

Supporting information:

Covalent assembly of a two-dimensional molecular “sponge” on a Cu(111) surface: Confined electronic surface states in open and closed pores

Aneliia Shchyrba,^a Susanne C. Martens,^{a,b} Christian Wäckerlin,^{c,‡} Manfred Matena,^a Toni Ivas,^a Hubert Wadepohl,^b Meike Stöhr,^d Thomas A. Jung,^{c,*} and Lutz H. Gade^{b,*}

^a Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland.

^b Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.

^c Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland.

^d Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

Present address: [‡] Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

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1. Molecular structure of *N,N'*; *N'',N'''*-diborylene-3,4,9,10-tetraaminoperylene (1).

The molecular structure of (1) by X-ray diffraction was characterized by X-ray diffraction (Figure S1). As has been described in the main text, the dimensions of the molecule are as follows: **HB – BH** 13.7 Å; **B-B** 11.4 Å and in width: **H3-H9** 6.6 Å; **H2A-H8** 6.6 Å.

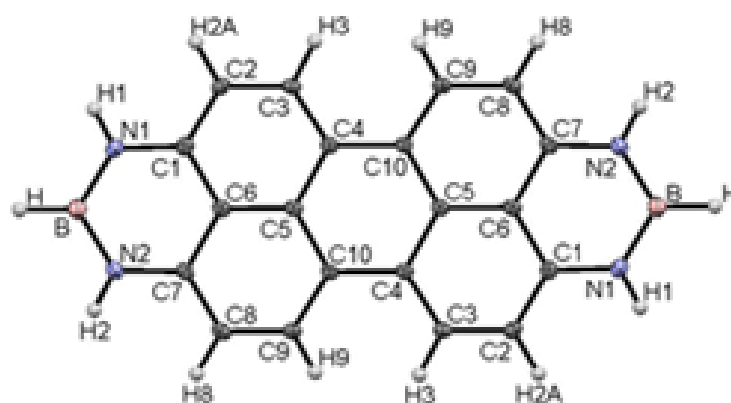


Fig. S1 Molecular structure of *N,N'*; *N'',N'''*-diborylene-3,4,9,10-tetraaminoperylene (1).

Crystal data: $C_{20}H_{14}B_2N_4 \cdot 2(C_4H_8O)$, monoclinic, space group $P2_1/c$, $a = 11.8021(4)$, $b = 11.1964(3)$, $c = 10.1080(3)$ Å, $\beta = 115.025(4)^\circ$, $V = 1210.30(8)$ Å³, $Z = 2$, $\mu = 0.082$ mm⁻¹, $F_{000} = 504$. $T = 110(1)$ K, θ range 3.6 to 28.9°. Index ranges h, k, l : -15 ... 15, -15 ... 15, -13 ... 13. Reflections measd.: 23170, indep.: 3021 [$R_{int} = 0.027$], obsvd. [$I > 2\sigma(I)$]: 2453. Final R indices [$F_o > 4\sigma(F_o)$]: $R(F) = 0.0513$, $wR(F^2) = 0.1426$, $Goof = 1.09$.

Data collection: Agilent Technologies Supernova-E CCD diffractometer, Mo- K_α radiation, microfocus X-Ray tube, multilayer mirror optics, $\lambda = 0.7107$ Å. Lorentz, polarization and semi-empirical absorption correction.¹ Structure solution: charge flip.² Refinement: full-matrix least squares methods based on F^2 ;³ all non-hydrogen atoms anisotropic, hydrogen atoms taken from difference fourier maps and refined.

CCDC 988044 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Details of the experimental methods

Preparation procedures for all samples were carried in ultra-high vacuum with a base pressure $5 \cdot 10^{-10}$ mbar. The Cu(111) substrate was prepared by repeated cycles of sputtering with Ar⁺ ions (at energy ~ 2000 eV, ion current ~ 10 μ A) and annealing to ca. 450°C in order to achieve atomically flat and clean surfaces with extended terraces. The purity of the substrate was verified by X-Ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). The molecules were deposited by thermal evaporation from a commercial evaporator (Kentax). The deposition rates were tracked by a quartz-crystal microbalance.

The STM measurements were performed at helium temperatures (~ 5 K) on the Omicron LT-STM. The bias voltage is with respect to the sample, i.e. negative voltage corresponds to the occupied states of the sample. The STM micrographs were recorded in the constant current mode.

The Scanning Tunneling Spectroscopy (STS) measurements were acquired with a lock-in amplifier frequency of 512 Hz and modulation amplitude of 8 mV (zero-to-peak value). The initial tip settings were: 35 pA; 77.5 mV. The condition of the tip was verified before and after acquisition of the STS spectrum by recording dI/dV spectra on the bare Cu(111) surface.

XPS measurements were performed at room temperature (RT) with a monochromatic Al-K _{α} X-Ray source. The resolution reaches a value ~ 1 eV of full width at half maximum (FWHM). The calibration of the energies was performed via reference measurements on a clean Au crystal (Au 4f_{7/2} $\equiv 84.0$ eV).

3. Identification of the reaction product between (1) and TMA on Cu(111)

Deposition of borylene functionalized molecule **1** and trimesic acid (TMA) onto room temperature Cu(111) substrate and annealing to 120°C results in the formation of aperiodic molecular network, observed by means of STM (Fig. S2c). In order to investigate the nature of the resulting polymer, we probed the chemical environment of C, B, N (present in **1**) and C, O (present in TMA) before and after annealing by measuring XPS of C1s, B1s and O1s core levels. The B1s and O1s spectra are presented in the main text, C1s and N1s spectra are shown in Figure S2.

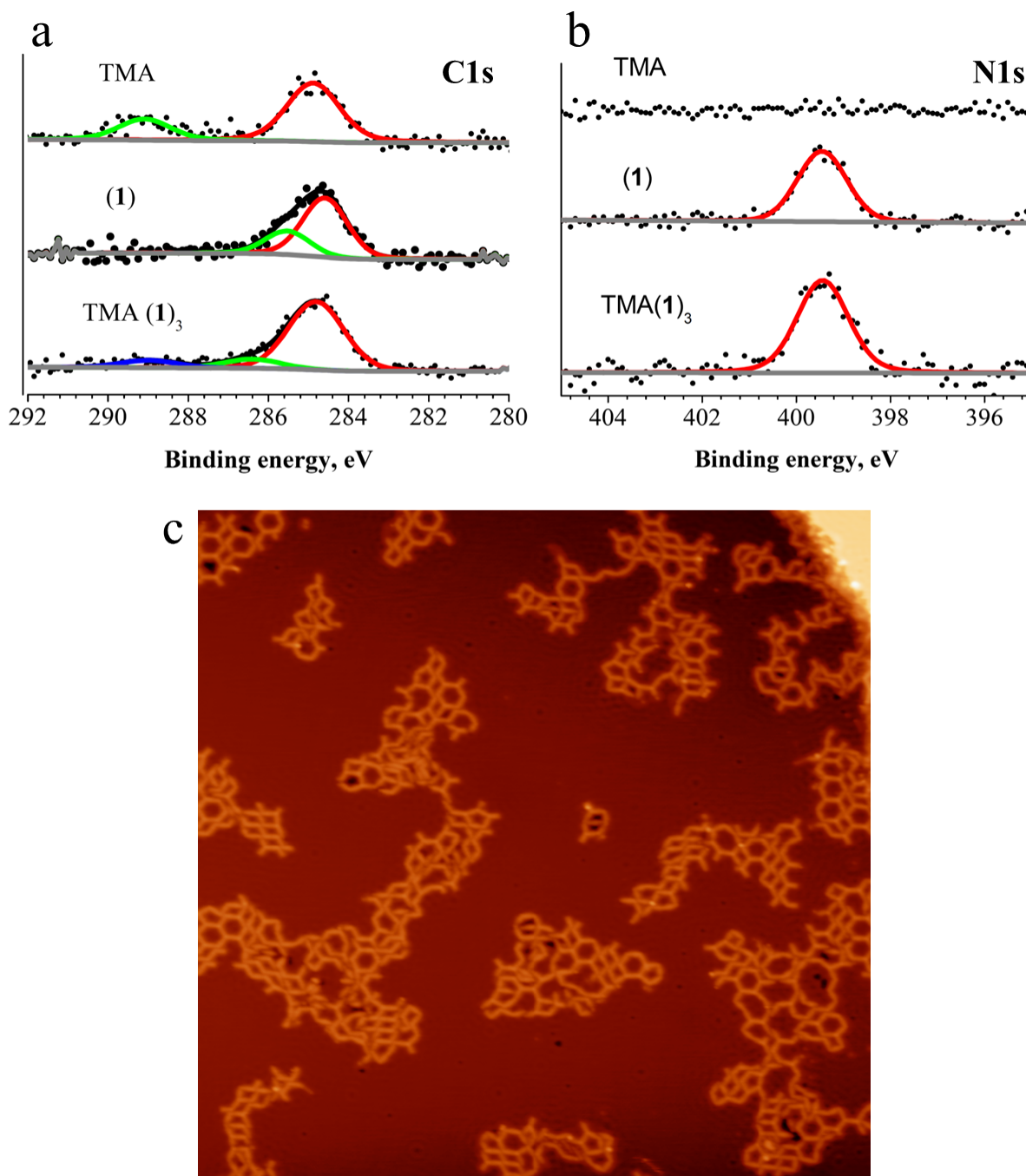


Fig. S2 The XPS data of each reactant (TMA and **1**) deposited onto Cu(111) at RT and the resulting reaction product (TMA(**1**)₃) are presented under each other for comparison: (a) C1s spectra and (b) N1s spectra. (c) The STM overview (at 5K, 100x100 nm²) of the aperiodic molecular network formed at Cu(111) after annealing to 120°C.

First, we sublimed sub-monolayer of TMA on Cu(111). The resulting amount of C is 4.3 % and O1s - 3.4 % with respect to the Cu surface. The experimental ratio C:O can be estimated to 9:7.1, which reflects well the stoichiometry of TMA (C₉O₆). B1s, N1s were not detected. The two peaks in C1s correspond to C*-C and C*=O.

The next step was an investigation of sub-monolayer of (**1**) on Cu(111). The XP spectra of C1s, N1s and B1s reveal 3.34 % of carbon, 0.61% of nitrogen and 0.19% of boron with respective ratio C:N:B equals 20:3.65:1.19, reflecting well the stoichiometry of the molecule (C₂₀N₄B₂). Oxygen was not observable in O1s spectra. XPS reveals one peak in the N1s spectra, corresponding to the BH-group, and two peaks in C1s, corresponding to C*-C and C*-N.

Finally, to the previous sample of **1** on Cu(111) a sub-monolayer amount of TMA was added and the sample was annealed (to ca 120°C). The resulting sample contained: 5.48% C1s; 0.83% O1s; 0.57% N1s and 0.21% B1s. The B1s binding energy (BE) of the resulting product (presented in the main text) differs significantly 191.6 eV in comparison to B1s of unreacted **1** (190.25 eV) on Cu(111). The N1s BE is not modified upon reaction.

The summary of N1s, O1s, B1s binding energies for all 3 samples (TMA, **1**, TMA(**1**)₃) are presented in a Table S1.

Molecule	N1s BE, eV	O1s BE, eV	B1s BE, eV
TMA	-	531.6; 533.5	-
1	399.4	-	190.25
TMA(1) ₃	399.4	532.0; 533.3	191.6

Table S1. Binding energies of the N1s, O1s and B1s for TMA, **1** and TMA(**1**)₃ on Cu(111) support a covalent reaction between TMA and **1** after annealing to 120°C with the formation of TMA(**1**)₃, as a resulting product.

4. STM overviews of unreacted (**1**) on Cu(111)

We have investigated the behaviour of borylene-functionalized molecule **1** on Cu(111) surface upon deposition at RT. The STM micrographs reveal no long-range order and randomly distributed molecular conglomerates (Fig. S3a). Among the conglomerates, can be distinguished two types of trimers, which are pro-chiral (Fig. S3 b,c). Possible model for these types of nodes are reflected on the schemes (Fig. S3 d-e).

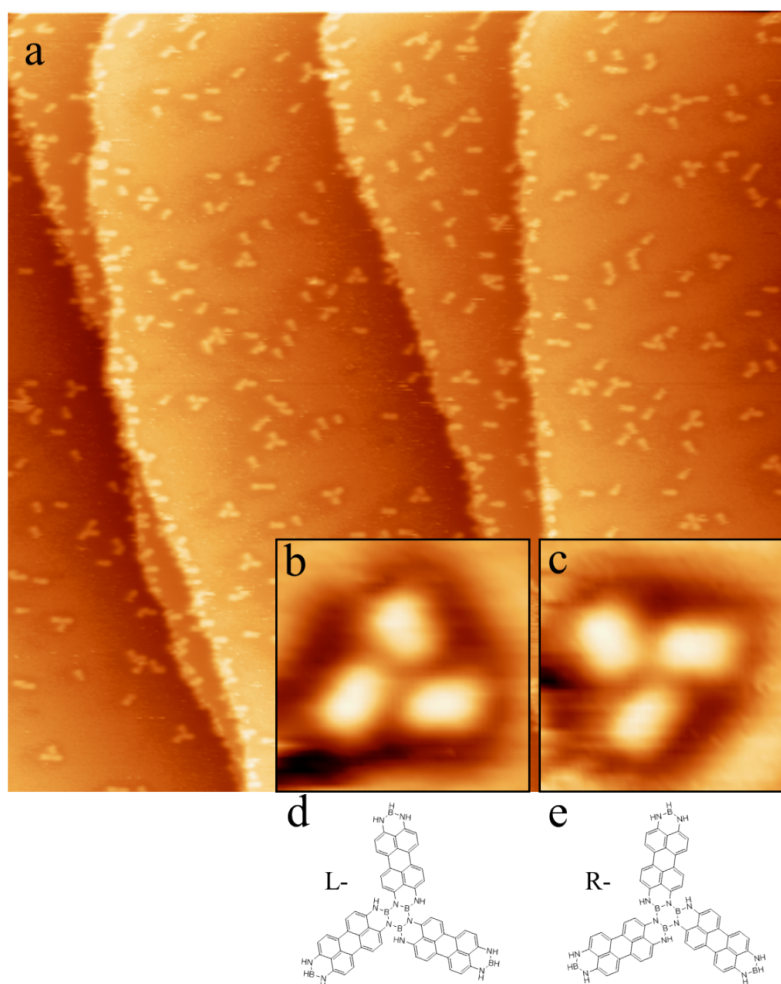
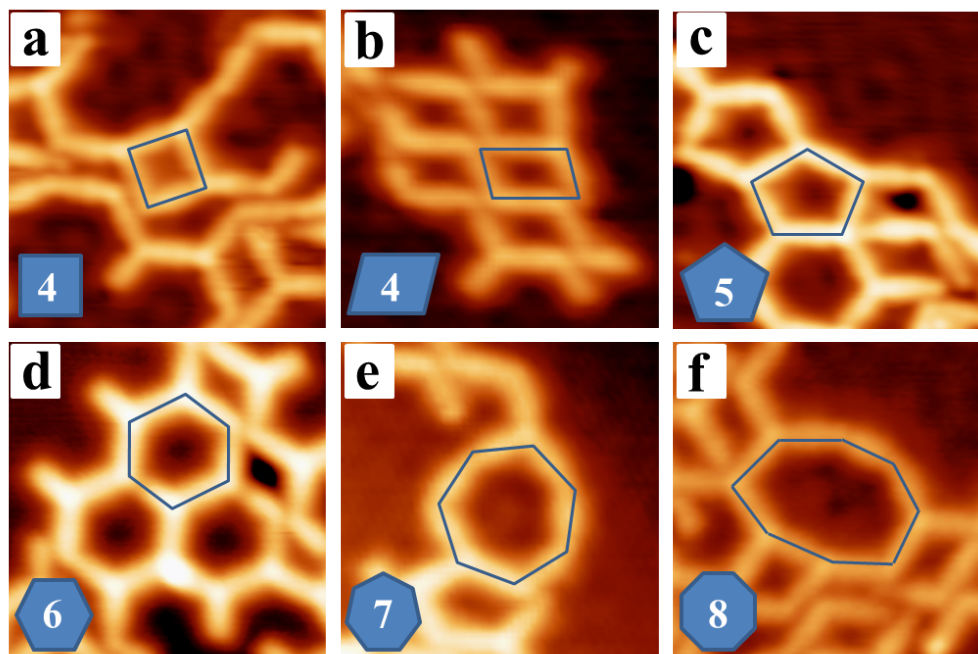


Fig. S3 Deposition of **1** onto Cu(111) at RT results in the formation of H-bonded molecular islands, as reflected on the (a) STM image (-1.5 V, 50 pA; 100x100 nm² at 5K). The assemblies are randomly distributed over the surface showing the local repulsion character. The frequently met pattern is characterized by the trimetric shape: (b), (c) pro-chiral L- and R- structures (-1.5V, 60 pA; 4x4nm² at 5K). (d),(e) The corresponding chemical schemes reflect possible types of intermolecular connection for L- and R- nodes, respectively.

5. Various shapes of the pores

Deposition of **1** and TMA results in the covalent molecular ‘sponge’-like network after annealing to 120°C (see chapter 3 and main text of the manuscript). The flexibility of the covalent connection between **1** and TMA allows for the formation of differently shaped pores (Fig. 1 of the main text). Typically 4-8 polygons can be identified from the STM images (Fig. S4).



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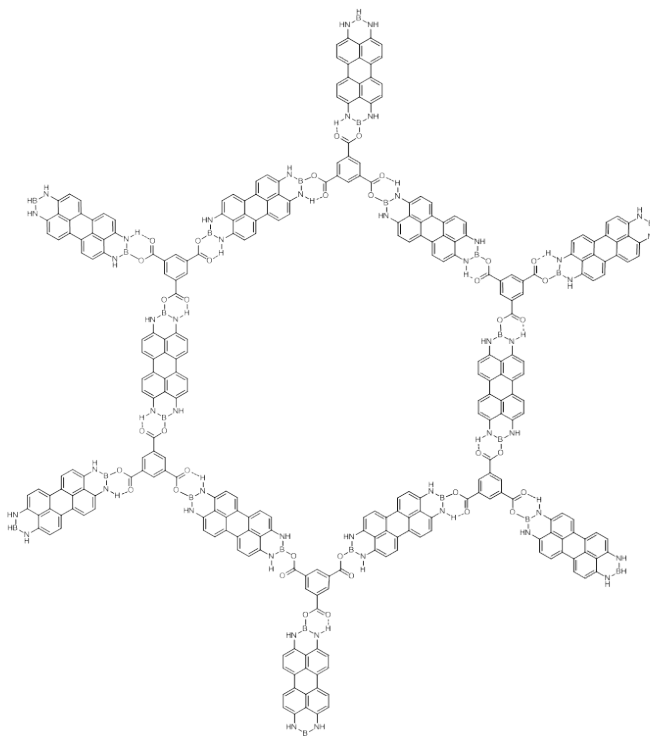


Fig. S4 Deposition of **1** and TMA on Cu(111) at RT and subsequent annealing to 120°C results in the formation of covalent networks. (a - f) The STM micrographs (10 x 10 nm²) reflect typical pores of various shape, containing 4 - 8 borylene-functionalized molecules. (g) Chemical scheme serves as one of the possible models for the hexagonally shaped pore.

6. Network formation on Ag(111)

We have shown in chapter 4 the occurrence of the on-surface reaction between **1** and TMA after annealing on Cu(111) with resulting covalent networks. In order to verify the influence of the substrate, the same preparation procedure has been performed on the less reactive Ag(111) substrate. Deposition of **1** and TMA on Ag(111) and annealing to 120°C results in similar polymer architectures as on Cu(111) (Fig. S5). The pores have different size and shape (Fig. S5 b,c). Excess of one of the pre-cursors can lead to the trapping of molecule inside of the formed pores. This fact indicate that pores can serve as a host system for molecular adsorbates (Fig. S5d).

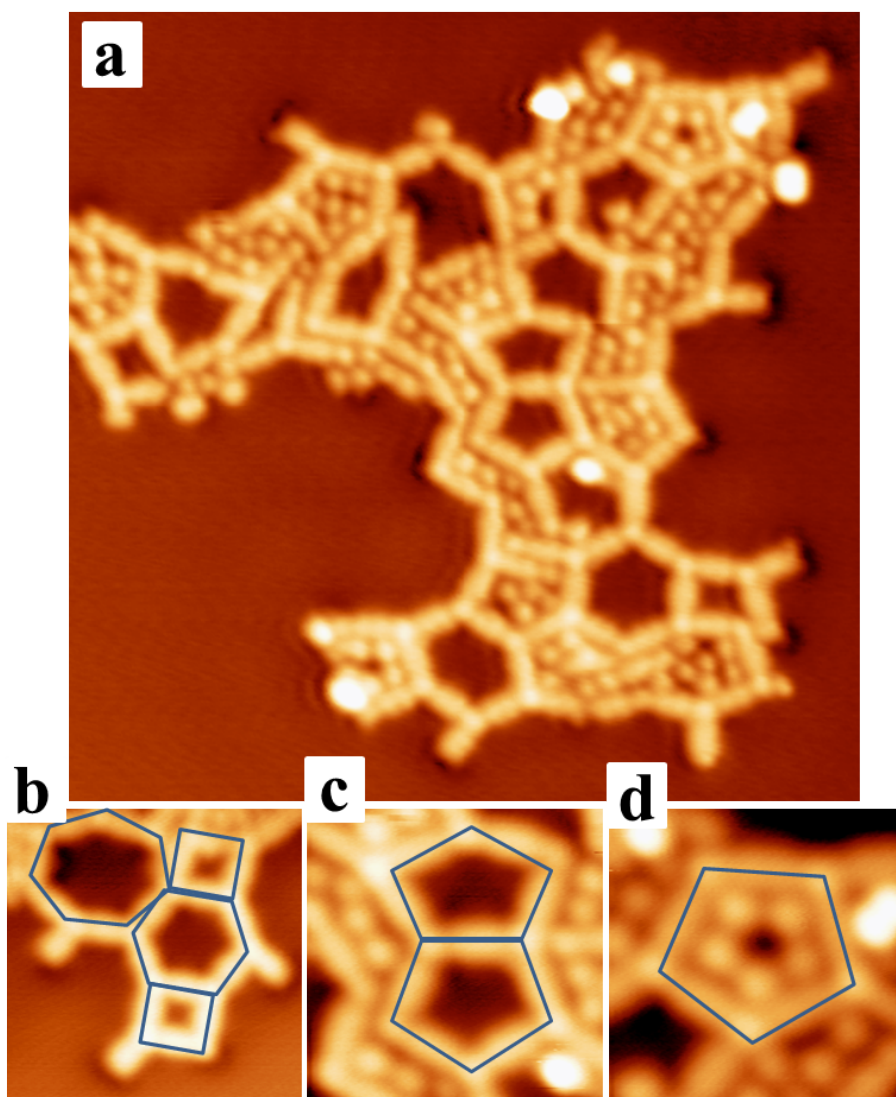


Fig. S5 (a) Deposition of **1** and TMA on Ag(111) at RT and subsequent annealing to 120°C results in the formation of networks similar to the ones observed on Cu(111). The STM micrograph reveal pores containing trapped in inside precursors, which were in excess (25 x 25 nm²). (b, c) Pores have different size and shape (10 x 10 nm² and 6 x 6 nm², respectively). (d) Each pore can serve as a host for the smaller adsorbates: STM image of the pentagonal pore and 5 TMA molecules inside (5 x 5 nm).

7. Pore area value and the energy of the confined surface state in the TMA(1)₃ polygons

n	Area, nm ²	Energy with respect to E _F , meV
4 - square	3.65	90
4 - parallelogram	3.72	180
5	6.01	265
6	9.26	336
7	11.9	360
8	14.46	382

Table S2. The values of the area, extracted from the STM images, and energy of the confined state measured in the center of the pore.

References:

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2. (a) L. Palatinus, *SUPERFLIP*, EPF Lausanne, Switzerland, 2007; (b) L. Palatinus, G. Chapuis, *J. Appl. Cryst.* 2007, **40**, 786.
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