Electronic Supplementary Material (ESI) for RSC Advances.

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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Contents for Supporting Information:

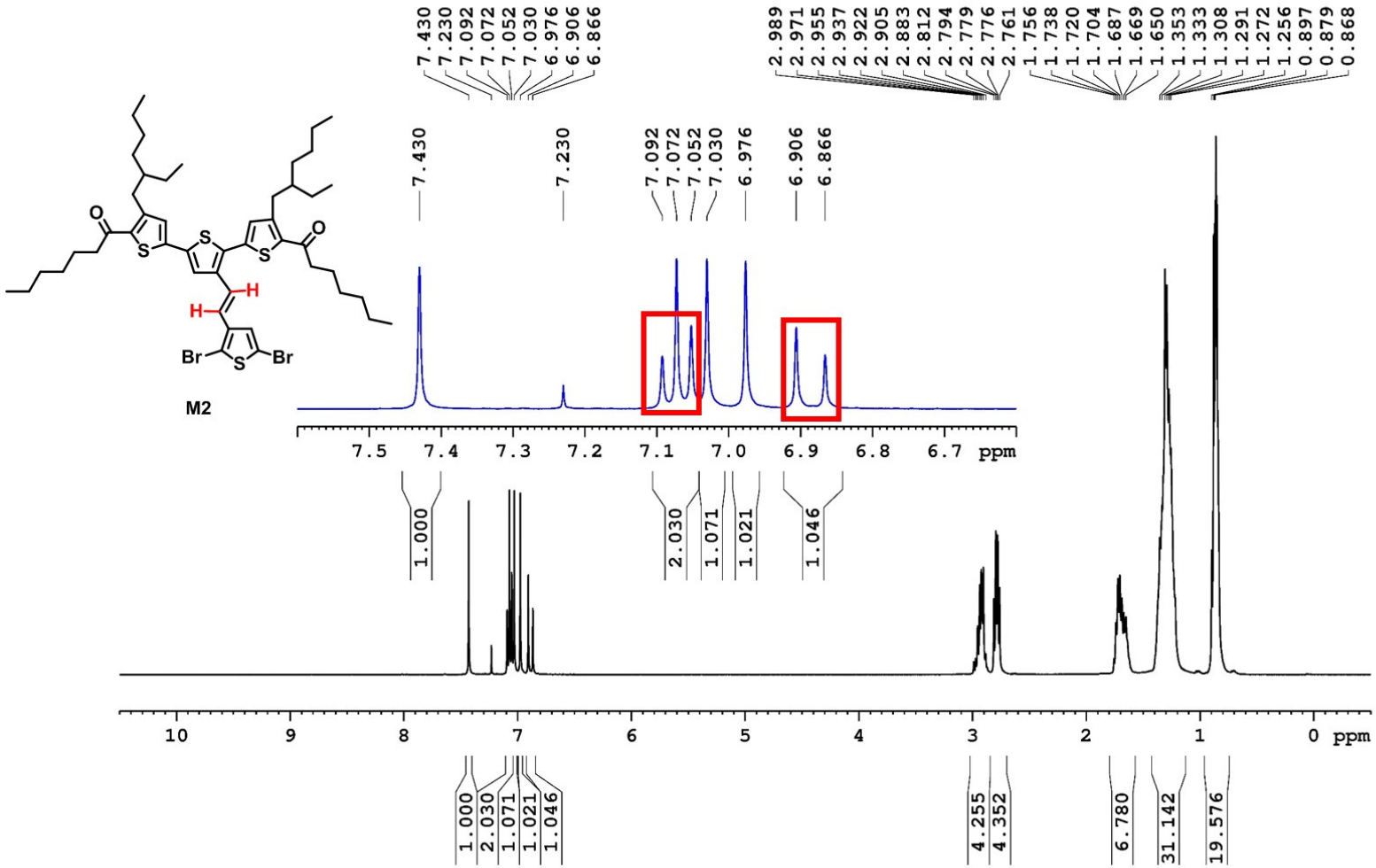

Figure S1. ^{1}H-NMR spectrum of compound **M2**

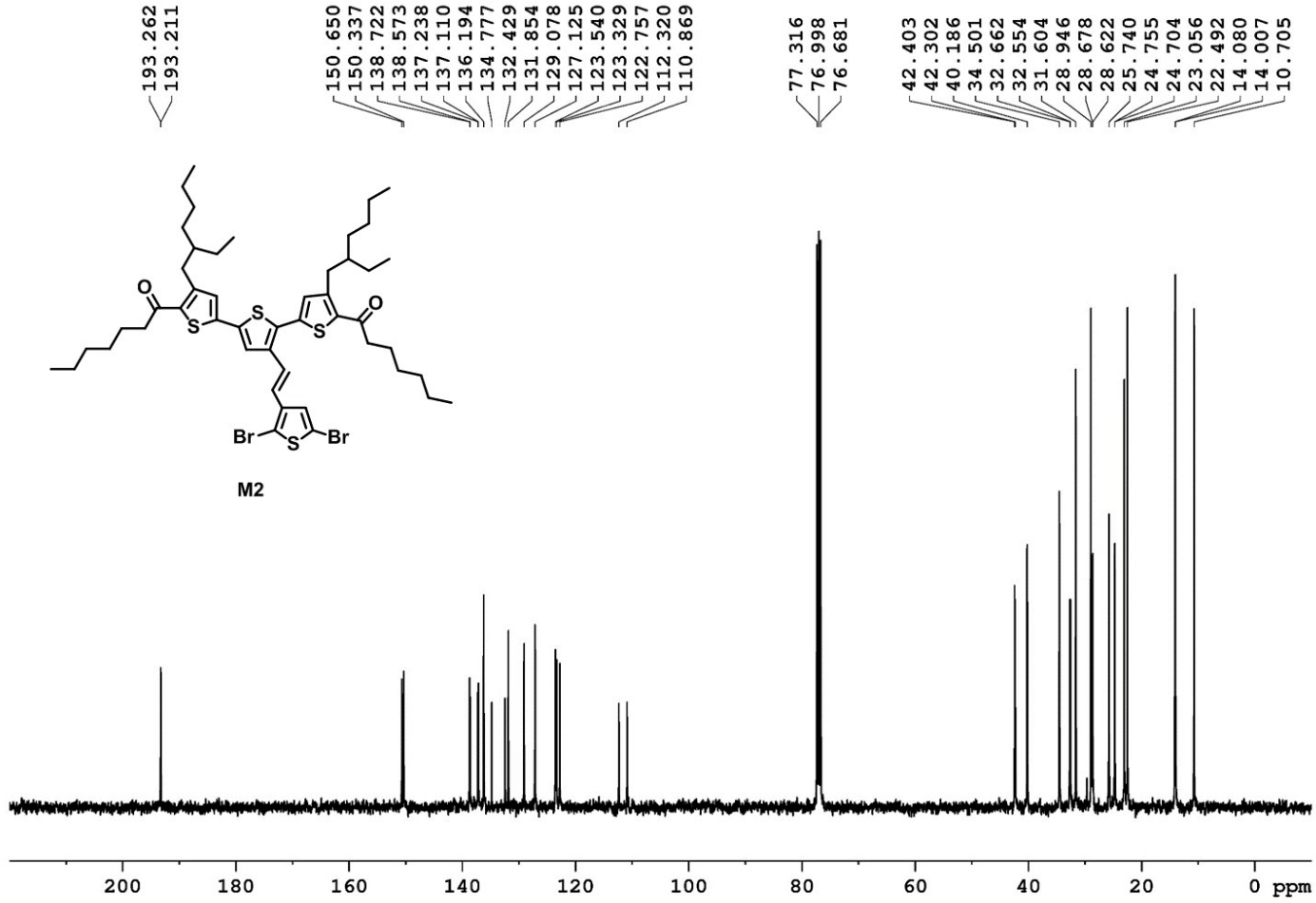

Figure S2. ^{13}C-NMR spectrum of compound **M2**

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

Entry	Solvent	Concentration (M)	Catalyst[a]	Condition[b]	Mn (kDa)[c]	PDI
1	Toluene	0.01	A, 5 mol%	1	5.2[e]	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	*p*-xylene	0.05	A, 3 mol%	2	14.0	2.36
8	***p*-xylene**	**0.05**	**B, 3 mol%**	**2**	**14.0**	**4.61**
9	*p*-xylene	0.05	A, 3 mol%	3	12.1	2.60
10[d]	Toluene	0.01	A, 5 mol%	4	12.0	3.61

[a]A：$Pd(PPh_3)_4$; B：Pd_2dba_3, P(*o*-tol)$_3$; [b]**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. [c]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_n and PDI of the polymers were estimated by GPC using polystyrene as standards in THF. [d]conventional heating. [e]Soxhlet extractions by only using methanol to remove impurity and chloroform to obtain the target polymer.

◎ PESA spectrum of polymer films

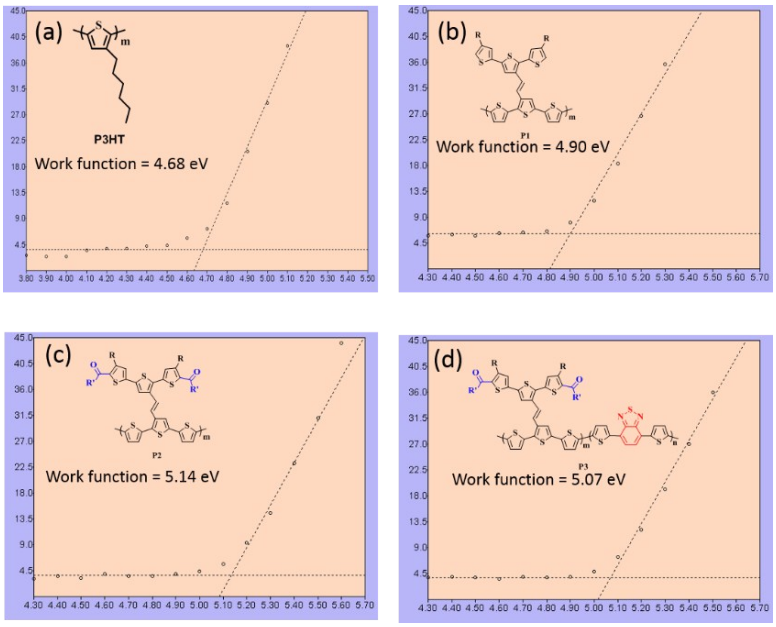

Figure S3. PESA spectrum of (a**) P3HT**; (b**) P1**; (c**) P2**; (d) **P3** film prepared by spin-coating followed by thermal annealing at 120°C for 15 min and measured under identical condition.

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

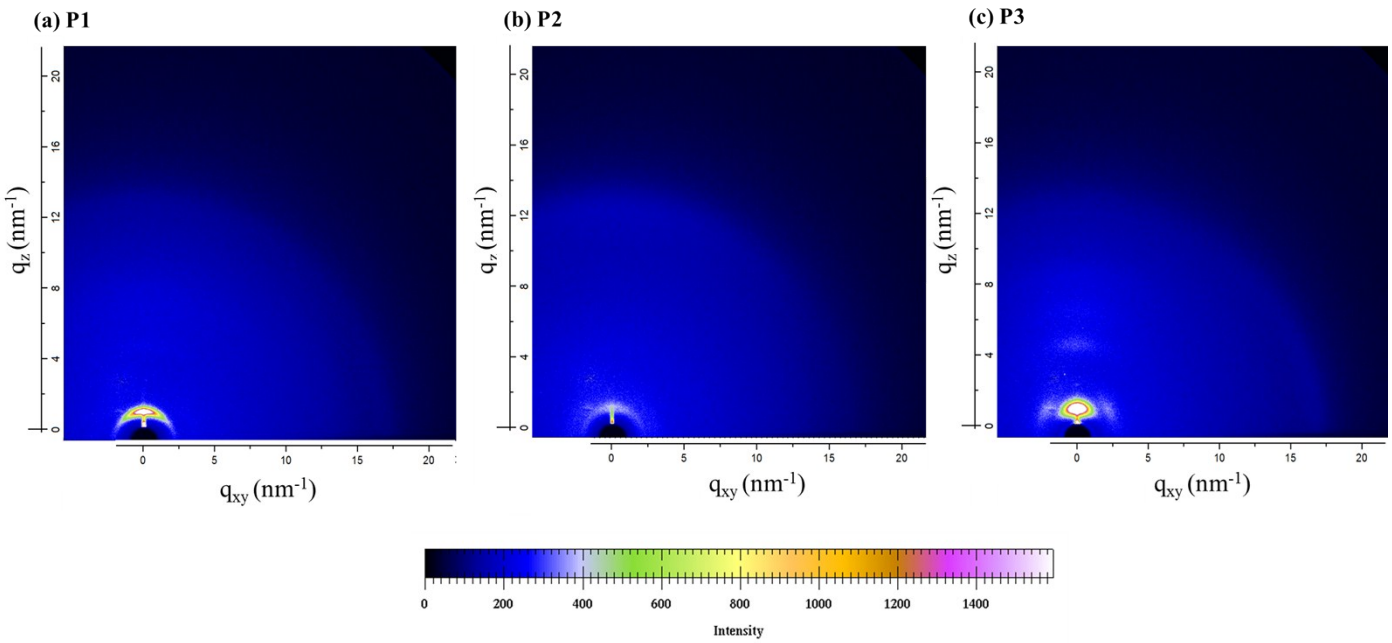

Figure S4. Two-dimensional grazing incidence X-ray diffraction (GIXRD) from thin films of (a) **P1**; (b) **P2**; (c) **P3** prepared by drop-cast followed by thermal annealing at 120°C for 15 min and measured under identical condition.

◎ Dark *J*-*V* curves of polymer/$PC_{61}BM$ devices.

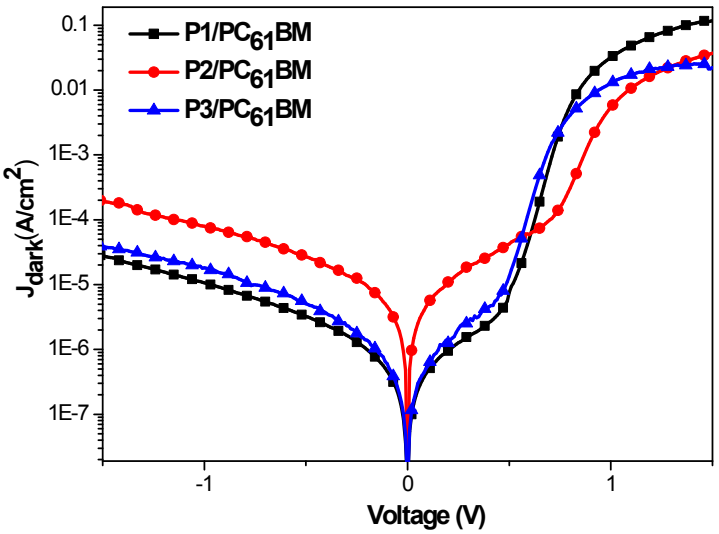

Figure S5. Dark *J*-*V* curves of polymer/$PC_{61}BM$ devices.

◎ Mobility of polymer with/without $PC_{61}BM$.

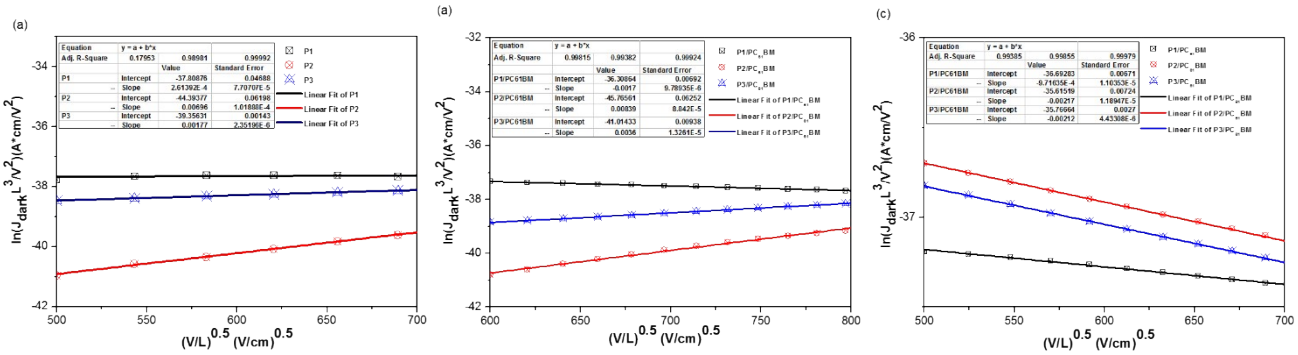

Figure S6. $\ln(J_{dark}L^3V^{-2})$ versus $(VL^{-1})^{0.5}$ plots of (a) the pristine polymers for the measurement of hole mobility; the polymers blend $PC_{61}BM$ for the measurement of (b) hole and (c) electron mobility by the SCLC method.

Table S2. Mobility of **P1**, **P2** and **P3** with/without $PC_{61}BM$ by the SCLC method.

	Pristine polymer hole mobility (cm^2/(V*sec))	**Blend with $PC_{61}BM$ hole mobility** (cm^2/(V*sec))	**Blend with $PC_{61}BM$ electron mobility** (cm^2/(V*sec))	h^+/e^-
P1	3.9×10^{-4}	2.1*10-4	2.5*10-4	0.84
P2	3.8×10^{-5}	1.1x10-6	3.5x10-4	0.003
P3	1.0×10^{-4}	8.4x10-5	3.3x10-4	0.25

◎ TGA and DSC.

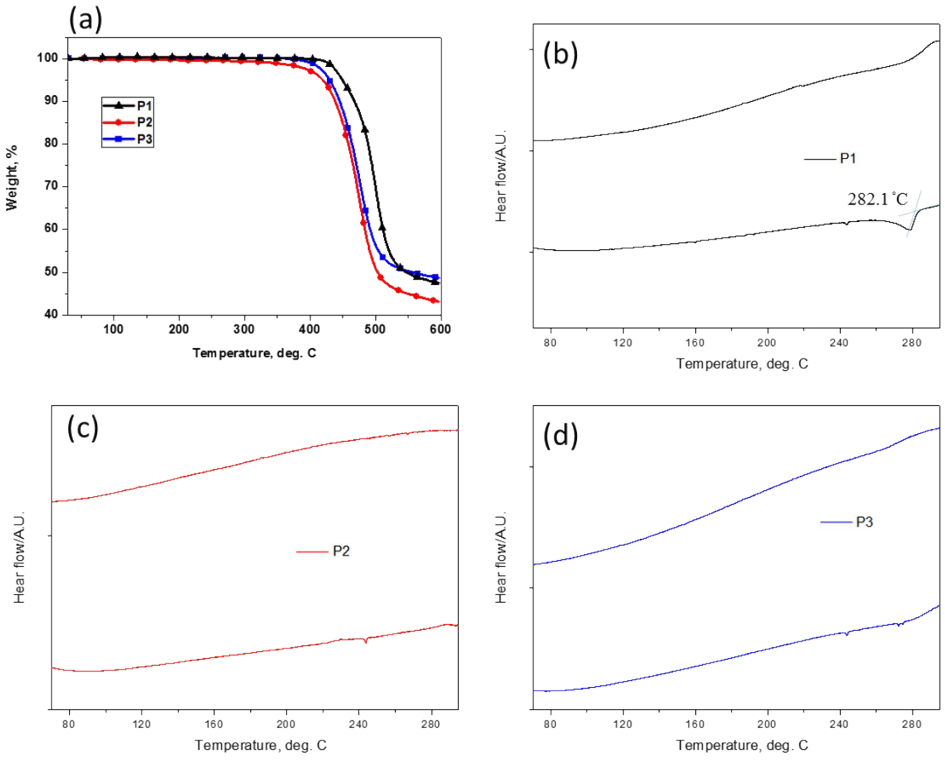

Figure S7. (a) TGA and (b-d) DSC second heating profiles of **P1**, **P2**, and **P3** with a heating rate of 10 °C/min under N_2 atmosphere and a cooling rate of 10 °C/min.