

STM studies of the bimolecular layer of CoPc and F₁₆CuPc on Ag(100) with non-equal composition

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ARTICLE INFO

Keywords:

Ag(100)
Metal-organic interface
Metal-phthalocyanine
Donor-acceptor layer
STM

ABSTRACT

The bimolecular layer composed of cobalt phthalocyanine (CoPc) and hexadecafluoro copper phthalocyanine (F₁₆CuPc) deposited at room temperature on Ag(100) was investigated by scanning tunneling microscope. The coexistence of ordered bimolecular chessboard-like structure with 2D molecular gas phase is observed after deposition 0.7 ML of CoPc and 0.1 ML F₁₆CuPc. The 2D gas phase contains mostly CoPc molecules. In the ordered domains, the CoPc:F₁₆CuPc ratio is about 1.2, i.e. around five and a half times lower than the deposition ratio. The molecular ratio, higher than one, in the chessboard-like structure arises from the substitution of F₁₆CuPc by cobalt compound. A slight increase (up to ca. 1.6) of the molecular ratio is observed close to the border of the ordered domain with CoPc rich 2D gas phase. Almost complete molecular monolayer was prepared by adding about 0.2 ML of CoPc. Thenceforth, the coexistence of chessboard-like bimolecular structure with monomolecular CoPc ordered domains is found. The addition of CoPc does not change the CoPc:F₁₆CuPc ratio assembled in the bimolecular chessboard-like structure.

1. Introduction

Recently the metal-organic (m-o) interfaces have attracted a lot of attention in the surface science studies due to their significance to performance of organic electronic devices [1,2]. The electronic properties of m-o junctions depend on the chemical composition of a molecule [3–6]. Metal-phthalocyanines (C₃₂H₁₆MN₈, MPc) absorbed on noble metal surfaces usually behave as donors, whereas their fully fluorinated counterparts (C₃₂F₁₆MN₈, F₁₆MPc) as acceptors [4–7]. The mixed donor-acceptor layers are of interest in view of possibility to steer m-o interface properties with various molecular proportions of components [8–11].

The monomolecular monolayers of MPcs or F₁₆MPcs on metal surfaces usually self-assemble in the ordered structures at room temperature (RT) [12]. For the submonolayer regimes, the molecules are observed in 2D gas phase on the Ag(111) or Ag(100) surfaces [13–17] or in the ordered islands on Ag(110) [14]. To transform 2D gas phase into ordered domains, the certain amount of organic material (namely critical coverage) is necessary [13]. Similar to monomolecular films, the first layers of bimolecular films (composed of porphyrins) are usually organized into ordered domains on metal substrates [18–31]. The scanning tunneling microscopy (STM) studies were performed at RT on bimolecular layers consisted of MPcs and metal-tetraphenylporphyrins (MTPP) on Au(111) [19–22]. After adsorption of 0.3 ML of CoPc with

0.5 ML of CoTPP, the coexistence of ordered domains with 2D molecular gas phase composed of CoPc was observed [19]. The ordered domains consist of both types of molecules distributed randomly in the islands, no compositional order was detected [19]. The compositionally ordered structure was found for mixture F₁₆CoPc with NiTPP with deposition ratio 1:2 [21,22]. In such arrangement single F₁₆CoPc has four nearest neighbors of NiTPP and vice versa. These compositional order is consequence of attractive interactions between periphery hydrogen atoms in NiTPP with periphery fluorine atoms in F₁₆CoPc. Apart from bimolecular ordered domains, two other phases were found i.e. the ordered phase of pure NiTPP and the disordered phase of NiTPP-F₁₆CoPc mixture [22].

For the mixtures of fluorinated with non-fluorinated MPcs, the chessboard-like structure with the molecular ratio close to one, was observed on Ag(111), Au(111), Ag(100) or highly-oriented pyrolytic graphite (HOPG) [15,23–27]. The coexistence of domains of the chessboard-like structure with monomolecular F₁₆CuPc was found on the HOPG surface covered with 0.4 ML of CuPc and 0.6 ML of F₁₆CuPc at 77 K [26]. In the chessboard-like arrangement, due to interactions between the periphery H and F atoms, the MPc is surrounded by four nearest neighbors of F₁₆MPc, and vice versa [15,23–27]. The attractive interactions steer the lateral arrangement of the molecules, providing the uniform distribution of features across the surface. For example, codeposition of hexadecafluoro iron phthalocyanine (F₁₆FePc) with

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<https://doi.org/10.1016/j.susc.2019.121534>

Received 1 August 2019; Received in revised form 7 November 2019; Accepted 15 November 2019

Available online 21 November 2019

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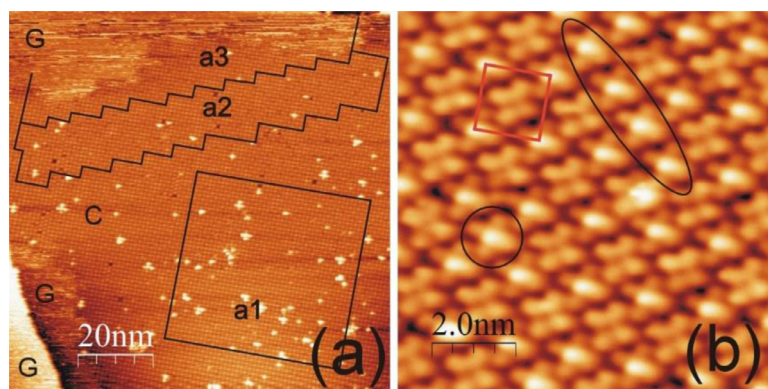


Fig. 1. STM images of CoPc- F_{16} CuPc mixture on Ag(100) with global ratio 7:1. Taken for (a) $U = -1.16$ V; $I = 0.16$ nA; (b) $U = -1.44$ V; $I = 0.16$ nA.

manganese phthalocyanine (MnPc) on oxygen reconstructed Co(001) and Ag(111) surface allows the fabrication of 2D array of spins on the surface [24]. The mixed layers can be also used to tune the lateral dipole density. That was achieved by deposition of mixture of F_{16} CuPc with chloroaluminum phthalocyanine (ClAlPc) with the molecular ratios 1:2, 1:1 and 2:1 on HOPG at 77 K [27]. For all investigated ratios, the compositionally ordered structures were detected. Varying the relative molecular ratio allows to tune the distance between molecules with permanent dipole. The compositional order of layer with non-equal compositions were ascribed to interactions between permanent dipole moments of ClAlPcs [27]. The possibility of tuning the bimolecular arrangements by the variation of molecular ratio was found for coadsorption of F_{16} CuPc with: p-sexiphenyl (6P) on HOPG [28], di-indenoperylene (DIP) on HOPG, Au(111) and Cu(111) [28,29] and pentacene (PEN) on HOPG [28] and Au(111) [30,31]. Varying the molecular ratio allows to change lateral intermolecular distances between F_{16} CuPc (acceptors) on the surface. For PEN: F_{16} CuPc ratios higher than 3:1, the F_{16} CuPc molecules are distributed randomly in the PEN matrix on Au(111). For F_{16} CuPc-rich mixtures on Au(111), the 1:1 bimolecular phases and pure F_{16} CuPc domains were developed. In the pure F_{16} CuPc domains small amount of PEN molecules were incorporated in the vicinity of domain boundaries [31]. The coadsorption of DIP with F_{16} CuPc on Au(111) with ratio 1:2 leads to coexistence of disordered binary structure with pure F_{16} CuPc domains [29].

The electronic and magnetic properties of metal-MPC interfaces depend on chemical composition of MPC. By preparing the bimolecular mixtures with various molecular ratios one could change the distribution of given MPCs on the surface. In this work we study the properties of CoPc- F_{16} CuPc mixture on Ag(100) developed after deposition of molecules with considerable excess of cobalt compound. The high mobility of MPCs at RT allows the development of bimolecular ordered domains on the surface. The surplus of CoPc molecules is responsible for development of defects in the chessboard-like structure. Despite the huge disproportion in the amount of components deposited on the surface, the bimolecular domains contain only small excess of CoPcs. The rest of deposited CoPcs are located in the 2D gas or in the monomolecular ordered phase.

2. Experimental procedures

The measurements were performed under ultra-high vacuum (UHV) conditions and at RT. The UHV chamber was equipped with Aarhus 150 STM. The STM images were recorded in constant current mode using filled state imaging (i.e. for negative polarity) with the tungsten tip cleaned in situ by argon ion sputtering. The STM data were analyzed using the WSxM software from Nanotec [32].

The Ag(100) sample was cleaned by the cycles of argon ion sputtering with ion current and energy of about 30.0 μ A and 1.3 keV respectively for 10 min followed by annealing at ca. 900 K. After this

procedure the STM images reveal flat surface terraces with average width of 200 Å. The CoPc (from SigmaAldrich, purity 97%) and F_{16} CuPc (from TCI American purity 98%, cleaned by sublimation) were deposited from separate homemade effusion cells. The molecular sources were calibrated separately by preparations of monomolecular monolayers. Presence of monolayer on the surface was checked by STM and low energy electron diffraction. The temperatures of crucibles were chosen so that the deposition rates were of about 0.05 ML/min, for both molecules.

3. Results and discussion

In this work we study the bimolecular mixture composed of CoPcs and F_{16} CuPcs molecules. We deposited on the surface about 0.8 ML of mixture in total, with non-equal proportion between components. There was around 7 times more CoPcs (14 min of deposition) than F_{16} CuPcs molecules (2 min of deposition). The deposition proceeded as follow: firstly, around 0.1 ML of F_{16} CuPc was evaporated, then around 0.7 ML of CoPc was added. Please note that the molecules of the first component (F_{16} CuPc) were in the 2D gas phase at RT in submonolayer regime on the Ag substrate [15]. Therefore, they were mobile when the second component (CoPc) was added.

After the deposition, the coexistence of the 2D gas phase (labeled by G in Fig. 1(a)) with the ordered molecular islands (labeled by C in Fig. 1(a)) was found by STM. The presence of 2D gas phase confirms that the coverage is, indeed, lower than the monolayer. The molecules which are not arranged into the ordered layer have space to stay mobile on the surface. In the STM images, it is possible to distinguish immobile CoPcs from F_{16} CuPcs by their appearance. Using the negative polarity, the CoPc molecules can be identified by presence of bright molecular center [15]. Based on that, the composition of molecular islands can be determined. High-resolution STM image of the ordered domain with the unit cell marked by red square is shown in Fig. 1(b). From this image it is clear that the molecules in the ordered domain are arranged in $(5\sqrt{2} \times 5\sqrt{2})R45^\circ$ chessboard-like structure. Such structure has been observed after deposition of 1 ML of CoPc - F_{16} CuPc mixture on Ag (100) with the deposition CoPc: F_{16} CuPc ratio close to one [15].

Direct determination of composition of 2D gas phase is not possible, since the mobility of MPCs on Ag(100) at RT prevents molecular identification. To determine the details of composition of the ordered islands we counted the numbers of each type of MPC embedded in three selected areas (labelled as a1, a2 and a3 in Fig. 1(a)). Region a1 is surrounded by the immobile molecules in the ordered layer. It is presented here as a representative region for an arrangement inside the ordered layer. It contains 1678 MPCs where 896 are CoPcs and 782 are F_{16} CuPcs. The ratio is 1.15. Two types of point defects can be responsible for determination of the molecular ratio higher than one. First, there are single vacancies - F_{16} CuPc molecule is missing, second, there are replacements of F_{16} CuPc by CoPc (an example is marked in

Fig. 1(b) by black circle). There are also substitutions of $F_{16}CuPc$ in the nearest neighbor unit cells, which create the defects (e.g. labelled by ellipse in Fig. 1(b)) - few CoPcs assembled in a row. In the region a1 there are only two $F_{16}CuPc$ vacancies and fifty substitutions, therefore, the substitutions of molecules are responsible for the determined ratio. To find out if the excess of CoPcs observed in region a1 is associated with bigger amount of CoPc molecules deposited on the surface, we analyzed the data from Ref. [15] taken for the deposition ratio equal to one; i.e. the same amount of CoPc and $F_{16}CuPc$ was deposited on the surface. For this case the molecular ratio determined from three large-scaled STM images recorded for three different areas is equal to 1.00 ± 0.02 . We conclude that the deposition ratio equal to seven is responsible for small excess of CoPc molecules found in the chessboard-like structure.

The second region, which was explored is region a2, contains 1217 MPcs, from which 705 are CoPcs and 512 are $F_{16}CuPcs$. The ratio here is equal to 1.38 and is slightly higher than one determined for region a1. The area is closer to the phase boundary with 2D gas. Slightly higher excess of CoPc molecules is associated with somewhat bigger number of defects in layer. There are sixty four substitutions, and only four vacancies in the a2 region. The ratio is still quite low in comparison to the deposition ratio.

The last region we have studied is region a3. It contains the border of the ordered domain with 2D gas phase. The movie constructed from 23 images of this region is provided as the video in the Supplementary Materials. The movie reveals the phase boundary time evolution. The registration rate of each image was $(10 \pm 1) \text{ \AA/s}$ and the time for single image acquisition was 1 min 37 s. Three chosen STM images are shown in Figs. 1(a) and 2(a–b). It is visible, both, from the movie as well as from the comparison of Fig. 2(a) with (b) that the shape of the edge of the molecular island fluctuates. The attachments and detachments of both types of MPcs to and from the ordered structure are observed (see the Supplementary Materials.). The island edge appears frizzy due to motion of molecules during scanning procedure. There is no accumulation of CoPcs directly at the border line. Both types of molecules are detected there.

In Fig. 2(a) the STM image with the lowest number of immobile MPcs (550 molecules) is shown, whereas in Fig. 2(b) with the highest number (723 molecules) assembled in area a3. In Fig 2(c) the changes in the number of molecules immobilized in the ordered layer in each STM image is presented as a function of frame number, which is correlated with time. Only part of the island is visible in the STM image, therefore we could not determine the total number of attachments and detachments to and from the island. From the Fig. 2(c) it is, however, clear that the total number of immobile MPcs in region a3 fluctuates around the value of 648. The fluctuations are also observed in the number of CoPcs and $F_{16}CuPcs$ immobilized in the chessboard-like

structure. For all frames the number of CoPcs, which is between 339 and 454, is higher by about 150 molecules than the number of $F_{16}CuPcs$ (between 211 and 269). The ratio versus time (frame number) is plotted in the upper part of the graph (the ratio is given in the right-hand y-axis). The ratio varies from 1.48 to 1.71 and fluctuates around a value of 1.59. In the plot, the ratios for a1 and a2 areas, are marked by dashed and dotted line, respectively. For all the frames, the ratio in a3 area is higher than in the region a1 and a2 but still much lower than the ratio deposited on the surface. This allows us to conclude that 2D gas phase is CoPc rich and the molecular ratio here is higher than the deposition ratio.

Above analysis suggests that the ratio determined in the chessboard-like structure is correlated with the distance of selected area to the phase boundary with 2D gas phase. The closer location of area to 2D gas phase, the higher molecular ratio is. This relation likely arises from the combination of non-equal amount of deposited CoPc and $F_{16}CuPc$ and attractive interaction between them. The creation of chessboard-like structure is clearly preferred by the system. However, due to non-equal deposition, the amount of $F_{16}CuPc$ to build nearly perfect chessboard-like structure is limited. At the same time there are, more than needed, CoPc molecules available during the growth of the island. Development of chessboard-like islands binds $F_{16}CuPcs$ from gas phase, which causes the increase of the molecular ratio of the gas phase and increase of the probability of assemblage of CoPc instead $F_{16}CuPc$ in the structure. As a result, the substitution defects start to appear in the structure. We expect that the least defected chessboard-like structure is developed nearby its nucleation center.

In order to find out if it is possible to assemble more substitutional CoPc in chessboard-like structure ca. 0.2 ML of CoPc was added to the sample. After that, the surface terraces were covered with ordered molecular layers, see Fig. 3(a). Additionally, the small areas covered by 2D gas phase, close to step edges and between domains, are detected. This is indication that the full monolayer was not achieved. The added CoPcs immobilize MPcs, which previously were in 2D gas phase. The development of monomolecular domains containing CoPc molecules is observed. In Fig. 3(a) the upper terrace, in the bottom part of the image, is covered by two ordered molecular domains: $(5\sqrt{2} \times 5\sqrt{2})R45^\circ$ and $(\sqrt{26} \times \sqrt{26})R11^\circ$. The first one consists of two types of molecules, whereas the second one is monomolecular and consists only of CoPcs. The same monomolecular structure as on the upper terrace is also visible on the lower terrace. The $(\sqrt{26} \times \sqrt{26})R11^\circ$ structure was previously characterized in Ref. [15].

For all of our data the monomolecular and bimolecular phases are separated by small area of 2D gas phase or by irregular phase boundary. The zoom of the boundary is provided in the Supplementary Materials. There is no smooth transition from chessboard-like structure to CoPc monomolecular phase. Additionally, the border of the bimolecular

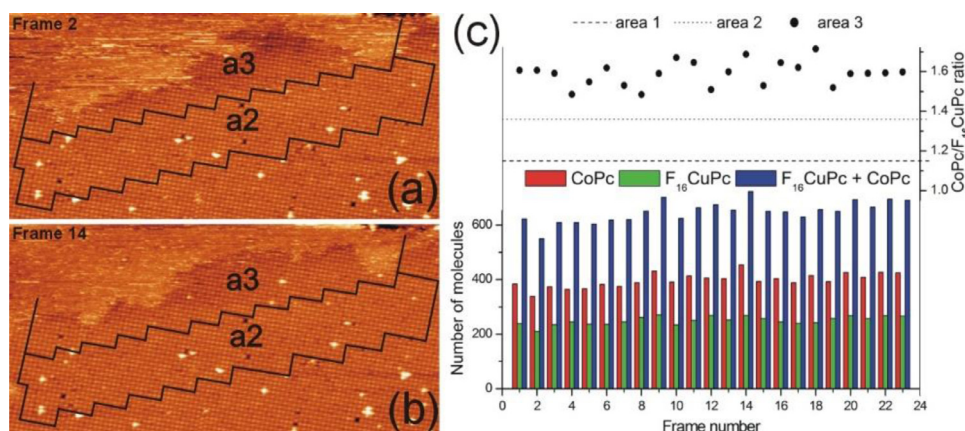


Fig. 2. (a-b) STM images $100 \text{ nm} \times 48 \text{ nm}$, taken for $U = -1.44 \text{ V}$; $I = 0.16 \text{ nA}$, (a) the minimum (b) the maximum value of MPcs in the a3 area. (c) Lower graph: number of MPcs, upper graph: the molecular ratios as the function of frame number.

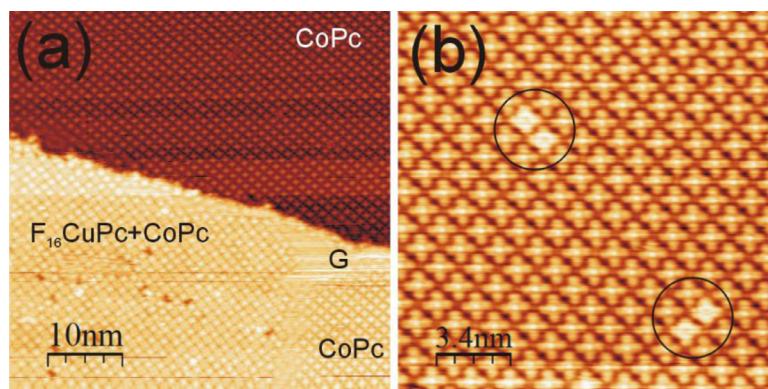


Fig. 3. (a) STM image of the coexistence of chessboard-like structure with CoPc ($\sqrt{26} \times \sqrt{26}$)R11° domains, taken for $U = -1.53$ V; $I = 1.64$ nA; (b) Four ‘guests’ $F_{16}CuPc$ molecules in ($\sqrt{26} \times \sqrt{26}$)R11° CoPc structure, taken for $U = -0.50$ V; $I = 0.39$ nA.

islands, (before and after adding 0.2 ML of CoPcs) are not decorated by CoPcs molecules. That suggests that the islands, which were on the surface before adding 0.2 ML of CoPcs, are not the nucleation centers of development of monomolecular domains.

In the ($\sqrt{26} \times \sqrt{26}$)R11° structure we observe CoPc substituted by $F_{16}CuPc$ molecules, the example such defects are marked by black circles in Fig. 3(b). In the figure we see two $F_{16}CuPc$ molecules next to each other, however, in a different place (not shown here) the single substitutions are also observed.

We counted the MPcs assembled in the bimolecular domain visible in Fig. 3(a). The domain contains 545 MPcs, from which 320 are CoPcs and 225 are $F_{16}CuPcs$. The ratio is 1.42 and it is comparable to the ratio determined for area a3, which was at the border of chessboard-like structure with 2D CoPc rich gas phase (see in Fig. 1(a)). We did not find the areas of chessboard-like structure with significantly higher molecular ratio than these obtained for the deposition ratio of seven. Addition of CoPc molecules did not significantly increase the number of CoPc molecules assembled into the chessboard-like structure. It likely happened because almost all of $F_{16}CuPcs$ were already bounded in bimolecular domain. We believe that the island fluctuations visible in Fig. 2 are associated with equilibrium fluctuations between solid and 2D gas phase on the surface. The addition of CoPcs immobilizes the CoPc from 2D gas phase and develops the monomolecular CoPc domains.

The comparable molecular ratio in the chessboard-like structure before and after adding CoPc supports our earlier claim that the substitution of $F_{16}CuPcs$ by CoPcs in chessboard-like structure occurs during the islands growth. Once the islands are arranged the contact with CoPc rich phase is not sufficient to increase the molecular ratio assembled in the structure. That means that CoPcs at RT are not able to penetrate into already arranged bimolecular structure. Occasional substitutional $F_{16}CuPcs$ assembled in CoPc monomolecular phase supports the argument that the number of $F_{16}CuPcs$ in 2D gas phase in first experiment is rather small.

Apart from ($\sqrt{26} \times \sqrt{26}$)R11° structure, one more monomolecular arrangement of CoPc was detected by STM, showed in Fig. 4(a). The unit cell for this structure is marked by red rhombus. The lattice constant is (14.7 ± 0.2) Å. The angle between unit vectors is $(67.1 \pm 1.9)^\circ$.

One of the unit vectors is rotated by 11° clockwise from the [011] direction, the second is rotated counterclockwise by 11° from the [01–1] surface direction. The molecular axis (labeled as MA in Fig. 4(a)) is rotated by $(31.1 \pm 1.9)^\circ$ with respect to the [011] surface direction and it is the same angle as for previously reported CoPc structures [15]. Basing on this information we deduced the transformation matrix as $\begin{pmatrix} 5 & 1 \\ 1 & 5 \end{pmatrix}$. The model of the structure is presented in Fig. 4(b). As in Ref. [15] in the model we assumed that CoPcs adsorbs with cobalt metal atom in the surface hollow site. According to our

knowledge such arrangement of CoPc molecules was not previously observed on Ag(100). The molecular density of both observed monomolecular CoPc domains ($(\sqrt{26} \times \sqrt{26})R11^\circ$ and $\begin{pmatrix} 5 & 1 \\ 1 & 5 \end{pmatrix}$) is lower than for $(5 \times 5)R0$ and $(5 \times 5)R37^\circ$ structures, commonly observed for 1 ML of MPc on Ag(100) [15,33–35]. The development of less packed CoPc domains similar as presence of 2D gas phase is associated with the coverage slightly lower than monolayer. Less dense phases are likely the intermediate states between 2D gas phase and the most common $(5 \times 5)R0$ arrangement. The transformation of MPc structure into denser phases caused by increasing molecular coverage were reported i.e. for CuPc or FePc on Ag(111) [13,17].

4. Conclusions

In this work the bimolecular films of CoPc and $F_{16}CuPc$ on Ag(100) were investigated by STM. For deposition of 0.7 ML of CoPc + 0.1 ML of $F_{16}CuPc$ the ordered chessboard-like structure coexists with 2D molecular gas phase. The CoPc: $F_{16}CuPc$ ratio of molecules assembled in the ordered domains, determined by STM is ca. 1.2. It is over five and half times lower than the deposition ratio. The small excess of CoPcs in the chessboard-like structure emerges from replacements of $F_{16}CuPc$ by CoPc. Our data suggests that 2D gas phase is CoPc rich with the molecular ratio higher than the deposition ratio.

After addition of about 0.2 ML of CoPc the coexistences of bimolecular chessboard-like structure with monomolecular CoPc ordered domains and small patches of 2D gas phase are observed. The CoPc: $F_{16}CuPc$ ratio determined for chessboard-like structure, before and after adding 0.2 ML of CoPc, is comparable, which suggests that the substitution of $F_{16}CuPc$ by CoPc molecules in bimolecular layer occurs during the growth of the domains.

Two types of arrangements of monomolecular CoPc phase were found i.e. ($\sqrt{26} \times \sqrt{26}$)R11° and $\begin{pmatrix} 5 & 1 \\ 1 & 5 \end{pmatrix}$. The latter, according to our knowledge, was not reported previously for MPc on Ag(100). Both detected monomolecular phases are less dense than commonly observed for CoPc on Ag(100) $(5 \times 5)R0$ structure.

Declaration of Competing Interest

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the

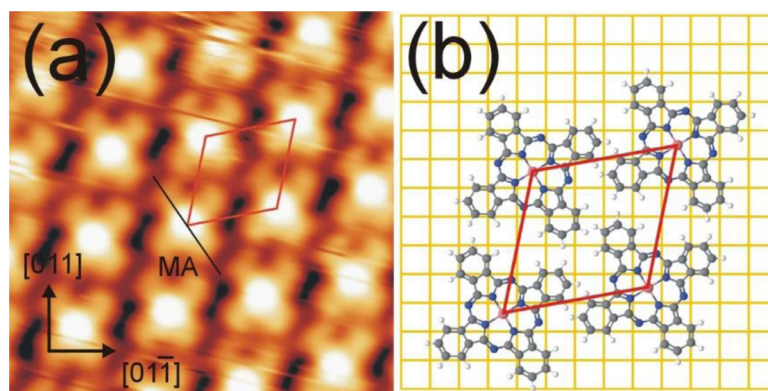


Fig. 4. CoPc structure described by transformation matrix $\begin{pmatrix} 5 & 1 \\ 1 & 5 \end{pmatrix}$ (a) high resolution STM image $6 \text{ nm} \times 6 \text{ nm}$, taken for $U = -2.75 \text{ V}$; $I = 0.60 \text{ nA}$; (b) corresponding model.

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Acknowledgments

We would like to thank Piotr Wiczorek for his technical assistance. This work was financed by National Science Center, Poland in the years 2016–2018 as a research project number 2015/19/N/ST3/01044.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.susc.2019.121534.

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