

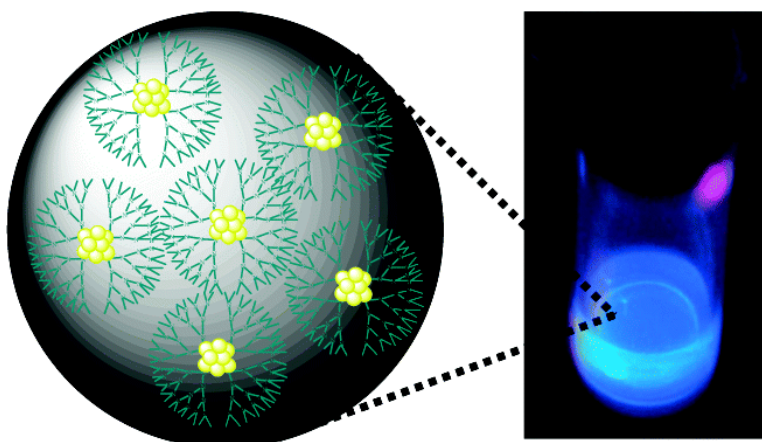
Communication

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## High Quantum Yield Blue Emission from Water-Soluble Au<sub>8</sub> Nanodots

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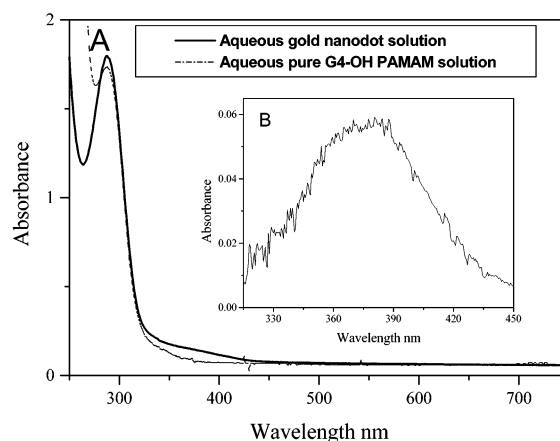
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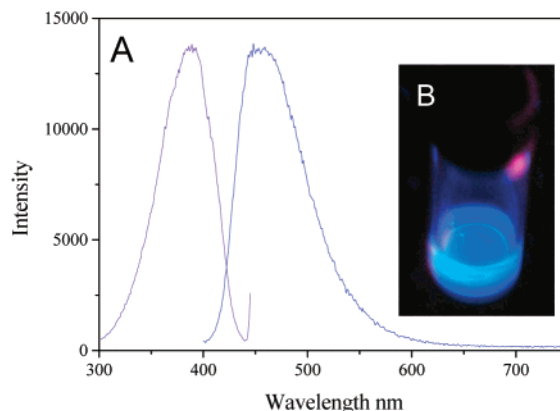
Usually occurring at the nanoscale, material properties drastically change as their sizes approach characteristic length scales. Such confinement effects often yield nanomaterials with greatly improved and potentially controllable properties. Metals exhibit a particularly wide range of material behavior along the atom to bulk transition.<sup>1–11</sup> At sizes comparable to the Fermi wavelength of an electron, optical properties are significantly modified, and discrete nanocluster energy levels become accessible.<sup>1–3</sup> Such metal nanoclusters, composed of only several tens of atoms, exhibit molecule-like transitions as the density of states is insufficient to merge the valence and conduction bands.<sup>5,7–9</sup> Such studies have yielded fluorescent, surface passivated Au nanoclusters ranging in size from 28 atoms to smaller particles (<1.2 nm) with emission in the near-IR,<sup>4</sup> red,<sup>10</sup> and blue,<sup>11</sup> with increasingly higher energy emission with decreasing nanocluster size. Although Au nanoclusters with million-fold enhanced fluorescence quantum yields  $\phi_F$ , relative to that of bulk gold films,<sup>12</sup> have been created, the  $10^{-3}$ – $10^{-4}$  quantum yields and polydisperse nanoparticle size distributions have precluded them from being good fluorophores.<sup>4,10</sup> Herein, we report water-soluble, monodisperse, blue-emitting Au<sub>8</sub> nanodots that, when encapsulated in and stabilized by biocompatible poly(amidoamine) (PAMAM) dendrimers,<sup>13</sup> exhibit a fluorescence quantum yield of  $41 \pm 5\%$ , a more than 100-fold improvement over other reported gold nanoclusters.<sup>4,10</sup>

Widely used to prepare larger metallic and semiconductor nanoparticles,<sup>14–17</sup> second and fourth generation OH-terminated PAMAM (G2-OH and G4-OH, respectively, Aldrich) were utilized to stabilize and solubilize gold nanoclusters in both aqueous and methanol solutions. By dissolving 0.5  $\mu\text{mol}$  of G4-OH or G2-OH and 1.5  $\mu\text{mol}$  of  $\text{HAuCl}_4 \cdot n\text{H}_2\text{O}$  (Aldrich) into 2 mL of distilled water (18 M $\Omega$ ), gold ions were sequestered into dendrimers and reduced by slowly adding an equivalent of  $\text{NaBH}_4$  into the solution. Reduced gold atoms aggregate within the dendrimers to form small nanodots (dendrimer-encapsulated nanoclusters) and large nanoparticles. The solution was stirred for 2 days until reaction and aggregation processes are completed. Solutions were subsequently purified through centrifugation (13 000g) to remove the large gold nanoparticles,<sup>16</sup> leaving a clear, colorless, Au nanodot solution. Although weak as compared to the 285 nm pure dendrimer peak, a clear absorption spectrum of dendrimer encapsulated gold nanodots is obtained by subtracting the pure dendrimer absorption. It can be seen from Figure 1B that a new absorption band at 384 nm with a bandwidth of  $\sim 60$  nm (fwhm) appears in the final fluorescent Au nanodot solutions. Contrary to the absorption spectrum of large gold nanoparticles, no surface plasmon absorption at 520 nm is observed from this solution, indicating that the nanodots are smaller than  $\sim 2$  nm.<sup>16</sup>

Strong blue luminescence with excitation and emission maxima at 384 and 450 nm, respectively, is clearly observed from these dendrimer encapsulated gold nanodot solutions (Figure 2A). The



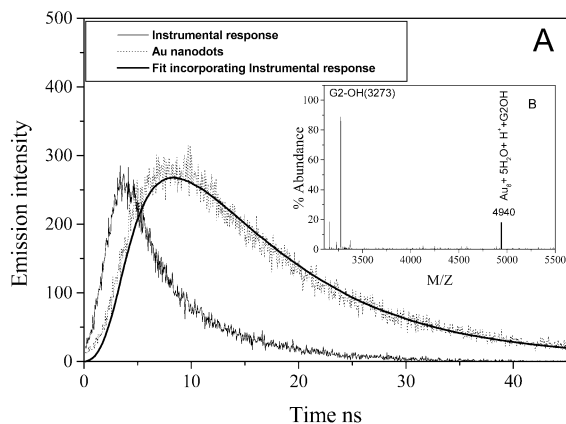
**Figure 1.** (A) UV-vis absorption spectra of aqueous gold nanodot and pure dendrimer solutions. (B) Subtraction of absorption spectra in A reveals the 384-nm absorption of PAMAM encapsulated Au nanodots.



**Figure 2.** (A) Excitation and emission spectra of G4-OH PAMAM encapsulated gold nanodots at room temperature. (B) Emission from Au nanodots under long-wavelength UV lamp irradiation (366 nm).

fluorescence excitation maximum and bandwidth are identical to the nanodot absorption band in Figure 1. While G2-OH and G4-OH dendrimers yield indistinguishable fluorescent solutions, G0 dendrimers yield only nonfluorescent solutions with black gold solids under the same synthetic conditions. These heterogeneous solutions suggest that, unlike larger second and fourth generation PAMAM, small zeroth generation dendrimers do not adequately protect and stabilize gold nanoclusters. Amazingly, for 384-nm excitation, integrated fluorescence quantum yields for G4-OH and G2-OH encapsulated gold nanodots are  $41 \pm 5\%$  using similarly emitting quinine sulfate as the reference. The quantum yield further increases in methanol to  $52 \pm 5\%$ . The time dependence of the emission shows that there are two lifetime components (Figure 3A), which are characteristic of gold nanodot emission.<sup>4</sup> The short lifetime component is 7.5 ns, which is dominant (93%) in the emission and likely arises from singlet transitions between low-

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**Figure 3.** (A) Lifetime measurement of gold nanodots in aqueous solution. Instrumental response and nanodot data with fit exhibit the 7.5 ns (93%) and 2.8  $\mu$ s (7%) lifetimes. (B) ESI mass spectrum of G2-OH PAMAM encapsulated gold nanodots with expected  $m/z$  of 4940 for G2-OH + Au<sub>8</sub> + 5H<sub>2</sub>O + H<sup>+</sup>.

lying d bands and excited sp bands of gold nanodots. The long lifetime component (2.8  $\mu$ s, 7%) may be due to a triplet–singlet intraband transition.<sup>4,10</sup>

The well-defined dendrimer structure enables analysis of encapsulated nanocluster sizes with electrospray ionization (ESI) mass spectrometry. As shown in Figure 3B, Au<sub>8</sub> is the dominant Au-containing component in the fluorescent solutions, and its abundance directly correlates with fluorescence intensity, independent of sample preparation. In fact, depending on reduction conditions, Au concentrations, and dendrimer generations, different Au-containing peaks can appear in the mass spectra. In all cases (>20 differently prepared samples), fluorescence intensity was only related to the abundance of the Au<sub>8</sub>-containing species observed in the mass spectra. In accord with stable nanoclusters having eight valence electrons (one from each Au atom),<sup>18</sup> this dominant nanocluster is confirmed to be in the overall neutral oxidation state as even 100-fold excess of highly reducing BH<sub>4</sub><sup>-</sup> does not alter the nanodot fluorescence. Confirmed through expected shifts relative to the dendrimer parent peak upon dissolution in D<sub>2</sub>O instead of H<sub>2</sub>O, five molecules of water were also found to be associated with the hydrophilic PAMAM dendrimer–Au complex. While five molecules of water appears to be the favored number, smaller peaks corresponding to Au<sub>8</sub> with other numbers of water molecules ranging from one to six were also observed in the mass spectra of other similarly prepared samples. The peaks containing Au<sub>8</sub> were only observed in the fluorescent Au nanodot solutions, and fluorescence intensities of differently prepared solutions are directly proportional to the relative abundance of the Au<sub>8</sub> nanodot peaks alone. Additionally, Au nanodot preparations using both HAuCl<sub>4</sub> and AuBr<sub>3</sub> yield indistinguishable fluorescent solutions with identical mass spectra. This indicates that the highly efficient blue emission results from Au<sub>8</sub> nanodots.

As mentioned above, luminescence from gold nanodots is thought to arise from transitions between the filled d band and sp conduction

bands.<sup>4,10,19</sup> As nanocluster size decreases, the spacings between discrete states in each band increase, leading to a blue shift in fluorescence relative to that from larger nanodots. The more than 100-fold fluorescence quantum yield enhancement over that of differently prepared larger nanoclusters probably results from two factors. The lower density of states present in very small Au<sub>8</sub> nanoclusters minimizes internal nonradiative relaxation pathways. Additionally, the larger dendrimer cage better protects these nanoclusters/nanodots from quenchers in solution. This latter interpretation is suggested by the zeroth generation dendrimer being unable to stabilize fluorescent Au nanodots. Additionally, in the purified solutions, there are no large gold nanoparticles to quench the nanodot fluorescence.<sup>20,21</sup>

In conclusion, monodisperse Au<sub>8</sub> nanodots were synthesized and stabilized in dendrimer PAMAM aqueous solution. Au<sub>8</sub> nanodots show strong size-specific emission, with a quantum yield of ~41% in aqueous solution. Practical applications of gold nanodots as a novel fluorophore become possible due to the more than 100-fold enhancement in quantum yield.

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