



Detection of Polychlorinated Pesticides by Surface-Enhanced Raman Scattering on Silver Nanoparticles Functionalized with α,ω -Aliphatic Diamines

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Abstract –Silver nanoparticles (Ag NPs) were functionalized with linear α,ω -aliphatic diamines (AD) to improve the sensing ability towards organochloride pesticides. The AD/AgNPs combined system was previously characterized by plasmon resonance and Surface-enhanced Raman Scattering (SERS). SERS spectra provided the limit of detection and the interaction mechanism between diamines and pollutants were deduced.

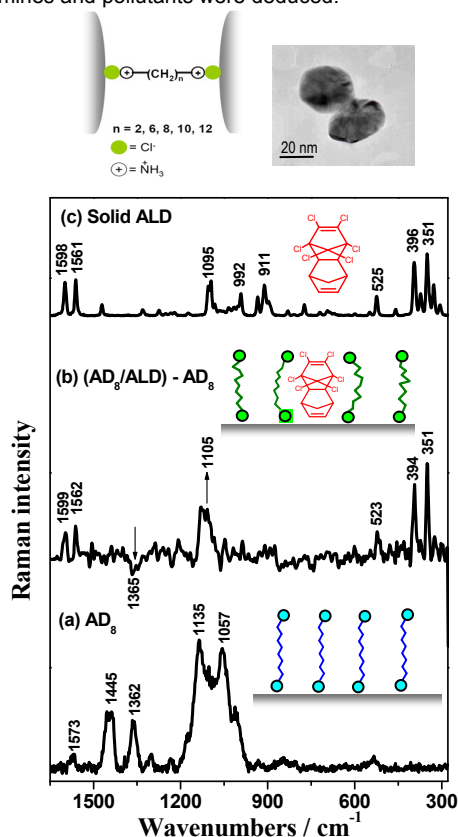


Figure 1: Top: NP-AD_n-NP interparticle HS induced by diamines and dimer formation. Bottom: SERS spectra of (a) AD₈ (10⁻³ M) and (b) AD₈/ALD (10⁻³ M/10⁻⁴ M) difference spectrum. (c) Raman spectrum of ALD in the solid state. All the spectra were recorded at $\lambda_{exc} = 514.5$ nm. [Inset] Schemes of the interaction of the pesticide aldrin with the interparticle cavities induced by the self-assembly of AD₈.

Surface-Enhanced Raman Scattering (SERS) is possible thanks to localized surface Plasmon resonance (LSPR) occurring in nanostructures metal surfaces inducing high electromagnetic field intensification in certain points or areas of the surface. This effect leads to a significant increase of the Raman cross section which makes this technique one of the most sensitive to detect pollutants and even single molecules [1]. The most effective locations for extremely high enhancements are interstitial sites of nanometer-scale between nanoparticles (NPs), named hot spots (HS). Therefore, the controlled fabrication of nanostructured junctions in SERS substrates is now a critical target in nanotechnology. An ideal situation for building interparticle HS is the use of bifunctional molecules which act as NPs linkers. The functionalization of silver NPs by bifunctional viologen dications gives rise to the formation of highly sensitive interparticle junctions by simultaneously creating intermolecular cavities (IC) where it was possible the approaching of pollutants, with low affinity toward the metal surface, near to these so-formed HS [2].

Another group of bifunctional molecules with promising properties in the creation of HS+IC sites are α,ω -aliphatic diamines (AD). The influence of these diamines on the NPs architecture could be interesting as these compounds can also act as linkers of NPs. In fact, these diamines are completely protonated in the colloidal suspension, presenting two positively charged nitrogen atoms at the side ends of the alkyl chains which are able to form ion pairs with the halide anions adsorbed on the metal surface. Besides, the coulombic repulsions between the amino head groups may result in the formation of cavities within the formed SAM. In addition, the use of these compounds as NP linkers and host molecules in the design of LSPR nanosensors could be advantageous because of

the relative weakness of their Raman features and their structural simplicity. In fact, the structure of AD is characterized by the existence of an aliphatic chain between two amino groups which length will determine the NP-NP interparticle distance (Figure1, top).

In this work a systematic analysis of the self-assembly of linear α,ω -aliphatic diamines with different length (AD_n where n = 2, 6, 8, 10 and 12; Fig. 1), on Ag metal surface was previously performed. One characterized this system we have applied it in the detection of polychlorinated pesticides, as it is illustrated in Figure 2, bottom, for the case of the pesticide aldrin (ALD).

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