

Nanoscale Surface Chemistry of Self-assembly and Directed-assembly of Organic Molecules on Solid Surfaces and Synthesis of Nanostructured Organic Architectures

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Methods for creating advanced materials such as 2-D and 3-D nanostructured materials and devices using chemical approaches typically include both molecular self-assembly through weak noncovalent interactions and directed-assembly of molecules via the formation of strong covalent bonds with solid surfaces. The application of the self-assembly and directed-assembly to the syntheses of nanoscale materials and devices is determined by a thorough understanding of various surface chemistry at nanoscale involved in these assembly processes as these assemblies originate from surface reactions or/and interfacial non-covalent interactions at nanoscale. We term the surface science involved in the syntheses of nanomaterials and fabrication of nanodevices as nanoscale surface science. Although tremendous studies have been carried out in the syntheses and functions of nanostructured organic/inorganic 1-D/2-D/3-D materials and devices, the nanoscale surface chemistry and the connection *between* the surface chemistry *and* materials synthesis and properties were few addressed. This dissertation research explored experimentally the nanoscale surface chemistry occurred in the self-assembly and directed-assembly of various organic molecules on solid surfaces and the synthesis of nanostructured organic architectures on solid surfaces, and successfully developed conceptually new synthetic methodologies which produce nanostructured organic architectures. It mainly focused on (1) development of experimental techniques (instrumentation) for the dissertation research, (2) nanoscale surface chemistry and mechanism of the self-assembly processed via weak noncovalent interactions and the directed-assembly carried out with strong chemical bonds, and (3) syntheses of nanostructural organic architectures. This dissertation presents a series of key advances toward mechanistic understanding of molecular self-assembly and directed-assembly and creation of 2-D and 3-D nanostructured organic architectures on solid surfaces.

Mechanistic Studies of Molecular Self-assembly via Weak Non-covalent Interactions

In molecular self-assembly, an ordered supramolecular species with new structure and property forms spontaneously from its original component. The self-assembly of organic molecules and the formation of organic architectures on solid surfaces are key for many promising applications such as molecular electronic devices, biomolecular recognition chips, tribology, corrosion inhibition, and 3-D nanopatterning. Here the self-assembly of several categories of organic molecules on solid surfaces was used as a model system for mechanistic studies at atomic level. A homemade high-resolution scanning tunneling microscope (STM) (Figure 1) was used for obtaining surface topography and electronic structure of the assembled systems on solid surfaces.

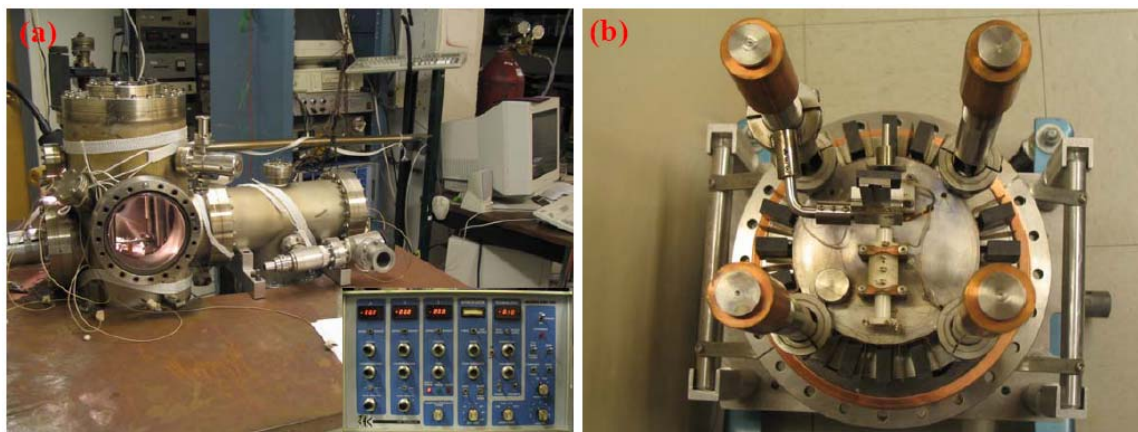


Figure 1. (a) *Homemade temperature-variable STM system.* (b) *Homemade STM head.*

As schematically shown in Figure 2, for each molecule of a self-assembled monolayer on a solid surface its adsorption includes at least three categories of non-covalent forces. They are the interactions between adjacent molecules in a lamella, the interactions between adjacent molecules of two neighboring lamellae, and the interactions between molecules and the solid surface. The competition and balance of these interactions determine structure and property of the self-assembled system. Our studies^{1,2} showed that lattice match *between* alkyl chain of organic molecules such as ester and *di-alcohol and* graphite substrate could change molecular conformation upon self-assembly, further inducing new chirality for achiral molecules. For example, the originally bent ester molecule is distorted into a linear configuration upon self-assembly on graphite (Figure 3) due to the requirement

of lattice match for maximization of molecule-substrate interactions. This result suggests a strategy for producing chiral structure from achiral materials via self-assembly.

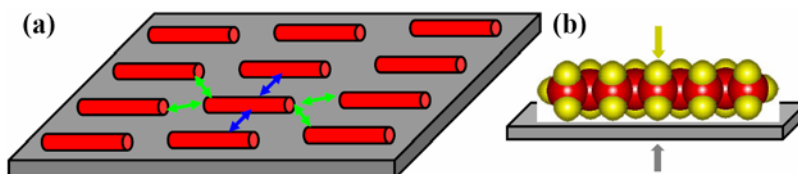


Figure 2. (a) Scheme of intermolecular interactions in a lamella and intermolecular interactions between two adjacent lamellae. (b) Side view of a self-assembled monolayer showing molecule-substrate interactions. Each red bar shows an organic molecule.

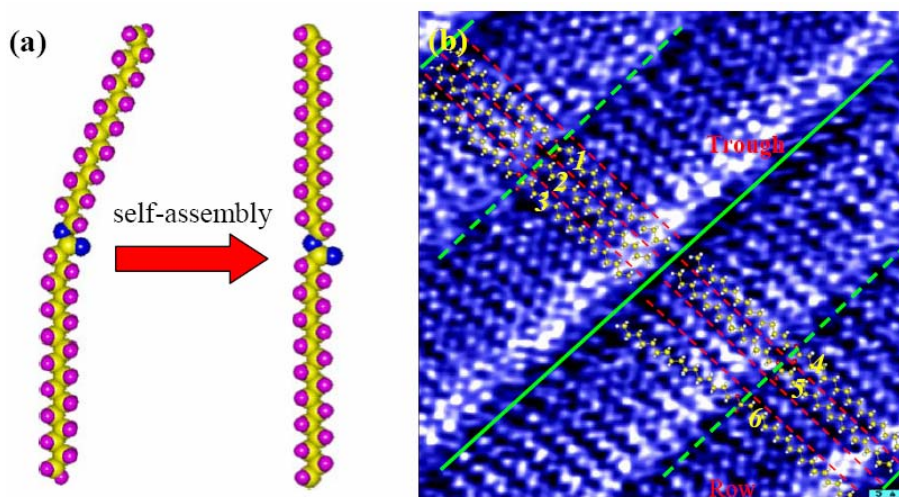


Figure 3. (a) Scheme showing the distortion of an ester molecule from the originally bent conformation into a linear conformation. (b) STM image of the self-assembled stearic acid palmityl ester molecules on HOPG with atomic resolution. The superimposed molecular models 1-5 with a linear shape match with the molecular images under them. Molecular model 6 with an originally bent conformation clearly offsets from the image under it.

We revealed that the intermolecular interactions, particularly the interactions of molecular functional groups play a dominant role in determining molecular packing pattern in self-assembled systems. For example, the shape and size of anhydride group of arachidic anhydride make this molecule adopt an unusual interdigitated packing to reduce intermolecular repulsion, therefore forming two 2-D chiral structures with opposite chirality (Figure 4).³ In addition, the hydrogen bonding between molecular functional groups is another important factor in dominating self-assembled structure. We first addressed that the relative hydrogen bond density between acid solvent molecules and *di*-acid solute molecules determines whether a solute-solvent coadsorption occurs or not (Figure 5a)⁴. For example, octanoic acid (C8, solvent) has a larger hydrogen-bond density than HOOC-(CH₂)_n-

COOH ($n=18$) (C20, solute); they coadsorb (Figure 5b). However, this solvent has a lower hydrogen-bond density than HOOC-(CH₂)_n-COOH ($n=12$) (C14, solute); they do not coadsorb (Figure 5c). This finding will direct the synthesis of composite architectures from various solvents. On the other hand, our studies show the intermolecular steric repulsion at atomic level can result in distinctly different self-assembled structure and even induce chirality. The simplest example is the odd-even effect on structure and chirality of carboxylic acid self-assembled on graphite (Figure 6).^{3,5} CH₃(CH₂)_{n-2}COOH ($n=$ odd) exhibits a different molecular packing and chiral structure in contrast to CH₃(CH₂)_{n-2}COOH ($n=$ even). We systematically revealed more odd-even effects on structures and functions of different organic architectures assembled on solid surfaces.⁶ These revealed odd-even effects are important for understanding functions and properties of the assembled organic architectures and devices.

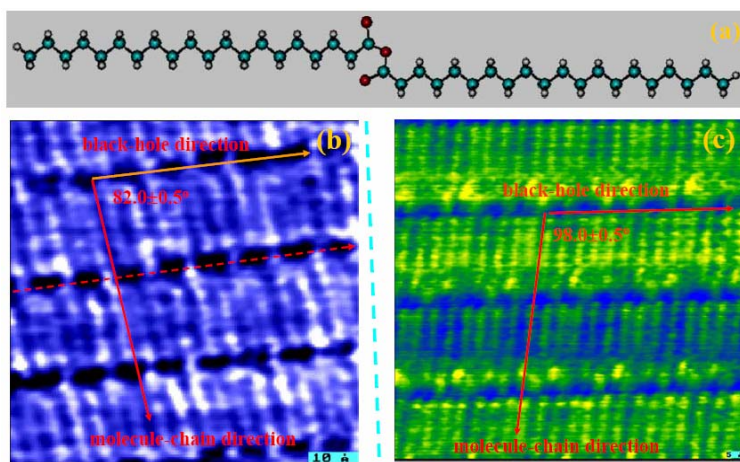


Figure 4. (a) Molecular structure of arachidic anhydride. (b) and (c) STM images of the two self-assembled chiral domains of arachidic anhydride with opposite chirality.

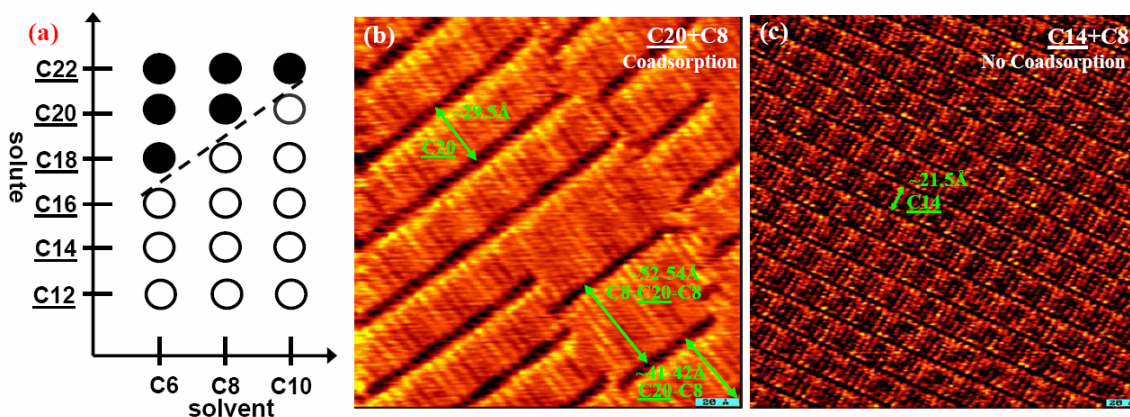


Figure 5. (a) Coadsorption and relative hydrogen-bond density of solvent and solute molecules in organic self-assembled systems. Solid circles show coadsorption. Hollow circles show no coadsorption. (b) STM image showing coadsorption between solvent (C8) and solute (C20) molecules. (c) STM image showing no coadsorption between solvent (C8) and solute (C14) molecules.

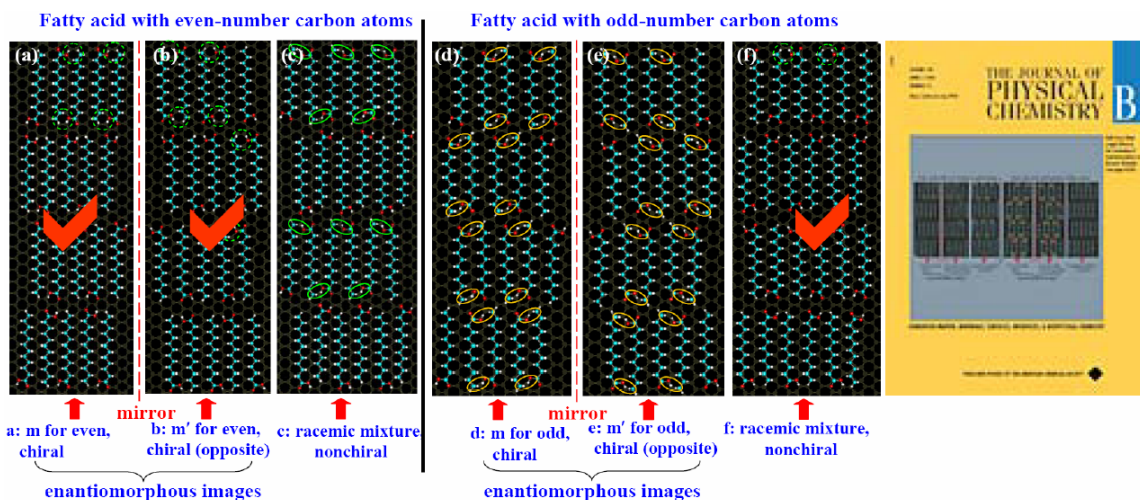


Figure 6. Odd-even effect on molecular packing pattern and chirality for *n*-carboxylic acid. $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ and $\text{CH}_3(\text{CH}_2)_9\text{COOH}$ represent even- and odd- acids, respectively. Even-acid forms enantiomorphous images with opposite chirality (Figures 6a and 6b). Odd-acid forms a nonchiral racemic mixture (Figure 6f).

Syntheses of Nanostructured Organic Architectures on Solid Surface by Molecular Self-assembly via Precisely Controlling Weak Non-covalent Interactions

Multi-component organic architectures can offer multiple functionalities of organic materials and flexibility of fine-tuning chemical, physical, mechanical and electronic properties of materials and devices. We developed a new methodology to precisely and controllably grow ordered *stoichiometric nanostructured multi-component* organic architectures. One of our examples is the synthesis of a nanomesh via co-self-assembly of multi-component organic molecules by precisely controlling nanoscale surface chemistry involved in this process on the basis of the above mechanistic understanding for molecular self-assembly.⁷

Figure 7a is a STM image of 5-octadecyloxyisophthalic acid (5OIA) thin film. The superimposed molecular models in Figure 7a and the molecular packing pattern in Figure 7b clearly show the formation of an ordered and homogeneous single-component structure. For the organic architecture synthesized from 5OIA and octanoic acid, a distinctly different structure was obtained

(Figure 7c), in which 5OIA self-assembles with octanoic acid at the molecular level. The two molecules alternately pack in each lamella, forming a homogenous stoichiometric crystalline organic architecture. Nanoholes (marked with pink boxes in Figures 7c and 7d) with a size of $13.5 \text{ \AA} \times 8.5 \text{ \AA} \times 1.8 \text{ \AA}$ were formed due to the different chain-lengths of the two molecules, consistent with the line-profile analyses (Figures 7e and 7f) for Sections 1 and 2 of Figure 7c. The ordered homogeneous arrangement of nanoholes forms a homogeneous organic architecture of nanomesh. In addition, with this strategy we synthesized a series of nanomeshes with different size of nanoholes via using carboxylic acid with different length as the coadsorbed component. Figure 7g is another example of a homogeneous multi-component system of 5OIA and terephthalic acid (Figure 7h).⁸

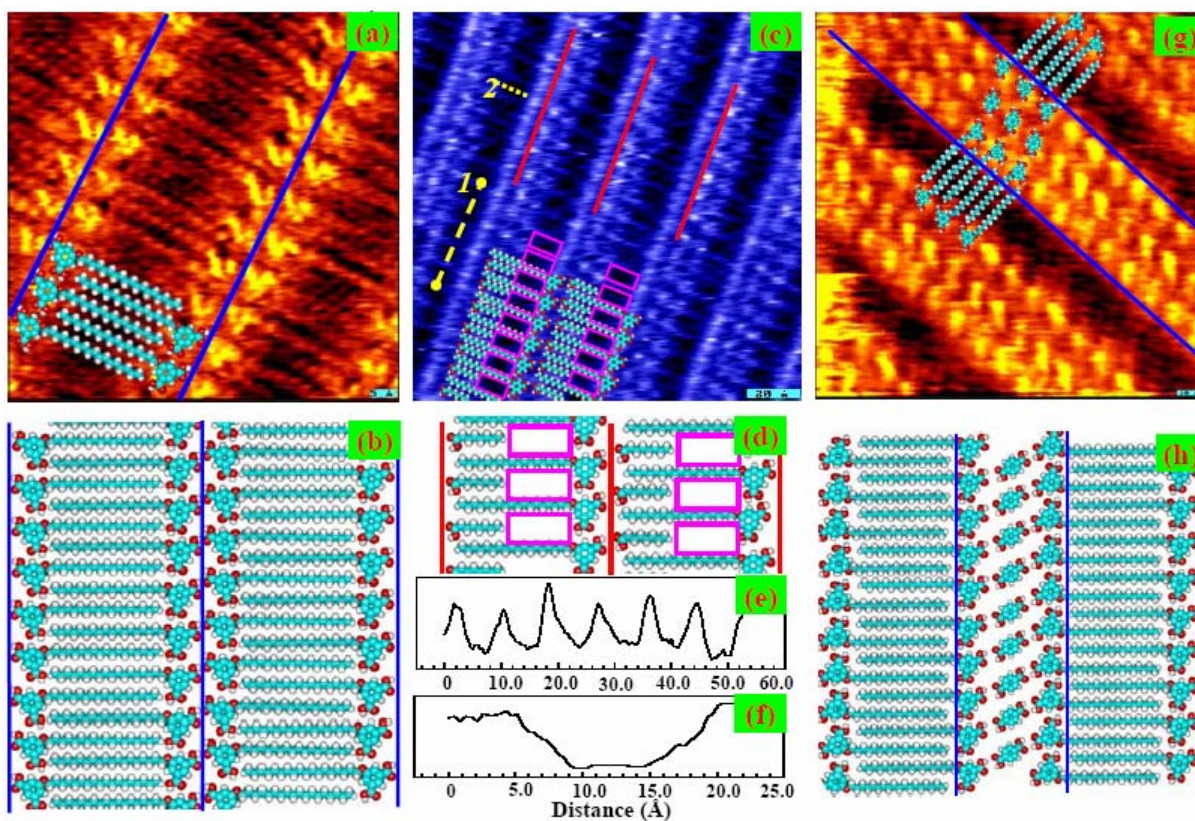


Figure 7. (a) STM image of the self-assembled 5OIA. (b) Molecular packing pattern in this image. (c) STM image of nanomesh made of homogeneously arranged nanoholes. (d) Molecular packing pattern in this nanomesh. (e) and (f) Line-profile analyses for the size of the nanoholes. (g) STM image and (h) molecular packing pattern of co-self-assembled 5OIA and terephthalic acid.

We first demonstrated this stoichiometric molecule-by-molecule co-self-assembly for fabricating nanostructured organic architectures on solid surfaces. By using this methodology, more organic architectures with different nanostructures were synthesized very recently.^{9,10} This methodology also provides a promising approach to fabrication of conductive molecular wires/nanowires and nano-circuits on the surface of a solid substrate by precisely controlling the weak intermolecular and molecule-substrate interactions in self-assembled systems.

Surface Chemistry and Mechanism of Directed-Assembly of Organic Molecules via Strong Chemical Bonds and Growth of Organic Multilayer Architectures

Compared to weak noncovalent interactions in molecular self-assembly, molecules are chemically bound on a well-defined solid surface with high chemical reactivity in directed-assembly. The reactivity of molecular functional groups with the solid surface is extremely important in the directed-assembly via chemical reaction. By assembling bi-functional or multi-functional molecules via the formation of chemical bonds, solid surfaces can be modified and functionalized. The functionalized surface plays an important role in a wide spectrum of technological fields such as the development of new-generation microelectronics and biosensing techniques.

It is important to note that due to electrical considerations, the thickness of silicon oxide layer used in electronic devices, such as transistors, has to be proportional to the gate length. While silicon oxide has managed to scale comfortably over the last 30 years from over 100 nm down to a few nanometers, it has almost reached its physical limit of 1.2 nm. At 1.2 nm the oxide consists of only four atomic layers and can no longer function as an insulator due to tunneling current losses. One promising approach considered is the move from oxides to organic thin film assembled on silicon surface. The organic thin film synthesized via directed-assembly has flexibility in the control of thickness and properties for the different needs in the fabrication of various microelectronics including transistors. On the other hand, the controllable growth of an organic multi-layer architecture on

semiconductor surface is extremely important for designing biosensing devices utilizing the molecular recognition mechanism because the assembled organic/biological molecules on semiconductor surface can display specific biocompatibility for certain biological molecules or proteins or cells. A change of physical property such as tunneling current can be used to monitor the specific biocompatibility. By identifying biocompatibility of protein or cell in this way, new diagnostic methods and sensing technologies can be developed.

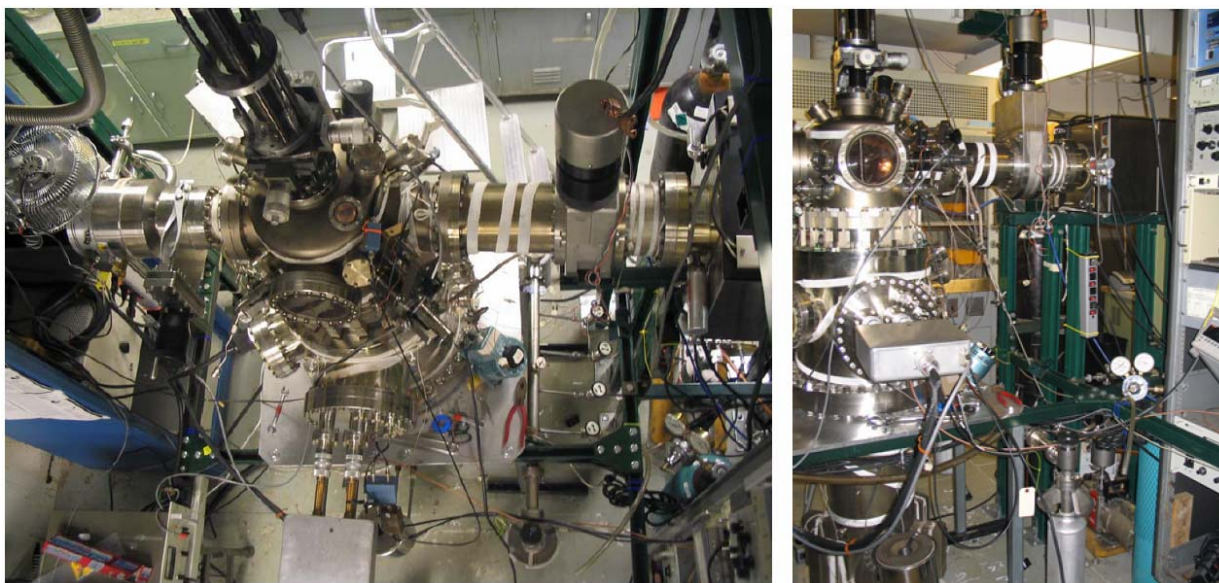


Figure 8. *Homemade high-resolution electron energy loss spectrometer/ultra-high vacuum system for studying the nanoscale surface chemistry in the directed-assembled organic architectures on silicon surfaces.*

In the directed-assembly of organic molecules on silicon surface, we carried out a thorough mechanistic study for various organic molecules and synthesized well-defined organic architectures which could be used for the development of silicon-based microelectronics and biosensing devices. For mechanistic studies of the directed-assembly of organic molecules and vibrational identification of the synthesized organic architectures, we successfully designed and built a high-resolution electron energy loss spectrometer/ultrahigh vacuum system (Figure 8). Si(111)- 7×7 was used as a solid surface here (Figures 9a and 9b). This surface provides a number of spatially and electronically inequivalent reactive sites. Because of the large difference in electron density among surface atoms containing dangling bonds, an adatom coupled with one adjacent rest atom can act as a dipole-like reactive site

(Figure 9c). In addition, the electron-deficient adatom can be a binding site of electron-rich functional group to form dative bond. The directed-assembly mechanisms including dissociation via M-H (M=O, S, or N) groups, formation of dative bond between electron-rich functional group and electron-deficient surface adatom, step-wise [2+2]-like cycloaddition, and [4+2]-like cycloaddition, were revealed for different organic molecules.¹¹

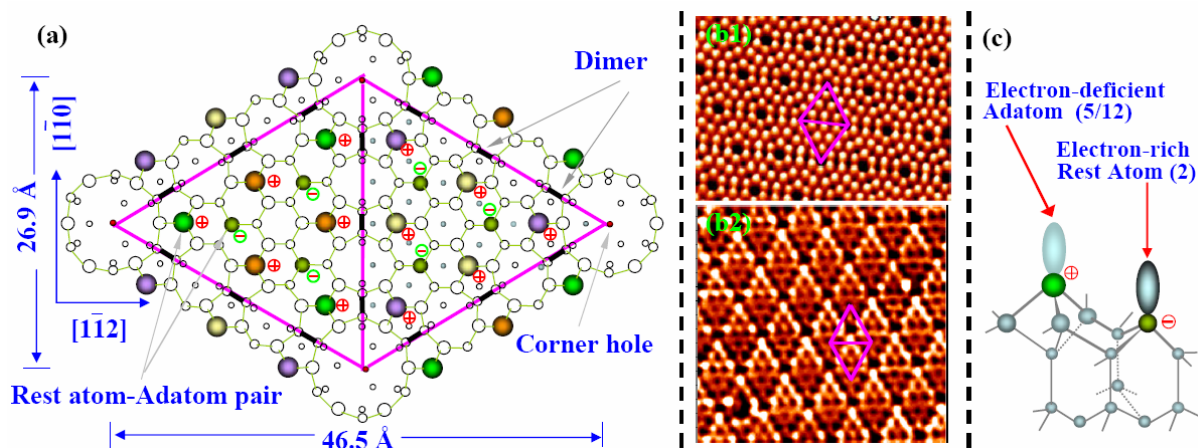


Figure 9. (a) Structure of one unit-cell of Si(111)-7×7 surface. (b) High-resolution STM image of Si(111)-7×7 surface (b1 is image of unoccupied state; b2 is image of occupied state.).(c) One reactive site (adatom-rest pair) for directed-assembly of organic materials on this surface.

The competition and selectivity of different functional groups of the assembled molecules were thoroughly investigated. For example, our recent systematic studies for the directed-assembly of various simple and complex aromatic molecules (Figure 10a) on Si(111)-7×7 discovered that the selection of reaction channel for these molecules is determined by the electronic contribution of heteroatoms for the formation of the aromatic conjugation of $(4n+2)$ π electrons, the geometric arrangement and the electronegativity of the heteroatoms on the aromatic ring, and molecular polarity.^{12,13} Based on the mechanistic studies of the directed-assembly of multi-functional organic molecules on silicon surface, a novel layer-by-layer strategy was designed and used for a controllable growth of organic multi-layer architectures (Figure 10b). This layer-by-layer alternate growth technique will open up a door for controllably fabricating molecular multi-layer architectures which is crucial for a wide spectrum of technological applications.

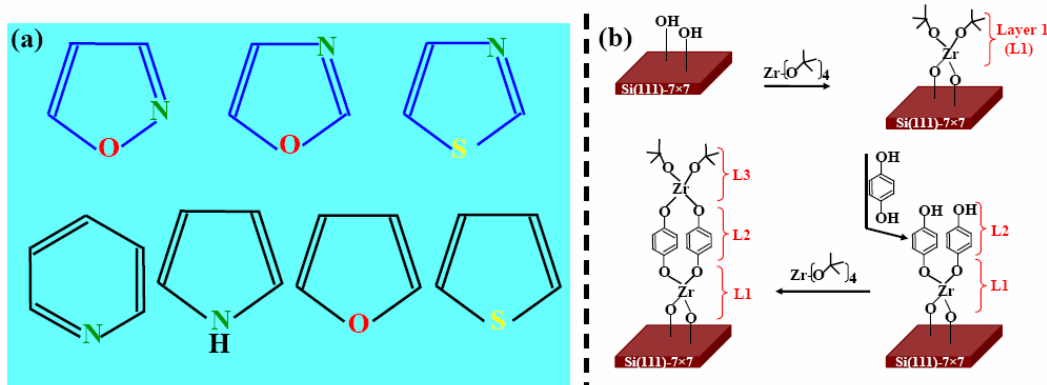


Figure 10. (a) Studied aromatic molecules. (b) Layer-by-layer directed-assembly strategy for a controllable synthesis of molecular multilayer architecture on Si(111)-7×7.

Conclusions

Nanoscale surface chemistry in the self-assembly and directed-assembly of organic molecules on different solid surfaces and conceptually new methodologies for the syntheses of 2-D and 3-D nanostructured organic architectures, were revealed. 2-D multi-component stoichiometric organic architectures such as nanomeshes were synthesized via co-self-assembly, which represents critical steps towards the design of 2-D nanostructural compositing materials. The directed-assembly of organic molecules via strong chemical bonds can be carried out through several uncovered reaction channels. The competition and selectivity of multiple reaction channels in the directed-assembly of multi-functional molecules on silicon surface were systematically studied. Methodology for developing silicon-based 3-D organic architecture was designed for significant applications in a wide spectrum of technological fields.

References

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