

## NOBLE METAL COLLOID AND Co-PORPHYRIN HYBRID SENSITIVE TO 4-AMINOSALICYLIC ACID

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### Abstract

A hybrid organic-inorganic nanomaterial (*Co-3OHPP/n-Au*) composed of Co(II) 5,10,15,20-meso-tetra(3-hydroxyphenyl)porphyrin (*Co-3OHPP*) and gold nanoparticles (*n-Au*) was tested as sensitive material for the optical detection of 4-aminosalicylic acid (*PAS*). This novel nanomaterial is able to detect 4-aminosalicylic acid in a reasonable concentration domain, covering one order of magnitude:  $1.24 \times 10^{-5} - 3.9 \times 10^{-4}$  M. The dependence between the intensity of absorption and the concentration in 4-aminosalicylic acid is linear, with a fair correlation coefficient of 95 %. This hybrid material can be further included in simple devices for the rapid and facile dosage of this antituberculosis drug in body fluids.

### Introduction

Aminosalicylic acid has bacteriostatic activity against *Mycobacterium tuberculosis* but it has seriously debilitating side effects. It is currently used only in the severe cases of multi-drug resistant TB. The controlled release of this drug was attempted by the intercalation of 4-amino salicylic acid (*PAS*) anions into biocompatible zinc layered hydroxide, using zinc oxide as starting material, and the creation of a nanocomposite [1].

The detection of *PAS* in body fluids is necessary [2], in spite of the fact that the detection of amino acids in general is affected by the continuous change of their ionic form with pH [3].

Among the detecting methods, the chromatographic ones [4] require laborious preparations of the samples. A method that uses samples without pretreatment implies capillary zone electrophoresis [5].

Porphyrins and metalloporphyrins provide recognition sites for amino acids and oligopeptides through their central metal ion and various functional groups at the four meso- and eight  $\beta$ -positions of pyrroles. Immobilized metallo-phenylporphyrins can be used as sensitive and selective sensors for different L-amino acids at pH 7 as they provide two avenues of interaction: the first via the metallic center of porphyrin and the second between the  $\pi$ - $\pi$  electrons of the macrocycles with the analytes [3].

In the present work a hybrid organic-inorganic nanomaterial (*Co-3OHPP/n-Au*) composed of Co(II) 5,10,15,20-meso-tetra(3-hydroxyphenyl)porphyrin (*Co-3OHPP*) and gold nanoparticles (*n-Au*) was tested as sensitive material for the optical detection of 4-aminosalicylic acid (*PAS*) (Figure 1).

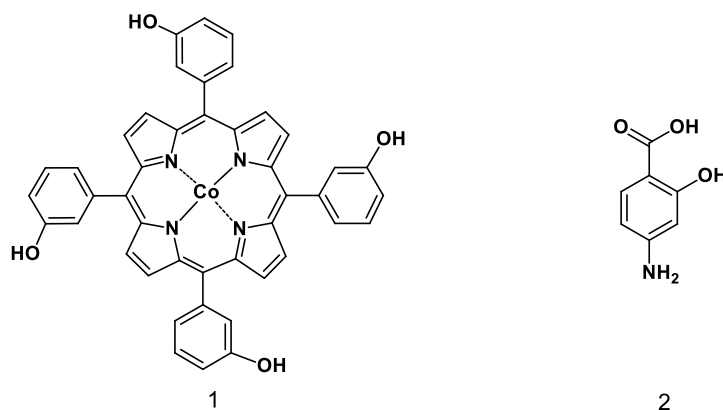


Figure 1. The structure of the investigated compounds

### Materials and methods

A JASCO model V-650 spectrometer was used for the UV-vis measurements in 1 cm quartz cuvettes at room temperature. Atomic force microscopy (AFM) measurements were performed on a Nanosurf®EasyScan 2 Advanced Research AFM (Switzerland) microscope. The samples were deposited onto pure silica plates from solvent mixtures (THF-water). Images were obtained in noncontact mode at room temperature.

Solvents (THF) were acquired from Merck and used without any further purification. The synthesis, optical and morphological characterization of the hybrid material was presented in previous work [6]. The 4-aminosalicylic acid (purchased from Merck) was solved in distilled water to obtain a final solution of  $4.23 \times 10^{-3}$  molar concentration.

The tested organic-inorganic hybrid material was obtained as follows: to 3 mL gold colloid solution ( $c = 4.58 \times 10^{-4}$  M)(Figure 2a) was added 1 mL of Co-porphyrin solution in THF ( $c = 5.15 \times 10^{-5}$  M)(Figure 2b) under intense stirring. The obtained hybrid presents the largest plasmonic band as compared to the initial materials' spectra (Figure 2c) [6].

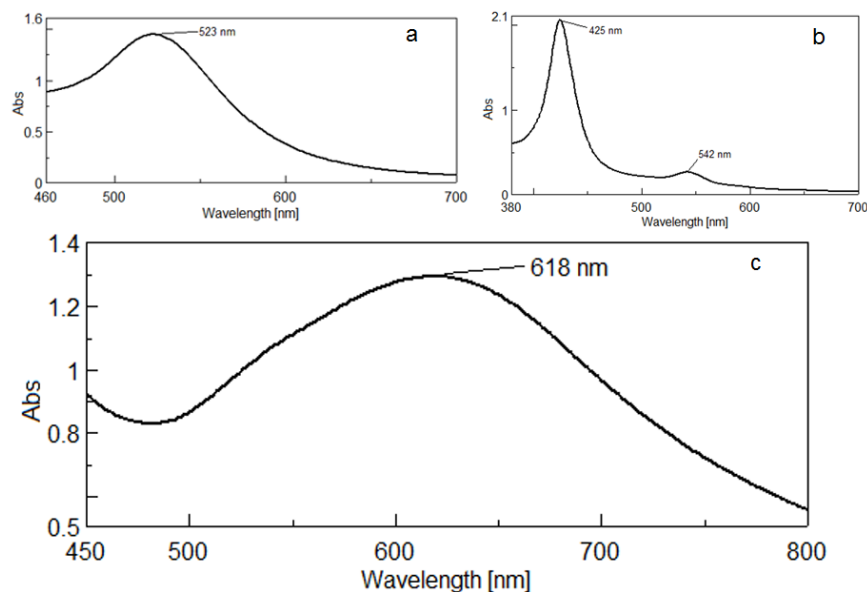
Figure 2. UV-vis spectra of the gold colloid solution ( $c = 4.58 \times 10^{-4}$  M)(a); of the Co-porphyrin ( $c = 5.15 \times 10^{-5}$  M) (b); and of the hybrid material (c)

Figure 3 depicts the AFM images of the obtained hybrid material, in which the triangular platelets of the hybrid form both H and J type aggregates by self-assembly.

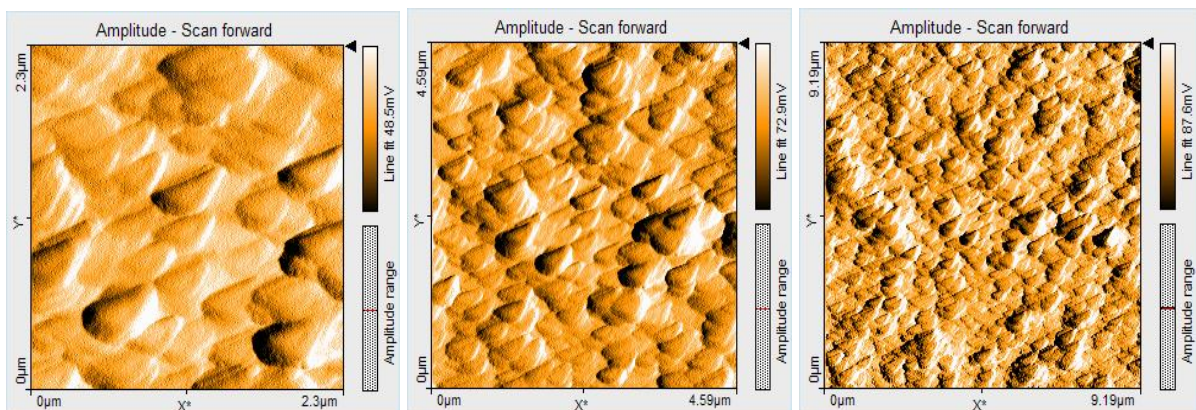


Figure 3. AFM images at 2, 4 and 9 micrometers respectively for the *Co-3OHPP-nAu* hybrid

The sensitivity tests were performed as follows: to 3 mL hybrid solution were added portions of 20  $\mu\text{L}$  of 4-aminosalicylic acid solution, the mixtures were stirred for 30 seconds and the UV-vis spectra were recorded for each step.

### Results and discussions

The optical response of the *Co-3OHPP-nAu* hybrid to the adding of 4-aminosalicylic acid solution was monitored by UV-vis spectroscopy (Figure 4). It can be observed that the plasmonic band presents a red shift and a decreasing intensity with the increase in *PAS* concentration, from 620 nm ( $c = 2.8 \times 10^{-5}\text{M}$ ) to 677 nm ( $c = 1.1 \times 10^{-3}\text{M}$ ). An isosbestic point can also be noticed at 680 nm on the plasmonic band. The detectable concentration domain for which the dependence between the intensity of absorption and the 4-aminosalicylic concentration is linear spans from  $1.24 \times 10^{-5}\text{M}$  to  $3.9 \times 10^{-4}\text{M}$ .

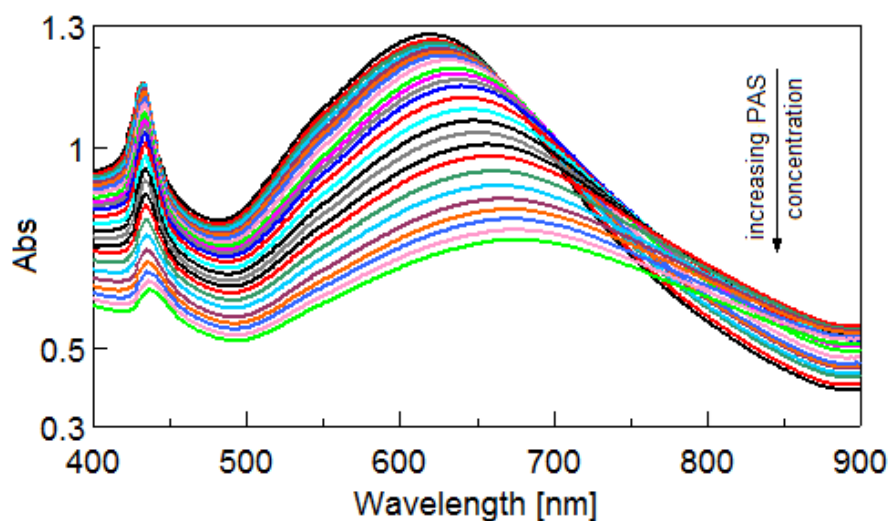


Figure 4. Overlapped UV-vis spectra registered during adding of increasing amounts of *PAS* solution to the *Co-3OHPP/nAu* hybrid material

The dependence between the intensity of absorption and the concentration in 4-aminosalicylic acid is linear, with a good correlation coefficient of 95 %.

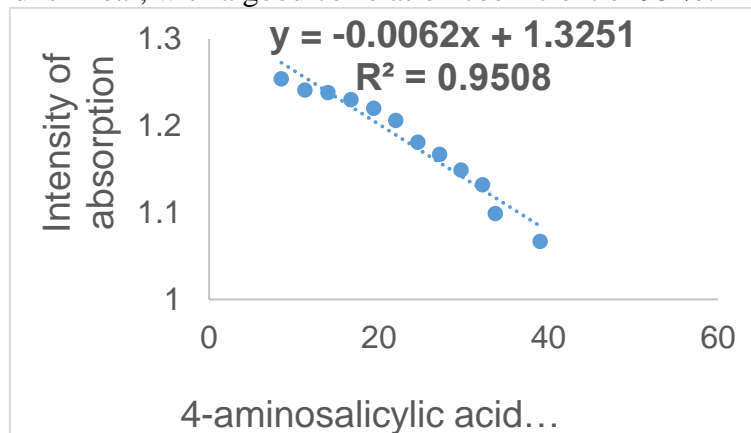


Figure 5. The linear dependence between the intensity of absorption of the hybrid plasmon and the increasing *PAS* concentration

### Conclusion

A hybrid organic-anorganic nanomaterial composed of a Co-metallated symmetrical porphyrin, Co(II) 5,10,15,20-meso-tetra(3-hydroxyphenyl)porphyrin and gold nanoparticles was tested as sensitive material for 4-aminosalicylic acid detection. It can be concluded that this novel optically active nanomaterial is able to detect 4-aminosalicylic acid in a large concentration domain, covering one order of magnitude:  $1.24 \times 10^{-5} - 3.9 \times 10^{-4}$  M. The dependence between the intensity of absorption and the concentration in 4-aminosalicylic acid is linear, with a fair correlation coefficient of 95 %. This hybrid material can be further included in simple devices for the rapid and facile dosage of this antituberculosis drug in body fluids.

### Acknowledgements

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