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Band Formation from Coupled Quantum Dots Formed by a Nanoporous Network on a Copper Surface — [Source link](#)

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Electronic confinement imposed by a nanoporous network: Band formation from coupled quantum dots

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One sentence summary

We provide the first experimental evidence for the formation of an artificial electronic band structure resulting from the confinement of a two dimensional free electron gas imposed by a supramolecular porous network, which can be considered as periodic array of coupled quantum dots.

ABSTRACT (125 words maximum. Used 120 words)

The properties of crystalline solids can to a large extent be derived from the scale and dimensionality of periodic arrays of coupled quantum systems like atoms and molecules. Periodic quantum confinement in two dimensions has been elusive on surfaces mainly because of the challenge to produce regular nanopatterned structures capable of trapping electronic states. We report on the practical implementation of this type of confinement by demonstrating that the two dimensional free electron gas of the Cu(111) surface state can be trapped within the pores of an organic nanoporous network, which can be regarded as a regular array of quantum dots. Moreover, a shallow dispersive electronic band structure is formed, which is indicative of electronic coupling between neighbouring pore states.

TEXT (1776 words, max. 2500)

Crystalline solids exhibit properties which derive to a large extent from the periodic arrangement and interactions of their component quantum systems, such as atoms or molecules. Their electronic and optical properties depend essentially on the emergence of new electronic states arising from the periodic coupling of their components by quantum effects. Extending the principle of such periodic coupling beyond the molecular regime has given rise to metamaterials which are composed of regularly repeated units (1), in most cases nanoparticles (2, 3).

Quantum effects due to confinement of electronic states have been extensively studied for surface states of noble metals which are characterized by a quasi two-dimensional (2D) electron gas. These may be visualized by scanning tunneling microscopy (STM) as standing wave patterns arising from scattering at steps and defects (4, 5) or at large organic molecules (6). Examples of such surface state confinement comprise thin films (7), artificial nanoscale structures (8, 9), vacancy and ad-atom islands (10, 11), self-assembled one-dimensional (1D) chains (12, 13), vicinal surfaces (14-16) and zero-dimensional (0D) quantum dots (2).

In spite of these previous examples, *periodic* quantum confinement in 2D at surfaces has always been elusive. This has been mainly due to the difficulties encountered in the production of strictly regular nanopatterned structures capable of trapping electronic states. Such periodic confinement is expected to induce regularly distributed discrete energy levels that could be experimentally observed through the appearance of non-dispersive subbands,

as previously reported for thin films (7) or 1D systems (13, 15, 16). The size of the confining entities embedded within the 2D periodic nanostructures should be larger than or comparable to a critical length of ~ 2 nm, as experimentally observed for 1D structures (15). The design of such structures is more readily achieved using molecules as building blocks than atomic units, given the fundamental dimensions of these arrays. Potential candidates for molecular systems which might exhibit this 0D periodic electronic confinement are porous molecular surface networks. Their production is based on molecular self-assembly, which makes use of concepts established in supramolecular chemistry, and has the advantage that identical parts are produced at once. This is in contrast, for instance, to assembly based on atom-by-atom positioning techniques (8, 9). Self-assembled nanoporous networks have been obtained using either hydrogen bonding motifs (17) or metal-complexation (18) on metal surfaces. Within the pores of these molecular nanoporous networks electronic confinement is to be expected.

In this work we report on the interplay of the surface state electrons of Cu(111) with a supramolecular porous network adsorbed on the Cu surface that leads to the formation of a 2D electronic band structure through the coupling of confined electronic states. For the case at hand, we chose a perylene derivative, 4,9-diaminoperylene-quinone-3,10-diimine (DPDI), as organic building block (Fig. 1A) which is known to form on Cu(111) a highly ordered network upon thermal dehydrogenation (19). By choice of the appropriate molecular coverage before annealing (20) a highly stable hexagonal $p(10 \times 10)$ organic superstructure is generated, as shown in Fig. 1B (19). As will be demonstrated, each pore of our porous network confines the surface state of the Cu substrate in what can be described

as a 0D quantum dot. Due to the imperfect confinement observed for all 0D cases studied so far on surfaces (8-12), the quantum dots couple with their neighbors resulting in shallow dispersive electronic bands. A consequence of this work is the perspective to engineer these artificially created electronic structures by modification of the dimensions of the molecular network periodicities together with the appropriate choice of the substrate.

To study the interaction between the electronic surface state and our porous network structure, scanning tunneling spectroscopy (STS) was used, since it provides access to the local (electronic) density of states (LDOS) (21). Spectra recorded inside a pore display a peak at -0.22 V which is not observable on the bare metal (Fig. 2A). This peak is thought to arise from the confinement of the surface state electrons inside the pore, in analogy to previous work (8-11). The confinement of this discrete state is demonstrated by recording simultaneously topography (Fig. 2B) and dI/dV -signal (Fig. 2C) at the peak energy, the latter showing in first order the local distribution of this state. Since each pore features a confined state it can be considered as a single quantum dot, since the electronic confinement occurs in all three spatial directions.

As a consequence of the inherent periodicity of the molecular network a regular ‘quantum dot array’ is generated, as depicted in Fig. 2C.

It should be noted that the width of the STS peak in Fig. 2A suggests imperfect confinement, which has been previously observed for isolated 2D nanocavities (8-11) as well as for 1D confinement (12). Such cases can be explained by lossy scattering at the confining boundary whereas inelastic electron-electron and electron-phonon scattering in

small nanocavities are thought to be less important (11). Likewise, for our 2D periodic dehydro-DPDI network, which is commensurate with the Cu(111) substrate, the confined electronic states are expected to ‘leak’ into neighboring pores. This would result in electronic coupling between the quantum wells of neighboring pores, which should be visible in the electronic structure of the system.

In order to probe the electronic structure of our ‘quantum dot array’, the system was investigated with angle-resolved photoemission spectroscopy (ARPES). This is a laterally averaging surface sensitive technique, by which the binding energy of the occupied states of the system is determined as a function of the electron momentum. In Fig. 3A, ARPES normal emission spectra recorded at room temperature (RT) are shown for the clean Cu substrate and for the Cu substrate covered by different amounts of the dehydro-DPDI network. For the extreme cases (the clean Cu substrate and the highest molecular coverage) the spectra display a single component line shape, whereas all the other spectra exhibit a double peak line shape. A detailed analysis of the spectra (fitted using two Lorentzian components together with a constant background and multiplied by a Fermi-Dirac distribution) shows that the double peak consists of the components observed for the extreme cases while only their relative intensities vary depending on the network coverage (Fig. 3B). The component marked red is attributed to the clean surface state and maintains its binding energy and width throughout the molecular coverage range, but its intensity decreases as the molecular network coverage increases. In the following it will be referred to as the “pristine state”. The component marked black, on the other hand, is related to the influence of the molecular network and increases with increasing coverage. In analogy to

the pristine case, it has a constant width and a constant binding energy. Its value of 0.23 ± 0.03 eV is in very good agreement to the STS spectrum shown in Fig. 2A. Since its binding energy and peak width are independent of the surface coverage its origin can be attributed to a single pore with its surrounding molecular border while the overall island size shows no influence. This component will henceforth be referred to as the “confined state”.

While isolated nanocavities exhibit discrete electronic states, the periodic influence of the porous network on the 2D free electron gas of the surface state, along with the imperfection of its confinement, is expected to induce an electronic band in analogy to the band structure of a solid created by the periodic potential of its atoms. The existence of such cooperative behavior can be investigated by studying with ARPES the electronic structure of both the pristine Cu(111) surface state and the confined state as a function of the surface parallel momentum. The ARPES data displayed in Fig. 3C exhibit for both states dispersive bands. One band (highlighted in red) follows the characteristic parabolic dispersion of the Cu surface state (22), whereas the second band (highlighted in black) is related to the periodic potential of the porous network. This interpretation is supported by the periodic continuation of the band within Brillouin zones of higher order which possess the same periodicity as the molecular network (10 times smaller than the substrate). This periodicity is indicated by white lines in Fig. 3C, which are separated by $|k_{\text{parallel}}| = 0.142 \text{ \AA}^{-1}$. Furthermore, weak photoemission intensity very close to the Fermi energy and around the \overline{M} symmetry points can also be observed in Fig. 3C, especially for the case of 0.55 ML which was acquired at 60 K. In analogy to the 1D case (15,16), we attribute this

intensity to the existence of the 2nd subband which has its lowest binding energy at ~60 meV. This value matches perfectly the onset of the second peak observed in the pore STS spectrum of Fig. 2A. Thus, the energy gap between the subbands originating from the confined network is ~90 meV.

The rather shallow dispersing band (bandwidth of ~80 meV) is an indication for the strong confinement of the surface state inside the pores. Further backup of our interpretation stems from both STS measurements performed on top of dehydro-DPDI molecules and photoemission spectra acquired on a sample fully covered by a *close-packed* structure of dehydro-DPDI (19) (see supporting online material). For this non-porous organic network of the same building block no remains of the surface state were found which additionally corroborates the strong confinement of the surface state within the pores. In analogy to the textbook case of electronic states in the solid crystal (23), it is the balance of confinement and coupling between neighbouring quantum systems that leads to the formation of an electronic band. In our case, the final electronic structure results from the dimensions of the porous network together with the interaction of the molecular backbone with the 2D surface electronic state.

Our results provide the first experimental evidence of periodic 2D confinement by a porous molecular network, which can be regarded as a regular array of 0D quantum dots. A notable consequence of such periodic influence on the otherwise free-electron-like surface state is the formation of an artificial electronic band structure. The established and

prospective possibilities to control the structures of porous networks, together with the characteristic degree of coupling between ad-molecules and the surface state, will allow the fabrication of related systems with different band structures resulting in ‘2D electronic metamaterials’ in analogy to the well-established optical metamaterials (24, 25). These findings may also provide new insight into the behavior of molecular guests within porous host networks on surfaces (26, 27), and the expected influence of the guests on the electronic band structure may even induce long-range effects in their host-guest behavior (28). Moreover, the resulting electronic bands may play a decisive role in the stabilization of the porous networks themselves.

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20. 1 monolayer (ML) refers to a full coverage of a close-packed assembly of DPDI. A full surface coverage of the porous network occurs at a coverage of ~ 0.70 ML¹⁹.
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29. We would like to express our gratitude to H. -J. Güntherodt for his continuous support. We gratefully acknowledge J. Osterwalder and T. Greber for fruitful

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Supporting Online Material

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Materials and Methods

Supporting text

Figs. S1, S2, S3, S4, S5

Supporting references and notes

FIGURES AND LEGENDS

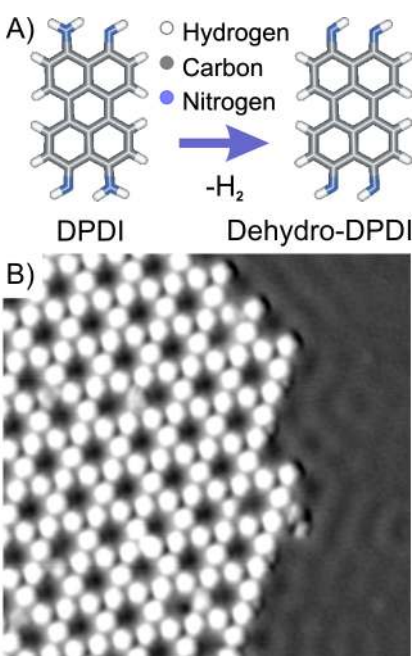


Figure 1: Interaction of the dehydro-DPDI network with the surface state of the underlying substrate. The formation of this porous network is based upon a thermally induced dehydrogenation of DPDI on Cu(111). A) Molecular structure of DPDI and its dehydrogenated form. B) STM image for submonolayer coverage of DPDI deposited on Cu(111) after thermal annealing at 500K. Dehydro-DPDI acts as both hydrogen-bond donor and acceptor to produce a very stable self-assembled porous network (image size: 29x29 nm², -0.1 V, 50 pA) (19). The network periodicity is 2.55 nm with a pore diameter of ~1.6 nm. Standing wave patterns in the Cu surface state arise from the scattering of the delocalized electronic states at the border of the adsorbate adlayer. This can be observed at low tunneling bias (4-6).

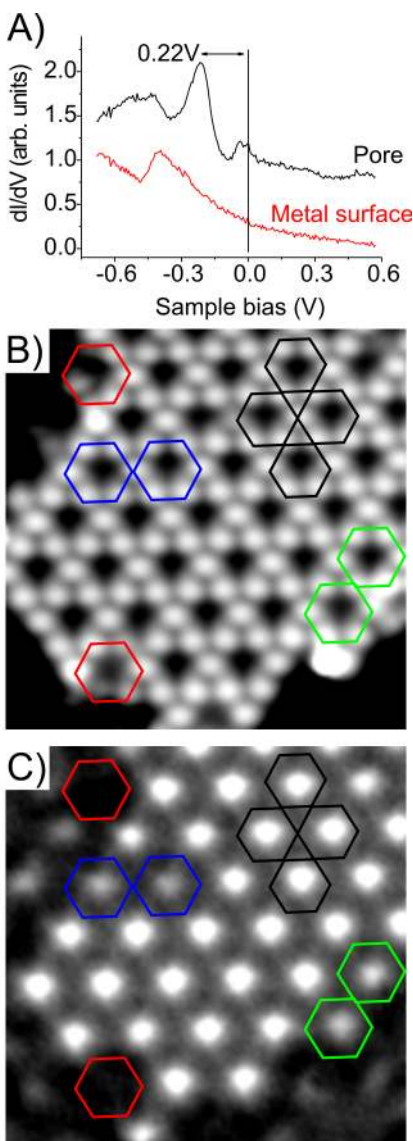


Figure 2: Study of the electronic confinement of the surface state within the pores of the network, corresponding to an array of 0D quantum dots. A) STS spectra obtained at 5K on the clean Cu surface (red) and inside a pore of the dehydro-DPDI network (black). The latter spectrum exhibits a maximum at -0.22 V which is attributed to a confined surface state (LockIn: $V_{\text{rms}} = 6$ mV, $f = 513$ Hz, initial tip parameters: -0.8 V, 80 pA). B) STM image of the porous network (13.6×13.6 nm², -0.20 V, 70 pA) and C) simultaneously recorded dI/dV map at 5K (LockIn: $V_{\text{rms}} = 8$ mV, $f = 513$ Hz). A confined electronic state is

observed inside the molecular pores. The black hexagons highlight the molecular positions. Defective pores severely affect the confined state (red hexagons) although not every defect annihilates the confined state (green hexagons). In some cases the confined state is affected although topography does not indicate any defects (blue hexagons). These observations could be explained by irregularities of the substrate within the pore (e.g. trapped Cu-adatoms or holes).

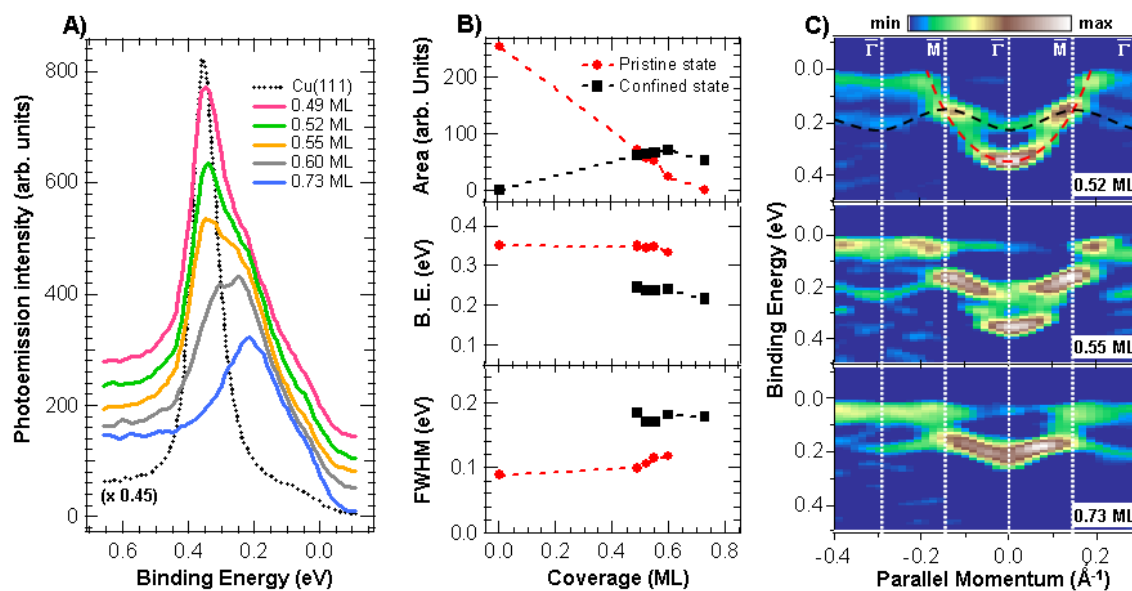


Figure 3: Band dispersion resulting from the periodic influence of the porous network on the surface state studied with ARPES for different molecular coverages. A) Normal emission spectra at RT showing the emerging confined state which progressively replaces the original Cu(111) surface state (scaled, black dotted line) with increasing molecular coverage. B) Peak area, binding energy (B.E.) and full width at half maximum (FWHM)

resulting from the analysis of the pristine and the confined states presented in A. C) Energy dispersion curves (EDC) of the pristine state (red dashed line) and the confined state (black dashed line) measured along the $\overline{\Gamma M}$ high symmetry direction and visualized as the 2nd derivative of the photoemission intensity for three different coverages. The 2nd derivative was used to enhance features of the EDC. Both EDCs at 0.52 ML and 0.73 ML have been acquired at RT, whereas 60 K was the acquisition temperature for 0.55 ML. The vertical white dotted lines refer to the new symmetry points induced by the molecular network. The red and black dashed lines on the top graph indicate the averaged positions of the maxima of both Lorentzian components fitted for all EDCs.

SUPPORTING ONLINE MATERIAL

1. - Materials and methods

The organic molecular network has been prepared by thermal deposition of DPDI (4,9-diaminoperylene-quinone-3,10-diimine) onto a clean Cu(111) single crystal surface held at RT. Afterwards, the sample was annealed at 500 K to create the hexagonal network which shows a commensurate $p(10 \times 10)$ structure in low energy electron diffraction (LEED), observed for all the coverages presented here. This self-assembled network completely covers the surface at a molecular coverage of ~ 0.7 ML (19, 20). Once formed, it is stable up to 600K due to its registry with the underlying substrate (19).

The STS spectra, topographic images, and dI/dV maps have been acquired using a commercial Omicron low temperature scanning tunnelling microscope (LT-STM) (Omicron NanoTechnology GmbH) at 5 K equipped with either wire cut PtIr tips or etched tungsten tips. The STM was operated by the Nanonis SPM control system (Nanonis GmbH) which also provides an internal lock-in amplifier. For the acquisition of STS spectra, STM tips were initially “calibrated” by reproduction of the well-known spectrum of the surface state. In all experiments the bias voltage was applied to the tip. However, the bias voltages given in the manuscript refer to a grounded tip to allow a direct comparison with the ARPES results. The free software WSxM (30) was used for data processing of the STM data.

ARPES spectra have been acquired at RT (unless otherwise stated) at the COPHEE end-station located at the Swiss Light Source (SLS) using a commercial monochromatized He-lamp source (31). The energy and angular resolution was $90 \text{ meV} / 0.5^\circ$ at $h\nu = 21.22 \text{ eV}$ and RT and the spot size was $\sim 6 \text{ mm}$, so that the sample was completely illuminated during

data acquisition. No radiation damage on the molecular overlayer was observed, as no appreciable changes of the normal emission spectra were recorded during the duration of the data acquisition.

2.- Supporting text

A summary of our main results is shown in Fig. S1. Periodic 0D confinement of the surface state of Cu(111) is imposed by means of an adsorbed molecular network. Each of the pores in the molecular network exhibits a confined electronic state, as displayed in Figs. S1A and S1B. However this confinement is shown to be imperfect so that the confined states ‘leak’ into neighboring pores. This induces cooperative electronic coupling between the quantum dots which results in the development of an electronic band, as shown in Fig. S1C. Our findings are in analogy to the band structure of a solid created by the periodic potential of its atoms. This is an experimental evidence of an artificial electronic band structure created by the periodic influence of the molecular network on the free-electron-like surface state.

In this supporting discussion we include i) scanning tunneling spectroscopy (STS) and angle-resolved photoemission spectroscopy (ARPES) data of the molecules forming the network, ii) information on the use of the 2nd derivative of the photoemission intensity for the ARPES data, and finally, iii) the proof that the reported electronic band only exists when the molecular network is present on the surface.

i) STS and ARPES of dehydrogenated DPDI molecules

Fig. S2 shows STS spectra obtained either on top of a dehydro-DPDI molecule of the porous network (black spectrum) or on the clean surface (red spectrum). The molecular spectrum exhibits two peaks at approximately -0.22 V and 0.07 V. Noticeably, the onset of the surface state is not present in the spectra taken on top of the dehydro-DPDI. STS has proven to be able to detect shifts of the surface state induced by molecules: In the case of

PTCDA (3,4,9,10-perylene tetracarboxylic dianhydride), another perylene derivative, Nicoara *et al.* (32) could determine a small shift induced by the weakly bound molecules (physisorbed, according to Ref. (33)) when deposited on Au(111). The same molecules become strongly bound (chemisorbed, according to Ref. (34)) when deposited on Ag(111) and in the corresponding STS spectra a characteristic feature is observed which resembles the surface state. This feature was initially interpreted as a dispersing state deriving from the LUMO + 1 of the free PTCDA (35) and later as the upshifted Shockley state of Ag(111) (36).

In our case neither ARPES (Fig. S3) nor STS showed any evidence of the surface state directly below the molecules. This is interpreted as a strong influence of the dehydro-DPDI molecules on the Cu(111) surface state. In this context the porous network is thought to act as a strong perturbation (and not as a weak modulation of the surface state) resulting in a shallow dispersing electronic band.

ii) Energy dispersion measured with ARPES

Fig. S4 demonstrates the use of the 2nd derivative of the photoemission intensity since it provides better contrast of small DOS features within the photoemission data, as previously shown (15, 16). In this figure, the photoemission energy distribution curves for the clean surface and for four different amounts of the dehydro-DPDI network is duplicated in two columns. The left column represents the photoemission intensity after removal of the Fermi step. In these plots the pristine state signal dominates, except for the highest coverage, and the contribution from the confined state is masked by it. The confined state band can be observed only very weakly in this data, especially outside from the 1st Brillouin

zone. On the other hand, the 2nd derivative from the raw data reproduces the binding energy positions obtained from normal emission and helps visualizing both band dispersions by enhancing the existing features. It is very instructive to see how the confined state band increases its intensity with respect to the pristine state originating from the clean network areas.

iii) Emergence of the confined state band with the presence of the molecular network

In Fig. S5 we demonstrate that the confined bands are only present after network formation. For samples covered with 0.49 ML of DPDI the electronic state is shifted by 85 meV towards the Fermi energy when compared to the clean surface state. On the other hand, when the same sample is annealed to 500 K and the porous dehydro-DPDI network is present on the surface, the Shockley state from the pristine areas is recovered and the band related to the molecular network emerges.

3.- Supporting figures

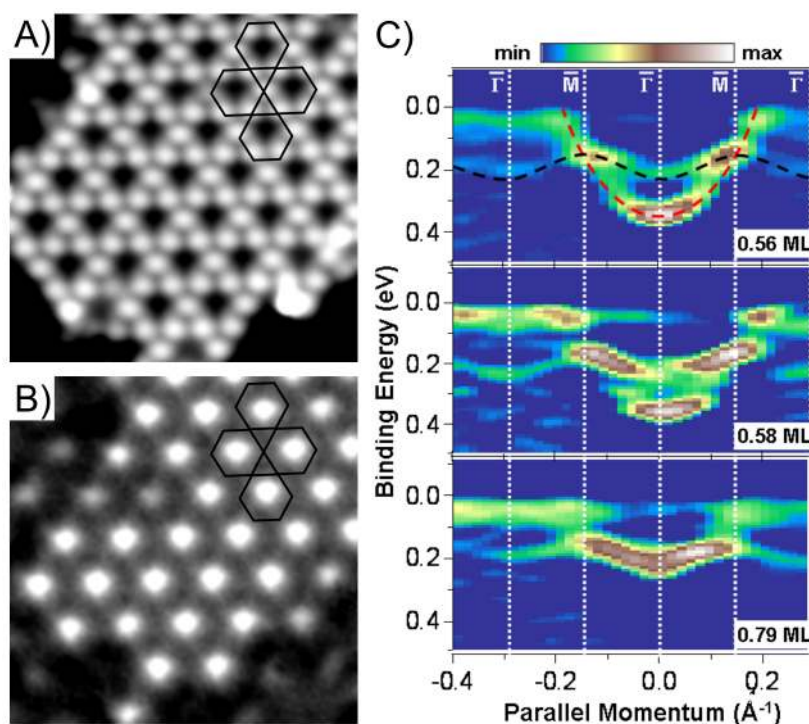


Figure S1: Surface state confinement resulting from a porous supramolecular network studied with complementary local and non-local techniques. A) STM image of the porous network ($13.6 \times 13.6 \text{ nm}^2$, -0.20 V , 70 pA) and B) simultaneously recorded dI/dV map (LockIn: $V_{\text{rms}} = 8 \text{ mV}$, $f = 513 \text{ Hz}$). A confined electronic state is observed inside the molecular pores. The hexagons highlight the molecular positions. C) Band dispersion resulting from the periodic influence of the porous network on the surface state studied with ARPES at different molecular coverages. The EDCs are measured along the $\overline{\Gamma M}$ high symmetry direction. The colour scale represents the 2nd derivative of the photoemission intensity.

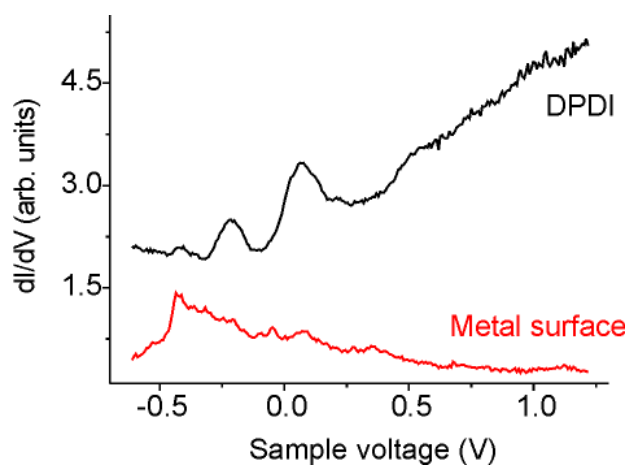


Figure S2: Low temperature (5K) STS spectra obtained on the pristine Cu surface (red) and on top of a dehydrogenated DPDI molecule of the molecular network (black) (LockIn: $V_{\text{rms}} = 7$ mV, $f = 313$ Hz, initial tip parameters: -0.8 V, 90 pA).

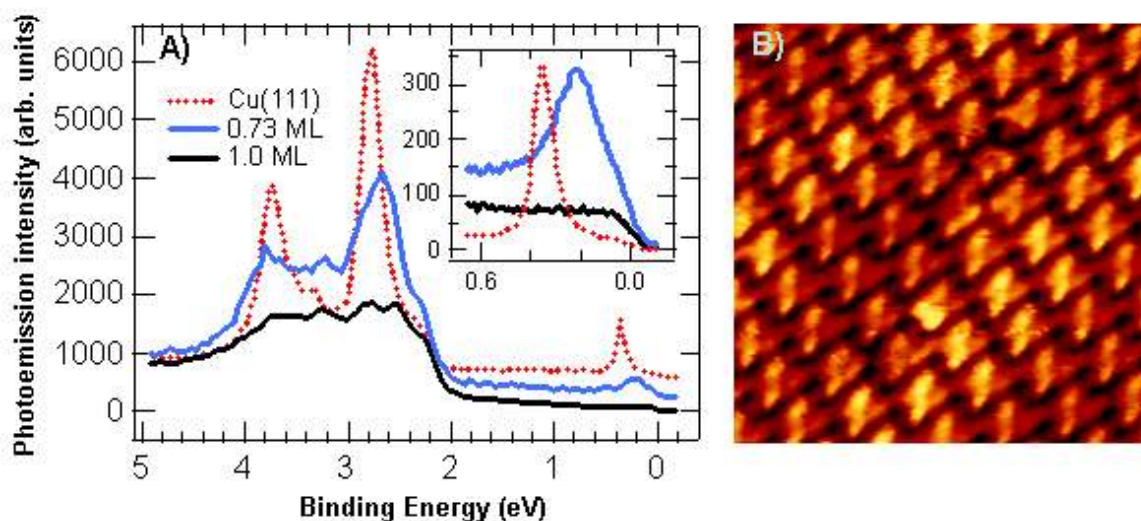


Figure S3: Investigation of the changes in the electronic structure when the molecular network (0.73 ML) is substituted by a close-packed assembly of dehydro-DPDI (1ML). A) Normal emission spectra of the full valence band comprising the *d*-bands (below 2 eV) and the surface related states (close to the Fermi energy). A close-up of the spectra near the Fermi energy is shown in the inset. For the porous network the surface state (red dotted line) is replaced with the confined state (blue spectrum). At a coverage of 1ML a close-packed assembly is formed (19, 20) which does not reveal any occupied surface related electronic state (black spectrum). B) STM image for 1ML of dehydro-DPDI on Cu(111) annealed at 500K (9x9 nm², -0.9 V, 84 pA).

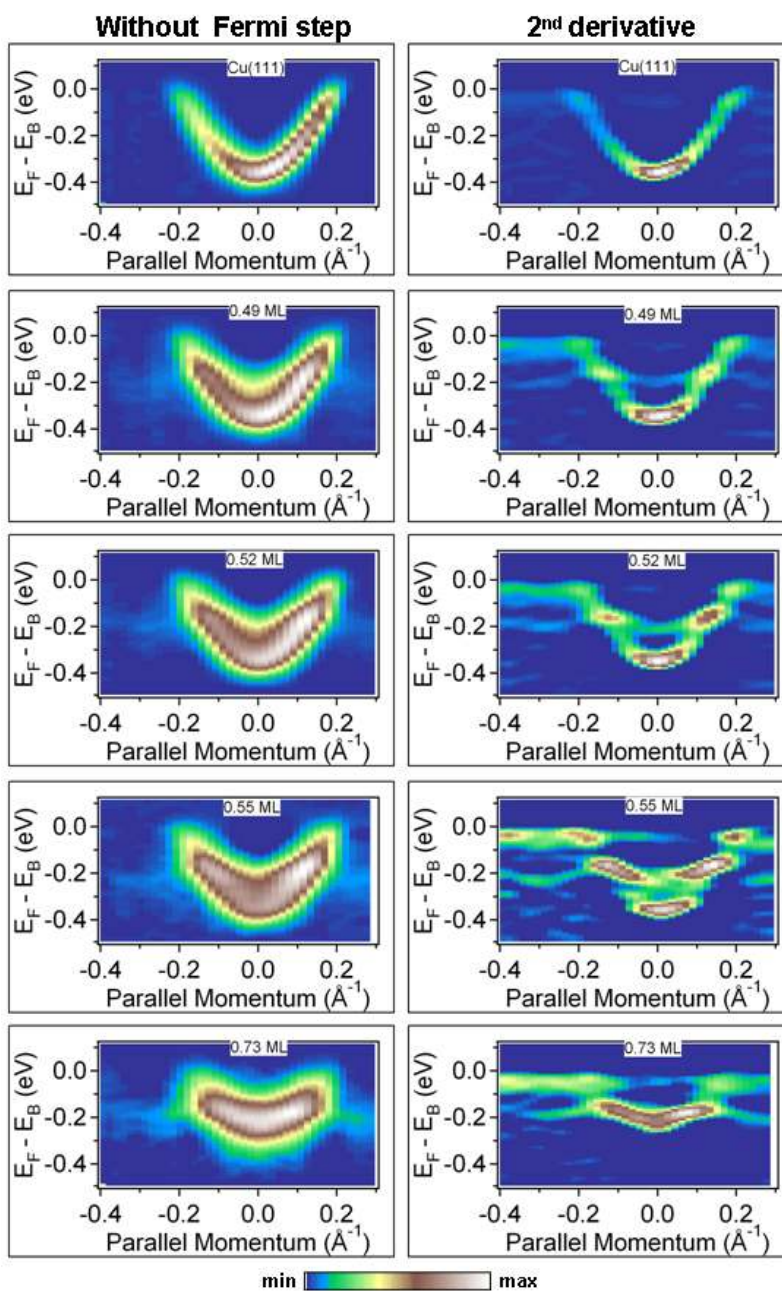


Figure S4: EDC curves measured along the $\overline{\Gamma M}$ high symmetry direction for the clean Cu surface (top) and the Cu surface covered with four different amounts of the dehydro-DPDI network. The effect of applying the 2nd derivative on the raw data (right column) can be directly compared to the smoothed data after removal of the Fermi step (left column). The bands related to the molecular network are clearly observed in all cases except for the

clean Cu(111) at the top. All the presented EDCs have been measured at RT, except for the case of 0.55 ML which has been acquired at 60 K.

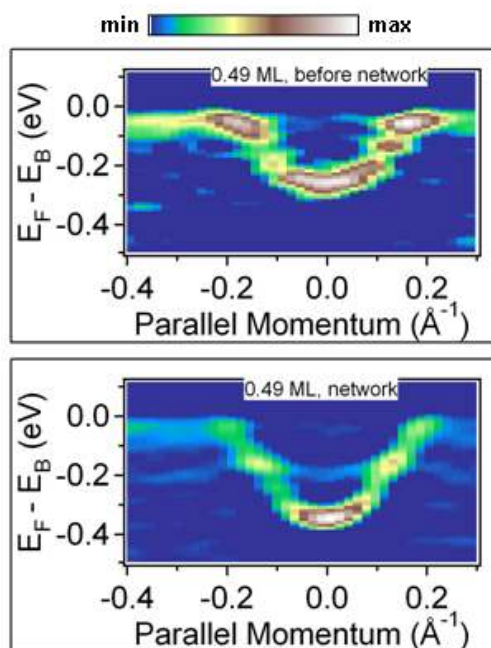


Figure S5: 2nd derivative of EDC curves measured along the $\overline{\Gamma M}$ high symmetry direction for 0.49 ML before (top) and after (bottom) network formation. The confined state exists only when the network is present on the surface.

4.- Supporting references and notes

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