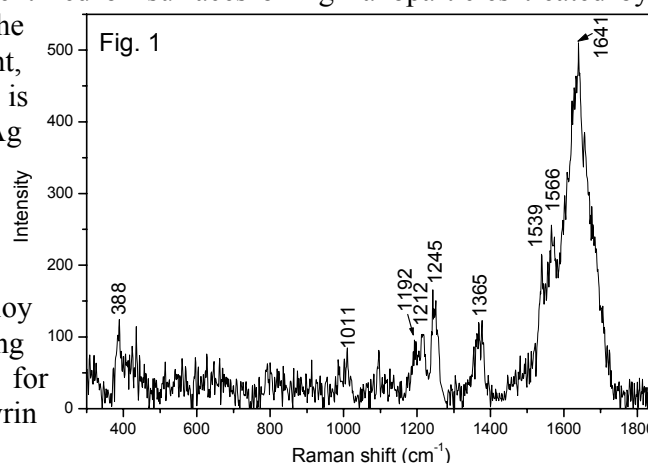


## Surface-enhanced Resonance Raman Scattering of Free-base Porphyrins for Ultrasensitive Spectral Detection and Surface Probing

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Recent development of SERS and SERRS (surface-enhanced /resonance/ Raman scattering) spectroscopies is strongly stimulated by their ultrasensitivity currently achieving a single molecule detection level, as well as by their recent incorporation into the expanding field of plasmonics [1]. Free-base (f.b.) porphyrins, a class of biologically important chromophores, have been the subject of interest as target adsorbates for both sensitive and selective SERRS spectral detection [2]. In this brief overview we demonstrate that, due to their unique molecular structure and reactivity towards plasmonic metal nanoparticle surfaces, f.b. porphyrins can also be employed as surface probes. Using a cationic f.b. 5,10,15,20-tetrakis (1-methyl-4-pyridiniumyl)porphine (H<sub>2</sub>TMPyP) as an example, we show that after identification of all observable SERRS spectral forms with help of factor analysis [3] and their assignment to the corresponding surface species, we obtain a tool for probing the impact of chemical modifications of Ag nanoparticle surfaces. Treatment of Ag nanoparticles by various selected ions has been performed (i) after the Ag nanoparticle preparation by a chemical procedure and/or by laser ablation (LA) of a Ag target in the aqueous ambient, or, alternatively, (ii) in the course of their preparation by LA. On Ag nanoparticle surfaces stabilized by weakly adsorbed anions, the porphyrin becomes readily metallated yielding Ag<sup>+</sup>-TMPyP surface species. By contrast, the native structure of the cationic f.b. porphyrin molecules becomes preserved in the case of their electrostatic bonding to molecular anions strongly bond to Ag nanoparticle surface. Finally, Ag(0)-TMPyP surface species have been identified on surfaces of Ag nanoparticles treated by chloride or thiosulphate anions. In the particular case of chloride-treatment, formation of Ag(0) adsorption sites is accompanied by formation of compact Ag nanoparticle aggregates with numerous “hot spots” [4]. In accord with our expectations, the SERRS spectral detection limit of Ag(0)-TMPyP in such a system is as low as  $1 \times 10^{-11}$  M (Fig. 1). The possibilities to employ the results of the surface probing for tailoring the Ag nanoparticle surface modifications for ultrasensitive detection of specific porphyrin surface species will be discussed.



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