Supplementary Information

π -Extended Low Bandgap Polymer Based on

Isoindigo and Thienylvinylene for High Performance

Polymer Solar Cells

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Experimental

Materials

6,6'-Dibromo-N,N'-(2-decyltetradexyl)-isoindigo and 1,2-(*E*)-bis(5'-trimethyl stannanyl-2'-C-thienyl)ethylene were prepared by following the method reported in literatures ^[S1,S2]. 6-Bromooxindole and 6-bromoisatin were purchased from TCI. $PC_{61}BM$ and $PC_{71}BM$ were purchased from Nano-C. Unless otherwise stated, all of the chemicals were purchased from Aldrich.

Synthesis of PiITVT and PiI2T

For synthesis of PiITVT, 6,6'-dibromo-N,N'-(2-decyltetradexyl)-isoindigo (200 mg, 0.183 mmol), 1,2-(*E*)-bis(5'-trimethylstannanyl-2'-C-thienyl)ethylene (94.7 mg, 0.183 mmol), and tri(o-tolyl)phosphine (4.5 mg, 0.015 mmol) in toluene (10 ml) were placed in a vial, and the vial was purged with Ar gas for 20 min. After tris(dibenzylideneacetone)dipalladium(0) (1.7 mg, 0.002 mmol) was added into the reaction vial, the mixture was stirred for 3 h at 130°C in a microwave reactor. The reaction mixture was precipitated in methanol with a small amount of hydrochloric acid, and then soxhlet-extracted successively with methanol, ethyl acetate and chloroform. The chloroform fraction was concentrated and precipitated into methanol to afford the polymer (184 mg, 89.3% yield). Elemental Anal. Calcd: for $(C_{74}H_{112}N_2O_2S_2)_n$: C, 78.95; H, 10.03; N, 2.49; O, 2.84; S, 5.70. Found: C, 77.86; H, 9.88; N, 2.39; O, 3.82; S, 5.94. PiI2T was synthesized according to a reported method,^[S3] except that a microwave reactor was used in the polymerization step.

Characterization

Molecular weight and its polydispersity of synthesized polymer were determined by GPC (Knauer K-501 pump with a K-2301 refractive index detector) using chloroform as an eluent. The UV-visible absorption spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer.

Cyclic voltammetry was conducted on a potentiostat/galvanostat (VMP 3, Biologic) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluoro-phosphate in acetonitrile. Pt wires (Bioanalytical System Inc.) were used as both counter and working electrodes, and silver/silver ion (Ag in 0.1 M AgNO₃ solution, Bioanalytical System Inc.) was used as a reference electrode. XRD patterns were obtained from an X-ray diffractometer (New D8 Advance, Bruker) using Cu-K α radiation (λ = 1.5418 Å) at a scan rate of 2° min⁻¹. Grazing incidence X-ray scattering experiment of the thin films was performed at the Stanford Synchrotron Radiation Light Source on beam 11-3. The scattering signal was recorded on a 2-D image plate (MAR-345) with a pixel size of 150 µm. The samples were 15 mm long in the direction of the beam path, and the detector was located at a distance of 450 mm from the sample center (distance calibrated using a lanthanum hexaboride standard). The incidence angle of 0.1° was chosen which gave the optimized signal-to-background ratio and the X-ray wavelength was 0.9758 Å. The beam size was 50 µm by 150 µm, which resulted in a beam exposure on the sample of 150 µm wide over the entire length of the sample. The data was processed and analyzed using WxDiff software package.^[S4] The photovoltaic performance was measured under nitrogen atmosphere inside a glove box. The current density-voltage curves were characterized with a Keithley 4200 source-meter under AM 1.5 G (100 mW cm⁻²) simulated by a Newport-Oriel solar simulator. The EQE was measured using a lock-in amplifier with a current preamplifier (K3100, Mac Science Co.) under short circuit current state with illumination of monochromatic light. The morphology of the active layer film was observed by TEM (JEM-1010, JEOL) with an accelerating voltage of 80 kV. The geometries of TVT and iT were optimized by the DFT calculation using the Gaussian 03 software package. Hybrid three-parameter B3LYP functional combined with 6-31G(d) basis set was used.

Device fabrication

ITO-coated glass (15 Ω sq⁻¹) was cleaned with acetone and isopropyl alcohol, and then dried at 120 °C for 30 min. After complete drying, the ITO-coated glass was treated with UV-ozone for 15 min. PEDOT:PSS was spin coated onto the ITO with 40 nm in thickness, and the PEDOT:PSS film was annealed at 150 °C for 10 min in a N₂-filled glove box. Polymers and PCBM were dissolved in solvent and then the solution was stirred for 8 h at room temperature. After the solutions were placed on a hot plate at 70 °C for a while, the solutions were spin-coated on the top of PEDOT:PSS layer. Ca (20 nm in thickness) was thermally evaporated on the top of the active layer, and then Al (100 nm) was thermally deposited on the Ca layer under high vacuum (< 10⁻⁶ Torr). For measurement of the SCLC hole mobility, hole-only devices were fabricated with ITO/PEDOT:PSS/active layer/Au configuration.

References

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- [S2] B. Lim, K.-J. Baeg, H.-G. Jeong, J. Jo, H. Kim, J.-W. Park, Y.-Y. Noh, D. Vak, J.-H. Park, J.-W. Park, D.-Y. Kim, *Adv. Mater.* 2009, 21, 2808.
- [S3] T. Lei, Y. Cao, Y. Fan, C.-J. Liu, S.-C. Yuan, J. Pei, J. Am. Chem. Soc. 2011, 133, 6099.
- [S4] S. C. B. Mannsfeld, M. L. Tang, Z. Bao, Adv. Mater. 2011, 23, 127.

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Figure S1. GPC trace of PiI2T and PiITVT eluted with chloroform (CF) at room temperature.



Figure S2. Thermogravimetric analysis of PiI2T and PiITVT under N₂ atmosphere.



Figure S3. Effect of PiITVT concentration in CF on the absorption spectra.



Figure S4. UV-vis absorption spectra of (a) PiI2T and PiITVT solution in chloroform, (b) PiI2T:PC₇₁BM and PiITVT:PC₆₁BM blend film.

Table S1. Summary of intermolecular distance (d), coherence length (L_c) and the average

Blend film	Direction	Reflection plane	d (Å)	L _C (Å)	L ₀ /d
Pil2T:PC ₇₁ BM	Out-of-plane	(100)	19.0	58.8	3.09
	In-plane	(100)	20.4	128.0	6.27
		PCBM	4.4	12.8	2.91
PiITVT:PC ₆₁ BM	Out-of-plane	(100)	20.6	67.2	3.26
	In-plane	(100)	22.3	151.3	6.78
		PCBM	4.5	14.4	3.2

number of chains in a crystallite (L_C/d) determined from GIWAXS data



Figure S5. Comparison of (a) $PC_{61}BM$ and (b) $PC_{71}BM$ as acceptor in PiITVT-based polymer solar cells.

p:n (acceptor)	$J_{\rm SC}$ [mA cm ⁻²]	V _{oc} [V]	FF	PCE [%]
1:1 (PC ₆₁ BM)	10.6	0.92	0.54	5.27
1:1.5 (PC ₆₁ BM)	12.4	0.92	0.58	6.61
1:2 (PC ₆₁ BM)	11.6	0.92	0.58	6.19
1:1 (PC ₇₁ BM)	12.4	0.90	0.54	6.03
1:1.5 (PC ₇₁ BM)	10.8	0.91	0.57	5.60
1:2 (PC ₇₁ BM)	12.3	0.88	0.56	6.06

Table S2. Summary of photovoltaic properties of $PiITVT:PC_{61}BM$ (or $PC_{71}BM$) with different blend ratio.

Device configuration: glass/ITO/PEDOT:PSS/active layer/Ca/Al

Solvent: CF:DCB (4:1 v/v)

Energy & **Environmental Science** 4 Current density (mA/cm²) 2 CF CF:DCB (9.5:0.5) 0 CF:DCB (9:1) CF:DCB (8:2) -2 CF:DCB (7:3) CF:DCB (6:4) -4 -6 -8 -10 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0 Voltage (V)

Figure S6. Effect of the mixing ratio of CF to DCB on J-V curves of PiI2T:PC₆₁BM (1:1.5 w/w) polymer solar cells.



Figure S7. Effect of the mixing ratio of CF to DCB on J-V curves of PiITVT:PC₆₁BM (1:1.5 w/w) polymer solar cells.



Figure S8. TEM images of PiITVT:PC₆₁BM (1:1.5 w/w) blend cast from (a) pure CF, (b) CF:DCB (95:5 v/v), (c) CF:DCB (8:2), (d) CF:DCB (7:3) and (e) CF:DCB (6:4) (all scale bars indicate 500 nm).

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Figure S9. J-V curves of PiI2T:PC₆₁BM (1:1.5 w/w), PiI2T:PC₇₁BM (1:1 w/w) and **PiITVT**:PC₆₁BM (1:1.5 w/w) polymer solar cells with DIO (4 vol%).



Figure S10. Dark current density-effective voltage characteristics of hole single carriers (SCLC mobilities) in PiITVT:PC₆₁BM (1:1.5 w/w) thin film cast from CF:DCB (9:1 v/v) and PiI2T:PC₇₁BM (1:1 w/w) thin film cast from CF:DIO (96:4 v/v).