Self-assembled π -conjugated macromolecular architectures - A soft solution process based on Schiff-base coupling

Masashi Kunitake,^{1,*} Rintaro Higuchi,¹ Ryota Tanoue,¹ Shinobu Uemura²

¹ Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan. Tel: +81-96-342-3673

² Department of Advanced Materials Science, Kagawa University, 2217-20, Hayashi-cho, Takamatsu, Kagawa 761-0396, Japan.

*E-mail address: kunitake@kumamoto-u.ac.jp

Abstract

Two-dimensional supramolecular covalent macromolecular architectures were visualized directly by in-situ scanning tunneling microscopy and colorful π -conjugated nanofilms with unique mesostructures formed spontaneously on hydrophobic substrates from aqueous solutions in the presence of simple aromatic building block molecules under ambient conditions. We thus report the results of surface-mediated polycondensation and chemical liquid deposition. The Schiff base coupling reaction applied for this soft solution process is a dynamic reversible covalent coupling reaction that can be managed by careful changes in solution conditions based on ‘adsorption’ and ‘polymerization’ equilibria. This low-cost and eco-friendly ‘bottom-up’ method allows great diversity in terms of the design of primary polymeric chemical structures by the selection of building blocks without the need to consider the solubility of the polymer. This paves the way to a true ‘bottom-up’ assembly of a vast array of solid-supported, designer supramolecular nanoarchitectures with potential use as functional materials for next-generation organic electronics.

Keywords

Covalent supramolecular nanoarchitectures; Thermodynamic self-assembly; Schiff base coupling reaction; dynamic reversible reaction; Poly(azomethine), Surface-mediated polycondensation; Chemical liquid deposition; Soft solution process; “Bottom-up” nanotechnology

1. Introduction

The construction of sophisticated, supramolecular architectures through self-assembly has attracted considerable attention as a “bottom-up” nanotechnology over the last two decades.[1,2] Initially, sophisticated structures were mainly based on fundamental interests regarding structural beauty rather than functionality in supramolecular chemistry. Currently, top-down methodologies such as photolithography are approaching the theoretical limit and, therefore, bottom-up methodologies based on self-assembly to build up well-defined functional nanostructures on certain substrates starting from atoms or molecules are desired. The construction of two- and three-dimensional (2-D, 3-D) macromolecular architectures that consist of functional building blocks on well-defined solid surfaces is a crucial milestone to bridge the “top-down” and “bottom-up” nanotechnologies and also to bridge supramolecular chemistry and nanomaterial science. The preparation and characterization of polymeric ultrathin films on solid substrates has been researched intensively both fundamentally and industrially. The diversity and controllability of a structure and correlations between function and structure are of interest at the nano- and mesoscale. Among the various methods, the Langmuir-Blodgett method[3,4] and the layer-by-layer method,[5,6] in which molecules are deposited onto substrates, are used as preparation methods for laminated ultrathin films, and these have received much attention because of the layered structures produced with relatively high precision at the molecular level.[7,8]

Sophisticated crystalline nanomaterials that consist of highly regularized pores, metal–organic frameworks (MOFs), porous coordination polymers,[9] and covalent organic frameworks[10,11] have been aggressively researched for application in gas storage, separations, sensors, and catalysis etc.[12] Although these materials are generally synthesized as crystalline powders, the preparation of substrate-supported polycrystalline MOF films, referred to as surface-anchored metal-organic

frameworks (SURMOFs), have received recent attention to extend their application range.[13-15] Ideally, SURMOFs should be highly oriented, nearly uniaxial MOF multilayers and have a highly commensurate relationship with their substrate lattice. However, they should not be polycrystalline films wherein MOF nanocrystals are scattered over the substrate. Several methods have been developed to fabricate SURMOFs and these are discussed in terms of the arrangement of porous channels or cavities and their thickness.

In this review, we summarize our recent research into 2-D and 3-D π -conjugated macromolecular architectures on surfaces constructed by surface-mediated selective polycondensation based on Schiff base coupling. Sophisticated structures in the nano/meso scale were constructed by a soft solution process in aqueous solutions under ambient conditions. The pursuit of methods for the design and preparation of nanoarchitectonic systems with integrated functionality through bottom-up methodologies remains a driving force in molecular nanotechnology.

2. Thermodynamic self-assembly of 2-D π -conjugated macromolecular adlayers

2-1. 2-D Supramolecular arrangements and their scanning tunneling microscopy (STM) imaging in aqueous solutions

The construction and in-space visualization of molecular adlayers on well-defined surfaces have been extensively investigated using a combination of supramolecular chemistry and scanning probe techniques over the previous decade.[16,17] Scanning tunneling microscopy (STM) can potentially be used to visualize molecules with sub-molecular resolution. Molecular imaging to determine arrangements in arrays, orientations, and even inner structures of molecules has been achieved in

air[18-20], under ultrahigh vacuum (UHV)[21-23] and in solutions[24-27]. *In situ* STM imaging is a powerful tool for the characterization of self-assembled molecular systems at solid-liquid interfaces especially for static nanostructures, dynamic formation mechanisms, and intermolecular interactions.[28] The formed structures have mainly been discussed in terms of intermolecular interactions in supramolecular chemistry rather than the epitaxial arrangements of surface chemistry.

Ordered adlayer systems in solutions are generally constructed by spontaneous adsorption from a solution phase followed by 2-D self-assembly or 2-D crystallization on surfaces induced by intermolecular interactions. As thermodynamic self-assembly in solutions require the surface diffusion of molecules at room temperature, relatively weak adsorption mechanisms such as physisorption are used. Under appropriate conditions, highly ordered molecular adlayers with supramolecular arrangements are formed as stable structures on a reversible adsorption system, and these are thermodynamically governed by phase equilibria.

Phase equilibria in solution are roughly classified as “adsorption–desorption” or “dispersion–aggregation”, and these are shown as vertical arrows and horizontal arrows in Figure 1, respectively. Reversible adsorption (physisorption) controls the molecular distribution on an interface based on the relevant adsorption–desorption equilibrium. Additionally, a “dispersion–aggregation” equilibrium also exists at solid-liquid or air-liquid interfaces, which is similar to that in solution. The equilibrium on the surface is primarily a function of temperature and surface concentration. Solution conditions such as solvent properties (polarity) and the concentrations of sample and salt also influence the equilibrium because these change the solubility of the target molecules. In addition, the adsorbate–substrate interaction also strongly influences the equilibrium distribution.

Figure 1. Thermodynamic equilibria between a homogeneous solution, an air-liquid interface, and a solid-liquid interface.

Thermodynamic self-assembly and high-resolution STM imaging of various artistic 2-D supramolecular systems have been achieved in solution by careful condition selection. In many cases, an “order-disorder” and “order-order” phase transition of 2-D assemblies was observed as a function of surface coverage.[29] In addition, adjusting the thermodynamic self-assembly conditions can also be achieved by electrochemical potential because the adsorption strength is a function of the potential.[30-31] Potential control in mV units is advantageous for the observation of phase transitions as very delicate tuning of the surface concentration can be achieved.

As typical examples of self-assembled structures including “order-order” phase transitions, Figure 2 shows highly ordered adlayer structures of two triangular building block molecules, trimesic acid (TMA),[32] and 2,5,8-triamino-tri-s-triazine (melem) [33] with their “order-order” phase transitions. Two ordered phases, namely a “honeycomb network” and a “close-packed structure” were observed and are reversibly controlled by the set conditions. The “honeycomb network” structures of TMA and melem were observed for each adequate condition for lower surface coverage at more negative potentials or at

lower concentrations compared with the conditions used for the “close-packed” structure phase with the highest coverage. In the "honeycomb network", TMA and melem molecules are connected to each other via hydrogen bonds. Increasing the surface coverage induces a transformation from a "honeycomb network" to a "close-packed" structure with much higher coverage by cutting off intermolecular hydrogen bonds in the network. This suggests that specific and strong intermolecular interactions, which can overcome the loss of thermodynamic energy because of low coverage, are necessary to construct a non-close packed network structure with a cavity.

Figure 2. Typical STM images (A, C, E, and G) and their structural models (B, D, F, and H) of polymorphic self-assembled structures at the solution–solid interface, and a diagram showing molecular dynamics and functions at the solution–solid interface (the bottom). (A-D) Trimesic acid. (E-H) Melem. Reproduced in part by permission of The Royal Society of Chemistry.

The construction of diverse multiple-component supramolecular architectures has also been achieved by thermodynamic self-assembly by fine tuning the adsorption conditions. Different

bi-component self-assembled structures comprising melamine and melem have been formed onto Au(111) by varying the concentrations of melamine and melem, and the electrochemical potential.[34] Diverse hydrogen-bonded network structures with different bi-component molar ratios were reversibly constructed by systematically changing the solution concentrations of melamine and melem and the electrochemical potential, as shown in Figure 3. Structural phase transitions between the melem mono-component honeycomb network, the bi-component honeycomb network, and the melamine mono-component honeycomb network were directly and reversibly observed by controlling the electrochemical potential. The close structural similarity and multiple hydrogen bonds between melamine and melem allow us to achieve controllable systematic diversity with long-range periodicity in the bi-component nanoarchitectures.

Figure 3. *In situ* STM images and corresponding arrangement models for bi-component self-assembled structures of melamine and melem. Reprinted in part with permission from ref. 34. Copyright 2013 American Chemical Society.

2-2 Surface-mediated selective polycondensation for covalently bonded 2-D supramolecular structures

Substrate supported 2-D assembled systems are commonly self-produced through relatively weak non-covalent interactions such as van der Waals interactions,[35] hydrogen bonds,[36] and

π - π stacking.[37] Although non-covalent intermolecular interactions are advantageous for the construction of extended molecular architectures in frameworks by self-assembly, the construction of covalently bonded nanostructures onto well-defined substrates is a crucial step in bottom-up technology for the actual use of nanomaterials or nanodevices without controversy.

Covalently bonded 2-D supramolecular structures synthesized by the bottom-up approach have been reported and most covalent self-assemblies have been achieved by an on-site thermal reaction under UHV conditions, such as thermally initiated C-C coupling[38-40], Ullmann coupling between aromatic halogen molecules[41-43], esterification between boronic acid and hydroxyl units[44,45], and azomethine (Schiff base) coupling between a primary amine and aldehyde units[46,47].

The step-wise synthesis of graphene nanoribbons (GNRs) from building block molecules onto a surface under UHV has attracted attention recently because of the high potential for excellent thermal, electronic, and magnetic properties of future devices.[48] The preparation of GNRs on surfaces has been achieved by the sublimation of aromatic building block molecules bearing reactive halogen atoms on the metal surfaces, which act as a catalyst and undergo two-step thermal reactions, thermal coupling initiated typically at 200 °C, and subsequent cyclodehydrogenation induced at 400 °C. A variety of GNRs with linear, zigzag, and branch shapes have been constructed on surfaces under UHV by the selection of building blocks.

As expected, it is difficult to avoid unfavorable irreversible cross-linking, which leads to the formation of disordered 2- or 3-D nanostructures in the substrate in covalently bonded molecular systems. The irreversibility of the connecting reactions provides a major problem for covalent self-assembly. The existence of a dynamic reaction equilibrium for the coupling of building blocks enables the self-organization processes to reach their most thermodynamically stable structure and this has been done by trial and error. Thermodynamic self-assembly based on reversibility and the robust

toughness imparted by covalent bonding are perceived as a trade-off. Therefore, under UHV conditions, successful preparative strategies have employed kinetically controlled, thermally activated reactions conducted at very low surface coverage to limit the supply of molecular building blocks. Moreover, many covalent architecture systems are constructed at high temperature in UHV, and STM observations are conducted at room temperature or lower.

In contrast, different tactics have been required for self-assembly based on reactions in solution for the soft solution process because of the severely limited temperature range compared with UHV systems. To overcome this, we have proposed equilibrium polycondensation reactions to connect building blocks in extended frameworks. Specifically, the use of aromatic primary amine and aromatic aldehyde units as complementary reactive substituents for aromatic Schiff base (also known as imine or azomethine) coupling.[49-52] The reaction between primary amines and aldehydes can be achieved spontaneously even in aqueous media at room temperature. The Schiff-base reaction has been widely applied for the synthesis of discrete supramolecules and 2-D[53] as well as 3-D nanoarchitectures. [54] However, it is not well known that the coupling reactions are essentially reversible despite the covalent bonds. The reversibility and thermodynamic control of this solution reaction allowed us to extend the conventional 2-D molecular self-assembly process from non-covalently bonded systems to covalently bonded systems.

The important concepts of this methodology are the spontaneity and the selectivity of the polycondensation reaction on the substrate surface, even under solution conditions wherein homogeneous solution reactions do not occur at all.[55] This has been achieved by the very careful control of conditions, which regulates two major equilibria: “adsorption-desorption” and “coupling-decoupling”. Figure 4B shows conceptually the construction of extended covalently linked, π -conjugated macromolecular architectures through surface-mediated polycondensation. Similar to

non-covalent self-assembled systems, the selection of solution conditions is necessary to allow surface diffusion and to thermodynamically manage the surface coverage of building blocks.

The reaction equilibrium is essentially controllable by solution pH. For instance, when 4,4'-diaminostilbene dihydrochloride (ASB) and terephthalaldehyde (TPA) are mixed in water at basic pHs relative to pK_a at room temperature, the reaction proceeds immediately with the irreversible sedimentation of an oligomeric product. At acidic pHs below the pK_a of the primary amino group, the reaction results in a monomeric dispersion as the equilibrium shifts from “coupling” to “breakdown” because of the protonation of primary amino groups. Therefore, the solution pH was carefully selected for each combination of molecular building blocks and was slightly acidic relative to the pK_a of the molecules bearing primary amino units. This resulted in protonation and a rare inhibition of the reaction in a homogeneous solution.

Figure 4. General reaction formula for Schiff base coupling (A), and typical appearance (B) of the reaction aqueous solution in the presence of ASB and TPA under different pH conditions. The schematic

representation of the adsorption and reaction equilibria for thermodynamic self-assembly at the liquid-solid interface (C). Reprinted in part with permission from ref. 49. Copyright 2011 American Chemical Society.

2-3 2-D Supramolecular adlayers of linear aromatic polymers

Surface-mediated polycondensation with various combinations of aromatic diamine and dialdehyde produces 2-D arrays of π -conjugated linear polymer arrays on iodine-modified Au(111) (I/Au(111)). [49,50] Chemically inert and hydrophobic I/Au(111) surfaces are some of the most suitable substrates for thermodynamic self-assembly in aqueous media. As shown by the typical *in situ* STM images in Figure 5, extended mosaic patch-like ordered domains of π -conjugated linear polymer arrays were observed. The presence of a nearly continuous molecular layer and associated chain termination at the phase boundaries proves that polymer formation occurred through surface propagation and that no sedimentation of polymeric or oligomeric species from the solution was evident.

Interestingly, when the meta-substituted building molecule isophthalaldehyde (IPA) was used with ASB, a domain consisting of zigzag lines was observed (Fig. 5C). The twist angle (ca. 120°) was consistent with that expected of a polymer with a flat orientation. This obviously affirms polymer formation through a surface reaction.

High-resolution STM images clearly revealed that each domain consisted of parallel lines where the aligned spots in each domain come from the benzene rings in the extended π -conjugated polymer chain. Each feature in the STM images agrees well with corresponding stretched and flat orientations from structural models in terms of size and conformation. The degree of polymerization, as estimated by the domain lengths along the direction of the polymer chain revealed that the individual polymer

chains are commonly composed of several tens (approaching a maximum of one hundred) of benzene units.

Figure 5 Typical STM images (A, B, and C) with corresponding models (A and B) of the linear and zigzag polymer array structures obtained from combinations of ASB-TPA (A and B), and ASB-IPA (C), respectively. Reprinted with permission from ref. 49. Copyright 2011 American Chemical Society.

2-4 Porphyrin based 2-D mesh frameworks and supramolecular arrays of discrete reaction products

Following the “on-site” successive polycondensation of π -conjugated 1-D polymeric systems, the ability to apply this synthetic methodology toward the fabrication of 2-D π -conjugated supramacromolecular frameworks was pursued.[49,51] Compared with chain polymerization on substrate surfaces such as polyacetylene and polythiophene initiated by local bias[56] or electrochemical control[57,58], surface-mediated successive polymerization enables the preparation of sophisticated cross-linked nanostructures like meshes or honeycombs by varying the number and relative arrangements of predefined reaction points, as for non-covalent hydrogen bonded network systems. The “on-site” polycondensation of aromatic dialdehydes and 4-fold 5,10,15,20-tetrakis-(4-aminophenyl)-21,23H-porphyrin (TAPP) provides adlayers for nanomesh

frameworks. As shown in Figure 6, typical high-resolution STM images clearly show various 2-D supramolecular frameworks composed of TAPP covalently bonded with linker molecules.

High-resolution imaging allows us to discriminate between TAPP and FeTAPP on each molecule. Furthermore, molecular dynamics can also be visualized by *in situ* imaging. The real-space visualization of covalent bond breakage and formation within the framework has been achieved through in situ STM imaging (Fig. 6 D–F). This direct observation of bond formation and dissociation clearly demonstrates the reversibility of this process at the solid-liquid interface. Moreover, the incorporation and removal of unconnected TAPP molecules in the cavities of the mesh frameworks were often observed as a host-guest reaction (Fig. 6C). Various nanomesh structures are designed as a combination of building blocks and are prepared by thermodynamic self-assembly. The symmetry of the linker molecules is crucial to form a mesh. 2,5-Thiophene dicarboxaldehyde (TCA) gave a disordered structure with TAPP because of the bent connection angle (Fig. 6 G). On the other hand, 2,2'-bithiophene-5,5'-dicarboxaldehyde (BCA) containing two thiophene moieties formed an ideal square mesh (Fig. 6H) because of linear connections.

Figure 6. Typical *in situ* STM images of 2-D covalently bonded nanomesh architectures for TAPP-TPA (A, C and D-F), FeTAPP-TPA (B), TAPP-TCA (G), and TAPP-BCA (H) on iodine-modified Au(111) in acidic solution. Reprinted in part (C-F and H) with permission from ref. 49. Copyright 2011 American Chemical Society.

Similar to the “order to order” phase transitions that depend on surface coverage as mentioned above for non-covalent systems, two different ordered structures are frequently observed for all TAPP-linker covalently bonded framework systems. Porous nanomesh frameworks are categorized as bonding-driven structures, and they generally form with relatively lower concentrations of building blocks. At relatively low surface coverage, a high-symmetry mesh structure is thermodynamically favored. Upon an increase in concentration, a coverage-driven structure (Fig. 7B) consisting of a close-packed 2-D array of linear polymers is favored. In the array, each porphyrin molecule is linearly connected with linkers at two diagonally opposite corners. The energy loss from the cleavage of azomethine bonds is compensated for by stabilization because of higher surface coverage. In other words, the energetic losses because of lower surface coverage resulting from the cavities in the mesh are overcome by the increased stability of the covalently bonded framework.

The ‘order to order’ phase transition between bond-driven and coverage-driven structures proves that covalent-bonded architectures on solid-liquid interfaces depend on a well-balanced equilibrium point. Therefore, the structure is changeable and may be fragile under the reaction solution conditions compared with UHV systems. For UHV systems, ordered adlayers are generally prepared by the thermal treatment of sublimated materials at high temperature to increase the surface diffusion of molecules. However, the structures created by the surface-mediated selective polycondensation can be stabilized by a change in the environmental conditions. After their removal from solution, the structures are exposed

to air. In neutral or higher pH solutions or aprotic solvents, the structures should be stable because the azomethine bonds are not cleaved.

Figure 7. *In situ* STM images (A and B) of a TAPP-TPA nanomesh and a linear polymer array obtained at relatively low (A) and high (B) TAPP concentrations and a schematic representation of the structural transition between “nanomesh” and “close-packing” according to the surface molecular coverage (C).

When mono-substituted building blocks are applied instead of cross-linkers for a similar surface reaction, simple discrete reaction products might form and become ordered on a surface (Fig. 8).[52] When the surface condensation reaction between TAPP and the monocarboxaldehyde (BA) was conducted on I/Au(111) in a solution containing TAPP and BA, the highly ordered close-packed arrays only consisted of a high-symmetry product, para TAPP-BA₂. The high selectivity toward the reaction products was only achieved at the surfaces upon a supramolecular reaction, but not in homogeneous media. The high-symmetry products, para TAPP-BA₂ and TAPP-BA₄ favor close packing with high coverage. Moreover, the TAPP-BA₂ ordered array might be energetically more

stable than a TAPP-BA₄ ordered array. It should be emphasized that position selectivity is thermodynamically achieved by two simultaneous equilibrium processes: a surface reaction and self-assembly on the surface.

Figure 8. *In situ* STM images of the TAPP-BA (A and C) product and intact TAPP (B) on I/Au(111) surfaces. Corresponding models (B' and C') of TAPP and para-TAPP-BA₂ and a schematic representation of the reaction (D).

[3] 3-D π -conjugated macromolecular architectures prepared by chemical lipid deposition (CLD)

As mentioned above, the specific conditions are crucial to manage the adsorption-desorption and coupling-decoupling equilibria for the construction of 2-D extended covalently bonded macromolecular nanoarchitectures based on Schiff base coupling. When the equilibria shifted slightly toward the adsorption or coupling sides, it was found that continuous polycondensation and deposition on the substrates occurred beyond a molecular adlayer. We have investigated such continuous deposition using novel chemical liquid deposition (CLD) methodology to prepare thin films on substrates by

self-assembly.[59] Chemical vapor deposition (CVD), in which sublimation and chemical reactions on a substrate is conducted in a vacuum chamber to produce ultrathin films on substrates is widely used, even in the semiconductor industry, because of the high-purity and high-performance of the products in addition to controllability.[60,61] A few CLD concepts, especially for organic materials, have been reported before the CLD method was proposed for surface-selective Schiff base coupling reactions. Electro- and electro-less deposition of metals or electroactive molecules can be classified as a classic CLD method. [62,63]

3-1 *In situ* STM observation of secondary adlayers of poly(azomethine)

Partially adsorbed secondary adlayers with “on-top” epitaxial behavior have frequently been observed by *in situ* STM, although multilayers have not been observed by STM because of the lack of conductivity. These secondary adlayers suggested the potential for the 3-D growth of π -conjugated polymers as thin films by continuous surface-selective Schiff base coupling. Figure 9 shows a typical STM image of secondary adlayers of 4,4-azodianiline (ADA) and TPA formed onto 2-D polymer arrays. The alignment of the polymer chains in the adlayers possesses a certain regularity in terms of a regular interval between the polymer chains. Each propagation row of the secondary polymer was found to be parallel at constant intervals. In the case of a secondary adlayer with relatively low coverage, the interval was found to correspond to three polymer rows. The adlayer with higher coverage possessed empty canals with the same interval between the pairs of polymer rows. The weak repulsive interaction between the polymer chains (rows) cooperatively controls the structures of the polymeric adlayers in an epitaxial fashion against an underlying polymeric adlayer and intermolecular interactions. These results encouraged us to construct supramolecular 3-D architectures onto 2-D structures while maintaining its structural mode by continuous deposition as an extension of thermodynamic self-assembly.

Figure 9. Typical *in situ* STM images (A and B) and the corresponding model (C) of the propagation of the polymer on polymer (ADA–TPA) adlayers. Image B is the 3-D representation of A. Reprinted in part with permission from ref. 50. Copyright 2012 American Chemical Society.

3-2. Poly(azomethine) ultrathin films prepared by CLD

As expected, the continuous lateral film growth of similar poly(azomethine) systems consisted of aromatic amine and aromatic aldehyde were achieved under typically less acidic conditions, which pushes the reaction equilibrium toward the product. Essentially, the basis of CLD is the same as for the formation of 2-D polymeric architectures, which have been visualized by EC-STM.

Figure 10 shows photographs of various π -conjugated polymeric ultrathin films on highly oriented pyrolytic graphite (HOPG) prepared by simple immersion in an aqueous solution containing ASB and TCA, *o*-phthalaldehyde (PDA), *m*-IPA or TPA under careful pH control as a typical example of CLD. Surprisingly, various colorful films were spontaneously formed on HOPG by simple immersion in the solution despite it being a combination of very simple building blocks. The color of the polymer films became deeper with an increase in the deposition time (Fig. 10, A and B). Because of the angle dependence of the UV-Vis reflection spectra, structural color originating from the surface structure influenced the UV-Vis spectra. However, the absorption band energy was predominantly determined by

Figure 10. Appearance of poly(azomethine) CLD films deposited on HOPG with various combinations of monomers (A–D) and with different deposition times (a–e), and UV-Vis absorption spectra of the films: ASB-TCA (A, pH 2.8) and ASB-IPA (C, pH 4.5). The deposition times are (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h, and (e) 24 h. The black dotted line corresponds to the aqueous solution that reacted for 24 h. Reproduced from Ref. 59 with permission from The Royal Society of Chemistry.

the chemical nature of the film because the influence of deposition time is greater than the angle dependence.

The CLD films on HOPG formed for almost all the combinations mentioned in Figure 10. As an exception, no film deposition was observed for the ASB-PDA combination. o-Substituted PDA might disturb the propagation of an ASB-PDA polymer structure. No structure was observed by EC-STM for this system. To induce CLD, the pH of the solution was carefully selected for each combination of molecular building blocks. Generally, the pH conditions used to induce CLD were slightly higher than the suitable pH condition used for the 2-D molecular arrays of the polymers on Au(111). For example, in the case of the ASB–TCA combination the pH values were 2.5 and 2.8, which are slightly less than the pKa of ASB, when used for the construction of a monolayer on Au(111) and for CLD on HOPG, respectively. No deposition was observed for aqueous solutions with a pH less than 2.3 or greater than ca. 8, which is probably due to the protonation of most of the amino units and the sedimentation of oligomeric products from the homogeneous solution, respectively. The deposition rate changed with pH

Figure 11. Photographs of the deposited CLD films of ASB-TPA on each substrate or interface. The conditions of the deposition are similar to those of HOPG. Reproduced from Ref. 59 with permission from The Royal Society of Chemistry.

and the highest deposition rate was at a pH near the pKa of ASB. In the spectra, an obvious red shift was observed and it depends on the deposition time while the absorbance increased with an increase in the deposition time. The red shift from 556 nm (3 h deposition) to over 800 nm (24 h deposition) is attributed to the extension of the π -conjugated system and is caused by interchain π -stacking rather than a covalent elongation of the polymer chains. The absorbance peak was consistent at ca. 460 nm and no red shift was observed for the ASB–IPA polymer films although the absorbance increased with deposition time, indicating continuous deposition (Fig. 10C). This is due to a disconnection of the π -conjugated systems in the polymer structure by the meta-positioned connection of IPA.

The substrate is crucial in CLD. On a hydrophilic surface such as clean glass, surface-induced polycondensation cannot start because the building blocks are not supplied by the partition or from the solution to the substrate surface and the dehydration reaction is thus suppressed. On hydrophobic substrates such as hydrophobic glass chemically treated with n-octyltriethoxysilane, deposited gold, iodine-modified gold, or mercury, CLD can be achieved as shown in Figure 11. Among the hydrophobic substrates for CLD, freshly cleaved HOPG is an ideal substrate because it is hydrophobic, atomically flat, and relatively chemically inert toward physical adsorption. In addition, specific graphene nanosheets can be used as a substrate, similar to a HOPG surface. It must be emphasized that despite the reaction equilibrium the polymer films formed by CLD are extremely stable and insoluble in common organic solvents as we found. Even in very acidic solutions, no polymer film damage was observed and this suggests that the pristine aromatic polymer backbones aggregate strongly by interchain π - π stacking.

3-3. Unique surface morphologies produced by poly(azomethine) type CLD

The polymer films produced by CLD do not have completely layered crystal structures, which would be expected for 2-D molecular adlayers. They frequently have unique surface morphologies in the mesoscale. Typically, granular and sponge-like network morphologies have been observed for CLD films of aromatic diamines and dialdehydes. During the early stage of deposition, granular morphologies are generally observed. However, a sponge-like network structure then frequently grows. Figure 12 shows a typical network structure of ASB–TCA polymers after 24 h deposition on HOPG. The networks consist of branched polymer bundles of 45–55 nm in diameter. In the structure, rigid aromatic polymer chains align and stack to form bundles. Similar network structures can be produced on other substrates such as hydrophobic glass. The porous network formed by CLD obviously proves that the propagation and deposition of the polymers proceeds simultaneously at the surface and that no sedimentation occurs. The surface morphologies are strongly influenced by the deposition rate and the

Figure 12. Typical FE-SEM image of a sponge-like network structure of ASB-TCA films deposited on HOPG and schematic representations of the deposition mechanisms based on “random walk” diffusion and linear diffusion for CLD conducted in solution and CVD in vacuum, respectively. Reproduced in part from Ref. 59 with permission from The Royal Society of Chemistry.

structures of the building blocks. As a deposition tendency, faster and slower deposition results in granular and sponge-like network surface structures, respectively.

This unique film growth mechanism is attributed to the characteristics of the CLD methodology as a wet process. The morphologies are produced as shown in Figure 13 with a comparison of the CVD process. When the formation rate is limited by the supply of monomers, the propagation and deposition of polymers occurs selectively at hills on the surface. The hills are favored by monomer supply by diffusion from the solution phase more than the valleys are. Molecular diffusion in solution is by “random walk” because of Brownian motion, and not linear diffusion as is the case for sublimation in a vacuum. Therefore, the slow speed of deposition typically with relatively low monomer concentrations without mixing favors the construction of a unique surface morphology with a high surface area, as mentioned previously.

As a more unique meso structure, the epitaxial growth of vertical nanowalls of aromatic

Figure 13. FE-SEM images of ANWs composed of (A, B) ASB-4HIP, (C) ASB-IPA, and (D) APE-4HIP deposited on HOPG at tilt angles of (A, C, D) 0°, and (B) 45°. The conditions for CLD were as follows: deposition time = (A, C, D) 24 h and (B) 8 h, temperature = 30 °C. Reprinted from Ref. 64. Copyright 2014 with permission from Elsevier.

poly(azomethine) were formed on HOPG by CLD when using the hydroxyl-substituted aromatic dialdehyde, 4-hydroxyisophthalaldehyde (4HIP), and several aromatic diamines.[64] As shown in Figure 13, numerous straight lines that represent standing poly(azomethine) nanowalls (ANWs) fully covered the HOPG. The triangular alignment of ANW obviously indicated epitaxial growth against the surface lattice of HOPG (inset of Figure 13A). Figure 14 shows the time course of ANW growth. For a deposition time from 10 min to 1 h, relatively short flakes (100–400 nm) that were elongated in an epitaxial fashion were observed at multiple points on the substrate. Perpendicular growth eventually led to standing ANW after the in-plane growth process of the flakes. Perpendicular nuclear growth occurs from the horizontal edges of the nanowalls.

The chemical structural dependence of a combination of building blocks is definitive and crucial for the vertical growth of standing ANWs. A hydroxyl-substituted aldehyde building block might be necessary to enhance the planarity of polymer backbones. High crystallinity because of a planar polymer chain will provide a nanowall structure. The selection of building blocks directly affects the

Figure 14 FE-SEM images of ASB-4HIP ANWs after deposition for (A) 1 h, (B) 3 h, and (C) 12 h, at 30 °C (pH = 2.6) and the formation mechanism of vertical ANWs by CLD. Reprinted from Ref. 64. Copyright 2013 with permission from Elsevier.

electronic and optical properties. Despite their similarities in terms of nanowall morphology, ANWs of ASB-4HIP and APE-4HIP have contrasting fluorescence properties. Despite the lack of fluorescence of ASB-4HIP ANWs, the APE-4HIP ANWs do fluoresce (inset in Fig. 13D). Interestingly, this result indicates that the fluorescence of CLD films directly depends on the primary chemical structures in the polymer main chain rather than intermacromolecular π - π stacking, which might determine the mesostructure of standing nanowalls.

Kimura and coworkers have reported the reaction-induced crystallization of poly(azomethine) in solution[65]. They have reported polycondensation in a homogeneous solution leading to the formation of crystalline precipitates or dispersion particles with unique morphologies such as needle-like[65] and disc-like[66]. The reaction induced crystallization and CLD are essentially based on the same principle.

The factors that control the mesostructures are a combination of building blocks, the sort of solid substrate and film growth (deposition) conditions. The combination of building blocks determines the primary chemical structure of the polymers that are formed by CLD. The formation of sponge-like network structures that consist of polymer bundles seems to require a bending moiety in the primary chemical structure of the polymer chain. On the other hand, a standing nanowall structure should be based on the stacking of relatively wide planer moieties of aromatic units.

In terms of film growth (deposition) conditions, the control of pH is crucial in managing the CLD conditions in which the homogeneous reaction is suppressed. The building blocks and salt concentrations, and the temperature are strong influences because these factors directly affect the supply of building blocks on a surface. An advantage of CLD that should be emphasized is the potential for heterodeposition. By simply changing the reaction solution using different combinations of building blocks, heterostructures have been constructed with high designability.

This sort of solid substrate also strongly influences the polymer film structures in terms of mesostructures, although the surface structure of the polymer thin films on a substrate prepared by deposition is not influenced much by the structure and nature of the substrate. A sponge-like network structure was constructed on various substrates such as HOPG and hydrophobized glass. However, vertically standing nanowalls have only been constructed on HOPG. The epitaxial influence of the substrates is obvious from the orientation of nanowalls.

3-4. Catalytic reactivity of Schiff base coupling for various building block combinations and reactive fields

The results of Schiff base reactions with different combinations of various aromatic diamine molecules and dialdehyde molecules and different reaction sites are summarized in Table 3-1. The reactivity of Schiff base coupling is predominantly determined by a combination of amine and aldehyde molecules; the reaction is particularly affected by the pKa of the amine in homogeneous aqueous dilute solutions. Generally, the reaction with protonated amines is prohibited and an amine molecule with a higher pKa possesses higher reactivity because of the higher electronic density of the amine unit. For instance, the order of reactivity of the three diamine aromatic molecules is ASB > AB > ADA.

A comparison of the catalytic reactivity of Schiff base coupling for reactive fields would be interesting. The formation of monolayers or thin films of the reaction products definitively proves the catalytic role of the surfaces. As mentioned repeatedly, the Schiff base reaction on a hydrophobic surface accelerates the hydrophobic surface-catalyzed dehydration reaction. The formation of CLD films also reveals that the polymer surface catalyzes the dehydration reaction. As a typical example, homogeneous reactions between ADA and TPA or TCA is prohibited across the entire pH range but

obvious surface-mediated selective polycondensation is achieved, even under acidic conditions, on a hydrophobic substrate such as iodine-modified Au(111) and HOPG.

Basically, CLD films were formed at equal or higher pH than that used to construct the monolayers. Except for those containing o-substituted PDA, CLD films were formed on hydrophobic surfaces using any combination regardless of ordered structures in the adlayers. Although the chemical structure of the diamine molecule predominantly determines their reactivity, the chemical structure of the dialdehyde also has an influence. Typically, in the case of the ASB–PDA (ortho-substituted) system, oligomeric dispersion occurs, which proves that a coupling reaction exists in homogeneous solutions. The *in situ* STM imaging of ASB-PA revealed a disordered adlayer of dimeric products and no continuous deposition of CLD film on HOPG is apparent.

Poly(azomethine)s are known to be π -conjugated polymers. The application of these polymers in organic solar cells has been reported. The macromolecular adlayers and CLF films prepared by surface-mediated Schiff-base coupling are π -conjugated semiconductive polymers. For instance, the

Table 3-1. Summary and a comparison of the reactivity of Schiff-base coupling and typical pH conditions for homogeneous aqueous solutions and monolayer/CLD film formation on the substrates with different combinations of building blocks.

Aldehyde	ASB (pKa=3.5)			ADA (pKa=2.1, 3.9)			AB (pKa=2.9, 6.0)		
	In homogeneous solution (at pH)	Monolayer on I/Au(111) (at pH)	CLD Film on HOPG (at pH)	In homogeneous solution (at pH)	Monolayer on I/Au(111) (at pH)	CLD Film on HOPG (at pH)	In homogeneous solution (at pH)	Monolayer on I/Au(111) (at pH)	CLD Film on HOPG (at pH)
TPA (<i>p</i> -)	Origimeric sedimentation (3.5)	Ordered array (2.5-3.0)	Film formation (2.6-2.8)	Not reacted (2.3-6.0)	Ordered array (3.0)	Film formation (3.0)	Not reacted (4.0); Origimeric sedimentation (6.0)	Ordered array (2.5)	Film formation (4.5)
IPA (<i>m</i> -)	Origimeric sedimentation (3.5)	Zigzag array (3.5)	Film formation (3.2)	—	—	Film formation (4.2-4.9)	Origimeric sedimentation (6.0)	Indistinct, but layer exists (6.0)	Film formation* (4.2)
PDA (<i>o</i> -)	Dispersion of origimeric product (3.5)	Disordered adlayer of dimeric product (3.5)	No-formation (2.6-3.9)	—	—	—	—	—	—
TCA	Origimeric sedimentation (3.5)	Ordered array (2.5)	Film formation (2.4-3.0)	Not reacted (2.3-6.0)	Disordered adlayer (2.5)	Film formation (3.1)	Origimeric sedimentation (6.0)	Ordered array (5.0)	—
BCA	—	Disordered adlayer (3.0)	—	—	Indistinct, but layer exists (3.0)	—	—	—	—

— Not measured

* Obtained with 0.5 mM monomer solution

electrochemical band gap (E_g) for the ASB–TCA CLD films on HOPG was determined to be 1.6 eV, indicating a semiconductive material. The E_g values of the CLD films were obviously lower than the E_g values of soluble poly(azomethine)s bearing alkyl side-chains with a similar chemical structure to the main aromatic chain.[67,68] A smaller E_g and a large red shift probably come from the delocalization of π -conjugated systems as a result of (1) interchain π -stacking and (2) restricted conformations of pristine aromatic polymer backbones with extended planar conformations.

4. Conclusions and outlook

We introduce here a surface-mediated, soft solution synthetic methodology based on the thermodynamic control of an equilibrium polymerization reaction on surfaces for the preparation of 2-D and 3-D covalently bonded supramacromolecular architectures. Because of the high degree of reversibility and controllability of the reaction, the pH controlled Schiff-base coupling is quite useful in supramolecular chemistry as a dynamic reversible covalent coupling reaction with a high reaction equilibrium rate even at room temperature. The basic concept of the careful control of dynamic reversible reactions for thermodynamic equilibria can be generalized by the design and construction of various supramolecular systems through the use of a wide array of equilibrium coupling reactions. This soft solution process is not limited to a planar 2-D surface and it can be readily applied to arbitrary 3-D micro- and macrostructured objects. A combination of top-down lithography and the discussed bottom-up assembly allows us to undertake arbitrary patterned deposition by the strong surface selectivity of the reaction; no deposition occurs onto hydrophilic glass.

Aromatic poly(azomethine)s prepared by the method are valuable as organic semiconductor materials. This ‘bottom-up’ methodology allows us to explore the design of primary polymeric chemical structures by the selection of building blocks selected from an infinite list of molecules to moderate

electronic and photonic properties without needing to consider the solubility of the polymer. In addition, the construction of a heterojunction is also possible by changing the solutions. A primary chemical structure can be built from simple aromatic molecules.

Furthermore, CLD is a low-cost and eco-friendly soft solution process. In contrast to the massive dry process used in UHV, the materials can be constructed in a straightforward manner, which can essentially occur in a beaker containing water at room temperature. Surface-mediated selective polycondensation paves the way to the true ‘bottom-up’ assembly of a vast array of solid-supported, designer supramolecular nanoarchitectures with potential use as functional materials for next-generation organic electronics.

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