# STUDIES ON ADSORPTION OF THIOLATED MONONUCLEOTIDES AND SINGLE STRANDED DNA ON GOLD SURFACE BY SERS

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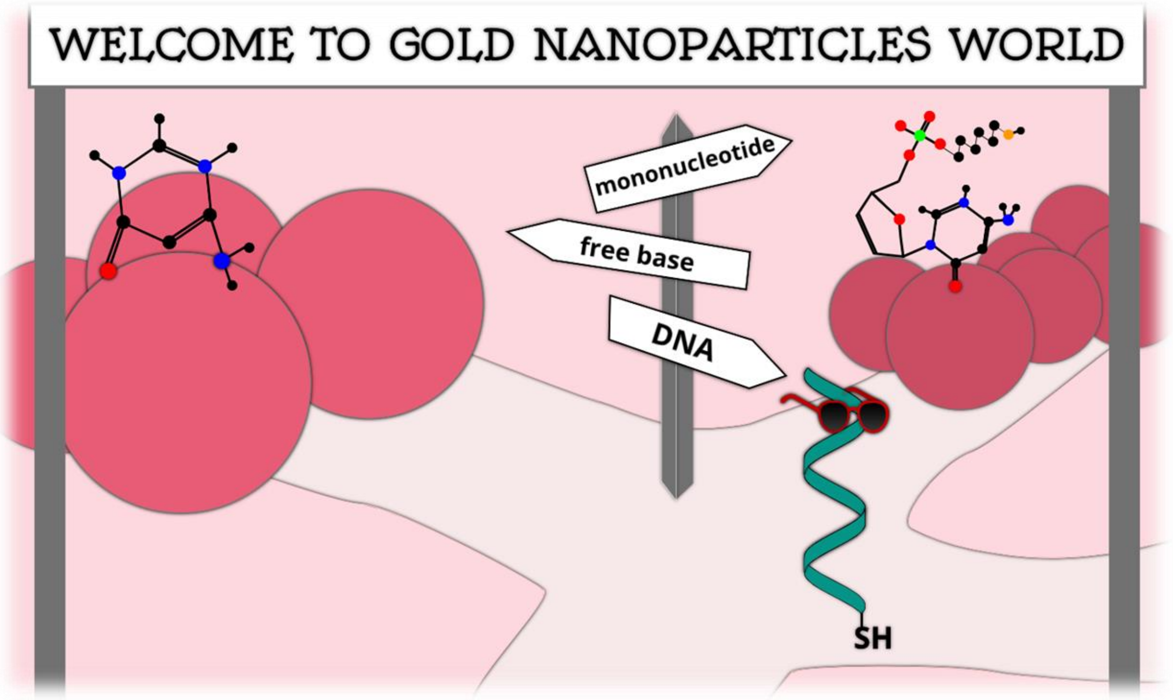

# A. Introduction

Immobilization of DNA strands on the plasmonic metal surface (gold or silver) is a crucial step in designing sensors for DNA detection based on surface-enhanced Raman spectroscopy (SERS) measurements. Typically, thiolated single-stranded DNAs are attached to the gold surface via sulphur-gold bond. They form the dense, homogenous layers with DNA strands oriented perpendicularly to the surface. Such structure of the layer allows an efficient hybridization of thiolated DNA with other DNA strands.

My work shows that chemisorption of thiolated molecules sometimes doesn't work according to this model.

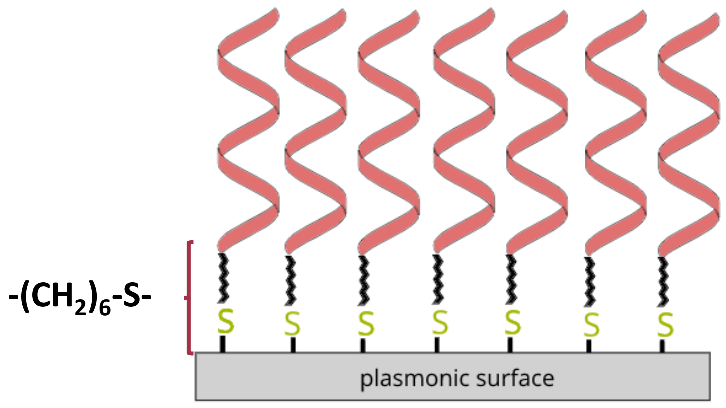


**Fig 1.** The structure of the single-stranded thiolated DNA monolayer on the plasmonic metal surface.

| **Free nucleobases:** | **Thiolated mononucleotides:** | **Thiolated single-stranded DNA:** |
|---|---|---|
| Adenine | A-$(CH_2)_6$-SH | CA-$(CH_2)_6$-SH |
| Cytosine | C-$(CH_2)_6$-SH | C CCA-$(CH_2)_6$-SH |
| Guanine | G-$(CH_2)_6$-SH | C CCC CCA-$(CH_2)_6$-SH |
| Thymine | T-$(CH_2)_6$-SH | C CCC CCC CCA-$(CH_2)_6$-SH |
| | | C CCC CCC CCC CCC CC**A**-$(CH_2)_6$-SH |
| | | C CCC CCC C**A**C CCC CCC-$(CH_2)_6$-SH |
| | | **A** CCC CCC CCC CCC CCC-$(CH_2)_6$-SH |

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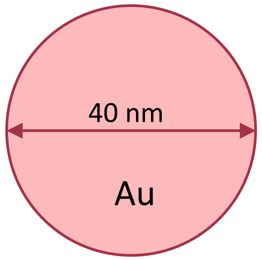


+ **SERS**

# B. Adsorption of Different Thiolated Mononucleotides

## Thiolated mononucleotides containing adenine[1]

The similarities of the wavenumbers of most bands in both SERS spectra (see Fig. 2) suggests that the thiolated mononucleotide containing adenine interacted with the gold surface mainly via the adenine moiety (see Fig. 3). Lack of the characteristic bands from thiol moiety suggests that this thiolated mononucleotide doesn't link with gold surface through Au-S bond. Similar effect was observed for thiolated mononucleotide containing cytosine.

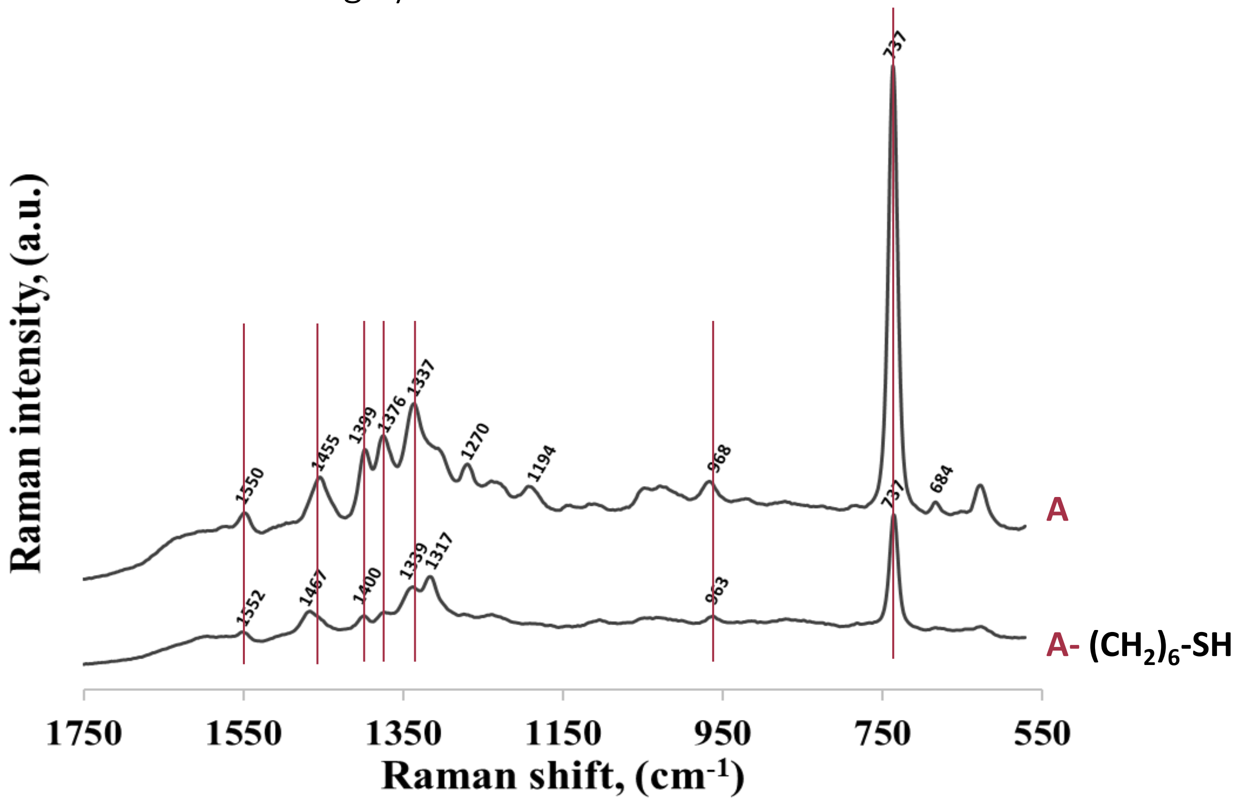


**Fig 2.** SERS spectra of thiolated mononucleotide containing adenine and adenine.

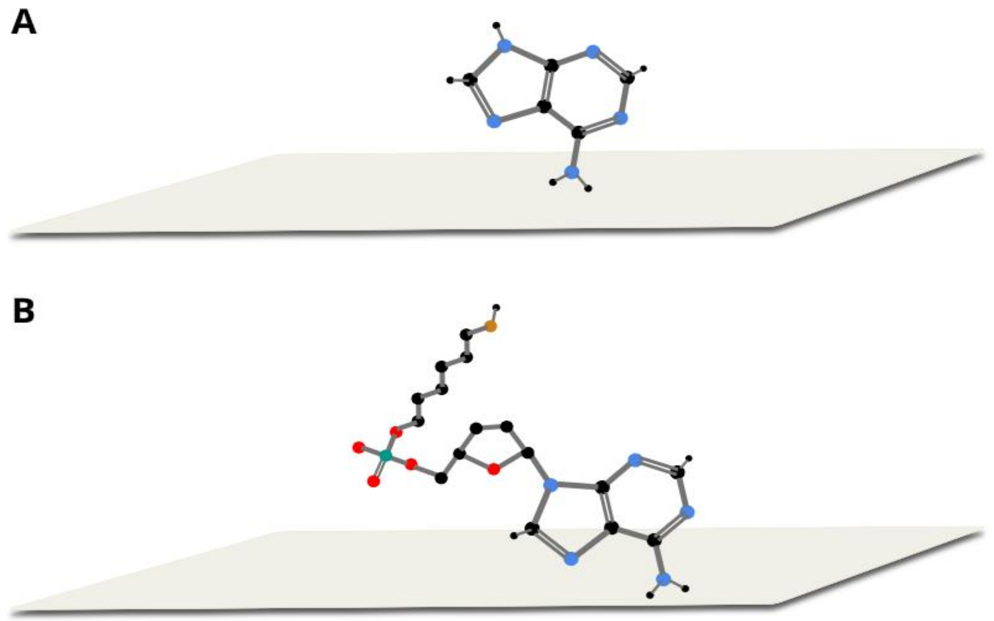


**Fig 3.** Proposed orientation of adenine (A) and thiolated mononucleotide containing adenine (B) on gold colloidal nanoparticles.

[1] E. Pyrak et al., *Molecules*, 24 (2019) 3921

# C. Adsorption of Different Thiolated Mononucleotides

## Thiolated mononucleotides containing guanine[1]

The measured spectrum of mononucleotide containing guanine is significantly different than the respective SERS spectrum of guanine adsorbed on the surface of gold nanoparticles (see Fig. 4), suggesting stronger contribution of the phosphate group, sugar and hexanethiol influencing its orientation on metal surface (see Fig 5). Similar effect was observed for thiolated mononucleotide containing thymine.

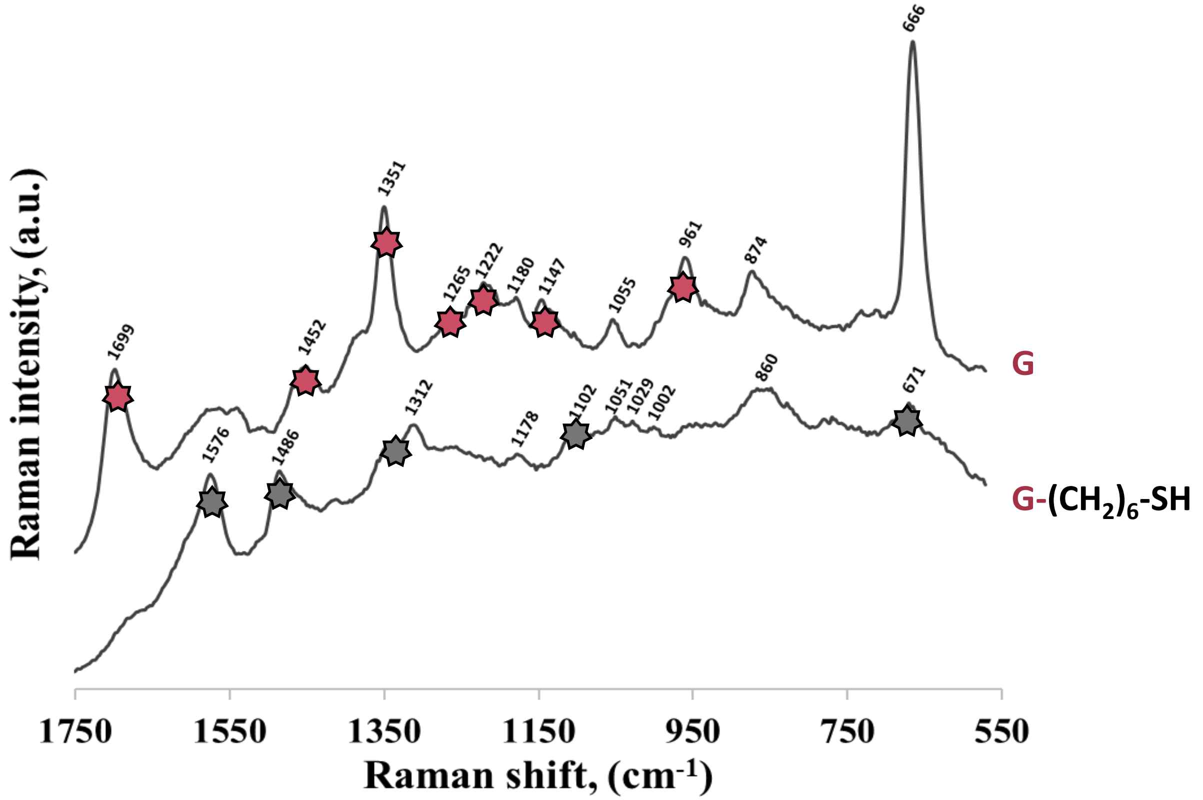


**Fig 4.** SERS spectra of thiolated mononucleotide containing guanine and guanine on gold colloidal nanoparticles.

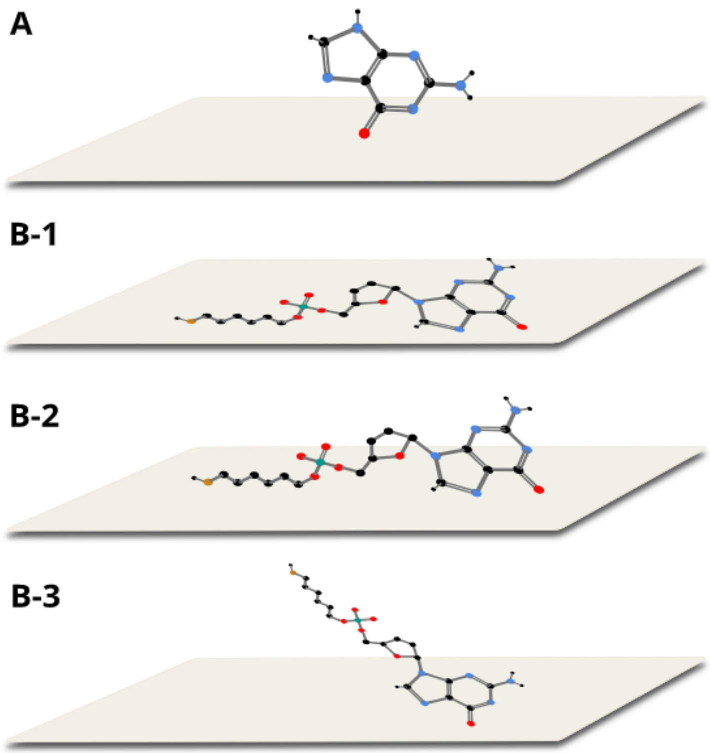


**Fig 5.** Proposed orientation of guanine (A) and thiolated mononucleotide containing guanine (B) on gold colloidal nanoparticles.

[1] E. Pyrak et al., *Molecules*, 24 (2019) 3921

# D. Adsorption of thiolated single stranded DNA chains

**The influence of the adenine in single-stranded DNA[1]**

The structure of the layer formed on the gold surface by the thiolated mononucleotide containing adenine is different than the structure of the layer formed by the thiolated single-stranded DNA containing adenine and other bases, even than DNA composed of two nucleobases.

**The influence of the adenine position in the DNA chain[1]**

SERS spectra of three different thiolated single-stranded DNAs with adenine located: at the 5′ end, in the middle of the chain, and at the 3′ end are practically identical suggesting that the adenine–gold interaction is strong enough to change the orientation of whole DNA strand.

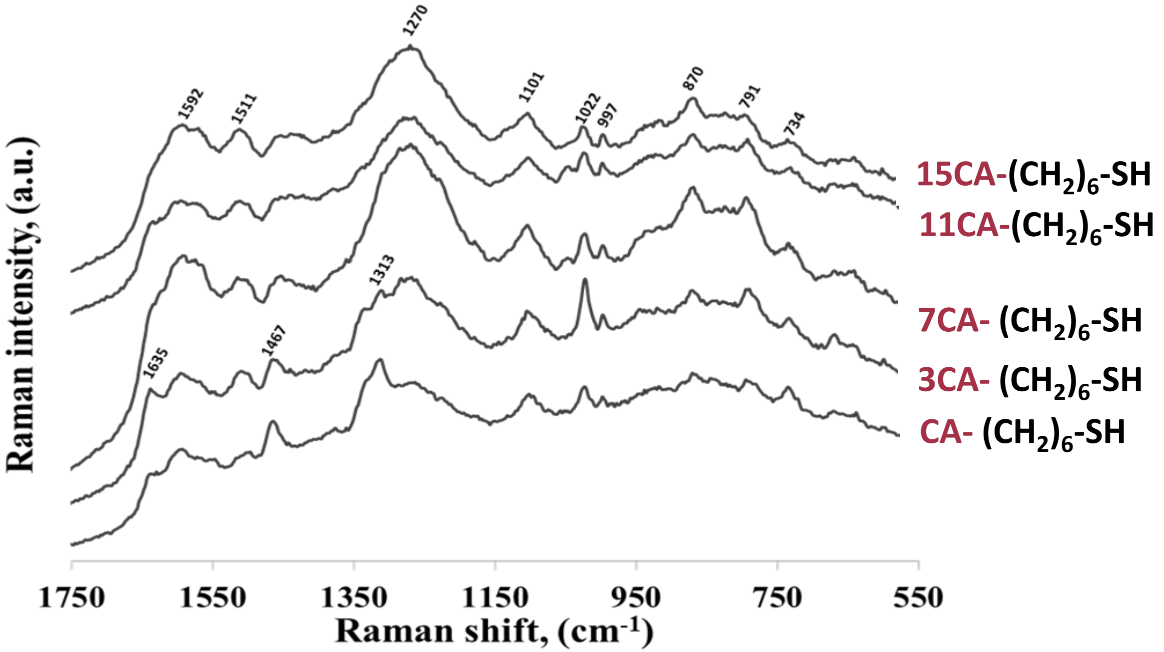


**Fig.6** SERS spectra of five different thiolated single-stranded DNA containing one adenine and cytosines.

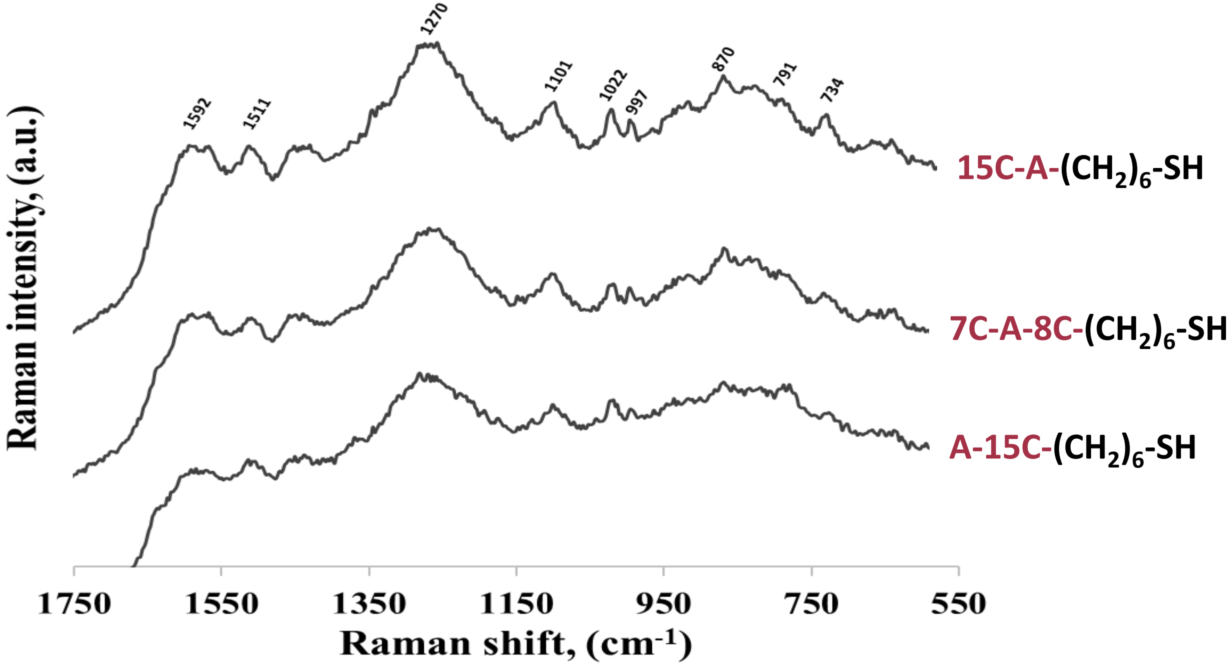


**Fig .7** SERS spectra of single-stranded DNA composed of the 15 cytosines and one adenine located in different positions.

[1] E. Pyrak et al., *Molecules*, 24 (2019) 3921

# E. Conclusions

1: Type of the nucleobase has a significant impact on the thiolated mononucleotide orientation on the gold nanoparticle surface.

2: Molecules modified with thiol moiety don't always interact with the gold surface through forming Au-S bond.

3: The structure of the layer formed on the gold surface by the thiolated mononucleotide containing adenine is different than the structure of the layer of thiolated single-stranded DNA, even containing only two nucleobases.

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