Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

2-D assembly of Supramolecular Nanoarchitectures on Mg(0001)

1. Experimental Section

STM experiments were performed in a homemade scanning tunneling microscope mounted on a chamber kept under ultra-high vacuum (UHV) conditions; which is also equipped with a standard experimental setup to allow the preparation process of the samples *in-situ*. The system relies on a single STM tip made of tungsten (W), fabricated by electrochemically etching. During the scans, the STM is operated in the constant current mode, with typical tunneling current and sample bias values of 1.0 nA and -1.0 V, respectively.

The XPS data were acquired in the X-Ray beamline PEARL in the synchrotron facilities at the Paul Scherrer Institute (PSI), Switzerland. The data for the Mg2p, C1s, N1s and O1s were acquired with a beam energy of 160 eV, 370 eV, 500 eV, and 675 eV, respectively. The pass energy of the analyser was set at 20 eV. The spectra were referenced using the $Au4f_{7/2}$ line at 84.1 eV. All the experiments were carried out under UHV (~ 3×10^{-10} mbar) at RT.

1.1 Substrate Preparation

The substrate used is a Mg(0001) monocrystal provided by Mateck. This substrate act as a template for the growth of molecular networks. Hence, it is important to perform a cleaning process to obtain atomically clean surfaces with few surface defects and well-defined terraces with transversal lengths of at least 100 nm. This length is ideal to study the self-assembly of molecules and metal atoms on the surface. The cleaning process was performed in an UHV chamber with a base pressure of 5.0×10^{-10} mbar. If the monocrystal was previously exposed to air conditions, the surface is degassed in 16 cleaning cycles on 3 different stages. The first stage involved 9 consecutive cycles of Ar^+ sputtering (kinetic energies of 0.5 keV) during 15 minutes, followed by a flash annealing at 403 K, and a slow cooling down below 313 K. The second stage involved 5 cycles of Ar^+ sputtering during 10 minutes, followed by a flash annealing at 398 K, and a slow cooling down below 313 K. The third stage involved 2 cycles of Ar^+ sputtering during 10 minutes, followed by a flash annealing at 393 K, and a slow cooling down below 313 K. This resulted in smooth and clean terraces of around 70 nm width, with low amounts of impurities (**Figure 1-SI)**. If the monocrystal already resides in the chamber, only 2 cycles are required: the first cycle involves Ar^+ sputtering during 15 minutes, followed by a flash annealing at 403 K, and a slow cooling down below 313 K. The second cycle involves Ar^+ sputtering during 10 minutes, followed by annealing at 393 K during 5 minutes, and a slow cooling down below 313 K. This resulted in flat and clean terraces:

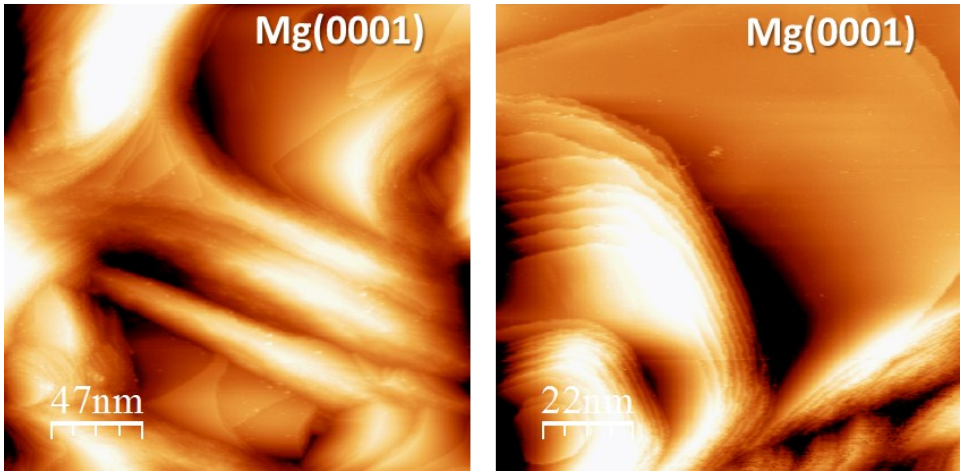


Figure 1-SI: STM image of typical atomically clean Mg(0001) surfaces at RT, with smooth terraces with a length of up to 70 nm.

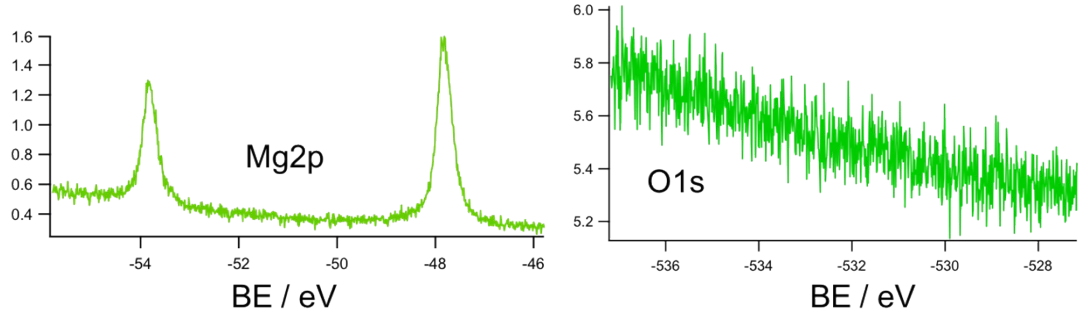


Figure 2-SI: To test the cleaning process, HR-XPS measurements were performed. The spectra in the Mg2p and in the O1s transition, show no evidence of oxide formation.

1.2 Sample preparation

The experiments were performed in a UHV chamber with a base pressure of 4.0×10^{-10} mbar. TAPT molecules were deposited by thermal evaporation from a quartz crucible by heating it up to 513 K. During molecular deposition, the pressure in the chamber was kept below 2.0×10^{-9} mbar, while the temperature of the substrates was kept at RT. TPA molecules were deposited by organic molecular beam epitaxy from a Knudsen cell at 448 K. During deposition, the substrate was kept at RT. Before deposition, the molecules were fully degassed, thus during their deposition on the substrates, the pressure in the chamber was not higher than 2.0×10^{-9} mbar.

2. TAPT Molecules Deposited on Mg(0001)

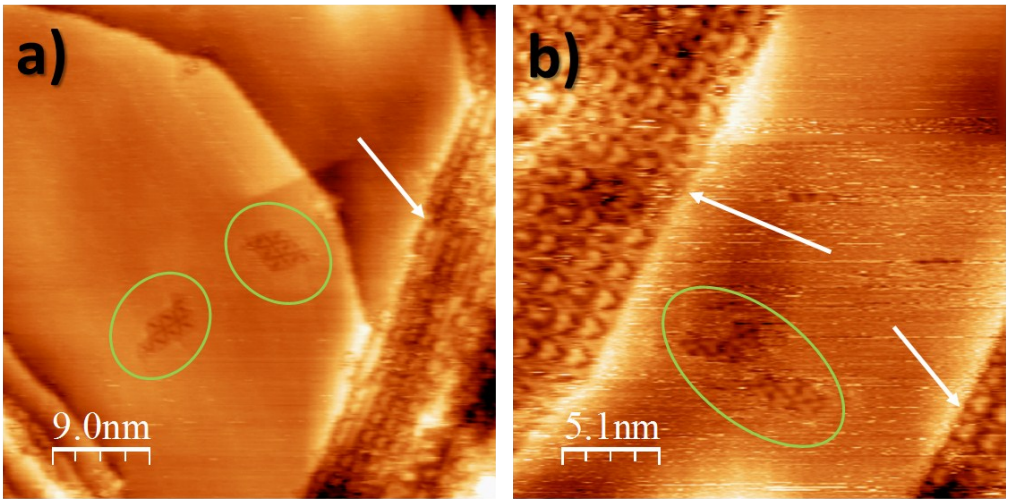


Figure 3-SI: (a) TAPT molecules on Mg(0001), lying on the terraces (highlighted by the green circles) and on the step edges (indicated by the white arrows). (b) The TAPT molecules arrange along the step edges.

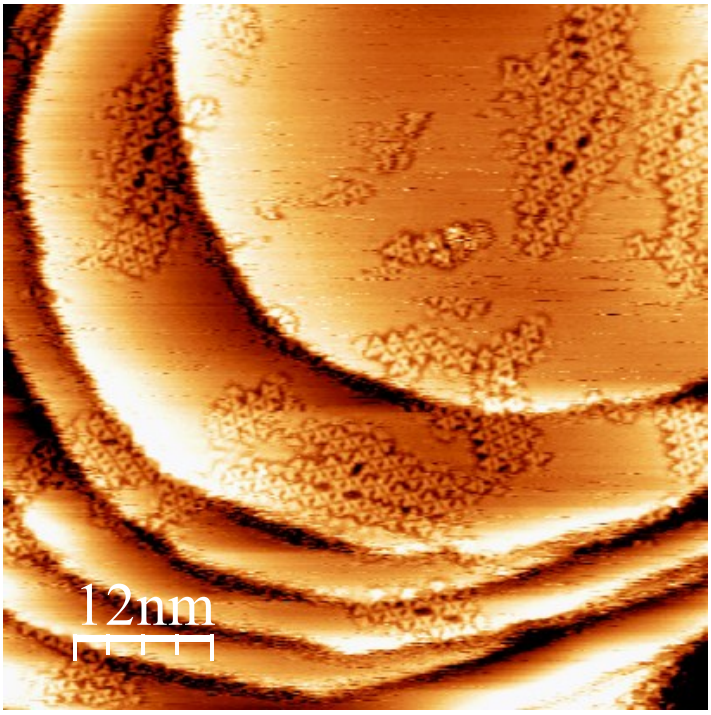


Figure 4-SI: (a) TAPT molecules forming a compact structure on the Mg(0001) terraces at low coverage.

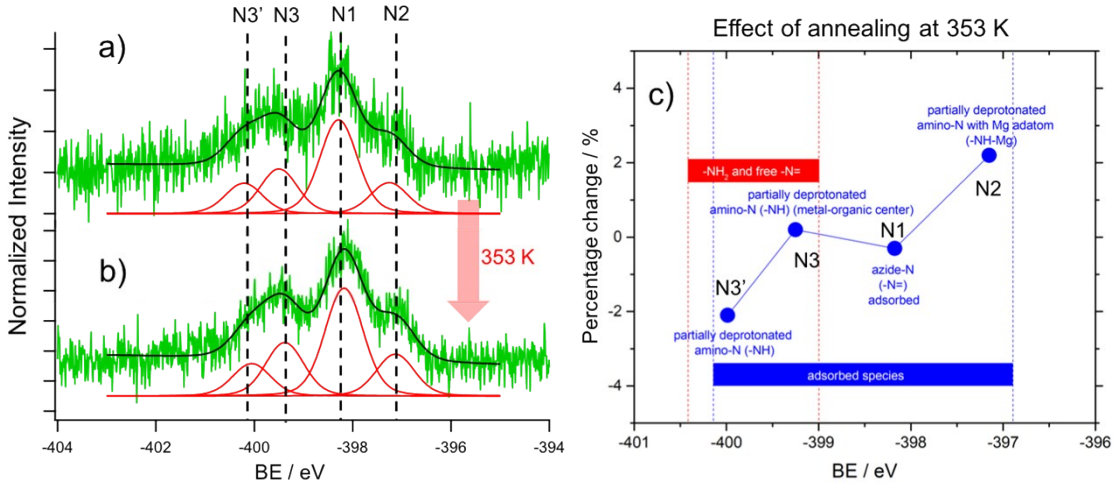


Figure 5-SI: HR-XPS spectra in the N1s region, corresponding to the interaction of TAPT molecules deposited on a Mg(0001) substrate (a) before and after (b) annealing at 353 K. (c) Graph showing the variations in the relative percentage area of the peaks at each binding energy. The blue line shows the direct effect of the annealing on the system based on TAPT molecules on Mg(0001). The change in the proportion of the peaks could help in the corroboration of the adsorbed species. The **N1** feature remains almost constant after annealing. Thus, it can be interpreted that the amount of TAPT molecules adsorbed on the surface is the same before and after annealing. Nevertheless, there is an increment in the signal attributed to semi-protonated amino groups coordinated with Mg (**N2**) by 2% and a decrease in the signal **N3'**. As it was described above, the **N3** and **N3'** signals are in the region of binding energies where the N1s transition of weakly adsorbed or fully deprotonated species takes place. Therefore, it can be concluded that the process of annealing at 353 K induces the semi-deprotonation of amino groups and consequently the formation of metal-organic coordination.

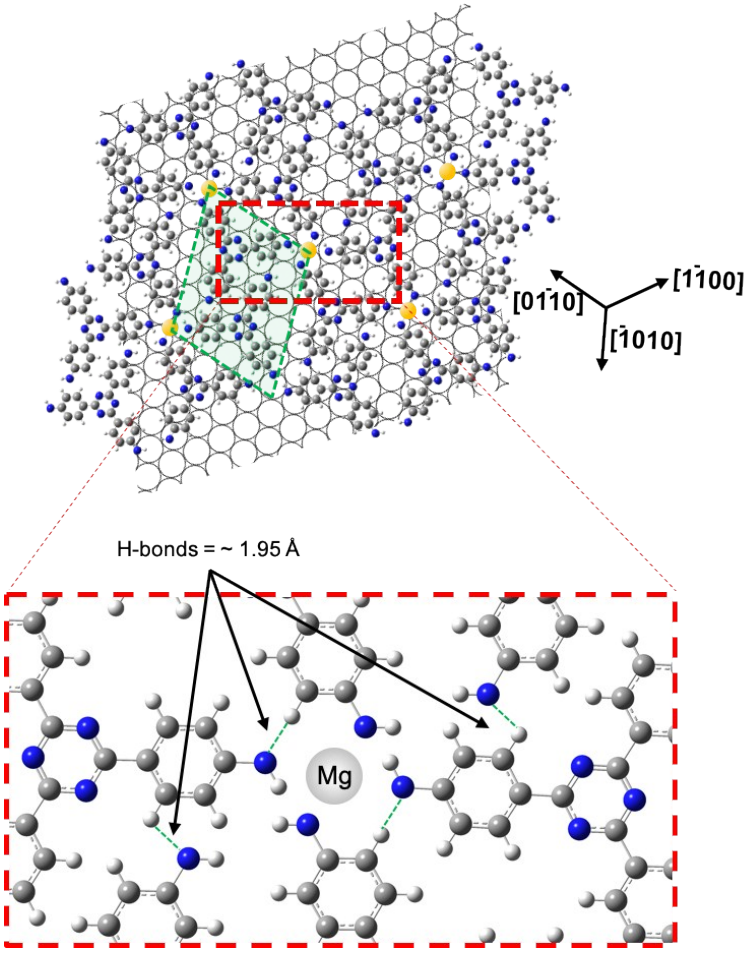
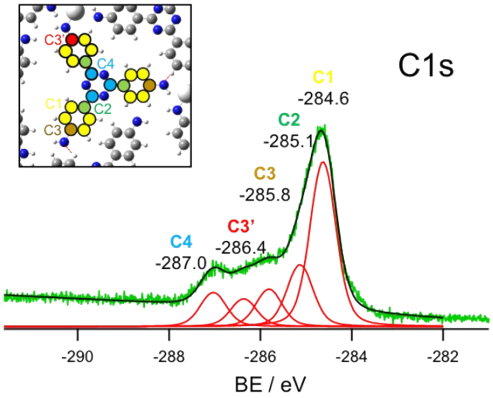


Figure 6-SI: Tentative model of TAPT molecules adsorbed on Mg(0001) and a zoom-in of the Mg active center. According to this model, the N3 and N3' peaks obtained in the HR-XPS spectrum from Figure 3(d), are attributed to the semiprotonated amino groups (adsorbed on the surface) interacting by the H-bonds with the adjacent aromatic rings. A small difference of 0.6 eV between these peaks could be attributed to the slightly different environments of these semi-deprotonated amino groups forming a H-bond near the metal–organic center.



	C1	C2	C3	C3'	C4
Theoretical model	4	1	0.66	0.33	1
HR-XPS	3.6	1.3	0.80	0.59	0.8

Figure 7-SI: HR-XPS spectrum in the C1s region for TAPT molecules deposited on a Mg(0001) substrate. In the insets, the different kind of C atoms on the theoretical model are depicted by circles with different colors. The table at the bottom shows the comparative relative composition of every specie. Considering the C atoms in free TAPT molecules, an ideal C1s spectrum should contain 4 peaks (depending on the resolution of the analyzer): **C1**, belongs to the C1s transition of the 12 equivalent C atoms in the middle of the 3 phenyl rings (yellow circles); **C2**, 3 C atoms in the phenyl rings directly bonded to the C atoms from triazine ring (green circles); **C3**, 3 C atoms in the phenyl rings directly bonded to the semi-deprotonated amino groups (red and brown); and **C4**, the 3 C atoms in the triazine ring (cyan circles). Therefore, the ideal proportion of the C1s peaks **C1:C2:C3:C4** should be **4:1:1:1**. However, in the theoretical model one semi-protonated amino group is coordinated with Mg while the other two with H-bonds. Hence, the **C3**-feature of an ideal spectrum should be divided into two sub-features: **C3** (brown circles) and **C3'** (red circle) with a **0.33:0.66** relative composition. Thus, according to the theoretical model, the relative composition of C atoms should be **4:1:0.66:0.33:1**. The best fitting of C1s spectrum shows a relative composition of **3.6:1.3:0.8:0.6:0.8**. The agreement with the composition in the theoretical model is reasonable, considering the presence of non-adsorbed species on the surface and uncertainties in the fitting procedure.