

Fluorescence Emission from Dendrimers and Its pH Dependence

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There has been a great interest in the development of dendrimers which have morphological architectures differing from those of the typical polymers.^{1–3} Although dendrimers possess a precise composition and constitution, so far their structures are not necessarily clear, because no direct techniques can provide detailed information on their structures. In past years, some experimental works^{4–8} and molecular simulations^{9,10} have been reported concerning size, shape, and segmental distribution of dendrimer molecule.

The properties and applications of poly(amido amine) (PAMAM) dendrimer and its derivatives have been investigated extensively.^{11–15} Some researchers have used fluorescent probe techniques to investigate the properties of PAMAM dendrimer.^{16–20} Meanwhile, a weakly fluorescent “background” from the PAMAM dendrimers was observed by different research groups.^{16,18,21} Importantly, Larson and Tucker²² studied a weak but detectable fluorescence emission from carboxylate-terminated PAMAM dendrimer by two fluorescence techniques (excitation–emission matrices and lifetimes).

In this Communication, we report a strong fluorescence emission from fourth generation (G4) NH₂-terminated PAMAM dendrimer upon adjusting the pH value. It was found that there was a remarkable difference in fluorescence properties between G2 and G4 PAMAM dendrimers, and, moreover, both of them showed pH dependence in fluorescence intensity. The strong fluorescence was also observed from OH-terminated and carboxylate-terminated PAMAM dendrimers, and from NH₂-terminated poly(propyleneimine) dendrimer (PPI).

All dendrimers were purchased from Aldrich Chemical Co. and used without further purification. In our experiments, distilled deionized water (Millipore filtration system) was used. All solutions prepared were 0.7 mM in water. Prior to fluorescence measurement, solutions were kept at room temperature for 24 h.

Figure 1 shows excitation and emission fluorescence spectra of G2 and G4 NH₂-terminated PAMAM dendrimers. G4 presents two excitation bands at 250 and 390 nm, and an emission band at 450 nm. In comparison with G4, G2 showed very weak fluorescence bands that blue-shifted in an emission spectrum. These results indicated that the dendrimer structure or the microenvironment of the functional group significantly influenced the fluorescence properties. It is known that lower generation PAMAM dendrimers have an expanded or “open” configuration, but as the generation of dendrimer grows, the terminal functional groups become crowded and cause the dendrimers to take a densely packed globular structure.^{4,16,23}

Both G2 and G4 NH₂-terminated PAMAM dendrimers showed a significant pH-dependent fluorescence property in the pH range from 13 to 1 (as shown in Figures 2 and 3). For G4, when the pH decreased from 11 to 6, there was little change in the emission intensity. However, as the pH was reduced further, there appeared a rapid increase of fluorescence intensity, which reached maximum at about pH 2.5; the emission band position scarcely changed in this processing. On the other hand, the fluorescence intensity of

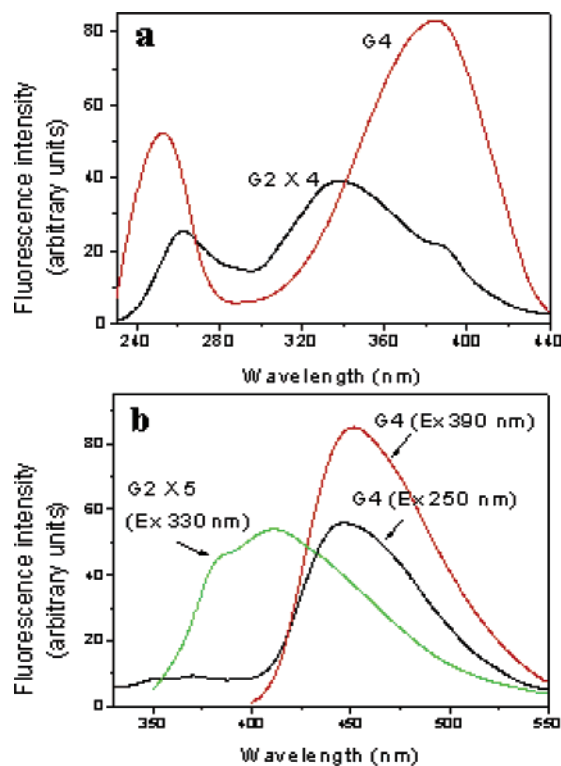


Figure 1. Fluorescence spectra of G2 and G4 NH₂-terminated PAMAM dendrimers at pH 2. (a) Excitation spectra emitted at 450 nm. (b) Emission spectra excited at different wavelengths.

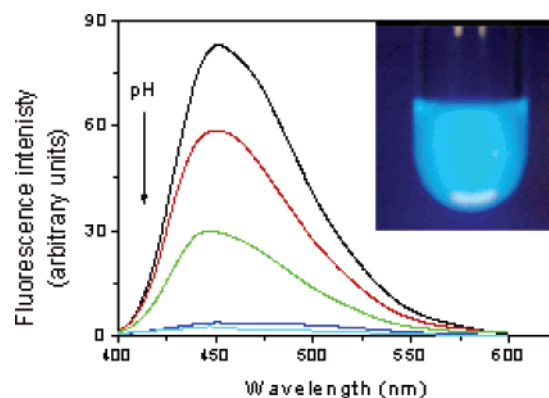


Figure 2. Fluorescence emission spectra of G4 NH₂-terminated PAMAM dendrimer at different pH values: pH 2, 4, 5, 9, and 11 (from top to bottom, excitation at 390 nm). Inset: An illumination photograph of aqueous 0.7 mM solution of G4 at pH 2. The solution was excited by a 4.5-W UV lamp.

G2 increased gradually from pH 11 to 4, where the maximum intensity was achieved. The above phenomenon can be explained on the basis of the following assumptions: (i) It is worth noting that pH 6 is the critical point in Figure 3, which correlates well

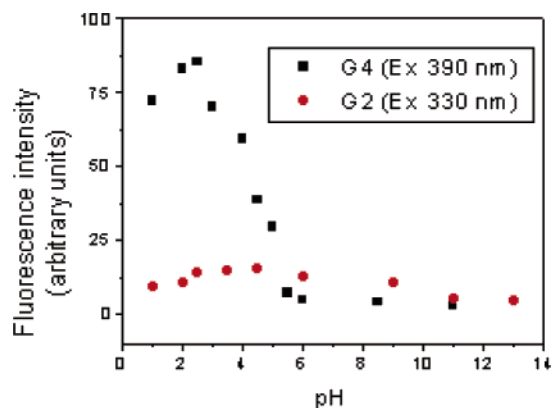


Figure 3. pH-dependent fluorescence intensity of G2 and G4 NH₂-terminated PAMAM dendrimers in the pH range from 1 to 13. Emissions of G2 and G4 were at 410 and 450 nm, respectively.

with the pK_a values^{14,15} of tertiary amines in PAMAM dendrimer. Below pH 6, the protonation of tertiary amine groups fills the whole dendritic interior with cations, and the strong charge–charge repulsion makes the structure of PAMAM dendrimer more rigid.^{8,13} (ii) The strength of the hydrogen bond in the dendrimer is enhanced under acidic condition.²³ (iii) It is also possible that chemical reaction of functional groups along dendrimer branches takes place under acidic conditions to form new fluorescent chemical species.²⁴

The fact that the strong fluorescence from these dendrimers was not observed previously^{16,18,21,22} may be due to an unsuitable pH value and a lower dendrimer concentration (linear relation between fluorescence intensity and concentration shown in Figure S1, Supporting Information). In addition, two discrete fluorescence lifetimes were found with similar values (around 1.7 and 7.5 ns) for G4 NH₂-terminated PAMAM dendrimer at different pH values. This result implied that the fluorescent species did not change at different pH values.

It is noted that, during the review of our manuscript, Lee et al.²⁴ reported a strong blue photoluminescence from OH-terminated PAMAM dendrimers after oxidation with (NH₄)S₂O₈. They also found that the same treatment for NH₂-terminated PAMAM produced very weak luminescence. They concluded that the backbone of the PAMAM dendrimer was not important in the formation of the luminescence centers but rather that the terminal-OH group played a key role. However, in our experiment, PAMAM dendrimers with different terminal groups, such as NH₂, OH, and carboxylate, produced similar fluorescent bands and intensities at the same dendrimer concentration at pH 6, as shown in Supporting Information (Figure S2). Importantly, we also found that G5 PPI dendrimer showed a strong emission band at 465 nm, with the excitation band at 430 nm, which was obviously different from PAMAM dendrimers (see Supporting Information, Figure S3). These results indicated that the backbone of the dendrimer played the key role in inducing the fluorescence if dendrimers were treated with acidification.

Zheng et al.²⁵ have reported fluorescence emission from G4 OH-terminated PAMAM dendrimer-encapsulated Au nanoparticles. The fluorescence band positions of excitation and emission reported in ref 25 were very close to those of G4 in Figure 1. It can be assumed that the fluorescence emission of hybrid nanoparticles comes from pure PAMAM dendrimer but not directly from Au nanoparticles.

From the classic viewpoint, the functional groups in PAMAM or PPI dendrimers could not emit the observed blue fluorescence. Now, it is difficult to explain the ultimately novel fluorescence phenomenon on the basis of our present experiments. Nevertheless, the phenomenon observed in the present work was highly reproducible. We also tested a sample of G4 NH₂-terminated PAMAM dendrimer synthesized in laboratory,⁸ and the obtained fluorescence phenomena were similar to those from commercial dendrimers. Furthermore, it was found that there was a general shift to longer fluorescence lifetimes with increasing generation.²² These data make the existence of a contaminant in the studied samples improbable.

In conclusion, a strong fluorescence emission was observed from different kinds of dendrimers under acidic conditions. There was a remarkable difference in fluorescence properties between G2 and G4 NH₂-terminated PAMAM dendrimers. It can be assumed that the backbone of the dendrimer played the key role in forming the novel fluorescent center.

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Supporting Information Available: Fluorescence spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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