

IMPROVEMENT OF OPTICAL PROPERTIES BY FLUORESC EIN  
COMPLEXATION  
WITH NANO-Pt- AND NANO-Ag -PORPHYRIN HYBRIDS

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### Abstract

Hybrid organic-inorganic nanomaterials based on Pt and Ag colloids, namely nano-Ag-5,10,15,20-tetrakis-(4-aminophenyl)-porphyrin-Zn(II) (*ZnTAPP-AgNPs*) and nano-Pt-5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin-Zn(II) tetrachloride (*ZnTMePyP-PtNPs*) were obtained and their capacity to form improved optically active complexes with fluorescein was investigated. By interaction with minute quantities of fluorescein the intensity of absorption of the plasmonic bands of the *ZnTAPP-AgNPs* and *ZnTMePyP-PtNPs* hybrids increases. *ZnTMePyP-PtNPs* hybrid will be further tested in clinical trials because it allows for a larger concentration domain of fluorescein complexation and more accurate dosage. All the sensitive materials are easy to prepare and respect the rules of sustainable chemistry.

### Introduction

In recent years scientists were interested in obtaining more fluorescent molecules and hyperchromic optical effects in order to study the mechanisms of molecular interactions. For this purpose, porphyrins were complexed with fluorescein and novel dyads were obtained in various methods. For example, tetraphenylporphyrin was complexed with a fluorescein molecule via a flexible four carbon atoms linker [1]. The intramolecular interactions were studied for this heterodimer by means of absorption and fluorescence spectroscopy in various solvents. The prototropic equilibrium of fluorescein dyes as function of pH is extensively presented in literature [2]. The presence of color of the dyads containing fluorescein (structure in Figure 1) indicates the structural form having hydroxyl and carboxyl active groups.

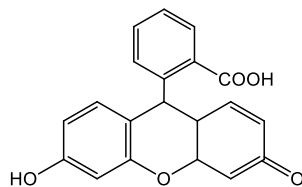


Figure 1. Fluorescein structure

Having hydroxyl and carboxyl active groups, the formation of the dyad can take place at different active sites [3]. The ester bond between the two chromophore molecules is performed in this case via a three carbon atoms flexible bridge. The same authors obtained Zn, Cu and Ni metal fluorescein-porphyrin dyads and analysed their photophysical properties [4]. They concluded that only the  $Zn^{2+}$  complex exhibits fluorescence emission and possesses a shorter fluorescence lifetime as compared to the free porphyrin dyad. They attributed this fact to the increase in electron density by the presence of  $Zn^{2+}$  ions in the complex.

A fluorescence strengthening was observed for the supramolecular system formed between 5-(p-hydroxyl-propanbrominephenyl)-10,15,20-triphenylporphyrin that was coupled with fluorescein and further complexed with copper(II) 5-(p-amino-phenyl)-10,15,20-triphenylporphyrin by hydroxyl-amino type hydrogen bonding [5].

Porphyrins tagged with fluorescein were obtained as dyads by linking the two molecules by a triazole bridge [6]. The intramolecular energy transfer was more efficient in DMSO as solvent than in chloroform.

The scope of our work was to obtain porphyrin-fluorescein complexes that exhibit better optical properties than the starting materials using a simple investigation tool like optical spectrophotometry. For this purpose, hybrid nanomaterials consisting of metalloporphyrins and noble metal Pt and Ag colloids, namely nano-Ag-5,10,15,20-tetrakis-(4-aminophenyl)-porphyrin-Zn(II) (*ZnTAPP-AgNPs*) and nano-Pt-5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin-Zn(II) tetrachloride (*ZnTMePyP-PtNPs*) were obtained and their capacity to form improved optically active complexes with fluorescein was investigated. Figure 2 a and b depicted the porphyrins structures.

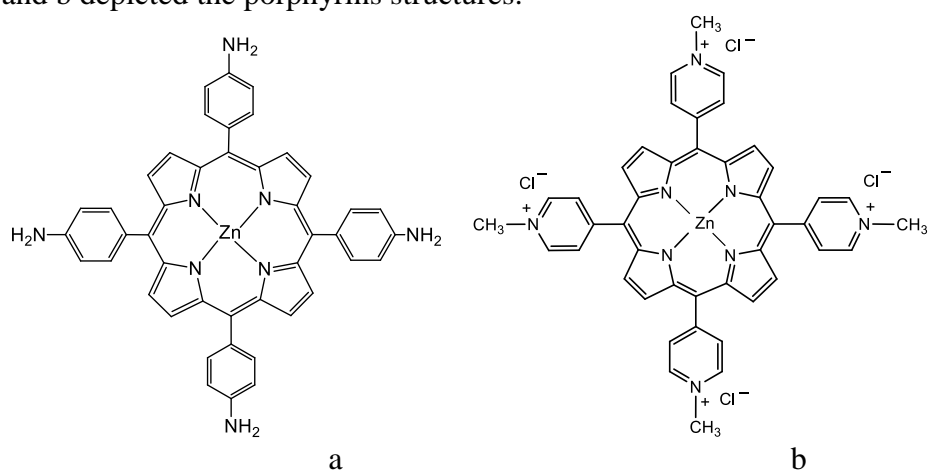


Figure 2. Structures of Zn-5,10,15,20-tetrakis-4-aminophenyl porphyrin (*ZnTAPP*)(a) and 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin-Zn(II) tetrachloride (*ZnTMePyP*)(b)

## Materials and methods

The metalloporphyrin 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin-Zn(II) tetrachloride (*ZnTMePyP*) was obtained by our group and previously reported [7]. The metalloporphyrin 5,10,15,20-tetrakis-(4-aminophenyl)-porphyrin-Zn(II) (*ZnTAPP*) was purchased from Por-Lab GmbH (Germany). Fluorescein Standard (Free acid) was provided by Fluka. Solvents, DMSO and THF, were acquired from Merck and were used without further purification. The formation of the hybrid nanomaterial stabilized with polyethyleneglicole (PEG), *ZnTAPP-AgNPs* was previously reported [8] and the formation of the hybrid nanomaterial *ZnTMePyP-PtNPs*, was performed by adapting the procedures used in previous experiments already published by our group [7, 9]. A fluorescein solution having the concentration of  $1.805 \times 10^{-3}$  M in THF was used for the detection experiments.

**Apparatus.** A JASCO UV- V-650 spectrometer (Japan) was used for recording UV-visible spectra using standard 1 cm pass cells.

## Results and Discussions

**The UV-vis spectra** of the starting materials are presented in Figures 3 and 4. The UV-vis spectrum of fluorescein (Figure 3a) does not have important peaks in the spectral domain of interest (350 – 550 nm). It can be seen that the interaction between the

metalloporphyrin and the silver colloidal nanoparticles leads to an enlargement of the plasmonic band ( $\lambda_{\text{max}} = 437 \text{ nm}$   $I = 1.97$ ) (Figure 3d) of the silver colloid alone (Figure 3b) and also to an increase in intensity as compared to the Soret band of the Zn-metalloporphyrin ( $\lambda_{\text{max}} = 428 \text{ nm}$   $I = 1.85$ ) (Figure 3c).

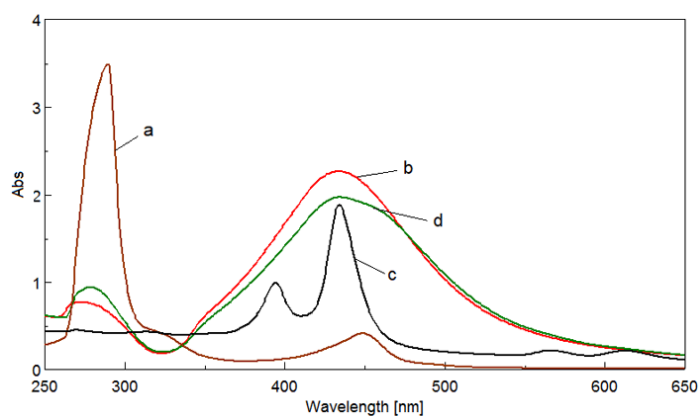


Figure 3. Overlapped UV-vis spectra of: fluorescein solution in THF (a); stabilized silver colloidal solution (b); **ZnTAPP** solution in THF (c) and the hybrid plasmonic nanomaterial **ZnTAPP-AgNPs** (d)

In the case of the hybrid nanomaterial formed between water soluble 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin-Zn(II) tetrachloride (**ZnTMePyP**) and platinum colloid (Figure 4) it can be concluded that the intensity of absorption of the hybrid (Figure 4d) is decreased as compared both to the intensity of absorption of the porphyrin base (Figure 4c) and to the intensity of absorption of the nanoplatinum colloid (Figure 4b).

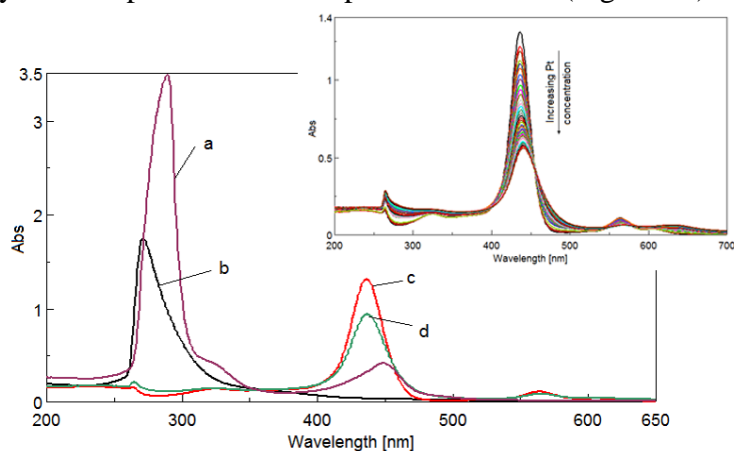


Figure 4. Overlapped UV-vis spectra of: fluorescein solution in THF (a); stabilized platinum colloidal solution (b); **ZnTMePyP** solution in water (c) and the hybrid plasmonic nanomaterial **ZnTMePyP-PtNPs** (d) presented also in detail by successive adding of Pt colloid

The fluorescein standard used in this experiment (Figure 1) has hydroxyl and carboxyl active groups and the interaction with the amino-substituted Zn-porphyrin and the silver colloidal nanoparticles leads to a dramatic increase in the intensity of absorption of the hybrid nanomaterial, as can be seen in Figure 5.

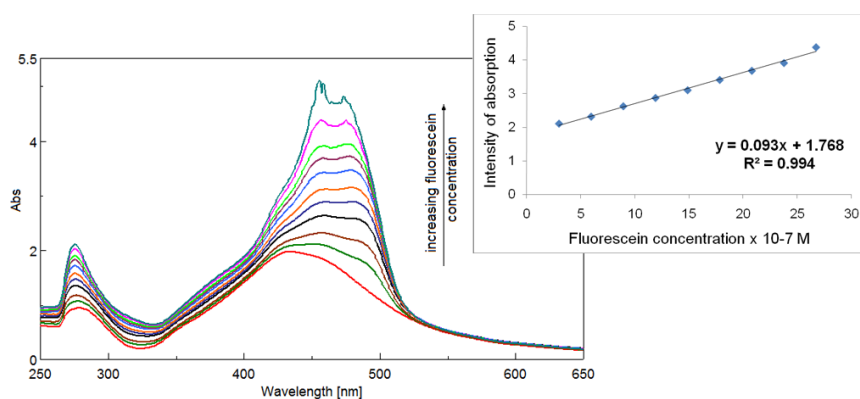


Figure 5. Overlapped UV-vis spectra after successive adding of fluorescein to **ZnTAPP-AgNPs** Dependence between the intensity of absorption at 457 nm and the fluorescein concentration

The concentration domain in which the dependence between the intensity of absorption of the plasmonic band and the concentration of fluorescein is linear spans from  $2.97 \times 10^{-7}$  M to  $2.67 \times 10^{-6}$  M (Figure 5 detail) and presents an excellent correlation coefficient of 99.4%

The demand for complexes with fluorescein used in smaller amounts justifies the experiment for obtaining fluorescein complexes with **ZnTMePyP-PtNPs** hybrid. The sequential adding of 0.001 mL fluorescein solution in THF ( $c = 1.805 \times 10^{-3}$  M) to 3.2 mL of **ZnTMePyP-PtNPs** hybrid nanomaterial in water was performed. The solutions were stirred for 30 seconds on a sonication bath and the UV-vis spectra were recorded (Figure 6).

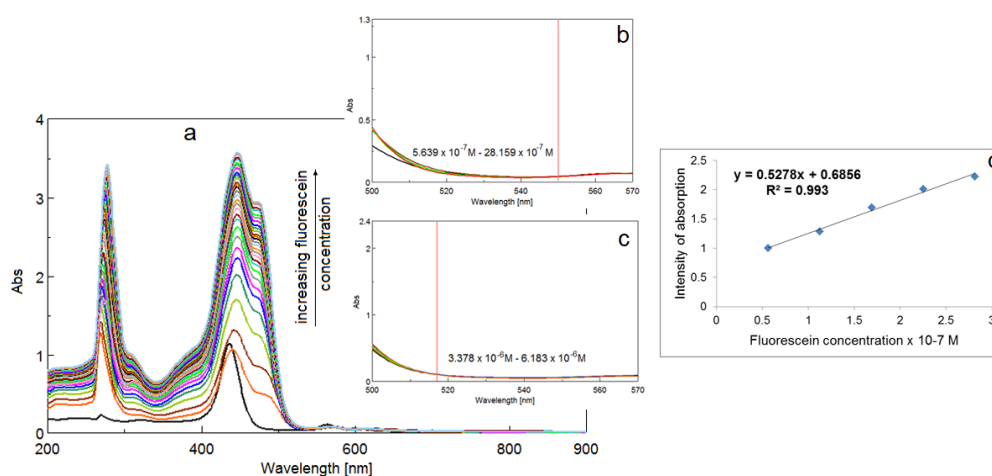


Figure 6. Overlapped UV-vis spectra for the sequential adding of fluorescein solution to the **ZnTMePyP/PtNPs** hybrid material. Details of the isosbestic points at 550 nm (b) and at 515 nm (c). Linear dependence between the intensity of absorption and the fluorescein concentration (d)

It can be observed that the intensity of absorption increases strongly and constantly after each fluorescein adding in the 250 – 650 nm wavelength domain. Another feature that confirms the formation of complexes between the **ZnTMePyP-PtNPs** hybrid material and fluorescein is the presence of two isosbestic points that appear, as a function of fluorescein concentration, at 550 nm and 515 nm respectively (Figure 6b and 6c). The increase in intensity of absorption is a linear function of the fluorescein concentration (Figure 6d).

## Conclusion

Although the synthesis of dyads between porphyrins and fluorescein is known to require tedious workup and high temperatures and leads to a decreased intensity of absorption of the obtained material [4] by comparison to the initial porphyrin, in our case, the intensity of absorption of the plasmonic bands of the *ZnTAPP-AgNPs* and *ZnTMePyP-PtNPs* hybrids increase in intensity by interaction with fluorescein.

*ZnTMePyP-PtNPs* hybrid will be further tested in clinical trials because it allows for a larger concentration domain of fluorescein complexation and more accurate dosage.

All the sensitive materials are easy to prepare and require no high temperatures or purification steps.

## Acknowledgements

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