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Polarization induced energy level shifts at organic semiconductor interfaces probed on the molecular scale by scanning tunnelling microscopy

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The inter- and intra- molecular energy transfer that underlies transport, charge separation for photovoltaics, and catalysis are influenced by both the spatial distribution of electronic states and their energy level alignment at interfaces. In organic materials, the relevant length scales are often on the order of a single molecular unit. Scanning tunneling microscopy (STM) and spectroscopy (STS) stands as one of few techniques with the ability to resolve both the spatial structure of these interfaces while probing energy levels on the nanometer scale.

Here, we have used STM/STS in a spectroscopic mapping mode to investigate the spatial shifts in energy levels across well-defined 2-dimensional nanoscale clusters of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) decoupled from an Ag(111) substrate by a bilayer of NaCl. We find a striking difference between the HOMO and LUMO states of molecules residing at the edges of these clusters and those in the centre. Edge molecules exhibit a gap that is up to 0.5eV larger than observed for inner molecules. Most of this difference is accounted for by the shift of the occupied states, strongly influencing level alignment for a boundary region of single molecular width. As STS is a single-particle spectroscopy –adding or removing a charge –the energy levels measured are influenced by the local polarization environment. The shifts observed for several different geometries of islands correspond well with calculations of the stabilization of this transient charge via the polarization of the other molecules in the cluster.

These effects are expected to influence organic semiconductors that exhibit hopping-like transport, and processes such as charge separation occurring at interfaces in organic photovoltaic devices. As the polarizability of most molecular semiconductors is anisotropic, the structure and orientation of molecules at interfaces will play a significant role in the resulting energy level alignment.

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