

Interfacial properties of hybrid nanomaterials

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Abstract. A brief summary of our ongoing efforts to understand the surface properties of nanoparticles using fluorophores, namely pyrene alkanethiols, is presented. Excited state interactions were investigated by varying the length of the spacer group and the concentration of fluorophore. The flexible long alkyl chain tethering pyrene in **Au-P2/Au-P3** allows free interaction between fluorophores resulting in excimer formation whereas the intermolecular interactions are limited in the **Au-P1** system due to the restriction imposed by the curvature of spherical gold nanoparticle. A gradual increase in the peak intensity ratio of III/I band of the normal fluorescence of pyrene was observed indicating that the surface of nanoparticle is more polar than the bulk solvent (toluene).

Keywords. Gold nanoparticle; pyrene; surface polarity; excited state.

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1. Introduction

Surface properties of metal and semiconductor nanoparticles are quite different from that of bulk material and an in-depth understanding of these aspects is essential for the utilization of various nanomaterials for optoelectronic devices and biomolecular research [1–3]. However, it is difficult to probe the surface properties of nanomaterials by adopting conventional methods. Photoresponsive molecules have been widely used as a ruler for probing the physical properties of microheterogeneous environment [4,5]. For example, the viscosity and polarity of various microdomains in biomolecular systems were investigated by probing the optical responses of fluorophores. Although exciting advances have been made in recent years in the design of nanomaterials, investigations on the surface properties of such systems using fluorophores are rather few. This was based on a general belief that the metal surfaces strongly quench the singlet-excited state of fluorophores through an energy transfer process [6–8]. Contrary to this belief, recent studies from our group [2,9,10] and others [11,12] have shown that there is a dramatic suppression in the quenching of emission upon binding the fluorophore onto Au nanoparticle and their photophysical properties are quite different. In order to investigate the mechanistic details of various deactivation channels, we have functionalized gold nanoparticles with various photoactive molecules [2] (for example, pyrene [10,13], fullerene and

spiropyran [14]). A brief account of our recent efforts [10] in (i) understanding the surface properties of gold nanoparticles by varying the distance of fluorophores from nanoparticle surface and (ii) the excited state interactions of fluorophore bound on nanoparticle are presented here.

2. Results and discussion

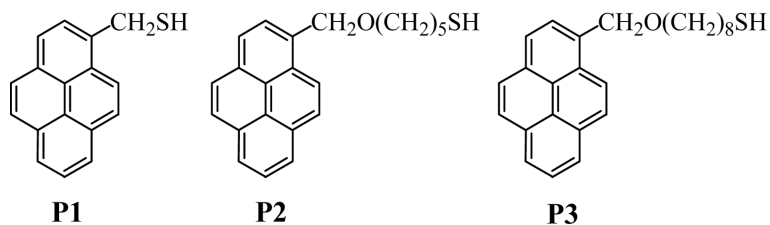
2.1 Synthesis and characterization

Pyrene chromophores possessing thiol groups (**P1**, **P2**, and **P3**) were functionalized on Au nanoparticles by adopting a biphasic synthetic procedure [9,10]. Details of the synthesis, adopted for preparing pyrene-functionalized Au nanoparticles (**Au-P1**, **Au-P2**, **Au-P3**) (scheme 1) were presented in an earlier report [10].

Not all ligands may react with Au nanoparticles during the preparation of functionalized nanoparticles, and the concentrations of the unreacted molecules were accounted from the absorption spectra of the filtrates obtained during the purification process. The average number of pyrene alkanethiols per Au nanoparticle was estimated by (i) assuming that the reacted fluorophores are evenly distributed on each nanoparticles and (ii) adopting a tight-packed spherical model suggested by Terril *et al* [15]. This model assumes the gold core as a sphere with density 58.01 atoms/nm³ covered with a skin of hexagonally close packed gold atoms with the number density of surface gold atoms as 13.89 atoms/nm² [15]. The average diameter of Au nanoparticle is ~2.2 nm, and on this basis, we have estimated the number of gold atoms as ~323, similar to that reported by Fox and co-workers [16]. Based on the assumption that Au nanoparticles are spherical in shape, the number of pyrene molecules functionalized on the surface of gold were estimated as approximately 30, 45 and 55 for 15, 30 and 60% loadings. Hybrid nanomaterials were purified and further characterized using high-resolution transmission electron microscopy (HRTEM), FTIR and ¹H NMR spectroscopy. Details of these aspects were summarized in ref. [10].

2.2 Ground state interactions

Monolayer protected gold nanoparticles possess a characteristic surface plasmon absorption band at around 520 nm, arising from the interaction of external



Scheme 1. Pyrene alkanethiols.

electromagnetic radiation with the highly polarizable Au $5d^{10}$ electrons of Au nanoparticles. The absorption spectra of pyrene-capped gold nanoparticles, normalized at 520 nm, with different loadings of **P1**, **P2** and **P3** are presented in figure 1 [9,10]. In the present case, the absorption spectra of **Au-P1**, **Au-P2** and **Au-P3** possess two sets of bands; an absorption band in the UV region, characteristic of functionalized pyrene molecules and a broad band in the visible region (~ 520 nm), attributed to the surface plasmon absorption of Au nanoparticles. A significant dampening and broadening of surface plasmon absorption was noticed in all the three systems. Dampening of surface plasmon band is a characteristic of smaller gold nanoparticles (<5 nm), capped with organic molecules such as thiols. In the case of **P1**, the structured absorption bands are found to be significantly perturbed when functionalized on to the surface of Au nanoparticle (figure 1A, curves a to c), indicating a strong ground state interaction between the plasmon electrons of Au nanoparticle and the π -electrons of pyrene chromophore. Pyrenyl moiety on **Au-P1** is very close to the metal surface and the possibility of electronic perturbation is very high. Similar ground state interaction was observed between 1-pyrenemethylamine and tetraoctylammonium bromide stabilized Au nanoparticle [17]. In contrast, the absorption spectra of **Au-P2** and **Au-P3** are almost the additive spectra of dodecanethiol-capped gold nanoparticles and pyrene alkanethiols of respective loadings. The structured absorption bands of pyrene remain more or less unperturbed (figure 1B, 1C; curves b–d), indicating the absence of any ground state interaction. The possibility of end-terminated pyrene chromophores in **Au-P2** and **Au-P3** directly interacting with gold is very less due to the presence of

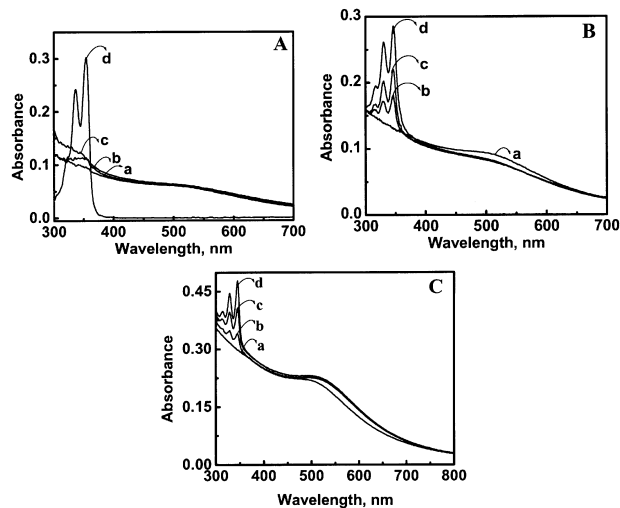


Figure 1. Absorption spectra (in toluene) of Au nanoparticles functionalized with dodecanethiol (trace a in B and C) and a mixture of pyrene alkanethiols and dodecanethiol, in different molar ratios, (**A** for **P1**): (a) 3:17, (b) 3:7, (c) 3:2, (d) unbound P1; (**B** for **P2**): (b) 3:17, (c) 3:7, (d) 3:2; (**C** for **P3**): (b) 3:17, (c) 3:7, (d) 3:2 (reprinted from ref. [10] with permission from the American Chemical Society).

densely packed alkyl chains and the hydrophobic repulsive interactions with the alkyl chain moieties [9,10].

2.3 Excited state interactions

Pyrene has a characteristic structured emission between 375 and 390 nm, corresponding to the singlet excited state of its monomer. A broad emission band between 450 and 550 nm is observed when the concentration of pyrene is high enough to form excited state dimers (excimer) [18]. It is well-established that the optimum condition for excimer formation in pyrene is a parallel, sandwich type arrangement with an interplanar separation of 3.53 Å [18].

The excimer formation of pyrene alkanethiol functionalized on gold nanoparticles is strongly dependent on the loading of the chromophores and the length of the spacer groups (figure 2). In all the three cases, the structured bands, characteristic of the monomer emission of pyrene were observed between 375 to 390 nm. No excimer emission was observed even at a high loading of 60% pyrene in the case of **Au-P1** (figure 2A), where pyrene is linked to Au nanoparticle by a methylene group. In contrast, the excimer emission centered around 480 nm become prominent for **Au-P2** and **Au-P3** systems at higher loadings (figures 2B and 2C). It may be noted that **Au-P2** and **Au-P3** nanoassemblies possess seven and ten spacer groups between Au nanoparticle and pyrene chromophore. The flexible chain tethering pyrene in Au-P3 is sufficiently long to protrude outside the dodecanethiol layer

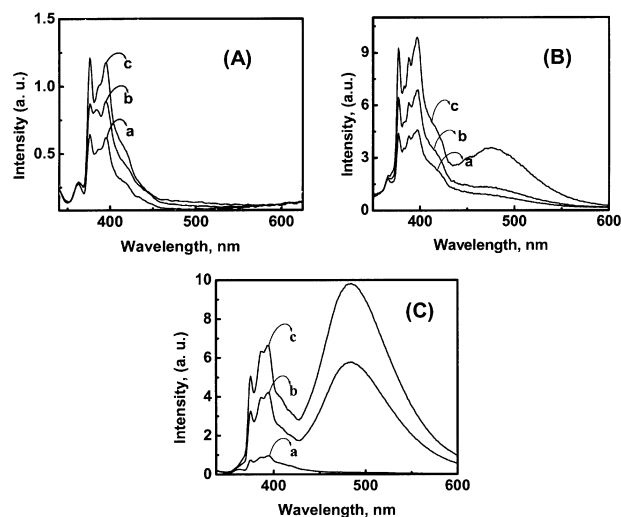
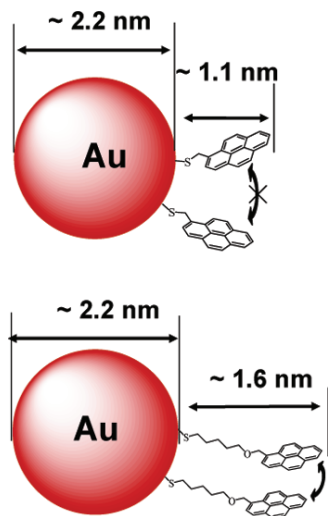


Figure 2. Emission spectra of Au nanoparticles functionalized with different loadings of pyrene thiols. **(A)**: (a) 15%, (b) 30%, (c) 60% of P1; **(B)** (a) 15%, (b) 30%, (c) 60% of P2; **(C)**: (a) 15%, (b) 30%, (c) 60% of P3, in toluene (excitation wavelength 328 nm, Au concentrations were kept constant by optically matching the solutions at 520 nm) (reprinted from ref. [10] with permission from the American Chemical Society).

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Scheme 2. Representation of pyrene alkanethiols on Au surface.

allowing free interaction between pyrene molecules, at higher loadings. On the other hand, pyrene chromophores in **Au-P1** are linked to Au nanoparticles by a single methylene group and the interplanar distance between the pyrene molecules is larger due to the restrictions imposed by the curvature of gold surface (scheme 2). In the case of **Au-P1**, no excimer emission was observed even at 60% loadings. It may be because the pyrene chromophores are deeply embedded inside dodecanethiol.

2.4 Surface polarity of nanoparticles

Pyrene-based fluorophores possess structured emission peaks and are the best suited for studying the polarity of the environment [4,18,19]. It has been reported that there is a significant enhancement in the emission intensity of the 0-0 vibronic band at the expense of other bands on varying the solvent polarity. The relative intensity of III to I peak is often used to measure the polarity of the medium (Ham effect) [19]. To study the polarity of the nanoparticle's surface environment, the relative intensities of the peak I (379.9 nm) and III (387.9 nm) were compared as a function of the length of spacer (figure 3). It was observed that for the single methylene-spaced pyrene–Au nanoparticle system (**Au-P1**), the ratio III/I is 0.8 whereas for the **Au-P2** and **Au-P3** systems with seven and ten spacer groups, the ratios turn out to be 0.98 and 1.18 respectively (table 1). This gradual increase in the ratio suggests that the local environment near the nanoparticle surface is more polar compared to the bulk medium (toluene).

2.5 Light-induced electron transfer processes

Close vicinity of a metal nanocore alters the excited deactivation pathways of the surface-bound fluorophores. For example, Dulkeith *et al* have observed a distance-dependent quenching of excited states of chromophores on metal nanoparticles [20].

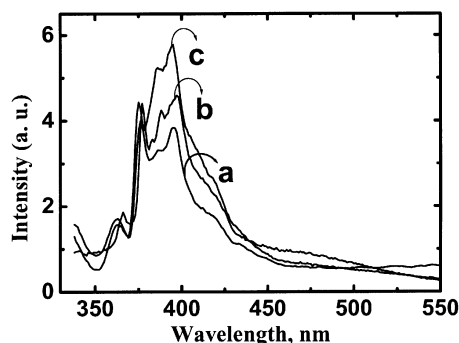


Figure 3. Emission spectra of (a) **Au-P1**, (b) **Au-P2** and (c) **Au-P3** at 15% loading.

In the case of pyrene alkanethiol functionalized on Au nanoparticle, the excimer formation depends strongly on the local concentration of pyrene on the surface of nanoparticles and length of the spacer groups used. Also it is observed that the emission yield of pyrene alkanethiol functionalized on Au nanoparticle is lower than that of unbound molecules in polar solvents. However, due to the strong overlap and plasmon absorption with the pyrene emission it is difficult to quantify these results and obtain an understanding on various deactivation channels. The possible deactivation pathways of the photoexcited pyrene bound to Au nanoparticle were further investigated by following time-resolved fluorescence studies. The unbound pyrene alkanethiols follow a biexponential decay, with a long-lived component ($\tau_1 \sim 8$ ns) and a short-lived component ($\tau_2 \sim 1.8$ – 2.5 ns). The long-lived component was attributed to the inherent lifetime of pyrene alkanethiols and the short-lived component is assigned to the decay of quenched pyrene alkanethiol molecules, resulting from the interaction with another ground state pyrene alkanethiol molecule, leading to the formation of excited state dimers. In addition, an extremely short-lived species was observed when pyrene alkanethiols (**P1** and **P2**) were functionalized on the surface of Au nanoparticles (**Au-P1**, $\tau_3 = 27$ ps and **Au-P2**, $\tau_3 = 48$ ps). It is observed that the relative abundance of the short-lived species (τ_3) increases significantly with increase in solvent polarity. Lifetimes of the long-lived (τ_1) and short-lived (τ_2) components and their relative distribution remain more or less unaffected for **Au-P3**, in toluene. These results rule out the possibility of any quenching process (electron or energy transfer) in nonpolar solvents (toluene) when **P3** is bound to Au nanoparticle. The transient absorption

Table 1. The ratio of III/I peak in comparison with the spacer groups between chromophore and nanoparticle core.

Nanohybrid system	Spacer	III/I
Au-P1	–(CH ₂)–	0.89
Au-P2	–CH ₂ O(CH ₂) ₅ –	0.98
Au-P3	–CH ₂ O(CH ₂) ₈ –	1.18

studies using **Au-P1** system have revealed the formation of pyrene radical cation further confirming the electron transfer process from bound pyrene to Au nanoparticle [13].

3. Conclusions

Thiol derivatized pyrene fluorophores were successfully employed to probe the polarity of the nanoparticle surface and it is concluded that the local environment close to the surface of Au nanoparticle is more polar compared to the bulk medium (toluene). Excited state properties of the fluorophore on the surface of nanoparticle depend mainly on fluorophore–nanoparticle distance and the concentration of fluorophore functionalized on the surface. Time resolved studies indicate that the light-induced electron transfer process is favored from pyrene to the Au core in polar solvents.

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