Supporting Information

Growth of Regular Nanometric Molecular Arrays on a Functional 2D template Based on a Chemical Guest-Host Approach

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1. The AMC assembly.

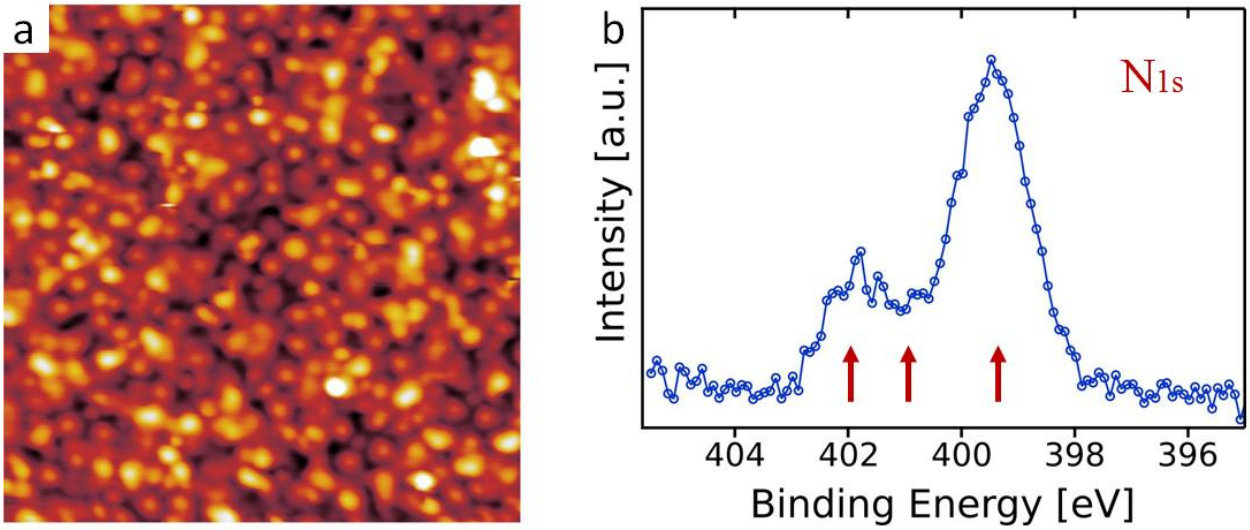

Figure S1. The STM image of AMC assembly on Au(111) surface reported in panel a (from figure 2 of manuscript) shows the absence of order and the formation of clusters. This is confirmed by the chemistry of the system, as revealed by the N1s XPS spectrum reported here in panel b. The peak presents at least three components, that can be attributed to different interaction schemes the amino groups are involved in[1,2]. The main one, close to 399 eV, indicates that most of the amines of the AMC molecules are in their neutral state. On the other hand, the component close to 402 eV is compatible with an ionic NH_3^+ state of the functional groups, whereas the intermediate component at 401 eV can be associated with a lone pair-mediated interaction of the functional groups. Even if a detailed description of the intermolecular interactions cannot be inferred from these evidences, we can state that the AMC molecules are in a not homogeneous chemical state.

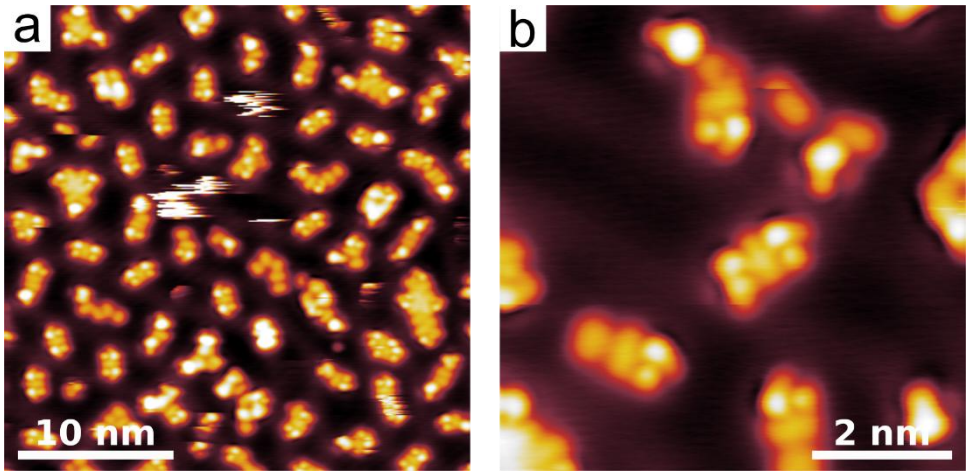

Figure S2. STM images of a low coverage sample of AMC on Au(111). Crown molecules assemble into small clusters of different size and shape. Since the first stages of deposition no order can be observed in the AMC assembly. Image parameters: (a, b) $V_s = -0.2$ V, $I_t = 0.02$ nA.

2. The CTTP Monolayer

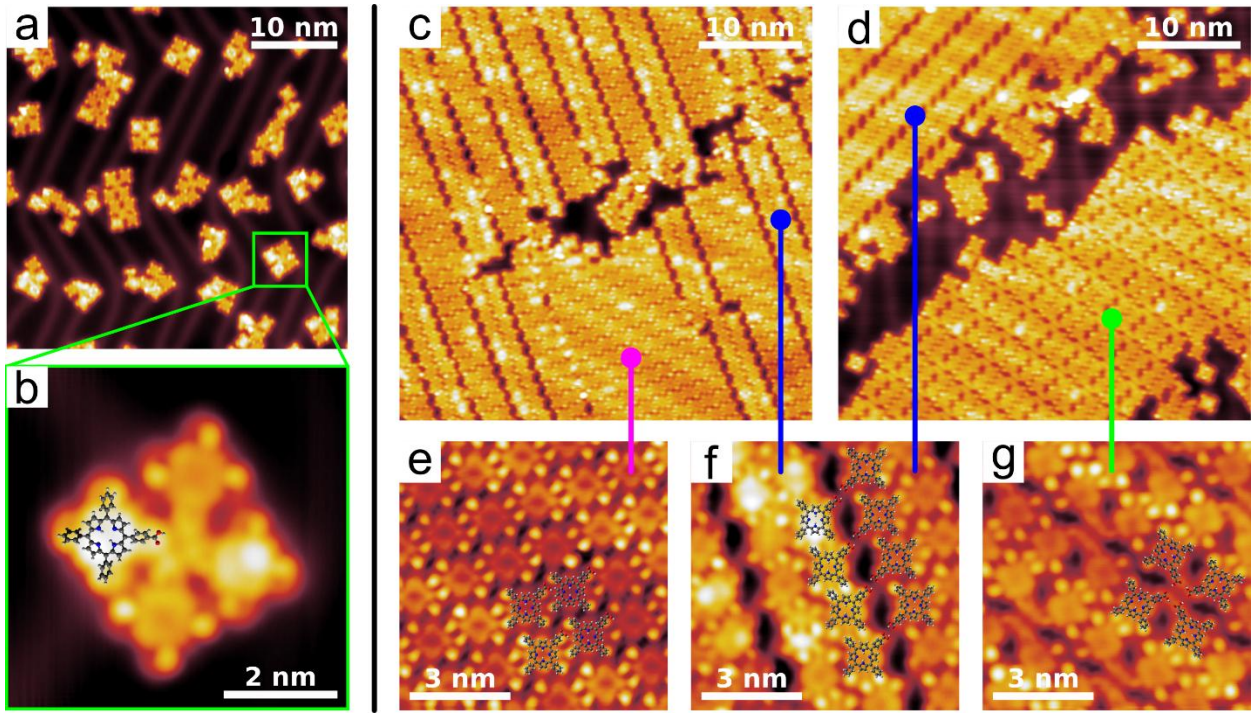

Figure S3. STM images of CTPP on Au(111) at low (a-b) and high coverage (c-g). (a) At low coverage, CTPP assembles in complexes of (b) four molecules via their carboxylic terminations, which can be easily identified because of their flatter appearance compared to the phenyls. The latter (b) resembles the high coverage phase in (g). (c-d) Large images showing the three coexisting different phases of the self-assembly of CTPP. The relative

population of the phases depends on the monolayer growth conditions: low growth rates preserve the four molecules cross-like structure (b, g), while high growth rates favour the compact (e) and double-chain (f) phases. (e) The CTTP monolayer presents a compact phase very similar to that of not functionalized tetraphenylporphyrines, where a T-like mutual geometry between phenyls of adjacent molecules rules the assembly. Image parameters: (a) $V_s = -0.5$ V, $I_t = 0.2$ nA. (b) $V_s = -0.5$ V, $I_t = 1.0$ nA. (c) $V_s = -0.5$ V, $I_t = 0.2$ nA. (d) $V_s = -0.5$ V, $I_t = 0.3$ nA. (e) $V_s = -0.5$ V, $I_t = 2.0$ nA. (f) $V_s = -0.5$ V, $I_t = 1.0$ nA. (g) $V_s = -0.5$ V, $I_t = 0.5$ nA.

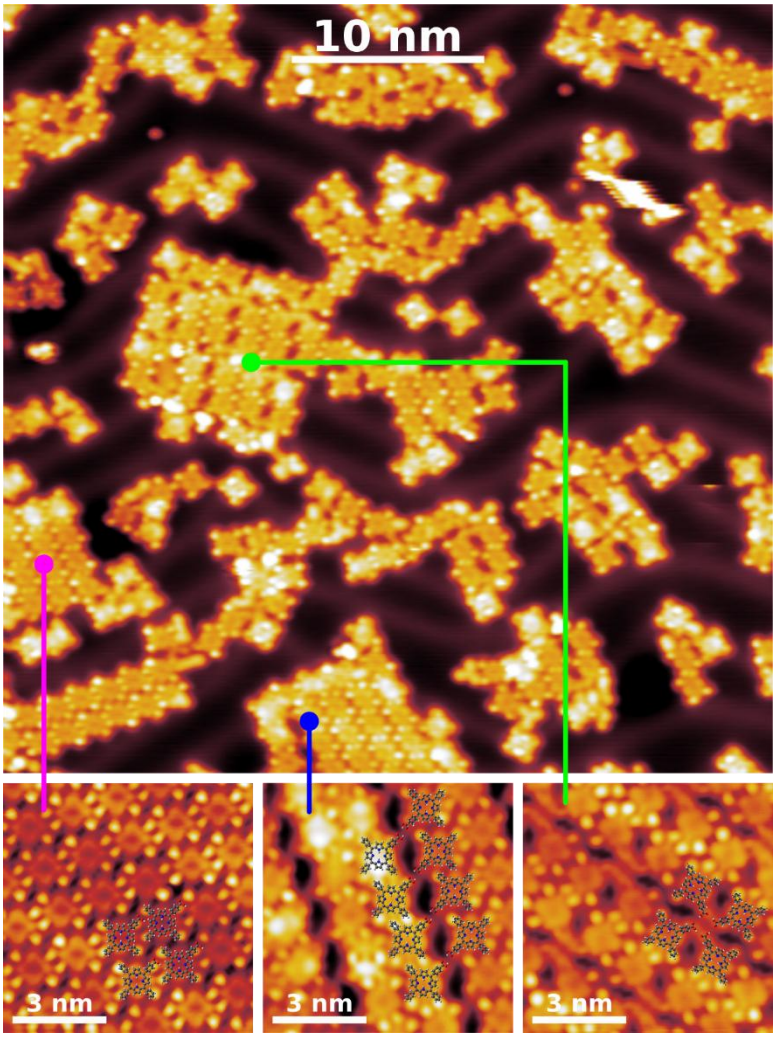

Figure S4. STM image of CTPP on Au(111) at a coverage of half monolayer where small islands showing all the three high coverage phases are visible. Image parameters: $V_s = -0.5$ V, $I_t = 0.3$ nA. This image suggests that the CTPP phases coexist since the first stages of aggregation of molecular clusters aggregation. The population of the compact phase is lower than the sum of population of the cross-like and double-chain phases, unless the coverage becomes higher than 0.7-

0.8 ML.

3. The NMA/CTTP guest-host architecture

The guest-host process has been tested on a second amino-molecule, the 1-Naphthylmethylamine (NMA), as a guest. NMA assemble on Au(111) surface forming n-leaf clover like structures, with n=3-6.[3]

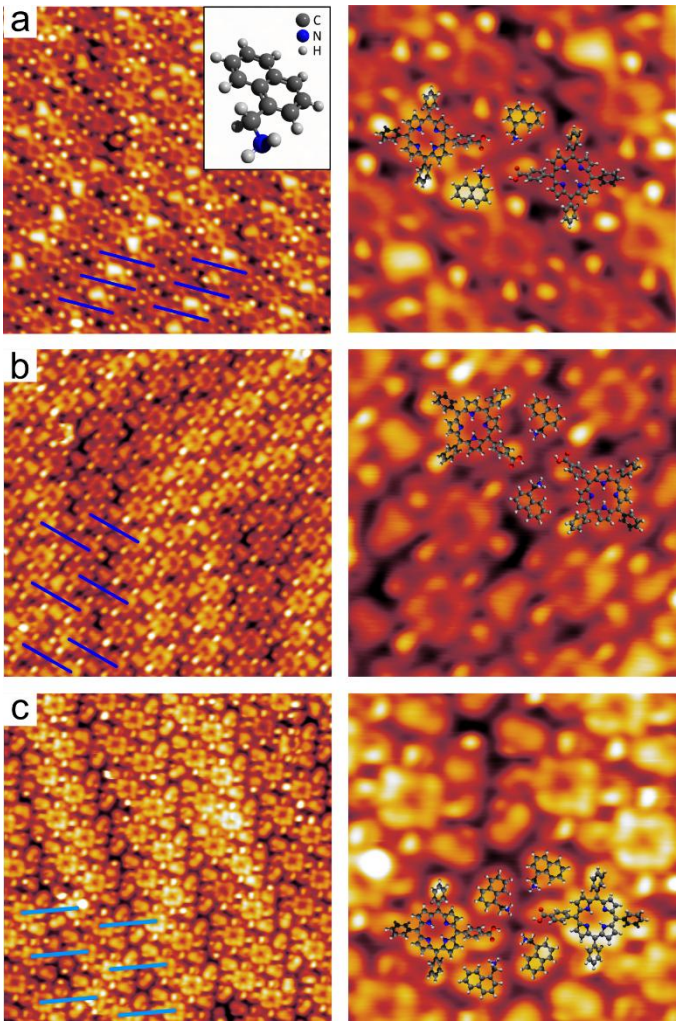

Figure S5. When intercalated onto the CTPP SAM template show different phases. We find three different coexisting phases of the NMA-CTPP assembly. The first two phases are NMA/CTPP 1∶2 (a) and 1∶1 (b) phases, which are equivalent to the two AMC/CTPP phases in Figure 3 in the main text. The NMA/CTPP 2∶1 phase (c) is characterized by four NMA molecules for each couple of CTPP-CTPP. The presence of this phase, not found for AMC/CTPP, is likely due to the molecule size of NMA which is considerably smaller than AMC, and therefore can establish a 4 NMA to 2

CTPP bonding scheme. The blue lines on the images help to identify the periodicity of the supramolecular architecture. For each image, on the right, there is a zoomed image with superimposed models of NMA and CTPP to help the reader to identify each molecule. Images parameters: (a) $V_s = -0.1$ V, $I_t = 0.3$ nA. (b) $V_s = -0.1$ V, $I_t = 0.2$ nA, 15×15 nm^2. (c) $V_s = -0.1$ V, $I_t = 70$ pA. All images size: 15×15 nm^2 (5.0×5.0 nm^2 zoomed).

References

1 A. Cossaro, M. Dell'Angela, A. Verdini, M. Puppin, G. Kladnik, M. Coreno, M. de Simone, A. Kivimäki, D. Cvetko, M. Canepa and L. Floreano, *J. Phys. Chem. C*, 2010, **114**, 15011–15014.

2 A. Cossaro, M. Puppin, D. Cvetko, G. Kladnik, A. Verdini, M. Coreno, M. De Simone, L. Floreano and A. Morgante, *J. Phys. Chem. Lett.*, 2011, **2**, 3124–3129.

3 Z. Feng, C. Castellarin Cudia, L. Floreano, A. Morgante, G. Comelli, C. Dri and A. Cossaro, *Chem. Commun. (Camb).*, 2015, **51**, 5739–42.