

Original article

Formation of heterocaryotic and homonuclear bridged–dimeric complexes on surface

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ABSTRACT

The formation of coordinated dimeric complexes bridged by axial ligands on surface is observed with the help of a 1,3,5-tris(10-carboxydecyloxy)benzene (TCDB) template through scanning tunneling microscopy (STM). STM images of molecular adlayers of zinc tetraphenylporphyrin (ZnTPP), zinc phthalocyanine (ZnPc), and their mixture are reported. ZnTPP and ZnPc can spontaneously form highly an ordered structure with a 1:1 molar ratio, which is different from that of individual ZnPc. The coordinated bimolecular complexes bridged with axial ligands, simply as ZnPc–DPP–ZnTPP and ZnPc–DPE–ZnPc, are presented and the corresponding surface structures are compared. ZnPc and ZnTPP can be connected by an axial ligand DPP and formed assembled structures out of surface. Two types of arrays with entirely new structure are obtained for the ZnPc–DPE–ZnPc complex. These bridged hybrid complexes provide an example of design of self-organized crystals on the basis of coordination through non-covalent interactions.

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1. Introduction

Coordination chemistry has emerged as a promising strategy for the construction of advanced materials with well-defined nanoscale structures [1–5]. The non-covalent interactions between organic ligands and metals are an essential feature in the design of materials' structure. In particular, directional interactions between the designed functional groups control the supramolecular structure. Metal–organic complexes have promising prospects for the applications in the fields of chemical separation, catalysis, optoelectronics, magnetic, and are a class of important source materials in preparing nano-devices [6–10]. Although the research is mainly focused on their three-dimensional crystals at present, this class of complexes are also a hot research topic in supramolecular chemistry [4–10].

Scientists have evaluated the assembly structures and properties of such aggregates on surface through the scanning tunneling

microscopy (STM) technique, which can provide clear images with atomic resolution [12–17]. Hereinto, metal complexes of porphyrin and phthalocyanine have received considerable attention due to their large π systems. Based on the self-assemblies of porphyrins and phthalocyanines as well as the coadsorption structure of their mixtures [18,19], various stable and periodic structures have been prepared using intermolecular coordination interactions, such as one-dimensional coordination polymer, two-dimensional coordination grid and three-dimensional complex structures [4,11,17,20,21]. The other reason of such studies is that metal–ligand bonds carry great advantages such as fewer synthesis steps, faster synthesis process, self-repair ability, which are effective in self-assembling and preparing periodic nanostructures.

Recently, we studied the adsorption behavior of coordination complexes in a supramolecular template on a highly oriented pyrolytic graphite (HOPG) surface using STM under atmospheric conditions [22,23]. It was found that two zinc phthalocyanines (ZnPc) can coordinate with 1,3-di(4-pyridyl)propane (DPP) and formed a well-ordered self-assembled structure with a molecular template. From both fundamental and technological points of view, formation and characterization of axial coordination with the central metal are of great importance because the obtained

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complexes are closely related to the crystal engineering applications. While previous reports on coordinated cluster ZnPc–DPP–ZnPc are encouraging for surface aggregation in different templates, rational design of materials is in question. Is there only ZnPc suitable for forming such complexes? How to design the chemical structures?

Therefore, this study will be focused on other molecules that can form coordinated complex structures on the HOPG surface. On the basis of previous study, in this work we firstly studied the physical and chemical co-absorption behaviors of ZnPc and zinc tetraphenylporphyrin (ZnTPP) with DPP. And then we selected another analogous dipyridyl molecule 1,2-di(4-pyridyl)ethylene (DPE) to investigate whether it can coordinate with ZnPc on the HOPG surface. After analysis of the results, it can be concluded that new complexes with different structures were fabricated on the HOPG surface and a synergistic effect of a pre-fabricated template was also observed.

2. Experimental

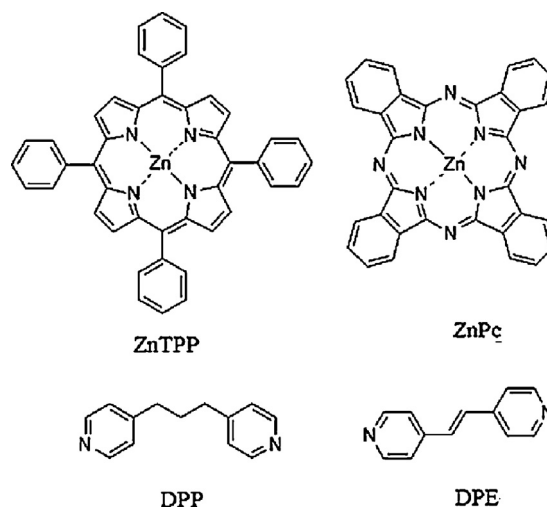
Materials: The materials studied include 1,3,5-tris(10-carboxydecyloxy)benzene (TCDB), Zinc phthalocyanine (ZnPc), zinc tetraphenylporphyrin (ZnTPP), 1,3-di(4-pyridyl)propane (DPP), 1,2-di(4-pyridyl)ethylene (DPE). TCDB was synthesized according to the methods reported. ZnPc, ZnTPP, DPP, DPE, and solvent 1-phenyloctane were purchased from Tokyo Chemical Industry Co., Ltd. These reagents were used without any purification.

Preparation of sample and measurements: The compounds (TCDB, ZnPc, ZnTPP, DPP, DPE) were dissolved in 1-phenyloctane with concentrations less than 10^{-4} mol/L. The solutions of the target compounds were deposited onto the freshly cleaved highly oriented pyrolytic graphite (HOPG) surface. STM imaging was performed at the solid–liquid interface after a short period of time under ambient conditions. Then, 0.4 μ L of 1-phenyloctane solution containing DPP or DPE was deposited onto the assembly structure. STM was conducted at the solid–liquid interface after staying for 20 min. STM with a digital instruments nanoscope III controller was used to acquire the reported constant current images using Pt0.8Ir0.2 tips.

3. Results and discussion

3.1. Self-assembly of ZnPc/ZnTPP in TCDB template

The chemical structures of studied compounds are shown in Scheme 1. Because of the relative inertness on the HOPG surface, ZnPc and ZnTPP molecules diffuse over the surface, and thus single isolated molecules cannot be seen by the STM technique under ambient conditions. Very recently, porphyrin and phthalocyanine molecules have been investigated on several metal surfaces [23–29]. In this study, a network of 1,3,5-tris(10-carboxydecyloxy)benzene (TCDB) was formed and used as a template for the adsorption of ZnPc and ZnTPP molecules on the HOPG surface



Scheme 1. Chemical structures of ZnPc, ZnTPP, DPP and DPE.

[30,31], and the dimeric complexes of ZnPc or ZnTPP bridged by the DPP or DPE ligand formed in a TCDB template on surface were investigated.

Firstly, the formation of two-dimensional bimolecular ZnPc and ZnTPP structures in TCDB is observed by STM. When ZnPc and ZnTPP are deposited onto the HOPG surface in a 1:1 molar ratio, a well-ordered closely-packed bimolecular structure of ZnPc and ZnTPP can be observed as shown in Fig. 1a. It should be noted that ZnTPP molecules cannot be accommodated by the TCDB cavities possible due to the molecular size matching and the weak guest–host intermolecular interactions, while one TCDB cavity can hold one or two ZnPc molecules [23]. From the point of view of the chemical structure, ZnTPP exhibits relatively high-degree distortion, while ZnPc has a robust and planar aromatic structure that contributes to the aggregation on surface. As marked by the white rectangle, there might still be a small region in which one TCDB cavity holds two ZnPc molecules. In other area, however, ZnTPP and ZnPc coadsorbed in one TCDB cavity, and formed the host–guest structure.

A high-resolution STM image displayed in Fig. 1b shows a looser molecular packing than the ZnPc case. It is proposed that a well-ordered 1:1 structure is shown with one ZnPc and one ZnTPP held in each TCDB cavity. After careful analysis, we can find that the molecular packing positions are slightly different between strips marked by the red and light blue arrows, respectively. Molecules ZnTPP and ZnPc were represented by red and light blue squares. In the region highlighted by white dotted rectangle, the relative position of ZnTPP and ZnPc in these two strips changed. From the proposed schematic molecular model shown in Fig. 1c, ZnTPP and ZnPc in one TCDB cavity might move and formed such structures. It should be noticed that there is no remarkable contrast in tunneling

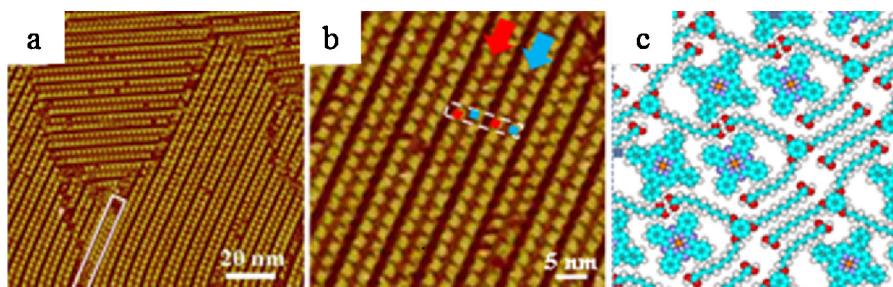


Fig. 1. (a) Large-scale and (b) high-resolution STM images for the self-assembled structure of ZnTPP and ZnPc in a TCDB network. (c) The suggested molecular model of image (a) and (b).

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