Fluorescence Energy Transfer in Dendritic Poly(L-lysine)s Combining Thirty-two Free Base- and Zinc(II)-porphyrins in Scramble Fashion

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Dendritic poly(L-lysine)s combining thirty-two free base- and Zn(II)-porphyrins in scramble fashion were successfully synthesized and exhibited highly efficient (85%) fluorescence energy transfer from Zn(II)-porphyrins to free base-porphyrins.

We previously reported the incorporation of a large number of porphyrin rings near the surface of dendritic poly(L-lysine)s.[1,2] A dendrimer combining thirty-two free base(H_2)-porphyrin rings, for instance, showed extremely strong split CD at Soret band in toluene/DMF (9/1, v/v), while it is silent in CD in DMF. This fact suggested that porphyrin rings could be arranged together in close vicinity on the single macromolecule with the molecular weight more than 50000 in certain conditions.

The energy transfer systems from Zn(II)-porphyrins to H_2-porphyrins have been extensively studied so far by designing a number of porphyrin ring assemblies.[3,4] More recently, design syntheses of porphyrin dendrimers are also reported under the same attempt to build the model systems as light-harvesting antenna system.[5,6] In the course of study on the porphyrin arrangement on various dendritic poly(L-lysine)s, we considered three types of separate incorporation of Zn(II)- and H_2-porphyrins. As illustrated in Figure 1, hemisphere, bouquet, and double strata fashions are challenging in synthetic approaches. The hemispherical dendrimer with Zn(II)- and H_2-porphyrins was very recently synthesized and unfortunately only 43% of fluorescence energy was transferred from Zn(II)-porphyrins to H_2-porphyrins.[2] Therefore, in the present study, we carried out the synthesis of **1a**-**1c** (Figure 1) containing a mixture of different porphyrins in scramble fashion and subjected to the fluorescence measurements to estimate the efficiency in the fluorescence energy transfer near the surface of dendritic poly(L-lysine)s.

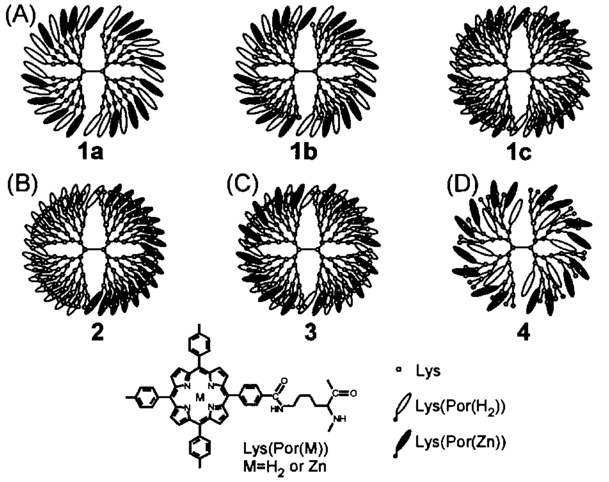

Figure 1. Illustration of four types of dendritic poly(L-lysine)s combining a large number of H_2- and Zn(II)-porphyrins. (A) Scramble fashion, (B) Hemisphere fashion, (C) Bouquet fashion, and (D) Double strata fashion.

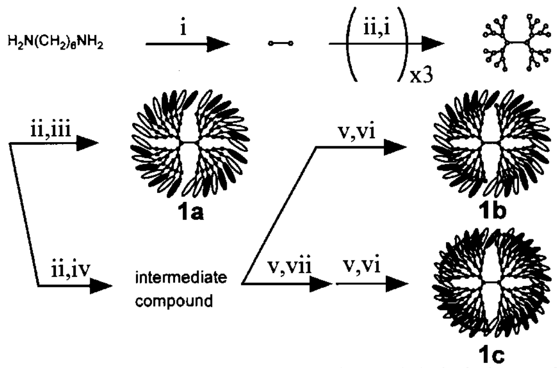

Figure 2. Synthetic route for dendritic poly(L-lysine)s combining thirty-two porphyrins in scramble fashion.
i) Boc-L-Lys(Boc)-OH, BOP/HOBt. ii) TFA. iii) Boc-L-Lys(Por(H_2))-OH and Boc-L-Lys(Por(Zn))-OH, HATU. iv) Fmoc-L-Lys(Por(H_2))-OH and Fmoc-L-Lys(Por(Zn))-OH, HATU. v) 20% piperidine in DMF. vi) Boc-L-Lys(Boc)-OH, HATU. vii) Fmoc-L-Lys(Fmoc)-OH, HATU.

The synthesis was carried out according to Figure 2.[7] At the fifth generation, the equimolar mixture of Boc-Lys(Por(H_2))-OH and Boc-Lys(Por(Zn))-OH was incorporated to give **1a** by the aid of HATU. Separately, the equimolar mixture of Fmoc-Lys(Por(H_2))-OH and Fmoc-Lys(Por(Zn))-OH was condensed to prepare the intermediate for **1b** and **1c**. After removal of Fmoc group, the incorporation of Boc-Lys(Boc)-OH gave **1b**. Further incorporation of Fmoc-Lys(Fmoc)-OH and subsequent Boc-Lys(Boc)-OH gave **1c**.

The three dendrimers **1a**, **1b**, and **1c**, which are the mixtures with different numbers (around sixteen) of metallated

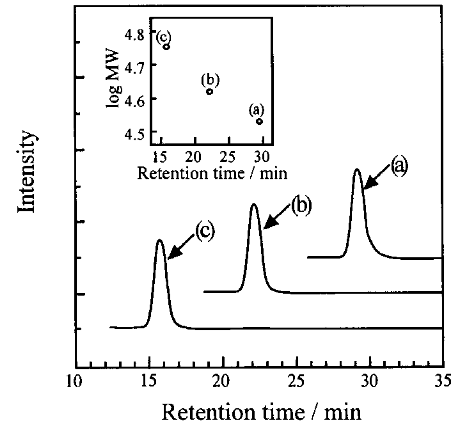

Figure 3. Analytical size-exclusion chromatograms of dendrimers **1a** (a), **1b** (b), and **1c** (c) with DMF. The mean molecular weights are 34131, 41436, and 56047, respectively.

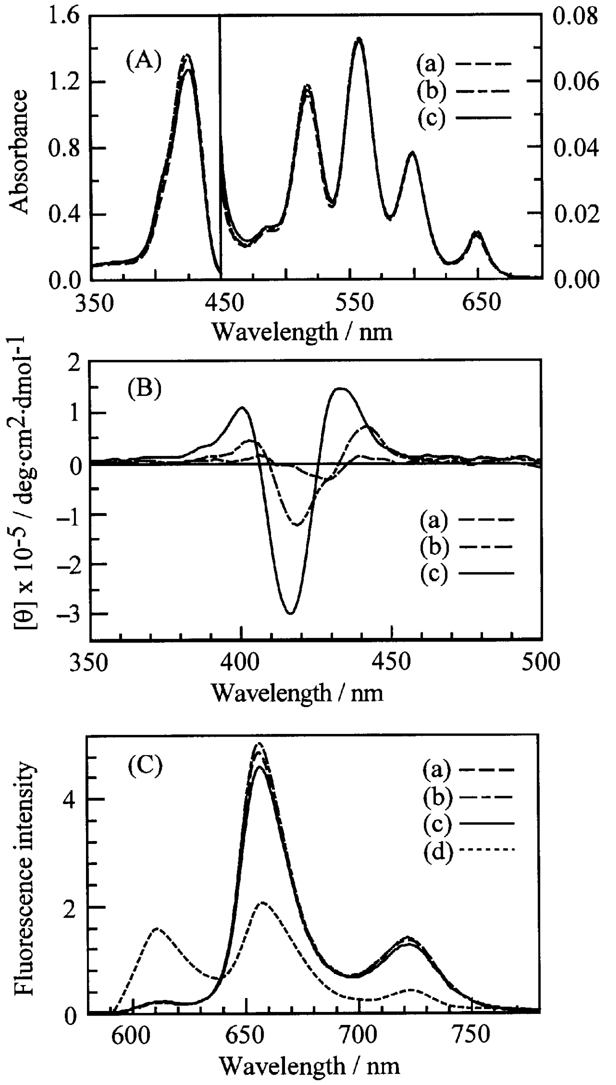

Figure 4. Spectroscopic properties of dendrimers **1a** (a), **1b** (b), **1c** (c), and 1:1 mixture of dendrimers with all H_2-porphyrins and dendrimers with all Zn(II)-porphyrins (d) in toluene/DMF (9/1, v/v). Concentrations of porphyrins : 5.6 x 10^{-6} mol·dm^{-3}. (A) UV-vis spectra. (B) CD spectra. (C) Fluorescence spectra. Excitation at 560 nm.

porphyrins, were analyzed by size-exclusion chromatography (TSKgel G3000HXL (7.8 × 300 mm) column, DMF) as shown in Figure 3. They were well separated by the difference in mean molecular weights. However, three dendrimers did not show the linear relationship between log MWs and retention times. The slow elution of **1a** may be caused by the interaction of porphyrin rings, which are more exposed at the surface, with the column.

The three dendritic poly(L-lysine)s **1a**, **1b**, and **1c** covered by different number of layers of L-lysine (0, 1, and 2, respectively) were characterized by UV-vis absorption, CD, and fluorescence spectra measurements. Though the environment of porphyrin moieties are different in the degree of exposure to solvent, the absorption spectra in toluene/DMF (9/1, v/v) of **1a**, **1b,** and **1c** were similar to each other (Figure 4A). The profile of Q bands suggested that the dendrimers contain H_2- and Zn(II)-porphyrins in almost 1:1 ratio. The CD spectra of these dendrimers in toluene/DMF (9/1, v/v) showed Cotton effect at the Soret band. The most covered compound **1c** showed the strongest CD ($[\theta]_{418}$ - $[\theta]_{435}$= 4.5 × 10^5 deg·cm^2·dmol^{-1}) for the Soret band as previously observed (Figure 4B).[1]

As shown in Figure 4C, obtained were almost same fluorescence spectra for **1a**, **1b,** and **1c** in toluene/DMF (9/1, v/v) upon the excitation at 560 nm of Zn(II)-porphyrin. The extra L-lysine layers seemed ineffective in the fluorescence incident. They showed extremely weak emission at 610 nm, which corresponds to Zn(II)-porphyrins. The quenching at 610 nm synchronized with the significant increase in fluorescence at 720 nm. The efficiency (85%) in energy transfer was estimated from the quenching of emission at 610 nm compared with that of the mixture of dendrimers combining all Zn(II)-porphyrins and all H_2-porphyrins (Figure 4C, line (d)). The average distance from Zn(II)-porphyrins to H_2-porphyrins in dendrimers of scramble fashion could be estimated as about 25 Å, if thirty-two porphyrins were scattered on the surface of a sphere with radius of about 40 Å. Considering the through-space-fluorescence-energy-transfer from Zn(II)-porphyrins to H_2-porphyrins beyond this long distance, the 85% energy transfer could be said rather efficient than expected. Actually, we observed only 43% energy transfer on the porphyrins in hemisphere fashion.[2] We further observed 50% energy transfer in Boc-Lys-(Por(Zn))-Lys[Boc-Lys(Por(H_2))]-$NHCH_3$, a reference compound of a set of Zn(II)-porphyrin and H_2-porphyrin with center-to-center distance of about 40 Å. This fact also suggests that there might be interactions between porphyrin rings in scramble fashion on the surface of the dendrimer.

Based on the results with the dendrimers in scramble fashion in the present study, further syntheses and analyses of dendrimers in bouquet and double strata fashions are in progress. Such strategy in designing the model system with efficient fluorescence energy transfer may open the way for a succeeding study of the light harvesting porphyrin dendrimers.

References and Notes

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7 Abbreviations used are as follows: Boc-Lys(Boc)-OH, di-*t*-butyloxycarbonyl-L-lysine; BOP, benzotriazol-1-yloxytris- (dimethylamino)phosphonium hexafluorophosphate; HOBt, 1-hydroxybenzotriazole; TFA, trifluoroacetic acid; DIEA, diisopropyl ethylamine; HATU, *O*-(7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate; Fmoc-, 9-fluorenylmethoxycarbonyl-.