

# Tunable Work Function and Energy-Level Alignment by Partially Deprotonated Carboxylic Acid Layers on Silver

V. Stará<sup>1</sup>, P. Procházka<sup>1</sup>, J. Planer<sup>1</sup>, T. Krajňák<sup>1</sup>, A. Shahsavari<sup>1</sup>, A. O. Makoveev<sup>1</sup>, T. Skála<sup>2</sup>, M. A. Blatnik<sup>1</sup>, J. Čechal<sup>1,3</sup>

<sup>1</sup> CEITEC - Central European Institute of Technology, Brno University of Technology, Czech Republic.

<sup>2</sup> Faculty of Mathematics and Physics, Charles University, Czech Republic

<sup>3</sup> Institute of Physical Engineering, Brno University of Technology, Czech Republic.

cechal@fme.vutbr.cz (J. Č.)

The energy level alignment between a metal electrode work function and the position of organic semiconductor frontier orbitals (HOMO or LUMO) is required to reduce contact resistance and enhance the efficiency of organic-semiconductor-based devices. Here, we present monolayer thick charge injection layers (CILs, Fig. 1a) based on aromatic carboxylic acids (4,4'-biphenyl dicarboxylic acid, BDA; and 1,3,5-tris(4-carboxyphenyl)benzene, BTB) that can induce an energy level shift in the subsequent layers by up to 0.8 eV (Fig. 1b).

The CILs were structurally characterized using STM and low-energy electron microscopy (LEEM) and their chemical change followed with XPS. By gradual on-surface deprotonation of both BDA and BTB, we achieve a highly tunable shift in the work function of the system (Fig. 1c). By means of photoelectron spectroscopy employing synchrotron radiation and DFT calculations, we show that the work function and energy-level positions in the CIL increase linearly with the density of dipoles that are formed upon the deprotonation of carboxylic groups. The energy level position of the subsequent layers follows the changes in the CIL [1].

**Acknowledgement:** This research has been supported by GAČR, project No. 22-04551S. We acknowledge CzechNanoLab Research Infrastructure (LM2023051) and e-INFRA CZ (ID:90140) supported by MEYS CR, and the CERIC-ERIC Consortium for access to experimental/computational facilities and financial support.

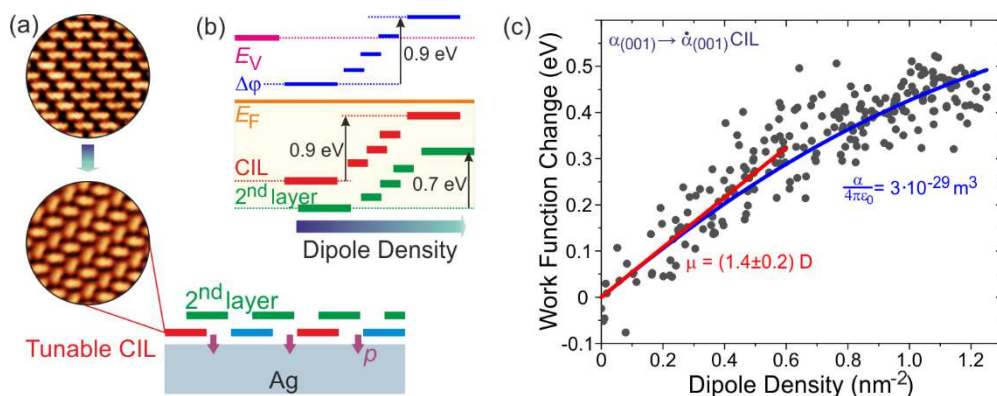


Fig. 1. (a) Schematics of studied system comprising two layers of carboxylic acids: tunable CIL (the first layer) and non-deprotonated second layer. STM images show change of CIL structure induced by its thermal deprotonation. (b) Changes in energy level positions in CILs, second layer, and work function  $\Delta\phi$ . (c) The work function change as a function of electric dipole density during the isostructural  $\alpha_{(001)} \rightarrow \beta_{(001)}$  transformation.

[1] V. Stará, P. Procházka, J. Planer, A. Shahsavari, A. O. Makoveev, T. Skála, M. Blatnik, J. Čechal, Phys. Rev. Appl. **18**, 044048 (2022)