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Controlling the Dimensionality and Structure of Supramolecular Porphyrin Assemblies by their Functional Substituents: Dimers, Chains, and Close Packed 2D Assemblies

Cristian Iacovita,^[a] Petra Fesser,^[b] Saranyan Vijayaraghavan,^[a] Mihaela Enache,^[c] Meike Stöhr,^[c] François Diederich,^[b] and Thomas A. Jung ^{*,[a,d]}

Porphyrin macrocycles are essential to the functionality of many biochemical systems, owing to their unique structure and electronic systems, which can host different metals and bind diverse ligands. They constitute versatile building blocks for the assembly for complex well defined supramolecular architectures. This occurs in 3D crystals as well as within biomolecular assemblies and has more recently also been implemented to produce supra-molecular ad-surface assemblies, which bring along the advantage of individual addressability^[1]. For the latter achievement, a variety of meso-substituted derivatives have been employed to steer the formation of specific arrangements either via noncovalent^[1-10, 12-14] or covalent^[11] interactions. For other classes of molecules, dipolar, charge-transfer mediated or even repulsive interactions^[15-20] were found to be the driving forces for the observed molecular superstructures. Of particular interest have been systems where molecular modules can undergo different competing interactions and thereby exhibit complex multiphase behavior^[10]. The system presented here deals with the control of

dimensionality of molecular assemblies via the complex interplay of short and long-range attractive and repulsive interactions. Herein, we report a low-temperature scanning tunneling microscopy (STM) investigation on the self-assembly process of a Zn(II) porphyrin^[21] (Figure 1a) on Ag(111). The important feature of this molecule, in the context of its self-assembly, is the “tail” appended at one meso-position of the porphyrin core, which consists of a phenylene spacer, an acetylene and a *N, N*-dimethylanilino (DMA) moiety. This tail induces a permanent electric dipole moment of 2.38 Debye (Figure 1b) across the molecule. This dipole moment gives rise to electrostatic interactions, which here leads to an unprecedented complex behaviour. The molecules were deposited on an atomically clean Ag(111) surface under ultrahigh vacuum conditions and were investigated by STM, in order to check for their conformational and self-assembly behavior, aiming for a later co-deposition of an electron acceptor, possibly reacting covalently with the electron rich acetylene integrated in the molecule’s tail. Such a covalent reaction with tetracyanoquinodimethane (TCNQ) molecule on Au(111) has been recently reported^[21].

At an early adsorption stage (molecular coverage of ~0.1 monolayer (ML), where 1 ML is defined as the amount of deposited molecules that entirely covers the substrate), the molecules prefer to adsorb on the Ag terraces in separate dimers (Figure 1c). They are randomly distributed across the terraces and are always oriented along one of the equivalent crystallographic axes of the threefold symmetric Ag(111) surface (Figure 1c). The individual molecules in the dimer exhibit six bright spots, three brighter and three slightly dimmer ones. Each of the spots is assigned to one *tert*-butyl group (Figure 1d)^[1-5]. The visibility of all *tert*-butyl groups indicates a conformational adaptation of the molecule upon adsorption on the Ag(111) surface, where the dihedral angle between the porphyrin ring and the phenyl groups is estimated to be about 20°, compared to 90° in the gas phase^[2]. Besides the six bright *tert*-butyl groups, each molecule displays a short line with distinctively less intensity, which represents the tail^[9, 12, 13]. Moreover, the confinement of the molecule on the Ag(111) surface leads to two conformational enantiomers^[8, 13] that exhibit two-dimensional chirality (Figure 1d). Therefore, equal amounts of two homochiral dimers, denoted here as LL and RR, were observed on the surface (Figures 1c and 1d). The dimers

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can be easily distinguished from one another by applying a simple convention: starting from the center point of the dimer, for the RR dimers (R = right) the brighter spots are distributed clockwise, while the LL dimers (L = left) follow an anticlockwise direction (Figure 1d and 1e).

Figure 1. a) Chemical structure of the investigated Zn(II) porphyrin, equipped with three meso-(3,5-di-*tert*-butyl)-phenyl groups and one phenylene-acetylene-DMA substituent. b) The electrostatic potential of the deposited porphyrin (blue = positive partial charge, red = negative partial charge). The black solid arrow shows the electric dipole vector. c) STM image of ~ 0.1 ML of molecules on Ag(111) (88×83 nm², $I = 10$ pA, $U = 2.0$ V). The set of the three white and red lines indicate the orientation of both LL and RR dimers. They form an angle of 30° . d) High-resolution STM image of both LL and RR dimers (24×8 nm², $I = 20$ pA, $U = 2.0$ V). The white arrow indicates the position of the DMA group. e) Molecular models developed for the two dimers shown in d). ‘Green’, ‘yellow’, and ‘red’ color has been used to indicate the conformation of the DMA and *tert*-butyl substituents, respectively. The ‘red’ CH₃ groups point up-wards, which leads to a strong STM contrast, while the ‘yellow’ CH₃ groups point to the substrate and consequently show less STM contrast^[8]. Black double arrows illustrate intermolecular van der Waals interactions of the DMA groups (green) with the di-*tert*-butyl-phenyl legs, while the black solid arrows show the attractive dipole-dipole interaction.

The molecules in both dimers (LL and RR) align in an antiparallel configuration, forming a closed structure, where the DMA group of the molecule’s tail is located close to the di-*tert*-butyl-phenyl substituents (or dtb-groups) of the opposite molecule (white arrow in Figure 1d). The methyl groups of both DMA units and the dtb-groups interact via van der Waals forces (see the black double arrows in Figure 1e). Furthermore, the antiparallel alignment of the permanent electric dipole moment inherent in each molecule (see the black solid arrows in Fig. 1e), gives rise to an attractive dipole-dipole force, which leads to the observed dimeric arrangement (closed dimers) of the molecules.

With increasing coverage, the molecules arrange in quasi-linear individual chains (Figure 2a). The chains do not extend beyond step edges, exhibit variable lengths, some of them larger than 100 nm and follow the high-symmetry substrate directions (Figure 2a). Taking a closer look at an individual chain, one can recognize repeating building blocks consisting of two types of dimers, one of them being slightly tilted with respect to the second one. Note that in this case, the molecules forming the dimers are arranged in opposite orientation (Figure 2c and 2d). In the contact region, a sort of cross-link junction is formed, with four *tert*-butyls groups interlinked^[8], via van der Waals interactions as they are indicated by black double arrows in Figure 2d. In addition, the high-resolution STM image (Figure 2c)

indicates that the building block is composed of two homochiral linear dimers of opposite conformational chirality. They can be identified by the arrangement of the brighter three spots within each of the four molecules forming a section of the chain (highlighted by black solid and dashed ovals in Figure 2c). This assignment of the conformational isomers to their STM characteristics is in agreement with the convention made for the closed dimers as depicted in Figure 1d and 1e. Both forms of the linear dimers (RR and LL) are integrated into the observed chains by multiple van der Waals interactions between the *tert*-butyl groups. These interactions are indicated by the black solid lines in Figure 2d. As a result of this chain assembly, the RR-LL dimer coupling forms an angle of around $+15^\circ$ while the LL-RR dimer forms an angle of -15° (Figure 2c). This results in a zig-zag arrangement of the homochiral dimers within the self-assembled heterochiral chain. Frequently, the chains change their principal direction, by introducing a “stacking fault”. This stacking fault depends on the position of the LL dimer which in continuation of the chain can be linked either to the right (building block α in Figure 2d) or to the left (building block β in Figure 2d) side of the RR dimer.

Figure 2. a) Large scale STM images for ~ 0.6 ML of Zn(II)porphyrin molecules on Ag(111) (300×300 nm², $I = 20$ pA, $U = 2.0$ V). b) A close up view of parallel chains. The sign + denote the localized positive charges, which generate long-range repulsive interactions between the chains (45×45 nm², $I = 30$ pA, $U = 1.50$ V). c) High-resolution STM image of a chain. The molecules are clearly discernible and can be seen as an array of linear dimers. The black solid and dashed ovals enclose the six *tert*-butyl groups of each R and L molecule respectively (10×10 nm², $I = 20$ pA, $U = 1.0$ V). d) The corresponding molecular model for the bottom tetramers (α and β) depicted in (c). The black double arrows illustrate the cross-linked junction realized in between molecules from both RR and LL linear dimers. The black solid lines denote the intermolecular interactions of the RR dimer with the neighboring LL dimer.

It is noteworthy that the chains, formed at increased molecular density on Ag terraces, still do not touch each other, which provides an indication for the presence of repulsive inter-chain forces (Figure 2a and 2b). The distance between neighboring parallel chains amounts to ~ 2 nm (Supporting Information, Figure S1). The positive partial charges localized on the dimethylamino

moieties of the DMA groups for all the molecules create an electrostatic field on each side of the chain. Hence, we presume that in the region between two neighboring parallel chains, considerable repulsive Coulomb interactions are present (Figure 2b), leading to the separation of the chains even at considerably high coverage.

Figure 3. a) Large scale STM image on Ag(111) with about 0.8 ML coverage ($90 \times 90 \text{ nm}^2$, $I = 20 \text{ pA}$ and $U = 2.0 \text{ V}$). Three symmetry-equivalent domains of a compact 2D layer are observed in coexistence with the chains described earlier. b) Close-up view of the closed-packed assembly ($20 \times 20 \text{ nm}^2$, $I = 10 \text{ pA}$ and $U = 1.5 \text{ V}$). c) High-resolution STM image taken at the domain border ($10 \times 10 \text{ nm}^2$, $I = 10 \text{ pA}$ and $U = 1.5 \text{ V}$). The black arrows indicate the orientation of the tails in both RR and LL closed dimers. The black solid and dashed ovals enclose the *tert*-butyls groups of each R and L molecule, respectively. d) The molecular model for the closed-packed assembly. The four blue molecules illustrate the different dimers.

Upon increasing the density of the molecules on the Ag terraces, for coverages higher than 0.7 ML, one can find close packed 2D molecular assemblies coexisting along with the chains (Figure 3a). Interestingly, there is still free surface area observed between the 2D islands and the chains, which indicates again repulsive interaction. In the close-packed domains, rows of molecular features with rectangular symmetry can be identified with their long axes alternating in parallel and orthogonal direction with respect to the row. Adjacent rows are shifted relative to each other by half of the period (see the white lines drawn in Figure 3b), thereby composing a compact 2D layer with apparent two-fold symmetry.

The high-resolution STM image (Figure 3c), taken at a domain border, reveals the coexistence of both molecules in R and L conformation with their tails enclosing an angle of 45° . On the basis of the convention introduced above, it is found that the features observed in alternating direction are composed of RR and LL dimers, respectively (Figure 3c). An attractive dipole-dipole interaction links the molecules in these closed dimers, just as in the isolated dimers. The dimers are held together within the 2D pattern by multiple van der Waals interactions between the *tert*-butyl groups of the molecules. Consequently, the number of the

intermolecular interactions, which contribute to the 2D condensation energy, increases in the close-packed arrays. Consistent with this discussion, we propose a repetition cell composed of two neighboring RR and LL closed dimers (see the blue blended molecules in Figure 2d). On the other hand, the close packing of the dipoles suggests a lower Coulomb energy. The balance of van der Waals contacts and dipole-dipole interactions enables the transition from the predominant chains to the nucleation of 2D islands. Note that such complexity has also been demonstrated in some other cases, i.e. for the complex porphyrin self-assembly, directed by entropically mobile alkoxy chains and dtb substituents. The complexity of dipole interactions modified by the adsorption and assembly also led to complex multimorphism for subPc^[22] also in coexistence with C₆₀^[23].

In summary, we have observed a case of complex multimorphism: the controlled transition in dimensionality of the self-assembly of a dipolar porphyrin derivative in three stages from 0D dimers, to 1D chains, and 2D islands, depending on the increasing submonolayer coverages. In all these phases the molecules are adsorbed on the Ag(111) substrate in two different conformational isomers denoted R and L, which at low coverage ($\sim 0.1 \text{ ML}$) self-assemble in homochiral dimers (RR and LL) reflecting pairwise chiral recognition. Remarkably, at intermediate coverage, the molecules associate in a completely different manner, dominated by the condensation of the apolar substituents of molecules in homochiral pairs and the large separation of the dipole pairs. By linking up the LL and RR pairs in alternating order, 1D chains are formed, which repel each other. Attractive van der Waals interactions between di-*tert*-butyl phenyl substituents thereby compete with the long-range electrostatic interaction, originating from the partial positive charges located at the dimethylamino centers in the DMA units of the molecules tail. Upon further increase in coverage, the repulsive inter-chain interactions are overcome and both homochiral dimers build up an extended 2D heterochiral, overall racemic network. Common to all the described structures is the observation of a well-defined chiral pattern, suggesting that the self-assembly is either depending on site-specific adaptation of the conformational chirality, or more probable by chiral recognition of the molecules, occurring in both helicities after their symmetry has been broken by surface molecular interaction upon adsorption.

Experimental Section

The STM measurements: The experiments were performed in a UHV system consisting of different chambers for sample preparation and characterization, at a base pressure of 10^{-10} mbar. The Ag(111) single crystal was prepared by subsequent cycles of sputtering with Ar⁺ ions and annealing at approximately 450°C . The Zn(II) porphyrin molecules were sublimed (sublimation temperature of 330°C) from a commercial Knudsen-cell-type evaporator (Kentax UHV equipment) onto the substrate held at room temperature, while the rate was monitored by a quartz crystal microbalance (QMB). The STM images were acquired in constant current mode by using a commercial Omicron low-temperature scanning tunnelling microscope (LT-STM, Omicron Nanotechnology GmbH) operated at 77 K . The tips were mechanically formed from Pt/Ir (90/10) wires. The STM was operated by the Nanonis SPM controller system (SPECS GmbH). The bias voltages refer to a grounded sample. The software WSxM was used for data processing^[24]. The synthesis of the porphyrin has been described elsewhere^[21].

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Keywords: porphyrin • chiral recognition • self-assembly • scanning tunnelling microscopy • repulsive interactions

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Entry for the Table of Contents (Please choose one layout only)

Layout 1:

Chiral recognition in Porphyrin Dimers, Chains, and Closed Packed Networks

C. Iacovita, P. Fesser, S. Vijayaraghavan, M. Enache, M. Stöhr, F. Diederich, T. A. Jung* 1-4

Controlling the dimensionality and structure of supramolecular porphyrin assemblies by their functional substituents: Dimers, Chains, and Close packed 2D assemblies

A staging of supramolecular aggregation from (0D) clusters to (1D) chains and (2D) assemblies as a function of molecular coverage of dipolar porphyrins adsorbed on the Ag(111) surface is described. It displays a complex interplay of both attractive and repulsive molecule-molecule interactions, the emergence of chirality and the registry of the substrate. Self-assembled chains show a repulsive behavior, which can be used as an additional repulsive interaction to fine-tune the engineering of surface assemblies.

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Supporting Information

Controlling the Dimensionality and Structure of Supramolecular Porphyrin Assemblies by their Functional Substituents: Dimers, Chains, and Close-packed 2D Assemblies

Cristian Iacovita, Petra Fesser, Saranyan Vijayaraghavan, Mihaela Enache, Meike Stöhr, François Diederich, and Thomas A. Jung, *

Fig. 1S1. a) Histogram of the inter-chains separations of the Zn(II)porphyrin at 0.7 ML indicating preferred distances of 4, 6, 8, 10, 12, 14, 16 and 18nm ± 0.15 nm. b) STM topographic image of two parallel chains. The double arrows show the inter-chains separations defined as the distance between the partially positively charged DMA units.