

Photophysical Behavior of Various Sized Colloidal Gold Clusters Capped with Monolayers of an Alkylstilbenethiolate

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trans-4-(Mercaptoheptoxy)stilbene (**S₇-SH**) was capped as a monolayer on colloidal gold clusters of diameters ranging from 1.4 to 5.2 nm. The resulting shell–core nanostructured composite showed emission from the metal and the appended arene. Differential surface area, rather than gold cluster size per se, accounted for the observed decreases in fluorescence intensity of the excited stilbene moiety upon shrinking the metal core size. Tight packing by an organic monolayer bound to the surface of the Au core was achieved most easily on large composite particles, whereas thiolatestilbene **S₇-SH** groups bound to the surface of the smallest metal clusters were found to be conformationally more labile.

Introduction

A thorough knowledge of the photochemical activity of self-assembled monolayers (SAMs) of functionalized organic thiols on noble metal surfaces is required in order to develop novel optical and electronic materials^{1,2} responsive to surface adsorption. In particular, the synthesis of monolayer-protected Au nanoparticles in organic solutions by Brust² and co-workers³ has opened a new route to the characterization of functional SAMs capped on Au clusters.^{4–7} These substrates can serve as valuable model compounds that can characterize perturbations of excited-state reactivity for probe molecules bound or adsorbed to nanoscaled metal clusters. Understanding these interactions is important if optical signaling is to be employed in metal-based fluorescent sensors.

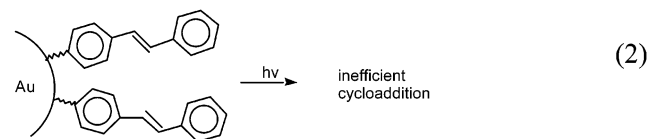
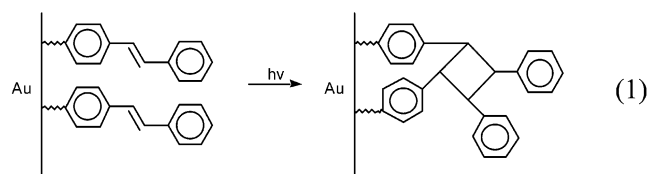
Unlike the organization of a densely packed monolayer achieved on a flat support, a thiol-capped Au cluster may exhibit high surface curvature, a high density of step edges, and an abundance of small metal facets, which can produce relatively loose packing of the thiols bound to the cluster.^{6b} Thus, cluster size is a crucial factor in controlling the topography and physical properties of composites in which thiols are bound at the surface of a metal cluster. When the diameter of the Au core is 5 nm, a cluster has roughly the dimensions of a rounded cube with 16 atoms on an edge; when the diameter is 1 nm, a cluster has roughly the dimensions of a rounded cube with an average of three atoms on an edge.

Stilbene is a chromophore known to be sensitive to its molecular environment, both in solution and in the solid state.^{12,13} Previous research in our group revealed that the *trans*-to-*cis* photoisomerization of a cyano-substituted stilbenethiol **NC-S₁₀-SH** as a monolayer on planar gold is blocked because



of restricted motion in the highly crystalline, densely packed monolayer.^{2d} In contrast, photochemical geometric isomerization

of a stilbene group present at the outer edge of a less densely packed monolayer on a core metallic cluster can readily take place. This difference was rationalized as a consequence of conformational flexibility permitted by loose association of adjacent thiols bound to the Au nanoparticulate core.^{6a,8} Differences in surface packing density also result in quite different photoreactivity toward dimerization in alkenes present in monolayers on planar gold arrays or as encapsulating layers on clusters. Thus, the tightly packed, π -stacked stilbene moieties present in a monolayer densely packed on a planar gold array efficiently participate in photodimerization to [2 + 2] cycloaddition product, eq 1, whereas only 15% of the stilbene moieties in a monolayer capping a gold nanoparticle (diameter = 2.5 nm) are sufficiently well-ordered to participate in photodimerization,⁹ eq 2, even with very long radiation periods. To better understand such subtle effects, we have undertaken here a further investigation of photoreactive organic monolayers covalently bound to the surface of metallic clusters of variable size.



The synthesis of relatively monodisperse alkanethiolate-protected metal clusters with diameters ranging from 1.3 to 5.6 nm has been reported.¹⁰ Very small clusters (<~50 metal atoms) capped by nonabsorptive thiols act like large molecules, and the optical properties of the metal cluster, including the intensity and absorption maximum of its surface plasmon band, have been strongly correlated with its size.¹¹ We are interested in the selective synthesis of monodisperse shell–core organic–inorganic composites in which a probe molecule is attached to

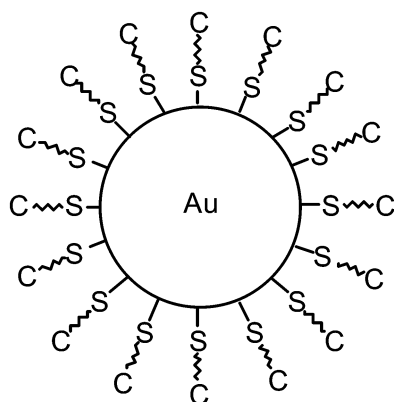


Figure 1. Schematic view of a gold nanoparticle encapsulated by an organic thiol bearing an absorptive chromophore C. The curved line represents an alkyl chain of undefined length and C represents a general chromophore.

TABLE 1. Preparation Conditions of Stilbenethiolate S₇-SH-Au Clusters and Diameters of the Metallic Cores

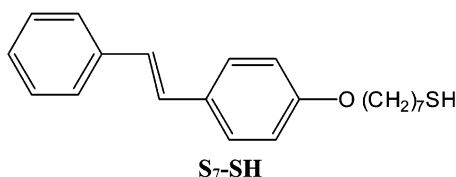
	no. 1	no. 2	no. 3	no. 4	no. 5	no. 6
thiol:HAuCl ₄	1/1	1/2	1/4	1/8	1/12	1/16
diameter of core (nm)	1.4	1.8	2.5	3.5	4.4	5.2
total Au atoms ^a	116	225	459	1289	2951	6299
surface Au atoms ^a	96	140	234	482	876	1472
thiolate stilbene number ^b	55	76	105	209	391	558
coverage, % ^c	57	54	45	43	45	38

^a Cited from ref 10 according to the corresponding core size.

^b Calculated from the mole ratio of Au/stilbene by referencing the total Au atoms number of (a). ^c Calculated from thiol atom/surface Au atom.

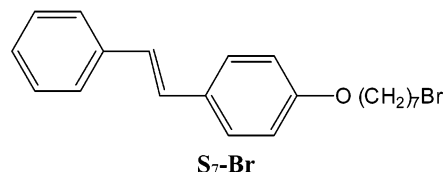
the organic shell that encapsulates the metallic core, Figure 1. Emission from the attached chromophore and from the metal plasmon band can then be used to define electronic interactions across the inorganic–organic interface. In these investigations, we wished to determine whether the size of the core nanoparticle might influence the efficiency of interfacial electronic coupling.

Monitoring the efficiency of excited-state reactivity of a stilbene present at the periphery on an organic encapsulant on a gold cluster will provide valuable information about the optoelectronic characteristics of these novel photoresponsive shell–core nanoparticles. In this paper, a series of stilbene-thiolate-protected Au clusters **1–6** (see Table 1), in which a gold cluster of 1–5 nm is capped by an alkylstilbene thiol **S₇-SH**, are examined spectroscopically with a focus on the dependence of the fluorescence intensity of an attached stilbene on the internal metal cluster core size.



Experimental Section

Chemicals. Chemical reagents (Aldrich) were used as received. All solvents were spectroscopic grade (Fisher or Aldrich). Water (MilliQ) used in the colloidal gold synthesis had a resistance of higher than 4 MΩ. Commercial solvents were used without further purification. Deuterated solvents were obtained from Isotech and Aldrich. *trans*-4-(Mercaptoheptoxy)-stilbene (**S₇-SH**) was prepared from the corresponding bromide **S₇-Br** as described earlier.⁹



Preparation of Clusters. The syntheses of monodisperse gold clusters of various sizes capped with a densely packed layer of **S₇-SH** were achieved by a standard procedure that changed the molar ratio of **S₇-SH** to HAuCl₄·3H₂O in the synthesis mixture.^{3,10} To a vigorously stirred solution of 0.5 g of tetraoctylammonium bromide (2 equiv) in 20 mL of toluene was added 0.06 g of HAuCl₄·3H₂O (1 equiv) in 5.0 mL of deionized water. The yellow HAuCl₄ aqueous solution became clear, and the toluene phase became orange-brown as the ion pairs were transferred interfacially. The organic phase was isolated, the desired amount of thiol was added, and the resulting solution was stirred for 10 min at room temperature. The resulting solution was then vigorously stirred as NaBH₄ (0.08 g, 10 equiv) in 5.0 mL of deionized water was added over a period of 5 min. The dark organic phase was further stirred at room temperature for 12 h. The organic phase was collected, and the solvent was removed under vacuum. The black solid was suspended in 30 mL of ethanol, collected on a 0.2 μm membrane filter, and washed with ethanol and acetone. The purity of the capped cluster was monitored by ¹H NMR and absorption spectroscopies. After the solvent was evaporated, the thiol-coated cluster was redissolved in CH₂Cl₂ or CHCl₃.

Identical results were obtained if longer reaction times (48 h) were employed.

Spectra. ¹H NMR spectra were recorded on a Varian UNITY plus-300 spectrometer at room temperature by using CD₂Cl₂ as solvent. The clusters were dissolved in CH₂Cl₂ to produce a 10^{−5} M solution of the stilbene moiety. The resulting solution was deaerated by bubbling with Ar for 15 min. Absorption spectra were monitored with a Shimadzu 3101PC spectrophotometer; emission spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

Transmission Electronic Microscopy (TEM). Samples for TEM were prepared by casting 1 drop of ~1 mg/mL cluster solution in CH₂Cl₂ onto standard carbon-coated Formvar films (20–30 nm) on copper grids (200 mesh, SPI) and drying in air. Phase-contrast images of the particles were obtained with a Topcon 002B electron microscope operating at 120 keV. Size distributions of the Au cores were measured from enlarged TEM image photographs for about 200 individual cluster core images.

Results and Discussion

A standard route to thiol-capped colloidal gold clusters involves treatment of a dilute HAuCl₄ solution with sodium borohydride in the presence of the capping thiol.³ Although the temperature and rate of addition of reductant have been used to control the particle size of the cluster,¹⁰ we conducted our synthesis at constant temperature and mixing rates and controlled the size of the colloidal gold cluster by varying the molar ratio of stilbenethiolate **S₇-SH** to HAuCl₄. Six differently sized metal cores were obtained in this way (the corresponding metal core diameters of these six clusters are listed in Table 1). TEM measurements showed that when the molar ratio was varied from 1:1 to 1:16, the Au core diameter increased from 1.4 to 5.2 nm, Figure 2. The clusters can be redissolved in CH₂Cl₂ or CHCl₃, with solubility decreasing in the series upon increasing size of the Au core. No spectral evidence for further aggregation upon redissolution was evident.

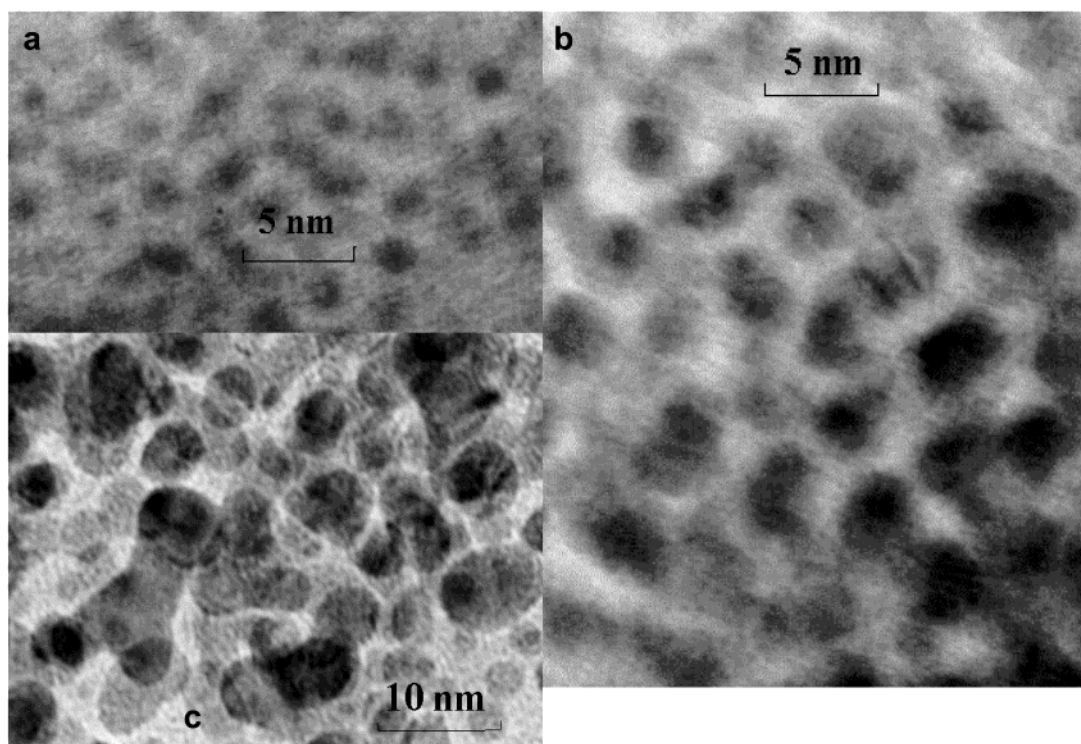


Figure 2. Transmission electron micrographs of films cast by (a) cluster **1**, (b) cluster **3**, and (c) cluster **6**. (The sizes of these clusters are defined in Table 1.)

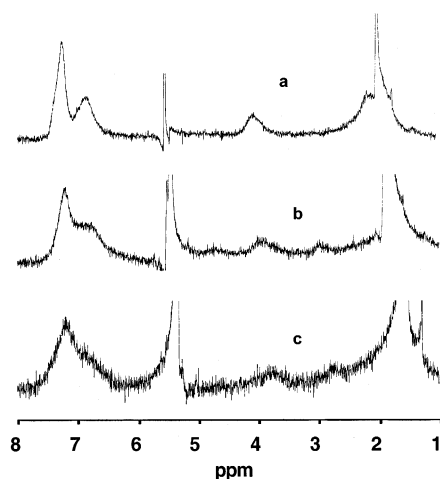


Figure 3. ^1H NMR spectra of (a) cluster **1**, (b) cluster **3**, and (c) cluster **4** in CD_2Cl_2 . (The sizes of these clusters are defined in Table 1.)

Because the solubility of the largest cluster **6** was poor in organic solvents, ^1H NMR spectra of only the smaller clusters could be obtained, Figure 3. In these shell–core composites, adsorptions from the stilbene moieties are broadened, indicating that the bonded thiol was packed in a gel-like state on the gold surface and that the motions of the end groups are severely restricted.¹⁴ Even more significant broadening was observed in the larger clusters, as is consistent with tighter packing on those surfaces with lower curvature. Although tetraoctylammonium bromide was present in the organic phase as phase transfer catalyst in the syntheses, no detectable amount of residual tetraoctylammonium bromide (less than 5 molar %) remained on the capped composites after washing, as judged by the integration of the broadened peak evident at high field. Thus, emission quenching of the excited stilbene by dissolved bromide ion, whether in solution or bound to the metal cluster (see below), can be neglected.

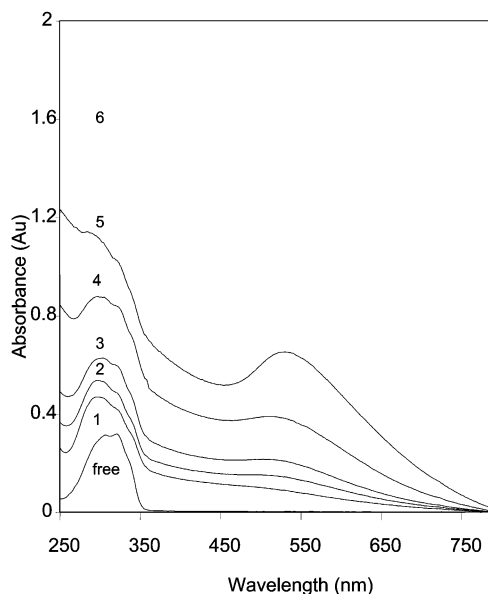


Figure 4. Absorption spectra of clusters **1–6** (see Table 1) and unattached bromide **S₁-Br** (1.0×10^{-5} M) in degassed CH_2Cl_2 .

The clusters **1–6** displayed a π, π^* stilbene transition in their absorption spectra at 300 nm, which is blue-shifted from that of unattached compounds **S₇-SH** or **S₇-Br** (at 307 nm), and a broadened plasmon band with a maximum near 530 nm, Figure 4.⁹ The amount of stilbene bound as a capping monolayer on each Au core was estimated by the change of concentration of uncapped stilbene in solution before and after cluster formation (see Experimental Section). All the clusters **1–6** have nearly identical absorbance at the maximum for stilbene, implying an identical concentration of stilbene (1.0×10^{-5} M).

The absorption from the capped stilbene moieties in clusters **1–6** is also accompanied by that of the Au core, which has significant absorption in the 300–400 nm wavelength range,

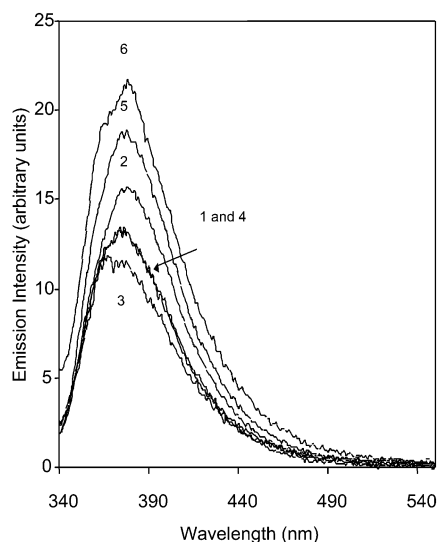


Figure 5. Fluorescence spectra of clusters **1–6** (1.0×10^{-5} M, defined in Table 1) in degassed CH_2Cl_2 .

Figure 4. A resolution of the separate spectral contributions of the two absorbing units, based on the emission intensity of unattached chromophore, **S₇-SH** or **S₇-Br**, in various concentrations of Au clusters protected with hexanethiol, could be obtained by correcting for the corresponding absorption from the analogous shell–core cluster of the same gold size prepared from dodecanethiol¹⁵ rather than stilbene **S₇-SH**. By subtracting the absorption spectrum of a same-sized hexanethiolate cluster from that of the stilbene-capped clusters in Figure 4, we can obtain the spectra assigned to the stilbene.

For clusters **1–6**, the absorbance intensity of the gold plasmon band is enhanced significantly upon increasing the gold core size, large clusters having been obtained from solutions with higher molar ratios of Au:thiol.¹⁰ Although the intensity of the plasmon band increases with particle size, its peak position does not change in this series. Because the driving force for electronic coupling that likely leads to quenching remains constant within this series, differential quenching must reflect differences in surface packing or surface energy rather than energetic differences in the capping layer or metal core size.

When the clusters were photoexcited at 300 nm, fluorescence was observed at 378 nm (Figure 5), slightly red-shifted from that observed for the homogeneously dispersed but unattached compound **S₇-Br** in CH_2Cl_2 (at 373 nm). According to Whitten and co-workers, the red-shift of a stilbene emission can be ascribed to aggregation of the aromatic moieties by π -stacking.¹³ When the stilbene concentration was normalized to 10^{-5} M, the observed fluorescence quenching can be calculated as a function of cluster size.

The emission intensity of a monolayer-protected cluster of capped stilbene thiol on colloidal Au was roughly 10-fold lower than that of the corresponding free (unattached) stilbene **S₇-SH** at an equivalent concentration. This lower emission intensity is as expected from strong electronic coupling between the excited chromophore and the metallic core.¹⁶ The emission intensity at 378 nm generally decreased upon shrinking the size of the Au core (Figure 5), except in clusters **3** and **4**.

In a control experiment, the emission intensity at 378 nm of a solution containing a constant concentration (10^{-5} M) of bromide **S₇-Br** decreases with increasing concentration of a 1.2 nm hexanethiol-protected cluster, Figure 6. Thus, a dissolved stilbene can be quenched by a separate capped cluster when both are present in a homogeneous solution.^{17a} Much weaker

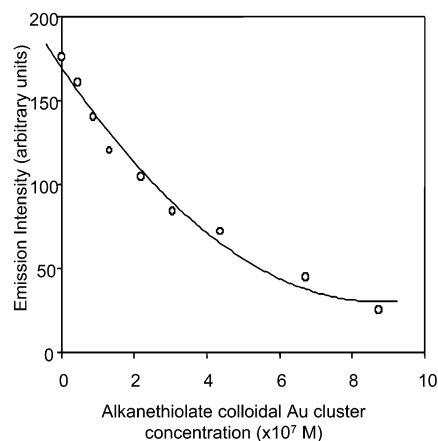


Figure 6. Dependence of the emission intensity of bromide **S₁₀-Br** (1.0×10^{-5} M) at 378 nm on the concentration of hexanethiol-protected Au cluster in degassed CH_2Cl_2 .

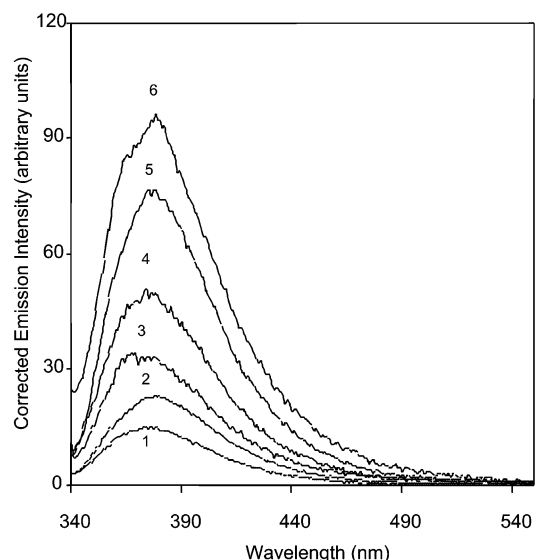


Figure 7. Corrected fluorescence spectra of clusters **1–6** (1.0×10^{-5} M, defined in Table 1).

quenching was observed, however, for the corresponding 5.2 nm capped cluster, presumably because of tighter surface packing of the thiols bound on the larger facets.

We can correct quantitatively for reduction in emission intensity deriving from the gold cluster itself by subtracting the absorption spectrum of a hexanethiol-protected cluster absorbance at the excitation and emission wavelengths.¹⁵ The corrected fluorescence spectra show that the observed emission intensity at 378 nm for the capped clusters increases monotonically upon increasing the size of the Au core, Figure 7. However, although the absorbance coefficients of Au clusters **1–6** do change with core particle size, the positions of their absorption maxima do not shift significantly, Figure 4. The observed absorption is thus calculated to be proportional to the size-dependent surface area in clusters **1–6**, establishing that the magnitude of fluorescence quenching by the Au core is roughly independent of the core size.

There are two possible factors that can affect the emission intensity of chromophores capped on Au clusters of different particle sizes: (1) changes in quenching efficiency by differently sized Au cores and (2) differences in local packing status of the appended thiol present on the surface of the Au nanoparticle. Fluorescence intensity of chromophores capped on the surfaces of differently sized Au clusters can be considered as deriving

from an oscillating excitation dipole, and an image electron–hole pair can be induced by generation of an excited state near the surface of the metal.^{17b} Hence, the emission intensity can be affected by the potential of the metal surface to which a chromophore is attached.¹⁸ Since no changes were attributable to different gold cluster size (apart from surface area effects), the observed change in fluorescence intensity of terminal stilbene for clusters **1–6** thus can thus be ascribed to local conformational flexibility of the stilbene chromophore bound on its surface.

The ¹H NMR spectra (described above) indicated that the terminal stilbene units on small Au cores experience substantially greater freedom of motion than those on larger Au cores.¹⁴ In addition, core sizes established from the respective TEM images give the total number of gold atoms in the cluster and the number of surface Au atoms per particle.¹⁰ From the mole ratio of stilbene/Au in the clusters, the number of thiolate stilbene per particle was obtained, Table 1. The numbers of surface thiols calculated in this way agreed with that obtained for hexanethiol clusters obtained from TGA measurements.¹⁰ The calculated ratio of thiolate stilbene/surface Au atom decreased as the core size was increased, indicating that more thiols were capped on edges and corners in the small clusters. The fraction of the surface gold atoms in the large cluster was 38%, close to that reported earlier for 2D SAMs (33%). Therefore, we conclude that monolayers bound to small metal clusters are more flexible, while those bound to large clusters are more tightly packed. The thermal motions allow chain folding that brings the chromophores closer to the Au core so that the excited chromophore can be quenched by the metallic core via energy transfer through space, which will lower the observed fluorescence emission intensity.¹⁵ The decrease in fluorescence intensity from the attached stilbene moieties in clusters **1–6** upon shrinking the core particle size can thus be ascribed to decreases in local order of the surface-bound thiols on the surface of the smaller Au core, rather than to different efficiencies for quenching for differently sized shell-core composites.

Conclusions

We have prepared a series of differently sized gold clusters capped by *trans*-4-(mercaptoheptoxy)stilbene (**S₇-SH**) by modifying the molar ratio of thiol **S₇-SH** to HAuCl₄ during its reductive preparation. TEM measurements show that the metal core sizes range from 1.4 to 5.2 nm. The ¹H NMR spectra of these shell–core composites were broadened, indicating that the bonded thiols were packed in a gel-like state on the gold surface and that motions of the appended chromophore end groups were severely restricted, with tighter packing observed with the larger clusters.

A blue-shift of the π,π^* absorption and a red-shift of the fluorescence of the composites can be ascribed to aggregation of the bound stilbene thiol moieties by π stacking. When the attached stilbene thiol completely covers the metallic core, the absorbance of the plasmon band is significantly enhanced upon increasing the core size. The emission intensities of the clusters were much less intense than that of a solution of the analogous unattached stilbene thiol or stilbene bromide at a nearly equivalent concentration in the presence of a similarly sized alkane-thiol-protected cluster. The efficiency of electronic coupling between the metal core and the attached stilbene was thus independent of the size of the Au core, after an appropriate correction for differential surface area was taken into account. Differences in emission intensity were explained by variance in conformational freedom of the attached thiols along the series.

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