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Synthesis and spectroscopic observation of dendrimer-encapsulated gold nanoclusters

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We report on the observation of the excitation/emission spectrum of a dendrimer-encapsulated gold nanocluster; the synthesis of Au-PAMAM was based on reduction of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ co-dissolved in methanol together with fourth-generation OH-terminated PAMAM.

Confinement of an electron within a metallic nanostructure at sizes comparable to the Fermi wavelength of the electron¹ results in electronic energy states which exhibit molecule-like transitions as the density of these states is too low for reproducing bulk properties of the metal. Such nanostructures present new materials with controllable (size-dependent) properties.^{2,3} A new synthesis of small metal clusters based on sequestration of metals from the solution into dendrimers has been recently reported by Zheng *et al.*⁴ and triggered intensive discussion in the literature.^{5,6}

Discrete band electron configuration has been predicted and was experimentally observed a while ago for cluster sizes as small as 3 atoms.⁷ It has been realized, however, that fluorescence emission is hindered by the rapid dissociation of the cluster from its electronically excited state.⁷ The stabilization of the metal cluster within a host matrix has been introduced as a solution to the photodissociation problem, and the UV fluorescence of Ag_8 clusters encapsulated into liquid argon droplets has been unequivocally observed.⁸ Aiming at production of metal nanoclusters at room temperature, the synthesis of an extremely stable 28-atom gold cluster capped by a monolayer of 16 tripeptide glutathione units has been developed.⁹

However, it was undoubtedly a remarkable achievement when water-soluble, monodisperse, blue-emitting Au_8 nanoclusters were stabilized by encapsulation in biocompatible poly(amidoamine) (PAMAM) dendrimers, and were reported to exhibit a stable fluorescence of high quantum yield of $41 \pm 5\%$.⁴ Subsequently, Zheng *et al.* described the synthesis of size-controlled Au nanoclusters characterized by excitation/emission spectra spanning the spectral range from UV to near-infrared.¹⁰ Stable, highly efficient gold nanocluster-based fluorophores protected by a biologically compatible dendrimer matrix represent very attractive optical labels for biological applications.¹¹ However, the production of these gold nanoclusters remained unique to one research group for several years. Attempts to follow the reported chemical

path have failed to find spectroscopic signatures of the gold nanoclusters.⁵ In place of the fluorescence emission at 450 nm characteristic of Au_8 nanoclusters, the chemical and spectroscopic analysis showed profound blue emission at the same wavelength whose origin was unambiguously assigned to hydroxyl-terminated PAMAM. Moreover, Wang and Imae have reported considerable enhancement of typically weak (background-level) fluorescence emission at 450 nm upon pH adjustment of NH_2 -terminated fourth-generation (G4) PAMAM whose maximum intensity was achieved at low pH values (pH 2).⁶ Based on these observations, the authors attributed the strong blue fluorescence to solely the PAMAM dendrimer and ruled out the contribution of gold nanoclusters. Although Zheng *et al.* have also noticed a similar fluorescence signal merging to that of Au_8 , they were, nonetheless, able to separate them using a signal processing algorithm.⁴ Contrarily, Lee *et al.*, Wang and Imae maintained that the observed signal originated purely from OH- or NH_2 -terminated PAMAM.^{5,6}

In order to shed light on the Au-PAMAM synthesis ambiguity, we report on our synthesis of the Au-PAMAM, a modified synthesis of that described by Lee *et al.*,⁵ and spectroscopic observations of the resultant product. Widely used to prepare larger metallic and semiconductor nanoparticles, fourth generation OH-terminated PAMAM (G4-OH, Aldrich) was utilized to stabilize and solubilize gold nanoclusters in both aqueous and methanol solutions. By dissolving 5 μmol of G4-OH PAMAM and aqueous HAuCl_4 (25 mM, 10 μmol) (Aldrich) in 40 mL of methanol, gold ions were sequestered into dendrimers for a few days and reduced by slowly adding NaBH_4 (30 μmol) into the solution. Reduced gold atoms aggregate within the dendrimers to form small dendrimer-encapsulated nanoclusters and large (few nm) nanoparticles. The solution was then stirred for a further few days to complete the reaction and aggregation processes. It was subsequently purified through centrifugation (5500 rpm) to remove the large gold nanoparticles, leaving a clear, colorless solution. We tested three samples prepared following this described procedure. In addition, pure G4-OH PAMAM dendrimer was used as the control sample. The series of excitation and emission spectra of these samples were acquired using a Jobin Yvon Horiba Fluorolog-3 fluorescence spectrometer with a 450 W Xe lamp and PMT detector.

As expected, we observed a strong fluorescence band from the treated G4-OH PAMAM solution. We were not able to detect any emission from the control sample. Excitation and emission spectra of the treated dendrimer are presented in Fig. 1.

The excitation/emission peaks at 382/445 nm agree very well with the previously reported data on G4-OH PAMAM.⁵ We also

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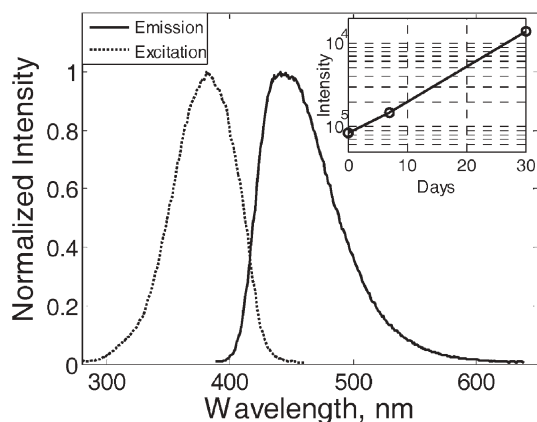


Fig. 1 “Blue” emission and corresponding excitation spectra of the G4-OH PAMAM solution. Inset: Semi-logarithmic plot of the evolution of the emission signal in time.

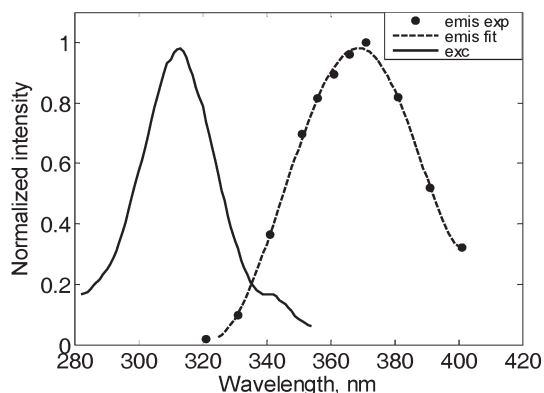


Fig. 2 Excitation (solid) and emission (dots and dashed) spectra of the sample in the UV spectral range ascribed to dendrimer-encapsulated Au₄. Dots denote experimental data fitted with a 5th order polynomial (dashed).

observed a noticeable effect of aging (see Fig. 1, inset) of a gold-dendrimer sample, reported by Lee *et al.*⁵ and Wang and Imae.¹² We observed a 15-fold increase in the blue fluorescence yield over 30 days as compared to that of the freshly prepared sample. The rapid growth of the fluorescence yield is expected to slow down after 20 days according to the experimental data obtained in Ref. 12.

Most remarkably, in addition to the expected fluorescence signal, we observed a UV fluorescence signal whose excitation and emission spectra are presented in Fig. 2. Since the UV emission spectral signal was obscured by the presence of the strong PAMAM signal, we reconstructed it from the set of excitation spectra recorded at 10 nm intervals.

The presence of these spectral bands should be attributed to the Au nanoclusters, since the pure dendrimer showed no traces of such signals. The excitation, emission spectra peaks occurred at 313 nm (3.96 eV)/371 nm (3.34 eV), respectively, and were observed repeatedly for two samples, whereas one sample did not exhibit any gold-associated signals. Adopting the jellium model described by Zheng *et al.*,¹⁰ the gold nanocluster size should be

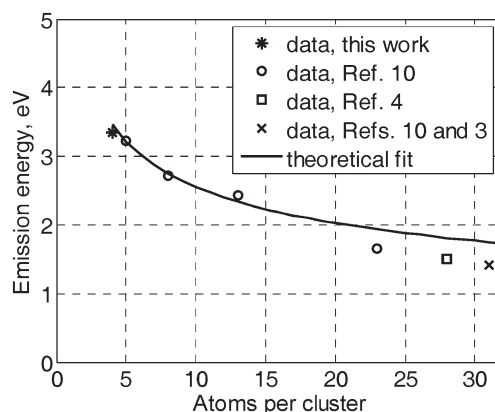


Fig. 3 Plot of the emission energy, E versus number of gold atoms per cluster, N . The reported data points (legend) were fitted by the theoretical curve (solid line): $E = E_i/N^{1/3}$, $E_i = 5.5$ eV – the work function of gold. The data point (cross) was obtained experimentally and confirmed theoretically.

ascribed to 4 atoms, although the jellium model predicts a slightly larger bandgap of 3.55 eV than that observed in our experiments (see Fig. 3). The excitation bandwidth (FWHM) of Au₄ G4-OH PAMAM of 34 nm (0.38 eV) is considerably narrower than that of the typical fluorescent dye, and is very consistent with the observations by Zheng *et al.* reporting FWHM of Au₅ G4-OH PAMAM of 0.42 eV.¹⁰ The emission curve of the dendrimer-encapsulated Au₄ is broader than that reported by Zheng *et al.*¹⁰ for larger Au-clusters and it tails off on the long-wavelength side of the frequency spectrum. Even though the signal processing artefact associated with the presence of the strong G4-OH PAMAM emission signal cannot be ruled out, an alternative mechanism of the spectral broadening has been proposed in the earlier publications, *e.g.* in the context of the spectral response of the stable Au₂₈-clusters.⁹ The spectral broadening may be attributed to the presence of two spectrally overlapping emission bands in the dendrimer-encapsulated Au₄, implying that the luminescence involves two different electronic states.

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