Communication

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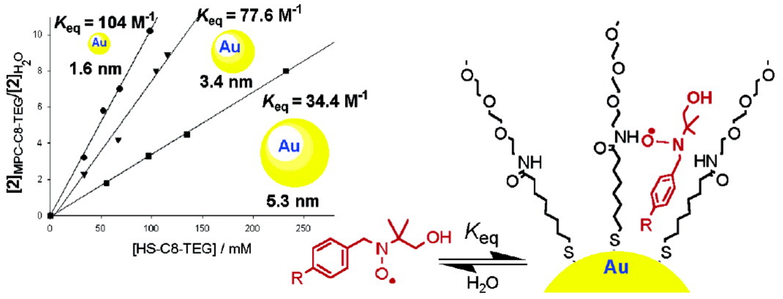

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Effect of Core Size on the Partition of Organic Solutes in the Monolayer of Water-Soluble Nanoparticles: An ESR Investigation

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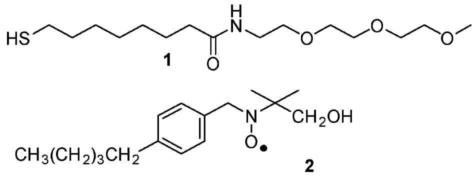
Organic thiols are known to interact strongly with gold nanoclusters, forming a passivating monolayer that stabilizes these nanostructures against their growth (monolayer-protected gold clusters, Au-MPC).[1] The physical and chemical properties of the thiols forming this monolayer dictate the solubility of Au-MPCs in a particular solvent and their interactions with solutes. Indeed, the passivating monolayer provides a pseudo-phase different from the bulk solvent in which molecules (or ions) may be hosted. Similarly to lipid membranes, water-soluble Au-MPCs featuring a monolayer made of thiols comprising a hydrophobic portion and a polar headgroup are able to host hydrophobic molecules with the important difference that the thiols are anchored on the surface of the gold nanocluster while membrane lipids are not. The packing of the thiols may be very tight, as demonstrated by phase transitions from an ordered gel to a partly disordered liquid crystal phase observed in the presence of a monolayer of Au-MPCs upon increasing the temperature.[2]

The size of the gold core affects many properties of Au-MPCs. These may be related to the core itself (i.e., optical properties) or to the monolayer.[1,3] However, a study of how the size of Au-MPCs affects the interaction of organic solutes with the monolayer has never been reported. In view of the use of functional Au-MPCs as nanozymes[4] (i.e., catalysts with enzyme-like properties) and, hence, of their ability to *bind* and subsequently modify a substrate, this appears to be a relevant issue. This communication specifically addresses this point.

ESR spectroscopy has been shown by us to be an excellent tool to monitor the partition of lipophilic nitroxides between the monolayer of water-soluble nanoparticles (MPC-C8-TEG) and bulk water.[5] The monolayer of these nanoparticles was made by thiol **1** comprising a short alkyl chain close to the Au surface and a triethylene glycol monomethyl ether unit. The results obtained with *para*-substituted benzyl hydroxyalkyl nitroxides have clearly demonstrated the inclusion of the nitroxide probes in the more hydrophobic environment of the monolayer. This is associated with large spectral changes of the hyperfine splitting constants, a(N) and $a(2\text{H}_\beta)$, due to the less polar environment experienced by the guest molecules when solubilized in the monolayer. The reduction of a(N) is due to the larger weight in lower polar environment of the monolayer of the nitroxide mesomeric forms in which the unpaired electron is localized on the oxygen rather than on the nitrogen atom.[6] The ease by which ESR spectroscopy is able to differentiate paramagnetic species experiencing different microscopic environments in solution prompted us to investigate the effect of the core size on the capacity of the monolayer to "bind" a organic radical probe.

Scheme 1



Gold nanoparticles protected by a monolayer of thiols **1** (HS-C8-TEG) of different size were prepared following reported procedures. Homogeneous-phase synthesis was used to prepare nanoparticles of 1.6 and 3.4 nm average core diameter.[7] For larger nanoparticles having an average core diameter of 5.3 nm, we followed the two-step procedure described by Brust.[8] The composition of these water-soluble MPCs was determined by TEM and thermogravimetric analysis (TGA) (see Supporting Information).[9]

The radical we have used in this study is the *para*-pentylbenzyl hydroxyalkyl nitroxides **2** that, because of the aliphatic chain, presents a large affinity for the organic monolayer. The nitroxides were generated directly inside an ESR tube by oxidizing the parent amine[10] (1 mM) with Oxone (1 mM)[11] in the presence of a variable amount of MPC-C8-TEG having different average Au core sizes ranging from 1.6 to 5.3 nm. In all cases, the spectra of **2** were characterized by the presence of additional signals, beside those due to the free species, which were attributed to the radical embedded in the MPC monolayer (see Figure 1). Inspection of Table 1 shows that the values of both a(N) and $a(2\text{H}_\beta)$ decrease when the aminoxyl is located in the less polar environment of the monolayer, remaining approximately constant by increasing the diameter of the Au core. This indicates that the polarity of the environment surrounding the nitroxide function is similar in all

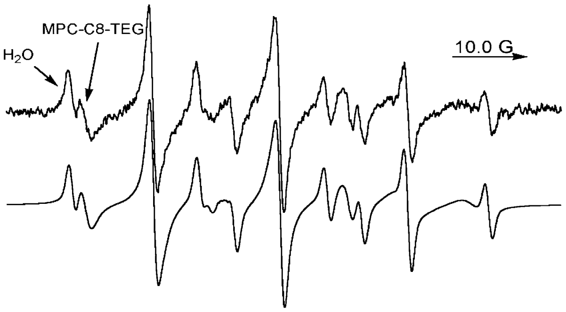


Figure 1. ESR spectrum of **2** recorded in the presence of 1.6 nm diameter MPC-C8-TEG (53.8 mg/mL) (top) and its computer simulation (bottom).

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Table 1. MPC Composition, ESR Spectral Parameters for **2** in Water and in the MPC Monolayer at 298 K, and Partition Equilibrium (K_{eq}) Constants

size (nm)	a(N) (G)	$a(2H_\beta)$ (G)	g-factor	HS-C8-TEG[a] (% w/w)	K_{eq} (M^{-1})[b]
in water	16.32	10.35	2.0056		
1.6	15.67	8.97	2.0057	41.2 (41.2)	104.0 ± 7.4
3.4	15.70	9.00	2.0057	22.1 (22.1)	77.6 ± 9.0
5.3	15.62	8.87	2.0057	14.0 (14.0)	34.4 ± 1.5

[a] In the monolayer, determined by TGA and TEM (ref 9); calculated values are in parentheses. [b] $T = 298$ K; errors refer to twice the standard deviation.

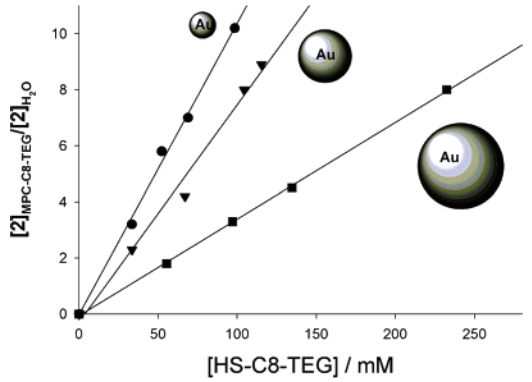

Figure 2. Plot of the ratio between the concentration of **2** partitioned in the monolayer and that of the free species (● 1.6 nm; ▼ 3.4 nm; ■ 5.3 nm) as a function of [HS-C8-TEG] bound to the gold.

cases, and that the N−O group is deeply inside the monolayer with the polar O−H group close to the hydrophilic region.[12]

The solubilization of the radical probes in the monolayer is also confirmed by the lower height of the high-field ESR lines of the complexed species, due to slower motion of the probe when it is bound to the monolayer.[13] By plotting the ratio between the concentration of the probe bound to the monolayer and that of the free species in water, obtained from the ESR spectra, against the concentration of HS-C8-TEG (Figure 2), the equilibrium constant, K_{eq}, for the partition of the probe between the two phases could be determined (see Table 1).

Inspection of these data clearly shows that the solubilization of the organic probe in the monolayer strongly depends on the nanoparticle diameter. In particular, K_{eq} increases as the nanoparticle diameter decreases. The decrease of the core size of the nanoparticle determines an increase in the corresponding radius of curvature and a decrease of the packing of the thiols chains upon moving away from the Au surface. Accordingly, it is conceivable that the thiol chains bound to the smaller nanoparticles experience a larger conformational freedom so that the accommodation of the hydrophobic guest requires a smaller energetic cost than that required in the presence of thiol chains bound to larger particles in which the monolayer is much more packed.

Our experimental results support those reported by Murray and co-workers who demonstrated that S_N2 reactions occur more readily on the surfaces of nanoparticles than on planar surfaces.[14] The headgroups of ω-bromoalkanethiolates are less densely packed on curved surfaces than they are on planar surfaces; this lower density allows backside attack of the incoming nucleophile (amine) to occur. The present results are also in accord with those recently reported by Workentin, showing that aryl ketones present on the monolayer of Au nanoparticles have a decreased reactivity in the Norrish type II photoreaction as the Au core size increases.[15] Moreover, the present data account for the solubility found in apolar solvents of nanoparticles made of thiol **1**.[7] Actually, smaller particles are more soluble than the larger ones because their hydrocarbon portion is more accessible for solvation by apolar molecules.

In conclusion, we have determined, for the first time, that the core size of metallic nanoparticles impart to the protective organic monolayer different solvating properties. In particular, by using ESR spectroscopy, we were able to measure the partition isotherms of an organic probe between an aqueous solution and the monolayer of water-soluble Au-MPC of different sizes. We thus confirm that ESR spectroscopy is a simple and powerful tool to investigate the binding properties of nanoparticles that are difficult to obtain by other techniques.

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Supporting Information Available: TEM and TGA analysis of the Au-MPCs used, some representative ESR spectra of **2**, detailed radical ratios determined from the ESR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) We have assumed an average composition of: $Au_{116}(SR)_{50}$ (MW = 38 852) for nanoparticles (NP) with an average core diameter of 1.6 nm, σ 0.3 nm; $Au_{1415}(SR)_{246}$ (MW = 357 475) for NPs with an average core diameter of 3.4 nm, σ 1.1 nm; $Au_{5093}(SR)_{510}$ (MW = 1 166 521) for NPs with an average core diameter of 5.3 nm, σ 1.0 nm (see Supporting Information).

(10) The amine precursor was obtained by reacting 2-methylalanine with p-pentylbenzoyl chlorides followed by reduction with 2 equiv of $LiAlH_4$ (see ref 5).

(11) We have previously demonstrated that the MPC-C8-TEG are quite stable under the oxidation conditions used to generate the nitroxides (see ref 5).

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