Observation of coexistence of 1D and 2D nanostructures in cobalt dipyrromethene trimer complexes adsorbed on a graphite surface

S.B. Son a, S.J. Lee a, J.R. Hahn a,*, L. Ma b, J.-Y. Shin b, D. Dolphin b

a Department of Chemistry, Chonbuk National University and Research Institute of Physics and Chemistry, Deok-jin Gu, Jeonju 561-756, Republic of Korea
b Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1

The adsorption of functional molecules on solid surfaces is becoming an important aspect of nanotechnology [1]. Molecular electronics—the integration of functional molecules to make specific functionalities on an integrated circuit—is a promising approach to reducing device size. In the fabrication of functional structures and devices, porphyrins are important materials because their conjugated and highly delocalized p-bonds yield various unusual chemical and physical properties [2–4]. To date, the assembly method has been widely used to construct 2D and 3D molecular structures through specific molecule–molecule and molecule–substrate interactions, whereas the formation of 1D molecular structures has been less explored. One-dimensional templates, such as step edges on a surface, have frequently been proposed to form 1D molecular arrays.

The rigid-planar nature of porphyrins has advantages in the assembly of 2D nanostructures on solid surfaces [5]; however, the lack of conformational flexibility can also be limiting. Porphyrin complexes are held together by covalent bonds, but self-assembled porphyrin structures are held together by weaker interactions such as hydrogen bonding and metal coordination, affording very versatile systems. Recently, dipyrromethenes, which can form neutral complexes with various metal ions, have been introduced as flexible and versatile ligands in the area of supramolecular chemistry. For example, bisdipyrromethene metal complexes featuring double helical structures or triangular structures have been reported [6–8].

In the present study, we used scanning tunneling microscopy (STM) to examine the nanostructures formed by cobalt dipyrromethene trimer (CDT) complexes adsorbed on a highly ordered pyrolytic graphite (HOPG) surface. We observed long 1D molecular chains isolated on terraces and 2D hexagonal patterns confined by a 1D chain and/or a graphite step edge. These 1D and 2D structures are attributed to ‘edge-on’ and ‘face-on’ complex alignments on the surface, respectively. In both configurations, substrate-mediated molecule–molecule interactions may play a significant role in stabilizing the nanostructures.

The CDT complex shown in Fig. 1 was prepared in the University of British Columbia [6–8]. The structure and purity of the compound were confirmed by 1H nuclear magnetic resonance spectroscopy. The complex is composed of three cobalt dipyrromethene monomers surrounding a cavity in the middle. It was possible to obtain single crystals of this trimer suitable for X-ray diffraction analysis. Molecular modeling predicts an outer diameter of the trimer of 2.6 nm and a height of 2.1 nm. For adsorption of the CDT complexes onto a graphite surface (Advanced Ceramics, grade ZYA), the complex was first dissolved in dichloromethane at a concentration on the order of $1.0 \times 10^{-5}$ M. Dichloromethane was chosen as the solvent because it can be removed from the surface under the conditions used. A droplet of the solution was applied onto a freshly cleaved surface and left to dry in air either at room temperature or at 100 °C for several hours. The droplet spread evenly over the surface, resulting...
in uniform coverage of the entire surface with CDT. All solvent appeared to have evaporated within a few minutes, leaving behind adsorbed CDT complexes. We expect that heating at 100 °C would remove any residual solvent molecules trapped in the CDT nanostructures on the surface.

STM images were obtained using a commercial scanning tunneling microscope (NT-MDT and NanoSurf) under ambient conditions [9]. STM tips were mechanically cut from a 0.25 mm Pt/Ir wire. Constant current mode (topographical imaging) was employed to investigate the static properties of the structures. All of the images shown are raw data with mean plane subtraction to reduce the thermal drift effect. The features of the adsorbed CDT complexes appear the same on the substrates evaporated at room temperature and 100 °C, indicating that the morphology of the sample evaporated at room temperature is not influenced by any residual solvent molecules that may have remained. The concentration and volume of the solution used in the experiment were carefully chosen to ensure that the amount of CDT adsorbed on the graphite surface was sufficient to take STM images.

STM imaging revealed two types of CDT molecular assemblies coexisting on the same graphite surface, as shown in Figs. 2 and 3. These molecular arrangements were observed by repeated scanning under very mild tunneling conditions. 1D chains of the type shown in Fig. 2(a) were found to have lengths extending up to a few hundred nanometers (not shown). At room temperature, where thermal mobility is appreciable, well-ordered and isolated chains were observed on the terraces of the surface; this finding indicates that there are significant adsorbate–substrate interactions in this system.

Fig. 1. Molecular structure of a cobalt dipyrromethene trimer complex with dimensions indicated.

Fig. 2. (a) STM topographical image showing a 1D molecular chain structure of cobalt dipyrromethene trimer complexes adsorbed on a graphite surface and (b) cross-sectional cuts taken along the chain (black) and along the direction perpendicular to the chain (red). The image was obtained at a sample bias voltage of 200 mV and a tunneling current of 45 pA. Thermal drift was not compensated for in the STM image. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 3. (a) STM topographical image showing both a 1D chain and a 2D hexagonal pattern of cobalt dipyrromethene trimer complexes adsorbed on a graphite surface and (b) a cross-sectional cut taken across the structures. (c) Magnified STM topographical image of the hexagonal pattern. The images were obtained at a sample bias voltage of 200 mV and a tunneling current of 100 pA. Thermal drift was not compensated for in the STM image.
The 1D chains consisted of a repeated pattern of protrusion features, where each chain was surrounded by large areas of pristine graphite, where the trigonal asymmetry of the graphite layer was imaged with atomic resolution. Fig. 2(b) shows cross-sectional cuts taken along the chain (black) and along the direction perpendicular to the chain (red). The spacing of the features along the chain was determined to be 3.4 nm by averaging the values measured from several images. The mean full width at half maximum (FWHM) of each protrusion unit was 1.6 nm. The 1D chains were exclusively observed on terrace regions, in contrast to previous reports of metal complexes forming chains along graphite step edges [10] or of the formation of arrays of 1D structures [11]. It is difficult to determine the internal structure of each protrusion from the present images. Multiple-tip effects, which can produce misleading features in STM images, were removed by a repeated tip sharpening process in situ at a graphite step edge. However, the dimensions of each protrusion in the STM image correspond to the molecular dimensions, suggesting that each protrusion corresponds to one CDT complex.

Fig. 3(a) shows the 2D hexagonal pattern formed by the adsorption of CDT complexes on the graphite surface. This pattern has a lattice constant of 3.12 nm, which is 12 times the graphite lattice spacing. Fig. 3(b) shows a cross-sectional cut across the boundary in Fig. 3(a). The topographical corrugations over the hexagonal structures are less than 0.07 nm high while over the boundary the height is about 0.2 nm or higher. The size of each protrusion is similar to the dimensions of a CDT complex. The features within each protrusion in Fig. 3(c) are not clearly resolved, which may be due to the weak bonding of each unit in the CDT complex. We found that the boundary of the 2D hexagonal pattern in Fig. 3(a) consists of a chain of higher protrusions, similar to the 1D chain in Fig. 2(a). The hexagonal patterns were found to extend for a few hundred nanometers and to stop either at a graphite step edge or at a 1D chain of protrusions. The height of the boundary protrusions is greater than that of the hexagonal pattern corrugations but slightly lower than that of an isolated 1D chain.

Many reports [12–19] on the structural analysis of various adsorbed porphyrin or phthalocyanine molecules help in the understanding our results. By using substituted long-chain alkanes as molecular anchors [12], Qi et al. found that both phthalocyanines and porphyrins can be immobilized at a graphite surface to allow high-resolution STM studies. Manipulation of individual porphyrin molecules using the STM tip has been demonstrated [13]. Moresco et al. reported the possibility of using a metallo-porphyrin (copper-tetra-3,5-di-t-butylphenyl porphyrin, Cu-TBPP) as a molecular switch at low temperatures [14]. In addition, the influence of molecular functionalities on the structure of self-assembled porphyrin wires and meshes has been reported [15]. Moreover, other studies have shown that porphyrin molecules adopt two possible adsorption and stacking configurations—’face-on’ and ’edge-on’—on a surface [16,17]. In the ’face-on’ configuration, the porphyrin molecules lie on the surface with the molecular plane parallel to the surface plane, whereas in the ’edge-on’ configuration the planes of the porphyrin molecules are either tilted with respect to, or perpendicular to, the substrate. Porphyrin structures adopting a ’face-on’ configuration have been widely observed using STM [12,18], whereas the direct observation of ’edge-on’ porphyrin structures has been rarely reported.

Cross-sectional cuts through both the 1D chain and 2D hexagonal CDT structures [Figs. 2(b) and 3(b)] show that the average topographical heights of these structures are 0.33 and 0.04 nm, respectively; that is, the isolated 1D chains are 8 times higher than the 2D hexagonal patterns. This suggests that the CDT molecules in the 1D chain are in some form of ’edge-on’ alignment whereas the hexagonal pattern is comprised of compounds in a configuration close to the ’face-on’ alignment. For porphyrins, the ‘edge-on’ stacking optimizes the π–π interactions between the conjugated porphyrin rings, affording a highly conjugated and delocalized π-system [20]. However, in the present molecular system, the distance between adjacent 1D protrusions along the chain is 3.4 nm on average, which is too far to have π–π interactions between the CDT complexes. It is possible that a substrate-mediated molecule–molecule interaction plays a major role in connecting the molecules in the 1D chain features. Graphite layers have metal-like electronic conductivity along the layer, which allows electronic perturbations to propagate a few nanometers along the layer [21,22]. The observations that the 1D chains were always located on terraces and were not mobile at room temperature indicate a significant interaction between the chains and the surface layer. In the case of the 2D hexagonal pattern, the symmetry of the pattern is the same as that of the graphite layer, which again suggests a significant interaction between the pattern and the surface layer. Further, the lack of definition of each protrusion indicates a more dynamic distribution of the CDT inside the trimer, and no conclusions could be drawn about the internal coordination structure of ligands.

The measured heights of the 1D chains are much smaller than the geometric dimensions of the complex. This difference may be due either to a much higher tunneling barrier above the complexes or to poor conductivity associated with the complex. For example, a self-assembled monolayer of dodecanethiol adsorbed on gold has a layer thickness of 1.2 nm, whereas STM measurements give a monolayer height of only 0.18 nm above the substrate [23,24]. In the case of Cu-TBPP adsorbed on the Cu(2 1 1) surface, the measured height of the molecule is 0.2 nm, which is much less than the expected value of 1.1 nm [15].

An interesting feature of the 2D hexagonal patterns is that they stop at either a 1D chain or at a graphite step edge. In fact, we observed that the 2D patterns are always accompanied by 1D chains, indicating that the hexagonal patterns cannot form without a 1D chain as a boundary. Therefore, the 1D and 2D structures may start to form independently and then the 1D chain blocks the growing of the 2D pattern. Alternatively, the 1D chain may act as a seed for the growth of the 2D hexagonal pattern with a ’face-on’ alignment on the graphite surface. The height of the 1D chains at the boundaries of the 2D patterns is lower than that of the isolated chains, indicating a tilted ’edge-on’ alignment at the boundary.

In summary we directly observed coexisting 1D and 2D CDT nanostructures adsorbed on a graphite surface using STM. The 1D and 2D patterns are attributed to ’edge-on’ and ’face-on’ molecular alignments on the surface, respectively. The isolated 1D chains formed on terraces with a significant interaction with the substrate. All 2D hexagonal patterns were accompanied by a 1D chain as a boundary. These adsorption features stand in contrast to those of porphyrin-based nanostructures. This difference may be due to dipyrrmethene complexes having greater conformational flexibility compared to porphyrins. The present results could be of use in areas such as molecular electronics, optoelectronics, and sensor development.

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References