

Supporting Information for

**Effect of Alkyl Chain Topology on the Structure, Optoelectronic Properties
and Solar Cell Performance of Thienopyrroledione-Cored Oligothiophene
Chromophores**

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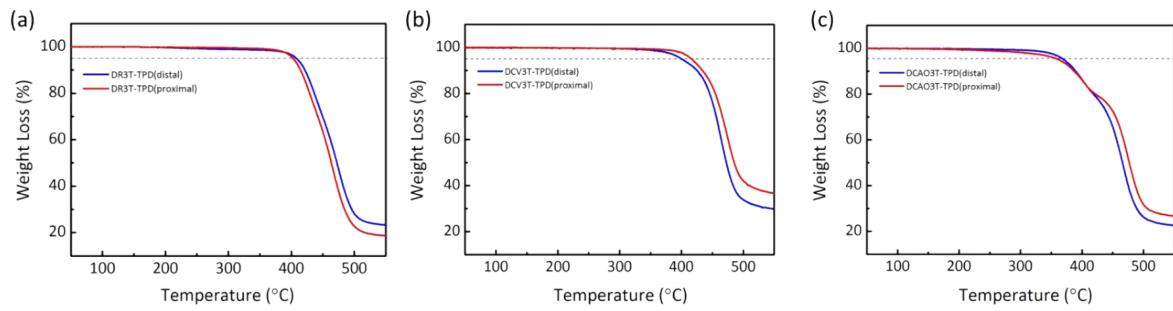


Figure S1. TGA thermograms of (a) DR3T-TPD, (b) DCV3T-TPD and (c) DCAO3T-TPD.

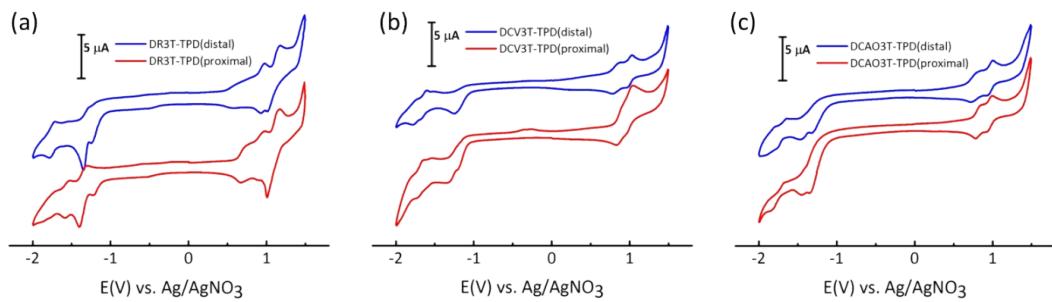


Figure S2. Cyclic voltammograms for (a) DR3T-TPD, (b) DCV3T-TPD and (c) DCAO3T-TPD.

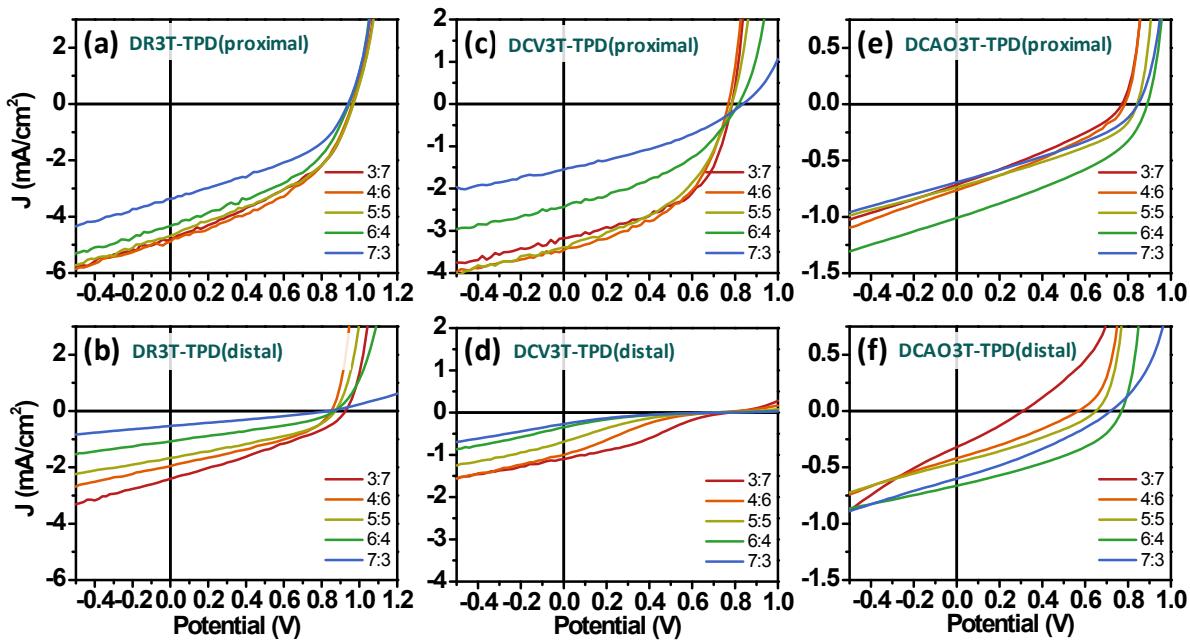


Figure S3. J - V characteristics of BHJ devices with various Donor:PC₇₁BM ratios.

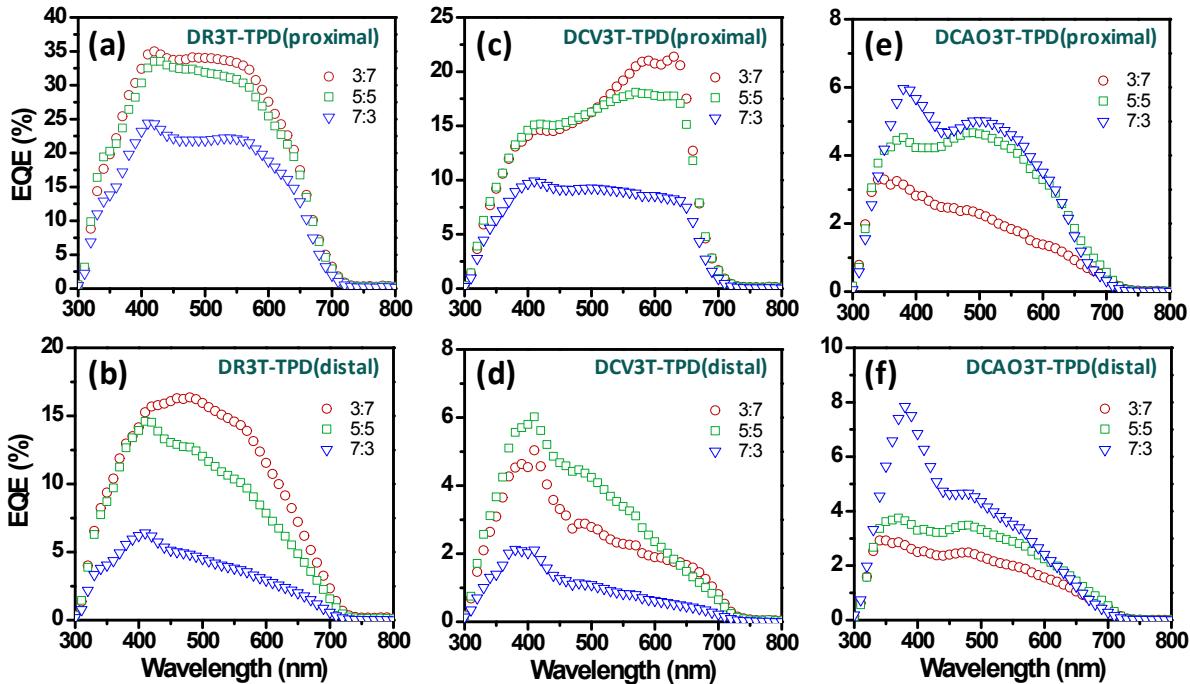


Figure S4. EQE characteristics of BHJ devices with various donor:PC₇₁BM ratios.

Table S1. Summary of photovoltaic characteristics of Donor:PC₇₁BM bulk heterojunctions.

Material	Isomer	Blend Ratio	<i>J_{sc}</i> (mAcm ⁻²)	<i>V_{oc}</i> (V)	<i>FF</i>	PCE (%)
DR3T-TPD	proximal	3:7	4.81	0.966	0.404	1.88
DR3T-TPD	proximal	4:6	4.89	0.962	0.429	1.98
DR3T-TPD	proximal	5:5	4.68	0.968	0.421	1.91
DR3T-TPD	proximal	6:4	4.33	0.946	0.417	1.71
DR3T-TPD	proximal	7:3	3.36	0.940	0.402	1.27
DR3T-TPD	distal	3:7	2.40	0.926	0.318	0.71
DR3T-TPD	distal	4:6	1.95	0.850	0.370	0.61
DR3T-TPD	distal	5:5	1.67	0.871	0.368	0.53
DR3T-TPD	distal	6:4	1.08	0.869	0.332	0.31
DR3T-TPD	distal	7:3	0.53	0.833	0.280	0.12
DCV3T-TPD	proximal	3:7	3.18	0.785	0.514	1.28
DCV3T-TPD	proximal	4:6	3.46	0.768	0.478	1.27
DCV3T-TPD	proximal	5:5	3.39	0.784	0.443	1.18
DCV3T-TPD	proximal	6:4	2.44	0.816	0.396	0.79
DCV3T-TPD	proximal	7:3	1.55	0.837	0.354	0.46
DCV3T-TPD	distal	3:7	1.10	0.773	0.292	0.25
DCV3T-TPD	distal	4:6	1.00	0.704	0.193	0.14
DCV3T-TPD	distal	5:5	0.69	0.714	0.152	0.08
DCV3T-TPD	distal	6:4	0.35	0.722	0.130	0.03
DCV3T-TPD	distal	7:3	0.27	0.763	0.131	0.03
DCAO3T-TPD	proximal	3:7	0.71	0.771	0.316	0.17
DCAO3T-TPD	proximal	4:6	0.76	0.784	0.332	0.20
DCAO3T-TPD	proximal	5:5	0.74	0.843	0.369	0.23
DCAO3T-TPD	proximal	6:4	1.01	0.889	0.387	0.35
DCAO3T-TPD	proximal	7:3	0.69	0.847	0.345	0.20
DCAO3T-TPD	distal	3:7	0.32	0.310	0.278	0.03
DCAO3T-TPD	distal	4:6	0.42	0.568	0.296	0.07
DCAO3T-TPD	distal	5:5	0.46	0.650	0.318	0.09
DCAO3T-TPD	distal	6:4	0.66	0.770	0.391	0.20
DCAO3T-TPD	distal	7:3	0.60	0.718	0.311	0.13

Table S2. Summary of photovoltaic characteristics of DR3T-TPD(proximal):PC₇₁BM with thermal annealing.

Blend Ratio	Annealing	J_{sc} (mAcm ⁻²)	V_{oc} (V)	FF	PCE (%)
3:7	As-cast	4.81	0.966	0.404	1.88
3:7	80 °C	4.02	0.965	0.333	1.29
3:7	110 °C	3.27	0.848	0.307	0.85
4:6	As-cast	4.89	0.962	0.42	1.98
4:6	80 °C	4.10	0.996	0.337	1.37
4:6	110 °C	3.00	0.836	0.325	0.82
5:5	As-cast	4.68	0.968	0.421	1.91
5:5	80 °C	4.01	1.008	0.351	1.42
5:5	110 °C	3.12	0.855	0.353	0.94
6:4	As-cast	4.33	0.946	0.417	1.71
6:4	80 °C	3.91	0.99	0.357	1.38
6:4	110 °C	2.85	0.835	0.363	0.86
7:3	As-cast	3.36	0.94	0.402	1.27
7:3	80 °C	3.44	0.987	0.362	1.23
7:3	110 °C	2.29	0.797	0.365	0.67

Table S3. Summary of photovoltaic characteristics of DR3T-TPD(proximal):PC₇₁BM processed with various processing additives.

Blend Ratio	Additive	J_{sc} (mAcm ⁻²)	V_{oc} (V)	FF	PCE (%)
4:6	None	4.89	0.962	0.429	1.98
	0.1% DPE	3.94	0.866	0.397	1.35
	0.2% DPE	4.31	0.868	0.408	1.53
	0.4% DPE	4.45	0.846	0.389	1.47
	0.6% DPE	4.11	0.799	0.356	1.17
	0.6% DIO	1.91	0.711	0.273	0.37
	0.6% CN	3.89	0.748	0.269	0.78
	0.02% PDMS	4.54	0.851	0.394	1.52
	0.06% PDMS	5.12	0.924	0.426	2.01
	0.1% PDMS	4.39	0.881	0.399	1.54
	0.15% PDMS	1.52	0.891	0.317	0.43
	5:5	None	4.61	0.909	0.398
	0.6% DPE	3.53	0.805	0.332	0.94
	0.6% CN	2.65	0.777	0.264	0.54

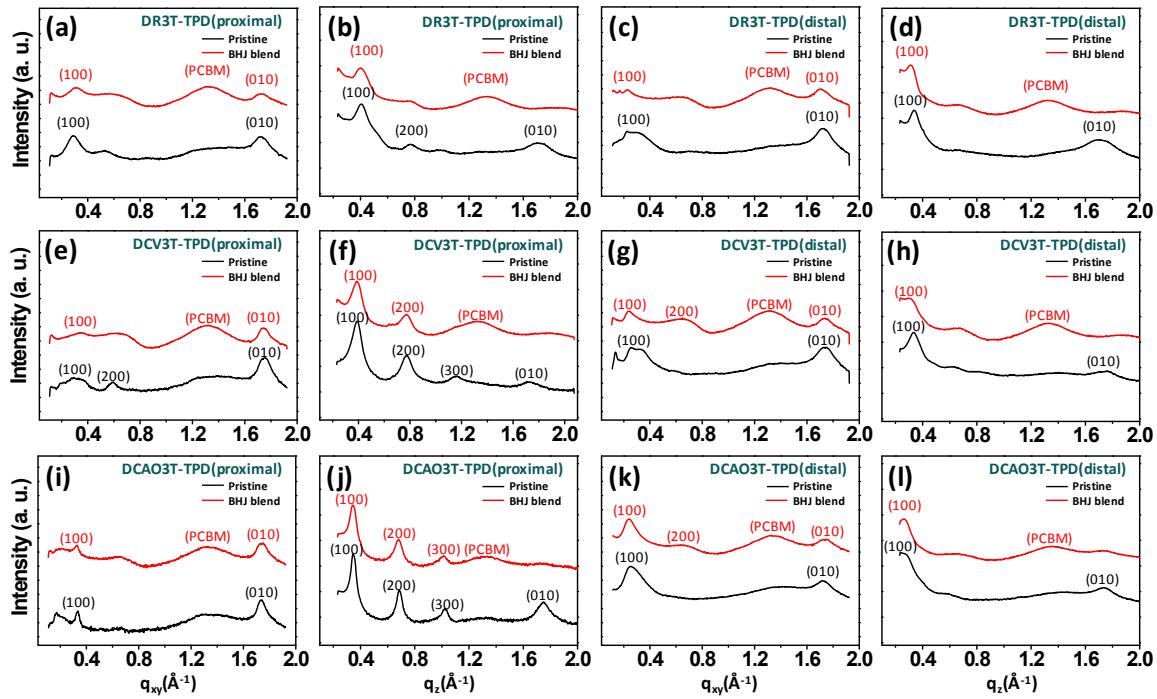


Figure S5. GIWAXS horizontal and vertical line-cuts. (a, b) DR3T-TPD(proximal), (c, d) DR3T-TPD(distal), (e, f) DCV3T-TPD(proximal), (g, h) DCV3T-TPD(distal), (i, j) DCAO3T-TPD(proximal), (k, l) DCAO3T-TPD(distal). First and third columns correspond to line-cuts in the in-plane direction, while second and fourth columns correspond to vertical line-cuts in the out-of-plane direction.

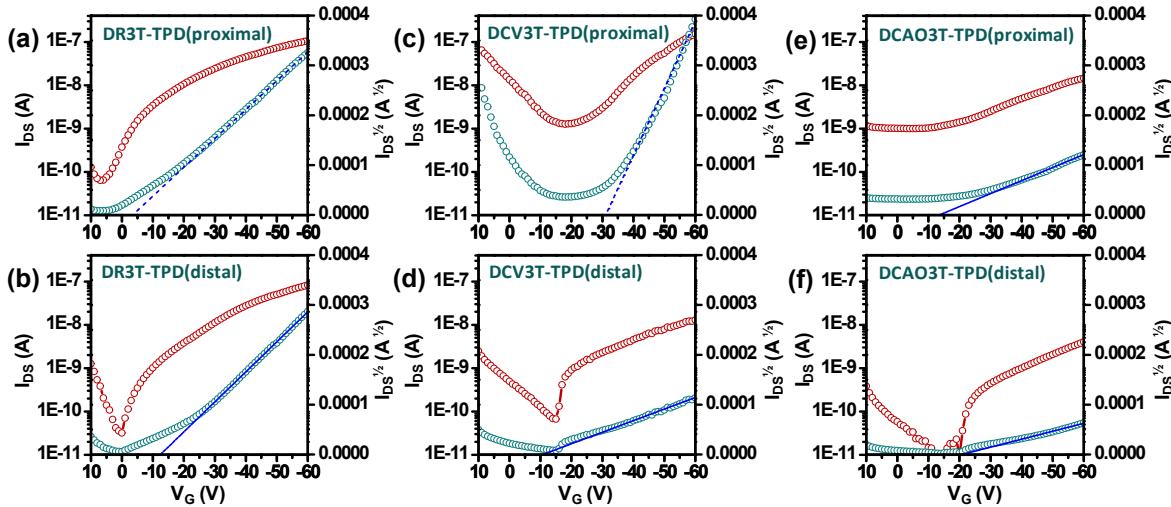


Figure S6. Transfer characteristics of FETs based on (a) DR3T-TPD(proximal), (b) DR3T-TPD(distal), (c) DCV3T-TPD(proximal), (d) DCV3T-TPD(distal), (e) DCAO3T-TPD(proximal), and (f) DCAO3T-TPD(distal).

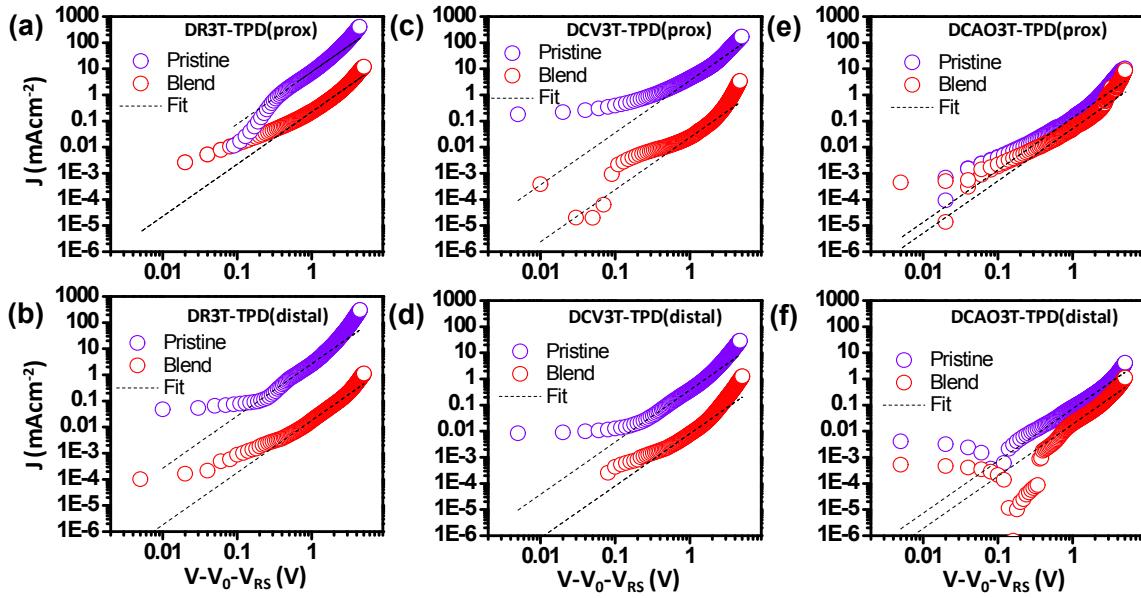


Figure S7. J - V characteristics of hole-only diodes, comparing pristine molecules and BHJ films. (a) DR3T-TPD(proximal), (b) DR3T-TPD(distal), (c) DCV3T-TPD(proximal), (d) DCV3T-TPD(distal), (e) DCAO3T-TPD(proximal), (f) DCAO3T-TPD(distal).

Table S4. Summary of SCLC hole mobilities.

Material	Isomer	μ_h	μ_h	Ratio
		(Pristine) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	(Blend) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	(Blend/ Pristine)
DR3T-TPD	proximal	2.5×10^{-4}	1.0×10^{-5}	0.041
DR3T-TPD	distal	7.2×10^{-5}	8.3×10^{-7}	0.012
DCV3T-TPD	proximal	1.6×10^{-4}	6.6×10^{-7}	0.004
DCV3T-TPD	distal	1.8×10^{-5}	2.2×10^{-7}	0.012
DCAO3T-TPD	proximal	6.1×10^{-6}	2.4×10^{-6}	0.385
DCAO3T-TPD	distal	3.3×10^{-6}	8.6×10^{-7}	0.259