

Manipulating the Intermolecular Stacking of Polymeric Donors for Efficient Organic Solar Cells

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1. Materials and synthesis

1.1 Materials

All reagents and chemicals were purchased from TCI Co., Sigma-Aldrich Co., and Alfa Aesar Co. and were used without further purification unless otherwise stated. The acceptor material ITIC was purchased from Derthon Co.

1.2 Synthesis

Chemical 1: The synthesis process was according to previous reports (F, A. Arroyave, C. A. Richard, J. R. Reynolds, *Org. Lett.*, **2012**, 14, 6138; S. L. Fronk, Y. Shi, M. Siefrid, and et. al., *Macromolecules*, **2016**, 49, 9301). The synthetic details of *fused*-DTBTz and 2Br *fused*-DTBTz were according to our previous work (L. Yu, Y. Li, Y. Wang, and et. al., *ACS Appl. Mater. Inter.* **2019**, 11, 31087), and the synthetic details polymers are listed below:

fused-DTBTz: 1.2 g (5.21 mmol) Chemical 1 and 0.7 g (6.25 mmol) t-BuOK were dissolved in 10 mL THF and refluxed for 1 h. Then 1.12 mL (6.22 mmol) 9-(bromomethyl)nonadecane was added to the solution and refluxed for additional 14 h. After the completion, the mixture was extracted three times with dichloromethane (DCM) and dried with anhydrous Na₂SO₄. The solvent was removed by rotary evaporator. The crude product was subjected into silica gel column chromatography with petroleum ether as eluent to give compound *fused-DTBTz* as yellow oil (44%).

2Br fused-DTBTz: 0.3 g (0.58 mmol) *fused-DTBTz* was added to a mixture of 20 mL N, N-dimethylformamide and 0.5 mL acetic acid. Then 0.23 g (1.29 mmol) N-bromosuccinimide was added in small portions. After the completion, the mixture was extracted three times with DCM and dried with anhydrous Na₂SO₄, and the solvent was removed by rotary evaporator. The crude product was subjected into silica gel column chromatography with petroleum ether as eluent to give *2Br fused-DTBTz* as light-yellow solid (90%).

PY3: 100.4 mg (0.15 mmol) *2Br fused-DTBTz*, 135.7 mg (0.15 mmol) 2F-BDT-Sn, and 8.7 mg (0.0075 mmol) Pd(PPh₃)₄ were put into a flame-dried and Argon-filled flask. After adding 10 mL dried toluene, the solution was purged with argon for 30 min. Then the solution was heated to 110 °C and refluxed for 24 h under an Ar atmosphere. After cooling to room temperature, the solution was dropped into 100 mL methanol and filtered, followed by Soxhlet extraction successively with methanol, acetone, hexane and hexane/dichloromethane (v/v=2:1) as the solvents to remove the residual monomers, oligomers and low-weight polymers. The final polymer was collected using CHCl₃ as the eluent and precipitated against methanol. The residue was filtered and dried in a vacuum oven at 45 °C to afford *PY3* as red solids (79%).

PY4: The synthesis was prepared by using a similar synthetic procedure described above for *PY3*. The final polymer was collected using CHCl₃ as the eluent and precipitated against methanol. The residue was filtered and dried in a vacuum oven at 45 °C to afford *PY4* as red solids (61%).

2. Characterization and methods

2.1 Device fabrication

All devices are the conventional structure of ITO/PEDOT:PSS/BHJ/PDINO/Al fabricated in the glove box. ITO substrates (sheet resistance = 15 Ω /square) were ultrasonically washed by deionized water, acetone, and isopropanol, and the dried ITO was subjected to UV/ozone treatment. The aqueous solution of PEDOT:PSS was spin-coated on the ITO substrate at 4000 rpm for 30 s, and annealed at 150 °C for 15 min. PY3 and PY4:ITIC-2F were dissolved in chloroform at a weight ratio of 1:1.5 (total 24 mg mL⁻¹). The PY3 and PY4:ITIC-2Cl were dissolved in chlorobenzene to ensure a weight ratio of 1:1.25 (22.5 mg mL⁻¹). The blend was spin-coated on PEDOT:PSS with a thickness of about 100-140 nm, and annealed at 130 °C or 140 °C for 10 min. PDINO was dissolved in methanol with the concentration of 1 mg mL⁻¹ to form the electron transfer layer. Finally, 60 nm thick Al was evaporated to complete the device, and the active area of each device is 0.1 cm².

2.2 Instrumentation

¹H NMR and ¹³C NMR were performed on a Bruker Advance III 600 MHz instrument with CDCl₃ as the solvent and tetramethylsilane as the internal reference. The absorption spectra were measured by Shimadzu UV-vis 2550 scanning spectrophotometer. TGA measurement was recorded using a SDT Q600 V20.9 Build 20 at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. Gel permeation chromatography (GPC) was performed with trichlorobenzene as eluent and polystyrene was used as the standard. CV was measured by the electrochemical workstation (CHI660E) in a three-electrode electrochemical cell (Pt wire as a counter electrode, glassy carbon electrode as working electrode, and Ag/AgCl electrode as a reference 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. The surface morphology of films was investigated by AFM (Agilent AFM 5400). TEM were measured by using a HITACHI H-7650 electron microscope with an acceleration voltage of 100 kV. Film thickness of the devices was determined by the profilometer (Veeco Dektak 150).

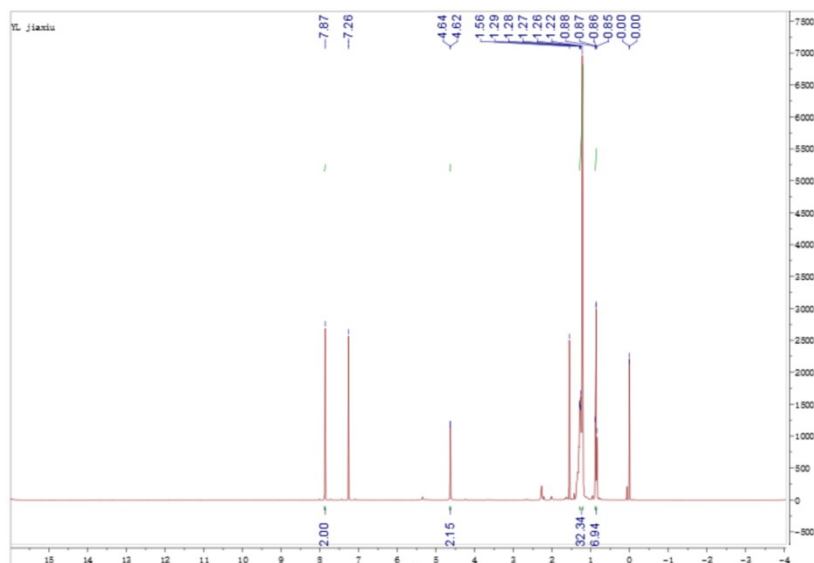


Figure S1. ^1H NMR spectra of *fused-DTBTz* and *2Br fused-DTBTz*.

Table S1. The Photovoltaic Parameters of the Optimal Device with PY3:IT-4Cl, PY3:IT-4F, PY4:IT-4Cl and PY4:IT-4F under Different Conditions

Blend	D/A (w/w)	Annealing ($^{\circ}\text{C}$)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE_{max} (%)
PY3:IT-4Cl	1:1	140	0.832	17.16	68.7	9.82
PY3:IT-4Cl	1:1.25	140	0.780	19.31	71.4	10.75
PY3:IT-4Cl	1:1.5	140	0.810	19.53	70.2	11.10
PY3:IT-4Cl	1:1.5	130	0.798	19.09	73.5	11.20
PY3:IT-4F	1:1.5	no	0.909	17.15	65.6	10.22
PY3:IT-4F	1:1.5	130	0.891	18.01	65.5	10.51
PY4:IT-4Cl	1:1.25	130	0.817	21.12	70.3	12.14
PY4:IT-4F	1:1.25	130	0.874	20.26	70.7	12.51