Linear Side Chains in Benzo[1,2-b:4,5-b′]dithiophene–Thieno[3,4-c]pyrrole-4,6-dione Polymers Direct Self-Assembly and Solar Cell Performance

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Résumé en anglais	While varying the size and branching of solubilizing side chains in π-conjugated polymers impacts their self-assembling properties in thin-film devices, these structural changes remain difficult to anticipate. This report emphasizes the determining role that linear side-chain substituents play in poly(benzo[1,2-*b*:4,5-*b*′]dithiophene–thieno[3,4-*c*]pyrrole-4,6-dione) (PBDTTPD) polymers for bulk heterojunction (BHJ) solar cell applications. We show that replacing branched side chains by linear ones in the BDT motifs induces a critical change in polymer self-assembly and backbone orientation in thin films that correlates with a dramatic drop in solar cell efficiency. In contrast, we show that for polymers with branched alkyl-substituted BDT motifs, controlling the number of aliphatic carbons in the linear N-alkyl-substituted TPD motifs is a major contributor to improved material performance. With this approach, PBDTTPD polymers were found to reach power conversion efficiencies of 8.5% and open-circuit voltages of 0.97 V in BHJ devices with $PC_{71}BM$, making PBDTTPD one of the best polymer donors for use in the high-band-gap cell of tandem solar cells.
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