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Patterned Deposition of a Mixed-Coordination Adenine−Silver Helicate, Containing a π-Stacked Metallacycle, on a Graphite Surface

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Surface modifications to create preconceived patterns are generally accomplished by various top-down lithographic techniques.[1] Alternatively, certain bottom-up approaches such as self-assembly may provide facile entry into programmed structures of predictable organization.[2] In this context, coordination polymers and metal−organic frameworks may serve as versatile building blocks for the bottom-up approach to exploit their varied multidimensional motifs in patterning suitable surfaces, with or without chemical modifications.[3] It can be envisaged that properties of coordination polymers and metal−organic frameworks related to catalysis, magnetism, luminescence, and as storage materials, can be readily transferred onto selected surfaces by the patterning process.

Recently, we reported formation of a homoadenine metallamacrocyclic structure stabilized by intervening silver ions.[4] This structure assembled at near neutral pH and afforded graphite patterning bearing close resemblance to the solid-state structure. Continuing with our efforts, we became interested in evaluating silver−adenine interaction at alkaline pH, having derived inspiration from pH-dependent conformational transitions in polyadenylic acid,[5] and the possibility of patterning ensuing coordination motif on surfaces such as graphite, silicon, and mica.

The coordination number of silver normally varies from two to four, while higher coordination numbers and mixed-valence silver ions are rarely encountered.[6] Interestingly, silver−adenine complex (**1**), at alkaline pH, led to a mixed silver coordination environment in the solid state (Figure 1a) and exhibited formation of a silver-coordinated homoadenine duplex where two nonintervening supramolecular helicates of opposite orientations were stabilized via Ag−purine interactions and by a virtual metallamacrocycle.

Complex **1** was prepared by metalation of 9-allyladenine with silver nitrate in 50% aqueous methanol adjusted to pH 8.3 with ammonium hydroxide solution (see Supporting Information[7]). Complex **1** was found to crystallize in the space group $P21/n$ (No. 14). The asymmetric unit consisted of two silver ions neutralized by four nitrate anions, out of which one Ag is tetracoordinated to two N1 nitrogens and two nitrate counteranions, while the other one exhibits pentacoordination to two N7 atoms, two nitrate counteranions, and an ammonia molecule (Figure 1a). This situation is unique and differs from the usual alternating N1 and N7 linear coordination. This spatial predisposition leads to a coordination helicate with intervening silver ions possessing alternating tetra- and pentacoordination environment (Figure 1b).

The nonintervening coordination helices possess two adenine residues per turn and with a pitch of ~2.5 Å (Figure 2a). The distance between two successive silver atoms is 13.07 Å; Ag−N1 is ~2.24, Ag−N7 is ~2.2, and Ag−NH_3 nitrogen is 2.5 Å, respectively. The nitrate counteranions are located ~2.5 and ~2.8 Å from tetra- and pentacoordinated silver, respectively. Consequently, distorted tetrahedral and square-pyramidal geometries were observed for tetra- and pentacoordinated silver, respectively (Figure 1a).

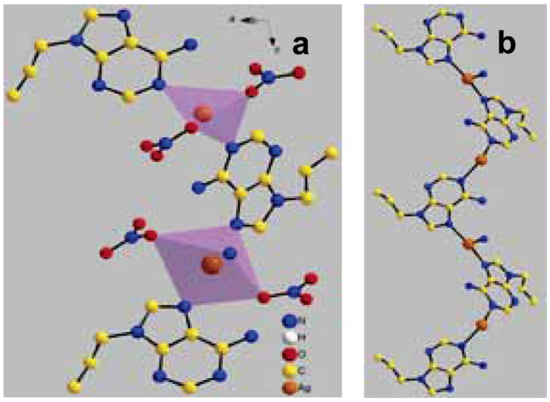

Figure 1. (a) Crystal structure of **1** showing both tetra- and pentacoordinated Ag(I). (b) Helical motif with N7−Ag−N7 and N1−Ag−N1 coordination. Hydrogen atoms are omitted for clarity.

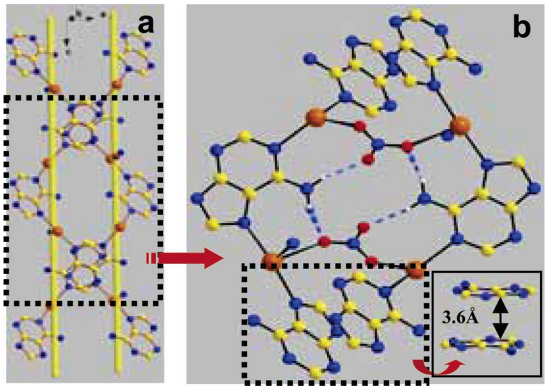

Figure 2. (a) Two helices with opposite orientations. Hydrogen, allyl and nitrate groups are omitted for clarity. (b) Expanded view of the virtual metallacycle: nitrate bridging and hydrogen bonding between two helical strands. Hydrogen and other atoms not involved in hydrogen bonding are omitted for clarity. Inset shows the separation between two stacked adenine rings providing closure to the virtual metallacycle.

A key stabilizing interaction in the helical structure is a virtual metallamacrocycle composed of coordinated and stacked adenine ligands. Besides silver−adenine interactions, it is stabilized by bridging nitrate counteranions tethering helical strands via silver ions present on the two helices and also by hydrogen bonding between nitrate anions and N6 exocyclic amino group (Figure 2b).[7] The closure of virtual metallacycle is achieved via favorable π−π-stacking interaction between the two adenine rings, with a separation of ~3.6 Å between the purine ring centroids. Favorable contribution of π-stacking is well-known for metal-organic frameworks and self-assembling supramolecular systems.[8]

We further wished to determine if the solid-state helical lattice structure **1**, which exhibits luminescence,[7] could be readily transferred to pattern a surface to fabricate artificial surfaces with a

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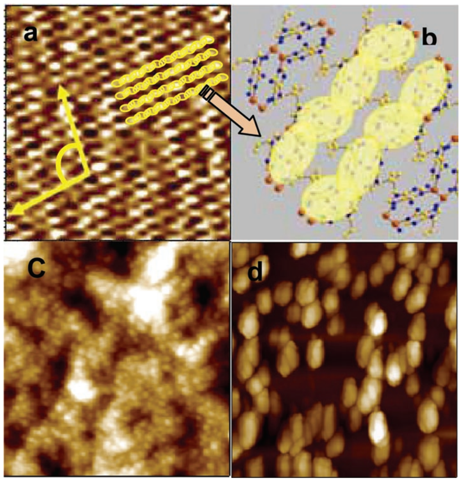

Figure 3. (a) AFM micrograph of **1** with a repetitively patterned surface (a) on HOPG. Image size is 400 × 400 Å^2. (b) Proposed model of coordination helicate deposition. Transparent ovals are used to signify similarities between AFM image and the crystal structure: (c) on Si(100) wafer, (d) on mica surface. Panels c and d are 1000 × 1000 nm^2 dimension.

function. To achieve this goal, we employed an admix of ammoniacal silver nitrate and 9-allyladenine, adjusted to pH 8.3, to pattern surfaces such as highly oriented pyrolytic graphite (HOPG) or silicon wafer or mica.[7]

Analysis of the noncontact mode AFM micrographs for the HOPG surface afforded a remarkable similarity between the surface deposition pattern and the crystal structure of **1** (Figure 3a,b). Interestingly, the angle between the two axes of zigzag and stepladder patterns observed in the AFM micrograph, was found to be 96 ± 2° throughout the probed surface (Figure 3a). This angle is nearly equal to the crystal angle $\beta = 96.96^\circ$, formed between the crystal axes *a* and *c*, observed in the solid-state structure of **1**.[7] Such a notable similarity between a discreet solid-state structure and reproducible surface patterning reveals persistent silver−adenine interaction in solution. As a control experiment, 9-allyladenine ligand alone did not exhibit structured deposition on the graphite surface.

In contrast, the deposition of **1** on a Si(100) wafer as well as mica surface lacked obvious pattern formation (Figure 3c,d). Analyses of silicon and mica surfaces revealed a nonuniform deposition of **1** with a maximum surface roughness of ∼5 and ∼7.5 nm, respectively. This suggests that silver−adenine coordination helicate prefers a graphite surface, but lacks ordering on silicon and mica. The preferential deposition on the graphite surface may be attributed to known adenine−graphite interactions.[9] These results, together with other recent reports,[4,10] affirm that surface−ligand and hydrogen-bonding interactions could be crucial in dictating stable patterning and retention of crystal structure on surfaces.

As a conclusion, we have the described molecular structure of a novel mixed-coordinate silver−adenine helicate, where single-stranded coordination helices are stabilized by anion bridges, $\pi-\pi$ stacking, and hydrogen bonding interactions and facile deposition of this metalated complex on a graphite surface. The AFM micrograph pattern of **1** on the HOPG surface was remarkably similar to the crystal structure. These results suggest utility of shape-persistent coordination motifs for fabricating functionalized surfaces for advanced nanoscale applications.[11]

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Supporting Information Available: Synthesis and characterization data for **1**, crystallographic information and tables (including CIF), and AFM sample preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

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