

Figure S1: Projected 4s densities of states (PDOS) for Cu atoms on the diagonal of the Moiré supercell (in the  $N_{top}$  and  $N_{fcc}$  regions) and a free surface for comparison. Vertical axis in units of states/eV.



Figure S2: Relationship between geometric and electronic structure in h-BN Moiré on Cu(111), along the cell diagonal. a) Lateral distance (Å) of B atoms to Cu atoms in the underlying *top*, *hcp* and *fcc* layers and vertical distance  $d_{\rm Cu}$  to the surface (shifted down by 2.5 Å). Lines drawn to guide the eye. b) Energy (eV) of the  $p_z$  flank onset (defined as the point where PDOS has a value of 0.035 states/eV) of PDOS projected on B atoms along the cell diagonal. Lines drawn to guide the eye. c) Approximate work function (eV) from electrostatic potential at 3.40 Å above the surface. Horizontal axis shows distance (Å) from the bottom left N atom in the cell.