Electronic Supplementary Information (ESI)

Interaction of cyclosporin A molecules with alkali and transition metal atoms on Cu(111)

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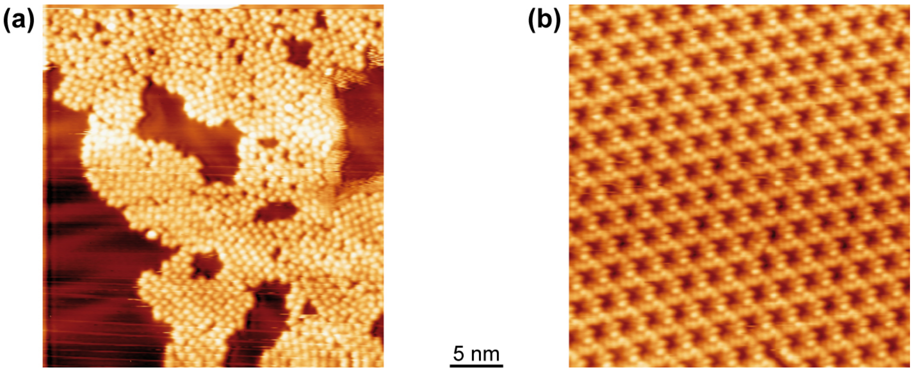
Methods

Sample preparation

Single crystal surfaces of Cu(111) and Au(111) were prepared by repeated cycles of Ar$^+$ sputtering and subsequent thermal annealing. The quality and cleanliness of the substrate surface was assessed by STM images. CsA molecules (Sigma, $\geq$98.5%) were dosed by organic molecular beam epitaxy (sublimation temperature 470 K) onto the substrates held at room temperature under UHV conditions for $\sim$ 40 min. K (SEAS Getters S.p.A. alkali metal dispensers), Co (Alfa Aesar, 0.1 mm wire, 99.995%) and Fe (Alfa Aesar, 0.1 mm wire, 99.998%) were dosed by physical vapor deposition by using in house developed sources. The parameters for the Co and Fe sources were calibrated against the formation of the corresponding metal clusters on single metal surfaces. The amount of dosed potassium was estimated by the percentage of the formed guanine-potassium network on the Au(111) surface (see figure below) [1]. The potassium source was operated then under the same power conditions and the CsA/Cu(111) surface placed at the same geometry. We note that this method gives a rough estimation of the dosed K atoms, however the uptake from CsA might differ from the guanine uptake. The coordination structure described as CsA-K$_2$ in the manuscript was highly reproducible and observed on the Cu(111) substrate upon saturation of CsA with K in more than five independent experiments.



STM images of (a) the guanine and (b) guanine-K porous assembly network which exhibits a stoichiometry of (3 guanine molecules) : (4 K atoms). (a: $I_\mathrm{t} = 0.06$ nA, $U_\mathrm{s} = -1.49$ V; b: $I_\mathrm{t} = 0.07$ nA, $U_\mathrm{s} = -1.74$ V)

STM measurements

STM measurements were performed in a custom-made UHV system equipped with an Aarhus-type variable-temperature STM (STM Aarhus 150, SPECS Surface Nano Analysis GmbH) at a base pressure of $\sim 2 \times 10^{-10}$ mbar. All STM images were recorded in constant-current mode using electrochemically etched tungsten tips and processed with the WsXM program [2]. The surfaces investigated by STM were cooled at a temperature of 100 K to suppress mobility. The tunnelling bias is applied to the sample.

Density functional theory (DFT) calculations

Geometry optimization of the CsA on Cu(111) was performed by using the QuickStep module within the CP2K simulation package. We applied the Kohn-Sham method [3] within the DFT [4] in order to obtain the electronic structure and from it the Hellmann-Feynman forces, that were used to optimise the geometry of the adsorbed molecules. Because the adsorption is weak, mainly via the van der Waals interactions we applied the revB86-vdW-DF2 functional [5,6] as the approximation in the Kohn-Sham equations. Double-zeta valence and polarisation (DZVP) Gaussian basis set of the MOLOPT type [7,8] and a plane wave basis set up to a cut-off energy of 600 Ry were employed in the Gaussian plane wave (GPW) method [9] to expand the wave functions and the electron density, respectively, together with pseudo potentials á la Goedecker-Teter-Hutter (GTH) [10]. The occupation number of the orbitals were broadened with a Fermi-Dirac distribution at 1000 K, and only the Γ point was used in the integration of the first Brillouin zone; given the large cell, 13×12 atoms of Cu(111) per layer, we expect this to yield only small error. Two rigid layers of the substrate, at the experimental lattice constant of Cu, 3.61 Å, were included, and the unit cell was 33.1845 Å× 26.5280 Å× 30 Å, the latter including the vacuum to separate subsequent replicas of the atomic slab. In the initial structures the molecule was placed well above the surface, and then it was relaxed. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was used as the method in the geometry optimisation.

References

1. Xu, W.; Wang, J.-G.; Yu, M.; Lægsgaard, E.; Stensgaard, I.; Linderoth, T. R.; Hammer, B.; Wang, C.; Besenbacher, F. Guanine- and potassium-based two-dimensional coordination network self-assembled on Au(111). *J. Am. Chem. Soc.* **2010**, *132*, 15927.

2. Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; Gómez-Herrero, J.; Baro, A. M. Wsxm: A software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* **2007**, *78*, 013705.

3. Kohn, W.; Sham, L. J. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **1965**, *140*, A1133-A1138.

4. Hohenberg, P.; Kohn, W. Inhomogeneous electron gas. *Phys. Rev.* **1964**, *136*, B864-B871.

5. Hamada, I. Van der Waals density functional made accurate. *Phys. Rev. B* **2014**, *89*, 121103.

6. Lee, K.; Murray, É. D.; Kong, L.; Lundqvist, B. I.; Langreth, D. C. Higher-accuracy van der Waals density functional. *Phys. Rev. B* **2010**, *82*, 081101.

7. VandeVondele, J.; Hutter, J. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J. Chem. Phys.* **2007**, *127*, 114105.

8. VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Quickstep: Fast and accurate density functional calculations using a mixed gaussian and plane waves approach. *Comput. Phys. Commun.* **2005**, *167*, 103-128.

9. Lippert, B. G.; Parrinello, J. H.; Michele. A hybrid gaussian and plane wave density functional scheme. *Mol. Phys.* **1997**, *92*, 477-488.

10. Goedecker, S.; Teter, M.; Hutter, J. Separable dual-space gaussian pseudopotentials. *Phys. Rev. B* **1996**, *54*, 1703-1710.

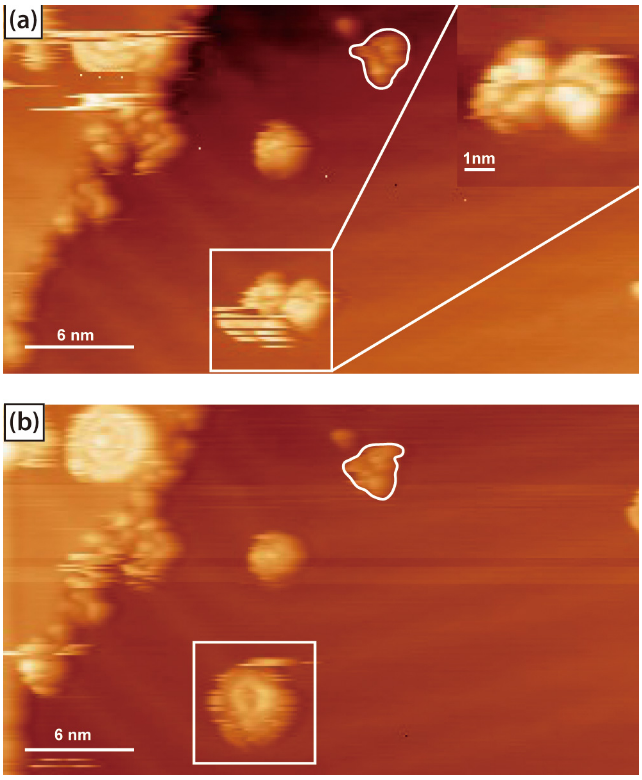


Figure S1: Large scale STM image of CsA molecules on Au(111). Two examples of monomers are indicated by white outlines. The inset in (a) shows a dimer, whereas the square in (b) indicates a rotating monomer. ($I_\mathrm{t} = 0.06$ nA, $U_\mathrm{s} = -2.02$ V)

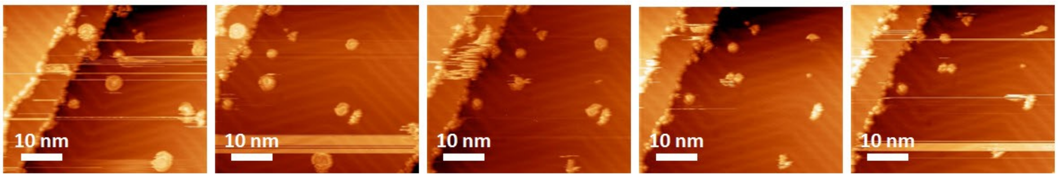


Figure S2: Consecutive STM images of CsA molecules on the Au(111) surface showing both rotational and translational motion.

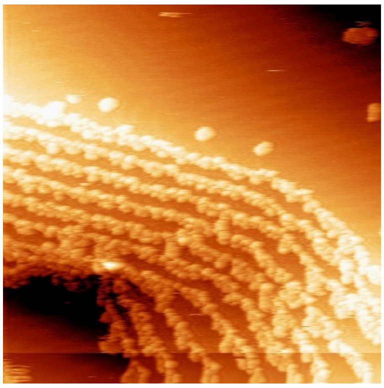


Figure S3: CsA molecules adsorb and are pinned on the step edges of Au(111).

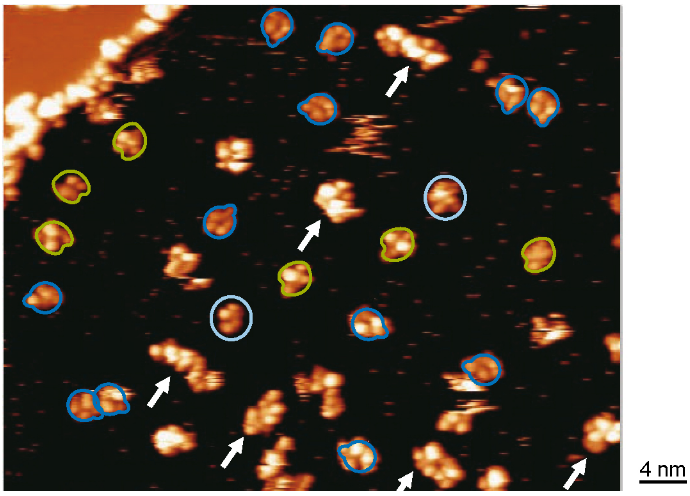


Figure S4: Sample of the CsA adsorption type assignment in an entire STM image ($I_t = 0.07$ nA, $U_s = -2.09$ V). Type I, type II, and unidentified molecular conformers are indicated by the blue, green and light blue outlines, respectively. Dimers and larger oligomers are indicated by white arrows. Molecules that were not stable under the tip were not accounted for.

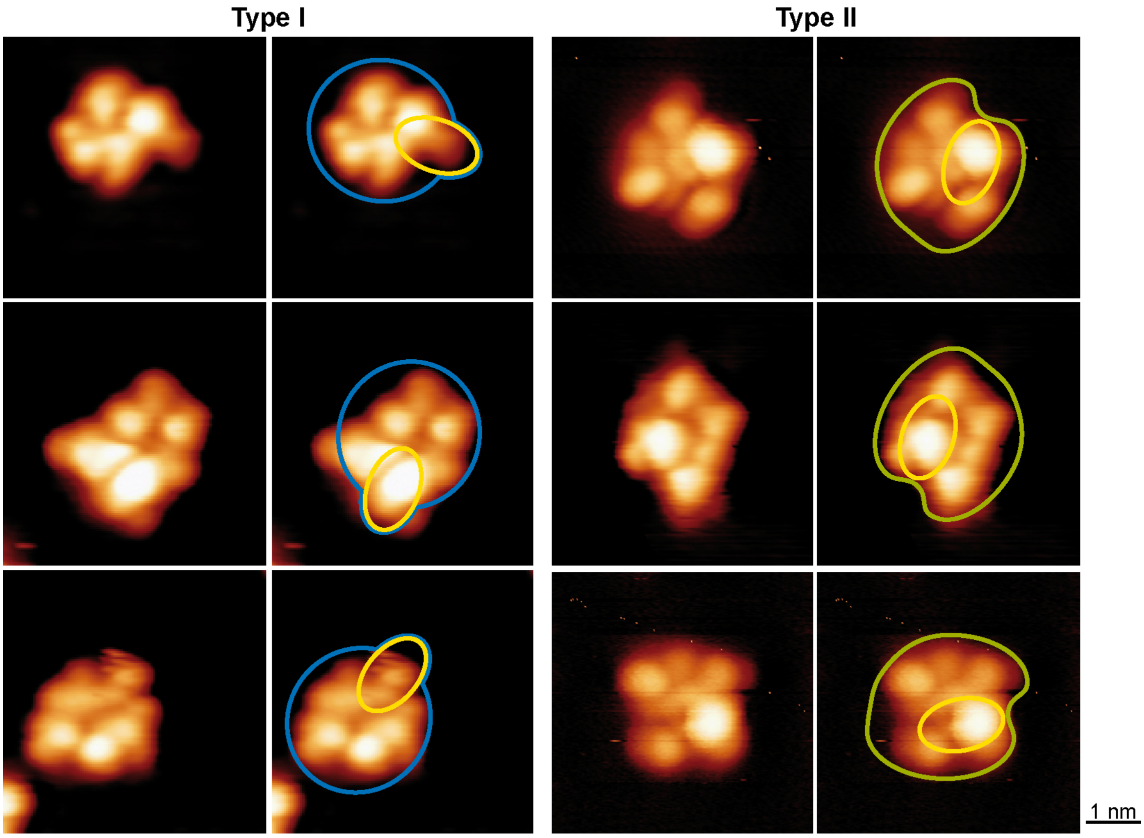


Figure S5: Different STM images CsA molecules of types I and II. The characteristic MeBut 1 residue is marked in yellow.

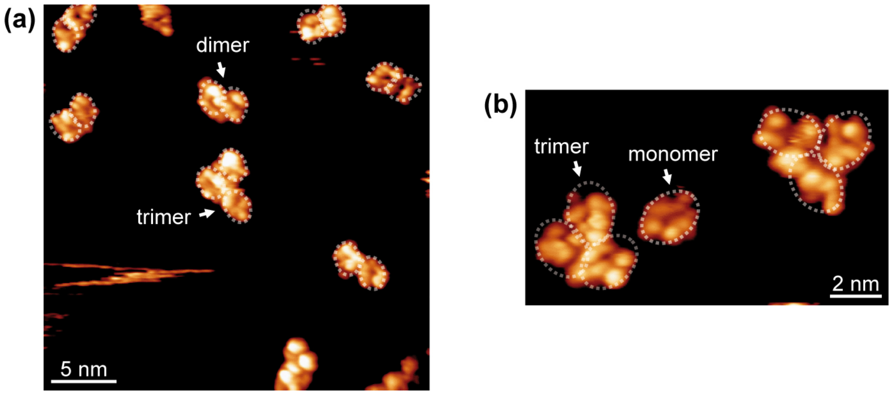


Figure S6: Type I CsA supramolecular assembly on Cu(111). Monomers in dimers and trimers are outlined. (a: $I_t = 0.06$ nA, $U_s = -2.43$ V; b: $I_t = 0.08$ nA, $U_s = -2.43$ V)

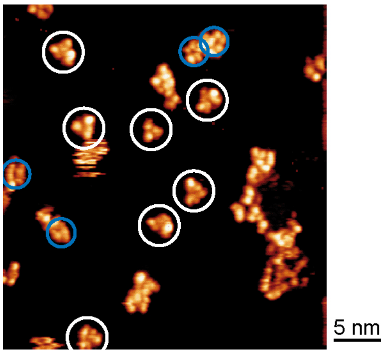


Figure S7: Sample of the CsA and CsA-K assignment in an entire STM image. CsA and CsA-K are indicated by the blue and white circles, respectively. Dimers and larger oligomers were not accounted for.

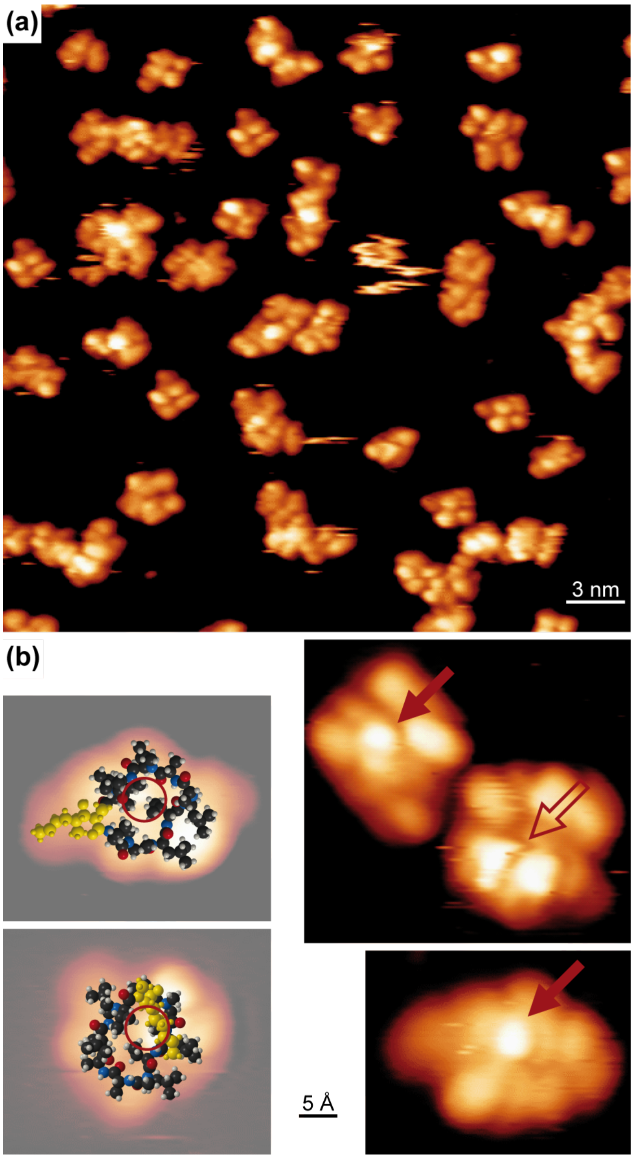


Figure S8: Fe coordinated CsA on Cu(111). (a) Overview STM image of CsA with Fe. (b) High resolution images of CsA-Fe monomers in the same scale. The monomers feature an additional protrusion in the centre indicated by solid arrows or circles. An empty arrow points to an additional protrusion ascribed to Fe, which is located atop of a CsA residue. Overlaid models of both type I and II CsA conformations on the STM images on the left show reasonable agreement with the arrangement of the molecular backbone: the core features are still visible and the position of the MeBut 1 group seems determinable. These findings clearly signal that Fe may bind both to the cavity and the periphery of CsA molecules on Cu(111).

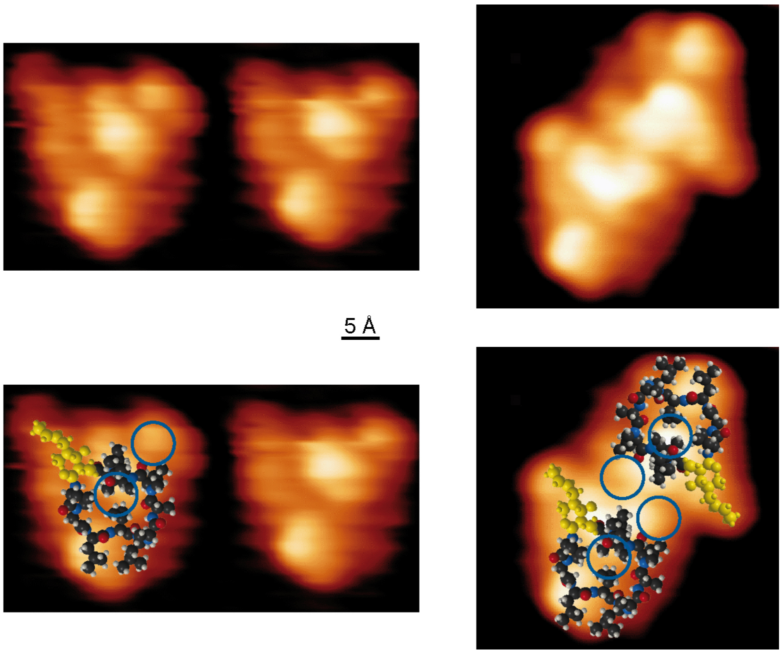


Figure S9: Co coordinated CsA on Cu(111): Comparison of STM data to molecular models.