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Self-Assembly Surface-Mediated Controlled by Interfacial Charge-Transfer¹ OLIVER MONTI, NAHID ILYAS, BRET MAUGHAN, Univ of Arizona, PERCY ZAHL, ROCIO CORTES-RODRIGUEZ, PETER SUT-TER, Brookhaven National Laboratory — Precise control of molecular self-assembly is desirable and essential to understand electronic structure and dynamics at organic semiconductor interfaces. Self-assembly into ordered supramolecular structures for such pi-conjugated molecules is determined by a subtle balance between surface-molecule and molecule-molecule interactions, and a predictive mechanistic understanding has remained a substantial challenge for most commonly used organic semiconductors. Here we show by a combination of low-temperature scanning tunneling microscopy and two-photon photoemission spectroscopy for the model system of chloro-boron subphthalocyanine on Cu(111) that interfacial charge-transfer results in fundamentally different self-assembly mechanisms for different molecular orientations on the surface. We uncover a novel mechanism that controls thin film growth for an important class of organic semiconductors. We conclude that the adsorption geometry may be exploited in self-assembly to control electronic structure and dynamics at organic semiconductor interfaces.

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Oliver Monti Univ of Arizona

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