

Supramolecular Assembly of Interfacial Nanoporous Networks with Simultaneous Expression of Metal–Organic and Organic-Bonding Motifs

Saranyan Vijayaraghavan,^[a] David Ecija,^{*,[a]} Willi Auwärter,^{*,[a]} Sushobhan Joshi,^[a] Knud Seufert,^[a] Mateusz Drach,^[b] Damian Nieckarz,^[b] Paweł Szabelski,^[b] Claudia Aurisicchio,^[c] Davide Bonifazi,^[c, d] and Johannes V. Barth^[a]

Abstract: The formation of 2D surface-confined supramolecular porous networks is scientifically and technologically appealing, notably for hosting guest species and confinement phenomena. In this study, we report a scanning tunneling microscopy (STM) study of the self-assembly of a tripod molecule specifically equipped with pyridyl functional groups to steer a simultaneous expression of lateral pyridyl–pyridyl interactions and Cu–pyridyl coordination bonds. The assembly protocols yield a new class of porous open assemblies, the formation of which is driven by multiple interactions. The tripod forms a purely porous organic

network on Ag(111), phase α , in which the presence of the pyridyl groups is crucial for porosity, as confirmed by molecular dynamics and Monte Carlo simulations. Additional deposition of Cu dramatically alters this scenario. For submonolayer coverage, three different porous phases coexist (i.e., β , γ , and δ). Phases β and γ are chiral and exhibit a simultaneous expression of lateral pyridyl–pyridyl interactions and

twofold Cu–pyridyl linkages, whereas phase δ is just stabilized by twofold Cu–pyridyl bonds. An increase in the lateral molecular coverage results in a rise in molecular pressure, which leads to the formation of a new porous phase (ϵ), only coexisting with phase α and stabilized by a simultaneous expression of lateral pyridyl–pyridyl interactions and threefold Cu–pyridyl bonds. Our results will open new avenues to create complex porous networks on surfaces by exploiting components specifically designed for molecular recognition through multiple interactions.

Keywords: metal–organic coordination • scanning probe microscopy • self-assembly • porous networks • supramolecular chemistry

Introduction

The tools of supramolecular chemistry provide versatile protocols to create myriad functional molecular nanostructures on surfaces by means of self-assembly.^[1] Within these nano-

architectures, 2D molecular porous networks are particularly relevant. They represent a family of model systems that exhibits a periodic spatial arrangement of voids and thus offers enormous potential as secondary templates to host guest species.^[2,3] Notably, they have proven to be valuable and versatile open nanoarrays for the specific positioning of adsorbates,^[4,5] electron-confinement phenomena,^[6,7] and controlling the dynamic properties of caged species.^[8]

The final structure of the 2D porous network is determined by a very subtle balance between molecule–substrate and molecule–molecule interactions. Substantial effort in the field was focused on weak interactions, including van der Waals forces and/or dipole–dipole interactions,^[9] hydrogen bonds,^[4,10] and metal–organic coordination,^[11] due to their higher propensity for self-correction in contrast to covalent bonding schemes,^[12] which results in a better network regularity. Hereby, the emphasis has recently been shifted to metal–ligand interactions since they show an adequate balance between stability and lability.^[13]

To date, most of the reported surface-confined porous architectures studied under ultra-high vacuum conditions are based on uni- or bimolecular systems and are stabilized by just one type of interaction. Occasionally, a supramolecular assembly has exhibited a serendipitous complex interplay between two different types of interactions, typically of different bond strength.^[14]

[a] S. Vijayaraghavan, Dr. D. Ecija, Dr. W. Auwärter, S. Joshi, Dr. K. Seufert, Prof. Dr. J. V. Barth
Physik Department E20
Technische Universität München
85748 Garching (Germany)
Fax: (+49) 89-2891-2608
E-mail: david.ecija@tum.de
wau@tum.de

[b] Dr. M. Drach, D. Nieckarz, Dr. P. Szabelski
Department of Theoretical Chemistry
Maria-Curie Skłodowska University
Pl. M.C. Skłodowskiej 3, 20-031 Lublin (Poland)

[c] Dr. C. Aurisicchio, Prof. Dr. D. Bonifazi
Department of Chemistry and Namur Research College (NARC)
University of Namur (UNamur)
Rue de Bruxelles 61, 5000 Namur (Belgium)

[d] Prof. Dr. D. Bonifazi
Department of Chemical and Pharmaceutical Sciences and
INSTM UdR of Trieste, University of Trieste
Piazzale Europa 1, Trieste (Italy)

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We recently developed an interest in the formation of regular porous networks based on multiple interactions (i.e., different binding types of comparable strength). With this aim, we exploit the linking characteristics of a tripod molecule peripherally equipped with three pyridyl functional groups (see module **1** in Figure 1a). In an earlier report, we showed that this molecular module displays a simultaneous expression of metal–organic and pyridyl–pyridyl interactions on Cu(111), thus favoring the formation of 2D short-range disordered crystalline networks.^[15]

Herein, we report a scanning tunneling microscopy (STM) study of the 2D molecular porous networks created by the deposition of module **1** on Ag(111) and describe their response in the presence of Cu adatoms at different molecular coverages, a scenario in which an interplay between molecular bonds of a different nature is visualized, the balance of which determines the final organization.

Results and Discussion

Molecule **1**, 1,3,5-tris(pyridin-4-ylethynyl)benzene, possesses three pyridyl groups connected to a central aryl ring through ethynyl moieties (see Figure 1a). The functional terminal groups are programmed to steer coordination bonds through pyridyl–metal–pyridyl interactions,^[16–18] together with lateral pyridyl–pyridyl links,^[15] presumably a variant of the recently suggested proton-acceptor ring interaction.^[19]

2D molecular porous network on Ag(111): The deposition of a submonolayer coverage of **1** on Ag(111) held at 350 K results in the formation of extended 2D molecular hexagonal porous networks (see Figure 1b), named phase α , with an average pore-to-pore distance of (20 ± 1) Å and a circular pore size of approximately 35 Å², as estimated from a careful inspection of the cavities in high-resolution STM images. An increase in the molecular coverage to saturation promotes the formation of a perfect porous molecular monolayer.

High-resolution STM data (see Figure 1c) allow us to discern the layer organization and submolecular features. Each molecule is characterized by four lobes, which correspond to the central aryl and the three peripheral pyridyl groups, respectively. Remarkably, the molecular appearance in the STM images preserves a strict threefold symmetry (i.e., apparent opening angles of 120° between pyridin-4-ylethynyl functions). Thus, the intrinsic flexibility attributed to the ethynyl moiety, previously encountered on Cu(111),^[15] is not expressed in the present system. In addition, we observed two different molecular orientations related by a 60° rotation. As clearly depicted experimentally in Figure 1c and by the corresponding atomistic model in Figure 1d, the network is essentially stabilized by lateral pyridyl–pyridyl interactions, following a pattern in which each molecule is in contact with three neighbors through two lateral pyridyl–pyridyl interactions, thereby resulting in six noncovalent bonds. In analogy to the deposition of **1** on Cu(111), we

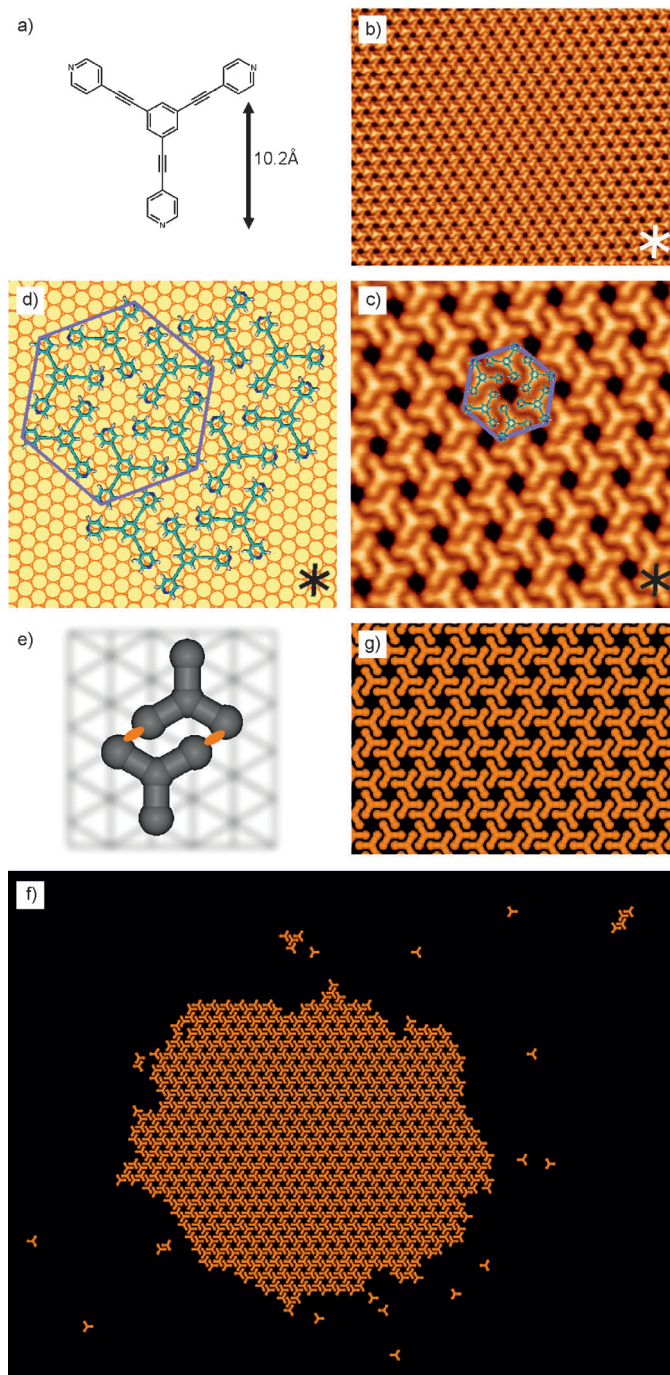


Figure 1. Phase α : Hexagonal molecular porous network obtained by the deposition of molecule **1** on Ag(111). a) Structure of 1,3,5-tris(pyridin-4-ylethynyl)benzene, compound **1**. b) Large-scale STM image displaying the porous assembly. c) Submolecular resolution STM image of detailed section of (b) exhibiting the threefold appearance of molecule **1** on Ag(111). d) Atomistic model of the assembly. The rosette motif described in the text is highlighted by a violet hexagon. The close-packed directions of the Ag(111) surface are depicted by white or black stars. Image size: b) 403×325 Å and c) 129×129 Å. Tunneling parameters: b, c) $I = 0.2$ nA, $V_{\text{bias}} = -1.7$ V. e) Configuration of a pair of adsorbed molecules **1** used in the MC simulations, developing into phase α . The lateral noncovalent interactions stabilizing the configuration are indicated in orange. f) Snapshot of the equilibrated self-assembled pattern of 1000 molecules as obtained from MC simulations, in which only directional noncovalent interactions from Figure 1e rule the arrangement. g) Detailed image of a region of Figure 1f.

assign this recognition motif to a noncovalent interaction^[19] with a characteristic projected N...H distance of (1.8 ± 0.5) Å, similar to the values measured on Cu(111)^[15] and at solid–liquid interfaces.^[20] With this arrangement, each pore is surrounded by six molecules in a rosette-like fashion. Moreover, the molecular superlattice is commensurate with respect to the Ag(111) substrate as reflected by the absence of a moiré pattern. We tentatively propose a molecular adsorption site geometry in which the compound is placed with an aryl on a hollow site.^[21]

The supramolecular network features organizational chirality and accordingly two mirror-symmetric domains of the hexagonal porous network have been observed, designated the α (displayed in Figure 1b–d and in Figure S1a,c of the Supporting Information) and α' network (see Figure S1a,b of the Supporting Information). Hereby, the unit-cell vectors of the supramolecular hexagonal porous pattern form an angle of -23° for chirality α and of 23° for chirality α' relative to the close-packed directions of Ag(111).

To obtain deeper insight^[22] into the stability and the porosity of phase α , we performed molecular dynamics (MD) simulations in which the Ag(111) substrate was explicitly taken into account assuming islands of six molecules under periodic boundary conditions (see Videos S1–S4 in the Supporting Information). A configuration of six linkers arranged like a rosette pore is stable at 100 K, presenting twelve N...H associations (see Video S1 in the Supporting Information). Importantly, two different close-packed assemblies of the modules turned out to be unstable (see Videos S2 and S3 in the Supporting Information). Finally, a simulation that employed tripod modules equipped with phenyl substituents instead of pyridyl termini was not able to create a rosette-like pore (see Video S4 in the Supporting Information). Altogether, these results prove that the lateral directional noncovalent interactions are responsible both for the stability and the porosity of phase α .

To further corroborate this conclusion, we performed separate lattice gas Monte Carlo (MC) simulations (see Figure 1e–g), which were parameterized according to the previous MD output to account for the dominant contribution of the lateral pyridyl–pyridyl interactions in the stabilization of the rosette motif (i.e., only the interactions marked in orange in the configuration from Figure 1e are considered). As a result, large assemblies of the molecule have been modeled, thereby confirming the dominant role of the lateral pyridyl–pyridyl contacts in the formation of phase α .

A comparison of our results with the self-assembly patterns formed by the tripod molecule on highly ordered pyrolytic graphite (HOPG) at the liquid–solid interface^[23] reveals the importance of the molecule–substrate interactions in the case of Ag(111). On HOPG, these interactions are considered negligible, and the architectures could be predicted by density functional theory (DFT) and MC simulations (without including the substrate) and experimentally inspected by STM. However, on Ag(111), molecule–substrate interactions are more relevant, which are properly parameterized in the molecular dynamics simulations described above; together

with the lateral pyridyl–pyridyl contacts they give rise to the formation of phase α , which differs from the structures reported at the liquid–solid interface.

Polymorphism through multiple interactions at submonolayer coverage: The deposition of small amounts of Cu atoms on a previously prepared submonolayer of α -network dramatically changes the self-assembly scenario. Up to three new phases appear, which coexist with phase α , labeled as phase β , γ , and δ . As detailed below, phases β and γ are governed by multiple lateral pyridyl–pyridyl interactions and pyridyl–Cu–pyridyl bonds, whereas phase δ is fully stabilized by pyridyl–Cu–pyridyl coordinative bonds. Remarkably, the deposition of an excess amount of Cu atoms, verified by the presence of Cu clusters on the steps, yields different patches of phase β , phase γ , and phase δ . In any scenario, phase β is the most abundant, which indicates its higher stability.

Figure 2a–c displays an overview STM image, a high-resolution STM image, and an atomistic model of phase β . The assembly is a complex porous network made of four types of pores: a small quasicircular pore of approximately 35 \AA^2

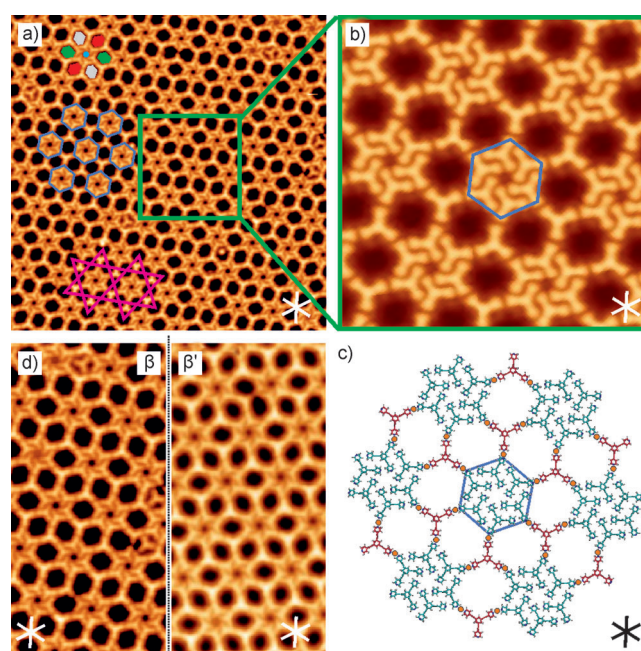


Figure 2. Phase β : A hierarchic molecular porous assembly based on multiple interactions obtained by the deposition of **1** and Cu atoms on Ag(111) for a local stoichiometric ratio of 0.75:1 (Cu/molecule). a) Large-scale STM image of the porous assembly. The rosette pores are highlighted by dark blue hexagonal contours. In the top left part of the image, the different oriented pores B are filled in with colors white, red, and green, whereas the rosette pore is marked with light blue. The assembly of pores B in positions of a kagomé lattice is displayed by the magenta lines. b) Detailed image of (a) exhibiting submolecular resolution features of the assembly. c) Atomistic model of (b) displaying two types of recognition motifs: a lateral pyridyl–pyridyl interaction and a non-straight twofold pyridyl–Cu–pyridyl bond. d) High-resolution STM images showing the organizational chirality displayed by phase β , labeled as β and β' . The close-packed directions of the Ag(111) surface are depicted by white or black stars. Image size: a) $443 \times 443 \text{ \AA}$, b) $140 \times 140 \text{ \AA}$, and d) $144 \times 287 \text{ \AA}$. Tunneling parameters: $I = 0.2 \text{ nA}$, $V_{\text{bias}} = -0.7 \text{ V}$.

(displayed in light blue in Figure 2 and identical to the pores of phase α) and three differently oriented pores, designated pores B and related by a 60° rotation, which have a similar size and distorted-hexagonal shape of approximately 280 \AA^2 (colored white, green, and red, respectively, in Figure 2a). The small pores are arranged on the surface following a hexagonal pattern, separated by $(51 \pm 2) \text{ \AA}$. The unit-cell vectors of this hexagonal pattern form an angle of 23° with respect to the close-packed directions of the Ag(111) surface. On the other hand, the arrangement of the distorted-hexagonal pores follows a kagomé-type assembly,^[6,24] as depicted by the magenta lines in Figure 2a.

As in phase α , the molecular species (Figure 2b) are visualized as modular tripods that exhibit perfect threefold symmetry and are arranged in four different orientations. Each molecule appears as a four-lobed structure, in which the lobes correspond to the central aryl and the peripheral pyridyl groups, respectively.

The stability of the network is provided by two different recognition motifs (see Figure 2c): 1) A head-to-head orientation between two neighboring pyridyl groups with a projected $\text{N}\cdots\text{Cu}$ distance of $(2.2 \pm 0.5) \text{ \AA}$, and 2) a lateral interaction between two adjacent pyridyl rings. In analogy with phase α , motif 2 is assigned to a noncovalent interaction with an average projected $\text{N}\cdots\text{H}$ length of $(1.8 \pm 0.5) \text{ \AA}$. In addition, on the basis of the assembly of molecule **1** on Cu(111),^[15] we assign motif 1 to a nonstraight (tilt angle of approximately 15°) pyridyl–Cu–pyridyl metal–organic interaction, in which the coordinated Cu atom is not resolved.^[15,16,25] Remarkably, in any phase that exhibits pyridyl–Cu–pyridyl interactions, an increase in the apparent height of the molecular moiety involved in the Cu–pyridyl bond is detected relative to other moieties that establish lateral pyridyl–pyridyl contacts, which reinforces our hypothesis about the formation of a metal–organic bond. In summary, the network is stabilized by multiple noncovalent interactions of different natures, which results in a complex hierarchic organization: Six molecules form a porous rosette-like structure, identical to that found in phase α , through lateral pyridyl–pyridyl interactions. Simultaneously, the rosette structures (depicted in blue in Figure 2c) are connected with each other in a hexagonal fashion by establishing pyridyl–Cu–pyridyl bonds with two differently-oriented molecular species (displayed in red in Figure 2c). The remaining surface voids create the distorted-hexagonal pores, to be named B pores. In summary, phase β is a hierarchic porous network that exhibits two levels of hierarchy: a first level to create the rosette motif that involves lateral pyridyl–pyridyl interactions, and a second level that joins the rosettes through metal–organic coordination. Overall, the local Cu/molecule stoichiometric ratio is 0.75:1. In principle, pyridyl–pyridyl interactions are expected to be weaker than coordinative pyridyl–Cu–pyridyl linkages. However, as a whole, the cyclic rosette motif is strong enough to be part of the first level of hierarchy. This is unprecedented in 2D hierarchic assemblies that involve coordination bonds in which the metal–ligand interactions typically prevail for the first level

of hierarchy and other noncovalent bonds intervene in the next levels of hierarchy.^[3]

Owing to the inclusion of the rosette motif, the self-assembly of phase β results in two mirror-symmetric domains that extend over entire surface terraces, designated as the β and β' network (see Figure 2d). Hereby, the unit-cell vectors that describe the hexagonal arrangement of the rosettes form an angle of $+23^\circ$ for chirality β and of -23° for chirality β' with respect to the close-packed directions of Ag(111).

Figure 3a displays a large-scale STM image of phase γ , which is visualized as a 2D molecular porous assembly com-

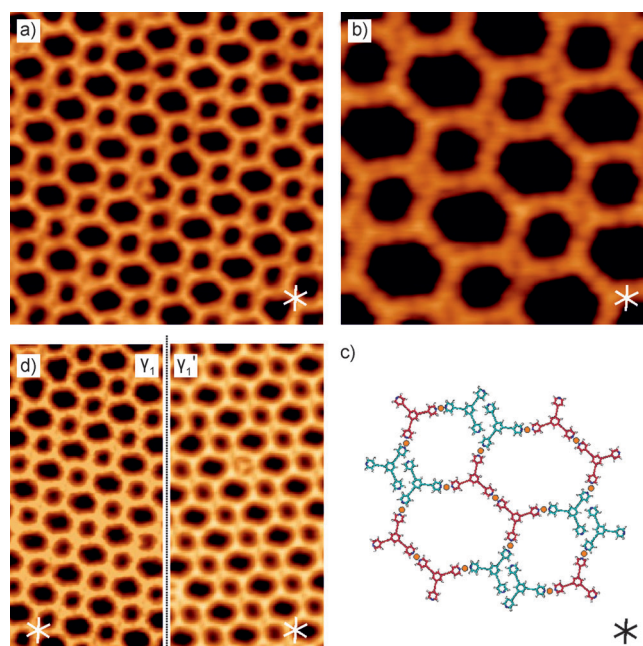


Figure 3. Phase γ : A 2D molecular porous assembly based on multiple interactions obtained by the deposition of **1** and Cu atoms on Ag(111), for a local stoichiometric ratio of 1.25:1 (Cu/molecule). a) Large-scale STM image displaying the alternating rows of pores. b) High-resolution STM image of a detailed region of (a) exhibiting submolecular resolution. c) Atomistic model of the assembly revealing the simultaneous expression of lateral pyridyl–pyridyl and pyridyl–Cu–pyridyl interactions. d) STM images comparing two chiral-symmetric domains. The close-packed directions of silver are depicted by white or black stars. Image size: a) $251 \times 251 \text{ \AA}$, b) $111 \times 111 \text{ \AA}$, and d) $300 \times 150 \text{ \AA}$. Tunneling parameters: a) $I = 0.1 \text{ nA}$, $V_{\text{bias}} = -0.7 \text{ V}$; b) $I = 0.2 \text{ nA}$, $V_{\text{bias}} = -1 \text{ V}$; d) $I = 0.1 \text{ nA}$, $V_{\text{bias}} = -1 \text{ V}$.

posed of alternating rows of two different kinds of pores. The small pores have a mean area of approximately 280 \AA^2 , forming rows with an interpore distance of $(31 \pm 1) \text{ \AA}$; whereas the bigger voids comprise approximately 520 \AA^2 with an interstructure distance of $(31 \pm 1) \text{ \AA}$. High-resolution STM data in Figure 3b and its corresponding model in Figure 3c reveal that phase γ exhibits noticeable similarities to phase β : 1) The molecules similarly appear in the STM images and display four identical orientations as those of phase β ; 2) phase γ is also stabilized by a simultaneous expression of lateral pyridyl–pyridyl interactions and pyridyl–Cu–pyridyl metal–organic coordinations, which exhibit the

same bond lengths; and 3) the small pores are identical to pores B found in phase β (depending on chirality; see below), whereas the big voids are new and thus are labeled as pores C. There are no rosette motifs; that is, the differences between phases γ and β arise from different organizational schemes; for phase γ they employ a local 1.25:1 (Cu/molecule) stoichiometric ratio, which is higher than in the case of β . Hereby, two different oriented molecules (displayed in blue in Figure 3c) are involved in a simultaneous expression of interactions, a lateral pyridyl–pyridyl link and a nonstraight pyridyl–Cu–pyridyl contact (tilt angle of approximately 15°), whereas the other two different oriented molecules just establish straight pyridyl–Cu–pyridyl coordination bonds (depicted in red in Figure 3c).

With regard to the self-assembly of phase γ , a statistical analysis of STM data shows the presence of three organizational domains, to be named domain γ_1 , γ_2 , and γ_3 , rotated by 60° . As depicted in Figure 3a–c, domain γ_1 forms an angle of 11° with respect to the close-packed directions of Ag(111). In addition, due to the presence of the lateral pyridyl–pyridyl interactions, which express chirality on the surface, phase γ displays three organizational chiral domains, labeled γ'_1 , γ'_2 , and γ'_3 (see Figure 2d for a comparison of the two mirror-symmetric domains γ_1 and γ'_1).

Finally, Figure 4a shows a large-scale STM image of phase δ , which is again a molecular porous network, exhibiting distorted hexagonal pores with a size of approximately 500 \AA^2 and arranged in a hexagonal fashion with an inter-pore distance of $(32 \pm 1) \text{ \AA}$. High-resolution STM images and a tentative atomistic model (see Figure 4b,c) decipher the pattern of interactions that stabilize the network: Two different oriented molecules are engaged in a pyridyl–Cu–pyridyl interaction following a Cu/molecule stoichiometry of 1.5:1. Remarkably, as observed in phases β and γ , the coordination bond features a similar bond length and it is not straight (tilt angle of approximately 15°), which, together with the assembly pattern, gives rise to a distorted hexagonal appearance of the cavities, named pores D. Since there are no traces of lateral pyridyl–pyridyl interactions, phase δ represents a pure 2D metal–organic network.

Concerning the organizational self-assembly, phase δ presents two orientational domains rotated by 36° . Figure 4a–c displays domain δ_1 , in which the unit-cell vectors that describe the hexagonal assembly of the pores form an angle of -13° with the close-packed directions of Ag(111).

Self-assembly modified by molecular pressure: The coexistence of phases α , β , γ , and δ at submonolayer coverage is due to a very subtle balance between molecule–substrate interactions and the simultaneous expression of lateral pyridyl–pyridyl and metal–organic bonds that govern the molecule–molecule interactions. Clearly, passing from phase α to δ , a noticeable increase in the porosity (defined as the fraction of the surface of the voids with respect to the surface of the supramolecular architecture) of the networks is observed. Provided there are enough Cu adatoms, a rational way to promote homogeneous molecular patterns on

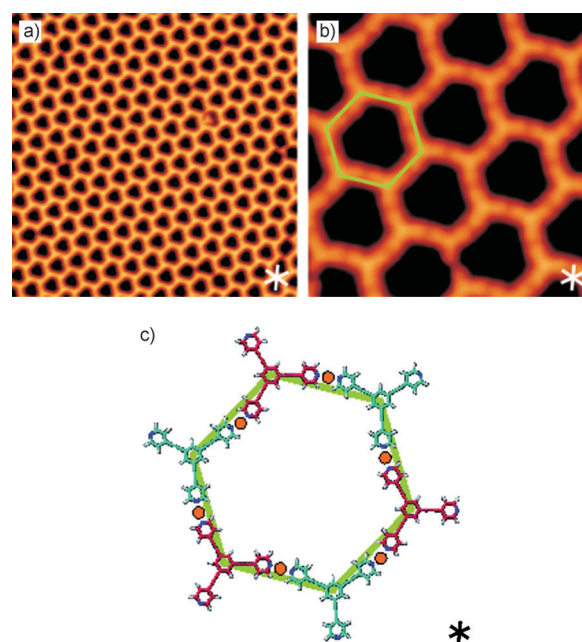


Figure 4. Phase δ : A 2D molecular porous network based on pyridyl–Cu–pyridyl interactions obtained by the deposition of **1** and Cu atoms on Ag(111), presenting a local stoichiometric ratio of 1.5:1 (Cu/molecule). a) Large-scale STM images of the two domains of the 2D porous assembly. b) High-resolution STM image of (a) displaying submolecular recognition and exhibiting the head-to-head pyridyl–Cu–pyridyl recognition motif stabilizing the network. c) Schematic model of image (b). The close-packed directions of silver are depicted by white or black stars. Image size: a) $443 \times 443 \text{ \AA}$, b) $111 \times 111 \text{ \AA}$. Tunneling parameters: a) $I = 0.2 \text{ nA}$, $V_{\text{bias}} = -1 \text{ V}$; b) $I = 0.2 \text{ nA}$, $V_{\text{bias}} = -0.6 \text{ V}$.

Ag(111) would be to enhance the intrinsic in-plane compression pressure built up by the molecules confined on the surface due to an increase in the molecular coverage, which, in principle, could favor the formation of phase β given its lower porosity and higher molecular density.^[18] In fact, for a molecular coverage of about 0.8 ML (ML = monolayer), after the dosage of Cu atoms, we observe the coexistence of phases α (organic superlattice) and β , whereas phases γ and δ are not present.

Surprisingly, for a molecular coverage close to monolayer saturation (above 0.9 ML), a new phase ϵ appears after deposition of Cu, which coexists with minority domains of phase α . A large-scale STM image and a high-resolution STM image, along with a tentative atomistic model are depicted in Figure 5. Remarkably, we observe the formation of a 2D hierarchic porous assembly that exhibits two levels of hierarchy. The first one corresponds to the purely organic rosette motif described above. Secondly, rosette elements are positioned on the surface in a hexagonal lattice, being joined together by threefold pyridyl–Cu–pyridyl coordination bonds. As a result, phase ϵ , like phases β and γ , is governed by a simultaneous expression of interactions, although in this case the metal–organic bond is threefold, whereas for phases β and γ it is twofold. A comparison in Figure 5a between phases γ and ϵ reveals that the same two molecular

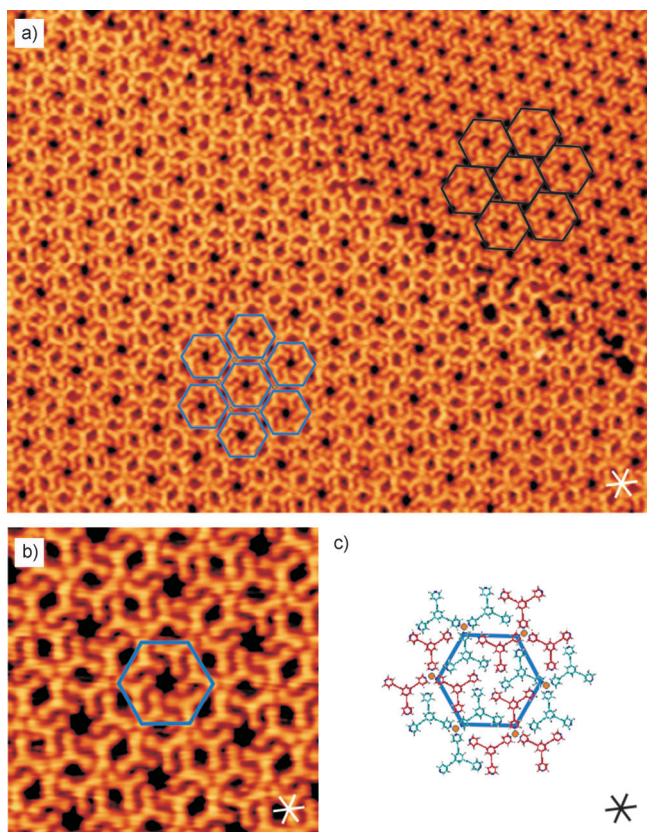


Figure 5. Phase ϵ : A 2D molecular porous network exhibiting simultaneous expression of threefold Cu–pyridyl interactions and lateral pyridyl–pyridyl links, obtained by the deposition of 0.9 ML of molecule **1** and Cu on Ag(111), and presenting a 1:3 Cu/molecule ratio. a) Long-range STM image of the coexistence of phases α (nonmetalated) and ϵ . b) Detailed image of (a) displaying submolecular resolution of phase ϵ . c) Atomistic model of phase ϵ . The black and violet hexagons represent the contour of the rosette motif in phase α and in phase ϵ , respectively. The close-packed directions of silver are depicted by white or black stars. Image size: a, d) 440×344 Å, b, e) 111×111 Å. Tunneling parameters: a) $I = 0.2$ nA, $V_{\text{bias}} = -1$ V; b) $I = 0.4$ nA, $V_{\text{bias}} = -1$ V.

orientations are involved in the formation of both phases. In particular, phase ϵ follows a design pattern in which each molecular module establishes four lateral pyridyl–pyridyl interactions and one pyridyl–Cu–pyridyl bond, thereby exhibiting a 1:3 Cu/molecule ratio. Within the experimental error, the lateral pyridyl–pyridyl interactions present an identical projected N...H distance to that of phase α , whereas the N–Cu projected bond length is (1.9 ± 0.5) Å. Interestingly, as a result of the hierarchic self-assembly, phase ϵ exhibits the rosette pores in a hexagonal lattice, like phase α , but with a different interpore distance and orientation with respect to the Ag(111) substrate. Thus, the molecular pressure together with the simultaneous expression of multiple interactions suggests that new ways can be exploited to tune the assembly of the pores of molecular networks. In particular, for phase ϵ the interpore distance between the rosette substructures is (33 ± 1) Å, whereas the unit-cell vector of their hexagonal assembly forms an angle of $+18^\circ$ with respect to the close-packed directions of Ag(111).

We have tried to estimate the binding energy per molecule of each phase by taking into account recent results, which report a binding energy of $0.101 \text{ eV}^{[26]}$ for pyridyl–pyridyl interactions and of $0.2 \text{ eV mol}^{-1[27]}$ for a Cu–pyridyl bond. Our calculations show a preference for the fully metalated phase, which is not consistent with a simultaneous expression of a lateral pyridyl–pyridyl interaction and a Cu–pyridyl bond, as experimentally observed by the coexistence of different phases. These results suggest that to have multiple interactions taking place at the metal–vacuum interfaces the inter-pyridyl noncovalent binding energy has to be closer to that of Cu–pyridyl bonds in our scenario than in the previous reports.

Conclusion

We have studied the self-assembly of a tripod molecular compound on Ag(111) tailored to feature multiple interactions in the presence of Cu adatoms (i.e., lateral pyridyl–pyridyl and pyridyl–Cu linkages).

The deposition of the tripyridyl module on bare Ag(111) results in the formation of a 2D molecular hexagonal porous network (phase α) essentially governed by lateral pyridyl–pyridyl interactions, with a characteristic rosette pore shape surrounded by six interacting molecules.

At submonolayer molecular coverage, a subsequent deposition of Cu atoms dramatically alters the self-assembly scenario and gives rise to a coexistence of three different 2D molecular porous phases: β , γ , and δ . Whereas phases β and γ are ruled by a simultaneous expression of both pyridyl–Cu–pyridyl and lateral pyridyl–pyridyl interactions, phase δ is solely comprised of pyridyl–Cu–pyridyl metal–organic coordination bonds. Remarkably, phase β exhibits a two-level hierarchic design in which the rosette motifs are placed in a hexagonal arrangement, with a higher interpore distance than in phase α , being connected together by additional linkers to establish twofold Cu–pyridyl bonds with the rosettes.

By increasing the molecular coverage, the influence of the molecular pressure is manifested in a reduction of the previous polymorphism. At a coverage of 0.8 ML, only phase β is detected in coexistence with phase α . Close to monolayer saturation, a new phase evolves (phase ϵ), which coexists only with residues of phase α . Phase ϵ is described as a two-level hierarchic porous assembly in which the rosettes are hexagonally distributed on the surface and are directly linked to each other by threefold Cu–pyridyl bonds, thus giving an intermediate interpore distance relative to phases α and β .

In addition, phases α , β , and γ feature chiral organizations, a property that enhances the potentials of the surface-confined molecular porous networks described in this paper for hosting functional chiral guests. In this sense, the simultaneous expression of multiple interactions on a surface represents an alternative strategy to design complex hierarchic networks at surfaces to possibly feature self-adaptive prop-

erties. Hereby, the different molecular adsorption modes observed for this tripod molecule on different substrates, threefold on Ag(111) and on HOPG,^[23] but distorted on Cu(111),^[15] highlights the potential of these molecular species for engineering self-healing and self-adaptive systems.

By taking into account the versatility of both organic chemistry and surface-confined supramolecular chemistry, we consider that our work will pave new avenues towards the design of increasingly complex molecular porous networks.

Experimental Section

All STM experiments were performed in a custom-designed ultra-high-vacuum (UHV) system that provided a base pressure below 1×10^{-10} mbar.^[28] The monocrystalline Ag(111) was cleaned by repeated Ar⁺ sputtering cycles at an energy of 800 eV, followed by annealing at 730 K for 10 min. Subsequently, a submonolayer coverage of molecule **1** was deposited by organic molecular beam epitaxy from a thoroughly degassed quartz crucible held at 463 K. During deposition, the Ag(111) surface was kept at 340 K, respectively, and the pressure remained $< 5 \times 10^{-10}$ mbar. When necessary, Cu atoms were evaporated from a homemade water-cooled cell by resistively heating a W filament surrounded by a Cu wire of high purity (99.9999%) on the sample kept at 340 K. All STM images were acquired by using a low-temperature CreaTec-STM^[29] with the sample held at 6 K with electrochemically etched W tips. In the figure captions, V_{bias} refers to the bias voltage applied to the sample. With regard to coverage, we define 1 ML as one surface fully covered by molecules to give rise to phase α . Atomistic modeling of the distinct phases were performed in the framework of the Hyperchem 7.5 Software Package.^[30] The WSxM software was used for the analysis of STM images.^[31]

All molecular dynamics (MD) simulations were performed with the Gromacs 4.5.5 software package.^[32,33] The calculations were carried out using an NVT ensemble at 100 K with a Nosé–Hoover thermostat. The interaction parameters for molecule **1** were taken from OPLS-AA force field, whereas for the Ag(111) surface the modified GoIP model^[34] with the parameters for silver from the literature^[35] was used. The simulation box ($58 \times 50 \times 80$ Å) consisted of four layers of silver atoms (400 atoms each) and six molecules of **1**. Long-range electrostatic interactions in the system were calculated by using the particle mesh Ewald method with cutoff equal to 12 Å. To calculate van der Waals interactions the same cutoff (12 Å) was used. All MD runs were performed for 5 ns.

The Monte Carlo simulations were performed using a 120×120 triangular lattice of equivalent adsorption sites with the conventional canonical ensemble Monte Carlo method with Metropolis sampling.^[36] To eliminate edge effects, periodic boundary conditions in both directions were applied. The tripod molecule **1** was represented by the rigid C_3 -symmetric planar structure that comprises four identical segments (core and three one-membered arms) showed in Figure 1. It was assumed that one molecular segment occupies one lattice site. The molecules were assumed to interact through a short-ranged segment–segment interaction potential limited to nearest-neighbors on a triangular grid. To account for the dominant contribution of the directional N···H interactions in the stabilization of the rosette motif, only the interactions marked in orange in the configuration from Figure 1 were considered, and their energy was set to -2.5 , expressed in kT units. For all remaining molecular configurations (not shown) the segment–segment interaction energy was equal to zero. The simulations were performed for 1000 molecules of **1**. To equilibrate the system, up to 10^4 MC trial moves per molecule were used.^[36]

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