

## Supporting Information

### Methyl Functionalization on Conjugated Side Chains for Polymer Solar Cells

#### Processed from Non-chlorinated Solvents

Chun-Hui Zhang,<sup>†a,e</sup> Fengyuan Lin,<sup>†a,c</sup> Wei Huang,<sup>†a</sup> Jingming Xin,<sup>†b</sup> Jiang Wang,<sup>a</sup> Zhichao Lin,<sup>a</sup> Wei Ma,<sup>\*b</sup> Tingbin Yang,<sup>\*a,d</sup> Jiangbin Xia,<sup>e</sup> Yongye Liang<sup>\*a</sup>

<sup>a</sup> Shenzhen Key Laboratory of Printed Electronics, Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, P. R. China. E-mail: liangyy@sustech.edu.cn

<sup>b</sup> State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-mail: msewma@xjtu.edu.cn

<sup>c</sup> State Key Laboratory of High Power Semiconductor Laser, Changchun University of Science and Technology, Changchun 130022, P.R. China

<sup>d</sup> Core Research Facilities, Southern University of Science and Technology, Shenzhen 518055, P. R. China. E-mail: yangtb@sustech.edu.cn

<sup>e</sup> College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, P.R. China

---

## Materials and methods

ITIC<sup>1</sup> was purchased from Vizuchem Co., LTD and Y6<sup>2</sup> was purchased from Derthon Co., LTD, while the derived acceptor Y6(BO) with 2-butyloctyl side chains on *N,N'*-position was prepared by a similar preparing method of Y6. All solvents used for reactions and devices fabrication were purified using a solvent purification system (Innovative Technology, Inc.) before use, except otherwise specified. PEDOT:PSS (Clevios AI4083) was obtained from NCM International. 1,2,4-Trimethylbenzene and diphenyl ether (DPE) were purchased from Sigma-Aldrich and used directly without further purification. PDINO<sup>3</sup> was synthesized according to the literature.

<sup>1</sup>H NMR spectra in CDCl<sub>3</sub> were obtained on a BRUKER AVANCE 400 system (400 MHz). GPC was performed at 170 °C on PL-GPC220 using polystyrene as the standard and 1,2,4-trichlorobenzene as the eluent. Absorption spectra were measured with a UV-Vis-NIR spectrophotometer (UV3600, Shimadzu). Cycle voltammetry (CV) measurements were carried out using an electrochemical workstation (CHI600E) to determine the ionization potential (IP) and electron affinity (EA) values of the materials. Organic films were dip-coated from chloroform solutions on a glass carbon working electrode (2 mm in diameter). CV curves were measured under an argon atmosphere in a CH<sub>3</sub>CN solution containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, with a Pt wire as the counter electrode, Ag/Ag<sup>+</sup> as the reference electrode and ferrocene as the external standard. The photoluminescence (PL) spectra was measured with a fluorescence spectrometer (FL920, Edinburgh Instrument). The thickness of the films was measured using a XP-200 Stylus profilometer (KLA Tencor). AFM images of active layers were characterized with an Asylum MFP-3D-Stand Alone microscope at tapping mode condition. TEM images were recorded on FEI Helios Nanolab 600i. The TEM samples of the blend films were prepared on copper grids and dried in a nitrogen filled glove box. GIWAXS and RSoXS measurements were performed at beamline 7.3.3 and 11.0.1.2 at the Advanced Light Source (ALS). GIWAXS samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.11°-0.15°, selected to maximize the scattering intensity from the samples.

---

The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. Samples for R-SoXS measurements were prepared on a PEDOT:PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick Si<sub>3</sub>N<sub>4</sub> membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). 2-D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-*b*-styrene-*b*-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm × 200 μm.

### **PSCs device fabrication and characterization**

PSCs were fabricated with the conventional structure: ITO/PEDOT:PSS/Active layer/PDINO/Ag. The ITO-coated glass substrates were sequentially cleaned with detergent/water, acetone, and isopropyl alcohol in an ultrasonic bath for 20 min, and then dried in an oven at 80 °C. The ITO substrates were treated in UV-Ozone for 15 min before spin-coating the top layer. The PEDOT:PSS layer was spin-coated at 3000 rpm for 30 s onto the pre-cleaned ITO substrate and annealed at 150 °C for 15 min in ambient. The active layer was spin-coated onto the substrate in glove-box. The polymer:ITIC PSCs were processed from toluene with 1% (v/v) DPE as the additive and the total concentration is 16 mg mL<sup>-1</sup>. The PMT49:Y6 PSCs were processed from chloroform with 0.5% (v/v) chloronaphthalene as the additive and the total concentration is 16 mg mL<sup>-1</sup>. The PMT50:Y6(BO) and PEHTT:Y6(BO) PSCs were processed from 1,2,4-trimethylbenzene with 0.5% (v/v) chloronaphthalene as the additive at 2500 rpm and the total concentration is 30 mg mL<sup>-1</sup>. The TMB solution was stirred at 85 °C for 5h before spin-coating. The thickness of the active layer is controlled to be about 100 nm. The PDINO layer that serves as an electron transport layer is spin-coated from ethanol solution (1 mg mL<sup>-1</sup>) at 3000 rpm. Finally, the Ag electrode with a thickness of about 100 nm is thermally evaporated under vacuum at a pressure of 1 × 10<sup>-6</sup> mbar, with a device effective area of 0.045 cm<sup>2</sup>.

---

The  $J$ - $V$  curves of the devices were measured under AM1.5G solar simulator illumination ( $100 \text{ mW cm}^{-2}$ , Enlitech) on a computer-controlled Keithley 2400 Source Measure Unit. The external quantum efficiency (EQE) data were obtained on QE-R3011 (Enlitech).

### **Hole-only and electron-only devices**

The device architecture for hole-only devices was ITO/PEDOT:PSS/Active layer/MoO<sub>3</sub>/Ag and the architecture for electron-only devices was ITO/ZnO/Active layer/PDINO/Ag. The hole transport layer and electron transport layer were prepared as the same in PSCs fabrication procedure, and MoO<sub>3</sub> serving as electron blocking layer was thermally evaporated before Ag.

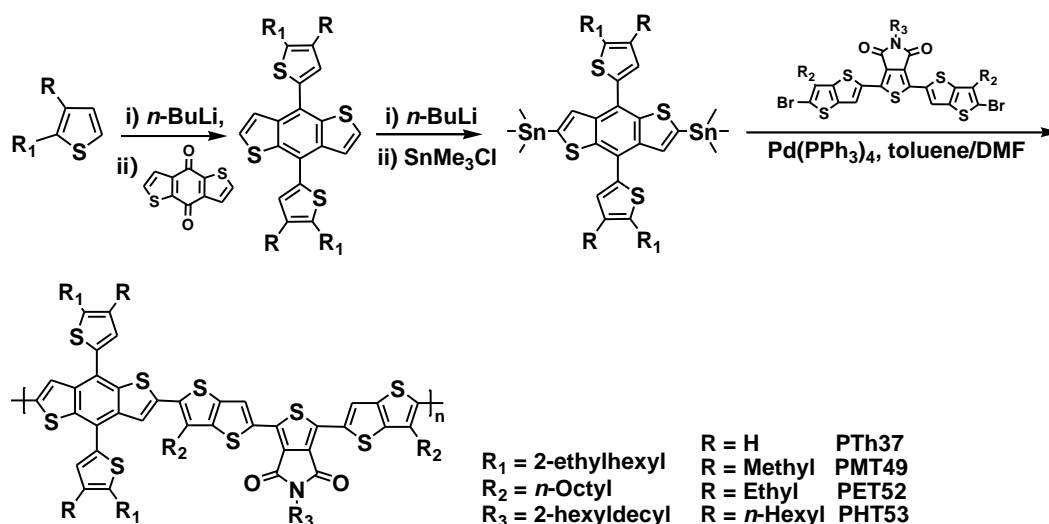
The hole-only device and electron-only devices were measured using a computer-controlled Keithley 2400 Source Measure Unit. And the charge mobility was determined by fitting the  $J$ - $V$  curves to the space-charge-limited current (SCLC) mode, described by equation below:

$$J = (9/8)\epsilon_0\epsilon_r\mu V^2/L^3$$

where  $J$  is the current density,  $L$  is the thickness of the active layer,  $\mu$  is the charge mobility,  $\epsilon_r$  is the relative dielectric constant and assumed to be 3,  $\epsilon_0$  is the permittivity ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ ), and  $V$  is the voltage drop across the device.

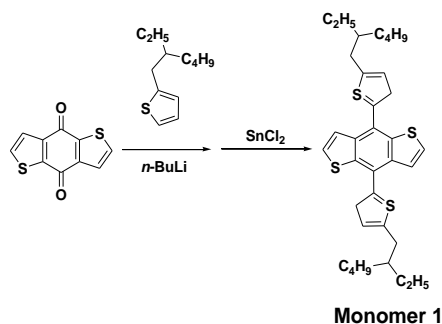
### **Materials synthesis**

---



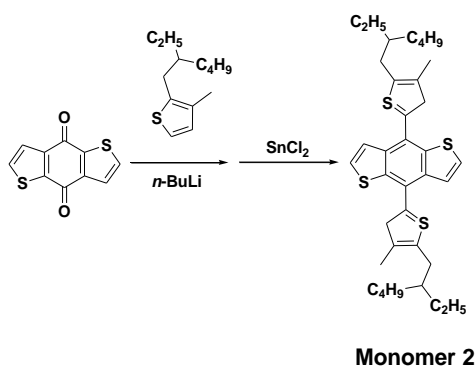
Scheme S1. Synthetic route to PTh37, PMT49, PET52 and PHT53.

#### 4,8-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (Monomer 1)



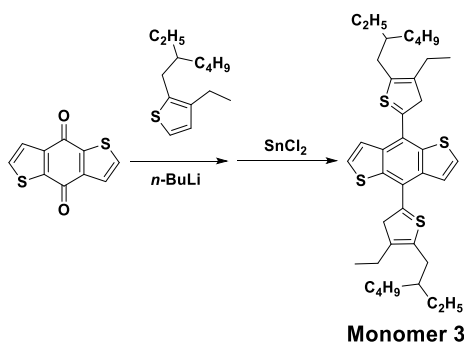
Monomer (1) was prepared according to the literature <sup>[4-6]</sup>. Yield: 78.6%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.63 (d, 2H), 7.45 (d, 2H), 7.26 (d, 2H), 6.87 (d, 2H), 2.83(d, 4H), 1.66 (m, 2H), 1.45-1.28 (br, 16H), 0.96-0.88 (m, 12H).

#### 4,8-(5-(2-ethylhexyl)-4-methylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (Monomer 2)



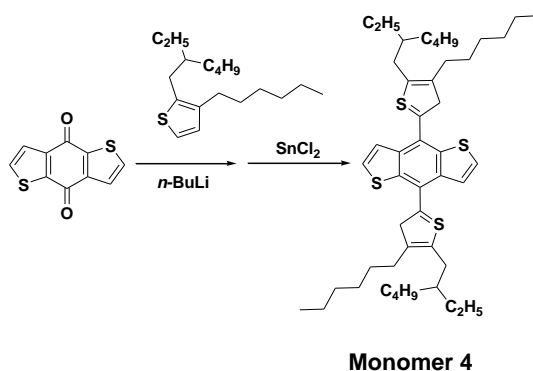
Monomer (2) was prepared in a similar method of monomer (1) but replacing 2-(2-ethylhexyl)thiophene with 2-(2-ethylhexyl)-3-methylthiophene. Yield: 62.3%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.67 (d, 2H), 7.44 (d, 2H), 7.16 (s, 2H), 2.75 (d, 4H), 2.26 (s, 6H), 1.64–1.69 (m, 2H), 1.27–1.48 (m, 16H), 0.93–0.97 (m, 12H).

#### 4,8-(4-ethyl-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (Monomer 3)



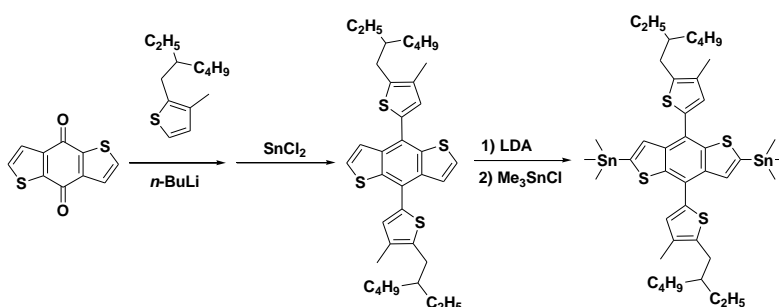
Monomer (3) was prepared in a similar method of monomer (1) but replacing 2-(2-ethylhexyl)thiophene with 3-ethyl-2-(2-ethylhexyl)thiophene. Yield: 62.3%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.67 (d, 2H), 7.45 (d, 2H), 7.18 (s, 2H), 2.75 (d, 4H), 2.42 (t, 4H), 1.60–1.70 (m, 6H), 1.25–1.55 (m, 28H), 0.90–0.98 (m, 18H).

#### 4,8-(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (Monomer 4)



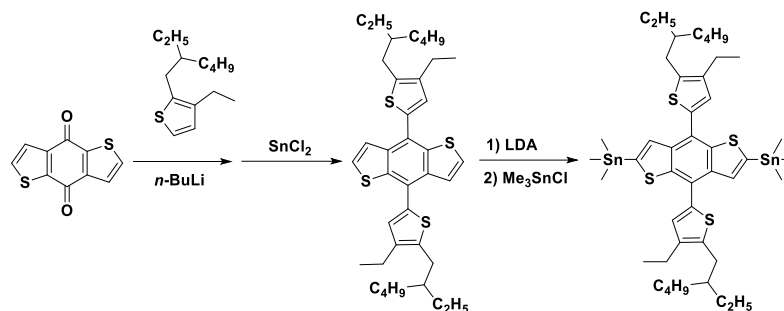
Monomer (4) was prepared in a similar method of monomer (1) but replacing 2-(2-ethylhexyl)thiophene with 2-(2-ethylhexyl)-3-hexylthiophene. Yield: 56.8%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.68 (d, 2H), 7.44 (d, 2H), 7.22 (s, 2H), 2.75 (d, 4H), 2.60 (t, 4H), 1.62–1.67 (m, 6H), 1.27–1.51 (m, 28H), 0.88–0.98 (m, 18H).

**4,8-(5-(2-ethylhexyl)-4-methylthiophen-2-yl)-(2,6-(trimethyltin))benzo[1,2-*b*:4,5-*b'*]dithiophene**  
e



4,8-(5-(2-ethylhexyl)-4-methylthiophen-2-yl)-(2,6-(trimethyltin))benzo[1,2-*b*:4,5-*b'*]dithiophene was prepared in a similar method of (4,8-bis(5-(2-ethylhexyl)-4-methoxythiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) <sup>[4]</sup> but replacing 2-(2-ethylhexyl)-3-methoxythiophene with 2-(2-ethylhexyl)-3-methylthiophene. Yield: 85.3%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.74 (s, 2H), 7.27 (s, 2H), 2.78-2.75 (m, 4H), 2.68-2.62 (t, 4H), 1.71-1.65 (m, 2H), 1.48–1.27 (m, 22H), 0.98–0.90 (m, 12H), 0.40 (s, 18H).

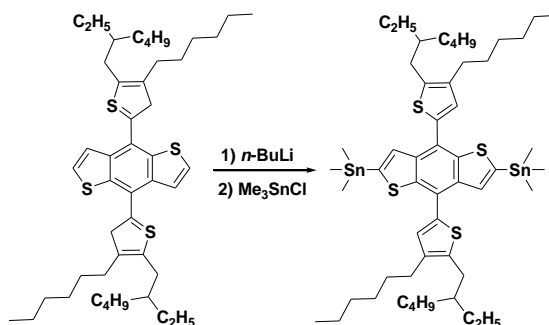
**4,8-(4-ethyl-5-(2-ethylhexyl)thiophen-2-yl)-(2,6-(trimethyltin))benzo[1,2-*b*:4,5-*b'*]dithiophene**



4,8-(4-ethyl-5-(2-ethylhexyl)thiophen-2-yl)-(2,6-(trimethyltin))benzo[1,2-*b*:4,5-*b'*] was prepared in a similar method of

(4,8-bis(5-(2-ethylhexyl)-4-methoxythiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane)<sup>[4]</sup> but replacing 2-(2-ethylhexyl)-3-methoxythiophene with 3-ethyl-2-(2-ethylhexyl)thiophene. Yield: 73.6%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.74 (s, 2H), 7.27 (s, 2H), 2.78-2.75 (m, 4H), 2.68-2.62 (t, 4H), 1.71-1.65 (m, 2H), 1.48-1.27 (m, 22H), 0.98-0.90 (m, 12H), 0.40 (s, 18H).

#### 4,8-(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)-(2,6-(trimethyltin))benzo[1,2-*b*:4,5-*b'*]dithiophene



4,8-(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)-(2,6-(trimethyltin))benzo[1,2-*b*:4,5-*b'*]dithiophene was prepared with a similar method as for monomer (5) but replacing 2-(2-ethylhexyl)-3-methoxythiophene with 2-(2-ethylhexyl)-3-hexylthiophene. Yield: 70.2%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.73 (t, 2H), 7.23 (s, 2H), 2.71-2.81 (m, 4H), 2.62 (t, 3 J = 7.2 Hz, 4H), 1.63-1.71 (m, 6H), 1.27-1.49 (m, 28H), 0.90-0.97 (m, 18H), 0.40 (t, 18H).



PTh37 was synthesized according to our previous work. Yield: 86.8%.  $M_n$ : 30.1 kDa; PDI: 2.03.

### **PMT49**

Into a 25 mL pre-dried flask, 4,8-(5-(2-ethylhexyl)-4-methylthiophen-2-yl)-(2,6-(trimethyltin))benzo[1,2-*b*:4,5-*b'*]dithiophene (154.9 mg, 0.1661 mmol), Br<sub>2</sub>-tt-TPD (172.1 mg, 0.1661 mmol) was first dissolved in degassed toluene (3.3 mL) and dry DMF (0.33 ml), then Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mg, 0.0043 mmol) was added under argon atmosphere. The mixture was reacted at 120 °C for 12 hours. The crude product was collected by precipitating from MeOH. The solid was then rinsed in a Soxhlet extractor with MeOH, acetone, hexane and chloroform successively. The solution in chloroform was concentrated, and then precipitated in MeOH. After drying at a reduced pressure, 238 mg of the polymer was obtained. Yield: 96.6%.  $M_n$ : 43.5 kDa; PDI: 1.95.

### **PET52**

PET52 was prepared with a similar procedure as for PMT49 using 4,8-(4-ethyl-5-(2-ethylhexyl)thiophen-2-yl)-(2,6-(trimethyltin))benzo[1,2-*b*:4,5-*b'*] (156.9 mg, 0.1633 mmol), Br<sub>2</sub>-tt-TPD (169.2 mg, 0.1633 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (4.9 mg, 0.0042 mmol) in degassed toluene (3.2 ml) and dry DMF (0.32 ml). 220 mg of the polymer was obtained. Yield: 89.2%.  $M_n$ : 49.7 kDa; PDI: 1.96.

### **PHT53**

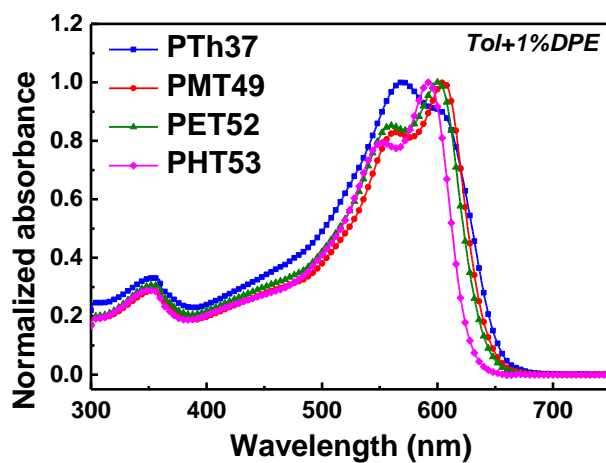
PHT53 was prepared with a similar procedure as for PMT49 using 4,8-(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)-(2,6-(trimethyltin))benzo[1,2-*b*:4,5-*b'*]dithiophene (152.3 mg, 0.1463 mmol), Br<sub>2</sub>-tt-TPD (146.9mg, 0.1418 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (4.8 mg, 0.0042 mmol) in degassed toluene (2.8 ml) and dry DMF (0.28 ml). 199 mg of the polymer was obtained. Yield: 86.5%.  $M_n$ : 91.5 kDa; PDI: 2.07.

---

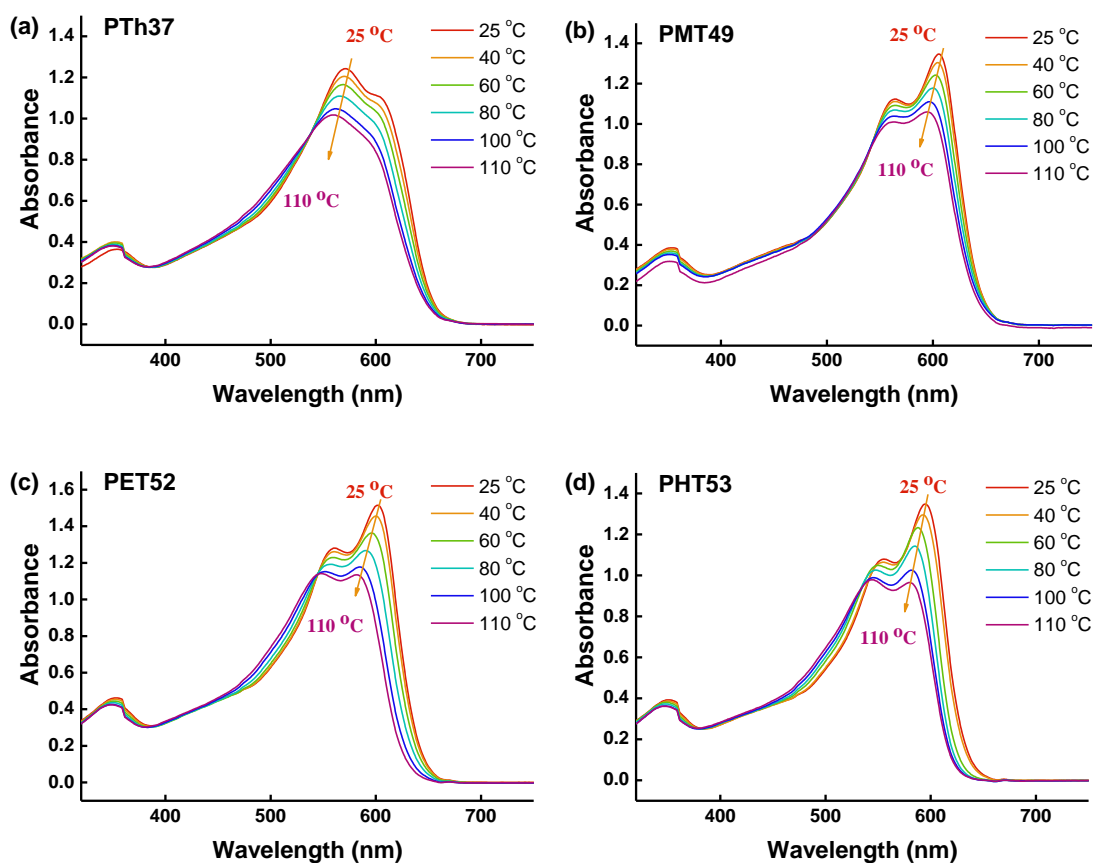
## **PMT50**

PMT50 was prepared with a similar procedure as for PEHTT<sup>7</sup> but replacing 2-(2-ethylhexylthio)thiophene with 2-(2-ethylhexylthio)-3-methylthiophene. The molecular weight of PMT50 was determined by GPC and found to be 31.6k/1.85 ( $M_n$ /PDI), versus 24.2k/2.18 for PEHTT.

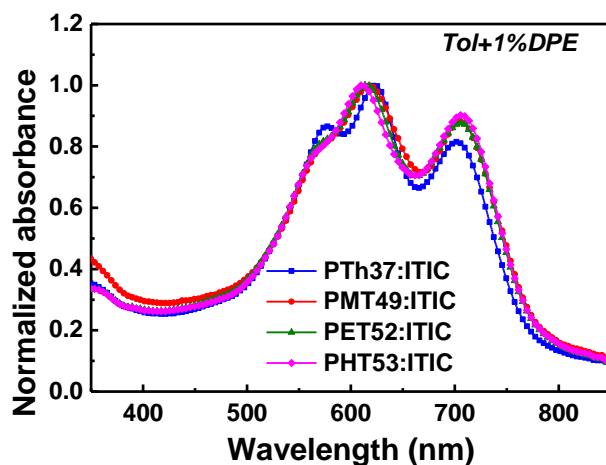
---



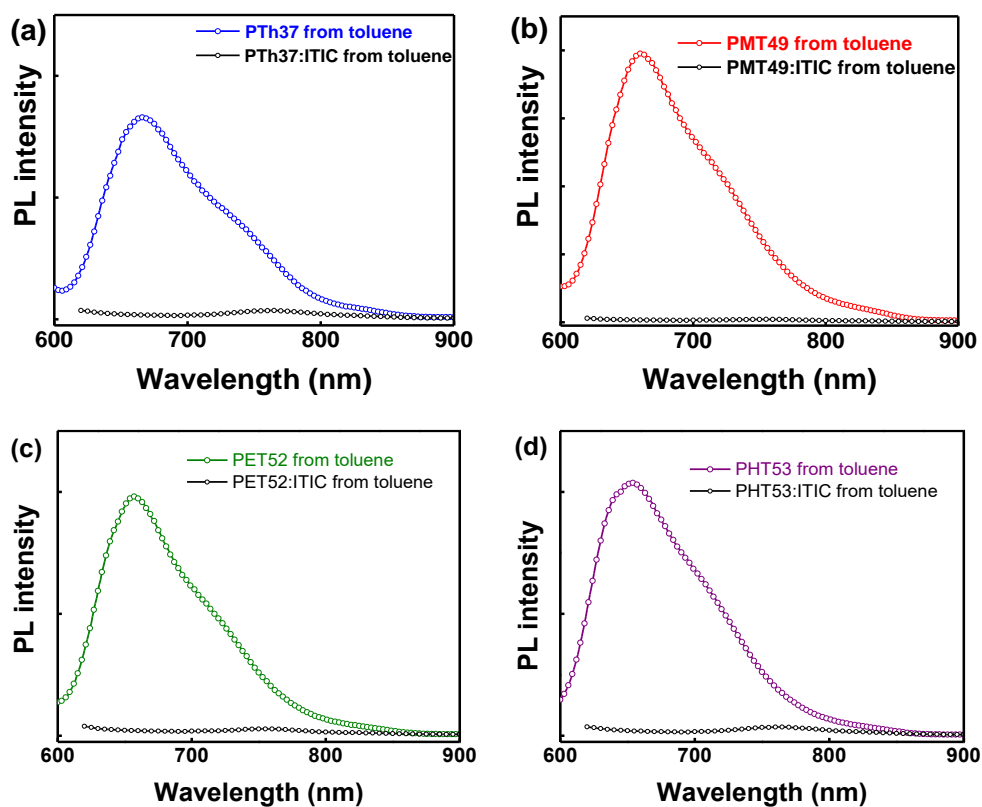
**Fig. S1** Normalized absorption spectra of PTh37, PMT49, PET52, PHT53 in toluene.



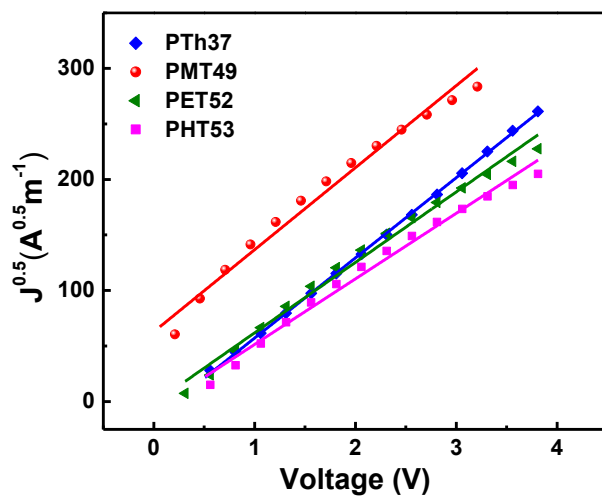
**Fig. S2** Temperature-dependent UV-Vis absorption spectra for PTh37, PMT49, PET52 and PHT53, measured from dilute toluene solutions.



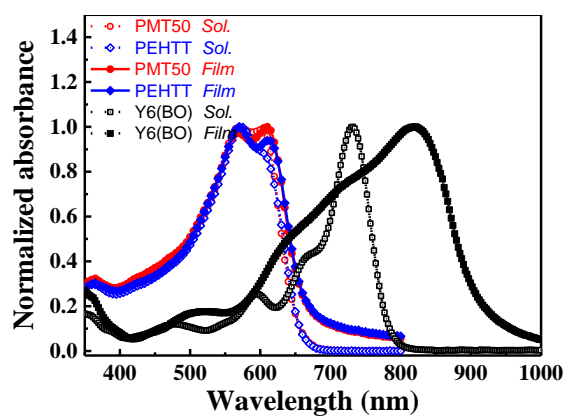
**Fig. S3** UV-vis absorption spectra of PTh37:ITIC, PMT49:ITIC, PET52:ITIC, and PHT53:ITIC processed from toluene.



**Fig. S4** PL spectra for PTh37:ITIC (a), PMT49:ITIC (b), PET52:ITIC (c) and PHT53:ITIC (d).



**Fig. S5**  $J^{0.5}$ - $V$  plots for hole-only devices based on pristine polymer films.



**Fig. S6** Normalized UV-Vis absorption spectra of pristine PMT50, PEHTT and Y6(BO) in dilute TMB solution and film spin-coated from TMB solutions.

**Table S1** Summary of device parameters of the conventional polymer solar cells based on PMT49:Y6 (1:1.2, w/w), under AM1.5G solar radiation ( $100 \text{ mW cm}^{-2}$ ).

Concentration ( $\text{mg mL}^{-1}$ )	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE <sup>a</sup> (%)
<b>16</b>	<b>0.810</b>	<b>24.99</b>	<b>70.3</b>	<b>14.2</b>
	<b>[0.810±0.01]</b>	<b>[25.06±1.25]</b>	<b>[69.6±0.9]</b>	<b>[14.1±0.21]</b>
14	0.810	24.83	68.0	13.6
	[0.810±0.01]	[24.56±0.95]	[67.8±0.5]	[13.4±0.18]
12	0.807	23.16	68.3	12.8
	[0.810±0.01]	[23.06±0.86]	[68.1±0.6]	[12.6±0.32]

<sup>a</sup> Average data in brackets were obtained from 10 devices.

## References

- 1 Y. Lin, J. Wang, Z.-G. Zhang, H. Bai, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2015, **27**, 1170–1174.
- 2 J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li and Y. Zou, *Joule*, 2019, **3**, 1140–1151.
- 3 Z. Zhang, B. Qi, Z. Jin, D. Chi, Z. Qi, Y. Li and J. Wang, *Energy Environ. Sci.*, 2014, **7**, 1966–1973.
- 4 F. Lin, W. Huang, H. Sun, J. Xin, H. Zeng, T. Yang, M. Li, X. Zhang, W. Ma and Y. Liang, *Chem. Mater.*, 2017, **29**, 5636–5645.
- 5 W. Huang, M. Li, F. Lin, Y. Wu, Z. Ke, X. Zhang, R. Ma, T. Yang, W. Ma and Y. Liang, *Mol. Syst. Des. Eng.*, 2018, **3**, 103–112.
- 6 W. Huang, M. Li, L. Zhang, T. Yang, Z. Zhang, H. Zeng, X. Zhang, L. Dang and Y. Liang, *Chem. Mater.*, 2016, **28**, 5887–5895.
- 7 C.-H. Zhang, W. Wang, W. Huang, J. Wang, Z. Hu, Z. Lin, T. Yang, F. Lin, Y. Xing, J. Bai, H. Sun and Y. Liang, *Chem. Mater.*, 2019, **31**, 3025–3033.