

*Electronic Supplementary Information*

**Benzotrithiophene and benzodithiophene-based polymers for efficient polymer solar cells with high open-circuit voltage**

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## 1. Characterization

### a) Normalized UV-vis spectra of polymer/PC<sub>71</sub>BM/DIO

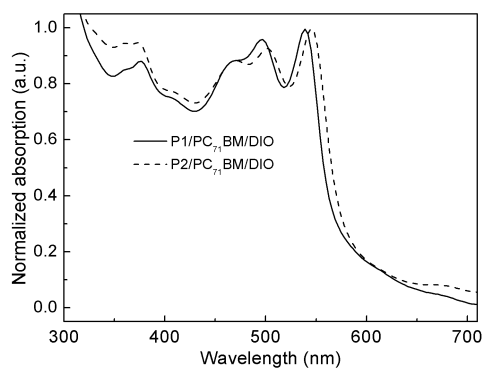


Fig. S1 Normalized UV-vis spectra of polymer/PC<sub>71</sub>BM/DIO.

### b) NMR spectra of monomers and polymers

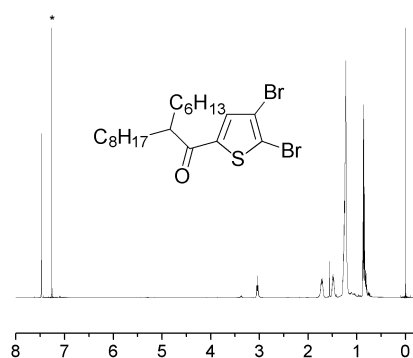


Fig. S2 <sup>1</sup>H NMR spectra of compound **1** in CDCl<sub>3</sub>.

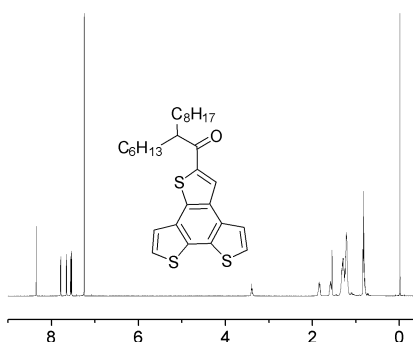
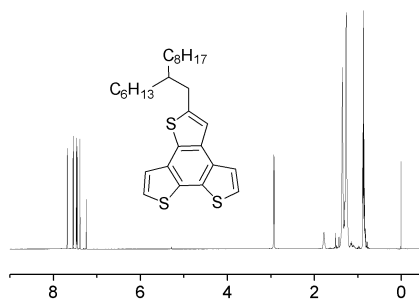
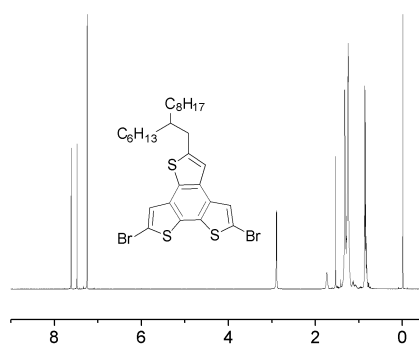


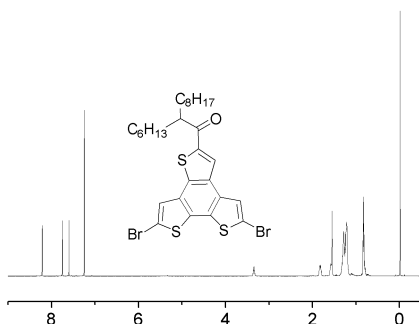
Fig. S3 <sup>1</sup>H NMR spectra of compound **3** in CDCl<sub>3</sub>.



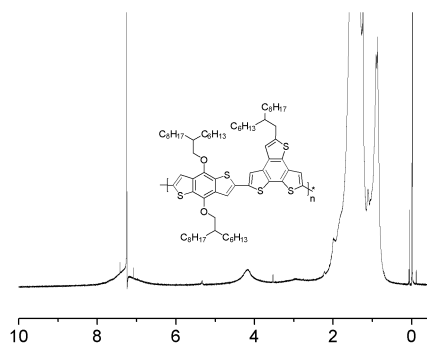
**Fig. S4**  $^1\text{H}$  NMR spectra of compound **4** in  $\text{CDCl}_3$ .



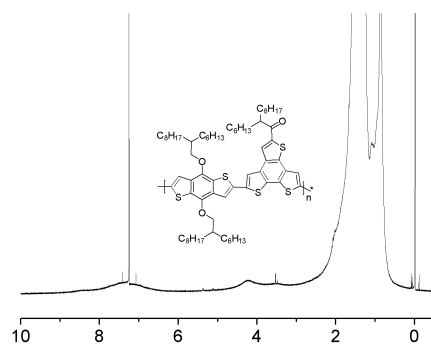
**Fig. S5**  $^1\text{H}$  NMR spectra of compound **5** in  $\text{CDCl}_3$ .



**Fig. S6**  $^1\text{H}$  NMR spectra of compound **6** in  $\text{CDCl}_3$ .



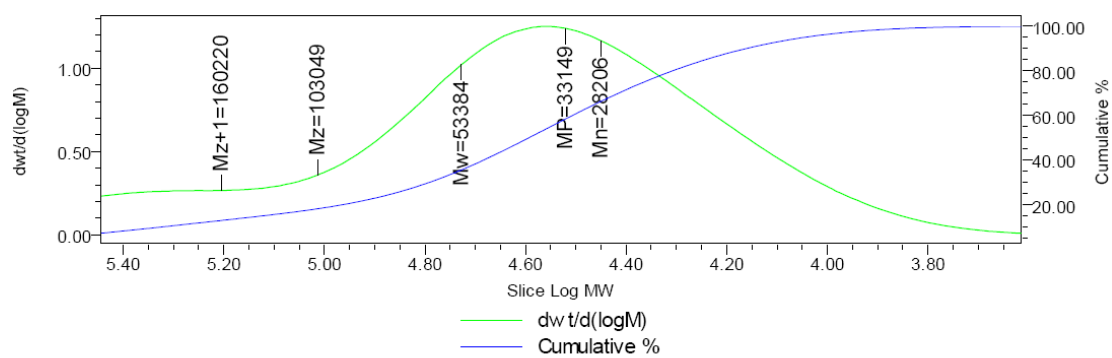
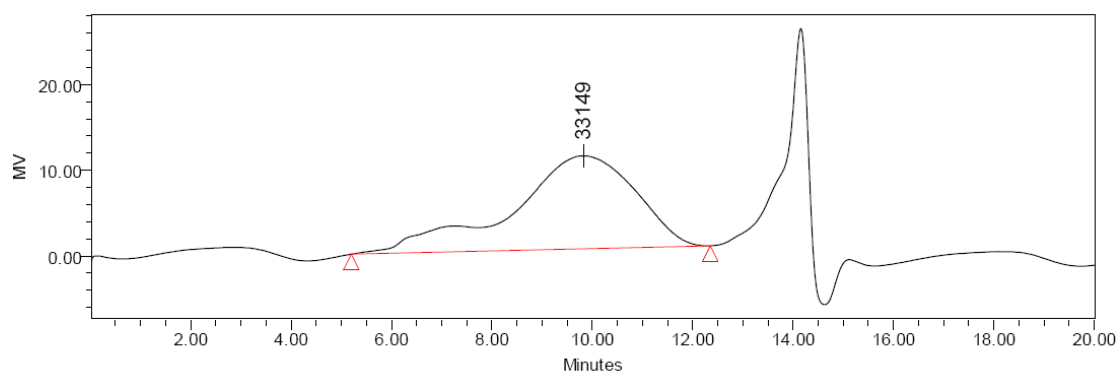
**Fig. S7**  $^1\text{H}$  NMR spectra of **P1** in  $\text{CDCl}_3$ .



**Fig. S8**  $^1\text{H}$  NMR spectra of **P2** in  $\text{CDCl}_3$ .

c) GPC curves

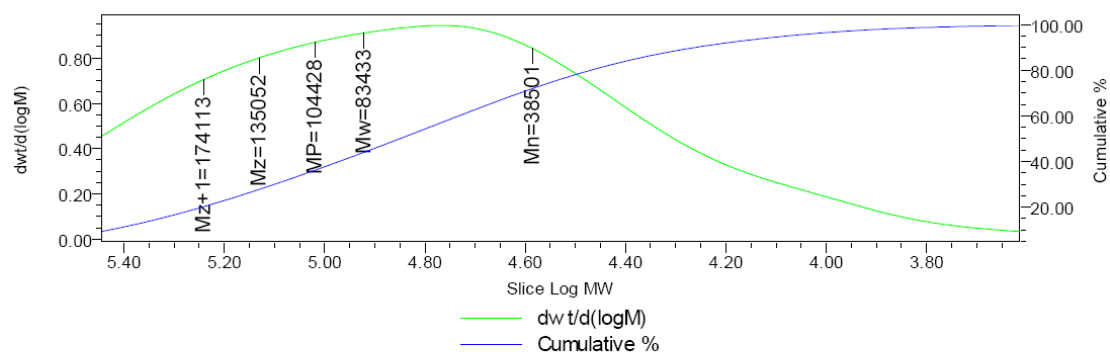
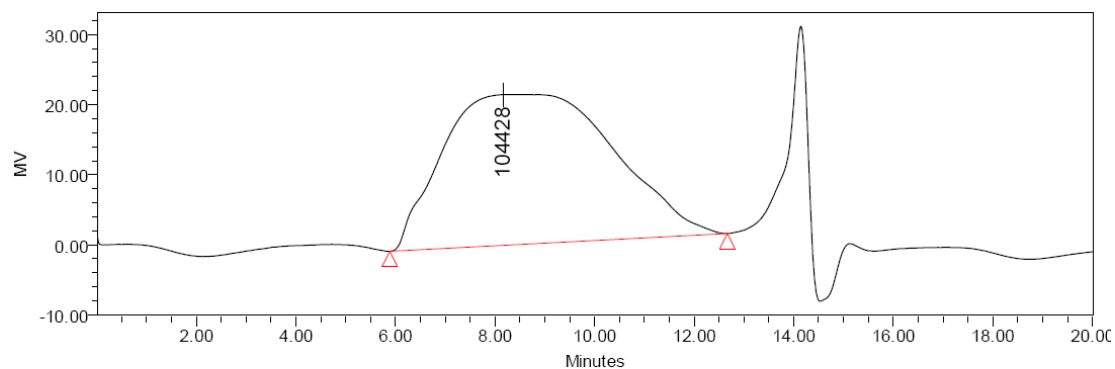
GPC results of **P1**



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	9.828	28206	53384	33149	103049	1.893

### GPC results of P2



GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	8.164	38501	83433	104428	135052	2.167