Molecular chessboard assemblies sorted by site-specific interactions of out-of-plane d-orbitals with a semimetal template

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Abstract: We show that highly ordered 2D chessboard arrays consisting of a periodic arrangement of two different molecules can be obtained by the self-assembly of unsubstituted metal-phthalocyanines (metal-Pcs) on a suitable substrate serving as the template. Specifically, CuPc:MnPc and CuPc:CoPc mixtures sort into highly ordered Cu:Mn and

Cu:Co chessboard arrays on the square $p(10\times 10)$ reconstruction of bismuth on Cu(100). Such created bimolecular chessboard assemblies emerge from the site-specific interactions between the central transition-metal ions and the periodically reconstructed substrate. This work provides a conceptually new approach to induce 2D chessboard patterns in that no functionalization of the molecules is needed.

KEYWORDS bimolecular self-assembly, template substrate, site-specific interactions, phthalocyanine, semimetal

The monocomponent self-assembly of tetrapyrroles, such as porphyrins (P) or phthalocyanines (Pc) at surfaces is a straightforward approach to obtain highly ordered 2D layers.^{1–3} For bicomponent mixtures Hipsps *et al.*^{4,5} showed that perfluorinated tetrapyrroles, *e.g.* Pc (CoF₁₆Pc) and unsubstituted tetraphenyl-P (NiTPP) on Au(111), order into periodic 2D chessboard layers. These layers consist of alternating CoF₁₆Pc and NiTPP molecules in both directions and thereby maximize the polar C—F—H interactions between the two components. Perfluorination has subsequently been proven as a robust avenue to obtain Pc-based chessboard arrays,^{6–8} which have controllable magnetic functionalities, if different central metal ions are used.⁹ The perfluorination approach has been extended to mixtures with other molecules^{10–12} and was used to order molecules also in the second layer.¹¹ If the two macrocycles differ, *e.g.* if one component is P and the other Pc, sorting has been observed for specific combinations of molecules and substrates.^{13,14} Also, an intriguing chessboard arrangement of the axial Cl-ligand has been observed in bilayers of pure ClAlPc^{15,16} and for SnPc¹⁷ where the Sn atom is vertically displaced. In case of binary mixtures of tetrapyrroles with identical macrocycles but different central metal ions, however, the two different centers were observed at random positions within the self-assembled lattice, due to the absence of specific molecule–molecule interactions.^{9,18}

Furthermore, moiré patterns of graphene or hexagonal boron nitride (*h*-BN) on suitable metal substrates have been used recently as templates to induce well-defined molecular arrangements in monocomponent P or Pc layers.^{19–26} Binary mixtures of Pc and tert-butyl Pc assembled on the moiré patterns of graphene on Ru(0001) showed short range 1D ordered arrangements, but long range 2D order comparable to *e.g.* a chessboard pattern was not observed.²⁷

Here we demonstrate that bicomponent mixtures of Pcs, which differ exclusively in their central metal ions (Mn, Co, Cu), sort into highly ordered bimolecular chessboard arrays on the p(10×10) reconstruction of bismuth on Cu(100).^{28–31} The sorting effect is based on site-specific molecule–substrate interactions between the central transition metal ions and the bismuth template. It is enabled by the square symmetry and the pitch of 1.8 nm of the Bi reconstructed substrate which both match the four-fold symmetry of the Pc molecules and the pitch of the Pc chessboard arrays.

STM images, obtained on the *in-situ* prepared p(10×10)-Bi reconstruction on Cu(100), reveal square pores (dark contrast) separated by rims and nodes (bright contrast) with an average pitch of 1.8 nm (Figure 1a, b). As reported in ref. 29, the reconstruction is not perfectly periodic and the size of the pores varies slightly. Differential conductance (dI/dV) spectra recorded at the nodes, rims and pores (Figure 1c) exhibit a u-shape, indicating a reduced density of states around the Fermi level compared to native Cu(100), in-line with the semi-metallic character of bulk Bi.^{30–32} In contrast, bare Cu(100) features a roughly constant dI/dV spectrum due to its about constant density of states around the Fermi level (E_F).³³ Consequent to the comparably lower density of states of the reconstructed Bi ad-layer at and around E_F and due to their in-plane delocalization,³¹ a rather weak interaction with molecular adsorbates is expected.³² This is in some analogy to the charge distribution of graphene or *h*-BN leading to a lower interaction with planar polycyclic aromatic compounds.^{19–26}

Figure 1. Overview (a) and close-up (b) STM images of the $p(10\times 10)$ -Bi/Cu(100) reconstruction. The reconstruction consists of a network of nodes (imaged bright, pink dot), connected by rims (orange dot) and surrounding pores (imaged dark, yellow dot). The Bi reconstruction is not strictly periodic,²⁹ *i.e.* the pore size varies. It is locally chiral at the nodes, as seen by their pin-wheel appearance (P – counterclockwise rotation of the node with respect to the ridge; M – clockwise rotation). (c) The characteristic u-shape of the virtually identical dI/dV spectra (set point: -3 V, -400 pA) obtained at these three sites indicates a lower density of states around the Fermi level compared to native Cu(100).^{30,31}

Deposition of a binary mixture of CuPc and MnPc (scheme in Figure 2a) by sublimation onto the reconstructed Bi samples held at room temperature leads to self-assembled molecular domains with each molecule appearing as a four-leaved clover (Figure 2b, c).

As shown by Hipps *et al.*, the contrast at the center of metal-Pcs allows for their identification.^{18,34} Cu^{18,34} and Ni^{4,5,34} centers have been imaged as depressions, while Mn⁹, Fe³⁴ and Co^{4,5,18} centers have been imaged as protrusions. This is because the square-planar ligand field of the Pc macrocycle implies that Mn ($3d^5$), Fe ($3d^6$) and Co ($3d^7$) have out-of-plane 3d states around the Fermi level (E_F) but not Cu ($3d^9$) and low-spin Ni ($3d^8$).³⁵ The out-of-plane 3d states protrude into the vacuum and are therefore imaged higher (coded bright) in the constant current STM mode. Consequently, the lack of out-of-plane 3d states in CuPc around E_F is the reason why its center is imaged lower (coloured dark).^{18,34} By comparing the contrast on the metal centers relative to the contrast on the Pc lobes (*cf.* line profiles in Figure

S1 in Supporting Information), CuPc (center lower than lobe) is clearly distinguished from MnPc and CoPc (centers higher than lobes). This approach works despite the fact that the absolute contrast on the lobes may be slightly modulated by the Bi reconstruction (*cf.* Figure 3a-c for images of pure CuPc, MnPc and CoPc). In addition, the molecules can be identified by performing tunneling spectroscopy (Figure S7 in Supporting Information).

Figure 2. Scheme of phthalocyanine (Pc) containing Mn (red), Co (blue) or Cu (green) (a) and STM images of a bimolecular CuPc:MnPc layer on p(10×10)-Bi/Cu(100) (b, c). MnPc and CuPc are identified by the respective bright and dark image contrast in their centers. The molecules self-assemble into a chessboard-lattice consisting of alternating MnPc and CuPc (b,c). (c) For visibility, the color scale is wrapped around making the substrate appear brighter. The two mirror domains (*P* and *M*) of the molecular chessboards are indicated by red and blue squares.

The characteristic STM contrast at the centers of the Pc (MnPc bright and CuPc dark) allows to directly see that the bimolecular mixture of CuPc:MnPc on the p(10×10)-Bi reconstruction forms a strictly periodic chessboard layer consisting of alternating MnPc and CuPc molecules (Figure 2b, c). Two mirror domains⁹ of this chessboard lattice are observed.

At this point, before discussing the driving forces behind the chessboard formation, we first extend the discussion to the self-assembly of pure CuPc, MnPc and CoPc and of their binary mixtures (CuPc:MnPc, CuPc:CoPc and MnPc:CoPc) on p(10×10)-Bi/Cu(100) (Figure 3).

Detail and overview images are supplied in Figure S2 and Figure S3 in Supporting Information. Pure CuPc self-assembles into extended domains of about 100 molecules, quite in contrast to pure CoPc and pure MnPc which aggregate into smaller domains of about 20 molecules (Figure 3a-c). In the pure CuPc domains (Figure 3a), every second molecule appears slightly brighter or darker, *i.e.* a bright/dark single component chessboard-like contrast is observed in the STM image. For pure CoPc and pure MnPc (Figure 3b, c), no single component chessboard contrast is observed.

Figure 3. Scanning tunneling microscopy (STM) images of transition metal Pcs on p(10×10) reconstructed Bi/Cu(100): pure CuPc, MnPc and CoPc (a-c) and binary mixtures (CuPc:MnPc, CuPc:CoPc and CoPc:MnPc) (d-f). The colored crosses assign the type of Pc (CuPc: green; MnPc: red; CoPc: blue) and their orientation designates the alignment of the Pc lobes. CuPc self-assembles into extended islands, while MnPc and CoPc form only smaller islands. In case of CuPc, the orientation and the contrast of every second molecule is slightly different (light and dark green crosses). Among the binary mixtures, CuPc:MnPc and CuPc:CoPc assemble into a chessboard lattice.

Like in the pure CuPc domains, every second molecule has a slightly different orientation. Interstitial CuPc molecules are observed occasionally in place of MnPc or CoPc. In case of CoPc:MnPc only small domains are observed, in which the molecules do not form chessboard arrays. The scale bar applies to all images. For visibility, the color scale is wrapped around, making the substrate appear brighter.

Among the bicomponent mixtures, CuPc:MnPc and CuPc:CoPc self-assemble into extended chessboard arrangements of ~ 100 molecules (Figure 3d,e). In contrast, for CoPc:MnPc the observed molecular domains are small and chessboard-order is absent, with the exception of small (and rare) 3×3 domains (Figure 4f). In CuPc:MnPc, interstitial CuPc molecules taking the place of MnPc molecules are occasionally observed due to the slightly higher amount of CuPc deposited (Figure 3d). In all three systems where a chessboard assembly (CuPc:MnPc and CuPc:CoPc) or chessboard-like contrast (pure CuPc) is observed, the molecules are observed to be slightly rotated with respect to each other (*cf.* the different orientations of the crosses in Figure 3). Specifically, the CuPc molecules in the chessboards (in case of pure CuPc those with dark appearance) are oriented such that their benzo-groups point towards the aza-nitrogens of MnPc, CoPc or bright CuPc, respectively (Figure 2b and Figure S2 in Supporting Information). While this alternating orientation is not observed in chessboard arrays of Pcs based on perfluorination,^{6–8} or in most assemblies of unsubstituted Pcs,^{18,34} it has been observed for SnPc on Ag(111)¹⁷ and has been attributed the interaction with the Ag(111) substrate. Therefore we tentatively assign it to the specific interactions of the molecules with the Bi reconstruction, but we cannot exclude weak hydrogen-bond like interactions.

The structures of the single and bicomponent Pc layers with respect to the $p(10 \times 10)$ Bi reconstruction are analyzed in Figure 4. Figure 4a displays the distances and orientations determined between the next-nearest-neighbor Pcs and between adjacent nodes of the Bi

reconstruction with identical chirality (black) in the single component islands (CuPc, CoPc, MnPc). The orientations are measured with respect to the vertical axis of the STM images. Figure 4b shows the same for the binary mixtures (CuPc:MnPc, CuPc:CoPc and CoPc:MnPc). The numerical values are also presented in Table S1 and Table S2 in Supporting Information. Figure 4c summarizes the adsorption sites determined at the edges of the molecular layers (*cf.* Figure S4 and Figure S5 in Supporting Information), *i.e.* MnPc in CuPc:MnPc, CoPc in CuPc:CoPc and bright CuPc in pure CuPc strongly prefer to adsorb on the Bi node. Consequently, the molecules appearing as dark CuPc in all three layers adsorb in the pores. Note that the loosely periodic structure of the substrate allows for its extrapolation below the molecular layer only at the edges.

Figure 4. Polar plot of the MPc – MPc distance and orientation of (a) pure CuPc, MnPc and CoPc and (b) binary mixtures (CuPc:MnPc, CuPc:CoPc and CoPc:MnPc) on p(10×10) reconstructed Bi/Cu(100) and of the Bi reconstruction. For chessboard layers (pure CuPc, CuPc:CoPc and CuPc:MnPc), the distances and orientations of the two mirror domains are identical with the values from the two chiral nodes. In contrast for non-chessboard layers (pure MnPc, pure CoPc and CoPc:MnPc), the orientations of the domains and the Bi nodes are different. (c) Sketch of the adsorption sites in the

pure CuPc, MnPc:CuPc and CuPc:CoPc chessboard layers as determined at the edges of the islands (cf. Figure S4 and Figure S5 in Supporting Information) showing that MnPc, CoPc and bright CuPc adsorb on the nodes and that dark CuPc adsorbs in the pores. (d) The combination of adsorption sites, the compatible distances and orientations implies that the chessboard layers are commensurate with the Bi reconstruction, as illustrated by the translation molecules schemes of CuPc:MnPc (Figure 2b) onto an image of the Bi reconstruction.

All distances are identical within the error margins. For the chessboard layers (CuPc:CoPc and CuPc:MnPc) and for pure CuPc which exhibits a chessboard contrast, the orientations of the mirror domains are the same as the orientations between pores with identical chirality. For non-chessboard layers (pure MnPc, pure CoPc and CoPc:MnPc), the lattice orientations are different from the lattice orientations of the Bi reconstruction. The identical distances and the matching orientations of the chessboard layers and the Bi nodes imply that they are commensurate with the Bi reconstruction. Therefore, all MnPc molecules in CuPc:MnPc can simultaneously be adsorbed on the nodes, while all CuPc molecules can be adsorbed in the pores. This is also shown graphically in Figure 4d by superposition (only translation) of the molecular schemes from the CuPc:MnPc layer (Figure 2b) onto the $p(10\times10)$ -Bi reconstruction. The above commensurability is also true for CuPc:CoPc.

This analysis shows that the chessboard lattice formation is driven by the Bi reconstruction which acts as a template. We note that the chessboard-arrays are highly periodic while the $p(10\times10)$ -Bi reconstruction is not strictly periodic.²⁹ This suggests an adsorbate induced modification of the reconstruction, as often observed for FePc monolayers³⁶ or adsorbed metal atoms,³⁷ which disrupt the herringbone reconstruction of Au(111). This observation is further consistent with Bi/Cu(100) being highly diffusive, for example being able to wet a Cu surface across almost one millimeter within 11 hours at 513 K.³⁸ Thus, we conclude that during the deposition and self-assembly process of the molecules at room temperature, the Bi

reconstruction below the molecules is modified to accommodate the nearly defect-free chessboard array. In fact, based on the matching orientations between Bi nodes with identical chirality and the mirror domains of the chessboard layers, we speculate that all Bi nodes below a molecular mirror domain have the same chirality.

In view of the above shown data on pure MnPc, CoPc and CuPc and of their respective bimolecular mixtures, we can now discuss the origins of the sorting into chessboard layers. Based on the preferred adsorption sites and in consistency with reports for tetrapyrroles on periodically corrugated graphene and *h*-BN surfaces,^{19–21} we identify the difference in the adsorption energy in the pore and on the node of the Bi reconstruction as the driving force. As reported by Meyerheim *et al.*²⁸ on the basis of surface X-ray diffraction data, the node and the pore of the p(10×10)-Bi reconstruction differ structurally. In particular Bi atoms on the node are ~0.4 Å higher above the Cu surface and therefore less hybridized with the Cu substrate than those in the pore. This implies a stronger interaction with the molecules. The fact that the monocomponent CuPc layer exhibits a chessboard contrast with alternating rotation between identical CuPc molecules, which differ solely in their adsorption site, is further evidence that the formation of the chessboard lattice is a template effect of the p(10×10)-Bi reconstruction and that it is not induced by molecule–molecule interactions.

Since the molecules differ only in their central metal atoms, their 3d electronic configurations and their interactions with the Bi reconstruction must be the origin of the different assemblies of the monocomponent and bicomponent Pc layers. As discussed above, CoPc and MnPc possess out-of-plane 3d states close to the Fermi level, but CuPc does not.^{22,39–42} This leads to a weaker interaction between metal surfaces and CuPc compared to metal-Pcs with out-of-plane orbitals, such as MnPc and CoPc.^{42–45} A weak electronic coupling between the substrate and CuPc is also inferred from the observation of vibronic satellite peaks²⁶ in the *dI/dV* spectra of CuPc on the Bi reconstruction (Figure S7 and S8 in

Supporting Information). In case of MnPc, the stronger interaction between the substrate and MnPc compared to CuPc promotes the lowest energy arrangement of them, where MnPc adsorbs on the Bi nodes. The same argument holds for CuPc and CoPc. Moreover, consistent with this simple model, we do not observe chessboard arrangements for CoPc:MnPc where both molecules have out-of-plane 3d states. The different assemblies might be further stabilized by hydrogen-bond like interactions between the aza-N of one Pc and the benzo-group of the next Pc or due to intermolecular charge transfer⁸, electric dipole-dipole (quadrupole-quadrupole) interactions.¹⁵⁻¹⁷ For the verification of these additional interactions, further experimental validation is required.

Our above discussed simple model based on site-specific interactions between the 3d orbitals of the metal-Pc and the square p(10×10)-Bi template on Cu(100) implies that a different template would result in a different molecular assembly. To test the hypothesis, we have studied the self-assembly of a CuPc:MnPc mixture on the striped c(9√2×√2)R45°-Bi reconstruction^{29,30} on Cu(100) (Figure 5). Indeed, for the same ratio between molecules, the CuPc:MnPc mixture self-assembles into a complex striped arrangement rather than into the chessboard pattern. The excess MnPc due to this striped arrangement (CuPc to MnPc ratio 7:3) forms separate small MnPc domains (Figure S6 in Supporting Information).

Figure 5. Close-up (a) and overview (b) STM images of CuPc:MnPc on the striped $c(9\sqrt{2}\times\sqrt{2})R45^\circ$ -Bi reconstruction on Cu(100). The color of the crosses assigns the type of Pc (CuPc: green; MnPc: red) and their orientation designates the alignment of the Pc lobes. The orange rhomboids designate the unit cells. For visibility, the color scale in b) is wrapped around.

In conclusion, we demonstrate the sorting of surface adsorbed phthalocyanine molecules, which differ only in their central metal ions (Mn, Co, Cu), into bimolecular chessboard arrays. The sorting mechanism depends on the site-specific interactions between the central transition-metal ions and the matching squarely symmetric Bi reconstruction acting as a template, in contrast to the non-matching hexagonal symmetry of graphene and *h*-BN templates. Our approach goes beyond established concepts for the bottom-up self-assembly of highly ordered 2D layers, because it circumvents the engineering of suitable molecule–

molecule interactions by their functionalization. Aside from providing a proof-of-principle demonstration, molecular layers consisting of architected multicomponent *e.g.* bimetallic layers are of interest for applications in catalysis⁴⁶ and spintronics.⁹ Moreover, we show that the Bi reconstruction leads to a significant decoupling of the molecular adsorbates. Its squarely symmetric periodic moiré pattern represents an interesting alternative to the hexagonally symmetric moiré patterns of graphene or *h*-BN. Its intrinsic local chirality and the high spin-orbit coupling of the post-transition element Bi are highly desirable properties to be used in design of electron spin-filters.⁴⁷

Methods

The Cu(100) single crystal was prepared in ultra-high vacuum by Ar⁺ ion sputtering and annealing. The Bi reconstructions were prepared by e-beam evaporation of the well outgassed material onto the sample kept at 295 K and subsequent annealing to 475 K. The phthalocyanines were sublimed sequentially onto the sample kept at 295 K. The scanning tunneling microscopy (STM) experiments were performed at 5 K using a PtIr (10% Ir) tip in constant current mode. dI/dV spectroscopy (lock-in: 513 Hz, zero-to-peak amplitude: 8 mV) was performed with open feedback loop. The imaging parameters (bias voltage, tunnel current set point) for the STM images were: 1a: (−10 mV, −300 pA), 1b: (−5 mV, −400 pA), 2a: (−5 mV; −6 pA), 2b: (−1000 mV; −30 pA), 3a: (−1000 mV; −20 pA), 3b: (2.8 mV; 30 pA), 3c: (1000 mV; 10 pA), 3d: (−5 mV; −6 pA), 3e: (−1000 mV; −10 pA), 3f: (−1000 mV; −10 pA), 4d: (−5 mV, −400 pA), 5a: (−2000 mV; −20 pA), 5b: (−2000 mV; −20 pA). A positive bias voltage corresponds to tunneling into unoccupied states of the sample.

ASSOCIATED CONTENT

Supporting Information.

Supporting Information Available: central metal dependent STM contrast, detail and overview images of Pcs on p(10×10)-Bi, adsorption sites of Pcs on p(10×10)-Bi, distances

and orientations of Pc domains on p(10×10)-Bi, overview image of CuPc:MnPc on striped c(9√2×√2)R45°-Bi, additional dI/dV spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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