

X-Ray Analysis of a DNA Encapsulated Silver Nanocluster with Near-IR Emission

DNA-templated silver nanoclusters have attracted a lot of attention due to their intriguing photophysical properties. Herein, we solved the crystal structure of a DNA-encapsulated, near-IR emitting Ag_{16} nanocluster (DNA- Ag_{16}NC). The individual Ag_{16}NC was confined by two DNA decamers that take on a horseshoe-like conformation. The tight wrapping of the two DNA strands around the cluster indicates that the Ag_{16}NC is almost fully shielded from the solvent environment. This structural insight will help to clarify the relationship between structure and photophysical properties for this class of emitters and allow us to design new DNA- AgNCs .

DNA-templated silver nanoclusters (DNA- AgNCs) that display bright emission are composed of DNA oligomers and usually contain less than 30 silver atoms. So far, many attempts have been made to characterize the exact composition and structure of these DNA- AgNCs using several techniques. However, only one crystal structure is reported to have been solved, by Huard *et al.* [1]; in their study, cationic silver-DNA precursor was first crystallized and then chemically reduced. This crystal structure contains a silver cluster with novel Ag-Ag interactions and a segment with cationic silver-mediated base pair interactions, similar to our previously reported silver-DNA hybrid nanowire [2]. In the present study, we obtained the crystal structure of a HPLC-purified magenta-colored near-infrared (NIR) emissive DNA- Ag_{16}NC that was formed in solution before crystallization [3].

The NIR-emissive DNA- Ag_{16}NC was formed in solution by two DNA decamer fragments 5'-CACCTAGC-GA-3', purified by HPLC and then crystallized by the hanging drop vapor diffusion method in a condition containing MOPS (pH = 7), spermine, $\text{Ca}(\text{NO}_3)_2$ and polyethylene glycol 3350 at 293 K. X-ray data was collected at 100 K with synchrotron radiation at the BL-17A beamline. In order to obtain a strong anomalous signal

from the silver atoms, an X-ray beam with 2.0 Å wavelength, which is the longest wavelength available in the beamline, was chosen for the data collection. Initially, diffraction data were taken using 1° oscillation with 1 s exposure per frame, which is the general experimental condition for DNA crystals in the beamline. However, the crystal was X-ray radiation sensitive, so that diffraction spots gradually disappeared during the data collection, while there was no visible change in the color and shape of the crystal after 360 s X-ray exposure. The sensitivity of silver ions and silver clusters to X-ray exposure is well documented. Therefore, the final X-ray data set was collected using 1° oscillation with 0.1 s exposure per frame. In this condition, radiation damage was not observed during the data collection. The initial phase was determined by the single-wavelength anomalous dispersion (SAD) method, then a molecular model of the crystal was constructed and finally refined at a resolution of 1.8 Å (PDB-ID = 6JR4).

Two DNA decamers took on a horseshoe-like conformation and confined the Ag_{16}NC , whose diameter and height were 7 Å and 15 Å, respectively. Surprisingly, no canonical Watson-Crick base pairs were observed. The two DNA strands were mainly linked via silver-atom-mediated interactions and only a few hydrogen bonds

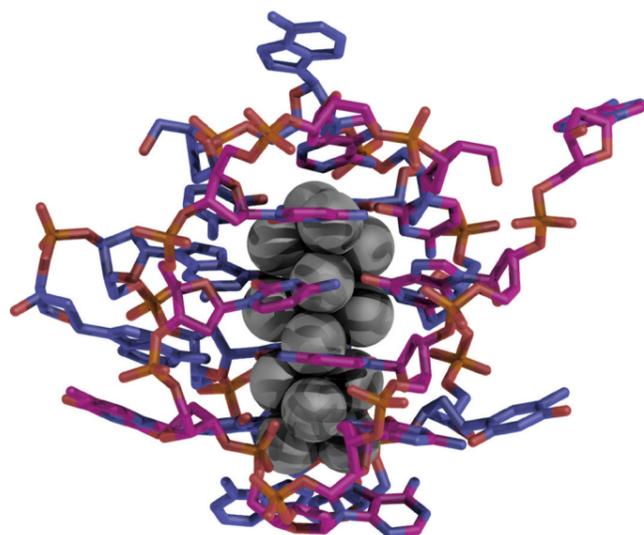


Figure 1: Crystal structure of the DNA- Ag_{16}NC

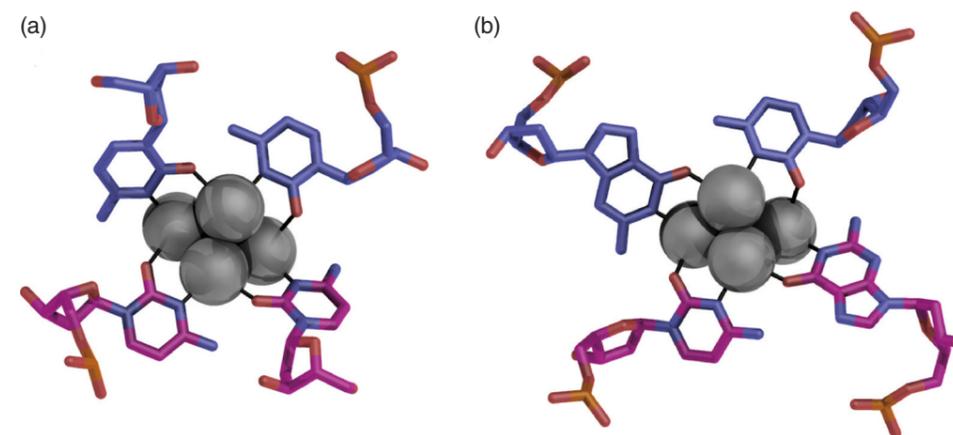


Figure 2: Silver-mediated C-quartet (a) and CGCG-quartet (b) found in the DNA- Ag_{16}NC

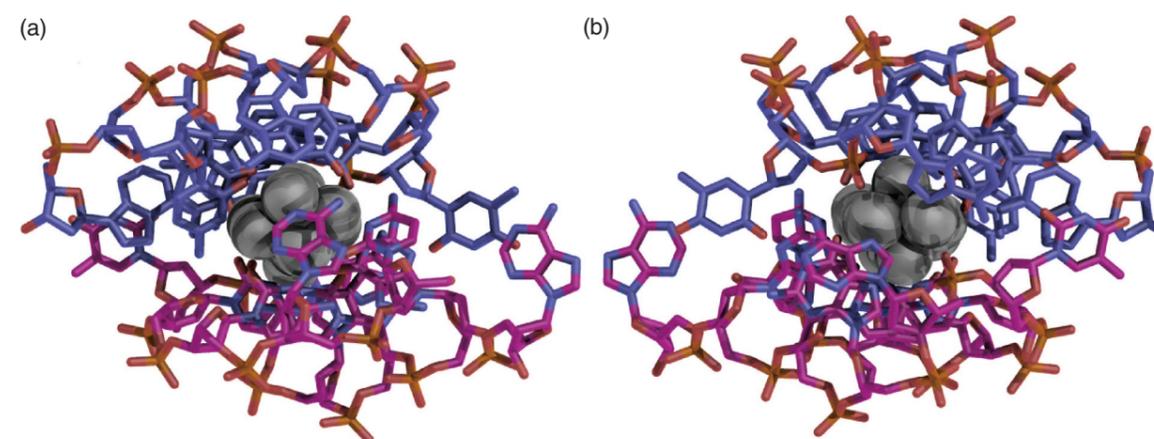


Figure 3: Top-down view (a) and bottom-up view (b) of the DNA- Ag_{16}NC

(Fig. 1). In the DNA- Ag_{16}NC , several silver-atom-mediated interactions including C-quartet [Fig. 2(a)], CGCG quartet [Fig. 2(b)], CC base pair and GG base pair were observed. In these interactions, Ag-N and Ag-O distances were in the range of 2.2–2.4 Å and 2.4–2.9 Å, respectively. The Ag-Ag distances, mostly 2.7–2.9 Å, the shortest being 2.6 Å and a few up to 3.1 Å, were far shorter than the sum of their van der Waals radii (3.44 Å) and were similar to or rather shorter than their metallic radii (2.88 Å). This observation agrees with the fact that the metallic bond distance between two neighboring atoms involved in a cluster tends to be shorter than that observed in bulk metal. The Ag_{16}NC is sealed with an adenine A2 on the top [Fig. 3(a)] and with two adenines A6 at the bottom [Fig. 3(b)]. Two residues T5 and A10 make no coordinate bonds to the Ag_{16}NC . The former residue plays an important role: it enables the required folding of the DNA strand around silver atoms, promoting the formation of the cluster. On the other hand, our recent study confirmed that the latter residue is not necessary for the cluster formation [4].

The structural insight obtained in this study will help clarify the relationship between the structural proper-

ties and the emission features, and might enable the design of a new range of monodisperse, biocompatible and water-soluble AgNCs with fascinating photophysical properties. Interestingly, the Ag_{16} nanocluster is so tightly embedded in the DNA scaffold that it is almost fully shielded from the surrounding solvent. We hope that the presented data will be the starting point for the rational design of DNA- AgNCs in future.

REFERENCES

- [1] D. J. E. Huard, A. Demissie, D. Kim, D. Lewis, R. M. Dickson, J. T. Petty and R. L. Lieberman, *J. Am. Chem. Soc.*, **141**, 11465 (2019).
- [2] J. Kondo, Y. Tada, T. Dairaku, Y. Hattori, H. Saneyoshi, A. Ono and Y. Tanaka. *Nat. Chem.*, **9**, 956 (2017).
- [3] C. Cerretani, H. Kanazawa, T. Vosch and J. Kondo. *Angew. Chem. Int. Ed.* **57**, 17153 (2019).
- [4] C. Cerretani, J. Kondo and T. Vosch. *RSC Adv.* **10**, 23854 (2020).

BEAMLINE

BL-17A

J. Kondo¹, C. Cerretani², H. Kanazawa¹ and T. Vosch² (¹So-phia Univ., ²Univ. of Copenhagen)