Electronic Supplementary Information

Conformation-controlled Networking of *H*-bonded Assemblies on Surfaces

Manfred Matena,[‡,¶] Anna Llanes-Pallas,[†,¶] Mihaela Enache, [‡] Thomas Jung,[¥] Johan Wouters,[#] Benoît Champagne,[#] Meike Stöhr,*[,‡] and Davide Bonifazi.*[,†,#]

1. Experimental Section

The experiments were performed in a UHV system, consisting of different chambers for sample preparation and characterization (base pressure of 10^{-10} mbar). As substrate a Ag(111) single crystal was used which was prepared by subsequent cycles of sputtering with Ar^+ ions and annealing at 500°C. The molecules were deposited onto the Ag surface from a glass crucible that was heated inside a commercial evaporator (Kentax UHV equipment) while the rate was controlled by a quartz crystal microbalance. During molecule deposition the sample was at room temperature. The samples were analysed with a commercial LT-STM (Omicron NanoTechnology GmbH) at 77K and with LEED (Low Energy Electron Diffraction) at room temperature. The tunneling voltages given in the text refer to the sample.

2. X-ray crystal structure determinations

Single crystals of **1** crystallized from DMF solution have been obtained in a sealed tube after 10 days. Empirical formula = C28 H24 N6 O4, 2(C3 H7 N O), M = 654.7 g.mol^{-1}, Monoclinic, $C2/c$ (No. 15), a = 27.586(5) Å, b = 11.284(5) Å, c = 11.317(5) Åb = 109.164(5)°, V = 3507(2) Å^3, T = 298(2) K, Z = 3, D_{calc} = 1.240 g.cm^{-3}, μ (Mo) = 0.087 mm^{-1}, F(000) = 1384, 3043 unique reflections (R_{int} = 0.0209). Final R = 0.0610 for 2278 reflections with $I > 2\ \sigma(I)$ and $\omega R2$ = 0.2048 for all data. Intensity data were collected on a Gemini R Ultra diffractometer equipped with CCD detector using Mo radiation 0.71073 Å. The images were interpreted and integrated with the program CrysAlisPro from Oxford Diffraction. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL program package. Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). CCDC-709109 contains the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44–1223–336033; or deposit@ccdc.cam.ac.uk).

3. Computational studies

Full geometry optimizations were carried out using the B3LYP/6-311G** method. All structures are characterized by 3N-6 real vibrational frequencies. The electronic energies were then determined, on the B3LYP geometries, performing single point energy calculations at the MP2/6-311G** level of approximation while basis set superposition errors were corrected using the counterpoise scheme. Then, thermal corrections were evaluated at the B3LYP/6-311G** level to obtain the enthalpy and Gibbs free enthalpy at 77 K. The efficiency of the scheme was tested against MP2 geometry optimizations and CCSD(T) single point energy calculations by considering the formation of the NHMe-CO-Me dimer. All calculations were performed using the Gaussian 03 quantum chemistry package.[1] The calculations have been performed on the Interuniversity Scientific Computing Facility (ISCF) installed at the FUNDP for which the authors gratefully acknowledge the financial support of the F.R.S.-FRFC and the 'Loterie Nationale' for the conventions No. 2.4578.02 and 2.4617.07, and of the FUNDP.

---

[1] Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004

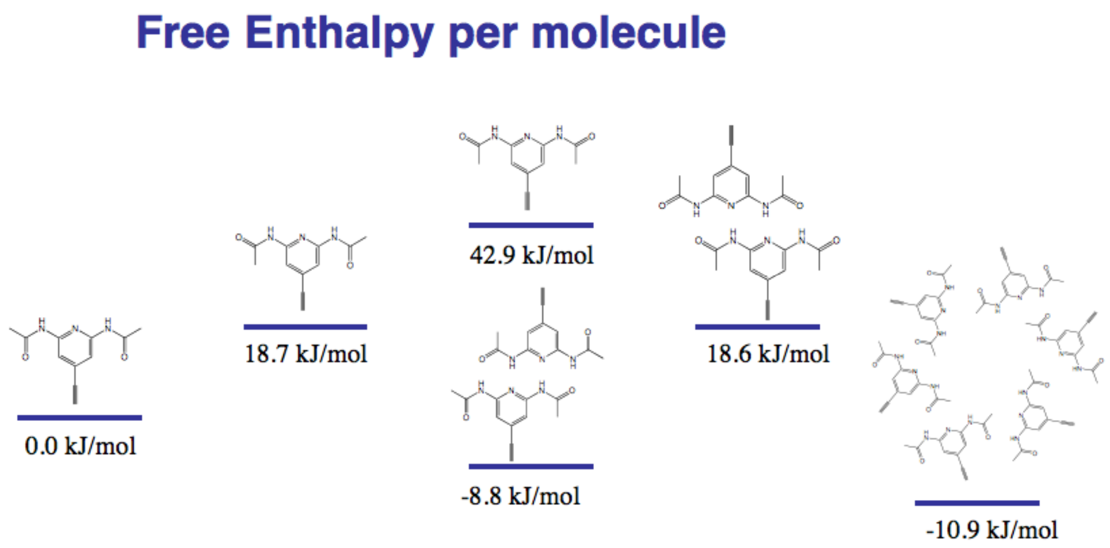

Figure S1. Energy level diagrams displaying the Δ*H*° of formation of the different conformers and *H*-bonded dimers.

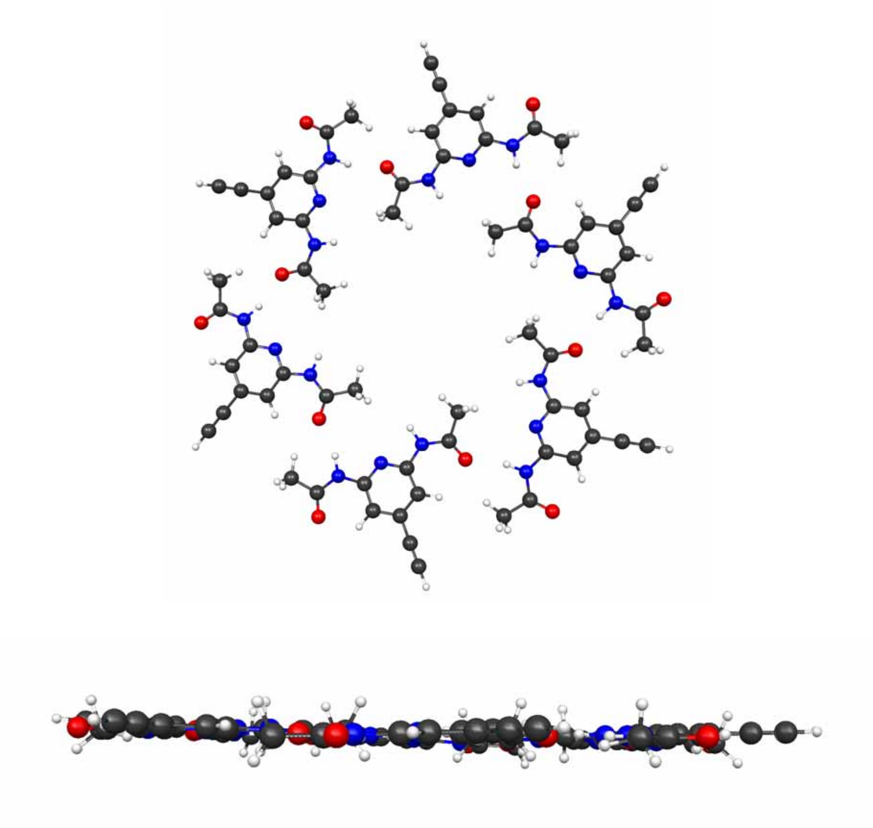

Figure S2. Optimized geometry in vacuum of the hexameric arrangement as observed on Ag(111) surfaces.

3. LEED measurements for molecule 1 on Ag(111)

LEED measurements were performed to determine the unit cell for both the hexagonal porous network and the close-packed assembly obtained after annealing the sample at 150°C. All LEED patterns were taken for samples held at room temperature (Figure S3b and c for the porous network and Figure S4 a-c for the close-packed assembly). The sample was slightly tilted with respect to normal incidence to obtain the diffraction spots of first order which would be otherwise hidden by the electron gun. The analysis of the LEED pattern supports for both molecular assemblies a superstructure which is commensurate to the underlying Ag substrate. For the porous network the following matrix describes the molecular ad-layer (Park and Madden):

$$\begin{pmatrix} 11 & 1 \\ 10 & 11 \end{pmatrix}.$$

For the close-packed assembly the matrix reads as follows:

$$\begin{pmatrix} 8 & 3 \\ 2 & 4 \end{pmatrix}.$$

The software LEEDpat 2.1 (K. Hermann and M. A. van Hove, LEED pattern simulator LEEDpat Version 2.1 2006) was used to simulate the LEED patterns (Figures S3a and S4d). The information on the dimensions of the unit cell and the structural data of the molecule were used to determine the length of the H-bonds for the porous network: the $CO\cdots H$ distance amounts to about 2 Å. The angle between the unit cell vectors of the hexagonal network and the close-packed structure was used to compare the STM results with the LEED results.

We found that both measurement techniques lead to the same results.

The following more detailed considerations support this statement. As both assemblies could not be observed at the same time it is assumed that the sample is always mounted in the same way in the STM with respect to the x- and y-scanning directions of the STM and that no rotation of the sample with respect to these scanning directions happens. This is a reasonable assumption because the setup used for the STM experiments does not allow for a rotation of the sample. This means that the angle between both assemblies is unique except for an integer multiple of 60° that can be added (what is a result of the six-fold rotational symmetry of the topmost layer of the substrate).

Taking into account that each domain can be mirrored at the principal directions of the substrate, this leads to more than one possible angle between the two assemblies. For the close-packed assembly, the mirror operation results in non-congruent unit cells. Thus, an STM image of the close-packed assembly can unambiguously be attributed to one of the patterns (either the pattern or its mirrored counterpart) determined by LEED. This attribution is not possible for the porous network as the mirror operation results in congruent unit cells (Figure S5a). This means for our case that there are two possible angles that were determined to 12.93° and 3.49° (average of both unit cell vectors of the porous network minus angle of the long unit cell vector of the close-packed assembly). Both values compare very well with the angles derived from STM (Figure S5b-d and caption).

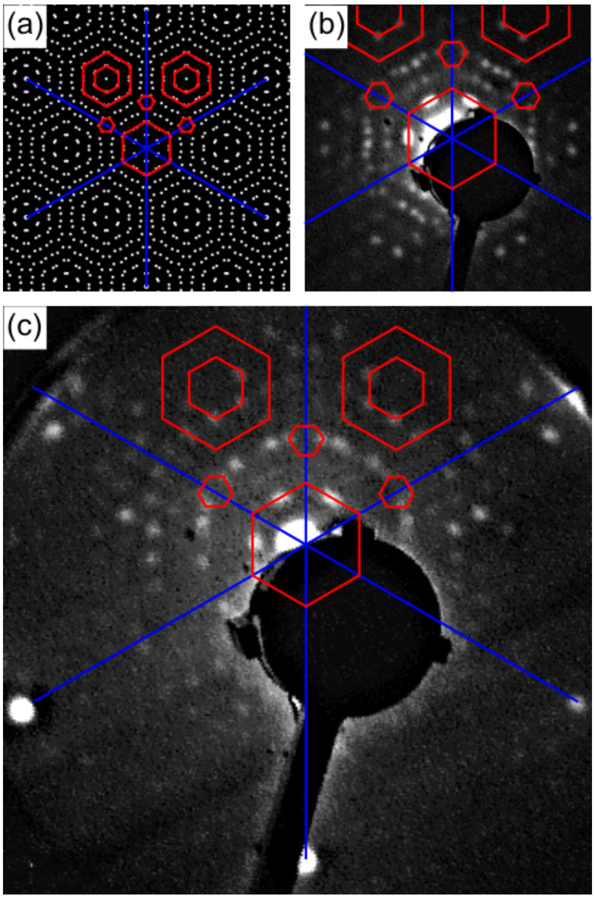

Figure S3. LEED patterns for the porous network on Ag(111). a) Simulated LEED pattern. b), c) LEED pattern taken at an energy of 23 eV and 37 eV, respectively. The blue lines indicate the principal directions of the Ag substrate. The red lines highlight symmetries of the pattern in order to facilitate the comparison of the different figures. of (b) 23eV and (c) 37eV.

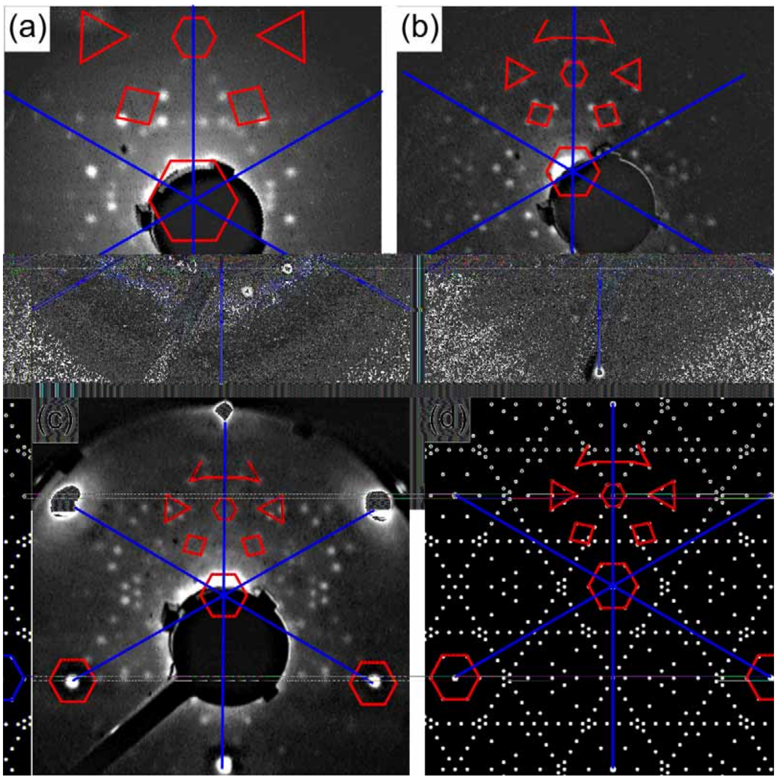

Figure S4. LEED patterns for the assembly of **1** on Ag(111) observed after annealing at 150°C. The blue lines indicate the principal directions of the Ag substrate. The red lines highlight symmetries of the pattern in order to facilitate the comparison of the different figures. The LEED patterns were taken at energies of (a) 15eV, (b) 30eV and (c) 42eV. d) Simulated LEED pattern.