



Spectroscopic investigation on porphyrins nano-assemblies onto gold nanorods

Mariachiara Trapani^a, Giovanna De Luca^{b,c}, Andrea Romeo^{a,b},
Maria Angela Castriciano^{a,*}, Luigi Monsù Scolaro^{a,b,**}

^a CNR-ISMN, Istituto per lo Studio dei Materiali Nanostrutturati, Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, University of Messina, V.le F. Stagno D'Alcontres, 31 98166 Messina, Italy

^b Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, University of Messina and C.I.R.C.M.S.B., V.le F. Stagno D'Alcontres, 31 98166 Messina, Italy

^c CNR-IPCB Istituto dei Polimeri, Compositi e Biomateriali - P.le Enrico Fermi 1, 80055 Portici (NA), Italy

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ABSTRACT

The interaction between gold nanorods (Au NRs), synthesized by a conventional seeded growth protocol, and the anionic tetrakis-(4-sulfonatophenyl)porphyrin (TPPS₄) has been investigated through various spectroscopic techniques. At neutral pH, the formation of H-aggregates and the inclusion of porphyrin monomers in CTAB micelles covering the nanorods have been evidenced. Under mild acidic conditions (pH = 3) a nano-hybrid assembly of porphyrin J-aggregates and Au NRs has been revealed. For the sake of comparison, Cu(II) and Zn(II) metal porphyrin derivatives as well as a cationic porphyrin have been studied in the same experimental conditions, showing that: i) CuTPPS₄ forms porphyrin H-dimers onto the Au NRs; ii) ZnTPPS₄ undergoes to demetallation, followed by acidification of the central core and eventually aggregation onto Au NRs; iii) cationic porphyrin does not interact with Au NRs.

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1. Introduction

Gold nanoparticles (Au NPs) with different sizes and shapes, such as spheres, rods, prisms, wires, platelets and ribbons have attracted large interest in many research fields [1]. Due to their relatively easy synthetic methods and their peculiar shape and size dependent optical properties, Au NPs are interesting nanomaterials for a variety of applications [2–11]. In particular, gold nanorods (Au NRs) have been extensively explored in several fields, such as in catalysis, sensing, optoelectronics and biomedicine [12–17]. Due to their anisotropic shape, Au NRs show two distinct spectroscopic features: a band localized at 520–530 nm, deriving from the oscillation of electrons along the short axis of the structure called transverse plasmonic (TP) band, and a band called longitudinal plasmonic (LP), due to the electron motion along the long axis of the rod, at higher wavelength (around 700 nm), that can be finely tuned by changing the aspect ratio (length/width ratio). These interesting Au NRs properties justify the efforts focused on improving their synthetic methods as well as reproducibility, yield and

their aspect ratio. Several synthetic procedures based on photochemistry [18,19], wet chemistry [20], use of templating reagents [21], or electrochemistry [22,23], have been developed. In this regard, it is important to point out that Au NRs features are strictly related to the nucleation and the growth steps that are extensively sensitive to physical and chemical parameters of the medium [24,25]. Among the different approaches, the seeds mediated synthesis, in presence or in absence of silver nitrate, is rather easy and convenient in directing elongated one-dimensional nanostructures and providing a bilayer that imparts a positive charge and a high stability to the nanorods [24,28,29]. The quite complex chemistry of Au NRs has been related to three distinct interfaces which play an important role in the growth mechanism and the functionalization processes: i) the metal-surfactant interface, ii) the hydrophobic surfactant bilayer and iii) the surfactant interface with the bulk solution [26]. In recent years, significant progress has been made to improve the electronic, magnetic and optical properties of these nanomaterials, by developing methods for Au NRs assembly in ordered structures through coupling among neighboring nanorods [27–29]. The controlled organization of these nanoparticles allows a better tuning of their electronic coupling making them potentially suitable in many technological areas such as photonics [30,31], nanoelectronic [32] and sensing [29,33,34]. Furthermore, the possibility to incorporate various organic, inorganic, biological, and pharmaceutical molecules makes them good candidates for biomedical applications [35–37]. Self-assembly can be achieved via supramolecular approach by functionalization

* Correspondence to: M.A. Castriciano, CNR-ISMN, Istituto per lo Studio dei Materiali Nanostrutturati, V.le F. Stagno D'Alcontres, 31 98166, Messina, Italy.

** Correspondence to: L. Monsù Scolaro, Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, C.I.R.C.M.S.B., V.le F. Stagno D'Alcontres, 31 98166, Messina, Italy.

E-mail addresses: castriciano@pa.ismn.cnr.it (M.A. Castriciano), lmonsu@unime.it (L.M. Scolaro).

of Au NRs with organic or inorganic components as well as biomolecules [38–41]. In this framework, due to their interesting spectroscopic properties and their ability to form self-assembled structures, porphyrins represent intriguing candidates to realize hybrids nanocomposite materials [42–45]. Gold nanorods and a hematoporphyrin-doped mesoporous silica shell were used for the generation of singlet oxygen with higher yield with respect to free porphyrin [46]. Au nanorods/nanospheres have been obtained using anionic porphyrins as linking agents [38]. The H-type aggregates of meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS₄), at various porphyrin concentrations, have been reported to work as linear or bifurcated junctions of Au nanorods/nanospheres [38]. Herein we report on the spectroscopic behavior of hybrid systems obtained by interaction between the water-soluble TPPS₄ porphyrin and Au NRs, pointing on the formation of porphyrin H-aggregates and monomers in CTAB micelles covering the nanorods at neutral pH, and peculiar J-type porphyrin aggregates onto Au NPs in mild acidic conditions (pH = 3). It is well known in literature that, TPPS₄ porphyrin shows the peculiar ability to self-aggregate forming J-type arrays whose sizes span from nano- up to microscale. These aggregates exhibit interesting nonlinear optical and optoelectronic properties mainly related to their structure [47–50]. The hierarchical self-assembling process, driven by electrostatic (including hydrogen bonding) and hydrophobic interactions occurring between adjacent porphyrins, shows different thermodynamically and kinetically controlled paths related to porphyrin concentration and medium conditions such as pH and ionic strength [51–57]. We anticipate that Au NRs are able to efficiently trigger the growth of TPPS₄ J-aggregates under experimental conditions unusual for obtaining this type of structures in the absence of the metallic entities. Moreover, this assembly strategy allows us to conjugate anisotropic metal nanocrystals into hybrid architectures. The merging of the optical and photophysical properties of the components make the Au NRs@J-agg assemblies interesting candidates for potential multitopic applications, ranging from optics, electronics, sensing, biomedicine and catalysis.

2. Experimental Methods

2.1. Chemicals

Hydrogen tetrachloroaurate (III) hydrate (99.9%) was supplied by Strem Chemicals. Sodium borohydride (98%), cetyltrimethylammonium bromide (CTAB, 98%), silver nitrate, L-ascorbic acid were purchased from Aldrich Chemicals co. and used as received. Hydrochloric acid (37%) was obtained from Fluka. The porphyrins 5,10,15,20-tetrakis(4 sulfonatophenyl)porphyrin (TPPS₄) and meso-tetrakis(4-(N-methylpyridium-4-yl))porphyrin (H₂TMPyP) were supplied by Aldrich Chemicals co. and their copper(II) and zinc(II) metal derivatives were synthesized according to literature [58,59]. Stock porphyrin solutions were prepared in dust free Milli-Q water and the concentration was determined by the known extinction molar coefficients at the Soret maxima (TPPS₄: $5.33 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda = 414 \text{ nm}$; CuTPPS₄: $4.16 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda = 412 \text{ nm}$; ZnTPPS₄: $6.83 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda = 421 \text{ nm}$; H₂TMPyP: $2.22 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and CuTMPyP: $2.31 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda = 424 \text{ nm}$).

2.2. Preparation of Au NRs

Au NRs were prepared according to a seed-mediated synthesis reported in literature with some slight modifications [60].

2.3. Preparation of Gold Seeds

HAuCl₄ · 3H₂O (0.25 mL, 0.01 M) was added to an aqueous solution of CTAB (7.5 mL, 0.1 M), and the mixture was stirred for some minutes at room temperature. After mixing, an aqueous ice-cold NaBH₄ solution (0.6 mL, 0.01 M) was added. Gaseous products were allowed to escape during the reaction. Aging of seed nanoparticles was carried out in a

bath at 28 °C for 2 h in order to react the excess of sodium borohydride with water.

2.4. Growth of Au NRs

A 0.1 M solution of ascorbic acid (0.032 mL) was added to a solution where CTAB (0.01 M, 4.75 mL), HAuCl₄ (0.01 M, 0.2 mL) and AgNO₃ (0.01 M, 0.030 mL) were previously mixed. At last, 0.01 mL of seeds solution was added and the mixture was left at 28 °C for 3 h. Growth of Au NRs from seeds was monitored by UV/Vis absorption spectroscopy.

2.5. Au NRs and Porphyrin Assemblies

In order to remove excess CTAB, 2 mL aliquots of a solution containing Au NRs was centrifuged at 11,000 rpm for 30 min and the pellet resuspended in pure water. The overall procedure was repeated twice. To study the interaction between metallic nanostructures and porphyrins, 500 µL of purified Au NRs and porphyrin stock solutions with known concentration were used (1.5–5 µM).

2.6. Methods

UV/Vis spectra were collected using a Hewlett-Packard mod. 8453 diode array spectrophotometer using 0.2 or 1 cm pathlength quartz cells. Kinetic experiments were carried out in the thermostated compartment of the spectrophotometer, with a temperature accuracy of ± 0.1 K. The analysis of the kinetic profiles has been performed by a non-linear fit of the absorption data according to Eq. (1):

$$\text{Ext} = \text{Ext}_0 + (\text{Ext}_\infty - \text{Ext}_0)(1 - \exp(-(kt)^n)) \quad (1)$$

with Ext₀, Ext_∞, k, and n as the parameters to be optimized (Ext, Ext₀, Ext_∞ are the extinction at time t, at starting time and at the end of aggregation, respectively). Fluorescence, excitation and Resonance Light Scattering (RLS) spectra were recorded on a Jasco model FP-750 spectrofluorometer. For RLS, a synchronous scan protocol with right angle geometry has been adopted [61].

3. Results and Discussion

Au NRs were synthesized through a seed mediated chemical approach in presence of CTAB [22], that assists and stabilizes the gradual formation of elongated nanostructures [20,62]. Fig. 1 shows the evolution of the UV/Vis absorption spectra during the growth of Au NRs from the initial seeds. During this process, the longitudinal absorption band shows a blue-shift, probably due to a change in the aspect ratio of the nanorods [60]. These solutions appear stable at temperature higher than 28 °C. Indeed, in accordance to the Krafft temperature,

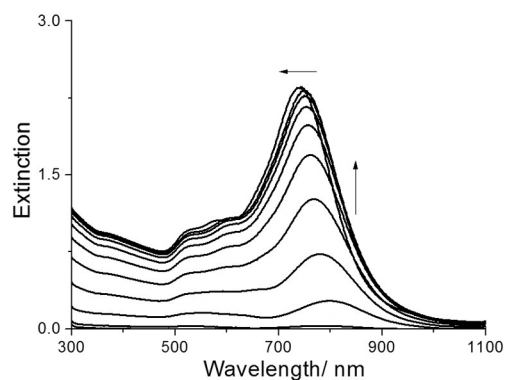


Fig. 1. Time dependent UV/Vis spectral changes for the growth of Au NRs from seeds (total time = 10,800 s). [ascorbic acid] = 0.1 M, [CTAB] = 0.01 M, [HAuCl₄] = 0.01 M, [AgNO₃] = 0.01 M, T = 301 K.

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