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Submolecular visualisation of palladium acetate complexation with a bipyridine derivative at a graphite surface

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In situ **complexation of palladium acetate by a monolayer of a bipyridine derivative at a graphite/liquid interface has been observed using scanning tunneling microscopy.**

With the continuing need for miniaturization of electronics, surface nano-patterning as a requisite to move from nanoscience to nano-technology has been of much interest in the last decade.[1] Nano-patterning has gained a growing momentum recently,[2] due to the wide range and better understanding of exquisite tools to advance this field especially scanning tunneling microscopy (STM).[3] With STM, the self-assembly of a wide range of organic compounds has been studied at the solid/liquid interface.[4,5] STM allows not only for the study of the molecular organization in the monolayer, but also for the evaluation of dynamic[6] and chemical[7–9] phenomena within the monolayer and between the monolayer and the liquid layer (supernatant solution) on top of the monolayer. Metal complexes on surfaces are of great technological and fundamental interest.[10–12] STM investigation in this direction has been mostly concerned with the electronic properties of the metal complexes on different surfaces.[13,14] Recently nanostructures of different metal complexes deposited on surfaces have been reported.[15–18] The inherent coordination properties of transition metals and the possibility to exchange weakly coordinated ligands with stronger coordinated ligands, might enable their use in building specifically functionalized three-dimensional (3D) nanostructures. In this communication, we report on the STM investigation of *in situ* complexation of $Pd(OAc)_2$ by a monolayer of a bipyridine derivative at a graphite surface. The formed monolayer can be used as a template to build nanostructures.

Prior to imaging, **$C_{19}BiPyC_{19}$** (Fig. 1) and $Pd(OAc)_2$ were dissolved in 1-phenyloctane (Aldrich, 99%). The reported STM images were acquired in the variable current mode (constant height) under ambient conditions. In the STM images, white corresponds to the highest and black to the lowest tunnelling current. STM experiments were performed using a Discoverer scanning tunneling microscope (Topometrix Inc., Santa Barbara, CA) along with an external pulse/function generator (model HP 8111 A), with negative sample bias. Tips were etched electrochemically from Pt/Ir wire (80%/20%, diameter 0.2 mm) in a 2 M KOH/6 M NaCN solution in water. The experiments were repeated in several sessions using different tips to check for reproducibility and to avoid artefacts. Note that during the experiments, the STM tip is immersed in the supernatant solution. Different settings for the tunneling current and the bias voltage were used. All STM images contain raw data and are not subjected to any manipulation or image processing.

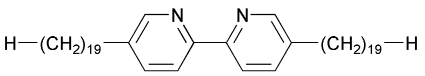

Fig. 1 Chemical structure of **$C_{19}BiPyC_{19}$**.

Upon applying a drop of **$C_{19}BiPyC_{19}$** solution on the graphite surface (HOPG), a physisorbed monolayer is spontaneously formed at the graphite/1-phenyloctane interface. Fig. 2(a) shows an image of such a monolayer observed with STM. The image is submolecularly resolved, which enables us to identify the two aromatic rings forming the bipyridine moiety (indicated by the two red arrows) as well as the aliphatic chains. The lamella is defined by two black troughs, which are characteristic for terminal methyl groups (indicated by the two yellow arrows). The bipyridine moieties appear to form an angle of 64 ± 2° while the aliphatic chains form an angle of 49 ± 2°, with respect to the lamella axis. For clarity, one **$C_{19}BiPyC_{19}$** molecule has been superimposed on the STM image. Based upon the contrast of the BiPy moieties in the STM images it is obvious that all the molecules are equivalent along the lamella axis, and the molecules appear to be fully extended. A molecular model for the observed packing is shown in Fig. 2(b). The distance between two neighbouring molecules within a lamella measured along the lamella axis a is 6.9 ± 0.3 Å, the lamella width ΔL equals 47.2 ± 1.6 Å. The packing parameters acquired from the STM image indicate that the BiPy moieties are adsorbed parallel to the graphite plane, and there is no interdigitation of the aliphatic chains from neighbouring lamella.

After the successful imaging of the **$C_{19}BiPyC_{19}$** monolayers at the graphite/1-phenyloctane interface, a drop of $Pd(OAc)_2$ in 1-phenyloctane was applied to the same location of the initial drop. A spontaneous change of the monolayer packing pattern was observed. Fig. 3(a) shows an image of the monolayer with the new packing pattern. The image is submolecularly resolved, which again enables us to identify the aliphatic chains as well as the complexation sites (indicated by the red arrow). The BiPy moieties cannot be indicated; instead well defined big bright

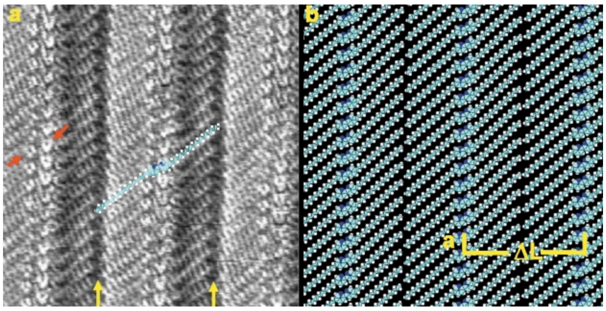

Fig. 2 (a) STM image showing a **$C_{19}BiPyC_{19}$** monolayer physisorbed at the graphite/1-phenyloctane interface. Red arrows point to the aromatic rings forming the BiPy moiety, yellow arrows define the lamella boundaries. One molecule model is superimposed for clarification. The different contrast of the alkyl chains on either side of the BiPy cores is due to a scanning artefact. The image area is 9.1×9.1 nm^2, $V_{set} = -0.244$ V, $I_{set} = 1.2$ nA. (b) Molecular model of the monolayer where $a = 6.9 \pm 0.3$ Å, $\Delta L = 47.2 \pm 1.6$ Å. The *cis* conformation of the BiPy units has been assumed arbitrarily.

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structures appear (yellow arrows). The distance between two successive bright structures measured along the lamella axis *a* is 9.4 ± 0.1 Å, which is significantly larger than the distance of 6.9 ± 0.3 Å between BiPy moieties before the addition of the $Pd(OAc)_2$. A change in the packing pattern of the aliphatic chains is also evident; the chains appear to interdigitate. This can be explained as follows: the distance between the neighbouring molecules increases to 9.4 Å in order to accommodate the $Pd(OAc)_2$ in between the BiPy moieties, causing the aliphatic chains to interdigitate and reduce the free space in the monolayer. This explanation is further supported by the change in ΔL from 47.2 ± 1.6 Å to 35.2 ± 1.2 Å after the addition of $Pd(OAc)_2$. It should be noted that the orientation of the aliphatic chains with respect to the lamella axis changes from 49 ± 2° to 87 ± 2° after addition of $Pd(OAc)_2$. The contrast arising from the complexed molecules suggests that the $Pd(OAc)_2$ is adsorbed on the graphite surface in between the **C_{19}BiPyC_{19}** molecules, where the palladium atom is on the graphite surface while the two acetate ligands are pointing towards the supernatant solution. To further clarify the packing pattern two complexed molecules have been superimposed on the STM image. A molecular model for the observed monolayer packing is shown in Fig. 3(b).

In order to demonstrate the possibility of using the above mentioned procedure as a template for building nanostructures, the stability of the formed template in air is a necessity. To achieve this, a solution of **C_{19}BiPyC_{19}** in 1-heptanol was applied to the graphite surface and left to dry under ambient conditions. The monolayer was submolecularly resolved (Figure not shown), and the packing parameters of the monolayer did not change from those obtained at the graphite/1-phenyloctane interface. A drop of $Pd(OAc)_2$ in 1-heptanol was then applied on top of the dry monolayer, and again left to dry under ambient conditions for two days. Fig. 4 shows an image of the complexed monolayer acquired by STM. The image shows similar features as those obtained at the graphite/1-phenyloctane interface.

In conclusion, **C_{19}BiPyC_{19}** molecules self-assemble at the graphite/1-phenyloctane interface into lamellar arrays, and the *in situ* complexation of $Pd(OAc)_2$ at the bipyridine moeities has been successfully observed using scanning tunneling microscopy. The stability of such monolayers under ambient conditions was demonstrated by the successful imaging of the dry complexed monolayers after a few days from deposition on the graphite surface from 1-heptanol solution. These data demonstrate the possibility of using organic molecules as templates for building nanostructures.

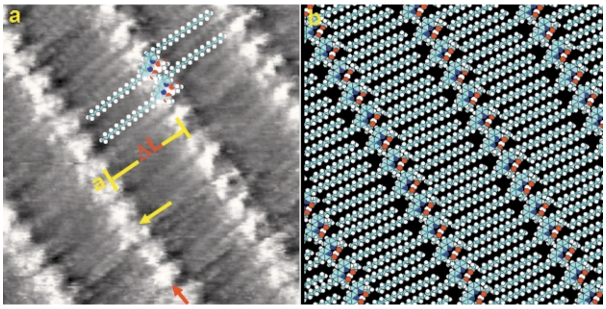

Fig. 3 (a) STM image showing a **C_{19}BiPyC_{19}** monolayer physisorbed at the graphite/1-phenyloctane interface after addition of $Pd(OAc)_2$ solution. The red arrow points to the position in which the BiPy moiety was expected, the yellow arrow indicates a complexation site. Two [$(Pd(OAc)_2)$(**C_{19}BiPyC_{19}**)] molecules are superimposed for clarification. The image area is 10.2 × 10.2 nm², $V_{set} = -0.486$ V, $I_{set} = 1.2$ nA. **(b)** Molecular model of the monolayer where $a = 9.4 \pm 0.1$ Å and $\Delta L = 35.2 \pm 1.2$ Å.

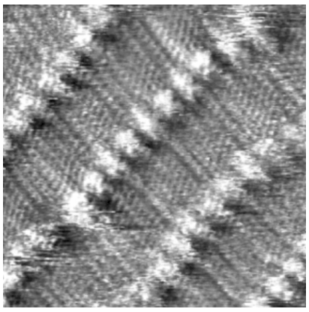

Fig. 4 STM image showing a **C_{19}BiPyC_{19}** monolayer physisorbed at the graphite/air interface after addition of $Pd(OAc)_2$ in 1-heptanol and drying for two days under ambient conditions. The image area is 10.2 × 10.2 nm², $V_{set} = -0.498$ V, $I_{set} = 1.00$ nA.

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