Crystallographic Processing of Scanning Tunneling Microscopy Images of Cobalt Phthalocyanines on Silver and Graphite

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Monolayers of cobalt phthalocyanine (CoPc) on silver (111) and highly (0001) oriented pyrolytic graphite (HOPG) were imaged with a scanning tunneling microscope (STM) at cryogenic temperatures (around 30 K) at Chemnitz University of Technology, Figs. 1a and 2a. Domains of regular arrays with periodicity in two dimensions (2D) and a variety of plane symmetries [1] were observed.

Crystallographic image processing (CIP) [2] was used to quantify deviations from the plane symmetry groups and to obtain symmetrized versions of the content of the average unit cells of these arrays, Figs. 1b,c and 2b-e. While classical Fourier filtering may be considered to be the simplest form of CIP (Figs. 1c, 2c,e), our full utilization of CIP also delivers the symmetry averaged periodic motif as well as information on the point symmetry of molecules in regular 2D periodic arrays [3]. Supported by the experimental data of ref. [4], we speculate on the basis of our CIP results that the CoPc molecules are inclined relative to the HOPG substrate at cryogenic temperatures [3].

Although only demonstrated for STM images in this paper, CIP is applicable to all kinds of scanning probe microscopy (SPM) images of 2D periodic arrays. A dedicated computer program for CIP of SPM images is under development, see Fig. 3. This program will allow for the extraction of the point spread function of a SPM from an image of a highly symmetric calibration sample and the usage of this function for the correction of subsequently recorded SPM images. Also, we will utilize geometric Akaike criteria [5] for decisions on which plane group an experimental SPM image most likely possesses. The first author of this paper asks the scientific community to send him raw images of 2D periodic arrays so that he can demonstrate the benefits of CIP to a wider audience (in future joint publications) [6].

References
[1] T. Hahn (editor), *International Tables for Crystallography. Brief Teaching Edition of Volume A, Space-group Symmetry*, 5th rev. ed., Chester, International Union of Crystallography, 2005.
[2] P. Moeck, in: *Microscopy: Science Technology, Applications and Education*, Microscopy Book Series, Vol. **4**, A. Méndez-Vilas and J. Diaz eds., 2011, http://www.formatex.org/microscopy4/.
[3] P. Moeck, J. Straton, M. Toader, M. Hietschold, *Proc. Fall 2010 Meeting of the Materials Research Society*, http://journals.cambridge.org/action/displayJournal?jid=OPL
[4] T. Kataoka, H. Fukagawa, S. Hosoumi, K. Nebashi. K. Sakamoto, and N. Ueno, *Chem. Phys. Lett.* 451 (2008) 43.
[5] K. Kanatani, *Inter. J. of Computer Vision* 26 (1998) 171.
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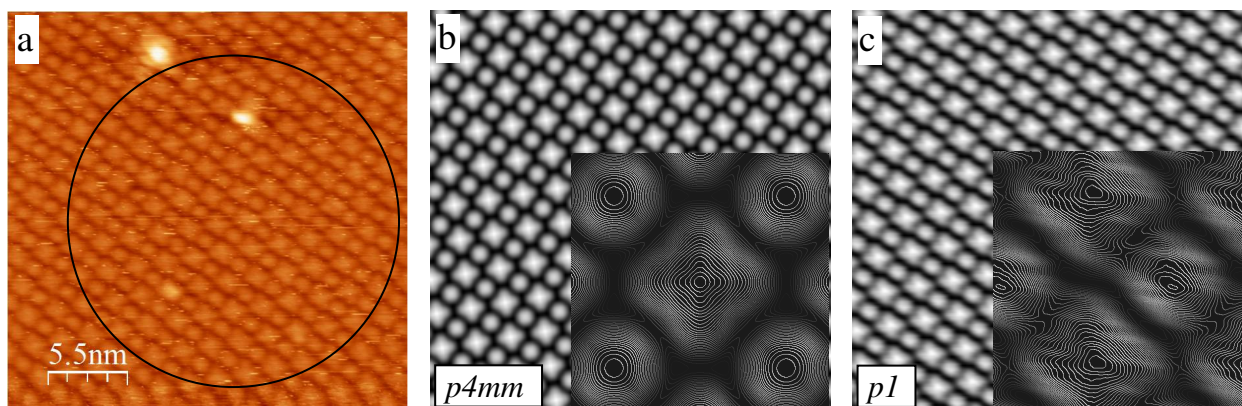
FIG. 1. CoPc on Ag (111), I_T = 150 pA, U_T = -1.0 V; **(a)** Raw STM data with selection for the application of the CIP procedures; **(b)** *p4mm* enforced version of this data (on the basis of a circular selection of 512 pixels diameter, which contained about 90 periodic motifs) with a quadratic unit cell inset as contour plot; and **(c)** translation averaged (*p1* enforced, i.e. classical Fourier filtered) version of the data (on the same basis) with an oblique unit cell inset as contour plot. For convenience, the contour plot insets were rotated clockwise by approximately 8º.
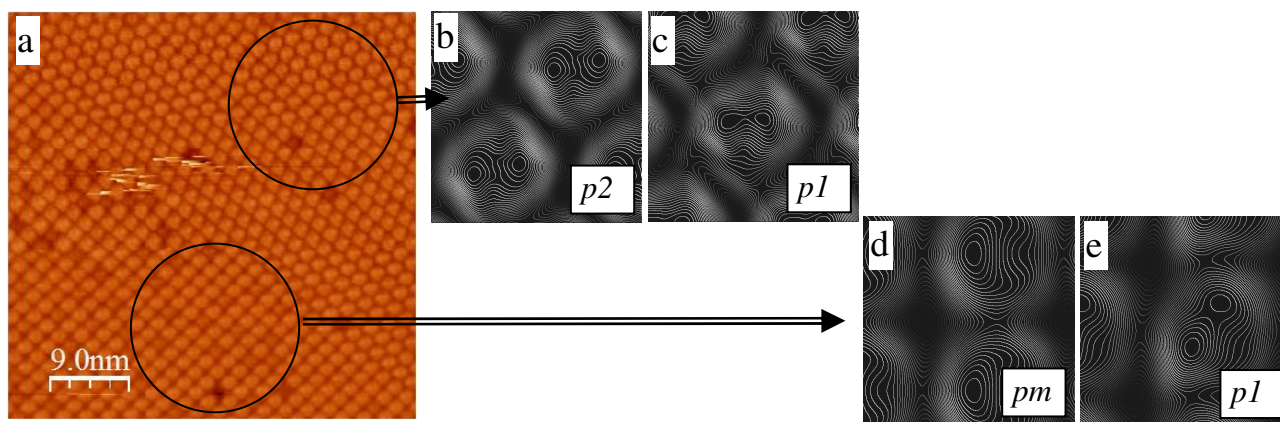

FIG. 2. CoPc on HOPG, I_T = 80 pA, U_T = +1.0 V; **(a)** Raw STM data with two domains and selections for the application of the CIP procedures; **(b)** *p2* enforced motif as contour plot for the selected data from the upper domain (on the basis of the upper circular selection with a diameter of 126 pixels, which contains about 85 periodic motifs); **(c)** translation averaged motif as contour plot for the same data (from the upper domain); **(d)** *pm* enforced motif as contour plot for the selected data from the lower domain (on the basis of the lower circular selection with a diameter of 126 pixels, which contains about 90 periodic motifs); and **(e)** translation averaged motif as contour plot for the same data (from the lower domain).
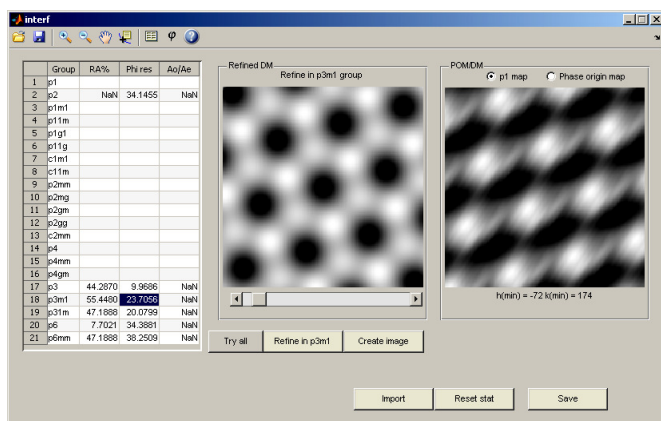

FIG 3. Screenshot of one of the interactive windows of PSU's CIP program for SPM. The right panel shows translation averaged STM data of a regular 2D periodic array of fluorinated CoPc molecules on HOPG. For illustrative purposes, the middle panel shows this data symmetrized to the plane group of HOPG. This group could be a supergroup of the molecular array. We assume that the molecules are arranged in the *c1m1* subgroup of this plane group and are not lying flat on the substrate [3]. We are in the process of utilizing geometric Akaike criteria [5] to test this hypothesis.