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# Modified Structure of Two-Dimensional Polythiophene Derivatives by Incorporating Electron-Deficient Units into Terthiophene-Vinylene Conjugated Side Chains and Polymer Backbone: Synthesis, Optoelectronic and Self Assembly Properties, and Photovoltaic Application

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- <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of M2
- © Conditions and results (GPC) for microwave-assisted Stille polymerization of P1.
- PESA spectrum of polymer films
- © Two-dimensional grazing incidence X-ray diffraction (GIXRD) of pristine polymer thin film.
- Dark *J-V* curves of polymer/PC<sub>61</sub>BM devices.

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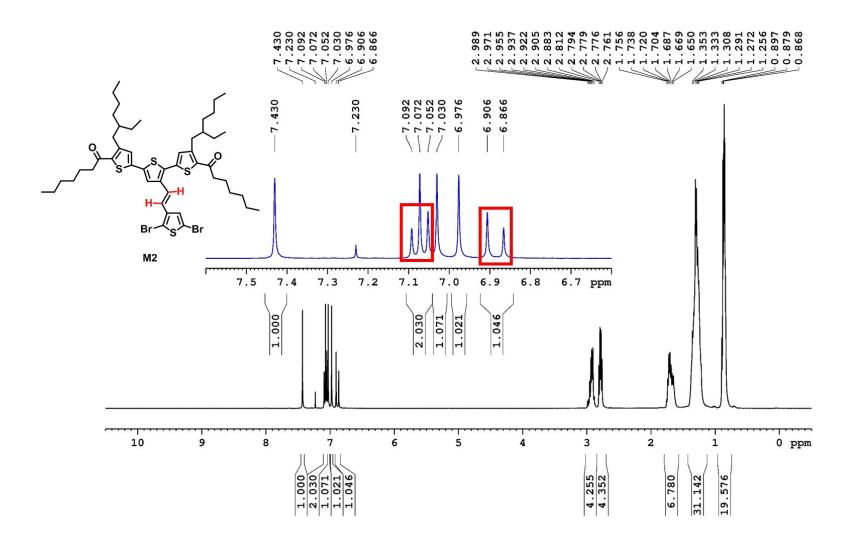
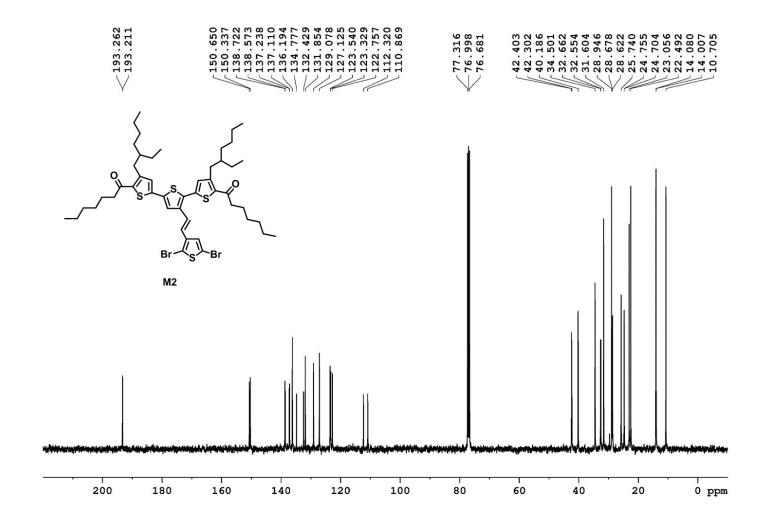


Figure S1. <sup>1</sup>H-NMR spectrum of compound M2



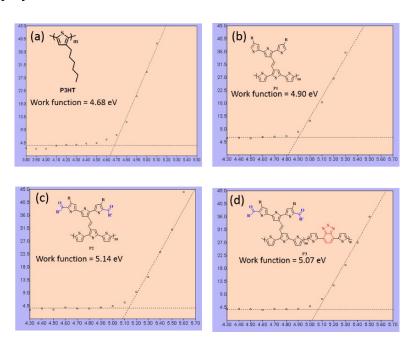
**Figure S2.** <sup>13</sup>C-NMR spectrum of compound **M2** 

**Table S1.** Conditions and results (GPC) for microwave-assisted Stille polymerization of P1.

Entry	Solvent	Concentration (M)	Catalysta	Conditionb	Mn (kDa)c	PDI
1	Toluene	0.01	A, 5 mol%	1	5.2e	1.85
2	Toluene	0.01	A, 5 mol%	2	9.5	2.32
3	Toluene	0.05	A, 5 mol%	1	11.0	2.61
4	Toluene	0.05	A, 3 mol%	1	12.0	2.58
5	Toluene	0.05	A, 1 mol%	1	13.2	2.59
6	Toluene	0.05	B, 5 mol%	1	10.0	4.33
7	<i>p</i> -xylene	0.05	A, 3 mol%	2	14.0	2.36
8	<i>p</i> -xylene	0.05	B, 3 mol%	2	14.0	4.61
9	<i>p</i> -xylene	0.05	A, 3 mol%	3	12.1	2.60
10 <sup>d</sup>	Toluene	0.01	A, 5 mol%	4	12.0	3.61

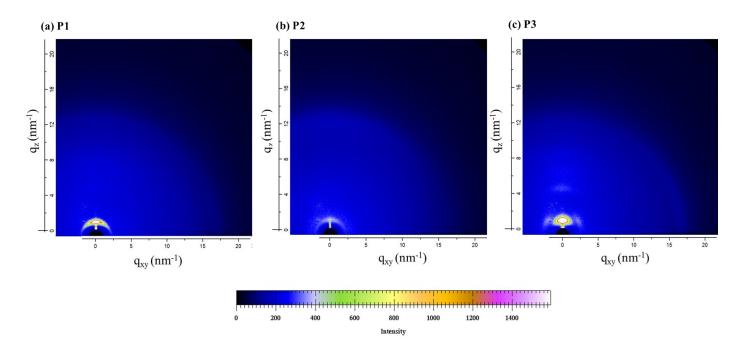
<sup>a</sup>A: Pd(PPh<sub>3</sub>)<sub>4</sub>; B: Pd<sub>2</sub>dba<sub>3</sub>, P(*o*-tol)<sub>3</sub>; <sup>b</sup>Condition (1) raise temperature from r.t. to 200 °C as fast as possible; hold the temperature 30 min; cool down to 55 °C. Condition (2) raise temperature from r.t. to 200 °C as fast as possible; hold the temperature 60 min; cool down to 55 °C. Condition (3) raise temperature from r.t. to 250 °C as fast as possible; hold the temperature 30 min; cool down to 55 °C. Condition (4) reflux 2 days. °Soxhlet extractions by using methanol and hexane quickly to remove the small molecules and oligomers and finally chloroform to obtain the target compounds for optimizing polymerization conditions. M<sub>n</sub> and PDI of the polymers were estimated by GPC using polystyrene as standards in THF. <sup>d</sup>conventional heating. °Soxhlet extractions by only using methanol to remove impurity and chloroform to obtain the target polymer.

# © PESA spectrum of polymer films



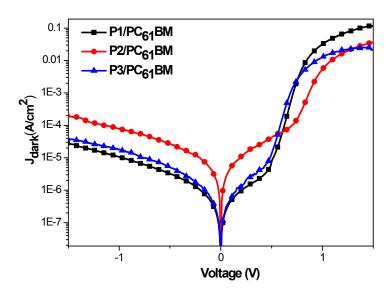
**Figure S3.** PESA spectrum of (a) **P3HT**; (b) **P1**; (c) **P2**; (d) **P3** film prepared by spin-coating followed by thermal annealing at 120°C for 15 min and measured under identical condition.

© Two-dimensional grazing incidence X-ray diffraction (GIXRD) of pristine polymer thin film.



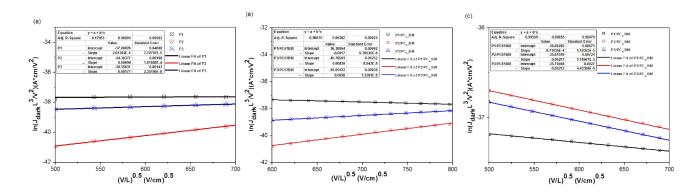
**Figure S4.** Two-dimensional grazing incidence X-ray diffraction (GIXRD) from thin films of (a) **P1**; (b) **P2**; (c) **P3** prepared by drop-cast followed by thermal annealing at 120°C for 15 min and measured under identical condition.

○ Dark *J-V* curves of polymer/PC<sub>61</sub>BM devices.



**Figure S5.** Dark J-V curves of polymer/PC<sub>61</sub>BM devices.

# ◎ Mobility of polymer with/without PC<sub>61</sub>BM.

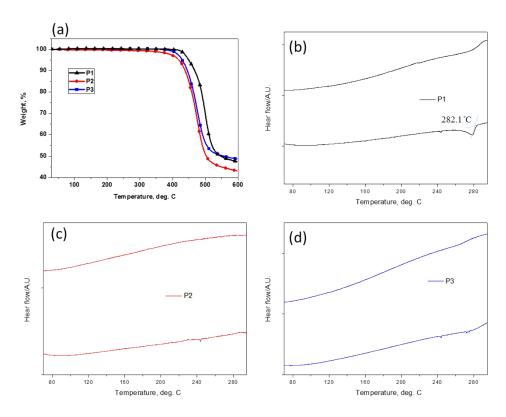


**Figure S6.**  $ln(J_{dark}L^3V^{-2})$  versus  $(VL^{-1})^{0.5}$  plots of (a) the pristine polymers for the measurement of hole mobility; the polymers blend  $PC_{61}BM$  for the measurement of (b) hole and (c) electron mobility by the SCLC method.

**Table S2.** Mobility of **P1**, **P2** and **P3** with/without PC<sub>61</sub>BM by the SCLC method.

	Pristine polymer hole mobility (cm^2/(V*sec))	Blend with PC <sub>61</sub> BM hole mobility (cm^2/(V*sec))	Blend with PC <sub>61</sub> BM electron mobility (cm^2/(V*sec))	h+/e-
P1	3.9×10 <sup>-4</sup>	2.1*10-4	2.5*10-4	0.84
P2	3.8×10 <sup>-5</sup>	1.1x10-6	3.5x10-4	0.003
Р3	1.0×10 <sup>-4</sup>	8.4x10-5	3.3x10-4	0.25

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**Figure S7.** (a) TGA and (b-d) DSC second heating profiles of **P1**, **P2**, and **P3** with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere and a cooling rate of 10 °C/min.