High-Performance Non-Fullerene Polymer Solar Cells Based on

Naphthobistriazole Wide Bandgap Donor Copolymers

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1. General Information

Materials: All solvents and reagents were purchased from commercial sources and used without further purification unless stated otherwise. All reactions were carried out under the nitrogen atmosphere. Tetrahydrofuran (THF) was distilled over sodium/benzophenone before use to ensure an anhydrous state. Anhydrous N, N-Dimethylformamide (DMF), toluene and chlorobenzene (CB) were purchased from Sigma-Aldrich and used as received. Naphtha[1,2-c:5,6-c]bis(1H-[1,2,3]triazole)(3)¹, 4,8-Di[2-(2-ethylhexyl)thiophen-5-yl]-benzo[1,2-b:4,5-b']dithiophene(M2)², (4,8-bis(4-fluoro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (M3)³ were prepared according to the previously reported literatures.

Measurements: ¹H NMR and ¹³C NMR spectra were measured on a Bruker AV-500 MHz spectrometer with tetramethylsilane (TMS) as the internal reference. MALDI-TOF-MS spectra was measured on a Bruker BIFLEXIII mass spectrometer. Molecular weights of the copolymers were obtained on an Agilent Technologies PL-GPC 220 hightemperature chromatograph in 150 °C and 1,2,4-trichlorobenzene using a calibration curve of polystyrene standards. Thermogravimetric (TGA) measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a NETZSCH (DSC200F3) apparatus at a heating or cooling rate of 10°C min⁻¹ under a nitrogen atmosphere. UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Cyclic voltammetry (CV) was measured on a CHI660A Electrochemical Workstation equipped with a glass carbon working electrode, a platinum wire counter electrode, and a Ag/Ag⁺ reference electrodes with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a scan rate of 100 mV s⁻¹. Potentials of the saturated calomel reference electrode were internally calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc⁺), which has a known reduction potential of -4.8 eV. The deposition of a copolymer on the working electrode was done by the evaporation of a chloroform solution. The geometry of the copolymers was optimized by using Density Functional Theory (DFT) method at a B3LYP/6-31G(d) level to optimize the ground state geometries., all the alkyl chains were replaced by methyl groups substituents for calculations. Photoluminescence was measured with a SHIMADZU RF-5301PC fluorimeter. The transient photocurrent of devices was measured by applying 580 nm laser pulses with a pulse width of 120 fs and a low pulse energy to the short-circuited devices in dark. The laser pulses were generated from optical parametric amplifier (TOPAS-Prime) pumped by a mode-locked Ti: sapphire oscillator seeded regenerative amplifier with a pulse energy of 1.3 mJ at 800 nm and a repetition rate of 1 kHz (Spectra Physics Spitfire Ace). 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.

PSCs Fabrication and Characterization: All of the solar cell devices with a conventional configuration of ITO/PEDOT: PSS/active layer/PFN-Br/Ag were fabricated. Firstly, the ITO glass substrates were pre-cleaned sequentially by using detergent, ethanol, acetone, and isopropyl alcohol under sonication, and dried in oven at 70 °C for 10 h before to use. Followed by treating with oxygen plasma for 4 min, the PEDOT: PSS was spin-coated onto the ITO glass at 3000 rpm for 30 s and then annealed at 150 °C for 10 min in air. Subsequently, the substrates were transferred into a N₂protected glove box for spin-coating the active layer. The donor polymer (PBTZNT or PFBTZNT) and the small molecule acceptor m-ITIC were dissolved in CB solution (with variant blend ratios, the total concentration of the donor polymer and the acceptor is 10 mg mL⁻¹). The mixed solution was spin-coated at the top of the PEDOT: PSS layer at 2000 rpm for 30 s to form the active layer with a film thicknesses approximately 100 nm. Then, the active layers were treated with thermal annealing at 120 °C for 5 min. Finally, the interface layer (5 nm) of PFN-Br in methanol (0.5mg mL⁻¹) was spin-coated on the blended films, and then the top electrode silver (100 nm) was deposited onto the interlayer PFN-Br by thermal evaporation though a shadow mask in a vacuum chamber with a base pressure of 1×10^{-6} mbar. The active layer area of the device was 0.04 cm². The current density-voltage (J-V) characteristics were recorded using a computer-controlled Keithley 2400 source meter under an AM 1.5G solar simulator (Taiwan, Enlitech SS-F5) at an light intensity of 100 mW cm⁻², which was tested by a calibrated silicon solar cell (certified by National Renewable Energy Laboratory) before to test. The EQE spectra were performed on a commercial EQE measurement system (Taiwan, Enlitech, QER), respectively.

The hole-only and electron-only mobilities of polymer: m-ITIC blend films and the polymer neat films were determined from space-charge-limited current (SCLC) devices. The devices were fabricated with the structures of ITO/ZnO/ blend films (or neat film)/Ca/Al for electron-only mobility and ITO/PEDOT: PSS/blend films (neat film)/MoO3/Ag for hole-only mobility, respectively. The mobilities were determined by fitting the dark *J–V* current to the model of a single carrier SCLC which were calculated on the basis of the following equation.

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

where J is the current, ε_0 and ε_r are the permittivity of free space and relative permittivity of the material, respectively. and μ_h , V and d is the zero-filed mobility, the effective voltage, and the thickness of the organic layer, respectively. The effective voltage can be obtained from the equation $V = V_{appl} V_{bi} V_s$, where V_{appl} , V_{bi} and Vs are the applied voltage, the offset voltage and the voltage drop, respectively. The electron- and hole-mobility can be calculated from the slope of the $J^{1/2} - V$ curves

2. Synthesis and Characterization



Scheme S1 The synthetic routes of the monomer M1.

Naphtha[1,2-c:5,6-c]bis(1H-[1,2,3]triazole) (3)

Compound 2 (2.06 g, 6.0 mmol) and two drops HOAc was added in 200 ml water and slightly stirred and warmed until the solid was totally dissolved. NaNO₂ (2.07 g, 30 mmol) was dissolved in water (20 mL) and was then added into the solution of compound 2 dropwise and the reaction was stirred for about 1 h until no more solid was precipitated. The dark solid was collected by Buchner funnel and washed by the cold water and methanol. After dried under vacuum, the crude product was used directly in the next reaction without further purification. (1.2 g, crude yield = 92%)

Naphtha[1,2-c:5,6-c]bis(2-butyloctyl-[1,2,3]triazole) (4)

Compound 3 (2.3 g, 10.9 mmol) was dissolved in anhydrous DMF(100mL)in a three-neck flask under an argon atmosphere. Potassium carbonate(5 g, 36 mmol) was added by one portion under the protection of argon. The reaction was warmed to 70°C and stirred under reflux condition for 1h. Subsequently, 5-(iodomethyl) undecane (14.2g, 48mmol) was added by one portion. The reaction was stirred under the protection of argon overnight. Subsequently, the reaction quenched by water. The mixture was extracted three times with dichloromethane (DCM) and washed 3 times with water. The organic phase was dried over MgSO4 and concentrated. The crude product was purified by silica column chromatography using a mixture of dichloromethane (DCM)and petroleum ether (1:2, v/v) as the eluant to afford compound 4 as Brownish yellow oil (1.76g, yield: 29.5%).

¹H NMR (500 MHz, CDCl₃) δ: 8.50-8.48 (d, 2H), 7.99-8.01 (d, 2H), 4.69-4.70 (d, 4H), 2.33 (m, 4H), 1.17-1.48 (m, 32H), 0.49-0.79 (m, 12H).

3,7-Dibromo-naphtha[1,2-c:5,6-c] bis (2-butyloctyl- [1,2,3] triazole) (5)

Compound 4(1.76g,3.2mmol) was added in hydrobromic acid (20 mL) slightly stirred and warmed until the solid was totally dissolved. Bromine (1.54 g, 9.6mmol) was added dropwise and the reaction was stirred overnight under reflux. After reaction, the excessive solution of sodium bisulfite was added to remove the excess bromine. Then the crude product was poured into 200 ml water and was extracted by dichloromethane (DCM) for three times and washed by water. After dried under vacuum, the crude product was used directly in the next reaction without further purification. (2.15g, crude yield =95%).

3,7-Di(thiophen-5-yl)-naphtho[1,2-c:5,6-c]bis(2-butyloctyl-[1,2,3]triazole) (6)

Compound 5 (2.15g, 3.04mmol), tributyl-(2-thienyl)- stannane (3.4g, 9.12mmol) and Pd (PPh₃)₄Cl₂ (20 mg) was added into anhydrous THF, the mixture was stirred under the protection of argon and refluxed overnight. Subsequently, the reaction quenched by water. The mixture was extracted three times with dichloromethane (DCM) and washed 3 times with water. The organic phase was dried over MgSO4 and concentrated. The crude product was purified by silica column chromatography using a mixture of dichloromethane (DCM) and petroleum ether (1:3, v/v) as the eluant and recrystallized from methanol to yield pure product as a light yellow solid (1.41g, yield=65%). ¹H NMR (500 MHz, CDCl₃) δ : 8.70 (s, 2H),7.27-8.28(d, 2H), 7.44-7.46 (d, 2H), 7.22-7.24 (m, 2H), 4.77-4.78 (d, 4H), 2.38 (m, 4H), 1.18-1.62 (m,32H), 0.77-0.97 (t, 12H).

3,7-Di(2-bromo-thiophen-5-yl)-naphtho[1,2-c:5,6-c] bis (2-butyloctyl- [1,2,3] triazole) (M1)

Compound 6 (1.41g, 1.98mmol) was dissolved in THF (60mL); and then N-bromosuccinimide (NBS) (0.78g, 4.36mmol) was added in several portions. The mixture was reacted for 12h at the room temperature. After evaporating the solvent, the crude product was purified with silica column chromatography using a mixture of dichloromethane (DCM)and petroleum ether (1:4, v/v) as the eluant and recrystallized from isopropanol to give product as a orange solid. (1.24g, yield = 72%).¹H NMR (500 MHz, CDCl₃) δ : 8.57 (s, 2H),7.96-7.97(d, 2H), 7.17(d, 2H), 4.74-4.76 (d, 4H), 2.35 (m, 4H), 1.22-1.48 (m,32H), 0.81-0.94 (t, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 142.45, 141.45, 140.49, 130.85, 127.55, 123.13, 122.07, 117.60, 113.63, 60.14, 39.20, 31.79, 31.40, 31.14, 29.57, 28.50, 26.17, 22.96, 22.69, 14.09, 14.07; MS (MALDI-TOF) calcd for C₄₂H₅₆Br₂N₆S₂, 868.24; found, 868.16.









Scheme S2 The synthetic routes of the copolymers

Synthesis of PBTZNT:M1(86.9 mg, 0.1 mmol), M1(90.5 mg, 0.1 mmol) and anhydrous chlorobenzene (2 mL) were added to a 25 mL double-neck round-bottom flask protected with N2. The mixture was purged with argon for 15 min. Then catalyst Pd₂(dba)₃ (1.8 mg) and P (o-tol)₃ (4.8 mg) was quickly added under a stream of argon. The reaction mixture was stirred and heated to 140°C for 48 h. Then 2-(tributylstannyl)thiophene and 2-bromothiophene were added to end cap the polymer chain. Subsequently, the reaction mixture was cooled to room temperature and dropped into methanol. The resulting precipitate was collected by filtration, and then subjected to Soxhlet extraction successively with methanol, acetone, hexane and dichloromethane to remove the oligomers and impurities, and finally extracted by chlorobenzene. The chlorobenzene solution was then concentrated by evaporation, precipitated into methanol. The solid was collected by filtration and dried under vacuum to get the polymer as purple solid (119.2 mg, 92.6%). Mn= 39.3 kDa, Mw= 79.0 kDa, PDI= 2.01

PFBTZNT were synthesized according to the similar procedures for PBTZNT from corresponding monomers. Yield (90.6%) GPC: Mn= 37.0 kDa, Mw= 62.1kDa, PDI= 1.77

3. Supplementary Figures and Tables



Figure S4 TG and DSC curves of the copolymers



Figure S5 (a) UV-vis absorption spectra of the PBTZNT and PFBTZNT in CB solution; (b) UV-vis absorption coefficient spectra of blend films



Scheme S6 (a) UV-vis absorption spectra of the PBTZNT in solution and as thin film; (b) UV-vis absorption spectra of the PBTZNT in solution and as thin film.



Figure S7 Cyclic voltammetry (CV) curves of the PBTZNT and PFBTZNT.

Table S1. Molecular weights and thermal properties of the PBTZNT and PFBTZNT

Polymer	Mn (kDa)	PDI	Td (°C)
PBTZNT	39.3	2.01	446.1
PFBTZNT	37.0	1.77	451.5

Table S2. Photovoltaic parameters of devices with structure of ITO/PEDOT: PSS/PFBTZNT: m-ITIC/PFN-Br/Ag (D/A=1:1, wt: wt) processed

Blending ratio	Salvant	Solvent	Voc	J _{sc}	FF	PCE
(wt: wt)	Solvent	additive	(V)	(mA cm ⁻²)	(%)	(%)
1:1	CF	N/A	0.92	16.87	60.21	9.34
1:1	СВ	N/A	0.91	17.28	61.53	9.67
1:1	DCB	N/A	0.91	15.53	64.60	9.18

by different solvents without any post-processing conditions under AM 1.5G, 100 mW cm⁻² illumination.

Table S3. Photovoltaic parameters of devices with structure of ITO/PEDOT: PSS/PFBTZNT: m-ITIC/PFN-Br/Ag (CB) with different donor: acceptor ratios.

Blending ratio		Solvent	Voc	J _{sc}	FF	PCE
(wt: wt)	Solvent	additive	(V)	(mA cm ⁻²)	(%)	(%)
1.5:1	СВ	N/A	0.92	16.55	59.96	9.16
1:1	СВ	N/A	0.91	17.28	61.53	9.67
1:1.5	СВ	N/A	0.90	17.46	60.35	9.53

Table S4. Photovoltaic parameters of devices with structure of ITO/PEDOT: PSS/PFBTZNT: m-ITIC/PFN-Br/Ag (CB;D/A=1:1, wt: wt) with

lifferent additive concentration.						
Blending ratio	Caluant	Solvent	Voc	J _{sc}	FF	PCE
(wt: wt)	Solvent	additive	(V)	(mA cm ⁻²)	(%)	(%)
1:1	СВ	N/A	0.91	17.28	61.53	9.67
1:1	СВ	0.5%CN	0.92	17.18	66.14	10.43
1:1	СВ	1%CN	0.91	17.11	67.90	10.52
1:1	СВ	2%CN	0.91	17.22	68.77	10.72
1:1	СВ	3%CN	0.90	16.43	69.81	10.37
1:1	CB	0.5%DIO	0.92	17.09	65.45	10.27

1:1	СВ	1%DIO	0.84	7.21	45.30	2.73

Table S5. Photovoltaic parameters of devices with structure of ITO/PEDOT: PSS/PFBTZNT: m-ITIC/PFN-Br/Ag (CB;D/A=1:1, wt: wt; 2%CN) with different thickness of active layer.

Thickness	V _{oc}	J _{sc}	FF	PCE
(nm)	(V)	(mA cm ⁻²)	(%)	(%)
107	0.90	17.20	66.66	10.36
100	0.91	17.22	68.77	10.72
91	0.91	17.07	68.57	10.63
83	0.91	16.06	70.09	10.19

Table S6. Photovoltaic parameters of devices with structure of ITO/PEDOT: PSS/PFBTZNT: m-ITIC/PFN-Br/Ag (CB;D/A=1:1, wt: wt; 2%CN;

100nm) with different thermal annealing temperature and time.

		Voc	J _{sc}	FF	PCE
TA temperature	TA time	(V)	(mA cm ⁻²)	(%)	(%)
N/A	N/A	0.91	16.72	64.93	9.89
80°C	10min	0.91	16.77	68.40	10.42
100°C	10min	0.91	17.63	68.72	11.02
120°C	10min	0.91	16.66	68.54	10.38
100°C	5min	0.91	16.89	69.18	10.65
100°C	20min	0.91	16.94	67.50	10.36

Table S7. Photovoltaic parameters of devices with structure of ITO/PEDOT: PSS/PFBTZNT: m-ITIC/PFN-Br/Ag (CB;D/A=1:1, wt: wt; 2%CN;

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6)/A	TA	TA time	Voc	J _{sc}	FF	PCE
SVA	temperature	IA time	(V)	(mA cm ⁻²)	(%)	(%)
N/A	100°C	10min	0.91	17.63	68.72	11.02
CF 45s	100°C	10min	0.91	17.46	66.04	10.45
THF 45s	100°C	10min	0.90	17.26	68.17	10.64

100nm) with different solvent annealing.



Figure S8 J^{1/2}-V characteristics of (a) Electron-only and (b) hole-only J^{1/2}-V characteristics of the PBTZNT: m-ITIC and PFBTZNT: m-ITIC blend films; (c) hole-only of the PBTZNT and PFBTZNT neat films from SCLC

Table S8. Ele	ctron/hole mobilit	v of the donor po	lymer: m-ITIC blend fi	Ims and the pristine	donor polymer films
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Film	μ _h (cm²·V ⁻¹ ·s ⁻¹)	μ _e (cm²·V ⁻¹ ·s ⁻¹)	$\mu_{ m h}$ / $\mu_{ m e}$
PBTZNT: m-ITIC	2.61×10 ⁻⁴	1.85×10 ⁻⁴	1.41
PFBTZNT: m-ITIC	5.22×10 ⁻⁴	3.11×10 ⁻⁴	1.68
PBTZNT	1.66×10 ⁻³		
PFBTZNT	2.38×10 ⁻³		



Figure S9 Transient photocurrent measurements of the optimized devices based on PBTZNT: m-ITIC and PFBTZNT: m-ITIC

Reference

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