Supporting Information for

Trifluoromethylated thieno[3,4-*b*]thiophene-2-ethyl carboxylate as building block for conjugated polymers

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Contents

1. TGA and DSC thermograms of polymers

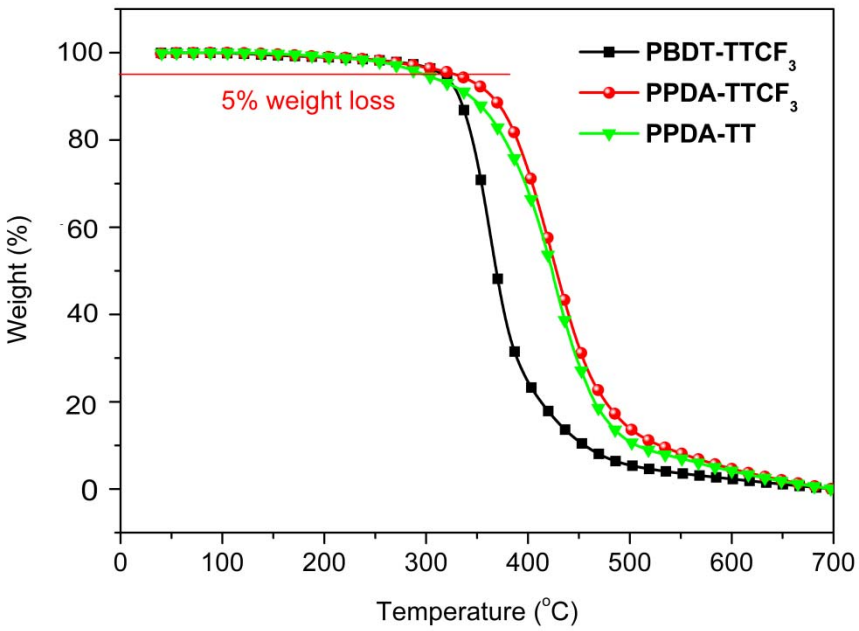

Fig. S1. TGA thermograms of polymers at temperature ramp of 20 °C min^{-1} under a N_2 atmosphere.

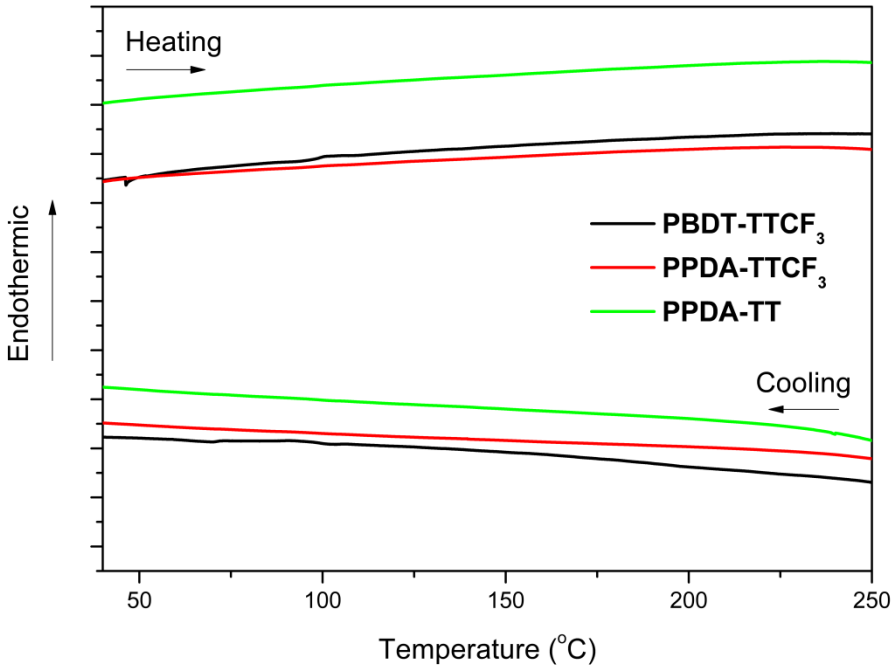

Fig. S2. DSC thermograms of first cooling and second heating scan of polymers at temperature ramp of 10 °C/min.

2. NMR spectra

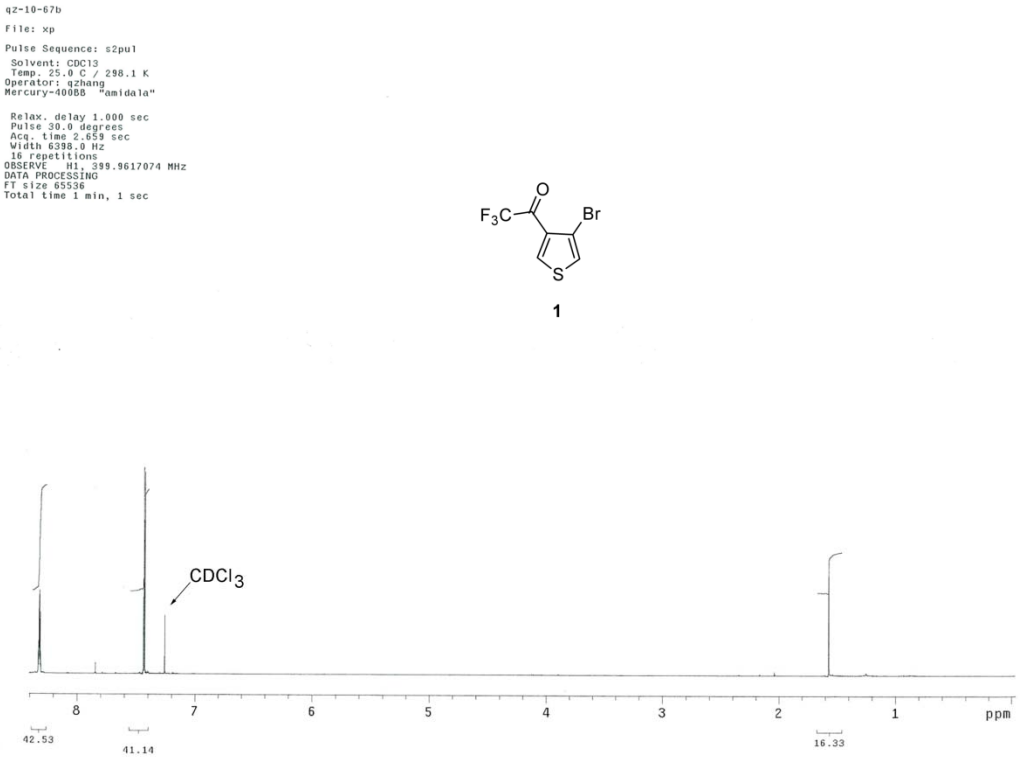

Fig. S3. ^{1}H NMR spectrum of compound **1.**

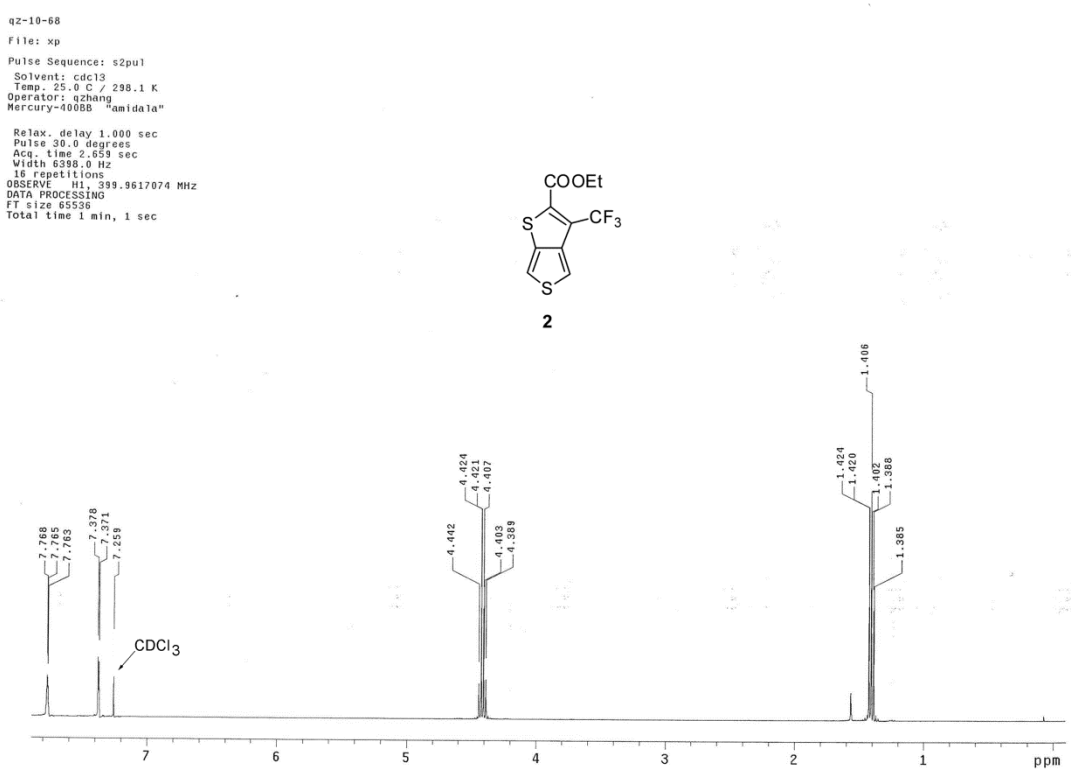

Fig. S4. ^{1}H NMR spectrum of compound **2.**

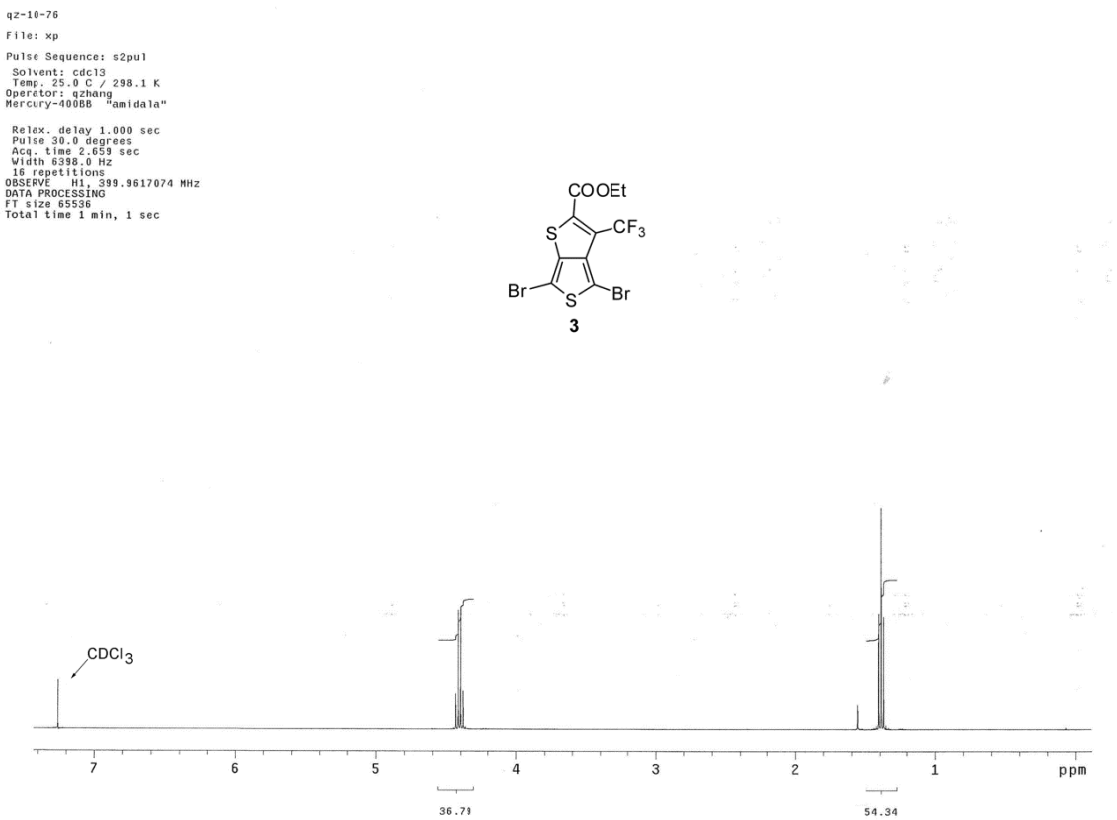

Fig. S5. ^{1}H NMR spectrum of compound **3.**

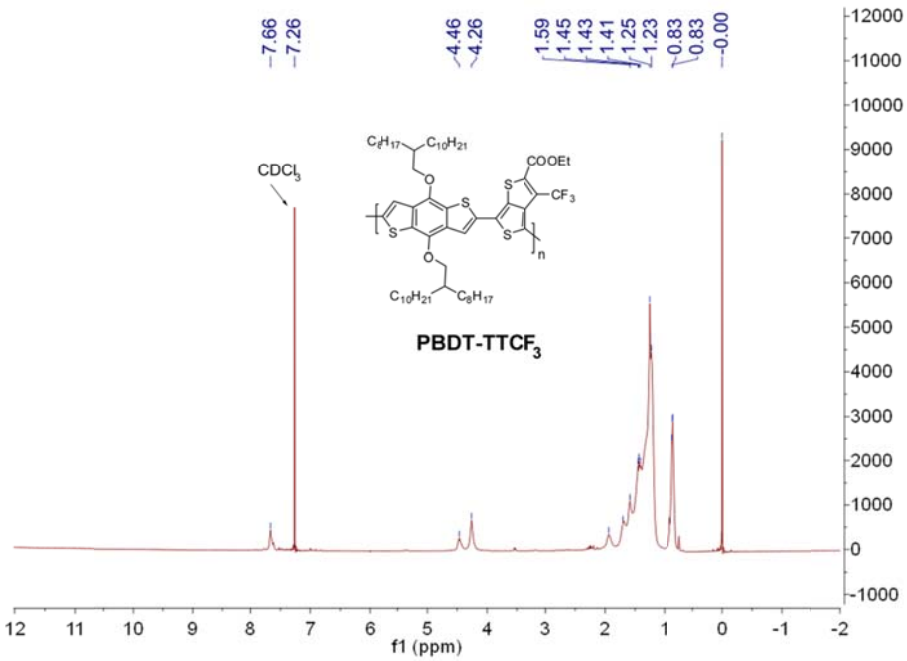

Fig. S6. ^{1}H NMR spectrum of polymer **PBDT-TTCF$_3$**.

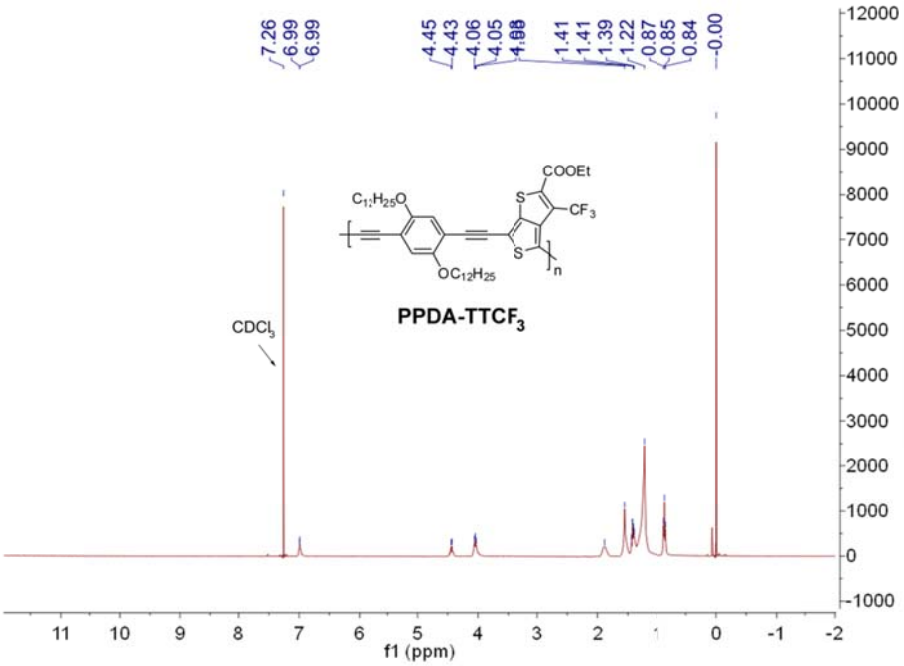

Fig. S7. ^{1}H NMR spectrum of polymer **PPDA-TTCF$_3$**.

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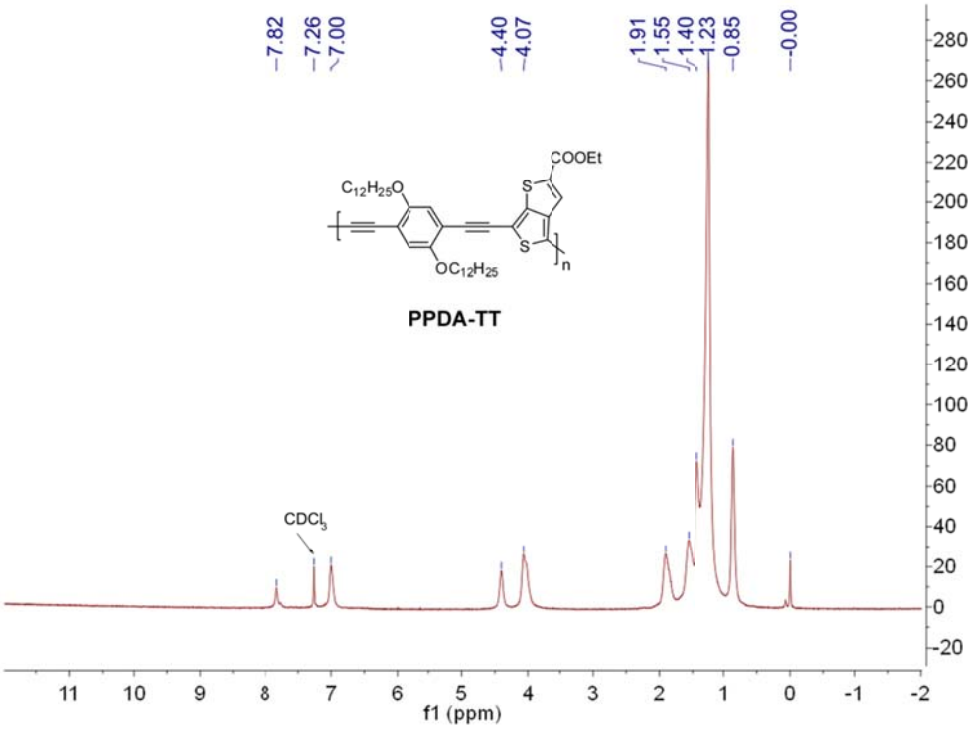
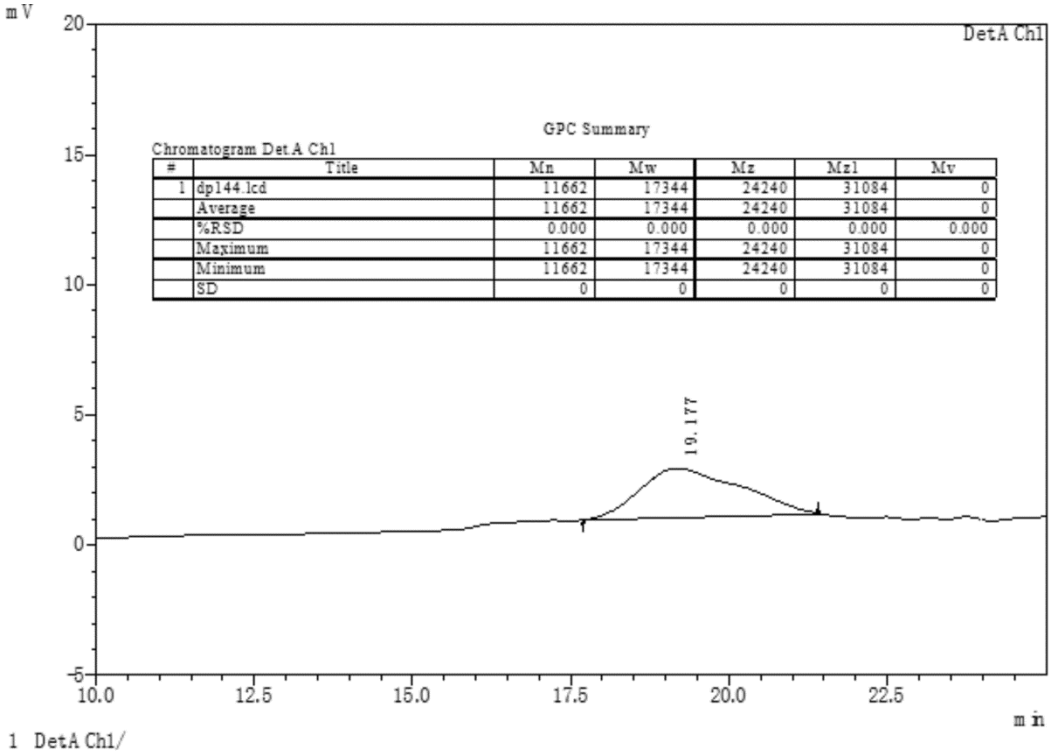


Fig. S8. ^{1}H NMR spectrum of polymer **PPDA-TT**.

3. GPC curves of polymers

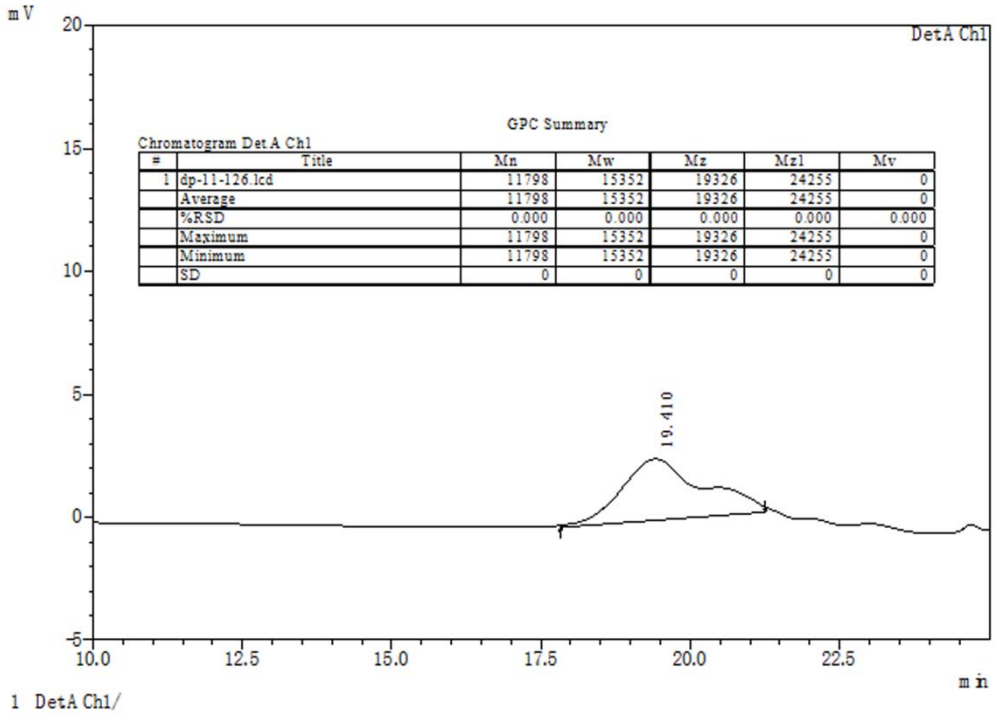


GPC Summary

Chromatogram Det.A Ch1

#	Title	Mn	Mw	Mz	Mz1	Mv
1	dp144.lcd	11662	17344	24240	31084	0
	Average	11662	17344	24240	31084	0
	%RSD	0.000	0.000	0.000	0.000	0.000
	Maximum	11662	17344	24240	31084	0
	Minimum	11662	17344	24240	31084	0
	SD	0	0	0	0	0

Fig. S9. GPC curve of **PBDT-TTCF$_3$**.

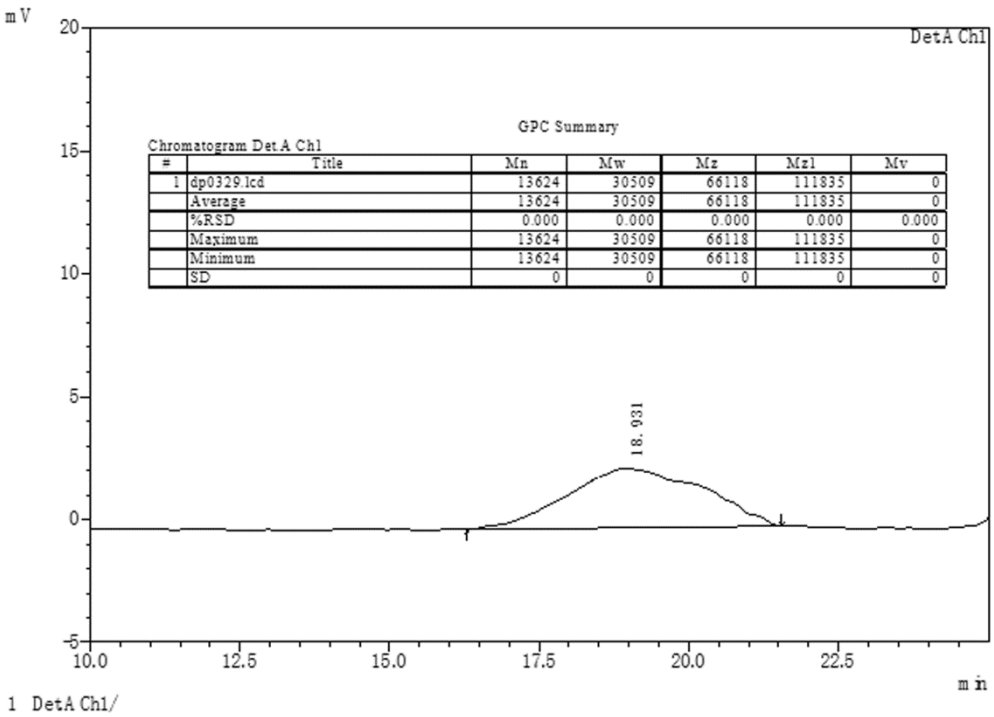


GPC Summary

Chromatogram Det.A Ch1

#	Title	Mn	Mw	Mz	Mz1	Mv
1	dp-11-126.lcd	11798	15352	19326	24255	0
	Average	11798	15352	19326	24255	0
	%RSD	0.000	0.000	0.000	0.000	0.000
	Maximum	11798	15352	19326	24255	0
	Minimum	11798	15352	19326	24255	0
	SD	0	0	0	0	0

Fig. S10. GPC curve of **PPDA-TT**



#	Title	Mn	Mw	Mz	Mz1	Mv
1	dp0329.lcd	13624	30509	66118	111835	0
	Average	13624	30509	66118	111835	0
	%RSD	0.000	0.000	0.000	0.000	0.000
	Maximum	13624	30509	66118	111835	0
	Minimum	13624	30509	66118	111835	0
	SD	0	0	0	0	0

Fig. S11. GPC curve of **PPDA-TTCF$_3$**

4. UV-vis absorption spectra of polymer thin-films

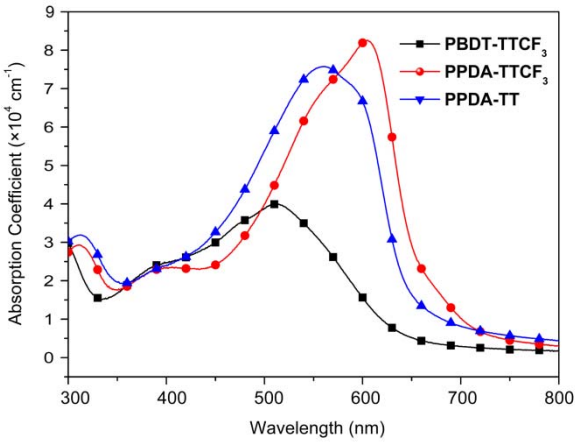


Fig. S12. UV-vis absorption spectra of thieno[3,4-b]thiophene-based polymer thin-films

5. The *J-V* characteristics of devices based on the polymer/$PC_{61}BM$ blends (w/w=1:1, without 1 vol % DIO).

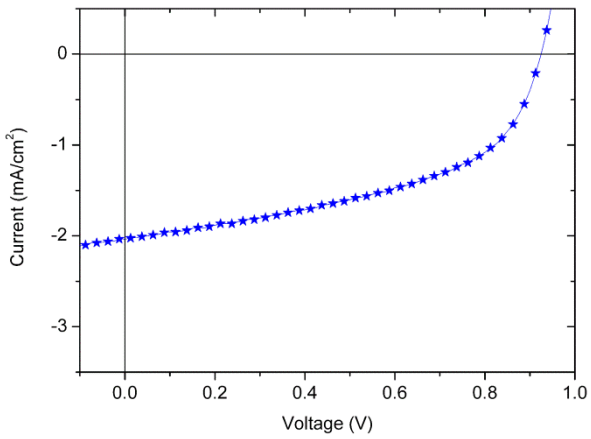


Fig. S13. The *J-V* characteristics of devices based on the polymer/$PC_{61}BM$ blends with weight ratio of 1:1 fabricated from CB solutions without 1 vol % DIO.

6. Hole mobilities of polymers investigated by the space charge limited current (SCLC) method

The hole-only device structure is ITO/PEDOT:PSS/polymer/MoO_3/Al, which is fabricated to investigate the hole mobility using the space charge limited current (SCLC) method. The hole mobility is determined by fitting the dark J-V curves for single carrier devices to SCLC model at low voltages, where the current is given by $J = 9\varepsilon_0\varepsilon_r\mu_h V^2/8d^3$, where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the polymer, μ_h is the zero-field mobility, and d is the thickness of polymer film. In this measurement, the film thicknesses are 35 nm, 40 nm, 40 nm for **PBDT-TTCF$_3$**, **PPDA-TT** and **PPDA-TTCF$_3$** respectively. The applied bias voltage is corrected for the built-in potential so that $V = V_{appl} - V_{bi}$.

7. AFM study of polymers/$PC_{61}BM$ blend morphologies

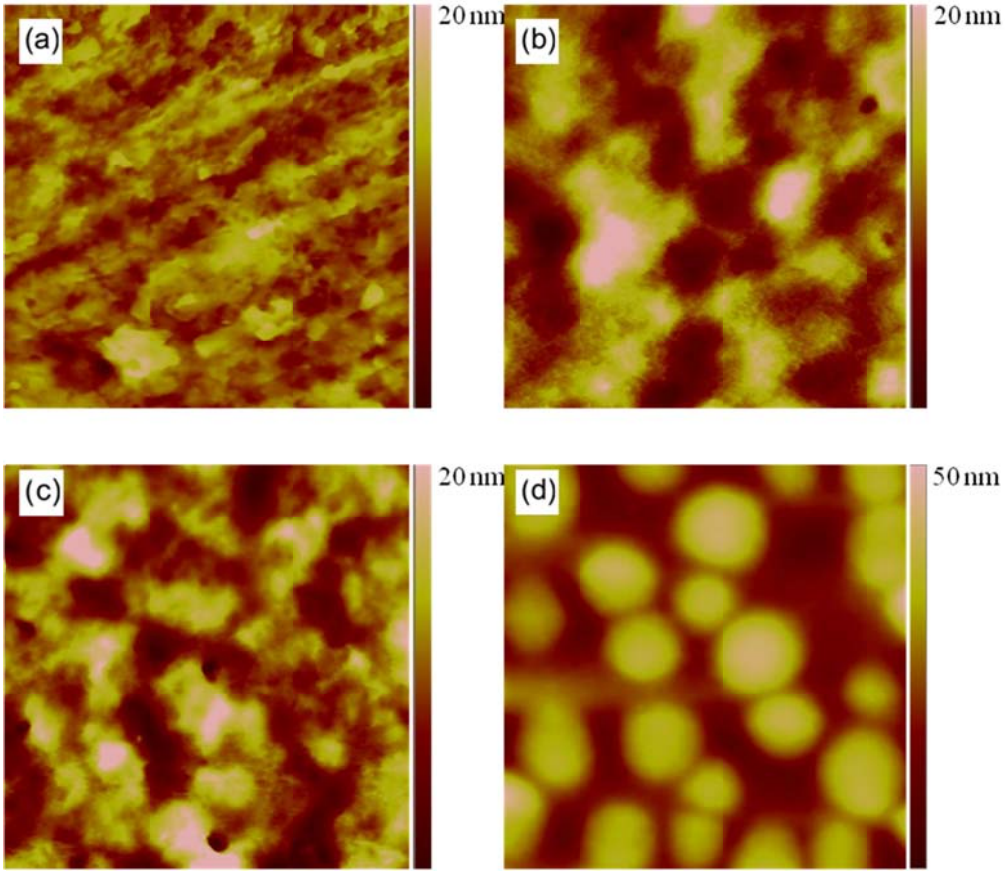


Fig. S14. AFM images (1×1 μm^2) of polymer/$PC_{61}BM$ blends at 1:1 ratio by weight: (a) **PBDT-TTCF$_3$**/$PC_{61}BM$ film with DIO; (b) **PPDA-TT**/$PC_{61}BM$ with DIO; (c) **PPDA-TTCF$_3$**/$PC_{61}BM$ with DIO; (d) **PPDA-TTCF$_3$**/$PC_{61}BM$ without DIO.