

Crystallographic STM image processing of 2D periodic and highly symmetric molecule arrays

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Abstract — Crystallographic Image Processing (CIP) is applied to experimental Scanning Tunneling Microscopy (STM) images of regular (2D periodic) arrays of organic molecules on noble metal substrates. The crystallographically averaged (surface) lattices, structural motifs, and plane symmetry groups of the arrays are determined. An assessment of the samples with the goal of utilizing highly symmetric molecular arrays as calibration samples for STM is made. A brief introduction to the CIP procedures is given in an appendix.

Index Terms – Scanning Tunneling Microscopy, Image Processing, Surface Crystallography.

INTRODUCTION

The supramolecular approach [1] to building arrays of “nano-optoelectronics devices” from the bottom up on a solid substrate has attracted much attention in recent years. For example, self-assembled monolayers of transition-metal phthalocyanines were grown on highly (0001) oriented pyrolytic graphite, silver (111) [2], gold (111) [3], or copper (001) [4] and subsequently analyzed by STM. There are also recent STM studies of regular 2D periodic monolayer arrays of cobalt (II) hexadecafluorophthalocyanine ($F_{16}CoPc$) molecules on silver (110) [5] and hexaazatriphenylenehexa-carbonitrile (HATCN) molecules on silver (111) [6].

In this paper, we report on the crystallographic processing of two STM images of 2D periodic arrays of cobalt phthalocyanine (CoPc) molecules on the (111) surface of two noble metals. The CIP of STM data of a regular array of $F_{16}CoPc$ (fully fluorinated cobalt phthalocyanine) molecules on silver (110) and HATCN molecules on silver (111) complement our study. These molecule arrays were grown by two different techniques; molecular beam epitaxy in the case of the silver substrates [2,5,6] and spontaneous solution-phase redox deposition in the case of the gold substrate [3].

Our earlier results of CIP of STM data of 2D periodic arrays of phthalocyanines are summarized in refs. [7,8]. Reference [9] is available in open access on the Internet and gives a comprehensive introduction to CIP for Scanning Probe Microscopy (SPM). Because of the straightforward access to ref. [9], we will explain key CIP procedures only

very briefly in an appendix and give their main results for the above mentioned four samples in the main part of this paper.

Standard Fourier filtering of STM images [10] may be considered as the simplest form of CIP and is equivalent to translation averaging or, in other words, the enforcing of the plane symmetry group $p1$. The 16 other (higher symmetric) plane groups all combine translation symmetries with point symmetries [11] so that both kinds of 2D symmetries are enforced simultaneously by the application of CIP. To distinguish the latter kind of symmetry averaging of 2D periodic motifs from Fourier filtering (aka simple translation averaging), we propose to call it crystallographic averaging.

CoPc MOLECULE ARRAY ON GOLD (111)

Figure 1 shows the STM data of a 2D periodic array of CoPc molecules on Au (111) as grown by spontaneous solution-phase redox deposition, ref. [3]. As determined by CIP, the unit vectors of the translation averaged surface lattice differ by 2.7 % in length and intersect at an angle of 90.8°.

The application of a modified geometric Akaike criterion [13,14] allows us to conclude that this lattice would be a square Bravais lattice when random errors in the STM imaging process were removed. (More information on this “best model selection process” in the presence of Gaussian noise is given in the appendix. It is also assumed that systematic errors are smaller than the random errors in the imaging process.) A square lattice can only support plane groups $p4$ and $p4mm$.

The plane symmetry group is most likely $p4$ with the image intensity Fourier coefficient (FC) residuals: 13.3 % for the amplitude and 12.8° for the phase angle. (These quantitative measures of the deviation of a 2D periodic image from the exact definition of a plane symmetry group [11] are briefly explained in the appendix together with other important crystallographic concepts.)

The $p2$ maximal type I (*translationsgleiche* and non-isomorphic) subgroup (of $p4$) possesses the FC phase angle residual 12.1°, which is only slightly smaller. Mirror and

glide lines can be excluded on the basis of the CIP analysis, since the FC amplitude and phase angle residuals for the corresponding plane groups are about twice as high as their counterparts for plane group $p4$.

A more or less central circular area of the STM data in Fig. 1 with a diameter of 512 pixels was selected for the CIP. This area contained approximately 40 molecules so that the results can be considered as quite representative. Note that the molecule possesses the 2D point symmetry 4 in the $p4$ enforced contour plot inset in the upper right corner of Fig. 1. The translation averaged (i.e. Fourier filtered [10]) data, upper left inset of Fig. 1, show the molecule only with point symmetry 1, i.e. no symmetry other than the identity element. Both contour plot insets in Fig. 1 show the measured (and CIP symmetrized and averaged) local density of electronic states (LDOS) of a CoPc molecule on Au (111) divided into 32 equally spaced contour levels. All other contour plots in this paper have the same LDOS contour level resolution.

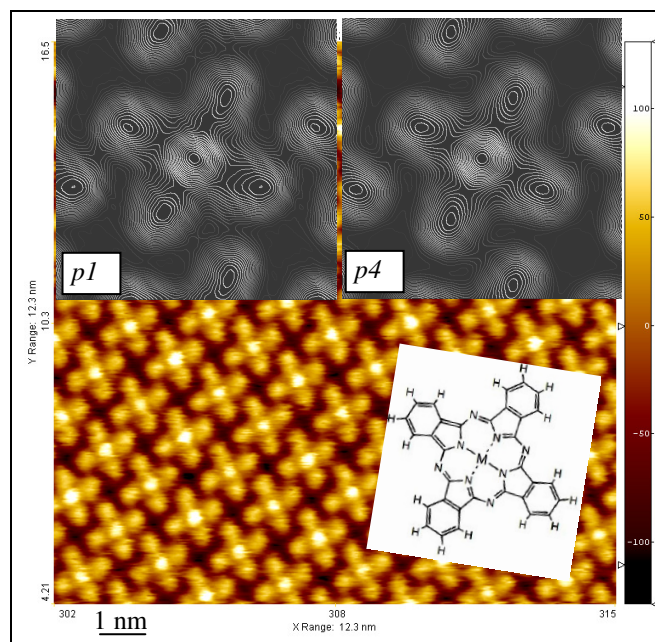


Fig. 1 Experimental STM data of a 2D periodic array of CoPc molecules on Au (111). The upper left inset shows the standard Fourier filtered (i.e. translation averaged or synonymously $p1$ enforced) motif (and its surrounding). The upper right inset shows a single CoPc molecule, i.e. the periodic motif of this array, (and its surrounding) after crystallographic averaging in plane group $p4$. The inset at the bottom is a sketch of a flat lying metal (element "M") Pc molecule with 2D point symmetry $4mm$ [12].

Somewhat loosely speaking, the CIP enforcing of plane group $p4$ removed the effects of the "less than perfect STM imaging process" from both the whole array and the individual CoPc molecules. Both random and systematic errors in the STM imaging process have been corrected.

CoPc MOLECULE ARRAY ON SILVER (111)

Figure 2 shows the STM data of a 2D periodic array of CoPc molecules on Ag (111) as grown by molecular beam epitaxy [2]. The unit vectors of the translation averaged surface lattice differ by 1 % in length and intersect at an

angle of 91.1° . The application of a modified geometric Akaike criterion [13,14] allows us again to conclude that this lattice would be a square Bravais lattice when random errors in the STM imaging process were removed.

The plane symmetry of the array is most likely $p4mm$ with a two-molecule motif. The corresponding FC residuals for this group (amplitude 37.4 %, phase angle 9.3°) are only slightly larger than for its maximal type I subgroups $p4$ (36.6 %, 9.3°), $c2mm$ (32 %, 5.1°), and $p2mm$ (27.9 %, 9.1°), which all possess only half as many point symmetry elements per lattice point. While plane group $p4$ would be consistent with the same square lattice, plane group $p2mm$ would only require a less symmetric rectangular Bravais lattice. Since we already concluded on the basis of the application of a modified geometric Akaike criterion that the experimental lattice is best described by a square, it is unlikely that plane group $p2mm$ would be the correct plane symmetry when the effects of the less than perfect STM imaging process were removed.

After the CIP, both molecules possess the site symmetry $4mm$. This is clearly revealed in the $p4mm$ contour plot inset in the upper right corner of Fig. 2. In the translation averaged data in the upper left corner of Fig. 2, the point symmetry of both molecules is only 1.

A circular area of the STM data in Fig. 2 with a diameter of 512 pixels was selected for the CIP. This area contained approximately 90 motifs, i.e. 180 molecules, and can be considered as sufficiently representative of the whole array.

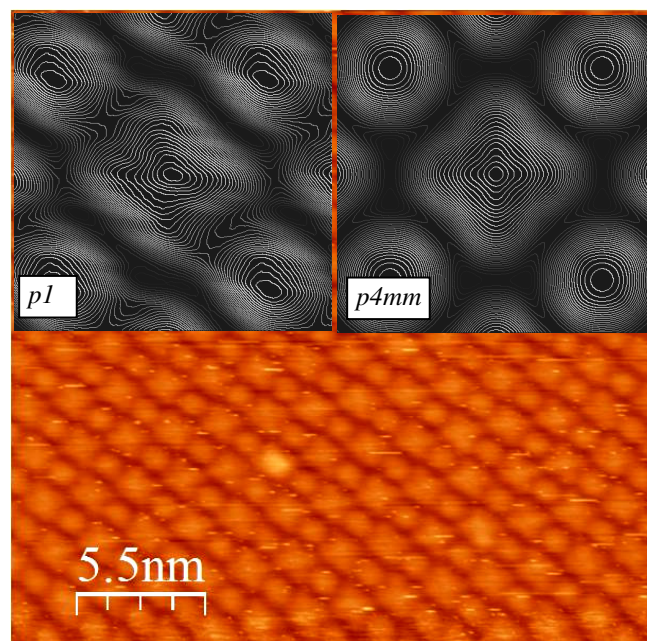


Fig. 2 Experimental STM data of a 2D periodic array of CoPc molecules on Ag (111). Sample bias +1.0 V, tunneling current 150 pA. The upper left inset shows the translation averaged motif (and its surrounding). The upper right inset shows two CoPc molecules, i.e. the crystallographic averaged periodic motif of this array (and their surrounding).

F₁₆CoPc MOLECULE ARRAY ON SILVER (110)

Figure 3 shows the STM data of a 2D periodic array of F₁₆CoPc molecules on Ag (110) as grown by molecular beam

epitaxy [5]. CIP delivered translation averaged unit vectors of the surface lattice that differ by 6.5 % in length and intersect at an angle of 108.2°. This represents an oblique unit cell that contains one molecule as the periodic motif (or one lattice point in other words) and is, therefore, primitive.

Since the lengths of the unit cell vectors are not very different and the intersecting angle is not close to either 120° or 90°, it is reasonable to assume that a primitive unit cell with unit vectors of equal lengths could serve as a viable alternative choice to convert the above mentioned CIP results (on the translation averaged lattice parameters) into the most likely 2D Bravais lattice of the array in the absence of random and systematic imaging errors. The corresponding centered cell would contain two molecules and its size would be twice that of the primitive unit cell with lattice vectors of equal length. Per definition, the corresponding Bravais lattice contains two lattice points. On the basis of the CIP results, the lattice vectors of this unit cell possess an a/b length ratio of 0.7333 and a lattice vector intersection angle of 85.7°, which is rather close to 90°.

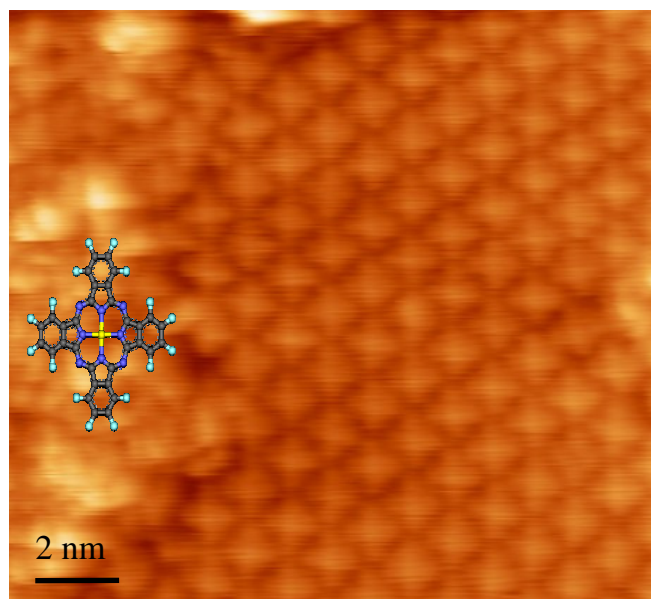


Fig. 3 Experimental STM data of a 2D periodic array of $F_{16}CoPc$ molecules on Ag (110). Sample bias: -2V and the tunneling current: 200 pA. A sketch of a slightly deformed $F_{16}CoPc$ molecule with 2D point symmetry $2mm$ is shown as inset.

A modified geometric Akaike criterion [13,14] allows us to conclude that this lattice would be a rectangular-centered 2D Bravais lattice when random errors in the STM imaging process were removed. A centered 2D Bravais lattice can only support plane groups $c2mm$ and cm , whereby the latter possesses two different settings. These plane groups do, however, possess type I subgroups that are based on primitive unit cells which can also be oblique due to a lack of mirror or glide lines [11].

An oblique (primitive) 2D Bravais lattice would only support twofold rotation points as site symmetries. The corresponding plane group would be $p2$ and possess a phase residual of 10.4°. Figure 4 shows contour plots of the

periodic motif with and without plane symmetry $p2$ enforced on the oblique unit cell.

Note that there will be another contour plot with plane symmetry $p2$ enforced on the “quasi-centered” unit cell that is in the “disguise” of plane group $c211$ a type I subgroup of $c2mm$. The two molecules of the periodic motif will not lie on positions with site symmetry 2 in that $p2$ group so that they will not possess twofold rotation points at their centers. Since they will be related to each other by twofold rotation points, both molecules of the periodic motif will be identical. From all of this, a different phase residual is to be expected for that $p2$ group. Since the periodic motif in the quasi-centered cell is “more complex” and twice as large, the phase residual of the $p2$ subgroup that is based on this unit cell should be larger than its counterpart residual on the basis of the primitive (oblique) cell.

Figure 5 shows contour plots of the periodic motif on the basis of primitive (and oblique) subgroups of $c2mm$ with and without plane group $p2$ enforced. The phase residual for plane group $p2$ in this quasi-centered unit cell (of Fig. 5) is 13.1°. This is indeed somewhat larger than the phase residual for $p2$ on the basis of the primitive (oblique) unit cell mentioned above, Fig. 4.

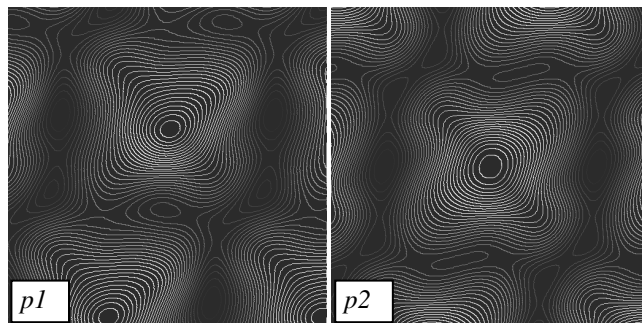


Fig. 4 Contour plots of $p1$ and $p2$ enforced versions of the experimental STM data of Fig. 3 on the basis of the oblique Bravais lattice (with surface lattice vectors that differ by 6.5 % in length and intersect at an angle of 108.2°). Note that one single molecule represents the periodic motif in both cases since the lattice is primitive.

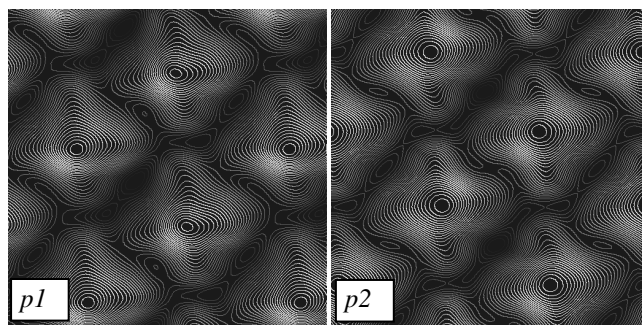


Fig. 5 Contour plots of $p1$ and $p2$ enforced versions of the experimental STM data of Fig. 3 on the basis of primitive (and oblique) subgroups of $c2mm$. Note that two molecules represent in both cases the periodic motif.

While these two molecules are allowed to be different in the $p1$ contour plot, they need to be identical in its $p2$ counterpart. The surface lattice is both primitive and oblique (a/b length ratio of 0.7333 for the lattice vectors and an intersection angle of 85.7°), but oriented analogously to the rectangular-centered Bravais lattice that would be obtained when the errors in the STM imaging process were removed. Because of this analogous orientation and size, we refer to this lattice as “quasi-centered”.

Figure 6 shows finally contour plots for the rectangular-centered unit cell with plane groups $p2mm$ and $c2mm$ enforced. The amplitude residual for $p2mm$ is 17.4 % and its phase residual is 18.1°. While the amplitude residual of 17.5 % of $c2mm$ is comparable to that of $p2mm$, its phase residual is only 13.8°. Plane group $p2mm$ is one of the four type IIa (*klassengleiche* with the same conventional cell, maximal non-isomorphic) subgroups of $c2mm$ [11].

The other three type IIa subgroups of $c2mm$, i.e. $p2gg$, $p2mg$ and $p2gm$, all possess higher amplitude and phase residuals than their supergroup. These are very interesting results and lend support to our earlier conclusion that the rectangular-centered Bravais lattice would be the correct choice.

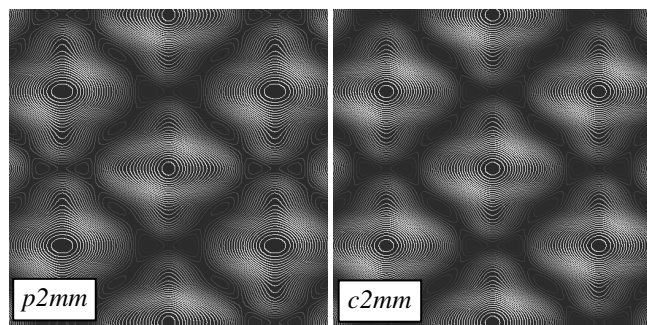


Fig. 6 Contour plots of $p2mm$ and $c2mm$ enforced versions of the experimental STM data of Fig. 3 on the basis of the centered-rectangular unit cell. While the molecules are allowed to be different in the $p2mm$ contour plot, they need to be identical in its $c2mm$ counterpart. In both of these plots, the molecules need to possess point symmetry $2mm$. While two molecules represent the periodic motif in the $p2mm$ plot, the $c2mm$ plot can be understood to feature one molecule per one half of the unit cell.

The two (*cm*) type I subgroups of $c2mm$ possess the same (17.5 %) amplitude residual and phase residuals of 8.8° (for $c1ml$) and 8.3° (for $c1lm$). The third type I subgroup of $c2mm$ is $c211$, in other words $p2$ (as shown in Fig. 5, right hand side), with the above mentioned phase residual of 13.1°. Note that this phase residual is reasonably close (but smaller) than the phase residual of its type I supergroup $c2mm$. The so called Ao/Ae ratio (see appendix for a brief explanation) of the $c2mm$, $c1ml$, and $c1lm$ groups were all zero.

From all of this, the conclusion has to be that the molecules in Fig. 3 possess site symmetry $2mm$ and are arranged in plane group $c2mm$ when the effects of the less than perfect STM imaging process are removed. Site symmetry $2mm$ means that the molecules must be distorted. A slight distortion from $4mm$ (for an undistorted molecule) to $2mm$ (for the average molecule in the array) is indeed discernable in the contour plot in the right hand side of Fig. 6.

A more or less central circular area of the STM data in Fig. 3 with a diameter of 256 pixels (and which excluded the defective area to the left) was selected for the CIP. This area contained approximately 35 molecules. The data in Fig. 3 are visibly quite noisy and show a very high spatial frequency modulation that is oriented approximately horizontally. CIP was, therefore, combined with noise filtering in order to remove this kind of distortion. The combination of noise

filtering and CIP enforcement of plane group $c2mm$ seems to have removed the effects of the less than perfect STM imaging process from both the whole array and the individual $F_{16}CoPc$ molecules. Experimental data such as shown in Fig. 3 may, however, represent the lower “data quality” limit for which CIP will produce useful results.

Our earlier study of regular arrays of $F_{16}CoPc$ molecules on Ag (110) revealed somewhat more densely packed domains that possessed only plane group $p2$ [7]. We also note that two densely packed oblique lattice domains and a more loosely packed domain with a rectangular (pseudo-square) lattice were described in ref. [5] for the same materials system.

HATCN MOLECULE ARRAY ON SILVER (111)

Figure 7 shows the STM data of a monolayer of hexaazatriphenylenehexacarbonitrile molecules on silver (111). As determined by CIP, the unit vectors of the translation averaged surface lattice differ by 0.5 % in length and intersect at an angle of 119.9°. A modified geometric Akaike criterion [13,14] allows us to conclude that this lattice would be a hexagonal 2D Bravais lattice when random errors in the STM imaging process were removed. A hexagonal unit cell supports plane groups $p3$, $p3m1$, $p31m$, $p6$ and $p6mm$.

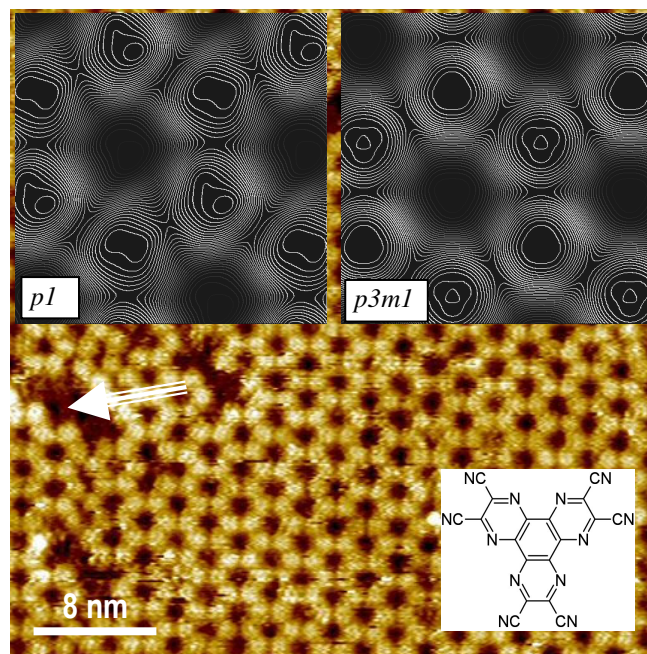


Fig. 7 Experimental STM image of a 2D periodic array of hexaazatriphenylenehexacarbonitrile molecules on silver (111), ref. [6]. The upper left inset shows the standard Fourier filtered motif (that encompassed two molecules) and its surrounding. The upper right inset shows two HATCN molecules, i.e. the periodic motif of this array, (and its surrounding) after crystallographic averaging in plane group $p3m1$. The arrow points to a patch of about ten aggregated molecular vacancies. The inset at the bottom is a sketch of a flat on a substrate lying HATCN molecule with 2D point symmetry $3m$ [6].

The CIP analysis (combined with some noise filtering) indicates that the plane symmetry group of the molecular array is probably $p3m1$ with the image intensity FC

residuals: 13.1 % for the amplitude and 4.8° for the phase angle. The FC residuals for its type I subgroup $p3$ are 12.8 % and 3.9°, i.e. only slightly lower than for $p3m1$. The multiplicity of the general position of $p3$ is, however, only half that of $p3m1$.

Neither of these two plane groups contains sets of twofold rotation points or a mirror line along the short diagonal of the unit cell (such as plane group $p6$ and $p31m$ do) so that an identical appearance of the symmetrized LDOS of the two molecules within one unit cell is not enforced. Correspondingly, there is a clearly visible difference between both molecules in the $p3m1$ contour plot inset of Fig. 7.

Note that the FC phase angle residuals of $p31m$, $p6$, $p6mm$ are with 8.1°, 8.3° and 8.3° significantly larger than for $p3m1$, while the FC amplitude residuals (13.1 %, 12.8 %, and 13.1 %) are for all groups comparable. The multiplicities (of the general position) are for the first two of these plane groups identical to that of $p3m1$, while $p6mm$ possesses a multiplicity that is twice as high. Also note that the phase angle residual for $p2$, i.e. one of the two type I subgroups of $p6$, is quite high at 7.9°, so that there are probably no sets of twofold rotation points in the molecular array.

If one were to require that both molecules in the hexagonal unit cell need to appear identical in STM images, one should conclude that $p6mm$ might be the correct plane symmetry when the effects of the less than perfect STM imaging process were removed. Whether $p3m1$ or $p6mm$ were to be the correct plane symmetry, in both cases the molecules would retain their $3m$ point symmetry. If the mirror lines within the molecules were broken, the plane group of the molecule array must be either $p3$ or $p6$. The comparatively modest spatial resolution in the experimental data of Fig. 7 does, however, not lend strong support to such a hypothesis.

The central 512 pixel diameter circular area of the STM data in Fig. 7 contains approximately 500 molecules and was selected for the CIP. Despite the presence of patches of up to about ten aggregated molecular vacancies (as marked by an arrow in Fig. 7), the crystallographic averaging over such a large array should ensure reproducible results.

Combining noise filtering with CIP enforcing of plane group $p3m1$ seems to have removed the effects of the less than perfect STM imaging process (at least partially) from both the whole array and the individual HATCN molecules.

REGULAR MOLECULAR ARRAYS AS CALIBRATION SAMPLES FOR STM?

Both CoPc molecule arrays are quite highly symmetric and could, therefore, serve as calibration samples for STMs. The point spread function of a STM could be derived by CIP on the basis of such a calibration sample and utilized for the correction of STM images that were subsequently recorded under essentially the same experimental conditions and with the same scanning probe tip [9]. For such a calibration sample, laboratory environment stability, non-toxicity, costs, and simplicity in the fabrication process would be essential.

Although it remains unclear if the underlying plane symmetry of Fig. 7 would be $p3m1$ or $p6mm$ (or perhaps

even $p3$ or $p6$) when the effects of the less than perfect STM imaging process were to be removed, an HATCN molecule array on Ag (111) may still serve as a calibration sample. This is because $p3$ is a type I subgroup of $p3m1$, which is in turn a type I subgroup of $p6mm$. Analogously, $p6$ is a type I subgroup of $p6mm$. The point spread function that one would extract on the basis of a $p3$ or $p3m1$ or $p6$ enforced array would not be “completely incorrect”; it would just be not as “detailed” as it possibly could be.

The F_{16} CoPc molecules on silver (110) array, on the other hand, would probably not make a good calibration sample because there are at least three different molecule domains [5,7,8]. This is probably the result of the comparatively low plane symmetry ($c2mm$) of this substrate compared to (111) oriented Au or Ag substrates (which possess plane symmetry $p6mm$). Due to the fluorination of the cobalt phthalocyanine molecules and the corresponding increase in the electro affinity, a stronger interaction is to be expected for the F_{16} CoPc molecules compared to CoPc molecules [15]. This may contribute to the somewhat undesired presence of more than one array domain, although it may mean an increased stability of the sample.

The $c2mm$ domain F_{16} CoPc molecules on silver (110) possesses a comparatively high symmetry and seems to exist with preference in areas adjacent to accumulations of monolayer defects, see left hand side of Fig. 3. The latter feature could possibly come in handy when one searches for this particular domain.

SUMMARY AND CONCLUSIONS

CIP was demonstrated on experimental STM images of regular monolayer arrays of small molecules on noble metals. Highly symmetric 2D periodic arrays such as the ones that are formed by CoPc molecules on (111) oriented gold and silver may serve as calibration samples in order to derive and utilize the point spread function of a STM. The same could be concluded for an HATCN molecule array on Ag (111). The first author of this paper asks the scientific community most politely to send him raw SPM images of 2D periodic arrays so that he can demonstrate the benefits of CIP to wider audiences in future joint publications.

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APPENDIX

Having its roots in electron crystallography [16], the essence of CIP is crystallographic averaging over many unit cells of a 2D periodic array in order to derive the content of one unit cell at a higher signal to noise ratio. For computational efficiency, this averaging is performed in Fourier space. The Fourier synthesis of the symmetry averaged Fourier coefficients of the SPM image intensity leads to the CIP processed (and plane symmetry enforced) SPM image in direct space.

As a consequence of the multiplicity of general position of the 16 higher symmetric plane groups [11] (which is equal to the number of point symmetry elements per lattice point), CIP effectively averages over two to twelve times larger arrays than

standard Fourier filtering. This enhances the signal to noise ratio of the SPM imaging process significantly.

CIP also allows for the quantification of the deviation of a 2D periodic array from the mathematical definition of the 16 higher symmetric plane symmetries. In order to quantify deviations from these plane groups, the electron crystallography community uses Fourier coefficient amplitude (A_{res}) and phase (ϕ_{res}) residuals [9,16]:

$$A_{res} = \frac{\sum_{H,K} \left| |A_{obs}(H,K)| - |A_{sym}(H,K)| \right|}{\sum_{H,K} |A_{obs}(H,K)|} \quad \text{in \% and}$$

$$\phi_{res} = \frac{\sum_{H,K} w(H,K) \cdot |\phi_{obs}(H,K) - \phi_{sym}(H,K)|}{\sum_{H,K} w(H,K)} \quad \text{in degrees,}$$

where the subscripts stand for *observed* and *symmetrized*, w is a relative weight proportional to A_{obs} , and the sums are taken over all Fourier coefficients labeled H and K .

The amplitudes of Fourier coefficients that must be systematically absent when certain symmetry elements are present [11] form the basis of the so called Ao/Ae ratio [9,16]. For those plane groups for which it is defined, Ao/Ae ratios larger than zero provide an additional quantifiable measure for how much an experimental SPM image of a 2D periodic array deviates from the corresponding plane symmetry. (Except for the identification of the most likely plane group of the $F_{16}CoPc$ molecule array on Ag (110), the Ao/Ae ratios were unimportant in the context of this paper.) The Fourier coefficient residuals, the Ao/Ae ratios, and the multiplicity ratios for subgroups and supergroups form traditionally the basis for concluding which plane symmetry group an experimentally obtained 2D periodic image most likely possesses. Such decisions have traditionally been somewhat subjective within the electron crystallography community.

A first step in the direction of reducing this subjectivity has been our utilization of a modified geometric Akaike information criterion [13,14] for concluding what the most probable Bravais lattice of a 2D periodic array would be when imaging errors were removed. Ref. [14] derives the number of constraints on the geometric shapes of a trapezoid, parallelogram, rectangle, rhombus, and square.

These numbers of constraints guide us in interpreting the last four of these shapes as oblique, rectangular, hexagonal, and square 2D Bravais lattices when the effects of a less than perfect imaging process are removed. The noise is thereby assumed as Gaussian with a mean of zero and concerns the position of the four vertices of the unit cell in direct space. As mentioned above in the main text, rectangular-centered Bravais lattices are currently determined on the basis of the (oblique, "twice as large") "quasi-centered unit cell" as derived by CIP. In the future, we will modify our geometric Akaike information criterion further and also try to include experimental error bars of the parameters of the various lattices (as determined by CIP).

Formally similar ideas should in the future help removing subjectivity in decisions between plane (type I or II) subgroups and supergroups. In the main part of the paper, we provided the residuals for subgroups and supergroups for this reason. The number of constraints on the intensity value of pixels in the general position of subgroups and supergroups should play a formally analogous role to the above mentioned number of constraints on the geometric shapes of quadrilaterals.