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Enhanced Sensitized NIR Luminescence from Gold Nanoparticles via Energy Transfer from Surface-Bound Fluorophores

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Systems that show luminescence in the NIR region are attracting increasing attention for their applications in the fields of diagnostics[1] and telecommunication.[2] Besides the molecular approach, which has led to the synthesis of extremely efficient dyes,[3] nano-objects such as quantum dots[4] and nanorods[5] have been recently proposed as promising alternatives to conventional luminophores. In this context, only a few examples of luminescence from gold nanoparticles have been reported, all showing a strong dependence of the emission properties on the nature of the ligands. In the case of large nanoparticles (radius > 2 nm) Gittins and co-workers observed a very weak plasmon emission in the visible region ($\Phi = 10^{-6}$) upon photoexcitation.[6] A more intense ($\Phi \approx 10^{-3}$) luminescence in the NIR region has been reported by Whetten[7] and by Murray[8] in the case of smaller monolayer-protected gold clusters. Furthermore, to our knowledge, only one example of luminescence sensitized via static energy transfer from a dye to gold nanoparticles has been reported to date.[9] However, in that case, only a minor fraction of the dye, electrostatically adsorbed to the surface, was involved in the process, and as a consequence, most of the absorbed light was not funneled to the nanoparticles' luminescent excited states. What we report here is the first case in which an extremely efficient transfer of excitation from fluorophores directly bound to the surface leads to a strong sensitized luminescence from gold nanoparticles.[10]

In particular, the luminescence quantum yield of 1.8 nm triphenylphosphine (TPP)-stabilized gold nanoparticles not only increases by at least 2 orders of magnitude if TPP is replaced with the pyrene derivative **P** shown in Figure 1 but is further enhanced by a factor of 3 if excitation is performed via excitation energy transfer from the pyrene molecule bound to the nanoparticles' surfaces.[11] Moreover, due to the high efficiency of the energy transfer process, the fluorophores behave as an efficient light-harvesting system that strongly increases the excitation efficiency and thus the brightness of the nanoparticles.

We modified the synthetic strategy proposed by Hutchison in order to prepare phosphine-stabilized 1.8-nm diameter gold nanoparticles.[12] Luminescence in the NIR for gold nanoparticles of this size was reported by Murray for particles stabilized with tiopronin ligands ($Au_{201}Tiopronin_{85}$).[8c] Synthesis of samples **N0** and **N2** was carried out in the presence of TPP or **P** respectively. **N1** was prepared from a mixture of the two ligands (see Supporting Information).[11] The ratios of **P** to gold atoms in the purified samples are reported in Table 1.

Absorption spectra of nanoparticles **N1** and **N2** are dominated by the contributions of the pyrene chromophores in the UV regions and are almost superimposible on the absorption spectrum of **N0** in the visible−NIR range (Figure 1). However, if the absorption spectra of **N1** and **N2** are compared with a suitable combination of the spectra of **N0** and **P**,[13] as in Figure 1, it becomes evident that the absorption bands of pyrene are significantly broadened and red-shifted when it is bound to the nanoparticle surface, indicating a strong interaction among the gold core and the pyrene moieties and between the chromophoric units themselves.[14] The absence of the plasmon resonance band for all samples is in agreement with the diameter measured in the TEM experiments ($d = 1.8 \pm 0.5$ nm).[15]

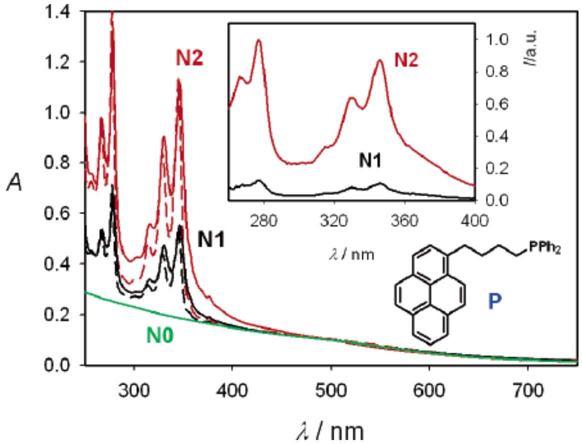

Figure 1. Absorption spectra of nanoparticles **N0**, **N1**, and **N2** (continuous line). In the case of **N1** and **N2** the spectra resulting from an additive combination of the spectra of the components **N0** and **P** (ref 13) are shown as dashed lines. (Inset) Corrected luminescence excitation spectra of nanoparticles **N1** and **N2** at 740 nm.

Table 1. Photophysical Properties of Nanoparticles **N1** and **N2**

	d/nm[a]	Au:**P**[b]	Φ_{345}[c]	stΦ_{450}[d]	$\langle\tau\rangle/\mu s$[e]
N1	1.8 ± 0.6	8.3	3×10^{-3}	1.5×10^{-3}	0.5
N2	1.8 ± 0.5	3.3	1.5×10^{-2}	4.5×10^{-3}	0.7

[a] Average diameter. [b] Molar composition ratio between gold atoms and molecules of **P**. [c] NIR luminescence quantum yield upon excitation at 345 nm. [d] NIR luminescence quantum yield upon excitation at 450 nm. [e] Average excited-state lifetime.

We investigated the luminescence behavior of these systems upon excitation either of the dye or of the metal core. The solutions were diluted by a factor of 12 in order to avoid inner filter effects.[16] Nanoparticles **N0** show almost no luminescence ($\Phi < 10^{-4}$) upon excitation either at 345 or 450 nm. The presence of the pyrene derivative **P** on the surface, on the other hand, causes a strong enhancement of the luminescence. Luminescence spectra recorded upon direct excitation of the metal core ($\lambda_{exc} = 450$) in the case of **N1** and **N2** (Figure 2, inset) show broad emission bands in the NIR region. Table 1 shows that the luminescence quantum yield is 3 times higher with the highest loading of pyrene.

As far as the excited-state lifetimes are concerned, in both cases a multiexponential decay was recorded; the average excited-state

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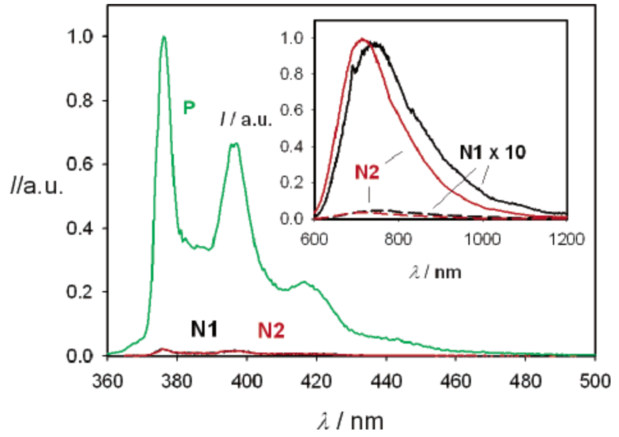

Figure 2. Corrected luminescence spectra of nanoparticles **N1** and **N2** and of **P**, upon excitation at 345 nm. (Inset) Corrected luminescence spectra of nanoparticles **N1** and **N2** upon excitation at 450 nm (dashed lines) and 345 nm (continuous lines).

lifetimes are reported in Table 1. The higher luminescence quantum yield of **N2** corresponds to a longer average lifetime, suggesting that the presence of **P** prevents nonradiative deactivation processes from occurring. Unfortunately, the impossibility of recording the decay for **N0** due to the weakness of the signal did not allow a deeper investigation of this kind of nanoparticles. The luminescence spectra resulting from excitation at 345 nm show, in the region between 360 and 500 nm, a very weak band with the typical structure of the pyrene fluorescence (Figure 2). An excited-state lifetime shorter than 0.5 ns was measured both for **N1** and **N2** for the residual emission. Overall, the average efficiency of the quenching process is extremely high (>95%) and fast enough to prevent pyrene excimer formation. Both Förster[17] and NSET[18] theories are compatible with the observed quenching; the synthesis of different ligands with increasing chain length are in due course in our laboratories in order to investigate the nature of the mechanism involved in the energy transfer process.

The same luminescence bands in the NIR region observed by direct excitation of the gold clusters result from the excitation of the pyrene molecules bound to their surfaces at 345 nm (Figure 2, inset). The presence of a very strong contribution of the typical bands of the pyrene in the excitation spectra recorded at 740 nm (Figure 1, inset) definitely supports the occurrence of a very efficient energy transfer process that leads to the sensitized emission of the gold core. Surprisingly the luminescence quantum yield, calculated in the case of a 100% efficient energy transfer process, is, upon sensitized excitation, considerably higher both for **N1** and **N2**. This unprecedented result confirms that the luminescence of gold nanoparticles in some cases originates from excited states located near the metal surface;[7,8b,d] the population of these states is in fact more efficient if it takes place by transferring energy from excited fluorophores which are located close to the surface than it is via relaxation after direct excitation of the gold core. In addition to causing the effect on the luminescence quantum yield, the fluorophores bound to the surface play other interesting roles. Excitation efficiency at 345 nm is, in fact, strongly increased due to the high absorbtivity and the large number of pyrene molecules bound to the surface, and of course, to the high efficiency of the energy transfer process. The overall effect upon sensitized excitation is to make the brightness of the system 1 order of magnitude higher than upon direct excitation.

In conclusion, the described systems showed extremely valuable features since NIR emissions, large Stoke's shifts, and long lifetimes are all desirable properties for analytical applications in biology and medicine. Finally the replacement of pyrene with other fluorescent molecules could allow the fine-tuning of the excitation wavelength, leading to a new generation of probes for the NIR region.

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Supporting Information Available: Synthesis of the samples and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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