Porphyrid-Cored Arylether Dendrimers with Vinyl Groups in the Periphery

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Benzyl arylether dendrimers with zinc porphyrin core and terminal vinyl groups have been synthesized and their photophysical properties and the influence of dendritic environments were investigated. Free base porphyrin-cored benzyl arylether dendrimers 1a-1c and 3a-3c, and their zinc derivatives 2a-2c and 4a-4c have been prepared. Absorption spectra are similar for all porphyrin-cored benzyl arylether dendrimers, except that absorption intensity at 280 nm increases in the higher generation of dendrimer. Fluorescence spectra are similar with two bands for all free base porphyrin dendrimers 1a-1c and 3a-3c, although fluorescence intensity ratio of shorter wavelength emission band to longer wavelength band varies with the generation of dendrimer. Emission efficiencies of 1a-1c and 3a-3c are lower than that of TTP. Emission efficiencies of 2a-2c and 4a-4c are higher than that of ZnTTP. Absorption and emission properties of 1a-1c, 2a-2c, 3a-3c, and 4a-4c were affected negligibly with dendritic environments.

Key Words: Arylether dendrimer, Porphyrin, Absorption spectra, Fluorescence spectra

Introduction

Natural photosynthesis converts light energy into chemical energy and its mimicry leads to design and development of a variety of artificial photosynthetic systems and optoelectronic devices such as solar cells.5-7 Porphyrin in plants and photosynthetic bacteria plays a key role in the efficient capture of light energy and photoinduced electron transfer to reaction center.1,5 A number of systems containing porphyrin moiety has been designed and prepared for molecular energy storage devices, artificial light-harvesting antenna, and long-range electron transfer systems. Optimum fabrication of covalently and noncovalently linked array composed of donor and acceptor units requires the efficient solar energy capture, efficient electron transfer, and inefficient back electron transfer. Dendrimers are the nano-sized material of current interest because of their structural uniqueness and a variety of potential applications for functional molecular devices.8 Dendritic architecture allows feasible molecular design and well-defined structure, in which the position of porphyrin and other functional groups is precisely controlled. Various porphyrin-functionalized dendrimers9 have been studied for numerous applications such as artificial photosynthesis,8,9-19 optoelectronic device,20-23 host-guest chemistry,24-26 medical application,27-29 and catalyst.30-35

It was known that treatment of the allyl end groups of dendrimer with Grubbs' Ru catalyst could afford the intramolecular polymerized product, through a ring-closing metathesis.55 For porphyrin-core dendrimer with many homocallyl end-groups. Zimmerman et al.55 reported that peripheral allyl groups are cross-linked by the treatment with Grubbs' Ru catalyst and the intramolecular-polymerized product was generated in the form of caged porphyrin, which is a precursor of synthetic host by molecular imprinting inside dendrimer. However, dendritic zinc porphyrins containing multiple terminal allyl groups in the dendrimer periphery56 have been scarcely reported, although it could not only locate multiple functional groups into the outmost dendritic layer by modification of terminal allyl groups, but also play a role as synthetic host through the intramolecular cross-linking and subsequent removal of porphyrin core.

In this study, various arylether dendrimers with porphyrin core and terminal vinyl groups have been synthesized and their photophysical properties and the influence of dendritic environments were investigated.

Experimental Section

Spectroscopic measurements. 1H NMR spectra were measured on a 400 MHz Bruker Advance 400 NMR spectrometer in chloroform-d6. MALDI-TOF Mass spectra were measured on Applied Biosystem Voyager-DE STR System 4407 Mass Spectrometer using 2,5-dihydroxybenzoic acid in a matrix. Absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Steady-state fluorescence spectra were recorded on a SLM-Amicon AB2 luminescence spectrophotometer. The concentrations were controlled so that the absorbances of the solutions at the excitation wavelength of 515 nm (for free base porphyrin derivatives) or 550 nm (for zinc porphyrin derivatives) have the value of 0.07-0.08, to avoid inner filter effects. Fluorescence quantum yields Φ1 were determined using 5.10.15,20-tetrakis(4-methylphenyl)porphyrin (TTP) as a standard (Φ1 = 0.69 in CH3Cl) or zinc 5,10,15,20-tetrakis(4-methylphenyl)porphyrin (ZnP) as a standard (Φ1 = 0.031 in CH3Cl).11,32

Materials and synthesis. The following materials were purchased from the indicated suppliers and used as received: Terakis(4-carboxyphenyl)porphyrin was purchased from TCI. 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin33 and Gn-OH43,45 (n = 1-3) were prepared as described in the literature. 1-{3-(Dimethylamino)propyl}-3-ethylcarbodiimide
ly-dichloride (EDC), 4-dimethylamino-pyridine (DMAP),
dimethylformamide were purchased from Aldrich. 
Silica gel 60 (230-400 mesh. Merck) and silica gel 60 F254(Merck 
25) were used for silica gel column chromatography. Methyl-
ene chloride, methanol, chloroform, and ethyl acetate were 
purchased from DAE JUNG Chemical Co. and solvents 
were dried and distilled by general purification methods.

**General procedure for the preparation of 1a-c, 5-(4-
Carboxyphenyl)-10,15,20-triphenylporphyrin (1.0 equiv.) 
was dissolved in CHCl3/DMF (1:1) and then Gn-OH (4.9 
equiv.). EDC (5.6 equiv.) and DMAP (5.6 equiv.) were 
added successively. The reaction mixture was stirred at room 
temperature. The solvents were removed in vacuo and then 
CHCl3 and H2O were added to the resulting residue. 
The CHCl3-later was separated and successively washed with 
aqueous saturated NaCl solution and aqueous saturated 
NaHCO3 solution. The CHCl3-later was dried with anhy-
drous MgSO4 and concentrated under reduced pressure and 
the resulting residue was purified by preparative TLC using 
33% ethyl acetate-hexane as the eluent to give 1a-1c.

For example, in the case of synthesis of 1a, 5-(4-carboxy-
phenyl)-10,15,20-triphenylporphyrin (80 mg, 0.11 mmol) 
was dissolved in 10 mL of CHCl3/DMF (1:1) and then 
Gn-0H (0.14 g, 0.56 mmol), EDC (0.12 g, 0.62 mmol) and 
DMAP (76 mg, 0.62 mmol) were added successively. The 
reaction mixture was stirred at room temperature for 24 
hours. The solvents were removed in vacuo and then CHCl3 
(20 mL) and H2O (20 mL) were added to the resulting 
residue. The next steps were accomplished according to 
the procedure described above.

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(20 mL) and H2O (20 mL) were added to the resulting 
residue. The next steps were accomplished according to 
the procedure described above.

**General procedure for the preparation of 2a-2c. 1a-c 
were dissolved in MeOH/CH2Cl2 (1:4) and then 
Zn(OAc)2 (4.0 equiv.) was added. The reaction mixture was 
removed at room temperature. The solvents were removed in 
vacuo and the resulting residue was purified by preparative 
TLC using 33% ethyl acetate-hexane as the eluent to give 2a-2c.

For example, in the case of synthesis of 2a, 1a (14 mg, 15 
mmol) was dissolved in 3 mL of MeOH/CH2Cl2 (1:4) and then 
Zn(OAc)2 (11 mg, 60 mmol) was added. The reaction 
mixture was stirred at room temperature for 40 min.

**General procedure for the preparation of 3a-3c. 3a-
OH (4.9 equiv.) was dissolved in DMF and then EDC (5.6 
equiv.). DMAP (5.6 equiv.), and trisakis(4-carboxyphenyl)- 
porphyrin (1.0 equiv.) were added successively. The reaction 
mixture was stirred at room temperature in the dark. The 
solvent was removed in vacuo and then CH2Cl2 and 
H2O were added to the resulting residue. The CH2Cl2-later 
was separated and successively washed 3 times with H2O. The 
CH2Cl2-later was dried with MgSO4 and concentrated under 
reduced pressure and the resulting residue was purified by

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silica gel column chromatography using 5% ethyl acetate-chloroform as the eluent and then further purified by preparative TLC using 2% methanol-chloroform as the eluent to give 3a–3c.

For example, in the case of synthesis of 3a. G1-OH (0.11 g, 0.43 mmol) was dissolved in 5 mL of DMF and then EDC (95 mg, 0.50 mmol), DMAP (61 mg, 0.50 mmol), and terakis[4-carboxyphenyl]porphyrin (70 mg, 89 imol) were added successively. The reaction mixture was stirred at room temperature for 2 days in the dark. 3a: 66 mg (44% yield); 1H NMR (400 MHz, 

Results and Discussion

The porphyrin-incorporated arylether dendrimers are expected to act as light-harvesting antenna for energy transfer, as a number of peripheral C–C double bonds could be easily modified with various energy donors or acceptors. Benzyl arylether dendrimers with 3,5-bis(but-3-enyloxy)phenyl groups in the periphery and porphyrin in the core1a–1c and 3a–3c, and zinc porphyrin in the core 2a–2c and 4a–4c were prepared (Figure 1). Their photophysical properties and the influence of dendritic environments were investigated.

Absorption and fluorescence spectra of free base porphyrin-cored benzyl arylether dendrimers 1a–1c and 3a–3c, and their zinc derivatives 2a–2c and 4a–4c with porphyrin or zinc porphyrin in the core and 3,5-bis(but-3-enyloxy)phenyl groups in the periphery were measured in dichloromethane and the data are summarized in Table 1. Absorption and fluorescence (λex = 515 nm) spectra of free base porphyrin-cored arylether dendrimers 1a–1c and 3a–3c were shown in Figure 2 in comparison with those of 5,10,15,20-tetrakis(4-methylphenyl)porphyrin (TTP) and similar to one another, except 280 nm band.

Absorption bands of 280 nm, 418 nm, 514–648 nm are due to dendron groups. Soret and Q absorption of porphyrin moieties, respectively. Absorption intensity at 280 nm increases in the higher generation of dendrimers. Fluorescence spectra
Reagents and conditions: (a) CH3Cl2, DMF, rt, EDC, DMAP; (b) CH3Cl2, CH3OH, rt, Zn(OAc)2.

Figure 1. Synthesis of arellether dendrimers 1a-1c, 2a-2c, 3a-3c, and 4a-4c with porphyrin or zinc porphyrin in the core and 3,5-bis(but-3-enoxy)phenyl groups in the periphery.

are similar with two bands at around 652 and 718 nm for all free base porphyrin-cored arellether dendrimers 1a-1c and 3a-3c. Although fluorescence intensity ratio of 652 nm to 718 nm is different with one another and smaller than for TTP. Fluorescence quantum yields of 1a-1c and 3a-3c are similar irrespective of dendrimer generation and are lower than that of TTP. Under the dendritic environments, emission efficiencies of porphyrin decreases.

Absorption and fluorescence (λex = 550 nm) spectra of zinc porphyrin-cored arellether dendrimers 2a-2c and 4a-4c were shown in Figure 3 in comparison with those of zinc 5,10,15,20-tetrakis(4-methylphenyl)porphyrin (ZnTTP) and similar to one another except the 280 nm band and remarkable red shift in 4c. Absorption intensity at 280 nm increases in the higher generation of dendrimer. Absorption bands of 280 nm, 420 nm, 547-592 nm are due to dendron groups, Soret and Q absorption of zinc porphyrin moiety, respectively. Fluorescence spectra are similar with two bands at around

<table>
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<th>λem (nm)</th>
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<tr>
<td>ZnTTP</td>
<td>420, 548, 586</td>
<td>596, 646</td>
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596 and 646 nm for all zinc porphyrin-cored arylether dendrimers 2a-2c and 4a-4c, except the distinct red shift in 4e. For fluorescence spectra of 2a-2c, band intensity at 596 nm is lower than ZnTTP and band intensity at 646 nm is higher than ZnTTP. For 4a and 4b, fluorescence intensities at both 596 nm and 646 nm are higher than ZnTTP. Fluorescence intensity of 4c is much higher than ZnTTP at 602 nm, but only a little higher than ZnTTP at 650 nm. Fluorescence quantum yields of 2a-2c and 4a-4c are slightly higher than that of ZnTTP and fluorescence intensity ratio of 596 nm to 646 nm differs from one another with generation of dendrimer. Under the dendritic environments, emission efficiencies of zinc porphyrin increases slightly.

However, with increase of the generation of dendron, absorption and fluorescence of porphyrin-cored dendrimers do not significantly change within the experimental error. For example, fluorescence quantum yields of 3a, 3b, and 3c lie in the range of 0.071-0.077 and those of of 4a, 4b, and 4c lie in the range of 0.039-0.042. In other words, absorption and emission properties were affected negligibly with dendritic environments.

Further studies with zinc porphyrin-cored arylether dendrimer 4e such as the introduction of functional moieties through terminal vinyl groups, the formation of caged zinc porphyrin by intramolecular polymerization of terminal allyl groups with Grubbs' Ru catalyst, and noncovalent interaction with electron acceptors are under investigation.

In summary, arylether dendrimers with multiple vinyl groups in the periphery, and porphyrin or zinc porphyrin in the core 1a-1c, 2a-2c, 3a-3c, and 4a-4c were prepared and their photophysical properties and the influence of dendritic environments were investigated. Absorption spectra are similar for all porphyrin-cored arylether dendrimers, except that absorption intensity at 280 nm increases in the higher generation of dendrimer. Fluorescence spectra are similar with two bands for all porphyrin-cored arylether dendrimers, although fluorescence intensity ratio of shorter wavelength emission band to longer wavelength band varies with the generation of dendrimer. Fluorescence quantum yields of free-base porphyrin dendrimers 1a-1c and 3a-3c are lower than that of TTP. Under the dendritic environments, emission efficiencies of zinc porphyrin dendrimers 2a-2c and 4a-4c are slightly higher than that of ZnTTP. However, absorption and emission properties were affected negligibly with dendritic environments.

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