

Investigation of Luminescent Poly(propylene imine) Dendrimer

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Luminescence phenomenon from NH₂-terminated third generation poly(propylene imine) dendrimers in water was investigated. Two excitation bands (340 and 370 nm) and corresponding emission bands (~400 and ~450 nm, respectively) were detected. Emission bands were intensified with time, heating and air-bubbling and converged at certain intensities, where the ~400 nm band was red-shifted. The initially weak emission band at ~450 nm in an alkaline solution was intensified up to the comparable intensity to the strongest emission band at ~400 nm in an acidic solution, after long time. While ¹H NMR spectra depended on pH owing to the protonation of amine, those were slightly affected by the time, heating and air-bubbling. However, no new ¹H NMR signals appeared even after long time, indicating no finding of chemical structure change of dendrimer. This suggests that the luminescent property should result from any interaction of amine with oxygen but not the chemical reaction.

Keywords: Poly(propylene imine) Dendrimer, Luminescence, Fluorescence, NMR, Poly(amido amine) Dendrimer.

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1. INTRODUCTION

Poly(amido amine) (PAMAM) and poly(propylene imine) (PPI) dendrimers,^{1–4} ones of typical dendrimers, have no particular traditional fluorophor. However, since weak fluorescence from them has been observed,^{5–12} fluorescence behavior has been investigated more detail for different dendritic polymers without traditional fluorophors.^{13–17} Lee et al.¹³ reported strong blue photoluminescence from oxidized OH-terminated PAMAM dendrimers, and Wang and Imae^{14,17} confirmed pH dependence of photoluminescence from NH₂-terminated PAMAM dendrimers. Blue photoluminescence was also observed on aqueous solutions of hyperbranched poly(amino ether)s.¹⁵

The identification of the fluorophor is, therefore, necessary to interpret the fluorescent properties of PAMAM or PPI dendrimers and related compounds. These polymers have commonly amine groups in their chemical structure, and it can be assumed from the previous reports that the ingested oxygen should be concerned with the fluorescent properties. Therefore, whether the chemical reactions happen and the oxygen is concerned in the reaction or not must be clarified.

In this work, aqueous solutions of the third generation (G3) PPI dendrimer are investigated in relation to its fluorescent behavior. This dendrimer has interior tertiary amines (pKa 6.1) and terminal primary amines (pKa 9.75).¹⁸ Hence, the pH values were selected; acidic pH (both primary and tertiary amines are protonated), neutral pH (only primary amines are protonated) and alkaline pH (neither primary nor tertiary amines are protonated). The luminescence behavior of the dendrimer was recorded by a fluorescence spectrometry as a function of pH, time, air-bubbling and temperature. The chemical structures of dendrimer involving luminescence were monitored by ¹H NMR spectrometry.

2. EXPERIMENTAL DETAILS

NH₂-terminated G3 PPI dendrimer was received from Aldrich Chemical Co. Methanol, hydrochloric acid, D₂O and CDCl₃ were purchased from Wako Pure Chemical Industries, Ltd. All chemicals were used without further purification. Water was purified using a Millipore Milli-Q Lab purification system. Aqueous solutions of dendrimer were prepared at 3.5 mM for ¹H NMR spectra and at 0.7 mM for other measurements. The pH of the solutions was adjusted by using an aqueous solution of hydrochloric acid.

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Fluorescence spectra were collected at 25 °C on a Hitachi F3010 fluorometry using a 10 mm-path quartz cell. Excitation and emission wavelengths used were at 340 or 370 nm and at 450 nm, respectively. ¹H-NMR spectra were recorded on a JEOL 400 NMR instrument using D₂O and CDCl₃ as solvents.

3. RESULTS AND DISCUSSION

3.1. Effects of pH, Time and Air-Bubbling on Luminescence of Aqueous Solutions of PPI Dendrimer

After aqueous solutions of NH₂-terminated G3 PPI dendrimer were prepared at pH 3.8, 7.5 and 10.6, two kinds of treatments were handled on the solutions at every pHs; N₂ gas or dry air was bubbled in each solution for 5 min. The pH values are above pK_a (9.75) of primary amine, below pK_a (6.1) of tertiary amine, and between them. In each solution, there were two excitation bands at ~340 and ~370 nm (see Fig. 1(a)). The excitation band at ~340 nm was especially strong in an acidic solution but weakened with increasing pH. Alternatively, the excitation band at ~370 nm was major at alkaline pH, but its intensity was only half of the band intensity at ~340 nm in an acidic solution.

Figures 1(b) and (c) show emission spectra of N₂-bubbled solutions excited at 340 and 370 nm, respectively. The emission intensity was maximized at ~400 or ~450 nm for respective excitations. Since the excitation bands at 340 and 370 nm are major at acidic and alkaline pH, respectively, emission bands at ~400 and ~450 nm can be attributed to fluorophors relating to protonated and non-protonated amine species, respectively. The emission intensity of a ~400 nm band increased with increasing acidity in accordance with the variation of excitation intensity, but the emission of a ~450 nm band was weak and maintained similar intensities at all pHs. These results suggest that a dendrimer with protonated tertiary amines displays strong emission, which works with wavelength and intensity of excitation.

Figure 2 shows time effect on emission spectra of an aqueous alkaline solution of PPI dendrimer. The emission band at $\lambda_{\text{ex}} = 340$ nm increased along with shift from ~400 to ~435 nm with time. This suggests that the contribution of the 450 nm emission band increased, although it was minor at the first stage after the preparation. Then the composition of two bands brings the shift of apparent band peak. On the other hand, the intensity of the band at ~450 nm at $\lambda_{\text{ex}} = 370$ nm increased without wavelength-shift and got close in intensity to the band at $\lambda_{\text{ex}} = 340$ nm after 90 days. It is implied that although the emission spectra of PPI dendrimer at two excitation wavelengths were initially different each other, they came close in their position and intensity with time. This indicates the difference in the time dependence of emission bands at

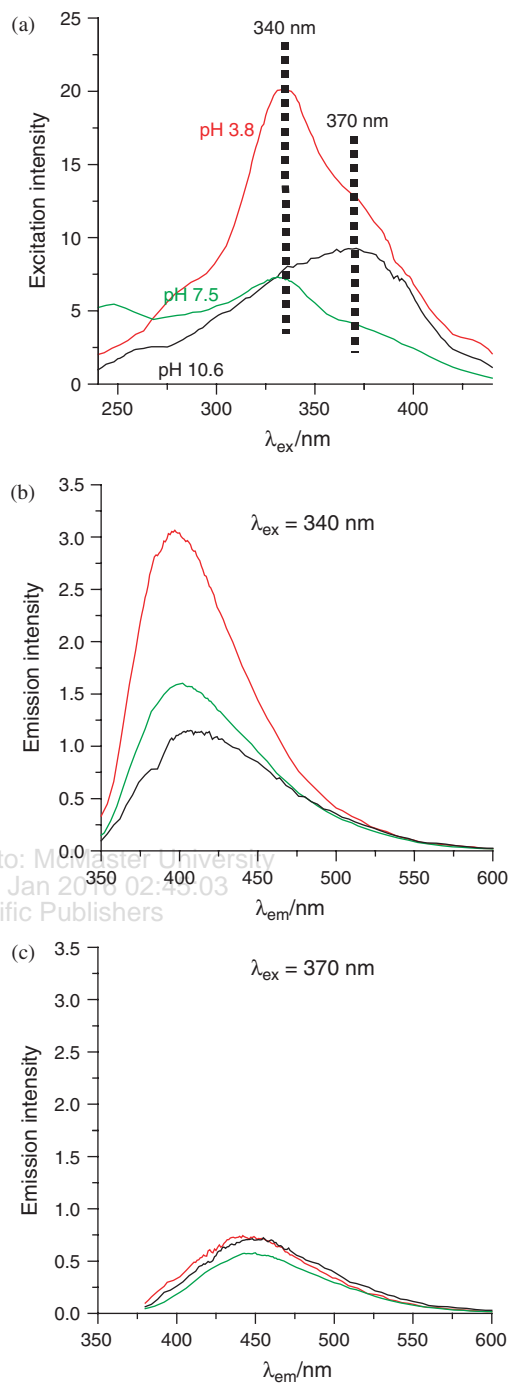


Fig. 1. Fluorescence spectra of aqueous solutions of NH₂-terminated G3 PPI dendrimer just after N₂-bubbling. (a) Excitation spectra at $\lambda_{\text{em}} = 450$ nm; (b) emission spectra at $\lambda_{\text{ex}} = 340$ nm; (c) emission spectra at $\lambda_{\text{ex}} = 370$ nm. (Red line) pH 3.8; (green line) pH 7.5; (black line) pH 10.6.

~400 and ~450 nm. Similar time effects were observed for both N₂- and air-bubbled solutions, although the emission intensities after long time were slightly stronger for the latter.

The intensities of emission bands of solutions (excited at 340 nm) at different pHs are plotted as a function of

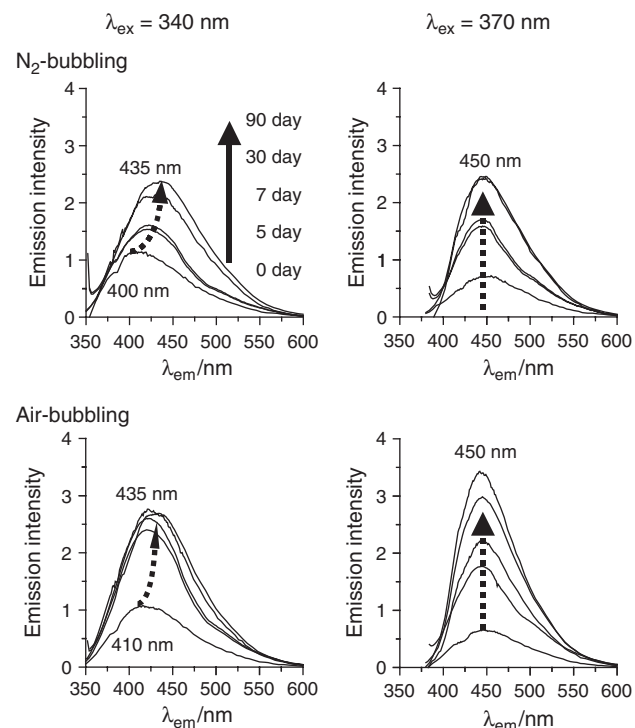


Fig. 2. Time effect on emission spectra (excited at 340 or 370 nm) of aqueous alkaline solutions of NH₂-terminated G3 PPI dendrimer after N₂- and air-bubbling.

time in Figure 3, where the results for N₂- and air-bubbled solutions are compared. The aspect of time course was different at every pHs. At the acidic solution (Fig. 3(a)), the emission band was intensified for 3~5 days but decreased down to a certain intensity after that, because the excess oxygen probably behaved as a quencher. The intensities at initial days and the maximum intensity were higher for

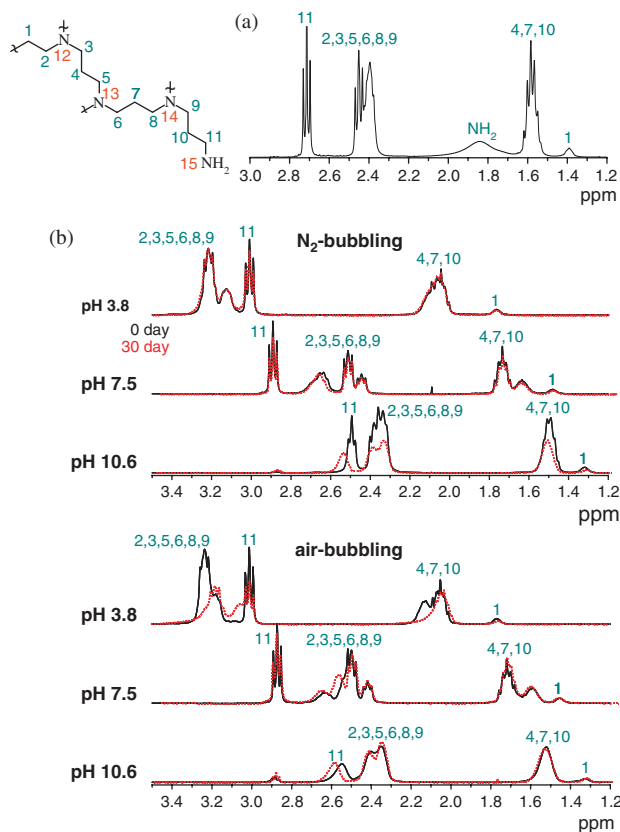


Fig. 4. ¹H NMR spectra of solutions of NH₂-terminated G3 PPI dendrimer after N₂- and air-bubbling. (a) In CDCl₃; (b) in D₂O. (Solid line) just after bubbling; (dot line) after 30 days.

an air-bubbled solution than for a N₂-bubbled solution but the intensities at long aging were equivalent for two kinds of bubbling. At the neutral condition (Fig. 3(b)), the emission intensity increased with time but did not reach to

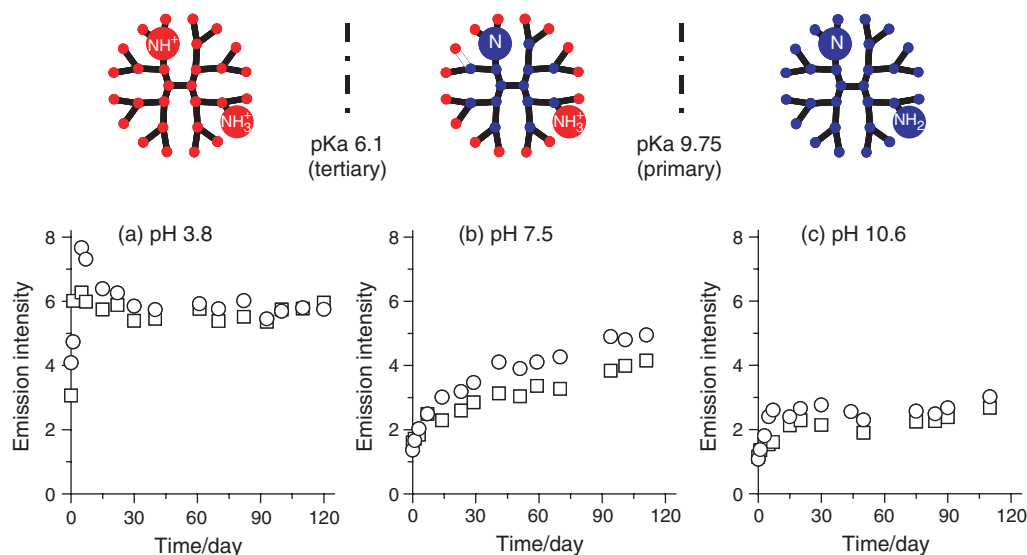


Fig. 3. Time-dependent emission band intensities (excited at 340 nm) of aqueous solutions of NH₂-terminated G3 PPI dendrimer. (a) pH 3.8; (b) pH 7.5; (c) pH 10.6. (Square) N₂-bubbled; (circle) air-bubbled. Illustration indicates the protonation state at each pH region.

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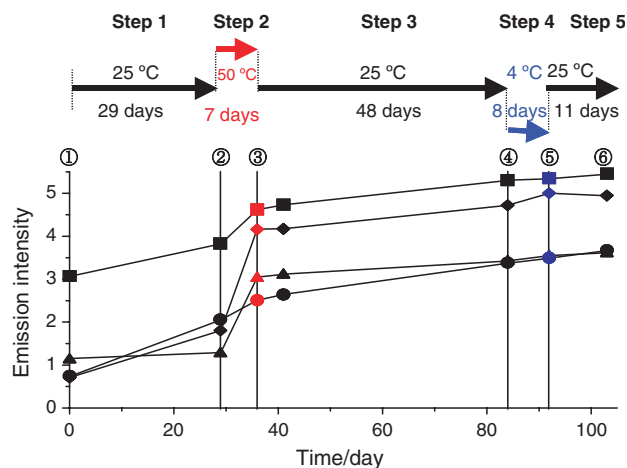


Fig. 5. Emission band intensities of N_2 -bubbled aqueous solutions of NH_2 -terminated G3 PPI dendrimer on heating-cooling processes. (Square) acidic solution, $\lambda_{ex} = 340$ nm; (circle) acidic solution, $\lambda_{ex} = 370$ nm; (triangle) alkaline solution, $\lambda_{ex} = 340$ nm; (diamond) alkaline solution, $\lambda_{ex} = 370$ nm.

saturation even at 120 days, although the band intensity was always stronger for an air-bubbled solution than for an N_2 -bubbled solution. Both air- and N_2 -bubbled solutions at alkaline pH behaved similarly on increase and saturation

of band intensities, while the intensities for the former were always slightly stronger than for the latter. Moreover, the emission intensity at saturation was weakest at alkaline pH. It is mentioned that air-bubbling affects the acceleration of luminescence at the initial stage but has no or less effect on the saturated intensities at long time, although the saturated intensities are influenced by pH.

3.2. Effects of pH, Time and Air-Bubbling on NMR Spectra of Aqueous Solutions of PPI Dendrimer

The 1H NMR spectra of NH_2 -terminated G3 PPI dendrimer in D_2O were measured at different pHs, times, and bubblings, and they are shown in Figure 4, where a spectrum of dendrimer in $CDCl_3$ is included. The spectrum in $CDCl_3$ exhibited intense multiplets below 3 ppm, being consistent with a previous report.^{4,19} A broad signal at 1.84 ppm is assigned to the terminal NH_2 protons, and the triplet near 2.71 ppm is to the protons of methylene groups 11 adjacent to terminal NH_2 . The resonances from the NCH_2 type methylenes appeared as multiplets near 2.45 and 2.39 ppm. The remaining upfield multiplets near 1.58 ppm are attributed to methylene groups 4, 7, and

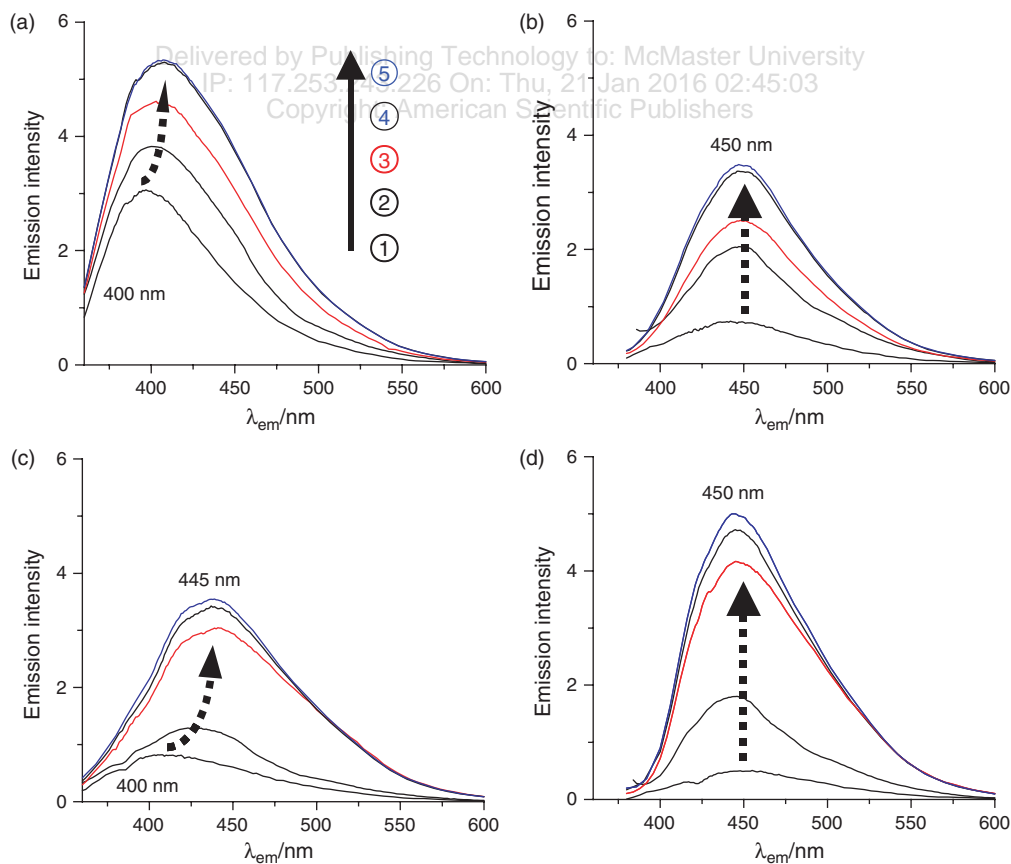


Fig. 6. Emission spectra of N_2 -bubbled aqueous solutions of NH_2 -terminated G3 PPI dendrimer on heating-cooling processes. The numbers in figure denote ones of process in Figure 5. (a) acidic solution, $\lambda_{ex} = 340$ nm; (b) acidic solution, $\lambda_{ex} = 370$ nm; (c) alkaline solution, $\lambda_{ex} = 340$ nm; (d) alkaline solution, $\lambda_{ex} = 370$ nm.

10 in the middle of propylene. The weak broad signal at 1.39 ppm is assigned to methylene 1 of the core.

As seen in Figure 4(b), in the ^1H NMR spectra for an aqueous (D_2O) solution of dendrimer at an alkaline condition, multiple signals of methylene group 11 and NCH_2 type methylenes appeared near 2.49 and 2.36 ppm, respectively. Multiplets of methylene groups 4, 7 and 10 and a weak signal of methylene 1 existed near 1.49 and 1.32 ppm, respectively, although no NH_2 signal appeared because of the exchange of proton to deuterium. The signals shifted to lower field with decreasing pH value. Especially, a signal of methylene group 11 shifted remarkably between alkaline and neutral conditions, because primary amine terminals were protonated at pK_a 9.75. On the other hand, there was a notable shift of multiplets from NCH_2 type methylenes between neutral and acidic conditions due to the protonation of interior tertiary amines.

In comparison of ^1H NMR spectra in Figure 4(b), it should be noted that there is no change on most signals for N_2 - and air-bubbled solutions at three pH values after just bubbling and 30 days. Especially, no significant time-dependency in the intensity indicates no chemical break on the backbone of molecules. The broadening and shift in some signals among resonances from the NCH_2 type methylenes were observed after 30 days in an air-bubbled solution. This suggests the environmental change around the tertiary amine like the constrained molecular motion. Although the broadening is especially remarkable at alkaline conditions, this behavior may be not necessarily related to the luminescence phenomenon. In addition, there were no detectable signals in the chemical shift region up to 10 ppm. These results denote that the remarkable variation on chemical structure of NH_2 -terminated G3 PPI dendrimer and the production of new compounds were not detectable from ^1H NMR spectra in the present investigations, except the change in the internal environment of the dendrimer.

3.3. Thermal Effect on Luminescence and NMR Spectra of Aqueous Solutions of PPI Dendrimer

The fluorescence spectra of N_2 -bubbled aqueous solutions of NH_2 -terminated G3 PPI dendrimer at pH 3.8 and 10.6 were investigated through variations of temperature and time at five steps, as illustrated in Figure 5. Emission spectra (excited at $\lambda_{\text{ex}} = 340$ and 370 nm) of acidic and alkaline solutions are shown in Figure 6, and variation of emission intensities at each step for all systems is plotted in Figure 5. At step 1, the freshly prepared solutions were left to stand for 29 days at 25 °C so that the emission intensities of the solutions were saturated as seen in Figure 3. Then the increase in emission intensity at 370 nm excitation was more remarkable than at 340 nm excitation. Next, the solutions were heated for 7 days at 50 °C (step 2). As seen in Figures 5 and 6, the intensities of emission

bands increased for both acidic and alkaline solutions, and, especially, the emission intensities for an alkaline solution were strengthened (about double). On the other hand, the wavelength of a main band red-shifted from ~ 400 nm for solutions at 340 nm excitation and came close to a wavelength for solutions at 370 nm excitation. This tendency is in agreement with time effect as seen in Figure 2. This means that the luminescence is effectively progressed by heating rather than time.

After heating, the solutions were stood at room temperature for 48 days (step 3), kept in a refrigerator (at 4 °C) for 8 days (step 4), and left to stand at room temperature for 11 days (step 5). During these steps, the emission spectra showed no specific changes in band position, and the emission intensity displayed only time-dependent increase. That is, cooling the solutions did not influence on luminescence. Then it can be referred that the enhancement of luminescence is temperature-irreversible. After five steps, the intensity of an alkaline solution at $\lambda_{\text{ex}} = 370$ nm came close to the strongest intensity of an acidic solution at $\lambda_{\text{ex}} = 340$ nm, and it became stronger than other two systems (an acidic solution at $\lambda_{\text{ex}} = 370$ nm and an alkaline

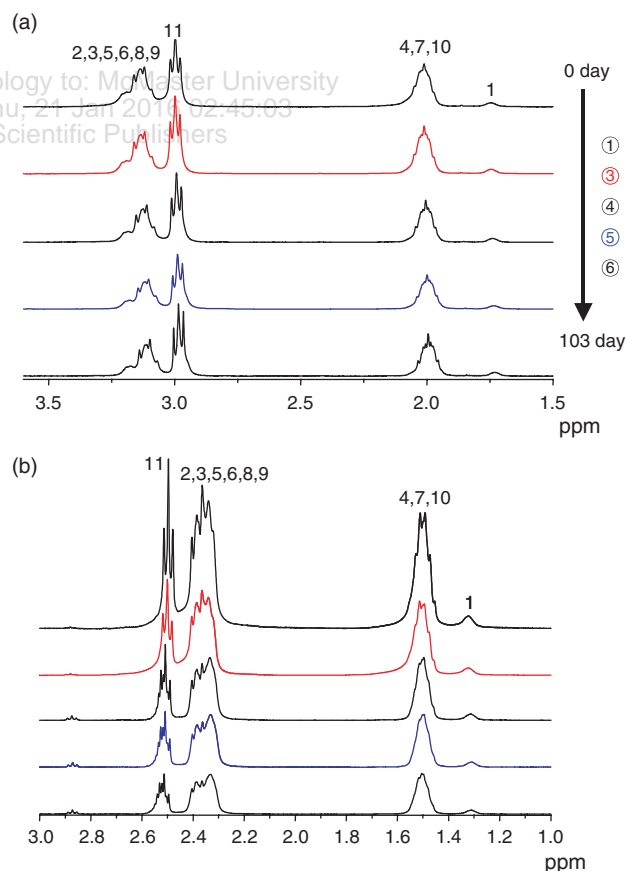


Fig. 7. ^1H NMR spectra of N_2 -bubbled aqueous solutions of NH_2 -terminated G3 PPI dendrimer on heating-cooling processes. The numbers in figure denote ones of process in Figure 5. (a) Acidic solution; (b) alkaline solution.

solution at $\lambda_{\text{ex}} = 340$ nm) in association with the excitation intensities as shown in Figure 1(a).

The variation of ^1H NMR spectra for acidic and alkaline solutions was examined through step 1 to 5 (Fig. 7). There was no change in all signals for an acidic solution despite different steps. On the other hand, although the signals for an alkaline solution also maintained their features during the treatment of all steps, the spectra were broadened observably through step 1 and 2 and gradually thereafter. It is indicated that the heating enhances the fluorescence behavior but the ^1H NMR spectra are free from the influence of temperature and only the molecular motion of dendrimers in an alkaline solution is restricted during thermal aging.

4. CONCLUSION

For aqueous solutions of NH_2 -terminated G3 PPI dendrimer, two distinct excitation bands at 340 and 370 nm were detected and the emission profile of this dendrimer was related to these excitation bands. When excited at 340 nm, an emission band at ~ 400 nm was dominant and strongest at acidic condition, relating to the intensity of excitation band. This relation is kept even after long time, where the emission band was intensified and saturated at certain intensity. On the other hand, although an emission band at weak 370 nm excitation was at ~ 450 nm and weak at whole pH region at the initial stage of the preparation, the intensity of this band increased with time and became comparable to that at 340 nm excitation. The remarkable difference during time course is the red-shift of emission band from ~ 400 nm at 340 nm excitation, while the emission at 370 nm excitation keeps always same wavelength with time.

Air-bubbling affected to intensify rapidly the emission in comparison with N_2 -bubbling, but the emission bands at bubbling of both gases completely came close each other at the condition of saturation like after long time. The elevation of temperature stimulated the increase in emission intensity and the shift in emission wavelength. The contribution of such factors resulted in the comparable emission intensities between an acidic solution at 340 nm excitation and an alkaline solution at 370 nm excitation, which are related to the most dominant excitation band at each solution. The results of previous report for fluorescence decay of a PAMAM dendrimer are now remained.¹⁷ Two discrete lifetimes were evaluated at acidic condition.

Regardless of the serious variation of emission bands at various conditions, the effect of such conditions on ^1H NMR spectra was less, since the fluorescence is much more sensitive than ^1H NMR. The ^1H NMR spectra of NH_2 -terminated G3 PPI dendrimer in water displayed

signals corresponding to component protons except NH_2 protons and varied with pH because of the protonation of amines. However, the variation of spectra was only the slight shift or broadening after time course, bubbling, and heating. It is noticed that no new ^1H NMR signals were observed even on any variation of conditions. These results confirmed that no major changes on the chemical structure of dendrimer were detectable from ^1H NMR spectra, although the suppression of molecular motion was indicated. It can be concluded that the origin of the luminescent properties should be the non-covalent interaction (complexation) of amine with oxygen but not be a product of the chemical reaction. The involvement of oxygen was confirmed from elemental analysis of neat and air-injected poly(ethylene imine) dendrimers.²⁰ The detectable amount of oxygen was incorporated in air-injected dendrimers.

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