Positional Selectivity of Reversible Azomethine Condensation Reactions at Solid/Liquid Interfaces Leading to Supramolecule Formation

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Abstract

We used *in situ* scanning tunneling microscopy to investigate the formation of two-dimensional supramolecules by means of reversible azomethine condensation reactions between aqueous 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TAPP) and terephthalaldehyde (TPA) or benzaldehyde (BA) at the solid/liquid interface of an iodine-modified Au(111) surface. A nanomesh and a close-packed array were formed by the reaction of TAPP with the dicarboxaldehyde. Formation of these structures was driven by Schiff base (azomethine) bonding and simultaneous self-assembly controlled by adsorption

and condensation equilibria. Surface cross coupling between TAPP and the monocarboxaldehyde (BA) formed highly ordered adlayers consisting solely of TAPP symmetrically disubstituted with two BA molecules attached at diagonally opposite corners. The position selectivity was achieved through simultaneous coupling reaction equilibria and the thermodynamic self-assembly.

Keywords

In situ scanning tunneling microscopy, Two-dimensional supramolecular assembly, Schiff base (azomethine) coupling, position-selective reaction

1. Introduction

The assembly of two-dimensional (2D) highly ordered molecular systems on well-defined surfaces can be visualized *in situ* by means of scanning tunneling microscopy (STM), and this technique has provided great insight into the thermodynamics of self-assembly processes. Molecular and supramolecular assemblies based on weak intermolecular interactions such as hydrogen bonding have been extensively studied,[1–6] and recently, there has been an increased focus on the preparation of 2D molecular systems based on metal–organic coordination and covalent bonding.[7,8] These systems are analogous to three-dimensional

Figure 1. (A) Azomethine formation and (B) chemical structures of building blocks used in this work.

porous molecular crystals such as metal–organic frameworks[9–11] and covalent organic frameworks.[12,13] The majority of studies have focused on the formation of 2D molecular assemblies under ultrahigh vacuum conditions on well-defined surfaces, and the formation of such assemblies at solid/liquid interfaces has met with only limited success. The use of covalent bond formation on surfaces under ultrahigh vacuum conditions by means of thermally initiated C–C couplings,[14–17] Ullmann couplings between aromatic halogen-terminated molecules,[18–21] esterification reactions between boronic acid and hydroxyl units,[22,23] and azomethine formation between primary amine and aldehyde units has also been reported.[24,25] In addition, simple thermal vapor approaches have been used to form massive 2D honeycomb structures composed of dehydrated boronic acids.[26–28]

We previously reported a solution-based method for preparation of extended π -conjugated polymeric nanoarchitectures in which the building blocks are held together *via* Schiff base bonds.[29–31] We have reported close-packed arrays of one-dimensional aromatic polymers and 2D macromolecular frameworks consisting of metal and metal-free porphyrins and aromatic linkage molecules at the interfaces between well-defined surfaces and aqueous solutions, and we studied the structures *in situ* by means of STM. Self-assembly of sophisticated covalent nanostructures is achieved by reversible polymerization under equilibrium conditions similar to those used for thermodynamic self-assembly based on noncovalent bonds, such as hydrogen bonds. Careful control of the solution conditions (e.g., reactant concentrations and pH) allows control over component adsorption and the condensation reaction equilibria. Solution-phase reactions can thus be limited compared with reactions that proceed on the substrate, where hydrophobic and chemically inert surfaces may control reactivity. A new method based on these principles has enabled the successive deposition of poly(azomethine) multilayers through chemical liquid deposition and

substrate-assisted polycondensation, where deposition of successive layers is achieved by tuning the reaction equilibrium.[32,33]

Here, we report an *in situ* STM investigation of 2D self-assembled adlayers formed by surface-selective “on-site” reversible azomethine condensation reactions between aqueous 5,10,15,20-tetrakis (4-aminophenyl)porphyrin (TAPP) and terephthalaldehyde (TPA) or benzaldehyde (BA) at the solid/liquid interface of an iodine-modified Au(111) surface (Figure 1). Supramolecular arrays formed from discrete azomethine products were compared with polymeric 2D covalent frameworks to evaluate reaction selectivity. Very recently, surface-assisted Ullmann coupling between 4,4''-dibromo-*m*-terphenyl molecules on Cu(111) under ultrahigh vacuum conditions has been reported with selectivity over the position of substitution.[34] Discrete macrocycle rings were the predominant products, and zig-zag oligophenylene chains were formed as minor products.

2. Material and methods

2.1 Chemicals

All chemicals were purchased from commercial suppliers and used without further purification.

2.2 Preparation of the reaction solutions.

TAPP (TCI, Tokyo, Japan) and TPA (95%; TCI) or BA (98%; Nacalai Tesque, Kyoto, Japan) were dissolved in 78 mM aqueous NaClO₄ (85%; Katayama Chemical, Osaka, Japan), which was the electrolyte for electrochemical STM. The pH of the monomer solutions was adjusted by the addition of several tens of microliters of 0.1 M aqueous HClO₄ (60%; Kanto Chemical, Tokyo, Japan) and 0.1 M aqueous NaOH (85%; Nacalai Tesque). For the discrete adlayer system, the typical concentrations of TAPP and BA were ~0.75 and 30 μ M,

respectively, and the pH was ~ 2.0 . For the polymeric adlayer system, the typical TAPP and TPA concentrations were 0.12–0.75 and 20 μM , respectively, and the pH was ~ 3.5 .

2.3 *In situ* STM observations

Au(111) single-crystal bead electrodes for STM observations were prepared from Au wire (99.999%; Tanaka Kikinzoku, Tokyo, Japan) by the Clavilier method, as previously reported.[35,36] Iodine-modified Au(111) electrodes were prepared by immersion in 10 mM aqueous KI (99.5%; Kanto Chemical) for several seconds, as previously reported.[37,38] STM observations were carried out with a Nanoscope E microscope (Digital Instruments, Santa Barbara, CA, USA), and all STM images were collected in constant-current mode. The iodine-modified Au(111) electrode was transferred to an STM cell filled with pH-controlled reaction solution. Tungsten wires (Nilaco, Tokyo, Japan) electrochemically etched with 1.0 M KOH (85%; Nacalai Tesque) were used as STM tips. Tips were coated with clear commercial nail polish to minimize faradaic current.

3. Results and discussion

During thermodynamic self-assembly based on relatively weak physical adsorption, molecular adlayers establish the most thermodynamically stable structure that depends on the surface concentration of molecules. The surface concentration is thermodynamically determined by partitioning between the solution and solid phases. Two main factors, surface coverage and bond formation, determine the most stable structure under a given set of reaction conditions. Both high-coverage structures and covalent bonding systems contribute to the energetic stability of the resulting ordered structure. However, there may be a trade-off between these two factors during self-assembly. 2D-network structures with a high degree of intermolecular bonding may give low surface coverage. Therefore, phase transitions between

different ordered structures such as bonding-driven and coverage-driven structures are frequently observed for 2D supramolecular structures based on hydrogen-bonded molecules such as trimesic acid and melem.[39–41] Bonding- and coverage-driven structures are also observed for azomethine-type covalently bonded frameworks.

Figure 2A and B shows typical high-resolution STM images of the polymeric adlayers that formed a nanomesh structure and arrays of independently self-assembled linear polymers on the iodine-modified Au(111) surfaces when grown from solutions containing TAPP and TPA. The square nanomesh structure (Figure 2A), which is categorized as a bonding-driven structure, formed at a TAPP concentration of 0.12 μM . When the TAPP concentration was increased to 0.20 μM , we observed a transition to a coverage-driven structure (Figure 2B) consisting of a 2D array of linear polymers having a close-packed structure with a density that was higher than that of the porous nanomesh, which was consistent with coverage-driven

Figure 2. Typical *in situ* STM images (A and B) and the corresponding models (A' and B') of a TAPP-TPA nanomesh (A and A') and a linear polymer array (B and B') formed by azomethine coupling on I/Au(111) at pH 3.5. The TAPP and TPA concentrations were 0.12 and 30 μM for (A) and 0.20 and 30 μM for (B), respectively.

ordering. The neighboring TAPP molecules in the array were bonded to each other *via* TPA molecules along the α direction. Bridging TPA molecules were clearly visible between the TAPP units. In this structure, each porphyrin molecule was linearly connected *via* azomethine bonds at two diagonally opposite corners. In the β direction, each TAPP unit of the one-dimensional polymer chains was interdigitated with close-packing, and there was no covalent bonding between the corners of the TAPP units in this direction.

Higher surface concentrations produce coverage-driven structures with higher packing densities. The energy loss from cleavage of azomethine bonds is compensated for by stabilization due to the higher surface coverage. At relatively low surface coverages, the high-symmetry mesh structure (Figure 2A), in which all the TAPP amino units are bonded with TPA, is thermodynamically favored. The energetic losses due to the lower surface coverage resulting from the cavities in the mesh are overcome by the increased stability of the covalently bonded framework.

Two major driving forces of bond-driven and coverage-driven allowed the selective formation of a 2D supramolecular assembly of discrete reaction products of the poly(azomethine) equilibrium at the solid/liquid interface. The “on-site” condensation between TAPP and the monocarboxaldehyde (BA), instead of TPA was performed to provide an example of a simple discrete surface reaction system. The solution containing TAPP and BA formed ordered adlayers consisting only of TAPP-BA₂ with each TAPP bonded to two BA molecules at diagonally opposite corners (Figure 3E'). In contrast, for a homogeneous organic solution, the fully substituted product, TAPP-BA₄, is the only major product.[42,43] For a TAPP solution with a relatively low BA concentration (<120 μ M), a 2D array consisting only of TAPP molecules was formed, and 2D arrays based on mono-, tri-, or tetrasubstituted TAPP were not observed. However, mixtures of homogeneous arrays of TAPP and disubstituted TAPP (TAPP-BA₂) were observed. STM images of these mixtures were useful because they

Figure 3. (A) Wide-area *in situ* STM image of a well-ordered molecular array of intact TAPP (domain I, upper left) and TAPP-BA₂ (domain II, lower right) obtained on I/Au(111) from an aqueous solution containing TAPP and BA. (B, D) Expanded STM images of the ordered adlayer structure of TAPP and TAPP-BA₂, respectively; the inset parallelograms show the unit cells of the ordered adlayers. (C, E) Single-molecule STM images and (C', E') corresponding space-filling models of TAPP and TAPP-BA₂, respectively.

allowed direct comparison of the details of the different array structures.

Figure 3 shows typical STM images of mixed domains of TAPP and TAPP-BA₂ arrays obtained on iodine-modified Au(111) from a solution containing TAPP and BA. The highly ordered close-packed arrays consisting of TAPP and TAPP-BA adducts exhibited high surface coverage. The unit cell parameters of the intact TAPP array (domain I) were $a = 1.41$ nm, $b = 1.81$ nm, and $\alpha = 79^\circ$ and were essentially the same as those of the close-packed arrays self-assembled in a homogeneous solution of TAPP in the absence of BA. The TAPP-BA₂ array (domain II) exhibited a similar molecular arrangement with a larger unit cell: $a = 1.43$ nm, $b = 1.91$ nm, and $\alpha = 77^\circ$.

Intact TAPP and substituted TAPP-BA₂ could be visually discriminated by high-resolution STM (Figures 3C and E). The STM images of TAPP-BA₂ showed bilateral symmetry clearly illustrating the formation of the TAPP disubstituted with BA at diagonally opposite corners.

Figure 4A and B shows typical high-resolution STM images of mismatched and matched domain boundaries between intact TAPP (domain I) and TAPP-BA₂ (domain II) adlayers, respectively. In Figure 4A, a clear gap is visible between the close-packed arrays of TAPP at the upper left (domain I) and the bilaterally symmetric TAPP-BA₂ at the lower right (domain II). In domains I and II, TAPP and TAPP-BA₂ are clearly resolved with four-fold and two-fold symmetry, respectively. During the observation, the mismatched boundary appeared to gradually change shape, whereas the matched phase boundary showed almost no change, suggesting that it is more stable.

Interestingly, unsymmetrical products such as trisubstituted TAPP (TAPP-BA₃) and monosubstituted TAPP (TAPP-BA) were frequently observed only at domain boundaries (arrows in Figures 4A and B). Molecular features of substituted porphyrins with one and three arms were attributed to the tri- and monosubstituted TAPP products (TAPP-BA₃ and TAPP-BA₁; Figures 4C and D, respectively).

These results suggest that the formation of TAPP-BA₂ occurred at the boundaries of

Figure 4 (A, B) *In situ* STM images of hetero domain boundaries of intact TAPP (I) and TAPP-BA₂ (II). (C, D) Single-molecule STM images and (C', D') corresponding models of TAPP-BA₃ and TAPP-BA₁ picked up from (A) and (B), respectively, as indicated by the arrows.

the arrays and that mono-, tri-, and, potentially, tetrasubstituted products were formed and broken down continuously on the surface under equilibrium conditions. The restricted motion of molecules at the boundaries allowed us to visualize reaction intermediates on the STM observation time scale, although surface diffusion of isolated TAPP molecules or analogs on the iodine-modified Au(111) surface was too rapid to allow imaging by STM.

Figure 5 shows a schematic of the reactions that produce the polymeric and discrete supramolecular systems. For the polymeric TAPP-TPA system, bonding- and coverage-driven structures were observed. The structural selectivity observed for the discrete TAPP-BA system was controlled by reaction equilibria rather than by surface coverage. Note that in the latter system, TAPP-BA₂ was the only major product even at high BA/TAPP ratios, and no arrays of TAPP-BA₃ and TAPP-BA₄ were observed.

The high selectivity for TAPP-BA₂ can be explained in terms of two aspects of the reaction process, as well as in terms of the thermodynamic stability of the reaction components. First, as a self-assembly component, the high-symmetry product, para TAPP-BA₂, is preferable to asymmetric products such as TAPP-BA, TAPP-BA₃, and ortho TAPP-BA₂. [High-symmetry products are advantageous for close packing in terms of coverage.](#) Second, the reaction of TAPP with BA was governed by the following equilibria: TAPP-BA $\leftrightarrow$ TAPP-BA₂ $\leftrightarrow$ TAPP-BA₃ $\leftrightarrow$ TAPP-BA₄. After TAPP-BA₂ molecules formed, they crystallized readily on the surface, and this crystallization inhibited further condensation reactions to form TAPP-BA₃ and TAPP-BA₄ owing to the lack of space and freedom of movement on the substrate, although TAPP-BA₃ molecules did form temporarily at the domain boundaries (Figure 4C).

The selectivity of the reaction might also be explained by the TAPP-BA₂ ordered array being energetically more stable than a TAPP-BA₄ ordered array. The interdigitated arrangement of the TAPP-BA₂ array may be stabilized by π - π stacking of the phenyl moieties

of the BA units of neighboring molecules, whereas a TAPP-BA₄ ordered array can be expected to have a low surface density with wider gaps between molecules.

Conclusions

We demonstrated Schiff base formation reactions that generated ordered supramolecular lattices of polymeric and discrete porphyrin molecules with specific chemical structures in terms of position selectivity with respect to reaction of the amines with the aldehydes. The reaction mechanisms were elucidated visually by means of *in situ* STM imaging at the liquid/solid interface at which the reaction occurred. The positional selectivity of the polymerization reactions was determined by surface coverage during self-assembly and by the equilibria of the azomethine condensation reactions. The self-assembly also determined the degree of substitution of discrete porphyrin building blocks in the molecular assemblies. These findings are of significance for the construction and STM imaging of 2D supramolecular systems on solid substrates and also for understanding the construction of three-dimensional supramolecular systems in homogeneous media.

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Figure Captions

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Figure 5. Schematic representation of supramolecule formation reactions on a solid/liquid interface for the (A) polymeric and (B) simple discrete systems.

Figure 5

Simple Reaction in Homogeneous Media

Position-Selective Reaction at Solid-Liquid Interface