압력 감지형 페인트용 발광 센서로 플라티늄포르피린 핵을 갖는 덴드리머의 제조에 관한 연구

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Synthesis of Platinumporphyrin-Core Dendrimers as Luminescent Sensors for Pressure Sensitive Paints

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Abstract

플라티늄포르피린 핵과 주위에 8, 16, 32 그리고 64 개의 벤질 단위를 갖는 새로운 덴드리머를 압력 감지형 페인트에 사용할 발광체로 합성하였다. 플라티늄포르피린 핵을 갖는 제1 세대의 덴드리머는 Lindsey형 합성법을 이용하여 제조하였으며, 제2 세대에서 제4 세대까지의 플라티늄포르피린 핵을 갖는 덴드리머는 플라티늄 테트라키스(3,5-디히드록시페닐)포르피린을 적합한 덴드론 브로마이드와 Williamson 에테르 합성법에 따라 알킬화반응시켜 제조하였다. 이러한 에테르 연결의 생성 반응들은 K_2CO_3 와 18-크라운-6를 사용하여 아세톤 용매에서 질소 기류 하에서 60 ℃에서 수행하였을 때 가장 좋은 결과를 주었다. 그리고 이렇게 합성한 덴드리머들을 ^{1}H-NMR, ^{13}C-NMR, Mass spectrum 이용하여 구조를 확인하고, 그리고 UV-VIS spectroscopy를 이용하여 분광학적인 특성을 조사하였다.

I . Introduction

There has been increased interest in the design and application of luminescent probes for such areas as O_2,[1] temperature,[2] and pH detection.[3] The prove molecules are frequently distributed through polymers or gels, which are applied as a thin film to a surface.[4-6]

The sensitivity of these luminescent proves is based on changes in luminescence intensity, lifetime(τ), and spectral emission bandpass.

The role of the luminescent proves is to absorb a photon of light resulting in promotion to an excited state species. The excited state species has several pathways in which to deactivate back down to the ground state. It may lose the energy as heat through nonradiative decay or as light through radiative emission. The energy of the excited state species may also be transferred through collisions with oxygen molecules, and it is this process of dynamic quenching which partially defines the pressure sensitivity of the coating containing O_2 sensitive luminophors.

The quenching of the excited state molecules is related to the Stern-Volmer(S-V) equation 1:

$$I_{REF}(P_{REF})/I(P) = A + K_{SV}B \qquad (1)$$

I_{REF} is the intensity at P_{REF} = 14.6 psi, B is air pressure(psi), and K_{SV} is the S-V constant. The pressure sensitivity or sensitivity coefficient(SC) of these coatings can be extracted from equation 1 as B/A. The higher the value of the SC, the greater the sensitivity of the coating.

So the coating containing the luminescent O_2 sensors afford a noninvasive approach to monitoring surface pressure by measuring the oxygen concentration.

The luminosity(L) of a pressure sensitive paint(PSP) can be qualitatively defined as the ratio of the detectable emitted light intensity(I_{em}, photon/s) to the illumination light intensity(I_{ex}, photon/s).[7]

The luminosity is a function of pressure; this is the basis for the operation of PSP. However, despite of the fact that luminosity inherently varies with pressure, the accuracy and precision of a PSP measurement systems is best under conditions where the luminosity is optimized.

Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(Ⅱ) and meso or beta substituted Pt porphyrins have been primarily used as luminescent oxygen sensors so far.

The low luminosity of these luminophors in a PSP limited their potential. One approach to increase the luminosity was to increase the luminophor concentration. This approach did not deliver significant gains, apparently due to aggregation or self-quenching effects.[8] Thus we planned two strategies to increase the luminosity of a PSP. First, the luminophors will be incorporated into dendrimer structures so that the concentration of the luminophors in the polymer binder can be increased. By using the luminophor as the "core" of the dendrimer, we expected to substantially decrease aggregation and self-quenching effects. This is because the dendrimer acts as a "steric shield" to prevent close approach(molecular scale) of the luminophor cores.[9]

Thus in this research we tried to synthesize convergent polyarylether type dendrimers with a platinumporphyrin as a luminescent core.

Ⅱ. Experimental

General directions. Silica for flash chromatography was Merck silica gel 60(230-400 mesh). Matrix-assisted laser-desorption ionization time-of-flight(MALDI-TOF) mass spectroscopy was performed on a Finnigan Lasermat. The energy source was a 337 nm nitrogen laser. Samples were prepared as 10 mg/mL solutions in tetrahydrofuran(THF). The matrix was a 0.3 M solution of indole acrylic acid in THF. 5 mL of the sample and 10 mL of matrix were combined and analyzed. All NMR spectra were recorded as solution in $CDCl_3$ on a Bruker WM 300 (300 MHz) spectrometer with the solvent proton signal as stsndard: 7.23 for ^1H and 77.0 for ^{13}C. The following abbreviations are used: Dendritic platinum-metallated porphyrin are referred to as $Pt[G\text{-}n]_4P$, where n designates the dendrimer generation. Ar refers to the aromatic repeat units within the dendrimer. Ph refers to the phenyl chain ends or "surface " groups of the dendrimer. Porph refers to the porphyrin ring, α and β refer to the corresponding sites on the pyrrole rings of the porphyrin.

General procedure for the Preparation of the benzylic Alcohol Dendrons.[10] A mixture of the appropriate benzylic bromide dendrons(2.05 equiv), 3,5-di-hydroxybenzyl alcohol(1.00 equiv), dried potassium carbonate(2.50 equiv), and 18-crown-6(0.20 equiv)

in dry acetone was heated to reflux and stirred vigorously under nitrogen for 48 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. the residue was partitioned between water and CH_2Cl_2 and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were dried($MgSO_4$) and evaporated to dryness. The crude product was purified by column chromatography. Analyses agreed with those published.[10a]

General Procedure for the Preparation of the Benzylic bromide Dendrons.[10a] To a mixture of the appropriate benzylic alcohol dendrons(1.00 equiv) and carbon tetrabromide(1.25 equiv) in a minimum amount of dry THF was added triphenylphosphine(1.25 equiv), and the reaction mixture was stirred under nitrogen for 20 min. The reaction mixture was then poured onto water and extracted with CH_2Cl_2. The combined organic extracts were dried($MgSO_4$) and evaporated to dryness. The crude product was purified by column chromatography. Analyses agreed with those published.[10a]

Tetrakis(3,5-dimethoxyphenyl)porphyrin. 3,5-Di-methoxybenzaldehyde(1.500 g, 9.026 mmol) and freshly distilled pyrrole(626 mL, 9.026 mmol) were dissolved in dry chloroform(903 mL) under nitrogen atmosphere. After adding $BF_3 \cdot OEt_2$(364 μL, 2.979 mmol) to the mixture, the solution was shielded from ambient light and stirred at room temperature for 90 min. After adding DDQ(1.537 g, 6.770 mmol), the mixture was stirred for an additional 90 min, then triethylamine(415 μL, 2.979 mmol) was added to neutralize the acid. The solvent was evaporated, and the residual solids were adsorbed onto silica(5 mL). The crude product was purified by chromatography through a 40 mL silica column eluting with a linear gradient starting with pure hexane and ending with pure CH_2Cl_2. After collecting the product fractions and evaporating the solvent, the product was obtained as purple crystals, yield 43%. UV/vis abs(ε) 424 nm(280,000), 516 nm(19,000), 548 nm(9,000), 586 nm(9,000), 648 nm(5,000). ^{1}H-NMR δ 8.95(s, 8H, β-H); 7.01(s, 8H, Ar-H); 6.65(s, 4H, Ar-H); 3.33(s, 24H, ArO-CH_3); -3.07(s, 2H, N-H). ^{13}C- NMR δ 156.60(ArC-OCH_3); 142.89(ArC-porph); 131.12(βC); 119.94(meso C); 114.19, 102.28(ArC-H); 48.64(Ar-OCH_3).

Tetrakis(3,5-dihydroxyphenyl)porphyrin. Tetra-(3,5-dimethoxyphenyl)porphyrin(740 mg, 0.866 mmol) was dissolved in dry CH_2Cl_2(20 mL) under nitrogen atmosphere. The solution was cooled to 0 ℃, and then BBr_3(7.27 mL, 7.271 mmol, 1M in CH_2Cl_2) was slowly added to the reaction mixture. After addition , the mixture was allowed to warm to room temperature as it stirred overnight. Enough methanol was then added

to deactivate any unreacted BBr_3. Then distilled water(30 mL) was added, and the mixture was stirred for 2 h. After evaporation of the organic solvents, a green powder was filtered from the water. It was dissolved in ether, washed twice with saturated $NaHCO_3$, washed once with distilled water, and then dried over $MgSO_4$. The solvent was evaporated, and the product was isolated as purple crystals that were dried under vacuum at 40 ℃(yield 95%). UV/vis abs(ε) 424 nm(242,000), 516 nm(14,000), 552 nm(5,000), 592 nm(4,000), 648 nm(2,000). ^{1}H-NMR (in acetone-d_6, 2.05 ppm) δ 8.93(s, 8H, β-H); 7.05(s, 8H, Ar-H); 6.64(s, 4H, Ar-H); 3.81(s, broad, Ar-OH). ^{13}C-NMR (in acetone-d_6, 29.2 ppm) δ 156.54(ArC-OH); 144.97(ArC-porph); 127.50(βC); 117.81(meso C); 114.15, 102.50(ArC-H). Mass spectrum(MALDI-TOF) *m/z* calculated 742.7; found 752.7.

Preparation of $Cl_2Pt(Ph-CN)_2$.[11] 150 mg(0.56 mmol) of $PtCl_2$ was dissolved in 8 mL of benzonitrile and the mixture was heated to 60 ℃ with stirring. After the $PtCl_2$ was completely dissolved, the solution was cooled to room temperature. To the solution, 100 mL of diethylether was added. The mixture was, then, placed in a refrigerator overnight. The yellowish crystals was obtained via filtration and vacuum drying for 2 h in 90% yield(186 mg, 0.50 mmol).

Platinum Tetrakis(3,5-dihydroxyphenyl)porphyrin. Tetrakis(3,5-dihydroxyphenyl) porphyrin(134 mg, 0.180 mmol) and $Cl_2Pt(Ph-CN)_2$ (210 mg, 0.445 mmol) were dissolved in 14 mL of benzonitrile. The solution was heated to reflux for 6 h, then the benzonitrile was removed by distillation under vacuum. the semisolid residue was extracted three times with 20 mL portion of acetone. After then the solution was concentrated and the crude product was purified by column chromatography eluting with a linear gradient starting with pure CH_2Cl_2 and ending pure ether. After collecting the product fractions and evaporating the solvent, the product was obtained as purple crystals, yield 82%. UV/vis abs(ε) 404 nm(465,000), 510 nm(45,000), 540 nm(18.000). ^{1}H-NMR (in acetone-d_6, 2.05 ppm) δ 9.16(s, 8H, AR-OH); 8.90(s, 8H, β-H); 7.32(d, 8H, Ar-H); 7.00(t, 4H, Ar-H). ^{13}C-NMR (in acetone-d_6, 29.2 ppm) δ 155.53(ArC-OH); 147.97(αC); 143.34(ArC-porphy); 129.50(βC); 118.62(meso C); 114.15, 101.50(ArC-H). Mass spectrum(MALDI-TOF) *m/z* calculated 935.8; found 942.7.

Pt[G-1]$_4$P. A mixture of 3,5-dibenzyloxybenzaldehyde(1.500 g, 4.711 mmol) and freshly distilled pyrrole(327 mL, 4.711 mmol) were dissolved in dry chloroform(903 mL) under nitrogen. Then $BF_3 \cdot OEt_2$(190 μL, 1.555 mmol) was added to the reaction mixture, and the mixture was shielded from ambient light as it was stirred at room

temperature for 90 min. After adding DDQ(802 mg, 3.534 mmol), the reaction mixture was stirred for an additional 90 min, and then triethylamine(217 μL, 1.574 mmol) was added to neutralize the acid. The solvent was evaporated, and the residual solids were separated by column chromatography through a 40 mL silica column eluting with a linear gradient starting with pure hexane and ending with pure CH_2Cl_2. After collecting the product fractions and evaporating the solvent, the product was obtained as purple crystals(32%).

Tetrakis(3,5-dibenzyloxyphenyl)porphyrin(220 mg, 0.150 mmol) and $Cl_2Pt(Ph-CN)_2$ (180 mg, 0.488 mmol) were dissolved in 15 mL of benzonitrile. The solution was heated to reflux for 10 h, then the benzonitrile was removed by distillation under vacuum. and the residual solids were adsorbed onto silica. The crude product was purified by column chromatography eluting with pure CH_2Cl_2. After collecting the product fractions, the solvent was evaporated to afford purple crystals(70%). UV/vis abs(ε) 404 nm(482,000), 510 nm(46,000), 540 nm(18,000). ^{1}H-NMR δ 8.97(s, 8H, β-H); 7.65(d, 8H, Ar-H); 7.43(m, 40H, Ph-H); 7.00(t, 4H, Ar-H); 5.21(s, 16H, Bn-H). ^{13}C-NMR δ 157.12(Ar C-O); 149.34(αC); 145.21(Ar C-porph); 136.35(Ph C-CH_2); 131.36(βC); 120.25(meso C); 115.15, 96.66(ArC-H). Mass spectrum(MALDI-TOF) *m/z* calculated 1656.8; found 1667.8.

Preparation of Porphyrin-Core Dendrimers(Gene-rations 2-4). The second-, third-, and fourth-generation porphyrin-core dendrimers were synthesized by coupling of platinum tetrakis(3,5-dihydroxyphenyl)porphyrin to the appropriate benzylic bromide dendron in a Williamson ether synthesis. Platinum tetrakis(3,5-dihydroxyphenyl)porphyrin (1.00 equiv) and the dendritic bromide(9.60 equiv) were dissolved in acetone under nitrogen atmosphere. To this solution, K_2CO_3(16.0 equiv) and 18-crown-6(1.60 equiv) were added, and the mixture was stirred and warmed to 60 ℃. The solvent was evaporated, and the residual solids were partitioned between water and CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×). The solvent was evaporated, and the residual solids were adsorbed onto silica(5 mL), and the crude product was purified by chromatography through a 40 mL silica column eluting with a linear gradient starting with pure hexane and ending with pure CH_2Cl_2. The product fractions were collected, and the solvent was evaporated. The product was dissolved in a minimum amount of $CHCl_3$, then precipitated into methanol. The precipitate was then dissolved in a minimum amount of ethyl acetate and reprecipitated into ether. The product was obtained as a dark purple powder.

Pt[G-2]$_4$P. This was prepared as above from platinum tetrakis(3,5-dihydroxyphenyl) porphyrin and [G-1] Br, yield 56%. UV/vis abs(ε) 404 nm(431,000), 510 nm(44,000), 540 nm(18,000). ^{1}H-NMR δ 8.91(s, 8H, β-H); 7.57(d, 8H, Ar-H); 7.43(m, 80H, Ph-H); 7.03(t, 4H, Ar-H); 6.75(d, 16H, Ar-H); 6.56(t, 8H, Ar-H); 5.11(s, 16H, Bn-H); 4.95(s, 32H, Bn-H). ^{13}C-NMR δ 160.09, 157.71(Ar C-O); 149.92(αC); 144.80(Ar C-porph); 139.15(Ar C-CH_2); 136.63(Ph C-CH_2); 132.10(βC); 128.46, 127.88, 127.43(Ph C-H); 120.25(meso C); 115.15, 106.43, 101.65. 96.66(Ar C-H); 70.00(Ar/Ph-CH_2). Mass spectrum(MALDI-TOF) *m/z* calculated 3354.8; found 3357.6.

Pt[G-3]$_4$P. This was prepared as above from platinum tetrakis(3,5-dihydroxyphenyl) porphyrin and [G-2] Br, yield 51%. UV/vis abs(ε) 404 nm(473,000), 510 nm(44,000), 540 nm(18,000). ^{1}H-NMR δ 8.96(s, 8H, β-H); 7.48(s, 8H, Ar-H); 7.17(m, 160H, Ph-H); 7.03(s, 4H, Ar-H); 6.75(d, 16H, Ar-H); 6.54(d, 32H, Ar-H); 6.43(t, 8H, Ar-H); 6.39(t, 16H, Ar-H); 5.09(s, 16H, Bn-H); 4.90(s, 32H, Bn-H); 4.78(s, 64H, Bn-H). ^{13}C-NMR δ 160.07, 160.03, 157.73(Ar C-O); 149.91(αC); 139.35, 139.21(Ar C-CH_2); 136.63(Ph C-CH_2); 128.43, 127.85, 127.42(Ph C-H); 120.58, 106.56, 106.20, 101.65, 101.52, 96.65(Ar C-H); 69.90(Ar/Ph-CH_2). Mass spectrum(MALDI-TOF) *m/z* calculated 6750.8; found 6769.2.

Pt[G-4]$_4$P. This was prepared as above from platinum tetrakis(3,5-dihydroxyphenyl) porphyrin and [G-3] Br, yield 12%. UV/vis abs(ε) 404 nm(452,000), 510 nm(43,000), 540 nm(18,000). ^{1}H-NMR δ 8.99(s, 8H, β-H); 7.48(s, 8H, Ar-H); 7.19(m, 320H, Ph-H); 6.72(s, 4H, Ar-H); 6.53-6.38(overlapping resonances, 168H, Ar-H); 4.91(s, 16H, Bn-H); 4.75-4.69(overlapping resonances, 224H, Bn-H). ^{13}C-NMR δ 160.05, 169.93, 159.82, 157.73(Ar C-O); 149.61(αC); 139.16, 139.08(Ar C-CH_2); 136.63(Ph C-CH_2); 132.10(βC); 128.43, 127.80, 127.46(Ph C-H); 106.42, 101.87(Ar C-H); 69.70(Ar/Ph-CH_2). Mass spectrum(MALDI-TOF) *m/z* calculated 13,542.7; found 13,562.3.

Ⅲ. Results and Discussion

Dendrimer[12] are well-defined macromolecules exhibiting a tree-like structure, first derived by the "cascade molecule" approach.[13] Dendrimer chemistry is a rapidly expanding field for both basic and applicative reason.[12] Such compounds are particularly interesting when they carry units capable of performing specific function(e.g., redox reactions and photo-induced processes). Transition-metal

complexes are useful components for constructing dendrimers because of their outstanding photochemical, photophysical, and electrochemical properties.[14 15] In dendrimers, transition metal units may be incorporated as a core, as components of the branches, and/or as peripheral units. When a dendrimer contains a photo- and/or electro-active unit as a core, the dendritic branches may modify the photochemical and eletrochemical properties of such a unit.[9,15,16 17] This effect may be exploited, for example, to improve the luminescence properties of the core or to decrease the rate of electron-transfer processes.

In the discussion below, the various generation dendritic molecules will be designated by use of the following notation [G-x]-f, in which [G-x] refers to generation number(x=0,1,2,...) and f refers to the functional group located at the focal point. After coupling to a core, the notation $[G\text{-}x]_n\text{-}[C]$ will be used where n represents the number of dendritic fragments(generation x) coupled to the core.

In our research, platinumporphyrin core dendrimers (Figure 1) as metal-containing dendrimers were synthesized.

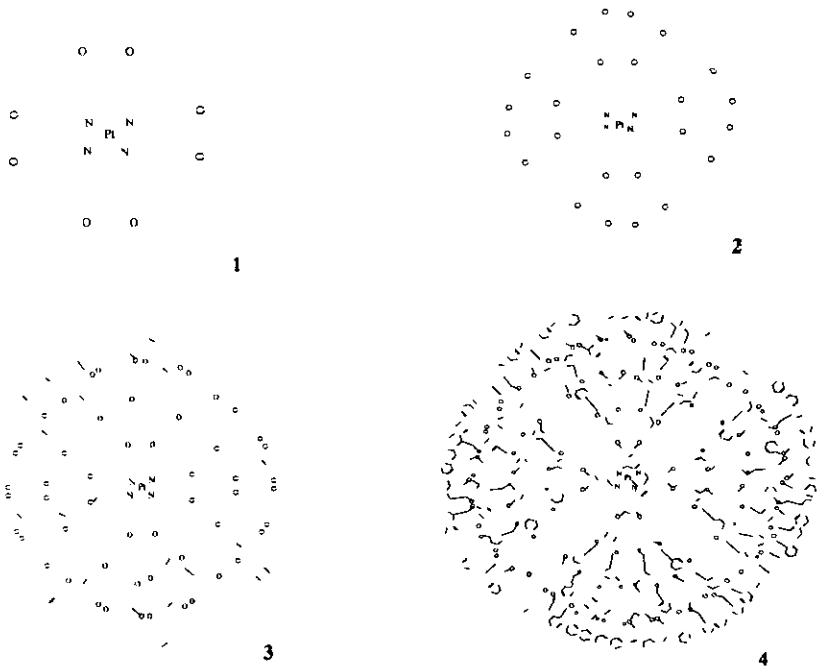


Figure 1. Series of porphyrin-core dendrimers prepared in this paper: 1, $Pt[G\text{-}1]_4P$; 2, $Pt[G\text{-}2]_4P$; 3, $Pt[G\text{-}3]_4P$; 4, $Pt[G\text{-}4]_4P$.

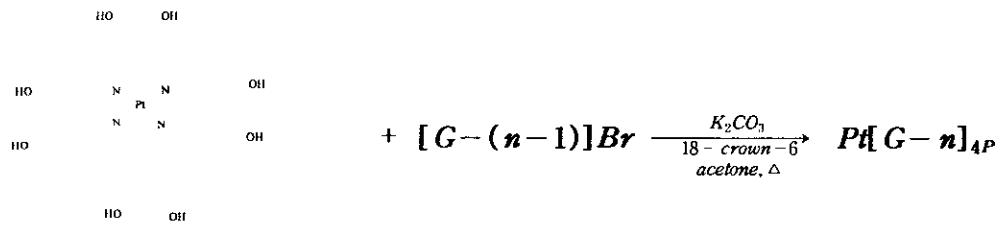
The first-generation porphyrin-core dendrimer was prepared through a Lindsey type synthesis[18] involving acid-catalyzed condensation of 3,5-dibenzyloxybenzaldehyde with pyrrole, followed by an oxidation step. After isolating the free-base product, the porphyrin core was metalated with platinum. The overall yield was 22%.

The second through fourth generation porphyrin-core dendrimers, also shown in Figure 1, were prepared by alkylating platinum tetrakis(3,5-dihydroxyphenyl)porphyrin with the appropriate dendron bromide in a Williamson ether synthesis(Scheme 1).

The reaction is best performed under nitrogen atmosphere, using potassium carbonate and 18-crown-6 in dry acetone at 60 ℃. Temperatures higher than 60 ℃ produced significant C-alkylation of the phenyl ring bound to the porphyrin core, evident in analysis of the product by 1H-NMR as two resonances of equal intensities at 7.82 and

8.59 ppm generated by the remaining phenyl protons of the C-alkylated moiety. Proton NMR showed the products to be fully alkylated at the phenolic oxygen. Yields for the second-, third-, and fourth-generation porphyrin-cored dendrimer were 56%, 51%, 12%, respectively. In the case of the fourth-generation porphyrin-cored dendrimer, Yield is very low compare to the yield of the second- or third-generation dendrimer. This can be attributed to increased steric congestion as Pt[G-4]$_4$P is a highly branched macromolecule of nominal molecular formula $C_{884}H_{748}N_4O_{120}Pt$ and molecular weight 13,543. MALDI-TOF mass spectroscopy showed a single product at the expected molecular weight(M+Na$^+$and M+K$^+$), and UV/vis spectrometry confirmed that the porphyrin core was intact.

Scheme 1



$$+\ [G-(n-1)]Br \xrightarrow[18-crown-6]{K_2CO_3} Pt[G-n]_{4P}$$
acetone, △

Compound Number	Generation	Nomenclature
1	n=1	$Pt[G-1]_4P$
2	n=2	$Pt[G-2]_4P$
3	n=3	$Pt[G-3]_4P$
4	n=4	$Pt[G-4]_4P$

Ⅳ. Conclusion

We have synthesized four porphyrin-core dendrimers. Each porphyrin ring is metallated with platinum and meso-substituted with a benbzyl ether dendrimer varying in size, from generation one to generation four. Metalation of their cores is possible using conventional approaches, while the modification of their periphery allows their fine-tuning for specific applications. Because the dendritic shell does not interfere with photooxidation or subsequent photochemical processes of the porphyrin core, these porphyrin-core dendrimers may be useful in conventional porphyrin-catalyzed chemistries. Specially designed dendrons with precise architectures incorporating rate enhancing ligands, guest-binding clefts, or solubilizng moieties, could be prepared using the conventional route to afford better performing porphyrin-core dendrimers.

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