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Self-assembled two-dimensional hexagonal networks

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A new compound, 1,3,5-tris(carboxymethoxy)benzene, which forms infinite two-dimensional hexagonal networks, has been synthesized. Its self-assembly behavior at gas–solid interfaces has been studied by scanning tunneling microscopy.

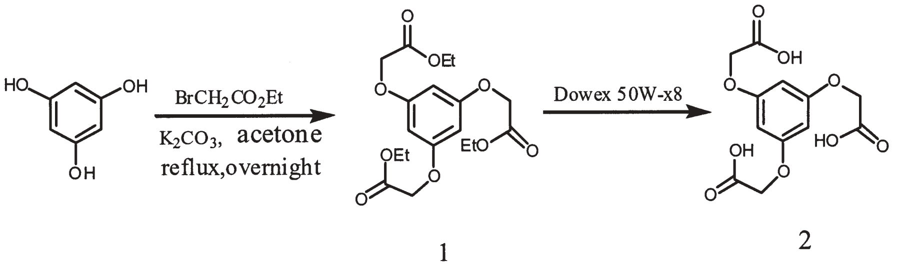
Supramolecular structures formed by the self-assembly of functional molecular building blocks are a promising class of materials for future technologies.[1–3] Particularly useful for their fabrication is hydrogen bonding,[4] which provides both high selectivity and directionality.[5] Among the various types of supramolecular structures, the hydrogen-bonded 2D hexagonal network formed by trimesic acid (1,3,5-benzene tricarboxylic acid, H_3TMA) is well known.[6] Early works were focused upon TMA itself and generated a large number of inclusion compounds, both with and without catenation.[7,8] That carboxylic acids can form homo- or heterodimers with a variety of complementary functional groups (*e.g.* pyridines, 2-aminopyridines, and pyrimidines) has allowed functionalized TMA,[9] its deprotonated forms,[10] and its metal complexes[11,12] to be exploited as templates in crystal engineering studies. Besides, TMA and many other molecules form host–guest systems,[13,14] which are of great significance in supramolecular chemistry and crystal engineering.

As is the case for TMA itself, inclusion compounds and host–guest systems containing TMA have been extensively studied; it is now of interest to further explore other molecules that have similar structures to TMA and behave like TMA. These molecules could then provide new hydrogen-bonded supramolecular synthons, which are the primary tools for crystal engineering, and, thus, provide alternatives to TMA. Here, we report the synthesis of 1,3,5-tris(carboxymethoxy)benzene (TCMB), which, like TMA, also possesses trigonal exodentate functionality that facilitates self-assembly in two dimensions.

While in supramolecular chemistry, host–guest complexes have mainly been investigated in solution and as bulk crystals, it is not always necessary to build three-dimensional structures. For potential technical applications, such as heterogenic catalysis, molecular electronics, organic network templates for structuring metal nano-assemblies, or biomolecules in sensor devices, only the surface is of interest. On the surface, ultrathin organic layers, such as self-assembling and Langmuir–Blodgett films are constructed. These films represent a novel class of materials with potential applications in advanced optical and electronic systems.[15,16] Recently, a lot of hydrogen-bonded systems which form 3D crystal structures have been assembled on solid supports to form highly stable 2D crystal structures which can be visualized by scanning tunneling microscopy (STM). STM is a powerful tool in the area of surface and interface analysis due to its ultrahigh resolution and adaptability to various environments. Organic species of all types, from benzene to polymers, have been characterized by STM.[17] It is of interest to determine whether the 2D structure of films resembles the intralayer alignment in the bulk 3D crystal.[18–20] A study of the adsorption of TMA to a single crystal graphite surface under ultra high vacuum conditions revealed that there are two coexisting phases that could be imaged with sub-molecular resolution by STM.[20] One of the two structures is composed of sixfold rings of TMA molecules with perfect arrangement of the hydrogen bonds, which is in agreement with the intralayer alignment in the 3D crystal. To date, we have not managed to obtain a single crystal of TCMB, but high resolution STM images show that it also forms hexagonal networks in the 2D crystal.

The synthetic route to the designed molecule, TCMB, is shown in Scheme 1. All chemicals used were purchased from Acros and used without further purification.

1,3,5-Tris(ethoxycarbonylmethoxy)benzene (**1**) was synthesized as follows: ethylbromoacetate (26.7 g, 0.16 mol) was slowly added to a stirred mixture of anhydrous potassium carbonate (22.1 g, 0.16 mol) in 500 ml acetone at room temperature. Next, anhydrous phloroglucinol (5.04 g, 0.04 mol) in 100 ml of acetone was added dropwise over a period of 1 h. After addition, the mixture was refluxed overnight. The salts formed were removed by filtration and the solvent volume was reduced by rotary evaporation. After cooling to room temperature, the solution yielded **1** as a yellowish solid, which was recrystallized from ethanol to provide colorless crystals. Yield: 10.7 g (70%). Mp 65–66 °C. ^1H NMR (300 MHz, $CDCl_3$): δ



Scheme 1

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1.30 (t, 9H, $J = 7.2$ Hz), 4.28 (m, 6H, $J = 7.2$ Hz), 4.55 (s, 6H), 6.13 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 168.5, 159.6, 95.1, 65.3, 61.4, 14.1. FT-IR (KBr) ν/cm^{-1}: 1749, 1607, 1219, 1159, 1091, 1035. EI-MS m/z: 384 (M^+). Elemental analysis for $C_{18}H_{24}O_9$ (M_w 384.3) found (calc.): C 56.53 (56.22), H 6.57 (6.30)%.

1,3,5-Tris(carboxymethoxy)benzene (**2**) was prepared as follows: compound **1** (5 g, 0.013 mol) was refluxed in water with 0.8 g. of Dowex 50 W-x8 (H^+ form). The ethanol formed upon hydrolysis was distilled as the azeotrope in order to drive the reaction to completion, thus forming the triacid **2**. After 8 h of reflux, the mixture was filtered to remove the resin. Upon cooling, the triacid solidified and was recrystallized from hot water. Yield: 3.6 g. (92%). Mp 285-287 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 4.67 (s, 6H), 6.13 (s, 3H). ^{13}C NMR (300 MHz, DMSO-d$_6$): δ 170.4, 159.8, 94.7, 65.0. FT-IR (KBr) ν/cm^{-1}: 3200–2500, 1748, 1714, 1602, 1233, 1175. FAB-MS(−ve) m/z: 299 ($[M - H]^-$). Elemental analysis for $C_{12}H_{12}O_9$ (M_w 300.2) found (calc.): C 52.67 (52.61), H 5.60 (5.30)%.

The solvent used in the STM experiments is a mixture of toluene (HPLC grade, Aldrich) and ethanol (A.C., Aldrich). The concentrations of all the solutions used are less than 1 mM. Samples were prepared by depositing a drop of the above solution on freshly cleaved highly oriented pyrolytic graphite (HOPG). Experiments were performed with a Nanoscope IIIA system (Digital Instruments, Santa Barbara, CA, USA) operating under ambient conditions. STM tips were mechanically firmed 90% Pt–10% Ir wires. All the STM images were recorded using the constant current mode of operation. The specific tunneling conditions are given in the figure captions.

Presented in Fig. 1(a) is a large scale STM image of TCMB molecules adsorbed on a HOPG surface over a scan area of 66 × 66 nm^2. The image illustrates that the TCMB molecules, appearing as bright spots with 6-fold symmetry, form a well-ordered two-dimensional array. Fig. 1(b) is a high resolution image of TCMB. The diameters of the hexagonal cavities are 1.9 ± 0.1 nm, compared to 1.5 ± 0.1 nm of TMA.[20] In the top right corner of Fig. 1(b), a model (constructed using Hyperchem software[21]) of four self-assembled rings composed of 16 molecules of TCMB is superposed on the STM image. The model and the image fit well. The blue hexagon at the bottom of Fig. 1(b) represents a unit cell, with a lattice constant of 1.1 ± 0.1 nm. Fig. 2 shows a schematic picture of TCMB hexagonal networks formed by hydrogen bonding. On the left is a molecular model proposed on the basis of STM observation using Hyperchem software; the model includes seven cavities. On the right is a molecular model constructed with ChemDraw Ultra[22] which shows how a hexagonal cavity is formed by the linking of six molecules in a circular pattern *via* hydrogen bonding. Each molecule is cooperatively connected by three cavities.

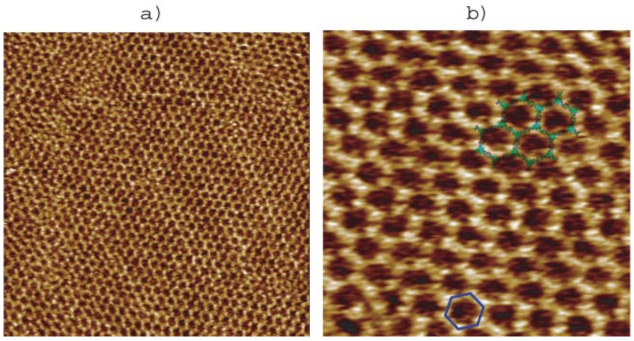

Fig. 1 (a) STM image (66 × 66 nm^2) of a self-assembled monolayer of TCMB on a HOPG surface. The imaging conditions are $I = 877$ pA and $V = 641$ mV. The z-axis is 0.5 nm. (b) A higher resolution STM image (19 × 19 nm^2) of TCMB. The imaging conditions are $I = 766$ pA and $V = 341$ mV. The z-axis is 0.5 nm.

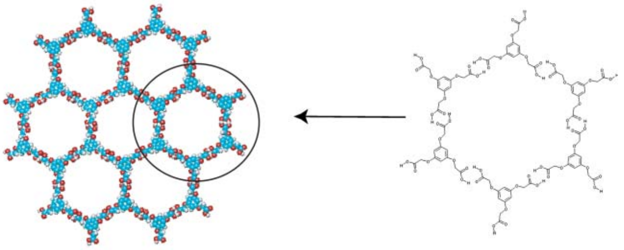

Fig. 2 Simulated molecular model representing the assembly structure of TCMB.

Due to the thermally activated diffusional motion of the molecules on the inert substrate at room temperature, most STM studies of organic molecules on graphite under ambient conditions are focused upon long chain alkyl-substituted molecules.[23] To the best of our knowledge, TCMB is one of the smallest organic molecules that has been imaged by STM on graphite under ambient conditions without using the matrix molecule coadsorption method. This shows that the strength of the hydrogen-bonding between the TCMB molecules on graphite is strong enough to support the two-dimensional networks.

Attempts were also made to obtain STM images of TMA. Maybe due to the lack of flexibility in its structure, we failed to obtain any images of well-ordered arrays of TMA on graphite.

In summary, it is illustrated that TCMB can form 2D hexagonal networks. Furthermore, because TCMB has longer chains than TMA, it seems likely that its structure is more flexible than that of TMA, which may mean that TCMB will form host–guest systems more easily.

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