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Scanning tunnelling microscopy study of a columnar metallomesogen: bis(β -diketonato)palladium(II) complexes on graphite

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Scanning tunnelling microscopy is used to analyse the structure of the columnar metallomesogen bis[1-(3,4,5'-trioctyloxyphenyl)-3-(4'-octyloxyphenyl)propane-1,3-dionato]palladium(II) [Pd(II)BPOC8], on the basal plane of highly oriented pyrolytic graphite. It is observed with near molecular level resolution that adsorbed molecules form a regular two-dimensional (2D) arrangement on the surface. The intermolecular spacing in the 2D crystallization is significantly shorter than in the intercolumnar mesophase, indicating that the alkyl chains of adjacent molecules interdigitate. Change in the carbon length of alkyl side chain groups results in a change in molecular periodicity in the 2D crystal. Models for the unit cell are proposed based on computer simulation.

1. Introduction

Self-assembled monolayers formed by organic molecules on substrate surfaces are of considerable importance for use in various technical applications. In particular, for molecules used in electronic devices, it is essential to understand that the memory, input/output, and processing units should be at well defined positions to enable communication between them. The surface-induced order can also be transferred into the bulk over comparatively large distances, influencing its structure and electro-optical properties. Thus, an understanding of how these functionalized organic molecules order on surfaces is crucial for optimizing their applications. However, a study of the ordering of organic materials on a solid surface is relatively difficult due to the presence of bulk material. Scanning tunnelling microscopy (STM), because of its ability to image directly the interfacial structure, with molecular and in many cases atomic resolution in real space, has emerged as a powerful tool for examining orientations, packing arrangements, and even the internal structures of organic molecules on surfaces.

In this paper, we report the self-assembling of a columnar metallomesogen on the (0 0 0 1) surface of highly oriented pyrolytic graphite (HOPG) studied by STM under the ambient environment. Liquid crystals

(LCs), have a self-assembly character by which thermally activated motion is suppressed via an interaction between neighbouring molecules. When LC molecules are absorbed on a substrate, the interaction between the molecules and the substrate surface can induce a change of LC phase to a two-dimensional 'solid' crystal. Since the uniform alignment of liquid crystals on substrate surfaces is very important in LC science and technology [1], the interfacial properties between the LC molecules and the surface need to be better understood [2–6]. In fact, the suppression of molecular motion is a necessary condition for molecular scale observation, and STM has been successfully applied to the direct observation of LC monolayers during recent years [5–7]. For example, STM studies on *n*-alkylcyanobiphenyls (*m*CBs: *m* = 7–12) have indicated that individual *m*CB molecules can be resolved in the images, and that distinction can even be achieved between aromatic and aliphatic moieties within each molecule [6]. It was also found that the surface ordering of *m*CB molecules is markedly dependent on the substrate surface as well as on the length of alkyl chain, and in turn a wide variety of electro-optic properties are affected [4, 6, 8–10]. These studies have so far been focused on rod-like LC molecules. Here, we present the STM image of columnar LC molecules incorporated with a metal centre on HOPG. The observation of individual molecules allows us to investigate the molecular alignment in the anchoring region at the molecule–substrate interface directly in real space.

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2. Experimental

The experiment was performed using a Nanoscope E scanning tunnelling microscope (Digital Instruments-DI) operating *in situ* at the liquid–solid interface under ambient conditions. We chose graphite (ZYG grade HOPG, Advanced Ceramics, Cleveland, OH, USA) to be the substrate in this study because monocrystalline HOPG is available and easy to cleave to expose new and clean surface. Due to the strong C–C covalent bondings within layers parallel to the cleaving surface, and weak van der Waals bonds between the layers, HOPG is chemically rather inert in air. A STM tip mechanically fabricated from a 0.25 mm diameter platinum–iridium (Pt:Ir = 80:20) wire (Omega) was used in this study; the STM image was recorded in constant current mode. The tunnelling conditions were optimized to attain the highest resolution. The voltage, V , corresponds to the tip bias with respect to the sample. STM images were slightly filtered in the space domain to remove dominant acoustic noise, to offset small inclination, and to enhance the image contrast. To ensure the accuracy of STM results, we repeated the imaging many times with different samples, tips, and tunnelling parameters.

The LC sample studied here was bis[1-(3',4',5'-trioctyloxyphenyl)-3-(4'-octyloxyphenyl)propane-1,3-dionate]-palladium(II), denoted Pd(II)BPOC8 [Pd(II)BPOC n , $n = 8$], which was reported by Fan and Lai [11]. The sample solution was prepared by adding ~ 4.0 mg of Pd(II)BPOC8 to 1.0 ml of 1-phenyloctane (HPLC grade, Aldrich). For the STM study of molecules adsorbed on a surface with the tunnelling tip immersed in solution, i.e. direct imaging of the liquid–solid interface, a suitable solvent is required. First, the solvent must be non-polar to allow the tunnelling current to be measured while the tip is under solution. Secondly, the solvent must have a low vapour pressure so that its evaporation is minimized during acquisition of images. Thirdly, the solvent selected must also be less strongly bound to the surface than the adsorbate of interest so that the adsorbate will not be displaced from the surface by the solvent [12]. 1-Phenyloctane has been demonstrated by many groups [12] as an appropriate solvent in STM studies and Pd(II)BPOC8 shows a reasonable solubility in it. The quantity of solute used depended on the condition necessary to achieve near saturation of the solution. The sample was then left to dissolve and thermally equilibrate for approximately 24 h prior to usage in the microscopy. A fresh drop of such prepared Pd(II)BPOC8 solution was placed on the HOPG surface before scanning to avoid crystallization of the bulk. LC phase behaviour and optical properties of Pd(II)BPOC8 have been reported previously [11].

Molecular models were constructed on a silicon graphics workstation using Cerius² 3.0 software package

(MSI-Molecular simulation Inc., CA, USA). The optimized Pd(II)BPOC8 molecules plating out on a single layer of HOPG surface were subjected to energy minimization using a Universal 1.02 force field in the module of OFF (open force field).

3. Results and discussion

Pd(II)BPOC8 is a columnar metallomesogen incorporating a Pd metal centre coordinated with β -diketonate as a rigid core. From polarizing optical microscopy (POM) and differential scanning calorimetry (DSC), it was previously shown that this sample in a bulk state undergoes phase transitions from a crystalline phase to a mesophase (columnar disordered Col^{hd}) at 77°C, and to an isotropic phase at 144°C (the clearing point) [11]. The molecular structure of Pd(II)BPOC8, as displayed in figure 1(a), is characterized by a flat aromatic core surrounded by eight flexible hydrocarbon chains. For a better interpretation of the STM image presented below, the dimension of the molecule can be useful. To this purpose, we have calculated the structure of Pd(II)BPOC8 as an isolated molecule by a geometrical optimization by Cerius² 3.0. The calculated molecular dimensions of Pd(II)BPOC8, as described in figures 1(b) (top view) and 1(c) (side view), are about 2.54 nm along the two molecular axes, with a diameter of the central aromatic core of 1.28 nm.

To perform the STM study, a saturated solution of Pd(II)BPOC8 in 1-phenyloctane ($\sim 6\mu\text{l}$) was directly applied to the basal plane of the HOPG surface. Before each experiment, the HOPG surface was freshly cleaved using Scotch tape and then imaged by STM to ensure the quality of substrate and tip before adsorbing the Pd(II)BPOC8 molecules. Since Pd(II)BPOC8 is crystalline or glassy solid at room temperature, 2D crystal was formed from solution in 1-phenyloctane. The STM image was obtained in constant current mode (scan rate 60 Hz). The tunnel current is usually set between 0.7 and 1.3 nA, with the tunnel bias between 750 and 890 mV (positive bias at the tip relative to the sample). Under such tunnelling conditions, the tip immerses into the Pd(II)BPOC8 film and probes the first adsorbed layer only. The underlying graphite lattice can also be visible *in situ* by lowering the bias voltage.

Figure 2 shows a typical STM image ($10 \times 10 \text{ nm}^2$) of Pd(II)BPOC8 adsorbed on a HOPG surface. It is observed that the Pd(II)BPOC8 molecules, appearing as bright spots, form a well ordered two-dimensional array on the HOPG surface. While it is easy to observe the individual molecules as fuzzy oval disks which appear organized on the surface, it is more difficult to resolve structure on the submolecular scale. Figure 3 is a combined top view (a) and section cut (b) of figure 2 which shows the detailed variation with height observed as a

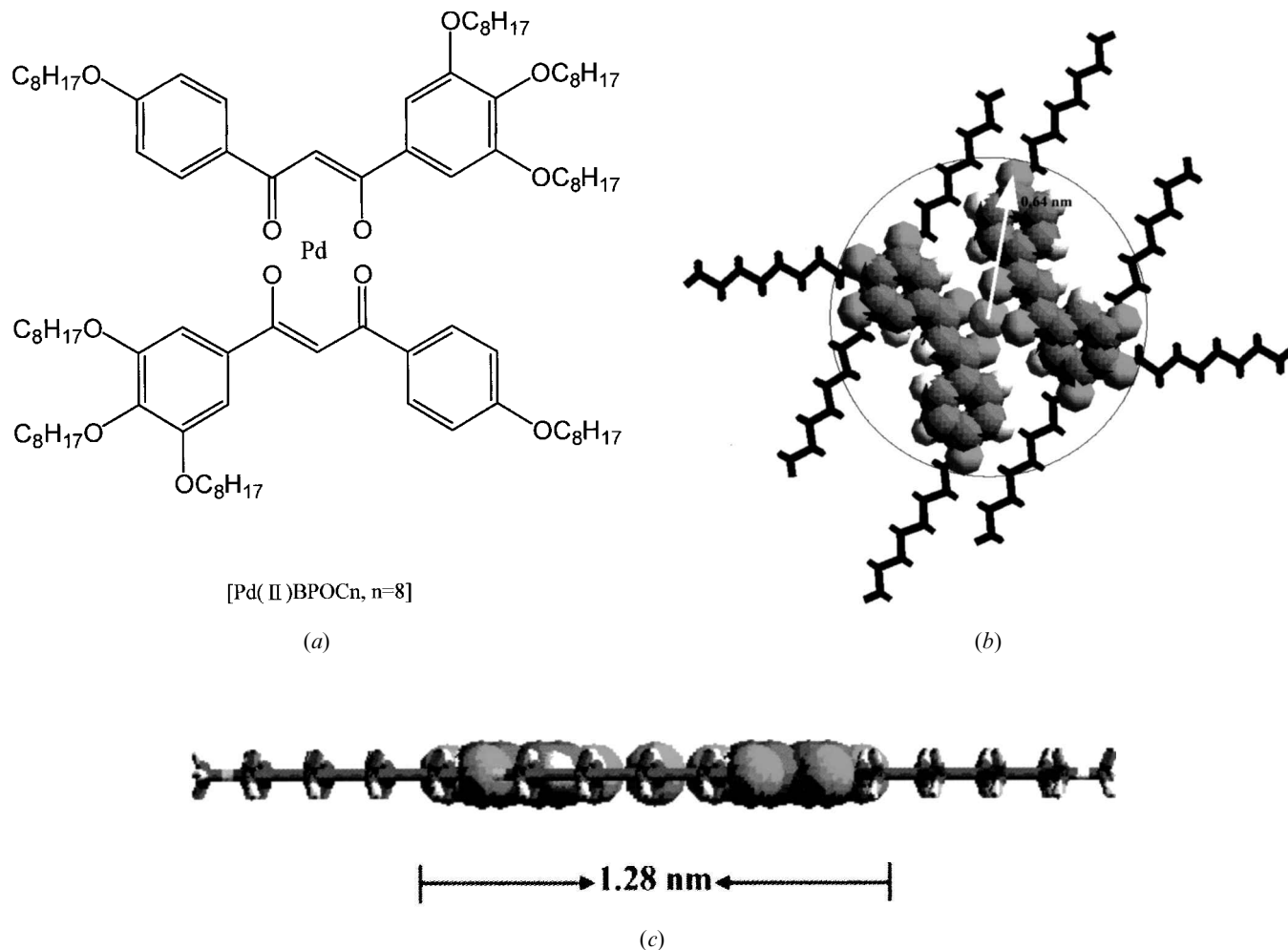


Figure 1. (a) Molecular structure of Pd(II)BPOC8. (b) Top view, and (c) side view of an optimized geometrical model for Pd(II)BPOC8: the molecular dimension is shown in the figure.

function of position over the surface scanned. The dotted lines in the 2D image of figure 2 served as the cut for the cross-sections shown in figure 3 (b). It is conspicuous that each oval disk has a bright (high) core composed of sparkle lobe 'flowers' with obscure but visible protrusion in the centre. The very intense bright centres should correspond to the Pd atoms. The less intense bright parts are attributed to the contribution from aromatic moieties of the molecules which in general enhance the tunnelling efficiency. On the other hand, the surrounding aliphatic chains reduce the tunnelling efficiency and image as dark contrast between the bright spots in the images [5, 6, 13]. The diagonal width of the central bright moieties is measured to be 1.25 ± 0.2 nm, which is in good agreement with the molecular dimension, i.e. the diameter of 1.28 nm estimated for Pd(II)BPOC8 as shown in figure 1 (b).

The image is filtered using the DI software, yet, there is still unremovable noise and the submolecular structure

of individual molecules is not well resolved. This is probably either due to the instrumental limitation or a high molecular mobility on the substrate under the experimental conditions. Since the STM observation was performed at room temperature and some of the molecules may still be capable of free movement without being anchored to the graphite substrate, the STM images are thus rather indistinct. The noise and low image resolution, however, does not affect the identification of Pd(II)BPOC8 molecule or their arrangement when adsorbed on HOPG.

The observed highly ordered molecular pattern indicates successful self-assembling of Pd(II)BPOC8 on HOPG which can be explained by the following discussion. Normally, the driving force for molecules containing alkyl groups to self-assemble on HOPG is primarily two-fold. One is due to the direct interaction between the alkane and the substrate, and the other is contributed by the 2D crystallization of alkanes [14].

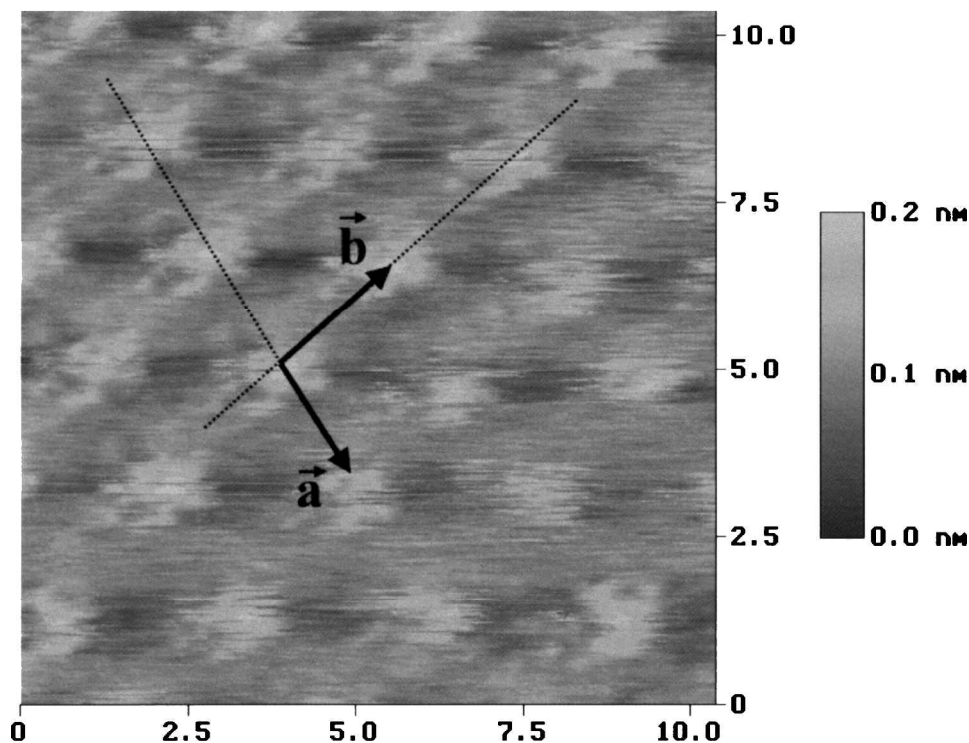


Figure 2. A $10 \times 10 \text{ nm}^2$ STM image of Pd(II)BPOC8 adsorbed on HOPG taken at 800 mV bias and tunnelling current of 1 nA.

In 1992, Hentschke and co-workers performed the theoretical calculation and found that each $\text{^-CH}_2\text{^-}$ of a long chain alkane adsorbed flat on graphite would provide an adsorption energy of *c.* 70 meV [14, 15]. In the case of Pd(II)BPOC8, one molecule comprises eight octyl groups, i.e. 64 $\text{^-CH}_2\text{^-}$ units, which would contribute the adsorption potential of *c.* 4 eV if the molecular plane of Pd(II)BPOC8 lies parallel to the graphite substrate. Such flat configuration is evident based on the observed uniform corrugation profile for the adsorbed monolayer in this system. In addition, 2D crystallization requires all alkyl chains to be densely packed with carbon skeletons arranged side by side. As shown below, a Pd(II)BPOC8 monolayer is formed through the interdigitation of alkyl chains between aromatic rings. Nevertheless, the two-dimensional network formed could be reproducibly observed but limited only to a small area. Attempts to scan in a larger area failed, indicating the instability of this self-assembly configuration.

As shown in figure 2, the packing arrangement in the monolayer of Pd(II)BPOC8 has nearly quadratic symmetry. The unit cell data of Pd(II)BPOC8 on HOPG are listed in the table. The intermolecular distances along two unit vectors, **a** and **b**, indicated by the arrows are $(20.7 \pm 2.1) \text{ \AA}$ and $(23.7 \pm 2.4) \text{ \AA}$, respectively, with an enclosed angle of $(103 \pm 3)^\circ$. Note that the intermolecular spacing in this two-dimensional crystal-

Table. Structure parameters of Pd(II)BPOC8 evaluated from STM data and molecular modelling.

Unit cell	STM data	Model
a		
b	$(20.7 \pm 2.1) \text{ \AA}$	23.8 \AA
\angle (enclosed angle between unit vectors a and b)	$(23.7 \pm 2.4) \text{ \AA}$ $(103 \pm 3)^\circ$	26.1 \AA 103°

lization is significantly shorter than the molecular dimension of Pd(II)BPOC8 shown in figures 1(b) or 1(c), indicating that the alkyl chains of adjacent molecules are all interdigitated. These values, however, are closer to the interlattice constant of a pure Pd(II)BPOC8 sample which displays the diffraction pattern of a two-dimensional hexagonal lattice as measured by variable temperature X-ray powder diffraction (XRD) with a periodic spacing of 27.0 and 23.0 \AA in the (1 0 0) face [11].

It is worth pointing out that the contrast of the central region is higher than that for the alkane regions in spite of the topographic structure of the molecule; i.e. the protruded positions of hydrogen atoms are positioned higher than β -diketonates as revealed in figure 1(c). Both electronic and topographic structures should be considered in analysing the observed STM contrast for

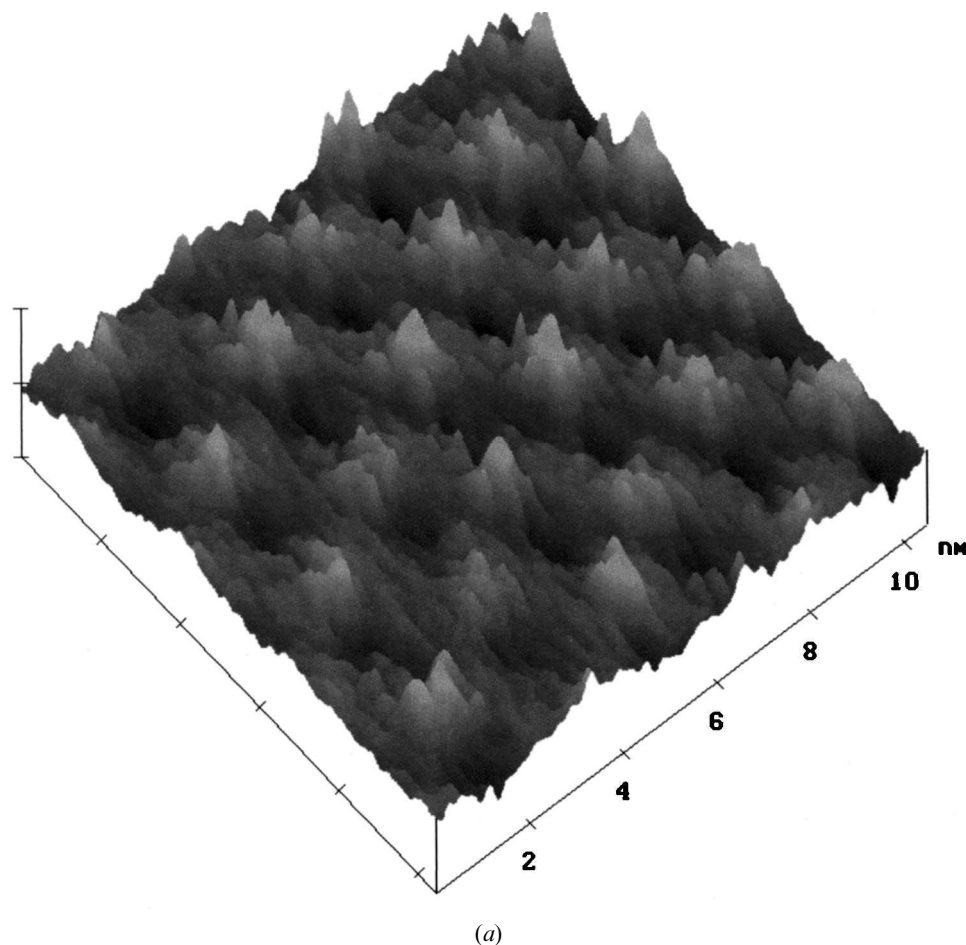


Figure 3. A combined top view and section cut of STM image shown in figure 2.

adsorbed molecules. Therefore, the observed higher contrast in the molecular centre is predominately due to the electronic structures of β -diketonates.

We have earlier discussed that the Pd(II)BPOC8 molecules and the underlying graphite atoms can be imaged with different bias voltages. However, once the adsorbate image has been lost by reducing the bias voltage at a constant current, the same adsorbate image can never be recovered, even after increasing the voltage back to its original value. Since reduction of the bias voltage at a constant current corresponds to a decrease in distance between the tip and the sample [16], it is possible that an irreversible removal of adsorbate molecules has taken place when lowering the tip. The temperature range of the mesophase for Pd(II)BPOC8 is 77.0–144.0°C. Therefore, under the STM scanning condition, a lateral diffusion or any process that can make up the molecular vacancy are expected to be suppressed. In other words, once a hole is produced by removing a set of adsorbate molecules from the HOPG surface, it is unlikely that the molecules will re-fill the hole to be imaged again.

Due to the limitation of image resolution and the fact that both the substrate lattice and adsorbed molecules cannot be observed simultaneously, the registry and unit cell structure were determined with the assistance of computer simulation. We first deduced a molecular model for one single Pd(II)BPOC8 molecule adsorbed on HOPG based on the following concerns [17]. (i) Fisher and Blöchl showed that the energetically most favourable position of an individual benzene ring is on top of a C atom of the graphite lattice [18]; therefore, in our model, all phenyl rings are arranged to centre on C atoms of the substrate. (ii) As discussed earlier, the heat of adsorption for hydrocarbons on the basal plane of graphite is relatively large; this was explained by a fortuitous match of the distance between the centres of the hexagons of the graphite lattice (2.46 Å) and the distance between alternate methylene groups ($\text{—CH}_2\text{—}$) of the hydrocarbon backbone (2.51 Å) [12]. Such a match allows the methylene groups of the alkyl chains to be located over the centres of the hexagons of the graphite lattice. In other words, all the alkyl chains of Pd(II)BPOC8 are adsorbed in all-*trans*-conformations

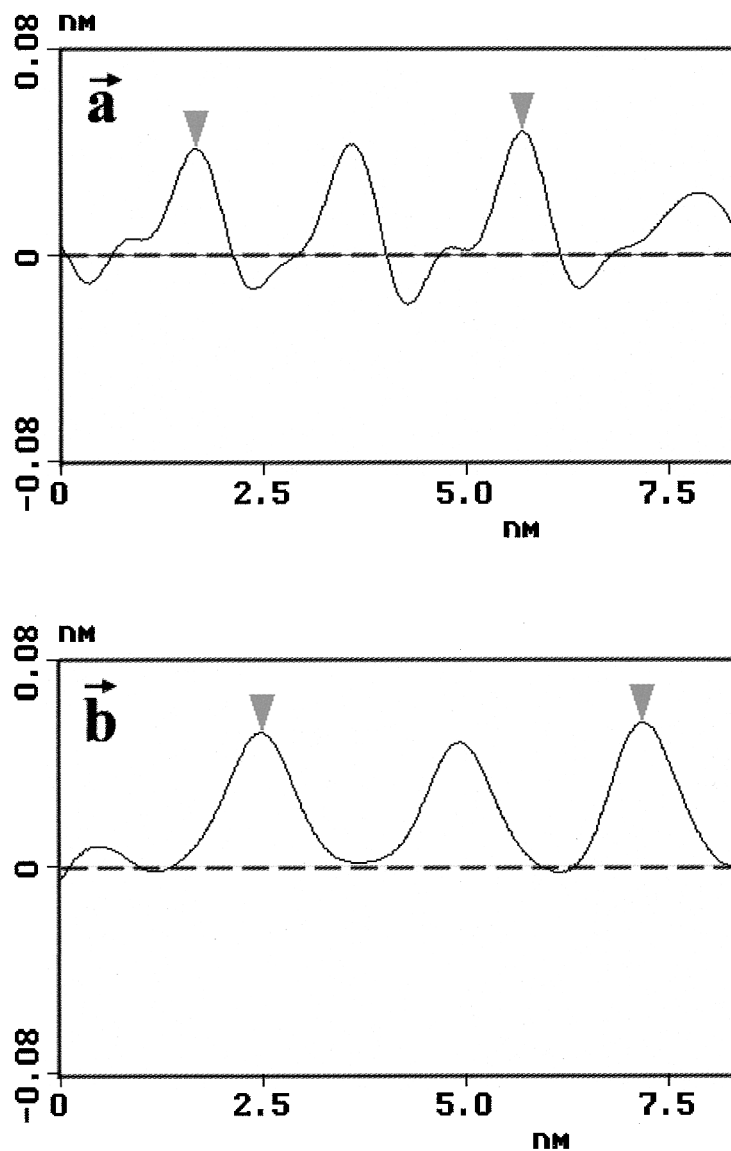


Figure 3. (Continued.)

(b)

parallel to the HOPG surface. This has been confirmed by numerous STM studies [12, 19, 20].

Since one Pd(II)BPOC8 molecule contains eight alkyl chains (C_8H_{17}), the above prerequisites lead to various possible molecular structures with altered possible orientations of the carbon skeleton. We have performed molecular mechanics simulations to search for the most stable one, which is shown schematically in figure 4. To construct the assembled overlayer of Pd(II)BPOC8 on HOPG, we have to conceive the way the alkyl chains are packed, bearing in mind the tendency to maximize van der Waals interactions between neighbouring molecules. We have also noticed from STM images that the contrast between the bright disks of molecular

centres is higher in the **a** direction than in the **b** direction. A densely packed molecular assemblage including sixteen Pd(II)BPOC8 molecules was then manually constructed on the basis of the optimized adsorbate structure. The unit cell data are also shown in the table. Since direct measuring of the relative height of Pd(II)BPOC8 above the substrate surface is not possible in this work, the initial distance of molecular plane was set to be 4.0 Å away from the basal plane of HOPG. The optimized molecular arrangement after the simulation is sketched in figure 5. Based on this model, the unit cell length in **a** and **b** directions is 23.8 and 26.1 Å, respectively, and the enclosed angle is 103°. The final distance of the Pd(II)BPOC8 overlayer from the HOPG is 3.2 Å.

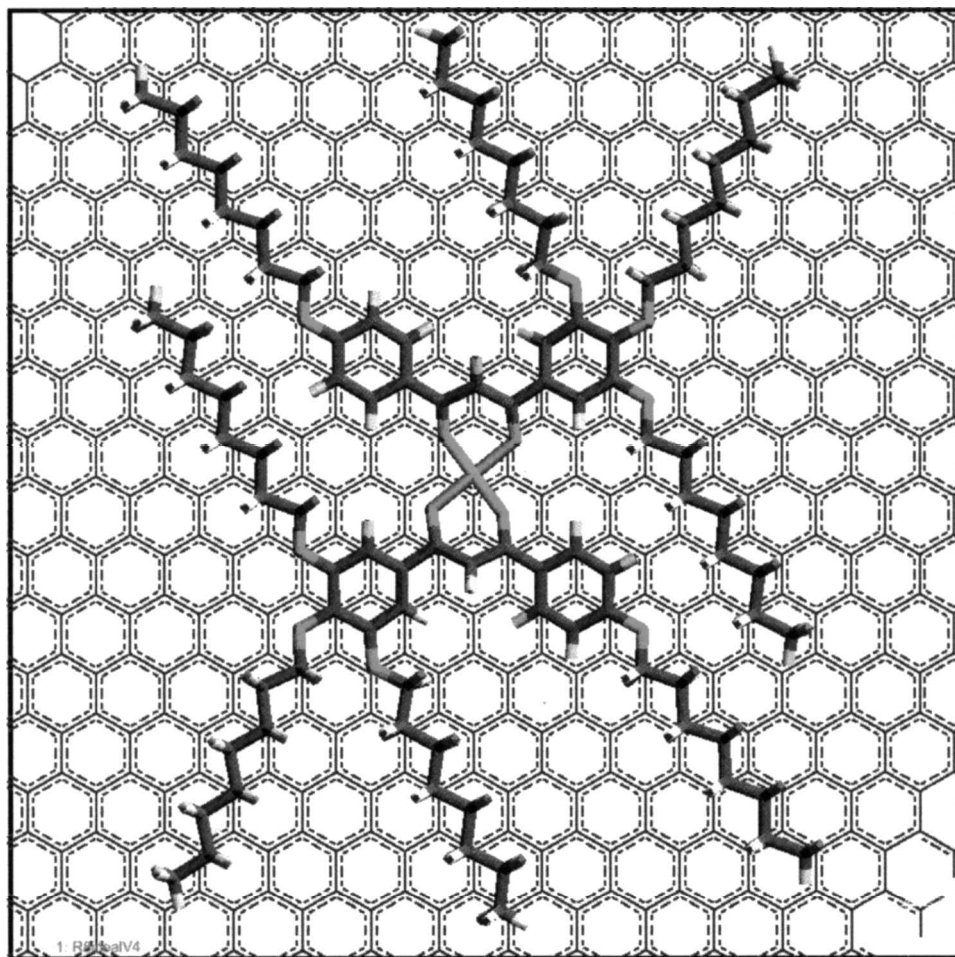


Figure 4. Illustration of a molecular model of one Pd(II)BPOC8 molecule absorbed on HOPG.

Within experimental uncertainty, the proposed structure is in agreement with the characteristic properties extracted from the STM images as presented above.

On the basis of the molecular structure of Pd(II)BPOC8, it is possible to vary the length of the equatorial flexible aliphatic chains, providing ideal model molecules with tunable intermolecular distances. As demonstrated by Pd(II)BPOC16, bis[1-(3',4',5'-trihexadecoxyphenyl)-3-(4'-hexadecoxyphenyl)propane-1,3-dionato]palladium(II), which shows a cognate STM image (not shown) on HOPG, the distance between molecules is apparently extended. Note, however, that the variation in the alkyl chain length induces different relative changes of the molecular periodicity in the two unit cell directions. An indication of a possible different structure of Pd(II)BPOC16 assembled on HOPG is currently under the investigation. Utilizing this feature, we may generate a two-dimensional ordered array with a controllable metal density which is 10^3 – 10^5 times higher than in a conventional type of integrated circuits.

4. Conclusions

Using STM, we have found that the columnar metallo-mesogen, Pd(II)BPOC8 forms a 2D crystal on a graphite surface. A structural model for the unit cell of the molecular lattice is proposed based on STM image and molecular modelling which assumes (i) commensurate registry of the molecules with all phenyl rings centred on C atoms of the substrate, (ii) all-*trans*-conformations of alkyl group parallel to the HOPG surface, and (iii) the tendency to maximize van der Waals interactions between neighbouring molecules. Finally, the variation in the alkyl chain length changes the molecular spacing accordingly.

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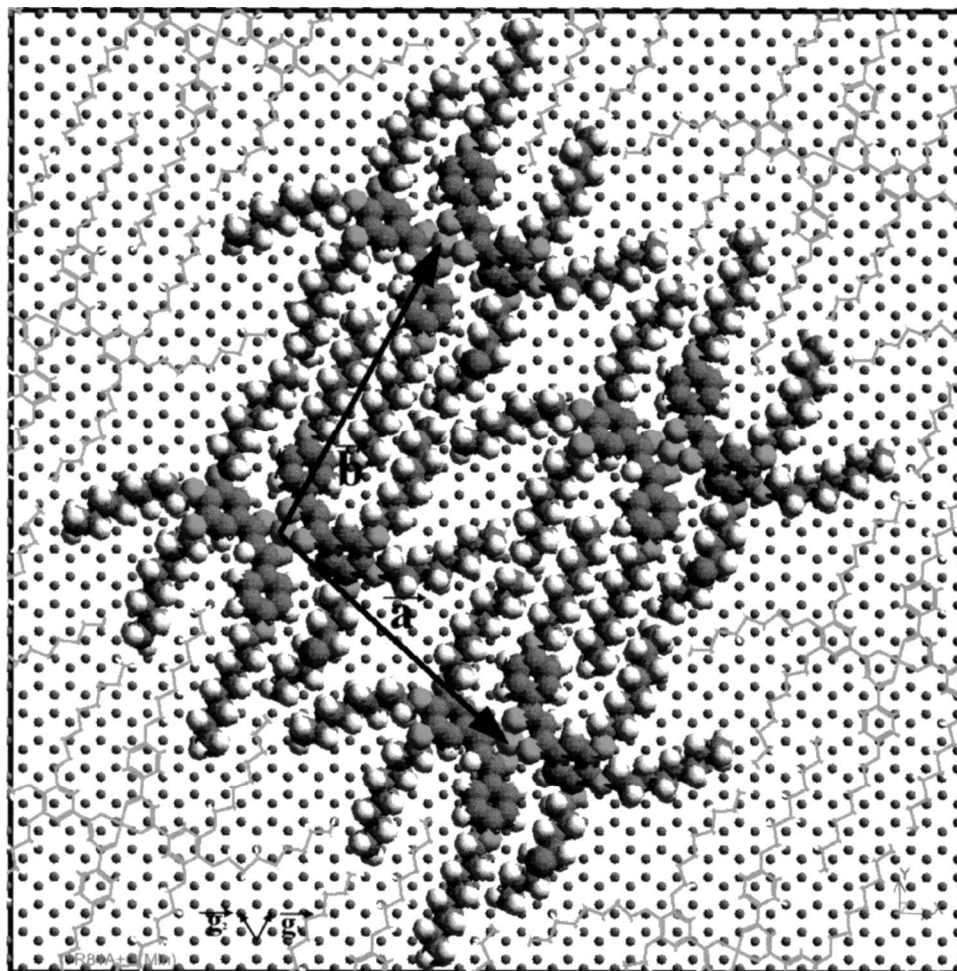


Figure 5. Molecular mechanics model of the two-dimensional arrangement of Pd(II)BPOC8 on HOPG.

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