Achieving 17.94% efficiency all-polymer solar cells by independently inducing D/A orderly stacking

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1. Experimental Procedures

1.1 Materials and characterization techniques

PM6 and PY-IT were purchased from Derthon Co.

The absorption spectra were recorded using a Hitachi U-4100 UV-Vis scanning spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI660D electrochemical workstation, equipped with a three-electrode cell consisting of a platinum working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire counter electrode. CV measurements were carried out in anhydrous acetonitrile containing 0.1 M n-Bu₄NPF₆ as a supporting electrolyte under an argon atmosphere at a scan rate of 100 mV s⁻¹ assuming that the absolute energy level of Fc/Fc⁺ was -4.80 eV. Thin films were deposited from chloroform (CF) solutions for the measurements of UV-vis absorption spectra. The contact angles and surface energies were obtained by CSCDIC-200S. Grazing incidence wide-angle X-ray scattering (GIWAXS) studies were measured synchrotron radiation center of Shanghai Synchrotron Radiation Facility (SSRF). Transmission electron microscopy (TEM) images were obtained by using a HITACHI H-7650 electron microscope with an acceleration voltage of 100kV. Atomic force microscopy (AFM) images were obtained using Agilent 5400 scanning probe microscope in tapping mode with MikroMasch NSC-15 AFM tips. Differential scanning calorimetry (DSC) measurements were performed by NETZSCH DSC 200F3 at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. The theoretical simulations and calculations of interactions were conducted by Gaussian 09 based on B3LYPD3/def2-SVP level of theory.

1.2 Device fabrication and evaluations

Preparation of rigid devices: All the rigid solar cells were fabricated with a conventional device structure of ITO/PEDOT:PSS/active layer/PDINN/Ag. The patterned ITO glass (sheet resistance = 15Ω / square) was pre-cleaned in an ultrasonic bath of acetone and isopropyl alcohol and treated by Plasma for 1 min. Then a thin layer (about 25 nm) of PEDOT:PSS was spin-coated onto the ITO glass at 4500 rpm and baked at 150 °C for 15 min. For the fabrication of bulk heterojunction (BHJ) APSCs, donor(s):acceptor based all-polymer solutions in chloroform (PM6 concentration: 7 mg/ml) with 1.5 vol% 1-chloronaphthalene (CN) were stirred for 2.5 hrs at 50 °C before spin-coating on the PEDOT:PSS layer to form the thin active layer about 110±20 nm. Donor(s):acceptor based all-polymer solutions in chloroform (PM6 concentration: 9 mg/ml) with 1.5 vol% 1-chloronaphthalene (CN) were stirred for 2.5 hrs at 50 °C before spin-coating on the PEDOT:PSS layer to form the thick active layer about 300±30 nm. The thickness of the thick active layer was measured using a Veeco Dektak 150 profilometer. For the fabrication of pseudo-planar heterojunction (PPHJ) APSCs, the donor(s) solutions in chlorobenzene (PM6 concentration: 10 mg/ml) were stirred for 2.5 hrs at 50 °C before spin-coating on the PEDOT:PSS layer to form the bottom layers about 60±20 nm. the acceptor top solutions in chloroform (PY-IT concentration: 7 mg/ml) with 1.5 vol% 1-chloronaphthalene (CN) were stirred for 2.5 hrs at 50 °C before spin-coating on donor layers to form the acceptor layers about 40±20 nm. Then PDINN (in CH₃OH, 1mg/mL) was spin-coating at 3000 rpm to form the electron transfer layer. Finally, Ag (100 nm) metal electrode was thermal evaporated under about 5×10^{-5} Pa

and the device area was 0.0936 cm² defined by shadow mask.

Preparation of flexible devices: The patterned indium tin oxide (ITO) coated PEN 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 twice for 30 s to improve their work function and clearance. subsequently, PEDOT: PSS 4083 was spin-coated on ITO substrates at 3000 RPM for 30 s on a rigid gasket. The solutions of the active layer were prepared the same as that of the rigid device. The mixed solutions were spin-coated onto the PEDOT: PSS modified ITO substrates for 30 s on a rigid gasket. The preparation of electron transport layer and electrode are the same as that of rigid device.

The current density-voltage (*J-V*) characteristics were recorded with a Keithley 2400 source measurement unit under simulated 100 mW cm⁻² irradiation from a Newport solar simulator. The external quantum efficiencies (EQEs) were analysed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. The hole mobility and electron mobility were measured by space-charge-limited current (SCLC) method with a device configuration of ITO/PEDOT:PSS/active layer/MoO₃/Ag and ITO/ZnO/active layer/PDINN/Ag structure, respectively. The SCLC is described by the Mott–Gurney law:

$$J = 9\varepsilon\mu V^2 / (8L^3)$$

where ε represents the dielectric constant of the metal, and μ is the carrier mobility, V is the voltage drop across the device and L is the thickness of the active layer.

1.3 The synthetic details for PBB2-H



BDT-H and Monomer 1 were purchased from commercial sources and used directly unless otherwise noted.

(5-(2-hexyldecyl)thiophen-2-yl)trimethylstannane (2). To a solution of compound 1 (2.23 g, 7.22 mmol) in 50 mL of dry THF at -78 °C was added 3.3 mL (7.95 mmol) of 2.4 M n-butyllithium in hexane. This mixture was stirred at this temperature for 30 minutes then warmed to room temperature and stirred for 30 minutes. The solution was subsequently cooled to -78 °C, and 8.66 mL (8.66 mmol) of tributyltin chloride was added. The solution was allowed to warm to room temperature and stirred overnight. Then the mixture was poured into a separatory funnel containing 200 mL water. To this was added diethyl ether and the organic layer was separated. The organic layer was further washed with brine, and then dried over anhydrous Na₂SO₄. The mixture was filtered and the solvent was removed via rotary evaporation. The compound **2** was obtained and used directly for the next step.

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

Compound 2 (564 mg, 1.2 mmol), 4,8-dibromobenzothiadizole (140 mg, 0.4 mmol)

and Pd(PPh₃)₄ (24 mg, 0.02 mmol), were dissolved in 10 mL of anhydrous toluene, and deoxygenated by Ar sparge for 30 min. The mixture was stirred at 120 °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 (silica gel, DCM: hexanes 1:3 in v/v) to afford the product (300 mg, 92%). ¹H NMR (400 MHz, CDCl₃) δ 9.14 (s, 2H), 7.74 (d, *J* = 3.6 Hz, 2H), 6.91 (d, *J* = 3.6 Hz, 2H), 2.86 (d, *J* = 6.7 Hz, 4H), 1.75 (m, 2H), 1.41 – 1.21 (m, 48H), 0.90 – 0.84 (m, 12H).

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

(5). A solution of compound 4 (847 mg, 1.05 mmol) in toluene 35 mL was added pentafluoroiodobenzene (1.02 g, 3.45 mmol) and t-BuOK (353 mg, 3.15 mmol). The mixture was stirred at room temperature for 30 min. After the reaction was completed, the solution was filtered through celite and washed with DCM. The solution was concentrated and purified by column chromatography (silica gel, DCM: hexanes 1:5 in v/v) to afford the product (1.07 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 3.6 Hz, 2H), 6.88 (d, *J* = 3.6 Hz, 2H), 2.85 (d, *J* = 6.7 Hz, 4H), 1.72 (m, 2H), 1.39 – 1.17 (m, 48H), 0.88 (m, 12H).

4,8-bis(5-(2-hexyldecyl)thiophen-2-yl)-2,6-di(thiophen-2-yl)benzo[1,2-d:4,5-

d']bis(thiazole) (6). Compound 5 (1.41g, 1.33 mmol), trimethyl(thiophen-2yl)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).

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) (7). In a dry flask, compound **6** (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%). The ¹H NMR spectrum of the Monomer 7 as follows:





Monomer **BDT-H** (0.05 mmol), monomer 7 (0.05 mmol) and Pd(PPh₃)₄ (2.9 mg) were mixed in 10 mL of toluene. 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 CH₂Cl₂ 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. (PBB2-H: 65 mg (yield: 84%). HT-GPC: Mn = 147 kDa; Mw = 316 kDa; PDI = 2.15)

2. Supporting Figures and Tables

	$J_{ m SC}$	V _{OC}	FF	РСЕ	
Active layer	(mA cm ⁻²)	(V)	(%)	(%)	Kef.
PBTA-BO:PNTB:N2200	15.77	0.84	74.98	10.09	1
PBTA-Si:PTzBI-Si:N2200	17.52	0.82	72.10	10.4	2
PBDB-T:PTB7-Th:DCNBT-TPC	21.9	0.81	68.3	12.1	3
PM6:PY-IT:BN-T	22.65	0.955	74.3	16.09	4
PM6:L15:MBTI	22.91	0.957	73.83	16.18	5
PTzBI-oF:PM6:PFA1	24.36	0.880	76.14	16.3	6
PM6:J71:PY-IT	23.29	0.942	75.2	16.52	7
PM6:PY-IT:PYC1-T	24.64	0.920	73.31	16.62	8
PM6:PM6TPO:PY-IT	24.80	0.945	72.52	17.0	9
PM6:PYT:PY2F-T	25.2	0.90	76.0	17.2	10
PM6:PY-1S1Se:PY-2Cl	25.74	0.914	77.2	18.2	11

 Table S1 Typical ternary APSCs reported in recent years.



Figure S1 The cyclic voltammetry (*C-V*) curve of PBB2-H.



Figure S2 The absorption spectra of PM6:PY-IT, PM6:PBB2-H:PY-IT and PBB2-H:PY-IT blend films.



Figure S3 The DSC curves of neat and blend materials.



Figure S4 The optimized geometries of PBB2-H, PM6, PY-IT.



Figure S5 Device structure of rigid APSCs.

Table S2 Photovoltaic parameters of PM6:PY-IT based APSCs with different PBB2-H contents.

Active layer	J_{SC} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
0 wt%	23.56	0.935	73.69	16.27 (16.01)
10 wt%	24.25	0.934	75.13	17.05 (16.83)
20 wt%	24.69	0.936	76.34	17.64 (17.47)
30 wt%	24.78	0.937	74.19	17.23 (17.01)
100 wt%	19.89	0.937	72.71	13.55 (13.24)



Figure S6 Device structure of flexible APSCs.

Active layer	$J_{ m SC}$	V _{OC}	FF	PCE
	(mA cm ⁻²)	(V)	(%)	(%)
PM6:PY-IT ^a	21.51	0.927	68.15	13.30 (13.15)
PM6:PBB2-H:PY-IT ^a	22.83	0.928	72.95	15.46 (15.12)
$PM6:PY-IT^b$	22.08	0.912	65.10	13.12 (12.82)
PM6:PBB2-H:PY-IT ^b	23.20	0.915	70.50	14.98 (14.53)

Table S3 The photovoltaic parameters of PM6:PY-IT and PM6:PBB2-H:PY-IT based flexibleAPSCs.

^{*a*} is the active layer thickness of about 110 nm; ^{*b*} is the active layer thickness of about 300 nm.



Figure S7 *J-V* curves of the electron-only and hole-only devices.

	J_{sat}	J_{SC}	J_{max}	η_{diss}	η_{coll}	τ
Active layer	(mA cm ⁻²)	(mA cm ⁻²)	(mA cm ⁻²)	(%)	(%)	(ns)
PM6:PY-IT	24.72	23.56	20.51	96.8	82.9	0.239
PM6:PBB2-H:PY-IT	25.19	24.69	22.43	98.0	89.0	0.225

Table S4 Parameters for PM6:PY-IT and PM6:PBB2-H:PY-IT based APSCs.



Figure S8 Time-resolved photoluminescence curves at 460 nm of PM6:PY-IT and PM6:PBB2-H:PY-IT based APSCs.



Figure S9 J_{SC} -light intensity and V_{OC} -light intensity characteristics of PM6:PY-IT and PM6:PBB2-H:PY-IT based APSCs.

 Table S5 Detailed GIWAXS data for the 010 peak of OOP direction of binary and ternary blend

 films.

	Out of	plane
Film	FWHM (Å ⁻¹)	CCL (Å)
PM6:PY-IT	0.354	17.74
PM6:PBB2-H:PY-IT	0.308	20.38
PBB2-H:PY-IT	0.322	19.50

	J_{SC}	V _{OC}	FF	PCE
Active layer	(mA cm ⁻²)	(V)	(%)	(%)
PM6/PY-IT (10/7)	24.24	0.924	74.22	16.62 (16.35)
PM6:PBB2-H/PY-IT (10:1/7)	24.65	0.925	75.11	17.12 (16.91)
PM6:PBB2-H/PY-IT:PBB2-H (10:1.5/7)	24.82	0.924	76.06	17.44 (17.12)
PM6:PBB2-H/PY-IT:PBB2-H (10:2/7)	24.95	0.923	75.25	17.32 (17.05)
PM6:PBB2-H/PY-IT:PBB2-H (10:1.5/7:0.5)	25.19	0.924	77.45	17.94 (17.72)
PM6:PBB2-H/PY-IT:PBB2-H (10:1.5/7:1)	25.06	0.925	76.12	17.65 (17.41)

Table S6 The photovoltaic parameters of binary and ternary APSCs with PPHJ structure.



Figure S10 The In (Jd^3/V^2) - $(V/d)^{0.5}$ curves of the hole-only and electron-only devices with PPHJ structure.

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