Synthesis and Single Aggregate Spectroscopy of a Novel Fluorescent Dendrimer with Highly Efficient Energy Harvesting

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A novel fluorescent dendrimer with a diphenylanthracene core and pyrenyl groups in the dendrons was synthesized. Fluorescence spectra and its decay curves proved spontaneous energy transfer from the pyrene units to the core diphenylanthracene, which was ascertained both in solution and for a single particle of the dendrimer aggregate.

Dendrimers are hyperbranched macromolecules with well-predictable three-dimensional architecture.[1–4] They are composed of core and dendron units which include building blocks and functional groups. Recently, dendrimers have attracted great attention as synthetic light-harvesting antennae,[5–10] which means that some dendrimers can emit strong fluorescence from their core unit owing to energy transfer from dendron units to the core unit even when the core unit does not absorb light directly. Low temperature structural relaxation in porphyrin-cored dendrimers was elucidated in our previous study.[11] In the present study, we synthesized a novel fluorescent dendrimer which contains pyrenyl groups in dendron units and a diphenylanthracene group in a core unit so as to show high-efficient energy transfer[12] to the core unit. The reasons why we chose pyrene and diphenylanthracene groups are as follows: the absorption wavelength of diphenylanthracene is almost overlapped by the emission wavelength of pyrene, the fluorescence lifetime of pyrene is long, and the fluorescence quantum yield of diphenylanthracene is almost unity. We report here synthesis of the dendrimer and the result of high efficient energy transfer from pyrene units to the core unit by measuring fluorescence spectra and lifetime. This dendrimer might be applied to a point light source. For example, when we attach it to the top of near-field scanning optical microscope (NSOM) probe as a point light source,[13] it may give a possibility of watching with NSOM a small object whose size is as big as one molecule.

The synthesis of the dendrimer with a diphenylanthracene core and dendrons with pyrenyl terminal groups (L2dendrimer) was carried out with a convergent method[3,14] as is shown in Figure 1. PyL1ester (**1**) was prepared by the reaction of 1-hydroxymethylpyrene and methyl 4-hydroxybenzoate in dry THF in the presence of triphenylphosphine and by adding diethylazodicarboxylate (DEAD) solution.[15] The reduction of **1** to PyL1OH (**2**) was performed by using lithium aluminum hydride (LAH). The reaction of **2** with methyl 3,5-dihydroxybenzoate in the presence of triphenylphosphine and DEAD resulted in PyL2ester, which was reduced with LAH to PyL2OH (**3**), the dendron with pyrenyl terminal groups. Then the dendron **3** was bonded with the aid of triphenylphosphine and DEAD to 9,10-bis(4-hydroxyphenyl)anthracene (**5**), which was prepared in advance from 9,10-bis(4-methoxyphenyl)anthracene (**4**) by using borontribromide. The resulting L2dendrimer (**6**) was characterized with ^{1}H NMR and MALDI TOF MS confirming its preparation.

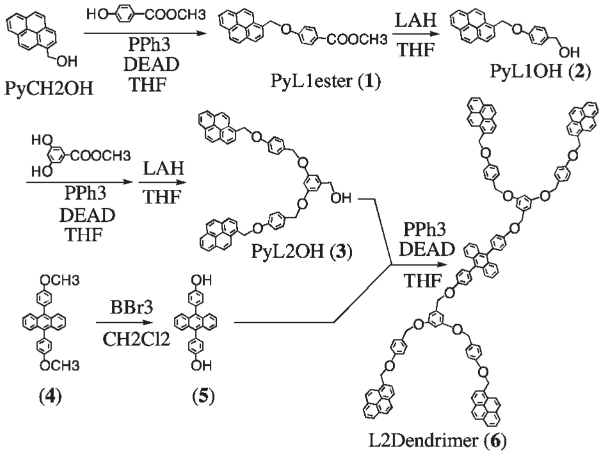

Figure 1. Synthetic route of the L2dendrimer with diphenylanthracene core and terminal pyrenyl groups.

The measurements of fluorescence and fluorescence excitation spectra were carried out for PyL2OH (**3**), 9,10-bis(4-methoxyphenyl)anthracene (**4**), and L2dendrimer (**6**) to know information on energy transfer from the dendron units to the core unit. The concentrations of the dendrimer and reference samples were set to be 1×10^{-5} M in dichloromethane so that we could ignore the influence of intermolecular interaction. The results are shown in Figure 2. The fluorescence spectrum of **6** shows almost the same emission profile as that of **4** when excited at 337 nm. On the other hand, the excitation spectrum of **6** shows almost the same profile as that of **3** when monitored at 426 nm where the strongest fluorescence intensity of **6** is observed. These results are

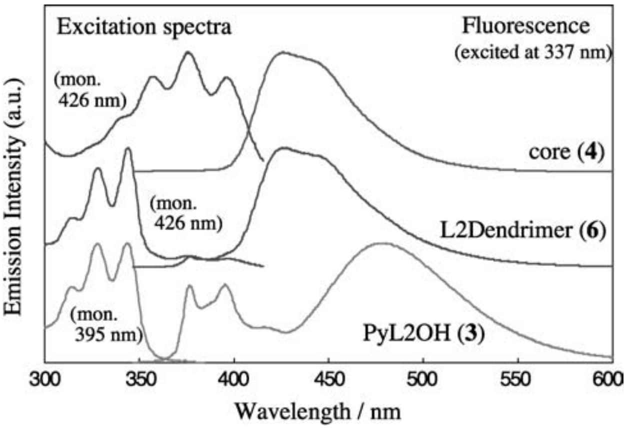

Figure 2. Fluorescence and its excitation spectra of core diphenylanthracene **4**, L2dendimer **6**, and L2dndron **3** in 1.0×10^{-5} M CH_2Cl_2 solution.

explained as follows. When we irradiate ultraviolet light at 337 nm onto **6**, the dendrimer **6** absorbs almost all of the irradiated light at the pyrene units and shows strong fluorescence only from the core unit due to energy transfer from the pyrene units to the core unit. Still more interesting to say is that though we could see a broad fluorescence peak attributed to pyrene excimer at 480 nm in the fluorescence spectra of **3**, we could not observe that kind of fluorescence peak in the spectra of **6**. This result suggests that energy transfer from pyrene units to the core unit takes place much faster than the excimer-forming motion between adjacent pyrene units in **6**.

Transient fluorescence decay curves for 1×10^{-6} M solutions of L2dendrimer **6**, and its reference samples, **3** and **4** were measured by using a sub-nano-sec pulsed N_2 laser and streak camera detection system. Details of the apparatus are given elsewhere.[16] The results for **3** and **6** are shown in Figure 3. First, we irradiated UV pulse at 337 nm onto **6** and carried out a transient decay measurement monitored at 406–477 nm. We could see the peaks of the irradiation laser light and the fluorescence from the core of **6** at almost the same time. Second, we irradiated UV pulse at 337 nm onto **3** and observed a time-decay monitored at 452–561 nm to see the fluorescence only from the excimer. We could see the peak of the fluorescence after 16 ns compared to the irradiation laser light. Therefore, we can say that excimer formation between adjacent pyrene units takes place within 16 ns, and this order of magnitude is in agreement with previous studies on excimer formation dynamics of oligomeric chains with chromophores at both chain ends in solution.[17,18] However, the rate of energy transfer in the L2dendrimer **6** was very fast and its time range was beyond the time resolution of the apparatus (100 ps). The average decay lifetime of **6** is 4.7 ns, which is almost the same as that of **4** (4.6 ns). The risetime of **3** (excimer) is 16 ns and the decay time of **3** (excimer) is about 22 ns.

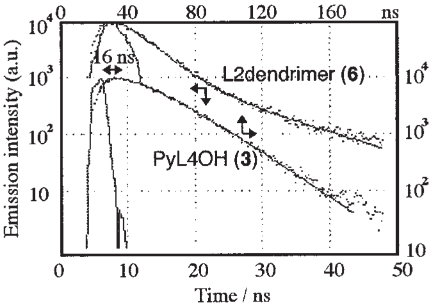

Figure 3. Fluorescence decay curves of L2dendrimer **6** and PyL2OH **3** in 1.0×10^{-6} M CH_2Cl_2 solution excited at 337 nm. Detection ranges are 406–477 nm (**6**) and 452–561 nm (**3**).

Finally, a single particle of L2dendrimer aggregate on a silica plate was prepared by spreading 1×10^{-8} M solution of **6** in CH_2Cl_2 onto the silica plate, and was observed with a confocal fluorescence microscope equipped with a time-resolved measurement using a mode-locked Ti-sapphire laser. Details of the apparatus are given elsewhere.[19] An optical image of the single aggregate under confocal microscope with a diameter of about 1 μm is shown in Figure 4. The fluorescence decay curve excited at 300 nm by the THG of Ti-sapphire laser with the pulse width of 2 ps showed no rise and the decay lifetime was about 1.6 ns (time resolution of the apparatus: 30 ps). Energy transfer from pyrene units to the core unit is proved to proceed very rapidly in less than 30 ps. The difference of its decay lifetime from that in solution suggests the existence of various deactivation processes from the excited state of diphenylanthracene unit due to their interaction in solid state.

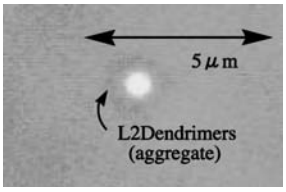

Figure 4. Fluorescence image of a single L2dendrimer aggregate observed with a confocal fluorescence microscope.

In conclusion, we synthesized an L2dendrimer which contains pyrene in dendrons and diphenylanthracene in a core. When UV light was irradiated at 337 nm onto this dendrimer, it emitted fluorescence almost only from the core unit due to the spontaneous energy transfer from the pyrene units to the core diphenylanthracene. Fluorescence decay lifetimes were measured both in solution and for a single particle of its aggregate.

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