

Local Electronic Structure of a Single-Layer Porphyrin-Containing Covalent Organic Framework

Chen Chen

Trinity Joshi, Huifang Li, Anton D. Chavez, Zahra Pedramrazi, Pei-Nian Liu, Hong Li, William R. Dichtel, Jean-Luc Bredas, Michael F. Crommie

University of California Berkeley, Berkeley, CA, USA

ars_chenchen@berkeley.edu

We have characterized the local electronic structure of a porphyrin-containing single-layer covalent organic framework (COF) exhibiting a square lattice. The COF monolayer was obtained by the deposition of 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMA) and 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TAPP) onto a Au(111) surface in ultrahigh vacuum followed by annealing to facilitate Schiff-base condensations between monomers. Scanning tunneling spectroscopy (STS) experiments conducted on isolated TAPP precursor molecules and the covalently linked COF networks yield similar transport (HOMO–LUMO) gaps of 1.85 ± 0.05 eV and 1.98 ± 0.04 eV, respectively. The COF orbital energy alignment, however, undergoes a significant downward shift compared to isolated TAPP molecules due to the electron-withdrawing nature of the imine bond formed during COF synthesis. Direct imaging of the COF local density of states (LDOS) via dI/dV mapping reveals that the COF HOMO and LUMO states are localized mainly on the porphyrin cores and that the HOMO displays reduced symmetry. DFT calculations reproduce the imine-induced negative shift in orbital energies and reveal that the origin of the reduced COF wave function symmetry is a saddle-like structure adopted by the porphyrin macrocycle due to its interactions with the Au(111) substrate.

References

- [1] Chen Chen, *et al.* ACS Nano 12(1) (2018), 385-391.

Figures

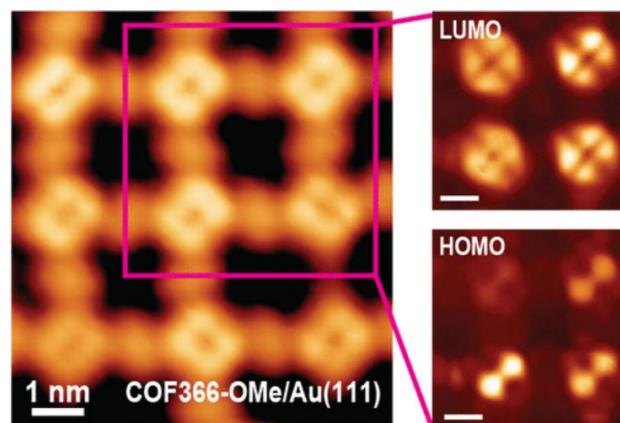


Figure 1: STM images of the single-layer covalent organic framework and the wavefunction distribution of the LUMO and HOMO states.