Electronic Supplementary Information

A new thieno-isoindigo derivative-based D–A polymer with very low bandgap for high-performance ambipolar organic thin-film transistors

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Table S1 Crystallographic parameters for polymer films of **PBTPBF-BT** and **PBIBDF-BT**.

Polymer	Lamellar spacing		π-π spacing	
	2θ (°)	d (Å)	2θ (°)	d (Å)
PBTPBF-BT	3.36	26.3	25.28	3.52
PBIBDF-BT[a]	-	28.5	-	3.55

[a] Values of the isoindigo derivative-based polymer were referred 12a.

Table S2 OTFTs performances of the polymers tested under vacuum.

Polymer	**T-annealing [°C]**	**Evaluation under vacuum conditions**					
		μ_h **(average)[a] [$cm^2V^{-1}s^{-1}$]**	I_{on}/I_{off}[b]	V_{th} **[V]**	μ_e **(average)[a] [$cm^2V^{-1}s^{-1}$]**	I_{on}/I_{off}[c]	V_{th} **[V]**
PBIBDF-BT	N/A	–	–	–	0.46 (0.29)	$10^4 – 10^5$	-0.4
	180	–	–	–	1.06 (0.79)	$10^4 – 10^5$	28.7
PBTPBF-BT	N/A	0.13 (0.10)	$10^2 – 10^3$	-15.5	0.08 (0.07)	$10^2 – 10^3$	47.0
	150	0.34 (0.30)	$10^3 – 10^4$	-26.4	0.13 (0.10)	$10^2 – 10^3$	55.6
	180	0.45 (0.38)	$10^4 – 10^5$	-21.3	0.22 (0.18)	$10^3 – 10^4$	56.9

[a]Average mobility from more than 8-10 devices; [b]Evaluated at $V_D = –20$ V; [c]Evaluated at $V_D = +20$ V.

Table S3 OTFTs performances of the polymers tested under air.

Polymer	T-annealing [°C]	Evaluation under air conditions					
		μ_h (average)[a] [$cm^2V^{-1}s^{-1}$]	I_{on}/I_{off}[b]	V_{th} [V]	μ_e (average)[a] [$cm^2V^{-1}s^{-1}$]	I_{on}/I_{off}[c]	V_{th} [V]
PBIBDF-BT[d]	N/A	0.39 (0.27)	$10^3 - 10^4$	-15.4	0.28 (0.20)	$10^3 - 10^4$	1.63
	180	0.36 (0.23)	$10^3 - 10^4$	-23	0.60 (0.37)	$10^3 - 10^4$	37.8
PBTPBF-BT	N/A	0.25 (0.21)	$10^3 - 10^4$	-19.5	0.03 (0.02)	$10^2 - 10^3$	76.6
	150	0.45 (0.36)	$10^2 - 10^3$	-14.4	0.02 (0.01)	$10^2 - 10^3$	69.1
	180	0.61 (0.53)	$10^2 - 10^3$	-16.2	0.07 (0.06)	$10^2 - 10^3$	76.2

[a] Average mobility from more than 8-10 devices; [b] Evaluated at V_D = –20 V; [c] Evaluated at V_D = +20 V. [d] The mobilities lower than those of the previous report (tested in low vacuum or glovebox, 12a).

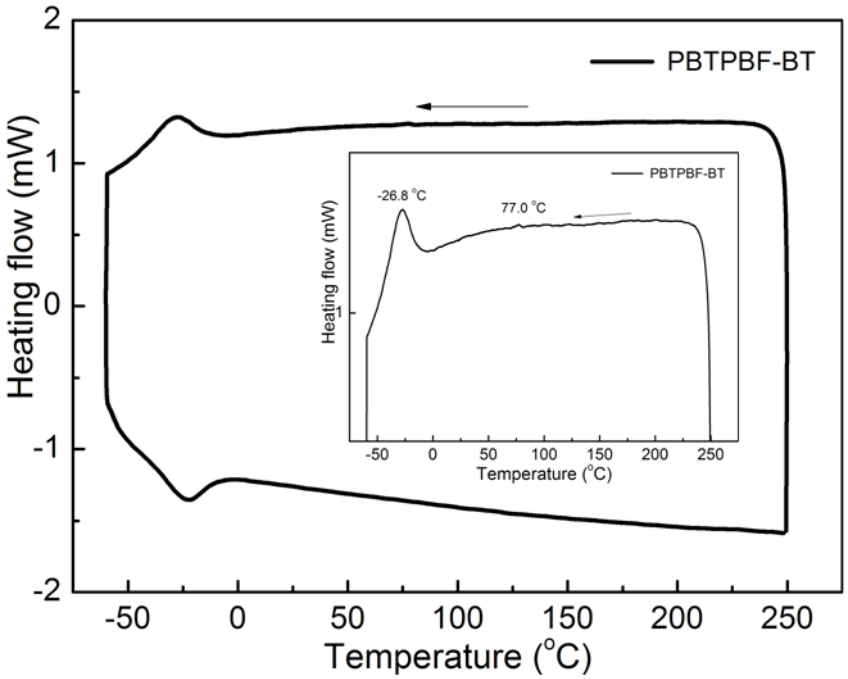


Fig. S1 The DSC curve of PBTPBF-BT.

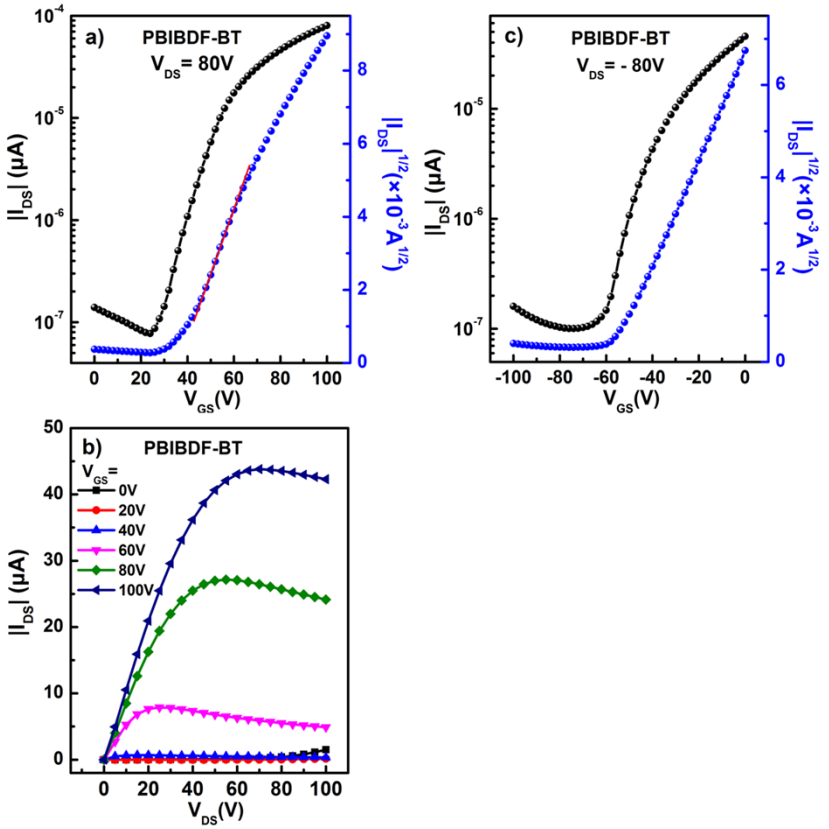


Fig. S2 the Output and transfer curves of **PBIBDF-BT** devices annealed at 180 °C and tested under vacuum. **PBIBDF-BT** exhibited n-channel transport in the vacuum with the electron mobility as high as 1.06 $cm^2V^{-1}s^{-1}$.

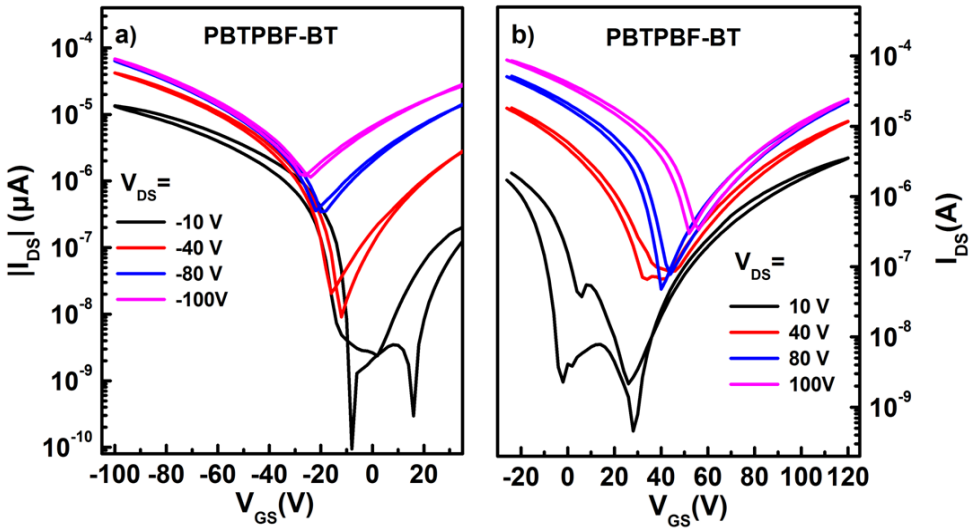


Fig. S3 The transfer characteristics of **PBIPBF-BT** devices annealed at 180 °C and test under vacuum condition. All the transfer curves for electron and hole transport showed negligible hysteresis.

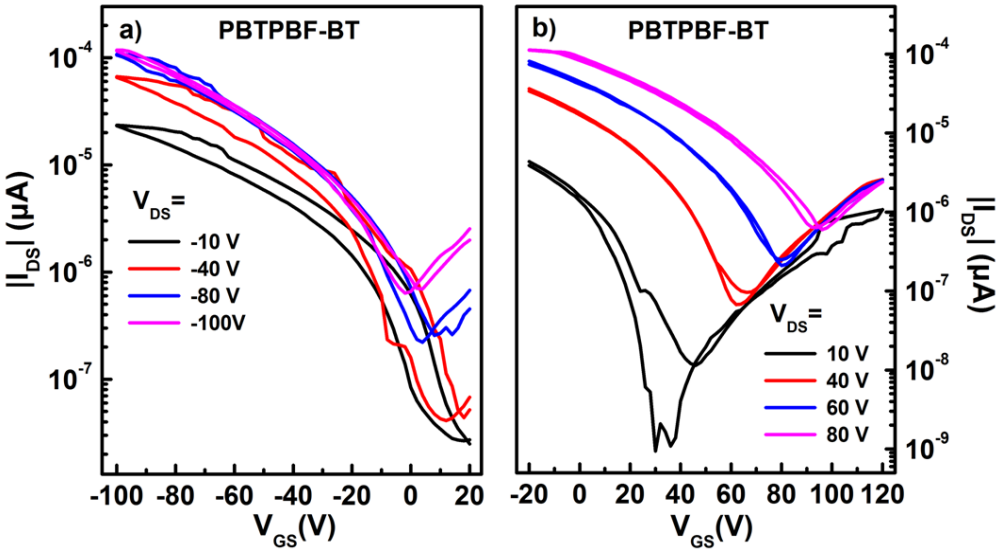


Fig. S4 The transfer characteristics of **PBIPBF-BT** devices annealed at 180 °C and test under air condition.

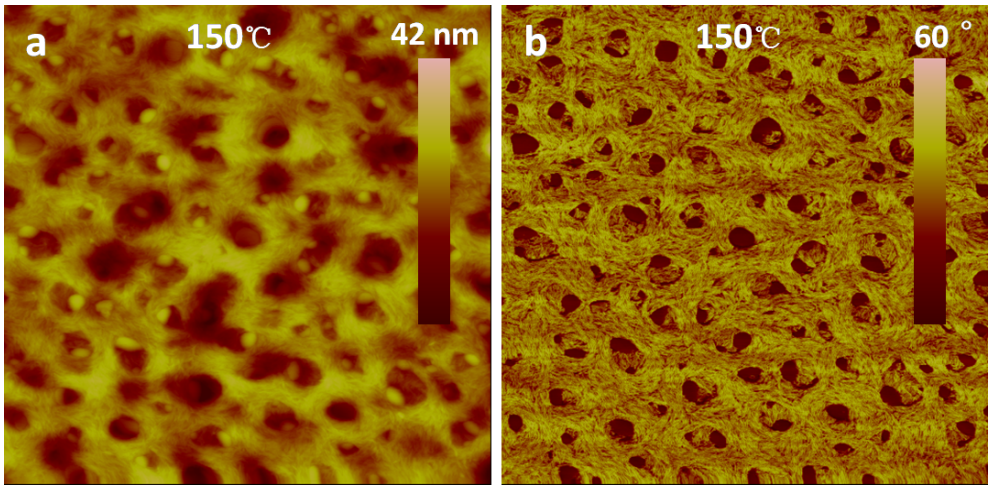


Fig. S5 AFM images (2 μm × 2 μm) of PBTPBF-BT thin film with the annealing temperature of 150 °C.

2. NMR spectra

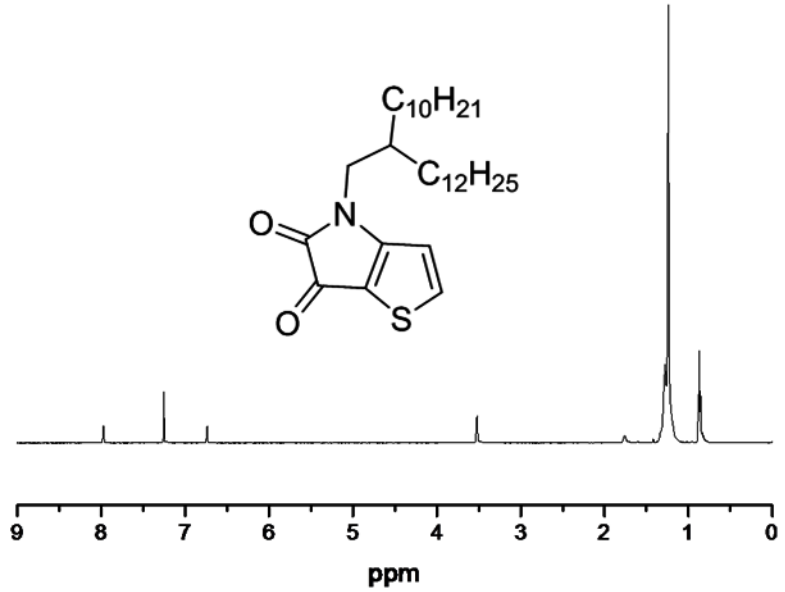


Fig. S6 ^{1}H NMR spectra of compound **2** in $CDCl_3$.

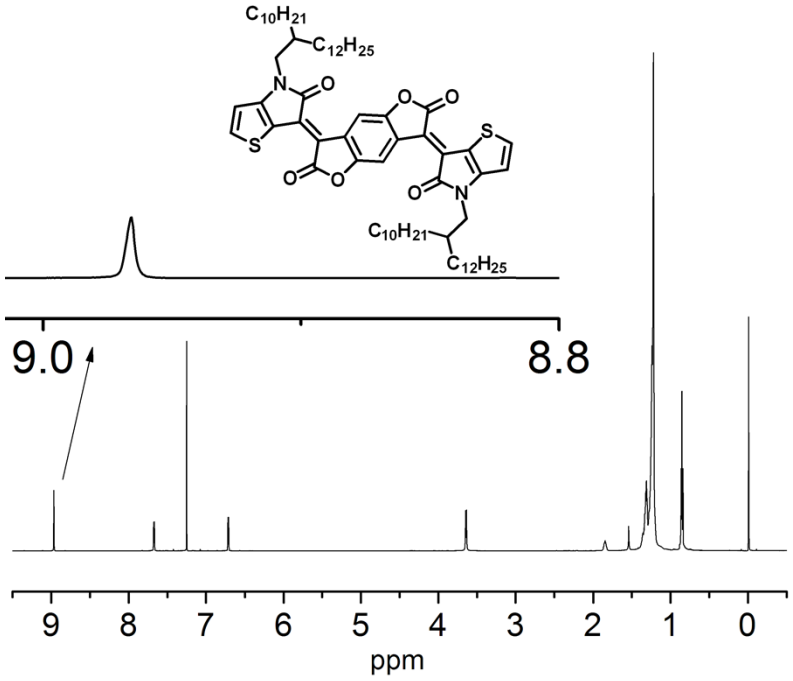


Fig. S7 ^{1}H NMR spectra of compound **3** in $CDCl_3$.

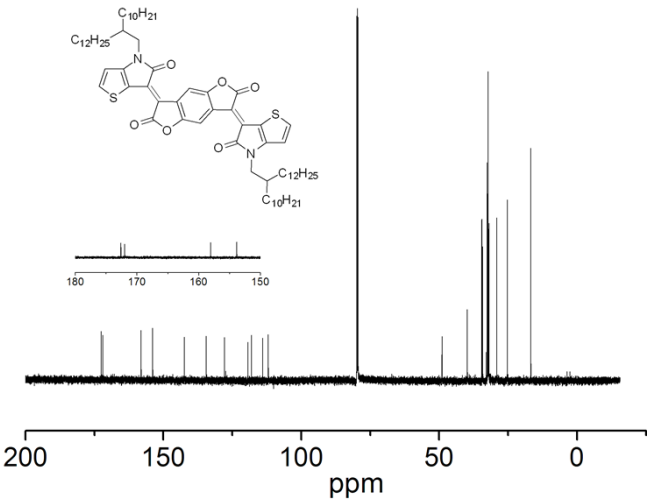


Fig. S8 ^{13}C NMR spectra of compound **3** in $CDCl_3$.

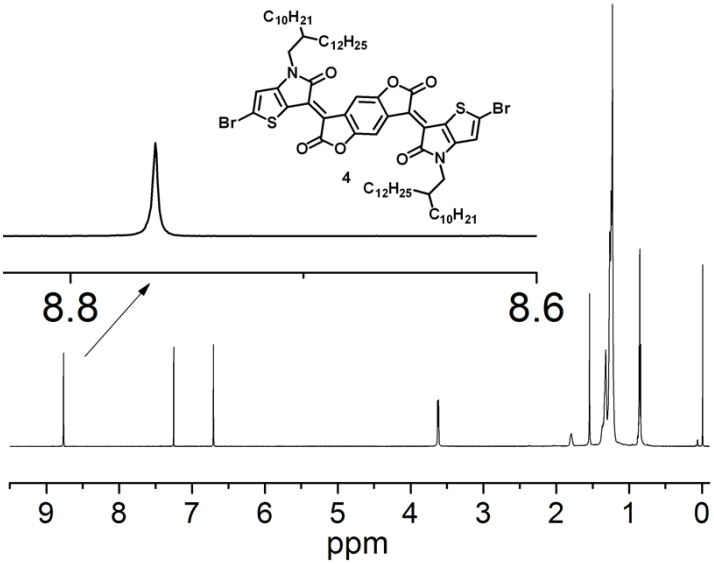


Fig. S9 ^{1}H NMR spectra of compound **4** in $CDCl_3$.

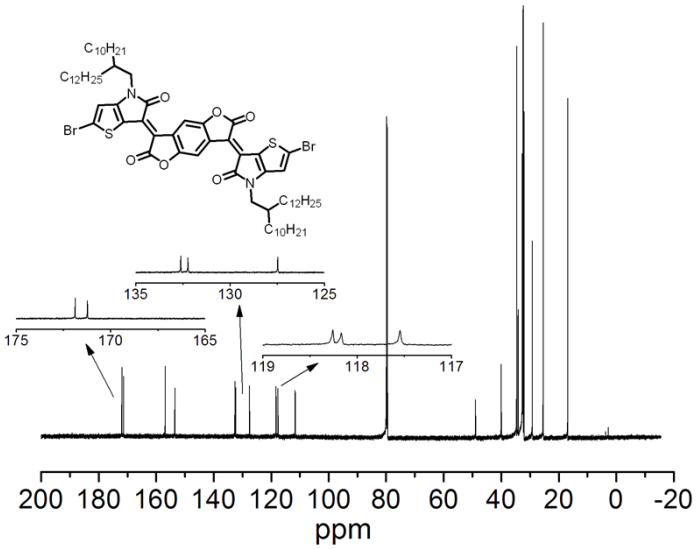


Fig. S10 ^{13}C NMR spectra of compound **4** in $CDCl_3$.

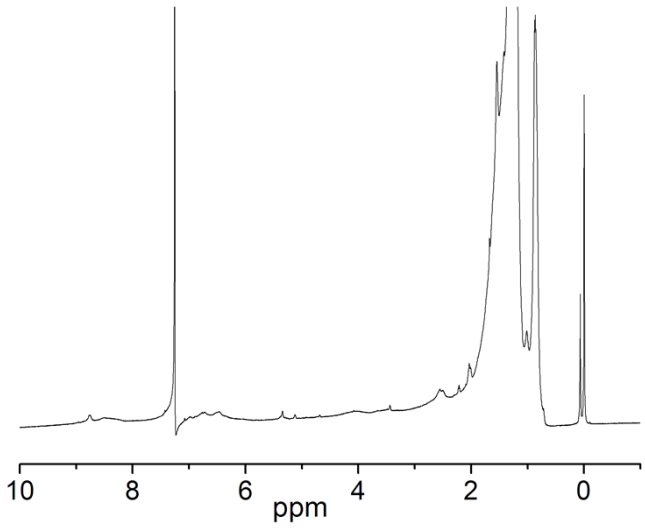


Fig. S11 ^{1}H NMR of **PBTPBF-BT**.

3. Mass spectrum and DSC curves of monomers

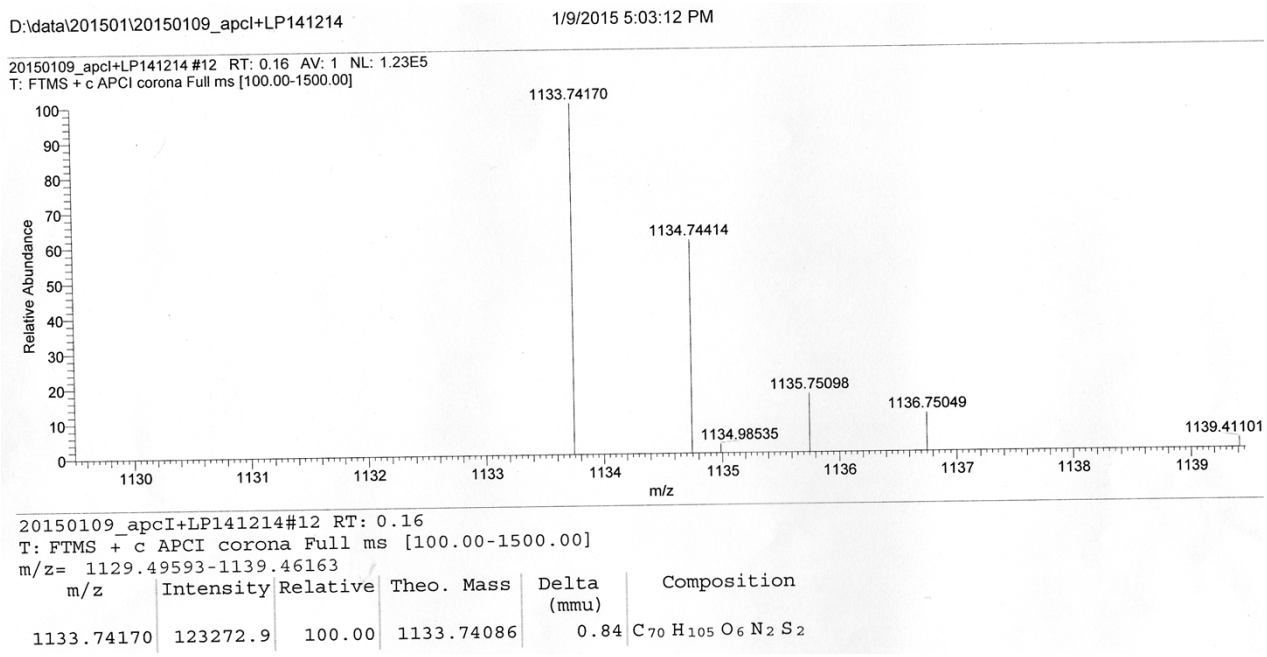


Fig. S12 The mass spectrum of compound **3**.

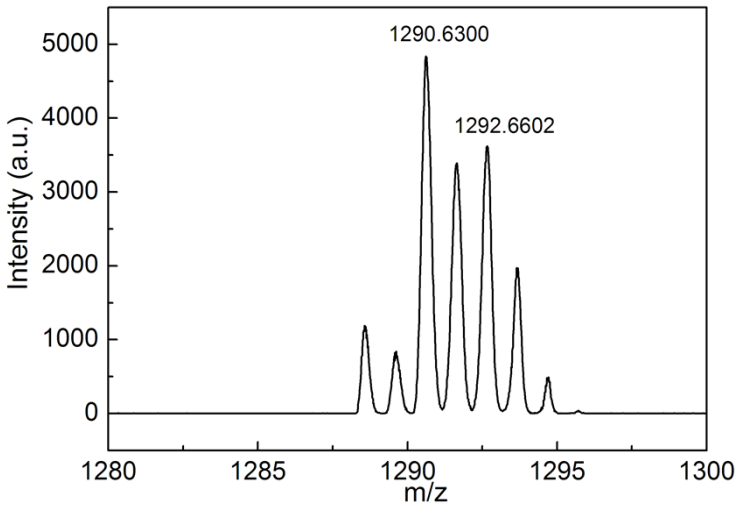


Fig. S13 The mass spectrum (MALDI-TOF) of **4**.

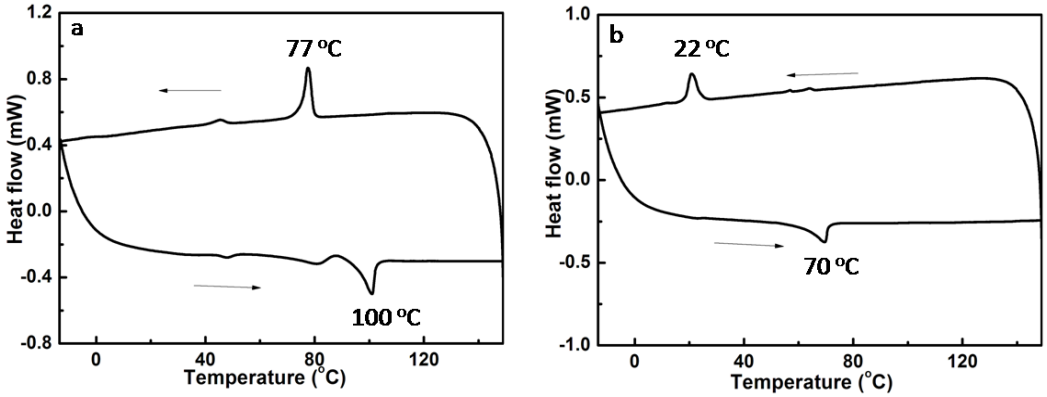
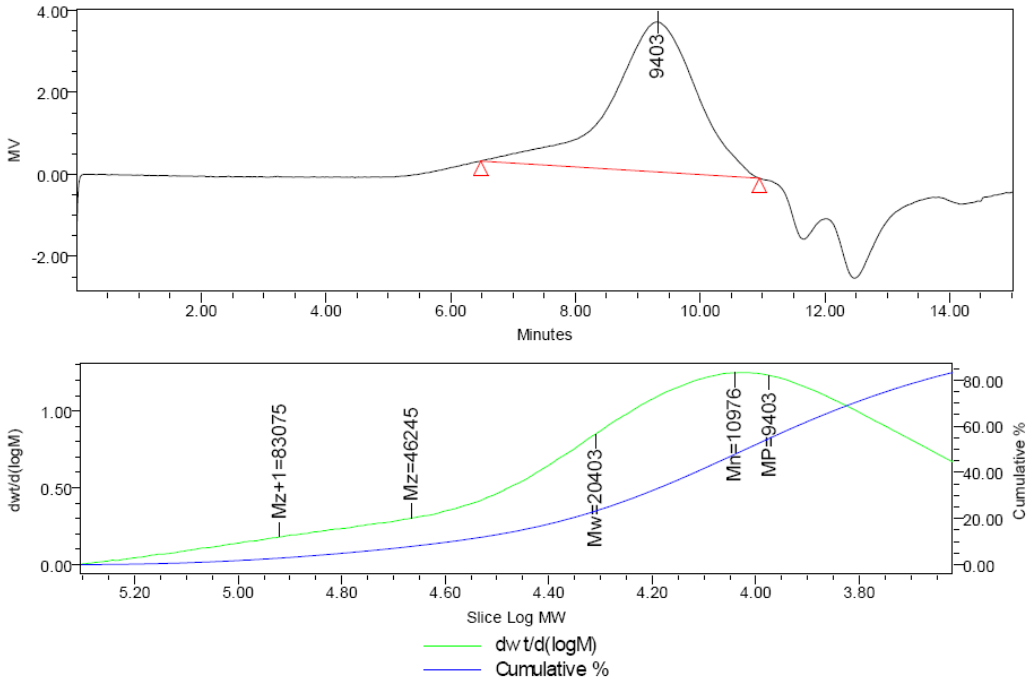


Fig. S14 The DSC curves of (a): compound **3** and (b): compound **4**.

4. GPC results



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	9.317	10976	20403	9403	46245	1.859

Fig. S15 GPC results of **PBTPBF-BT**.