Surface self-assembly of the cyanuric acid–melamine hydrogen bonded network

Luís M. A. Perdigão,[a] **Neil R. Champness***[b] **and Peter H. Beton***[a]

A hydrogen-bonded bimolecular network formed between cyanuric acid (CA) and melamine (M), CA·M, has been prepared by a surface-based self-assembly process; the monolayer CA·M network is prepared under ultra-high vacuum conditions either by sequential deposition of CA followed by M, or through simultaneous deposition of the component molecular species.

One of the most extensively studied structural motifs in supramolecular chemistry is the complementary hydrogen-bonding observed between diaminopyridine and diimide moieties.[1] This classic hydrogen-bonding interaction has been used extensively in the formation of tapes,[2–4] rosettes[5,6] and capsules[7–9] in the solution phase,[2,5–9] the solid-state,[3,4] at interfaces[10] and more recently on surfaces.[11–14] The interaction is observed in biologically relevant systems such as barbiturates and in a wide range of host–guest systems.[15] Most recently the diaminopyridine : diimide interaction has been used to stabilize nanoscale templates for fullerene cluster formation.[11,12]

The prototypical structure common to these studies is the highly symmetric hydrogen-bonded two-dimensional array of cyanuric acid (CA) and melamine (M) shown in Fig. 1. Despite the importance of this structure in supramolecular chemistry the solid-state structure was only published relatively recently.[16] We report molecular resolution imaging of CA·M networks formed as monolayers through surface based self-assembly[11–13,17] and show that our results underpin the rational design of supramolecular templates.[18]
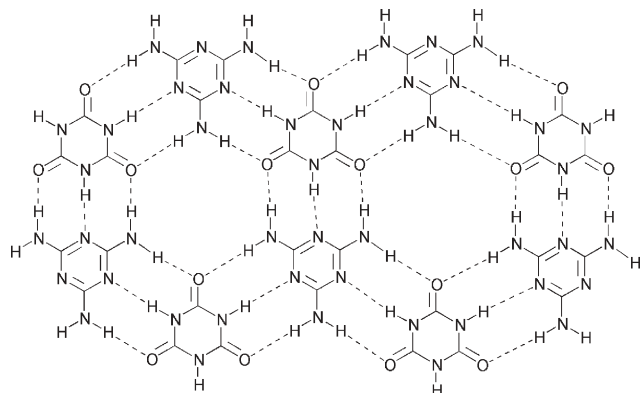

Fig. 1 A portion of the two-dimensional CA·M network.

[a]*School of Physics and Astronomy, The University of Nottingham, University Park, Nottingham, UK NG7 2RD*
[b]*School of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD*

The CA·M network was formed under ultra-high vacuum (UHV) conditions (base pressure 10^{-10} Torr) on a Ag–Si(111)$\sqrt{3} \times \sqrt{3}R30°$ surface.[19,20] Adsorbed organic molecules are known to diffuse readily at room temperature on this surface and form extended structures with long range order governed, primarily, by intermolecular interactions.[11–13,19,21] CA and M were deposited by sublimation and images of the surface were obtained using a scanning tunnelling microscope (STM) which is housed within the UHV chamber and operated in constant current mode at room temperature.

We found that a CA·M network can be formed either by sequential deposition of CA followed by M or, significantly, by simultaneous deposition of CA and M (Fig. 2, 3). CA forms large hexagonally ordered islands with a lattice constant which is equal to that of the Ag–Si(111)$\sqrt{3} \times \sqrt{3}R30°$ surface, 6.65 Å (Fig. 2). After sublimation of M a honeycomb structure is formed at the edges of the CA domain which we attribute to the formation of the CA·M complex (Fig. 3(a)). After leaving samples of co-existing islands of CA·M and hexagonal CA overnight (>10 h) the CA desorbed leaving *only* the less volatile bimolecular CA·M complex on the surface (Fig. 3(b)). No further changes to the CA·M islands were observed over a period of several days.

Interestingly, the CA·M complex can be formed directly, without traces of the single component CA islands, by simultaneous deposition of CA and M (Fig. 3(e, f)), indicating a significant preference for incorporation of CA molecules into the CA·M network under these conditions. Most importantly both methods of preparation result in networks uncontaminated by precursor phases—all CA and M molecules are incorporated in the network complex. This is a direct consequence of the greater stability of the CA·M phase as compared with CA or M islands.
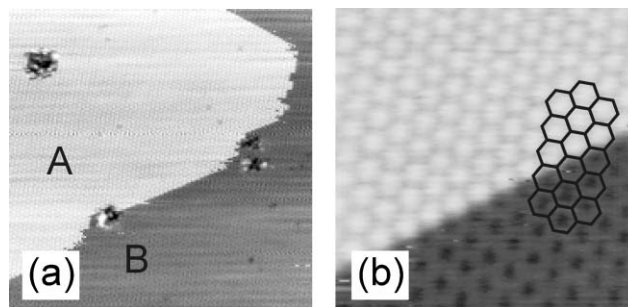

Fig. 2 (a) STM images of CA islands (region A) deposited on Ag–Si(111)$\sqrt{3} \times \sqrt{3}R30°$ (region B). (b) Image showing molecular resolution of CA island (upper half) and honeycomb structure of the Ag–Si(111)$\sqrt{3} \times \sqrt{3}R30°$ surface. Image dimensions and operation parameters: (a) 415 Å × 415 Å, −2 V, 0.05 nA; (b) 85 Å × 85 Å, −1.7 V, 0.05 nA.
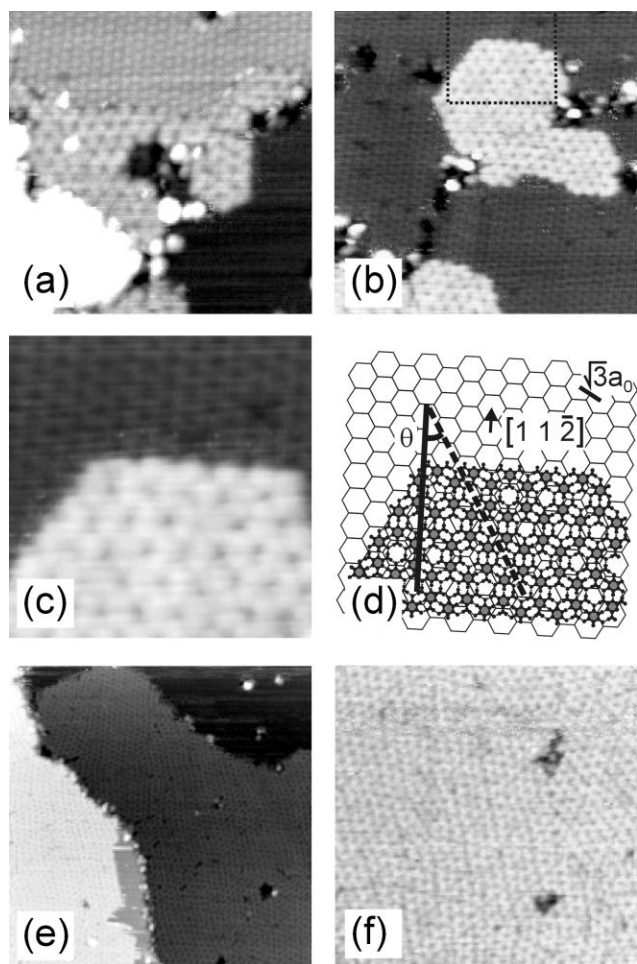
Fig. 3 (a) Surface after sequential exposure to CA then M. CA islands (upper part) are partially converted to the CA·M network (centre of image); (b) image taken after leaving a surface such as (a) overnight. Area highlighted by dotted line is shown in (c) at higher magnification; (c) higher magnification image of CA·M network island; (d) schematic representation of the CA·M network, shown in (c), on the Ag–Si(111)$\sqrt{3} \times \sqrt{3}R30°$ surface (represented by a regular array of hexagons in which the centres and vertices correspond respectively to Si and Ag trimers[19,20]). The angle θ (see text) is also illustrated; (e) image following codeposition of CA and M showing large islands of CA·M. A substrate step runs from top left to bottom centre; (f) the CA·M network within the large islands observed in (c). Tunnelling parameters for all images were −2.5 V sample bias and 0.03–0.05 nA feedback current. Image dimensions: (a) 175 Å × 175 Å, (b) 220 Å × 220 Å, (c) 80 Å × 80 Å, (e) 470 Å × 470 Å, (f) 250 Å × 250 Å.

Indeed, repeated attempts to prepare single component hydrogen-bonded arrays of M on the Ag–Si(111)$\sqrt{3} \times \sqrt{3}R30°$ surface at room temperature have proven to be unsuccessful, presumably due to a high mobility of this molecule under the conditions of the experiment coupled with a lower stability of any hypothetical hydrogen-bonded arrangement.

The CA·M complex forms domains oriented in several different directions (Fig. 4). In the case of simultaneous CA and M deposition, large islands are formed which are composed of CA·M domains in different orientations. At the boundaries between these domains abrupt changes in the local orientation are observed in some cases, while for other cases quasi-continuous variation of the
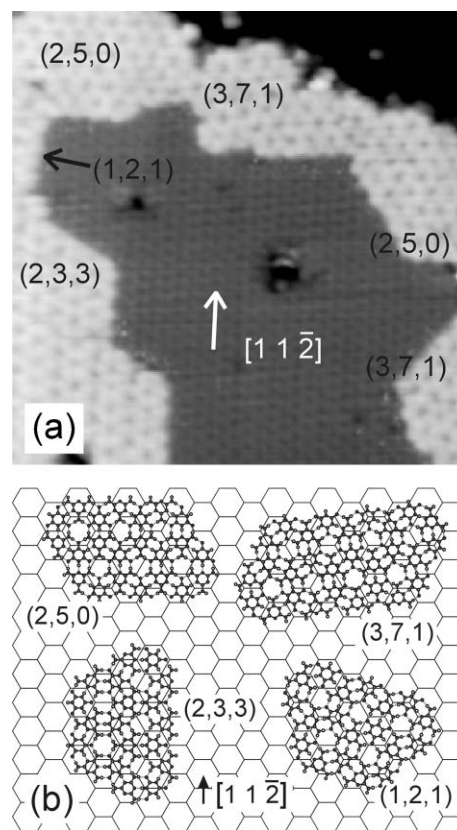

Fig. 4 (a) Image taken after leaving a surface, such as that shown in Fig. 3(a), overnight. CA·M domains with different alignment are identified by integers (l,m,n); (b) schematic showing arrangements of the CA·M on the Ag–Si(111)$\sqrt{3} \times \sqrt{3}R30°$ surface (represented by a regular array of hexagons in which the centres and vertices correspond respectively to Si and Ag trimers[19,20]). Domains are classified by integers (l,m,n) as explained in text.

ordering is observed. Co-evaporation leads to a higher surface coverage (up to 70%) of the CA·M network.

The relative orientations of different CA·M domains can be understood within a simple geometrical model. Two overlaid hexagonal structures will match periodically in a superstructure provided that there are integers l, m and n satisfying the condition:[19]

$$la_c = |m\underline{a} + n\underline{b}| = a_0\sqrt{(m^2 + n^2 + m.n)}$$

with a_c the unit cell dimensions of the CA·M network, $\underline{a}$ and $\underline{b}$ are the surface lattice vectors of the Si(111) substrate, and $a_0 = 3.84$ Å is the lattice constant of the unreconstructed silicon surface. The angle between the CA·M network and the [11$\bar{2}$] direction of the Si(111) substrate is given by:

$$\theta = \cos^{-1}[\sqrt{3}(m + n)/2\sqrt{(m^2 + n^2 + m.n)}]$$

We have identified the set of (l,m,n) integers corresponding to the orientations most commonly observed for surfaces prepared by sequential deposition (see Fig. 4(a)). The molecular models for these phases are shown in Fig. 4(b) and their properties, including periodicity and fractional coverage, are shown in Table 1. The period of three of these phases is within 0.05 Å of the value

Table 1 Angular mismatch, θ, and period, a_c of the domains classified by integers (l,m,n). Also shown is the percentage of the CA·M network found in each phase. Note that for the off axis domains (3,7,1) and (1,2,1) there are two equivalent phases rotated by $\pm \theta$ and the coverage for these two phases has been combined to provide the value above

l	m	n	θ	$a_c/\text{Å}$	Coverage (%)
2	5	0	30	9.60	17
3	7	1	23.4	9.66	34
2	3	3	0	9.68	18
1	2	1	10.9	10.16	23

determined for bulk CA·M (9.641 Å) using X-ray crystallography,[16] while the difference for the (1,2,1) phase is somewhat larger, ~ 0.5 Å, but still close to the bulk value. We also observe small areas of network which have a local orientation which cannot be readily identified and, in some cases, varies on a length scale comparable to the period. In most cases these are formed at substrate steps and domain boundaries.

Overall our results show that H-bonding dominates molecular ordering, but the additional stabilisation due to molecule–substrate interactions leads to a relaxation of the network to preferred orientational arrangements. The competition between intermolecular and molecule–substrate interactions results in a small variation of the possible lattice constants displayed by the network in different orientations as summarised in Table 1.

Our work is highly relevant to H-bonded surface templates[11–13,18] since it demonstrates that network dimensions may be systematically determined through selection of component molecules. The CA·M network is a close analogue of the pore arrays previously demonstrated for the combination of a perylene derivative and melamine.[11,12] The exchange of PTCDI for CA leads to a reduction in pore area, the critical parameter for template applications, from ~ 700 Å^2 to ~ 20 Å^2. Furthermore we show that, while important, a simple commensurability between network and substrate is not an absolute requirement and that some mismatch in lattice constants may be tolerated. Finally, the CA·M network has well defined molecular stoichiometry with monophase islands of CA or M *completely* absent, illustrating an approach for the synthesis of chemically pure bimolecular surface arrays with high surface coverage.

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