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Controlling the Edge-on vs. Face-on Stacking of Semicodundcting Polymers Using Diffusive Noncovalent Interactions

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In thin films of semiconductor polymers, the polymer chains often exhibit distinct orientation with respect to the substrate. The planar -face of the backbone typically orients either in an edge-on or face-on manner. Generally, an edge-on alignment is thought to be favourable for transport in thin film transistors, whereas face-on alignment is considered to improve vertical transport as desired in solar cells. However, molecular orientation is among the very few parameters that usually cannot be controlled when tailoring new semiconducting polymers. Here we show for an important class of semiconducting polymer that both the mode of orientation as well as the degree of alignment can be well controlled by exploiting diffusive non-covalent interactions along the backbone. Studying polydiketopyrrolopyrroles (PDPPs) as a case study, by strategically varying chemical structure we demonstrate systematic variation in molecular orientation with degree of chain planarization resulting from different degrees of diffusive non-covalent interactions. This observation opens the possibility of controlling and optimizing the orientation of semiconducting polymer chains in thin films by rational design.

Keywords or phrases (comma separated)

GIWAXS; semiconducting polymers; thin films;

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