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CHEMBIOCHEM Highlights

DNA Arrays with a Silver Lining

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The development of molecular electronics is one of the current focuses of bottom-up nanotechnology. DNA has been the building block for nanostructures with a variety of applications, and its use has been extended to the formation of conducting nanowires. The one-dimensional silver/DNA hybrid arrays reported recently are a step towards achieving longer DNA nanowires.

The utility of DNA as a material has been explored in recent years, specifically in areas of biomaterial design, drug delivery, biosensing, molecular computation, and in the development of nanoelectronics. The use of DNA as a conducting material for applications in molecular electronics has been largely debated over the years.[1] One-dimensional DNA arrays and chains have been created before, but their ability to conduct electricity and their use as "wires" have been impeded by the molecule's lack of electrical conductance. However, DNA has been used as a template for metallic nanowires with electrical properties. For example, 1D architectures formed from DNA such as cross-tile nanoribbons, triple-crossover nanotubes, and three-helix nanobundles have been used as templates for metallization.[2] Simple DNA duplexes that contain metal ions have also been shown to support electron transport.[3] However, the metal-containing DNA duplexes created so far have been short, with up to only ten contiguous metallo-base pairs.

Tanaka and co-workers have now addressed this drawback by creating DNA arrays containing metallo-base pairs.[4] In their study, they used a DNA dodecamer that crystallizes in the presence of silver nitrate to yield crystals in which the DNA duplex units are composed only of silver-mediated base pairs. They solved the X-ray crystal structure of the metal-containing DNA duplexes at 1.4 Å resolution (Figure 1 A). The dodecamer strands hybridize to each other to form an antiparallel right-handed duplex similar to the B-form conformation. The duplex revealed four types of silver-mediated base pairing: C-Ag-C, G-Ag-G, G-Ag-C and T-Ag-T. The group had earlier reported silver-mediated C-Ag-C base pairing,[5] but the other three metallo-base pairs were observed for the first time. A notable feature of the crystal structure is that the adenine residues in the dodecamer bulge out from the duplex due to the exclusively silver-mediated base pairing. These residues were found to be involved in crystal-packing interactions by forming AT-Ag-T triplets and AA stacks.

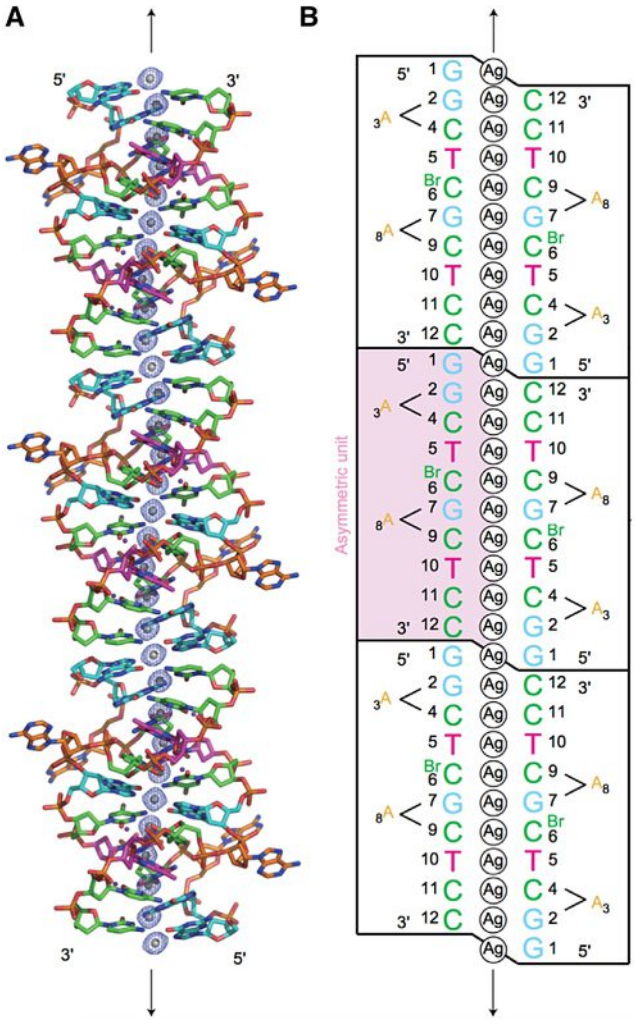

Figure 1. DNA duplex with silver-mediated base pairs. A) Crystal structure of the dodecamer duplex with metallo-base pairs. The adenine residues (orange) are bulged out of the duplex. B) A schematic showing three representative dodecamer duplexes in the array. The G overhangs of the duplexes are connected by G-Ag-G base pairs. Reproduced with permission from ref. [4]. Copyright: 2017, Nature Publishing Group.

Although the dodecamer duplex itself was held together by silver-mediated base pairs, the G overhang on the 5′-end of the dodecamers formed a G-Ag-G base pair, thereby linking continuous duplexes (Figure 1 B). This interduplex metallo-base pair contributes to connecting the silver–DNA hybrid units, with the helical axis that runs through the center of the metallo-base pairs forming an uninterrupted 1D array in the crystal. Moreover, inter-base pair hydrogen bonds, which were observed along the whole double helix, provided enhanced stability to this metallo-DNA duplex. The group also investigated

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the formation of silver–DNA hybrid units in solution by NMR spectroscopy.

With an aspect ratio of 50 000 (the diameter of the largest crystals was 0.1 mm, and the width of the continuous duplex DNA is 2 nm), this "nanowire" is longer than most previously reported. However, the ability of these molecular arrays to conduct electricity, especially over long ranges, is still unknown. Previous reports have shown electrical conductance over 34 nm (100 bp) by DNA monolayers on a gold electrode.[6] Charge transport in DNA nanowires can also be turned on or off by the conditional deposition of copper nanoclusters.[7] In addition, charge transport through DNA is sequence dependent[8] and relies largely on proper base-pairing patterns.[9] In this context, it would be interesting to study the conductance of the silver–DNA hybrid arrays reported by Tanaka and coworkers either in solution or in crystallo.

From a structural perspective, the metal-mediated base pairing leads to interesting options for DNA nanotechnology and molecular circuits. Firstly, it opens up more sequence design parameters, with the stability of noncanonical base pairs provided by metallization. Secondly, the metallized DNA itself imparts additional characteristics to such DNA nanostructures. Apart from featuring exclusively silver-mediated base pairs, the interduplex connection in this study is also provided by metal-mediated base pairing. It might be possible to use such interactions as part of a "metallo sticky end" to create higher-order DNA nanostructures. Such interactions can be used to construct thin molecular cables and devices that are capable of electrical conductance. Recent developments in charge transport through the use of DNA origami[10] open up newer possibilities to incorporate such metallo-base pairs for a range of nanoelectronics.

Conflict of Interest

The author declares no conflict of interest.

Keywords: DNA · metallo-base pairs · nanomaterials · nanowires · silver

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