

Competitive Photochemical Reactivity in a Self-Assembled Monolayer on a Colloidal Gold Cluster

Jun Hu, Jian Zhang, Fang Liu, Kevin Kittredge, James K. Whitesell,* and Marye Anne Fox*

Contribution from the Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

Received August 25, 2000. Revised Manuscript Received November 29, 2000

Abstract: A shell–core cluster **2** produced by depositing a self-assembled monolayer (SAM) of 6-thiohexyl-3-nitro-4-(4'-stilbenoxymethyl)-benzoate (**1**) on a nanoparticulate gold colloid preserves normal solution-phase photoreactivity of the *trans*-stilbene and *o*-nitrobenzyl ether moieties, but shows quenched fluorescence. Nearest-neighbor aggregation is weaker for **1** bound to the roughly spherical colloidal gold particle (in cluster **2**) than for analogous stilbenoids bound to a planar gold surface. Unlike the observed photochemical reactivity of stilbenylalkyl sulfides appended as SAMs on planar gold surfaces, the chromophores present in these shell–core nanocomposites **2** exhibit efficient *trans*-to-*cis* photoisomerization and blocked [2 + 2] photodimerization. Wavelength selectivity for photoisomerization and photocleavage proved to be elusive, but triplet sensitization of the geometric isomerization took place without photorelease of the attached group.

Introduction

The design, synthesis, and characterization of surface-modified nanoparticles are of fundamental importance in controlling the mesoscopic properties of new materials and in developing new tools for nanofabrication.^{1–4} Self-assembled monolayers (SAMs) of thiolates on colloidal gold clusters are therefore ideal substrates for investigating nanoparticle micro-fabrication techniques and the effect of surface-bound reagents on structure–property relationships.^{5–7} Although the materials properties of metal clusters capped by simple alkyl thiols have been described,⁸ photochemical characterizations of the supra-molecular structures of these capped nanoclusters are rare. This situation may reflect a general belief that the metal cores of such composite clusters may quench the appended excited states or otherwise complicate the observed photochemical and photophysical properties of the photosensitive capping reagent.

Recently we reported the photoreactivity of several chromophores bound as a SAM at the end of a long-chain alkyl spacer bearing a terminal thiol as an anchor on a planar gold film. In particular, we observed efficient photoisomerization of stilbene and photodimerization of attached stilbenes, coumarins, and anthracenes.^{9–11} These reports show that it is, indeed, possible to generate sufficiently long-lived excited states in SAMs functionalized with photoreactive moieties that effective photo-

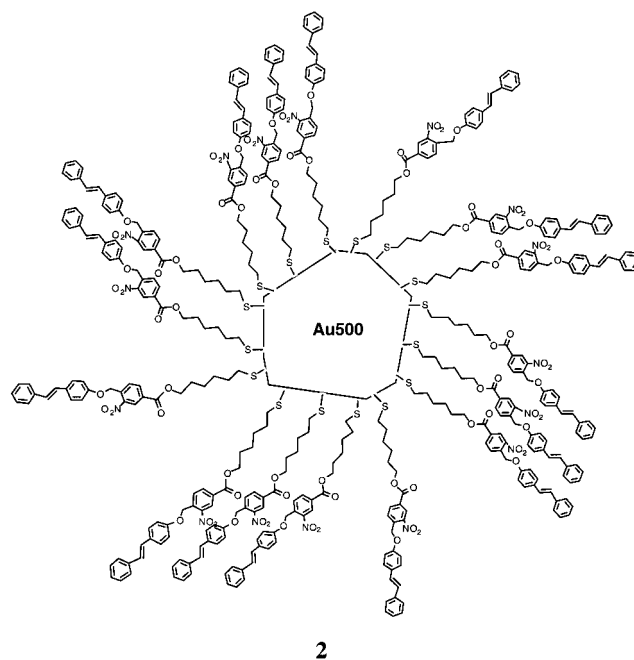


Figure 1. Schematic representations of a organic shell–metal core composite, illustrated with cluster **2**.

chemical modification of the metal–dielectric interface can be observed. They also demonstrate that photochemistry can be a useful tool in characterizing the local environment of covalently attached molecules present as monolayers on metal surfaces.

We report herein the photochemical reactivity of a shell–core nanocluster, Figure 1, in which an outer organic sphere of 6-thiohexyl-3-nitro-4-(4'-stilbenoxymethyl)-benzoate (**1**) caps a

(1) Fendler, J. H. *Chem. Mater.* **1996**, *8*, 1616.

(2) Qin, D.; Xia, Y.; Xu, B.; Yang, H.; Zhu, C.; Whitesides, G. M. *Adv. Mater.* **1999**, *11*, 1433.

(3) Letsinger, R. L.; Elghanian, R. V. G.; Mirkin, C. A. *Bioconjugate Chem.* **2000**, *11*, 289.

(4) Watson, K. J.; Zhu, J.; Nguyen, S.-B. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 462.

(5) Brousseau, L. C.; Zhao, Q.; Shultz, D. A.; Feldheim, D. L. *J. Am. Chem. Soc.* **1998**, *120*, 7645.

(6) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735.

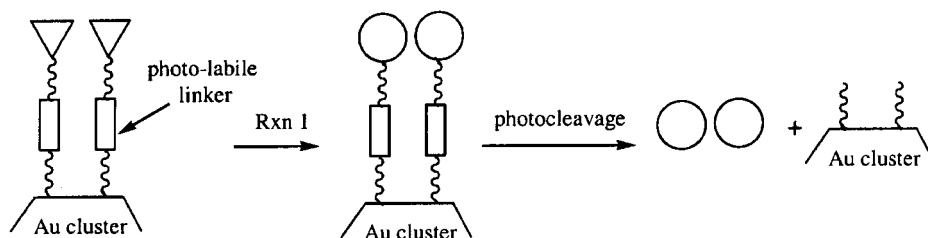
(7) Hayat, M. A., Ed. *Colloidal Gold: Principles, Methods, and Applications*; Academic Press: San Diego, 1991.

(8) Dai, H. L.; Ho, W., Eds. *Laser Spectroscopy and Photochemistry on Metal Surfaces*; World Scientific: Singapore, 1995; Parts I and II.

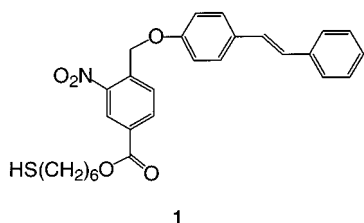
(9) Wolf, M. O.; Fox, M. A. *J. Am. Chem. Soc.* **1995**, *117*, 1845.

(10) Li, W.; Lynch, V.; Thompson, H.; Fox, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 7211.

(11) Fox, M. A.; Wooten, M. D. *Langmuir* **1997**, *13*, 7099.

Scheme 1. Photolysis To Release a Bound Reagent from a Covalently Bound Surface

metallic core comprised of colloidal gold of a defined dimension. This molecule is designed to use the metallic support to

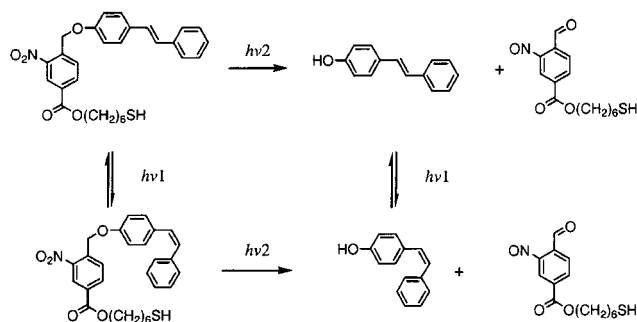
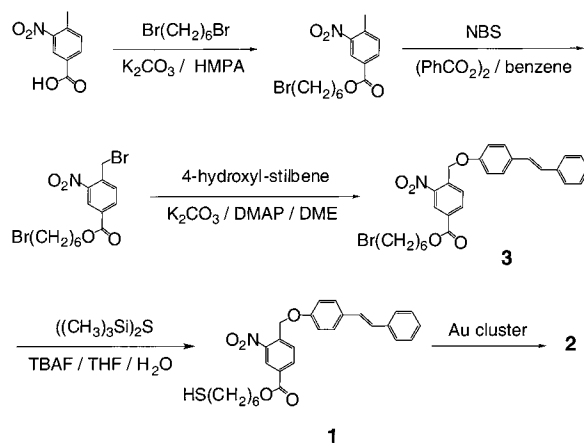


influence nearest-neighbor interactions and to include a photo-cleavable group that will release, in controlled fashion, the cluster-derived photoproduct formed under the influence of the surface bound reagents, Scheme 1. The insertion of a photolabile group also allows for easy separation of the photoproduct from the support.

By conducting these photolyses on a capped cluster rather than as a SAM on a planar surface, we can produce photoproducts in preparative quantities, and, hence, their structures can be compared with those of photoproducts derived from the same substrates when irradiated in homogeneous solution. Shifts in product distribution attained on this metallic cluster, rather than as a SAM on planar gold, can thus provide valuable information about local packing differences on these two- and three-dimensional arrays.

The stilbenoid end group was used as a photochemical probe of the relative efficiency of *trans*–*cis* isomerization^{4–6} and of [2 + 2] photodimerization.^{6,12,13} In particular, the [2 + 2] photoreaction is known to be a sensitive probe for the solid-state packing of stilbenoids in a crystalline solid,¹⁴ in a microemulsion,¹⁵ as an inclusion complex,¹⁶ or in a Langmuir–Blodgett film.¹⁷ We thus hoped that these photochemical investigations of capped metal clusters might provide new insight into the influence of the orientation of the appended chromophore on the cluster surface relative to that observed on a flat metal surface. If so, the extent of photodimerization might clarify the proximity of chromophores present in the organic shell.

The absorption maximum of the 3-nitrobenzyl ether group (at 240 nm) is significantly shifted from that of the *trans*-stilbene group (at 300 nm). If these separate chromophores were non-interactive or if the photodissociation and photoisomerization were to take place through excited-state surfaces with different

Scheme 2. Wavelength-Sensitive Photolysis of Thiol **1** in Methylene Chloride**Scheme 3.** Synthesis of SAM-Capped Cluster **2**

multiplicities, thiol **1** might present an excited-state manifold not directly governed by the Kasha–Vavilov law. If so, selective excitation at a chosen wavelength could, in principle, allow for the selective photoreaction of the stilbene or selective photocleavage of the linking group, Scheme 2. We wished, therefore, to determine whether one can carry out selective photochemistry with light sources of different wavelengths. Therefore, these photoreactive shell–core capped clusters may be of interest both as photoresponsive nanomaterials per se and as new probes for supramolecular organization.¹⁸

Results and Discussion

Synthesis and Characterization of Shell–Core Nano-clusters. Thiol **1** was synthesized from the corresponding bromide by trimethylsilylthioxy dehalogenation in THF, followed by desilylation in situ,¹⁹ Scheme 3. The thiolate-capped cluster **2** was synthesized by treating a colloidal suspension of gold stabilized by tetraoctylammonium bromide with thiol **1**.²⁰ This

(12) Binkley, R. W.; Flechtner, T. W. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1984; pp 375–417.

(13) Schechter, H.; Link, W. J.; Tiers, G. V. D. *J. Am. Chem. Soc.* **1963**, *85*, 1601.

(14) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641.

(15) Mishra, B. K.; Valaulikar, B. S.; Kunjappu, T.; Manohar, C. J. *Colloid Interface Sci.* **1989**, *127*, 373.

(16) Rao, K. S. S. P.; Hubig, S. M.; Moorthy, J. N.; Kochi, J. N. *J. Org. Chem.* **1999**, *64*, 8098.

(17) (a) Whitten, D. G. *Acc. Chem. Res.* **1993**, *26*, 502. (b) Whitten, D. G.; Chen, L.; Geiger, H. C.; Perlstein, J.; Song, X. *J. Phys. Chem. B* **1998**, *102*, 10098 and references therein.

(18) Turro, N. J. *NATO Sci. Ser., Ser. C* **1999**, *519*, 37.

(19) Hu, J.; Fox, M. A. *J. Org. Chem.* **1999**, *64*, 4959.

(20) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. J. *Chem. Soc., Chem. Commun.* **1994**, 801.

route is unusual, in that thiolate-capped colloidal gold nanoparticles are usually prepared by treating a dilute HAuCl_4 solution with a reducing agent, such as sodium borohydride, in the presence of a capping thiol.^{21–23} However, thiol **1** is susceptible to reductive decomposition, and a ligand exchange approach was adopted instead. The gold nanoparticles used in this synthesis contained on average about 500 gold atoms and exist as roughly faceted spheres contained within cubes with an edge length of about nine gold atoms. The nanoparticle had an average diameter in the range of 1.5–3.5 nm, with a maximum in the distribution at about 2.5 nm.²⁰

A self-assembled monolayer shell of an alkyl thiol on a colloidal gold core is likely to exhibit organization very similar to that observed with the corresponding SAM on a flat polycrystalline gold surface.²⁴ Powder X-ray diffraction and high-resolution transmission electron microscopy studies have shown that gold nanoparticles have highly faceted low-energy surfaces.²⁵ High-resolution X-ray photoelectron spectroscopy (XPS) studies also demonstrate nearly identical Au–S bonding in the two systems.²⁶

Cluster **2** displays a remarkably different solubility than its precursor tetraoctylammonium bromide-stabilized gold colloid. Whereas most clusters capped by long-chain alkyl thiolates on stabilized gold colloids form stable suspensions in toluene, the solubility of cluster **2** was appreciable only in methylene chloride, and cluster **2** could not be redispersed easily into solvents such as benzene and chloroform. Thus, the dispersibility of an organic-capped gold cluster is dominated by the physical characteristics of the metal–organic interface, i.e., the interactions between the appended chain, especially the end group, and the solvent. The solubility change accompanying thiol displacement of the tetraoctylammonium salt indicated that the displacement proceeded efficiently, producing gold nanoparticles that are effectively covered by the stilbene-terminated thiolate units.

The ^1H NMR spectrum of cluster **2** in deuterated methylene chloride at ambient temperature shows three slightly broadened peaks at high field, which can be assigned to residual tetraoctylammonium bromide, Figure 2. The signals from thiol **2** are broadened, indicating that the bonded thiol was packed in a gel-like state on the gold surface such that the motions of the end groups are severely restricted.²⁷

The structure of cluster **2** was also confirmed by transmission FT-IR spectroscopy. Although spectral bands characteristic of thiol **1** could be also observed in cluster **2**, peak broadenings and small resonance frequency shifts were also evident, Figure 3. For example, the broadening of the CH_2 peaks at 2850 and 2920 cm^{-1} was accompanied by the appearance of a CH_2 wag at 1344 cm^{-1} , indicating that the methylene units of the thiolate linker are not in a perfect crystalline state in the monolayer.^{28,29} Either the tetraoctylammonium electrolyte remains associated

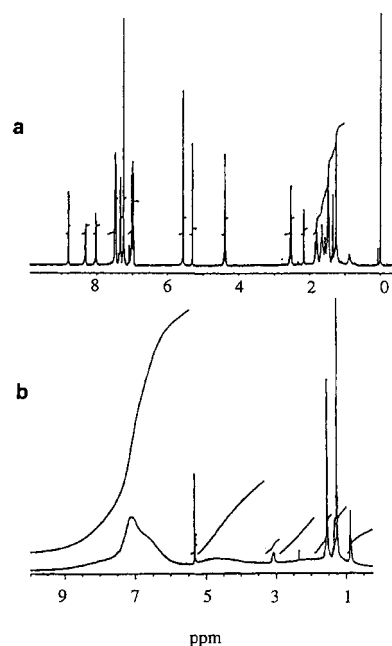


Figure 2. ^1H NMR spectra in CD_2Cl_2 of (a) thiol **1** and (b) cluster **2**.

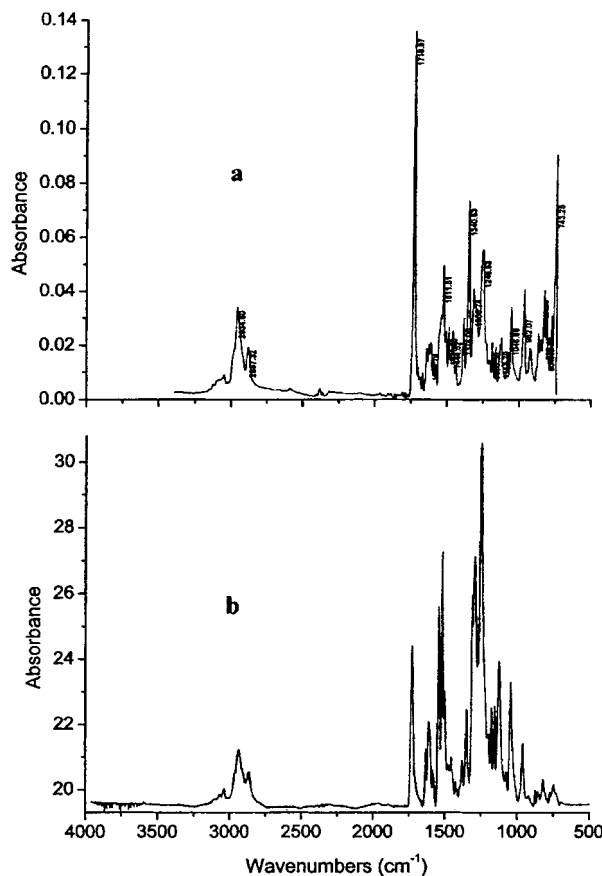


Figure 3. FT-IR spectra recorded as a thin film of (a) thiol **1** and (b) cluster **2**.

with the surface or the $-(\text{CH}_2)_6-$ alkyl spacer is amorphous at room temperature.

By comparing the integration intensities of the NMR signals attributed to the aromatic and aliphatic protons of **2**, we estimate residual tetraoctylammonium bromide present in the capped

(21) Turkevich, J.; Stevenson, P. C.; Hillier, P. *Discuss. Faraday Soc.* **1951**, *11*, 55.

(22) Cunnane, V. J.; Schiffrin, D. J.; Beltran, C.; Gebtran, G.; Solomon, T. *J. Electroanal. Chem.* **1988**, *247*, 145.

(23) Thomas, J. M. *Pure Appl. Chem.* **1988**, *60*, 1517.

(24) Hostetler, M. J.; Murray, R. W. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 42.

(25) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428.

(26) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1991**, *113*, 7152.

(27) Badia, A.; Lennox, R. B.; Reven, L. *Acc. Chem. Res.* **2000**, *33*, 475.

(28) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.

(29) Bain, C. D.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 506.

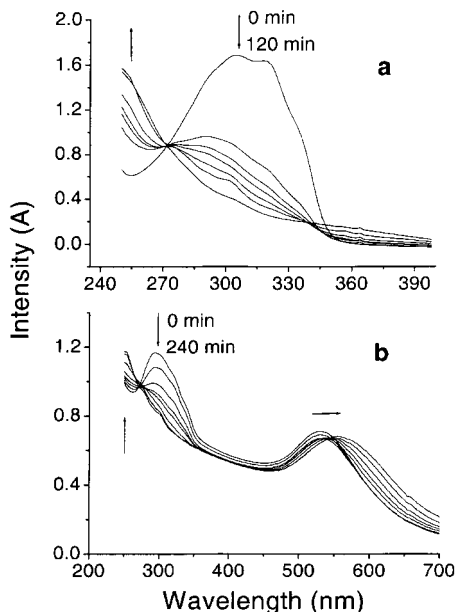


Figure 4. Absorption spectral monitoring of the 350 nm direct photolysis of (a) thiol **1** (1×10^{-5} M in CH_2Cl_2) and (b) cluster **2** (6×10^{-6} M in CH_2Cl_2).

cluster **2** to be less than 5 mol %. This analysis is also supported by the qualitative comparison of the intensities of the C–H vibrations (ca. 3000 cm^{-1}) in the IR spectra of **1** and **2**, where the relative intensities of these two families are virtually identical. Most likely, the small amount of residual electrolyte is localized at the edge of the faceted cluster, where covalent binding of the thiol to the gold surface is weakest. We thus conclude that the residual tetraoctylammonium bromide is not a significant inhibitor of close surface packing of thiol **1** in the equilibrated cluster **2**.

IR surface selection rules for SAMs on metal surfaces dictate that absorptions perpendicular to the surfaces will be enhanced, whereas parallel ones will be relatively attenuated.³⁰ The relative intensity of the ester carbonyl stretch (1716 cm^{-1}) in cluster **2** is significantly attenuated, whereas those of the C–O stretching peaks (1230 and 1272 cm^{-1}) are more intense. Thus, we infer that the bound thiolate is oriented at an angle from the surface of the colloidal gold nanoparticle, Figure 1, but that the average facet size in the gold cluster is smaller than that encountered upon vapor deposition of gold on a planar support.

Cluster **2** displays a characteristic gold plasmon band in its absorption spectrum (at about 526 nm, Figure 4), slightly shifted from the λ_{max} (530 nm) observed for the tetraoctylammonium bromide-stabilized gold sol before ligand exchange. This small shift indicates a modest change of the dielectric properties at the nanoparticle surface. A slightly broadened *trans*-stilbenoid absorption peak at 293 nm in the absorption spectrum of **2** is blue-shifted from the maximum at about 306 nm of the corresponding thiol **1** in solution. Whitten and co-workers have reported a 20 nm or so blue-shift in the absorption spectrum of stilbenoids that are π -stacked in the solid state.¹⁷ The smaller shift observed here indicates a lower density of packing of the stilbene units in cluster **2**. On the other hand, any significant dipolar interactions between the gold surface and the chromo-

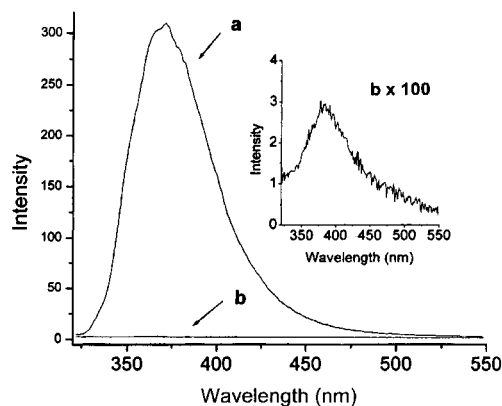


Figure 5. Fluorescence emission spectra recorded for (a) thiol **1** and (b) cluster **2**. Inset: spectrum of **2** with gain increased by 100 times.

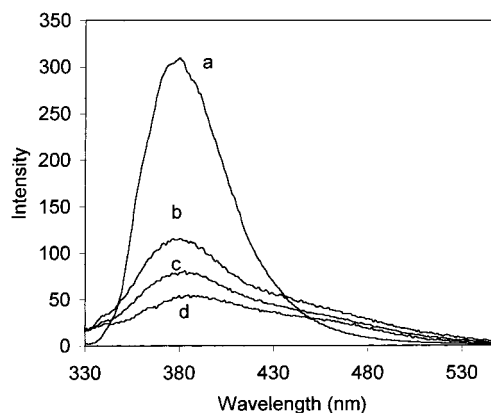


Figure 6. Dependence of fluorescence intensity on time after mixing of a 1×10^{-5} M solution of **1** in CH_2Cl_2 after treatment with a solution of tetraoctylammonium bromide-protected gold cluster. (a) Before mixing; (b) immediately upon mixing; (c) after 1 min of stirring; (d) after 3 min of stirring.

phore would stabilize the singlet excited state relative to the ground state, producing a red-shift in the absorption spectrum.³¹ It is possible that the smaller-than-expected blue-shift observed here might represent compensation of these opposing effects.

Perhaps the most striking spectroscopic change resulting from the assembly of thiol **1** in cluster **2** is the quenching of its fluorescence. Thiol **1** in methylene chloride displays a typical stilbenoid fluorescence spectrum with a broad emission at 370 nm, Figure 5, curve a. In cluster **2**, this emission is quenched, Figure 5, curve b. This result is as expected if the attachment of **1** to the colloidal gold cluster either enhances the rate of photoreaction (vide infra), increases the rate of intersystem crossing to a reactive but nonemissive triplet, or facilitates nonradiative decay of the bound singlet state.

It is also possible that some of the observed fluorescence quenching may derive from trivial reabsorption of the emission from **1** by the suspended colloidal gold clusters. The gold clusters do strongly absorb in the same spectral region of the emission of **1**. If trivial absorption were significant, fluorescence quenching would be immediate upon mixing of a solution of the thiol **1** with the tetraoctylammonium-protected gold cluster. Instead, the fluorescence intensity of such a solution weakens over a period of several minutes, Figure 6, showing that the fluorescence emission efficiency decreases as the thiol becomes

(30) (a) Blanke, J. F.; Vincent, S. E.; Overend, J. *Spectrochim. Acta, Part A* **1976**, *32*, 163. (b) Aguila, A.; Murray, R. W. *Langmuir* **2000**, *16*, 5949. (c) Hostetler, M. J.; Wingate, J. E.; Zhong, C. J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Morter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17.

(31) Nordlander, P. In *Laser Spectroscopy and Photochemistry on Metal Surfaces*; Dai, H.-L., Ho, W., Eds.; World Science: Singapore, 1995; Part I, Chapter 9, p 347.

bound to the cluster. Thus, direct quenching through bonds formed during binding of the fluorophore to the cluster is the dominant route for fluorescence quenching.

Because fluorescence can be considered as deriving from an oscillating excitation dipole, the emission from an excitation dipole near a metal surface is modeled by classical dipole antenna theory,³¹ and an image electron-hole pair can be induced by generation of an excited state near the surface of the metal. When the excited dipole is perpendicular to the metal surface, the image dipole and antenna dipole are 180° out of phase and cancel. When the excitation dipole is parallel to the surface, the image dipole reinforces the antenna excitation. The observed fluorescence quenching in cluster **2** supports the assertion that the thiol units are attached such that the *trans*-stilbene moieties are oriented at an angle from the surface such that there is a substantial electronic component roughly perpendicular to the surface of the metal particle. This implies that the singlet excitation dipole of *trans*-stilbene will extend along the axis that links the center of the two phenyl rings,³² producing substantial fluorescence quenching.

Direct Observation of Photochemical Reactions on Colloidal Gold Nanoparticles. The direct photolysis of thiol **1** was first examined in methylene chloride. When monitored by absorption spectroscopy, the absorption of **1** at 306 nm decreased as the absorption below 277 nm rose, with an isosbestic point at 277 nm, Figure 4. Such absorption changes are typical for *trans*-*cis* photoisomerization of stilbenoids.¹⁷ The growth of absorption beyond 345 nm, together with an isosbestic point at about 550 nm, indicates photodetachment of the *o*-nitrobenzyl ether moiety,³³ thus affecting directly the position and intensity of the plasmon band as the identity of the bound chemical species is altered. When the photolysis was scaled to preparative quantities and monitored by ¹H NMR spectroscopy, the bromide precursor **3**, instead of thiol **1**, was employed since **1** and **3** presented virtually identical excited-state profiles. The chemical shifts of the two *trans*-stilbene vinyl hydrogens in **1** (7.02 and 6.96 ppm, $J_{AB} = 16$ Hz) gradually converted into those characteristic of the *cis* form (7.09 and 7.06 ppm, $J_{AB} = 8.8$ Hz),³⁴ and the benzylic proton signals of the *o*-nitrobenzyl ether moiety (4.4 ppm) disappeared. The spectral bands assigned to both the *cis*- and *trans*-stilbenoids were present in the NMR spectrum of the bulk photolysis of *trans*-**3** at 350 nm. The photoinduced production of the *cis*-isomer was unambiguously established by the isolation of the *cis*-**3** and a mixture of both geometric isomers of 4-hydroxystilbene. We could observe no photodimerization product, within the limits of detection of this method (<5%). Therefore, the photoreaction of thiol **1** proceeds as shown in Scheme 2 through competing geometric isomerization and photocleavage.

The photoisomerization of the stilbene group in **1** is more efficient than the photodissociation of the *o*-nitrobenzyl moiety. By monitoring the course of the reaction by ¹H NMR spectroscopy, the progress of the two photoreactions (geometric isomerization and benzylic cleavage) could be deconvoluted, Figure 7. Under constant irradiation of dilute solutions (0.03 M in stilbene) at 350 nm, the photoisomerization reaches a photostationary state after about 25 min of irradiation, whereas the competing dissociation required about 60 min to complete. A much cleaner geometric photoisomerization was observed when the reaction was triplet photosensitized with 1,4-dibromonaphthalene (ET = 58.1 kcal/mol).³⁵ The photodissociation of

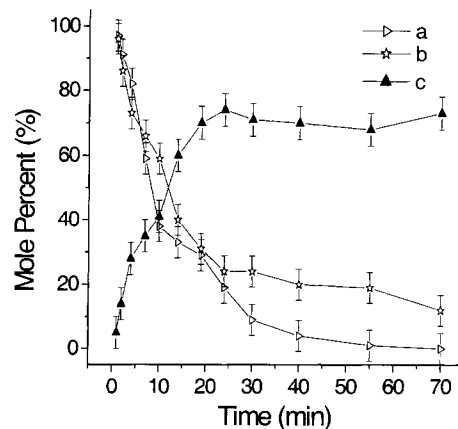


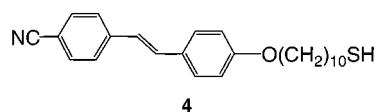
Figure 7. Reaction profile of the solution photolysis of **3** (0.03 M in CH₂Cl₂) obtained by ¹H NMR peak integration: (a) the sum of *cis*/*trans*-bromide **3**; (b) the sum of *trans*-bromide **3** and *trans*-4-hydroxystilbene; (c) the sum of *cis*-bromide **3** and *cis*-4-hydroxystilbene.

the *o*-nitrobenzyl linkage was suppressed upon triplet sensitization, although **1** did slowly disappear after prolonged irradiation. As expected from extrapolation of results obtained for stilbene itself and for **1** in dilute solution, no photodimerization product could be observed, even after extensive photolysis.

Direct irradiation of cluster **2** revealed photoreactivity of its stilbene group very similar to that in its precursor **1**. As shown in Figure 3, the *trans*-stilbene absorption peak at about 300 nm decreases upon irradiation at 350 nm with simultaneous growth in intensity below 270 nm with an isosbestic point at 270 nm, indicating production of the *cis*-isomer.¹⁷ It is interesting that a large shift of the gold plasmon band (from 530 to 550 nm) was observed as the photoreaction proceeded. Because the surface plasmon band is very sensitive to changes in properties at the metal/dielectric interface, the observed shift indicates a steep change in dielectric³⁶ that can be plausibly attributed to the photodetachment of the highly polar 4-hydroxystilbene group from the cluster surface.

Because the singlet state is effectively quenched by interactions with the gold core, it is likely that the geometric isomerization can take place from either the singlet or triplet manifold, as is typical for many simple olefins.³⁵ When the isomerization takes place through the triplet manifold, it will dominate over a lower quantum yield process. The lower quantum efficiency observed for all conversions in **2** than in **1** thus makes it difficult to rule out completely any singlet state involvement.

It is also interesting that the *trans*-to-*cis* isomerization is observed in cluster **2**, whereas the analogous *trans*-to-*cis* geometric photoisomerization is blocked in self-assembled monolayer **4**. The latter includes a similar stilbenoid bound at



an angle similar to that observed in **2**,⁹ but on planar gold with larger metal facets, better packing of the *trans*-stilbene groups sterically blocks the isomerization. In contrast, the corresponding *cis*-isomer of **4** is less well-packed and can photoisomerize easily. It seems likely, therefore, that the surface disorder

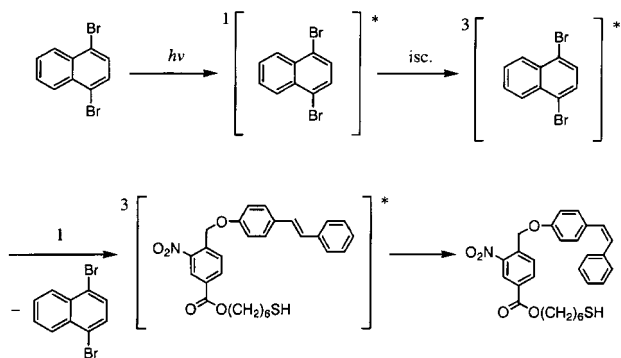
(32) Kawski, A.; Kubicki, A. *Acta Phys. Pol. A* **1991**, 79, 457.

(33) Pillai, V. N. R. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 9.

(34) Fisher, T. H.; Schultz, T. P. *Magn. Reson. Chem.* **1991**, 29, 966.

(35) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(36) Lazarides, A. A.; Schatz, G. C. *J. Phys. Chem. B* **2000**, 104, 460.

Scheme 4. Triplet Sensitization of Thiol **1**

characteristic of *cis*-**4** similarly characterizes the appended stilbene units in *trans*-**2**.

Likewise, [2 + 2] photodimerization could be observed with **4** on planar gold, but not with cluster **2**. The quantum yield for photocycloaddition of **4** is very low compared with that for geometric isomerization. It can be observed, in fact, only because of the absence of a photorelease pathway such as that available to **2**. It is not surprising that the photorelease route in **2** precludes the possibility of observing the sterically disfavored pericyclic photoreaction.

The efficiencies of both photoisomerization and photodissociation in cluster **2** were significantly lower than those in the soluble precursor **1**, Scheme 4. There are two probable causes for this reduction of photoefficiency. Suppression of geometric isomerization may arise either from steric hindrance associated with tight monolayer packing or from metal-based nonradiative quenching. The isomerization of the *trans*-stilbene moiety to the corresponding *cis*-isomer does involve a large geometric change which would be difficult were the stilbene units in **2** as closely packed in the cluster **2** as on a larger planar facet of SAM **4** on gold. Contrasting expectations from the broadened ¹H NMR spectrum, which indicates a gel-like packed state, and from the observation of *trans*-to-*cis* isomerization, which requires loose packing, provide a rationale for the observation that the photoisomerization could be retarded. However, were packing the dominant factor, the photodetachment of the *o*-nitrobenzyl group should be relatively facile, since it is less affected by packing. In fact, the release of the relatively large bound chromophore from the capped cluster surface is presumably sterically favorable. Retardation of both the photoisomerization and the photodissociation thus requires a significant role for surface quenching of the chromophore by the metal core.³

As in the solution-phase reaction, triplet-sensitized photolysis of cluster **1** gave no photodetachment product in 20 min of irradiation, Scheme 4. After prolonged irradiation, a very complex mixture was formed, although neither photodetachment nor [2 + 2] photocycloaddition products could be isolated. The absence of the cycloaddition product likely indicates that the stilbene units in cluster **2** are less well-packed than in the solid state or in a compressed Langmuir–Blodgett (L–B) film, where the π -stacked stilbenoid units of the “shell” in cluster **2** are apparently only loosely associated, but not nearly as tightly π -stacked as in the crystalline solid or in a L–B film.

Conclusions

We have prepared a photodetachable thiol linker for covalent surface modification of colloidal gold. Using this linker, we have constructed a densely covered shell–core nanoparticle in which a *trans*-stilbenoid is present as a capping group on size-selected

colloidal gold. Spectroscopic and solubility experiments indicate that the self-assembled array on cluster **2** has structural order similar to, but not identical with, that observed with long-chain alkyl thiolate SAMs on bulk polycrystalline gold. Thus, the end groups are less tightly packed in **2** than in the analogous stilbene **4** bound to larger planar gold facets. Fluorescence of the stilbene moiety in thiol **1** was quenched in cluster **2**, indicating strong electronic interaction between the excited stilbene and the metal surface.

Both the stilbene and the *o*-nitrobenzyl moieties were photochemically active in cluster **2** upon direct photolysis, but selective activation through excitation wavelength selection of either reaction (geometric isomerization of the stilbene or photodeprotection of the phenolic group) to the exclusion of the other proved to be elusive. However, triplet sensitization permitted selective excitation of the stilbene moiety without photodissociation of the *o*-nitrobenzyl linkage.

Both direct and sensitized irradiation led to geometric isomerization, in contrast to the unidirectional (*cis*-to-*trans*) isomerization observed with **4**. Photodimerization of the *trans*-stilbene units in cluster **2** was not observed, implying that the stilbene units in **2** are more loosely packed than in a typical L–B film or in a solid crystal in which face-to-face π -stacking of the stilbene moieties facilitates [2 + 2] cycloaddition at the olefinic π bond.

Inclusion of a photocleavable linker between a metallic surface and a reactive chromophore provides several advantages: an optical route for surface patterning, a photochemical method for release of a bound reagent from a covalently bound metal surface, and a new technique for exploiting local organization in choosing among competing photochemical pathways.

Experimental Section

General Procedures and Techniques. Unless specified in the synthetic procedures, all chemical reagents (Aldrich) were used as received. H₂AuCl₄ was purchased from Strem and tetraoctylammonium bromide from Fluka. Spectroscopic grade solvents from Fisher or Aldrich were used both for spectral measurements and for photochemical reactions. Pure water (Milli-Q) used in the colloidal gold synthesis had a resistance of higher than 4 M Ω . Tetrahydrofuran (THF), benzene, toluene, and diethyl ether were distilled from sodium benzophenone ketyl. Ethylene glycol was distilled from sodium metal, and methylene chloride was distilled from calcium hydride under argon prior to use. Deuterated solvents obtained from Isotech or Aldrich were used as received.

Air- and moisture-sensitive reactions were performed under an atmosphere (nitrogen or argon after a Drierite tower). Glassware was oven-dried at 140 °C or flame-dried if necessary. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254). Baxter silica gel 60 (230–400 mesh ASTM) was used for flash column chromatography. Melting points are uncorrected. ¹H NMR (300 MHz) and ¹³C NMR (75.5 MHz) spectra were recorded on a Varian UNITY Plus-300 spectrometer at room temperature with an internal standard (¹H, 7.24 ppm and ¹³C, 77.0 ppm). IR spectra were recorded on a Nicolet 510P FT-IR as thin films on NaCl plates. High-resolution mass spectra were obtained on a VG ZAB-E4F instrument using EI or CI ionization. Absorption spectra were monitored with an HP diode array spectrophotometer and a Shimadzu 3101PC spectrophotometer. Emission spectra were recorded on a Shimadzu RF-5301PC spectrofluorometer.

Synthesis of 6-Mercaptohexyl-3-nitro-4-(4'-stilbenoxymethyl)-benzoate **1.** Thiol **1** was prepared by following a procedure reported by Hu and Fox¹⁹ from the corresponding bromide (see Supporting Information).

Synthesis of Cluster **2.** The shell–core composite **2** was synthesized by treating a tetraoctylammonium bromide-stabilized gold colloidal suspension²⁰ with thiol **1** (0.20 g, 0.39 mmol) in toluene. The resulting

suspension was stirred under N₂ in the dark for 10 h. The capped nanoparticles precipitated and were collected by membrane filtration on a Millipore HTPP 0.4 μm filter. The dark solid precipitate was washed with copious amounts of toluene and ethanol to remove the electrolyte and unreacted thiol. A dark amorphous solid was obtained, which was resuspended in methylene chloride.

Photolysis Reactions. Photolyses were carried out with phosphor-coated low-pressure mercury arcs with emission centered at 350 or 300 nm in a Rayonet photochemical reactor (Southern New England Ultraviolet) at ambient temperature. When the progress of the reaction was monitored spectroscopically, a methylene chloride solution of thiol **1** or cluster **2** was placed in a Pyrex cell and degassed by bubbling Ar for 10 min before irradiation. For synthetic photoconversions, a solution of **1** or bromide **3** (7.4 mM in 50 mL of CH₂Cl₂) was placed in a Pyrex tube under Ar. The resulting solution was irradiated at 350 nm in a Rayonet photochemical reactor. After removal of solvent, the solid residue was separated by flash chromatography on silica gel to give 4-hydroxystilbene and **1** or **3** as mixtures of *cis*- and *trans*-stereoisomers. The *trans*-isomers were identified by comparing their ¹H NMR spectra with those of authentic samples. The formation of the *cis*-isomers was inferred from the product ¹H NMR spectrum for the olefinic protons^{19,37} and confirmed by their complete reconversion to the corresponding

trans-isomer in the presence of traces of I₂. Photoreactions of cluster **2** were monitored directly in an NMR tube by ¹H NMR spectroscopy. In the triplet-sensitized reactions, 1,4-dibromonaphthalene (20 equiv) was added to the reaction solutions to ensure that direct absorption of light by the substrate would be negligible.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Science, Chemistry Division. We thank our colleagues at North Carolina State University for sharing their research instruments and space while our laboratory renovations were completed.

Supporting Information Available: Synthesis and characterization of 6-bromohexyl-3-nitro-4-methyl-benzoate, 6-bromohexyl-3-nitro-4-bromomethyl-benzoate, and 6-bromohexyl-3-nitro-4-(4'-stilbenoxymethyl)-benzoate (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA003180L

(37) Friedrich, K.; Hennig, H. G. *Chem. Ber.* **1959**, *92*, 2944.