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Copolymers based on dithieno[3,2-b:2',3'-d]silole (DTS) and dithienylthiazolo[5,4-d]thiazole (TTz) are synthesized and tested in an all-solution roll process for polymer solar cells (PSCs). Fabrication of polymer:[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) solar cells is done on a previously reported compact coating/printing machine, which enables the preparation of PSCs that are directly scalable with full roll-to-roll processing. The positioning of the side-chains on the thiophene units proves to be very significant in terms of solubility of the polymers and consequently has a major impact on the device yield and process control. The most successful processing is accomplished with the polymer, PDTSTTz-4, that has the side-chains situated in the 4-position on the thiophene units. Inverted PSCs based on PDTSTTz-4 demonstrate high fill factors, up to 59%, even with active layer thicknesses well above 200 nm. Power conversion efficiencies of up to 3.5% can be reached with the roll-coated PDTSTTz-4:PCBM solar cells that, together with good process control and high device yield, designate PDTSTTz-4 as a convincing candidate for high-throughput roll-to-roll production of PSCs.

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