Quantum dot arrays in the form of molecular nanoporous networks are renown for modifying the electronic surface properties through quantum confinement. Here we show that, compared to the pristine surface state, the fundamental energy of the confined states can exhibit downward shifts accompanied by a lowering of the effective masses simultaneous to the appearance of tiny gaps at the Brillouin zone boundaries. We observed these effects by angle resolved photoemission for two self-assembled homothetic (scalable) Co-coordinated metal-organic networks. Complementary scanning tunneling spectroscopy measurements confirmed these findings. Electron plane wave expansion simulations and density functional theory calculations provide insight into the nature of this phenomenon, which we assign to metal-organic overlayer-substrate interactions in the form of adatom-substrate hybridization. The absence to date of the experimental band structure resulting from single adatom metal-coordinated nanoporous networks has precluded the observation of the significant surface state renormalization reported here, which we infer are general of low interacting and well-defined adatom arrays.

Over the last decades, the concepts of supramolecular chemistry have been successfully transferred to the construction of two-dimensional (2D) self-assembled molecular arrangements on metallic surfaces [14]. By selecting the proper tectons (molecular constituents and, if required, metal linkers) and depositing them onto selected substrates, long-range ordered, regular and robust nanoporous networks have been achieved, ranging from hydrogen- [5] or halogen-bonded [6], to metal-organic structures [7, 8]. Such regular structures stand out as ideal templates for nanopatterning organic and inorganic adsorbates by selective adsorption [9, 14]. Nanoporous networks, also referred to as quantum dot (QD) arrays since they can confine surface state (SS) electrons, provide a vast playground for studying and engineering the electronic properties of new and exotic 2D materials. Indeed, metal-organic networks are known to show novel magnetic properties [15, 16], catalytic effects [17], oxidation states [18], exotic tessellation [19, 21] and bear the prospect of exhibiting topological electronic bands [22, 23].

The dominant electronic signature around the Fermi level due to the presence of nanoporous networks comes from the substrate’s surface state electrons, which scatter at the molecular array and become confined within individual nanopores [24, 25]. The tunability of the confined electronic state has so far been achieved by varying the pore dimensions, i.e. the QD size [25, 26]. However, since the confining potential barriers are not infinite, these QDs are not independent but coupled, as has been shown by angle resolved photoemission (ARPES) through the existence of new dispersive electronic bands [24], as well as by Fourier-transform scanning tunneling spectroscopy (FT-STS) data [27]. These QD array bands can be modified through the condensation of guest atoms [28] or by changing the barrier width [6]. The standard fingerprints, whenever confinement of two-dimensional electron gases (2DEGs) occurs on noble metal surfaces, are in the form of an energy shift towards the Fermi level of its fundamental energy, an increase of the effective mass, and the appearance of energy gaps at the surface Brillouin zone (BZ) boundaries [6, 24, 29, 30].

In this work we show for two homothetic (scalable) metal-organic nanoporous networks (MONN) grown on Au(111) the first experimental evidence of energy downshifts and reduced effective masses compared to the pristine SS, simultaneous to the opening of zone boundary gaps that suggest electron confinement within the nanocavities. More specifically, these effects are gradual, i.e. they depend on the network dimensions. The interaction between the Au substrate and the MONN are at the base of these unexpected phenomena and it is not a consequence of the quantum confinement.
The studied scalable Co-coordinated networks were grown on Au(111) from two related dicarbonitile-polyphenyl derivatives. Specifically, we used dicarbonitile-terphenyl (Ph3) and dicarbonitile-sexyphenyl (Ph6) molecules and Co atoms in a 3:2 stoichiometry to fabricate the MONN. These tectons were sequentially evaporated (molecules first, then Co) onto Au(111) followed by a mild annealing to 400 K. That resulted in two scalable, periodic, long-range order and practically defect free QD arrays [shown in Figure 1(A-B)] and named hereafter Ph6Co and Ph3Co. In agreement with previous work [24], the networks exhibit sixfold symmetry with unit cell vectors of 3.53 nm (for Ph3Co) and 5.78 nm (for Ph6Co) along the [11\textit{2}] direction and enclose pore areas of 8 nm² and 24 nm², respectively. Note that the interaction of both networks with the substrate is assumed to be rather weak since the herringbone reconstruction is neither lifted nor modified in its periodicity [31, 32]. We experimentally probed these networks with ARPES [Helium I source (\(h\nu=21.2\) eV) at 150 K] and scanning tunneling microscopy/spectroscopy (STM/STS) at 5 K to obtain both spatially averaged and spatially highly resolved information [31]. The experimental data are complemented by Electron plane wave expansion (EPWE) simulations and Density Functional Theory (DFT) calculations [31].

The 2DEG onset of Ph6Co and Ph3Co networks formed on Au(111) is reliably determined by ARPES and only approximately by STS [6]. Moreover, ARPES –in contrast to STS– can resolve the QD array band structure from the MONN. However, this can be exceedingly challenging because the networks must be extended, almost defect-free and completely covering the probed surface (in absence of other coexistent molecular phases) [6, 24]. To achieve these conditions we evaporated the molecules and Co adatoms in orthogonal shallow gradient depositions on the Au(111) substrate, thereby ensuring the existence of an area with optimal coverage and the exact 3:2 stoichiometry [33]. Figure 1(C, D) shows the second derivative of the ARPES spectral density from Ph6Co and Ph3Co along the \(\Gamma M\) high symmetry direction. We observed a gradual downshift of the fundamental energy (\(\Gamma\) point) towards higher binding energies as the pore size is reduced, which can be quantified from the normal emission energy distribution curves (EDCs) [cf. Fig. 1(E) and Table 1]. Note that this clearly goes in the opposite direction to the energy shift expected from conventional lateral confinement systems. Simultaneously to this downshift, we observed a reduction of the effective mass (see Table 1), resembling a Fermi wave-vector pinning [31]. The partial confinement of the substrate’s 2DEG is inferred from the presence of small gaps (observed as slight intensity variations) at the symmetry points, which denotes weak scattering from the network barriers. Note that the absence of spin-orbit splitting in our data for Ph3Co and Ph6Co does not rule out this effect, as it could be masked by ARPES lineshape intrinsic broadening [31].

To unravel the potential energy landscapes generated by the molecular networks and their confining properties, we performed EPWE simulations. Such a semi-empirical model has been successfully used for similar systems [6, 25, 34]. The geometry of both systems for the simulations were defined following topographic STM images [see Figures 1(F, G)]. Assuming repulsive scattering potential sites for molecules

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**FIG. 1:** STM topographies of the single domain Co-coordinated hexagonal QD arrays using (A) dicarbonitile-sexyphenyl (Ph6) and (B) dicarbonitile-terphenyl (Ph3). Scale bar in red corresponds to 5 nm. (C, D) Second derivative of the spectral density obtained by ARPES at 150 K along the \(\Gamma M\) high-symmetry direction for both Ph6Co and Ph3Co nanoporous networks. The band structure exhibits downward shifts of the band bottom and gap openings at the superstructure symmetry points compared to the pristine Au(111) Shockley state (black dotted lines). (E) Energy distribution curves (EDCs) at normal emission (\(\Gamma\) point) for pristine Au(111) (green), Ph6Co (blue) and Ph3Co (red). A gradual downshift of the fundamental energy as the pore size is reduced (\(\Delta E_{\text{Ph6Co}} = 40\) meV and \(\Delta E_{\text{Ph3Co}} = 100\) meV with respect to the Au SS) is found. (F, G) 2D potential geometry used for the EPWE modelization, where green stands for the molecular repulsive potentials, purple for slightly repulsive Co regions and red for cavity regions with zero potential. (H, I) Band structure along \(\Gamma M\) direction of the overlayers simulated by EPWE based on the previous geometry. Matching the experimental ARPES data (gap openings and band-bottom shifts) requires a significant modification of the 2DEG energy reference (see text for details).
(\(V_{\text{mol}} = 250\text{ meV}\)) and Co atoms (\(V_{\text{Co}} = 50\text{ meV}\)), the experimental data were correctly reproduced. In particular, the ARPES energy gaps (\(\sim 25\text{ meV}\) for Ph6Co and \(\sim 30\text{ meV}\) for Ph3Co at \(\Gamma\)) reflect the weak scattering strength of the networks [Figures 1H, I]. However, such repulsive scattering is known to shift the 2DEG fundamental energy (at \(\Gamma\)) upwards, opposite to what is observed here. In this way, the ARPES dispersions can only be matched by EPWE when adopting higher binding energy references and smaller effective masses than the pristine Au(111) SS (see Table I). In other words, using the original dispersion of the Au(111) SS as scattering reference cannot correctly reproduce the experimental data.

Such an unexpected scenario questions the confining capabilities of these MONN. Using STS, we could verify that these networks do confine the Au SS, similarly to the ones generated onto Ag(111) by the same family of molecules [25]. In panel (A) (middle) of Figure 2 we present the Ph6Co STS data acquired at two different positions. The conductance spectra together with the \(dI/dV\) maps taken at different voltages [Figure 2B to E]) exhibit clear confinement resonances within the pores [6]. Such electron localization mirrors the one observed for the same network on Ag(111) [25]. In order to directly compare them we adapt the \(dI/dV\) spectra of ref. [25] by normalizing the energy axis by the ratio of the respective effective masses (\(m^*_{\text{Ph6Co}}/m^*_{\text{Au}} = 0.41/0.24\)) and shifting the onset of the Ag SS to the one of Au (\(-485\text{ meV}\) at 5 K). The agreement (lineshape and peak energies) between the two datasets is quite reasonable [cf. middle and top of Figure 2A], demonstrating that the confinement properties of Ph6Co are similar for the two substrates.

We can now address the 2DEG energy downshift with respect to the Au SS upon network formation using local techniques. The overall \(dI/dV\) lineshapes at the pore center exhibit broad peak widths (reflecting the ARPES bandwidth) and are quite asymmetric (with maxima being displaced towards higher energy) [6]. Such spectral asymmetry for \(n = 1\) at the pore center can be understood from a band structure perspective: the reduced onset contribution relates to electrons spreading out over the surface given their longer wavelength (\(\lambda = 2\pi/k\)) at the band bottom (\(k \sim 0\) around \(\Gamma\)). Contrarily, the STS is maximized at higher energies (close to the \(M\) point) since the electrons have much shorter wavelengths, thereby becoming much more sensitive to the network barriers and prone to be trapped within the pores. Figure 2J, shows the STS spectra of the two networks at the pore center compared to the Au(111) SS. For Ph3Co the onset is clearly shifted away from the Au SS onset, whereas for Ph6Co it is similar but still slightly displaced. This is also the case for these networks on Ag(111) (see S.I. 3I). For the Ph6Co, we simulated the STS point spectra and conductance maps [Figure 2A, F-I] using the same scattering parameters and effective mass reduction as described above for the ARPES electron bands. While the experimental and simulated STS spectra match reasonably well, we observe slight discrepancies for the conductance maps taken at higher energies. This can be ascribed to weak potential variations introduced by the recon-

|                | \(E_{\text{B}}^*(\text{eV})\) | \(m^*/m_0\) | \(E_{\text{Reff}}^*/m_{\text{Reff}}^*/m_0\) | \(E_{\text{Ref}}^*/m_{\text{Ref}}^*/m_0\) |
|----------------|-----------------|-----------|--------------------------------|-----------------|
| Au(111)        | 0.45            | 0.255     | 0.45                           | 0.26            |
| Ph6Co          | 0.49            | 0.24      | 0.52                           | 0.24            |
| Ph3Co          | 0.55            | 0.22      | 0.59                           | 0.21            |

TABLE I: ARPES experimental binding energies at \(\Gamma\) and effective masses (columns \(E_{\text{B}}^*\) and \(m^*/m_0\)) for the substrate and the two networks. The corresponding 2DEG references (fundamental energy and effective masses) required for matching ARPES with the EPWE simulations are indicated in the last two columns: \(E_{\text{Reff}}^*/m_{\text{Reff}}^*/m_0\) and \(E_{\text{Ref}}^*/m_{\text{Ref}}^*/m_0\).
In summary, ARPES and STS results reveal a gradual energy and mass renormalization of the Au(111) SS upon formation of two homothetic Co coordinated metal-organic networks. EPWE simulations only agree with the experimental data after the 2DEG reference is shifted to higher binding energies. Notably this downshift is gradual with decreasing pore size and is observable in spite of the confining attributes of the nanocavities (that upshifts the states). Our EPWE simulations can satisfactorily match our experimental data using repulsive potentials for both molecules and Co atoms. Overlayer-substrate interactions must be responsible for such...
counterintuitive effects upon the Au SS reference. Hybridization between the Co adatoms and the folded substrate bands with the Au SS appear as the most plausible cause, as deduced from DFT calculations. We predict that other MONNs grown on noble metal surfaces should show such subtle counterintuitive 2DEG energy renormalization whenever the SS character is preserved, i.e. for weak coupling cases.

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The effect of a Co network on the Au Shockley state cannot be tested with ARPES, since at low coverages Co atoms aggregate forming clusters at herringbone elbows (see SI).