**Supplementary Information**

# An Expanded Isoindigo Unit as a New Building Block for Conjugated Polymer Leading to High-Performance Solar Cells

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***Contents***

1. ***NMR spectra***

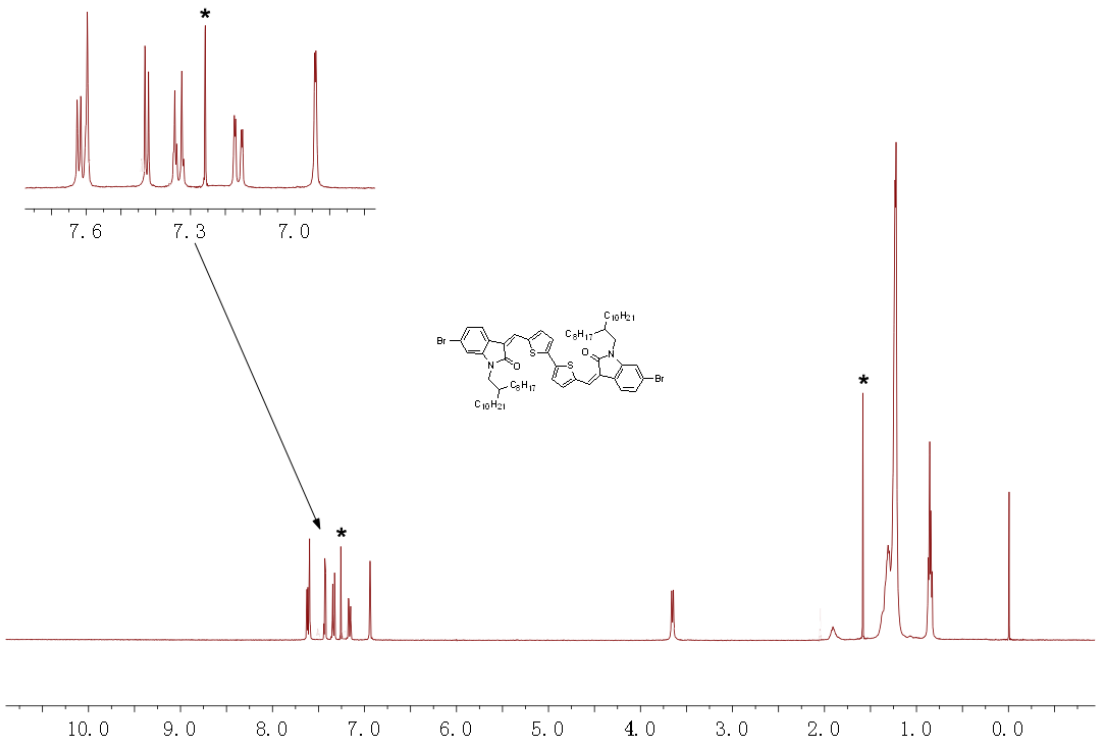



**Fig. S1** $^{1}$H NMR spectrum of (3Z,3′Z)-3,3′-(2,2′-Bithiophene-5,5′-diylbis(methan-1-yl-1-ylidene))bis(6-bromo-1-(2-octyldodecyloxy)indolin-2-one (**IBTI**)

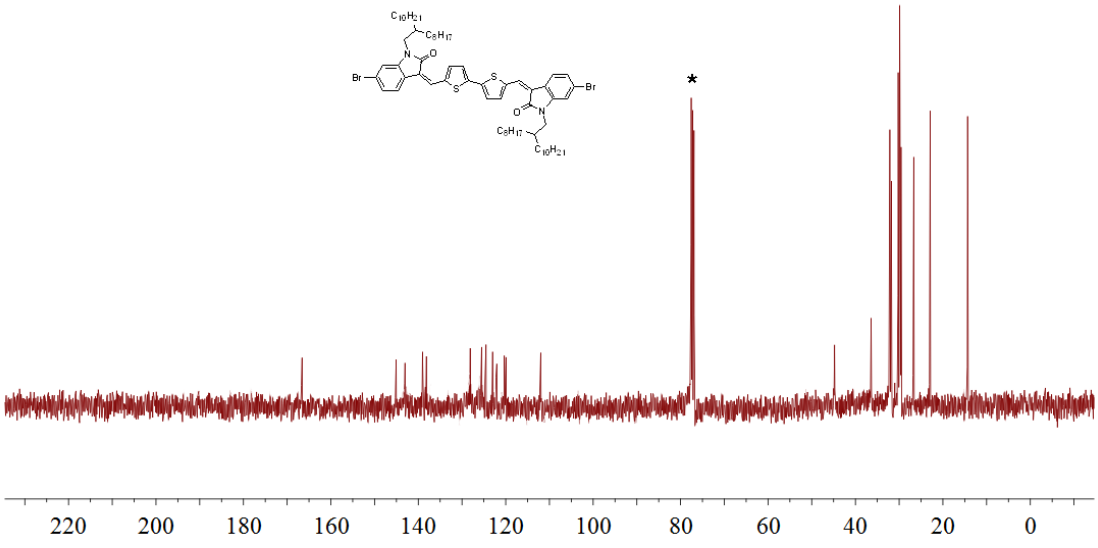


**Fig. S2** $^{13}$C NMR spectrum of (3Z,3′Z)-3,3′-(2,2′-Bithiophene-5,5′-diylbis(methan-1-yl-1-ylidene))bis(6-bromo-1-(2-octyldodecyloxy)indolin-2-one (**IBTI**)

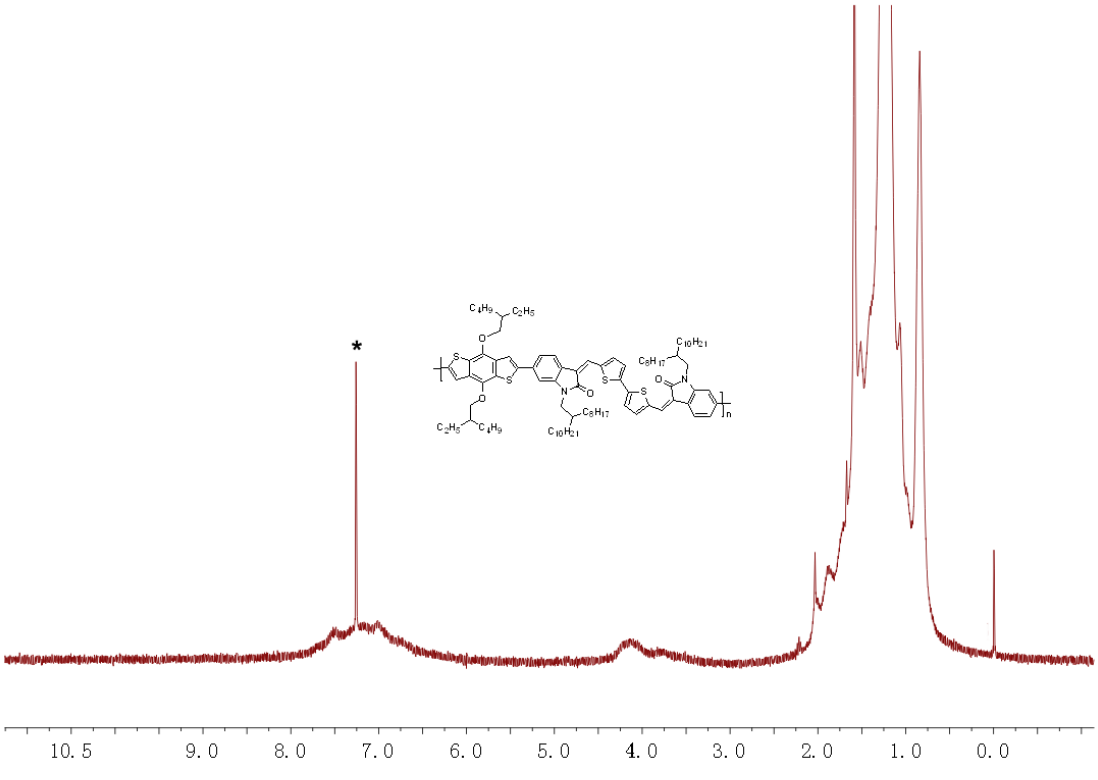



**Fig. S3** $^{1}$H NMR spectrum of **PBDT- IBTI**

## 2. *TGA and DSC thermograms of polymer*

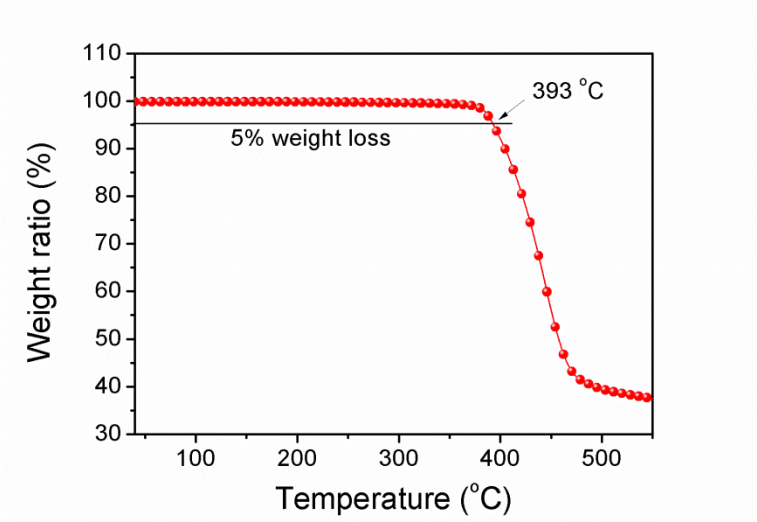



**Fig. S4** TGA plots of polymer **PBDT-I2TI** with a heating rate of 20 °C/min under a $N_2$ atmosphere.

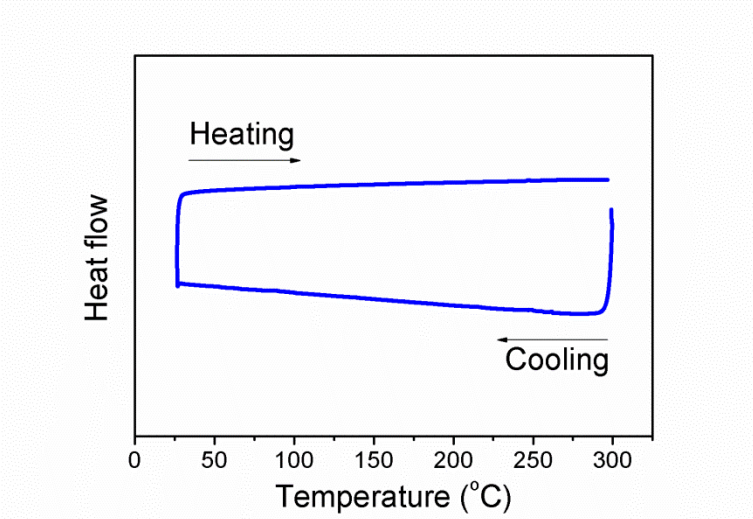
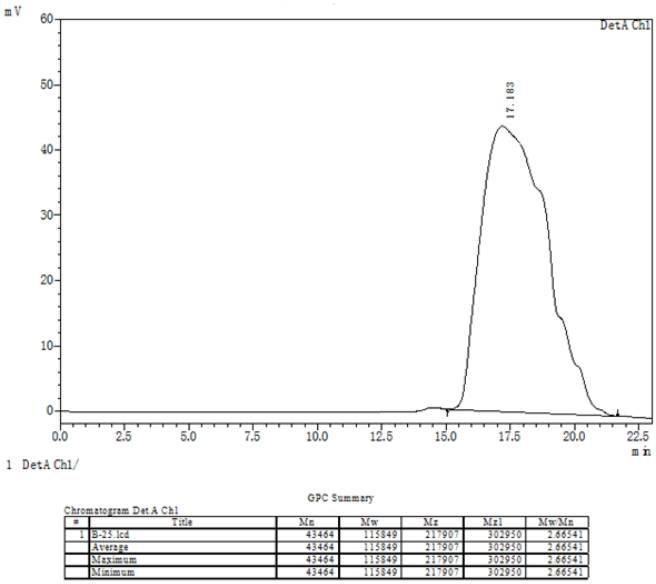



**Fig. S5** DSC thermograms of first cooling and second heating scan of polymer **PBDT-I2TI** at temperature ramp of 10 °C/min.

### *3. GPC curve*




| # | Title | Mn | Mw | Mz | Mz1 | MwMn |
|---|---|---|---|---|---|---|
| 1 | B-25.lcd | 43464 | 115849 | 217907 | 302950 | 2.66541 |
| | Average | 43464 | 115849 | 217907 | 302950 | 2.66541 |
| | Maximum | 43464 | 115849 | 217907 | 302950 | 2.66541 |
| | Minimum | 43464 | 115849 | 217907 | 302950 | 2.66541 |

**Fig. S6** GPC trace of polymer **PBDT-IBTI**, $M_n$ = 43.5 kDa, $M_w$ = 115.8 kDa, PDI = 2.67.

### 4. *Photovoltaic Properties*

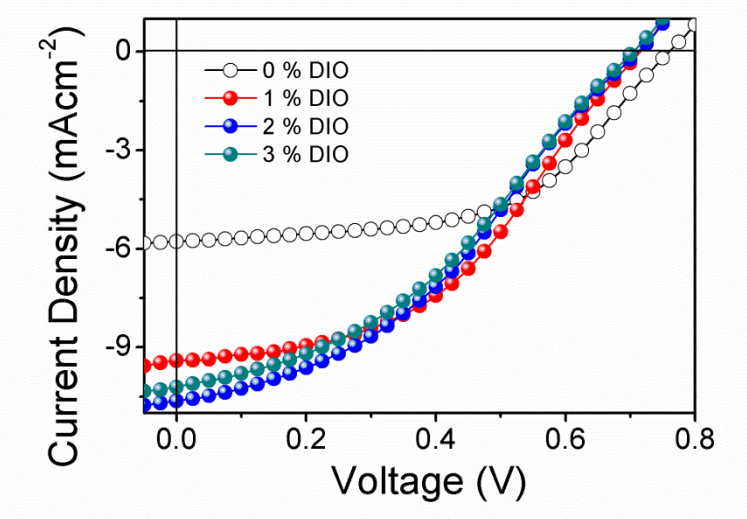



**Fig. S7** *J-V* curves of the PSC devices with conventional structures, active layer based on **PBDT-IBTI**:$PC_{61}BM$ (1:2, *w/w*) processed with DIO from *CB*.

**Table S1** The photovoltaic performances of the PSC devices with inverted structures under the illumination of AM1.5G, 100 mW $cm^{-2}$.

| D/A ratio [a] | $V_{oc}$ (V) | $J_{sc}$ (mA $cm^{-2}$) | FF | PCE (%) |
|---|---|---|---|---|
| 1:1 | 0.76 | 3.24 | 0.39 | 0.96 |
| 1:2 | 0.77 | 6.84 | 0.66 | 3.49 |
| 1:3 | 0.80 | 4.28 | 0.49 | 1.69 |

[a] polymer/ $PC_{61}BM$.