

Supporting Information

Low-Bandgap Conjugated Polymers for High Efficient Photovoltaic

Applications**

Yi-Chun Chen, Chao-Ying Yu, Yu-Ling Fan, Ling-I Hung, Chih-Ping Chen, Ching Ting**

Experimental

Materials and Equipment for Polymer Solar Cells

All chemicals were purchased from Aldrich and used as received unless otherwise specified. ^1H NMR (500 MHz) spectra were recorded using a Bruker spectrometer. Absorption spectra were recorded on a Perkin–Elmer Lambda 950 UV–Vis spectrophotometer. The molecular weights of the polymers were measured using the GPC method with polystyrene standards. CV traces were recorded using an Autolab PGSTAT302 operated at a scan rate of 50 mV s^{-1} , equipped with Pt electrodes and a Ag/Ag^+ (0.10 M AgNO_3 in MeCN) reference electrode in an anhydrous, N_2 -saturated solution of 0.1 M Bu_4NClO_4 in MeCN. Bu_4NClO_4 (98 %, TCI) was recrystallized three times from methanol/water (1:1) and then dried at $100\text{ }^\circ\text{C}$ under reduced pressure. A Pt plate coated with a thin polymer film was used as the working electrode; a Pt wire and an Ag/Ag^+ electrode were used as the counter and reference electrodes, respectively. The electrochemical potential was calibrated against Fc/Fc^+ . Samples for the TEM analysis were prepared by spin-casting from various blend solutions onto a PEODOT:PSS/glass substrate. The films were then floated onto water and placed on a 200-mesh copper TEM grid (Agar sci. Inc.). TEM images were obtained on a JEOL-2010 transmission electron microscope using the internal charge-coupled device (CCD) camera.

Synthetic Procedures for Monomers and Polymers

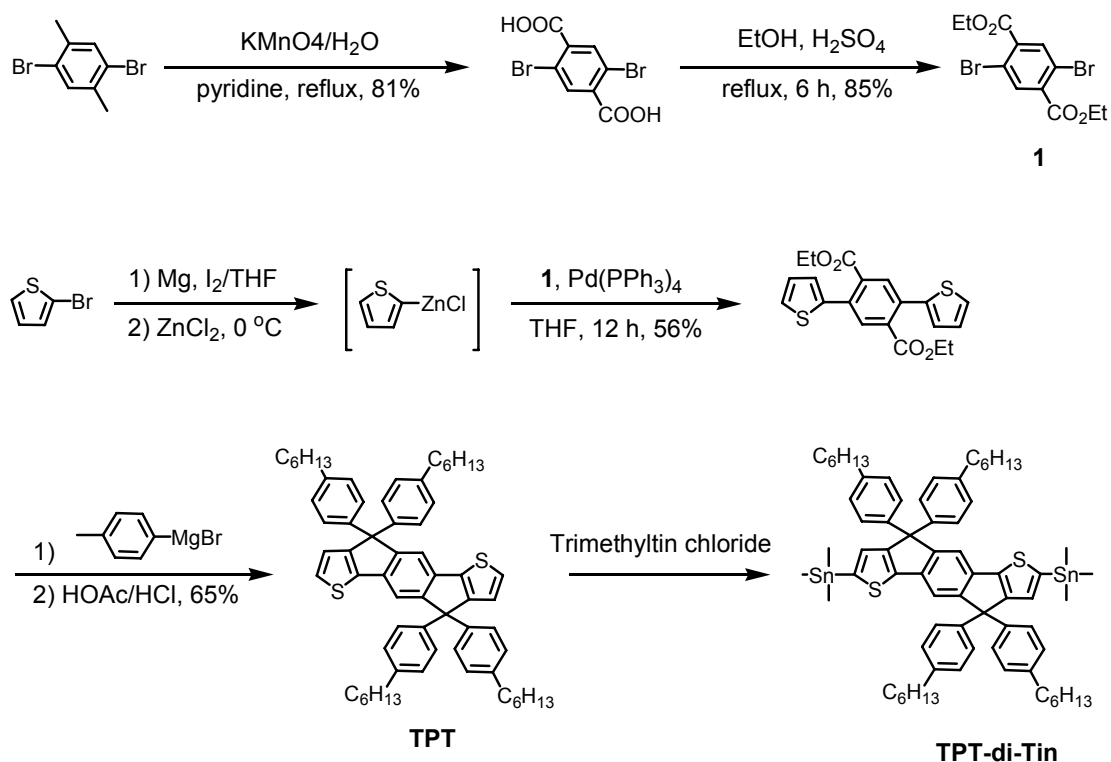
TPT-di-tin

The compound TPT have been already reported in our previous report [1], the detail of synthesis was shown in Scheme S1. TPT (0.91 g, 1mmol) was dissolved in dry THF (30 mL). The solution was cooled to -78 °C, and butyllithium (1.6M, 1.38 mL, 2.2 mmol) was added dropwise over 10 min. The reaction was stirred at this temperature for 1 h. Trimethyltin chloride (1 M in hexanes, 2.4 mL, 2.4 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. Water was added, and the reaction was extracted with diethyl ether. The organic layer was washed with water and dried over magnesium sulfate. Evaporation of the solvent afforded the bis(trimethyltin) monomer(**TPT-di-Tin**) as a light brownish viscous oil (1.14 g, 92%). ¹H NMR (CDCl₃, 500 MHz): 7.38 (s, 2H), 7.14 (d, 8H), 7.03 (d, 8H), 7.01 (s, 2H), 2.54 (t, 8H), 1.57 (m, 8H), 1.31 (m, 24H), 0.86 (t, 12H), 0.33(s, 18H). ¹³C NMR (CDCl₃, 100 MHz): 157.47, 153.52, 147.31, 142.43, 141.12, 140.93, 134.70, 130.57, 128.16, 127.96, 117.72, 62.08, 35.56, 31.71, 31.34, 29.16, 22.60, 14.07, -8.06.

α-PTPTBT polymer

TPT-di-Tin (0.6g, 0.487mmole), 4,7 dibromo-2,1,3 benzothiadiazole(0.1439, 0.487mmole) tris(dibenzylideneacetone)dipalladium (0) (17.88 mg, 0.0195 mmole), tri(o-tolyl)phosphine (47.45 mg, 0.156 mmole) were added to dry chlorobenzene (20 mL). The reaction mixture was purged with N₂ and subjected to three freeze/pump/thaw cycle to remove O₂. The mixture was heated in a microwave reactor for 30 min. The dark solution was poured into methanol (1 L) and the black precipitate was collected on a membrane filter. The polymer was washed for 72 h through Soxhlet extraction with methanol, acetone, and hexane sequentially; the soluble fraction was then collected through extraction with CHCl₃. The extract was

concentrated and precipitated into methanol to yield the polymer as a deep-blue product (80%). GPC (THF): $M_w = 60,900 \text{ g mol}^{-1}$; $\lambda_{\text{max}} = 570 \text{ nm}$. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.8–8.0 (br, 2H), 7.09–7.51 (br, 20H), 2.55 (t, 8H), 1.55 (m, 8H), 1.28 (br, 24H), 0.86 (t, 12H).



Scheme S1. Synthesis of TPT-di-tin monomer

TPT-di-tin

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***α* -PTPTBT polymer**

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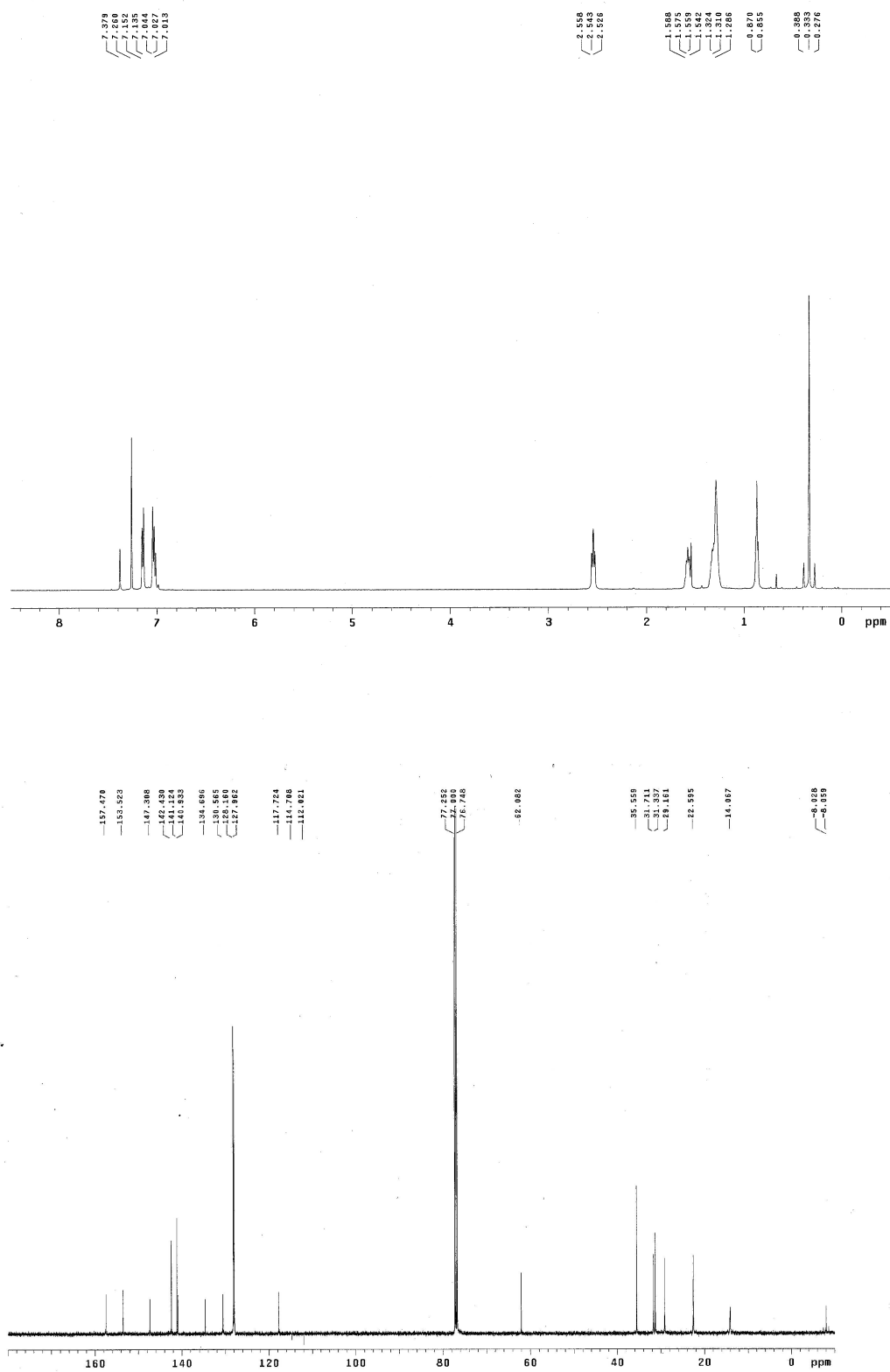


Figure S1. ^1H -NMR and ^{13}C NMR spectra of TPT-di-Tin monomer

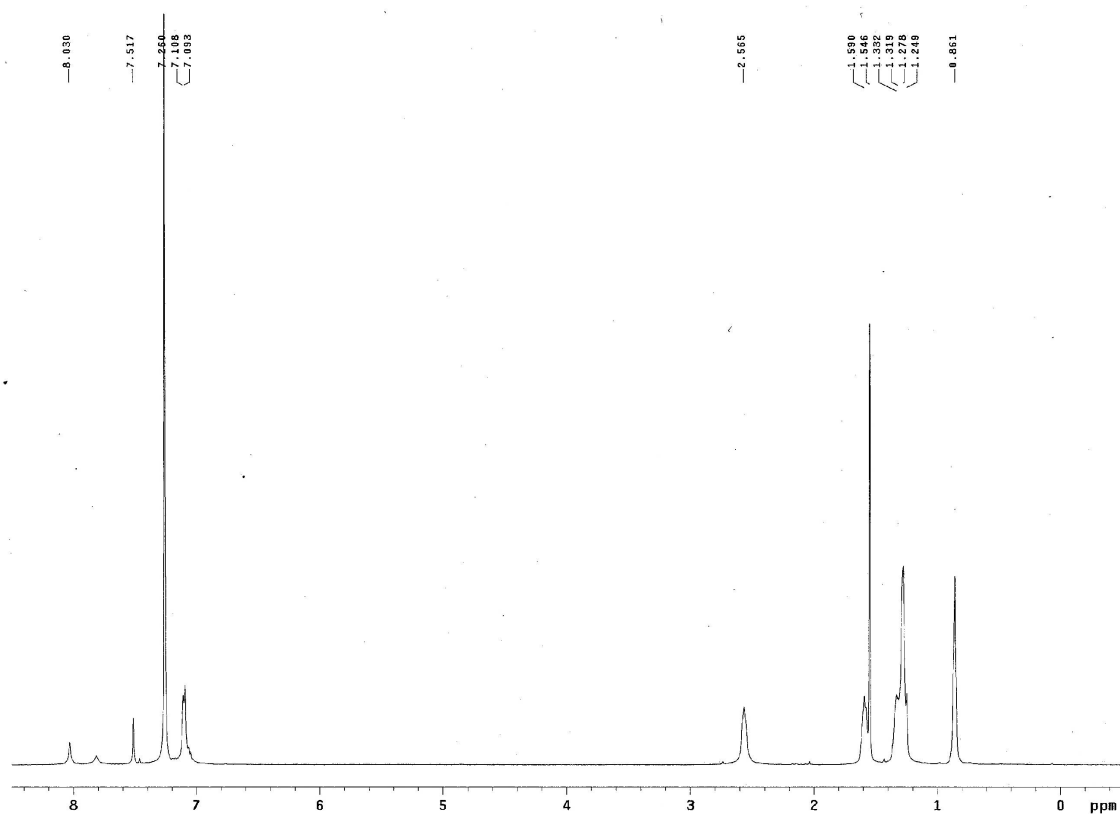


Figure S2. ¹H-NMR spectrum of *a*-PTPTBT

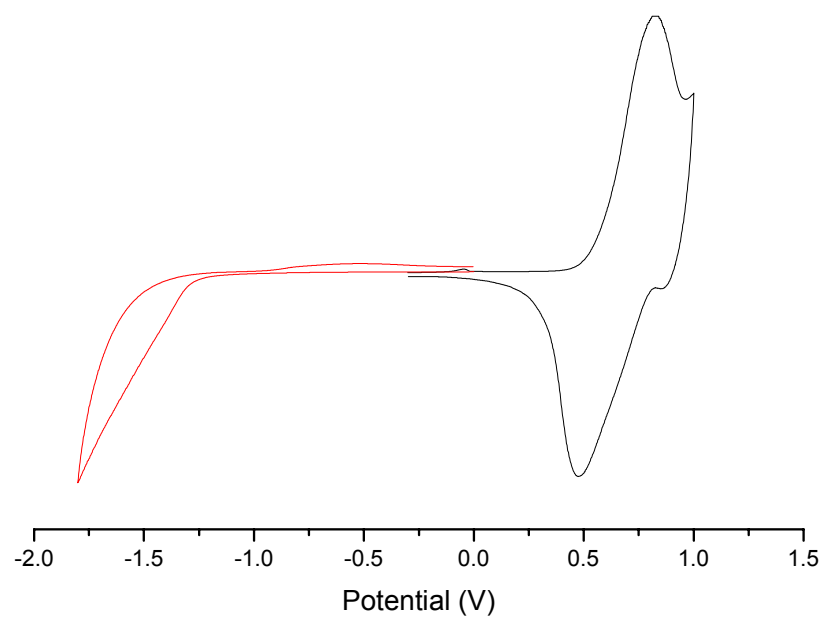


Figure S3. Cyclic voltammograms of *a*-TPTBT

Characterization of Mobility of Polymer

We fabricated hole-only devices using a high-work-function material, palladium (Pd), as the cathode to block the back injection of electrons. When a sufficient voltage is applied to this hole-only device, the transport of holes through the polymer film is limited by the space charge that accumulates. The space charge limited current (SCLC) is described by the equation

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu_h \frac{V^2}{L^3}$$

where ϵ_r is the dielectric constant of the polymer, ϵ_0 is the permittivity of free space, μ_h is the hole mobility, V is the voltage applied to the device, and L is the polymer thickness. The applied voltage was corrected for the built-in voltage (V_{BI}), which we estimated from the difference between the work function and the HOMO of polymers. The plots of $J^{0.5}$ with respect to V for the ***a*-PTPTBT** and random **PTPTBT** derived devices were straight lines; from the slope we calculated the field-independent mobility of respective devices.

Photovoltaic Cells Fabrication and Testing

All the bulk- heterojunction photovoltaic cells were prepared using the same preparation procedures and device fabrication procedure referring as following: The glass-indium tin oxide (ITO) substrates (obtained from Sanyo, Japan ($8\Omega/\square$)) were first patterned by lithograph, then cleaned with detergent, and ultrasonicated in acetone and isopropyl alcohol, and subsequently dried on hot plate at 120°C for 5 min, and finally treated with oxygen plasma for 5min. Poly(3,4-ethylene-dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, Baytron P-VP AI4083) was filtered through a $0.45\ \mu\text{m}$ filter before being deposited on ITO with a thickness around 30 nm by spin coating at 3000rpm in the air and dried at 150°C for

30 min inside glove box. The devices were fabricated using the *a*-PTPTBT concentration of 10 mg/mL, a spin rate of 1300 rpm for 30 s, and DCB as the solvent. The optimal thickness of the active layers obtained under these conditions was ~ 90-100 nm. Subsequently the device was completed by coating 30 nm thickness of Ca and an 80nm thickness of Al in $< 10^{-6}$ torr pressure respectively. The active area of the device is 5 mm². Finally the cell was encapsulated using UV-curing glue (purchased from Nagase, Japan). The fabricated device was then encapsulated using the UV-curable glue (Nagase). The fabricated device was then encapsulated using the UV-curable glue (Nagase). During the encapsulation process, the UV-glue was dispensed onto the edge of a piece of glass in the air. The UV-glue coated glass was transferred to the glove box to cover of the OPV device. The device was then sealed by pressing the UV-glue coated glass on top of the device and the device underwent UV curing (254nm) for 2mins. After encapsulation using UV-curing glue, we measured the *I-V* characteristics in air. *I-V* curves of the OPV devices were measured using a computer-controlled Keithley 2400 source measurement unit (SMU) equipped with a Peccell solar simulator under AM 1.5G illumination (100 mW cm⁻²). The illumination intensity was calibrated using a standard Si photodiode detector equipped with a KG-5 filter. The output photocurrent was adjusted to match the photocurrent of the Si reference cell to obtain a power density of 100 mW cm⁻². After encapsulation, all devices measurements were operated in an ambient atmosphere at 25 °C. The efficiency of 3.5% of a P3HT/PCBM reference cell measured under illumination in our laboratory was verified to be 3.4% under AM1.5G conditions (100 mW cm⁻²) in National Institute of Advanced Industrial Science and Technology (AIST, Japan).

Reference

1. Chan, S.-H.; Chen, C.-P.; Chao, T.-C.; Ting, C.; Ko, B.-T. *Macromolecules* **2008**, *41*, 5519.