Porphyrin-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.[1-5] 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.[6] 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 dendrimers[7] have been studied for numerous applications such as artificial photosynthesis,[8-19] optoelectronic device,[20-23] host-guest chemistry,[24-26] medical application,[27,28] and catalyst.[29]

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.[30] For porphyrin-core dendrimer with many homoallyl end-groups, Zimmerman *et al.*[26] 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 periphery[26] 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. ^{1}H NMR spectra were measured on a 400 MHz Bruker Avance 400 NMR spectrometer in chloroform-d_1. MALDI-TOF Mass spectra were measured on Applied Biosystem Voyager-DE' STR System 4407 Mass Spectrometer using 2,5-dihydroxybenzoic acid in THF as a matrix. Absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Steady-state fluorescence spectra were recorded on a SLM-Aminco 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 Φ_f were determined using 5,10,15,20-tetrakis(4-methylphenyl)porphyrin (TTP) as a standard (Φ_f = 0.09 in CH_2Cl_2) or zinc 5,10,15,20-tetrakis(4-methylphenyl)porphyrin (ZnTTP) as a standard (Φ_f = 0.031 in CH_2Cl_2).[31,32]

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-triphenylporphyrin[33] and Gn-OH[34,35] (n = 1-3) were prepared as described in the literature. 1-{3-(Dimethylamino)propyl}-3-ethylcarbodiimide hydrochloride (EDC), 4-dimethylamino-pyridine (DMAP), and dimethylformamide were purchased from Aldrich. Silica gel 60 (230-400 mesh, Merck) and silica gel 60 F_{254} (Merck 25) were used for silica gel column chromatography. Methylene 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-1c. 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin (1.0 equiv.) was dissolved in CH_2Cl_2/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 CH_2Cl_2 and H_2O were added to the resulting residue. The CH_2Cl_2 layer was separated and successively washed with aqueous saturated NaCl solution and aqueous saturated $NaHCO_3$ solution The CH_2Cl_2 layer was dried with anhydrous $MgSO_4$ 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-carboxyphenyl)-10,15,20-triphenylporphyrin (80 mg, 0.11 mmol) was dissolved in 10 mL of CH_2Cl_2/DMF (1:1) and then G1-OH (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 CH_2Cl_2 (20 mL) and H_2O (20 mL) were added to the resulting residue. The next steps were accomplished according to the procedure described above.

1a: 40 mg (40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78-8.87 (m, 8H, pyrrole), 8.45 (d, 2H, J = 8.2 Hz, Por-$\underline{Ar}$-CO_2-), 8.31 (d, 2H, J = 8.2 Hz, Por-$\underline{Ar}$-CO_2-), 8.20-8.22 (m, 6H, Por-$\underline{\mathrm{phenyl}}$), 7.73-7.81 (m, 9H, Por-$\underline{\mathrm{phenyl}}$), 6.73 (d, 2H, J = 2.2 Hz, dendron-$\underline{Ar}$-), 6.50 (t, 1H, J = 2.2 Hz, dendron-$\underline{Ar}$-) 5.88-5.94 (m, 2H, $-O-CH_2-CH_2-C\underline{H}=CH_2$), 5.47 (s, 2H, $-CO_2-C\underline{H_2}-Ar-$), 5.17-5.22 (m, 4H, $-O-CH_2-CH_2-CH=C\underline{H_2}$), 4.07 (t, 4H, J = 6.7 Hz, $-O-C\underline{H_2}-CH_2-CH=CH_2$), 2.52-2.59 (m, 4H, $-O-CH_2-C\underline{H_2}-CH=CH_2$), −2.92 (s, 2H, N$\underline{H}$) ppm; MALDI-TOF MS m/z 931.08 (M^+) (Calculated for $C_{63}H_{54}N_4O_4$: 930.41).

1b: Yield = 44%; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.78-8.86 (m, 8H, pyrrole), 8.45 (d, 2H, J = 8.2 Hz, Por-$\underline{Ar}$-CO_2-), 8.31 (d, 2H, J = 8.2 Hz, Por-$\underline{Ar}$-CO_2-), 8.20-8.22 (m, 6H, Por-$\underline{\mathrm{phenyl}}$), 7.73-7.79 (m, 9H, Por-$\underline{\mathrm{phenyl}}$), 6.41-6.82 (m, 9H, dendron-$\underline{Ar}$-), 5.86-5.90 (m, 4H, $-O-CH_2-CH_2-C\underline{H}=CH_2$), 5.47 (s, 2H, $-CO_2-C\underline{H_2}-Ar-$), 5.05-5.19 (m, 8H, $-O-CH_2-CH_2-CH=C\underline{H_2}$), 5.03 (s, 4H, $-Ar-O-C\underline{H_2}-Ar-$), 4.0 (t, 8H, J = 6.7 Hz, $-O-C\underline{H_2}-CH_2-CH=CH_2$), 2.48-2.54 (m, 8H, $-O-CH_2-C\underline{H_2}-CH=CH_2$), −2.78 (s, 2H, N$\underline{H}$) ppm; MALDI-TOF MS m/z 1282.73 (M^+) (Calculated for $C_{85}H_{78}N_4O_8$: 1282.58).

1c: Yield = 14%; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.77-8.84 (m, 8H, pyrrole), 8.46 (d, 2H, J = 8.0 Hz, Por-$\underline{Ar}$-CO_2-), 8.29 (d, 2H, J = 8.0 Hz, Por-$\underline{Ar}$-CO_2-), 8.20-8.22 (m, 6H, Por-$\underline{\mathrm{phenyl}}$), 7.73-7.78 (m, 9H, Por-$\underline{\mathrm{phenyl}}$), 6.37-6.85 (m, 21H, dendron-$\underline{Ar}$-), 5.80-5.89 (m, 8H, $-O-CH_2-CH_2-C\underline{H}=CH_2$), 5.48 (s, 2H, $-CO_2-C\underline{H_2}-Ar-$), 5.06-5.18 (m, 16H, $-O-CH_2-CH_2-CH=C\underline{H_2}$), 5.03 (s, 4H, $-Ar-O-C\underline{H_2}-Ar-$), 4.91 (s, 8H, $-Ar-O-C\underline{H_2}-Ar-$), 3.99 (t, 16H, J = 6.7 Hz, $-O-C\underline{H_2}-CH_2-CH=CH_2$), 2.44-2.53 (m, 16H, $-O-CH_2-C\underline{H_2}-CH=CH_2$), -2.79 (s, 2H, N$\underline{H}$) ppm; MALDI-TOF MS m/z 1987.23 (M^-) (Calculated for $C_{129}H_{126}N_4O_{16}$: 1986.92).

General procedure for the preparation of 2a-2c. 1a-c (1.0 equiv.) was dissolved in MeOH/CH_2Cl_2 (1:4) and then $Zn(OAc)_2$ (4.0 equiv.) was added. The reaction mixture was stirred 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 μmol) was dissolved in 3 mL of MeOH/CH_2Cl_2 (1:4) and then $Zn(OAc)_2$ (11 mg, 60 μmol) was added. The reaction mixture was stirred at room temperature for 40 min.

2a; 12 mg (80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88-8.95 (m, 8H, pyrrole), 8.45 (d, 2H, J = 7.5 Hz, Por-$\underline{Ar}$-CO_2-), 8.30 (d, 2H, J = 7.5 Hz, Por-$\underline{Ar}$-CO_2-), 8.21 (d, 6H, J = 5.9 Hz, Por-$\underline{\mathrm{phenyl}}$), 7.75 (d, 9H, J = 5.9 Hz, Por-$\underline{\mathrm{phenyl}}$), 6.72 (d, 2H, J = 2.2 Hz, dendron-$\underline{Ar}$-), 6.48 (t, 1H, J = 2.2 Hz, dendron-$\underline{Ar}$-) 5.87-5.97 (m, 2H, $-O-CH_2-CH_2-C\underline{H}=CH_2$), 5.44 (s, 2H, $-CO_2-C\underline{H_2}-Ar-$), 5.11-5.21 (m, 4H, $-O-CH_2-CH_2-CH=C\underline{H_2}$), 4.06 (t, 4H, J = 6.6 Hz, $-O-C\underline{H_2}-CH_2-CH=CH_2$), 2.54-2.60 (m, 4H, $-O-CH_2-C\underline{H_2}-CH=CH_2$) ppm; MALDI-TOF MS m/z 992.62 (M^-) (Calculated for $C_{63}H_{52}N_4O_4Zn$: 992.33).

2b: Yield = 31%; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.82-8.95 (m, 8H, pyrrole), 8.44 (d, 2H, J = 7.8 Hz, Por-$\underline{Ar}$-CO_2-), 8.30 (d, 2H, J = 7.8 Hz, Por-$\underline{Ar}$-CO_2-), 8.21 (d, 6H, J = 6.4 Hz, Por-$\underline{\mathrm{phenyl}}$), 7.75-7.78 (m, 9H, Por-$\underline{\mathrm{phenyl}}$), 6.41-6.82 (m, 9H, dendron-$\underline{Ar}$-), 5.81-5.91 (m, 4H, $-O-CH_2-CH_2-C\underline{H}=CH_2$), 5.47 (s, 2H, $-CO_2-C\underline{H_2}-Ar-$), 5.04-5.15 (m, 8H, $-O-CH_2-CH_2-CH=C\underline{H_2}$), 5.02 (s, 4H, $-Ar-O-C\underline{H_2}-Ar-$), 4.0 (t, 8H, J = 6.7 Hz, $-O-C\underline{H_2}-CH_2-CH=CH_2$), 2.47-2.53 (m, 8H, $-O-CH_2-C\underline{H_2}-CH=CH_2$) ppm; MALDI-TOF MS m/z 1344.93 (M^-) (Calculated for $C_{85}H_{76}N_4O_8Zn$: 1344.50).

2c: Yield = 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.82-8.95 (m, 8H, pyrrole), 8.38 (d, 2H, J = 8.1 Hz, Por-$\underline{Ar}$-CO_2-), 8.27 (d, 2H, J = 8.1 Hz, Por-$\underline{Ar}$-CO_2-), 8.20-8.26 (m, 6H, Por-$\underline{\mathrm{phenyl}}$), 7.74-7.77 (m, 9H, Por-$\underline{\mathrm{phenyl}}$), 6.41-6.80 (m, 21H, dendron-$\underline{Ar}$-), 5.73-5.83 (m, 8H, $-O-CH_2-CH_2-C\underline{H}=CH_2$), 5.46 (s, 2H, $-CO_2-C\underline{H_2}-Ar-$), 5.01-5.10 (m, 20H, $-Ar-O-C\underline{H_2}-Ar-$ & $-O-CH_2-CH_2-CH=C\underline{H_2}$), 4.91 (s, 8H, $-Ar-O-C\underline{H_2}-Ar-$), 3.79 (t, 16H, J = 6.7 Hz, $-O-C\underline{H_2}-CH_2-CH=CH_2$), 2.35-2.40 (m, 16H, $-O-CH_2-C\underline{H_2}-CH=CH_2$) ppm; MALDI-TOF MS m/z 2048.95 (M^+) (Calculated for $C_{129}H_{124}N_4O_{16}Zn$: 2048.83).

General procedure for the preparation of 3a-3c. Gn-OH (4.9 equiv.) was dissolved in DMF and then EDC (5.6 equiv.), DMAP (5.6 equiv.), and terakis(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 CH_2Cl_2 and H_2O were added to the resulting residue. The CH_2Cl_2 layer was separated and successively washed 3 times with H_2O The CH_2Cl_2 layer was dried with $MgSO_4$ and concentrated under reduced pressure and the resulting residue was purified by 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); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.81 (s, 8H, pyrrole), 8.47 (d, 8H, J = 8.3 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 8.29 (d, 8H, J = 8.3 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 6.73 (d, 8H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.50 (t, 4H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-) 5.88-5.96 (m, 8H, -O-CH$_2$-CH$_2$-C$\underline{\mathrm{H}}$ =CH$_2$), 5.47 (s, 8H, -CO$_2$-C$\underline{\mathrm{H}_2}$-Ar-), 5.11-5.22 (m, 16H, -O-CH$_2$-CH$_2$-CH=C$\underline{\mathrm{H}_2}$), 4.07 (t, 16H, J = 6.7 Hz, -O-C$\underline{\mathrm{H}_2}$-CH$_2$-CH=CH$_2$), 2.55-2.60 (m, 16H, -O-CH$_2$- C$\underline{\mathrm{H}_2}$-CH=CH$_2$), −2.82 (s, 2H, N$\underline{\mathrm{H}}$) ppm; MALDI-TOF MS m/z 1710.66 (M$^-$) (Calculated for $C_{108}H_{102}N_4O_{16}$: 1710.74).

3b: Yield = 19%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.83 (s, 8H, pyrrole), 8.47 (d, 8H, J = 8.3 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 8.30 (d, 8H, J = 8.3 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 6.82 (d, 8H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.64 (t, 4H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.61 (d, 16H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.42 (t, 8H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 5.81-5.91 (m, 16H, -O-CH$_2$-CH$_2$-C$\underline{\mathrm{H}}$=CH$_2$), 5.48 (s, 8H, -CO$_2$-C$\underline{\mathrm{H}_2}$-Ar-), 5.04-5.15 (m, 32H, -O-CH$_2$-CH$_2$-CH=C$\underline{\mathrm{H}_2}$), 5.03 (s, 16H, -Ar-O-C$\underline{\mathrm{H}_2}$-Ar-), 4.0 (t, 32H, J = 6.7 Hz, -O-C$\underline{\mathrm{H}_2}$-CH$_2$-CH=CH$_2$), 2.48-2.53 (m, 32H, -O-CH$_2$-C$\underline{\mathrm{H}_2}$-CH=CH$_2$), −2.80 (s, 2H, N$\underline{\mathrm{H}}$) ppm; MALDI-TOF MS m/z 3119.56 (M$^-$) (Calculated for $C_{196}H_{198}N_4O_{32}$: 3119.40).

3c: Yield = 17%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.79 (s, 8H, pyrrole), 8.45 (d, 8H, J = 8.2 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 8.27 (d, 8H, J = 8.2 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 6.82-6.35 (m, 84H, dendron-$\underline{\mathrm{Ar}}$-), 5.77-5.88 (m, 32H, -O-CH$_2$-CH$_2$-C$\underline{\mathrm{H}}$=CH$_2$), 5.47 (s, 8H, -CO$_2$-C$\underline{\mathrm{H}_2}$-Ar-), 5.04-5.15 (m, 64H, -O-CH$_2$-CH$_2$-CH=C$\underline{\mathrm{H}_2}$), 5.03 (s, 16H, -Ar-O-C$\underline{\mathrm{H}_2}$-Ar-), 4.93 (s, 32H, -Ar-O-C$\underline{\mathrm{H}_2}$-Ar-), 3.93 (t, 64H, J = 6.7 Hz, -O-C$\underline{\mathrm{H}_2}$-CH$_2$-CH=CH$_2$), 2.43-2.48 (m, 64H, -O-CH$_2$-C$\underline{\mathrm{H}_2}$-CH=CH$_2$), −2.83 (s, 2H, N$\underline{\mathrm{H}}$) ppm; MALDI-TOF MS m/z 5936.65 (M$^-$) (Calculated for $C_{372}H_{390}N_4O_{64}$: 5936.74).

General procedure for the preparation of 4a-4c. 3a-c (1.0 equiv.) was dissolved in MeOH/CH$_2$Cl$_2$ (1:4) and then Zn(OAc)$_2$ (4.0 equiv.) was added at room temperature. The reaction mixture was stirred 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 **4a-4c**.

For example, in the case of synthesis of **4a**, **3a** (22 mg, 13 μmol) was dissolved in 3 mL of MeOH/CH$_2$Cl$_2$ (1:4) and then Zn(OAc)$_2$ (9 mg, 51 μmol) was added. The reaction mixture was stirred at room temperature for 40 min.

4a: 9 mg (39 % yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.91 (s, 8H, pyrrole), 8.45 (d, 8H, J = 8.1 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 8.29 (d, 8H, J = 8.1 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 6.71 (d, 8H, J = 2.1 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.47(t, 4H, J = 2.1 Hz, dendron-$\underline{\mathrm{Ar}}$-) 5.87-5.97 (m, 8H, -O-CH$_2$-CH$_2$-C$\underline{\mathrm{H}}$ =CH$_2$), 5.44 (s, 8H, -CO$_2$-C$\underline{\mathrm{H}_2}$-Ar-), 5.10-5.21 (m, 16H, -O-CH$_2$-CH$_2$-CH=C$\underline{\mathrm{H}_2}$), 4.06 (t, 16H, J = 6.7 Hz, -O-C$\underline{\mathrm{H}_2}$-CH$_2$-CH=CH$_2$), 2.54-2.59 (m, 16H, -O-CH$_2$- C$\underline{\mathrm{H}_2}$-CH=CH$_2$) ppm; MALDI-TOF MS m/z 1772.51 (M$^+$) (Calculated for $C_{108}H_{100}N_4O_{16}Zn$: 1772.64).

4b: Yield = 80%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.91 (s, 8H, pyrrole), 8.45 (d, 8H, J = 8.2 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 8.30 (d, 8H, J = 8.2 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 6.81 (d, 8H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.62 (t, 4H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.59 (d, 16H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.41 (t, 8H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 5.80-5.90 (m, 16H, -O-CH$_2$-CH$_2$-C$\underline{\mathrm{H}}$=CH$_2$), 5.46 (s, 8H, -CO$_2$-C$\underline{\mathrm{H}_2}$-Ar-), 5.03-5.14 (m, 48H, -O-CH$_2$-CH$_2$-CH=C$\underline{\mathrm{H}_2}$), 5.02 (s, 16H, -Ar-O-C$\underline{\mathrm{H}_2}$-Ar-), 3.99 (t, 32H, J = 6.7 Hz, -O-C$\underline{\mathrm{H}_2}$-CH$_2$-CH=CH$_2$), 2.47-2.52 (m, 32H, -O-CH$_2$-C$\underline{\mathrm{H}_2}$-CH=CH$_2$) ppm; MALDI-TOF MS m/z 3181.60 (M$^-$) (Calculated for $C_{196}H_{196}N_4O_{32}Zn$: 3181.31).

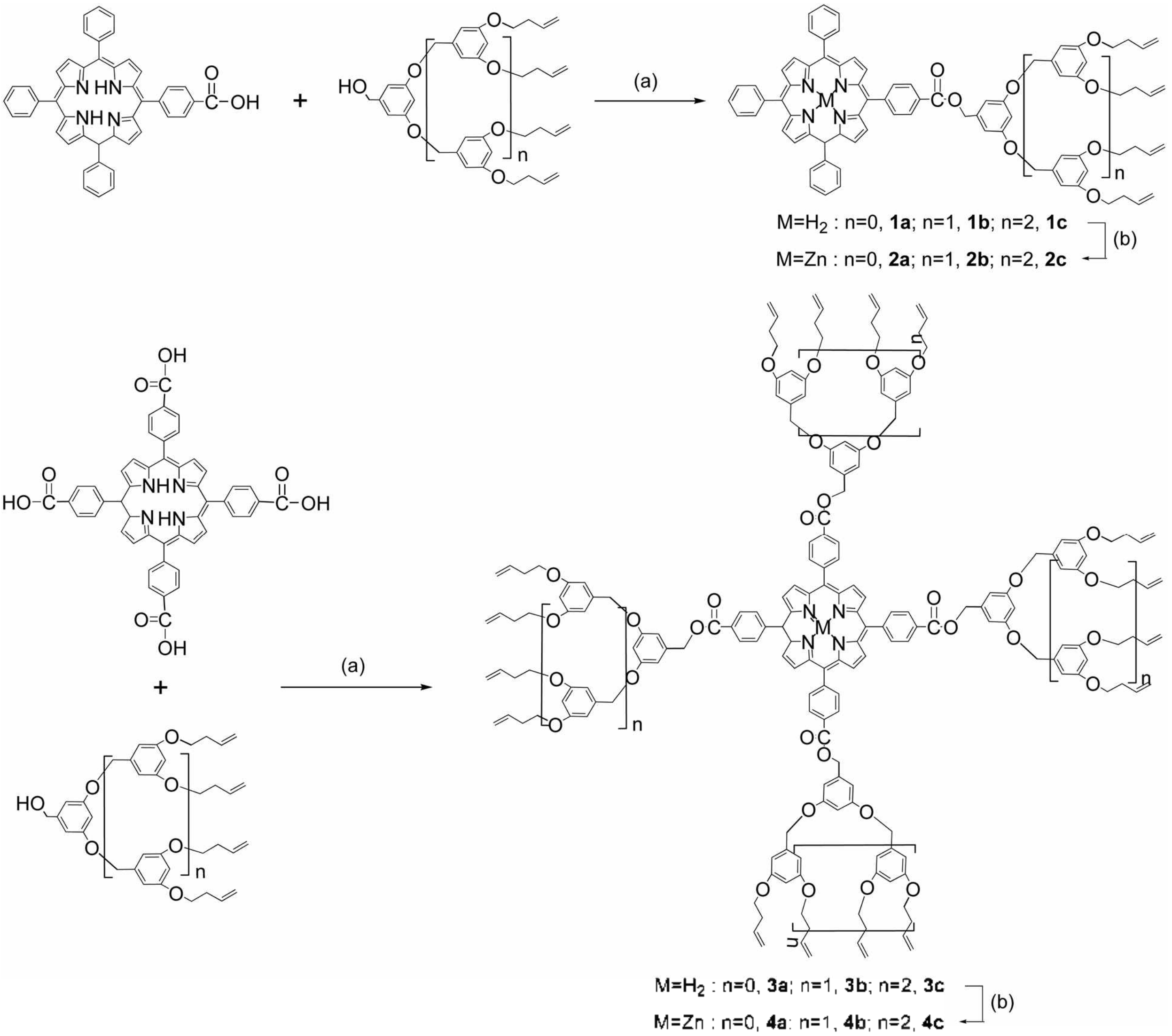
4c: Yield = 15%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.83 (s, 8H, pyrrole), 8.41 (d, 8H, J = 8.2 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 8.26 (d, 8H, J = 8.2 Hz, Por-$\underline{\mathrm{Ar}}$-CO$_2$-), 6.80 (d, 8H, J = 2.1 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.69 (d, 16H, J = 2.1 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.63 (t, 4H, J = 2.1 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.53 (t, 8H, J = 2.1 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.45 (d, 32H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 6.20 (t, 16H, J = 2.2 Hz, dendron-$\underline{\mathrm{Ar}}$-), 5.74-5.84 (m, 32H, -O-CH$_2$-CH$_2$-C$\underline{\mathrm{H}}$=CH$_2$), 5.47 (s, 8H, -CO$_2$-C$\underline{\mathrm{H}_2}$-Ar-), 5.01-5.10 (m, 80H, -Ar-O-C$\underline{\mathrm{H}_2}$-Ar- & -O-CH$_2$-CH$_2$-CH=C$\underline{\mathrm{H}_2}$), 4.91 (s, 32H, -Ar-O-C$\underline{\mathrm{H}_2}$-Ar-), 3.84 (t, 64H, J = 6.7 Hz, -O-C$\underline{\mathrm{H}_2}$-CH$_2$-CH=CH$_2$), 2.37-2.42 (m, 64H, -O-CH$_2$-C$\underline{\mathrm{H}_2}$-CH=CH$_2$) ppm; MALDI-TOF MS m/z 5998.88 (M$^-$) (Calculated for $C_{372}H_{388}N_4O_{64}Zn$: 5998.65).

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 core **1a-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 (λ_{ex} = 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 moiety, respectively. Absorption intensity at 280 nm increases in the higher generation of dendrimer. Fluorescence spectra



Reagents and conditions: (a) CH_2Cl_2, DMF, rt, EDC, DMAP; (b) CH_2Cl_2, CH_3OH, rt, $Zn(OAc)_2$.

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

are similar with two bands at around 652 and 718 nm for all free base porphyrin-cored arylether 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 (λ_{ex} = 550 nm) spectra of zinc porphyrin-cored arylether 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 1. Absorption and fluorescence spectral data of free base porphyrin-cored benzyl arylether dendrimers **1a-1c** and **3a-3c**, and their zinc derivatives **2a-2c** and **4a-4c** in dichloromethane

Compound	λ_a^{max}	λ_f^{max}	Φ_f
1a	418, 515, 550, 589, 645	651, 715	0.076
1b	418, 514, 550, 591, 644	651, 715	0.069
1c	418, 514, 550, 592, 645	651, 715	0.070
3a	420, 515, 550, 590, 643	651, 715	0.071
3b	420, 514, 550, 590, 644	651, 715	0.072
3c	421, 515, 550, 591, 646	651, 715	0.077
TTP	419, 516, 551, 592, 648	651, 715	0.090
2a	419, 547, 586	596, 646	0.030
2b	419, 547, 587	596, 646	0.032
2c	420, 549, 590	599, 646	0.035
4a	421, 548, 589	599, 645	0.039
4b	421, 549, 589	598, 645	0.038
4c	423, 553, 592	602, 650	0.042
ZnTTP	420, 548, 586	596, 646	0.031

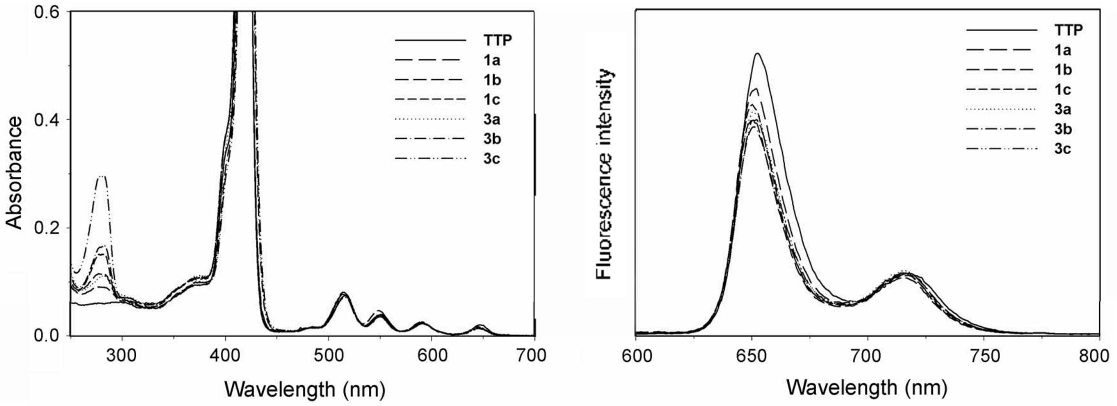


Figure 2. Absorption (left) and fluorescence (right) spectra of free base porphyrin-cored arylether dendrimers **1a-1c** and **3a-3c** in dichloromethane.

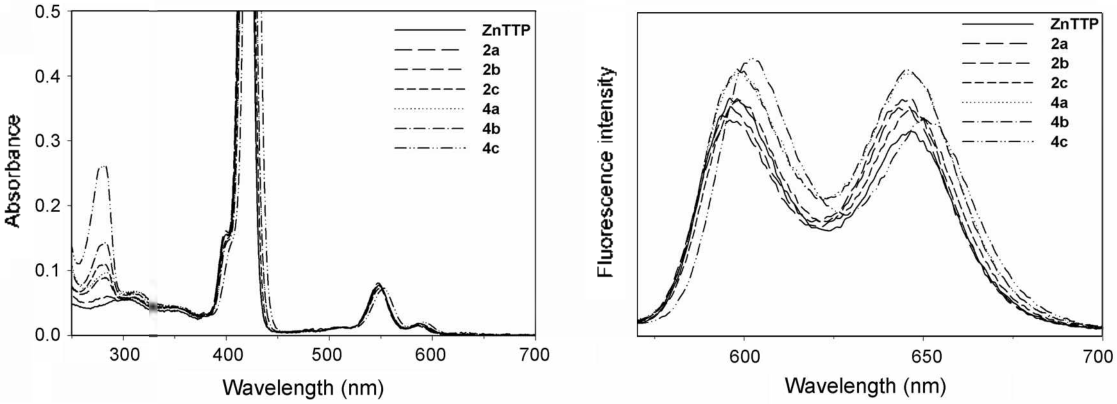


Figure 3. Absorption (left) and fluorescence (right) spectra of zinc porphyrin-cored arylether dendrimers **2a-2c** and **4a-4c** in dichloromethane.

596 and 646 nm for all zinc porphyrin-cored arylether dendrimers **2a-2c** and **4a-4c**, except the distinct red shift in **4c**. 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 **4c** 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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