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Synthetic Aspects of Porphyrin Dendrimers

Wouter Maes[a] and Wim Dehaen*[a]

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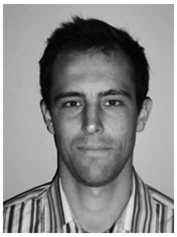
This Microreview presents a concise overview of the different synthetic approaches that have been applied to porphyrin dendrimers over the years, with the porphyrin macrocycle(s) being embedded variously as the dendritic cores, at the peripheries, within the branching units, or spread throughout entire dendritic architectures.

1. Introduction

Dendrimers are highly branched, monodisperse, well-defined macromolecules that are synthesized by iterative divergent or convergent protocols to different sizes or generations (G_n), ultimately affording globular structures up to the nanoscopic level.[1] The unique properties associated with the perfectly branched dendritic architectures are highly appreciated and have been validated in a substantial amount of different application domains during the last two decades.

The introduction of porphyrins into dendritic structures began in the early days of dendrimer chemistry, mainly as core entities, due to the morphological resemblance of these macrostructures to natural hemoproteins. Over the years, porphyrin macrocycles have also been introduced as dendritic surface groups or within the dendritic branches.[2] The combination of the peculiar photophysical and redox features of porphyrinoids and the perfectly synthetically controllable hyperbranched dendritic frameworks has enabled porphyrin/dendrimer hybrid molecules to be used in a broad array of diverse, mainly biomimetic, fields of application, ranging from reversible O_2 binding, light-harvesting (LH), artificial photosynthesis, and (oxidation) catalysis to biomedical applications [e.g., oxygen imaging and photodynamic therapy (PDT)] and optoelectronics [e.g., organic light-emitting diodes (OLEDs)].

In this Microreview we summarize the synthetic pathways that have been explored for the construction of various kinds of porphyrin dendrimers, with particular attention on the most recent contributions to the field. Emphasis has been placed on the structural diversity of porphyrin dendrimers, whereas the applications of the dendritic macromolecules are only briefly touched upon. Only entirely covalently constructed porphyrin dendrimers, in the strictest sense, are covered. Nondendritic oligomeric assemblies with embedded porphyrins, dendronized or dendritic star polymers and related materials, and structurally imperfect



Wouter Maes was born in 1978 in Neerpelt, Belgium. He obtained his PhD at the KU Leuven (Belgium) in 2005 under the supervision of Prof. W. Dehaen, working on the synthesis and application of dendrimers incorporating porphyrins and other heterocyclic building blocks. Since that time, he has been working as a postdoctoral fellow of the Fund for Scientific Research-Flanders (FWO-Vlaanderen) in the laboratory of Prof. W. Dehaen, focusing mainly on porphyrins and related macrocycles, and also (hetera)calixarenes. During this period he undertook short postdoctoral stays in Paris (with Dr. E. Rose, 3 months in 2007) and Oxford (with Prof. H. Anderson, 2 months in 2009), both in the field of (synthetic) porphyrin chemistry.

Wim Dehaen was born in 1962 in Kortrijk, Belgium. He obtained his PhD at the KU Leuven (Belgium) in 1988 under the guidance of Prof. G. L'abbé on a study involving the rearrangements of 5-diazoalkyl-1,2,3-triazole derivatives. After postdoctoral stays in Israel (1988–1990), Denmark (3 months in 1990), the UK (3 months in 1994), and Belgium (1990–1998) he was appointed associated professor at the KU Leuven (Belgium) in 1998, becoming a full professor at the same university in 2004. Up to 2009, over 250 publications on his work on heterocyclic and supramolecular chemistry have appeared in international journals.

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[a] Department of Chemistry, Katholieke Universiteit Leuven,
Celestijnenlaan 200F, 3001 Leuven, Belgium
Fax: +32-16-327990
E-mail: wim.dehaen@chem.kuleuven.be

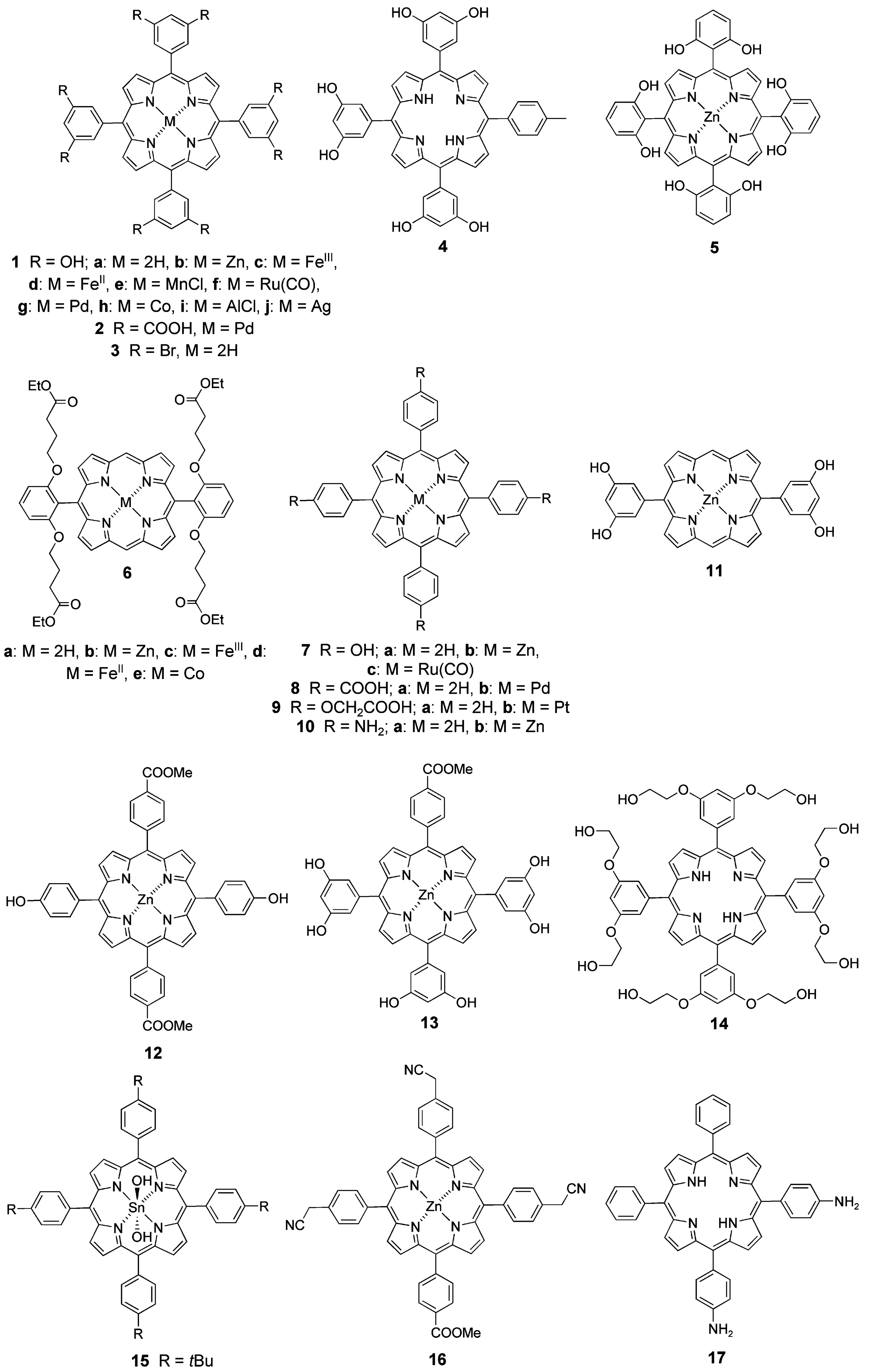


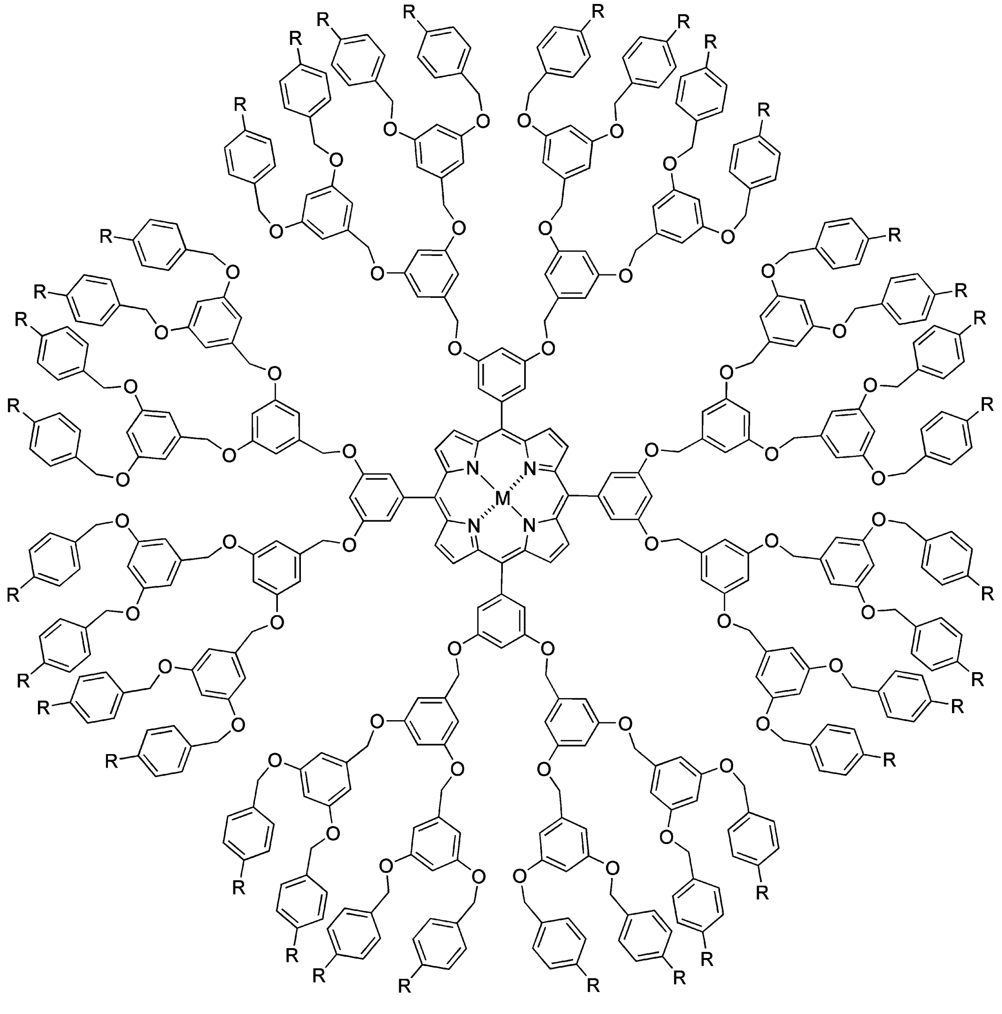
Figure 1. Porphyrin macrocycles **1**–**17** applied as dendritic core reagents.

hyperbranched porphyrin analogues are therefore not surveyed.[3,4] Dendritic systems incorporating porphyrinoid analogues, derived macrocycles or phthalocyanines, or dendrimers built by noncovalent supramolecular approaches[5] are also not discussed. The wide scope of porphyrin dendrimers synthesized to date is divided into three subclasses, based upon the subunits – core, branches, and periphery – that can be distinguished within the dendritic architecture. For each subclass, an example from our own research group is discussed, and dendrimers from other research teams are grouped according to their structural resemblance or the applied synthetic protocol. The description of the synthetic procedures mainly stresses the introduction of the porphyrin units, rather than the other dendritic segments. Synthetic methodologies for nonporphyrin-containing core entities, surface groups, or dendrons (e.g., standard Fréchet-type dendrons) are easily retrievable from the literature.

2. Porphyrin-Core Dendrimers

The majority of porphyrin dendrimers reported to date possess a (metallo)porphyrin unit as the interior core moiety only, in contrast to the regular trend observed in dendrimer chemistry in which functionalities are mostly introduced at the surfaces of readily (commercially) available dendritic structures, such as poly(amidoamine) (PAMAM) dendrimers. Encapsulation of a sterically shielded porphyrin core within a surrounding dendritic hydrophobic shell is obviously bio-inspired, mimicking natural hemoproteins and their associated biological functions. Pioneering work in the field of porphyrin dendrimers was performed in the laboratories of Aida, Diederich, and Suslick.[6–8]

The first example was described by Aida and co-workers in 1993;[6a] their convergent approach involved covalent attachment of various generations of Fréchet poly(benzyl ether) dendron bromides to free-base (Fb) 5,10,15,20-tetrakis(3,5-dihydroxyphenyl)porphyrin (**1a**) under alkaline Williamson ether conditions (Figures 1 and 2). The dendritic surfaces were varied from methyl ethers to esters and ionic (carboxylate or ammonium) functionalities to afford water solubility and electron- or energy-transfer events, and reversible O_2 binding within these structures was evaluated.[6] Mixed aldehyde condensations of 3,5-dimethoxybenzaldehyde and *p*-tolualdehyde with dipyrrylmethane and



18: M = 2H, Zn; R = CO_2Me, COO^-, $CONH(CH_2)_2N^+Me_3Cl^-$, $CONH(CH_2)_2NH_2$

Figure 2. Aida's four-layered porphyrin-core dendrimers **18**.

subsequent removal of the methyl ethers with BBr_3 afforded suitable porphyrin cores (e.g., A_3B-porphyrin **4**, Figure 1) for smooth construction of analogous porphyrin-centered dendrimers with designed structural defects.[6g]

Suslick et al. applied the $Mn^{III}Cl$ A_4-porphyrin core **1e** (Figure 1) to prepare Fréchet-type poly(phenyl ester) dendrimers **19** through dicyclohexylcarbodiimide-promoted (DCC-promoted) coupling {catalyzed by DPTS [4-(dimethylamino)pyridinium 4-toluenesulfonate]} of carboxy-terminated dendritic wedges with *tert*-butyl surface groups (Figure 3), and applied these dendrimers as oxidatively robust regioselective (ep)oxidation catalysts, benefiting from

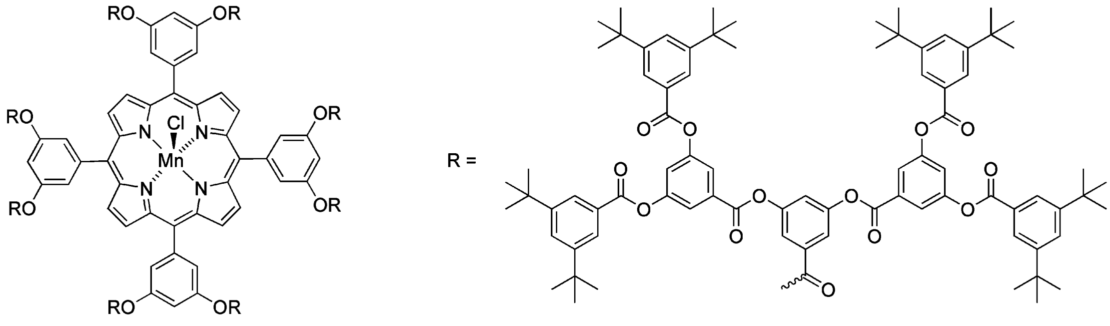


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Figure 3. Suslick's second-generation porphyrin dendrimer **19**.

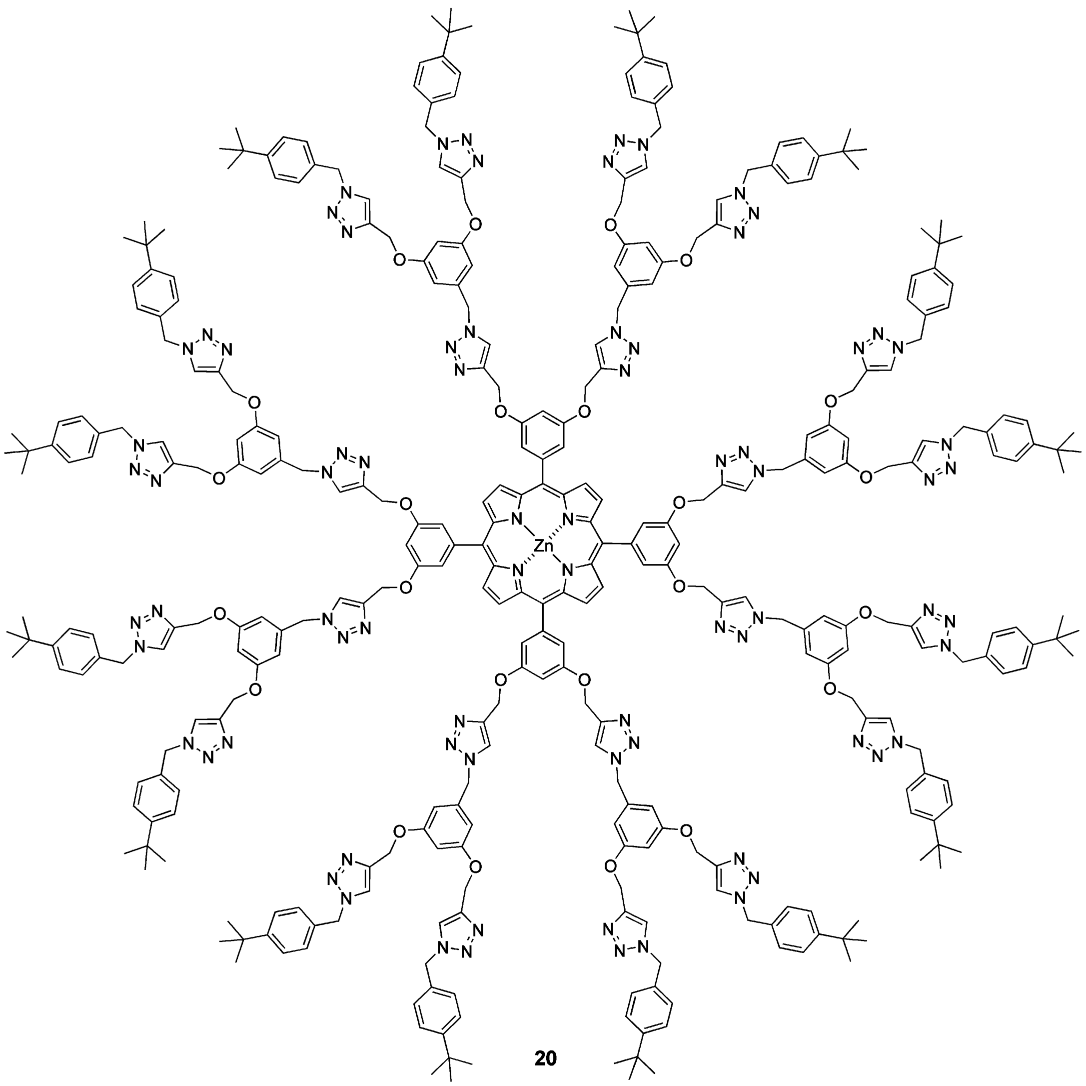

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Figure 4. Example of a porphyrin–core dendrimer (**20**) with two layers of internal triazole units (Kimura et al.).

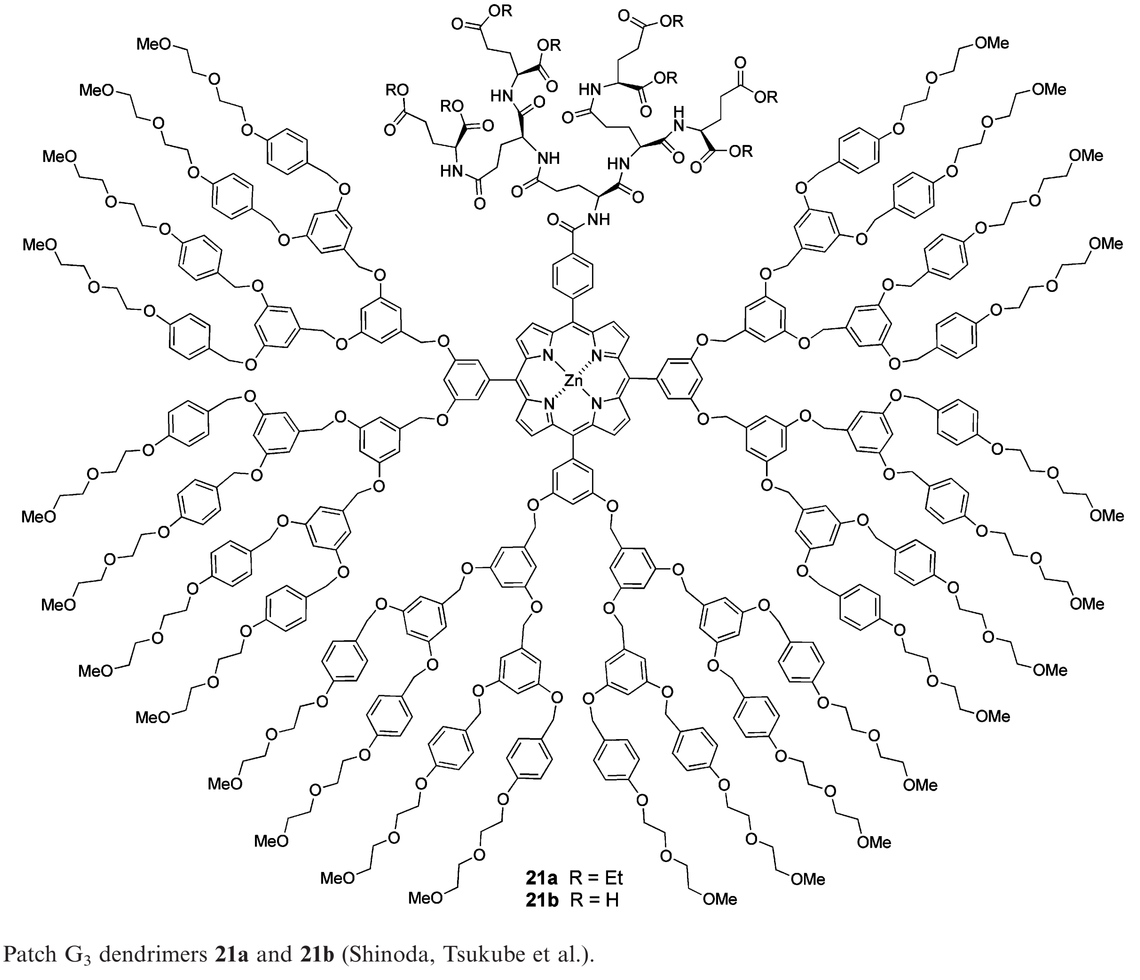
the steric protection of the catalytic metal center.[8a,8b] The same group also demonstrated strong control over axial ligation of nitrogen-centered Lewis bases in analogous Zn–porphyrin dendrimers through shape selectivity induced by the dendrons.[8c] In this study, small G_1 amide dendrons were alternatively attached to Zn–5,10,15,20-tetrakis(2,6-dihydroxyphenyl)porphyrin (**5**, Figure 1) (DCC/DPTS; 35% yield).

Diederich and associates constructed dendritic Fe–porphyrin heme analogues in a divergent fashion starting from the Zn–*trans*-A_2B_2-porphyrin **6b** (Figure 1), with successive construction of the aliphatic poly(ether amide) Newkome-type dendrons by peptide coupling protocols (iterative ester hydrolysis and DCC coupling).[7]

2.1. Fréchet-Type Dendrons

A number of related porphyrin-core dendritic structures based on Fréchet-type benzyl ether branches have been prepared during the last decade. Fréchet and co-workers prepared porphyrin-centered dendrimers (Ph surface groups) similar to those designed by Aida and evaluated the effect of the macromolecular dendritic architecture on site isolation.[9] In collaboration with the research groups of De Schryver and Fréchet, we have investigated the effect of the porphyrin core structure on the photophysical and hydrodynamic properties of porphyrin dendrimers in solution. For this purpose, three generations of dendrons were alternatively attached to the A_4-porphyrin core **7a** [5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin, Figure 1].[10a] The fluorescence quenching kinetics of this dendrimer series with different types of quenchers were studied more recently.[10b]

Nikles et al. prepared Fréchet-type porphyrin-centered dendrimers by anchoring poly(benzyl ether) bromide wedges to 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (**8a**, Figure 1), and performed preliminary studies on the hydrodynamic properties and fluorescence quenching within these structures.[11b–11d] First-generation porphyrin-core dendrimers with carbazole peripheral moieties were alternatively synthesized from Zn–5,10,15,20-tetrakis(3,5-dihydroxyphenyl)porphyrin (**1b**, Figure 1).[11a] Miller and co-workers attached two G_2 Fréchet dendrons to the A_2B_2-porphyrin core **11** [Zn–5,15-bis(3,5-dihydroxyphenyl)porphyrin, Figure 1] under standard alkaline conditions (K_2CO_3, 18-crown-6, acetone; 43% yield) and studied the electrochemistry within this dendritic system.[12] Che et al. employed Ru–porphyrin dendrimers, synthesized through convergent attachment of G_0–G_2 Fréchet-type dendritic mesylates (rather than the bromides) to polyphenolic



21a R = Et
21b R = H

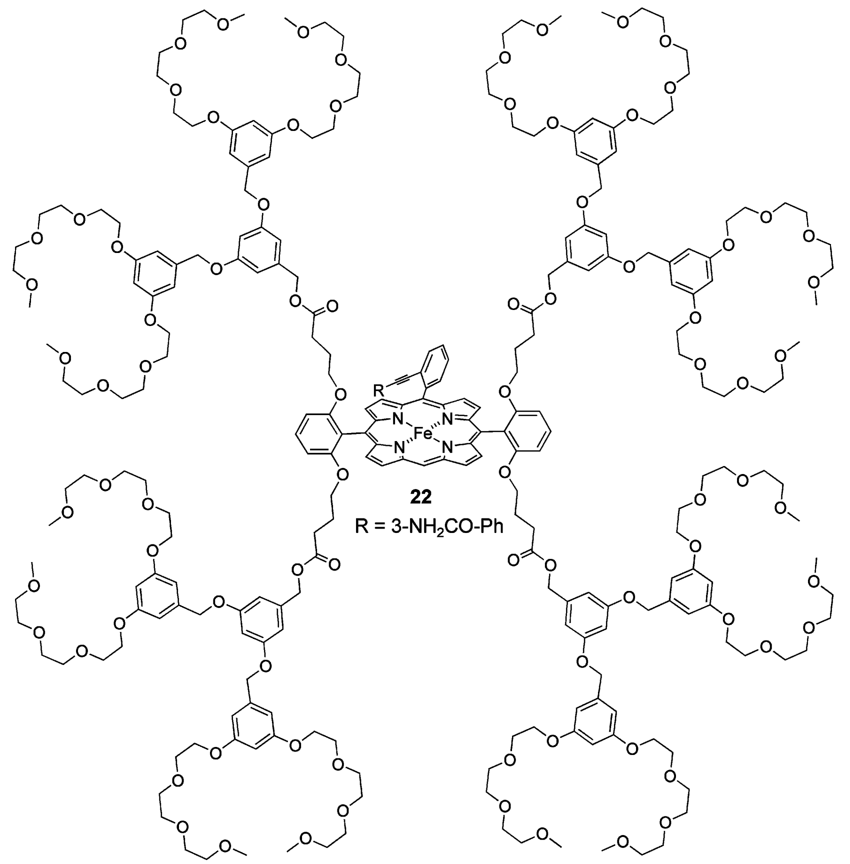
Figure 5. Patch G_3 dendrimers **21a** and **21b** (Shinoda, Tsukube et al.).

Ru(CO)–porphyrin cores **1f** or **7c** (Figure 1) in alkaline medium, as highly selective homogeneous catalysts for alkene epoxidation and cyclopropanation.[13]

Akai, Tsukube et al. (re)investigated energy transfer within Aida's four-layered benzyl ether dendrimer.[14] The morphology dependence of the excitonic energy transfer was studied by comparison of dendrimers with a different number of dendrons.[14b] Shinkai et al. revealed that Aida's porphyrin dendrimers can act as hosts for C_{60}, the affinity originating from the dendritic branches.[15] Kataoka and coworkers employed polyion complex micelles based on Aida's ionic porphyrin dendrimers (Figure 2) as supramolecular nanocarriers to enhance their photodynamic efficacy.[16] Aida et al. more recently reported a Zn–porphyrin dendrimer, synthesized from *trans*-A_2B_2 porphyrin core **12** (Figure 1), to which two G_2/G_3 poly(benzyl ether) dendrons were attached, that formed a *J*-aggregate through π-stacking.[17] Aggregation is promoted by the formation of a hydrogen-bonded supramolecular polymer through the remaining opposite carboxylic acid functions, obtained by straightforward hydrolysis of the ester moieties. Upon spin-coating, the dendron-coated porphyrin forms a chiroptically active film, and the structural flexibility allows spectroscopic visualization of vortex flows.

Zimmerman, Suslick, and co-workers applied porphyrin-centered dendrimers with homoallyl surface groups, synthesized from porphyrin core **1a** (Figure 1) to which eight G_3 dendritic Fréchet wedges with carboxyl focal units and peripheral 3,5-bis(but-3-enyloxy)phenyl moieties were attached under DCC coupling conditions (DPTS-catalyzed; 54% yield) for monomolecular imprinting in the dendritic interior.[18a] Neighboring double bonds on the periphery were cross-linked intramolecularly by use of the Grubbs (type I) catalyst (ring-closing metathesis) and the porphyrin core template could be removed by hydrolysis. Binding studies of the resulting imprinted host macromolecule showed selective and tight complexation of porphyrin guests with appropriate sizes and numbers of hydrogen bonding sites. This research was later extended to G_4 tetradendron dendrimers built around the tetraphenolic porphyrin core **7a** (Figure 1).[18c] Similar G_3 dendrimers containing an $Sn(Cl_2)$–metalloporphyrin core have been exploited for the construction of covalent organic nanotubes through successive oligomerization of the Sn–porphyrin interior with succinic acid as the bridging bidentate ligand, extensive cross-linking of the dendrons through their alkene terminals, and subsequent removal of the porphyrin template oligomer by transesterification.[18b]

Choi, Shin et al. synthesized analogous benzyl aryl ether dendrimers with a (Zn) porphyrin core through the reaction between 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (**8a**, Figure 1) and Fréchet dendrons with benzylic alcohol focal points and peripheral vinyl moieties in the presence of EDC {1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide} and DMAP [4-(dimethylamino)pyridine].[19]



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R = 3-NH_2CO-Ph

Figure 6. Hemoglobin model G_2 dendrimer **22** (Diederich et al.).

Very recently, several dendritic porphyrins in which benzyl ether dendritic azides were "clicked" to an acetylene-terminated Zn–porphyrin core (derived from **1b**, Figure 1) through Cu-catalyzed cycloaddition reactions (52–90%) to afford 1,2,3-triazole links (Figure 4) were designed by Kimura et al.[20] Axial ligation of the internal triazole moieties

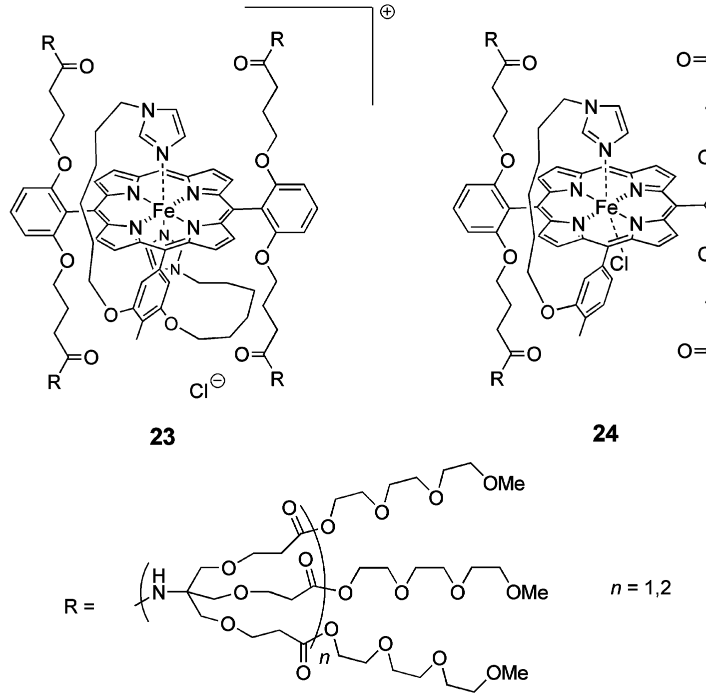


Figure 7. Fe–porphyrin core dendrimers **23** and **24** (Diederich et al.).

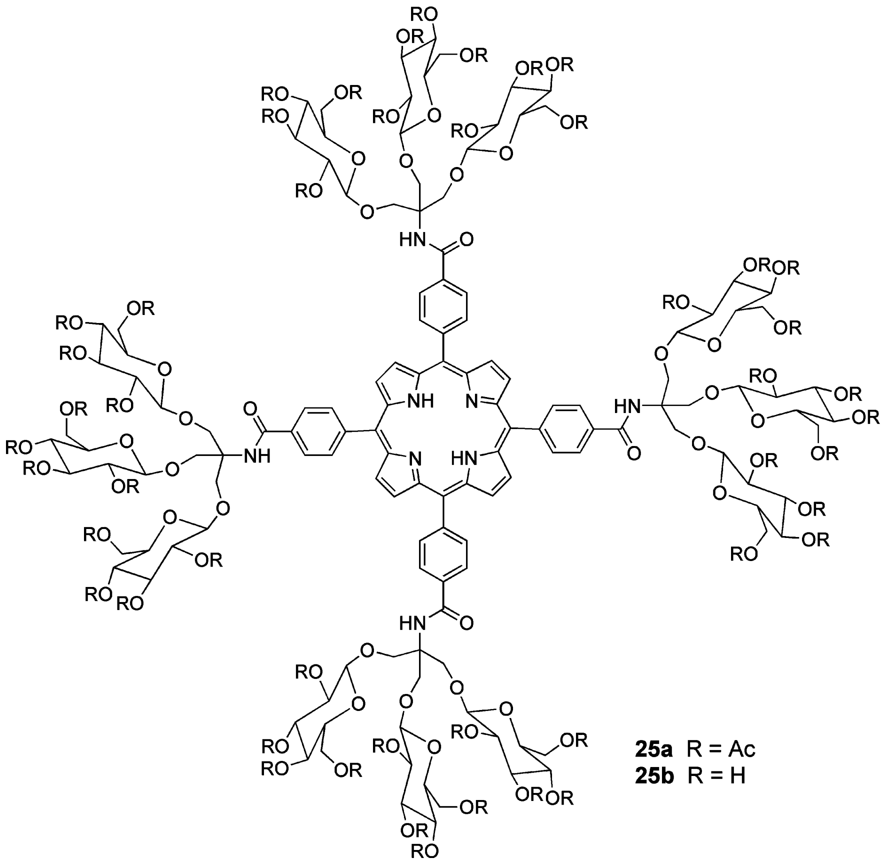


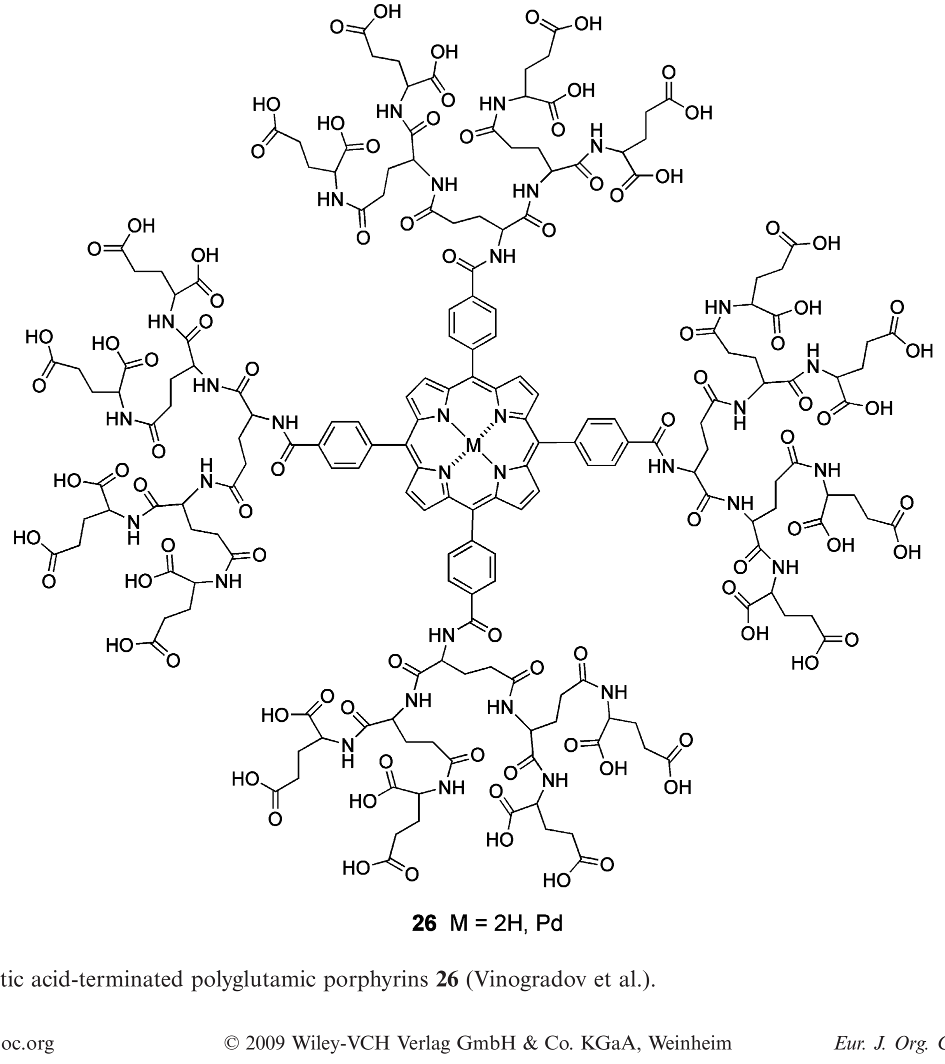
Figure 8. Porphyrin-centered glycodendrimers **25a** and **25b** (Stoddart et al.).

to the Zn–porphyrin center is observed, and the triazole links seem to constitute a favorable pathway for electron transfer.

Shinoda, Tsukube, and co-workers developed porphyrin dendrimers with asymmetrically substituted "patched" structures as synthetic nanoscale receptors.[21] "Proteo-dendrimers" **21**, in which three hydrophobic Fréchet dendrons with a hydrophilic polyether surface are combined with a poly(glutamic acid) dendron around a fluorescent Zn–porphyrin core (Figure 5), were synthesized from the starting A_3B porphyrin **13** (Figure 1) by convergent attachment of the G_x poly(benzyl ether) dendrons through their focal mesylate functions (64–76%) and subsequent amide formation [HOBt: 1-hydroxybenzotriazole; HBTU: 2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate; DIPEA: diisopropylethylamine] between the (deprotected) *meso*-carboxyphenyl unit and an amine-terminated heptaglutamic acid dendron (52–80%). The polyanionic peptide-patch dendrimer (**21b**) binds to cytochrome *c* through complementary electrostatic interactions, resulting in a stable supramolecular complex.[21a,21c,21d] Cytochrome *c* binding proteo-dendrimers of this type have recently been shown to be mitochondrial apoptosis inhibitors.[21d] Analogous dendrimers, each containing three Fréchet dendrons with a methyl ether periphery and a single nondendritic diamidopyridine residue, were constructed by a similar strategy, and these "pocket" dendrimers were investigated for bimolecular guest complexation by complementary hydrogen bonding and Zn coordination.[21b,21c]

Aida and Uyemura examined organocobalt dendritic porphyrins, synthesized according to the procedure reported by Suslick,[8a] based on (free-radical-tolerant) Fréchet-type poly(aryl ester) dendrons surrounding Co–porphyrin **1h** (Figure 1), as artificial coenzyme B_{12} models.[22] Selective, AIBN-initiated transformation of various alkyne substrates has been accomplished through steric control provided by the large dendritic shell.

Fréchet et al. prepared LH porphyrin dendrimers based on a poly(benzyl ether) framework and octafunctional (metallo)porphyrin cores (**1a**, **1b**, **1i**, **1j**, or the enlarged analogue **14**, Figure 1), and containing peripheral two-photon-absorbing (2PA) chromophores (AF-343) for photosensitization of singlet oxygen ($^1O_2$) through two-photon-excited fluorescence resonance energy transfer (FRET).[23] A triethyleneglycol periphery was applied to afford water solubility.[23b] Functionally layered LH dendrimers with naphthopyranone dyes in the interior and coumarins at the surface were constructed in a divergent way starting from porphyrin **14** (Figure 1) through a stepwise esterification/deprotection procedure.[24]



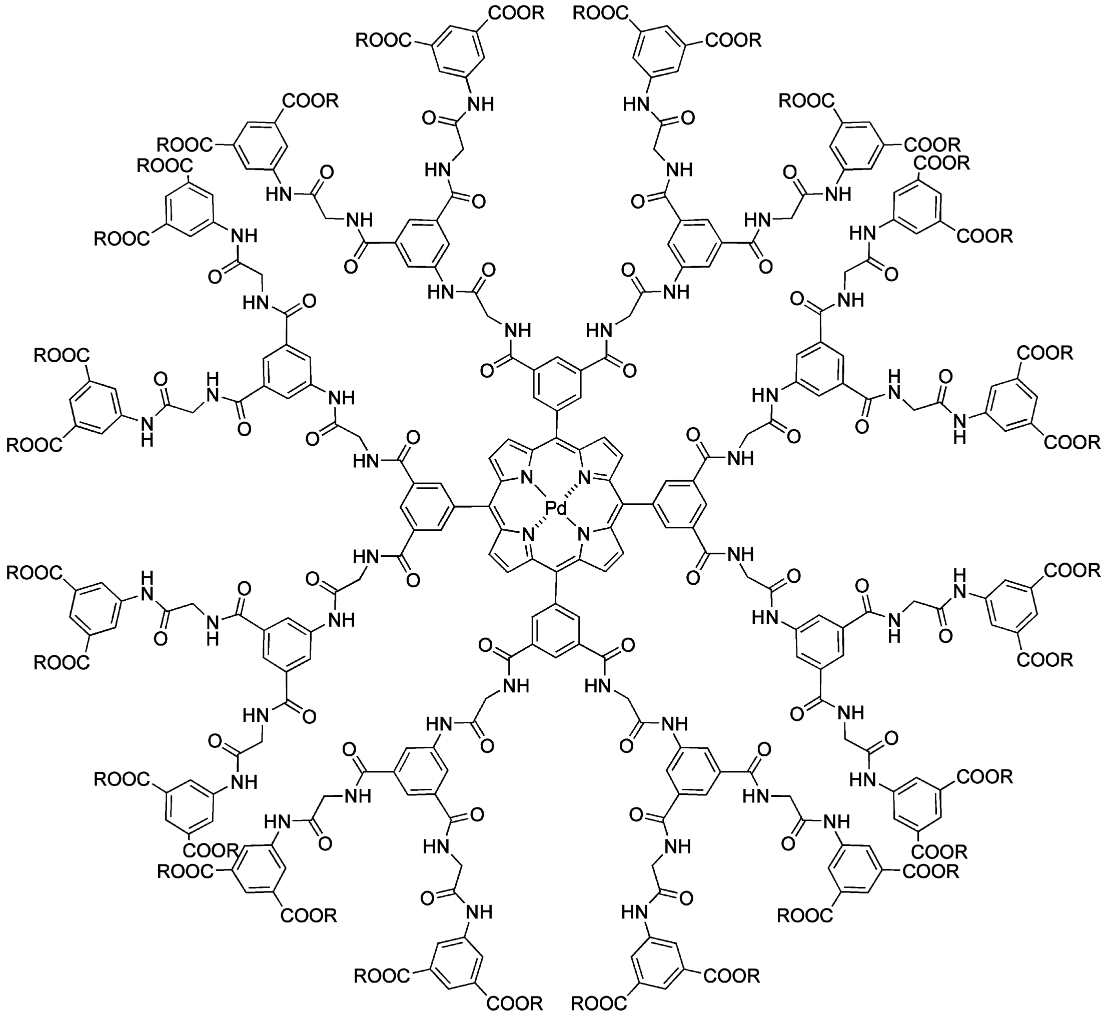
26 M = 2H, Pd

Figure 9. G_3 dendritic acid-terminated polyglutamic porphyrins **26** (Vinogradov et al.).

In order to gain more information on the possible involvement of a previously postulated hydrogen-bonding interaction, emanating from the proximal amide NH groups of Newkome-type dendrons, in the observed high O_2 affinity for their dendritic heme analogues,[7] Diederich and associates synthesized analogous (G_1/G_2) porphyrin dendrimers bearing Fréchet-type dendrons with triethyleneglycol monomethyl ether end groups and *distal* H-bond donor moieties introduced at a *meso*-position of the porphyrin core (Figure 6).[25] Because a Suzuki protocol (see further, section 2.2, Figure 7) was surprisingly found to be ineffective, the *ortho*-ethynylated *meso*-aryl ring required for precise positioning of the H-bonding functions was introduced during porphyrin macrocyclization through a mixed cyclocondensation of dipyrromethanes (one carrying the *ortho*-ethynyl substituent) and an aldehyde derived from 2,6-dimethoxybenzaldehyde (17% yield). After attachment of the dendrons by esterification under DCC coupling conditions (HOBt, DMAP; 88 and 66% yields for G_1 and G_2, respectively), the H-bond moieties were introduced by Sonagashira cross-coupling, and metallation afforded the final Fe^{II}–porphyrin dendrimers.

2.2. Polyamide Dendrons

Diederich and co-workers expanded their pioneering research on hemoprotein mimics with dendritic Fe–porphyrins carrying tethered imidazole ligands (**23**, **24**, Figure 7).[26] The required porphyrin cores were obtained from *trans*-A_2B_2 porphyrin **6a** (Figure 1) by a procedure involving *meso*-bromination and Suzuki coupling with imidazole-appended phenylboronic acids, whereas the flexible Newkome-type poly(ether amide) dendrons, with triethyleneglycol monomethyl ether end groups offering solubility in solvents of differing polarity, were now attached in a convergent way with use of HATU [2-(1*H*-7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate] as the coupling reagent. The dendritic porphyrins **24** each have a vacant axial coordination site, affording the potential to coordinate diatomic gas molecules (O_2, CO, NO), and they



27 R = Bu, H, PEG350

Figure 10. G_2 Pd–porphyrin poly(aryl amide) dendrimers **27** (Vinogradov et al.).

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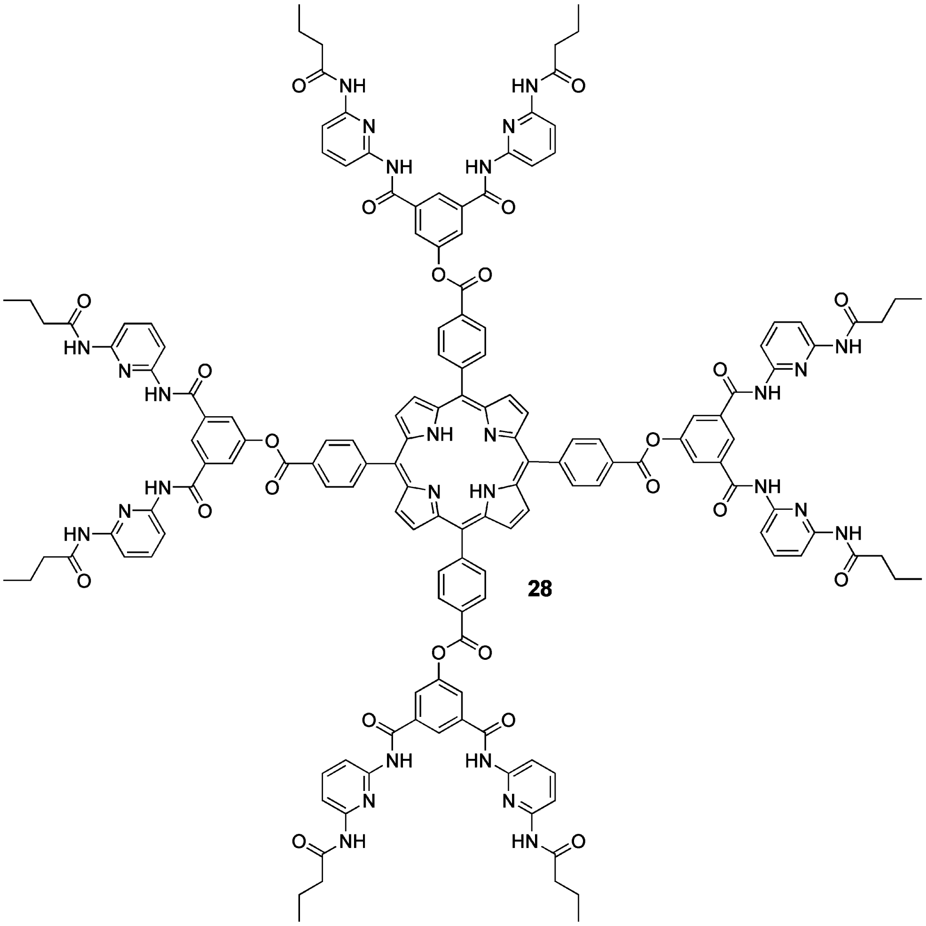

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Figure 11. Hamilton receptor G_1 porphyrin dendrimer **28** (Hirsch et al.).

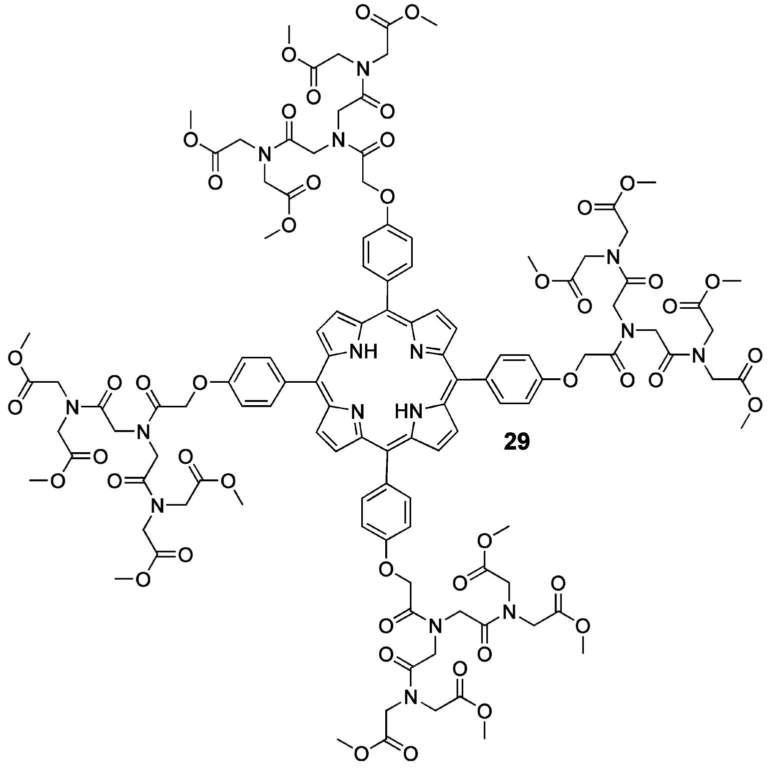

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Figure 12. G_2 porphyrin core polyamide dendrimer **29** (Singh et al.).

were used as heme monooxygenase model catalysts in olefin epoxidation and sulfide oxidation reactions.[26b,26c,26e]

Modarelli et al. introduced anthraquinone groups at the surfaces of Newkome-type (Zn or Fb) porphyrin-centered dendrimers (G_1–G_3) and studied photoinduced electron transfer within these macrostructures.[27a,27b] The synthesis was accomplished by starting from *meso*-tetrakis(4-carboxyphenyl)porphyrin (**8a**, Figure 1). The porphyrin macrocycle was first converted into the tetraacid chloride ($SOCl_2$), and the "three-to-one" polyamide branches were divergently constructed on this core by straightforward peptide coupling protocols (EDC/HOBt and peripheral ester hydrolysis; total yields 7–16%). Structure and aggregation studies on analogous dendrimers with methyl ester termini were performed by multidimensional NMR spectroscopy.[27c]

A similar synthetic sequence was applied by Stoddart and co-workers to anchor G_1 Newkome-type glycodendrons to the same tetraacid chloride porphyrin core (Et_3N/CH_2Cl_2; 16% yield).[28] The 12 peracetylated β-D-glucopyranosyl end groups create a carbohydrate shell around the porphyrin nucleus, and they could be quantitatively deprotected under Zemplén conditions (NaOMe, MeOH/THF) to afford water solubility (Figure 8).

Vinogradov et al. synthesized dendritic polyglutamic porphyrins (G_1–G_4) by a divergent approach employing 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (**8a**) or its Pd^{II} derivative **8b** (Figure 1) as the interior functional unit (Figure 9).[29a–29c] The branches were constructed by repetitive DCC-promoted condensation of L-glutamate monomers and subsequent deprotection through hydrolysis or hydrogenation, depending on the applied ester derivative. Phosphorescence quenching of the Pd–porphyrin dendrimers by O_2 was related to the dendritic size and solvent properties,[29b] whereas the polyglutamic "dendrimer-protected" Fb porphyrin fluorophores were shown to be convenient (membrane-impermeable) pH nanosensors.[29c,29g] The fourth-generation Fb porphyrin dendrimer was more conveniently synthesized by a combined convergent-divergent route involving condensation of G_2 tris(glutamic) dendrons with the porphyrin core **8a** (DCC methodology) and subsequent divergent propagation.[29g] The relative shielding efficiencies of different sorts of dendritic matrices were investigated by comparing the O_2 quenching of the phosphorescent Pd–porphyrin cores in polyglutamic, Fréchet-, and Newkome-type dendrimers.[29d,29e,29h] The dendritic macromolecules were synthesized in a convergent manner starting from the prefabricated dendrons and Pd–porphyrin cores (**1g** or **2**) by Williamson-ether or DCC coupling protocols.

The same group recently established a novel route to poly(aryl amide) dendrimers with flexible linkers by a haloacyl

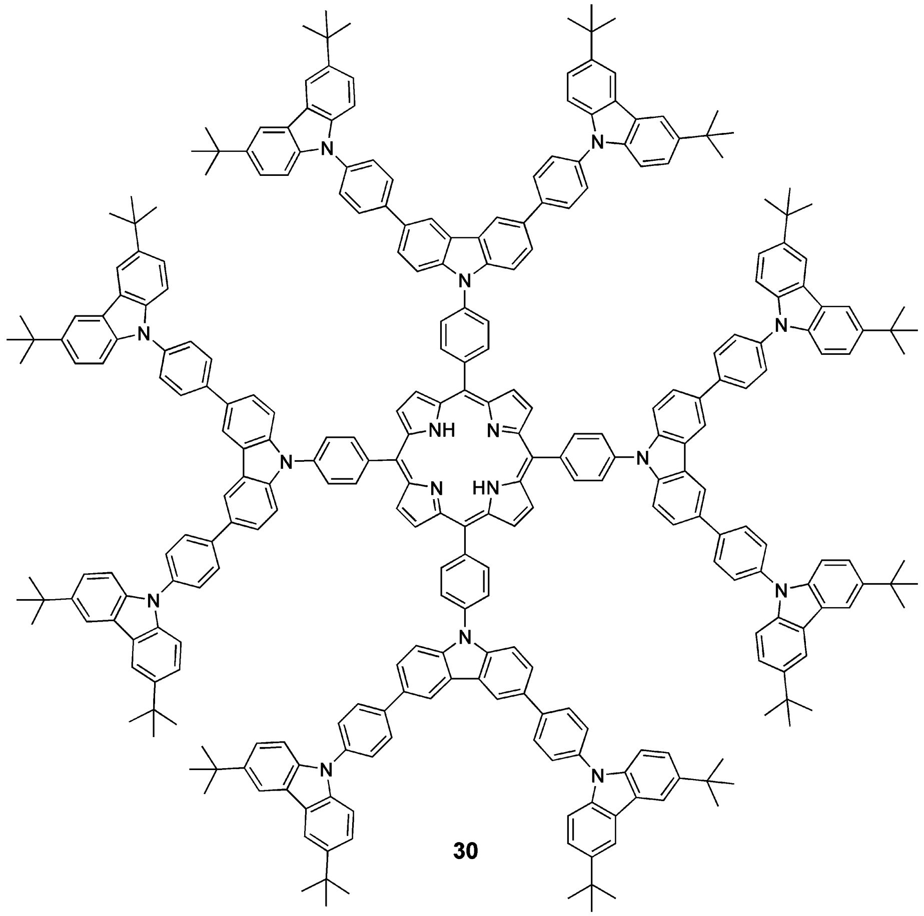

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Figure 13. Multicarbazole porphyrin dendrimer **30** (Dehaen et al.).

halide method based on glycineamide building blocks.[29i] Eight G_2 dendrons could be anchored on phosphorescent Pd–porphyrin core **2** (Figure 1) through their focal amino functions [CDI-promoted (1,1′-carbonyldiimidazole-promoted) coupling; 68% yield] (Figure 10). Hydrolysis of the butoxycarbonyl end groups afforded a water-soluble polyacid dendrimer, and further surface modification was achieved through esterification with monomethoxypoly(ethylene glycol)s (PEG350, by DCC/HOBt coupling; 80% yield). The compositions of the dendritic phosphors were later optimized for oxygen measurements in biological systems.[29j–29l]

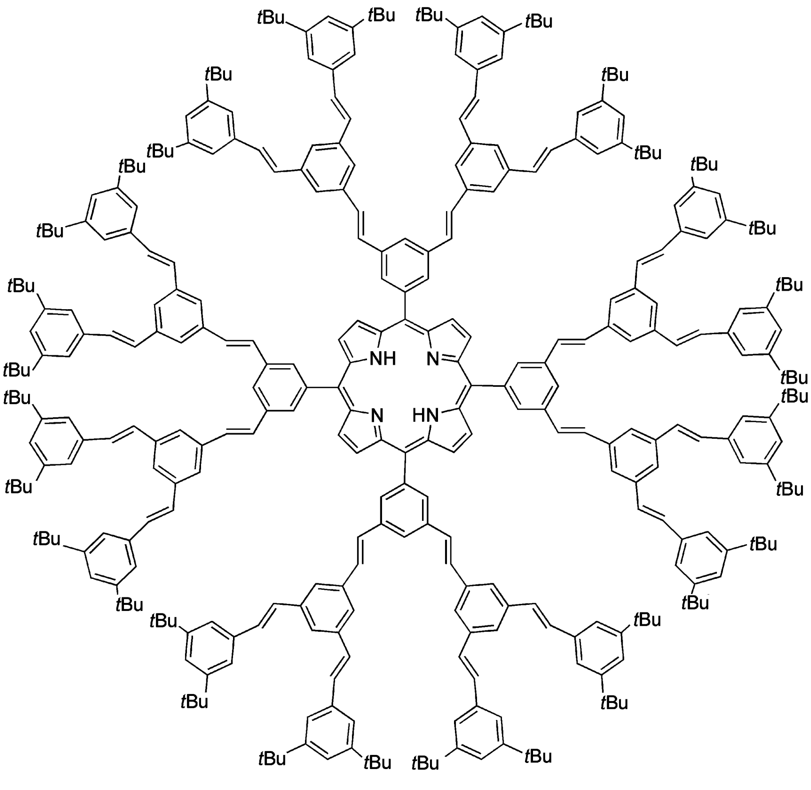
A dendritic nanoprobe with internally enhanced 2PA cross-section has been designed for oxygen microscopy in vivo. The optimized dendritic construct was synthesized by a combined convergent/divergent approach with a peptide coupling methodology and resembles porphyrin dendrimer **27**. It combines coumarin-343 2PA antenna moieties, channeling the excitation energy to a phosphorescent Pt–porphyrin core (**9b**, Figure 1), and oligoethyleneglycol residues (PEG750) attached to the end groups of four G_3 arylglycine dendrons.[29k,29l]

A new type of porphyrin core dendritic receptor, compound **28** (Figure 11), was reported by Hirsch and associates, and its complexation properties with chiral depsipeptide dendrons carrying cyanuric acid focal points, affording supramolecular chirality, were examined.[30a] For the construction of the dendritic cyanurate receptor, G_1 dendrons with an included Hamilton receptor binding motif were attached to porphyrin core **8a** (Figure 1) through peptide coupling reactions (EDC, DMAP, DMF; 5% yield). Alternatively, two G_1 dendrons with peripheral neopentyl substituents were coupled to the axial positions of $Sn(OH)_2$–porphyrin platform **15** (Figure 1) (EDC, DMAP, CH_2Cl_2; 13% yield).[30b]

Two generations of porphyrin-centered dendrimers with small polyamide dendrons were synthesized by a divergent route by Singh et al. in order to evaluate their third-order optical nonlinearities (Figure 12).[31] The dendrons were gradually grown on the porphyrin core **9a** (Figure 1) through stepwise activation with thionyl chloride, treatment with bis(methoxycarbonylmethylene)amine, and basic hydrolysis. Guo and co-workers synthesized a G_1 Cu–porphyrin dendrimer by treatment of a bromide-functionalized small bis(amide) dendron and 5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrin (the *meta* analogue of **7a**, Figure 1) and subsequent Cu insertion.[32] Taylor et al. have grafted G_1/G_3 polyurethane dendrons onto the A_4 porphyrin core **8a** (Figure 1) through a (modified) Curtius reaction employing diphenylphosphoryl azide (DPPA) and have established MALDI-TOF MS as an interesting tool for structural confirmation (dendritic purity) and for monitoring the reaction progress.[33]

2.3. Cyclocondensation of Dendritic Aldehydes

An alternative convergent pathway toward porphyrin-centered dendrimers is based on cyclocondensation of prefabricated dendritic wedges containing aldehyde focal



31

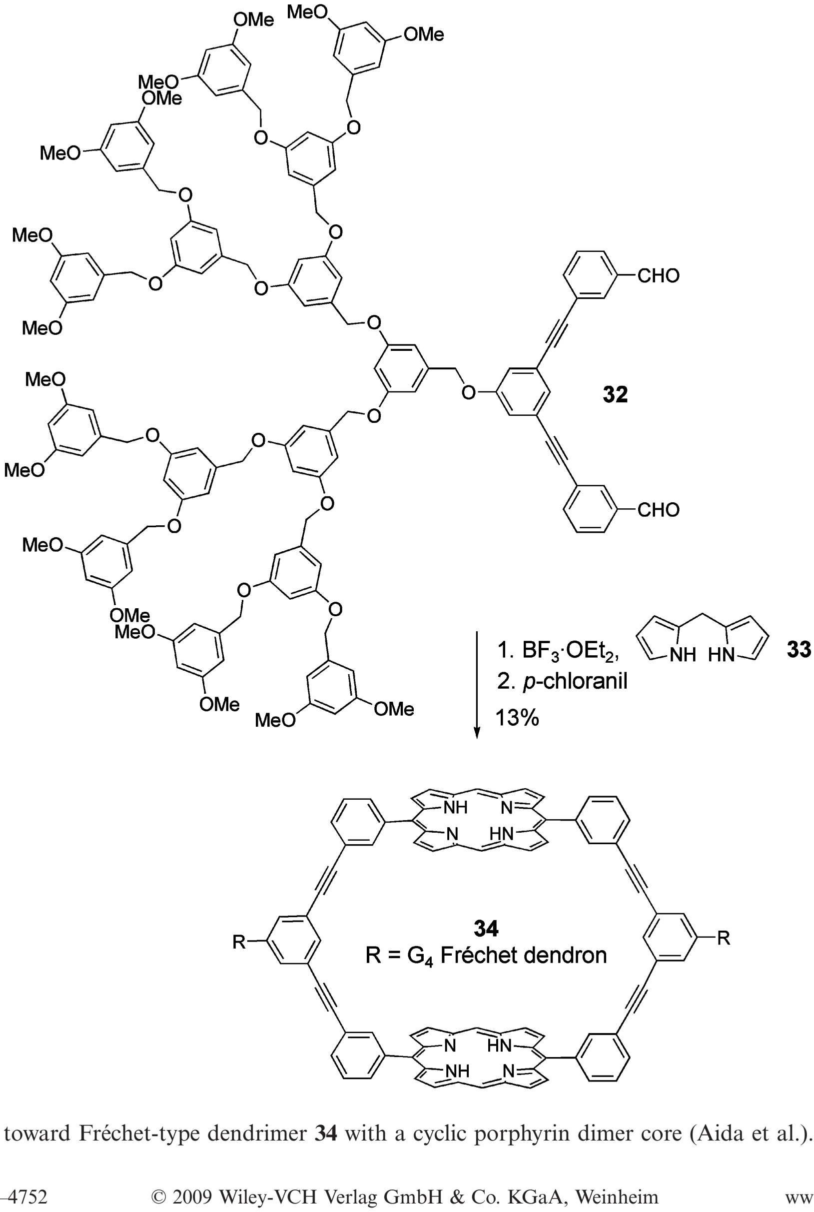
Figure 14. G_2 porphyrin-core stilbene dendrimer **31** (Burn et al.).

points with an equivalent amount of pyrrole to form the tetrapyrrolic porphyrin core (after oxidation of the porphyrinogen intermediate) at the ultimate synthetic step. Although this route suffers from steric limitations, it has generally provided rather high yields relative to traditional *meso*-tetraarylporphyrin synthesis from sterically not congested building blocks. Moreover, the absence of incompletely substituted dendrimers often allowed straightforward purification.

Fréchet and co-workers employed this strategy for the first time to avoid the long reaction times and harsh purification procedures generally observed in convergent routes toward Aida-type poly(benzyl ether) porphyrin dendrimers.[9a,9c] The dendritic aldehyde and pyrrole were combined in a one-pot, two-step Lindsey porphyrin synthesis (TFA catalysis, chloranil oxidation), affording 25–30% yields of G_1–G_3 porphyrin dendrimers. Similar G_1 dendrimers with dodecasubstituted porphyrin cores were prepared by Ryppa and Senge, starting from β-alkylated pyrrole derivatives (Lindsey approach: TFA catalysis, 29–41% yield).[34] An alternative divergent approach to these porphyrin dendrimers was shown to be impractical (incomplete reactions and purification issues) because of the substantial steric hindrance in β-substituted porphyrins.

In 2005, our group reported the synthesis of multicarbazole porphyrin dendrimers, and the photophysical features and redox behavior of these structures were investigated.[35] The carbazole-based dendritic aldehyde precursors were constructed through multistep procedures involving Cu-catalyzed Ullmann or Pd-catalyzed Suzuki reactions; subsequent condensation with pyrrole under Lindsey conditions ($BF_3{\cdot}OEt_2$ catalysis) afforded two generations of porphyrin dendrimers (e.g., **30**, Figure 13) containing up to 20 carbazole chromophores. The yields for the porphyrin formation range from 30% for the first-generation monocarbazole dendron to 8% for the sterically most congested G_2 dendron.

Related carbazole-based dendrimers with porphyrin cores were synthesized by Zhao and co-workers through a combination of Ullmann coupling and Adler condensation



Scheme 1. Synthetic route toward Fréchet-type dendrimer **34** with a cyclic porphyrin dimer core (Aida et al.).

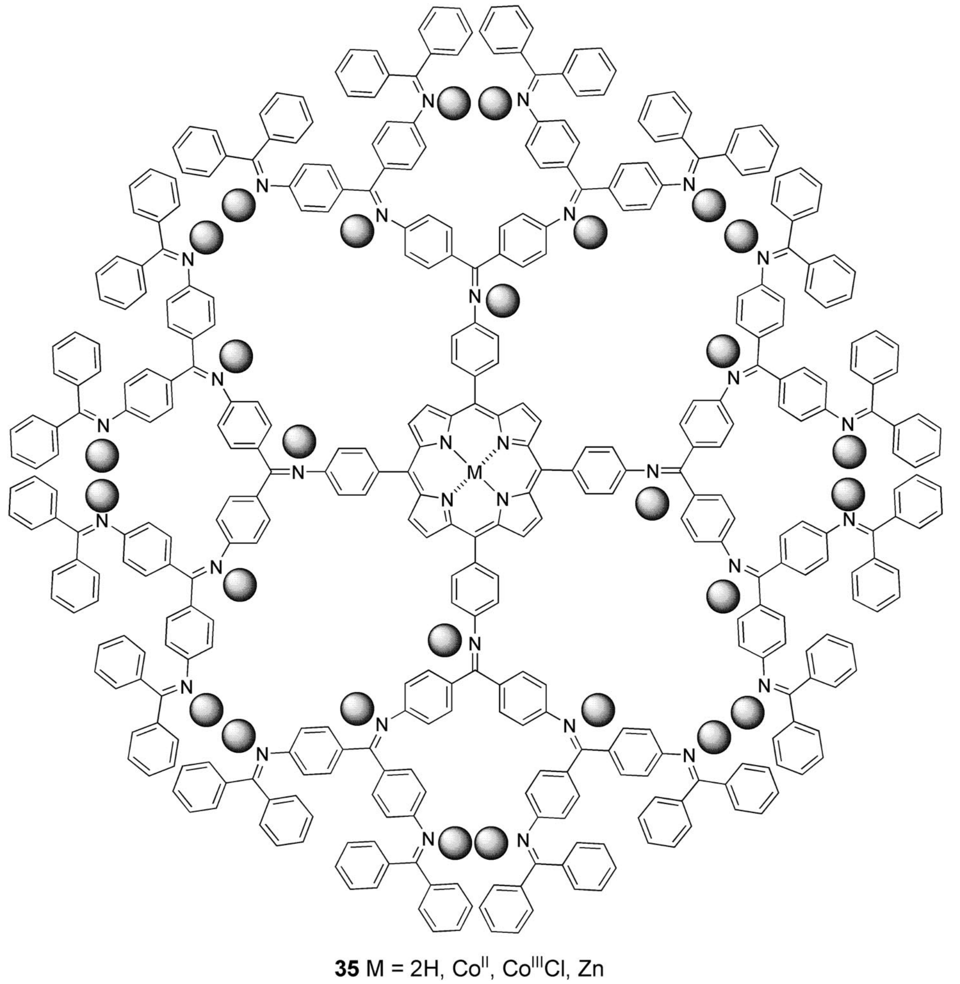
reactions (in the presence of 4-nitrobenzoic acid in xylene, 3–24 h reflux; 7–21% yields), and their intramolecular energy transfer properties were also examined.[36]

Burn, Samuel, and associates prepared *meta*-linked stilbene dendrons with *tert*-butyl surfaces conferring high solubilities, and aldehydes at their centers. Condensation with pyrrole under Lindsey conditions (TFA catalysis) and subsequent oxidation afforded electroluminescent dendrimers (G_1/G_2; 33/24% yield, Figure 14).[37] The porphyrin-centered dendrimers were explored as red-light-emitting components for the development of OLEDs,[37b–37d] whereas a G_1 Pt–porphyrin phosphorescent analogue was applied as a triplet-harvesting dopant for the control of electroluminescence in related *meta*-stilbene-based host dendrimers.[37e] Similar structures in which the dendrons are linked to the porphyrin cores through stilbene rather than regular phenyl units were also synthesized (G_1/G_2; 15/22% yields), and their electro-optical properties were compared to those of the previous dendrimer family.[37f]

Deng and Advincula reported the synthesis of thiophene dendrimers with porphyrin nuclei starting from oligothiophene-carbaldehyde dendrons under Lindsey conditions (TFA catalysis; G_1 8% yield, G_2 4% yield).[38]

Kim et al. studied inert and stable, nine-coordinate Er^{III}-cored complexes based on dendritic Pt–porphyrin ligands for optical amplification.[39] The A_3B porphyrin centered dendritic ligands were prepared by porphyrin formation from 5-[4-(methoxycarbonyl)phenyl]dipyrromethane and an aldehyde and dipyrromethane precursor carrying G_1–G_3 Fréchet poly(benzyl ether) dendrons (23–19% yield), followed by Pt insertion and hydrolysis of the ester moiety. The near-infrared (NIR) emission intensities of thin films of these complexes were strongly enhanced with increasing generation number, due to site isolation and LH effects. The G_1 dendritic Zn–porphyrin ligand and an analogue with an additional stilbene linker carrying a cyano moiety (to enhance the electron-injection properties) have been applied for the fabrication of dye-sensitized solar cells (DSSCs) based on solid polymeric electrolytes.[40] The extended π-conjugated porphyrin-core dendrimer was synthesized by grafting three G_1 Fréchet dendrons with benzaldehyde focal points onto A_3B porphyrin **16** (Figure 1).

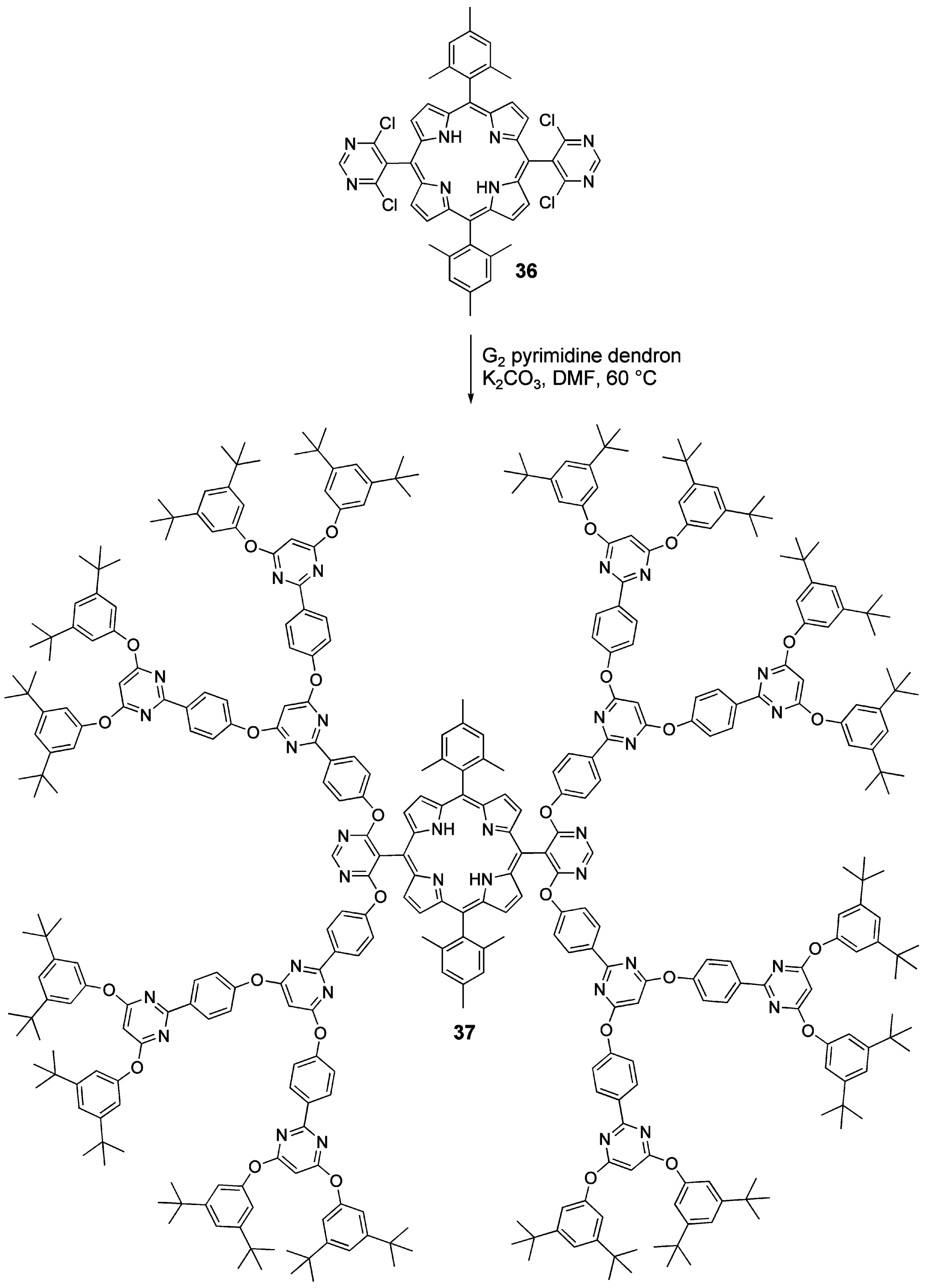
Aida and co-workers synthesized dendritic macromolecules with a face-to-face cyclic porphyrin dimer as the interior core unit.[41] Bis(aldehyde) precursor **32**, bearing a G_4



35 M = 2H, Co^{II}, $Co^{III}Cl$, Zn

Figure 15. G_3 phenylazomethine-porphyrin dendrimer **35**, spatially arranging 28 metal ions (Yamamoto et al.).

poly(benzyl ether) dendron, was condensed with dipyrromethane **33** ($BF_3{\cdot}OEt_2$ catalysis) and, after oxidation with *p*-chloranil, cyclic dimer **34** was obtained fairly selectively in 13% yield (14% for G_3) (Scheme 1).[41a] The bis(porphyrin)-core dendrimers form stable supramolecular complexes with fullerenes (C_{60}/C_{70}), due to the strong interaction at the porphyrin dimer center. Later the same group reported the fullerene-triggered supramolecular polymerization of an acyclic porphyrin dimer bearing only one G_4 poly(benzyl ether) dendron and six carboxylic acid functions at the *meso*-positions.[41b] The G_3 dendritic bromide was attached to a preformed porphyrin dimer scaffold containing a (silyl-protected) 3,5-dihydroxybenzyl Fréchet-type monomer unit under desilylating conditions.

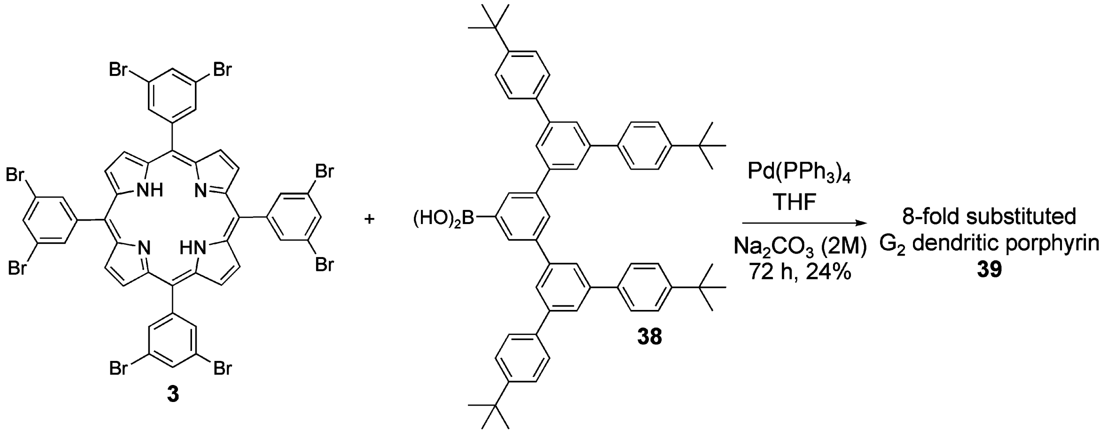


Scheme 2. Synthesis of G_2 pyrimidine–porphyrin dendrimer **37** (Dehaen et al.).

2.4. Miscellaneous Porphyrin-Core Dendrimers

Yamamoto and co-workers introduced porphyrin cores into their dendritic phenylazomethine (DPA) systems through coupling of G_1–G_4 benzophenone-functionalized dendrons to 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (**10a**, Figure 1) through a dehydration reaction based on $TiCl_4$ [DABCO (1,4-diazabicyclo[2.2.2]octane), chlorobenzene, 125 °C; 30–48 % yields] (Figure 15).[42] Because the DPA dendrons contain multiple interior imine functions, a controlled arrangement of metal ions with Lewis acidity (e.g., $SnCl_2$ or $FeCl_3$) can be complexed throughout these structures in a stepwise radial fashion. Complexation of a G_4 dendritic template (Fb porphyrin core) with $PtCl_4$, followed by pyrolysis at 1000 °C, afforded a Pt nanoparticle carbon nanocomposite, active as an electrochemical catalyst for O_2 reduction.[42f] The DPA dendrimers with a Co–porphyrin core could be applied for catalytic CO_2 reduction in the presence of a strong Lewis acid [e.g., $Ln(OTf)_3$] at a relatively low overpotential, due to the synergetic effect of the assembled metal ions and the porphyrin core involving a multi-electron transfer process.[42g] An analogous open-shell bis(dendronized) "pocket" G_4 dendrimer, synthesized from *cis*-A_2B_2-5,10-bis(4-aminophenyl)-15,20-diphenylporphyrin (**17**, Figure 1), showed an improved activity due to the greater accessibility of the catalytic center. Other asymmetric DPA-Zn–porphyrin dendrimers were synthesized similarly from mono-, bis-, and tris[*meso*-(*p*-aminophenyl)]-substituted porphyrins, and their physical properties and metal complexation were found to be highly morphology-dependent.[42i] The G_3 DPA dendrimer with Co–porphyrin center was also investigated as a dehalogenation catalyst.[42h] An enhanced activity was observed when Sm^{3+} or Tb^{3+} were bound to the DPA units, mediating electron transfer from the reducing agent (SmI_2) to the catalytic (Co–porphyrin) center. Recently, double-layer-type carbazole-phenylazomethine dendrimers with carbazole moieties at the outer layers and a Zn–porphyrin core (**10b**, Figure 1) were prepared and explored as hole-transporting and emitting layers for OLEDs.[42j,42k] Lee and Goodson have demonstrated entangled two-photon absorption in a G_3 DPA-porphyrin dendrimer.[42l]

In our group, an efficient convergent approach to heterocyclic porphyrin dendrimers has been developed.[43] Convergence of two research topics, the synthesis and application of dendrimers with internal heterocycles and the explo-



Scheme 3. Synthetic strategy for G_2 1,3,5-phenylene-based porphyrin dendrimer **39** (Kimura et al.).

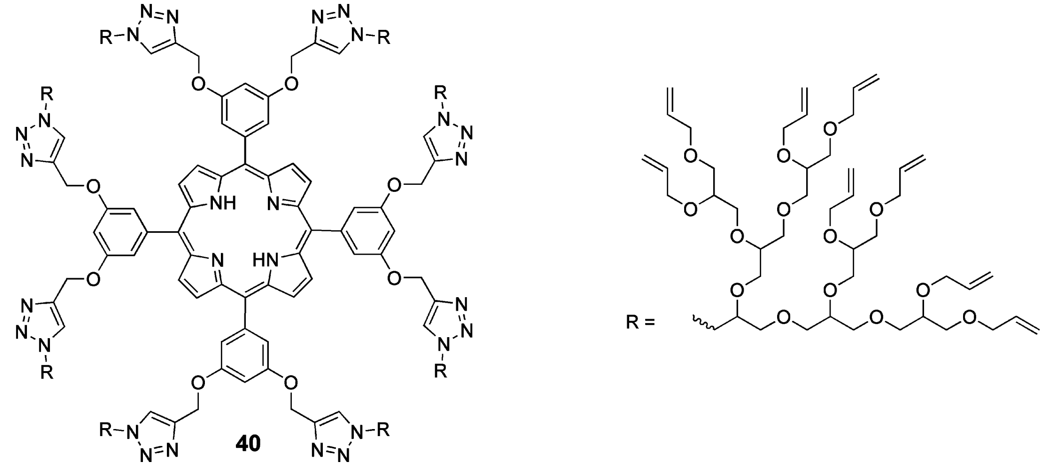
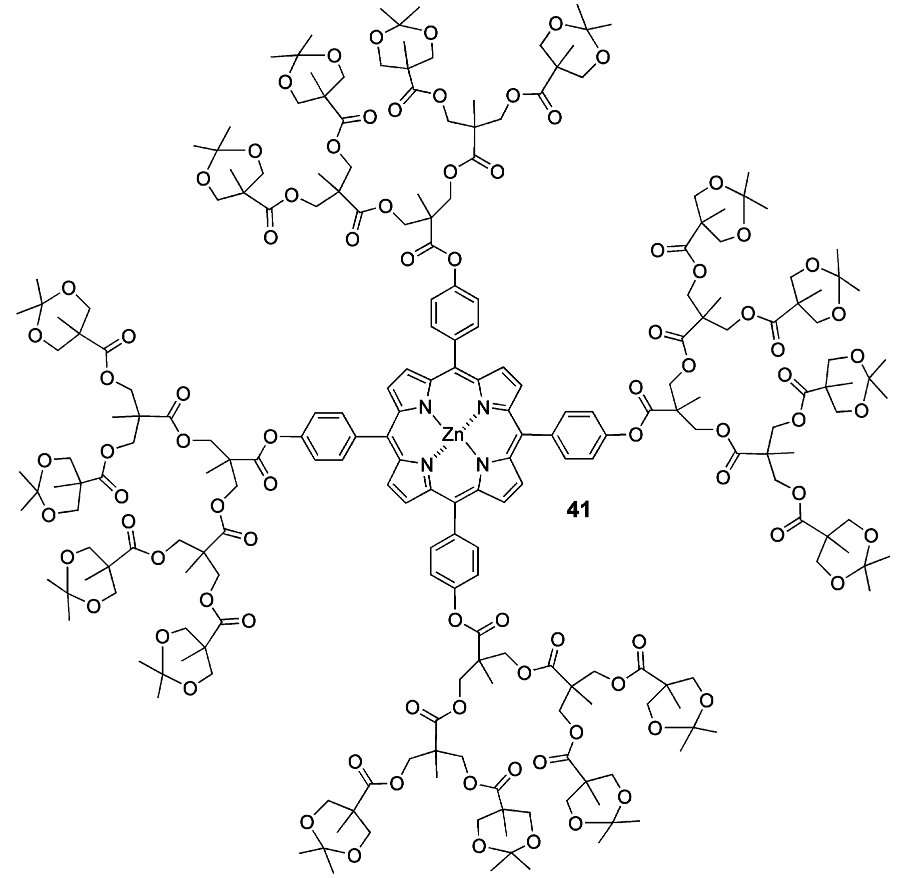
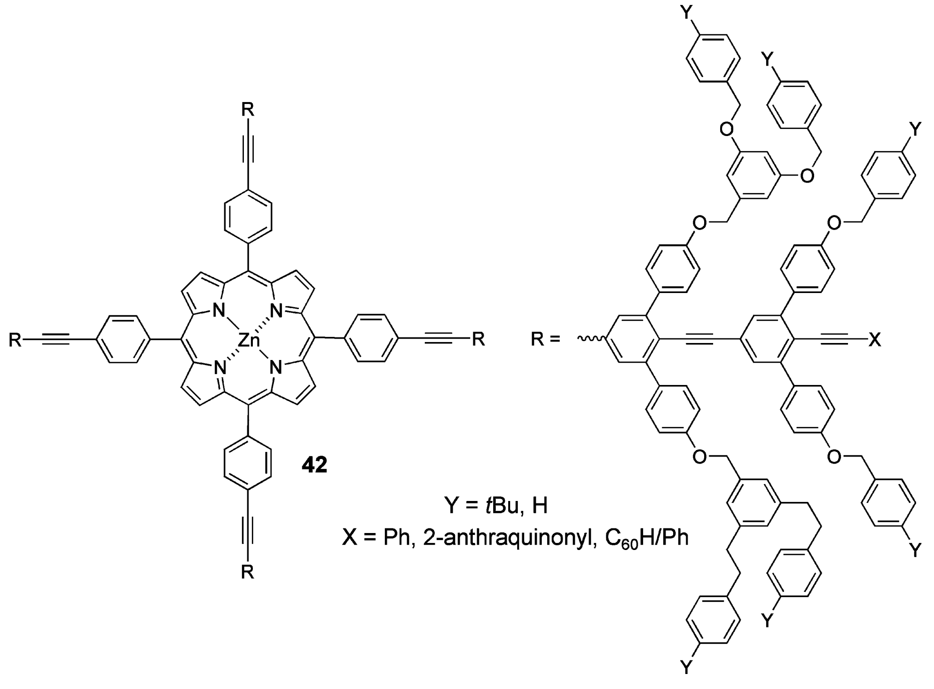


Figure 16. Porphyrin-centered polyglycerol dendrimer **40** (Zimmerman et al.).



41

Figure 17. Zn–porphyrin centered G_3 2,2-bis(methylol)propionic acid dendrimer **41** (Malmström et al.).



42

Y = *t*Bu, H
X = Ph, 2-anthraquinonyl, $C_{60}H$/Ph

Figure 18. Snowflake porphyrin dendrimers **42** (Okada et al.).

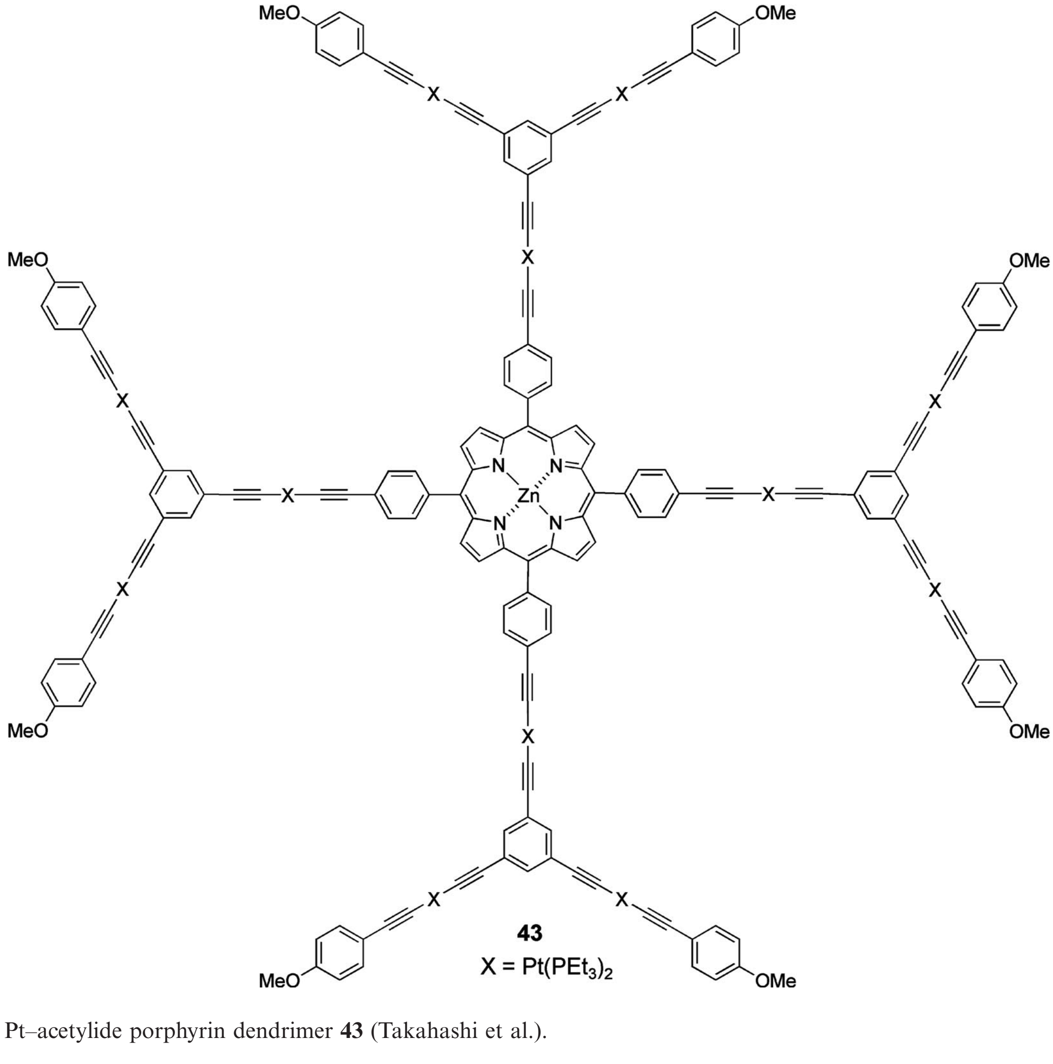
ration of *meso*-(dichloropyrimidinyl)-substituted porphyrinoids,[44–47] afforded porphyrin-centered dendrimers constructed from G_1–G_3 pyrimidine-based dendrons with phenolic focal points and *trans*-A_2B_2 pyrimidinylporphyrin **36** through straightforward nucleophilic aromatic substitution (S_NAr) reactions in high yields (70–80%) (Scheme 2).[43] Unlike most other reported porphyrin-core dendrimers, the dendrons are anchored to the *ortho*,*ortho′*-positions of the *meso*-pyrimidinyl substituent, which might provide a more densely shielded porphyrin center.

Rigid 1,3,5-phenylene-based porphyrin dendrimers **39** (G_1/G_2) were synthesized by Kimura and co-workers through Suzuki coupling (57/24% yields) of arylboronic acid dendritic wedges and 5,10,15,20-tetrakis(3,5-dibromophenyl)porphyrin (**3**, Figure 1) (Scheme 3).[48] Upon coupling of the G_3 dendron, a mixture of defect structures was obtained. Energy transfer within these systems was studied, and the porphyrin-core shape-persistent dendrimers (alternatively decorated with long alkyl end groups to induce self-organization) were also examined as host molecules for C_{60} and substrate-selective oxidation catalysts. First-generation triphenylene dendrons with benzyl bromide focal points were alternatively attached to porphyrin core **1a** (Figure 1) under alkaline conditions to obtain a partially flexible porphyrin dendrimer.[48b]

Related conjugated polyphenylene dendrimers with exterior benzoquinone groups were prepared by Modarelli et al., and electron transfer within these systems was also studied.[49] The dendritic wedges were either attached to *meso*-(bromophenyl)porphyrin cores under Suzuki cross-coupling conditions, or alternatively cyclocondensation of dendritic polyphenylenes with aldehyde focal moieties and pyrrole under Lindsey conditions ($BF_3{\cdot}OEt_2$ catalysis) was used to obtain the final porphyrin dendrimers. The latter, more general, approach allowed easier purification and afforded high yields (G_1/G_2; 64/54%).

Polyglycerol dendrimers with porphyrin interiors were recently synthesized by Zimmerman et al. (Figure 16).[50] Polyether dendrons with exterior allyloxy moieties and azide focal points were convergently “clicked” onto an octa-alkynylporphyrin core [prepared from **1a** (Figure 1) and propargyl bromide] through Cu-catalyzed 1,3-dipolar cycloaddition reactions ($G_{3.5}$/$G_{4.5}$; 65/66%).

Malmström et al. synthesized 2,2-bis(methylol)propionic acid (bis-MPA) dendrimers with porphyrin cores (Figure 17). The dendrons were divergently grown from a start-



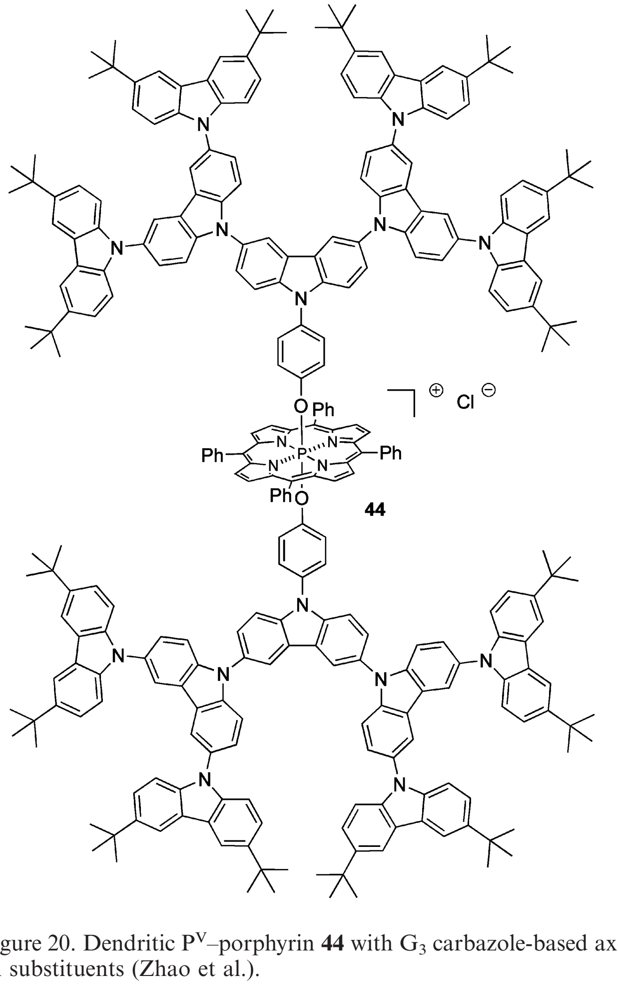
43
X = $Pt(PEt_3)_2$

Figure 19. G_1 Pt–acetylide porphyrin dendrimer **43** (Takahashi et al.).

ing 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (**7a**, or its Zn derivative **7b**, Figure 1) with acetonide-2,2-bis(methoxy)propanoic anhydride as the branching unit.[51a] Introduction of a propanol spacer on the porphyrin core, increasing the hydrolytic stability, was required to extend the divergent approach up to the fifth generation. Convergent DCC-promoted coupling of the (larger) dendrons to the porphyrin core gave defect dendritic structures resulting in the need for harsh purification procedures. The vibration and fluorescence spectra of these dendrimers were recently reported by Lindgren.[51b]

Okada and co-workers designed the "snowflake-shaped" porphyrin dendrimers **42**, featuring a rigid conjugated oligomeric network within flexible poly(benzyl ether) branches (Figure 18).[52] The synthetic strategy involved Sonogashira coupling of four snowflake dendrons to a Zn–tetrakis(4-ethynylphenyl)porphyrin core (**42**, R = H) through their iodo focal points. The electron- and energy-transfer properties of dendrimers carrying anthraquinonyl or fullerene (C_{60}) surface groups were also studied.

Takahashi et al. applied the same Zn–tetrakis(4-ethynylphenyl)porphyrin derivative to prepare organometallic Pt–acetylide dendrimers **43** by a convergent method (Figure 19).[53] Three generations of Pt–acetylide dendrons were grafted on a tetranuclear Pt–acetylide porphyrin core by a Cu-catalyzed reaction (73–41% yield).



44

Figure 20. Dendritic P^V–porphyrin **44** with G_3 carbazole-based axial substituents (Zhao et al.).

Lu, Zhao et al. employed axial ligation of phosphorus(V)–porphyrins as an alternative strategy directed towards porphyrin-core oligocarbazole dendrimers (Figure 20).[54] $[P^V(TPP)Cl_2]Cl$ (TPP = tetraphenylporphyrin) was applied as the core entity, and polycarbazole dendrons with focal phenol units were easily introduced through reaction with the reactive P–Cl bonds (pyridine, reflux; 79–63%).

2.5. Dendrons with Porphyrin Units at their Focal Points

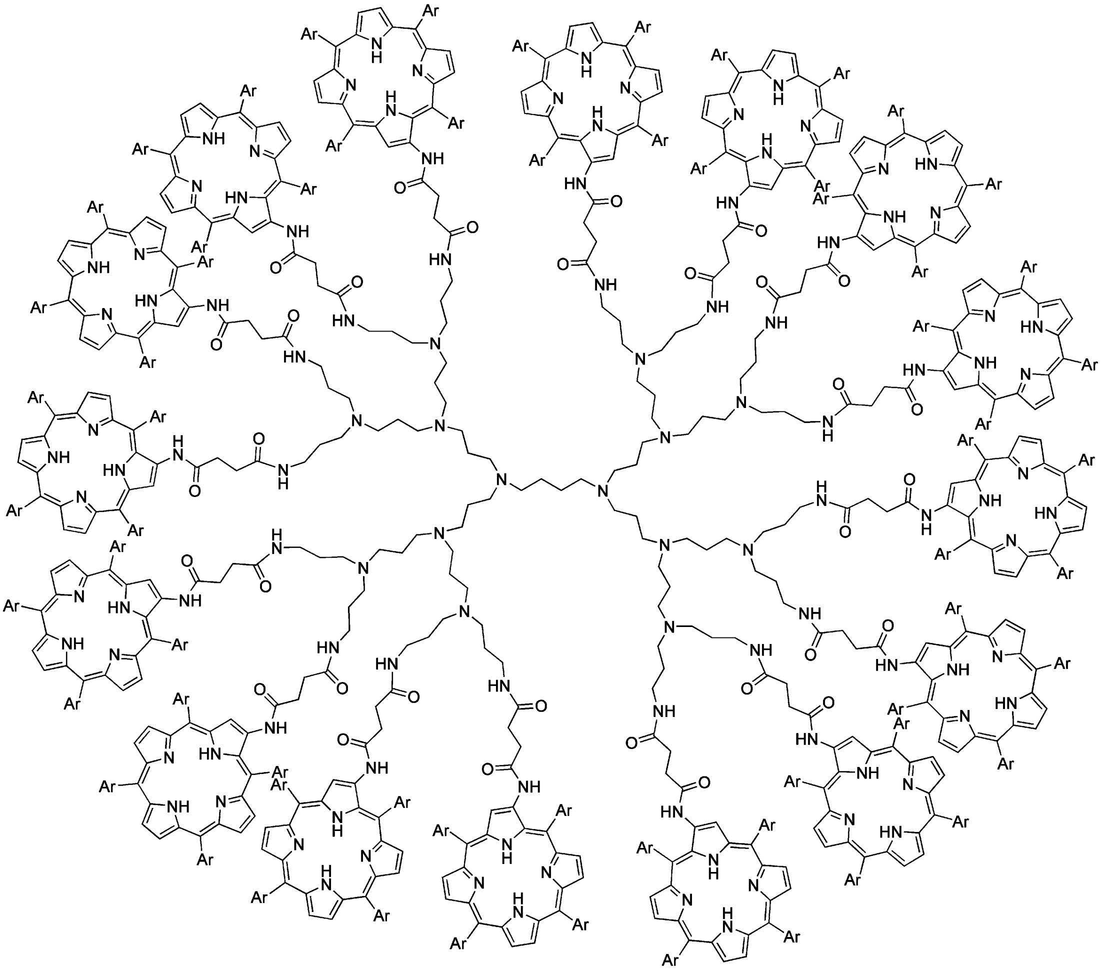
A number of research groups have synthesized macrostructures in which single dendrons are attached to porphyrin chromophores.[55,56] Nagata et al. synthesized photo- and redox-active layered nanostructures with porphyrin focal points and multiple internal quinone or ferrocene groups suspended through a (G_1–G_3) poly(benzyl ether) dendritic framework.[56a,56b] Hirsch and co-workers reported various dendritic systems with fullerene–metalloporphyrin dyad focal points in which Fréchet- or Newkome-type dendrons are attached to the fullerene moieties through cyclopropanation reactions.[56c,56d] Prato et al. also prepared a dendritic fullerene–porphyrin dyad, the structure of which includes a G_2 cyanobiphenyl-based liquid-crystalline dendron.[56e] Water-soluble amphiphilic poly(L-lysine) dendrons with carboxylate terminals and links to porphyrins (and a fullerene) were prepared by Nishino et al.[56f,56g] Fréchet-type dendrons attached to the axial position of a Rh^{III}–porphyrin through their focal dialkoxybenzyl groups were synthesized as novel carbon-centered free-radical equivalents by Kimata and Aida.[56h] Aida and associates also reported the synthesis and self-assembly of an amphiphilic Zn–porphyrin–fullerene dyad with a G_1 benzyl ether dendron carrying triethyleneglycol end groups attached to one of the *meso* positions.[56i] Rosilio and co-workers synthesized monodendron glycodendrimeric porphyrins in a project directed towards efficient targeting of photosensitizers.[56j]

3. Dendrimers with Porphyrins at Their Peripheries

Only a few examples of dendrimers with multiple porphyrins attached to the perimeters of (known) dendritic backbones have been synthesized to date.[2,4,57,59–67] The design of these macrostructures has often been inspired by the different photosynthetic LH antenna complexes used by nature.

Crossley et al. have applied poly(propylene imine) dendrimers (developed by Meijer and co-workers) to prepare porphyrin-appended dendrimers up to the fifth generation and containing 64 exterior porphyrin chromophores by a divergent method (Figure 21).[57] The porphyrin-surface dendrimers were prepared by coupling of G_x poly(propylene imine) dendrimers and an activated ester derived from a β-NH_2-monofunctionalized porphyrin. Ghiggino et al. investigated the dynamics of electronic energy transfer within these porphyrin-functionalized dendrimers,[57a] whereas the electrochemical properties of both the Fb and Zn–porphyrin dendrimers were explored by Bond et al.[57h] Larsen, Sundström, and co-workers studied energy-transfer processes between the porphyrin end groups and conformational dynamics within the Zn–porphyrin dendrimers.[57e–57g,57i] The efficiency of the energy transfer could be significantly enhanced through the addition of an extra carbon atom to the molecular spacer connecting the porphyrin chromophores to the dendritic framework.[57i] Fukuzumi and associates applied the Fb porphyrin dendrimers in conjunction with C_{60} for the construction of supramolecular photovoltaic cells by clusterization on nanostructured SnO_2 electrodes.[57b–57d,57j]

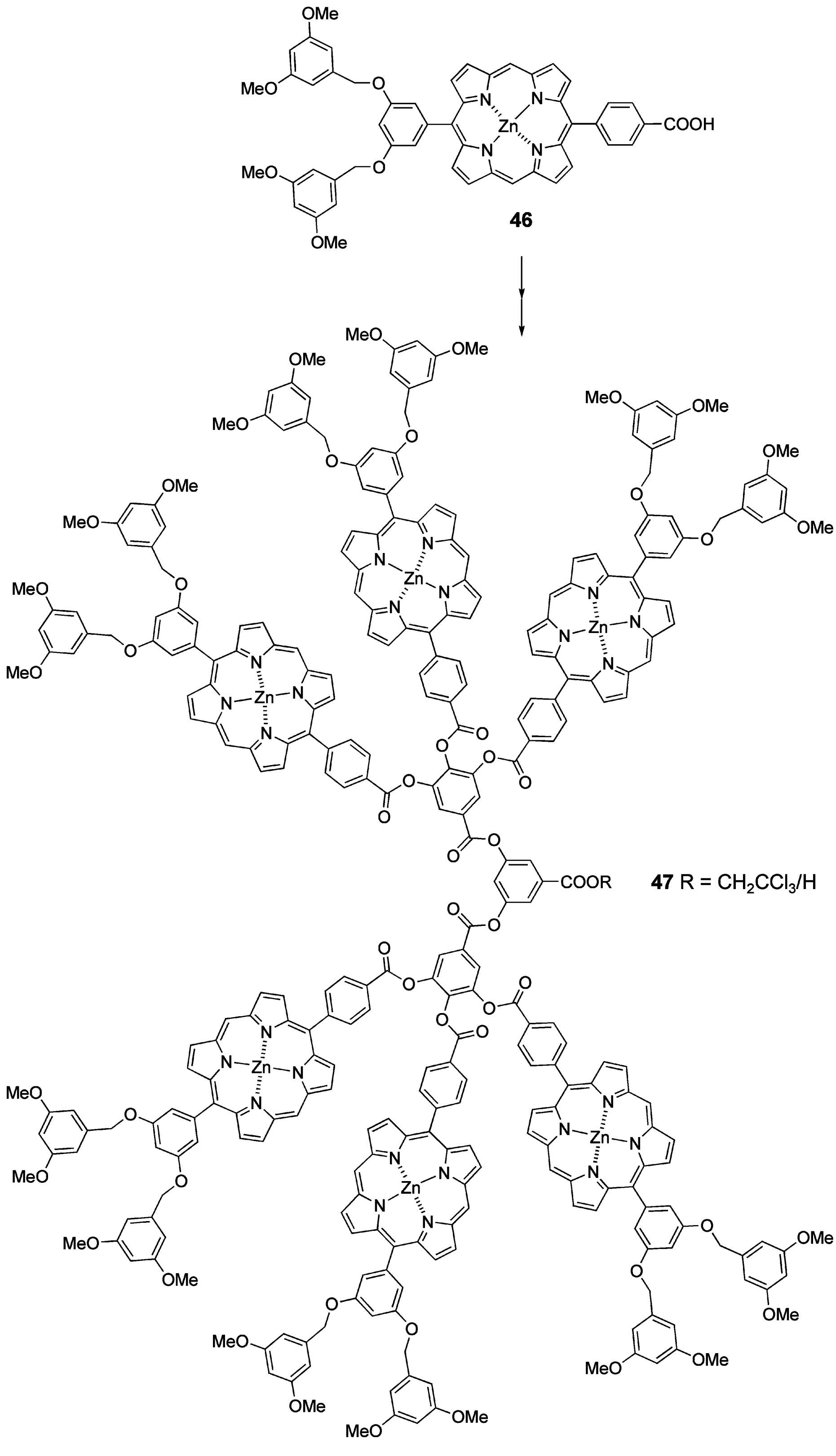
Aida et al. reported dendritic macromolecules functionalized with Zn–porphyrin moieties and peripheral G_1 Fréchet dendrons.[58,59a] Two- and three-branched oligo-Zn–porphyrin polyester dendrons were synthesized convergently from the starting Zn–porphyrin **46** (Scheme 4), which was in turn prepared from a *tert*-butyldiphenylsilyl-protected *meso*-(3,5-dihydroxyphenyl)porphyrin precursor and 3,5-dimethoxybenzyl bromide. The propagation scheme involved repetitive coupling of porphyrin **46** (or the corresponding next-generation dendrons) to 2′,2′,2′-trichloroethyl 3,5-dihydroxybenzoate (or 2′,2′,2′-trichloroethyl 3,4,5-trihydroxybenzoate) under DCC/DPTS coupling conditions and conversion of the resulting ester focal point into the corresponding carboxylic acid (Zn, AcOH). The oligoporphyrin dendrons were coupled to hexakis(4-hydroxyphenyl)benzene (DCC/DPTS) to afford the final multiporphyrin dendrimers. A cooperative effect in the chiroptical sensing of an asymmetric ligating bipyridine guest has been observed for these porphyrin-functionalized dendrimers.[59a] The Zn–porphyrin dendrimers were also used as a scaffold for the preparation of supramolecular segregated arrays of multiple porphyrin donor units and fullerene acceptors (through Zn–porphyrin–bipyridine entrapment), in which noticeable dendritic effects on the photoin-



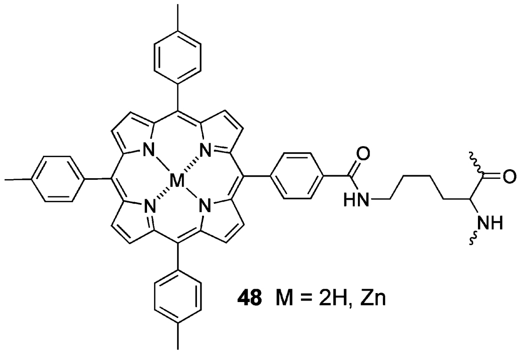
45 Ar = 3,5-di-*tert*-butylphenyl

Figure 21. Porphyrin-appended G_3 poly(propylene imine) dendrimer **45** (Crossley et al.).

duced charge separation were revealed.[59c] Further photophysical studies on these systems performed by Kim and co-workers focused on incoherent excitation energy migration processes in relation to the dendritic structure, together with control of the molecular structures and their photophysical features through bidentate guest complexation, overcoming the intrinsic flexibility of the dendrimers and the resulting heterogeneities.[59b,59d,59e]



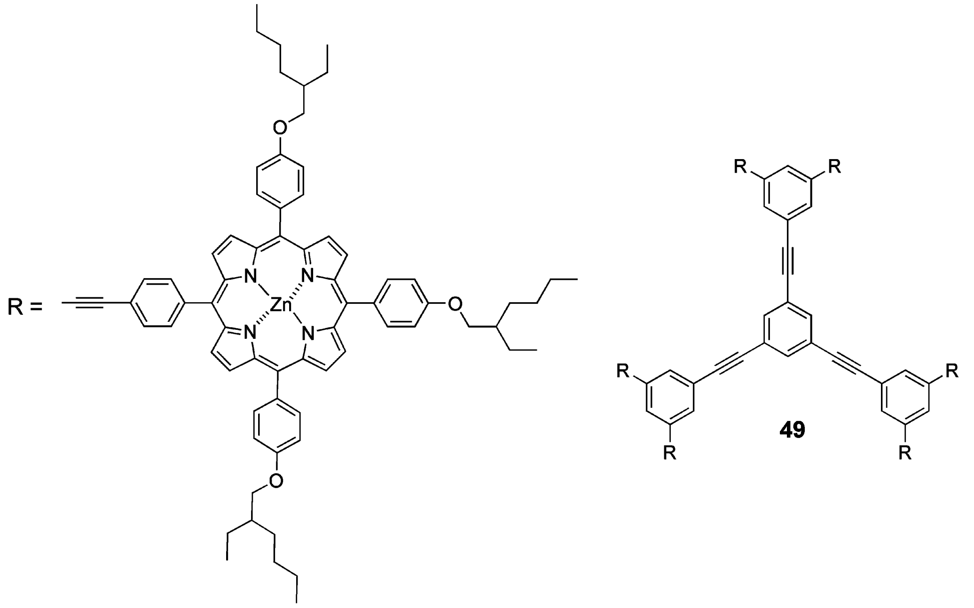
Scheme 4. Aida's three-branched hexakis(Zn–porphyrin) dendron **47** and porphyrin precursor **46**.



48 M = 2H, Zn

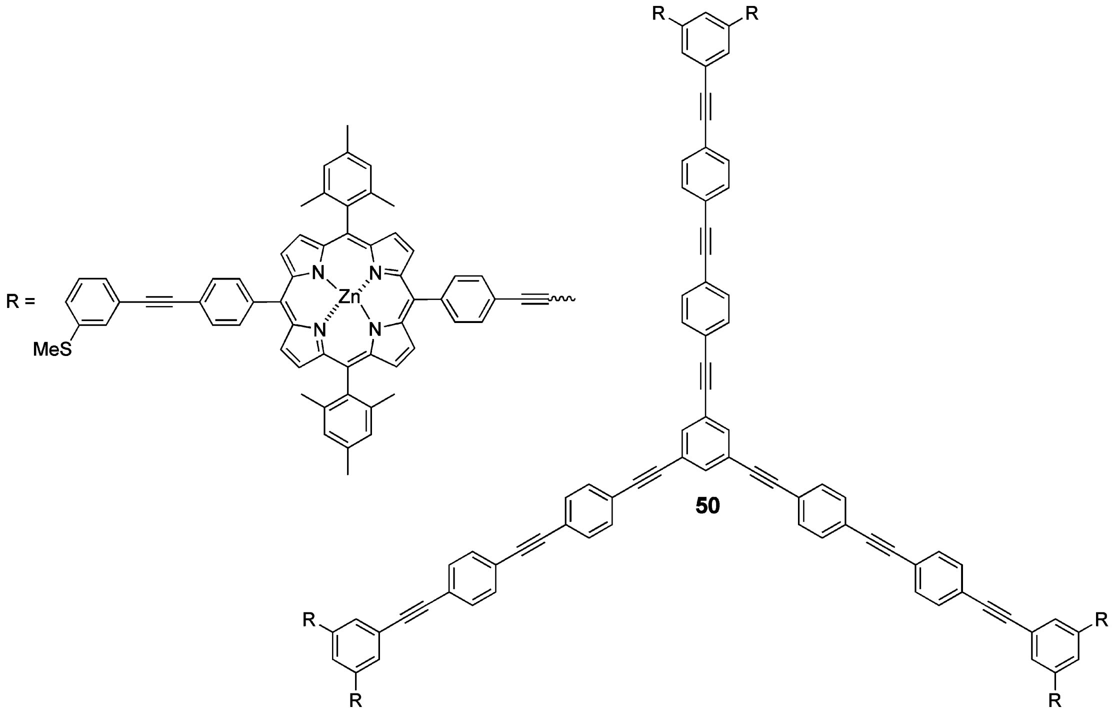
Figure 22. Porphyrin **48**, incorporated near to the surfaces of Nishino's poly(L-lysine) dendrimers.

Poly(L-lysine) dendrimers containing up to 32 Zn or Fb near-surface porphyrin units **48** (Figure 22) at the fifth generation (and covered by two additional L-lysine generations) were prepared by Nishino and co-workers through a divergent strategy employing synthetic peptide coupling reactions and Boc/Fmoc protection.[60] The Fb and Zn–porphyrin chromophores could also be combined within one single dendritic structure, either randomly distributed or separated hemispherically. Intramolecular fluorescence energy transfer from the Zn to the Fb porphyrin chromophores has been examined, with a higher efficiency (85%) being observed in the scrambled assembly.



49

Figure 23. Porphyrin–phenylacetylene dendrimer **49** (Shinkai et al.).



50

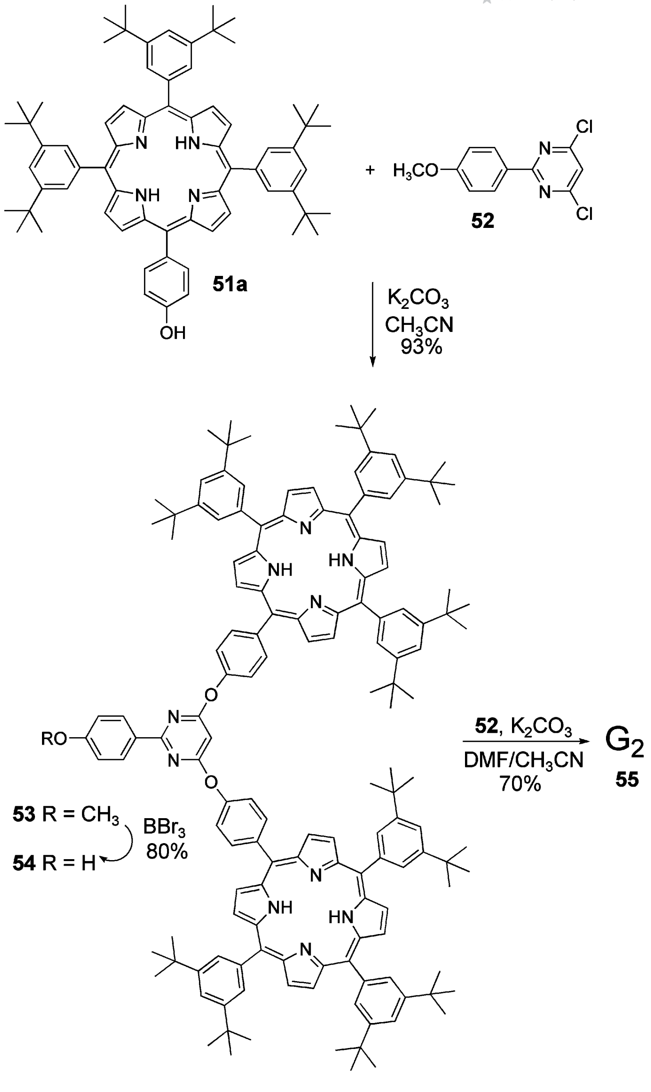
Figure 24. Benzene-centered dendritic hexaporphyrin **50** (Gossauer et al.).

Shinkai et al. designed a phenylacetylene dendrimer **49** with six peripheral porphyrin units (Figure 23), which was shown to be an efficient dendritic porphyrin receptor, binding three C_{60} molecules in a positive allosteric manner.[61] The dendrimer was constructed convergently from a starting AB_3 porphyrin (Zn–5,15,20-tris{4-[(2-ethylhexyl)oxy]-phenyl}-10-(4-ethynylphenyl)porphyrin) as the surface unit through iterative Sonogashira coupling and phenylacetylene deprotection reactions.

The similar rigid hexaporphyrin dendritic array **50**, and also smaller tris(porphyrin) arrays, were prepared by Gossauer et al. (Figure 24).[62] Their synthetic pathway started essentially from a 1,3,5-triiodobenzene core and Zn–5,15-bis(4-iodophenyl)-10,20-dimesitylporphyrin as the exterior porphyrin unit. The propagation involved conversion of the porphyrin precursor into a peripheral bis(phenylethynyl)-porphyrin bearing a *meta*-thioanisole unit and a (deprotected) *meso*-phenylethynyl moiety for further reactions, dimerization with [(3,5-diiodophenyl)ethynyl]trimethylsilane, elongation of the ethynylphenyl moiety with 4,4′-diiodotolane, and finally a triple reaction with 1,3,5-triethynylbenzene [$Pd_2(dba)_3$, $AsPh_3$, DMF, Et_3N; 28 %]. An alternative strategy was applied to prepare an analogous hexaporphyrin dendrimer with two Zn and four Fb porphyrin end groups, and the dynamics of electronic energy transfer within the multiporphyrin arrays were investigated.[62b]

In our own group we have explored porphyrin-functionalized dendrons as recyclable homogeneous photocatalysts in collaboration with the research team of Jacobs and De Vos.[63] The applied convergent synthetic strategy involved the attachment of AB_3 porphyrin **51a** through its phenol group to pyrimidine monomer **52**, and propagation through cleavage of the protective focal methyl ether with BBr_3 and a novel S_NAr reaction on the pyrimidine monomer (Scheme 5).[43] The resulting multiporphyrin dendrons showed high activity as catalysts for the light-induced generation of $^1O_2$ and are useful photosensitizers for the oxidation of various olefinic substrates to the corresponding allylic hydroperoxides. Moreover, efficient recycling of the dendrimer-enlarged porphyrin photocatalysts could be effected by solvent-resistant nanofiltration through an oxidatively stable membrane.

Liu et al. attached 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphyrin (**7a**, Figure 1) to the periphery (one third to half of the NH_2 end groups) of a G_5 PAMAM dendrimer with a cyclic 1,4,7,10-tetraazacyclododecane core via the dianhydride of an EDTA (ethylenediaminetetraacetic acid) linker for gene transfer purposes.[64] Similarly, Lai and co-workers more recently reported water-soluble PAMAM–porphyrin conjugates for non-toxic phototriggered gene transfection.[65] The surface of a starburst G_4 poly(amidoamine) dendrimer was modified by treatment with 5,10,15-tris(4-acetamidophenyl)-20-(4-carboxyphenyl)porphyrin under DCC/NHS (*N*-hydroxysuccinimide) coupling conditions, and the degree of porphyrin loading was estimated as 12 % (w/w) by UV/Vis spectroscopy. Roberts et al. applied PAMAM dendrimers as synthetic handles to link porphyrin chelators [5-(4-carboxyphenyl)-*N*-(4-nitrobenzyl)-10,15,20-tris(4-sulfonatophenyl)porphyrin] for radiocopper ions covalently to antibody molecules (amide formation with EDAC {1-[3′-(dimethylamino)propyl]-3-ethylcarbodiimide} and NHS).[66] Prato and co-workers decorated single-wall carbon nanotubes (SWNTs) with G_2 PAMAM dendrons functionalized with porphyrin termini.[67] 5-(4-Carboxyphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin was coupled to the amine moieties on the PAMAM surface in the presence of EDC and HOBt.



Scheme 5. Convergent propagation scheme directed towards the porphyrin-appended pyrimidine dendrons **53**–**55** (Dehaen et al.).

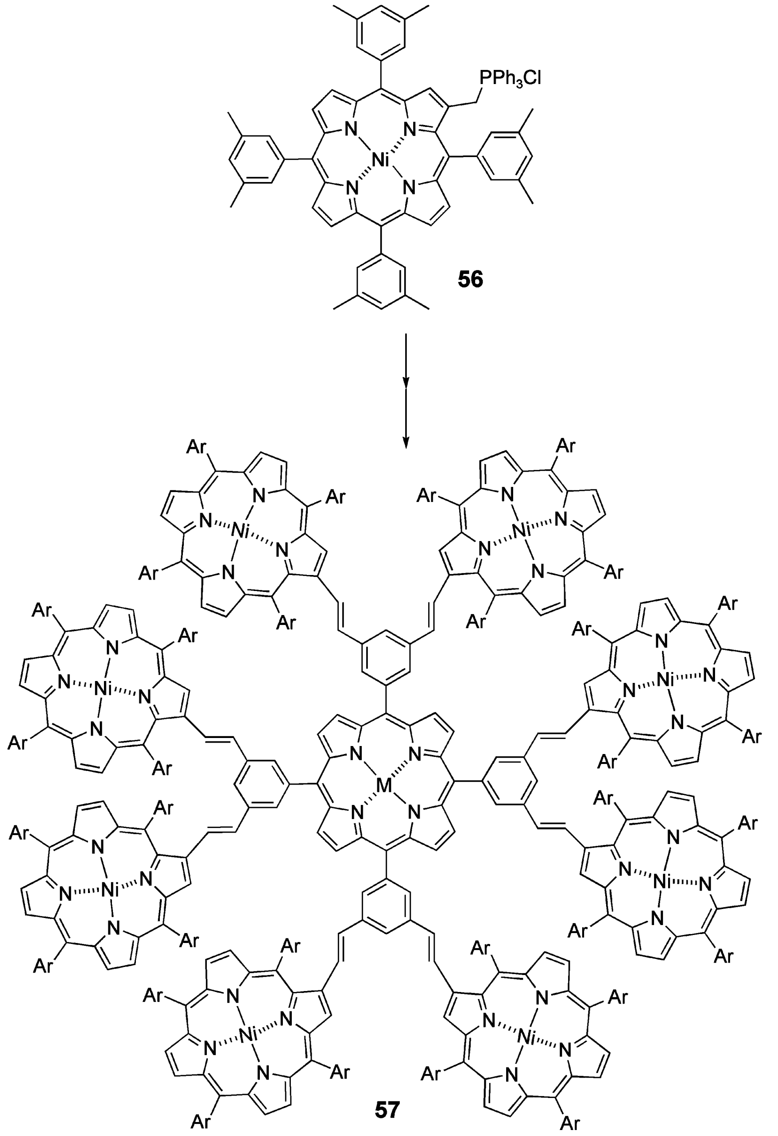
4. All-Porphyrin Dendrimers

“All-porphyrin” dendrimers, embedding porphyrins at every level of the branched macrostructure – as core unit, within the dendrons, and at the surface – are attractive materials for electronic and photonic nanodevices, artificial photosynthesis, and multisite catalysts, but are obviously the most challenging porphyrin dendrimers from a synthetic point of view.

A number of rather simple star-shaped pentaporphyrin systems that might be regarded as G_0 multiporphyrin dendrimers have been synthesized by different approaches over the years.[68] These structures, however, are not surveyed in detail.[4]

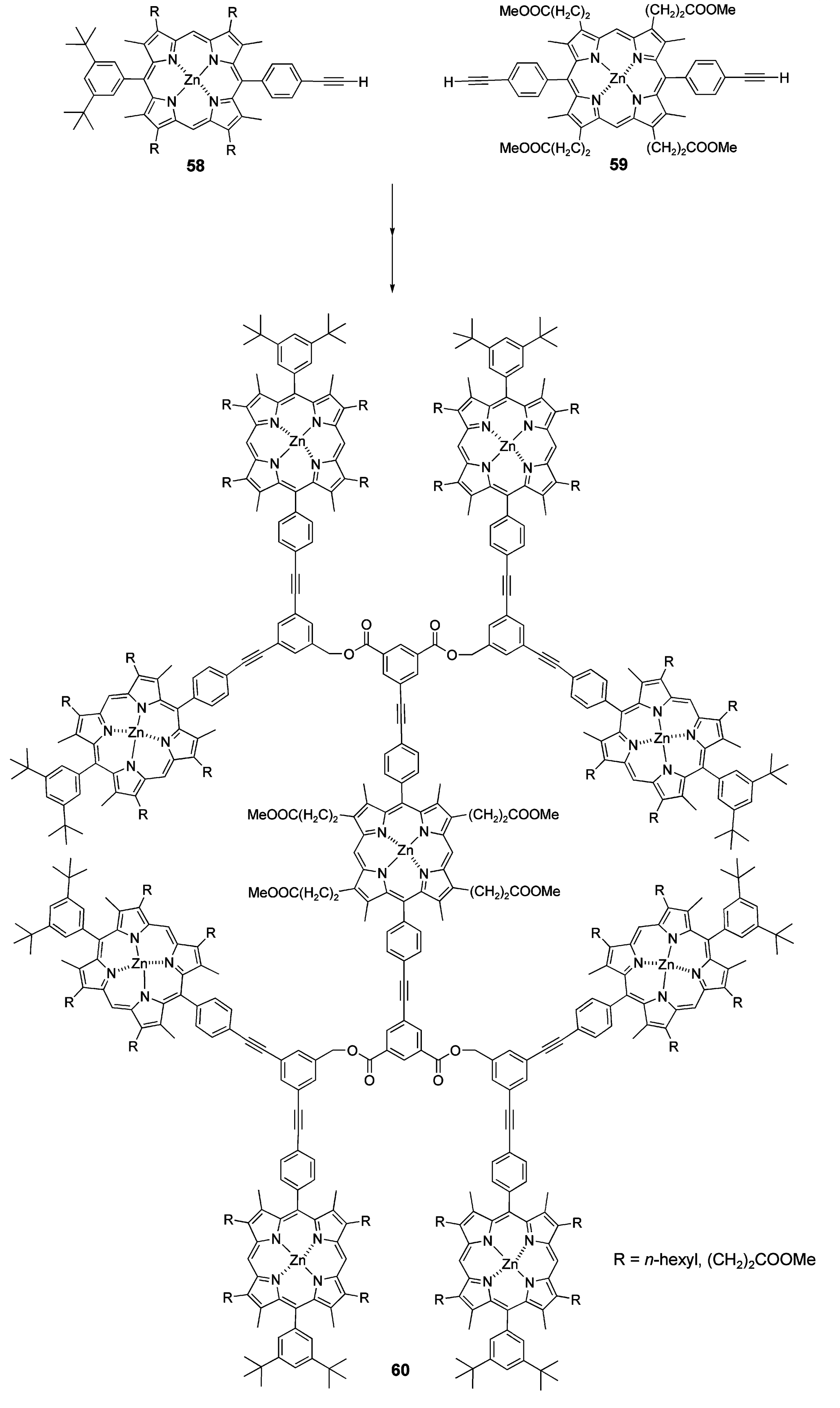
Burrell and Officer prepared dendritic penta- and nonaporphyrin arrays based on the β-functionalized Ni–tetrakis(3,5-dimethylphenyl)porphyrin–methylphosphonium salt **56** (Scheme 6).[69] A twofold Wittig reaction between the peripheral porphyrin **56** and 1,3,5-triformylbenzene afforded a stilbene-linked dimeric porphyrin (68 % yield), and cyclocondensation of this G_1 dendritic aldehyde with pyrrole under Lindsey conditions (TFA catalysis) resulted in the G_1 porphyrin dendrimer **57** (29 % yield). Analogous vinylene-linked G_x dendrons with exterior porphyrin units were constructed in consecutive Wittig reactions.

Sanders et al. reported the convergent synthesis of metalloporphyrin dendrimers containing nine porphyrin chromophores, connected through a combination of diphenylethyne and ester linkers by means of alternating high-yielding Pd-mediated and Mitsunobu coupling reactions. Their synthetic procedure involved the porphyrins **58** and **59** as building blocks and 3,5-diiodobenzyl alcohol and 5-iodoisophthalic acid as the branching units, and proceeded without any activation or deprotection steps (Scheme 7).[70] The combination of rigid and flexible linkers allows the dendrons to fold in a cooperative way, binding DABCO. The peripheral G_1 dendritic porphyrin dimers were alternatively attached to a Fb A_2B_2 porphyrin-tetraacid core by Mitsunobu coupling through their benzylic alcohol focal moieties (69 % yield).[70b] This strategy allows easy chromatographic separation of the nonaporphyrin

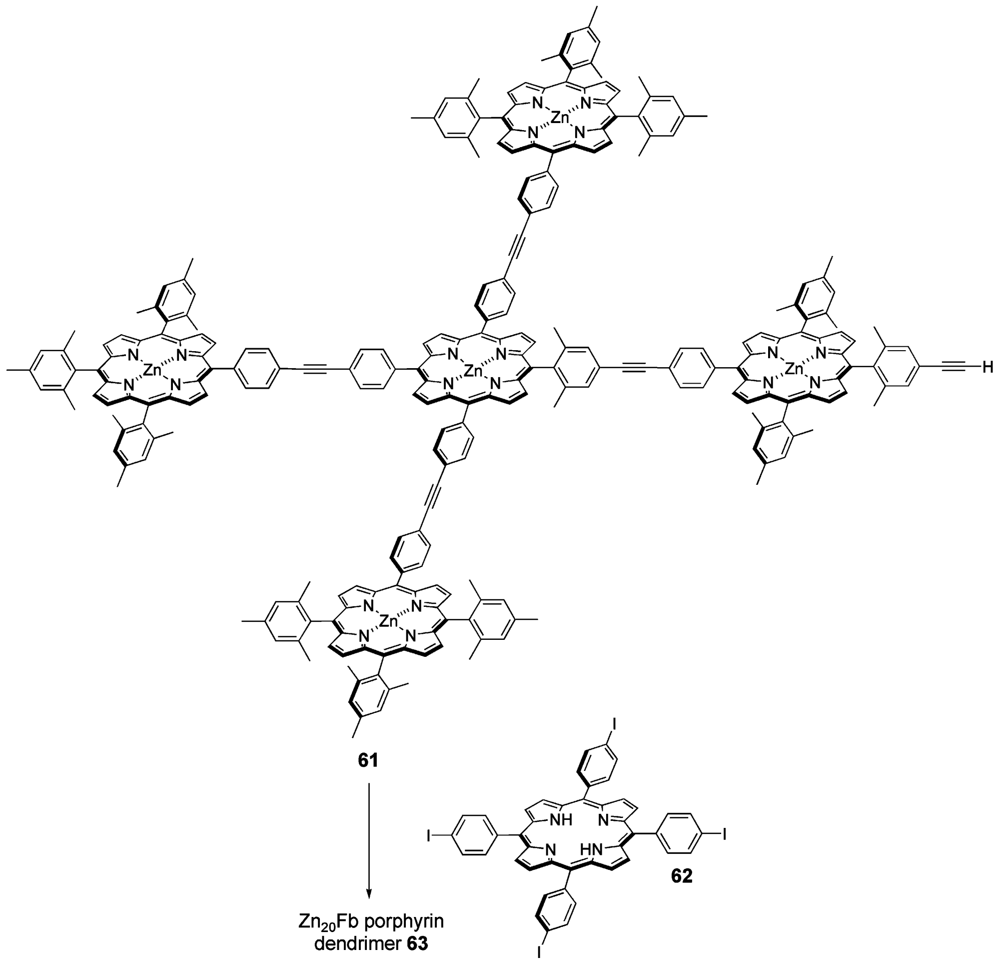


Ar = 3,5-dimethylphenyl; M = 2H, Zn

Scheme 6. Synthetic pathway toward the dendritic nonaporphyrin **57** (Officer, Burrell et al.).



Scheme 7. The dendritic nonaporphyrin array **60** and its precursors **58** and **59** (Sanders et al.).



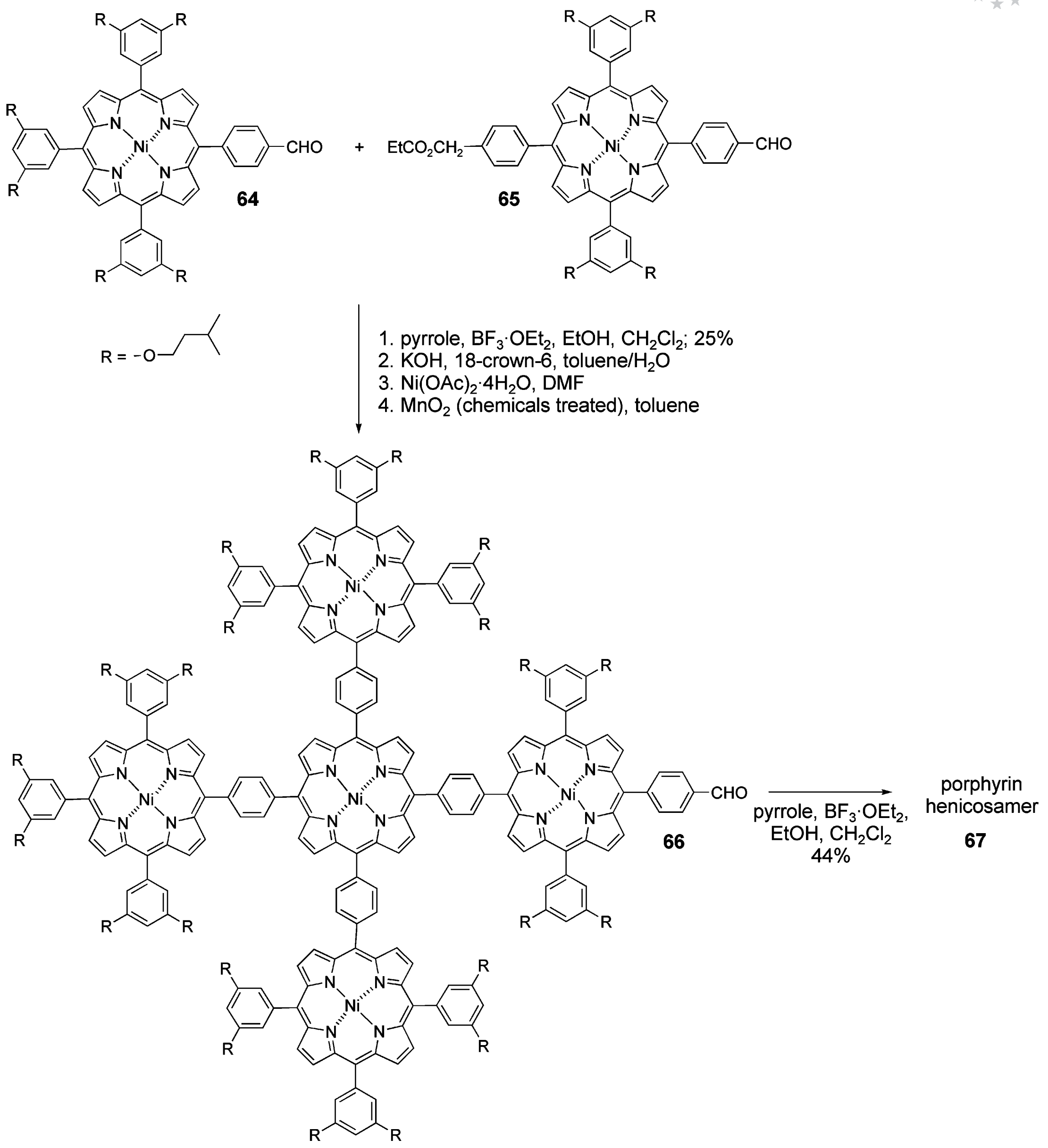
Scheme 8. Synthetic approach to the porphyrin dendrimer **63** (Lindsey et al.).

from more polar products resulting from incomplete coupling.

Lindsey's convergent synthetic strategy afforded dendritic multiporphyrins containing *n* Zn–porphyrins ($n = 4$, 8, or 20) and an Fb porphyrin core joined by semi-rigid diarylethyne linkers with favorable LH and hole-storage properties.[71] Their largest all-porphyrin dendrimer **63**, containing 21 porphyrin chromophores, was constructed stepwise from iodophenyl and ethynylphenyl-substituted *meso*-tetraarylporphyrin building blocks, with mesityl groups providing solubility, under standard Pd-mediated coupling conditions [$Pd_2(dba)_3$, $AsPh_3$, toluene/triethylamine] (Scheme 8).

The similar impressive dendritic array **67**, incorporating 20 Ni–porphyrins and one Fb porphyrin, was prepared by Sakata and co-workers through successive porphyrin-forming reactions, with a total yield of only 0.15% for the 17-step sequence (Scheme 9). The square-shaped sheet-like macromolecule was additionally characterized by direct observation of its molecular shape by STM (scanning tunneling microscopy).[72]

Choi, Aida et al. synthesized large multiporphyrin arrays in which light-absorbing Zn–porphyrin dendrons (containing one, three, or seven porphyrins) are attached to an energy-accepting Fb porphyrin core.[73] Their convergent growth approach used 5-(3,5-dihydroxyphenyl)-15-(4-methoxycarbonylphenyl)porphyrin as the main porphyrinic building block, and Fréchet-like stepwise construction of the dendrons afforded the heptameric Zn–porphyrin dendrons **68a** and **68b** (Figure 25). The dendron surface is equipped with G_2 Fréchet poly(benzyl ether) dendrons (for solubility). Linkage of the dendron **68b** to the Fb porphyrin core **7a** (Figure 1) afforded a giant multiporphyrin macromolecule (18%) consisting of 28 Zn–porphyrin units and an Fb porphyrin core, the largest multiporphyrin dendrimer synthesized to date. Ester-linked all-porphyrin dendrimers were also prepared, through connection of the peripheral (porphyrin) dendrons to a pentaporphyrin core derived from **8a** (Figure 1). The star-shaped dendritic arrays (in contrast to the cone-shaped dendrons), in which the chromophore units are arranged in an analogous fashion to those in the natural LH antenna complexes (bacterial LH2), show both a large absorption cross section and a high efficiency of vectorial energy transfer, without assistance of π-electronic conjugation. Through coupling of the (multi)porphyrin dendrons to a fullerene acceptor, the same group also provided a start towards the construction of electron transfer relays mimicking the natural photosynthetic reaction center.[74]

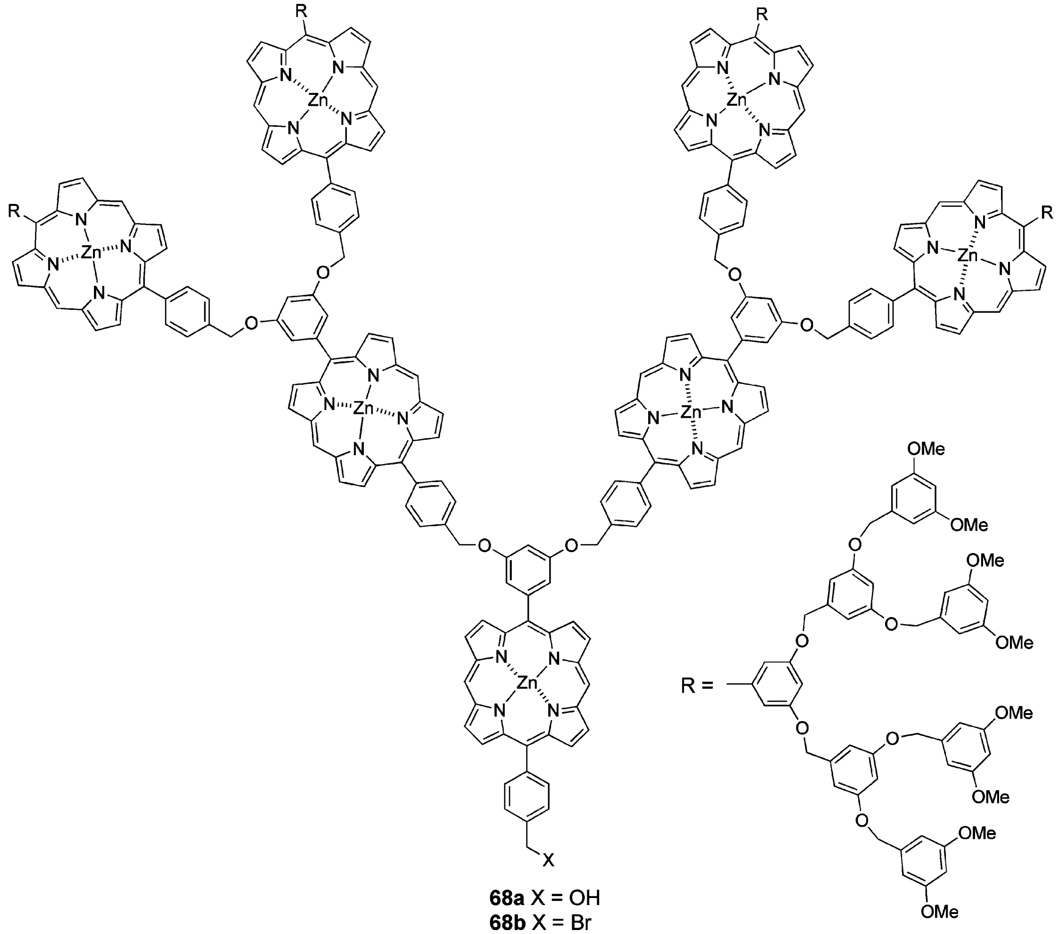


Scheme 9. Synthesis of the "mandala-patterned bandanna-shaped" all-porphyrin dendrimer **67** (Sakata et al.).

Solladié and co-workers extended their previously developed methodology for pentaporphyrins to a photoactive dendritic nonaporphyrin with (enantiopure) nucleosidic interporphyrin linkers.[68h,68j,75] The nucleoside–porphyrin conjugate **69**, bearing two Zn–porphyrins at the C-5′ position of a ribose sugar unit and an aldehyde moiety at the C-5 position of an uracil nucleic base, could be converted into the G_1 nonaporphyrin dendrimer **70** upon cyclocondensation with pyrrole under Lindsey conditions (Scheme 10).[75] Photoinduced processes occurring within the multiporphyrin structure have been studied in detail.[75b]

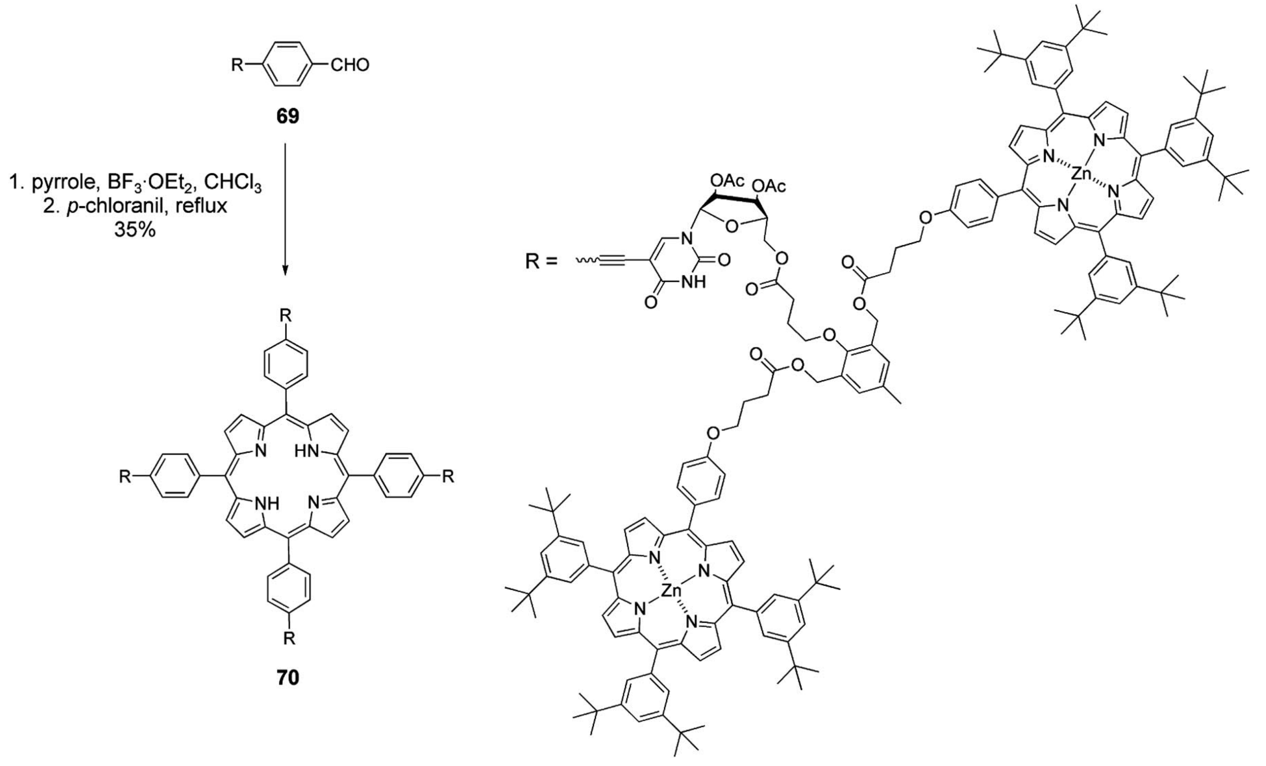
Our group has also contributed to the field of all-porphyrin dendrimers. In 2006 we reported an efficient synthetic protocol for novel multiporphyrin dendrons and dendrimers, constructed through consecutive S_NAr reactions with *meso*-(dichloropyrimidinyl)porphyrinic building blocks.[76] The dendron propagation involved a (high-yielding) S_NAr reaction with the peripheral AB_3 porphyrin **51a**, decorated with di-*tert*-butylphenyl groups to afford high solubility and thereby enabling easy synthetic routine handling and characterization, and the *meso*-(dichloropyrimidinyl)-substituted porphyrin AB_2 monomer **71a**, with subsequent deprotection of the benzyl-protected phenolic focal moiety (Scheme 11). The propagation was carried out up to the second-generation heptaporphyrin dendron **74a**. Moreover, the applied S_NAr approach was shown to be compatible with the stepwise introduction of different metal atoms – as a proof-of-principle Pt, Zn, and Ni were initially chosen – in the successive generations.

On application of analogous *meso*-(dichloropyrimidinyl)-substituted porphyrin cores (e.g., **36**, Scheme 2), the final multiporphyrin dendrimers were obtained. The largest



68a X = OH
68b X = Br

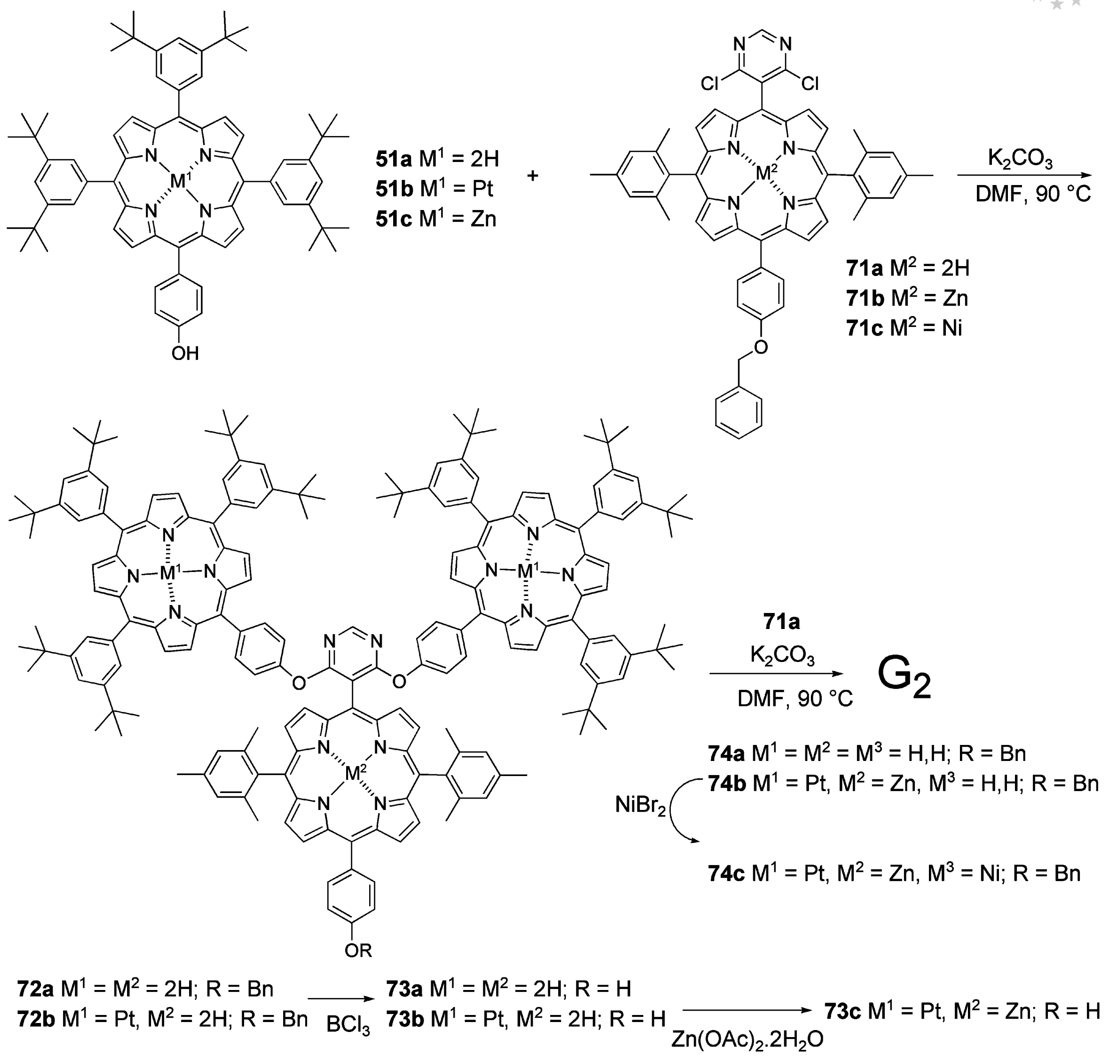
Figure 25. Heptaporphyrin dendrons **68a** and **68b** (Aida et al.).



69

70

Scheme 10. Synthesis of the nonaporphyrin dendrimer **70** through porphyrin formation from the aldehyde precursor **69** (Solladié et al.).



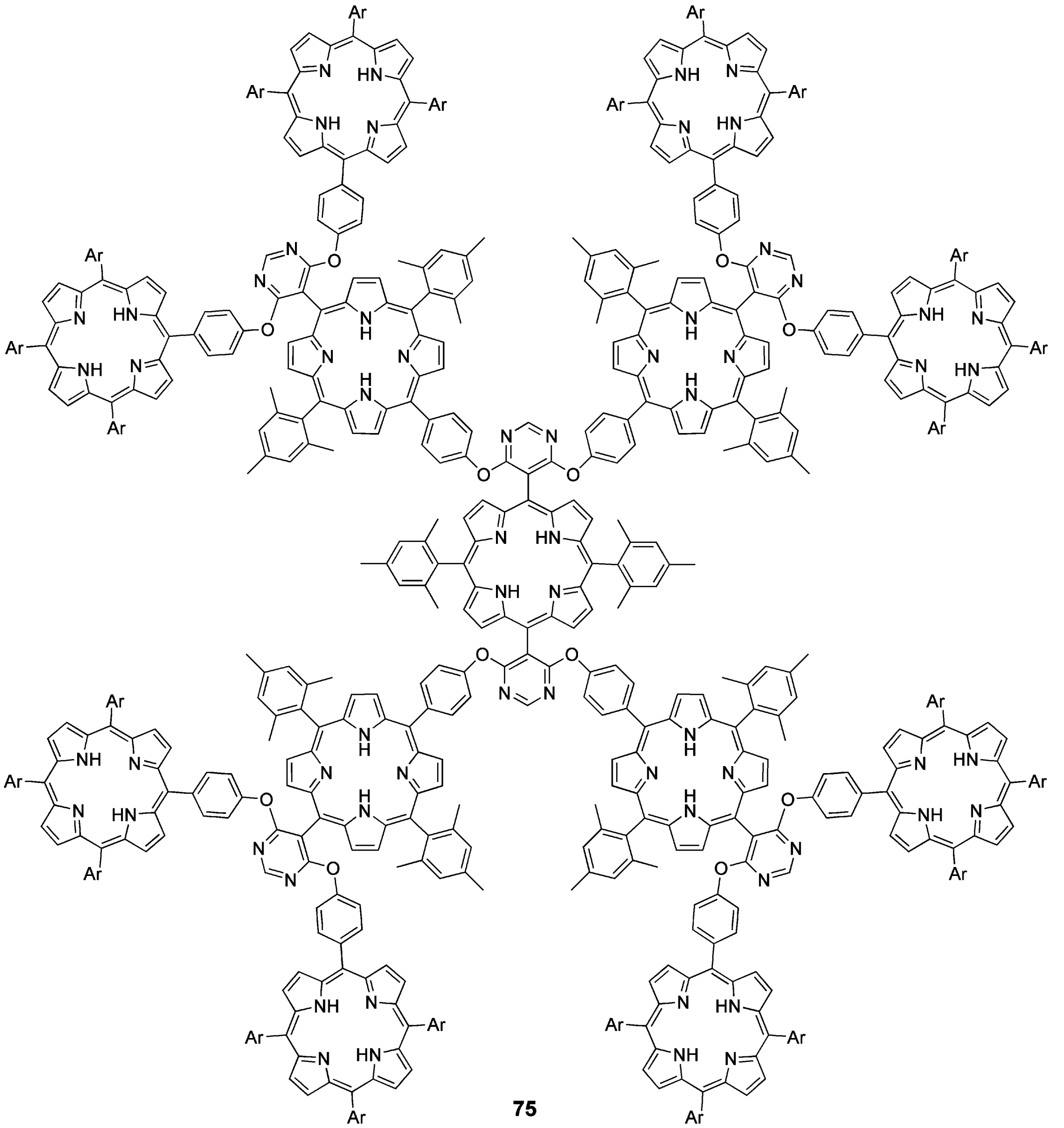
Scheme 11. Convergent synthesis of multiporphyrin dendrons **72**–**74** (Dehaen et al.).

member of the dendritic multiporphyrin family (the G$_1$ dendrimer **75**, Figure 26), containing 13 porphyrin chromophores joined by (hetero)aryl ether linkages and a unique *ortho*,*ortho'*-substitution pattern, could not efficiently be purified from the defect trisubstituted side product solely by column chromatography.[76]

Okada et al. recently elaborated their synthetic strategy for "snowflake-shaped" porphyrin-core dendrimers (see Figure 18, ref.[52]) to multiporphyrin dendritic systems.[77] A cross-shaped dendritic pentaporphyrin conjugated assembly was constructed by (Cu-free) Sonogashira coupling of a dendritic A$_3$B Zn–porphyrin to a dendritic Fb A$_4$ porphyrin core (15% yield).[77a] Fluorescence from the peripheral Zn–porphyrins was partially quenched through intramolecular energy transfer to the central Fb porphyrin. On the other hand, the LH G$_1$ multiporphyrin dendrimer **76**, composed of 12 porphyrin surface groups, a rigid conjugated phenylethynyl backbone, and a porphyrin core (Figure 27), was synthesized convergently, again based on the Sonogashira reaction as the key propagation step.[77b] Four snowflake tris(porphyrin) dendrons, constructed through Sonogashira and Suzuki cross-coupling reactions, were connected to tetrakis(4-ethynylphenyl)porphyrin as the core unit through their iodo focal points [Pd$_2$(dba)$_3$·CHCl$_3$, AsPh$_3$, THF, Et$_3$N; 23%]. The efficiency of the intramolecular singlet-energy transfer in these systems was also investigated.

5. Summary and Outlook

The field of porphyrin dendrimers has advanced a long way since the pioneering work of Aida, Diederich, Suslick, and others in the early 1990s. Increasingly complex synthetic molecular constructs incorporating multiple porphyrin chromophores at different sites within the hyperbranched architecture have been designed and synthesized. We have tried to provide an up-to-date overview of the porphyrin dendrimer macromolecules that have been prepared over the years, with a focus on their structural compositions and the applied synthetic routes, complementary to the earlier accounts and reviews on related topics. The main challenge nowadays is to find applications for porphyrin dendri-



75

Ar = 3,5-di-*tert*-butylphenyl

Figure 26. Multiporphyrin G_1 dendrimer **75** (Dehaen et al.).

mers in which the unique hallmarks of the dendritic architecture and the (multiple) porphyrin chromophores overcompensate the synthetic difficulties and high costs, enabling porphyrin dendrimers to evolve from useful model compounds into economically viable products. This overview of currently available structures might provide a useful starting point to those scientists interested in applying porphyrin dendrimers.[78]

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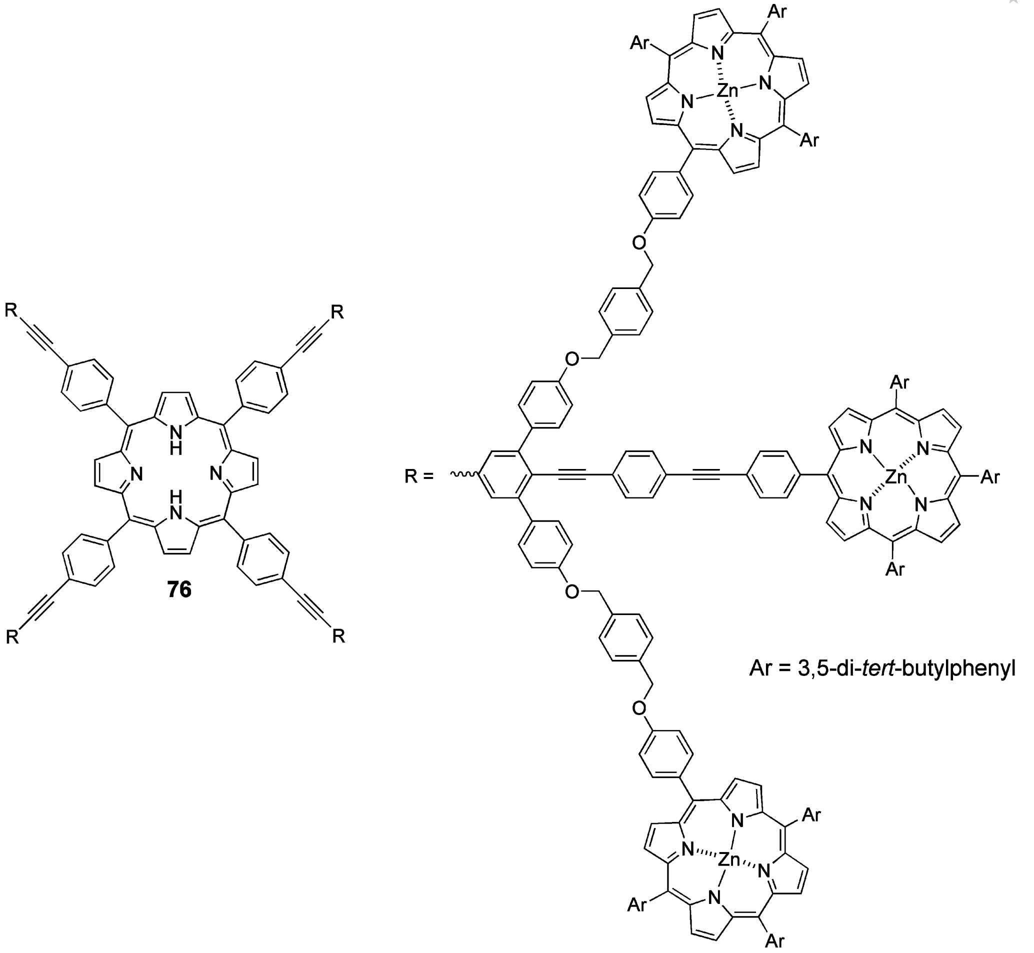

Figure 27. Snowflake multiporphyrin dendrimer **76** (Okada et al.).

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