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Synthesis of Multi(metallo)porphyrin Dendrimers through Nucleophilic Aromatic Substitution on *meso*-Pyrimidinyl Substituted Porphyrins

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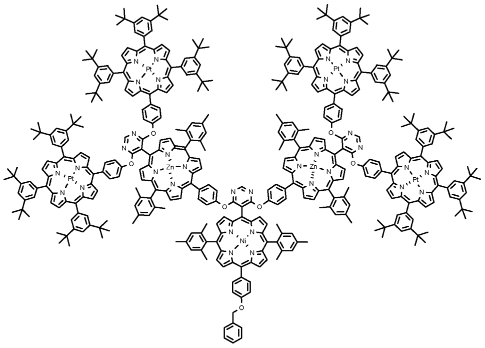

A convergent synthetic strategy toward novel all-porphyrin dendrimers, which can be regarded as synthetic model systems of the natural photosynthetic light-harvesting antennae, was successfully explored. The dendron propagation, based on nucleophilic aromatic substitution reactions on a *meso*-dichloropyrimidinyl substituted porphyrin AB_2 monomer, was carried out up to the second-generation dendron, and the used approach was proven to be compatible with the stepwise introduction of different metals in the successive generations. Three different metals (Pt, Zn, and Ni) could be introduced in the second-generation heptaporphyrin dendron. By applying analogous *meso*-dichloropyrimidinyl substituted porphyrin cores, novel multiporphyrin dendrimers were obtained.

Introduction

Spherical dendritic macromolecules have gained considerable attention during the past decade as a new class of monodisperse, well-defined, and highly branched polymers.[1] This huge interest was triggered by the desire to exploit their unique inherent structural properties in a broad range of applications. Porphyrins have been incorporated into the framework of dendrimers by numerous research groups. They mostly have been applied as central building blocks (cores) in dendrimer chemistry,[2,3] but dendrimers with porphyrins attached to the periphery of a known dendritic backbone have been synthesized as well.[4] Multiporphyrin dendrimers (containing porphyrin units at the periphery

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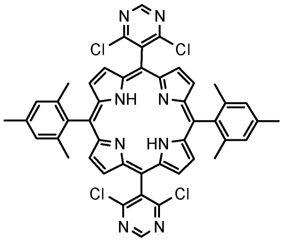
as well as at the branches and a porphyrin core) currently gain more and more interest as promising candidates for the construction of multisite catalysts, molecular electronic and photonic devices, and artificial light-harvesting systems.

In recent years, considerable effort has been devoted to the synthesis and study of covalently linked multiporphyrin arrays of different shapes and sizes due to their promising role in artificial photosynthesis.[5,6] Multiporphyrin dendrimers are of special interest since the dendritic architecture allows for maximum interactions between the chromophores, a necessary condition for efficient energy and electron-transfer processes.[7,8] However, access to such multiporphyrin compounds remains a difficult synthetic challenge. A series of pentaporphyrins, which could be regarded as the smallest members of the family of multiporphyrin dendrimers, have been prepared by different approaches.[9] Sanders et al. reported on the synthesis of metalloporphyrin dendrimers (containing up to nine porphyrins) through consecutive Pd-mediated and Mitsunobu couplings.[10] Lindsey's convergent synthesis afforded dendritic multiporphyrin arrays containing *n* Zn porphyrins ($n = 4$, 8, or 20) and one free-base (Fb) porphyrin joined by semirigid diarylethyne linkers.[11] Efficient excited singlet-state energy transfer occurs among the Zn porphyrins and ultimately to the sole Fb porphyrin in these arrays. A similar dendritic array incorporating 20 Ni porphyrins and one Fb porphyrin has been prepared by successive porphyrin-forming reactions.[12] Choi et al. synthesized arrays that contain energy-donating dendritic Zn porphyrin wedges (containing one, three, or seven porphyrin units) attached to an energy-accepting Fb porphyrin core.[13] Their star-shaped dendritic arrays (in contrast to the cone-shaped dendrons), in which the chromophore units could be arranged in a fashion analogous to those in the natural light-harvesting antenna complexes, can cope with both a large absorption cross section and a high efficiency of vectorial energy transfer. By coupling their dendrons to a fullerene acceptor, they gave an offset to the construction of electron-transfer relay systems mimicking the natural photosynthetic reaction center.[14]



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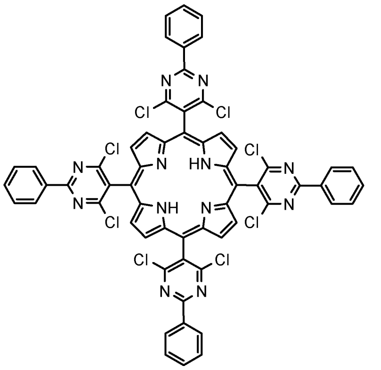

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FIGURE 1. *meso*-Dichloropyrimidinyl substituted porphyrin cores.

Our research group has been working on the synthesis of dendrimers through a nucleophilic aromatic substitution (NAS) approach that uses the substitution of (hetero)aryl halogenides with phenolates to build up dendrimers in a convergent way.[15] This approach allows the incorporation of heterocyclic building blocks in the dendritic framework, something that has rarely been done. In this manner, dendrimers consisting of 1,3,4-oxadiazoles,[15a] 1,3,5-triazines,[15b] pyrimidines,[15c] and 1,2,4-triazoles[15d] have been prepared. At present, the pyrimidine system seems to present an optimum within our strategy, combining an intermediate reactivity (allowing an easy synthesis) and a good structural stability. Heterocyclic dendrimers are promising candidates to be used in applications where a more rigid dendritic structure and a better resistance to the applied conditions are required (e.g., catalytic oxidations). Hence, pyrimidine dendrimers equipped with benzimidazole or porphyrin ligands at the periphery have been prepared, and they have been used as oxidatively stable, active, and selective

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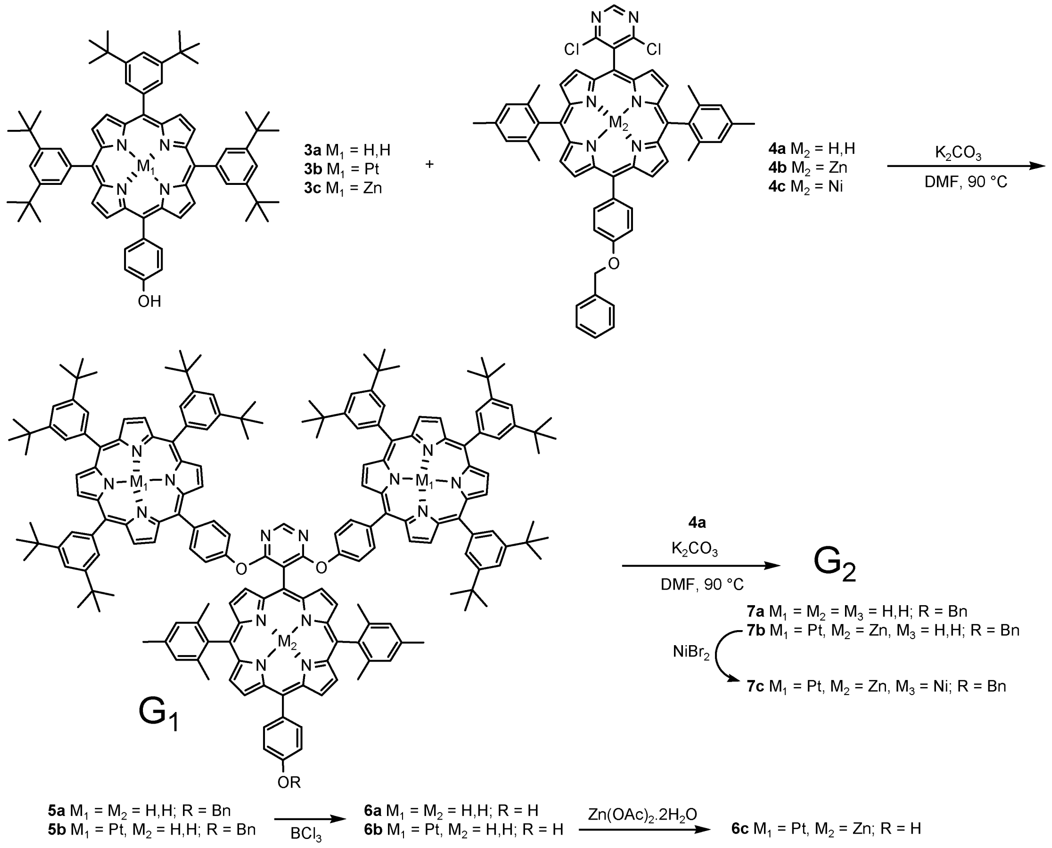
SCHEME 1. Convergent Propagation Strategy toward Multiporphyrin Dendrons



dendritic catalysts in oxidation reactions.[16] Very recently, our group also prepared dendrimers containing a porphyrin core and carbazole-based branches.[17] The light collected by the peripheral chromophores was quantitatively transferred to the core in these dendrimers.

In this article, we report on the efficient synthesis of novel (successively metalated) multiporphyrin dendrons and dendrimers built through NAS on *meso*-dichloropyrimidinyl substituted porphyrin building blocks.

Results and Discussion

Earlier synthetic efforts on porphyrinic systems in our group afforded a novel *meso*-dichloropyrimidinyl substituted A_2B_2 porphyrin **1** (Figure 1), which could be subjected to NAS[18a,b] (with a number of phenols) or Suzuki cross-coupling reactions[18c] (with arylboronic acids) to obtain highly sterically encumbered "double picket fence" porphyrins. This A_2B_2 porphyrin **1** seemed to be an ideal candidate to be used as a tetrafunctional porphyrin core, and pyrimidine-based dendrons of successive generations were coupled successfully to this core in high yields through their phenolic focal group.[15c] Inspired by the success of the NAS on bis(dichloropyrimidinyl)porphyrin **1**, we envisaged a strategy to synthesize "all-porphyrin" dendrimers through a similar approach.

Synthesis. First, a novel porphyrin AB_2 monomer **4a** was devised, containing both the dichloropyrimidinyl moiety and a benzyl-protected phenolic moiety (Scheme 1). This porphyrin monomer could be prepared through a MacDonald condensation of mesityldipyrromethane[19] with *p*-benzyloxybenzaldehyde and 4,6-dichloropyrimidine-5-carbaldehyde[20] under Lindsey conditions. Depending on the stoichiometric amounts of the aldehydes, both A_2B_2 porphyrins (5,15-bis(dichloropyrimidinyl)-porphyrin **1** or the 5,15-bis(*p*-benzyloxyphenyl)porphyrin analogue) could be isolated as side products with an obvious preference for the *meso*-dichloropyrimidinyl substituted A_2B_2 porphyrin **1**, which could be used later as the dendritic core. When 5 mmol of *p*-benzyloxybenzaldehyde and 7.5 mmol of 4,6-dichloropyrimidine-5-carbaldehyde were condensed with 10 mmol of mesityldipyrromethane, the desired monomer was obtained in 17% yield, while the A_2B_2 bis(pyrimidinyl)porphyrin was obtained in 8% yield. Both porphyrin monomer **4a** and porphyrin core **1** can thus be prepared in substantial amounts in the same one-pot procedure. The Zn(II)-metalated derivative **4b** was easily prepared through reaction of the free base with an excess of zinc(II) acetate in CH_2Cl_2. Ni(II)-metalated analogue **4c** could be obtained on reacting the free base with an excess of nickel(II) bromide in refluxing DMF.

3,5-Di-*tert*-butylphenyl substituted AB_3 porphyrin **3a**[21] (which could be denoted as the zeroth-generation dendron) was chosen as the peripheral porphyrin building block due to its favorable

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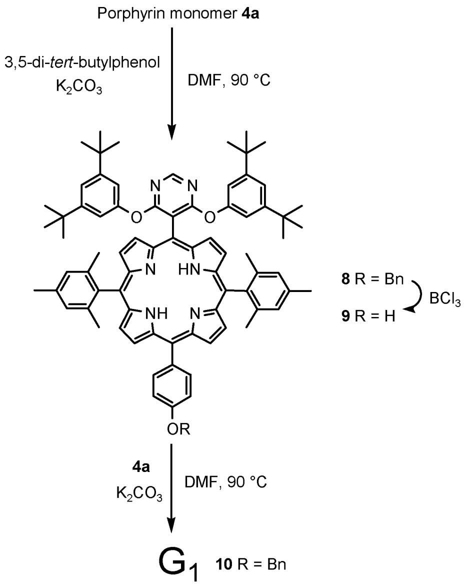
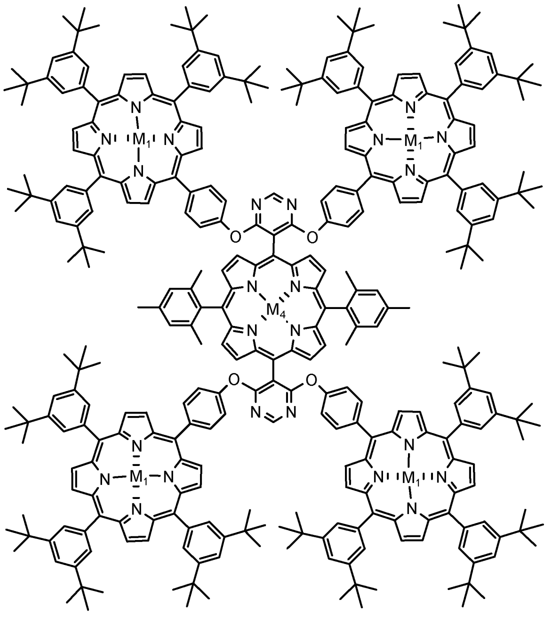
SCHEME 2. Alternative Propagation Strategy





11a $M_1 = M_4 = H,H$
11b $M_1 = Zn, M_4 = H,H$

FIGURE 2. Pentaporphyrin G_0 dendrimers **11a**,**b**.

solubilizing properties enabling easy synthetic routine handling and characterization of the multiporphyrin arrays (Scheme 1). The AB_3 porphyrin was synthesized by a mixed condensation of 3,5-di-*tert*-butylbenzaldehyde[22] and 4-hydroxybenzaldehyde with pyrrole under Lindsey conditions (16%).[21a]

Reaction of a slight excess of peripheral porphyrin **3a** (2.2 equiv) with porphyrin monomer **4a** afforded the protected first-generation (G_1) dendron **5a** (Scheme 1). The NAS proceeded smoothly, and trisporphyrin **5a** could, after chromatographic purification from the excess of peripheral porphyrin and trace amounts of the monosubstituted G_1 dendron, be isolated in a fairly acceptable yield of 85%. Initial problems regarding reproducibility of the NAS reaction were solved by careful purification of peripheral porphyrin **3a** and the use of optimized reaction conditions: NAS reactions were found to proceed smoothly in DMF at 90 °C (for 48 h) with potassium carbonate base.

Removal of the benzyl protecting group was achieved easily (84%) using boron trichloride affording a novel phenolic focal group ready for further elaboration of the dendritic structure. Deprotections were carried out at low temperature (−18 °C) to avoid any destructive fragmentation of the diaryl ether linkages.[15b] Deprotected G_1 dendron **6a** was subjected to a novel NAS reaction on porphyrin monomer **4a**, and G_2 dendron **7a** could be obtained in 55% yield (Scheme 1). This G_2 dendron already contains seven porphyrins linked through diaryl ether linkages.[23]

For the purpose of artificial photosynthesis (and other possible applications), it could be useful to introduce different metals in the various generations of porphyrin ligands to obtain an "energy funneling" effect from the outer porphyrins to a Fb porphyrin core resulting in an increased antenna effect.[8] Hence, our NAS approach toward multiporphyrin dendrimers was checked for its compatibility with the insertion of different metals in the successive generations. Several aspects were considered in the design of these multimetalated porphyrin dendrimers. At this time, emphasis was placed on easy synthesis rather than on spectroscopic features to provide a real energy funneling effect (*proof-of-principle*). First, metals were chosen as such to avoid paramagnetic complexes to enable easy NMR characterization of the dendrimers. Second, metals with the necessity of axial ligands to complete their coordination sphere were avoided for the cause of axial ligand uncertainty and their lability toward nucleophiles. Furthermore, the stability of the metal complexes under the applied propagation conditions should be considered.[24]

Peripheral porphyrin **3a** was easily metalated with either Zn (using zinc(II) acetate in CH_2Cl_2) or Pt (using platinum(II) chloride in boiling benzonitrile[25]), and the (orange-colored) Pt(II) derivative **3b** was chosen as the peripheral unit because of the high stability of the Pt(II) complex (stability class I: the metal is not even removed in boiling H_2SO_4).[24] Insertion of the second metal (Zn) was not undertaken at the monomer stage, but only after coupling of Pt(II) porphyrin **3b** to the free base porphyrin monomer **4a** and subsequent deprotection of the obtained G_1 dendron **5b** (Scheme 1). This strategy was chosen because of the acid lability of the Zn(II) complex. Treatment of Zn(II) porphyrin monomer **4b** with boron trichloride afforded the simultaneously debenzylated and demetalated porphyrin. The Pt(II) complex, however, proved to be stable under the applied deprotection conditions. Deprotected G_1 dendron **6b** ($M_1 = Pt$, $M_2 = H,H$) was easily metalated with Zn under the known conditions affording G_1 dendron **6c** with two different metals, Pt and Zn, respectively, in the successive generations. G_1 dendron **6c** was again coupled to the free-base porphyrin monomer **4a** to generate heptaporphyrin dendron **7b** (Scheme 1). The G_2 dendron could then be subjected to a novel metalation step to insert a third metal. As an example, Ni (through the use of nickel(II) bromide in refluxing DMF) was introduced in the interior generation to afford the trimetalated G_2 dendron **7c**

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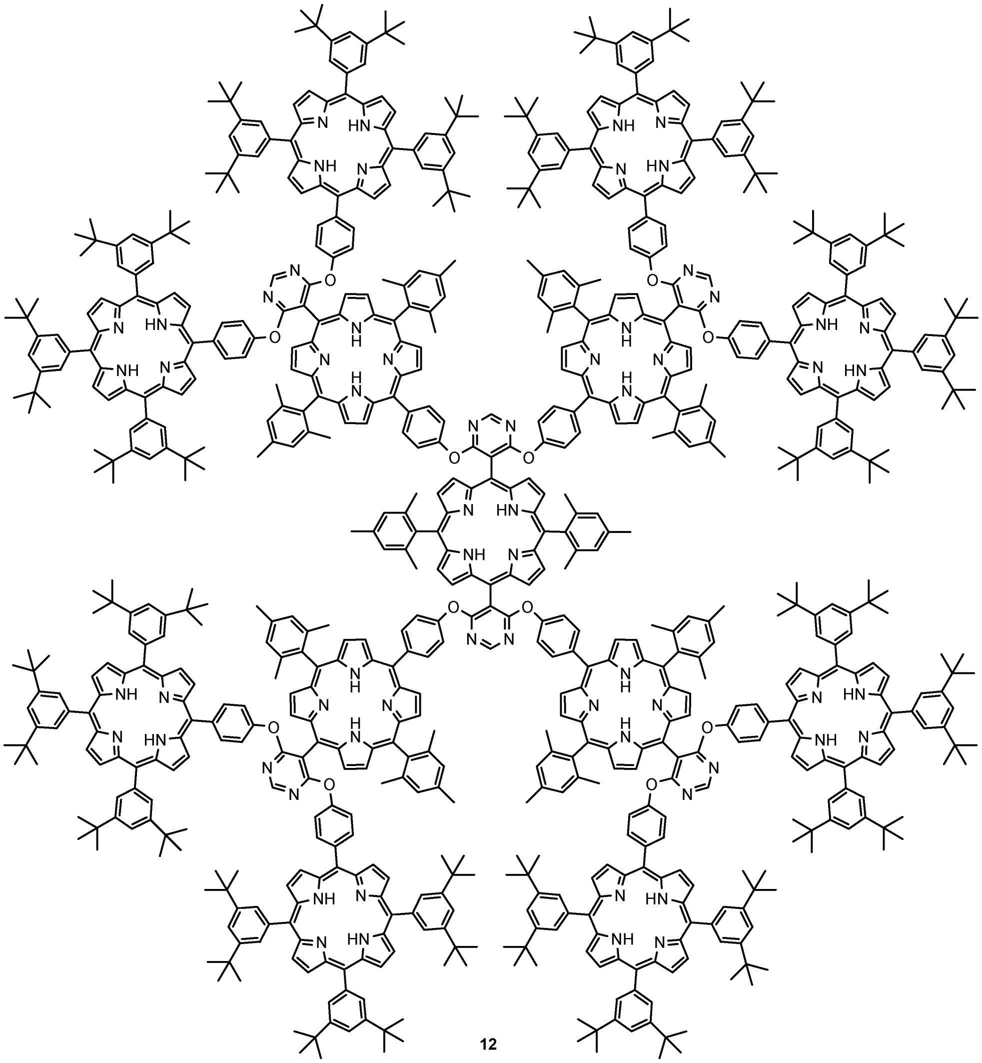

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FIGURE 3. G_1 dendrimer **12**.

(Scheme 1). During the Ni insertion, Zn was retained in the first-generation porphyrin ligands.

The mild, basic NAS conditions preserve the metalation state of the porphyrin ligands. However, since Zn was not retained in the deprotection step, a gentler protection/deprotection strategy will probably be necessary to prepare higher-generation multiporphyrin dendrimers equipped with different metals (e.g., Zn, Mg, and Cd) suitable for efficient light harvesting.

To avoid the tedious synthesis of two different porphyrinic building blocks **3** and **4** (low yields, exhaustive chromatographic purifications), an alternative route was devised using monomer **4a** as the only porphyrin. For this purpose, porphyrin monomer **4a** was substituted with 3,5-di-*tert*-butylphenol to afford porphyrin **8** (80%), which after deprotection with boron trichloride (78%) could serve as an alternative peripheral building block (Scheme 2). Phenolic porphyrin **9** was hence coupled to porphyrin monomer **4a** to obtain the analogous first-generation dendron **10** (73%).

The convergent approach to dendrimer synthesis implies that the synthesized dendrons are attached to a central core in the final step. To obtain multiporphyrin dendrimers, two polyfunctional cores (based on the same NAS chemistry) were considered. In addition to the earlier mentioned tetrafunctional porphyrin core **1**,[18] a novel analogous octafunctional *meso*-dichloropyrimidinyl substituted A_4 porphyrin **2** was synthesized from 4,6-dichloro-2-phenylpyrimidine-5-carbaldehyde and pyrrole (Figure 1).[16b,26] By applying this octafunctional core, an even faster growth of molecular size could be achieved.

Substitution of the chlorine groups of these cores by porphyrin dendrons can give access to multiporphyrin macromolecules. Peripheral porphyrin **3a** was coupled successfully to both cores, affording pentameric (**11a**,**b**, Figure 2, 65%) and nonameric (58%) multiporphyrin dendrimers.[27] Metalation (Zn was chosen as a model) could be achieved on both the individual building blocks and the free base pentaporphyrin.

Coupling of higher-generation multiporphyrin dendrons to both cores could give access to even larger dendritic structures. Increased steric hindrance can, however, prevent full functionalization of the core and hence presents a limitation to the applied convergent strategy. As an example, G_1 dendrimer **12** (containing 13 porphyrin units) was synthesized by substitution of G_1 dendron **6a** on A_2B_2 porphyrin core **1** (Figure 3). MALDI-TOF MS and ^{1}H NMR analysis of the obtained compound

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(26) Maes, W.; Vanderhaeghen, J.; Dehaen, W. *Chem. Commun.* **2005**, 2612−2614.

(27) This nonaporphyrin was already used in a study of porphyrin-functionalized dendrimers (porphyrin moieties at the periphery) as recyclable photocatalysts in a nanofiltration membrane reactor (see ref 16b).

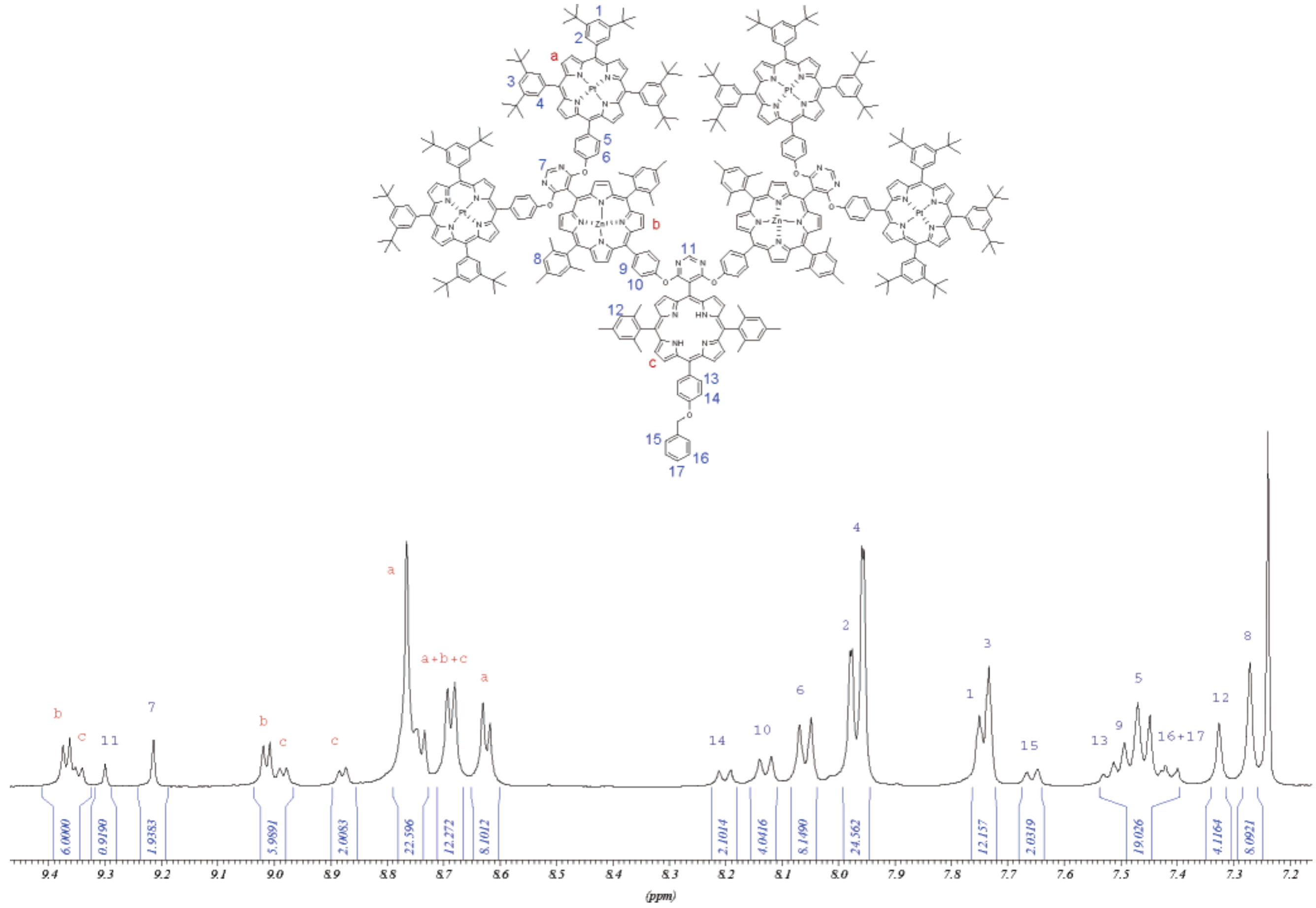

FIGURE 4. Aromatic region of the ^{1}H NMR spectrum of G_2 dendron **7b** (M_1 = Pt, M_2 = Zn, M_3 = H,H).

revealed the presence of the trisubstituted dendrimer in addition to the desired G_1 dendrimer **12** and chromatographic purification of the G_1 dendrimer from this analogue lacking one dendron could not be achieved.[28]

Characterization. Two important challenges concerning dendrimer synthesis are the efficient purification and thorough characterization of the dendritic macromolecules. The multiporphyrinic compounds in this work were all purified by simple column chromatography on silica (or preparative TLC for some higher-generation dendrons/dendrimers), and the products were obtained in essentially pure form without the use of preparative gel permeation chromatography (GPC) that is usually required to efficiently purify such multiporphyrin dendrimers. All porphyrins and multiporphyrinic compounds were fully characterized using NMR spectroscopy (^{1}H and additional ^{13}C and 2D experiments), mass spectrometry (electrospray or MALDI-TOF), and UV−vis spectroscopy. The ^{1}H NMR spectra of the different generation dendrons clearly show the signals corresponding with the different porphyrin layers, and the integration indicates which generation is involved. An example is given in Figure 4, in which the signals in the aromatic region of the ^{1}H NMR spectrum of G_2 dendron **7b** are easily connected to the different generation porphyrin ligands.

The successively metalated porphyrin ligands could also easily be identified by ^{13}C NMR spectroscopy. The metalloporphyrins show well-resolved carbon signals at distinct ppm values for their pyrrolic α- and β-carbon atoms, while the Fb porphyrins give rise to very broad signals for these carbon atoms (due to NH tautomerization). For some of the higher-generation dendrons and dendrimers, complete assignment of the signals in the ^{13}C NMR spectrum could not be accomplished due to the low abundance of some (core) signals. The electrospray mass spectra of the higher-generation dendrons and dendrimers display peaks consistent with multiply charged species. Due to the detection limit of the used electrospray mass apparatus (m/z ≈ 4000), MALDI-TOF MS spectra were taken for some higher-generation multiporphyrinic systems. MALDI spectra with very high resolution were obtained on using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (BMPM) as a matrix. Analytical scale GPC indicated that the prepared compounds were obtained pure and monodisperse (polydispersity (PDI) < 1.070). UV−vis analysis was carried out for the different generation multiporphyrins, and all spectra showed an intense Soret band and a number of Q-bands according to the metalation state. The higher-generation (metallo)porphyrin dendrons and dendrimers show absorption spectra that are composed of the signals of the different porphyrinic building blocks. The UV−vis spectrum of G_1 dendron **6b** (M_1 = Pt, M_2 = H,H), for instance, clearly shows absorption peaks due to the peripheral Pt porphyrins as well as the interior Fb porphyrin (Figure 5).

Conclusions

In conclusion, a novel convergent synthetic strategy, based on nucleophilic aromatic substitution on *meso*-dichloropyrim-

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[28] The MALDI-TOF MS spectrum has been enclosed in the Supporting Information.

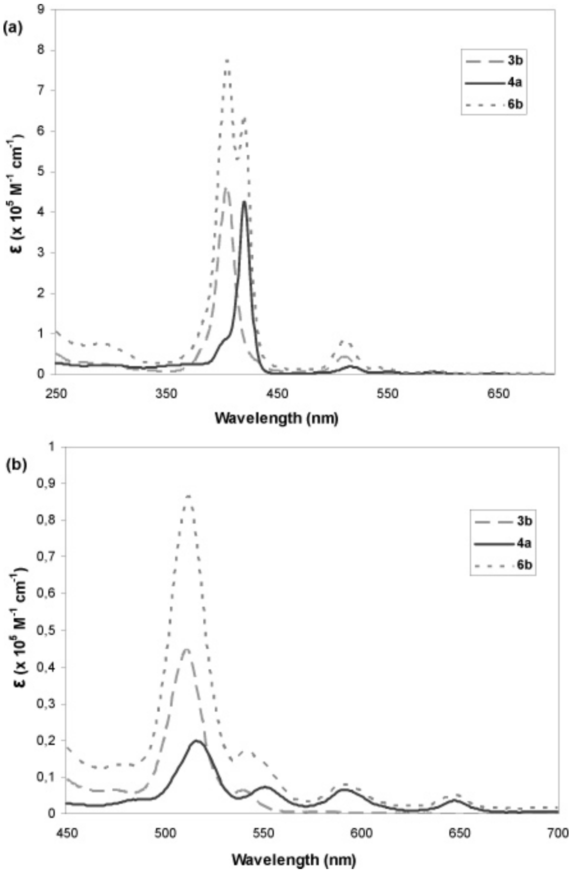

FIGURE 5. UV−vis absorption spectra of Pt G_0 dendron **3b**, porphyrin monomer **4a**, and G_1 dendron **6b**: (a) full spectrum, (b) enlarged Q-band region.

idinyl substituted porphyrin building blocks, has afforded all-porphyrin dendrons and dendrimers containing up to 13 porphyrins joined through diaryl ether linkages and equipped with different metals in the successive generations. Because of the ortho,ortho′-heteroaryl linkages, the porphyrins are closer together in space than in other multiporphyrinic systems reported.[5−14] The unique ortho,ortho′-substitution pattern and a proper choice of the metalation sequence could cause a significant change in the energy transfer properties, and hence, the obtained multiporphyrin arrays have potential to be used for further elaboration of the photosynthetic reaction process.

Experimental Section

5,10,15-Tris(3,5-di-*tert*-butylphenyl)-20-(4-hydroxyphenyl)-porphyrin (3a). Peripheral porphyrin **3a** (∼1 g) was prepared by a previously reported method (see ref 21a) and characterized by ^{1}H and ^{13}C NMR, MS (ESI/MALDI), and UV−vis spectroscopy. Purity was determined to be >95% by NMR spectroscopy.

Platinum(II) 5,10,15-Tris(3,5-di-*tert*-butylphenyl)-20-(4-hydroxyphenyl)porphyrin (3b). $PtCl_2$ (138 mg, 519 μmol, 5 equiv) was dissolved in PhCN (30 mL), and the solution was heated at reflux during 1 h, after which AB_3 porphyrin **3a** (100 mg, 103 μmol, 1 equiv) was slowly added to the hot solution and the mixture was heated at reflux for another 6 h. The solvent was evaporated and Pt(II) porphyrin **3b** was purified by flash chromatography (silica, eluent CH_2Cl_2/heptane 3:2), which afforded 104 mg (87%) of an orange-colored solid. MS (ESI) calcd for $C_{68}H_{76}N_4OPt$: 1160.4; found: *m/z* 1161.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83−8.75 (m, 8H, H_β-Pt porph), 8.04−7.95 (m, 6H), 7.98 (d, ^3J = 8.0 Hz, 2H), 7.78−7.75 (m, 3H), 7.07 (d, ^3J = 8.0 Hz, 2H), 1.50 (s, 54H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 (C_i-OH), 148.9 (C_i-*t*-Bu), 141.1 and 141.0 (C_α-Pt porph), 140.6, 134.8 (CH-*m*-OH), 134.0, 132.2, 130.9, 130.7, 130.5, 129.1 (CH), 129.0, 123.5, 121.6, 121.1 (CH), 113.6 (CH-*o*-OH), 35.1, 31.8 (CH_3); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 404.5 (5.667), 511.1 (4.635), 540.0 (3.807).

Zinc(II) 5,10,15-Tris(3,5-di-*tert*-butylphenyl)-20-(4-hydroxyphenyl)porphyrin (3c). $Zn(OAc)_2{\cdot}2H_2O$ (170 mg, 774 μmol, 5 equiv) was added to a solution of AB_3 porphyrin **3a** (150 mg, 155 μmol, 1 equiv) in CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 6 h (gradual color change from dark purple to pink-purple). The metalation progress was monitored by UV−vis spectroscopy. The solution was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and water. The organic layer was dried with $MgSO_4$, and the solvent was removed, affording Zn(II) porphyrin **3c** as a pink solid (in a quantitative yield). MS (ESI) calcd for $C_{68}H_{76}N_4OZn$: 1030.8; found: *m/z* 1028.5; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02−8.95 (m, 8H, H_β-Zn porph), 8.10−8.05 (m, 8H), 7.79 (t, ^4J = 1.5 Hz, 3H), 7.13 (d, ^3J = 9.1 Hz, 2H), 5.15 (s_{br}, 1H, OH), 1.53 (s, 54H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1 (C_i-OH), 150.4, 148.5, 141.9, 135.5, 135.4 (CH), 132.2 (CH), 131.7 (CH), 129.7 (CH), 129.6 (CH), 122.42, 122.36, 120.7 (CH), 120.3, 113.5 (CH-*o*-OH), 35.0, 31.8 (CH_3); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 292.7 (4.673), 401.5 (4.598), 421.6 (5.583), 549.6 (4.317), 588.1 (3.800).

5-(4-Benzyloxyphenyl)-15-(4,6-dichloropyrimidin-5-yl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (4a). To 850 mL of CH_2Cl_2, purged with Ar for 15 min (while stirring vigorously), were added mesityldipyrromethane (2.643 g, 10 mmol), *p*-benzyloxybenzaldehyde (1.060 g, 5 mmol), and 4,6-dichloropyrimidine-5-carbaldehyde (1.330 g, 7.5 mmol), immediately followed by the addition of $BF_3{\cdot}OEt_2$ (0.5 mL, 4 mmol), and the solution was stirred at room temperature for 1 h (under an Ar atmosphere and protected from light). *p*-Chloranil (2.460 g, 10 mmol) was subsequently added, and the mixture was heated at reflux for 1 h. The solvent was removed under vacuum, and the crude porphyrin was purified by column chromatography (silica, eluent CH_2Cl_2/petroleum ether 5:1). Porphyrin monomer **4a** was obtained as a purple solid (0.740 g, 17%). A_2B_2 porphyrin **1** was also obtained in a substantial amount (0.250 g, 8%). MS (ESI) calcd for $C_{55}H_{44}Cl_2N_6O$: 875.9; found: *m/z* 875.1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H, H_{pyrim}), 8.87 (d, ^3J = 4.8 Hz, 2H, H_β porph), 8.78 (d, ^3J = 4.4 Hz, 2H, H_β porph), 8.72 (d, ^3J = 4.8 Hz, 2H, H_β porph), 8.59 (d, ^3J = 4.4 Hz, 2H, H_β porph), 8.15 (d, ^3J = 8.4 Hz, 2H), 7.65 (d, ^3J = 7.4 Hz, 2H, H_o), 7.52 (t, ^3J = 7.4 Hz, 2H, H_m), 7.45 (t, ^3J = 7.4 Hz, 1H, H_p), 7.39 (d, ^3J = 8.4 Hz, 2H), 7.32 (s, 4H, H_{mesit}), 5.38 (s, 2H, CH_2), 2.66 (s, 6H), 1.89 (s, 12H), −2.46 (s_{br}, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (C−Cl), 158.9, 158.0 (CH_{pyrim}), 150−141 (br, C_α porph), 139.4, 138.0, 137.0, 135.5 (CH-*m*-OBn), 135.0, 134.4, 131.9 (br, CH_β porph), 130.2 (br, CH_β porph), 128.8 (CH), 128.2 (CH), 127.9 (CH_{mesit}), 127.7 (CH), 121.3, 119.2, 113.2 (CH-*o*-OBn), 106.9 (*meso*-C), 70.4 (CH_2), 21.7 (CH_3), 21.5 (CH_3); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 420.5 (5.631), 516.1 (4.299), 551.1 (3.864), 591.3 (3.817), 647.4 (3.557); IR (KBr) ν_{max} (cm^{-1}) 3315, 2917, 1605, 1505, 1451, 1391, 1340, 1226, 1173, 1022, 966, 808, 732.

Nickel(II) 5-(4-Benzyloxyphenyl)-15-(4,6-dichloropyrimidin-5-yl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (4c). $NiBr_2$ (25 mg, 114 μmol, 5 equiv) was added to a solution of porphyrin monomer **4a** (20.0 mg, 22.8 μmol, 1 equiv) in DMF (1 mL), and the mixture was heated at reflux for 5 min (color change from dark purple to red). The solution was diluted with Et_2O and washed with water. The organic layer was dried with Na_2SO_4, and the solvent was removed, affording Ni(II) porphyrin **4c** as a red solid (in a quantitative yield). MS (ESI) calcd for $C_{55}H_{42}Cl_2N_6NiO$: 932.6; found: *m/z* 933.2; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (s, 1H, H_{pyrim}), 8.75 (d, ^3J = 4.6 Hz, 2H, H_β-Ni porph), 8.64 (d, ^3J = 5.5 Hz, 2H, H_β-Ni porph), 8.58 (d, ^3J = 5.5 Hz, 2H, H_β-Ni porph), 8.45 (d, ^3J = 5.5 Hz, 2H, H_β-Ni porph), 7.93 (d, ^3J = 8.2 Hz, 2H), 7.58 (d, ^3J = 7.3 Hz, 2H, H_o), 7.46 (t, ^3J = 7.3 Hz, 2H, H_m), 7.41

(t, $^3J = 7.4$ Hz, 1H, H_p), 7.28 (d, $^3J = 8.2$ Hz, 2H), 7.21 (s, 4H, H_{mesit}), 5.29 (s, 2H, CH_2), 2.56 (s, 6H), 1.81 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9 (C-Cl), 158.7, 157.9 (CH_{pyrim}), 143.3 (C_α-Ni porph), 143.2 (C_α-Ni porph), 142.6 (C_α-Ni porph), 140.9 (C_α-Ni porph), 139.0, 137.9, 136.95, 136.86, 134.7 (CH-*m*-OBn), 134.1, 133.4, 133.0 (CH), 132.7 (CH), 131.3 (CH), 129.5 (CH), 128.7 (CH), 128.1 (CH), 127.8 (CH_{mesit}), 127.7 (CH), 119.8, 118.2, 113.3 (CH-*o*-OBn), 106.8 (*meso*-C), 70.3 (CH_2), 21.42 (CH_3), 21.40 (CH_3); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 297.0 (4.322), 416.1 (5.474), 529.3 (4.350), 559.8 (3.866).

General NAS Procedure. Porphyrin monomer **4a** (1 equiv) and the G_x dendron (3,5-di-*tert*-butylphenol, **3a**, **3b**, **6a**, **6c**, or **9**; 2.2 equiv) were dissolved together in DMF. K_2CO_3 (5 equiv) was added to this solution, and the mixture was heated at 90 °C during 48 h (under an Ar atmosphere). DMF was removed (under reduced pressure), and the residue was dissolved in Et_2O and washed with water, and the organic layer was dried with $MgSO_4$ and evaporated in a vacuum. The porphyrin dendrons were purified by column chromatography (silica).

General Deprotection Procedure. To a solution of the protected G_x dendron (**5a**, **5b**, or **8**; 1 equiv) in CH_2Cl_2 an excess of BCl_3 (1 M in hexane, 10 equiv) was added at −78 °C, and the mixture was kept at −18 °C (freezer) during 3 days. Ice water was added, and the organic phase was separated, washed with water, dried with $MgSO_4$, and evaporated in a vacuum. The porphyrin dendrons were purified by column chromatography (silica).

G_1 Dendron ($M_1 = M_2$ = H,H; R = Bn) (5a). Eluent CH_2Cl_2/hexane 2:1; Yield 85% (153 mg); MS (ESI) calcd for $C_{191}H_{198}N_{14}O_3$: 2737.7; found: *m/z* 2738.1 $[M + H]^+$, 1370.2 $[M + 2H]^{2+}$; MS (MALDI, IAA) *m/z* 2732.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.33 (d, $^3J = 4.4$ Hz, 2H, H_β porph mon), 9.27 (s, 1H, H_{pyrim}), 8.98 (d, $^3J = 4.4$ Hz, 2H, H_β porph mon), 8.88−8.76 (m, 20H, H_β porph), 8.18 (d, $^3J = 8.8$ Hz, 2H), 8.16 (d, $^3J = 8.4$ Hz, 4H), 8.05 (d, $^4J = 1.5$ Hz, 12H), 7.76 (t, $^4J = 1.5$ Hz, 6H), 7.63 (d, $^3J = 7.4$ Hz, 2H, H_o), 7.51−7.36 (m, 9H), 7.32 (s, 4H, H_{mesit}), 5.35 (s, 2H, CH_2), 2.63 (s, 6H), 1.97 (s, 12H), 1.50 (s, 108H), −2.26 (s_{br}, 2H, NH), −2.74 (s_{br}, 4H, NH); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 421.3 (6.062), 516.9 (4.644), 552.7 (4.337), 592.1 (4.099), 649.3 (4.053).

G_1 Dendron (M_1 = Pt, M_2 = Zn; R = H) (6c). Metalation procedure: cfr. **3c** (70 mg scale). MS (ESI) calcd for $C_{184}H_{186}N_{14}O_3Pt_2Zn$: 3097.1; found: *m/z* 3096.5 $[M + H]^+$, 1549.3 $[M + 2H]^{2+}$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.43 (d, $^3J = 5.1$ Hz, 2H, H_β-Zn porph), 9.28 (s, 1H, H_{pyrim}), 9.07 (d, $^3J = 4.4$ Hz, 2H, H_β-Zn porph), 8.94 (d, $^3J = 4.4$ Hz, 2H, H_β-Zn porph), 8.84−8.78 (m, 10H, H_β-Zn/Pt porph), 8.73 (d, $^3J = 5.1$ Hz, 4H, H_β-Pt porph), 8.68 (d, $^3J = 5.1$ Hz, 4H, H_β-Pt porph), 8.14−8.08 (m, 6H), 8.01 (d, $^4J = 1.5$ Hz, 4H), 7.99 (d, $^4J = 1.5$ Hz, 8H), 7.77−7.74 (m, 6H), 7.52 (d, $^3J = 8.0$ Hz, 4H), 7.30 (s, 4H, H_{mesit}), 7.08 (d, $^3J = 8.0$ Hz, 2H), 2.61 (s, 6H), 1.95 (s, 12H), 1.50 (s, 36H), 1.48 (s, 72H); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 293.8 (4.697), 404.9 (5.849), 422.3 (5.850), 511.0 (4.809), 547.8 (4.434), 589.4 (3.610); GPC ($CHCl_3$) $M_w = 2095$, $M_n = 1964$, PDI = 1.067.

G_2 Dendron (M_1 = Pt, M_2 = Zn, M_3 = H,H; R = Bn) (7b). Purification by preparative TLC (silica, eluent CH_2Cl_2/petroleum ether 1:1); Yield 48% (22 mg); MS (MALDI, BMPM) calcd for $C_{423}H_{414}N_{34}O_7Pt_4Zn_2$: 6997.1; found: *m/z* 6998.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (d, $^3J = 4.7$ Hz, 4H, H_β-Zn porph), 9.35 (d, $^3J = 4.7$ Hz, 2H, H_β-NH porph), 9.30 (s, 1H, H_{pyrim}), 9.21 (s, 2H, H_{pyrim}), 9.01 (d, $^3J = 4.7$ Hz, 4H, H_β-Zn porph), 8.98 (d, $^3J = 4.7$ Hz, 2H, H_β-NH porph), 8.88 (d, $^3J = 4.7$ Hz, 2H, H_β-NH porph), 8.80−8.73 (m, 22H, H_β porph), 8.68 (d, $^3J = 5.0$ Hz, 12H, H_β-Pt/Zn porph), 8.62 (d, $^3J = 5.0$ Hz, 8H, H_β-Pt porph), 8.20 (d, $^3J = 8.7$ Hz, 2H), 8.13 (d, $^3J = 8.4$ Hz, 4H), 8.06 (d, $^3J = 8.4$ Hz, 8H), 7.98 (d, $^4J = 1.6$ Hz, 8H), 7.95 (d, $^4J = 1.6$ Hz, 16H), 7.75 (s, 4H), 7.73 (s, 8H), 7.66 (d, $^3J = 7.2$ Hz, 2H, H_o), 7.54−7.38 (m, 17H), 7.33 (s, 4H, H_{mesit}), 7.27 (s, 8H, H_{mesit}), 5.39 (s, 2H, CH_2), 2.64 (s, 6H), 2.60 (s, 12H), 1.97 (s, 12H), 1.88 (s, 24H), 1.48 (s, 72H), 1.47 (s, 144H), −2.23 (s_{br}, 2H, NH); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 293.5 (4.982), 405.2 (6.090), 425.0 (6.078), 511.6 (5.065), 548.4 (4.719), 590.2 (4.075), 647.9 (3.517); GPC ($CHCl_3$) $M_w = 6851$, $M_n = 6585$, PDI = 1.040.

G_0 Dendrimer ($M_1 = M_4$ = H,H) (11a). To a solution of porphyrin **3a** (170 mg, 180 μmol) and A_2B_2 porphyrin **1** (34 mg, 40 μmol) in DMF (5 mL), Cs_2CO_3 (230 mg, 0.70 mmol) was added. The mixture was heated at 60 °C during 48 h. The mixture was than diluted with CH_2Cl_2, washed with water, and dried with $MgSO_4$. The crude dendrimer was purified by column chromatography (silica, eluent CH_2Cl_2) to obtain the pure pentaporphyrin **11a** as a purple solid (120 mg, 65%). MS (ESI) calcd for $C_{318}H_{342}N_{24}O_4$: 4564.4; found: *m/z* 2282.1 $[M + 2H]^{2+}$, 1522.2 $[M + 3H]^{3+}$, 1141.9 $[M + 4H]^{4+}$, 967.2 $[G_0]$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, $^3J = 4.8$ Hz, 4H, H_β porph core), 9.27 (s, 2H, H_{pyrim}), 9.04 (d, $^3J = 4.8$ Hz, 4H, H_β porph core), 8.84 (dd, 16H, H_β porph periph), 8.79 (dd, 16H, H_β porph periph), 8.17 (d, $^3J = 8.5$ Hz, 8H), 8.05 (d, $^4J = 1.7$ Hz, 8H), 8.02 (d, $^4J = 1.7$ Hz, 16H), 7.77 (t, $^4J = 1.7$ Hz, 4H), 7.70 (t, $^4J = 1.7$ Hz, 8H), 7.53 (d, $^3J = 8.5$ Hz, 8H), 7.36 (s, 4H, H_{mesit}), 2.63 (s, 6H), 2.09 (s, 12H), 1.50 (s, 72H), 1.44 (s, 144H), −2.00 (s_{br}, 2H, NH), −2.74 (s_{br}, 8H, NH); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 421.4 (6.361), 516.6 (4.970), 551.1 (4.836), 592.0 (4.560), 647.7 (4.464); GPC ($CHCl_3$) $M_w = 3965$, $M_n = 3839$, PDI = 1.033.

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Supporting Information Available: Additional experimental data and selected spectra (NMR, MS, GPC, and UV−vis) for the presented multiporphyrin dendrons and dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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