

Electronic Supplementary Information

High open circuit voltage polymer solar cells enabled by employing thiazoles in semiconducting polymers

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Table S1 The Stille coupling polymerization conditions and polymer molecular weights of BDT-DTzBT^a

Entry	Catalyst ^b	Solvent	Monomer concentration ^c	Temperature (°C)	Heat source	Yield (%) ^d	<i>M_n</i> (kDa) /PDI
1	Pd ₂ (dba) ₃ , P(<i>o</i> -Tolyl) ₃	CB/DMF	0.075 M	115	Oil bath	0	--
2	Pd ₂ (dba) ₃ , P(<i>o</i> -Tolyl) ₃	Tol/DMF	0.075 M	115	Oil bath	81	18.6/3.4
3	Pd ₂ (dba) ₃ , P(<i>o</i> -Tolyl) ₃	Tol/DMF	0.075 M	180	Microwave	0	--
4	Pd ₂ (dba) ₃ , [(<i>t</i> -Bu) ₃ P ⁺ H]BF ₄ ⁻	Tol/DMF	0.075 M	180	Microwave	0	--
5	Pd(PPh ₃) ₄	<i>o</i> -Xylene/DMF	0.075 M	120	Oil bath	0	--
6	Pd ₂ (dba) ₃ , P(<i>o</i> -Tolyl) ₃	CB	0.40 M	130	Oil bath	93	--
7	Pd ₂ (dba) ₃ , P(<i>o</i> -Tolyl) ₃	CB	0.60 M	130	Oil bath	72	--
8	Pd ₂ (dba) ₃ , P(<i>o</i> -Tolyl) ₃	<i>o</i> -Xylene/DMF	0.60 M	130	Oil bath	87	--
9	Pd ₂ (dba) ₃ , P(<i>o</i> -Tolyl) ₃	THF	0.20 M	80	Oil bath	0	--

^a All the crude polymers were extracted successively with acetone, hexane, dichloromethane, and chloroform.

^b The catalyst loadings were 3 mol % Pd₂(dba)₃ and 24 mol % [(*t*-Bu)₃P⁺H]BF₄⁻ for entry 4, 3 mol % Pd(PPh₃)₄ for entry 5, and 3 mol % Pd₂(dba)₃ and 24 mol % P(*o*-Tolyl)₃ for entry 1, 2, and 3, and 1.5 mol % Pd₂(dba)₃ and 9 mol % P(*o*-Tolyl)₃ the other entries.

^c Monomer concentration is the total concentration of both bis(trimethyltin) monomer and dibrominated monomer.

^d The yield of polymer fraction extracted by chloroform. For entry 1, 3, 4, 5, and 9, all polymers were completely washed away before extracting by chloroform. In sharp contrast, extraction of BDT-DTBT by chloroform almost give nothing.

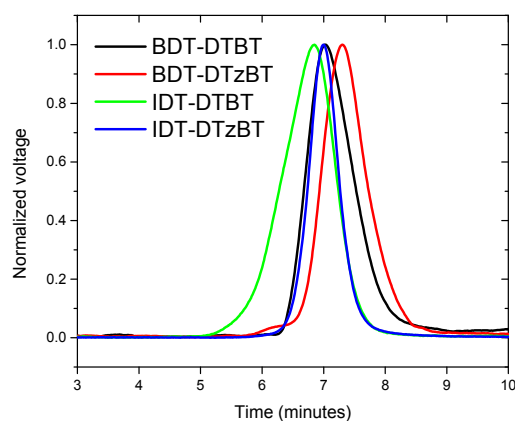
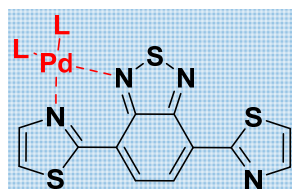


Fig. S1 GPC traces of the polymers measured with *o*-DCB as eluent at 140 °C.



Scheme S1 The possible chelating mode of palladium catalyst by thiazole-substituted BT moiety, leading to the formation of a thermodynamically stable six-member ring that contain palladium.

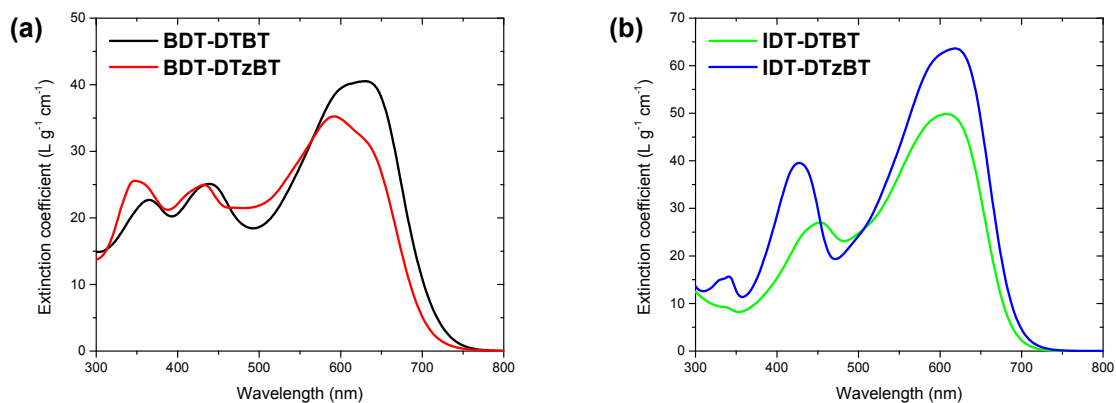


Fig. S2 Optical absorption spectra of the polymers with concentration of 0.05 mg mL⁻¹ in *o*-DCB: (a) BDT-DTBT and BDT-DTzBT; (b) IDT-DTBT and IDT-DTzBT.

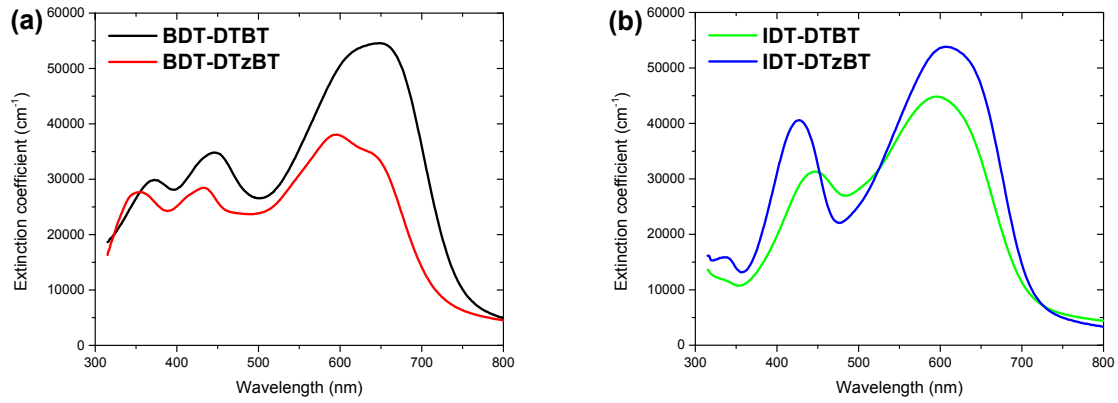


Fig. S3 Optical absorption spectra of the polymers with absorption coefficient in films: (a) BDT-DTBT and BDT-DTzBT; (b) IDT-DTBT and IDT-DTzBT.

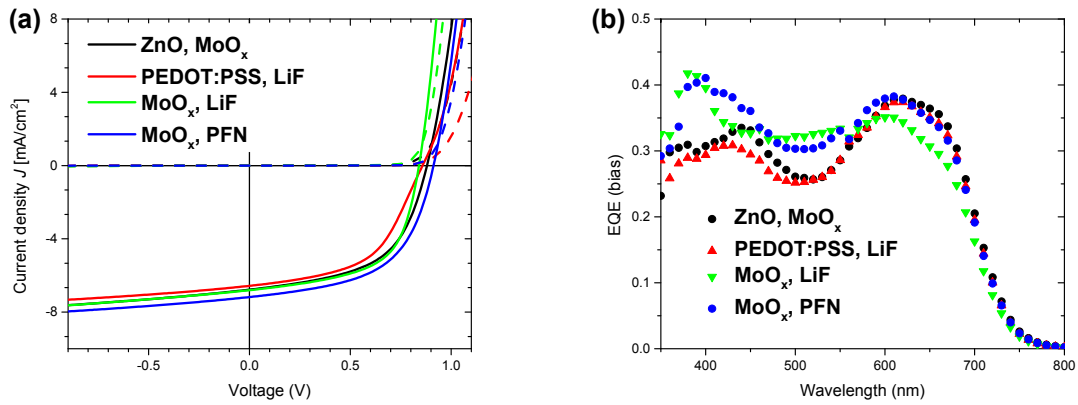


Fig. S4 (a) Current density–voltage (J – V) characteristics of the PSCs made from BDT-DTzBT with different contacts in dark and under AM1.5G illumination (100 mW cm^{-2}). (b) EQE spectra of the corresponding solar cells. The device structure of the PSCs is ITO/bottom contact/BDT-DTzBT:[70]PCBM (1:2)/top contact/Al (100 nm). The active layer of all PSCs were spin-coated from *o*-DCB with 3% 1-chloronaphthalene (CN).

Table S2 Performance parameters of the PSCs made from BDT-DTzBT with different contacts under AM1.5G illumination (100 mW cm⁻²). The device structure of the PSCs is ITO/bottom contact/BDT-DTzBT:[70]PCBM (1:2)/top contact/Al (100 nm).

Bottom contact	Top contact	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
ZnO	MoO _x	6.8	0.88	0.55	3.3
PEDOT:PSS	LiF	6.6	0.86	0.53	3.0
MoO _x	LiF	6.8	0.84	0.59	3.4
MoO _x	PFN	7.2	0.91	0.55	3.6

Table S3 Performance parameters of the PSCs based on BDT-DTzBT under different conditions.

Contact	Acceptor	Ratio	Solvent	Annealing	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
ZnO/~MoO _x	[60]PCBM	1:2	CB	-	3.54	0.881	0.424	1.32
			DCB	-	6.08	0.891	0.447	2.42
				100 °C, 10 min	5.73	0.778	0.455	2.03
			DCB (1% DIO)	-	4.46	0.905	0.394	1.59
			DCB (2.5% DIO)	-	7.08	0.869	0.472	2.90
			DCB (3% CN)	-	6.78	0.880	0.547	3.26
		1:1.5	DCB (3% CN)	-	6.48	0.894	0.404	2.34
		1:2.5	DCB (3% CN)	-	5.73	0.869	0.548	2.76
		1:3	DCB (3% CN)	-	4.71	0.875	0.541	2.23
PEDOT:PSS/~LiF	[60]PCBM	1:2	DCB (3% CN)	-	6.57	0.858	0.525	2.96
MoO _x /~LiF	[60]PCBM	1:2	DCB (3% CN)	-	6.81	0.841	0.588	3.37
MoO _x /~PFN	[60]PCBM	1:2	DCB (3% CN)	-	7.18	0.913	0.551	3.61
	[70]PCBM	1:2	DCB (3% CN)	-	7.17	0.936	0.558	3.74
			CF	-	2.97	0.954	0.525	1.49
			CF (3% DIO)	-	7.39	0.924	0.627	4.28
			CF (3% CN)	-	6.83	0.941	0.533	3.43
			CF (6% DCB)	-	4.21	0.961	0.519	2.10

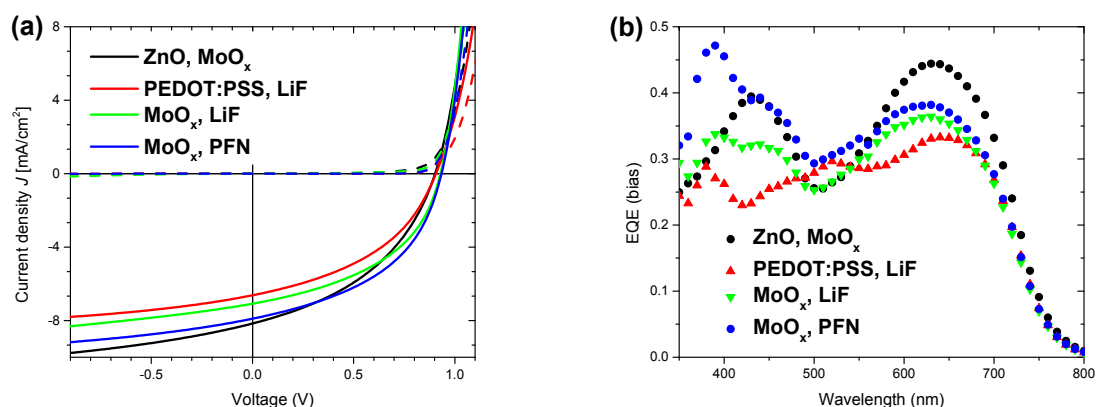


Fig. S5 (a) Current density–voltage (J – V) characteristics of the PSCs made from IDT-DTzBT with different contacts in dark and under AM1.5G illumination (100 mW cm⁻²). (b) EQE spectra of the corresponding solar cells. The device structure of the PSCs is ITO/bottom contact/IDT-DTzBT:[70]PCBM (1:3)/top contact/Al (100 nm). The active layer of all PSCs were spin-coated from *o*-DCB.

Table S4 Performance parameters of the PSCs made from IDT-DTzBT with different contacts under AM1.5G illumination (100 mW cm⁻²). The device structure of the PSCs is ITO/bottom contact/IDT-DTzBT:[70]PCBM (1:3)/top contact/Al (100 nm).

Bottom contact	Top contact	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
ZnO	MoO _x	8.2	0.90	0.42	3.1
PEDOT:PSS	LiF	6.6	0.91	0.43	2.6
MoO _x	LiF	7.1	0.93	0.46	3.0
MoO _x	PFN	7.9	0.93	0.46	3.4

Table S5 Performance parameters of the PSCs based on IDT-DTzBT under different conditions.

Contact	Acceptor	Ratio	Solvent	Annealing	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
ZnO/~ /MoO _x	[60]PCBM	1:2	DCB	-	7.28	0.944	0.363	2.50
			DCB	-	7.92	0.922	0.407	2.97
			DCB	130 °C	8.16	0.902	0.417	3.07
			DCB (2.5% DIO)	130 °C	7.61	0.891	0.393	2.66
			DCB (3% CN)	130 °C	7.44	0.901	0.400	2.68
		1:3	CB	130 °C	7.23	0.905	0.409	2.68
			CB (2.5% DIO)	130 °C	6.33	0.882	0.345	1.92
			CB (2% CN)	130 °C	6.58	0.904	0.390	2.32
			CF	130 °C	7.73	0.889	0.388	2.67
			CF (3% DIO)	130 °C	6.92	0.890	0.387	2.38
			CF (3% CN)	130 °C	7.76	0.898	0.413	2.87
			CF (6% DCB)	130 °C	7.75	0.932	0.420	3.03
			CF (10% DCB)	130 °C	7.89	0.924	0.420	3.06
			TCE	130 °C	7.13	0.914	0.411	2.68
		1:4	DCB	-	7.28	0.905	0.435	2.87
PEDOT:PSS/~ /LiF	[60]PCBM	1:3	DCB	130 °C	6.62	0.906	0.428	2.57
MoO _x /~ /LiF	[60]PCBM	1:3	DCB	130 °C	7.08	0.928	0.459	3.02
MoO _x /~ /PFN	[60]PCBM	1:3	DCB	130 °C	7.90	0.934	0.461	3.40
	[70]PCBM	1:3	DCB	130 °C	10.47	0.939	0.458	4.50

Table S6. Device statistics of polymer:[70]PCBM solar cells.^a

Polymer	J_{sc} (mA cm ⁻²)	$J_{sc}(\text{EQE})^b$ (mA cm ⁻²)	V_{oc} (V)	FF (-)	P_{max} (mW cm ⁻²)	PCE ^c (%)
BDT-DTBT	9.8	10.9	0.73	0.60	4.3	4.8
	9.7 ± 0.1		0.73 ± 0.01	0.59 ± 0.01	4.2 ± 0.1	
BDT-DTzBT	6.6	7.4	0.92	0.63	3.9	4.3
	6.5 ± 0.1		0.93 ± 0.01	0.63 ± 0.01	3.8 ± 0.1	
IDT-DTBT	8.4	9.8	0.75	0.49	3.1	3.6
	8.1 ± 0.2		0.72 ± 0.02	0.49 ± 0.01	2.9 ± 0.1	
IDT-DTzBT	9.4	10.5	0.94	0.46	4.0	4.5
	9.2 ± 0.2		0.93 ± 0.01	0.45 ± 0.01	3.9 ± 0.1	

^aMeasured with white light (100 mW cm⁻²) in a ITO/MoO_x(10 nm)/polymer:[70]PCBM/PFN/Al(100 nm) device configuration. Both maximum and device statistics from four devices are given. ^bDetermined by integrating the EQE with the AM1.5G solar spectrum. ^c Calculated using J_{sc} (EQE).

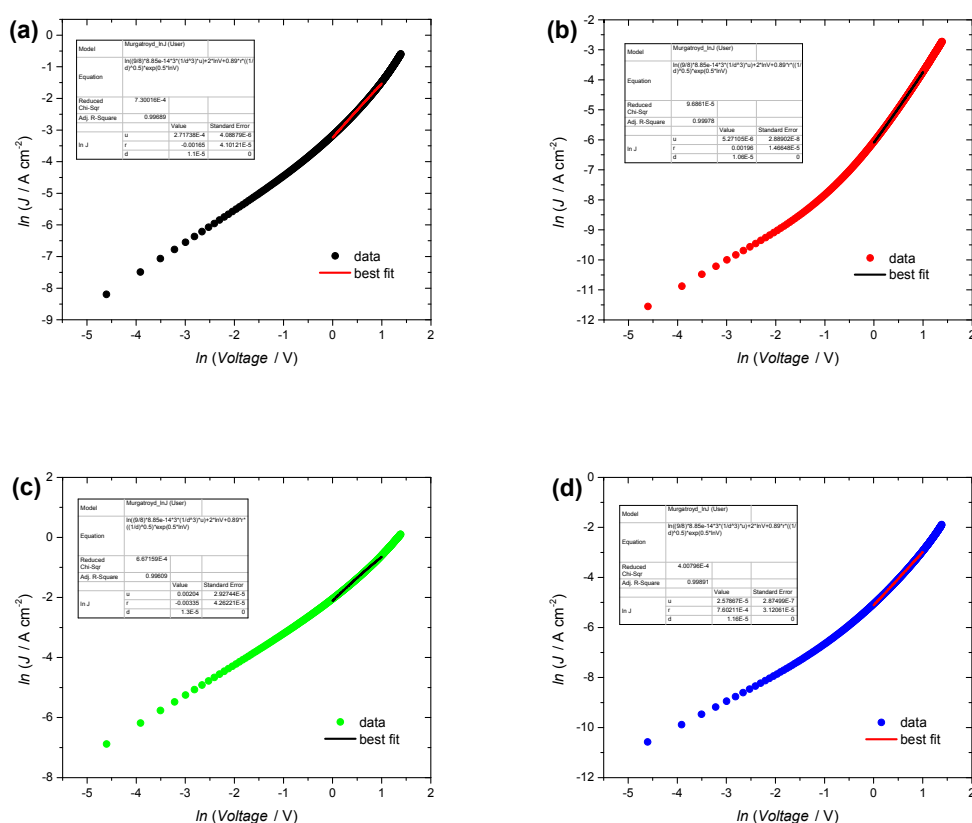


Fig. S6 Current density versus voltage characteristics of hole-only devices with a configuration of ITO/MoO_x (10 nm)/polymer:[70]PCBM/MoO_x (10 nm)/Ag (100 nm) plotted in the format of $\ln J \sim \ln V$: (a) BDT-DTBT, (b) BDT-DTzBT, (c) IDT-DTBT, and (d) IDT-DTzBT.

Table S7 Summary of the derived fitting data for the hole-only devices based on Mott-Gurneys law with field-dependent mobility.

Polymer	Zero-field mobility μ_0 ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Field-dependence factor γ ($\text{cm}^{1/2} \text{V}^{-1/2}$)	μ_{h} at $E = 2 \times 10^5 \text{ V cm}^{-1}$ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
BDT-DTBT	2.7×10^{-4}	-1.7×10^{-3}	1.3×10^{-4}
BDT-DTzBT	5.3×10^{-6}	2.0×10^{-3}	1.3×10^{-5}
IDT-DTBT	2.0×10^{-3}	-3.4×10^{-3}	4.6×10^{-4}
IDT-DTzBT	2.6×10^{-5}	7.6×10^{-4}	3.6×10^{-5}

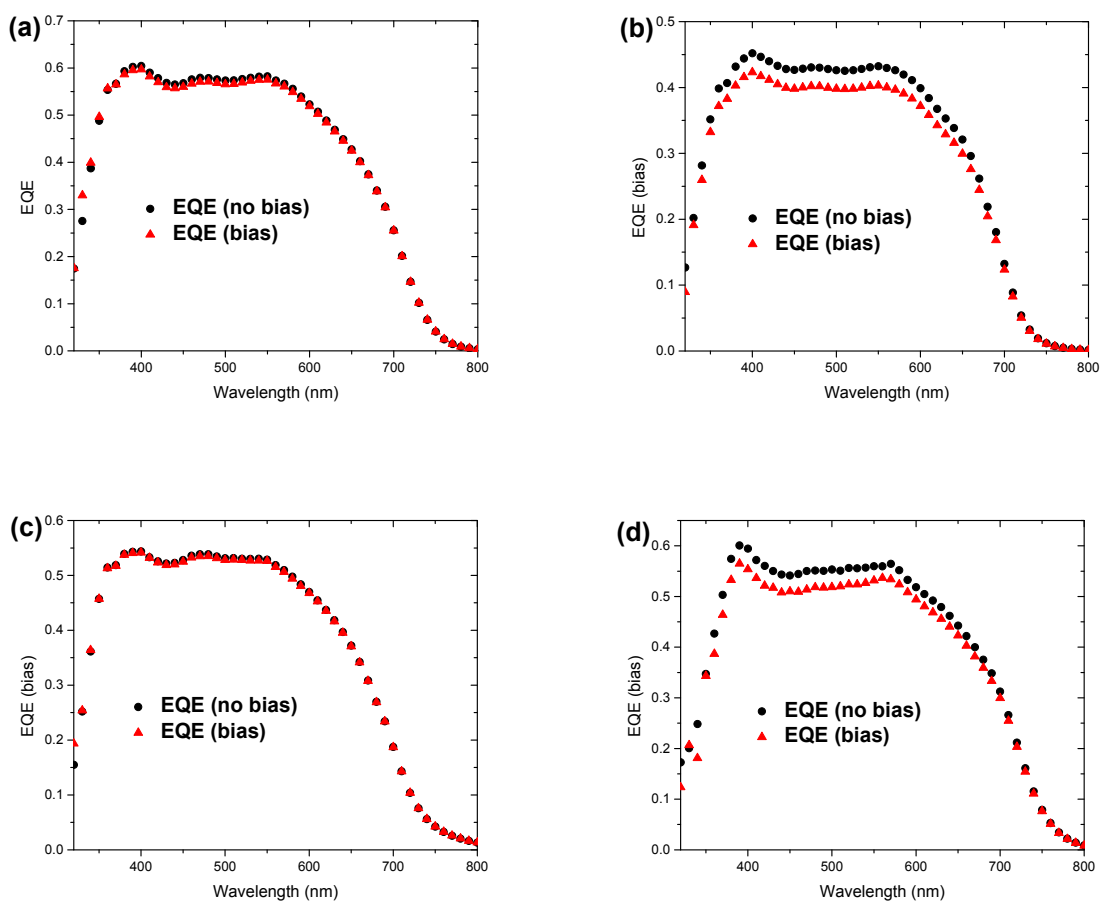


Fig. S7 EQE spectra measured with and without light bias of the polymer:[70]PCBM solar cells based on BDT-DTBT (a), BDT-DTzBT (b), IDT-DTBT (c), and IDT-DTzBT (d).

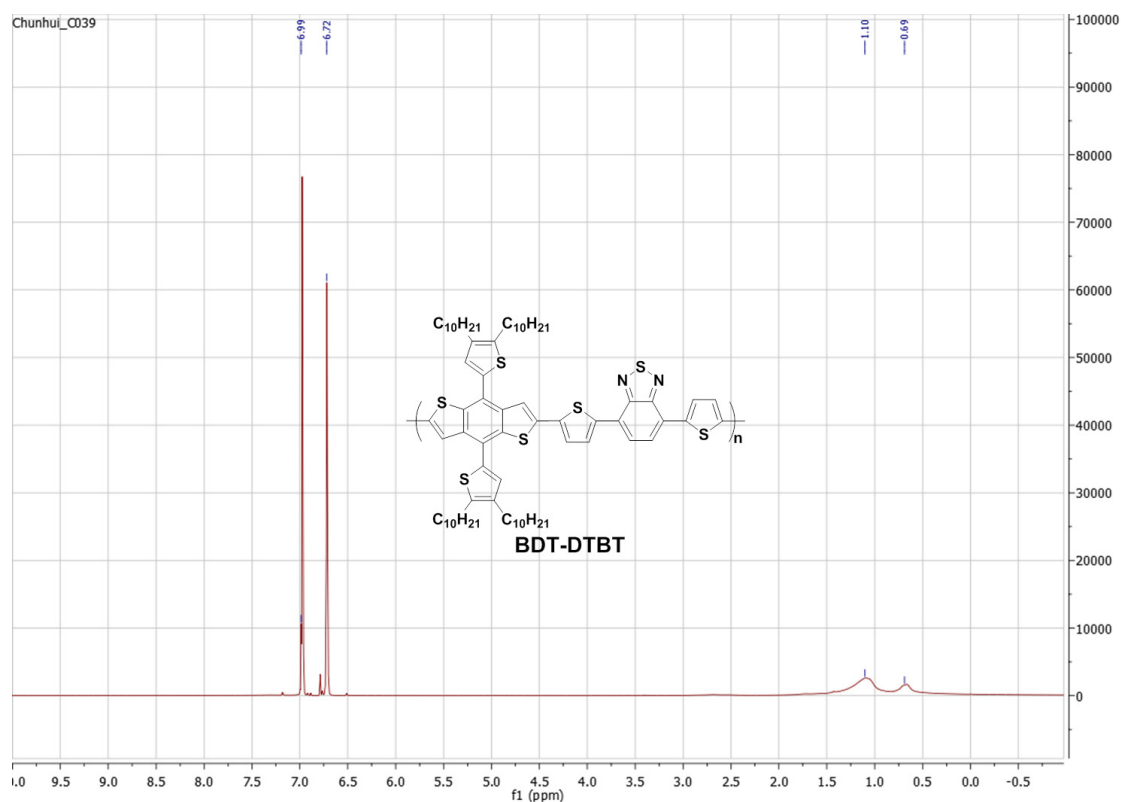


Fig. S8 ^1H -NMR of BDT-DTBT acquired from $o\text{DCB-}d_4$.

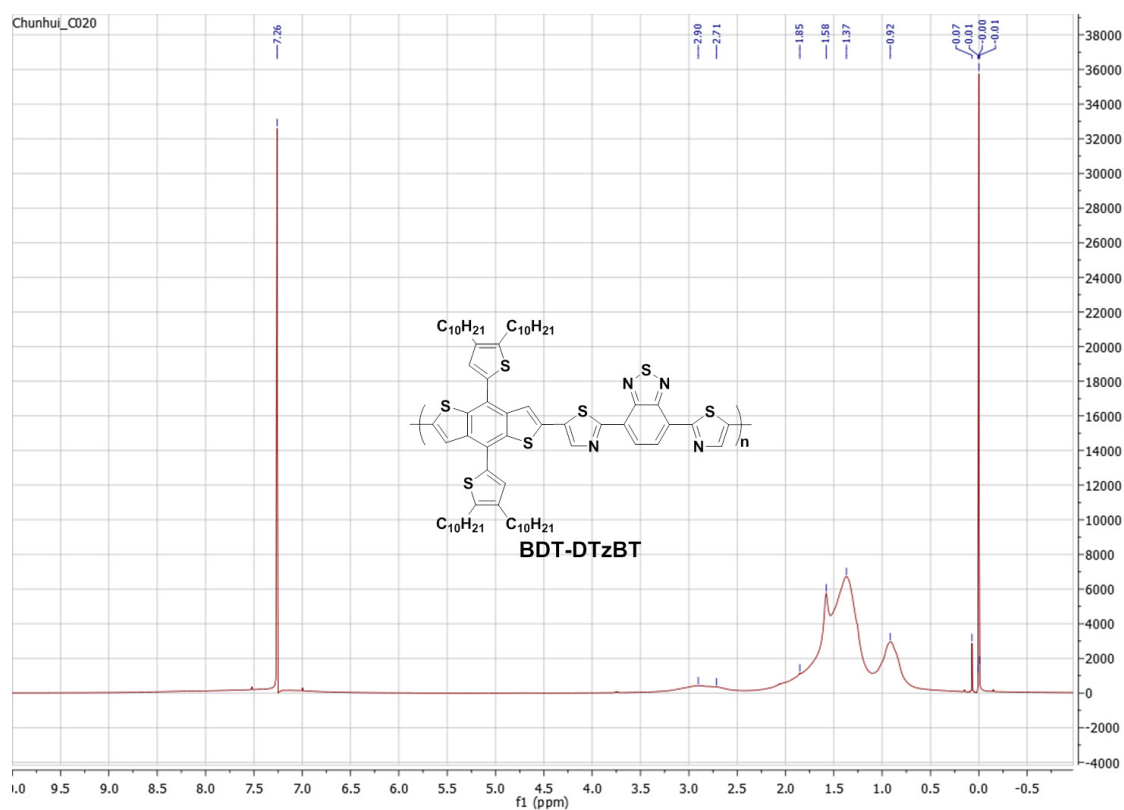


Fig. S9 ^1H -NMR of BDT-DTzBT acquired from CDCl_3 .

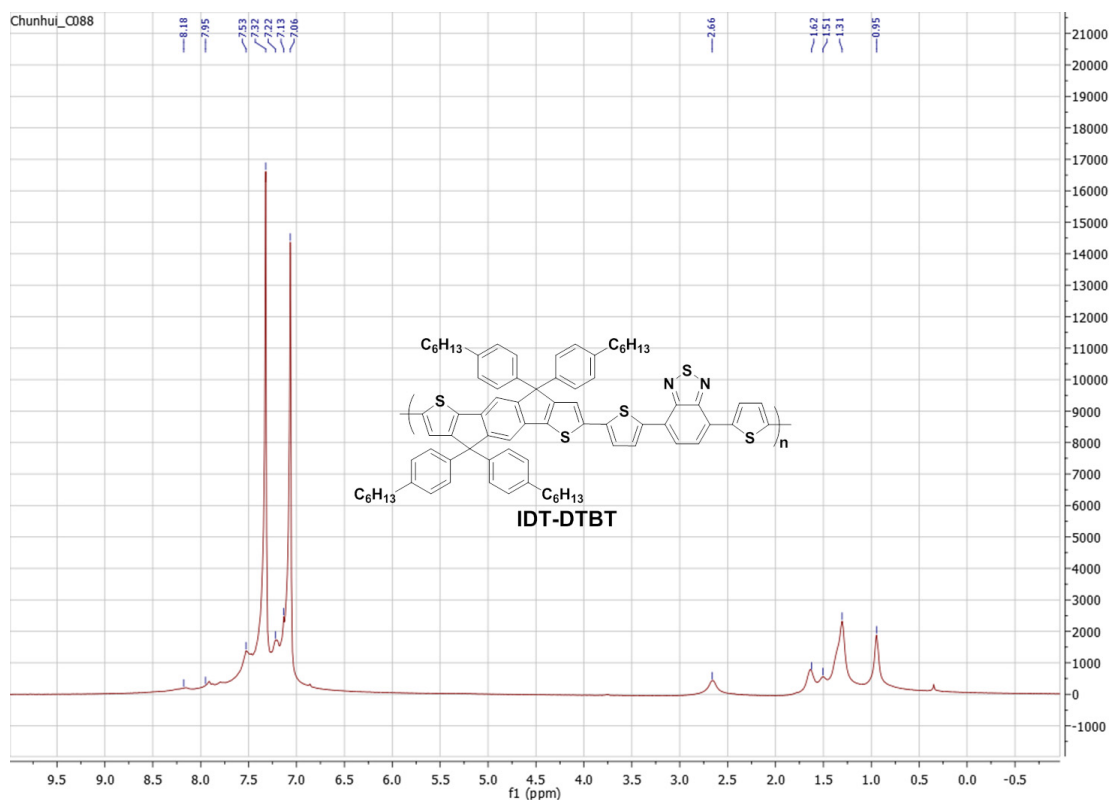


Fig. S10 ^1H -NMR of IDT-DTBT acquired from $o\text{DCB-}d_4$.

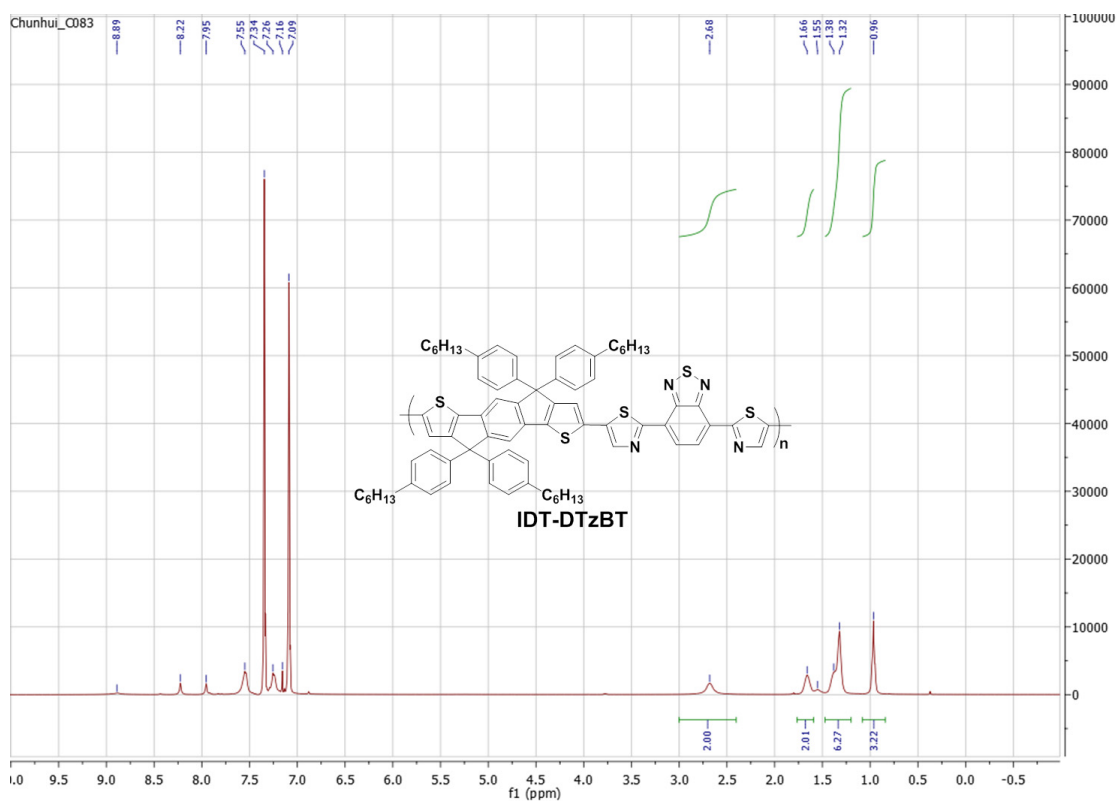


Fig. S11 ^1H -NMR of IDT-DTzBT acquired from $o\text{DCB-}d_4$.