Electronic Supplementary Information

Supramolecular H-bonded Porous Networks at Surfaces: Exploiting Primary and Secondary Interactions in a Bi-component Melamine-Xanthine System

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Table of Contents

S-2
S-4
S-6
S-7
S-10

1. Mass Spectroscopy

 N^3 -Methylxanthine and melamine analytes were purchased from TCI and Sigma-Aldrich, respectively. N^3 -Octadecylxanthine was prepared as described in ref.¹ Saturated solutions were prepared from both analytes in hot water using a bath sonicator for 10 min. The saturated solutions, containing 0.5% formic acid, were measured first separately, then a 50:50 (v/v) mixture of them. All mass spectrometric measurements were performed on a Waters Q-TOF Premier spectrometer (Waters, Milford, Massachusetts, USA) equipped with a built-in electrospray ion source. A high voltage of ca. 3000 V was used in the ion source. The instrument was scanned in the normal MS mode over the mass range 50-990 with a scan time of 2 s. In case of MS/MS measurements collision energy was set from 5 to 2 eV. Argon was used as collision gas; gas flow was 0.33 mL/min. Injection volume: 5 μ L; Injection speed: 200 μ L/min. Cone voltage: 32 V. Eluent: acetonitrile - water 1:1 (v/v).



Figure S1. MS spectrum of Melamine (M, MW: 126) in aq. 0.5% formic acid (Q-TOF instrument, positive ion mode).



Figure S2. MS spectrum of N^3 -Methylxanthine (*X*', MW: 166) in aq. 0.5% formic acid (Q-TOF instrument, positive ion mode). *Peaks caused by contamination of the needle with melamine.



Figure S3. MS spectrum bi-component mixture: N^3 -Methylxanthine (*X*', MW: 166) + Melamine (*M*, MW: 126) in aq. 0.5% formic acid (Q-TOF instrument, positive ion mode).



Figure S4. MS spectrum bi-component mixture: N^3 -Methylxanthine (X', MW: 166) + Melamine (M, MW: 126) in aq. 0.5% formic acid. Zoom range m/z 550 – 860.



Figure S5. MS spectrum bi-component mixture: N^3 -Methylxanthine (X', MW: 166) + Melamine (*M*, MW: 126) in aq. 0.5% formic acid CID spectrum of peak at m/z 625.

2. NMR

NMR spectra were recorded with a Varian Unity INOVA 600 MHz instrument equipped with a reverse probe. Appropriate amounts of X and M were weighted and added into NMR tubes. DMSOd₆ was added to each tube to obtain a 5.3 mM overall composition. Each sample was heated at 353.0 K in the instrument probe and allowed 20 min for dissolution and equilibration before acquiring the spectrum. All measurements were run in duplicate. Modified Job's plot² constructed from ¹H NMR experiments, confirm the existence of a X/M aggregate with 3:1 stoichiometry.



Figure S6. Modified Job's plot² of *X* and *M* (600 MHz, dmso-d₆, 353.0 K). $\Delta \delta$ = chemical shift change of the NH-1 proton of *X*.¹



Figure S7. X NH-1 signal shift in X/M mixtures as a function of X molar fraction.

3. STM investigation. Scanning Tunneling Microscopy (STM) measurements were performed using a Veeco scanning tunneling microscope (multimode Nanoscope III, Veeco) at the interface between highly oriented pyrolitic graphite (HOPG) and a supernatant solution, by using a scanner A (Veeco), therefore by mapping a maximum area of $1\mu m \times 1\mu m$. Diluted solutions of M and/or X were applied to the basal plane of the surface. For STM measurements the substrates were glued on a magnetic disk and an electric contact is made with silver paint (Aldrich Chemicals). The STM tips were mechanically cut from a Pt/Ir wire (90/10, diameter 0.25 mm). The raw STM data were processed through the application of background flattening and the drift was corrected using the underlying graphite lattice as a reference. The latter lattice was visualized by lowering the bias voltage to 20 mV and raising the current to 65 pA. Mother solutions of 1,3,5-triazine-2,4,6-triamine (melamine, M) and N^3 -ocadecylxanthine (X) were dissolved in 1,2,4-trichlorobenzene (TCB) at 95 °C and diluted to give 100 µM and 10 µM solutions. STM imaging was carried out in constant current mode yet without turning off the feedback loop, to avoid tip crashes. Monolayer pattern formation was achieved by applying onto freshly cleaved HOPG 4 µL of a solution that was heated at 60-70 °C to improve the solubility. Noteworthy, study of this system in different solvents, i.e. 1phenyloctane, nonanoic acid and tetradecane, did not produced any ordered monolayers, which can be attributed to the low solubility of molecules M and X in those solvents. The two aforementioned solutions have been diluted with TCB to yield concentrations of $1 \pm 0.1 \mu M$ and $3 \pm 0.5 \mu M$ of M and X, respectively, and mixed in 1:3 (M:X) ratio. By applying 4 μ L of this new solution to the HOPG surface, a porous network has been obtained at the solid-liquid interface, as visualized by STM imaging at room temperature. The STM images were recorded at room temperature after achieving a negligible thermal drift. All of the molecular models were minimized with Chem3D at the MM2 level and processed with QuteMol visualization software.³

4. Computational details

All calculations were performed using the 2012 version of Amsterdam Density Functional (ADF),⁴ and the QUantum-regions Interconnected by Local Descriptions (QUILD) program developed by Swart and Bickelhaupt.⁵ The applied level of density functional theory (DFT) was BLYP-D in combination with the TZ2P basis set: BLYP-D comprises the BLYP functional⁶ with dispersion corrections as proposed by Grimme.⁷ This approach has been shown to yield excellent structures and energies for multiply-hydrogen bonded DNA-base oligomers.⁸ The other reason for including dispersion corrections in the calculations is that, in this way, the new results can have a direct comparison to our previous 3-methylxanthine quadruplex calculations.⁸⁻⁹

Equilibrium structures were optimized using analytical gradient techniques and all energy minima except the two largest (12 and 9 units) ones were verified through vibrational analysis.¹⁰ In those cases where it was necessary the presence of a surface was taken into account by planar restraint. The overall bond energy ΔE_{bond} is made up of two major components [Eq. (1)]:

$$\Delta E_{\text{bond}} = \Delta E_{\text{def}} + \Delta E_{\text{int}} \tag{1}$$

The deformation energy ΔE_{def} is the amount of energy required to deform the individual monomer molecule from its equilibrium structure in the gas phase to the geometry that it acquires in the supramolecular complex. The interaction energy ΔE_{int} corresponds to the energy change when the geometrically deformed molecules are associated to form the optimized structure. ADF does not provide total energies, i.e., energies with respect to all nuclei and electrons separated at infinite distance). Instead, it yields energies with respect to separate fragments where default fragments are spherical spin-restricted individual atoms. Note that energy differences with respect to this atomic zero level provide exactly the same results as calculations with respect to any other point of reference.





Structure $M_3 X'_3$

Structure $M_3 X'_6$



Structure $M_3 X'_9$

Figure S8. Optimized H-bond distances (in Å, yellow numbers) and angles (in degree, cyan numbers) of the basic surface motif $M_3X'_9$ and the calculated subsystems (MX'_3 , X'_3 , $M_3X'_3$, $M_3X'_6$) in the interaction of melamine (M) and N^3 -methylxanthine (X'). All the calculations were performed in C_{3h} symmetry, except structure B where the optimization leads to a non-symmetric structure very close to a C_{3h} symmetric geometry(see main text).



Figure S9. Optimized H-bond distances (in Å, yellow numbers) and angles (in degree, cyan numbers) of hexameric melamine (M_6) in C_{6h} (left) and C_{3i} (right) symmetry.



Figure S10. The three optimized reference dimer structures M_2 (top), MX' (middle) and X'_2 (bottom) with optimal H-bond distances (in Å, yellow numbers) and angles (in degree, cyan).

5. References

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