

# Design and Synthesis of Robust Calixarene-Capped Metal Clusters and Aggregates as Catalytically Active Structures

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## Introduction

While supported nanoparticles are ubiquitous in catalysis, unsupported and coordinatively unsaturated metal colloids with accessible surfaces are unstable due to their intrinsically high surface energy and tendency to sinter. Monolayer-protected nanoparticles exhibit an improved stability, but the densely-packed ligand shell layer that confers this stability also inhibits accessibility to the nanoparticle surface. As a result, monolayer-protected nanoparticles cannot be used for the catalysis in spite of their extraordinarily high surface area. Calixarenes have been previously suggested to be useful building blocks for synthesizing a stable porous layer on the nanoparticle surface, which may allow for small molecule accessibility through the layer because of the calixarene's robust bulky structure and large cavity [1].

## Materials and Methods

Tetraoctylammonium bromide (TOAB)-stabilized gold nanoparticles were prepared in a biphasic mixture of dichloromethane and water by reducing  $\text{HAuCl}_4$  with  $\text{NaBH}_4$  [2]. A ligand of 5,11,17,23,29,35-hexa(*tert*-butyl)-37,39,41-tris(diphenyl phosphinomethoxy)-38,40,42-trimethoxycalix[6]arene (**1**) was synthesized [3] and added to the TOAB-stabilized gold colloid solution to obtain **1**-capped gold nanoparticles. The gold nanoparticles were characterized using a UV-Vis spectrometer (Cary-400, Varian) and a transmission electron microscope (CM200, Philips, Lawrence Berkeley Laboratory). Gold nanoparticles capped with various concentrations of **1** were titrated with a naphthalene-based fluorescent probe (2NT) whose emission was characterized with a fluorimeter (F-4500, Hitachi).

## Results and Discussion

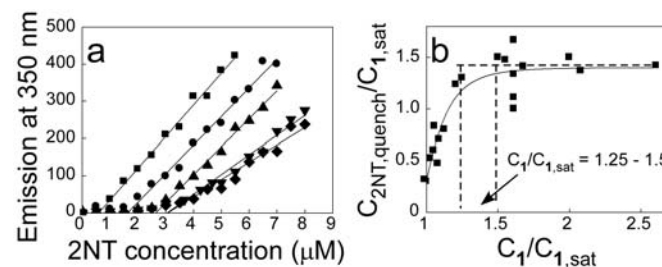
Gold nanoparticles saturated with **1** are highly stable compared with their corresponding TOAB-stabilized gold nanoparticles and those less saturated with **1**. The accessible surface of **1**-capped gold nanoparticles is proven via fluorescence of 2NT which quenches when it is bound to the gold surface [4]. As 2NT's fluorescence quenches when bound to the TOAB-stabilized gold nanoparticles, it quenches when added to the 4.0-nm gold nanoparticles saturated with **1** (Figure 1), which demonstrate the **1**-capped gold nanoparticles have a gold surface that can be accessed and bound to by 2NT. With increasing 2NT concentration,  $C_{2NT}$ , the excess 2NT unbound to the nanoparticles starts to exhibit the emission at a characteristic quenching concentration,  $C_{2NT, \text{quench}}$ , and the emission intensity increases linearly with  $C_{2NT}$ . With increasing the **1** concentration,  $C_1$ , the  $C_{2NT, \text{quench}}$  increases from 0.3 to 1.4 times  $C_{1, \text{sat}}$  at which the gold nanoparticles are saturated with **1**, and reaches the plateau at  $C_1/C_{1, \text{sat}} = 1.25 - 1.5$ . For  $C_{2NT, \text{quench}}/C_{1, \text{sat}} = 1.4$ ,  $\sim 30$  2NT molecules are bound to each nanoparticle, which indicates that  $\sim 720 \text{ \AA}^2$  of accessible surface exists on each 4.0-nm

nanoparticle or  $\sim 13\%$  of total gold atoms are exposed to the bulk solution when calculated on the basis of  $24 \text{ \AA}^2$  gold surface area per 2NT molecule bound to the gold foil [5]. Because **1** does not affect the fluorescence of 2NT and the  $C_{2NT, \text{quench}}$  reaches the plateau with increasing  $C_1$ , the increasing  $C_{2NT, \text{quench}}$  can be attributed to the geometry of **1** bound to the nanoparticle surface. While incomplete binding of calixarene to the nanoparticle has been suggested for the calix[4]arene [6], only one or two of **1**'s three phosphine groups may be bound to the nanoparticle when the excess **1** molecules are added. The mono- or bidentate geometry of **1** can make more accessible sites because **1** has a robust rigid structure and can form the shell layer with less close packing allowing the material transfer through the layer.

We have applied similar methods to gold clusters that have been recently synthesized in our research group, and also demonstrate accessible surface on these materials.

## Significance

We demonstrate the first accessible surface on calixarene-capped metal nanoparticles and  $\sim 1$  nm clusters, which presumably arises due to the steric bulk of the calixarene as a multidentate ligand on the metal surface.



**Figure 1.** (a) Representative subtracted emission of 2NT on gold nanoparticles capped with **1** for  $C_1/C_{1, \text{sat}} = 1$  (■), 1.25 (●), 1.5 (▲), 2 (▼), and 3 (◆), excited at 283 nm. (b) Saturation concentration of 2NT with varying **1** concentration. The concentration of gold atoms is 200  $\mu\text{M}$ .

## References

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