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Supporting Information

Facile green synthesis of isoindigo-based conjugated polymers using aldol polycondensation

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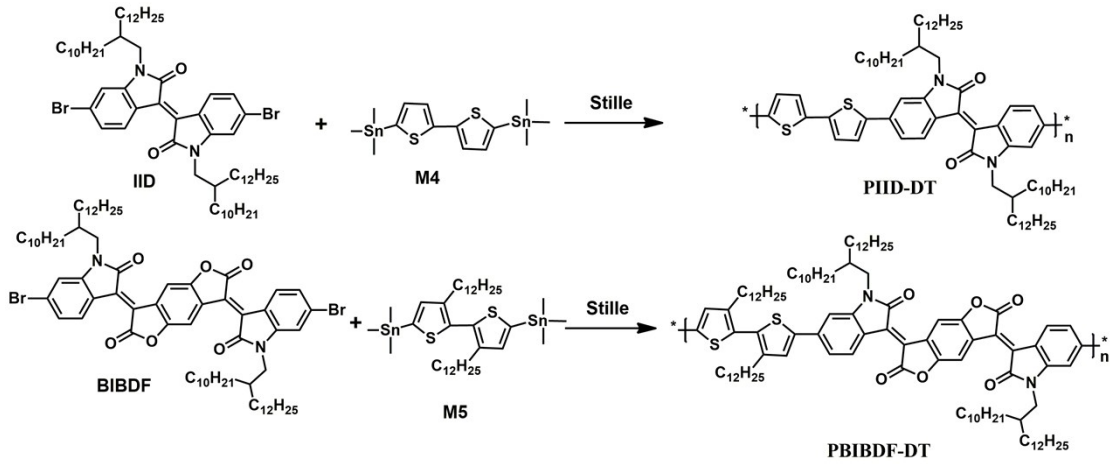


Scheme S1. Stille polymerization of PIID-DT and PBIBDF-DT.

Synthesis of PIID-DT (Stille). Tin-monomer **M4** (0.1 g, 0.21 mmol), **IID** (0.23 g, 0.21 mmol), $Pd_2(dba)_3$ (8 mg), $P(o\text{-}tol)_3$ (10 mg) and toluene (8 mL) were added to a Schlenk tube. The tube was charged with nitrogen through a freeze-pump-thaw cycle three times. The mixture was stirred at 105 ^oC. The viscosity of mixture became too large after stirring for about five hours. Then the mixture was cooled down to room temperature, and poured into methanol (100 mL) and stirred for 2 h. The precipitate was collected by filtration. The product was purified through Soxhlet extraction using methanol and hexane to remove oligomers. The remaining polymer was extracted with hot chloroform in an extractor for 12 h. After removing the solvent, a blue solid was collected (95 mg, 37.9%). ^1H NMR (400 MHz, Cl_2CDCl_2), σ(ppm): 9.00-9.30 (br, 4H), 6.88-7.50 (br, br, 8H), 3.70-3.88 (br, 4H), 0.98-1.95 (br, 82H), 0.65-0.95 (br, 12H). GPC: M_n = 20.16 kDa, *PDI* = 3.2.

Synthesis of PBIBDF-DT. The same procedure were used as those for PIID-DT. The compound used were $Pd_2(dba)_3$ (6 mg), $P(o\text{-}tol)_3$ (8 mg) **M5** (0.13 g, 0.16 mmol), **BIBDF** (0.20 g, 0.16 mmol) and toluene (8 mL). The highly viscous black solution was formed after stirring for about 24 h. After workup, black polymers were obtained (0.11 g, 43.3%). ^1H NMR (400 MHz, $CDCl_3$), σ(ppm): 8.90-9.15 (br, 4H), 6.85-7.20 (br, 6H), 3.65-3.75 (br, 4H), 2.50-2.70 (br, 4H), 0.95-1.95 (br, 122H), 0.65-0.95 (br, 18H). GPC: M_n = 29.83 kDa, *PDI* = 1.5.

Table S1 Optical properties of polymers synthesized by aldol and Stille polycondensation.

Polymer	λ_{max}^{abs} (nm) (solution)	λ_{max}^{abs} (nm) (thin film)	λ_{onset}^{abs} (nm) (thin film)	E_g^{opt} (eV)
PIID-DT (aldol)	705	709	780	1.59
PIID-DT (Stille)	699	709	780	1.59
PBIBDF-DT (aldol)	824	831	1050	1.18
PBIBDF-DT (Stille)	824	840	1040	1.19

Table S2 Crystallographic parameters for polymer films annealed at 260 °C.

Polymer (Aldol)	Lamellar spacing (100)		π-π spacing (010)	
	q_z (Å^{-1})	d (Å)	q_{xy}	d (Å)
PIID-DT	0.296	21.21	1.674	3.75
PBIBDF-DT (Edge on)	0.210	29.79	1.783	3.52
PBIBDF-DT (Face on)	0.23	27.30	1.782	3.52

Table S3 The device performances of isoindigo-based polymers made via Stille polymerization.

Annealing temperature(°C)	**p-channel**			
	$\mu_{h,max}$ ($cm^2V^{-1}s^{-1}$)	**$\mu_{h,avg}$ ($cm^2V^{-1}s^{-1}$)**	**I_{on}/I_{off}**	**V_{th} (V)**
PIID-DT				
RT	0.07	0.05±0.009	9×10^5	-21.1
180	0.38	0.26±0.064	3×10^6	-20.6
260	0.29	0.20±0.049	1×10^6	-13.3
PBIBDF-DT				
RT	-	-	-	-
260	0.60	0.49±0.127	6×10^5	6.0

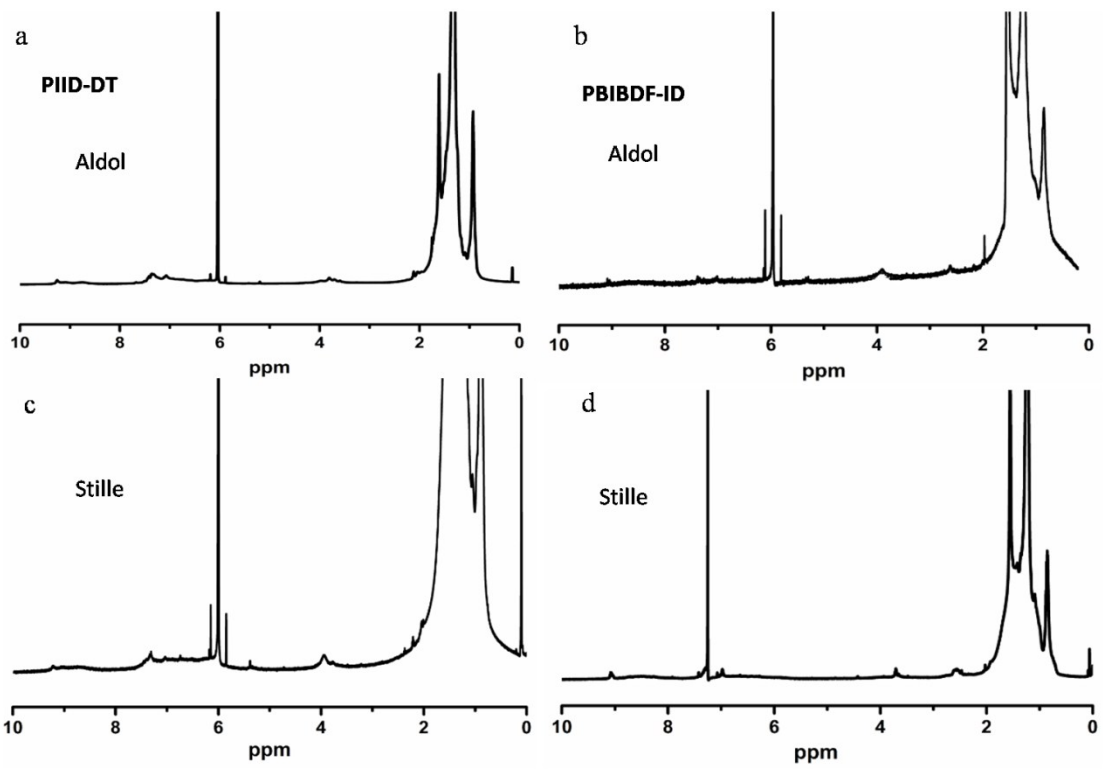


Fig. S1 The ^{1}H NMR spectra of two polymers prepared by aldol and Stille polycondensation.

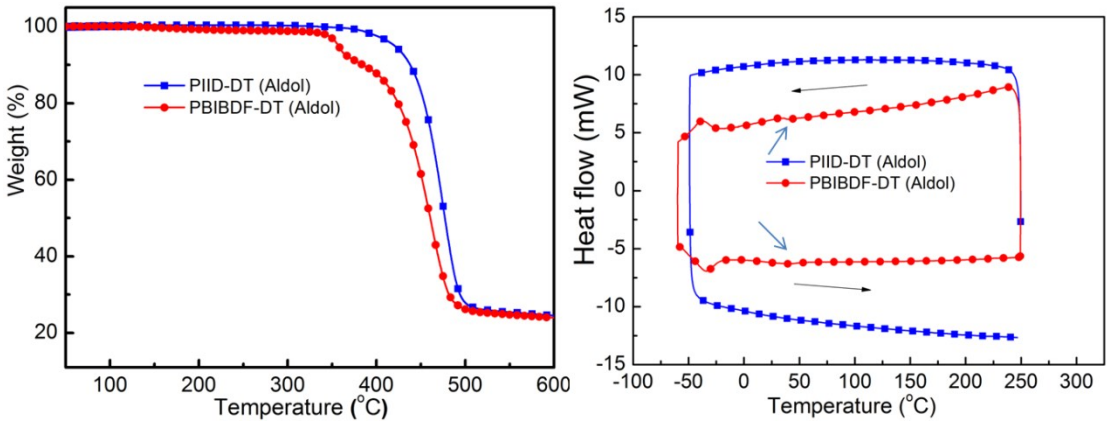


Fig. S2 TG and DSC curves of two polymers prepared by aldol polycondensation.

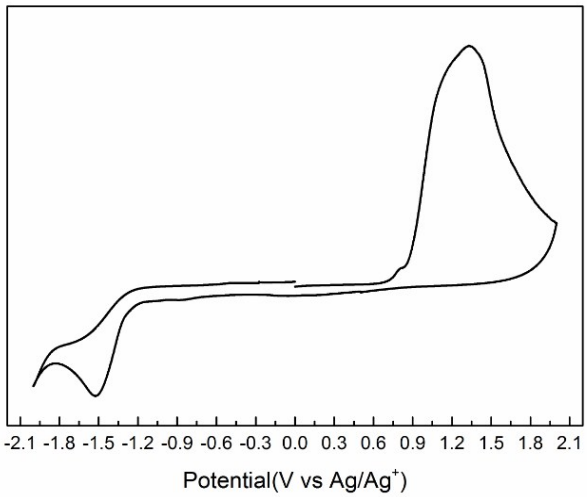


Fig. S3 Cyclic voltammograms of **PIID-BT** made by aldol polycondensation.
The potential were referenced to Ag/Ag^+ and the redox Fc/Fc^+ was assumed at an absolute energy of 4.8 eV to vacuum. The redox Fc/Fc+ was measured under the same conditions as polymer films and was located at 0.05 V related to the Ag/Ag+ electrode. The onset reduction potential and oxidation onset potential were -1.20 and 0.80 eV, corresponding to the LUMO and HOMO energy levels of -3.55 and -5.55 eV, respectively.

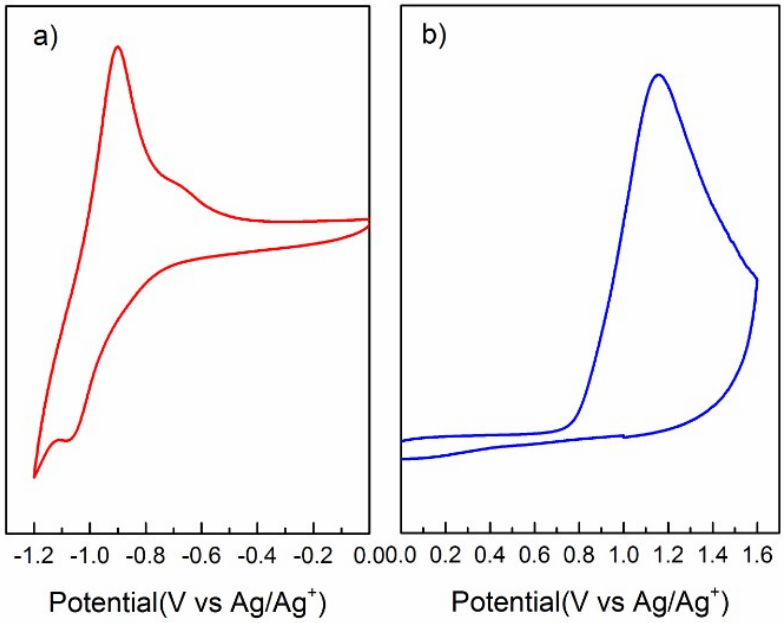


Fig. S4 Cyclic voltammograms of **PBIBDF-BT** made by polycondensation.
The onset reduction potential and oxidation onset potential were -0.70 and 0.75 eV, corresponding to the LUMO and HOMO energy levels of -4.05 and -5.50 eV, respectively.

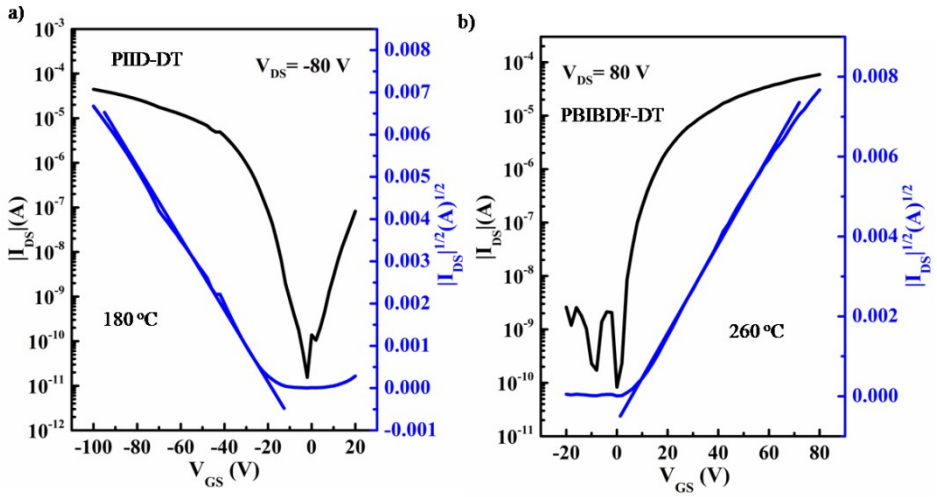


Fig. S5 Transfer characteristics of **PIID-DT** (a) and **PBIBDF-DT** (b) prepared by Stille polycondensation.

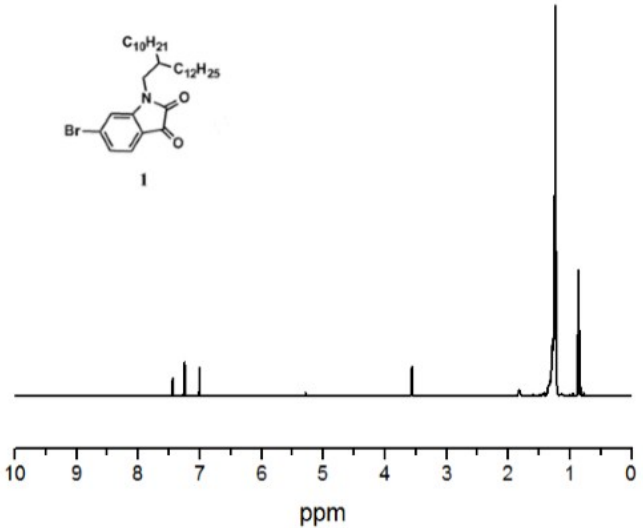


Fig. S6 ^{1}H NMR spectra of compound 1 in $CDCl_3$.

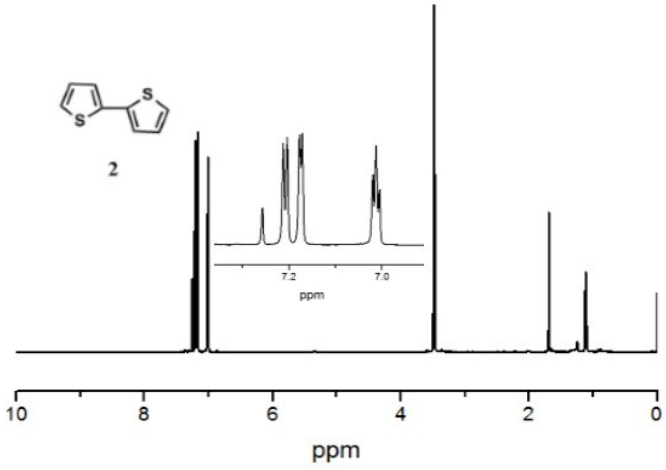


Fig. S7 ^{1}H NMR spectra of compound 2 in $CDCl_3$.

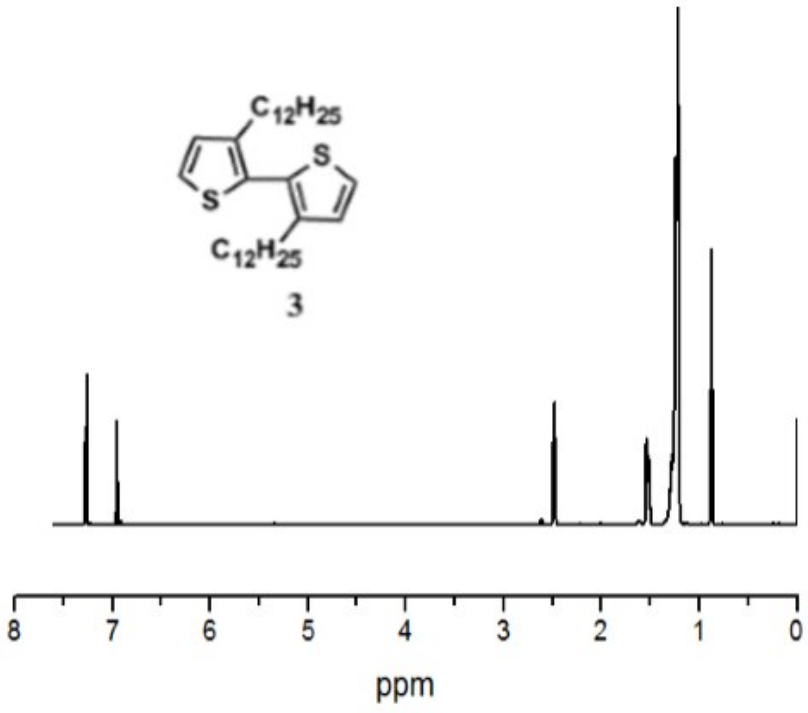


Fig. S8 ^{1}H NMR spectra of compound 3 in $CDCl_3$.

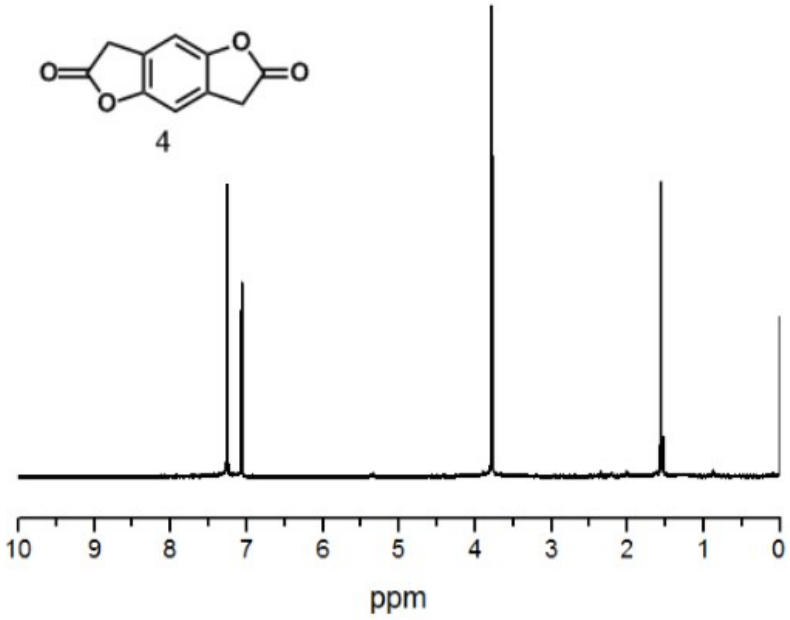


Fig. S9 ^{1}H NMR spectra of compound 4 in $CDCl_3$.

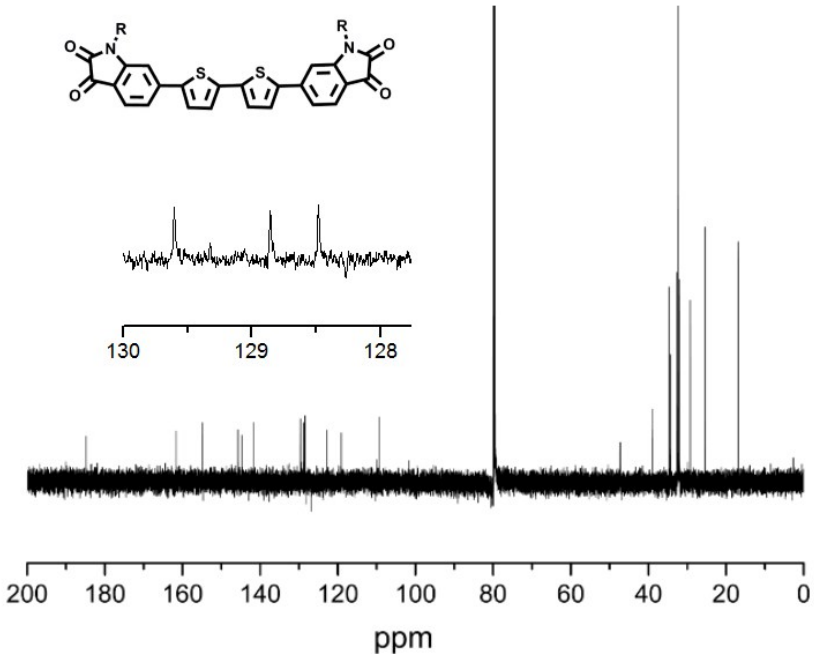


Fig. S10 ^{13}C NMR spectra of **M1** in $CDCl_3$.

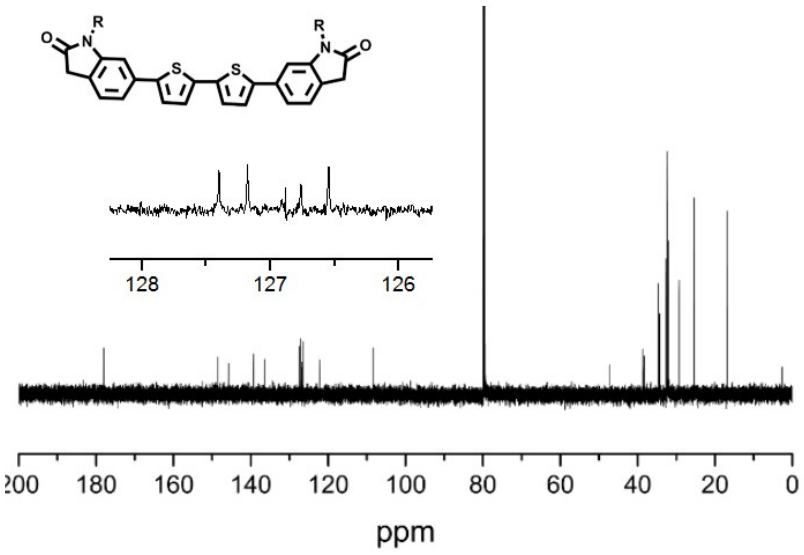


Fig. S11 ^{13}C NMR spectra of **M2** in $CDCl_3$.

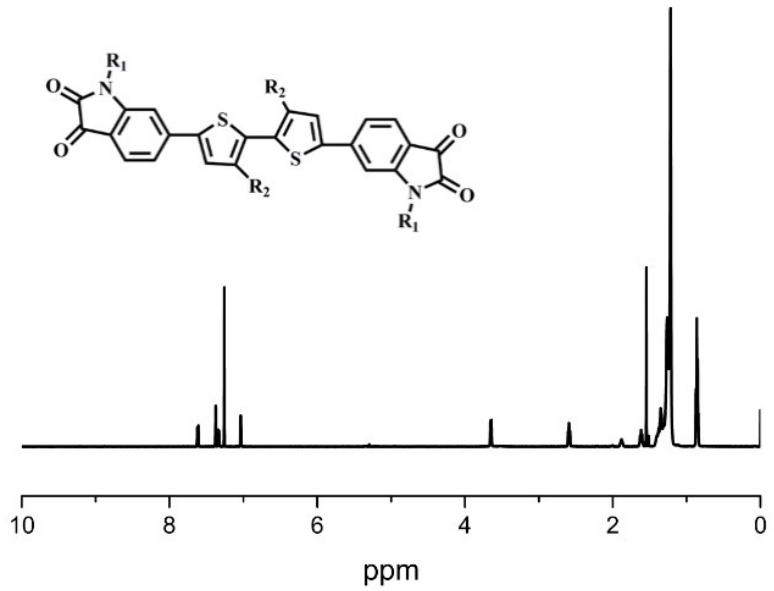


Fig. S12 ^{1}H NMR spectra of **M3** in $CDCl_3$.

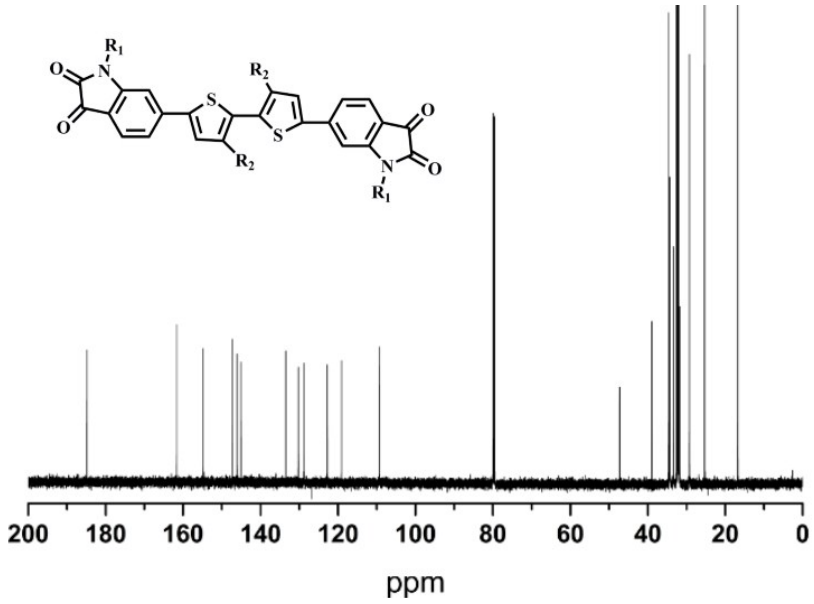
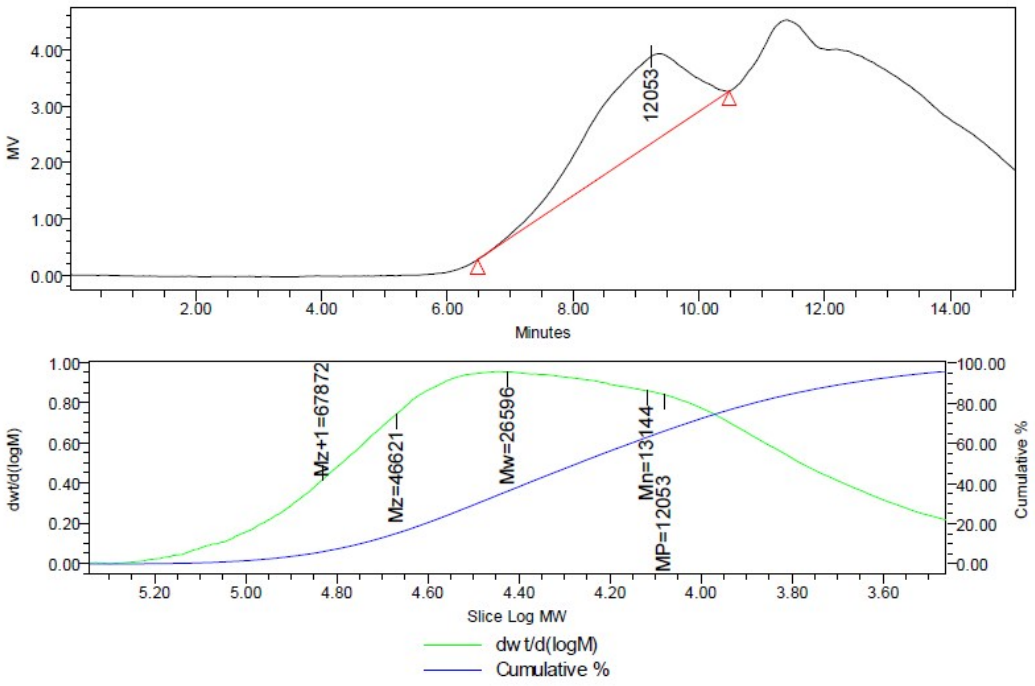


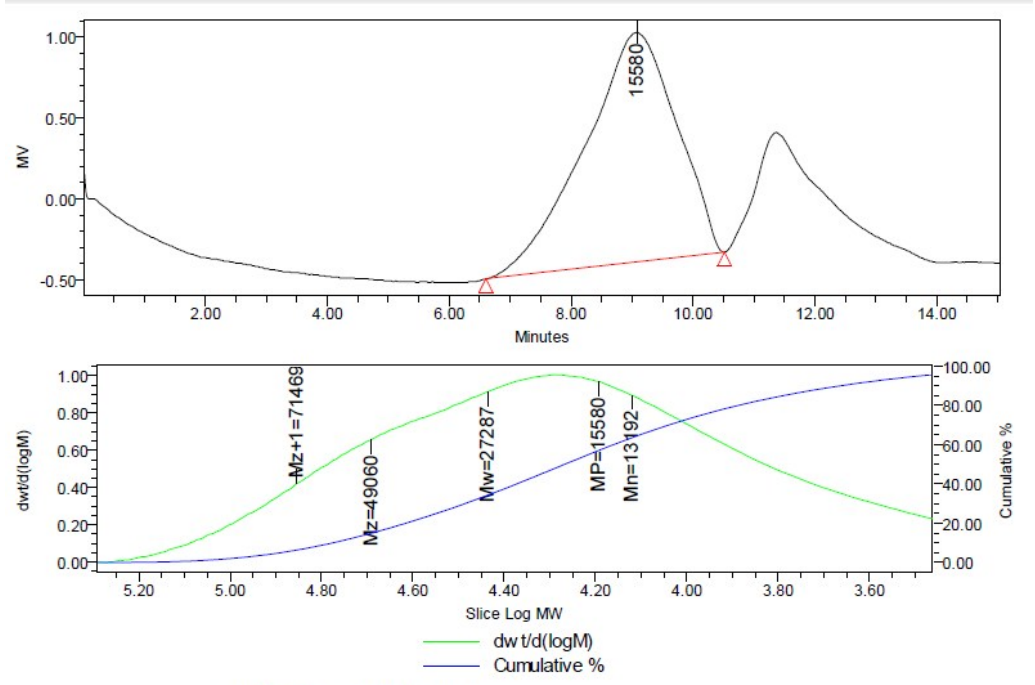
Fig. S13 ^{13}C NMR spectra of **M3** in $CDCl_3$.



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	9.250	13144	26596	12053	46621	2.023

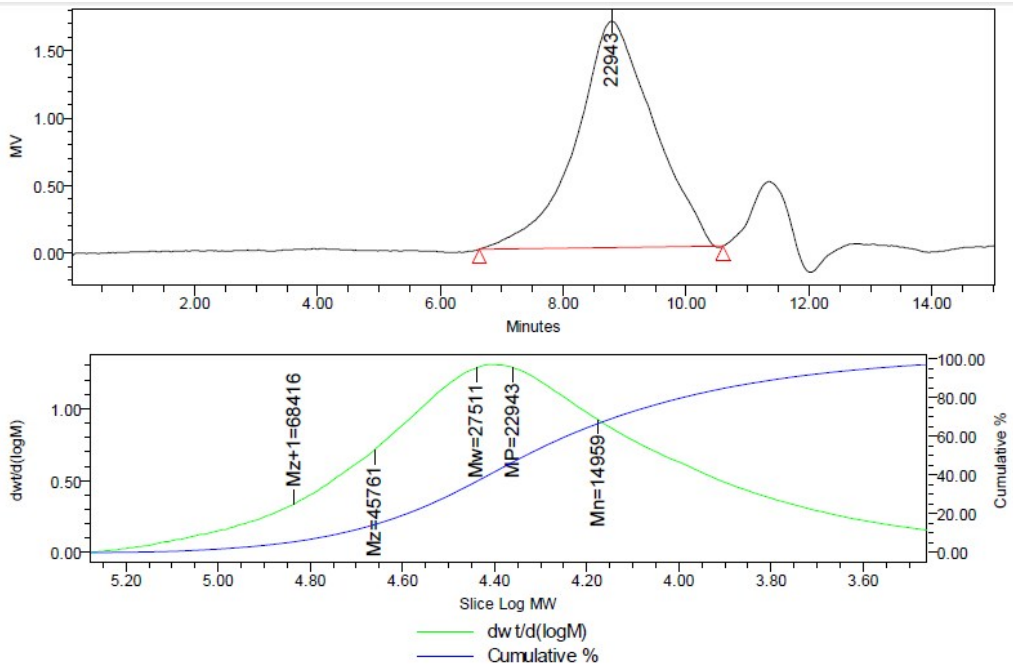
Fig. S14 The GPC sample results for **PIID-DT** (entry 1).



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	9.077	13192	27287	15580	49060	2.068

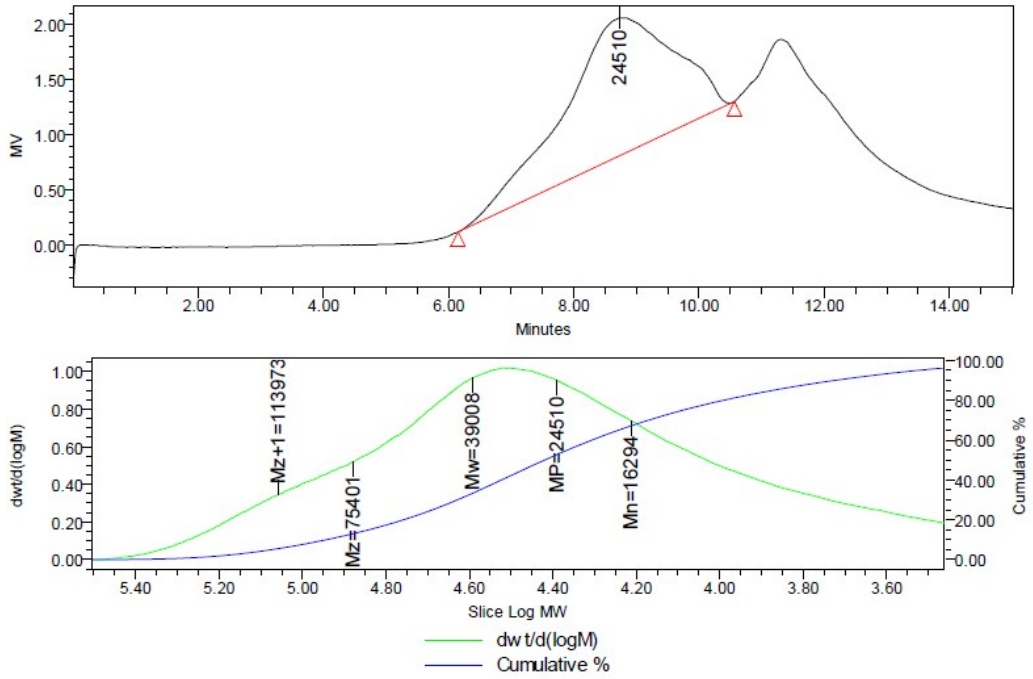
Fig. S15 The GPC sample results for **PIID-DT** (entry 2).



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	8.789	14959	27511	22943	45761	1.839

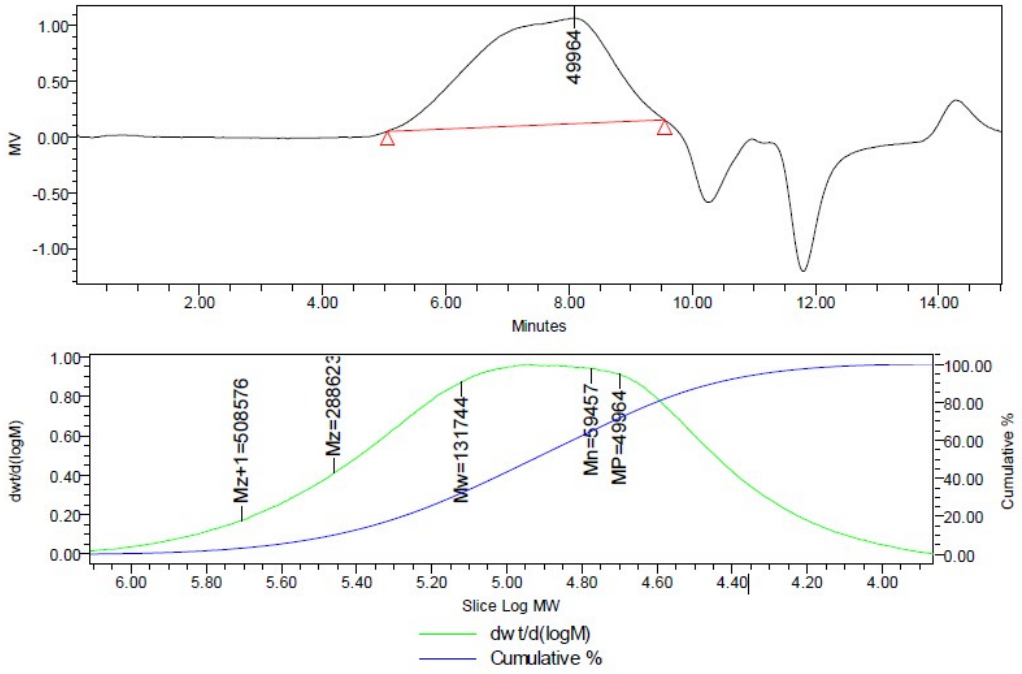
Fig. S16 The GPC sample results for **PIID-DT** (entry 3).



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	8.736	16294	39008	24510	75401	2.394

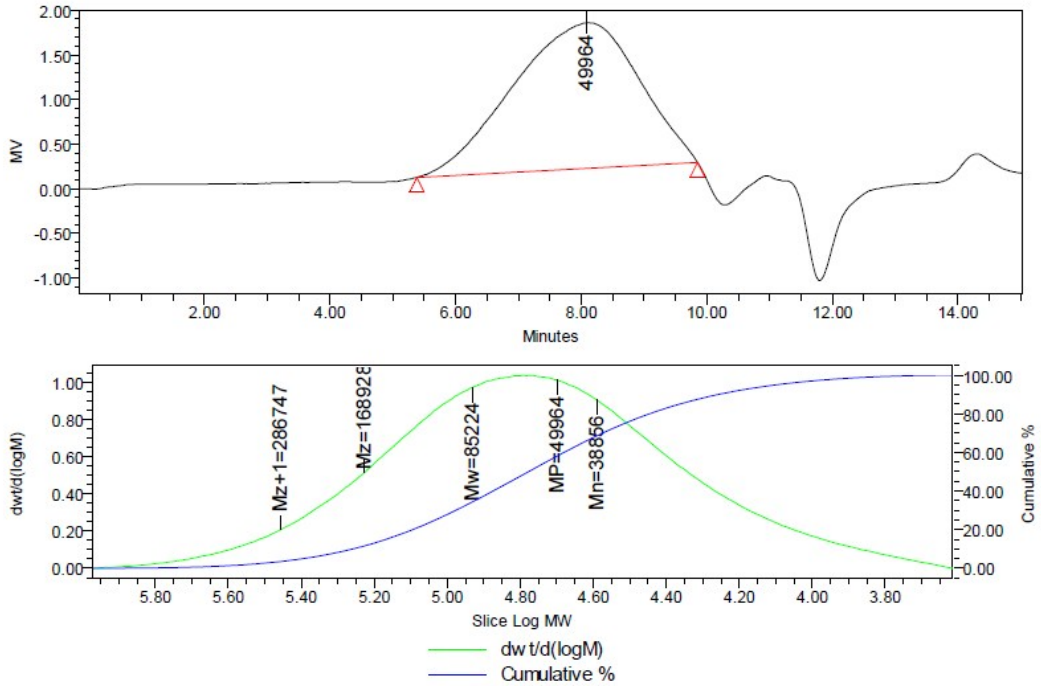
Fig. S17 The GPC sample results for **PIID-DT** (entry 4).



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	8.083	59457	131744	49964	288623	2.216

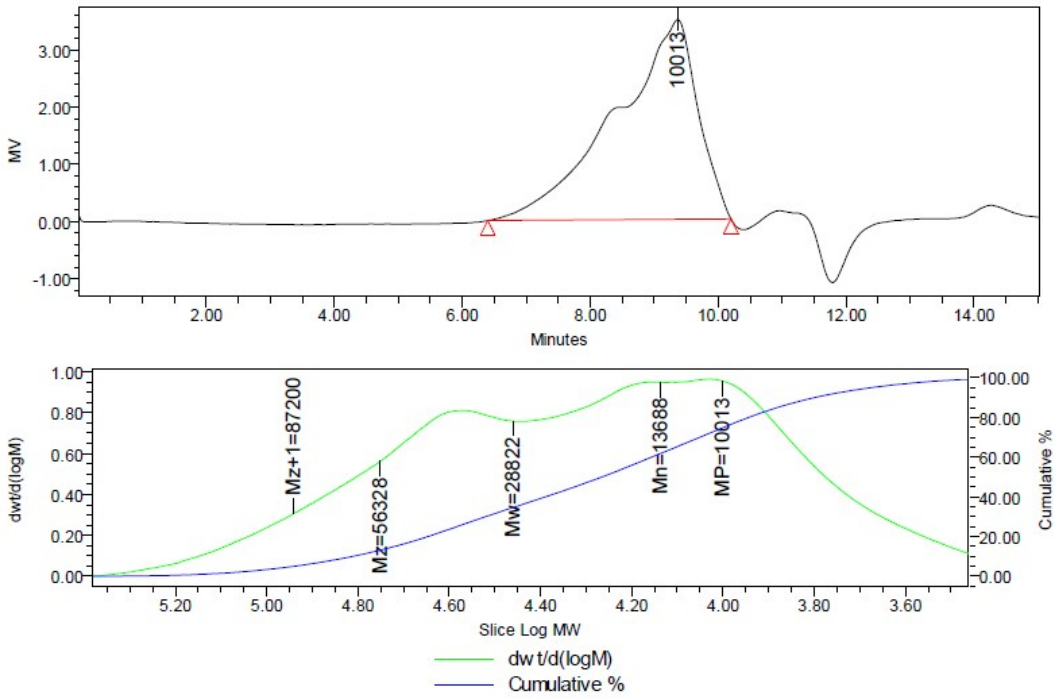
Fig. S18 The GPC sample results for **PIID-DT** (entry 6).



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	8.083	38856	85224	49964	168928	2.193

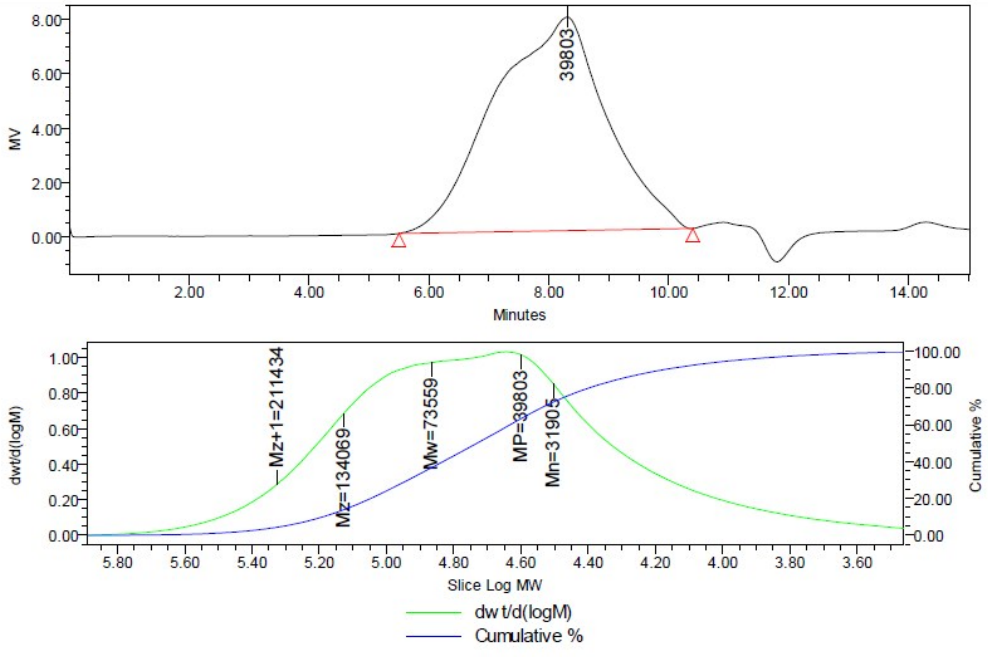
Fig. S19 The GPC sample results for **PIID-DT** (entry 7).



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	9.367	13688	28822	10013	56328	2.106

Fig. S20 The GPC sample results for **PBIBDF-DT** (entry 8).



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	8.308	31905	73559	39803	134069	2.306

Fig. S21 The GPC sample results for **PBIBDF-DT** (entry 9).