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Supporting Information

The Effect of Molecular Geometry on the

Polymer/Fullerene Ratio in Polymer Solar Cells

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Figure S1 400 MHz ¹H NMR spectra of polymer PTP8 in CDCl₃



Figure S2 400 MHz ¹H NMR spectra of polymer PTN8 in CDCl₃.



Figure S3 Optimized molecular orbital surfaces of the LUMO and HOMO of PTP8, PTN8 and PTN8'



Fig. S4 AFM images of **PTP8** and **PTN8** based blend cast from chloroform w/wo DIO (polymer/fullerene weight ratio 1/0.5).



Fig. S5 a-d) TEM and HAADF-STEM images of **PTP8** and **PTN8** based blends under the same processing conditions (with 0.5% DIO, D/A weight ratio 1/0.5).

Table S1 Optimized devices performance of PTP8:PC₇₁BM blends with varying D/A blend weight ratios.

D/A Ratio w/w	V _{oc} (V)	$J_{\rm sc}$ [mA/cm ²]	FF (%)	PCE (%)
1:1.0	0.93	10.50	55.7	5.44
1:0.8	0.96	11.00	58.5	6.18
1:0.6	0.97	10.32	57.6	5.77
1:0.5	0.98	10.51	58.1	5.98
1:0.3	1.00	8.42	48.0	4.04