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Visual Observation and Characterization of Fluorescent Poly(amido amine) Dendrimer in Film State

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The fluorescent property of PAMAM dendrimers were examined at film state rather than in solution. The O_2-treated PAMAM dendrimer displayed strong blue fluorescence due to its conservation of luminance in the film state and diminished its intensity with degas. The fluorescent property of PAMAM dendrimers was utilized as a fluorescent probe on functional patterned substrates for visual observation by a fluorescence microscope. G4 and G4.5 PAMAM dendrimers having peripheral groups of functional amine and carboxylate, respectively, were adsorbed selectively by electrostatic interactions on patterned carboxylic acid and amine terminated surfaces, respectively resulting in strong fluorescent patterns. This suggests the possible application of fluorescent PAMAM dendrimers as a fluorophor for the visualizable reactions. It was confirmed from an X-ray photoelectron spectroscopy that O_2 molecules interact with tertiary amine moiety in PAMAM dendrimers but not amide group. These results give us an important support for the principle of fluorescence phenomenon.

Keywords: Patterned Poly(amido amine) Dendrimer Film, Fluorescence Microscope, X-ray Photoelectron Spectroscopy.

RESEARCH ARTICLE

1. INTRODUCTION

The family of poly(amido amine) (PAMAM) dendrimer can be used to monitor the properties of biomaterials owing to its well-characterized architecture, biocompatibility, nonimmunogenicity, and water-solubility.[1] Number of studies about molecular assemblies of PAMAM dendrimers on various solid substrates are carried out by adsorption, self-assembled monolayer (SAM) and patterning techniques where the various peripheral groups (–OH, –COOH, $–NH_2$) of PAMAM dendrimers having high reactivity selectively bind to the functional substrates.[2–9] The SAM of dendrimers has been used as a DNA (or polyelectrolyte) detector and a biochemical sensor based on polyelectrolyte-ligand interaction.[10–13] The molecular assemblies of PAMAM dendrimers have also been patterned by techniques of microcontact printing,[14–17] scanning probe lithography[18] and photolithography,[19] which were examined by atomic force microscopy, scanning electron microscopy, etc. However, there are no reports of visual observation on selective adsorption of PAMAM dendrimers on solid substrates.

It has been found that the family of aged or O_2-treated PAMAM dendrimer emits blue photoluminescence under excitation around 360 nm. The fluorescence of PAMAM dendrimers and their derivatives or analogs has been studied by some research groups.[20–33] Therefore, it is expected that when the target materials are selectively labeled by fluorescent PAMAM dendrimer as a fluorescent probe, one is allowed to investigate properties and assembling of the objective materials by simple fluorescence technique. Incidentally, the visualization by a fluorescence microscopy has been carried out on PAMAM dendrimer-dyed fibers and dendritic nanohydrogels of PAMAM Dendron.[28–29] Additionally, it can be noticed that the current investigation of photoluminescence for the family of PAMAM dendrimer has been carried out only in solution.

In the present work, the selective adsorption of fluorescent G4 and G4.5 (G: generation) PAMAM dendrimers on patterned SAM substrates with different affinities to dendrimers is visually detected by a fluorescence microscopy. SAM preparation and photolithography are used to create the functional substrates with carboxylic acid- or amine-terminated pattern along with methyl-terminated pattern. Subsequently, the fluorescent property of dendrimers in a solid state on the substrates is successfully investigated

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under gas/degas process of oxygen. The present work indicates the extensive possibility for family of PAMAM dendrimer to be utilized even at the solid film as a fluorescence probe on the microscopic observation. Moreover, facile and highly sensitive detection of fluorescent dendrimer probe on a fluorescence microscope is the strong advantage on the various biomedical applications, sensing technology and molecular recognition.

2. EXPERIMENTAL DETAILS

2.1. Materials

Methanol solutions of G4 and G4.5 PAMAM dendrimers (PAMAM-NH_2, PAMAM-COO^-) were purchased from Aldrich Co., Ltd. These dendrimers contain 64 (amine) and 128 (carboxylate) terminal groups, respectively. *n*-octadecyltrimethoxysilane (ODS), 3-aminopropyltriethoxysilane (APS) and ammoniumpersulfate ($(NH_4)_2S_2O_8$) were obtained from Tokyo Chemical Industries, Co., Ltd., Acros Organics Co., Ltd, and Wako Chemicals Co., Ltd, respectively. Ethanol and toluene were products from Junsei Chemical Co., Ltd. Purified water was prepared by a Millipore milli-Q system.

2.2. Preparation

Silicon and glass substrates (Matsunami micro cover glass, 18×18 mm) were patterned by SAM procedure and photolithography.[19,34] Prior to the patterning on silicon or glass substrate, the substrates were carefully cleaned by ultrasonication for 5 min each in piranha solution, water, acetone, and ethanol, followed by drying in an oven. The substrates were further cleaned photochemically by irradiation of UV light in vacuum which is generated from an excimer lamp (Ushio Electric UER20-172V, $\lambda = 172$ nm with a power density of 10 $mWcm^{-2}$) in order to remove any organic contaminants. The UV irradiation was carried out at a pressure of 1.5×10^2 pa with a proximate gap of <10 nm between the substrate and photomask. The radiation at short wavelength produces the oxygen atoms and ozone molecules from atmospheric oxygen molecules by photoexcitation, which decompose the carbon–carbon and carbon–hydrogen bonds of organic molecules.[35]

Two different types of precursors, ODS and APS, were employed for the preparation of carboxylic acid and amine terminated patterns, respectively. The carboxylic acid (ODS-COOH) and amine (ODS-NH_2) terminated patterns were immersed in a 0.5 mM solution of G4 or G4.5 PAMAM dendrimer for 24 h and thus the dendrimer-treated substrates were denoted by PAMAM-NH_2/ODS-COOH, PAMAM-COO^-/ODS-COOH, PAMAM-NH_2/ODS-NH_2, and PAMAM-COO^-/ODS-NH_2. Prior to the immersion of these substrates, solutions of PAMAM dendrimers were aged for 7 days under the addition of an aqueous 0.1 M solution of ammoniumpersulfate. The dendrimer-treated substrates were dried by N_2 gas and then examined by optical and fluorescence microscopy.

The G4 and G4.5 PAMAM dendrimer films on well-cleaned quartz and silicon (*n* type (100) wafer, Nilaco Co.) substrates were prepared from 50 mm^3 of a 5 wt% PAMAM dendrimer solution by a spin coating method where the substrates were rotated at 100 rpm for 5 min. This process was repeated for four times and then the films were dried overnight at room temperature under vacuum. PAMAM dendrimer films on substrates were aged in the presence of O_2 gas and degassed. Then the films were analyzed by UV-visible absorption spectroscopy, fluorescence spectroscopy and X-ray photoelectron spectroscopy (XPS).

2.3. Measurements

UV-visible absorption spectra on quartz substrates were collected on a Shimadzu Bio Spec-1600 spectrometer. Fluorescence spectra were recorded on a Hitachi F-3010 fluorescence spectrophotometer, where the excitation source was Xenon lamp operated at 150 W. The optical (Halogen lamp, LHS-H100P-1, 12 V, 100 W) and fluorescence (super high pressure mercury lamp, Model C-SHG1, 100 W) microscopic images were taken on a Nikon-Eclipse TE 2000-U microscope. For fluorescence microscopic images, the silicon substrates were irradiated at 365 nm excitation wavelength by using DM 400 and RA 400 filters. XPS studies on quartz substrates were performed on a JPS-9000 MX JEOL photoelectron spectrometer using Mg$K\alpha$ monochromatized X-ray beam at a constant dwell time of 100 ms. X-ray scans were performed by using pass energies of 50 eV for wide scan and of 10 eV for narrow scan. The anode voltage and current were 10 kV and 10 mA, respectively. All core level spectra were obtained at a photoelectron takeoff angle of 90° with respect to the PAMAM dendrimer films.

3. RESULTS AND DISCUSSION

3.1. Visual Observation of G4 and G4.5 PAMAM Dendrimers on ODS-COOH and ODS-NH_2 Patterned Substrates

The functional patterned substrates allow us to investigate the properties and assembling of materials and can be used for various applications like sensing technologies, organic light-emitting diodes, organic thin-film transistors, etc.[36–41] Moreover, they can be model surfaces of biomaterials which are prepared readily by a large variety of available techniques.[42,43] The substrates with –NH_2 or –COOH surface pattern along with methyl surface pattern are ones of model surfaces of biomaterials. The fluorescent G4 and G4.5 PAMAM dendrimers possessing –NH_2 and –COO^- functional groups, respectively, on their periphery can be expected to be adsorbed selectively on these model

surfaces. The fluorescent PAMAM dendrimers were pretreated by adding an aqueous 0.1 M $(NH_4)_2S_2O_8$ solution and used throughout the patterning experiments, because this treatment enhances the fluorescence of PAMAM dendrimers even at very short time process.[25] Figure 1 shows the comparison of fluorescence intensity of persulfate-treated and untreated G4 PAMAM dendrimer on silicon substrate which was prepared by spin-coating dendrimer in water (0.5 mM) at 100 rpm for five times. The persulfate-treated dendrimer displayed a strong blue fluorescence emission band at 452 nm at excitation wavelength of 360 nm and an excitation band at 370 nm at emission wavelength of 452 nm. The fairly strong fluorescence intensity of persulfate-treated dendrimer superior to untreated one indicates the conservation of luminescence even at the film state.

Figure 2 denotes the procedure for the selective adsorption of PAMAM dendrimer on methyl/carboxylic acid-terminated patterned silicon substrates. For this purpose, the well-cleaned silicon substrates were put together with a few drops (0.2 cm^3) of ODS liquid in a Teflon container, which was covered tight with a lip and then retained in an oven at 150 °C for 3 h. The formation of ODS SAMs on substrates was examined by contact angle of pure water; the silicon substrate terminated with methyl groups brought about a highly hydrophobic contact angle at $86 \pm 2°$. The carboxylic acid pattern was prepared as rectangular closed area by exposing an ODS SAM substrate to UV light for 100 s under photo mask in the presence of oxygen gas. Then alkyl groups of ODS out of the photo mask underwent partial oxidation on the exposure process through UV light and were decomposed into carboxylic acid-terminated pattern,[19, 44, 45] which resulted in

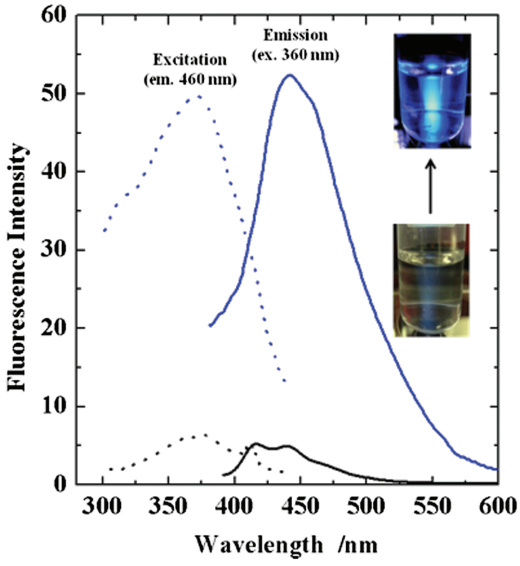


Fig. 1. Fluorescence spectra of pristine (black) and persulfate-treated (blue) G4 PAMAM dendrimer films on a silicon substrate. Insets are photos of 0.5 mM G4 PAMAM dendrimer solutions before preparing films.

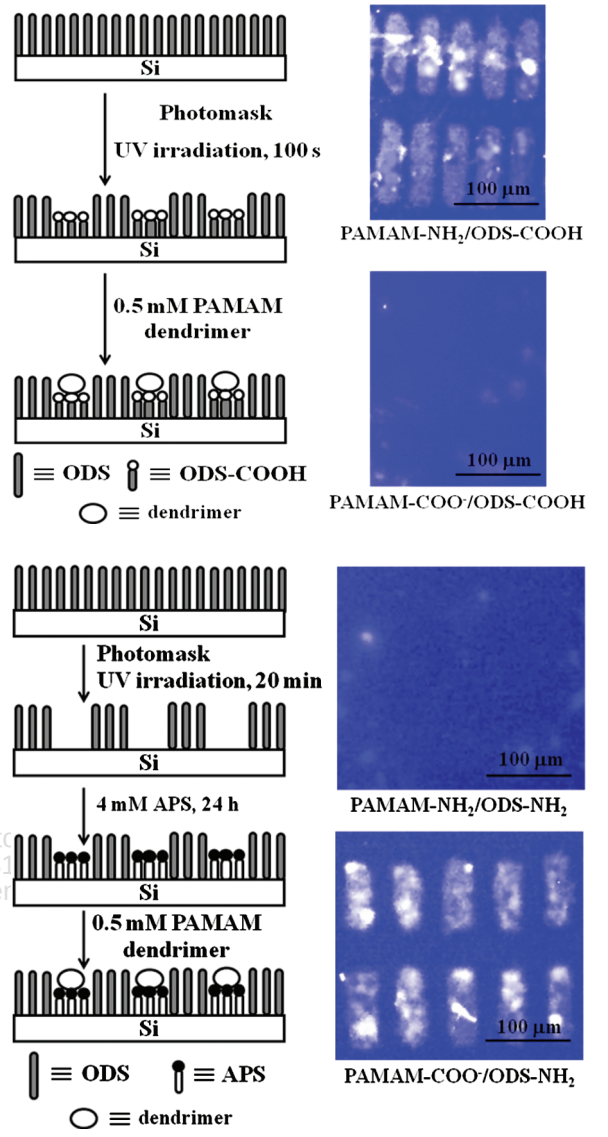


Fig. 2. A scheme of the pattern preparation on ODS SAM on a silicon substrate and the adsorption of PAMAM dendrimers on it. Photographs indicate fluorescence microscopic images after the adsorption procedure of G4 and G4.5 PAMAM (PAMAM-NH_2, PAMAM-COO^-) dendrimers. (top) Carboxylic acid pattern on an ODS SAM (ODS-COOH); (bottom) Amine pattern on an ODS SAM (ODS-NH_2).

the ODS-COOH patterned substrate with ODS frame. The water contact angle of the resultant substrate was $64 \pm 2°$.

After the adsorption of G4 PAMAM dendrimer, as shown in Figure 2, the fluorescence microscopic image of the substrate at excitation wavelength of 365 nm displayed strong fluorescent pattern with two distinct regions, that is, the dark frame and the bright fluorescent rectangles. The dark frame is indicative of the ODS SAM without adsorption of dendrimer, because amine-terminated G4 PAMAM dendrimer does not adsorb on methyl-terminated pattern. Whereas, the clear and well-defined fluorescent region suggests the adsorption of fluorescent G4 PAMAM dendrimer, since the peripheral amine groups of G4

PAMAM dendrimer bind on carboxylic acid-terminated substrate. Then the binding interaction should be electrostatic, because the adsorption process was carried out in water at neutral pH where amine and carboxylic acid are protonated and deprotonated, respectively.

The reverse effect is also expected i.e., G4.5 PAMAM dendrimer (with –COOH peripheral groups) will interact with amine-terminated substrate. Figure 2 shows the procedure for preparation of APS SAM pattern on ODS SAM substrate. The ODS SAM substrate loaded photo mask was irradiated by UV light for 20 min in the presence of oxygen so as to remove completely ODS SAM from the unmasked area.[45] The APS SAM was introduced on the ODS-removed pattern by immersion of patterned ODS substrates for 24 h in a 4 mM toluene solution of APS. Thus the resultant patterned substrate of ODS and APS (ODS-NH_2) was washed with toluene and ethanol, dried under N_2 atmosphere and maintained for 1 h at 120 °C in oven. Then G4.5 PAMAM dendrimers were adsorbed on the ODS-NH_2 patterned substrate. As expected, strong fluorescent pattern was displayed, as shown in Figure 2. The bright rectangular region is an outcome of an effective interaction between –COOH peripheral groups of G4.5 PAMAM dendrimers and NH_2 terminated pattern on the substrate. However, the dark frame region suggests that no such interaction was observed between G4.5 PAMAM dendrimer and methyl-terminated group of ODS SAM on the substrate.

The results described above indicate that the electrostatic interaction is a main driving force of the selective adsorption of dendrimers on the patterned substrates. In order to make sure this conclusion, the adsorption behavior of G4.5 PAMAM dendrimer on ODS-COOH or G4 PAMAM dendrimer on ODS–NH_2 was examined. As seen in Figure 2, distinct bright regions were not observed for both combinations, suggesting no considerable attraction between dendrimer and patterned substrate in this combination. Additionally, it can be insisted that the fluorescence microscopic observation is the highly excellent technique to detect the existence of PAMAM dendrimers on the selected area, since the distinction by the optical microscopic images is not easy for the dendrimers on glass substrates, which are prepared by the procedure same as that on silicon substrates, as shown in Figure 3.

3.2. Effect of O_2 Gas on G4 and G4.5 PAMAM Dendrimer in Film State

Different from previous works which were done in solutions,[13, 19, 24–26, 46] dendrimers in the film state provide us the solvent-free fluorescence behavior and the outright evaluation on the structural aspect of PAMAM dendrimers during aging under O_2 gas. Figure 4 shows emission fluorescence spectra for G4.5 PAMAM dendrimer film on a silicon substrate which was aged under O_2 gas at various time intervals. When the substrate was irradiated at 360 nm, a strong emission band was observed at 435 nm, and its intensity increased with increasing aging time. The same trend was also found in excitation fluorescence spectra: The strong excitation band was observed at 370 nm and intensified with increasing aging time at the emission of 460 nm, as shown in Figure 4. These results support

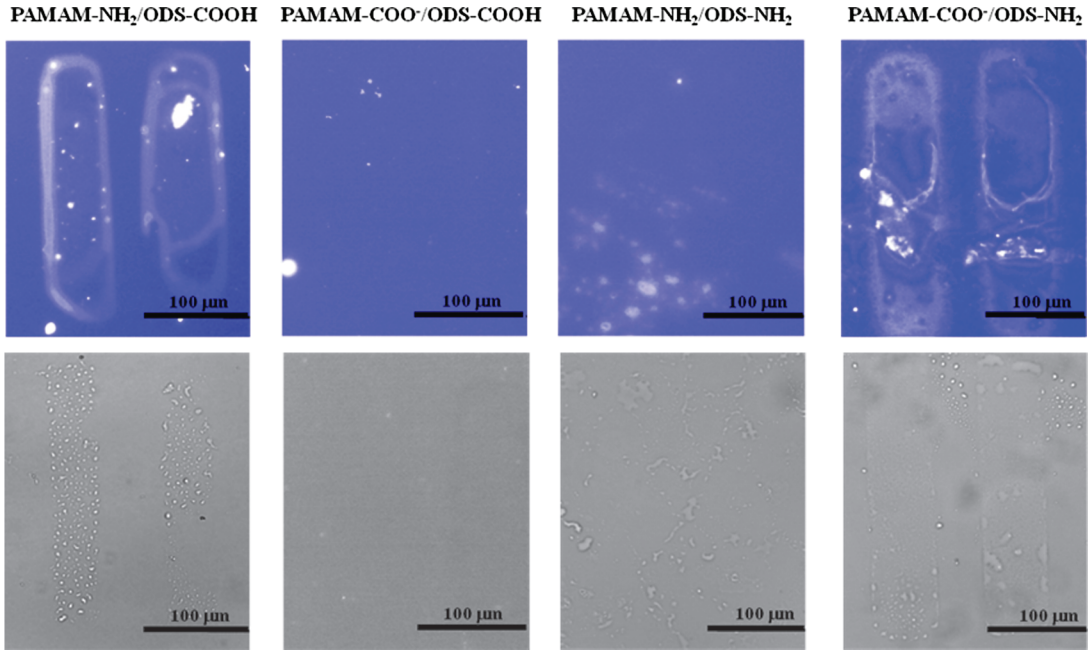


Fig. 3. Fluorescence (top) and optical (bottom) microscopic images of PAMAM-NH_2/ODS-COOH, PAMAM-COO^-/ODS-COOH, PAMAM-NH_2/ODS-NH_2, PAMAM-COO^-/ODS-NH_2.

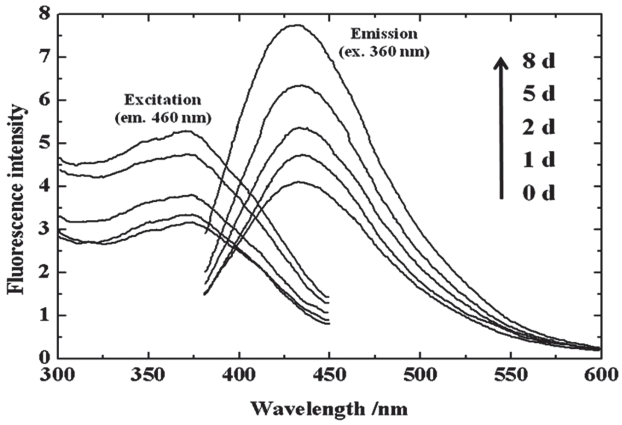


Fig. 4. Fluorescence spectra of a G4.5 PAMAM dendrimer film on a silicon substrate at different aging time under O_2 gas atmosphere.

that O_2 molecules are doped within PAMAM dendrimer in the film and participate in the enhancement of the fluorescence intensity.

O_2-treated PAMAM dendrimer films were overnight subject to vacuum condition in order to ensure the enhanced fluorescence property through doping O_2. The emission fluorescence intensity of O_2-treated G4.5 PAMAM dendrimer films decreased after vacuum treatment, as shown in Figure 5(top). As with the emission fluorescence intensity, the excitation fluorescence intensity also decreased after vacuum treatment. The similar trends on fluorescence variation were found again for G4 PAMAM dendrimer films, as seen in Figure 5(bottom). It should be noticed that the successive gas/degas process on G4 PAMAM dendrimer films reproduced the increase/decrease behavior of emission and excitation intensities (see Fig. 5(bottom, inset)). These results clearly indicate that O_2 molecules are doped within PAMAM dendrimer films by noncovalent binding to enhance the fluorescence property of PAMAM dendrimers.

According to the successive UV-visible absorption spectra for a G4.5 PAMAM dendrimer film on quartz substrate which was aged in the presence of O_2 gas at various time intervals as sown in Figure 6, an absorption band (maybe, assigned to n–π^* transition) was observed at 286 nm and intensified systematically with increasing aging time. Since the present experiments were carried out at solvent-free, this variation in the absorption band is the intrinsic behavior of PAMAM dendrimer. Therefore, it should be noticed that the local configuration of PAMAM dendrimer in the film may be changed during aging process under O_2 atmosphere. However, it must also be recognized that the position of the absorption band is lower than that of the excitation band.

The pristine and O_2-treated PAMAM dendrimer films on quartz substrate were examined further by high resolution XPS in order to investigate the influence of O_2 gas on the enhancement of fluorescence. High resolution spectra were recorded for the main core level peaks of C, N, and

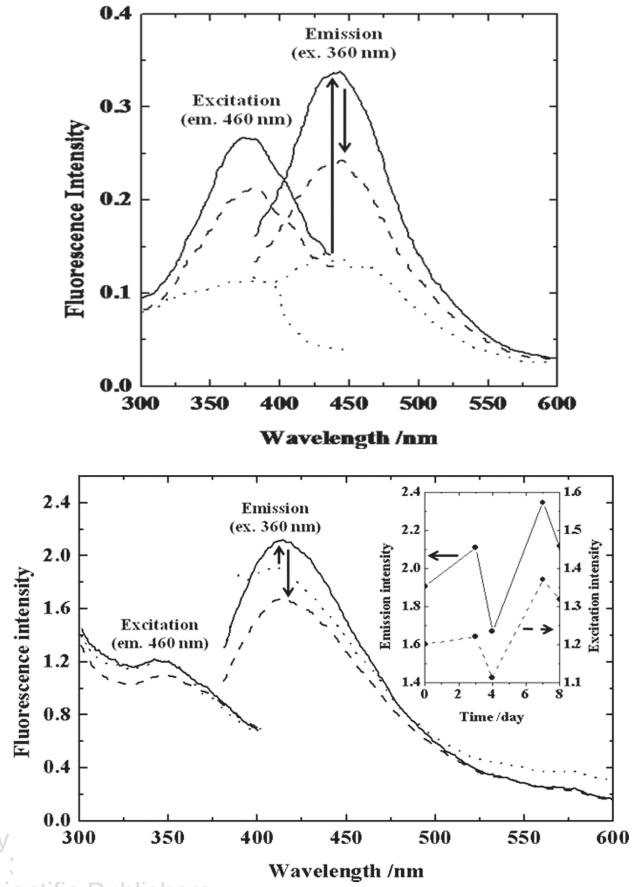


Fig. 5. Fluorescence spectra of PAMAM dendrimer films on a silicon substrate. Dotted line: pristine, solid line: O_2-treated (3 d), dashed line: degas-treated (overnight in vacuum). (top) G4.5, (bottom) G4. An inset is a plot of fluorescence intensity variation during two cycles of the O_2- and degas-treatments.

O and exemplified in Figure 7. The XPS was deconvoluted into component peaks and resultant data are summarized in Table I. The C1s region of a G4 PAMAM dendrimer film revealed clearly the different chemical states of carbon

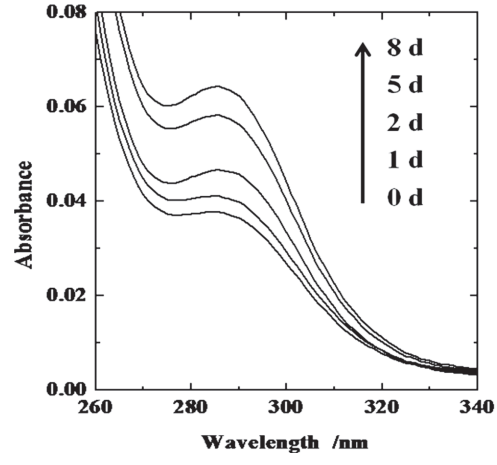


Fig. 6. UV-visible absorption spectra of a G4.5 PAMAM dendrimer film on a quartz substrate at different aging time under O_2 gas atmosphere.

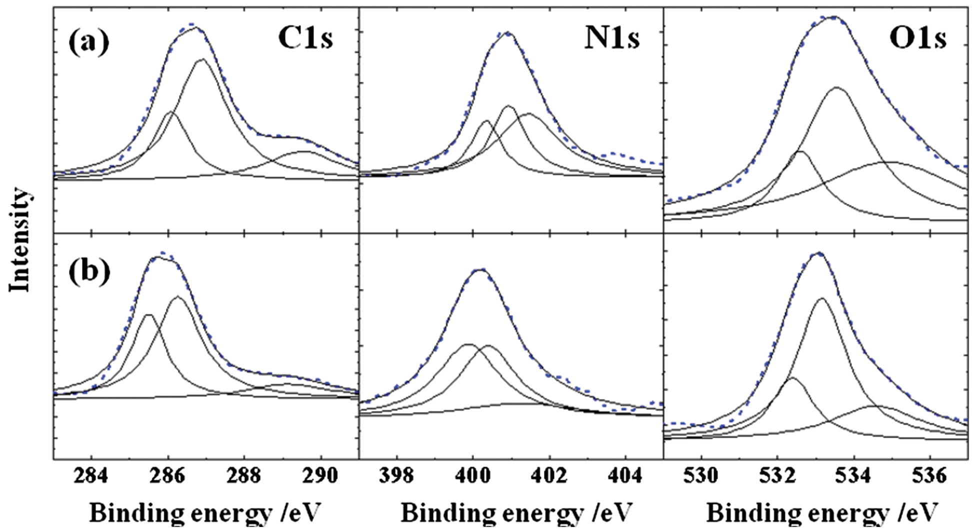


Fig. 7. Observed XPS of G4 PAMAM dendrimer films on a quartz substrate and deconvolution of C1s, N1s, and O1s peaks. (a) Pristine; (b) O_2-treated (8 d).

(see Fig. 7 and Table I).[47,48] The component peaks were obtained at binding energies of 286.1 (C–C=O), 286.9 (C–N), and 289.6 (C=O) eV for the pristine G4 PAMAM dendrimer film. The binding energy of C–N peak was considerably lowered to 285.6 eV after aged at O_2 atmosphere, while the binding energies of C–C=O and C=O peaks remained in the almost same energy. Changes were also observed in the N1s region for G4 PAMAM dendrimer film. The N1s spectra can be deconvoluted into three component peaks at the binding energies of 400.4 (N–H_2), 401.0 (N–C), and 401.5 (NH–C=O) eV. The amide nitrogen exists at higher binding energy than primary and tertiary amine nitrogen, since amide nitrogen bears the partial positive charge because of its resonance structure. Although the binding energies of the primary amine and amide nitrogen were not changed by O_2-treatment, the energy of the tertiary amine nitrogen shifted 1.2 eV and observed at 399.8 eV. In the broad O1s spectra for PAMAM dendrimer films, the O1s peak of the amide oxygen was observed at 533.3 eV and did not vary even after O_2-treatment. However, the peak of pristine dendrimer film at 535.0 eV lowered down to 534.4 eV after O_2-treatment. The third peak was observed at the binding energy of 532.6 eV, although the energy is scarcely susceptible for O_2-treatment. While both peaks at 535.0 and 532.6 eV are not assigned to oxygen in PAMAM dendrimer, the O1s peaks of surface oxide and hydroxyl of quartz substrate appear in this region. Then, it is difficult to distinguish the peaks of surface oxide or hydroxyl groups on quartz and those of other chemical states of oxygen such as free O_2 or H_2O, as previously reported.[48,49] Figure 8 displays XPS of a G4 PAMAM dendrimer film on a silicon substrate at different aging time under O_2 gas atmosphere. It is consistent with the results in Figure 7 that the C, N, and O peaks varied to lower binding energies with aging. However, it should be noticed that the remarkable variation of binding energy occurred after aging for three days, although the detectable change in fluorescence intensity was observed even after aging for one day under O_2 gas.

The XPS of G4.5 PAMAM dendrimer films behaved like that of G4 PAMAM dendrimer films on the effect of O_2-treatment (see Table I). Differently from invariable C1s peaks of C–C=O (286.9 eV) and C=O (289.6 eV), a C–N (287.3 eV) peak shifted to 286.2 eV. In the N1s region, while the peaks for tertiary amine and amide nitrogen were observed at the binding energy of 401.1 and 401.3 eV, respectively, the binding energy of tertiary amine nitrogen shifted to 400.5 eV but there was no considerable shift for amide nitrogen after the O_2-treatment. For the O1s region, the peaks at the binding energies of 532.5 eV (C–OH) and 533.1 eV (C=O) were invariable for both pristine and aged G4.5 PAMAM dendrimer film.

Table I. XPS peaks of pristine and O_2-treated G4 and G4.5 PAMAM dendrimer films (number: binding energy in eV).

PAMAM dendrimer film	C1s			N1s			O1s		
	C–C=O	C–N	C=O	NH_2	–N<	O=C–NH	OH	C=O	
Pristine G4	286.1	286.9	289.6	400.4	401.0	401.5	532.6	533.3	535.0
O_2-treated G4	286.2	285.6	289.5	400.4	399.8	401.4	532.5	533.2	534.4
Pristine G4.5	286.9	287.3	289.6	—	401.1	401.3	532.5	533.1	535.0
O_2-treated G4.5	287.0	286.2	289.6	—	400.5	401.1	532.4	533.1	534.1

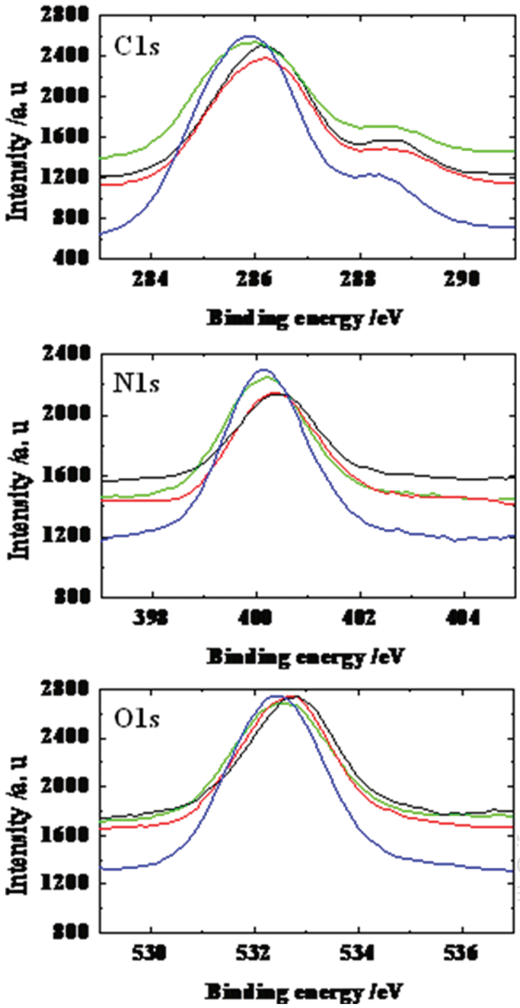


Fig. 8. Observed XPS of a G4 PAMAM dendrimer film on a silicon substrate at different aging time under O_2 gas atmosphere. Aging time: pristine (red), 3 d (black), 6 d (green), 20 d (blue).

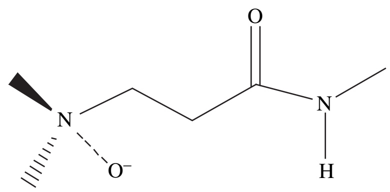
The binding energy at 535.0 eV of the pristine film lowered into 534.1 eV after O_2-treatment.

The PAMAM dendrimer consists of three different components, such as amide spacer, tertiary amine, and peripheral $–COO^-$ or $–NH_2$ (in the case of G4.5 and G4 PAMAM dendrimers, respectively) functional groups in their chemical structure. Then the XPS examination allows us to estimate the effect of O_2 treatment at atomic level. The XPS results for G4 and G4.5 PAMAM dendrimers are summarized in common as follows:

(1) The binding energies of carbon, nitrogen and oxygen in amide and primary amine are not affected by the O_2-treatment.

(2) The binding energies of carbon and nitrogen in tertiary amine are lowered on the process of the O_2-treatment.

(3) Besides peaks from PAMAM dendrimer, the additional component peak of O1s is observed at 535.0 eV and it is lowered after the O_2-treatment, suggesting the existence of other chemical states of oxygen, e.g., O_2



Scheme 1. Schematic representation of O_2-encapsulated, branched element of PAMAM dendrimer unit. O_2 molecules attack the tertiary amine moiety rather than the amide spacer moiety.

in the PAMAM dendrimer film. Then it is assumed that the tertiary amine moiety in the PAMAM dendrimer is attacked by O_2 as illustrated in Scheme 1 and, as a result, that the binding energies of tertiary amine moiety and O_2 are lowered, that is, the binding are stabilized. These results seem to be consistent with previous reports that tertiary amine should be a common moiety of PAMAM and related dendrimers with blue photoluminescence phenomenon,[46] that is, the family of PAMAM dendrimers with different terminal moieties (–OH, –COOH, $–NH_2$, etc.),[25,26,29] poly(alkyleneimine) dendrimers,[31,32] poly(amino ester) dendrimers,[27] poly(propyl ether imine) dendrimer,[33] polyethyleneimine[30] and triethylamine.[46]

4. CONCLUSIONS

Fluorescent G4 and G4.5 PAMAM dendrimers were characterized at film state. O_2-treated PAMAM dendrimer films displayed the luminescence which was detected by excitation and emission spectra. Selective adsorption of fluorescent PAMAM dendrimers on hydrophilic/hydrophobic patterned substrates was determined by means of a fluorescence microscope. It was conformed from strong luminescence on corresponding pattern that the peripheral $–NH_2$ and –COOH functional groups of G4 and G4.5 PAMAM dendrimers, respectively, were selectively adsorbed on carboxylic acid and amine terminated patterns, respectively by strong electrostatic interaction. However, no such fluorescence patterns were observed, if there were no strong interactions between PAMAM dendrimers and functionalized substrates. Luminescence intensity changed with O_2 filling and degas, indicating the nonchemical binding of O_2 with dendrimer. It could be newly mentioned from XPS that O_2-treatment affected tertiary amine moiety but not amide group in the PAMAM dendrimers.

Obviously, the present results suggest that the luminescent behavior occurs not only in solution but also even at film state. Moreover, the direct discovery of the affect of O_2 on tertiary amine in PAMAM dendrimer allows us to confirm previous assumption[46] for the luminescence mechanism of PAMAM dendrimers. The attractive features of the present technique are the simplicity, reproducibility, and sensitivity on the detection of the selective

adsorption of PAMAM dendrimers on functionalized substrates. Further, the fluorescent property of PAMAM dendrimers utilized through the present procedure is highly effective, suggesting that family of PAMAM dendrimers can be used to label and monitor the target systems as fluorophor. Especially, the fluorescent PAMAM dendrimers, which are nontoxic, can be selectively labeled to the functionalized systems such as biomaterials and valuably utilized as a sensor of selective molecular recognition in medical therapy and testing.

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