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Unconventional Molecular Weight Dependence of Charge Transport in a High Mobility n-type Semiconducting Polymer

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Semiconducting polymers are of interest for a range of applications including organic light-emitting diodes (OLEDs), polymer solar cells and flexible electronics. When used as the active layer in solution-processed organic field-effect transistors (OFETs) one usually finds that charge carrier mobility increases with increasing molecular weight, due to the ability of longer chains to bridge regions of local order. Here an unconventional molecular weight dependence of charge transport is reported in n-channel OFETs based on the semiconducting polymer poly{[N , N '-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)}, **P(NDI2OD-T2)**. Five different molecular weights have been studied (10 kDa, 17 kDa, 30 kDa, 35 kDa and 41 kDa) with the charge carrier mobility in top gate bottom contact (TGBC) OFETs found to systematically increase with decreasing molecular weight. To understand the origin of this effect, the aggregating behaviour of polymer chains in solution has been studied, as well as the thin-film microstructure. From optical absorption measurements, which are sensitive to the polymer chain conformation, it is found that low molecular weight chains have an open coil conformation while higher molecular weight chains adopt a collapsed, or aggregated conformation. Analysis of Atomic Force Microscopy (AFM) measurements suggest a higher degree of polymer chain alignment in low molecular weight samples. Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy measurements have also been performed that show a similar molecular orientation (backbone tilt) at the surface for all the molecular weight samples. Taken together, these results indicate that upon solution processing, the lower molecular weight samples are able to form more chain-extended thin-film morphologies that promote charge transport than the higher molecular weight samples that self-aggregate in solution produces less favorable morphologies.

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