

# Tailoring pores for guest entrapment in a unimolecular surface self-assembled hydrogen bonded network<sup>†</sup>

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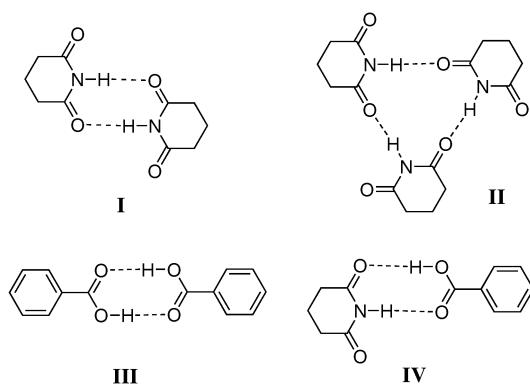
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A unimolecular hydrogen-bonded network is formed by a perylene-diimide derivative following surface self-assembly leading to the formation of pores of appropriate dimensions to accommodate regularly spaced guest C<sub>60</sub> molecules.

The surface-based self-assembly of hydrogen-bonded structures is an area of increasing scientific interest.<sup>1–9</sup> This interest arises due to fundamental interest in self-assembly processes,<sup>1</sup> potential applications in nanostructure fabrication<sup>2–5</sup> and the observation of unusual structural phenomena such as the formation of random frameworks with glass like structures.<sup>6,7</sup> Such structures typically rely upon the formation of robust supramolecular synthons such as that formed between imides and complementary species such as melamine<sup>2–4,8</sup> as well as others (Scheme 1).<sup>6,9,10</sup>

We<sup>11,12</sup> and others<sup>13</sup> have studied imide–imide interactions, using a variety of 3,4:9,10-perylenetetracarboxylic diimide (PTCDI) derivatives and related species,<sup>11,12</sup> and intermolecular carboxylic acid–carboxylic acid interactions<sup>6,9</sup> in a series of investigations and have become interested in the interplay between competing supramolecular synthons during the surface-based self-assembly process. Thus, we have targeted the synthesis and investigation of a molecule that combines both the imide moiety and carboxylic acid groups within a single molecule 1,7-bis(4-benzoic acid)-PTCDI, **1** (Scheme 2). Such a compound has the ability to adopt a range of potential intermolecular interactions involving imide or carboxylic acid groups.



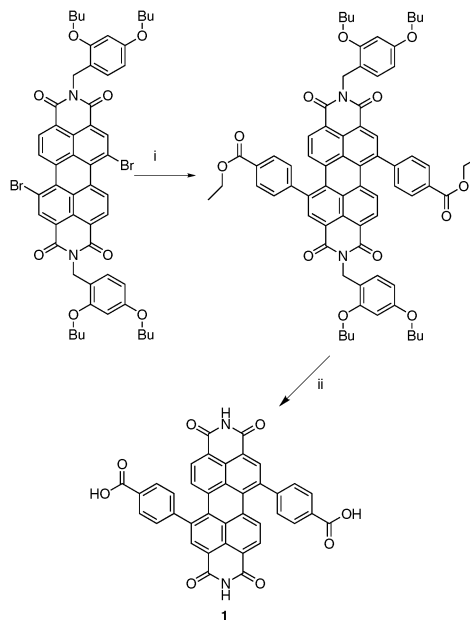
**Scheme 1** Anticipated supramolecular synthons adopted by imides and carboxylic acids.

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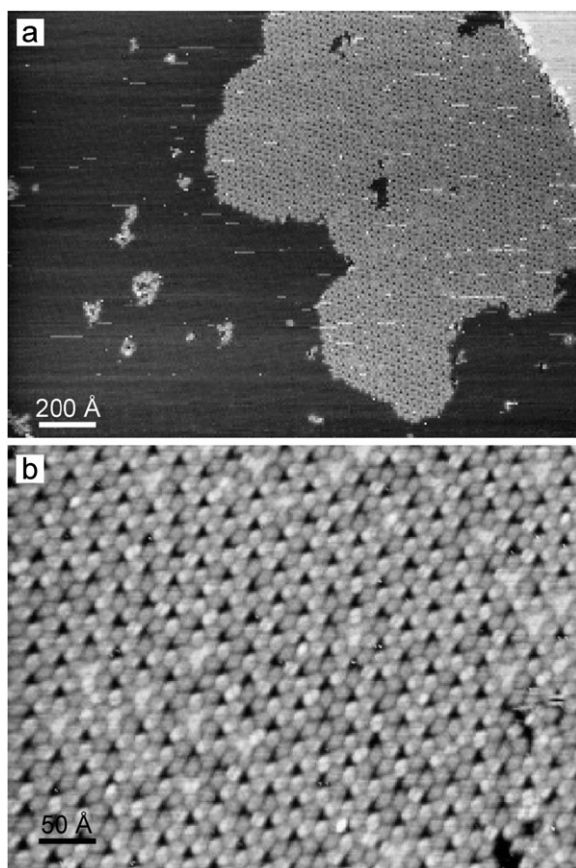


**Scheme 2** Synthesis of **1** (i) 4-ethoxycarbonylphenyl boronic acid, toluene, Pd(PPh<sub>3</sub>)<sub>4</sub>, Ag<sub>2</sub>O, CsF; (ii) MeSO<sub>3</sub>H, toluene.

Compound **1** was prepared using the synthetic pathway shown in Scheme 2.† Thus, the benzoic acid sidearms were introduced, in an ester protected form, to dibromo-PTCDI using Suzuki coupling reaction conditions.<sup>14</sup> By using the dibutylbenzoyl protected imide it is then possible to deprotect both imides and carboxylic acids in a single reaction using methanesulfonic acid.

Deposition of **1** onto a Ag–Si(111) $\sqrt{3} \times \sqrt{3}R30^\circ$  surface<sup>15</sup> under ultra-high vacuum (UHV) conditions leads to the assembly of a hexagonal two-dimensional network structure as revealed by room temperature scanning tunnelling microscopy (STM) (Fig. 1). Inspection of images where both the surface reconstruction and the molecular arrangement are visible reveals that the hexagonal molecular arrangement is commensurate with the reconstructed Ag–Si(111) $\sqrt{3} \times \sqrt{3}R30^\circ$  surface with a  $4 \times 4$  registry with a periodicity of 26.6 Å [ $4 \times a(\text{Ag–Si}) = 4 \times 6.64$  Å] and a unit cell vector parallel to the [1 1  $\bar{2}$ ] direction of the Ag–Si(111) $\sqrt{3} \times \sqrt{3}R30^\circ$  surface. Within the hexagonal network triangular cavities can be readily seen (Fig. 1).

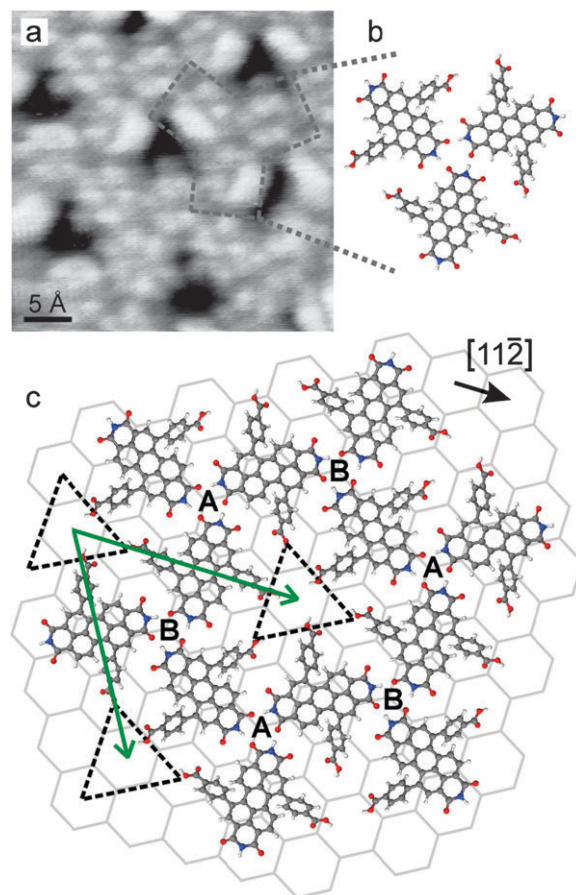
Closer inspection of the structure (Fig. 2) reveals that, the hydrogen-bonded network is formed exclusively by using inter-imide hydrogen bonds with the carboxylic acids playing no role in hydrogen-bonding interactions. A trimeric hydrogen bonded node is adopted (Fig. 2b, Scheme 1, configuration II) which is inherently chiral on the surface. The proposed configuration (Fig. 2c) indicates that adjacent nodes adopt alternate chiralities, labelled A and B. PTCDI and its derivatives are capable of



**Fig. 1** Two STM images showing the formation of self-assembled molecular islands. The scale bar is provided. The imaging parameters for both images,  $-2.5$  V sample bias,  $30$  pA tunnel current.

adopting a range of homomolecular hydrogen-bonding interactions, typically adopting a  $R^2_2(8)$  interaction between two imide groups<sup>12</sup> (Scheme 1, configuration **I**), but we have recently identified a threefold hydrogen-bonded vertex that can be adopted by such molecules<sup>11</sup> (Scheme 1, configuration **II** and Fig. 2b). DFT calculations have shown that such threefold interactions (configuration **II**) are more stable than corresponding bimolecular interactions (configuration **I**) observed for PTCDI species,<sup>11</sup>  $-0.78$  eV vs.  $-0.48$  eV (see ESI†). Interestingly, carboxylic acid $\cdots$ carboxylic acid  $R^2_2(8)$  (configuration **III**) and imide $\cdots$ carboxylic acid (configuration **IV**) interactions are calculated to give an additional  $-0.80$  or  $-0.61$  eV stabilisation, respectively, using the same parameters in the calculation. It is notable that DFT calculations indicate that of the competing interactions possible for compound **1**, configuration **III** affords the greatest additional stability, although the calculated values are similar in magnitude to those for the experimentally observed configuration **II**.

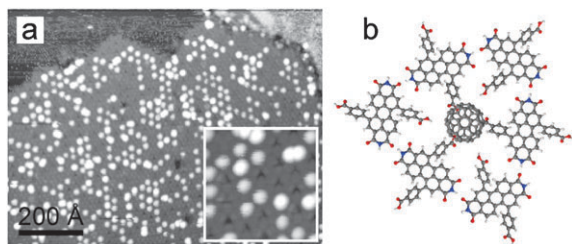
As a result of **1** adopting hydrogen-bonding configuration **II** the residual carboxylic acid groups protrude into the cavities of the framework significantly restricting the available space for guest species. Indeed it is also possible to distinguish the benzoic acid sidearms in the STM images (Fig. 2a), supporting the molecular model presented. Interestingly, geometry optimised calculations of a single molecule lead to two possible low-energy geometries differing in the manner that the benzoic acid sidearms



**Fig. 2** (a) High resolution, drift corrected, image of the arrangement. Imaging parameters  $+1.0$  V sample bias,  $100$  pA tunnel current. (b) Proposed trimer node corresponding to the region highlighted in (a). (c) Suggested molecular structure of the hexagonal network. Nodes designated A and B represent trimer nodes of alternating chirality. Unit cell vectors are shown in green and dashed triangles represent where the triangular cavities are observed. Grey hexagons represent the reconstructed  $\text{Ag-Si}(111)\sqrt{3} \times \sqrt{3}R30^\circ$  surface, with the center of the hexagons corresponding to silicon trimers.

protrude from the plane of the molecular core. We believe that the bright regions over the core of some molecules in the STM image in Fig. 2 could be related to the molecular configuration.

The ability of the network formed by **1** to act as a host for guest species was evaluated by investigating its ability to host  $C_{60}$  molecules. Networks formed by PTCDI derivatives, often in combination with melamine, have been shown previously to act as hosts for fullerenes with up to seven  $C_{60}$  molecules adopted within a single network pore.<sup>2-4</sup> In the current example the pore formed is significantly restricted due to the presence of the benzoic acid groups and as a result is expected to host small numbers of  $C_{60}$  molecules. Indeed it can be clearly seen (Fig. 2) that single molecules of  $C_{60}$  are hosted within each pore of the network (43%). Closer inspection of high resolution images indicates that some network cavities host two guest  $C_{60}$  molecules but the proportion of such doubly occupied cavities is low (7.5%) (for details of occupancy analysis see ESI†). Analysis of the  $C_{60}$  encapsulation in relation to the molecular configuration of the hydrogen-bonded network indicates that each  $C_{60}$  molecule overlap with three carboxylic acid groups



**Fig. 3** (a) STM image showing single  $C_{60}$  entrapment onto the molecular cavities. Inset, higher resolution image, note some cavities appear to host more than one  $C_{60}$  molecule. Tunneling parameters (both) +1.1 V sample bias, 0.03 nA tunneling current. (b) Proposed model for  $C_{60}$  encapsulation within the pore.

presumably sitting on the tripodal cup formed by these groups (Fig. 3). This is in contrast with previous  $C_{60}$  entrapment results where no overlapping between the host network cavities and guest species was observed. Adjacent  $C_{60}$  molecules are separated by a regular distance of 26 Å. Thus the network acts as a well-defined structure that has the potential to template the formation of regular two-dimensional arrays of individual fullerene molecules with well-defined spacings, a goal of fullerene-based approaches to quantum computing applications.<sup>16</sup>

In summary we have demonstrated the formation of a regular unimolecular hydrogen-bonded array in which imide...imide intermolecular interactions dominate the self-assembly process, over potentially competing carboxylic acid...carboxylic acid interactions. The resulting network forms unusual cavities that contain protruding carboxylic acid moieties defining the shape and size of the resulting pore for guest encapsulation. We are currently developing these strategies to tailor the host-guest properties of surface-based supramolecular networks.

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## Notes and references

† Synthesis and experimental conditions:  $N,N'$ -di[[(2,4-dibutoxy benzyl)-1,7-di(4-ethoxybenzoate)perylene-3,4,9,10-tetracarboxylic diimide] (2):  $N,N'$ -di[[(2,4-dibutoxy benzyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic diimide] (122 mg, 0.12 mmol) and CsF (72 mg, 0.47 mmol, 4 eq.) were added to a flame-dried flask. This was backfilled with  $N_2$  three times. Toluene (100 mL) was then added *via* cannula, and the reaction mixture was degassed with  $N_2$  for 20 minutes. The reaction was heated for at 70 °C 15 minutes under  $N_2$ . After this point, 4-ethoxycarbonylphenyl boronic acid (64 mg, 0.35 mmol, 3 eq.),  $Ag_2O$  (55 mg, 0.24 mmol, 2 eq.) and  $Pd(PPh_3)_4$  (20 mg, *ca.* 10 mol%) were added, the reaction temperature was increased to 80 °C and the mixture was heated for 24 h under  $N_2$ . The reaction was then cooled and the toluene removed *in vacuo*. The resulting purple residue was extracted from chloroform/water, dried with  $MgSO_4$  and evaporated to dryness. This was purified *via* column chromatography ( $SiO_2$ , 0–0.2% MeOH/ $CHCl_3$ ) to yield a dark purple powder (96 mg, 69% yield). The 1,7-isomer was isolated by recrystallisation from  $CH_2Cl_2/MeOH$ . MS (MALDI-TOF)  $m/z^+$ : 1154.5 (M);  $^1H$  NMR (400 MHz, chloroform- $d$ )  $\delta$ : 8.65 (s, 2H), 8.22–8.17 (m, 6H), 7.78 (d,  $^3J = 8.16$  Hz, 2H), 7.65 (d,  $^3J = 7.91$  Hz, 4H), 7.07 (d,  $^3J = 8.41$  Hz, 2H), 6.44 (s, 2H), 6.37 (d,  $^3J = 8.41$  Hz, 2H), 5.38 (s, 4H), 4.48 (q,  $^3J = 7.15$  Hz, 4H), 3.97 (t,  $^3J = 6.2$  Hz, 4H), 3.91 (t,  $^3J = 6.3$  Hz, 4H), 1.70–1.83 (m, 9H), 1.44–1.58 (m, 14H), 0.95 (q,  $^3J = 7.5$  Hz, 12H).  $^{13}C$  NMR (101 MHz, Chloroform- $d$ )  $\delta$ : 165.96, 163.23, 163.11, 159.62, 157.77, 146.46, 140.00, 134.98, 134.41, 132.65, 131.37, 130.65, 129.83, 129.16, 128.74, 127.91, 122.69, 122.38, 116.92, 104.47, 99.69, 67.90, 67.69, 61.38, 39.33, 31.37, 31.33, 19.38, 19.25, 14.37, 13.63, 13.84. CHN calculated: C 74.85%, H 6.11%, N 2.42%. Found: C 74.95%, H 6.16%, N 2.53%. 1,7-Di(4-benzoic acid)perylene-3,4,9,10-tetracarboxylic diimide: **2** (50 mg, 0.04 mmol) was dissolved in

toluene (50 mL) yielding a highly coloured pink solution. Methanesulfonic acid (5 mL) was added, and the mixture was heated at 110 °C overnight. During this time, all perylene-containing material was precipitated from the toluene, leaving a clear solution. This was then cooled and decanted, leaving a dark blue residue. This was then triturated with water and ethanol before being dried with  $N_2$  and under high vacuum, yielding a dark blue powder (25 mg, 90% yield) CHN calculated: C 72.38%, H 2.88%, N 4.44%; found: C 72.23%, H 2.76%, N 4.32%. MS (MALDI-TOF)  $m/z^+$ : 630.1 (M). The compound was found to be insoluble in all solvents to allow analysis by NMR spectroscopy. Surface deposition was performed by subliming **1**, at 445 °C for 20 min, onto the  $Ag-Si(111)\sqrt{3} \times \sqrt{3}R30^\circ$  surface under ultra-high vacuum (UHV).  $C_{60}$  was sublimed at 415 °C for 12 min onto the self-assembled array of **1**. Samples were not annealed following deposition. See ESI† for details of DFT calculations.

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