

# Directing two-dimensional molecular crystallization using guest templates†

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**The use of a coronene guest template directs the formation of a 2D Kagomé network in preference to alternative close packed and parallel hydrogen-bonded structures of tetracarboxylic acid tectons self-assembled from solution on a graphite surface.**

The exploitation of supramolecular chemistry for the controlled assembly of molecules has reached a level of maturity where the products of specific self-assembly processes can be predicted to a high level of accuracy in many cases.<sup>1,2</sup> In comparison to solution-phase self-assembly,<sup>1</sup> and to a lesser extent solid-state crystal engineering,<sup>2</sup> surface-based supramolecular chemistry is less well understood and has been receiving a great deal of attention over recent years.<sup>3</sup> Amongst the intermolecular interactions that have been used to facilitate controlled self-assembly processes on surfaces are hydrogen-bonding interactions.<sup>4</sup> Hydrogen-bonds represent versatile intermolecular interactions that can be designed into molecular building-blocks, or tectons, allowing the targeted design of specific self-assembled structures.

A recent study by Wuest and co-workers<sup>5</sup> elegantly illustrated the self-assembly of tetracarboxylic acid molecules on a highly oriented pyrolytic graphite (HOPG) surface following crystallization from heptanoic acid solutions. Imaging of the resultant structures by scanning tunneling microscopy (STM) reveals hydrogen-bonded framework structures that utilize inter-carboxylic acid hydrogen-bonding interactions. Two framework motifs are anticipated and observed, a so-called parallel network and a Kagomé network<sup>6</sup> (Scheme 1). The balance between the two polymorphic structural arrangements leads to frustrated 2D molecular crystallization.<sup>7</sup> Independently and in parallel to the studies by Wuest we have been investigating the assembly of related tetracarboxylic acid tectons. In this study we demonstrate an approach to overcome the crystallization frustration by the use of a guest templating molecule that significantly enhances the stability of the Kagomé network polymorph. The use of guest molecules to influence and to transform the structures of two-

dimensional surface networks has recently been demonstrated in networks that utilise alkyl-chain interdigitation for network formation.<sup>8</sup> However, our study illustrates that by judicious choice of guest molecule stronger intermolecular, network forming, interactions, in this instance hydrogen-bonds, can be controlled to direct two-dimensional network structures.

The tetracarboxylic acids **1** and **2** (Fig. 1(a) and (b), respectively) were prepared either by reported procedures (**1**)<sup>9</sup> or in the case of **2** via the Suzuki coupling of 2,6-dibromonaphthalene with diethyl isophthalate 5-boronic acid and subsequent hydrolysis (see ESI†). Both **1** and **2** form hydrogen-bonded arrays on the HOPG surface following deposition from a nonanoic or heptanoic acid solution. It can be seen that the structures formed by **1** (Fig. 1(c)) and **2** (Fig. 1(d)) differ in their hydrogen bonding arrangements and in forming two-dimensional sheet structures. The molecular arrangements for **1** and **2** vary in their respective hydrogen-bonding arrangements and can be interpreted in terms of the models illustrated in Fig. 2. Thus, **1** adopts the parallel structure observed previously for related tetracarboxylate molecules<sup>5</sup> with all four carboxylic acid groups of each molecule of **1** participating in double hydrogen-bonds. In contrast, **2** adopts a more close-packed structure (Scheme 1 and Fig. 2(b)), in which two carboxylic acid groups per molecule participate in intermolecular RCOOH...HOOCR double hydrogen-bonding interactions ( $R^2_2(8)$  graph set notation<sup>10</sup>), with the remaining carboxylic acid groups believed to adopt weaker OH...O or C-H...O interactions.

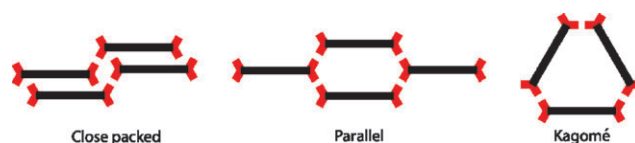
We have confirmed, using DFT calculations, that the proposed arrangements are stable and have lattice constants which are in excellent agreement with the values measured from our images (see ESI†).

In contrast to the study of Wuest and co-workers<sup>5</sup> our studies of **1** and **2** do not exhibit frustrated crystallization with no evidence for the formation of a Kagomé network. We were interested to investigate whether we could enhance the formation of the Kagomé network structure via the use of a guest species to act as a template for this structure. Thus, coronene was chosen as a guest molecule that was anticipated to act as a suitable template to favour the formation of the

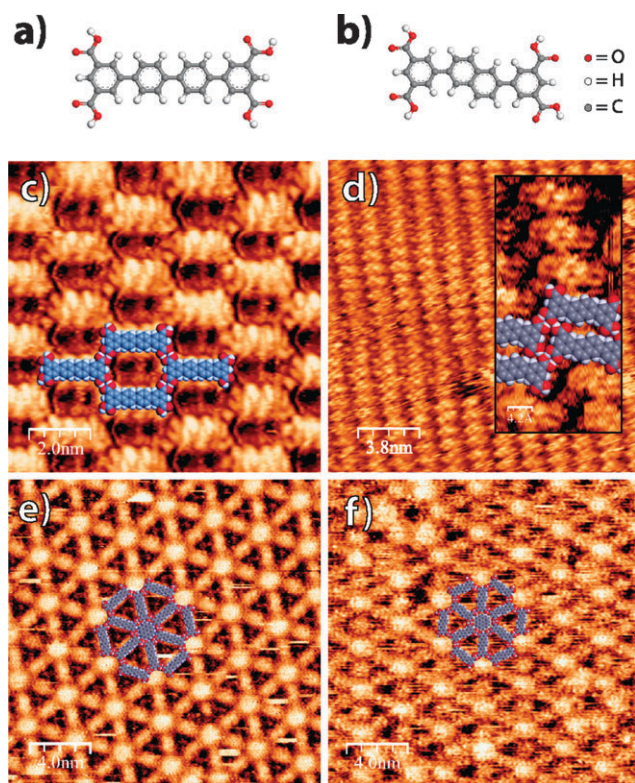
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Scheme 1

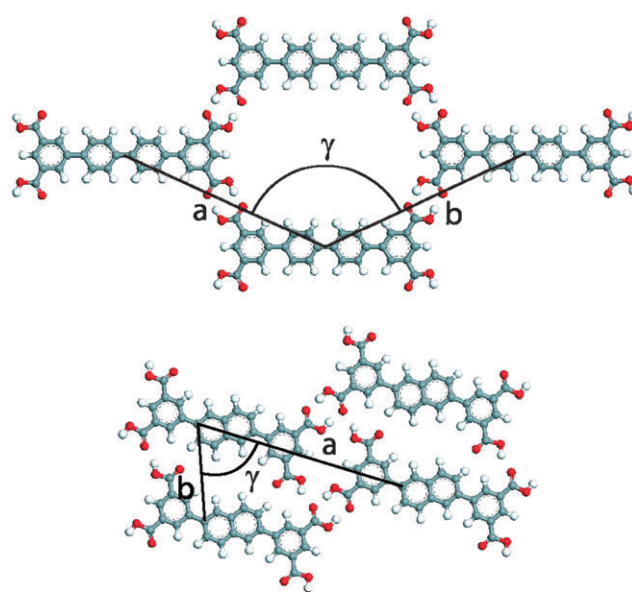


**Fig. 1** Tetracarboxylic acid tectons (a) **1** and (b) **2**. STM images of (c) **1** adsorbed on HOPG showing the parallel network structure and (d) **2** adopting a close-packed arrangement. Both molecules adopt a Kagomé network structure when co-adsorbed with coronene, (e) tecton **1**, (f) tecton **2**. Image dimensions and operation parameters: (c)  $100 \times 100 \text{ \AA}$ , +1.2 V, 100 pA; (d)  $190 \times 190 \text{ \AA}$ , -1.0 V, 200 pA (inset  $20 \times 40 \text{ \AA}$ ; -1.5 V, 300 pA); (e)  $200 \times 200 \text{ \AA}$ , +1.3 V, 5 pA; (f)  $200 \times 200 \text{ \AA}$ , +1.3 V, 5 pA. Schematic representations of compounds **1** or **2** overlaid to illustrate tecton arrangement.

Kagomé network (Scheme 1). The choice of coronene is based upon previous studies that have demonstrated that coronene is of a suitable size and shape to fit within the circular pores that can be formed by isophthalate moieties, such as those formed by trimesic acid,<sup>11</sup> extended isophthalate functionalised molecules<sup>12</sup> and related molecules.<sup>13</sup> Thus the addition of coronene as a template molecule was anticipated to favour the formation of the Kagomé network in the case of **1** and **2**.

Coronene was added to nonanoic acid solutions of **1** or **2** prior to surface deposition on a HOPG surface. STM images of the resulting structures confirm the formation of the Kagomé network structure for both **1** (Fig. 1(e)) and **2** (Fig. 1(f)) with coronene sitting in the circular hexa-isophthalate node of each framework. The networks have measured periods of  $3.2 \pm 0.2 \text{ nm}$  (**1**) and  $2.9 \pm 0.2 \text{ nm}$  (**2**). Following addition of coronene to the deposition solutions there is no evidence for the formation of the parallel or close-packed networks. Indeed only the Kagomé network, with co-adsorbed coronene, is observed on the surface. These images clearly demonstrate the successful use of a guest template in pre-determining the formation of a network arrangement that is less stable in the absence of the guest molecule.<sup>8</sup>

In the case of molecule **2** two enantiomorphic arrangements can be adopted by the molecule upon surface adsorption.



Unit cell parameters	Molecule 1 : parallel		Molecule 2: close packed	
	STM	DFT	STM	DFT
a	$2.0 \pm 0.1 \text{ nm}$	$1.97 \pm 0.01 \text{ nm}$	$2.0 \pm 0.1 \text{ nm}$	$1.95 \pm 0.1 \text{ nm}$
b	$2.0 \pm 0.1 \text{ nm}$	$1.97 \pm 0.01 \text{ nm}$	$0.9 \pm 0.1 \text{ nm}$	$0.90 \pm 0.1 \text{ nm}$
$\gamma$	$130^\circ \pm 1^\circ$	$130.1^\circ \pm 0.1^\circ$	$70^\circ \pm 1^\circ$	$68.9^\circ \pm 1^\circ$

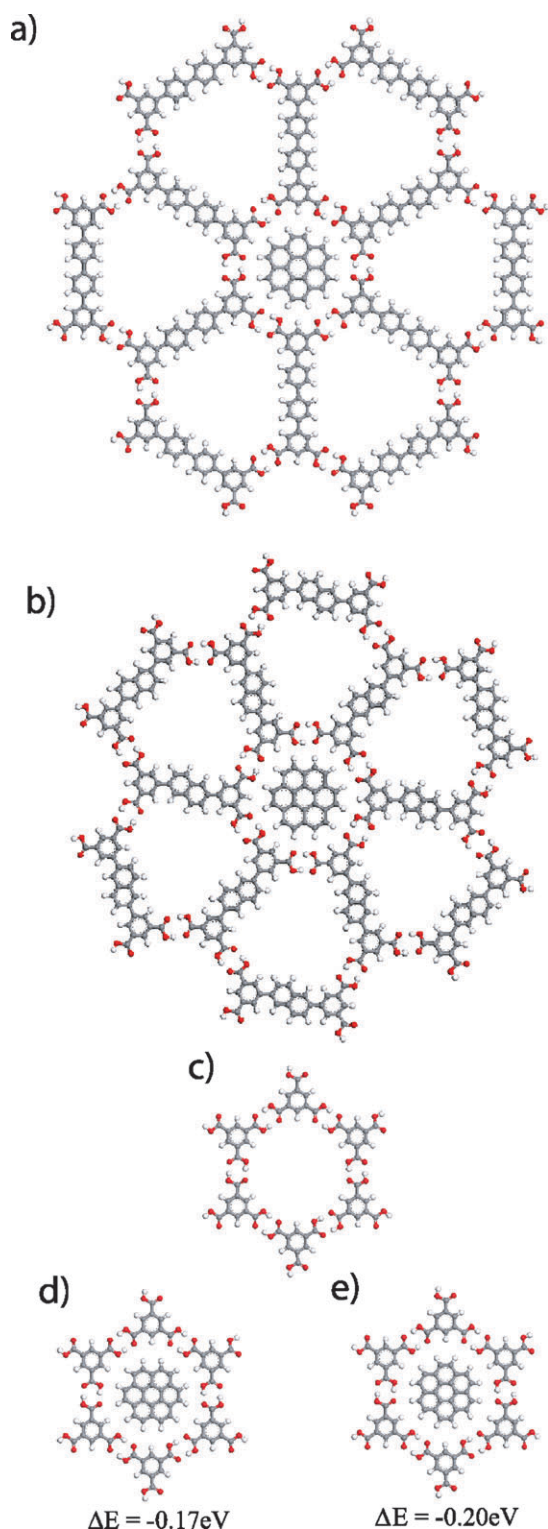
**Fig. 2** Schematic representations of the supramolecular arrangement observed for tecton **1** parallel network (above) and tecton **2** close-packed arrangement (below) with both measured and calculated unit cell parameters.

Although we cannot resolve the enantiomorphs from the STM images, simple geometric requirements mean that within a given Kagomé network all of the molecules of **2** must adopt the same enantiomorph. It is reasonable to conclude that both enantiomorphs are present on the surface in different chiral domains.

A model for the experimentally observed stabilization of coronene within the Kagomé network is shown in Fig. 3(a), (b). The stabilisation of the hexa-isophthalate node by the inclusion of a guest coronene molecule is supported by DFT calculations. Modeling of the Kagomé network hexa-isophthalate node using trimesic acid as a representative molecule to form this node, Fig. 3(c), gives an energy gain of -0.17 or -0.20 eV per coronene molecule depending on molecular orientation (Fig. 3(d), (e), see ESI†) and a theoretical estimate for the period of the network shown in Fig. 3(a), (b) of  $3.1 \pm 0.01 \text{ nm}$  ( $3.0 \pm 0.01 \text{ nm}$  for network formed from **2**) which is in excellent agreement with measured values. The stabilisation of the hexa-isophthalate node by coronene is clearly important in favouring the formation of the Kagomé network instead of other network arrangements. The calculation reported here does not assess the overall stabilisation of the whole Kagomé network as other factors, including surface/adsorbate and van der Waals interactions as well as solvent effects, are not taken into account. However, agreement between the reported calculations and the experimental results clearly confirm the value of this simple theoretical approach.

In summary we have demonstrated the successful application of a templating approach to surface-based crystallization by the use of a suitably designed guest molecule, coronene,





**Fig. 3** Schematic representations of the Kagomé network supramolecular arrangements observed with coronene positioned in the circular hexa-isophthalate sub-unit: (a) tecton **1**; (b) tecton **2**; (c) the circular hexa-isophthalate sub-unit observed with trimesic acid used in DFT calculations; (d), (e) the two orientations of coronene positioned within the circular hexa-isophthalate sub-unit observed with trimesic acid, similarly used in DFT calculations.

which significantly enhances the stability of one network arrangement, the Kagomé network, over another, the parallel network. We are currently developing these studies to other network types and guest species to further elaborate the tecton-based supramolecular approach to surface-based self-assembly.

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