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A Luminescent Silver−Adenine Metallamacrocyclic Quartet

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Nucleic acids offer a versatile platform for metal ion coordination resulting in stabilization of higher order superstructures.[1] The constituent heterocyclic nucleobases are bestowed with suitably predisposed metal ion binding sites, which are invoked for the generation of interesting supramolecular structural paradigms.[2] The occurrence of nucleic acid/nucleobase architectures also holds great significance in the cellular milieu where motifs such as guanine-(G) quartets and adenosine platforms are implicated for biological functions ranging from telomeric DNA stability to the stabilization of group I intron tertiary structure.[3]

In this context, the formation of nucleobase polyads in isolation is particularly challenging for mixed-metal and -nucleobase regimens.[4] Although several reports describe generation of base triples and cyclic structures with sandwiched metal ions, nucleobase quartet structures entirely composed of a unique base and a single intervening metal ion leading to the formation of metallamacrocylic tetrad have not been reported.

9-Substituted adenines offer three main donor sites (N1, N3, and N7) for metal ion coordination. While most of the reported examples concern bidentate coordination, tridentate coordination of adenine nucleobase has also been reported.[5] However, a 3N (μ-N1, N3, N7) coordination mode for 9-substituted adenine is rare, and thus far only one such example involving bimetallic Pt/2Ag coordination to 9-methyladenine has been reported by Lippert et al.[6]

We have been experimenting with polymerizable adenine nucleobases to create catalytic polymers where the activity profiles are dictated by judicious selection of impregnated metal ions.[7] In continuation, we wished to study coordination behavior of the silver−adenine complex on our way to prepare argentated adenyl homopolymers. Interestingly, 9-allyladenine (9-AA) afforded a 3N-coordinated, silver-tethered macrocyclic tetraplex **1**, which exhibited aggregative ordering on graphite surface and luminescent properties. **1** was prepared by the metalation of 9-AA with silver nitrate (1:1) in 50% aqueous methanol. Crystals suitable for X-ray diffraction studies were grown by careful layering of silver nitrate in water with 9-AA in methanol (see the Supporting Information).

It was found that **1** crystallizes in the orthorhombic space group *Fdd*2 (No. 43). The asymmetric unit consists of one silver ion neutralized by nitrate anion and simultaneously coordinated to three different nitrogens of three 9-AA molecules.[8] This leads to the formation of a metallamacrocyclic quartet, as part of a coordination polymer, where N1, N3, and N7 nitrogens are coordinated to silver ions (Figure 1a). Four silver atoms, located at each corner of a distorted rectangle, have interatomic distances of 7.71 and 6.95 Å for the two sides of this rectangle. The distances between silver and nitrogen atoms are Ag−N1 (2.40 Å), Ag−N3 (2.24 Å), and Ag−N7 (2.18 Å). The porous central part of the macrocycle comprises two inwardly projected allyl groups, and this void occupies ~10% of total cell volume (480.2 $Å^3$ out of cell volume 4824.8 $Å^3$ as calculated by PLATON).[8]

Interestingly, participating 9-AA ligands in this metalated quartet are contributed by two left-handed and two right-handed supramolecular helices, which are tethered by intervening silver atoms (Figure 1b). Diagonal helices are of the same handedness and form an infinite 1D helix with a pitch of 7.5 Å along the *c*-axis, involving N1 and N3 coordination (Figure 2a). Another perspective of 9-AA coordination, involving N3 and N7, can be viewed along the *c*-axis (Figure 2b).

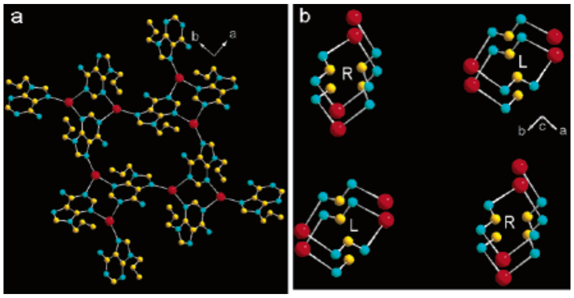

Figure 1. (a) Silver-mediated quartet formation in **1**. Color code: Red, silver; orange, carbon; blue, nitrogen. Hydrogen, nitrate ion, and solvent molecule are omitted for clarity. (b) Four quartet-forming helices. L and R denote their handedness. Both figures are viewed along the *c*-axis.

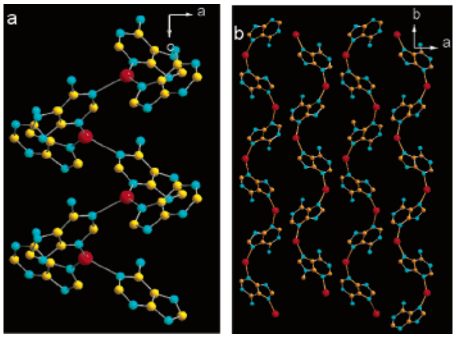

Figure 2. (a) A 1D helix as viewed along the *b*-axis. (b) View of crystal lattice along the *c*-axis, showing a 1D polymer due to coordination of N3 and N7. Hydrogen atoms, nitrate ion, and solvent molecules are omitted for clarity. Color code: silver, red; nitrogen, blue; carbon, orange.

Thus, the quartet structure of **1** is composed of four noninterpenetrating parallel strands where each one of them contributes a 9-AA ligand for coordination (Figure 3). Such an arrangement is evocative of DNA quadruplex formation involving the arrangement of four guanosine or adenosine residues into a cyclic tetramer via intermolecular hydrogen bonds, which may be further stabilized by the presence of metal ions.[3b]

Aggregative propensity of **1** on the graphite surface was also probed by noncontact mode atomic force microscopy (AFM). The use of graphite surface to study adenine adsorption has been previously described in context of prebiotic assemblies.[9] A solution of **1** in DMF (10 μL, 1 mM) was spread over a freshly cleaved graphite, followed by drying under mild air flow and high vacuum. The AFM micrograph showed a structured deposition of **1**, while the magnified image afforded a repetitive zigzag assembly of bright vertexes in a striking resemblance to the helical solid-state crystal

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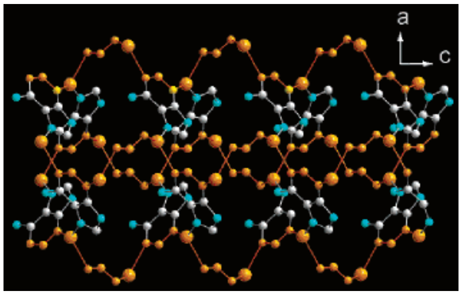

Figure 3. Four parallel nonpenetrating helices as viewed along the *b*-axis. Atoms constituting the helices are colored in orange. Hydrogen atoms and solvent molecule are omitted for clarity.

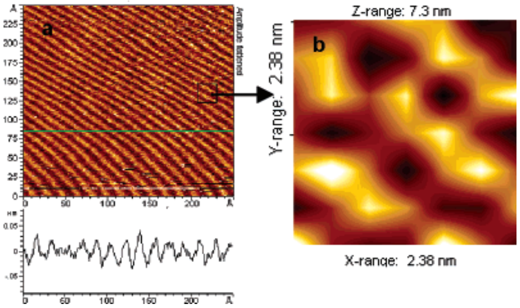

Figure 4. (a) AFM image of **1** on the graphite surface. (b) Magnified image.

lattice (Figure 4a,b). The distance between bright vertexes in the X- and Y-ranges is comparable to the distance between the silver atoms involved in quartet formation, as obtained from the crystal data (Figure 4b).[8] A similar observation has been reported in an STM micrograph of hydrogen-bonded guanine quartet.[10]

Metal-enhanced fluorescence modulates intrinsic fluorescence through various mechanisms, including enhanced excitation rates, increased quantum yields, and altered lifetimes with superior photostability.[11] As an example, insignificant intrinsic fluorescence of DNA was considerably increased when in close proximity to silver island films.[12] Thus, the premise of enhanced radiative decay rates of natural DNA bases and other weak fluorophores in the presence of silver prompted us to study luminescent behavior of metallamacrocycle **1**. When excited at 350 nm, **1** exhibited an emission with maxima at 421 nm (Figure 5). In a control experiment, unmetalated ligand 9-AA did not produce emission. Preliminary observation suggests an altered excited state for **1** due to silver coordination compared to adenine alone,[13] which also corroborates well with the luminescent properties reported with polynuclear d^{10} complexes.[14]

In conclusion, we have presented the molecular structure of a silver−adenine metallamacrocycle **1**, its propensity to aggregate, and its luminescent properties. This unusual coordination mode, resemblance to biological purine quartets, and the presence of silver-mediated helical motifs represent an interesting example of metal−nucleobase interaction, with possible application for the construction of architectures mimicking biological assemblies, controlling pore size to generate metallamacrocycles suitable for gas/H_2 storage, and as novel photoactive materials.

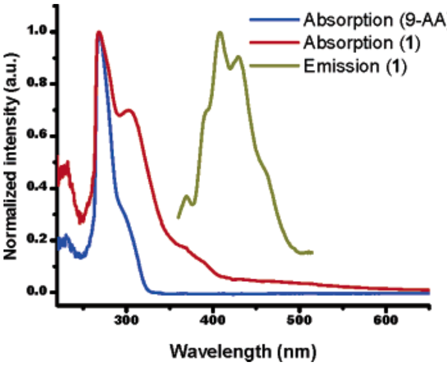

Figure 5. Absorption and emission spectra of 9-AA and **1**.

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Supporting Information Available: Synthesis and characterization data for **1**, crystallographic information and tables (including CIF), and AFM sample preparation and micrographs of 9-AA and graphite. This material is available free of charge via the Internet at http://pubs.acs.org.

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