

 ROBL-CRG	Experiment title: Determination of intermetallic distances in metal-modified DNA	Experiment number: 20-01-737
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Shifts: 6 / 3	Local contact(s): Andreas Scheinost / André Rossberg	<i>Received at ROBL:</i>
Names and affiliations of applicants (* indicates experimentalists): Jens Müller, Westfälische Wilhelms-Universität Münster, Germany Tim Richters*, Westfälische Wilhelms-Universität Münster, Germany		

Report:

The aim of the EXAFS measurements was the determination of an intermetallic distance in artificial nucleic acids with neighbouring Ag(I)-mediated base pairs. Such metal-modified nucleic acids hold great promise as they allow the site-specific introduction of metal-based functionality into self-assembling systems. However, experimental information on metal···metal distances within these systems is scarce. For the imidazole–Ag(I)–imidazole base pairs under investigation, no direct experimental information on the Ag···Ag distance is available at all. According to recent DFT calculations, this distance amounts to 3.42 Å (*J. Inorg. Biochem.* **2013**, 127, 203-210). During the measurements in January, two nucleic acids have been investigated both in solid state and in solution. The experiments indicate no structural difference of the short-range order between the solution and the lyophilised samples. Moreover, no concentration dependence was observed. The distances from Ag to C and N atoms from the imidazole moiety agree well with expected values. However, the EXAFS spectra of

both nucleic acids (sample 1 containing three neighbouring Ag(I)-mediated base pairs, sample 2 containing one Ag(I)-mediated base pair) indicate distinct Ag \cdots Ag distances of about 3.9 Å, with Ag \cdots Ag coordination numbers ranging between 1.5 and 1.8. As sample 1 should give an average coordination number of 1.3, and sample 2 should not show any close Ag \cdots Ag contact at all, the nucleic acids seem to have been contaminated with excess Ag(I). Accordingly, new nucleic acid samples were devised with either two neighbouring, one or no designated Ag(I)-binding sites (samples 3-5, respectively), also to simplify the interpretation of the experimental data. EXAFS spectra of solutions of these samples were recorded in March.

The spectra of samples 3 and 4 look very much alike, thereby confirming that Ag(I) is located within the binding site (contrary to sample 5, which does not have any designated Ag(I)-binding site). Again, the experimental Ag \cdots N and Ag \cdots C distances confirm that Ag is bound to the imidazole moieties. The information on the Ag \cdots Ag distances is buried in the residual after fitting the Ag binding to the imidazole residues. The high structural flexibility of DNA in solution and the labile coordination of the Ag(I) ions complicates further interpretation of the data, so that the existing software had to be significantly adapted. To date, preliminary Monte Carlo simulations are available for sample 3. Two different fits of more or less equal quality are possible, giving rise to structures with an Ag \cdots Ag distance of 3.28 Å and 3.92 Å, respectively (see figure). Once final simulations are available, a precise inspection of the geometry of the imidazole moieties is expected to assist an evaluation of the quality of each simulation.

