



## Formation of hydrogen bond-based 2D two-component supramolecular networks at liquid-solid surface



Wei Li<sup>a,\*</sup>, Xinli Leng<sup>b</sup>, Chengyong Xu<sup>a</sup>, Ning Liu<sup>a</sup>

<sup>a</sup> Department of Science, Nanchang Institute of Technology, Nanchang 330099, PR China

<sup>b</sup> Department of Physics, Nanchang Normal University, Nanchang 330032, PR China

### A B S T R A C T

Two kinds of variable binary supramolecular structures constructed by 1,3,5-benzenetricarboxylic acid (TMA) and terephthalic acid (TPA) on a highly oriented pyrolytic graphite (HOPG) were investigated by scanning tunneling microscopy (STM). Two different solvents (heptanoic acid and nonanoic acid) were utilized to affect the self-assembling structures of TMA and TPA at the liquid/HOPG interfaces. High-resolution STM measurement revealed that the functional networks of TMA/TPA are proposed from the hydrogen-bonding under different solvents environment, and the functionalized flower network could recognize three AgNO<sub>3</sub> molecules. These results could be helpful for designing functionalized molecular networks by multi-component self-assembling strategy.

### 1. Introduction

Self-assembly involving molecular recognition events play an irreplaceable role in natural [1,2] and man-made systems [3,4], which has vast potential in scientific research and nanotechnology. In general, self-assembly leads to the formation of nanoporous networks via non-covalent interactions, such as van der Waals interactions [5–8], hydrogen bonds [9–11], halogen bonds [12–14], metal-ligand coordination [15,16], etc. These supramolecular networks at different dimensions [17,18] composed of various building blocks interlinked through hydrogen bonding, are a promising class of materials for future technology. Specially, how to gain the controllable two-dimensional (2D) molecular assemblies might turn out to be crucial to the design and properties of functional surface [19,20].

Presently, numerous highly ordered 2D mono-component porous networks had been successfully obtained through synthesizing unit molecules with suitable chemical structures and functional groups [21, 22], choosing appropriate substrate surfaces [23,24], and adopting befitting experimental conditions, such as solvent, concentration, temperature and guest exchange [25,26]. These factors are of great importance for controlling the assembled structure and tuning properties of the obtained nanostructure. As for binary or multiple complexes, there usually happen two phenomena, phase separation at nanoscale, or the formation of randomly mixed monolayers. Self-assemblies of binary or multiple components might have potential advantages in the fabrication of the heterojunction materials for technology purpose. Therefore, the

controllable formation of multi-component assemblies with a well-defined ordering networks is still one big challenge to molecular self-assembly approaches. Among various experimental factors, it is no doubt that the choice of appropriate building blocks still play an important role in whole molecular self-assembly procedures.

Such 2D porous networks offer the possibility to immobilize functional guest molecules depending on the characteristics of the porous networks, such as size, shape, and symmetry. For most of the reported host-guest architectures, the interactions between guest molecules and inner cavity of the networks are typically van der Waals interactions or relatively weak hydrogen bonds with evenly distributed interaction sites within the cavity. However, this kind of guest selectivity is limited because of the relatively weak interaction between host and guest. It can be expected that a functionalized inner cavity would facilitate enhanced selectivity of the networks for guest molecules. For example, Y. B. Li et al. have demonstrated that nanoporous networks can be functionalized through inclusion of additional molecule within the networks [27]. In our previous report, the nitrite containing full orbital metals (AgNO<sub>3</sub> and Zn(NO<sub>3</sub>)<sub>2</sub>), the pristine nitrate molecules are directly embedded into the pores within the TMA networks [28]. Therefore, designing the cavities with suitable size and selecting appropriate molecules would be expected to immobilize the guest molecules.

In this work, the two-component self-assembly supramolecular structures of TMA and TPA at heptanoic acid and nonanoic acid liquid/HOPG interfaces were investigated by STM. One kind of TMA/TPA structure is rectangle honeycomb in nonanoic acid, the other is flower

\* Corresponding author.

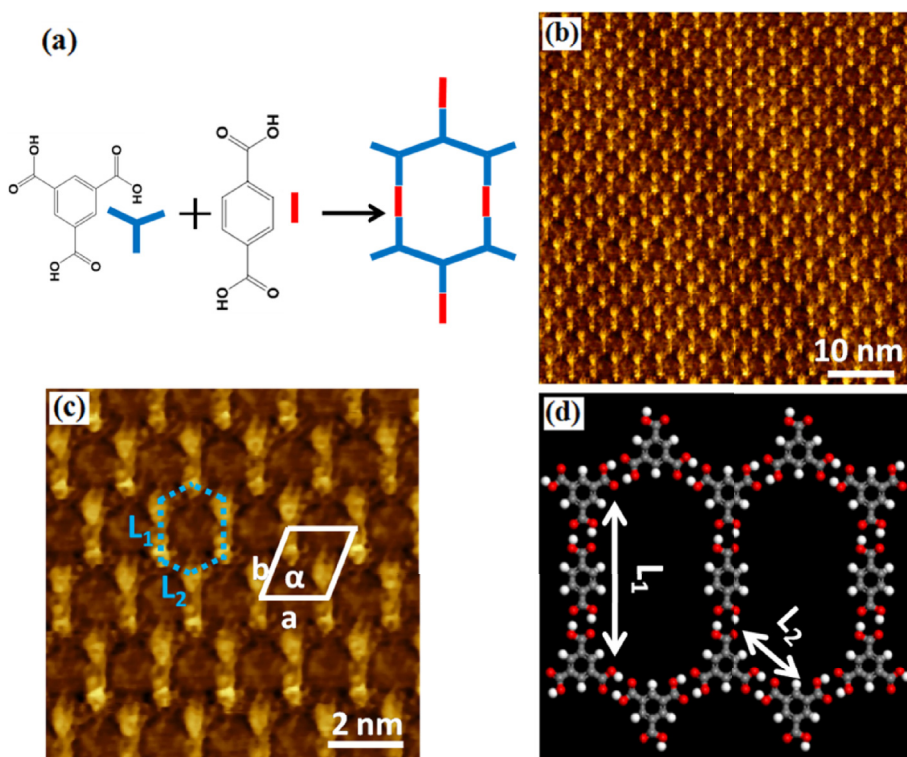
E-mail address: [liweidting@nit.edu.cn](mailto:liweidting@nit.edu.cn) (W. Li).

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**Fig. 1.** (a) Schematic diagram of the Self-assembly of TMA and PTA honeycomb structure on nonanoic acid/HOPG interface; (b) The large-scale STM image of TMA/TPA self-assembled nanoporous network on nonanoic acid/HOPG interface ( $I = 0.63$  nA,  $V = -0.5$  V); (c) The high-resolution STM image of TMA/TPA self-assembled nanoporous network ( $I = 0.68$  nA,  $V = -0.56$  V). The blue dashed line highlights functionalized nanoporous formed by TMA and PTA molecules; (d) Proposed molecular model for TMA/TPA self-assembled nanoporous network structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

structure in heptanoic acid. The possible factors affecting the structure on the surface are discussed based on the cooperative interaction. The results of STM measurements reveal that functionalized nanoporous networks could immobilize three  $\text{AgNO}_3$  molecules. Through those experimental results, we hope to explore new approaches toward constructing highly complex on-surface supramolecular architectures and put forward a step toward on-surface molecules devices.

## 2. Experimental section

### 2.1. Sample preparation

All chemical molecules and solvents for scanning tunneling microscopy (STM) experiments were purchased from Tokyo Chemical Industry (TCI) and used without further purification. Stock solution of 30 ml each of 1, 3, 5-benzenetricarboxylic acid (TMA), terephthalic acid (TPA) and  $\text{AgNO}_3$  was prepared by dissolving in nonanoic acid and heptanoic acid. The concentrations of all the solution for STM investigation were less than  $1.5 \times 10^{-5}$  M. STM samples were prepared by dropping about  $5 \mu\text{L}$  of above solutions on a freshly cleaved highly oriented pyrolytic graphite (HOPG, grade SPI-2) substrate. Then, the samples were kept at room temperature for about 3 h. After that, the samples were again investigated by STM at the liquid/solid interface.

### 2.2. STM measurements

All STM measurements were performed at liquid/solid interface and acquired in constant current mode under atmospheric conditions. All the STM images were acquired on a Pico-SPM (Molecular Imaging, Agilent Technology) scanning tunneling microscope operating in constant-current mode under ambient conditions of about  $25^\circ\text{C}$ . STM tips were made by cutting Pt/Ir (80/20) wire (California Fine Wire Co., Grover Beach, CA). Detailed tunneling conditions were given in the corresponding figure captions. All STM images presented in this study were extracted from raw data files using Pico Image Basic 6.2 program (Agilent, USA) and all samples to test repeatability and to make sure that

there were no artifacts caused by interactions between the tip and the sample. The drift is calibrated using the underlying graphite lattice as a reference.

## 3. Results and discussion

The two self-assembled chicken-wire and flower structures of pure TMA has been reported at the alkanolic acids-graphite interface [29]. In the previous report, it can be seen that all carboxy groups participate in the hydrogen bonding, resulting in unstrained networks. The main difference is that hydrogen bonding occurs only between molecular pairs for the chicken-wire structure, whereas for the flower structure, one-third of all hydrogen bonds involve three molecules, resulting in a circular hydrogen-bonding scheme. The structures indicate the possibility that other functional guest molecules with carboxy groups could form a new structure.

At the nonanoic acid/HOPG interface, we choose TPA, with a benzene in middle and two carboxy groups in two ends, as the functional guest molecule to modify the supramolecular network of TMA. The TPA represents a good module, which is capable of forming multi-dimensional hydrogen-bonded host-guest architectures. Fig. 1a shows the expected self-assembly structure. When the nonanoic acid solution including the TMA and TPA molecules is deposited on graphite surface, a new kind of porous network is formed and observed in Fig. 1b. It is clear that the new nanoporous network is different from that formed by pure TMA [30] or TPA [31]. When the molar ratio of TMA: TPA is adjusted to 2:1, the bi-component nanoporous cover the whole surface. More details of the structure are shown in the high resolution STM image in Fig. 1c, where the length of the hexagon gets longer. The length  $L_1$  of the hexagon is  $1.94 \pm 0.1$  nm, which almost equals to the total length of two TMA molecules adding one TPA molecule, where the length  $L_2$  is the same of the pure TMA. It is indicative of the formation of hydrogen bonds between TMA and TPA molecules, and all carboxylic acid groups participate in the formation of hydrogen bonding. A unit cell is determined for the adlayer. The measured unit cell parameters are  $a = 1.7 \pm 0.1$  nm,  $b = 2.6 \pm 0.1$  nm and  $\alpha = 70 \pm 10$ , respectively. According to the STM

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