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Journal of Colloid and Interface Science 306 (2007) 222–227
JOURNAL OF Colloid and Interface Science
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Fluorescence emission from PAMAM and PPI dendrimers

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Received 2 May 2006; accepted 13 October 2006

Available online 22 November 2006

Abstract

A strong fluorescence emission from poly(amido amine) (PAMAM) dendrimers with different terminal groups or a poly(propylene imine) (PPI) dendrimer was studied under different conditions by varying experimental parameters such as pH value, aging time, temperature, and concentration. The increase of fluorescence intensity was fast at low pH or high temperature but linear with respect to dendrimer concentration. It was reasonable that the formation of a fluorescence-emitting moiety had a close relation to protonated tertiary amine groups in PAMAM or PPI dendrimers. Furthermore, oxidation of the tertiary amines was confirmed to play an important role, which was evidently caused by oxygen in air. The results of fluorescence decay indicated that the deactivation of luminescence was raised with increasing temperature. Dendrimers emitted blue photoluminescence along fiber chain templates on a fluorescent microscope.

Keywords: Fluorescence; Emission; Photoluminescence; Poly(amido amine) dendrimer; Poly(propylene imine) dendrimer; Dendrimer; Oxidation; Fluorescence lifetime; Fluorescence microscope

1. Introduction

Dendrimers are morphological architectures differing from typical polymers. In the case of poly(amido amine) (PAMAM) dendrimers, the repeating units, consisting of an amido amine, are grown from an ethylene diamine core, and the dendritic structure can be obtained with different terminal groups such as amine (–NH_2), hydroxyl (–OH), and carboxylate (–COO^-) [1,2]. Poly(propylene imine) (PPI) dendrimers are another important class of dendritic polymers, and tertiary amines exist commonly in interiors of both dendrimers [3–6].

Properties and applications of PAMAM and PPI dendrimers have been investigated extensively [7–17]. Some researchers have used fluorescent probe techniques to investigate the properties of PAMAM dendrimers [18–25]. Meanwhile, a weak fluorescent "background" from the PAMAM dendrimers was observed by different research groups [26–31]. Larson and Tucker [32] studied a weak but detectable fluorescence emission from a COO^--terminated PAMAM dendrimer by two fluorescence techniques (excitation–emission matrix and lifetime). Lee et al. [33] reported a strong blue photoluminescence from OH-terminated PAMAM dendrimers, which were treated with oxidation. In our previous work, it was also found that different kinds of dendrimers with tertiary amine branching points could emit strong fluorescence by adjusting pH value [34]. Furthermore, we observed that fluorescence emitted from PAMAM dendrimers or fullerodendrons was obviously affected by nanoparticles [35,36]. Because PAMAM dendrimers are a kind of organic molecules without traditional fluorophores, observations of the fluorescence were unexpected and attracted much attention. However, the fluorescence, which was emitted from nanohydrogels fabricated by triethoxysilyl focal poly(amido amine) dendrons, was characterized even by fluorescent microscopy [37].

In this paper, we report strong fluorescence emission from several kinds of dendrimers, such as NH_2-terminated, OH-terminated, and COO^--terminated PAMAM dendrimers and an NH_2-terminated PPI dendrimer. Fluorescence emission and excitation spectra are compared among all of the tested dendrimers. The significant influence on the fluorescence properties of experimental factors (pH, temperature, time, concentra-

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0021-9797/$ – see front matter
doi:10.1016/j.jcis.2006.10.025

tion, and oxidation) has been studied. The variation of solution pH is especially noticeable because of protonation of amine groups (pK of primary amine = 9.20; pK of tertiary amine = 6.65) [38] as well as deprotonation of carboxylic acid groups. Moreover, the fluorescence lifetime has been discussed in relation to the formation of the fluorescence-emitting moieties in PAMAM dendrimers at varying pH or temperature. Evident fluorescent microscopic images of fluorescent dendrimer have been visualized by using fiber chain templates.

2. Experimental section

Fourth generation (G4) NH_2-terminated, G4 OH-terminated, and G4.5 COO^--terminated PAMAM dendrimers and a G5 NH_2-terminated PPI dendrimer were received from Aldrich under nitrogen atmosphere and stored at 0 °C. Before being used, the dendrimers were dried under reduced pressure and dissolved in water. Unless specially indicated, aqueous dendrimer solutions were prepared at a concentration of 0.7 mM. The pH of the solutions was adjusted using dilute hydrochloric acid or sodium hydroxide solutions. Other chemicals were of commercial grade and used without further modification.

Fluorescence spectra were recorded at 25 °C on a Hitachi F3010 fluorometry with a slit width of 5 nm at a scan rate of 240 nm/min using a 10-mm-path quartz cell. Excitation and emission wavelengths were 390 and 450 nm, respectively. Fluorescence decay measurements were performed with an IBH (Glasgow, UK) 5000U fluorescence lifetime spectrometer system equipped with a thermostat. An IBH NanoLED operating at 370 nm, giving 1.3 ns pulses, was used as the exciting light source. Excitation and emission wavelengths were fixed at 370 and 450 nm, respectively, by monochromators (5000 M). The measured decays were fitted to exponential decays of two lifetime components,

$$\langle\tau\rangle = (a_1\tau_1 + a_2\tau_2)/(a_1 + a_2),$$

using the DAS6, v. 6.1, software, where $\langle\tau\rangle$ is an average lifetime, and a_1 and a_2 are preexponential terms of independent component lifetimes τ_1 and τ_2, respectively.

Dendrimer-treated cotton fibers were prepared as follows; cotton fibrils were taken from nonwoven gauze sponges (Asahi Kasei Ltd. Co.) and washed thoroughly with acetone and ethyl alcohol. Bundles of cotton fibers were immersed in a solution of G4 NH_2-terminated PAMAM dendrimer (1.4 mM) at pH 6. After about 30 min, these bundles of fibers were picked up from the dendrimer solution and dried in air. The dendrimer-treated and untreated cotton fibers were properly mixed. A Nicon 80i fluorescent microscope was used to take images of cotton fibers. Two modes, a fluorescence mode (under UV irradiation with a filter DAPI) and a "fluorescence–transmission" mode (using UV irradiation and transmission light at the same time), were used.

3. Results

3.1. pH-dependence of emission intensity

The excitation fluorescence spectra of aqueous solutions of G4 NH_2-terminated PAMAM dendrimer exhibit an emission band at 450 nm and two excitation bands at 250 and 390 nm, although the remarkable absorption bands were not observed in the same wavelength region [34]. Fig. 1 shows emission intensities of aqueous solutions of G4 PAMAM dendrimer prepared at different pH values and aged for 7 days. A significant pH-dependent profile of fluorescent intensity in the pH range from 13 to 1 was observed. Within the pH range from 13 to 8, the emission intensity was very weak and had little change. However, as the pH was lowered further, fluorescence intensity displayed a rapid increase and became constant below pH 6, although the emission band position scarcely changed. It should be noted that the intensity-transition pH region in Fig. 1 was slightly discrepant from that (24 h aging) reported in our previous work [34], due to the time-dependence of dendrimer emission after adjusting pH, as will be discussed below.

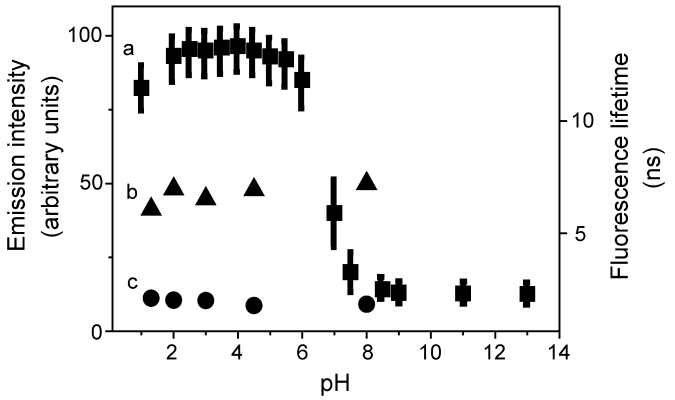

Fig. 1. The pH-dependent fluorescence intensity and lifetime of G4 NH_2-terminated PAMAM dendrimers: (a) emission intensity, (b) first-component lifetime, (c) second-component lifetime. Data were obtained after an aging time of 7 days at room temperature.

3.2. Time-dependence of emission intensity at different pH values

The pH values of aqueous solutions of G4 NH_2-terminated PAMAM dendrimer were varied to study the time-dependence of fluorescence intensity at different pH values. The emission intensities were monitored at time intervals after adjusting pH. Fig. 2 shows the remarkable difference in the time-dependence of fluorescence emission among different pH values (pH 4.5 and below): The fluorescence intensity increased faster for the solutions prepared at lower pH; that is, with lower pH value, it took a shorter time to achieve constant fluorescence intensity. For example, at pH 2, the fluorescence intensity was saturated at ~75 min. Based on each curve, the intensity increase followed a first-order reaction ($-\mathrm{d}I_{\mathrm{Em}}/\mathrm{d}t = kI_{\mathrm{Em}}$, where I_{Em} is emission intensity at time t, and k is a rate constant). The rate constants correlated well with the pH value, and they were in the order pH 2 > 3 > 4 > 4.5. These results reflect two important points: (i) The fluorescence-emitting moieties in PAMAM dendrimers grew gradually with time, and the characteristics of time dependence are similar to those of chemical reaction; (ii) The lower the pH value, the faster the formation of fluorescence-emitting moieties is. These are the key hints for the mechanism of the

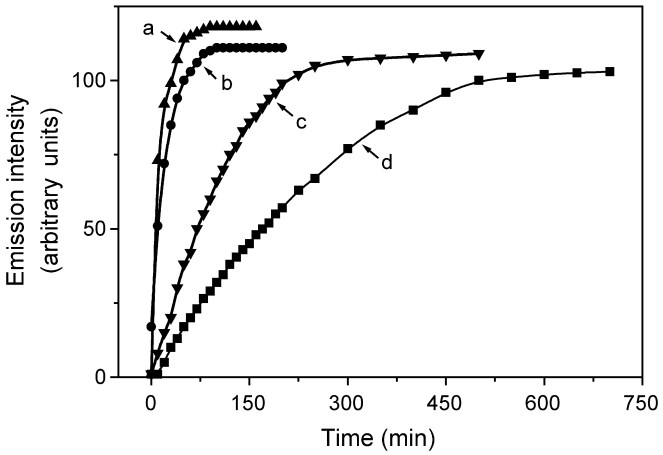

Fig. 2. The fluorescent intensity of G4 NH_2-terminated PAMAM dendrimers as a function of aging time after adjusting pH: pH (a) 2, (b) 3, (c) 4, (d) 4.5. All solutions were aged at room temperature.

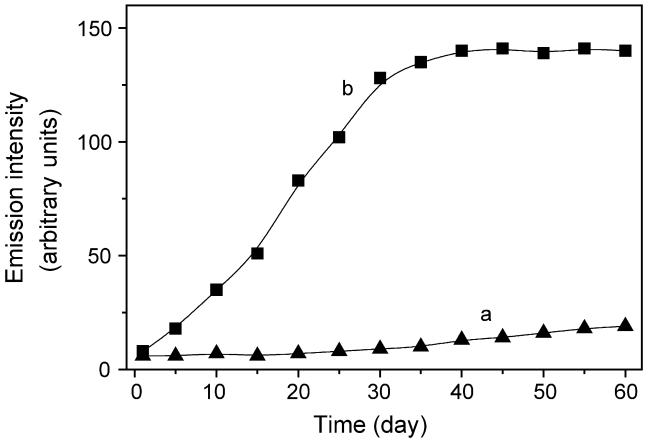

Fig. 3. The fluorescent intensity of G4 NH_2-terminated PAMAM dendrimers as a function of aging time at different temperatures: (a) 0 °C, (b) 45 °C. Both solutions were adjusted to pH 7 before aging.

formation of fluorescence-emitting moieties in dendrimer similar to the chemical reaction.

3.3. Effect of temperature on emission intensity

Two aqueous solutions of G4 NH_2-terminated PAMAM dendrimer were adjusted at pH 7, and they were kept at 0 and 45 °C. It is indicated by Fig. 3 that there was an obvious difference in time dependence of emission intensity at different temperatures. The fluorescent intensity increased fast for the solution at 45 °C, whereas a very slow increase was found at low temperature. This result proves that the higher the temperature, the faster the formation of fluorescence-emitting moieties is.

3.4. Effect of oxygen in air on emission spectrum

Keeping in mind that the fluorescence phenomenon in the present system might be similar to the chemical reaction, two aqueous solutions of G4 NH_2-terminated PAMAM dendrimer at an identical concentration (0.7 mM) were examined at different preparation conditions: one was bubbled with nitrogen gas

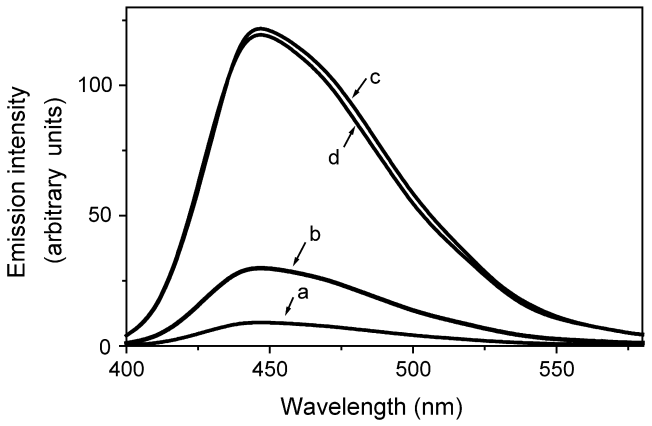

Fig. 4. Fluorescent emission spectra of G4 NH_2-terminated PAMAM dendrimers at pH 7: (a) just after preparation (aging: 0 days), (b) nitrogen-bubbled (aging: 25 days), (c) exposed to air (aging: 25 days), (d) exposed to air (aging: 15 days) after nitrogen-bubbled (aging: 25 days). All solutions were aged at room temperature.

and carefully sealed, and the other was exposed to air. To accelerate the reaction, the solutions were left at rest in an oven at 50 °C after being prepared at pH 7. A considerable difference developed between two specimens after 25 days (compare the changes from curve a to curve b and c in Fig. 4): Whereas the emission intensity of the nitrogen-bubbled solution was weak and changed slightly, the emission of the unbubbled solution was considerably increased. Importantly, in the next step, when the former solution was bubbled with air and kept at 50 °C for 15 days, its emission reached the same intensity as that of the latter (unbubbled) solution (compare curves c and d in Fig. 4). This result provided important evidence for the assumption that functional groups in the dendrimers can most likely interact with oxygen. In addition, the increase of emission intensity at a certain amount in the nitrogen-bubbled solution can be ascribed to the small amount of oxygen remaining in the aqueous solution.

3.5. Concentration-dependence of emission intensity

Fig. 5 shows the emission intensity from aqueous solutions of G4-NH_2 PAMAM dendrimer at pH 6 with various dendrimer concentrations. It was indicated that the emission intensity increased almost linearly with the concentration. This result confirms that there is no effect of intermolecular interaction on the fluorescence properties of the tested dendrimers under the present experimental condition.

3.6. Effects of pH and temperature on fluorescence decay

The fluorescence decays of G4 NH_2-terminated PAMAM dendrimer were measured at different pH values. Two discrete fluorescence lifetimes (around 1.5–1.9 and 6.9–8.3 ns) were found at pH 8 and below, as plotted in Fig. 1, although the intensities at pH 8 and above were very weak in comparison with those at lower pH and the lifetimes at higher pH than 8 were not detectable due to the weaker intensity. This indicates that the amount (number) of the fluorescence-emitting moiety depends on pH, that is, the protonation of tertiary amines.

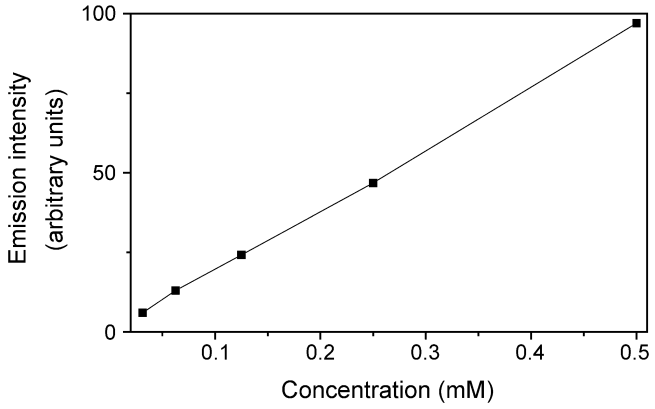

Fig. 5. The fluorescent intensity of G4 NH_2-terminated PAMAM dendrimers at pH 6 as a function of dendrimer concentration. Data were obtained after an aging time of 7 days at room temperature.

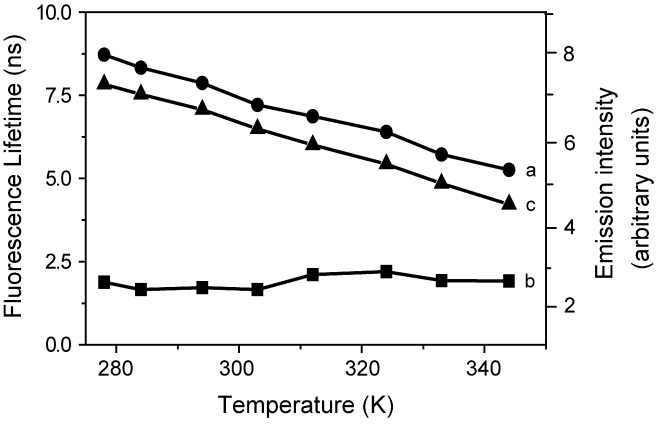

Fig. 6. The fluorescence lifetime and the emission intensity of G4 NH_2-terminated PAMAM dendrimers at pH 4 as a function of temperature: (a) first-component lifetime, (b) second-component lifetime, (c) emission intensity.

On the other hand, it was found from the temperature dependence of the fluorescence lifetime as seen in Fig. 6 that the variation of temperature from 5 to 70 °C for solutions at pH 4 had an impact on the fluorescence lifetime. While the second-component lifetime maintained a value of 1.7–2.2 ns, the first-component lifetime decreased from 8.7 to 5.3 ns with increasing temperature, in parallel with decrease fluorescent intensity (down to about half; see Fig. 6), as well as being observed in the static measurement (see Fig. 3). It was confirmed from these results that the collisional deactivation of luminescence increased with increasing temperature but not with pH variation. Furthermore, the observation of two discrete fluorescence lifetimes suggested the existence of either a single fluorescence-emitting moiety in two distinct structural microenvironments or two different fluorescence-emitting moieties with different lifetimes. Unfortunately, neither the former model nor latter one can be ruled out, as stated by Larson and Tucker [32].

3.7. Fluorescence from PAMAM dendrimers with different terminal groups

For G4 OH-terminated and G4.5 COO^--terminated PAMAM dendrimers, the same blue fluorescence was practically

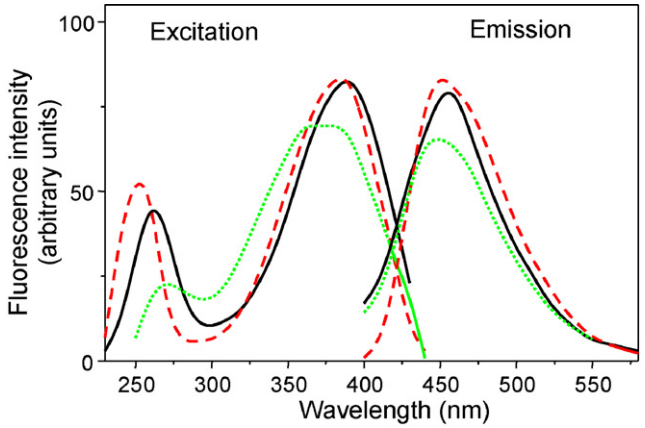

Fig. 7. Excitation and emission spectra of PAMAM dendrimers with different terminal groups at pH 6: (solid line) G4 NH_2-terminated, (dashed line) G4 OH-terminated, (dotted line) G4.5 COO^--terminated. All of these solutions were measured after an aging time of 24 h at room temperature.

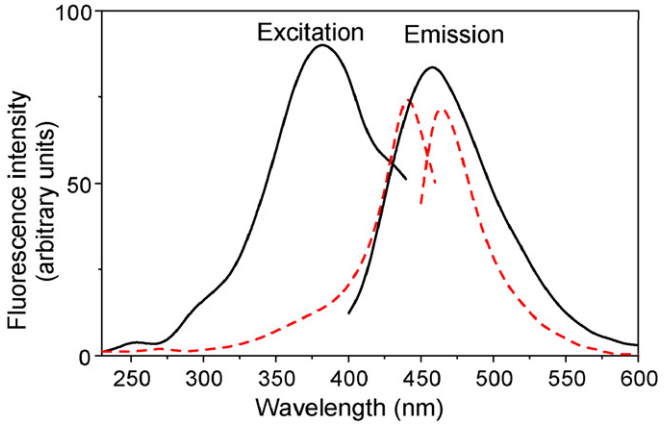

Fig. 8. Excitation and emission spectra of G5 NH_2-terminated PPI dendrimers measured at different aging times after preparing a solution at pH 6: (dashed line) 24 h, (solid line) 30 days. An aqueous PPI solution was aged at room temperature.

observed at pH 6 with emission and excitation bands very close to those of G4 NH_2-terminated PAMAM dendrimer, as seen in Fig. 7. Furthermore, there was no big difference in fluorescence intensity among the dendrimers with different terminal groups under the same experimental conditions. This observation suggested that the interiors of PAMAM dendrimers rather than the terminal groups played an important role in the formation of fluorescence-emitting moieties.

3.8. Fluorescence from PPI dendrimer

The fluorescence properties of the G5 NH_2-terminated PPI dendrimer in water were also examined at pH 6. It was found that emission and excitation spectra of PPI dendrimer gradually changed in the aging process after the PPI dendrimer was dissolved in water. Fig. 8 shows that the position of emission and excitation bands, respectively, shifted from 465 and 430 nm to 455 and 385 nm after an aging time of one month. In other words, fluorescence spectra of G5 NH_2-terminated PPI dendrimers came close to those of PAMAM dendrimers after

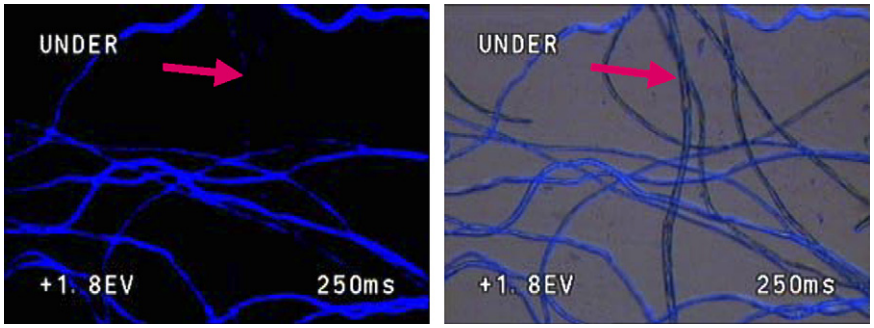

Fig. 9. Fluorescent microscopic images of cotton fibrils stained and unstained (control) by G4 NH_2-terminated PAMAM dendrimers (1.4 mM in water, pH 6). Arrow indicates an unstained fiber. Images were taken in different modes: (left) fluorescent mode, (right) fluorescence–transmission mode.

enough aging. This result indicates that PAMAM and PPI dendrimers have the common fluorescence-emitting moiety. Furthermore, because the tertiary amine is the only common functional group existing in both PAMAM and PPI dendrimers, it can be assumed that the tertiary amine is the active group forming fluorescence-emitting moieties.

3.9. Microscopic observation of fluorescence emission on cotton fibers

To stain cotton fibers by the fluorescence of dendrimers, the fibers were treated with a dendrimer solution, as described in Section 2. Optical fluorescence microscopic observation in Fig. 9 shows a significant difference in fluorescence emission between the stained and unstained (control) fibers. The observed blue photoluminescence is attributed to dendrimers on the fibers. It is evident that the unstained fibers, which could be observed only in the fluorescence–transmission mode (as indicated by arrows in Fig. 9), were not visible in the fluorescence mode.

4. Discussion

In the present work, emission spectra almost similar to those of the PAMAM dendrimers were observed even for the aged PPI dendrimer, indicating that both dendrimers have common fluorescence-emitting moieties. Since PAMAM and PPI dendrimers are synthesized by different methods, it is almost impossible for these two kinds of dendrimers to contain the same kind of impurities. In addition, it has been found that there were general shifts to longer wavelength fluorescence and longer fluorescence lifetimes with increasing generation [32,34]. Therefore, it is assumed at the present time that luminescence from impurities in the studied dendrimers is deniable.

It is reasonable to assume that the oxidation of functional groups within dendrimers plays a key role in the formation of fluorescence-emitting moieties, which can be caused by oxygen in air. This mechanism can be proposed on the basis of the present experimental results. Namely, in comparison with an aqueous dendrimer solution exposed to air, the fluorescence intensity of a nitrogen-bubbled dendrimer solution was very weak. Therefore, it can be assumed that the fluorescence-emitting moieties could not be formed in the absence of oxygen. The ^{1}H NMR measurement was carried out for nitrogen-bubbled and air-bubbled solutions of G3 PPI dendrimer. However, any serious difference such disappearance or occurrence of NMR signals was not observed, suggesting that the oxidation does not generate the chemical reaction species but should produce the oxygen-interacted moiety [39]. The analysis of the fluorescence intensity curves in Fig. 2 indicated that the oxidation might be a first-order reaction. The assumption of the oxidation was also supported by the fact that fluorescence intensity changed faster at higher temperature but almost linearly with dendrimer concentration. Since the emission intensity increased fast at lower pH values, acidic conditions may be favorable for oxidation. Lee et al. [33] reported strong blue photoluminescence from OH-terminated PAMAM dendrimers after oxidation with $(NH_4)S_2O_8$, and a conclusion similar to ours was drawn.

There are three kinds of functional groups existing in NH_2-terminated PAMAM dendrimers, that is amides, internal tertiary amines, and terminal primary amine. Therefore, it is necessary to determine which of them was oxidized to form the fluorescence-emitting moiety. In the present experiment, all tested dendrimers presented almost the same emission and excitation spectra, and, furthermore, the tertiary amine is the only functional group commonly existing in these dendrimers. Thus it is convincible that the formation of fluorescence-emitting moieties has a close relation to tertiary amine. However, for NH_2-terminated dendrimers, the contribution of terminal primary amines to fluorescent emission also cannot be ruled out. Lee et al. [33] concluded that the backbone of the PAMAM dendrimer was not important in the formation of the luminescence-emitting moiety, but the OH-terminal group played a key role. However, in our study, PAMAM dendrimers with different terminal groups produced similar fluorescence bands and intensities under conditions of the same dendrimer concentration and pH. These results indicated that the backbone of the dendrimer played the key role in inducing fluorescence.

It is a focused fact that the strong fluorescence from these dendrimers was not observed in the past decades, which may be due to three reasons: (i) Commercial dendrimers are usually stored in nitrogen atmosphere, which prevents them from being exposed to oxygen in air. (ii) Without adjusting pH, the pH value of aqueous solutions of PAMAM and PPI dendrimers is around 9, and the fluorescence-emitting moiety in dendrimer

cannot be readily formed at this pH value. (iii) What is most important is that there is no traditional fluorophore in PAMAM and PPI dendrimers. Here, it is worth noting that some works concerning photoluminescence phenomenon in the presence of PAMAM or PPI dendrimers have been reported previously. However, the influence of the strong fluorescence emission from dendrimers was not taken into consideration in most of these works, and the fluorescence was not visualized by using templates.

5. Conclusions

Strong fluorescence emission was observed from different kinds of dendrimers, and its intensity was strong under acidic conditions. The fluorescence intensity increased faster at lower pH values or higher temperatures and linearly with dendrimer concentration. The formation of a fluorescence-emitting moiety can be believed to have played a crucial role by the oxidization of internal tertiary amines in PAMAM or PPI dendrimers, which was evidently caused by oxygen in the air. The results of fluorescence lifetime supported the conclusion that the formation of a fluorescence-emitting moiety is in parallel with the protonation of tertiary amines, although the deactivation of luminescence increased with increasing temperature. The present work opens up the study of a new kind of fluorescent materials with unique properties. The blue photoluminescence of dendrimers was microscopically visualized as a fluorescent marker on dendrimer-treated cotton fibers. Thus it can be stated that the fluorescence property of PAMAM and PPI dendrimers will find applications in many fields, especially in the biomedical field, because these dendrimers possess excellent biocompatibility and unique mimic properties of biological macromolecules [3,4].

Acknowledgments

We gratefully thank Nicon Co. for the use of a fluorescent microscope and helpful discussion. This work was supported by a Grant-in-Aid for Scientific Research (B) (15350067) and for Scientific Research in Priority Area “Molecular Nano Dynamics” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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