

Supporting Information:

Pre-programmed bicomponent porous networks at the solid-liquid interface: The low concentration regime

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Experimental. Melamine (>99.0%) was obtained from Sigma-Aldrich and used without further purification. Mother solution of melamine (**2**) was dissolved in DMSO and diluted with trichlorobenzene (TCB) to give solutions 40 ± 25 and 2 ± 1 μM respectively. Preparation of molecule **1** has been described elsewhere [A. Llanes-Pallas, M. Matena, T. Jung, M. Prato, M. Stöhr, and D. Bonifazi, In Press]. The molecule was readily soluble in DMSO, diluted with TCB and used with concentration of 29 ± 19 and 3 ± 2 μM . Pattern formation was achieved by applying 5 μL of a vigorously shaken and warm (40 – 50°) solution 3 ± 2 μM in **1** 2 ± 1 μM in **2** onto freshly cleaved HOPG. Uncertainties values are derived from the standard deviation for the “limit values” of the balance’s linearity (XS105 Mettler Toledo ®) for maximum confidence. “Typical values” are reported as one order of magnitude lower. STM tip was approached and the solution imaged before the solvent was completely evaporated ($\sim 3\text{h}$). Imaging of the patterns occurred within minutes. Over 200 images from at least 3 different experiments were obtained for each monolayer pattern. Unit cells were corrected by the underlying graphite, except for unit cell of the porous network **1+2** pattern in which the unit cell was just averaged over 6 images. All images with superimposed molecular models were also corrected by the underlying graphite and the models were minimized with Chem3D at the MM2 level. Unit cell errors correspond to the standard deviation multiplied by a factor of 2. DFT calculations for hydrogen bond interaction between 3H-Pyridine-2,6-dione fragments and melamine fragments were performed with the quantum mechanical package GAMESS 04 [1] at the PBE 6-31G(d) level, where geometries converged typically to <0.0002 Hartrees. Unit cell determination and plane correction were made by the SPIP program. No filtering of any kind was applied to any of the images herein reported. The images in the supporting information were rendered with the help of the Gwyddion Program [2].

The molecular monolayer concentration C_s (pmol cm^{-2}) for a specific phase characterized by a unit cell was determined as follows,

$$C_s = n_{\text{unit cell}}^{\text{molecules}} [\text{cm}^{-2}] \cdot \frac{1 \times 10^{12} [\text{mol}^{-1} \cdot \text{pmol}]}{N_A [\text{mol}^{-1}]}, \text{ where } n_{\text{unit cell}}^{\text{molecules}} [\text{cm}^{-2}] = \left[\frac{N_{\text{unit cell}}^{\text{molecules}}}{A_{\text{unit cell}} [\text{cm}^2]} \right]$$

Determination of the total H-bond energy per picomol of adsorbed molecules E_{HA} (eV pmol^{-1}) for a specific phase characterized by a unit cell

$$E_{HA} = N_{\text{unit cell}}^{\text{H-bond interactions}} \cdot E^{\text{H-bond interaction}} [\text{eV}] \cdot \frac{N_A [\text{mol}^{-1}]}{N_{\text{unit cell}}^{\text{molecules}}} \cdot 1 \times 10^{-12} [\text{mol} \cdot \text{pmol}^{-1}]$$

where N_A is Avogadro’s Number.

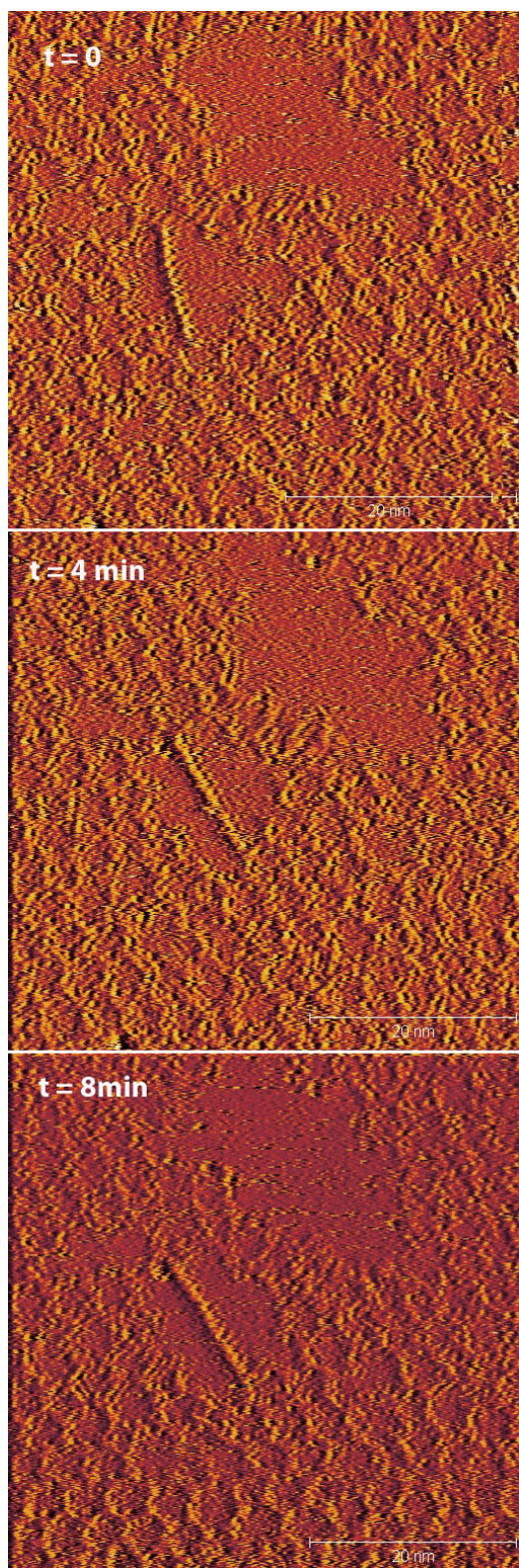


Figure S1. 50 x 50 nm STM constant height images of the porous network showing two hexagons linked by a 1D array.

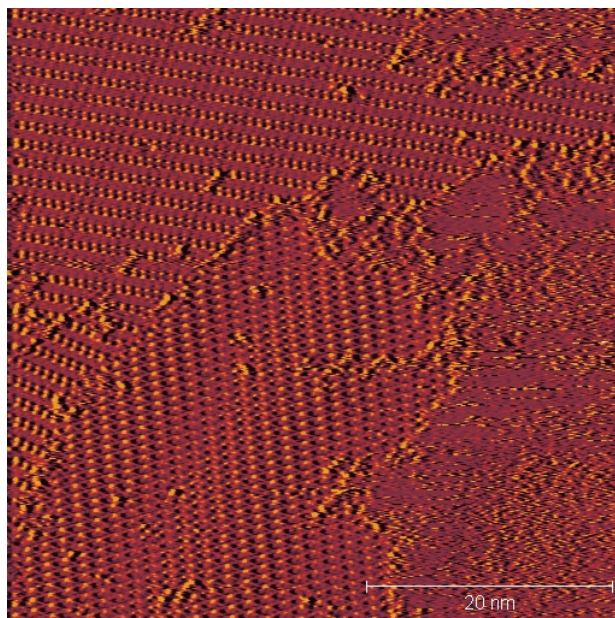


Figure S2. 50 x 50 nm STM constant height images of module **1**. The chains in figure S1 and S2 highly resemble chains of molecule **1**.

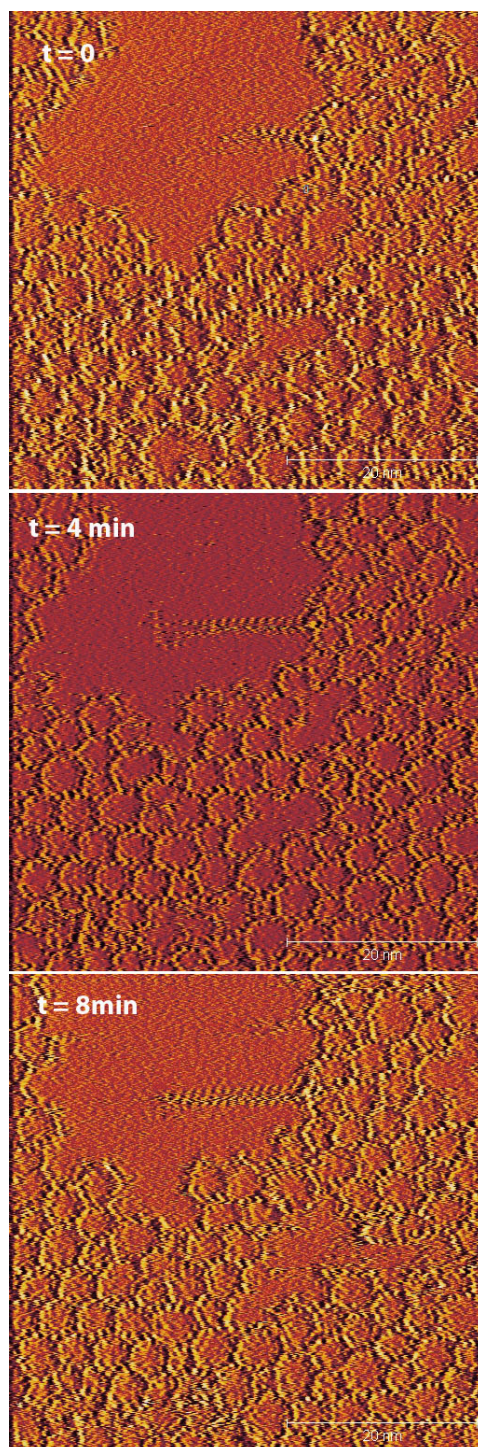


Figure S3. 50x50 nm STM constant height images of the porous network showing the evolution in a 1D array.

- [1] M.W.Schmidt, K.K.Baldrige, J.A.Boatz, S.T.Elbert, M.S.Gordon, J.H.Jensen, S.Koseki, N.Matsunaga, K.A.Nguyen, S.J.Su, T.L.Windus, M.Dupuis, J.A.Montgomery J. Comput. Chem. 14, 1347-1363 (1993).
- [2] D. Nečas, P. Klapetek, C. Anderson, M. Šiler, J. Bílek, N. Ocelic, R. Zitko, L. Chvátal, S. Neumann, J. Hořák, A. Ковалев, O. Davies, R. Würdemann, D. Kähler, M. Valtr, M. Hasoň, Gwydion 2.9. <http://gwyddion.net/> 2008.