ANOMALOUS FLUORESCENCE EMISSION FROM ORGANIC MOLECULE WITHOUT FLUOROPHORE ---- POLY (AMIDO AMINE) DENDRIMER

*Dongjun Wang, Toyoko Imae**

Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan

imae@nano.chem.nagoya-u.ac.jp

In this paper, we report an anomalous fluorescence emission from poly (amido amine) (PAMAM) dendrimer, which is a kind of organic molecules without fluorophore. It was found that there was a remarkable difference in fluorescence property between second- and fourth-generation (G2 and G4) PAMAM dendrimers, and, moreover, both of them showed pH-dependence in fluorescence intensity. It can be believed that this fluorescence emission, as named 'structure induced fluorescence', is contributed by overcrowded structure of functional groups in dendrimer.

Figure 1 shows excitation and emission fluorescence spectra of G2 and G4 PAMAM dendrimers. In comparison with G2, G4 showed strong fluorescence bands and red-shift in an emission spectrum; this difference maybe due to the higher crowding degree of functional groups in G4.

Both G2 and G4 showed a significant pH-dependent fluorescence property in the range of pH value from 13 to 1 (as shown in Figure 2 and 3). Protonation of amine groups increases with the decreasing of pH value. At lower pHs, charge-charge repulsion forces dendritic termini to the periphery in outward-folding way, and functional groups in dendrimer become more crowded. On the other hand, charge-charge repulsion makes the structure of dendrimer become more rigid. Therefore, fluorescence from G4 and G2 reached their intensity maximums at acidic condition, respectively. It should be noted here that pH 6 is the critical point for G4 (as shown in Figure 3), which correlates well to the pK_a values of amines in PAMAM dendrimer.

From the classic viewpoint, organic molecules without fluorophore, such as PAMAM dendrimer, could not emit fluorescence. Nevertheless, the phenomenon observed in the present work was a highly reproducible result. It is believed that functional groups in PAMAM dendrimer could be densely packed under suitable condition, because of its structure stability formed by covalent bonds. Therefore, it is possible for the overcrowded functional groups to construct a somewhat new kind of 'fluorophore'. On the contrary, the above highly crowded state can not be achieved by small organic molecules or classical micelles, although they have same functional groups or have a similar shape and size as dendrimers.

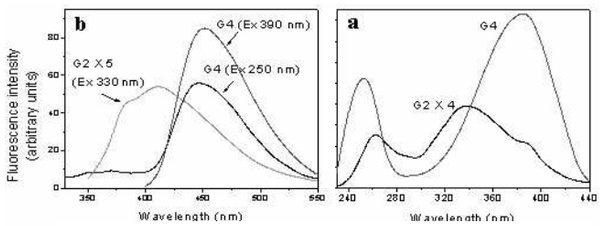

Figure 1. Fluorescence spectra of G2 and G4 at pH 2. (a) Excitation spectra emitted at 450 nm (b) Emission spectra excited at different wavelengths.

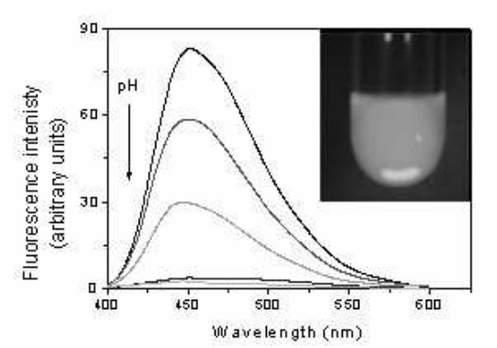

Figure 2. Fluorescence emission spectra of G4 at different pHs: pH 2, 4, 5, 9, and 11 (from top to bottom, excitation at 390 nm). Inset: an illumination photograph of aqueous 1 wt % solution of G4 at pH 2. The sample was excited by a 4.5 w UV lamp.

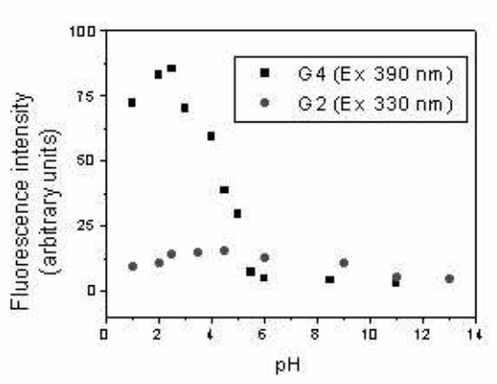

Figure 3 The pH-dependent fluorescence intensity of G2 and G4 in the pH range from 1 to 13. Emissions of G2 and G4 were at 410 nm and 450 nm, respectively.