<div align="center">**Supporting Information**</div>

Processing pyridyl-based polymeric additive for improved photovoltaic performance of a wide-bandgap π-conjugated polymer

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Instrumentation and characterizations

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV-500 MHz spectrometer with tetramethylsilane (TMS) as the internal reference. Molecular weights of the polymers were obtained on a Acquity Advanced Polymer Chromatography (Waters) at room temperature using a calibration curve of polystyrene standards with tetrahydrofuran as the eluent. 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 $Ag/AgNO_3$ reference electrodes. The measurements were carried out in dry acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under a nitrogen atmosphere at a scan rate of 100 mV s^{-1}. The potential of $Ag/AgNO_3$ reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc$^+$), which has a known reduction potential of –4.80 eV. The deposition of a copolymer on the working electrode was done by the evaporation of a chloroform solution. Dipole moments were obtained from Gaussion Calculation (B3LYP/6-31G*). Contact angle tests were performed on a Dataphysics OCA40 Micro surface contact angle analyzer. Tapping-mode atomic force microscopy (AFM) images were obtained by using a Bruker Multimode 8 Microscope. Transmission electron microscopy (TEM) images were obtained by using a JEM 2100F Microscope. X-ray photoelectron spectroscopy (XPS) were characterized with a Kratos spectrometer (Axis Ultra DLD) with a monochromatic Al Kα (hv = 1486.6 eV) radiation source. The instrument was calibrated using the C(1s) peak signal at 284.6 eV.

The current density−voltage (J−V) characteristics were measured under a computer controlled Keithley 2400 sourcemeter under 1 sun, AM 1.5G solar simulator (Taiwan, Enlitech SS-F5). The light intensity at each wavelength was calibrated by a standard silicon solar cell (certified by NREL) before the testing, giving a value of 100 mW cm^{-2}

during the test. The current density–voltage (J– V) characteristics of hole-only devices were recorded with a Keithley 236 sourcemeter under dark. The EQE spectra were performed on a commercial EQE measurement system (Taiwan, Enlitech, QE-R).

SCLC hole mobility measurements

Hole-only devices were fabricated with the device structure ITO/PEDOT:PSS(40nm)/polymer:PC$_{71}$BM/MoO$_3$(10 nm)/Al. The mobility was determined by fitting the dark current to the model of single carrier SCLC, which is described by the equation,

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

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

Fabrication of inverted PSCs

The ITO-coated glass substrates were cleaned by sonication in detergent, deionized water, acetone, and isopropyl alcohol, and dried in oven at 80 ℃ for 12 h before used. The ZnO precursor solution was spin-coated onto the ITO glass at 3000 rpm for 30 s, annealed at 200 ℃ on a hot plate in air for 1 h to make 30 nm ZnO layer. Then the

substrates were transferred into a N_2 protected glove box. The cross-linkable polymer PF$_3$N-OX (0.5 mg mL^{-1}) was spin-coated from its methanol:acetic acid (99:1 v/v) solution onto the substrates to form 5 nm thin film, and the cross-linking process was carried out by heating the half-dried films under 140 ℃ for 20 min. The active layer solutions were prepared by dissolving polymer:PC$_{71}$BM blend or polymer:PC$_{71}$BM:polymeric additive ternary blend into o-dichlorobenzene and heated at 50 ℃ overnight. After cooled down to R.T. and without any filtering, the active layer solutions were spin-coated onto PF$_3$N-OX to yield about 95nm thick active layers by adjusting the spin-coating speed. After that, about 10 nm molybdenum oxide (MoO$_3$) and 80 nm aluminum were thermally deposited on top of the active layer through a shadow mask in a vacuum chamber with base pressure of 3×10^{-6} mbar. The effective area of devices was defined to be 0.16 cm^2 by the shadow mask.

Synthesis of monomers and polymers

All reagents and chemicals were purchased from commercial sources (Aldrich, Alfa Aesar and Stream) and used without further purification unless otherwise stated. 2-(6-Thiopyridyl)-5,6-difluoro-4,7-bis(5-bromothiophen-2-yl)-2H-benzo[d][1,2,3]triazole (M2).

To the mixture of sodium tert-butoxide (0.38 g, 4.0 mmol) in CH$_3$CN (8 mL) was added 4-mercaptopyridine (0.35 g, 3.2 mmol). The white suspension was stirred for 30 min and 2-(6-bromohexyl)-5,6-difluoro-4,7-bis(5-bromothiophen-2-yl)-2H-benzo[d][1,2,3]triazole (**M1**, 1.27 g, 2.0 mmol) in 4 mL THF was then added slowly

via syringe. The reaction mixture was stirred at room temperature for 2.5 h and then poured into water. After extraction with dichloromethane, the concentrated organic layer was purified by column chromotography using 4:4:1 petroleum ether:dichloromethane:triethylamine as the eluent. Yellow solid. Yield: 76.2%. ^{1}H NMR (500 MHz, CHCl$_3$, ppm): 8.36 (d, 2H), 8.01 (d, 2H), 7.17 (d, 2H), 7.07(d, 2H), 4.79 (t, 2H), 2.96 (t, 2H), 2.20 (m, 2H), 1.57 (m, 2H), 1.46 (m, 2H), 1.25 (m, 2H). ^{13}C NMR (125 MHz, CHCl$_3$, ppm): 149.20, 146.36, 137.51, 133.85, 130.50, 129.33, 120.79, 116.19, 109.63, 56.93, 30.64, 29.84, 28.35, 28.30, 26.19.

PBTA-BO

2,6-Bis(trimethyltin)-4,8-di(2,3-dihexylthiophen-5-yl)-benzo[1,2-*b*:4,5-*b*']dithiophene (**M4**, 203.7 mg, 0.2 mmol), 2-(2-butyloctyl)-5,6-difluoro-4,7-bis(5-bromothiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole (**M3**, 128.6 mg, 0.2 mmol) , and 5 mL dry *o*-dichlorobenzene were combined in a microwave vial. The mixture was purged with argon for 20 min. Then Pd$_2$(dba)$_3$ (6 mg) and P(*o*-Tol)$_3$ (12 mg) was quick added under argon. After another purge with argon for 20 min, the microwave vial was sealed and transferred to a microwave reactor with parameters set to be 200 ^{o}C, 300 W, and 40 min. After cooled to room temperature, the deep red viscous solution was precipitated into 150 mL methanol. The obtained flocculent solid was filtered and extracted with methane, acetone, and hexane. The residual solid in the Soxhlet thimble was dissolved in acid-free chloroform. Sodium diethyldithiocarbamatre was added and the mixture was stirred for 8 h to remove the catalyst. Then the mixture was filtered, concentrated and chloroform (3 mL) was added. The polymer solution was

reprecipitated in methanol, filtered and dried under vacuum. Yield: 83.2%. Purple

metallic solid. GPC: M_n = 25.2 kDa, M_w = 42.8 kDa, PDI = 1.70. ^{1}H NMR (500 MHz,

CHCl$_3$, ppm): 8.12, 7.47-7.05, 4.72, 2.97, 2.77, 2.27, 1.85-0.85.

PBTA-Py

The polymerization process was the same as that for PBTA-BO except that

monomer 2-(6-thiopyridyl)-5,6-difluoro-4,7-bis(5-bromothiophen-2-yl)-2*H*-

benzo[*d*][1,2,3]triazole (**M2**) was used instead of 2-(2-butyloctyl)-5,6-difluoro-4,7-

bis(5-bromothiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole (**M3**). Yield: 85.7%. Purple

metallic solid. GPC: M_n = 8.4 kDa, M_w = 13.1 kDa, PDI = 1.56. ^{1}H NMR (500 MHz,

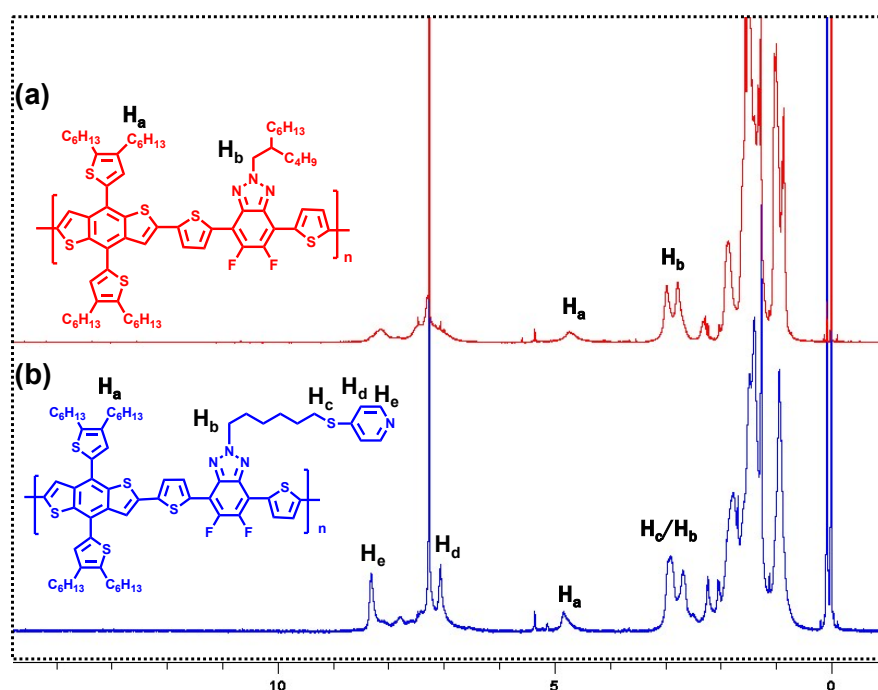CHCl$_3$, ppm): 8.31, 8.13, 7.47-7.05, 4.78, 2.97, 2.77, 2.22, 1.81-0.98.

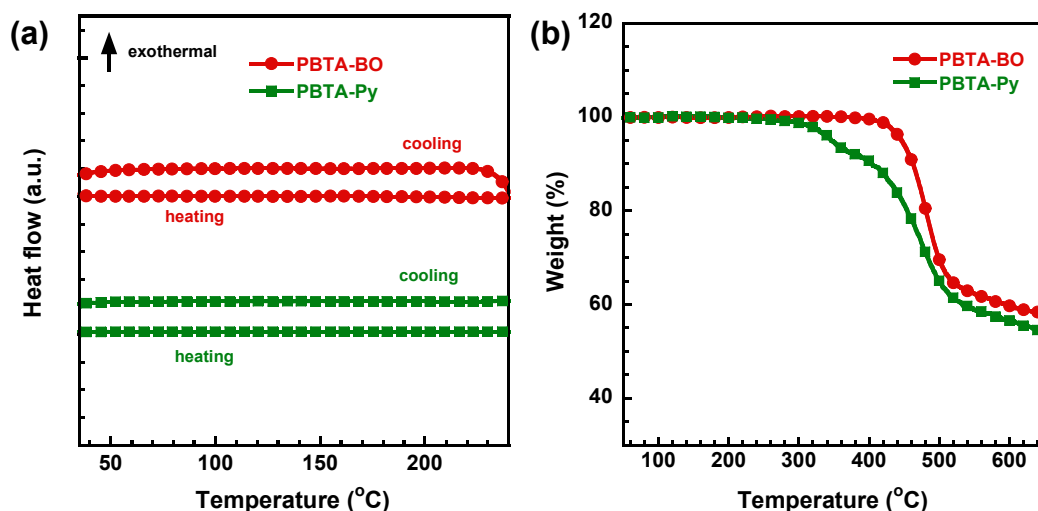**Figure S1.** ^{1}H NMR spectra of the alternating copolymers: (a) PBTA-BO and (b)

PBTA-Py.

Figure S2. (a) Differential scanning calorimetry thermograms of the donor and the polymeric additive at a heating or cooling rate of 10 ℃ min^{-1} under a nitrogen atmosphere. (b) The thermogravimetric analysis profile of the donor and the polymeric additive at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere.
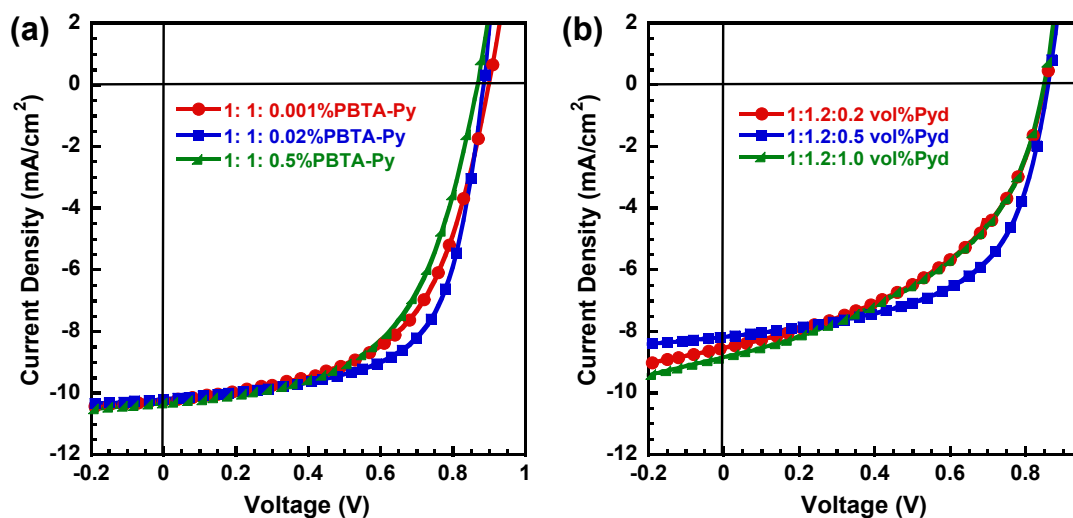

Figure S3. *J-V* curves for solar cells (a) with 1:1 donor-acceptor weight radio and various amounts of polymeric additive PBTA-Py, and that (b) with 1:1.2 donor-acceptor weight radio and various amounts of solvent additive Pyd.

Table S1. Photovoltaic performance of devices (PBTA-BO:PC$_{71}$BM = 1:1, wt:wt) w/ and w/o polymeric additive PBTA-Py under AM 1.5G, 100 mW cm^{-2} illumination.

Additive	Ratio (wt%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE [Avg.] (%) [a]
/	/	0.87	9.63	58.67	4.92 [4.75]
PBTA-Py	0.001%	0.90	10.24	56.49	5.21 [5.11]
PBTA-Py	0.02%	0.89	10.20	63.25	5.74 [5.72]
PBTA-Py	0.5%	0.87	10.23	55.72	5.01 [4.88]

[a] Measured by an inverted solar cell device with structure of ITO/ZnO/PF$_3$N-OX/photoactive layer/MoO$_3$/Al, data obtained from the average result of 8 devices.

Table S2. Photovoltaic performance of devices (PBTA-BO:PC$_{71}$BM = 1:1.2, wt:wt) w/ and w/o solvent additive Pyd under AM 1.5G, 100 mW cm^{-2} illumination.

Additive	Ratio (vol%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE [Avg.] (%) [a]
/	/	0.87	9.77	58.39	4.96 [4.69]
Pyd	0.2%	0.85	8.53	46.91	3.40 [3.32]
Pyd	0.5%	0.86	8.18	57.41	4.04 [3.96]
Pyd	1.0%	0.85	8.83	45.60	3.42 [3.38]

[a] Measured by an inverted solar cell device with structure of ITO/ZnO/PF$_3$N-OX/photoactive layer/MoO$_3$/Al, data obtained from the average result of 8 devices.

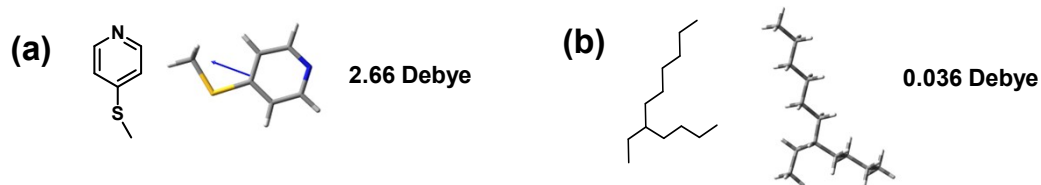(a) **2.66 Debye** (b) **0.036 Debye**

Figure S4. Dipole moments of the side-chain moieties in the acceptor units of polymeric additive (a) and donor host (b), obtained from Gaussion Calculation (B3LYP/6-31G*).
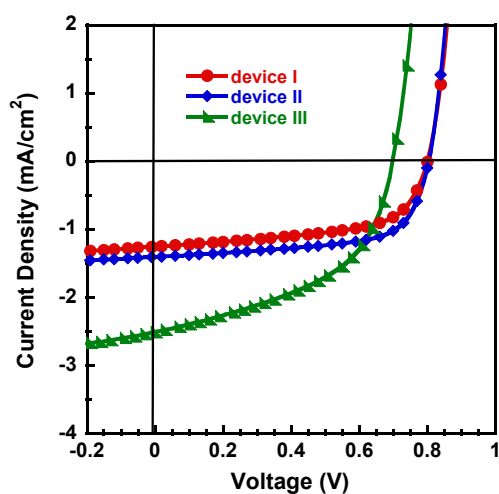

Figure S5. *J-V* curves for bilayer devices with various donor layers.

Table S3. Photovoltaic performance of bilayer devices under AM 1.5G, 100 mW cm^{-2} illumination.

device	V_{oc}	J_{sc}	FF	PCE	thickness
	(V)	(mA cm^{-2})	(%)	(%) [d]	(donor/PC$_{71}$BM, nm/nm)
I [a]	0.80	1.26	59.63	0.60	80/22
II [b]	0.80	1.41	64.95	0.73	82/22
III [c]	0.70	2.51	48.68	0.86	83/22

[a] donor layer: PBTA-BO; [b] donor layer: PBTA-BO/0.02 wt% PBTA-Py; [c] donor layer: PBTA-Py; [d] Measured by a conventional device structure of
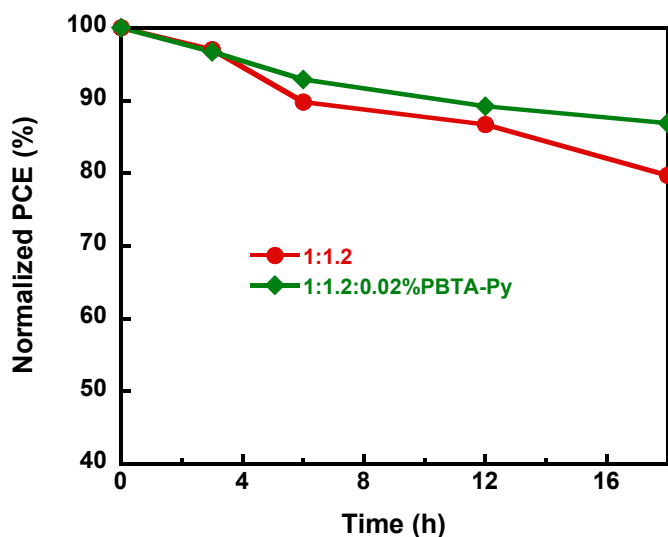
ITO/PEDOT:PSS/donor/PC$_{71}$BM/Ca/Al.

Figure S6. Photo-stability measurements (normalized PCE versus illumination time curves) of PBTA-BO:PC$_{71}$BM (1:1.2) and PBTA-BO:PC$_{71}$BM:PBTA-Py (1:1.2:0.02%) devices under continuous AM 1.5G illumination for 18 h in air.

Table S4. Photo-stability of PBTA-BO:PC$_{71}$BM (1:1.2) and PBTA-BO:PC$_{71}$BM:PBTA-Py (1:1.2:0.02%) devices under AM 1.5G, 100 mW cm^{-2} illumination in air.

donor:acceptor (wt:wt)	Solvent additive	PCE (%) [a]	Normalized PCE (%)	Time (h)
PBTA-	/	4.73	100.0	0
BO:PC$_{71}$BM		4.59	97.0	3
(1:1.2)		4.25	89.8	6
		4.10	86.7	12
		3.77	79.7	18

0.02% PBTA-Py	6.29	100.0	0
	6.08	96.7	3
	5.84	92.9	6
	5.61	89.2	12
	5.46	86.9	18

[d] Measured by an inverted device structure of ITO/ZnO/PF$_3$N-OX/active layer/MoO$_3$/Al.
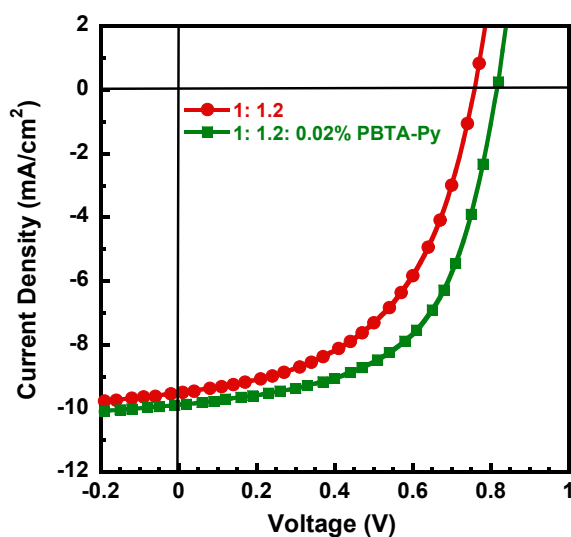

Figure S7. *J-V* curves for devices with the structure of ITO/ZnO/active layer/MoO$_3$/Al.

Table S5. Photovoltaic performance of devices with the structure of ITO/ZnO/active layer/MoO$_3$/Al, under AM 1.5G, 100 mW cm^{-2} illumination.

donor:acceptor	V_{oc}	J_{sc}	FF	PCE	thickness
	(V)	(mA cm^{-2})	(%)	(%)	(nm)
PBTA-BO:PC$_{71}$BM (1:1.2)	0.76	9.50	51.07	3.69	95
PBTA-BO:PC$_{71}$BM:PBTA-Py	0.82	9.89	56.75	4.60	98

（1:1.2;0.02%）