

Self-Assembly of Trimesic Acid at the Liquid–Solid Interface—a Study of Solvent-Induced Polymorphism

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A scanning tunneling microscope operated under ambient conditions was utilized to study the self-assembly of trimesic acid (TMA) at the liquid–solid interface. On a graphite substrate, two different open, loosely packed, two-dimensional hydrogen-bond networks were found. Both structures exhibit a periodic arrangement of ~ 1.0 nm wide cavities, which can be used for the co-adsorption of another species (guest) within the cells of this host system. These two polymorphs (“chickenwire” and “flower” structures) differ in their molecular packing density and hydrogen-bonding schemes. Using a homologous series of alkanolic acids as solvents, ranging from butyric to nonanoic, selective self-assembly of either the “flower” or “chickenwire” forms was achieved on a graphite surface. Solubility of TMA in these acid solvents was found to decrease with increasing chain length, and the longer-chain solvents favored formation of the chickenwire polymorph structure on the surface.

Introduction

Self-assembly of organic molecules is a widely discussed issue in current nanotechnology as it is believed to be an appropriate approach for efficient production of future molecule-based devices such as sensors and circuits. Many novel adsorbate–substrate systems are known to exhibit a high degree of order on a large scale, and scanning tunneling microscopy (STM) has proven its capability for investigations of submolecularly resolved structural and electronic properties.^{1–5} For some systems, hydrogen bonding is the predominant interaction between molecules and governs the self-assembly.^{6–13} Using the selectivity and directionality of hydrogen bonding to tailor nanostructures by specific design of building blocks based on these forces is, thus, very appealing.

Among self-assembled systems, open (loosely packed) structures are of current interest as host–guest systems exhibiting a periodic arrangement of voids that are capable of incorporating suitable species in otherwise equivalent cells.^{14,15} Trimesic acid (TMA), with its 3-fold symmetrically disposed carboxyl groups, is an excellent building block for such host–guest systems. In a low-temperature STM study under UHV conditions, TMA was shown to form two-dimensional hydrogen-bond host–guest systems on the basal plane of graphite with cavity diameters around 1.0 nm.¹⁶ Two different coexisting crystallographic phases—a “flower” structure and a “chickenwire” structure—were observed. On Cu(001), due to strong adsorbate–substrate interactions, a slightly distorted TMA chickenwire structure was found,¹⁷ and no large domains could be grown. Chickenwire packing is found in the bulk crystal structure where interpenetration of different TMA molecular planes leads to dense packing.^{18,19}

Co-deposition of TMA and iron atoms has also been observed on Cu(001) leading to the formation of chiral organo-metallic complexes consisting of four TMA molecules and one iron atom.²⁰ An electrochemical STM study of TMA on Au(111) revealed the formation of the chickenwire structure under suitable potential conditions.²¹ Additionally, altering of the potential conditions causes a transition to a densely packed structure.

The molecule 1,3,5-tris(carboxymethoxy)benzene, which has a structure similar to that of TMA, has carboxy-

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terminated side groups with increased length. Large ordered domains of this molecule have been grown on highly oriented pyrolytic graphite (HOPG) and imaged by STM under ambient conditions.²² As in the case of TMA, the system is not densely packed and can be considered to be a host–guest system with enlarged cavities.

The existence of both chickenwire and flower structures for TMA is an example of polymorphism, the observation of different crystalline forms of a given substance, a topic of some interest, particularly in the pharmaceutical industry. Control of the final solid state form of a manufactured drug is considered one of the ways to ensure its purity and to guarantee uniformity of properties.^{23–26} Techniques for achieving crystallization of a single polymorph are, thus, important and a topic of active research. For example, Matzger and co-workers have recently reported control of acetaminophen and carbamazepine crystal growth through the use of a library of polymer surfaces employed to heteroseed precipitation.²⁶ When crystallized from water solutions, acetaminophen forms either the thermodynamically stable monoclinic form, the less stable orthorhombic crystals, or a mixture of both polymorphs depending on the polymer used for seeding.

Polymorphism in two-dimensional surface adsorbate monolayer films (2-D crystal structures) has also recently attracted considerable attention.^{27–29} Because of their reduced dimensionality, 2-D systems provide an attractive, simplified venue in which to delineate the intermolecular driving forces for polymorphism.²² Furthermore, controlling the arrangement of molecules in a self-assembled monolayer film is obviously of significant interest in the development of any molecular-level mechanical or electronic devices and is, thus, of importance in the field of nanotechnology. Indeed the “Holy Grail” in both 2-D and 3-D crystallization is complete control of the structure of films or crystals via simple physical manipulation of temperature, pressure, surface structure, or solvent character.

Spontaneous formation of highly ordered molecular monolayers at the liquid–solid interface allows for quick and straightforward sample preparation and the study of solvent effects on self-assembly and 2-D polymorphism. In many cases, STM has proven to be a powerful technique for the investigation of these molecular films in equilibrium with the liquid phase. For example, systematic alteration of functional groups of alkanes provides insight into the ordering behavior of these compounds.^{30,31} Using STM “chemical marker groups” also helps to reveal the influence of chirality³² or chain length³³ on the interfacial self-assembly. In this paper, self-assembled TMA monolayers are investigated at the interface between the (0001) basal plane of HOPG and solutions of TMA in a homologous series of alkanolic acids (butyric to nonanoic). Depending

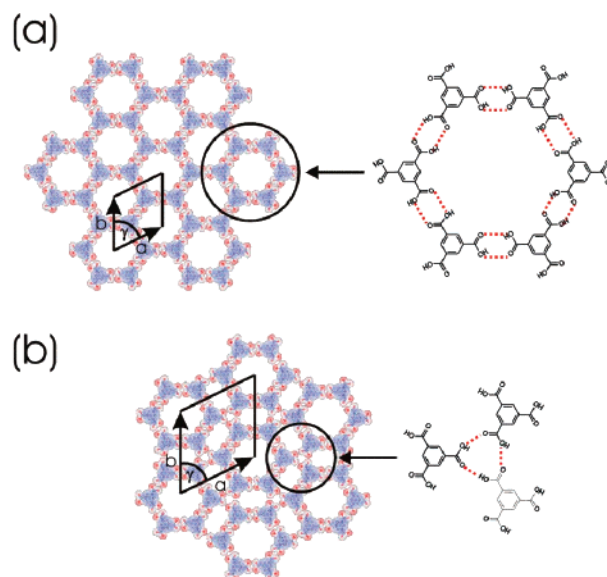


Figure 1. Models of the different crystallographic structures found with their corresponding hydrogen-bonding scheme: (a) chickenwire structure, $a = b = 1.7$ nm, $\gamma = 60^\circ$, area = 2.5 nm², 2 molecules per unit cell (b) flower structure, $a = b = 2.5$ nm, $\gamma = 60^\circ$, area = 5.4 nm², 6 molecules per unit cell.

on the solvent used, two different structures, similar to those already found earlier for evaporated films of TMA under UHV conditions,¹⁶ were observed. Solvent is the controlling factor in determining the self-assembly patterns, which are themselves polymorphic forms of TMA in a 2-D crystallization space.

Experimental Section

All experiments were conducted under ambient conditions at room temperature. Samples were prepared by depositing ~ 10 μ L of nearly saturated solution on the freshly cleaved basal plane of HOPG. Except for butyric acid, no significant leakage current could be detected for the solvents used. The vapor pressure of pentanoic acid and higher-chain length acids is sufficiently low to allow stable imaging for at least 30 min. STM tips were mechanically cut from a PtRh wire and used without insulation. Best imaging results were obtained for sample biases ranging from -1.0 to -1.5 V (sample negative) and tunneling current setpoints from 50 to 300 pA. Occasionally, short voltage pulses (sample bias $+1.5$ to $+5.0$ V) were applied for reconditioning of the tunneling tip. No general dependence of the images on the tunneling parameters could be detected. All topographs were taken in the constant current mode of operation and have been mean filtered for noise reduction.

In addition to the STM experiments, the solubility of TMA in the alkanolic acids was determined by measuring the volume of solvent needed to dissolve a fixed amount of TMA. The amount of TMA was chosen so that approximately 75 mL of solvent were necessary to just dissolve the solute. These measurements allow the dependence of TMA solubility on the chain length of the acid solvents to be roughly evaluated. The solubility measurements were conducted twice, and the results agreed within experimental error.

Results and Discussion

Although the interaction between a single TMA molecule and the graphite surface is not particularly strong, intermolecular hydrogen bonding stabilizes the TMA network, thereby allowing STM studies even at room temperature. In these experiments, both of the crystallographic structures known from the earlier UHV investigations¹⁶ were found, depending on the solvent used. Space-filling models of the two different hydrogen bond networks are depicted in Figure 1a and b. For heptanoic,

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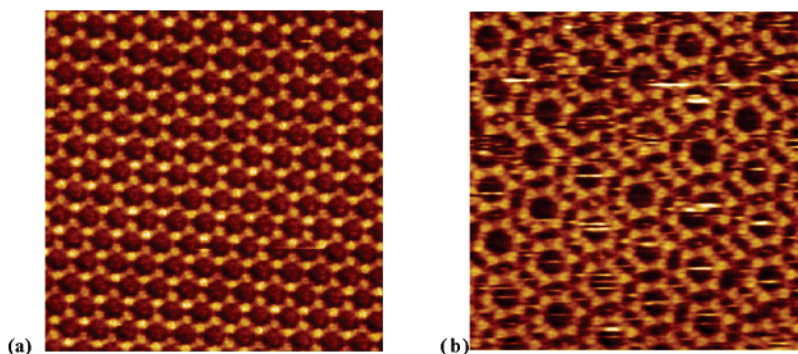


Figure 2. (a) $15 \times 15 \text{ nm}^2$ constant current STM image of a TMA monolayer at the interface between HOPG and a saturated solution of TMA in heptanoic acid ($\text{CH}_3(\text{CH}_2)_5\text{COOH}$), where TMA assembles in the chickenwire structure. (b) $15 \times 15 \text{ nm}^2$ constant current STM image of a TMA monolayer at the interface between HOPG and a saturated solution of TMA in pentanoic acid ($\text{CH}_3(\text{CH}_2)_3\text{COOH}$), where TMA assembles in the flower structure.

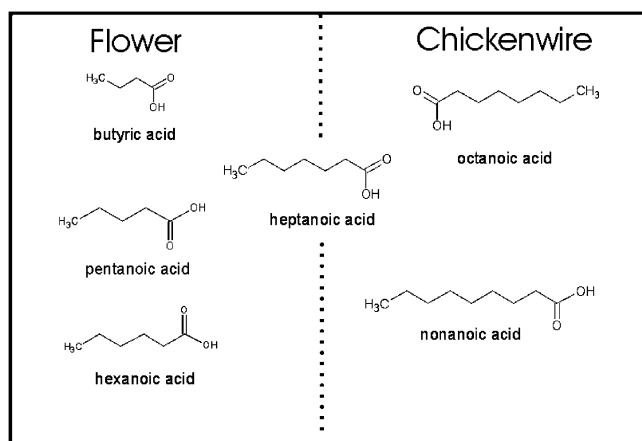


Figure 3. Overview showing the relation between TMA structure at the interface and solvent identity. In the case of heptanoic acid, both structures were observed, sometimes, co-existing.

octanoic, and nonanoic acid, the chickenwire structure was found. Figure 2a shows a molecularly resolved STM image of TMA in heptanoic acid, and Figure 1a shows the corresponding model. For saturated solutions of butyric, pentanoic, and hexanoic acid, the flower structure was successfully imaged. Figure 2b shows an STM topograph of TMA dissolved in pentanoic acid, and Figure 1b shows the corresponding model. In the case of heptanoic acid, indications of the coexistence of both structures were found, but no high-resolution images of domain boundaries could be obtained. Occasionally, the pure flower structure was observed as well with heptanoic acid. An overview showing the dependence of the observed structure on the solvents used is presented in Figure 3.

As pointed out previously, in both structures, all carboxyl groups participate in the hydrogen bonding, resulting in unstrained networks.¹⁶ The main difference is that hydrogen bonding occurs only between molecular pairs for the chickenwire structure, whereas for the flower structure, one-third of all hydrogen bonds involve three molecules, resulting in a circular hydrogen-bonding scheme. A comparable circular hydrogen-bonding mechanism among four carboxyl groups has also been suggested for tetracarboxyl-phenylporphyrins on graphite.³⁴ The two TMA polymorphs exhibit a 30% difference in molecular area density, $\rho_{\text{ch}} = 0.80 \text{ molecules/nm}^2$ for the chickenwire and $\rho_{\text{fl}} = 1.1 \text{ molecules/nm}^2$ for the flower structure,

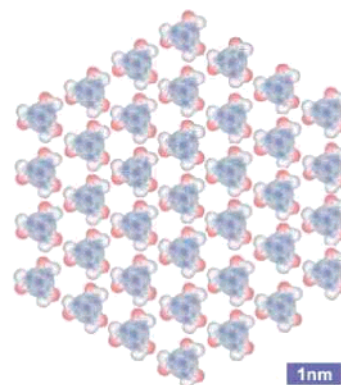


Figure 4. Possible densely packed 2-D TMA polymorph, based purely on 3-fold hydrogen bonding (“super flower structure”), not observed in the present study.

respectively. These values were determined by measuring the distance between the large circular voids, which allows for a unique calculation of the molecular densities based on the unit cells shown in Figure 1a and b. On the basis of the Principle of Closest Packing,^{35,36} the higher density of the 2-D flower structure suggests that it should be the most stable of the two polymorphs on the surface. (This assumes that a principle enunciated for three-dimensional crystals with weakly interacting building blocks also holds for hydrogen-bonded 2-D moieties.) It is worth noting that an even more densely packed TMA structure could conceivably be formed from a purely 3-fold hydrogen-bonded structure (“super flower structure”, see Figure 4), but this TMA form has not been observed in the present study.

Both structures show a hexagonal arrangement of circular voids with a diameter of approximately 1.0 nm. In the flower structure, these large circular cavities are surrounded by six elongated small voids. This results in a significant difference in the center-to-center distance between neighboring circular cavities, 1.7 nm for the chickenwire versus 2.5 nm for the flower structure, as indicated in Figure 1a and b. This huge difference can be utilized to identify either the chickenwire or the flower structure, even if good resolution of the voids cannot be obtained. For instance, in the case of butyric acid, imaging was more difficult because of the rather high vapor pressure of the solvent and the aforementioned STM offset current.

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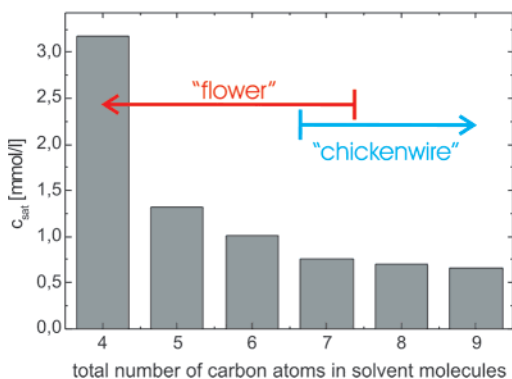


Figure 5. Solubility of TMA in alkanolic acids as determined by simple volumetric measurements. The saturation concentration decreases monotonically with increasing alkane tail chain length. Arrows show the TMA interface structure observed with each solvent.

Simple concentration measurements, as described previously, were conducted in order to estimate the solubility of TMA in each solvent. The results, depicted in Figure 5, show that for decreasing chain length of the alkanolic acid, the solubility of TMA increases. Thus, observed 2-D polymorph structures also correlate with changes in TMA solubility in the solution phase above the interface.

The observation of polymorphism driven only by solvent identity in this relatively simple system is quite interesting. Generally, polymorphism arises when one “crystalline” form of a species is more thermodynamically stable than the other, but the less stable form is kinetically favored. Normally, for 3-D systems in which multiple crystalline forms are observed, the differences in total free energy among the polymorphs are rather small and the less stable form can achieve a metastable phase or state. Under the right conditions, this less stable moiety will form first but ultimately reverts to the more stable polymorph.^{20,31}

We consider here two possible mechanisms for the observed solvent induced polymorphism: (1) stabilization of a specific basic precursor seed unit in solution (e.g., TMA dimer vs trimer) by a particular solvent, favoring either the chickenwire or flower structure; (2) solvent coadsorption and/or stabilization of the polymorph structures on the surface itself. Note that the essential unit of the chickenwire structure (Figure 1a) is a hydrogen-bonded dimer of TMA, while the flower structure has a TMA trimer as its basic unit. It is reasonable to speculate that the formation of these respective polymorphic films begins, respectively, with a dimer or trimer moiety landing on the surface followed by addition of TMA monomer to complete the surface structure. While seeding could be followed by addition of dimers and trimers to these initial adsorbate structures, the relatively high concentration of monomer in solution makes it the most likely candidate for growth of the interfacial film.

To produce the results observed here, short-chain carboxylic acids would then have to preferentially stabilize the trimer (Figure 1b), leading to a higher concentration of this species in solution and a more likely seeding event for the flower structure. This explanation is consistent with Ostwald’s Rule of Stages and the idea that the seeding event for formation of 3-D crystal polymorphs takes place in solution.^{25,37} Clearly, the nucleation kinetics for long- and short-chain solvent molecules interacting with TMA need not be the same. Solvation of the TMA likely involves

the formation of a hydrogen-bonded solvent–solute complex, whose stability can be expected to depend on the solvent’s acid ionization constant and the length of the hydrophobic hydrocarbon solvent chain. For the homologous series of solvent fatty acids studied here (butyric to nonanoic), the acid strength is almost independent of chain length. Thus, if solution stabilization of seed precursors is involved in the 2-D polymorphism observed in the present experiments, the solvation effects of the hydrophobic hydrocarbon tail are likely important in differentiating flower and chickenwire structures.

Though no evidence was found in the present study for transformation between the (presumably) less stable chickenwire structure and the flower structure (except in the case of heptanoic acid where both species were found on the surface), it is well known that polymorph transformation can take an exceedingly long time and hence cannot be ruled out for this system. If solvent stabilization of the trimer precursor is the controlling factor for formation of the flower structure in this system, kinetics must necessarily favor formation of the dimer precursors for the longer solvents. This is not surprising as dimer formation can be expected to proceed more expeditiously than trimer formation just on the basis of the probability of two versus three molecule encounters in solution. How or why this rate depends on the length of the hydrocarbon tail of the solvent is not yet clear; nevertheless, the dimer and trimer precursors in solution must certainly be in equilibrium with each other through encounters with monomer molecules. $[(TMA)_2 + TMA \rightarrow (TMA)_3]$ The shorter solvent molecules presumably shift this equilibrium to the right by stabilizing the trimer (or conceivably destabilizing the dimer). TMA is more soluble in short chain compared to long-chain solvents (see Figure 5); therefore, in the experiments described here (conducted in all cases with near-saturated TMA solutions) the shorter-chain solvent solutions have a higher TMA monomer concentration. Thus, the Law of Mass Action predicts a shift in the dimer/trimer equilibrium to favor the trimer for solvents with short chains. In addition, the rate of formation of trimers from encounters between dimers and monomers is likely to be more rapid in low-viscosity, short-chain solvents. This will also shift the equilibrium toward the trimer for these solvents, assuming (as seems likely) that trimer decomposition is independent of viscosity.

For 2-D crystallization, at least one additional scenario for control of the two polymorphic structures must also be considered when the film on the surface is in continuous contact with solvent, as is the case here. In such a situation, the solvent may actually stabilize the monolayer surface structure since it is in constant contact with the surface film, e.g., through co-adsorption of solvent molecules. If this happens, different solvents could stabilize different polymorphs, in which case, the observed structures might represent the thermodynamically most stable form in all situations. Of course, because of the large volume-to-surface ratio for 3-D crystals, such an effect is highly unlikely to be important for macroscopic crystals. Nevertheless, for 2-D monolayers, this mechanism cannot be completely ruled out in the present case because the entire “crystal” is fully exposed to solvent. Indeed, Hipps and co-workers, employing coronene as a solute and fatty acids as solvents, have just recently shown that solvent coadsorption can have a great impact on surface-adsorbed monolayer structures.³⁸ For this system on Au(111),

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alkanoic acids adsorb in an upright geometry surrounding coronene molecules lying flat on the surface. The driving force for this structure is most likely the increased adsorption energy of solvent molecules on a metallic substrate.

One potential explanation for such a stabilization in the TMA case, which might depend on the length of the solvent molecule chain, can be found in the void area density on the surface, greater for the chickenwire structure, that can accommodate solvent molecules. Thermal desorption experiments reveal that the adsorption energy of alkane-like molecules on graphite increases almost linearly with chain length due to the close registry between the carbon backbone and the graphite lattice distances.^{39–41} Though no co-crystallization of solvent and TMA were observed in any of the chickenwire- or flower-producing solutions studied, rapid exchange of solvent between the solution and surface regions would not be detectable via STM because of the slow time scale of the instrumental measurement. Small solvent molecules would, in general, be expected to fill some of the smaller surface voids in the flower structure better than large solvent molecules, leading to stabilization of this surface moiety in the case of short-chain solvents. If this happens, it is possible that the most thermodynamically stable form of the surface monolayers changes with solvent identity, and the observed 2-D polymorphism does not result from a kinetic/thermodynamic competition in solution.

The observation of these same two polymorphs at the vacuum–solid interface suggests that the overall energies of the chickenwire and flower structures are at least close.¹⁶ However, under such conditions, equilibrium must necessarily be achieved through surface diffusion, which sheds little light on the role of possible solution precursor seed moieties or solvent stabilization of the surface structures. The flower structure was more likely to be observed in the vapor deposition, UHV study under conditions where the

rate of TMA monomer deposition was highest.⁴² This observation lends support to the concept discussed above that a trimer is the precursor for the flower species since the trimer will always be favored at high surface concentration, even in a vapor deposition experiment.

Conclusion

Self-assembly of a two-dimensional, loosely packed hydrogen-bond network of TMA at the liquid–solid interface has been observed using STM. Two different crystallographic 2-D phases of TMA were identified and selected by varying the solvent. Although the molecules are rather small, both structures are sufficiently stable to allow for investigation with STM, even under ambient conditions and without the experimental effort of additional immobilization by sample cooling. On the basis of the Principle of Closest Packing,^{35,36} the more dense “flower” structure is likely the most thermodynamically stable of the two monolayer polymorphs. Studies of these adsorbed polymorph structures for TMA dissolved in a series of acid solvents [$\text{CH}_3(\text{CH}_2)_n\text{COOH}$ with $n = 2–7$] show that the flower structure is favored for the shortest-chain solvents, which also correspond to those in which TMA has the highest solubility. A possible explanation for this variation in monolayer identity is the stabilization, in short chain solvents, of a TMA trimer [$(\text{TMA})_3$] solution-phase nucleation species, which is a likely precursor to the flower form of TMA; however, an explanation based on differential solvent stabilization of the surface monolayer flower and chickenwire structures cannot be ruled out.

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