Spectroscopic studies upon silver nanoclusters formed on oligonucleotides containing a tricyclic cytosine analogue, tC

Agnieszka Borysowiec, Angelika Świtalska, Anna Dembska*

Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznanskiego 8, 61-614 Poznań, Poland e-mail: aniojka@amu.edu.pl

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Introduction

Silver nanoclusters (AgNCs) generated on DNA-templates belong to a new class of fluorescent tags showing excellent brightness, photostability as well as biocompatibility [1,2,3]. Moreover, AgNCs-DNA have been applied in various applications, from the detection of metal ions, small biomolecules (for example ATP, adenosine, biological thiols, theophylline), DNA/RNA, environmental monitoring to bioimaging and cancer therapy [3,4,5]. The aim of our research was to verify the influence of the fluorescent 1,3-diaza-2-oxophenothiazine, tC [6] on the absorption and emission properties of AgNCs synthesized by using tC-modified oligonucleotides.

The DNA templates used for synthesis of silver nanoclusters (AgNCs) are cytosine-rich (C-rich) oligonucleotides related to the RET sequence: 5'- *CCCCGCCCCGCCCCGCCCCA*-3' (Table 1) [7].

We synthesized the AgNCs on RET-related oligonucleotides by adding sodium borohydride to the mixture of silver nitrate and the oligonucleotides, under air [8].

Table 1. The oligonucleotide sequences.

System	DNA template
RET20-AgNCs	5'- *CCCCGCCCCGCCCCGCCCCA*-3'
RET19tC-AgNCs	5'- *CCCCGCCCCGCCCCGCCCtCA*-3'
RET14tC-AgNCs	5'- *CCCCGCCCCGCCCtCGCCCCA*-3'

Spectroscopic studies

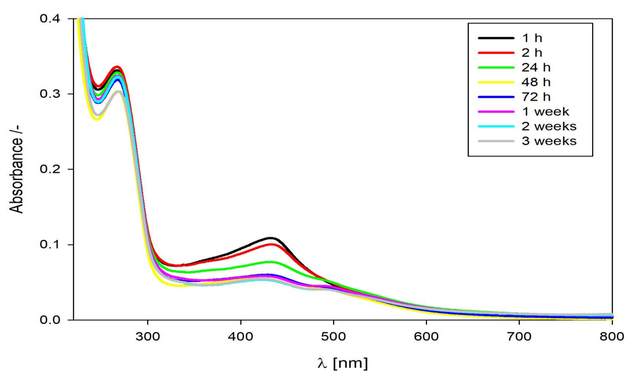

Fig. 1. Absorption spectra of RET20-AgNCs.

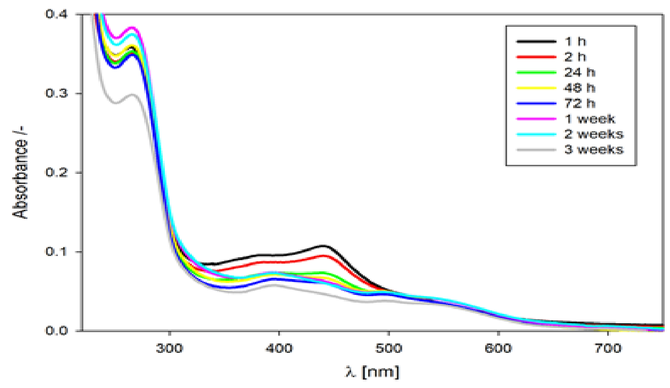

Fig. 2. Absorption spectra of RET19tC-AgNCs.

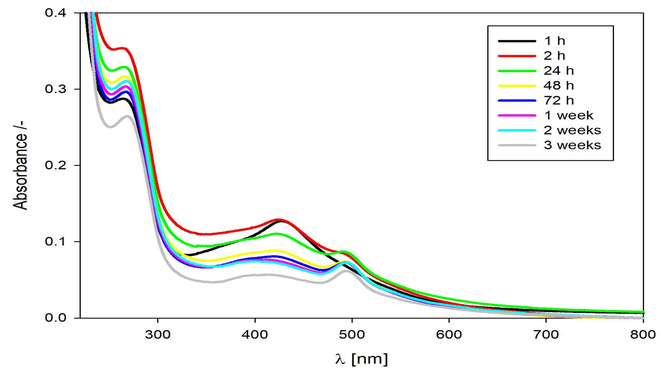

Fig. 3. Absorption spectra of RET14tC-AgNCs.

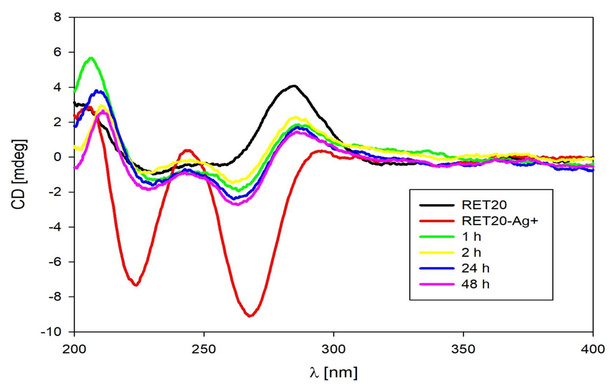

Fig. 4. CD spectra of RET20-AgNCs.

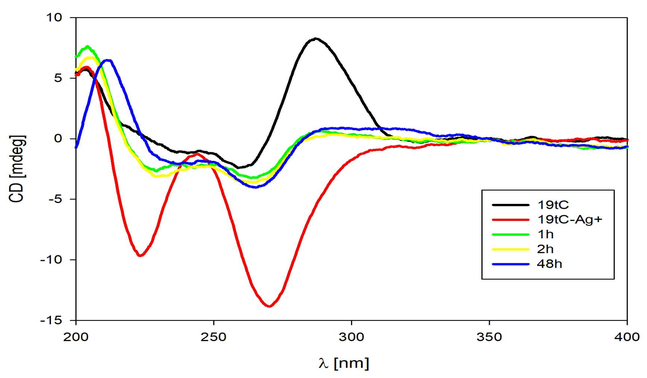

Fig. 5. CD spectra of of RET19tC-AgNCs.

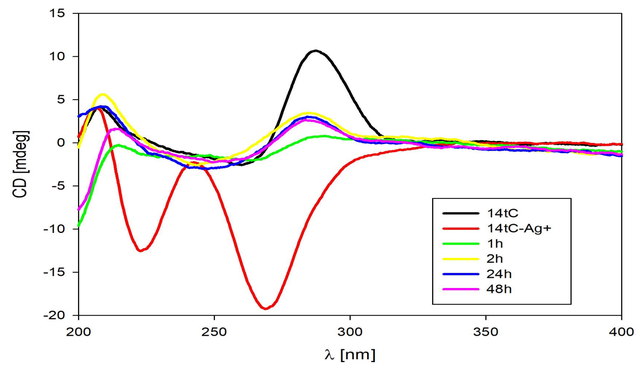

Fig. 6. CD spectra of RET14tC-AgNCs.

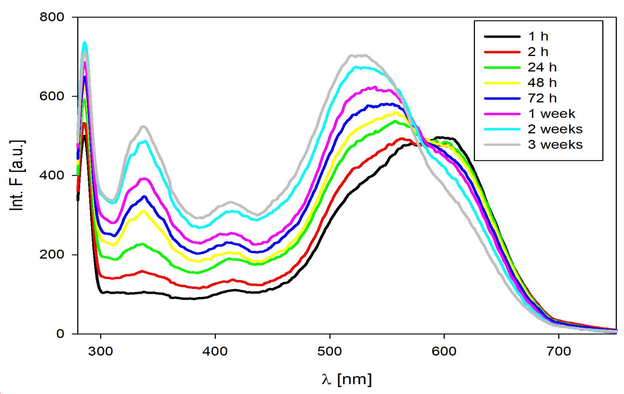

Fig. 7. Fluorescence spectra of RET20-AgNCs with excition wavelength set at 260 nm.

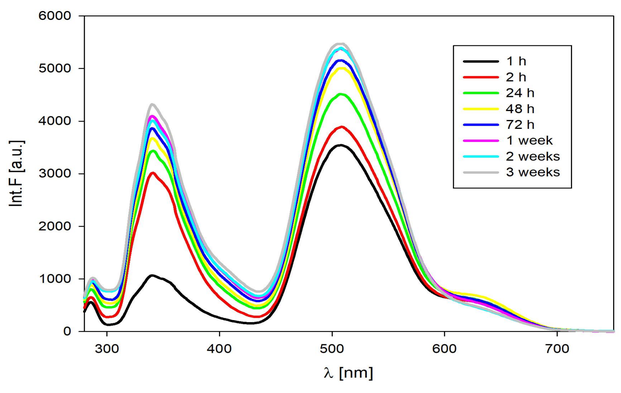

Fig. 8. Fluorescence spectra of RET19tC-AgNCs with excition wavelength set at 260 nm.

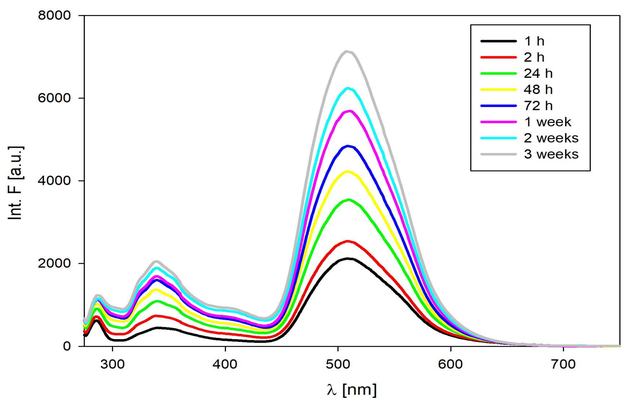

Fig. 9. Fluorescence spectra of RET14tC-AgNCs with excition wavelength set at 260 nm.

References

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Conclusions

- The presence of tC in the oligonucleotide sequence has a significant influence not only on the spectroscopic properties of RET-AgNCs, but also on their stability.
- The absorption spectra of freshly prepared RET20-AgNCs, RET19tC-AgNCs and RET14tC-AgNCs exhibit the peaks with local maximum at 440 nm (Figs. 1,2) and 425 nm (Fig. 3).
- The elliptical changes suggest that obtained nanoclusters retain the chirality of the DNA template (Figs. 4, 5, 6).
- The emission spectra of RET19tC-AgNCs (Fig. 8) and RET14tC-AgNCs (Fig. 9) exhibited fluorescence signal several times higher in the long-term range than RET20-AgNCs (Fig. 7).
- Comparing the emission spectra of RET14tC-AgNCs or RET19tC-AgNCs with RET20-AgNCs, it seems that in case of AgNCs templated on tC-modified ssDNA only slightly amount of "green" fluorescence (~520 nm) comes from Ag^0/cytosines nanoclusters.
- We test ability of silver nanoclusters templated on RET19tC to serve as pH probe, but the preliminary results indicated that system is not sensitive to small pH changes.