

Fluorescent Doughnut-Like Assembling of Wire-Type Dendrimers Depending on Their Generation Numbers and Degrees of Polymerization

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The self-assembled structures by evaporation of tetrahydrofuran (THF) solution of wire-type dendrimers have been studied by some spectroscopic and microscopic techniques. Doughnut-like structures were obtained for some dendrimers with generation number of 2 and about 28 nm length by depositions their THF solutions on a quartz substrate, while yarn-like and particle-like structures were obtained for other dendrimers. The size of the doughnut structure varied from 1 to 8 μm in diameter and between 30 and 150 nm in height. Confocal fluorescence microscopy, atomic force microscopy (AFM), and near-field scanning optical microscopy (NSOM) were applied to elucidate assembled structures and electronic properties in addition to conventional fluorescence spectroscopy. Polarization and local fluorescence measurements at some parts of doughnuts and particles were demonstrated, however, no correlation between molecular orientation/intermolecular interaction and doughnut structures was found. The doughnut formation mechanism is considered on the basis of evaporation processes observed from in situ experiments.

Introduction

Wire-type dendrimers, $L_n\text{PPE}_m$, where n and m show the generation number of dendritic wedges and the average degree of polymerization (DP) of backbone, respectively, are summarized in Figure 1 and Table 1. These consist of a rigid and fully conjugated poly(phenyleneethynylene) backbone wrapped with flexible poly(benzyl ether) dendritic wedges were recently synthesized and have received much attention.¹ Interestingly, the supramolecular rods harvest light over a wide range of wavelengths and convert it to blue light with high efficiency. The backbone collects photons in the whole wavelength range up to 450 nm, while the dendritic wedges collect photons of UV ranging from 220 to 300 nm and channel the energy to the backbone, thus, only blue fluorescence at 454 nm from the conjugated backbone was observed without any luminescence from the dendritic wedges in solution.¹ The most remarkable characteristic of the wire-type dendrimer is its molecular structure, that is, a very long one-dimensional structure due to rigid π -conjugated poly(phenyleneethynylene) backbone. Namely, the length of L3PPE130 reaches about 180 nm as a single molecule. Therefore, we expect unique assembled structures and accompanying photophysical properties in solid state. The association of the present long molecules might form straight fiber-like aggregates that can be applied in molecular device construction. Indeed, a relation between surface morphology and microscopic electronic properties, that is, height/thickness dependences of fluorescence properties in single molecular microcrystals and amorphous films are now receiving much attention.^{2–4} For example, it was demonstrated in films

TABLE 1: Weight-Average Molecular Weight (M_w) and Its Ratio to Number-Average Molecular Weight (M_n), M_w/M_n , of Wire-type Dendrimers

	M_w	M_w/M_n
L2PPE3	3 400	1.1
L2PPE19	21 500	3.4
L2PPE25	27 800	2.5
L3PPE19	41 700	1.6
L3PPE56	121 800	2.5
L3PPE130	280 000	6.5
L4PPE8	34 000	1.5

of a polythiophene derivative that protruding and flat areas give blue and red emissions, reflecting rather folded and extended polymer conformations, respectively.⁴

Recently, we have found the formation of a doughnut-like assembled structure when THF solutions of L2PPE19 and L2PPE25 were cast on a quartz substrate. For other dendrimers that possess different numbers of generation and DP, doughnut-like assembled structures were not observed under the same condition. In addition to doughnuts, μm -sized yarn-like and particle-like structures were formed, depending on n and m . The formation of such a doughnut-like structure has recently been observed in the evaporation process of some organic solutions, but only for porphyrin derivatives,^{6–8} monomeric collagen⁹ and metal particles.^{10,11} While De Schryver and Nolte examined various conditions of the solvent, vaporization speed, and concentration, whether the doughnut-like structural formation can be applied to other types of molecules or not are unknown. Several hypotheses have been put forward to explain the formation of doughnut from evaporating solutions. They have been attributed the formation to gas bubbles in the liquid film,^{6,7} or to solvent convection by the rim of a hole opening in an

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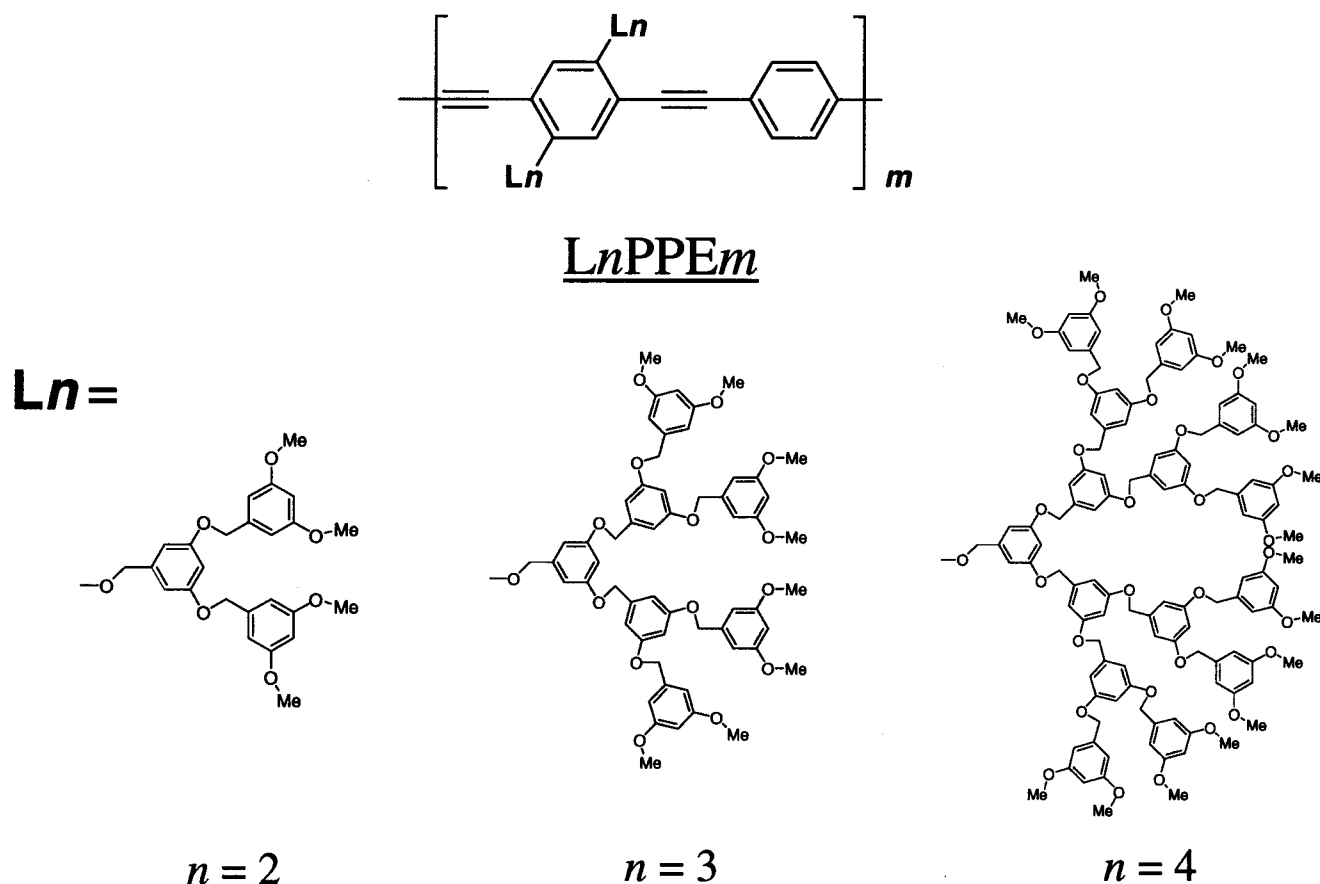


Figure 1. Chemical structures of wire-type dendrimers. n and m show the generation number of dendritic wedges and the average degree of polymerization (DP) of backbone, respectively.

unstable film.^{7,9–11} On the basis of the direct observation of doughnut formation of bis(21*H*,23*H*-5(4-pyridyl)-10,15,20-tris-(4-hexadecyloxyphenyl)porphyrin)platinum dichloride (PtP)/chloroform (CHCl₃) system in the in situ experiments, Latterini et al.⁸ reported the doughnut formation process involves three steps as follows; (1) film rupture after a period of spreading of the initial droplet and its thinning under evaporation, (2) coalescence of small droplets to bigger droplets until pinning at defects, and (3) final evaporation of the solvent and doughnut formation. Actually, it is reported that the final evaporation leads to piling of dispersed particles at an edge of macroscopic droplets.¹² Concerning photophysical properties and molecular orientation, Hofkens et al.⁷ reported that fluorescence decays at doughnut structures and other aggregates of PtP agreed with each other, and indicated from polarized NSOM images that the doughnuts are an amorphous conglomerate of aggregates. We think it is now the time to look for many examples which give interesting aggregates upon casting and spin-coating and to elucidate their molecular/electronic properties and formation processes.

In this letter we report a detailed investigation of doughnut and other assembled structures of wire-type dendrimers, LnPPEm, by use of confocal fluorescence microscopy, AFM and NSOM. In situ observation of their formation processes, measurement of the local photophysical properties and the molecular assembling conditions are reported and considered.

Experimental Section

The chemical structures, weight-average molecular weight (M_w), and its ratio to number-average molecular weight (M_n), M_w/M_n , of wire-type dendrimers are listed in Figure 1 and Table

1. Their synthesis is described elsewhere.¹ THF (Nacalai Tesque, Spectro-Grade) was used as a solvent without further purification. All quartz substrates were washed with detergent solution and immersed in water with sonication.

Fluorescence microscope images have been acquired using a conventional instrument (Olympus, universal fluorescence equipment) with a 40 \times , 0.85 NA objective lens. AFM images have been obtained by a tapping mode AFM (Digital Instrument, Nanoscope III a) using commercially available silicon cantilevers, and processed by horizontal leveling. NSOM images have been recorded using a modified commercial instrument (Seiko Instruments, SPA 300).³ The argon ion laser (454 nm, Omnicrome, 543-AP) was used as an excitation source for fluorescence measurement. The experiments were performed with homemade Al-coated optical fiber probes with ~ 100 nm aperture at the end. Topographic and fluorescence images were recorded simultaneously. The fluorescence spectra of single fluorescent doughnuts, yarns, and particles were measured using a confocal fluorescence microspectroscopy system with scanning piezo stage (Physik Instrumente, E-710) described elsewhere.⁵ A 100 \times , 1.25 NA oil immersion objective lens was used. As an excitation light, the third harmonic ($\lambda = 300$ nm, 2 ps, 82 MHz) of a mode-locked Ti:sapphire laser (3950-S2L, Spectra Physics) was introduced to the microscope. The fluorescence spectra were recorded with a polychromator (Oriol Instruments, model 77480) and an attached CCD camera (Andor, DU420-OE). Polarization effects on the fluorescence were examined by placing a $\lambda/2$ wave plate (Sigma Koki) and a Gran laser prism (Sigma Koki) in the excitation light path. The bulk fluorescence spectra were measured using a conventional fluorescence spectrometer (Hitachi, F-4500).

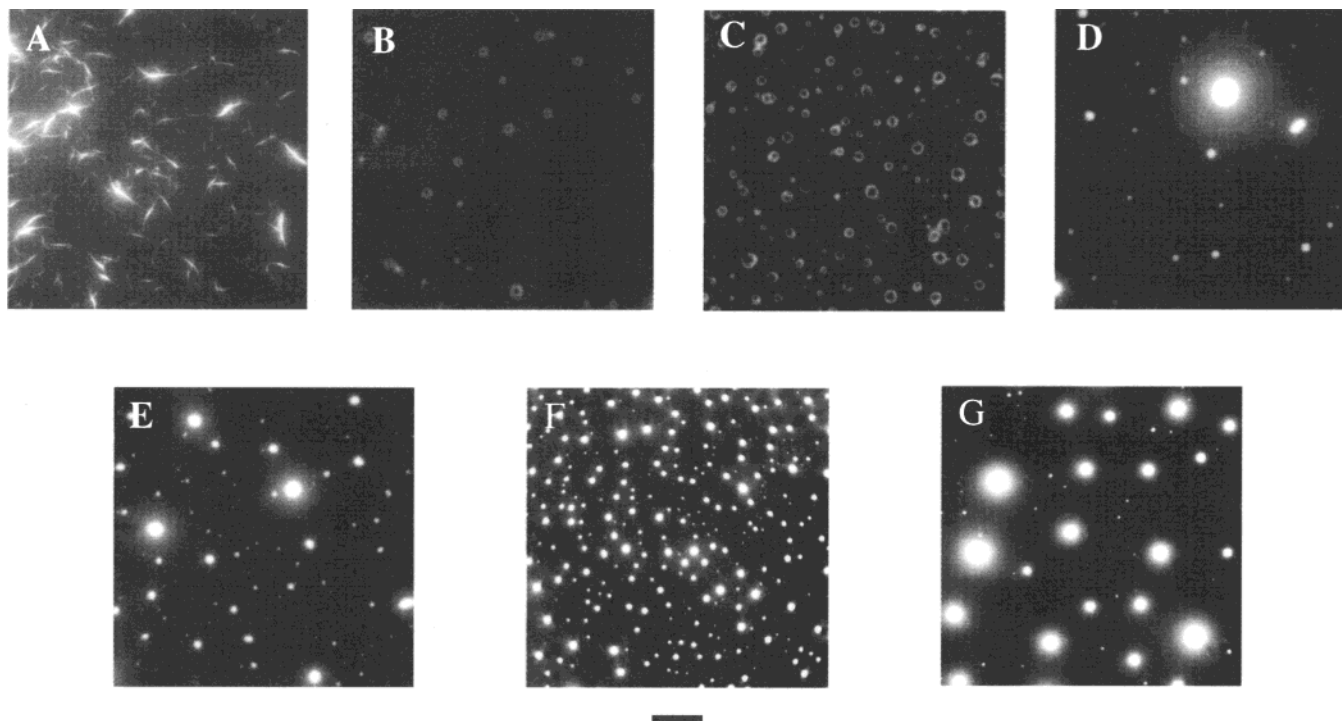


Figure 2. Fluorescence microscope images. (A) L2PPE3, (B) L2PPE19, (C) L2PPE25, (D) L3PPE19, (E) L3PPE56, (F) L3PPE130, and (G) L4PPE8. The scale bar below the image (F) represents 20 μm . Fluorescent doughnut-like structures were observed in images (B) and (C), molecular yarn-like structures in image (A), and fluorescent particles in other images.

Results and Discussion

Fluorescence microscope images of self-assembled structures of the wire-type dendrimers on a quartz substrates are shown in Figure 2. These assembled structures were obtained on a quartz substrate by casting their THF solution and drying in air at 21–22 $^{\circ}\text{C}$. All samples were prepared under the same condition. The concentration of their THF solutions was adjusted by setting optical density at each absorption peak wavelength of the conjugated backbone to 0.3. This corresponds roughly to 10^{-5} M. Depending on chemical structures, doughnut-like rings and yarn-like and particle-like structures are formed. It is interesting to note that a large number of fluorescent ring structures were observed only for L2PPE19 and L2PPE25 (B and C), yarn-like structures for L2PPE3 (A) that possesses the same generation number of the latter two, and particle-like structures for L3PPE19 (D) with almost the same DP as the DP values of L2PPE19 and L2PPE25.

The morphology and size of fluorescent ring structures for L2PPE25 were measured by AFM as shown in Figure 3. A line scan analysis of the AFM image in Figure 3A is shown in Figure 3B, where no appreciable amount of molecules was observed in the center of the ring. Thus, the fluorescent ring is considered to have a perfect doughnut structure. The size of the doughnut structures varied from 1 to 8 μm in diameter and between 30 and 150 nm in height. This doughnut structure is also characterized by observation of fluorescence NSOM images. In Figure 3C,D, a pair of simultaneous topographic and fluorescence images for another ring of L2PPE25 are shown as an example. Topographic and fluorescence images agreed well with each other, and no fluorescence was observed in the center of the doughnut. As seen in Figure 3C, agglomerates near the doughnut is lower than that of doughnut structure, while no fluorescence was observed from the agglomerates. Maybe they contain a nonfluorescent defect or an impurity. It should be emphasized that such agglomerates are exceptional and formation of

doughnut and other structures is perfect, although the solutions were simply cast.

To obtain detailed information about the different aggregation formation of doughnuts and particles, we carried out in situ observation. Fluorescence images of the evaporation processes were acquired in real time when THF solutions of the wire-type dendrimers were spread on a quartz substrate on the microscope stage at 21–22 $^{\circ}\text{C}$. The formation processes of each structure are given in Figure 4 and their characteristics are summarized as follows.

(1) Doughnut Structure Formation (L2PPE25). Initially, the solution spread homogeneously (image at 0 min). Because of solvent evaporation, the solution film became inhomogeneous; thus, in the image at 8 min, white (fluorescent solution film) and black (nonemissive quartz) areas were shown. At white areas, many small black holes opened,¹³ as marked by arrows in the expanded view at 8 min of Figure 4A. As the solvent further evaporated, the black area expanded, and the solution was left around the small holes (image at 12 min). However, in this process, the small holes did not expand. It is natural to consider that the displacements of the wire-type dendrimers are induced and their accumulation at edge of the small holes gave the doughnut-like distribution (image at 43 min). This process can therefore be assumed to be due to the analogous mechanism to gas bubbles.^{6,7}

(2) Particle Structure Formation (L3PPE130). Initially, the solution spread homogeneously (image at 0 min). As solvent evaporated, the solution film became inhomogeneous and was ruptured (image at 10 min).¹⁴ After the rupturing was repeated, the solution film became droplets (image at 12 min). Subsequently, the droplets shrank due to further evaporation, the dendrimers may be accumulated in the center, and particle structures were formed when the drying was completed (image at 40 min).

It is considered that the evaporation rate and solute concentration are very important factors for doughnut structure formation.

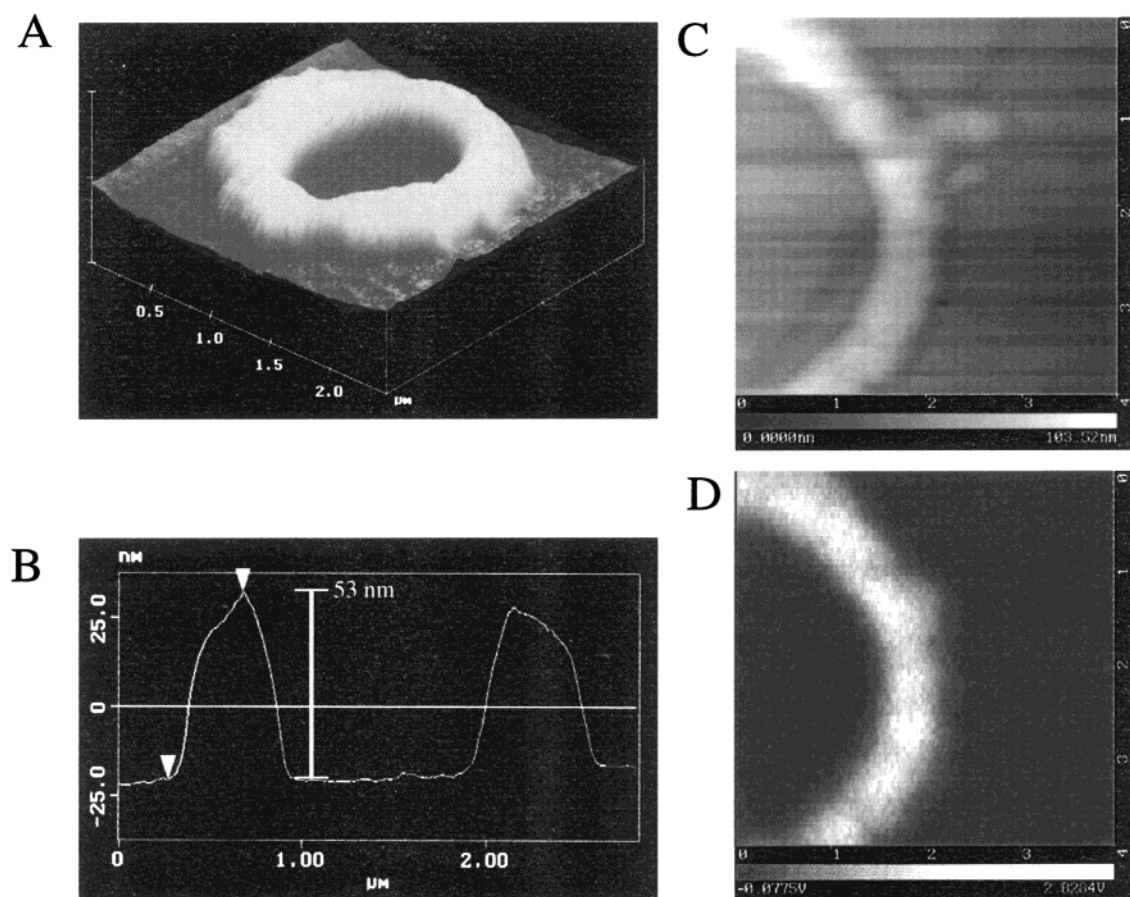


Figure 3. (A) A topographic image acquired by AFM on a fluorescent doughnut structure of L2PPE25. (B) A topographic line scan obtained from AFM image of (A). Topographic (C) and fluorescence (D) images acquired by NSOM on another fluorescent doughnut structure of L2PPE25.

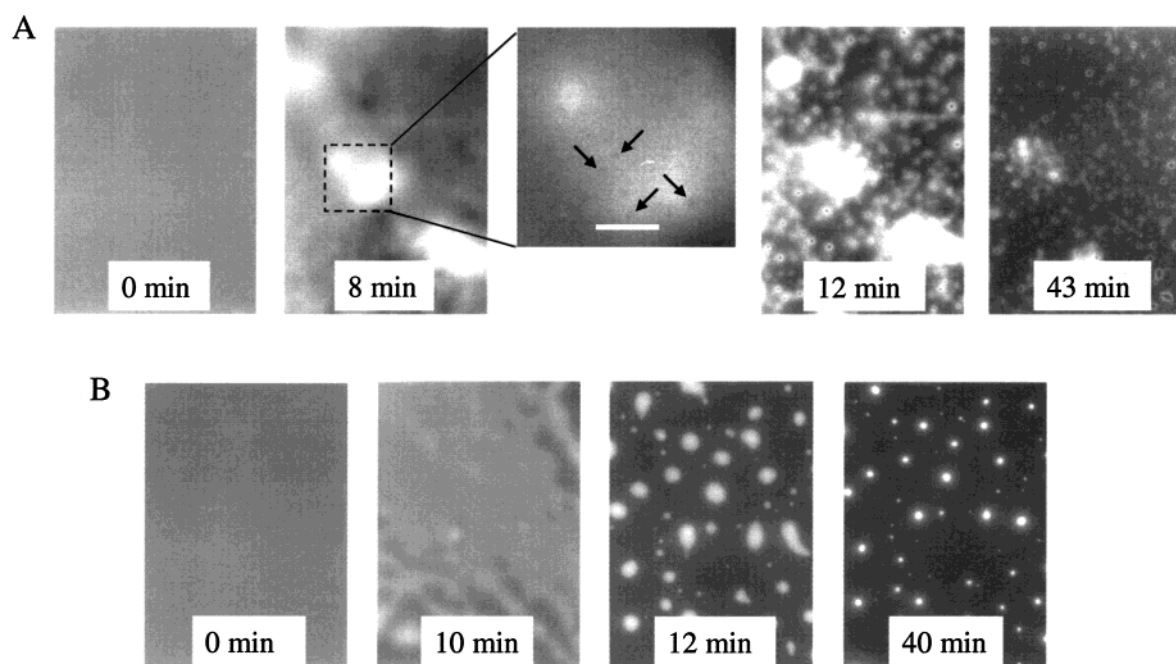


Figure 4. Fluorescence microscope images acquired during in situ observation of formation processes of (A) doughnut (L2PPE25) and (B) particle (L3PPE130) on a quartz substrate. The times after deposition of the solution are shown below each image. The scale bar below images (B) represents 100 μm . In the process of (A), the expanded view of the square enclosed with broken lines in image at 8 min is shown between images at 8 and 12 min. In the expanded view, the scale bar represents 20 μm .

Evaporation rate can be same in every case under the present experimental condition, while the LnPPEm concentration was adjusted by setting its optical density to 0.3 at each absorption

peak wavelength. Each wire-type dendrimer is composed of different DP; therefore, absorption peak wavelength that is assigned to conjugated backbone is slightly different. However,

Wautelet et al. studied ether-substituted poly(phenyleneethynylene) oligomers and polymers in THF, and reported that though absorption peak wavelength was red-shifted with increasing DP, molar extinction coefficient of the monomer unit at each wavelength is almost same.¹⁵ Swager et al. reported that the value is approximately the same as that of phenyleneacetylene, indicating that the polymer is regarded as if it is composed of isolated chromophores.¹⁶ Therefore, in the present case where the optical density is adjusted to the same, it is considered that the total number of the repetitive units is almost same. Thus, L_nPPE_m concentration of THF solutions is proportional to m^{-1} . Namely, the concentration of L3PPE130 is lower than that of L2PPE25 by 5.2, while the concentrations of L2PPE19, L2PPE25, and L3PPE19 solutions are almost the same. Furthermore, preliminary concentration effect was carried out in L3PPE19 that possesses the same DP as that of L2PPE19. However, in the region of 0.05~0.3 of optical density at the absorption peak, the doughnut structure has never been observed. Therefore, it is considered that the difference of the assembled structures does not result from the difference of evaporation rate and solute concentration.

Other important factor for doughnut structure formation is molecular structure. Schenning et al. reported,⁶ that the so-called picket-fence porphyrins which hardly stack gave no doughnut, while other porphyrins did. Therefore, they considered that π - π stacking interactions between molecules are necessary for the formation of the doughnut structures. Although π - π stacking of the present wire-type dendrimers should be largely different from that of the porphyrin derivatives, the former may also stack. Whether dendrimers stack with each other or not is reflected in the differences in absorption and emission spectra between the solution and doughnut/particle.

Thus, we consider the organization of the assembled structure may be due to properties of each wire-type dendrimer, that is, solubility, tendency to aggregate and diffusion coefficient, which are functions of molecular structure and molecular size, and eventually ascribed to intermolecular interaction between the dendrimer and the solvent.

To get more microscopic information of the doughnut structures, fluorescence spectra were measured at some parts of the doughnut structure of L2PPE25 and of the particle structure of L3PPE19 by using confocal fluorescence microspectroscopy system with about 1 μ m spatial resolution. Both spectra are similar to each other, and also identical with the spectra of the corresponding ensemble measured for bulk film including many doughnuts or particles on a substrate. Therefore, in wire-type dendrimers, morphology such as doughnut, yarn, and particle structures have no direct correlation with the fluorescence spectra. This means that electronic structure of the backbone poly(phenyleneethynylene) is not influenced by the agglomeration.

Furthermore, molecular orientation in the doughnuts, yarns, and particle structures were investigated by the excitation polarization effect upon the fluorescence intensity distribution.

The fluorescence intensity images obtained by confocal microspectroscopy system with horizontally and vertically polarized excitation lights were identical within experimental errors. The absence of fluorescence anisotropy in the fluorescence intensity images indicates that no ordered structure is formed over ca. 500 nm (spatial resolution). In our experimental setup, the polarizer is not set in the detection light path, so the fluorescence intensity distribution depends on the excitation efficiency. Therefore, the result suggests that the dendrimers are in a random orientation at every measured spot.

Here it is shown that the dendrimers with the second generation and about 20 DP give the characteristic doughnut structure, while its nature is not clarified yet. More systematic detailed study to elucidate the nature of characteristic formation of the various molecular aggregates is going on for the present wire-type dendrimers. This will contribute to the development of organic mesoscopic chemistry and is practically important for the future designing of molecular systems for nanometer-sized memory cells, electronics, and displays. The present work reports a new series of dendrimers giving special doughnut aggregation structures.

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