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Porphyrin-Based Two-Dimensional Coordination Kagome Lattice Self-Assembled on a Au(111) Surface

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A Kagome lattice is a geometric arrangement consisting of interconnected triangles and hexagons. This structure has been of interest because of its relevance in terms of novel physical properties related with geometrically frustrated magnetism.[1] However, natural Kagome structures are very rare. In recent years examples of molecular Kagome lattices have been synthesized through supramolecular assembly,[2] which exhibit interesting magnetic properties at room temperature. Due to their 2D geometry, it is appealing to form single-layer Kagome lattices supported on surfaces, which represent an ideal model system to study the intriguing physical properties of the Kagome structures. Supramolecular self-assembly has demonstrated the ability to create a large variety of two-dimensional (2D) crystals on surfaces.[3] Organic 2D Kagome lattices stabilized by H-bonds or van der Waals interactions were fabricated on surfaces through supramolecular assembly.[4] Here, we present, to our knowledge, the first example of a metal−organic coordination Kagome lattice using porphyrin ligands, which opens the possibility of introducing magnetic centers to the Kagome lattice through porphyrin core metalation.[5]

Porphyrins display intriguing properties, including electron and energy transfer, redox, and photophysical properties.[6] They have been employed as building components in supramolecular assembly. In particular, zeolite-like porous metal−organic frameworks formed by porphyrins have been studied intensively.[7] These materials exhibit remarkable structural versatility, rigidity, and integrity with potential functions including sensing, organic magnetism, and biomimetic photosynthesis. For 2D systems, adsorption and self-assembly of porphyrins and their derivatives on surfaces have been extensively studied.[8] It is well-established that porphyrin molecules adsorb in a flat-lying conformation with the macrocycle backbones parallel to surfaces. The adlayer structures are determined by intermolecular and molecule-to-substrate interactions. In most cases, porphyrin molecules form 2D close-packed structures.[8] Recently Grill et al. reported on open porphyrin networks formed through covalent polymerization.[9]

The porphyrin molecule used in our study is 5,10,15,20-tetra(4-pyridyl)-porphyrine (TPyP, inset in Figure 1). TPyP (97% purity, Sigma-Aldrich) was deposited by organic-beam evaporation on a clean single-crystal Au(111) surface which was held at room temperature under ultrahigh vacuum conditions. After proving the cleanliness by Auger electron spectroscopy measurements and post-annealing treatments, the samples were characterized *in situ* by an Omicron scanning tunneling microscope (STM) at room temperature. Figure 1 is a typical overview STM topography image acquired from a sample with 250 °C post-annealing, which shows islands of regular network structures with open voids. The islands can be as large as 200 nm depending on the post-annealing parameters. In total, four different network-lattice orientations were identified with angles of 11°, 15°, 19°, and 30° in between. Since we have not resolved the Au(111) surface atomic structure simultaneously with the network islands, we cannot determine the orientations of the islands with respect to the substrate atomic lattice.

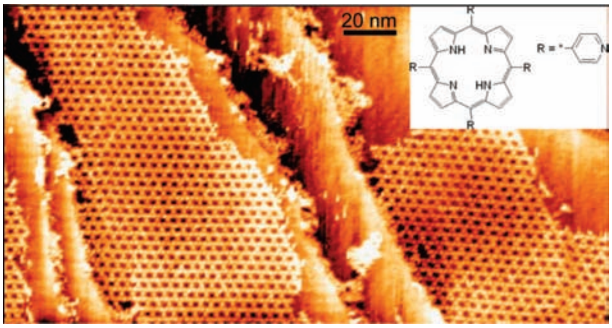

Figure 1. STM topography of network structures of TPyP self-assembled on a Au(111) surface. (I = 0.3 nA and U = −1.3 V). Inset: Chemical structure of TPyP.

Figure 2a is a high-resolution STM image showing individual TPyP molecules with submolecular resolution. One can identify that each TPyP molecule is attached to four neighboring TPyP molecules whereas three TPyP molecules form a symmetric three-branch joint, thus constructing a Kagome lattice as highlighted by the overlaid frame. The rhombic-shaped unit cell has a lattice constant of 4.1 ± 0.1 nm. Single TPyP molecules display a square shape with a valley in the middle, i.e., a saddle-like feature. This saddle-like feature was observed in previous STM studies of TPyP.[10] It was concluded that the two maxima that sandwich the saddle line correspond to the two opposed pyrrole groups and that the pyridyl end groups are located at the four corners of the square.[10] The submolecular resolution features allow us to determine the relative orientations of neighboring TPyP molecules, suggesting the TPyP molecules are arranged in a "corner-to-corner" manner; i.e., the neighboring TPyP molecules approach each other with their pyridyl end groups. The distance between the two approaching N atoms of the neighboring TPyP's can be determined by positioning the TPyP molecules of intrinsic molecular dimension at the Kagome lattice. A value of 5.4 ± 0.1 Å is obtained for the neighboring N−N distance. Such a structure excludes the intermolecular H-bonds that result in the hexagonal structures observed in the TPyP/Cu(111) system.[10b]

It is well-known that ad-atoms existing on metal surfaces can coordinate organic ligands on surfaces.[11] Based on the STM data we propose a model involving Au atom coordination, as drawn in Figure 2b and 2c. The neighboring N atoms are coordinated by a Au atom in a 2-fold linear configuration in which the N−Au distance is 2.7 Å. Although the 2-fold linear coordination is very rare in 3D coordination compounds, it was reported that pyridyl functions can coordinate Cu atoms in this geometry on surfaces.[10b,12] Klappenberger et al. proposed a very similar three-branch joint structure based on the linear 2-fold coordination of TPyP with Cu on a Cu(111) surface.[10b] In those examples, the N−Cu bond length is within a distance of 1.9 to 2.9 Å.

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The 2.7 Å N−Au bond length in our model falls in this range. The Au atoms are not resolved in the STM data, presumably due to the electronic effect which was reported before.[10b,12,13]

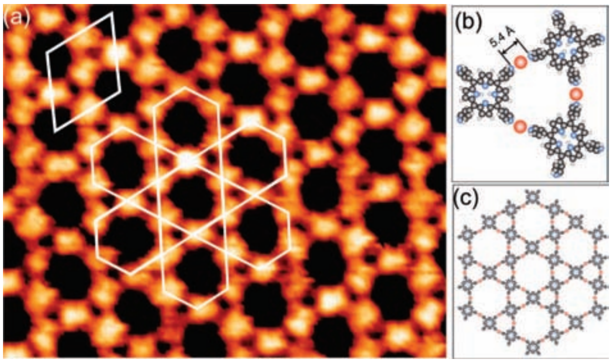

Figure 2. (a) High-resolution STM image (25 nm × 20 nm) of Au-TPyP network structures assembled on Au(111). ($I = 0.3$ nA and $U = -1.3$ V) The rhombic-shape frame defines the network unit cell with a constant of 4.1 ± 0.1 nm. The network frame highlights the Kagome lattice. (b and c) Structural model based on STM data of three-branch joint (b) and Kagome lattice (c). The nitrogen, carbon, and hydrogen atoms are shown in blue, gray, and white, respectively. Orange-color spheres between TPyP molecules represent Au ad-atoms.

In contrast to the disconnected three-branch joints observed on Cu(111) by Klappenberger et al.,[10b] the extended network structures formed on the Au(111) surface lead to the periodic Kagome lattice. We propose three possible mechanisms for this difference: (1) A careful inspection of the STM data revealed that the Au surface herringbone reconstruction beneath the Kagome lattice is lifted, whereas in the area without the Kagome network it is preserved. It was reported that the lifting of the herringbone reconstruction results in an enrichment of Au ad-atom density,[14] which favors the formation of Au-coordinated networks on the Au(111) surface. (2) It is understood that geometric matching of the network periodicity with the substrate lattice plays a critical role in the formation of 2D coordination networks because molecules and metal centers prefer to adsorb at certain sites of a substrate atomic lattice.[15] The nearest-neighboring atom distance is 2.88 Å for Au(111) and 2.55 Å for Cu(111), giving rise to an 11% difference. We postulate that the TPyP molecules and metal atoms of the Kagome network may readily adsorb at energetically favored sites on the Au(111) surface but not on the Cu(111) surface. (3) The higher reactivity or enhanced substrate−molecule interaction of the Cu(111) surface might hinder the formation of extended networks.

We have performed similar experiments on a Ag(111) surface and obtained the same results as Auwarter et al., that TPyP forms close-packed monolayers stabilized by intermolecular H-bonds.[16] Since the substrate lattice constant of Au(111) (2.88 Å) is very close to that of Ag(111) (2.89 Å), the substrate lattice matching effect is indiscernible. We propose that the different structures formed by TPyP on the two substrates are due to the specific coordination property of Au atoms; i.e., atoms of Au but not Ag readily engage in the 2-fold linear coordination with pyridyl functions on surfaces. It is interesting to note that a previous study of TPyP adlayers adsorbed at an electrochemical Au(111) interface reported the formation of close-packed adlayer structures.[17] We believe a deficiency of Au ad-atoms in the electrochemical environment inhibits forming coordination structures.

In summary, we have demonstrated the formation of a metal-coordinated Kagome network structure using porphyrin (TPyP) as building blocks. This system is of great interest since second type metal ions may be incorporated in the porphyrin cores, which will create bimetallic coordination systems with multiple functionalities. For example, as a next step we will use metalated porphyrins consisting of Fe or Co ions as ligands in the aim of bestowing magnetic properties upon this intriguing structure.[18]

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Supporting Information Available: Full author list of ref 18. This material is available free of charge via the Internet at http://pubs.acs.org.

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