

In situ observation of place exchange reactions of gold nanoparticles. Correlation of monolayer structure and stability†

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Place exchange reactions were studied using dye displacement: subtle changes in ligand structure greatly affected both the rate of displacement and the stability of the monolayer.

Place exchange chemistry of monolayer protected gold (Au) nanoparticles offers an effective and generalized method to fabricate functional 3-D nanoscopic surfaces in a wide variety of applications, from functional materials to biological active agents.¹ A number of interactions are involved in this process, including gold–thiol interactions, incoming thiol–bound thiolate interactions, and incoming thiol–surface monolayer interactions. Although a complete understanding of place exchange is still being pursued, the reaction is now generally considered to follow an associative mechanism; an incoming thiol attaches to the surface and a bound thiol leaves the gold surface in a simultaneous process.² In addition, due to the inhomogeneous nature of the particle shape, and the surface monolayer packing, exchange reactions are initiated at surface sites where monolayer packing is less dense, such as the edges and vertices of the gold particles, and diffuse into the terrace places until an equilibrium state is reached.^{2,3}

Proton NMR has been the primary method to study ligand exchange reactions on gold nanoparticles.^{2,4} However, the surface bound thiol ligands are usually present as much broader peaks relative to free thiols, which makes it difficult to integrate accurately. The structures of the bound thiol and the incoming thiol have to be easily distinguishable in the NMR spectrum, which limits the scope of thiols that can be studied. In addition, the amount of material required for NMR is large (typically > 5 mg of gold cluster for one NMR experiment).⁵

We have explored the use of fluorophore-labeled gold nanoparticles, **Au-FI**, to provide a facile probe of place exchange reactions (Fig. 1). This method is based on the quenching of fluorophores by Au nanoparticles.⁶ The optical properties of the thiol-Bodipy ligand,⁷ including high quantum yield and excellent photostability, provide a stable probe for a ligand exchange process. The high sensitivity of this fluorescence-based method allows systematic study of place exchange with structurally similar thiols. It also enables the observation of the early stages of place exchange reactions, which is difficult in NMR based methods. In addition, since no sample separation was needed, the exchange

reactions were monitored in real time. We report here the details of this place displacement approach, along with correlation between dye release kinetics and the corresponding monolayer stability.

The labeling of Au nanoparticles (2.6 ± 0.5 nm core) was achieved through ligand exchange of pentanethiol-covered Au nanoparticles with thiolated Bodipy dye (see ESI). The coverage of the dye was quantified using ¹H NMR resulting in a *ca.* 1 : 1 ratio of Bodipy dye and pentanethiol ligand. The presence of dye on the nanoparticle surfaces was clearly observed in the UV-Vis spectrum of **Au-FI** as a pronounced peak around 500 nm, matching the absorbance of the dye molecule (Fig. S2). The absence of free dye molecules in solution was further confirmed by ¹H NMR, as no sharp peaks of the fluorophore ligand were seen.

Three groups of thiols were chosen to study place exchange with the dye-labeled nanoparticles **Au-FI** (Fig. 2a). Group A includes thiols attached to primary, secondary and tertiary carbon atoms; Group B features linear and branched thiols; and Group C probes the effect of thiol chirality on place exchange reactions. In each group, the numbers of carbon atoms are identical, thus giving identical molecular weight of the thiols. It should be noted that the general lack of distinctive NMR peaks made these exchange processes difficult to study by a traditional NMR integration method.

In a typical experiment, thiol (final concentration 10 mM) was added to a methylene chloride solution of **Au-FI**, with a Bodipy concentration of $\sim 6 \mu\text{M}$ ⁸ and the solution was kept at 23 °C. The place exchange reaction was monitored by dye release from the nanoparticles, and the concomitant increase of fluorescence signal. The emission intensity at 507 nm was plotted against the reaction time as shown in Fig. 2b–2d.

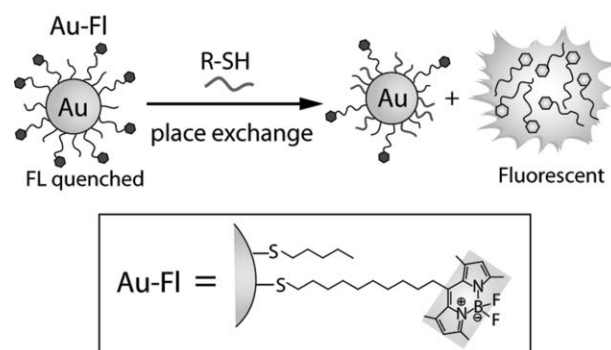


Fig. 1 Schematic depiction of place exchange on fluorophore-labeled gold nanoparticles, **Au-FI**.

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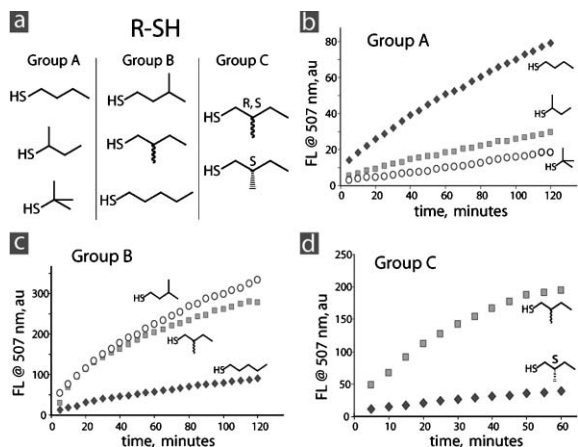


Fig. 2 a) Chemical structures of the thiol ligands; b), c), and d) place exchange of dye-labeled nanoparticles with three groups of thiols. The fluorescence intensity at 507 nm was plotted against reaction time.

The displacement of Bodipy by Group A thiols clearly showed that the primary thiol is more active than the corresponding secondary and tertiary thiols (Fig. 2b), demonstrating that steric hindrance near the thiol group significantly reduces its reactivity in place exchange reactions.⁹ Surprisingly, when the bulky group is removed from the thiol group by one carbon (Group B), the branched (bulkier) thiol exhibited higher activity than the linear thiol of the same molecular weight (Fig. 2c).

The enhanced activity of branched thiols can be rationalized by considering that place exchange, especially in the initial stages, predominantly takes place at the vertices and edges of the cluster, where the surface monolayer is not densely packed. These loose monolayer sites are open enough to accommodate the branched thiols in Group B. In addition, the branched thiols, once attached to the gold surface, may pack better than linear ones. This is supported by previous cyanide decomposition experiments showing that branched thiols form a more stable monolayer than the linear ones.^{2b} Furthermore, the branched thiol may also occupy more space on the cluster surface than the linear one, thus serving to destabilize the surrounding bound thiol more efficiently.

In addition to the above results, quite subtle changes in incoming ligand structure can have profound effects on the rate of displacement. For example, the rate of dye release by a racemic thiol mixture was dramatically faster than that of the homochiral thiol (Fig. 2d), an effect that to our knowledge has not been observed before. Given the identical chemical activity of the homochiral and the racemic thiols, the difference in displacement must arise from differences in the monolayer thiol packing.

Thermogravimetric analysis (TGA) was used to examine the stabilities of gold nanoparticles made with C5 thiols to determine whether the observed kinetic differences were manifested in monolayer stability. In all cases, a sharp transition in the TGA curve was recorded, corresponding to the cooperative loss of thiol ligands from nanoparticle surfaces. From the derivative thermogravimetric peaks (Fig. 3a) it is clear that the branched thiols from Group B form more stable monolayers than the linear isomer. Furthermore, the racemic homochiral thiol 2-methyl-1-butanethiol forms a more stable monolayer than the corresponding homochiral *S*-2-methyl-1-butanethiol. The TGA results provide possible

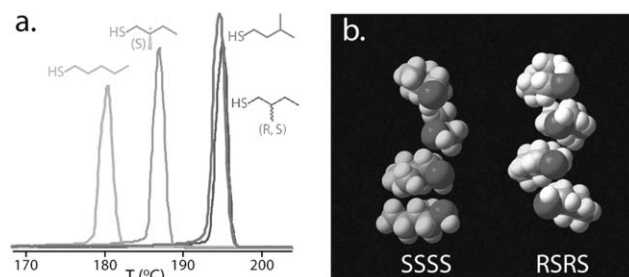


Fig. 3 a) Derivative thermogravimetric peaks of C5 thiol capped gold nanoparticles; and b) comparison of thiol packing between chiral (SSSS) and racemic mixture (RSRS) by molecular simulation of four thiol molecules constrained in a linear fashion.

thermodynamic insight into the dye releasing difference: in this study thiols exhibiting higher activity in place exchange reactions also form a more stable monolayer on Au nanoparticle surfaces. Further study will be required to establish the generality of this observation.

A simplified packing model was used to correlate the structures of homochiral and racemic 2-methyl-1-butanethiol monolayers with the observed differences in stability. The thiol atoms of a four-thiol cluster, *SSSS* and *SRSR*, were constrained with fixed distance (4.2 Å)¹⁰ in a linear fashion to simulate the spacing of Au atoms at the particle surface (Fig. 3b, see ESI). It is apparent from this simple model that the racemic mixture can form a zig-zag type structure that packs more efficiently than the analogous homochiral thiol.

In summary, fluorophore (Bodipy)-labeled nanoparticles were used to probe ligand exchange reactions of Au nanoparticles *in situ*. Combining displacement and TGA results, it is clear that both kinetic and thermodynamic factors play a role in place exchange reactions. The high activity of branched thiols in ligand exchange, and the high stability of the corresponding monolayer may be utilized to enhance nanoparticle monolayer stability. In addition, the findings on chiral thiols aid in better understanding of nanoparticle monolayer systems, and provide opportunities to construct monolayers of desired properties.

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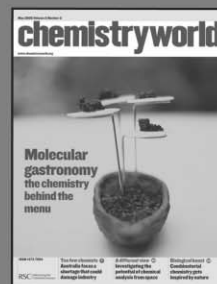
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