Electronic Supplementary Information: Surface state tunable energy and mass renormalization from homothetic Quantum dot arrays


EXPERIMENTAL & THEORETICAL METHODS

**ARPES measurements.** The Au(111) substrate was prepared by standard cycles of sputtering-annealing at 1 kV and 800 K. The molecules [dicyano sexyphenyl (Ph6) and dicyano terphenyl (Ph3)] were first thermally deposited onto the Au(111) crystal at room temperature from a quartz Knudsen cell and then the Co adatoms, followed by a mild annealing to 400 K. For the ARPES measurements, we evaporated the molecules and the Co adatoms in two orthogonal shallow deposition wedges using a fixed square mask while moving the sample laterally and vertically with a velocity controlled motor to obtain a region with exact 3:2 stoichiometry. Prior to forming this wedge we roughly determine the evaporation parameters for a full surface coverage of the MONN (checked using RT-STM). Afterwards, we apply the gradient method and use shallow deposition coverage wedges [1] in order to perform position dependent ARPES. Our ARPES 2D detector allows us to trace the electronic structure modification around the band bottom where we look for the sharpest 2DEG signal that in this case includes changes in the bottom energy, intensity modulations at the zone boundaries, and side replicas with respect to the pristine case.

The ARPES measurements were performed with a lab-based experimental setup using a display-type hemispherical electron analyzer (SPECS Phoibos 150, energy/angle resolution of 40 meV/0.1°) combined with a monochromatized Helium I source (hν=21.2 eV). Measurements were acquired with the sample at 150 K by moving the polar angle.

**STM measurements.** The experiments were carried out in a two-chamber ultrahigh vacuum system (base pressure of $4 \times 10^{-11}$ mbar) housing a commercial low temperature STM (Scienta Omicron GmbH). The Au(111) substrate was cleaned by repeated cycles of Argon ion sputtering followed by annealing at 800 K. The Ph3 (Ph6) molecules were heated to 445 K (550K) inside a commercial molecule evaporator (OmniVac) and deposited onto the Au(111) substrate held at room temperature. The Co atoms were deposited with an electron beam evaporator (Oxford Applied Research Ltd). STM measurements were performed at both 77 K and 4.5 K with a mechanically cut Pt/Ir wire in constant current mode. All bias voltages are given with respect to a grounded tip. The STM images were processed with the WSxM
software [2]. STS measurements were performed at 4.5 K by using a lock-in amplifier (typical modulation parameters used: amplitude of 10 mV (rms) and frequency of 677 Hz).

**EPWE simulations.** The combined Plane Wave Expansion (PWE) and Electron Boundary Element Method (EBEM) have been developed by García de Abajo and represent a scalar variant of the electromagnetic PWE/BEM extensively used for solving Maxwell’s equation and optical response for arbitrary shapes. It is based on Green’s functions for finite geometries and electron plane wave expansion for periodic systems. For the band structure calculations, particle-in-a-box model is extended to infinite 2D systems by defining an elementary cell and using periodic boundary conditions. Within PWE code, solutions of the Schrödinger equation are represented as a linear combination of plane waves and a satisfactory convergence was achieved with a basis set consisting of ~ 100 waves. More information can be found in [3, 4].

**DFT calculations.** Density Functional Theory calculations have been performed using the VASP code [5–7]. The interaction of the valence electrons with the ion cores was described with the projector augmented wave method (PAW) and the Perdew-Burke-Ernzerhof [8] exchange-correlation functional was used. An energy cutoff of 300 eV in the plane wave expansions and different K-point samplings, depending on the size of the surface unit cells, were employed and checked to be well-converged. A four layer Au(111) slab with hydrogen atoms passivating one of the two vacuum-metal interfaces was used to model the Au(111) surface state [9], while a Co atom was placed on the other interface at 2.5 Angstroms vertical distance at a fcc hollow site. At this distance the Co-Au(111) interaction is weaker than for the optimal adsorption distance but it is the way we mimic a less reactive Co atom in the metal-organic network. Table I summarizes the SS band bottom energies as function of adatom concentration obtained from these calculations.
### SUPPLEMENTARY TABLE

<table>
<thead>
<tr>
<th>Adatom concentration</th>
<th>Array size</th>
<th>Co/Au(111) $\Delta E_{SS}(eV)$</th>
<th>Au/Au(111) $\Delta E_{SS}(eV)$</th>
<th>Cu/Cu(111) $\Delta E_{SS}(eV)$</th>
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</thead>
<tbody>
<tr>
<td>0.25 ML</td>
<td>2x2</td>
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<td>-0.92</td>
<td>-0.93</td>
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<tr>
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<td>-0.65</td>
<td>-0.78</td>
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<tr>
<td>0.11 ML</td>
<td>3x3</td>
<td>-0.49</td>
<td>-0.49</td>
<td>-0.35</td>
</tr>
<tr>
<td>0.08 ML</td>
<td>3x4</td>
<td>-0.54</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table S I: Energy shift of the pristine SS with adatom concentration and array size obtained from our DFT calculations. The calculations, from left to right, correspond to the cases of Co/Au(111), Au/Au(111) and Cu/Cu(111). To account for the decoupling effect of the molecules, the adatoms are relaxed at $\sim 2.5 \, \text{Å}$ above the unreconstructed pristine surfaces. The calculations show a general increasing downward shift of the SS with adatom content. Note that the experimental amounts of Co used are significantly lower, corresponding to 0.015 ML for Ph3Co and 0.005 ML for Ph6Co.
Figure S1: The herringbone reconstruction of Au is preserved under the Ph3Co and Ph6Co networks, which is an indication of the low interaction between molecules and substrate [10, 11]. (A) 100 nm x 100 nm STM image of Ph3Co network on Au(111) at 77 K. This image highlights the growth of the Ph3Co network 30° rotated from [1\bar{1}0] direction of the surface as well as domain boundaries among molecular islands. STM parameters: V=-2 V, I=20 pA. (B) 25 nm x 25 nm STM close up image of Ph3Co network on Au(111) at 4.5 K. STM parameters: V=-1 V, I=10 pA. (C) 30 nm x 30 nm STM image of Ph6Co network on Au(111) at 4.5 K. The Ph6Co hexagonal network grows 30° rotated from [1\bar{1}0] direction of the surface. STM parameters: V= -0.5 V, I= 150 pA. (D) 80 nm x 80 nm STM long-range image of Ph6Co network on Au(111) at 4.5 K, highlighting its single domain and high quality. STM parameters: V= -0.5 V, I=10 pA. The compact high symmetry directions are indicated in B and C.
Figure S 2: ARPES and EPWE simulated electronic band structures, band bottom energies and Fermi wave-vector features. Second derivative electronic band structure of Au(111) SS (A), Ph6Co/Au [\Gamma M] direction in (B) and \Gamma K in (E) and Ph3Co/Au [\Gamma M] direction in (C) and \Gamma K in (F). (D) Schematic representation of the surface Brillouin zone defined by Ph6Co and Ph3Co networks and the \Gamma M and \Gamma K high symmetry directions considered in ARPES. (G) A gradual shift of the band bottom energy towards lower energies is experimentally observed (left), the largest one being for the Ph3Co case, while for Ph6Co a smaller shift is detected. This tendency is satisfactorily matched by EPWE simulations (right). (H) Experimental (top) and EPWE simulated (bottom) Fermi wave-vector features are plotted for both Ph3Co (red) and Ph6Co (blue) networks and compared to the pristine Au surface state (green). Despite the large band bottom energy variations at \Gamma, no population of the surface state is observed since the Fermi wave-vector remains pinned.
Figure S 3: Surface state energy variation upon Co, Ph3 and Ph6 gradient depositions. (A) The plot shows a tendency of the surface state to shift towards the Fermi level as the Co deposition is increased (likely due to Co clustering). For the diluted amount of Co required for both Ph3Co and Ph6Co network formations the surface state remains unaltered within the experimental error. (B) and (C) plots for Ph3 and Ph6 gradient depositions show that at low coverages the surface state remains energetically unchanged and gradually shifts towards the Fermi level, although it is more clearly observed for Ph6. The small energy variation at zero coverage for the Ph6 case is attributed to slight deviations from normal emission.

Figure S 4: Energy renormalization effects from dicarbonitrile-polyphenyl MONN on Ag(111). The left topographic images show two networks generated on Ag(111) when mixing with Co atoms the molecules Ph6 (top) and Ph4 (bottom) (shown in the insets). On the right, the different $dI/dV$ spectra at the pore centers (Ph6Co in red and Ph4Co in blue) are compared to the pristine Ag(111) SS (dotted gray line) close to its energy onset (band bottom SS energy). Similarly to the Au(111) case, we observe a clear downshift of the onset energy, as indicated by the horizontal arrow, that is dependent on the Co adatom concentration, i.e. it is larger for Ph4Co. This figure has been adapted from Ref. [4].
Figure S 5: Experimental confirmation of the downshift effect on two other MONNs with single metal coordination. (A) and (B) show topographic images of two ext-TPyB-Cu molecular networks generated on Cu(111) (adapted from [12]). In the H-phase (hexagonal network) the Cu adatoms coordinate with two adjacent molecules, whereas in the D-Phase we find two-fold and three-fold Cu-pyridyl coordination motifs. (C) ARPES EDCs at the $\Gamma$ point ($k=0$) of the two MONNs. Compared with the pristine Cu(111) surface state (Cu SS, gray discontinuous line) we observe a 2DEG renormalization when these MONNs are present on the metal surface.

Figure S 6: Position dependent STS for Ph6Co and dI/dV map of a pore at the 2DEG onset. (A) The STS spectra discard the existance of bound states at the Co adatom since their expected features and corresponding modulation with distance are not visible in our dataset. Topography (B) and corresponding $dI/dV$ map (C) for a Ph6Co pore at the 2DEG onset. At this energy the underlying herringbone reconstruction dominates the LDOS. Even if the STM data were taken with a slight double tip, no extra intensity is found at the Co adatoms with respect to the rest of the image. Note that the first confined resonance ($n = 1$) can only be visualized at higher voltages (see main text for details).
Figure S 7: Validation of the energy downshift of the 2DEG band bottom energy from homoatomic arrays grown on noble metal surfaces by means of DFT. The panels show the cases of (A) Au adatoms on Au(111) and (B) Cu adatoms on Cu(111) for 2x2 (0.25 ML) and 3x3 (0.11 ML) surface unit cells. Similarly to Fig. 3 of the main text, the hybridization between the pristine SS with the adatom d-bands (in blue) and the substrate’s folded bulk bands open tiny gaps and pushes downwards the 2DEG (vertical arrows), the shift being larger for higher adatom coverages. We represent the pristine SS by a full red line and the altered one with a dotted line as a guide to the eye. This downshift found both for homoatomic and heteroatomic arrays turns out to be recurrent, as long as the SS character is maintained, i.e. the existing hybridizations are not strong.
SUPPLEMENTARY REFERENCES


