

Controlling the Self-Assembly of Organic Semiconductors by Tuning the H-Bonded Assembly of Diketopyrrolopyrroles

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Organic semiconductors (OSCs) have emerged as a flexible, easy-to-process, and cost-effective alternative to inorganic semiconductors with applications in organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and organic light-emitting diodes (OLEDs) [1, 2]. Diketopyrrolopyrroles (DPP) is a commonly used building block in OSCs with excellent ambipolar mobilities. Recently, the hydrogen bonding (H-bonding) control of DPPs has garnered significant interest as an avenue to tailor the structure and properties of their semiconducting films [3, 4]. In this context, investigating the H-bonded assembly of DPP molecules on surfaces is pivotal to understanding their charge transport properties in OFETs. Here, we investigated the H-bonded self-assembly of N-unsubstituted DPP molecules diselenylDPP (DSeDPP), dithiazolylDPP (DTzDPP), and dithienothienylDPP (DTTDPP) at highly ordered pyrolytic graphite (HOPG)-solution interfaces using scanning tunneling microscopy (STM) and density functional theory (DFT). DSeDPP and DTzDPP form heteroassembly with the 1-octanoic acid solvent involving H-bonding between carboxyl and lactam groups or homoassemblies via H-bonding between the lactam groups. However, DTTDPP forms two homoassemblies with H-bonding between lactam groups or weak H-bonding between the lactam group and heteroaromatic ring. DFT simulations unraveled the inter- and intramolecular interactions in the self-assembled lattices, rationalizing the self-assembly behavior of the DPP molecules. Homoassembly with twisted conformations of molecules that enable intermolecular π -interactions along the edge-on direction on the surface is only observed for DSeDPP. The absence of homoassembly with twisted conformations of DTzDPP and DTTDPP arises from the higher strain energy in acquiring out-of-plane twists in these molecules. Our results show how the aromatic substituents dictate the supramolecular assembly of DPP molecules on surfaces, which could significantly influence the properties, such as the charge transport in their thin films.

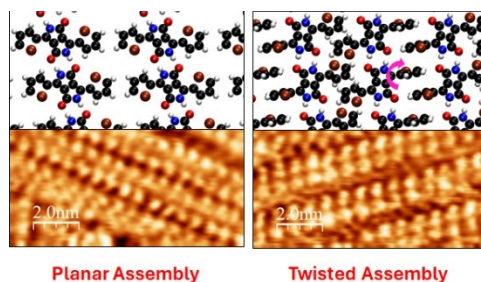


Fig. 1. Heteroaromatic substituents are found to significantly alter the preference of DPP molecules to form different self-assembled polymorphs on HOPG, which consist of planar or twisted conformations of the DPP molecules.

References

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