

NEW PORPHYRIN -BASED SPECTROPHOTOMETRIC SENSOR FOR Ag⁰ DETECTION

A. PALADE^a, G. FAGADAR-COSMA^{b*}, A. LASCU^a, I. CREANGA^a,
M. BIRDEANU^c, E. FAGADAR-COSMA^a

^a*Institute of Chemistry Timisoara of Romanian Academy, 24 M. Viteazu Ave, 300223-Timisoara, Romania*

^b*"Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Victoriei Square 2, 300006-Timisoara, Romania,*

^c*National Institute for Research and Development in Electrochemistry and Condensed Matter, 1 Plautius Andronescu Street, 300224-Timisoara, Romania*

An approach to obtain silver colloids of different sizes by reduction of silver nitrate with sodium citrate in bare form and stabilized with polyethyleneglycol was intended in the purpose of developing new hybrid porphyrin-based materials with extended optoelectronic properties. The plasmons were comparatively analyzed by UV-vis and AFM investigations. Unexpectedly, the stabilized colloid tends to aggregate giving rise to honeycomb like architectures.

A new complex based on 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin and freshly synthesized silver colloid was obtained and can be further used as a new optical sensor for Ag⁰ detection in very small concentrations (2.5x10⁻⁹ M to 0.82x10⁻⁷ M), broadening the known detectable concentration range for rare metals and improving their recovery.

The investigation of the behaviour of Ag⁺ ions towards the same bare porphyrin led to obtaining of Ag(II) 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin as a result of disproportionation of Ag(I) ions.

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1. Introduction

Due to the self-assembling property of porphyrins determining amazing optical effects and their capacity to host a wide range of metals, the study of metal-organic frameworks, both in solid state chemistry and in molecular engineering, is of increasing interest [1]. The statistical physics of planar arrays of molecular chains has been studied in the last decade [2-4].

Due to the fact that Gustav Mie theory has limited applicability to aggregated particles, theoretical work was also done by applying the so-called discrete dipole approximation (DDA) in which the particle is divided into small elements interacting with each other through dipole-dipole interactions, and subsequently a global evaluation of absorption and scattering is performed [5].

The incorporation of fluorescent tetrapyrrolic heterocycles exhibiting extended π -conjugation into plasmonic colloidal systems or other hybrid systems is of high interest nowadays due to the possibility of tuning the nano scale dimension of the material corroborated with high fluorescence and amazing photochemical stability making them true candidates for sensing [6-10] photosensitizing [11] and imaging [12, 13].

In this respect, the recovery of precious metals including silver is an ongoing topic, the methods used (electrolysis, metallic replacement and chemical precipitation) depending on the concentration of the metal. The detection of silver in various oxidation states (from 0 to +2) is often performed by various means, such as: ion-selective membrane electrodes [7, 14], differential

* Corresponding author: gfgadar@yahoo.com

pulse voltammetry [15], atomic absorption determination [16] or atomic emission of the silver atoms. A novel method, based on direct electrooxidation of AgNPs colliding with an electrode that is both viable and quantitative can be used for characterization and NP identification [17].

Regarding potentiometric sensors, a functionalized porphyrin, namely: tetra-(3-hydroxyphenyl) porphyrin was tested as ionophore in polymeric membrane cation-selective electrodes. The best results as silver-selective electrode has a working concentration range from 8×10^{-6} – 1×10^{-1} M, a slope of (64.5 ± 1.8) mV/decade of activity and very good values of the selectivity coefficients. The detection limit of the sensor is 7.0×10^{-6} M. The useful pH-range is 5–10. The sensor was used for the determination of chlorides in meat by potentiometric titration [7]. Another polymeric membrane selective to Ag(I) with application in analysis of natural water spiked with silver, based on calix[4]arene derivative as ionophore was reported [14]. The electrode response is stable over wide pH range of 1.0–6.0 and the response time of the sensor is 30 seconds. The detection limit of the electrode is 6.31×10^{-6} M, similar with our reported data [7].

On the other hand, silver nanoparticles are used by themselves as supporting material for the detection of various analytes. Tripolyphosphate modified silver nanoparticles are used for facile and rapid colorimetric detection of manganese ion (Mn^{2+}) with high sensitivity and excellent selectivity [18]. A multilayer nano-silver modified ITO electrode was applied to determine directly chloride anion in real samples, the newly proposed method being much more selective than the existing ones [19]. Nano-silver coated multi-walled carbon nanotubes advanced materials [20] were used as electrode for determination of trace thiocyanate from urine and saliva samples of smoker and non-smoker subjects up to 5×10^{-8} M.

In this work, our main goal was to achieve a new hybrid nanomaterial based on A_3B type porphyrin with freshly synthesized silver colloid and to observe its intrinsic optical properties. In this respect, Ag nanoparticles of diameter ranges from 39 to 55 nm and 80 to 120 nm were synthesized by modifying reported data [21, 22].

Usually the most investigated aspect in this combination is the transformation of the optical properties of the porphyrin, which is stabilized and prevented from aggregation by the association with nanometals, giving rise to wide-band absorption materials [23].

Due to the fact that in previous reported data [24–27] it was observed that by absorbing porphyrins onto silver colloids sometimes a metallation (the incorporation of a metal ion into the porphyrin core) takes place, our investigation was also focused on this aspect. Based on the knowledge that colloidal silver contains besides metallic silver particles also Ag^+ ions [28] and the diameter of a single silver atom is 0.288 nm, suitable to be accepted into porphyrin core, we determined the interaction of a carboxy-substituted meso porphyrin, namely: 5-(4-carboxyphenyl)-10,15,20-triphenyl-porphyrin, both with nano-silver colloidal particles but also with Ag^+ ions provided by silver salts.

If the ionic radii of the metal ions are too large to fit into the cavity, it might be located out of the porphyrin ligand plane, distorting it.

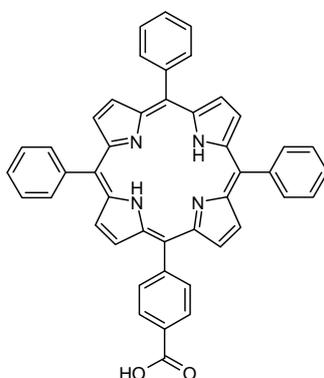


Fig. 1. Structure of 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin.

2. Experimental

Materials. The reagents used were *purum analyticum* obtainable from Merck (Germany) and Chimopar (Romania) and were used without further purification.

Method for obtaining 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin. The A₃B mixed substituted porphyrin, namely: 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin was obtained by two steps procedure. Firstly, Lindsey multicomponent method was used for synthesis of 4-(methoxycarbonyl)phenyltriphenylporphyrin [29, 30] followed by hydrolysis of methyl-ester porphyrin in basic condition [31].

General method for preparation of silver colloids was the same as in our previously published paper [22] using molar ratio silver nitrate/ sodium citrate = 1:2 (see UV-vis, Figure 3). From the obtained colloid, 50 mL were extracted and stabilized by adding 0.2 mg polyethyleneglycol (PEG, M=600) and stirring the mixture for additional 10 minutes.

Method for complexing nano-silver with 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin. To 4 mL porphyrin solution in DMF ($c=1.2 \times 10^{-5}$ M) successive portions of 100 μ L silver colloid solution ($c=0.11 \times 10^{-5}$ M) were added under intense stirring and the UV-vis spectra were recorded for each step.

Method for obtaining metalloporphyrin Ag (II) 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin

To a quantity of 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin 0.72×10^{-3} g (0.11×10^{-5} mole) dissolved in 2 mL DMF, a solution of AgNO₃ (3.7×10^{-3} g, 2.2×10^{-5} mole) in 2 mL DMF was added dropwise under intense stirring. The molar ratio porphyrin: silver salt was set up to 1:20. The mixture was stirred for 1 hour and 1 mL buffer solution (100 mL KH₂PO₄ and 51.8 mL NaOH 0.1M) was added to maintain constantly pH=6.9

Apparatus. Atomic force microscopy *AFM* measurements were performed on Nanosurf[®] EasyScan 2 Advanced Research AFM (Switzerland), equipped with a stiff ($450 \mu\text{m} \times 50 \mu\text{m} \times 2 \mu\text{m}$) piezoelectric ceramic cantilever. The surface imaging investigations were done in ambient conditions with samples deposited onto pure silica or glass plates by slow evaporation of the water. AFM images were obtained in contact mode. UV-visible spectra were recorded on a JASCO UV-visible spectrometer, V-650 model (Japan). Absorption, excitations and emission spectra were recorded in environmental conditions (temperature: 22 ± 2 °C), on 1 cm path length cells.

3. Results and discussions

The UV-vis spectrum of 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin belongs to *etio* type class (Figure 2) with the Soret band at 417.8 nm ($\log \epsilon= 5.56$) and the four Q-bands decreasing in intensity at 514 nm ($\log \epsilon= 4.28$), 549 nm ($\log \epsilon= 3.97$), 590 nm ($\log \epsilon= 3.77$) and 647 nm ($\log \epsilon= 3.74$) respectively, that are assigned to $a_{2u}(\pi) - e_g^*(\pi)$ transitions. The Q bands are decreasing in intensity in the following order: $Q_y(1,0) > Q_y(0,0) > Q_x(1,0) > Q_x(0,0)$.

The molar extinction coefficients of the Q-bands are at least one order of magnitude lower than the Soret band, hence, an analytical determination method based on Q-absorption may be less sensitive.

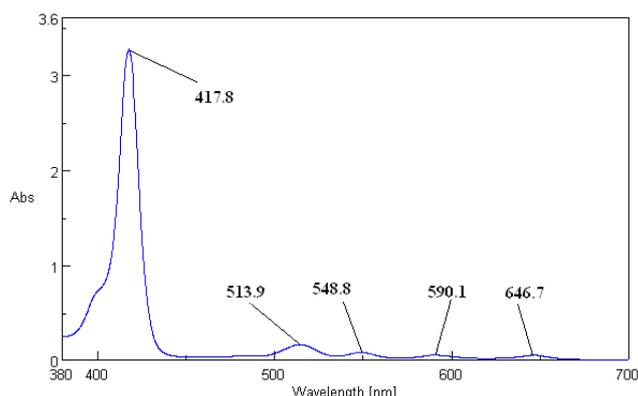


Fig. 2. The UV-vis spectrum of 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin in CHCl_3 $c=0.91 \times 10^{-5} \text{M}$

The UV-VIS spectra of the bare and PEG-stabilized silver colloids (Figure 3) prepared at molar ratio silver nitrate/ sodium citrate: 1:2 in the range 320 nm – 700 nm, show the typical absorption band for silver nanoparticles with plasmonic peak around 450-460 nm [32].

The optical properties of silver nanoparticles, also known as the surface plasmon absorption band, generated by the electric field of the incoming radiation will induce the formation of a dipole in the nanoparticle.

The movement of the conduction electrons in the particles, resulting in a displacement of the negative and positive charges in the metal, determines the particle polarization and the positive charge will act as a restoring force that tries to compensate it, so that it will produce oscillations of the electrons. The surface plasmon absorption band depends on the silver nanoparticles shape, their size, surrounding medium and possible aggregation processes of the colloids [33].

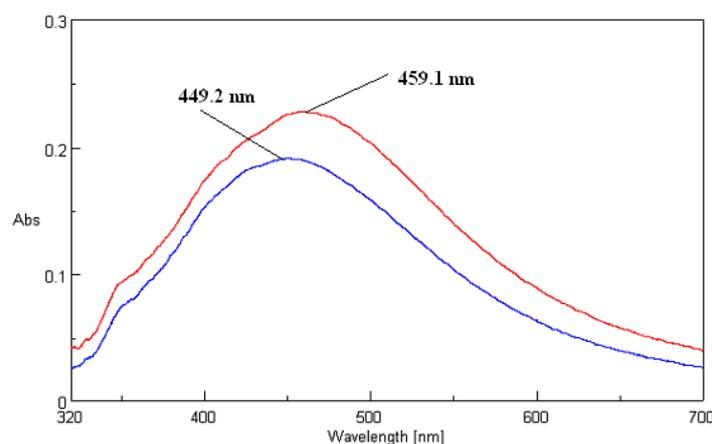


Fig. 3. Overlapping of UV-vis spectra of bare ($\lambda=449.2 \text{ nm}$) and stabilized ($\lambda=459.1 \text{ nm}$) Ag-colloids at the same concentration (10^{-6} M).

Analyzing the electronic spectra, it can be noticed that with the increase in particle size, corresponding to PEG stabilization, the absorption peak is both red and hyperchromically shifted [33, 34] as also AFM results certify.

The samples for AFM studies were obtained by deposition of the colloid solutions both on mica and glass in order to discern the influence of the surface tension upon the aggregation of the Ag colloidal particles.

In case of using mica as support, the Ag particles were prevented from agglomeration as can be seen in (Figure 4 A and B) no matter of the stabilizing agent. In Figure 4A, the size of the particles is smaller, in the range 39-55 nm in comparison with the PEG stabilized colloids, where the sizes are situated in the range 80-120 nm.

A different phenomenon is revealed in the case of deposition of bare Ag colloid on glass support. Because of hydrophilic effects, the Ag particles tend to evenly distribute on the surface, not showing sites of aggregation (Figure 5). Surface tension is responsible for the spherical shape of Ag nanoparticles.

If one discusses in terms of energy, the boundary molecules possess a higher energy. In order to minimize the colloid energy state, the number of higher energy boundary molecules must be minimized, thus resulting in minimized surface area, so that a surface will assume the smoothest shape it can.

Unexpectedly, the PEG stabilized Ag colloids (diameter ranging from 80 to 120 nm) deposited on glass support (Figure 6A) tend to aggregate and organize on the surface, showing honeycomb like architecture (Figure 6B).

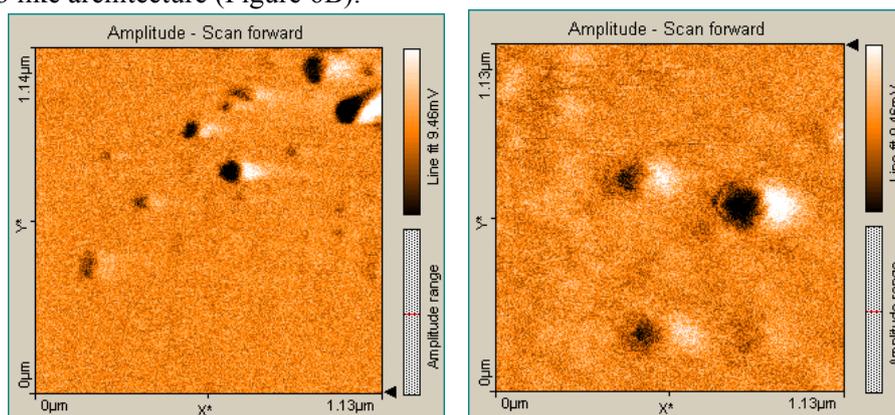


Fig. 4 A and B. 2D AFM images of A) bare Ag-colloid and B) PEG stabilized Ag-colloid.

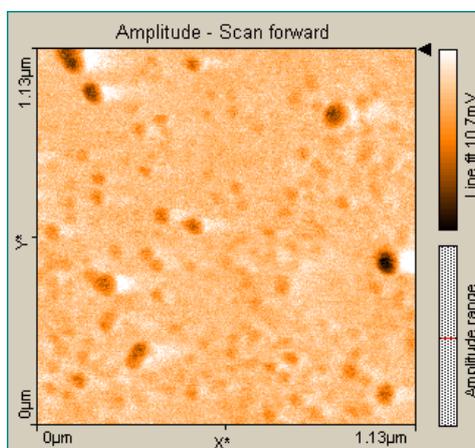


Fig. 5 2D AFM contact mode image of the deposition of bare Ag colloid (diameter ranges from 39 to 55 nm) on glass support.

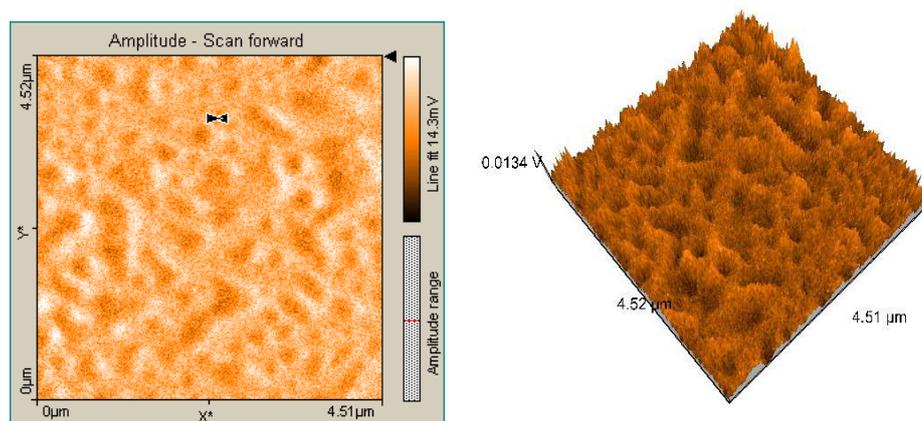


Fig. 6. 2D (A) and 3D (B) AFM images of the PEG stabilized Ag colloid deposited on glass support.

The experiments concerning expected complex generation of nano-silver with 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin gave different results as in case of the other A_3B phenyl-substituted porphyrin, namely: 5,10,15-tris-(4-pyridyl)-20-(3,4-dimethoxy-phenyl)-porphyrin [22].

In this specific case, the newly formed complex is not giving rise to a wide absorption band material, but the complex generation is obvious from presence of three isosbestic points, indicating equilibrium processes, situated on the descending branch of the Soret band (435 nm) and on both branches of the $Q_Y(1,0)$ band (located at 508 nm and 522nm, respectively), as illustrated in Figures 7 and 8.

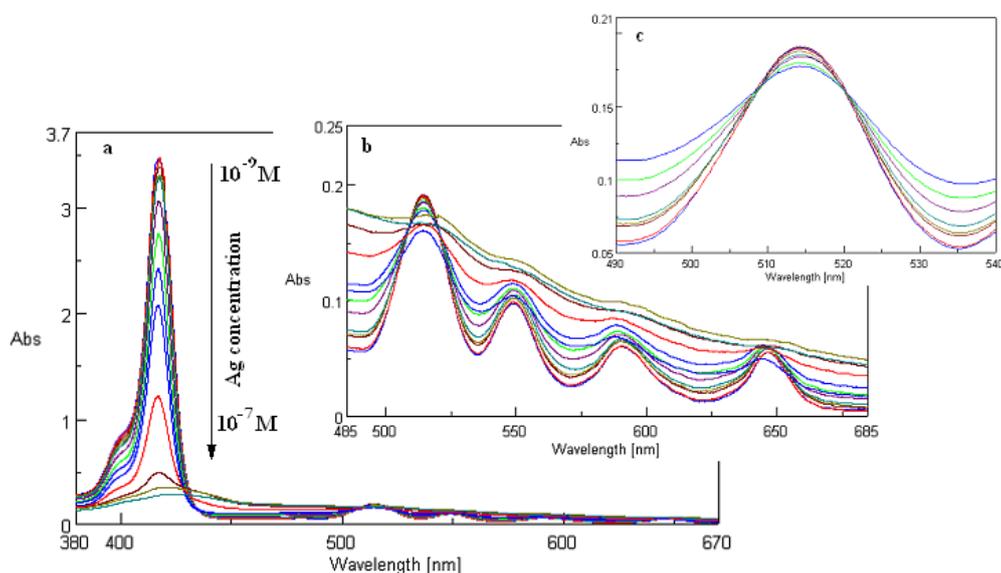


Fig 7. The superposed UV-vis spectra during addition of silver colloid into porphyrin solution (a); details of the Q bands (b); highlight of QIV bands with isosbestic points (c).

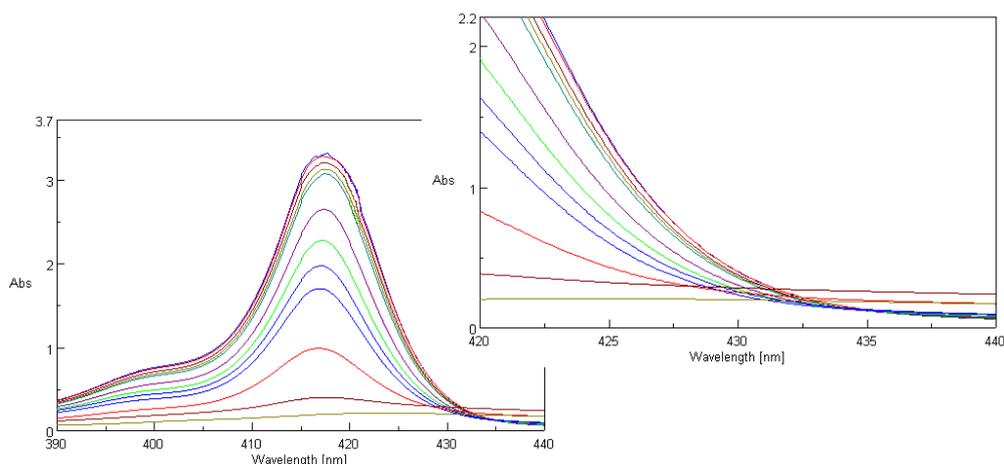


Fig. 8. The magnified UV-vis spectra of Soret band behaviour during addition of silver colloid into porphyrin (detail of isosbestic point).

Analyzing the relationship between the intensity of absorption and the concentration of the silver colloid (Figure 9), a linear dependence in the range of very small concentration was evidenced.

We were able to measure dilute Ag colloid concentrations in the range of 2.5×10^{-9} M to 0.82×10^{-7} M, so that we can consider 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin as a highly sensitive molecule for Ag^0 detection.

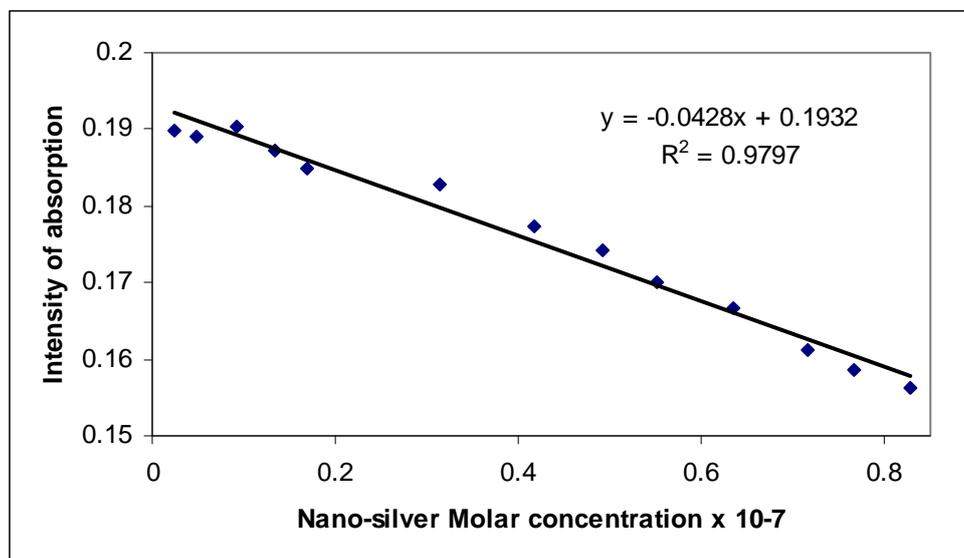


Fig. 9. Linear dependence in the range of very small concentration between the intensity of absorption and the concentration of the silver colloid.

The proposed binding from (Figure 10) is based on the fact that silver particles that are suspended in pure water to form a colloid will assume a negative charge that is called the zeta potential. (The zeta potential of silver colloids that contains no silver ions will have a higher negative potential of about -50 mV, as in our case when a large citrate excess was used) [35, 36]

Ionization of carboxylic acid from the *para* position of *meso* phenyl is occurring according with equation 1:



In this respect, positively charged H^+ , is attracted to the silver atom, leaving the negatively charged COO^- end to stick out into the solution.

It can be understood that since the silver colloidal particles possessed a negative charge due to both the adsorbed citrate ions and COO^- groups from 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin, a repulsive force worked along particles and prevented aggregation, as also AFM confirmed (Figure 5).

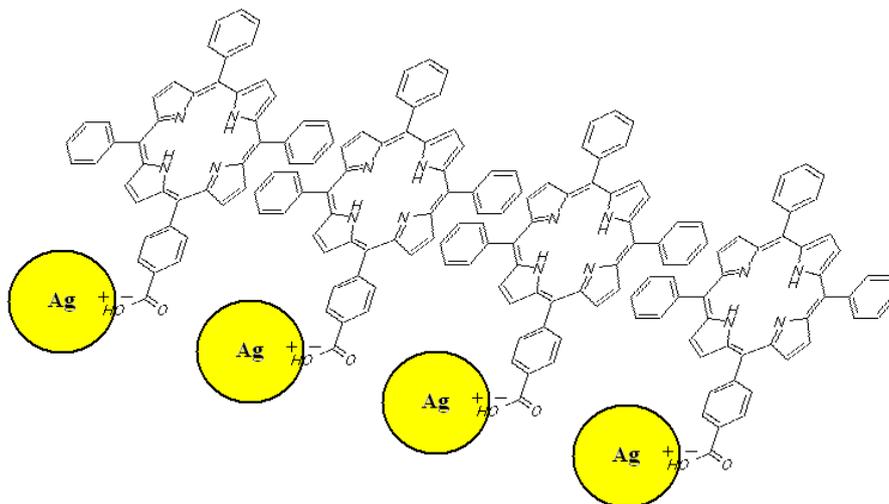
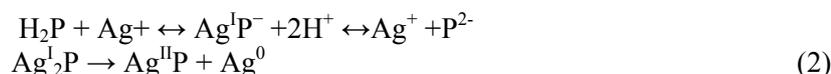


Fig. 10. Binding of porphyrin through Carboxylic groups.

In order to compare the behaviour of Ag^0 from different Ag ions in relationship to 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin, the synthesis of silver metalloporphyrin was performed.

Stable Ag(II) 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin was synthesized by mixing a porphyrin solution in DMF, with saturated silver nitrate DMF solution in large excess (molar ratio: porphyrin/ $AgNO_3=1:20$).

At the beginning of the reaction the red porphyrin solution becomes green due to the acidity caused by the dissociation of H^+ from pyrrole and at the end red colour is again pregnant due to formation of Ag(II) porphyrin as a result of disproportionation of Ag(I) ions [37] in macrocycle (equation 2):



As previously reported [38], in Ag(I) porphyrin the major visible Q band is located at 517 nm, but in our case (see Figure 11, last detail), the highest intensity Q band is located at 539.9 nm and the second one around 600 nm.

The metallation of the porphyrin base is accompanied by a simplified UV-vis spectrum, due to an increase in symmetry, resulting in the presence of only two Q bands, namely $Q(0, 1)$ and $Q(0, 0)$.

In detail of Figure 11, it is clear that the Soret band is red shifted with 9 nm in Ag (II) metalloporphyrin complex in comparison with corresponding bare porphyrin.

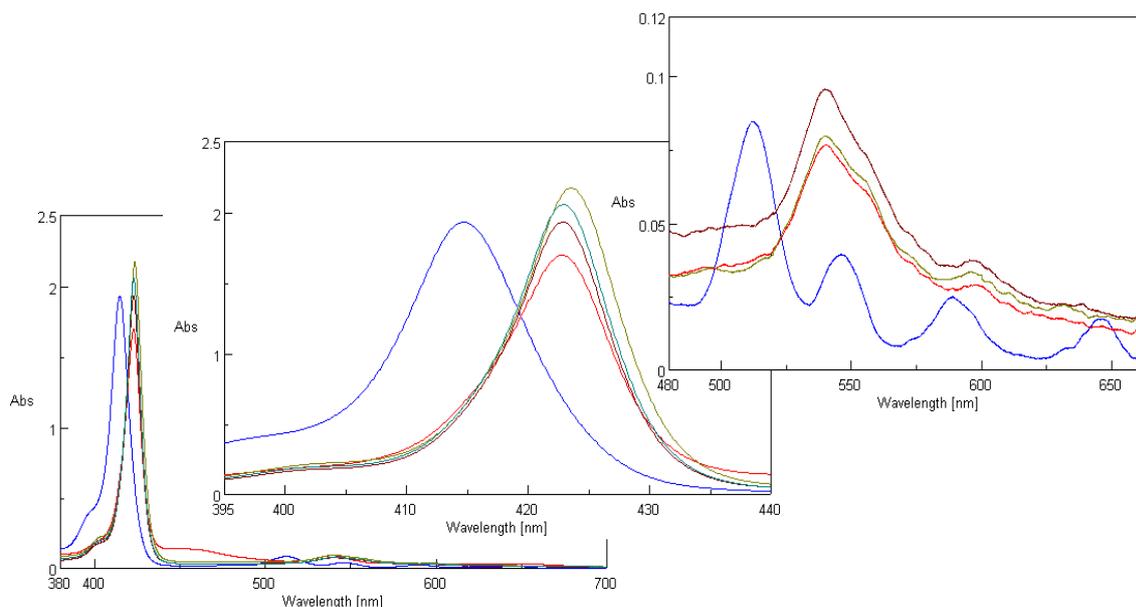


Fig. 11. Overlapped UV-vis spectra of Ag (II) metalloporphyrin complex in comparison with corresponding bare porphyrin. In detail, red shift of Soret band and reduction of the number of Q bands in the Ag-complex.

4. Conclusions

Silver colloids of diameter ranging from 39 to 55 nm and 80 to 120 nm were obtained by reduction of silver nitrate with large excess of sodium citrate in bare form and stabilized with polyethyleneglycol. The plasmons were comparatively analyzed by UV-vis and AFM investigations. Unexpectedly, the stabilized colloid tends to aggregate giving rise to honeycomb like architectures.

A new complex based on 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin and freshly synthesized silver colloid was obtained and its intrinsic optical properties were studied. As a consequence, 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin can function as a new optical sensor for Ag^0 detection in very small concentrations (2.5×10^{-9} M to 0.82×10^{-7} M), broadening the known detectable concentration range for rare metals and improving their recovery.

Our approaches were also focused on the behaviour of silver ions towards the same bare porphyrin and as a result we proved the obtaining of Ag (II) 5-(4-carboxy-phenyl)-10,15,20-triphenyl-porphyrin as a result of disproportionation of Ag(I) ions.

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