Photochemistry of chromophore-functionalized gold nanoparticles*

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Abstract: It is generally believed that metal nanoparticles strongly quench the singlet-excited states of chromophores when attached to nanoparticle surfaces, through an energy-transfer mechanism, which limits their application in optoelectronic devices and photonic materials. Recent studies of fluorophore-linked metal nanoparticles reveal that there is a dramatic suppression in the quenching of the singlet-excited state of these molecules and they possess unusual photophysical properties. A summary of our work on the photophysical and excited-state properties of chromophore-functionalized gold nanoparticles is presented in this article. Pyrene-capped gold nanoparticles showed normal fluorescence in nonpolar solvents and an intermolecular excimer formation at higher loadings. The quenching of the emission, observed in pyrene-labeled gold nanoparticles in polar solvents, is attributed to the formation of pyrene radical cation through a photoinduced electron-transfer process. We have also functionalized gold nanoparticles using a thiol derivative of fullerene. The quenching of fluorescence and decreased yields of triplet-excited state, observed in these systems, are attributed to an energy-transfer process.

INTRODUCTION

The fascinating colors of metal colloids have attracted the attention of people for a long time. The ancient Egyptians, for instance, used metal colloids to stain glass. Michael Faraday made the remarkable observation that colloidal gold exists in reduced state, as exceedingly fine particles, and these divided metals are responsible for their colors [1]. We now understand the colors of nanoparticles of noble metals such as Au, Ag, and Cu in terms of the strong absorption in the visible region, often referred to as "surface plasmon absorption". This absorption results when the incident photon frequency is resonant with the collective oscillation of the conduction electrons [2] and it is absent in bulk metal.

Metal and semiconductor nanoparticles possess interesting size- and shape-dependent optoelectronic properties [3,4]. Such nanoparticles are versatile building blocks for the construction of nanoscale devices through a "bottom-up approach", i.e., by functionalizing nanoparticles with molecules of specific properties and functions [5,6]. Exciting advances have been made in recent years, by several groups, in the design of such nanomaterials, which possess novel optical, electrical, and magnetic properties.

Several synthetic strategies, adopting chemical, radiolytic, as well as photolytic methods, have been reported for the preparation of metal nanoparticles [7–9]. Among these, the most popular one is the chemical method of preparation of nanoparticles, by reducing the appropriate metal salts in the pres-

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ence of a stabilizer [7]. Also, the methodologies for the preparation of metal nanoparticles of well-defined size and shape are documented [4,7].

Most of the early studies in the area of metal clusters have focused on the preparation of gold colloids in aqueous media; the notable ones are the original work by Faraday [1] and the classic reports by Turkevich et al. [10]. Colloidal gold prepared in aqueous medium, by chemical reduction, are usually capped with anions (e.g., citrate), and the negative surface charges provide the repulsive force between the particles, which prevents them from agglomeration [7]. For catalytic applications, quaternary ammonium halide-stabilized metal nanoparticles were earlier synthesized by Bönnemann et al. [11]. More recently, newer methods have been reported for the preparation of stable metal nanoparticles capped with monolayers of organic molecules possessing functional groups such as quaternary ammonium halides, amines, thiols, isothiocyanates, etc., which can often act as stabilizers of nanoparticles. Such monolayer-protected metal clusters (MPCs) are of interest in the design of nanostructured materials and can be visualized as three-dimensional assemblies possessing a core-shell structure (metal core covered with ligand shell) as illustrated in Fig. 1 [12,13]. The ability of functional groups such as thiols to self-assemble around metal nanoparticles is exploited for the preparation of MPCs. Solubility of MPCs can be tuned from aqueous to nonaqueous medium by varying the thickness and nature of the stabilizer layer [13,14].
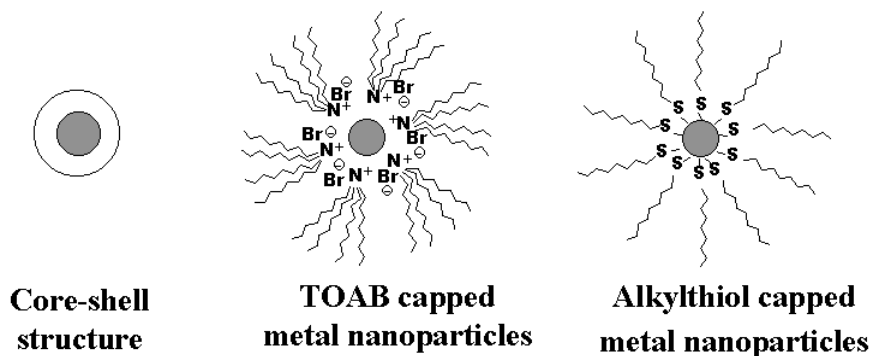

Core-shell structure   **TOAB capped metal nanoparticles**   **Alkylthiol capped metal nanoparticles**

Fig. 1 Monolayer-capped metal clusters (MPCs).

Most of the literature on the synthesis of MPCs adopts modifications of the method reported by Brust et al., and this procedure adopts a two-phase (water–toluene) extraction of $[AuCl_4]^-$ using a phase-transfer reagent (e.g., tetraoctylammonium bromide), followed by reduction [15]. This procedure was further modified, by "place exchange reaction" for the preparation of MPCs with alkanethiolate shells of varying thickness. MPCs stabilized by alkanethiolate monolayers are quite stable, isolable, and could be resuspended in a wide range of organic solvents.

Tailoring of the optical, as well as electrochemical properties of MPCs, is possible by capping metal core with photo/electroactive molecules as shell materials [6,12,16–23]. For example, extending the surface modification method to alkyl thiols possessing ω-functionalized chromophore results in the formation of a well-ordered and tightly bound photoresponsive shell of nanometric dimension, encapsulating the nanoparticle core. Thus, it is possible to tune the optoelectronic properties of MPCs by independently manipulating the properties of the shell. Such photoresponsive antennae systems may have potential applications in diverse optoelectronic devices (sensors, switches, biological probes, light-harvesting assemblies) and photonic systems [13]. Although the material properties of MPCs bearing functional alkyl thiols as shell materials are well investigated, their photophysical and photochemical properties have not received adequate attention. This, in part, has been due to the general belief that the metal nanoparticles strongly quench the excited state of chromophores when attached to nanoparticle surface through an energy-transfer mechanism. Such quenching can limit their applications in devices [6]. Interestingly, recent studies on the photophysical properties of chromophore-linked gold nanopar-

ticles, by our group and others, suggest a dramatic suppression in the quenching of singlet-excited state properties of these chromophores [6]. These results suggest that the photoactive molecules, when capped onto metal nanoparticles, possess unusual photophysical as well as excited-state properties, and a detailed summary of these aspects are presented here.

Surface plasmon absorption of TOAB-capped Au nanoparticles

Gold nanoparticles stabilized with tetraoctylammomium bromide (TOAB) possess well-defined surface plasmon absorption in contrast to alkanethiolate-protected Au clusters. Surface plasmon absorption properties are generally discussed within the framework of Drude model, according to which the plasmon peak position depends on the refractive index of the surrounding medium (*n*) and governed by eq. 1 [24],

$$\lambda^2 = \lambda_p^2(\varepsilon^\infty + 2\varepsilon_m)$$ (1)

where, λ_p is the bulk plasmon wavelength, ε^∞ is the high-frequency dielectric constant due to interband and core transitions, and ε_m is the medium dielectric constant [refractive index of the medium is directly related to its dielectric constant, i.e., $n = (\varepsilon_m)^{1/2}$]. Recently, we have investigated the interaction between TOAB-capped gold nanoparticles with solvents and functionalized organic molecules, by probing the changes in the surface plasmon absorption band [25]. Based on the interactions, solvents were classified into two general categories: (i) solvents that do not complex with Au nanoparticle surface and that can alter the refractive index and (ii) solvents that complex with the gold nanoparticle surface. Solvents such as cyclohexane, toluene, *o*-xylene, chlorobenzene, and *o*-dichlorobenzene fall in the first category, and the surface plasmon band gradually shifts toward longer wavelengths with increasing refractive index of the solvent. Plot of the square of the observed position of the surface plasmon band of TOAB-capped Au nanoparticles in these solvents as a function of the square of the medium dielectric function shows a linear relationship. In an earlier report, Murray and coworkers have shown that the surface plasmon absorption of alkanethiolate-protected clusters are unaffected by medium dielectric properties [26]. The contribution of the dielectric of the organic shell was not accounted for in the Drude equation and was modified by Murray and coworkers as in eq. 2 [27],

$$\lambda^2 = \lambda_p^2[(\varepsilon^\infty + 2\varepsilon_m) - 2g(\varepsilon_m - \varepsilon_s)/3]$$ (2)

where, *g* is the volume fraction of the shell layer that increases with chain length of the organic capping agent. The size of the core and organic shell becomes comparable for very small gold nanoparticles. For example, in the case of alkanethiolate-protected clusters, the diameter of core and shell are in the range of 1–2 nm, and this in turn reduces the sensitivity of the gold plasmon absorption to the changes in the solvent refractive index. It is possible to explain the solvent-sensitive nature of TOAB-capped gold colloids based on "*g*" value. The TOAB-capped gold colloids produce nearly spherical particles with diameter ranging from 5–6 nm and the contribution of *g* value becomes smaller with increase in the core size. Moreover, in the present case, TOAB-capped gold nanoparticles are stabilized through noncovalent interactions and hence it renders the bulk solvent molecules to penetrate through the shell and directly influence the surface plasmon band of the metal particle. Interestingly, the surface plasmon band position remains unaffected in polar solvents with nonbonding electrons (e.g., tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, and acetone), and is attributed to the direct interaction of these solvents with the gold surface. Such complexation processes may override the effects of refractive index since it substantially alters the electron density of the gold nanoparticle surface.

Surface binding properties of TOAB-capped Au nanoparticles

Functional groups such as amines, isothiocyanates, and thiols bind strongly to the gold surface and can provide a link between the photoactive group and the gold surface. We have used an amine as

well as thiol groups for organizing chromophores such as pyrene onto the gold nanoparticles. The surface-binding properties of TOAB-capped gold nanoparticles and functionalized organic molecules [1-aminomethylpyrene (Py–CH$_2$NH$_2$) and a model compound ^{15}N-labeled benzylamine (C$_6$H$_5$–CH$_2$NH$_2$)] (Scheme 1) were followed using various spectroscopic techniques [16,25]. The binding of ^{15}N-labeled benzylamine to gold nanoparticles was probed using ^{15}N NMR spectroscopy and two sets of signals were observed, one from the free molecule and the other from the molecule complexed to Au nanoparticles [25]. 1-Aminomethylpyrene is weakly fluorescent when dissolved in an organic solvent such as tetrahydrofuran (THF) ($\phi_f = 0.016$). The low fluorescence yield of Py–CH$_2$NH$_2$ is attributed to the intramolecular quenching of the singlet-excited state via an electron transfer from the lone pair of the nitrogen to the pyrene moiety. However, Py–CH$_2$NH$_2$···Au hybrid nanoparticles, dissolved in THF, emit bright blue light upon UV excitation, with 30-fold increase in the fluorescence quantum yield [16]. Surface binding of the amine group to gold nanoparticle suppresses the intramolecular photoinduced electron transfer from the lone pair of the amine to pyrene and thereby increases the efficiency of radiative deactivation of the singlet-excited state.
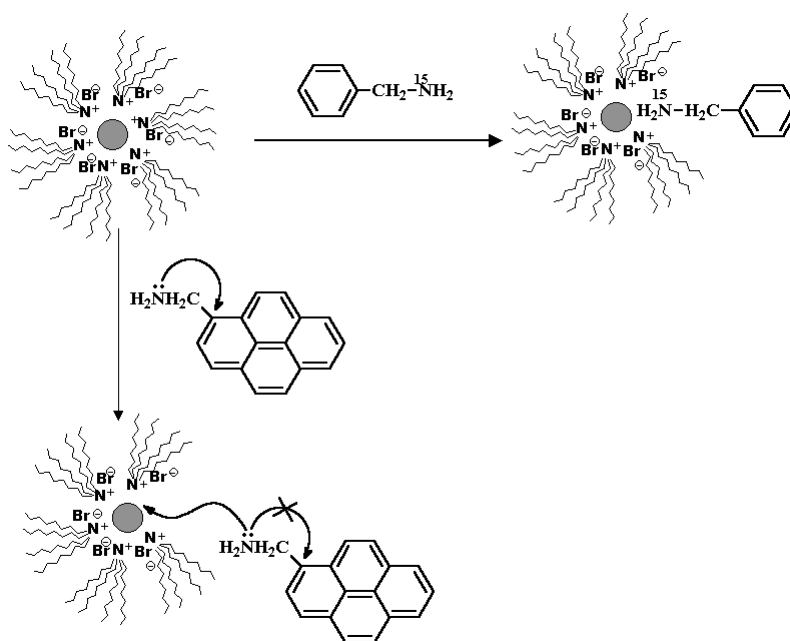
Scheme 1 Surface-binding properties of TOAB-stabilized Au nanoparticles.

## Photophysical properties of pyrene-functionalized Au nanoparticles

Synthesis of MPCs bearing chromophores such as pyrene [16,28], porphyrin [6,19], quinone [20], fluorescein [21], stilbinyl [22], and dansyl [23] units have been reported by various groups. We have recently synthesized nanoparticles of gold stabilized by thiol derivatives of pyrene (Py–R–S–Au), and the coverage of the photoresponsive molecules around metal nanoparticles was varied by cobinding with alkyl thiol (Scheme 2). In a typical preparation, gold nanoparticles capped with dodecanethiol and the thiol derivative of the chromophore were synthesized by reducing hydrogen tetrachloroaurate (III) hydrate in the presence of TOAB, adopting a two-phase extraction procedure [17]. The interaction between the gold nanoparticles and pyrene was monitored by following the changes in the absorption and emission spectra [28]. The absorption spectrum of the pyrene-capped Au nanoparticle (Py–R–S–Au) is almost an additive spectrum of dodecanethiol-capped Au nanoparticle and the thiol derivative of pyrene. The structured absorption bands of pyrene remain more or less unperturbed, indi-
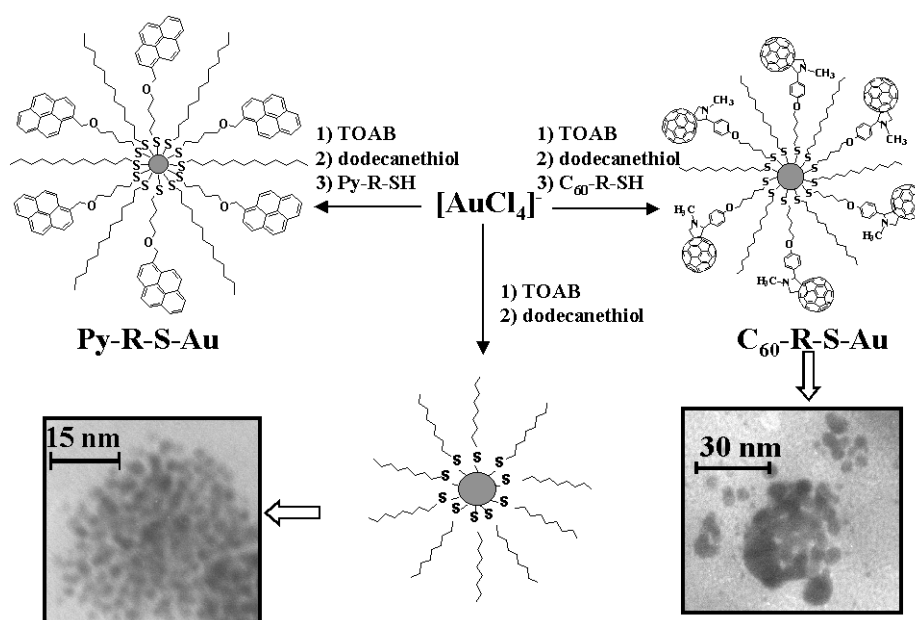
Scheme 2 Synthesis of Py–R–S–Au and C_{60}–R–S–Au nanoparticles.

cating the absence of any direct ground-state interaction. Py–R–S–Au nanoparticles possess structured bands, characteristic of the normal fluorescence of pyrene, and at higher surface coverage, an excimer emission was observed. The flexible linker between the nanoparticle and chromophoric unit provides a topographical control on the interactions between the chromophores in the three-dimensional mono-layers, leading to the formation of excimer on nanoparticle surface. Time-resolved emission studies were carried out in degassed solutions to obtain a better understanding of the excited-state dynamics of Py–R–S–Au nanoparticles [28]. Time-resolved fluorescence of thiol derivative of pyrene, monitored at 390 nm, showed biexponential decay, and, interestingly, an additional short-lived species was observed when capped on Au nanoparticles [28]. Lifetimes and the fractional contributions of all three species remain unaffected at different loadings of pyrene on Au nanoparticles, ruling out the possibility of self-quenching. Relative contribution of the short-lived species increased significantly with solvent polarity, and these results are attributed to photoinduced electron transfer from the excited state of pyrene to Au nanoparticles. Time-resolved absorption studies of Py–R–S–Au nanoparticles and the thiol derivative of pyrene were carried out for establishing the identity of the various intermediates formed [17]. The difference absorption spectrum of thiol derivative of pyrene was recorded by following the 337-nm laser pulse excitation (N_2 laser), in degassed THF solutions. A transient absorption with maximum around 425 nm, characteristic of triplet-triplet absorption of pyrene, was observed and is readily quenched in oxygenated solutions. In contrast, pulsed laser irradiation (337 nm) of Py–R–S–Au nanoparticle resulted in an electron transfer between gold nanoparticle and pyrene. The pyrene radical cation formed showed an absorption maximum at 400 nm and the charge separation sustained for several microsec-onds before undergoing recombination. The radical cation decayed with a lifetime of 4.5 µs and the presence of O_2 in the solution had no effect on the formation or decay of the transient. These results indicate that gold nanoparticles can act as a buffer to hold the charges.

Thus, in the case of Py–R–S–Au, the main deactivation channels of the singlet-excited-state energy are (a) normal fluorescence, (b) intermolecular excimer formation, and (c) the competitive elec-tron transfer to the gold nanocore [28]. These aspects are represented in Scheme 3. The first two processes, i.e., fluorescence and excimer formation, are favorable in nonpolar solvents, whereas the lat-
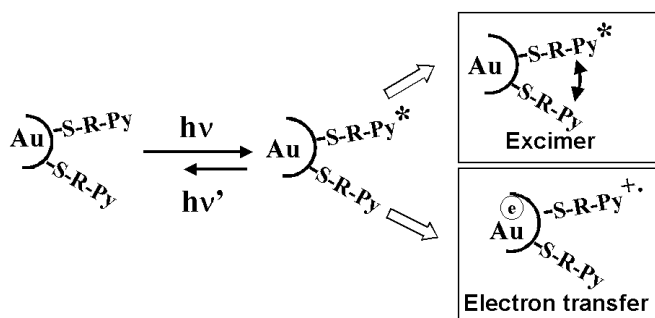
Scheme 3 Various photoprocesses in Py-R-S-Au nanoparticles.

ter process dominates in polar solvents. The suppression in the quenching of the singlet-excited state observed in these systems could be further extended for the development of optoelectronic devices. Time-resolved fluorescence studies, as well as the transient absorption studies, indicate that in polar solvents, photoinduced electron transfer is more favored from pyrene to Au core, and such processes may have potential applications as photocatalysts and light-harvesting devices.

Photophysical properties of fullerene-functionalized Au nanoparticles

We have also synthesized fullerene thiol-functionalized gold clusters [18], and these systems can be visualized as antenna systems containing gold nanoparticle as central core, surrounded by fullerene units forming a hydrophobic shell (Scheme 2). The transmission electron micrograph of C_{60}–R–S–Au nanoparticles and dodecanethiol-stabilized gold nanoparticles are compared. Gold nanoparticles stabilized with dodecanethiol possess a diameter of 2–3 nm. On the other hand, the C_{60}–R–S–Au nanoparticles tend to form optically transparent clusters of 10–30 nm diameter. In the present case, ~90 fullerene units are linked to a single gold nanoparticle, and the high concentration of C_{60} around Au nanoparticle may lead to the formation of small clusters. Interestingly, larger clusters are observed in the TEM picture, which may preferably be formed as a result of interparticle clustering (Scheme 4). The ease of suspending C_{60}–R–S–Au nanoparticles in organic solvents allowed us to probe the excited-state interactions by various spectroscopic methods. The quenching of fluorescence, as well as decreased yields of triplet-excited state, suggests an efficient singlet-energy transfer from fullerene to gold nanocore.

C_{60} moieties serve as excellent electron acceptors in donor acceptor dyad and triad systems [29]. A novel approach for charge stabilization was demonstrated in fullerene-based dyads by taking advan-
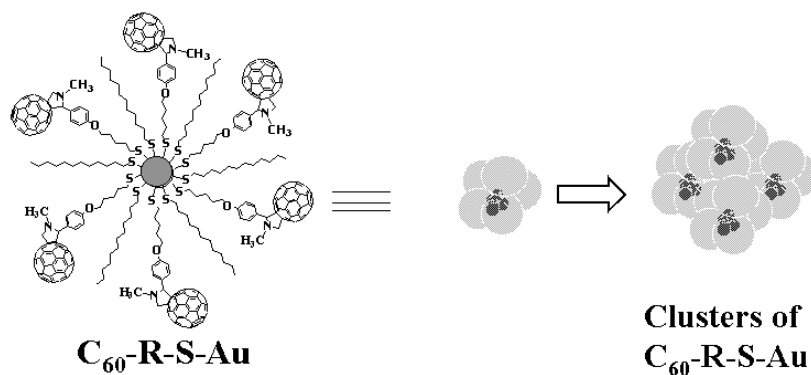
Scheme 4 Interparticle clustering of C_{60}-functionalized Au nanoparticles.

tage of the clustering behavior of C_{60} [30]. Laser excitation of the clustered dyads of fullerene yielded remarkably stable charge-transfer products, with lifetimes of several hundred microseconds. The close network of fullerene moieties in the cluster facilitates the hopping of electron from the parent fullerene to the adjacent molecule, thus increasing the spatial distance between the charge-separated pairs. Light-induced charge-transfer processes in C_{60}-based systems capped on metal nanoparticle may yield long-lived charge-separated products, and these aspects are currently under investigation.

CONCLUSIONS

The unexpected suppression in the quenching of emission, observed upon binding chromophores such as pyrene onto metal nanoparticle surface provides an excellent possibility to use the three-dimensional arrays of chromophore-functionalized nanoparticles, as antenna systems. Such nanometer-scale antenna systems may have application in optoelectronic and photonic devices. In polar solvents, photoinduced electron-transfer process is more favored from chromophore to Au core, and such chromophore-bound metal nanoparticles are useful in designing light-harvesting devices.

ACKNOWLEDGMENTS

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