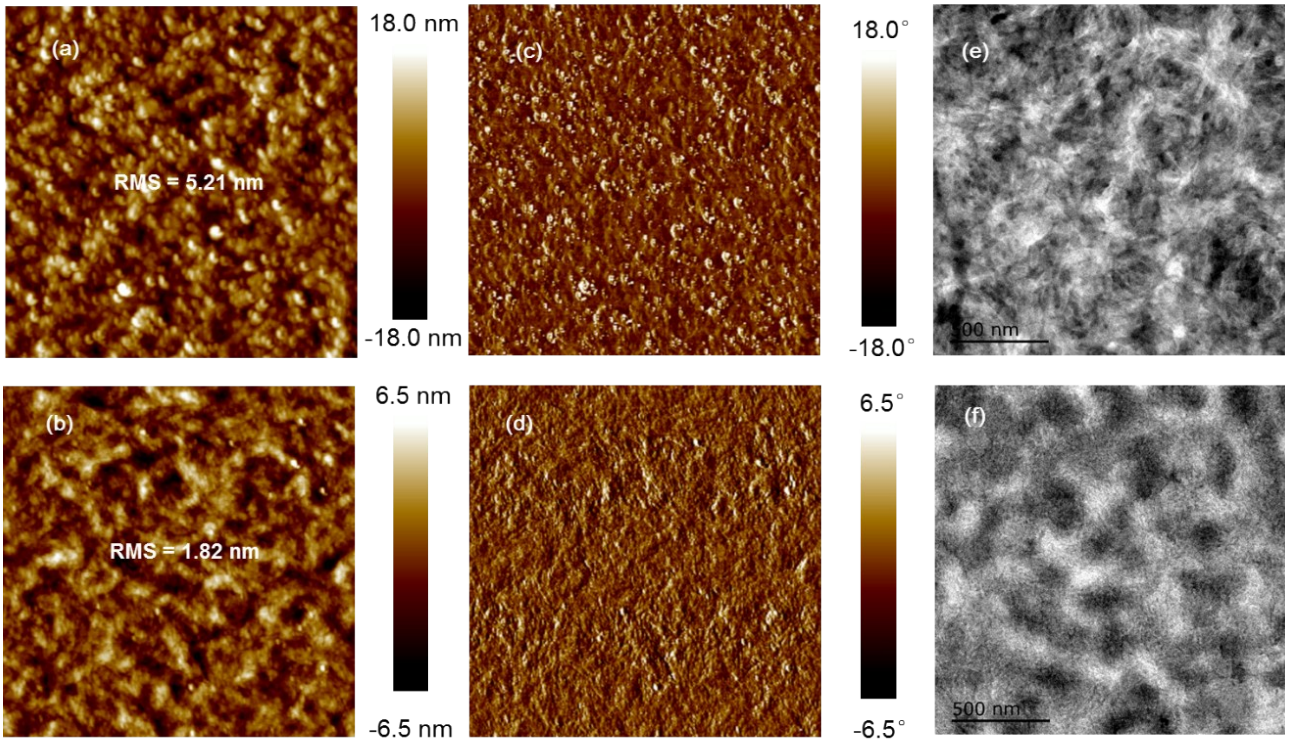
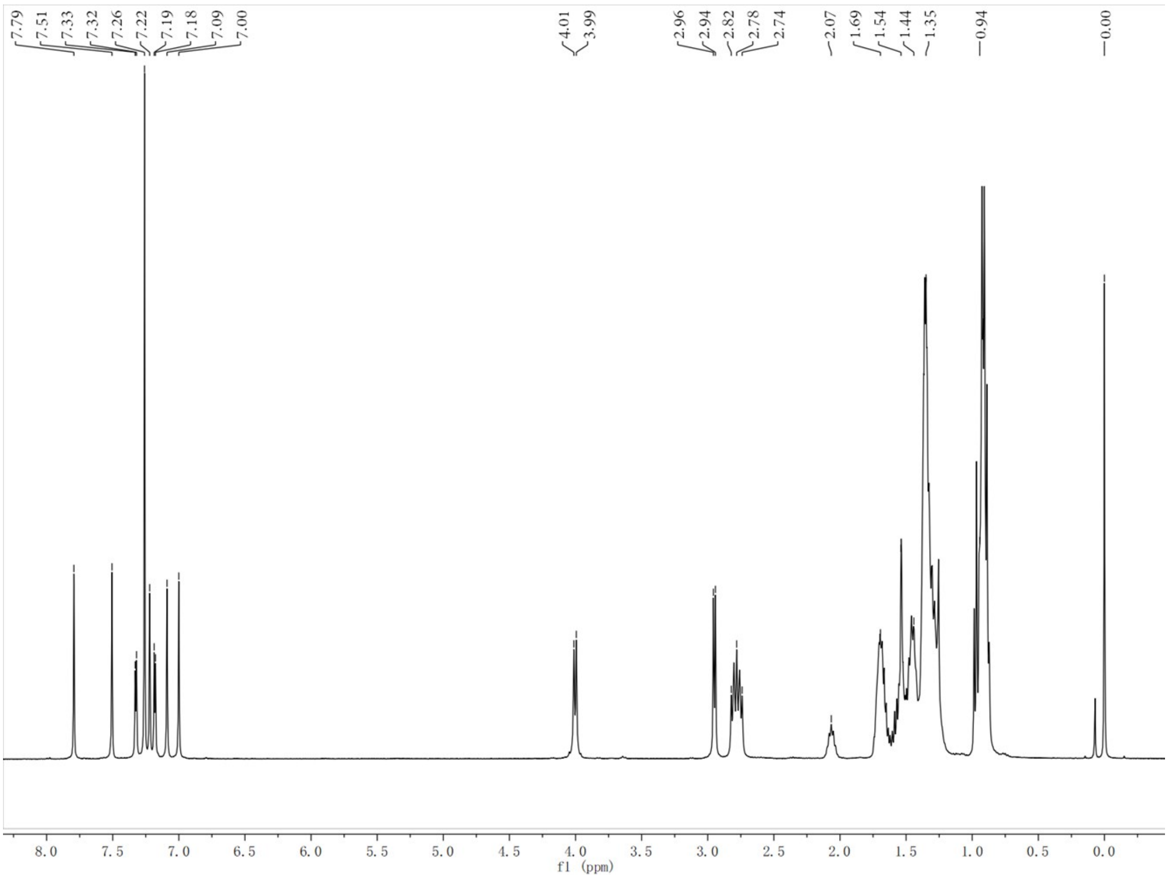
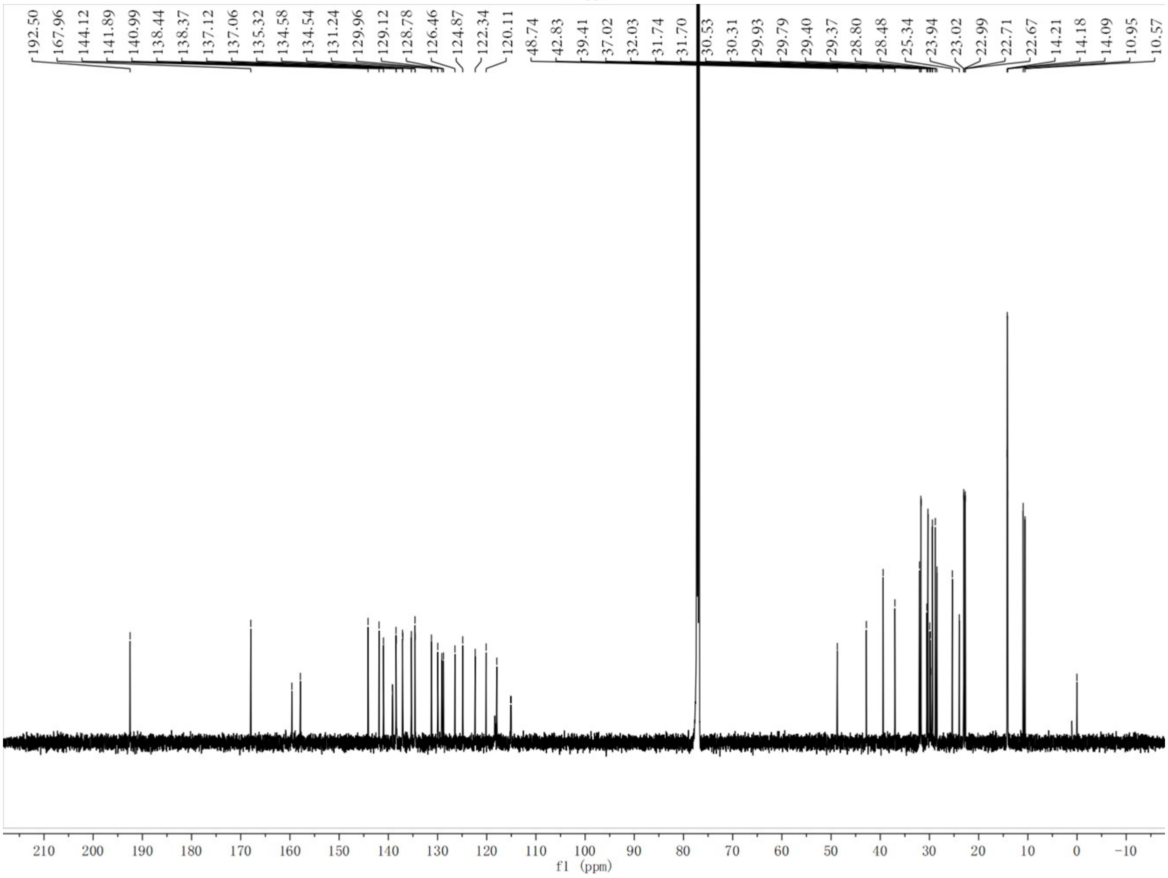


Figure S4 AFM height, phase, and TEM imagines of BDT3TR-SF:NBDTP-F$_{out}$ (a, c, e)and the BSFTR:NBDTP-F$_{out}$ (b, d, f) blends**.**

NMR Charts

BSFTR





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