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Intramolecular Energy Transfer in 1,3,5-Phenylene-Based Dendritic Porphyrins

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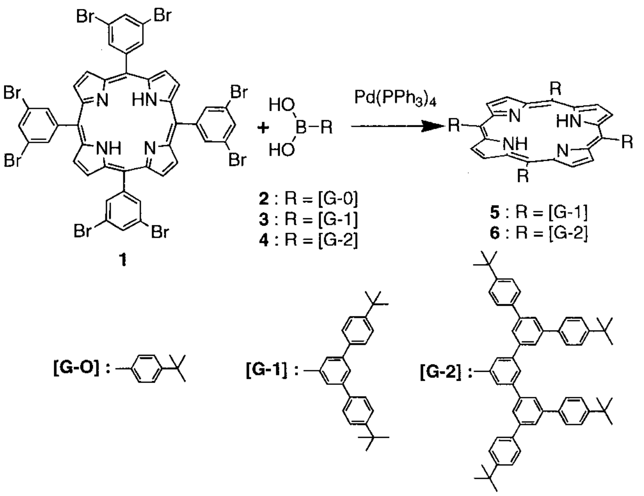
Dendrimers form highly symmetric layered molecules that adopt well-defined nanostructures.[1] There has been considerable interest in the incorporation of functional units on the exterior surface or in the interior of dendrimers.[2] Dendritic structures affect several functionalities through the control of the microenvironment around functional units. Dendritic porphyrins have exhibited interesting properties by the encapsulation of a porphyrin core in the interior of a dendritic structure.[3] The work on these dendritic porphyrins has focused on encapsulation in flexible dendron units; however, the effect of rigid dendron units as phenylene,[4] phenylacetylene,[5] and phenylenevinylene[6] dendron units on the porphyrin functionality has not been as extensively explored.[7] Recently, the dendritic structures have attracted increasing attention as synthetic light-harvesting antennas.[8] Moore et al. have reported a light-harvesting antenna by using rigid perylene-terminated phenylacetylene dendron units, and excitation energy was transferred efficiently through the phenylacetylene dendritic structure.[9] Jiang and Aida have investigated the efficient energy migration in the spherical dendritic porphyrins possessing flexible aryl ether dendrons.[10] Constructing a rigid dendrimer around a porphyrin core may result in interesting photochemical, electrochemical, and catalytic properties. We report here the synthesis, characterization, and photochemical behavior of 1,3,5-phenylene-based rigid dendritic porphyrins.

Scheme 1



A series of 1,3,5-phenylene-based dendritic porphyrins **5** and **6** were synthesized by using the methodology developed by Miller, Neenan, and co-workers (Scheme 1).[4a] The porphyrin core **1** was obtained from 3,5-dibromobenzaldehyde and pyrrole by the conventional method. The dendrons **2**−**4** were prepared stepwise through a Suzuki coupling reaction between arylboronic acid and 3,5-dibromo-1-(trimethylsilyl)benzene. Finally, the coupling of dendrons **2** or **3** to **1** using $Pd(PPh_3)_4$ as a catalyst proceeded smoothly to yield the dendritic porphyrins **5** and **6**. However, the third-generation porphyrin dendrimer could not be prepared from the coupling between **1** and **4**. The matrix-assisted laser desorption ionization time-of-flight mass spectrum (MALDI-TOF-Ms) of the resulting products indicated a mixture of defect structures by coupling 5 and 6 equiv of **4** to the porphyrin core **1**. As molecular weight increases, it becomes difficult to carry out a complete coupling reaction of a focal point of the dendron unit with the porphyrin core. The synthesized dendritic porphyrins **5** and **6** have been fully characterized by UV−vis, size-exclusion chromatography (SEC), MALDI-TOF-Ms spectroscopy, and ^1H and ^{13}C NMR (see Supporting Information). Examination of SEC showed that the observed molecular weight rises with each generation and that all products have sharp and symmetrical elution patterns with polydispersities (M_w/M_n) less than 1.02. MALDI-TOF-Ms spectra of dendrimers also confirmed their monodispersity and high purity. The first-generation **5** yields crystalline materials with a melting point at 287 °C as indicated by the DSC analysis. On the other hand, the second-generation **6** shows only a glass transition at 222 °C and no sign of crystallization up to 400 °C. This thermal behavior suggests that the second-generation **6**, possessing 28 benzene rings, is a glassy and amorphous material. Figure 1 shows ^1H NMR spectra of **5** and **6** in $CDCl_3$ at 25 °C, which provide the structural information. In the aliphatic region, a sharp singlet resonance corresponding to the *tert*-butyl protons is observed. This indicates that the peripheral *tert*-butyl groups interchange rapidly on the NMR time scale. Proton resonances in the aromatic region of **5** and **6** are distinguishable and assignable, as shown in Figure 1. Proton resonance of benzene units nearer the porphyrin core shifts downfield compared with that of the exterior benzene units, indicating the successive generation of a highly symmetric layered structure. Moreover, the pyrrole β proton signal of the porphyrin core also shifts downfield with the increase in generation number. As revealed by CPK models of the second-generation **6**, the dendritic porphyrin **6** represents a globular nanostructure with a diameter of ca. 3 nm as predicted from the CPK model.

UV−vis absorption spectra of **5** and **6** in CH_2Cl_2 are listed in Figure 2, and the absorption maxima (λ_{max}) and molar extinction coefficient (ϵ) are collected in Table 1. The absorption spectra are the sum of a porphyrin moiety and four 1,3,5-phenylene-based dendron units. The ϵ values of dendron units at 264 nm increased in proportion to the generation number. On the other hand, the Soret and Q-bands of the porphyrin moiety remained unaltered with the increase in generation number, suggesting that the electronic conditions of **5** and **6** are similar to each other. The dendritic porphyrins emitted fluorescence at 650 and 717 nm on excitation of the Soret band of the porphyrin core in degassed CH_2Cl_2 and exhibited nearly the same intensities in different generations. The phenylene-based dendron **4** emitted a strong fluorescence at 353 nm with excitation at 264 nm, as shown in Figure 3. When the dendritic

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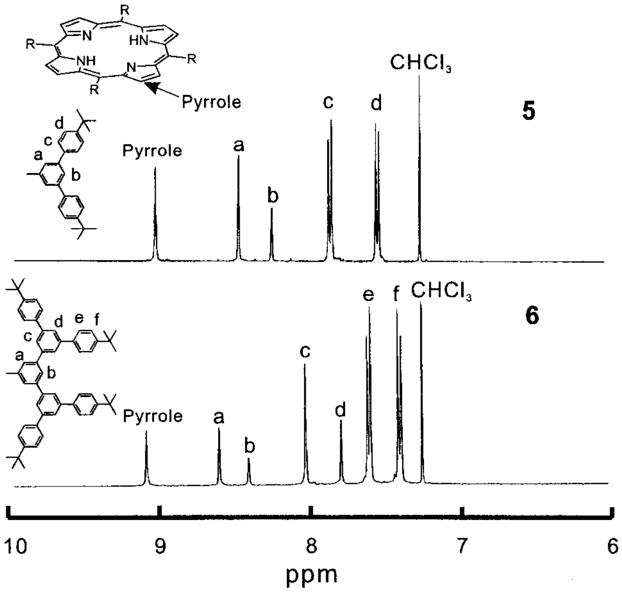

Figure 1. ^{1}H NMR spectra of dendritic porphyrins **5** and **6** in $CDCl_3$.

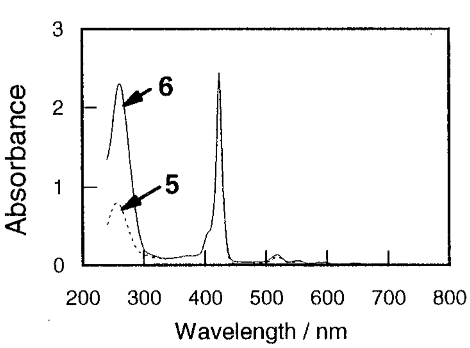

Figure 2. UV–vis absorption spectra of dendritic porphyrins **5** and **6** in CH_2Cl_2. The spectra are normalized to 5.0 μM concentration.

Table 1. Molecular Weight, Absorption, and Fluorescence Data for 5 and 6

dendrimer	mol wt		M_w/M_n[b]	diam (nm)[c]	λ_{max} (nm)[d] (log ϵ (M^{-1} cm^{-1}))	ϕ_{ET}[e]
	calcd	obsd[a]				
5	1671.0	1672	1.01	2.4	256 (520) 424 (5.69)	0.66
6	3335.9	3337	1.02	2.9	262 (5.66) 424 (5.68)	0.98

[a] Determined by MALDI-TOF-Ms. [b] Determined by SEC relative to the corresponding polystyrene standard. [c] Estimated by CCK models. [d] In CH_2Cl_2. [e] Quantum yield of energy transfer (ϕ_{ET}) in dendritic porphyrins estimated by comparing the absorption spectrum and excitation spectrum by monitoring the emission of the porphyrin moiety in CH_2Cl_2 at 25 °C.

porphyrins **6** were excited at 262 nm, where the 1,3,5-phenylene dendron units absorb, the emission was mostly from the porphyrin core, and the residual fluorescence from the dendron units was very weak. A mixture of **1** and **4** indicated no emission peaks from the porphyrin moiety with excitation at 262 nm. This result indicates the efficient intramolecular energy transfer from the phenylene-based dendron units to the porphyrin core within the dendrimer. The efficiency of energy transfer (ϕ_{ET}) can be estimated by comparing the UV–vis spectrum and excitation spectrum of the dendron units.[9,10] The ϕ_{ET} values in **5** and **6** were estimated to be 66 and 98%, respectively. Despite the large difference in the number of benzene units, the ϕ_{ET} value in **6** is very high compared to the previously reported value observed in the aryl ether dendritic porphyrin.[10] The high efficiency of energy transfer from phenylene-based dendron units to the porphyrin core can be ascribed to the efficient energy flow through the cross-conjugation of 1,3,5-phenylene dendron units as well as a larger overlap between the emission of the dendron units and the absorption of the porphyrin core.

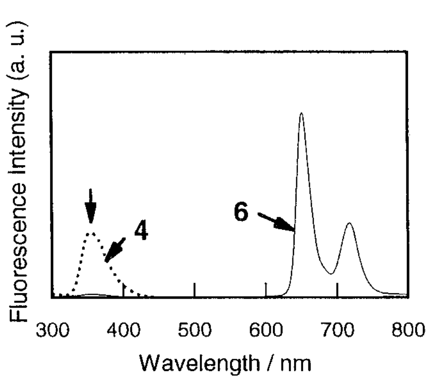

Figure 3. Steady-state fluorescence spectra of the dendritic porphyrin **6** and the dendritic ligand **4** in CH_2Cl_2. The excitation wavelength is 262 nm. All the spectra are normalized to a constant absorbance at the excitation wavelength.

We have synthesized and characterized novel rigid dendritic porphyrins **5** and **6**, in which the photoactive porphyrin core was encapsulated within the 1,3,5-phenylene-based dendron units. The energy transfer from the dendron units to the porphyrin core occurred with high efficiency due to their unique structures. Work on the further functionalities of catalytic and selective ligand-binding properties is in progress.

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Supporting Information Available: Synthesis and characterization of dendritic porphyrins **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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