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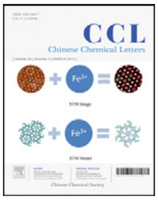

Review

Construction of two-dimensional (2D) H-bonded supramolecular nanostructures studied by STM

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ABSTRACT

In this review, a group of two-dimensional (2D) hydrogen-bonded supramolecular networks developed in our laboratory are discussed. Our attention is mainly focused on: (1) recognition of Fe^{3+} through two-component molecular networks; (2) site-selective fabrication of 2D fullerene arrays; and (3) fabrication of the nanoporous structure regulated by photoisomerization reaction process. It is envisioned that special supramolecular nanostructures, through H-bonding interactions, can be constructed or reconstructed to be further investigated toward the research of multi-component systems, molecule recognition, single molecular switches, and host–guest supramolecular chemistry.

1. Introduction

Based on molecular recognition and self-assembly, supramolecular chemistry has been recognized as an important concept in nanotechnology and widely studied in recent years [1,2]. Different from traditional chemistry, where chemical bonds play a major role, self-assembly of supramolecular nanostructures is mainly achieved through non-covalent interactions (*i.e.* hydrogen bonds, π–π stacking, electrostatic interactions, metal–ligand coordination and van der Waals interaction) [3–5]. The self-assembled process of molecules at surfaces or interfaces can be complicated since it involves interactions between molecules and molecules, molecules and substrate, as well as other environmental factors [6,7]. Due to high directionality and selectivity, hydrogen bonds represent versatile intermolecular interactions in obtaining and understanding specially designed supramolecular nanostructures [8–13].

With its resolution at atomic level, scanning tunneling microscopy (STM) has been proven to be a powerful tool in studying surface phenomena. When the metallic probe in STM closely approaches the conductive substrate, a distance-sensitive tunneling current will generate under the applied voltage between the two conductive media. The tunneling current, which decreases exponentially with the distance between the probe and the substrate, reflects the density of electronic states on atomic flat surface. By controlling the tunneling current, molecules adsorbed on surfaces with very high resolution can be observed. Through visualizing single molecules, the self-assembled structures of physical adlayers as well as the chemical reaction process at surfaces or interfaces can be studied.

Early experiments of molecules adsorption by STM are mainly carried out on metal surfaces under ultra-high vacuum (UHV) conditions. UHV conditions provide a perfect atmosphere to protect the substrate surface. However, special technical treatments are needed and their potential application is relatively limited. In recent years, more and more relevant experiments are performed in ambient environment, which add the flexibility in research. Both the methods require conductive substrates, molecules immobilization and thin adlayers [14–21].

In this review, we discuss a series of two-dimensional (2D) H-bonded supramolecular nanostructures on highly oriented pyrolytic graphite (HOPG) with the aid of scanning tunneling microscopy (STM) technique under ambient condition. Being conductive, atomically flat, stable and easy to clean, HOPG has several advantages as a substrate. We mainly focus on the construction of surface-confined 2D molecular frame via intermolecular hydrogen bonds of small organic molecules. Three parts herein are included: (1) recognition of Fe^{3+} through

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two-component molecular networks; (2) site-selective fabrication of 2D fullerene arrays; and (3) fabrication of the nanoporous structure regulated by photoisomerization reaction process. It is envisioned that, special supramolecular nanostructures can be constructed or reconstructed to be further investigated toward the research of multi-component systems, molecule recognition, single molecular switches, and host–guest supramolecular chemistry.

2. 2D H-bonded supramolecular networks on HOPG surface

2.1. Recognition of Fe^{3+} through two-component molecular networks

Construction of 2D H-bonded supramolecular networks is widely studied through systems with hydroxyl, carboxyl, and amino groups. In early reports, supramolecular structures formed by triacontanol ($CH_3(CH_2)_{29}OH$), isophthalic acid derivatives and 1-octadecylamine ($CH_3(CH_2)_{17}NH_2$) were illustrated by STM images [9]. Both hydrogen bonds and interactions between the long alkyl chains and the substrates contribute to the formation of stable lamellae. Most systems studied by STM involve organic compounds with high alkyl chains. However, some small molecules, such as benzene and naphthalene, are difficult to be observed by STM since the interaction between molecules and substrate are too weak to stabilize. Intermolecular H-bonding interactions are highlighted under such circumstances.

2,6,10-Tricarboxydecyloxy-3,7,11-triundecyloxy triphenylene (sym-TTT, Fig. 1(A)) is a symmetric triphenylene derivative with three carboxyl groups [22]. Previously, it has been reported that a hexagonal network can be formed by every six sym-TTT molecules with the seventh one in the center at the octanoic acid–HOPG interface [23]. From the STM results, it can be inferred that the entrapped carboxyl groups remain in a free state. To modify the supramolecular network of sym-TTT, melamine (Fig. 1(B)), a molecule with three-fold symmetry, was added as the functional guest molecule. The STM measurements reveal that in the sym-TTT/melamine nanoporous network, six melamine molecules can form a hexagonal cavity via N···H—N hydrogen bonds. Moreover, each melamine forms two hydrogen bonds (O···H—N (amino group of melamine) and O···H—N (nitrogen atom of melamine)) with one carboxyl group of the neighboring sym-TTT molecule to form perfect cocrystal structure (Fig. 1).

The nanopore formed by the melamine cluster is functionalized by the amino groups inside. Since it has been reported that Fe^{3+} can be coordinated by amine nitrogen [24], Fe^{3+} was chosen as the target guest metal ion to realize molecule recognition. STM observations further demonstrate that in the system of sym-TTT/melamine/Fe^{3+}trimmers (Fig. 2), the remained amino-groups of melamine are linked with one iron (III) ion through metal–ligand coordination to form four-ligand structure [25].

2D porous networks are often expected to immobilize functional guest molecules depending on the characteristics of

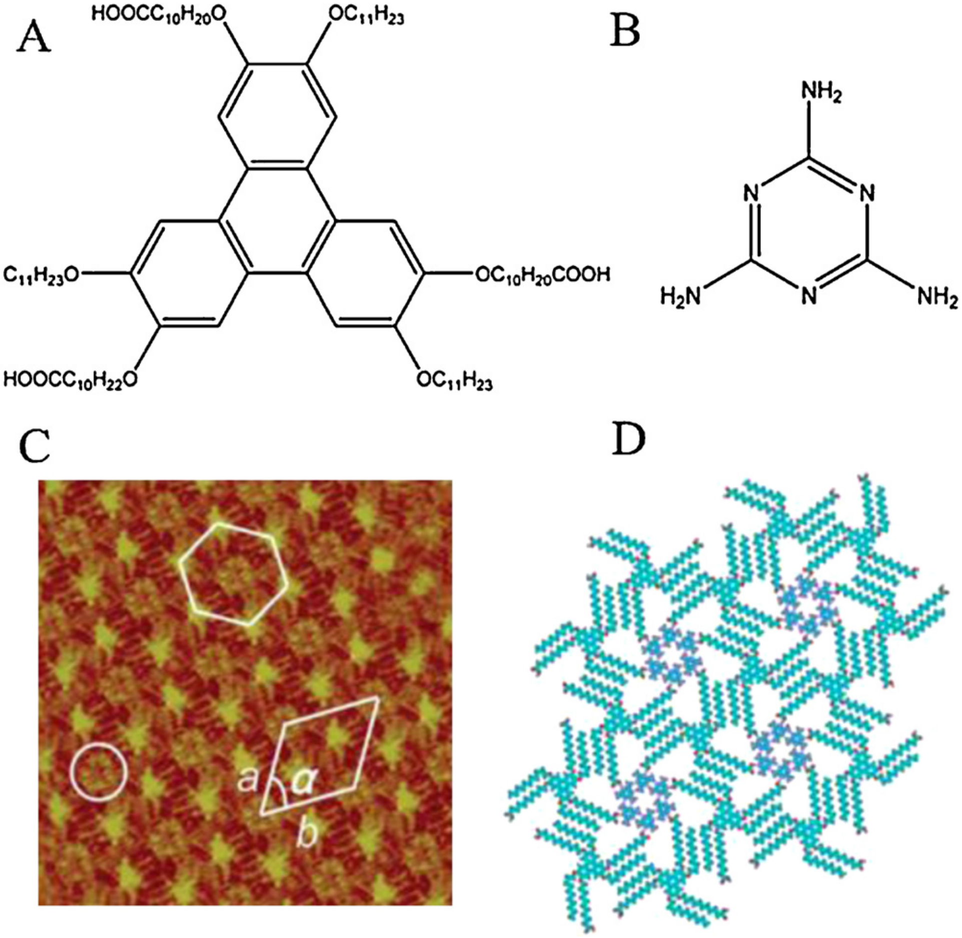

Fig. 1. (A) and (B) represent chemical structures of sym-TTT and melamine. (C) High-resolution STM image of sym-TTT/melamine network (19.7 nm × 19.7 nm, I = 398.5 pA, V = 924.8 mV). The white circle highlights functionalized nanopores formed by the six-melamine cluster. (D) Proposed molecular model for sym-TTT/melamine network structures [25]. Reproduced by permission of The Royal Society of Chemistry.