Supporting Information

Overlapping fasten packing enables efficient dual-donor ternary

organic solar cells with super stretchability

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Device fabrication and characterization

The patterned indium tin oxide (ITO) coated glass substrates (15 Ω per square) were successively cleaned by ultrasonic treatment in detergent, de-ionized and isopropanol, respectively. The cleaned ITO substrates were further dried by high purity nitrogen and treated by oxygen plasma for 70s to improve their work function and clearance. subsequently, poly(3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS, purchased from H.C. Starck co. Ltd.) solution was spin-coated on ITO substrates at 4500 RPM for 30 s and baked at 160 °C for 20 min in atmospheric air. Then ITO substrates coated with PEDOT: PSS films were transferred into a highpurity nitrogen-filled glove box to fabricate active layers and electron transport layer. The used acceptor material Y6-BO-4Cl purchased from Derthon photoelectric material technology Co. Ltd. PM6, PBB1-Cl and PBB2-Cl were synthesized by associate professor Wen. The active layer material was dissolved in chlorobenzene to prepare 22 mg/ml mixed solution and stirred for 3 hours. The proportions of D1 (PM6): D2(PBB1-Cl or PBB2-Cl) are 1:0, 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.5:0.5, 0:1 and the weight ratio of acceptor to donor is kept constant as 1:1.2. Then 0.5% chloronaphthalene (DIO) was added into the solution and stirred for half an hour. The mixed solutions were spincoated onto the PEDOT: PSS modified ITO substrates at 2700 RPM for 30 s to prepare the active layers. The prepared active layers were suffered from thermal annealing at 100 °C for 7 min. The prepared 1mg/ml PDINO (1 mg PDINO, 1 ml methanol were mixed and stirred for 3 hours) solutions were spin-coated onto the active layers at 3500 RPM for 25s. Finally, in the vacuum condition of 10⁻⁴ Pa, 100 nm aluminum (Al) were deposited by thermal

evaporation with a shadow mask. The flexible device is to stick the flexible substrate on the glass sheet for spin coating, and separate the glass before testing. The specific preparation method and conditions are consistent with those of rigid devices.

Device Measurement:

The current density-voltage (*J-V*) curves of all the polymer solar cells (OPVs) were measured by a Keithley 2400 unit in high-purity nitrogen-filled glove box. The AM 1.5G irradiation was provided by an XES-40S2 (SAN-EI ELECTRIC Co., Ltd) solar simulator (AAA grade, 70×70 mm2 photobeam size) with light intensity of 100 mW cm⁻². The external quantum efficiency (EQE) spectra of OPVs were measured by a Zolix Solar Cell Scan 100. The absorption spectra of films were measured with a Shimadzu UV-3101 PC spectrometer. The TEM and TEM images were measured in public laboratory of qingdao institute of energy. GIWAXS were measured at the synchrotron radiation center of Shanghai light source.

In-situ stress-strain test: For the tensile testing specimen, the active layers were blade-coated onto the PEDOT:PSS/glass substrate. To float the layers on the water surface, water was allowed to penetrate into the PEDOT:PSS layer. Subsequently, PEDOT:PSS was dissolved, and the active layer was delaminated from the glass substrate. By performing this process at the water surface, the floating active layer specimen could be obtained. The active layer specimen with a size of 2.54×0.5 cm was prepared by using a cutting plotter. The tensile test was performed by a linear stage with a strain rate of 1 µm/s. During the tensile test, stress and strain data were obtained through a load cell (Linkam TST350, UK) and a digital image correlation device. The corresponding test program is MDS (Demo machine).

Mechanical and thermal stability tests: This constant bending process of flexible device was carried out at a speed of 2 time/s under cylinders with different curvature, and the bending stability tests of each sample were completed within about 20min. The thermal and mechanical stability tests were carried out in the high-purity nitrogen glove box.

Contact angle test: The two liquid method is used to measure the contact angles. The active layers were bladecoated onto the glass substrate. The treatment of thin films is the same as that of devices. Subsequently, During the contact angle test with the contact angle measuring instrument, H_2O and CH_2I_2 droplets contact the surface of the film and quickly disengage. By using the video recording function of the instrument, the continuous image of the drop, contact and stability of the droplets on the surface of the active layer can be obtained, so as to accurately judge the contact angle image of CH_2I_2 droplets in the active layer.

Synthesis and characterization of polymers :



2,6-bis(4-(2-hexyldecyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bis(thiazole) (1).

4-(2-hexyldecyl)thiophene-2-carbaldehyde (1.54 g, 4.59 mmol), 2,5-diaminobenzene-1,4-dithiol bishydrochloride (511 mg, 2.09 mmol) and anhydrous N,N-dimethylformamide (45 mL) were placed in a Schlenk flask equipped with a magnetic stirrer. The resulting solution was heated at 120 °C and stirred for 16 h. Then, it was cooled down to room temperature and poured into deionized water; the resulting dark yellow precipitate was filtered off and dried under reduced pressure. The crude product was purified by flash column chromatography to give bisthiazole **1** as a yellowish solid (715 mg, 42% yield). ¹H NMR (600 MHz, CDCl₃) δ 8.41 (s, 2H), 7.48 (s, 2H), 7.10 (s, 2H), 2.59 (d, *J* = 6.9 Hz, 4H), 1.68-1.64 (m, 2H), 1.36-1.19 (m, 48H), 0.88 (q, *J* = 6.8 Hz, 12H).

2,6-bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bis(thiazole) (2).

In a Schlenk flask equipped with a magnetic stirrer, compound **1** (489 mg, 0.61 mmol) and Nbromosuccinimmide (270 mg, 1.52 mmol) were dissolved in a mixture of glacial acetic acid (3 mL) and anhydrous CHCl₃ (10 mL). The resulting reaction mixture was shielded from light and stirred for 4 h at room temperature. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography to afford dibromide **2** as a yellow solid (446mg, 76% yield). ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.37 (s, 2H), 7.30 (s, 2H), 2.54 (d, *J* = 7.2 Hz, 4H), 1.73-1.69 (m, 2H), 1.31-1.25 (m, 48H), 0.89-0.85(m, 12H).



Synthesis of 4,8-bis(5-(2-hexyldecyl)thiophen-2-yl)-2,6-di(thiophen-2-yl)benzo [1,2-d:4,5-d']bis(thiazole)

(4)

Compound **3** (1.41g, 1.33 mmol), trimethyl(thiophen-2-yl)stannane (988 mg, 4.0 mmol) and Pd(PPh₃)₄ were dissolved in 30 mL of anhydrous toluene, and deoxygenated by argon for 30 min. The mixture was stirred at 115 °C for 24 hours. The mixture was poured into water, extracted with dichloromethane, and dried over anhydrous Na₂SO₄. After concentration, the residue was purified by column chromatography to afford the product as a yellow solid (1.05 g, 81%).

¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, *J* = 3.6 Hz, 2H), 7.73 (d, *J* = 3.6 Hz, 2H), 7.52 (d, *J* = 4.9 Hz, 2H), 7.18-7.14 (m, 2H), 6.92 (d, *J* = 3.6 Hz, 2H), 2.90 (d, *J* = 6.6 Hz, 4H), 1.78 (br, 2H), 1.46-1.21 (m, 48H), 0.92-0.84 (m, 12H).

Synthesis of 2,6-bis(5-bromothiophen-2-yl)-4,8-bis(5-(2-hexyldecyl)thiophen-2-yl) benzo[1,2-d:4,5-d'] bis(thiazole) (5)

In a dry flask, compound **4** (480 mg, 0.49 mmol) was dissolved in 10 ml anhydrous THF under argon and cooled to -78 °C and n-BuLi (1.2 mL, 1.6 M in hexane) was added dropwise. The solution was stirred for two hours in the cold bath. After this period, a solution of tetrabromomethane (492 mg, 1.48 mmol) in 5 ml anhydrous THF was added. The reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was poured into water, extracted with dichloromethane, and dried over anhydrous Na₂SO₄. After concentration, the residue was purified by column chromatography to afford the product as a yellow solid (375 mg, 63%). ¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, *J* = 3.6 Hz, 2H), 7.39 (d, *J* = 3.9 Hz, 2H), 7.09 (d, *J* = 3.9 Hz, 2H), 6.88 (d, *J* = 3.6 Hz, 2H), 2.89 (d, *J* = 6.5 Hz, 4H), 1.77 (br, 2H), 1.46-1.23 (m, 48H), 0.93- 0.84 (m, 12H).

General procedure for the synthesis of polymers



Figure S1 The synthesis process of PBB1-Cl and PBB2-Cl.

Monomer **BDT-Cl** (0.05 mmol), monomer **2** or **5** (0.05 mmol) and $Pd(PPh_3)_4$ (2.9 mg) were mixed in 10 mL of toluene.¹ The flask was purged three times with successive vacuum and argon filling cycles. The reaction mixture was stirred for 18 h at 120 °C under argon atmosphere. After cooling to room temperature, the mixture was precipitated in 100 mL methanol. The precipitate was filtered and washed with methanol, acetone and CH_2Cl_2 successively in a Soxhlet apparatus to remove catalyst residues and oligomers. Finally, the polymer was extracted

with chloroform. The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 40 °C overnight to give the product.

PBB1-Cl: 52 mg (yield: 71%). HT-GPC: Mn = 66 kDa; Mw = 154 kDa; PDI = 2.32. Anal. calcd (%) for (C82H108Cl2N2S8)_n: C, 67.96; H, 7.51; N, 1.93. Found: C, 70.12; H, 7.53; N, 1.92.

PBB2-Cl: 63 mg (yield: 78%). HT-GPC: Mn = 61 kDa; Mw = 140 kDa; PDI = 2.28. Anal. calcd (%) for (C90H112Cl2N2S10)_n: C, 67.00; H, 7.00; N, 1.74. Found: C, 67.15; H, 7.02; N, 1.75.

Т	able S1	Recently reported m	nixed polymer based OSCs.	
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A ativa lavor	J_{SC}	FF	Voc	PCE	Dof
Active layer	(mA cm ⁻²)	(%)	(V)	(%)	Kel.
PM6:P1:Y6	25.45	73.7	0.87	16.2	2
PM6:J71:Y6	25.55	76.0	0.850	16.5	3
PBDT-ST:PNDT-ST:Y6-T	24.04	75.9	0.909	16.57	4
PM6:PDHP-Th:Y6	26.60	71.7	0.85	16.8	5
PM6:S3:Y6	25.86	79.17	0.856	17.53	6
PM6:TPD-3F:Y6	25.6	73.4	0.88	17.0	7
PM7:SiCl-BDT:Y7	27.73	70.43	0.86	17.40	8
PM6:PY2F-T:PYT	25.2	76.0	0.90	17.2	9
PM6:PBB2-Cl:Y6-BO-4Cl	26.77	75.04	0.850	17.09	Our work
PM6:PBB1-Cl:Y6-BO-4Cl	26.84	74.63	0.866	17.36	Our work



Figure S2 C-V plots of PBB1-Cl and PBB2-Cl films.

The HOMO and LUMO energy levels were calculated according to the following equations:

$$HOMO = -[E_{ox} + (4.80 - E_{Fc})] \text{ eV};$$
(1)

$$LUMO = -[E_{red} + (4.80 - E_{Fc})] \text{ eV};$$
⁽²⁾

where E_{ox} and E_{red} are the onset of oxidation and reduction potential, respectively.

Table S2 Optical and electrochemical properties of the polymers.

Demonstratio	E_{ox}	E_{red}	E_{Fc}	LUMO	НОМО
Donor materials	(V)	(V)	(V)	(eV)	(eV)
PBB1-Cl	1.29	-0.86	0.41	-3.53	-5.68
PBB2-Cl	1.24	-0.87	0.41	-3.52	-5.63

Table S3 The Photovoltaic performance of the devices with different PBB1-Cl contents under the illumination ofAM1.5G, 100 mW/cm².

PBB1-Cl	V _{OC}	J_{SC}	FF	PCE
(wt%)	(V) (1	(mA cm ⁻²)	(%)	(%)
0	0.845	25.68	72.94	15.83
20	0.866	26.84	74.63	17.36
50	0.902	23.70	70.09	14.98
100	0.970	20.45	63.57	12.62

 Table S4 The Photovoltaic performance of the devices with different PBB2-Cl contents under the illumination of AM1.5G, 100 mW/cm².

PBB2-Cl	V _{OC}	J_{SC}	FF	РСЕ
(wt%)	(V)	$(mA cm^{-2})$	(%)	(%)
0	0.845	25.68	72.94	15.83
20	0.850	26.77	75.04	17.09
50	0.885	21.07	72.08	13.44
100	0.948	17.73	66.24	11.14

The charge mobilities are generally described by the Mott-Gurney equation: 10

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{V^2}{L^3} \exp[0.89\gamma \sqrt{\frac{V}{L}}]$$
⁽³⁾

where J is the current density, ε_0 is the permittivity of free space (8.85×10⁻¹⁴ F/cm), ε_r is the dielectric constant of used materials, μ is the charge mobility, V is the applied voltage and L is the active layer thickness. The ε_r parameter is assumed to be 3, which is a typical value for organic materials, μ_0 is the charge mobility at zero electric field and γ is a constant. In this case, the charge mobilities were estimated using the following equation:

$$\ln(\frac{JL^3}{V^2}) = 0.89\gamma \sqrt{\frac{V}{L}} + \ln(\frac{9}{8}\varepsilon_r \varepsilon_0 \mu_0)$$
⁽⁴⁾



Figure S3. The $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ curves of (a) electron-only ITO/SnO₂/active layer/PDINO/Al devices and (b) hole-only ITO/PEDOT:PSS/active layer/MoO₃/Ag devices.



Figure S4 2D-GIWAXS images of PM6, Y6-BO-4Cl, PBB1-Cl and PBB2-Cl pure films.



Figure S5: The force curves of binary and ternary blend films. (Adhesion is defined as: $F = k \times D \times \Delta V$; k is the force constant (50 N/m), D is deflection sensitively (40.9355 nm/V). ΔV is the average of 20 values measured at different positions.)



Figure S6 The DFT calculation diagrams of the optimized stacking structures of PM6, PBB1-Cl and PBB2-Cl.

Table S5 The overlapping area length of PM6:PM6, PM6:PBB1-Cl and PM6:PBB2-Cl.

Calculation systems	Length (Å)		
PM6:PM6	6.76		
PM6:PBB1-Cl	11.95		
PM6:PBB2-Cl	12.09		

Table S6 The reorganization energy (RE) and effective transfer integrals (ETIs) between the two polymer units.

Intonno al applan intonaction	RE	ETIs
	$V_h ({ m eV})$	$V_h ({ m meV})$
PM6:PM6	0.284	0.502
PM6:PBB1-Cl	0.262	-6.559
PM6:PBB2-Cl	0.203	-3.459

Table S7 The photovoltaic parameters of PM6:Y6-BO-4Cl based binary and ternary flexible OSCs.

Active layer (D1:D2: A)	<i>V_{OC}</i> (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)	R_s ($\Omega \ { m cm}^2$)	R_{sh} ($\Omega \ { m cm}^2$)
PM6:Y6-BO-4Cl	0.833	24.79	65.02	13.44	4.5	1048
PM6:PBB1-Cl:Y6-BO-4Cl	0.860	25.81	67.37	14.96	3.6	1110
PM6: PBB2-Cl:Y6-BO-4Cl	0.846	25.33	67.49	14.47	4.1	1138



Figure S7 The transmission spectra of of glass/ITO and PEN/ITO.



Figure S8 The DSC curves during the heating process of PM6:Y6-BO-4Cl, PM6:PBB1-Cl:Y6-BO-4Cl and PM6:PBB2-Cl:Y6-BO-4Cl blend materials.





Figure S9 The changes of (a) binary OSCs, (b) PBB1-Cl and (c) PBB2-Cl based ternary blend films absorption spectra with heating time at 100 °C.

Figure S10. ¹H NMR spectrum of the compound 2.



Figure S11. ¹H NMR spectrum of the compound 5.

Reference

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