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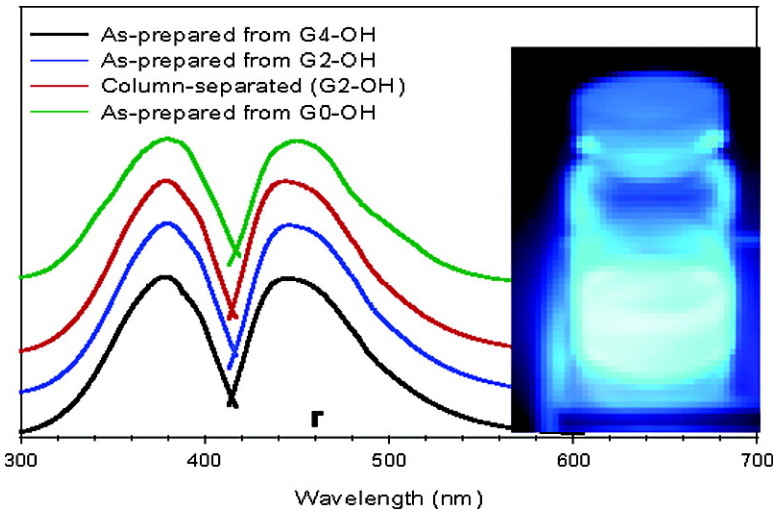

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Strong Blue Photoluminescence and ECL from OH-Terminated PAMAM Dendrimers in the Absence of Gold Nanoparticles

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Dendrimers have recently been of interest as new templates for the preparation of quantum dots of angstrom- to a few nanometer dimensions,[1−5] a size range where new optical, electrical, or magnetic properties are expected for metals or semiconductors. In addition the nanoclusters formed inside dendrimers are highly monodisperse, chemically stable, and free from agglomeration and are thus excellent systems for studies of quantum size effects. Au_8 nanoclusters encapsulated in dendrimers reportedly produce strong blue photoluminescence at 450 nm,[4] and we began an investigation of the electrochemistry and the production of ECL with such species. However, we found that photoluminescence with the same spectral profile was obtained without the addition of any Au species. Simple oxidation of OH-terminated PAMAM dendrimers, such as (fourth generation) G4-OH, G2-OH, or even G0-OH, e.g. with $(NH_4)_2S_2O_8$ (PS), produced species that showed blue photoluminescence with a high quantum yield.

The preparation method described below was quite simple and highly reproducible. A 0.2-mL aliquot of G2-OH (Aldrich, 20 wt % in MeOH) was added to 2.6 mL of distilled water, followed by addition of 0.2 mL of 0.1 M aqueous PS (Aldrich). After several hours, the colorless solution began to display blue luminescence under UV irradiation at 366 nm with the luminescence intensity gradually increasing with time up to several weeks. Moreover, the initially colorless solution changed to pale yellow after about a week. The UV−vis spectra shown in Supporting Information (Figure S1A) indicate that the characteristic absorption peak of pure PAMAM G2-OH dendrimer occurred below 300 nm. After the addition of PS, a new absorption band grew at around 380 nm, which slowly increased with time. This PS-treated G2-OH produced the strong blue luminescence shown in Figure 1. A PS-treated G2-OH aqueous solution diluted to 10 μM showed an emission band at 450 nm with the excitation band at 380 nm, coincident with the UV−vis absorption band (Figure S1A); both bands gradually increased with time, while their peak positions remained unchanged. With 380-nm excitation, the fluorescence quantum yield for this PS-treated G2-OH was 58 ± 5% with quinine sulfate (dissolved in 0.1 M sulfuric acid), showing a similar luminescence spectrum, used as reference.[6]

When the same treatment was applied to PAMAM G4-OH or G0-OH (technical grade, Dendritech Inc.), virtually the same blue photoluminescence was observed, with emission and excitation spectra very close to those of G2-OH (Figure 1A). The same treatment for amine-terminated PAMAM dendrimers, such as G4-NH_2, G2-NH_2, and G1-NH_2, produced only very pale-blue luminescence with intensities less than 0.01% of samples prepared from OH-terminated PAMAM. This observation suggests that the backbone of the PAMAM dendrimer is not important in the formation of luminescence centers but rather that the terminal −OH group plays a key role in generating the blue-luminescent species.

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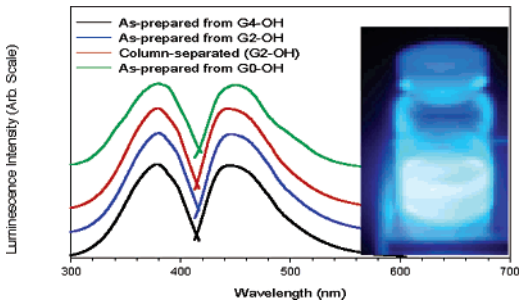

Figure 1. (A) Emission (EM) and excitation (EX) spectra for several PS-treated OH-terminated PAMAM dendrimers, concentrations of G4-OH, G2-OH, and G0-OH are 2.5, 10, and 40 μM, respectively. Each sample has been aged for 7 days. (B) Blue emission from the column-separated PS-treated G2-OH under 366-nm irradiation.

The chemical structure for this luminescence center is currently under investigation (see Supporting Information for preliminary characterization), but we speculate that the initial step of the reaction is the oxidation of a terminal −OH group by the PS, finally forming the blue-luminescent chemical species.

We also attempted to prepare Au_8 nanoclusters in the cavity of PAMAM G2-OH and G4-OH dendrimers by modifying the original procedure.[4] Ten micromoles of $HAuCl_4$ (Aldrich, 99.99%) was dissolved in 40 mL of MeOH (Aldrich, HPLC grade), and 5 μmol of G4-OH or 10 μmol of G2-OH was then added. The solution was magnetically stirred for 2 days in the dark. During this procedure some Au^{3+} ions were sequestered into the dendrimer, while other Au^{3+} ions precipitated as Au(0) from the solution. Thirty micromoles of fresh $NaBH_4$ dissolved in MeOH was then added dropwise to this solution to complete the reduction of Au^{3+} ions to metallic Au. The resultant solution was stirred for 4 days until the formation of any Au clusters was complete. Any Au^{3+} ions not sequestered into the dendrimer precipitated by the reduction of dendrimer or $NaBH_4$. The precipitated Au was collected by centrifugation, and a gravimetric analysis showed the weight percentage of Au in the G2-OH dendrimer to be 49 ± 5%. The luminescence properties of the prepared Au/G2-OH or Au/G4-OH samples after removal of the Au(0) were the same as those in the earlier report[4] and also the same as those of PS-treated dendrimers (Figure 2). However, the PS-treated dendrimers produced a 25−50-times higher luminescence intensity at the same dendrimer concentration.

We also prepared the Au/G2-OH in EtOH instead of MeOH under the same experimental conditions. In EtOH solution, most of the Au component was precipitated as Au(0) without being sequestered into the G2-OH (see Supporting Information). The Au incorporated into the G2-OH dendrimers represented only about 2% of the total gold added. Nevertheless, the resultant solution showed (Figure 2) an emission band at the same position and luminescence intensity comparable to that of Au/G2-OH prepared

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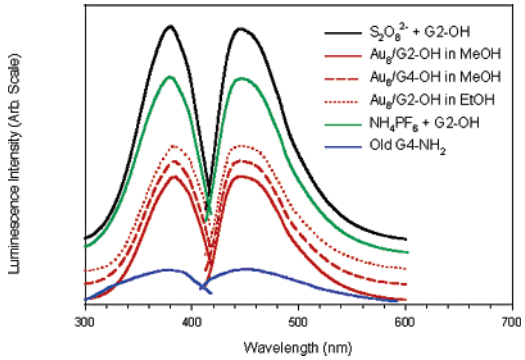

Figure 2. Emission and excitation spectra of several blue-luminescent species. The concentrations of PS-treated G2-OH, gold-treated G2-OH, gold-treated G4-OH, NH_4PF_6-treated G2-OH, and G4-NH_2 are about 10, 500, 250, 50, and 1000 μM, respectively.

in MeOH solution, clearly supporting that most of the blue luminescence originates from the dendrimer. The precipitation of Au(0) did not occur when NH_2-terminated dendrimers were employed, suggesting that Au^{3+} is reduced to metallic Au while oxidizing the OH-terminated dendrimer.

In a previous report, Au_8 was not formed in G0-OH, since this small-sized dendrimer was said to be unable to provide enough space to accommodate Au clusters.[4] However, we could prepare blue-luminescent material by treating G0-OH with PS, as shown in Figure 2, with the same conditions as for higher-generation dendrimers. The blue-luminescent chemical species could also be formed by simply adding NH_4PF_6 to G2-OH or G4-OH. In this case 2 μmol of G2-OH was added to 2 mL of 0.4 M NH_4PF_6. After a week, this solution produced the luminescence shown in Figure 2. Even a 3-year old sample of PAMAM G4-NH_2 (Starburst) produced a weak blue luminescence. Presumably, in these cases the dendrimers were oxidized during long exposure to the environment. Their luminescence intensities were quite different, but the spectral range of emission was the same (Figure 2).

The ECL of the PS-treated G2-OH could also be observed. The PS-treated G2-OH sample was dried in a vacuum at room temperature. The dried sample was then dissolved in 3 mL of H_2O/acetonitrile (50/50 by volume), with an estimated concentration of about 3.3 mM, and 0.1 M tetramethylammonium perchlorate (TMAP) was used as electrolyte. After purging with Ar gas and with a glassy carbon (3-mm diameter) working electrode, Pt wire counter electrode, and an Ag/AgCl reference electrode, ECL was observed when the electrode potential was cycled between +1.9 V and −2.5 V at a scan rate of 1 V/s (Figure 3A).[7,8] During the positive scan, a very small ECL peak occurred at ∼1.2 V and formed a plateau at 1.4 V. The ECL signal that appeared on the negative scan was relatively strong, appearing at about −1.8 V and increasing during the scan to more negative potentials. The ECL intensity of PS-treated G2-OH at negative voltages was appreciably stronger than background ECL of pure G2-OH.

When PS or sodium oxalate (10 mM) was added as a coreactant[9,10] to the PS-treated G2-OH solution, a considerable enhancement of the ECL signal was observed on the negative voltage scan, whereas the peaks at the positive voltage side were not appreciably changed. Because the ECL signal at −2.3 V was weak, its spectrum was obtained by employing several band-pass filters (average bandwidth, 10 nm) between the PM tube and glassy carbon electrode. As shown in Figure 3B, the maximum intensity occurred at 450 nm, suggesting that the ECL emission spectrum is very close to that of the photoluminescence and originates from the same species. From the applied potentials needed to produce ECL, the energy of the electron transfer was about 2.9 ± 0.1 eV, consistent with the optical transition of 2.8 eV from the photoluminescence spectrum. The data on the energy levels of HOMO and LUMO for this blue-luminescent species were 1.2 and −1.7 ± 0.1 V vs Ag/AgCl electrode (or 1.4 and −1.5 ± 0.1 V vs NHE), respectively.

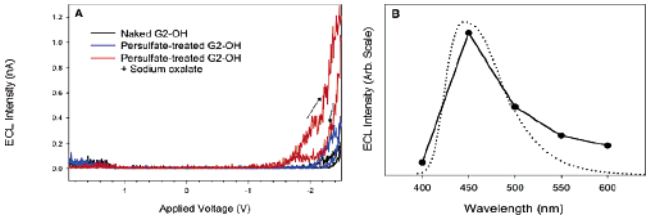

Figure 3. (A) ECL curves for naked G2-OH, PS-treated G2-OH, and PS-treated G2-OH with a coreactant (10 mM sodium oxalate). The concentration of G2-OH was 3.3 mM in H_2O/MeCN (50/50 by volume), and 0.1 M TMAP as electrolyte. Scan rate, 1 V/s, with first scan toward positive potentials. (B) Spectral profile of ECL signal emitted with −2.3 V scan at 1 V/s. The ECL signal passing through band-pass filters with 10-nm spectral width was detected with a PMT. The dotted line represents PL spectrum.

In conclusion, the strong blue luminescence found on treatment of dendrimers, Gn-OH (n = 2 or 4), with PS or Au(III)[4] mainly originates from oxidized OH-terminated PAMAM dendrimers. This blue-luminescent chemical species may have potential applications as a novel fluorophore or in aqueous ECL.

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Supporting Information Available: UV−vis spectra, preliminary characterization, preparation, and ECL details. This material is available free of charge via the Internet at http://pubs.acs.org.

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