

# Convergent Dendrons and Dendrimers: from Synthesis to Applications

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Received March 5, 2001

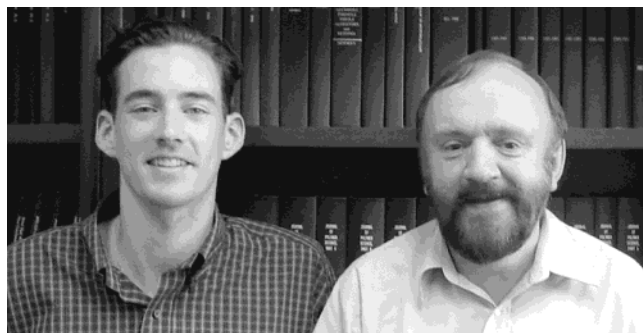
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## I. Introduction

Dendrimers represent a key stage in the ongoing evolution of macromolecular chemistry. From the origins of polymer chemistry until 20 years ago, a major focus had been the synthesis and characterization of linear polymers. Although the molecular interactions and the many conformations of linear polymers involve three dimensions, their covalent assembly is strictly a one-dimensional process. Half a century ago, in theoretical studies, Flory was among the first to examine the potential role of branched units in macromolecular architectures,<sup>1,2</sup> but it was not until the mid-1980s that methods for the orderly preparation of these polymers had been sufficiently developed to enable their practical study. In 1978, Vögtle developed an iterative cascade method for the synthesis of low molecular weight branched amines.<sup>3</sup> Using chemistry and conditions less prone to cyclization side-reactions and therefore more suitable for repetitive growth, Tomalia et al. disclosed the synthesis and characterization of the first family of dendrimers in 1984–1985.<sup>4,5</sup> The synthesis was initiated by Michael addition of a “core” molecule of ammonia to three molecules of methyl acrylate, followed by exhaustive amidation of the triester adduct using a large excess of ethylenediamine, a process that generates a molecule with six terminal amine groups. Iterative growth is then continued using alternating Michael addition and amidation steps with the appropriate excess of reagents. Optimization of this procedure enabled the synthesis of globular poly(amidoamine) (PAMAM) dendrimers on a commercial scale with molecular weights well above 25 000. Shortly thereafter, in 1985, Newkome reported preliminary results toward another family of trisbranched polyamide dendrimers,<sup>6</sup> and in 1993,

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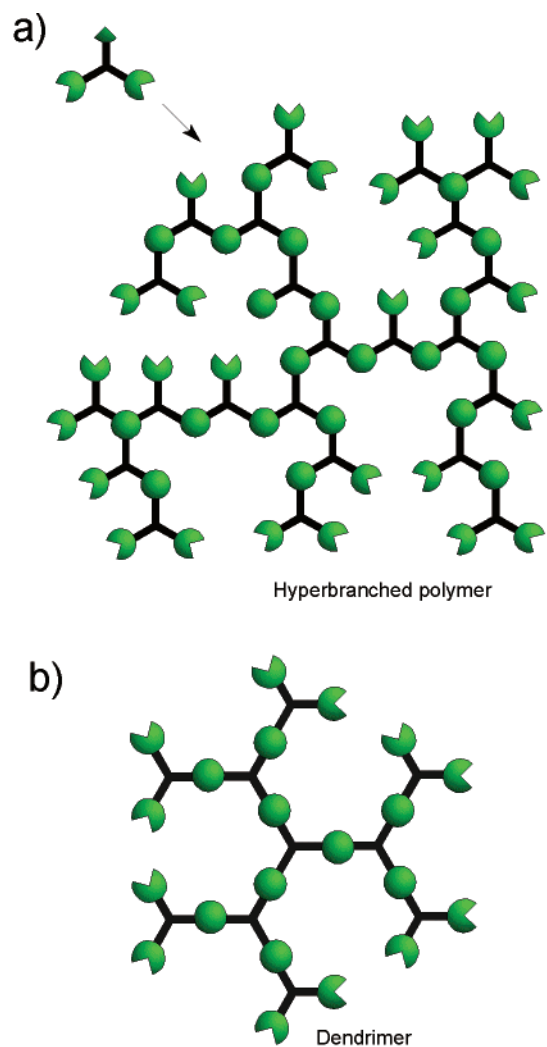
Scott M. Grayson (left) was born in 1974 in St. Louis, Missouri. He studied at Tulane University in New Orleans and graduated summa cum laude with a BS in Chemistry in 1996. After completing his M.Phil. in Archaeological Chemistry at the University of Bradford (Bradford, U.K.), under the guidance of Prof. Carl Heron, he returned to the US to pursue doctoral studies in chemistry. He is presently researching the applications of dendritic architectures with Professor Jean M. J. Fréchet at the University of California, Berkeley.

Jean M. J. Fréchet (right) obtained his first degree at the Institut de Chimie et Physique Industrielles (now CPE) in Lyon, France, and Ph.D. degrees at SUNY-CESF and Syracuse University. Following academic appointments at the University of Ottawa (1973–1986) and Cornell University (1987–1996), he joined the department of chemistry at the University of California, Berkeley. Fréchet is a member of the National Academy of Science, the National Academy of Engineering, and the American Academy of Arts and Sciences. His research is concerned with functional polymers from their design and synthesis to their applications.

improvements on Vögtle's original synthesis were disclosed by Meijer and Mülhaupt that enabled the production of poly(propylene imine) (PPI) dendrimers.<sup>7,8</sup> In 1989–1990, Hawker and Fréchet introduced the convergent growth approach to dendrimers,<sup>9,10</sup> the second general route to dendritic structures, and the primary subject of this review. Since these seminal reports, thousands of papers have been written about the synthesis, properties, and applications of dendrimers, and a diverse range of complex macromolecules have been assembled, capitalizing on the unique architecture of dendritic molecules and the properties they confer.<sup>11–28</sup>

## A. Structure

There are two basic types of polymers that consist entirely of branched repeat units: dendrimers and hyperbranched polymers. Hyperbranched polymers are usually the product of a noniterative polymerization procedure<sup>29–31</sup> and therefore exhibit an irregular architecture (Figure 1a) with incompletely reacted branch points throughout the structure.<sup>17,32,33</sup> Dendrimers, on the other hand, are highly ordered, regularly branched, globular macromolecules prepared by a stepwise iterative approach. Their structure is divided into three distinct architectural regions: (i) a core or focal moiety, (ii) layers of branched repeat units emanating from this core, and (iii) end groups on the outer layer of repeat units (Figure 1b). Dendrimers are differentiated from hyperbranched polymers by their structural perfection, leading to an exact number of concentric layers of branching points, or generations.



**Figure 1.**

At least three characteristic features of dendrimers are in sharp contrast to those of traditional linear polymers.

(i) A dendrimer can be isolated as an essentially monodisperse single compound, unlike most linear polymers whose synthesis affords a range of molecular species differing in molecular weight (MW). Size monodispersity results from a well-designed iterative synthesis that allows reactions to be driven to completion, side-reactions to be avoided, and in some cases, the dendritic products to be purified at intermediate steps during their growth.

(ii) As their molecular weight increases, the properties of dendrimers (e.g., solubility, chemical reactivity, glass transition temperature) are dominated by the nature of the end groups. Unlike linear polymers that contain only two end groups, the number of dendrimer end groups increases exponentially with generation, and therefore the end-groups frequently become the primary interface between the dendrimer and its environment.

(iii) In contrast to linear polymer growth that, theoretically, can continue ad infinitum barring solubility issues, dendritic growth is mathematically limited. During growth of a dendrimer, the number of monomer units increases exponentially with gen-

eration, while the volume available to the dendrimer only grows proportionally to the cube of its radius. As a result of this physical limitation, dendritic molecules develop a more globular conformation as generation increases. At a certain generation a steric limit to regular growth, known as the De Gennes dense packing<sup>34</sup> is reached. Growth may be continued beyond de Gennes dense packing but this leads to irregular dendrimers incorporating structural flaws.

## B. Applications

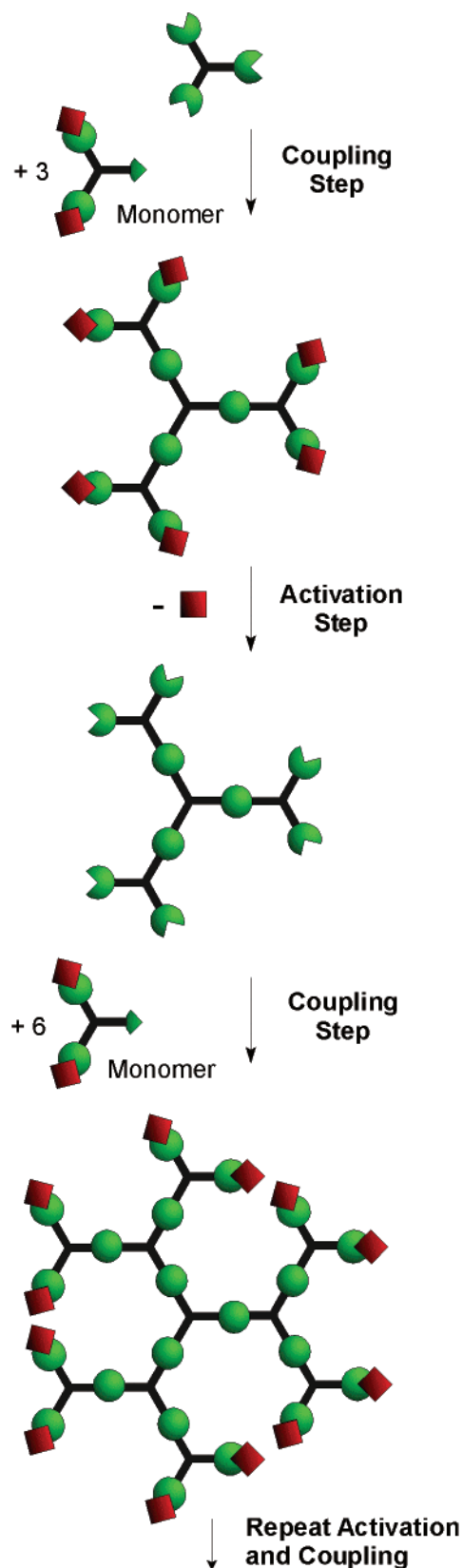
Because of their well-defined, unique macromolecular structure, dendrimers are attractive scaffolds for a variety of high-end applications. Their highly branched, globular architecture gives rise to a number of interesting properties that contrast those of linear polymers of analogous molecular weight.<sup>35–39</sup> When compared to linear analogues, dendrimers demonstrate significantly increased solubility<sup>35,36</sup> that can be readily tuned by derivatizing the periphery,<sup>40</sup> and they also exhibit very low intrinsic viscosities.<sup>11,37</sup> Unlike linear polymers, properly designed high generation dendrimers exhibit a distinct “interior” that is sterically encapsulated within the dendrimer, enabling applications as unimolecular container molecules.<sup>41</sup> For example, Meijer et al. have described an elegant “dendritic box” that can encapsulate various small organic molecules and control their release by modifying the steric crowding of the dendritic periphery.<sup>42</sup> Synthetic approaches have been developed that allow the functionalization of both the interior and exterior of these versatile macromolecules enabling them to operate as transition state catalysts with high turnover.<sup>43</sup> The encapsulation of function<sup>28</sup> provided by dendrimers has been utilized in a variety of light-harvesting,<sup>44</sup> emission,<sup>44</sup> and amplification<sup>45</sup> functions. Among many other applications under consideration, the use of dendrimers as components in drug or gene delivery is the object of numerous current studies.<sup>46–54</sup>

## C. Synthetic Approaches

Two complementary general approaches, the divergent and the convergent, have been used for the synthesis of dendrimers.<sup>15,17</sup>

### 1. Divergent Approach

The divergent approach, arising from the seminal work of Tomalia and Newkome, as well as the branched model work of Vögtle, initiates growth at what will become the core of the dendrimer and continues outward by the repetition of coupling and activation steps (Figure 2). Reaction of the peripheral functionalities of the core with the complementary reactive group of the monomer introduces a new latent branch point at each coupling site and results in an increase in the number of peripheral functionalities (Figure 2: coupling step). The peripheral functionalities on each monomer are designed to be inert to focal monomer functionality, thereby pre-



**Figure 2.**

venting uncontrolled hyperbranched polymerization. After driving the first coupling reaction to completion, these latent functionalities can be activated to afford a new layer of peripheral groups capable of coupling to additional monomer (Figure 2: activation step).

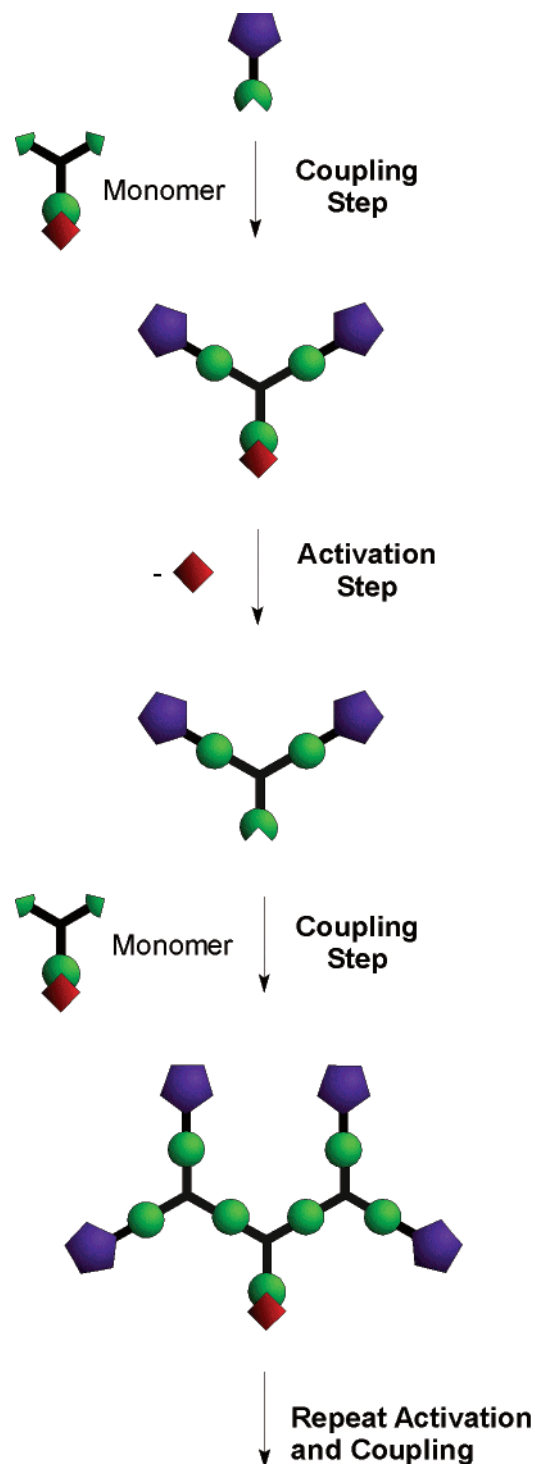
The activation of the peripheral group may involve its conversion to a reactive functionality, its coupling with a second molecule, or the removal of a protecting group. Repetition of the coupling and activation steps leads to an exponential increase in the number of reactions at the periphery; therefore, a large excess of reagents is required to drive both reactions to completion. Because of the difference in molecular weight, it may be possible to separate the macromolecule from the excess reagents by a simple distillation, precipitation, or ultrafiltration.

Given an appropriate choice of coupling and activation steps, reagents, and reaction conditions, the divergent approach is ideally suited for the large-scale preparation of dendrimers as the quantity of dendrimer sample essentially doubles with each generation increment. However, because the number of coupling reactions increases exponentially with each generation, the likelihood of incomplete functionalization or side reaction increases exponentially as well. Although removal of the monomer may be straightforward, any flawed molecules resulting from cyclizations or incomplete reactions cannot easily be removed because of their structural similarity to the intended product. In addition, if the activating agent itself is capable of initiating new growth, rigorous measures must be taken to ensure its complete removal in order to prevent the growth of smaller dendritic impurities. Because of this and the onset of De Gennes dense packing, high generation dendrimers produced using the divergent method, though quite monodisperse when compared to the narrowest polydispersity linear polymers, still contain an appreciable number of structural flaws. Of the many divergent syntheses studied to date, a few appear to be particularly noteworthy. These include Dow's PAMAM<sup>5,55</sup> and DSM's poly(propylene imine)<sup>8,56</sup> dendrimers, Newkome's arborols,<sup>6,57-61</sup> and Majoral's phosphorus-based dendrimers.<sup>62-64</sup>

## 2. Convergent Approach

The convergent method, first reported by Hawker and Fréchet in 1989–1990,<sup>9,10,65</sup> initiates growth from what will eventually become the exterior of the molecule (Figure 3), and progresses inward by coupling end groups to each branch of the monomer (Figure 3: coupling step). After completion of the coupling, the single functional group located at the focal point of the wedge-shaped dendritic fragment, or dendron, can be activated (Figure 3: activation step). Coupling of this activated dendron to each of the complementary functionalities on an additional monomer unit affords a higher generation dendron. After sufficient repetition of this process, these dendrons can be attached to a polyfunctional core through their focal point to form a globular multidendron dendrimer. Although again an iterative synthesis, the convergent route strongly contrasts its divergent counterpart since it involves only a small number of reactions per molecule during the coupling and activation steps.

Although the molecular weight of the dendron is effectively doubled at each coupling step, the contribution of the monomer to the mass of the product



**Figure 3.**

decreases exponentially as the generation number increases. Since coupling yields are not quantitative and purification results in some losses, the mass of the sample decreases with each additional generation. In addition, because the coupling reaction occurs at the focal point of the growing dendron, the preparation of very large dendrimers (typically above the sixth generation) is complicated by steric inhibition, resulting in decreased yields.

As mentioned earlier, each activation and coupling step in the convergent synthesis requires only a very

small number of transformations per molecule. As a result, the reactions can be driven to completion with only a slight excess of reagent, in contrast to the massive excess of reagent required for the divergent synthesis of high generation dendrimers. Product purification after the coupling step is also facilitated by the very small number of components in the reaction mixture. The dissimilarity between these components enables the effective use of chromatographic purification, ensuring that convergent dendrons are probably the purest synthetic macromolecules prepared to date.

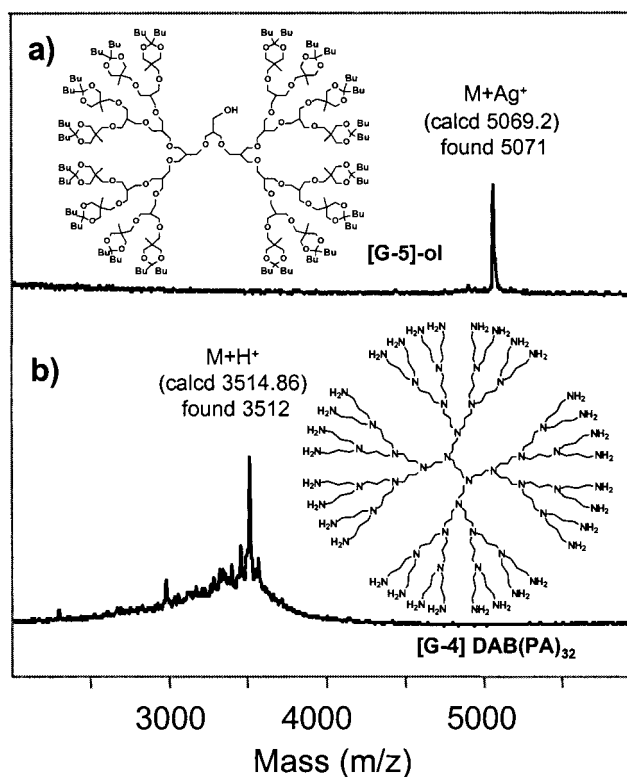
This review will focus on the development of the convergent approach to dendrimers since its conception over a decade ago. In addition to discussing a number of noteworthy convergent syntheses, it will also cover their chemical modification for incorporation of function. The divergent approach, which has provided numerous valuable contributions to the field of functional macromolecules, is beyond the scope of this review and has been covered elsewhere.<sup>20,22,24,26,28</sup>

## D. Features of the Convergent Synthesis

The convergent synthesis with its stepwise assembly of building blocks can be described as the "organic chemist's approach" to dendrimers. It provides greater structural control than the divergent approach due to its relatively low number of coupling reactions at each growth step, allowing access to dendritic products of unmatched purity and functional versatility. The ability to precisely place functional groups throughout the structure, to selectively modify the focal point or the chain ends, and to prepare well-defined unsymmetrical dendrimers are among the most attractive features of the convergent synthesis. Yet because it is less readily scaled up than the divergent synthesis, its commercialization is presently limited to one family of polyether dendrons by Tokyo Kasei Co., Ltd. in Japan.<sup>10</sup>

### 1. Structural Purity

A convenient way to examine sample purity involves the use of matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF MS). Figure 4 shows the mass spectrum of a convergently synthesized fifth generation aliphatic polyether dendron. In the mass spectrum, only one peak is observed, corresponding to the mass of the dendron plus a silver cation. The mass spectrum of a purchased sample of divergently prepared fourth generation poly(propylene imine) dendrimer, also displayed in Figure 4, exhibits a measurable amount of defective molecules as the sample could not be purified by chromatography. Detailed mass spectral studies by Meijer and co-workers have identified a number of recurring flaws within the PPI dendrimer synthesis including cyclizations and incomplete couplings. From mass spectral analysis, they approximate the purity of a fourth generation PPI dendrimer to be only 41%.<sup>66</sup> Although the structural purity obtained from the two approaches varies significantly, depending on the specific conditions employed



**Figure 4.**

during synthesis, the divergently prepared samples are generally mixtures of several closely related compounds with an extremely low overall polydispersity,<sup>67-69</sup> whereas the convergently prepared materials, with appropriate chromatographic purification, can be isolated essentially as a single molecular species of precise molecular weight and structure.<sup>70,71</sup>

### 2. Synthetic Versatility

The convergent approach has seen extensive use in the construction of functional macromolecules because of its ability to modify dendrons at both the focal point and the chain ends. This modularity is especially helpful in design optimization because the same dendritic structure can be modified, after the dendron synthesis, to vary the number and chemistry of functional moieties in the resultant dendrimer.<sup>72</sup>

In addition, structural variations involving the attachment of chemically different dendrons to a single monomer unit are possible. For example, it is possible to carry out a coupling reaction involving only one of the active functionalities of the monomer (Figure 5). The remaining site may then be coupled with an alternative dendron, affording a dendritic "copolymer." Appropriate variations of the chemistry and sequencing of such unsymmetrical growth enables accurate control over the exact number and placement of different peripheral groups, as well as different monomer units, throughout the dendritic structure. We first demonstrated this capability in 1990 with the preparation of unsymmetrically end-functionalized dendrimers and in 1991 with new types of dendritic copolymers that are not readily obtainable by other approaches.<sup>73,74</sup>

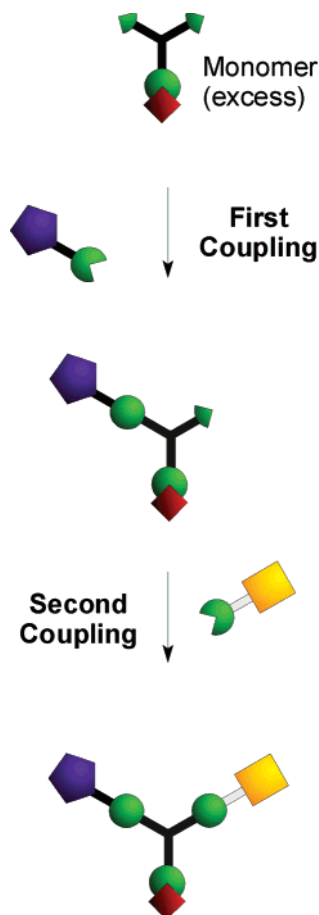


Figure 5.

## II. Convergent Synthesis of Dendrons and Dendrimers

In the past decade, a variety of convergent syntheses have been developed, incorporating a wide range of functionalities. While many are imaginative, only a few have proven sufficiently versatile and efficient to see consistent use since they were first reported. By far the most widely used convergent syntheses are the poly(aryl ether), developed by Fréchet and co-workers, and the poly(aryl alkyne) developed by Moore and co-workers. Other noteworthy syntheses include those of the poly(phenylene), the poly(alkyl ester), the poly(aryl alkene), and the poly(alkyl ether) dendrimers. All of these syntheses will be described in more detail below.

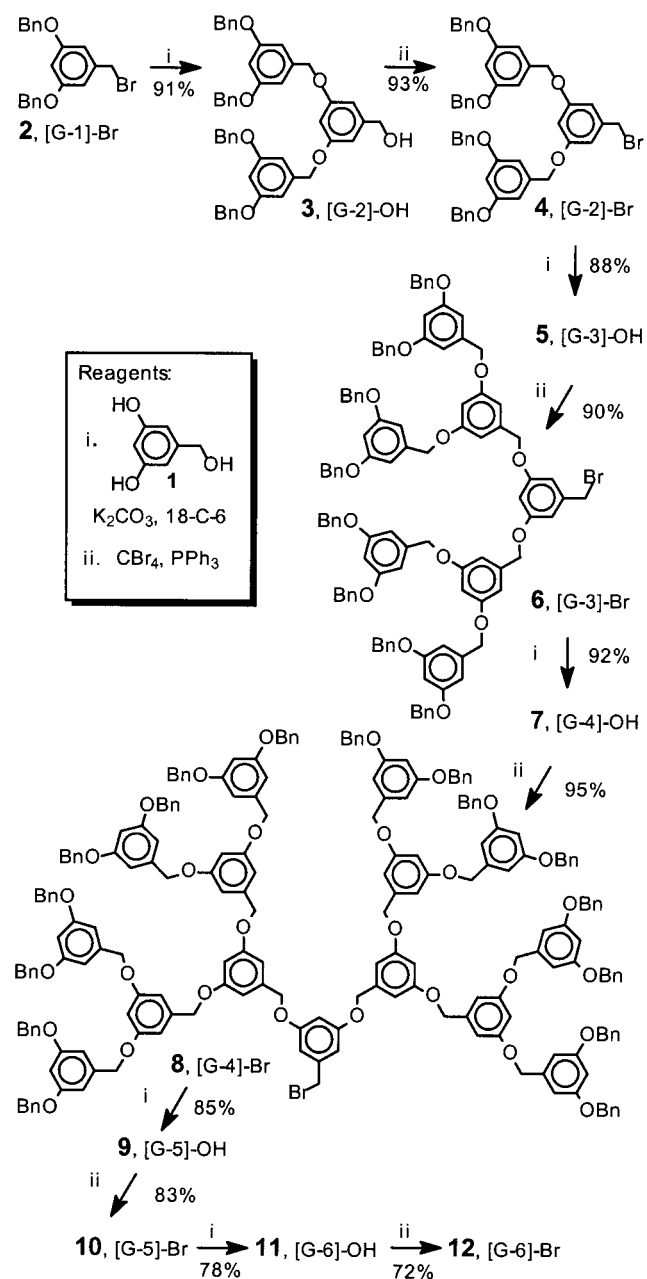
### A. Single-Stage Convergent Syntheses

An effective convergent synthesis requires a monomer that can undergo the activation and coupling steps in high yield and whose products can be readily isolated from excess starting material and byproducts. In addition, the coupling step must be very efficient to enable complete reaction even when involving sterically demanding high generation dendrons.

#### 1. Poly(aryl ether) Dendrimers

Developed by Hawker and Fréchet in 1989–1990, the poly(benzyl ether) synthesis<sup>10,65,75</sup> makes use of 3,5-dihydroxybenzyl alcohol (Scheme 1) as the mono-

### Scheme 1

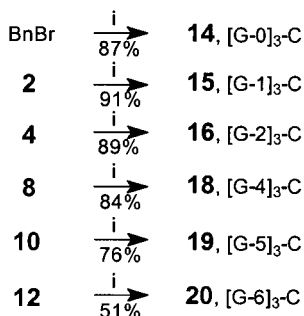
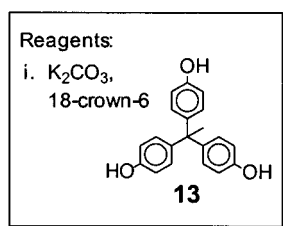
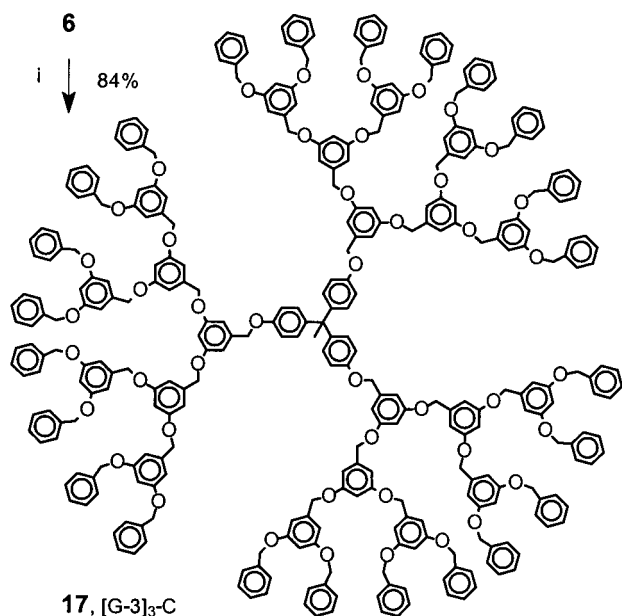


mer **1**. The two phenolic groups of this monomer were coupled to the benzylic bromide **2**, in the presence of potassium carbonate and 18-crown-6, producing the two new ether linkages of the second generation benzylic alcohol **3**. The focal benzylic alcohol functionality was then activated for the next coupling step by reaction with carbon tetrabromide and triphenyl phosphine affording brominated dendron **4**. The coupling step was then repeated using 2 equiv of activated dendron **4** and 1 equiv of the monomer, yielding the third generation benzylic alcohol, **5**. Subsequent repetitions of the Williamson coupling and bromination steps enabled the production of the sixth generation dendrons **11** and **12**. This effective synthesis was designed to incorporate the efficient Williamson coupling reaction between a highly nucleophilic phenolate, and a highly activated benzylic bromide, ensuring exceptional yields during all the generation growth steps. The benzylic substrate also

prevented elimination side reactions that frequently accompany nucleophilic displacements. Similarly, optimization of the activation step from a benzylic alcohol to the benzylic bromide ensured that this reaction could be achieved with consistently high yields. These considerations mandated our initial choice of monomer **1** in order to provide excellent yields and regioselectivity during its activation and coupling reactions.

A clear limitation of the convergent growth is observed when pursuing the synthesis at very high generation number, as steric constraints begin to hinder the coupling step. For example, in the poly(benzyl ether) synthesis depicted in Scheme 1, the yields obtained during the coupling reactions for the first four generations are consistently near 90%, but drop to 85% at the fifth generation coupling step and to 78% at the sixth. All of the dendrons from generation one through six can also be effectively coupled to a tris(phenolic) core **13** to form tridendron dendrimers **14–20**, though an analogous steric effect causes a slight reduction in yields for the larger dendrimers (Scheme 2).

Scheme 2



The poly(benzyl ether) dendrimer synthesis is one of only a few convergent syntheses that can produce dendrons and dendrimers in reasonable yields up to the sixth generation. These dendrons, now frequently referred to as “Fréchet-type” dendrons, have been utilized by a number of groups because they are

relatively readily accessed and exhibit the chemical stability associated with ether linkages.

The versatility of this Williamson type convergent dendritic synthesis can be witnessed by the number of variations (Figure 6) reported on the original

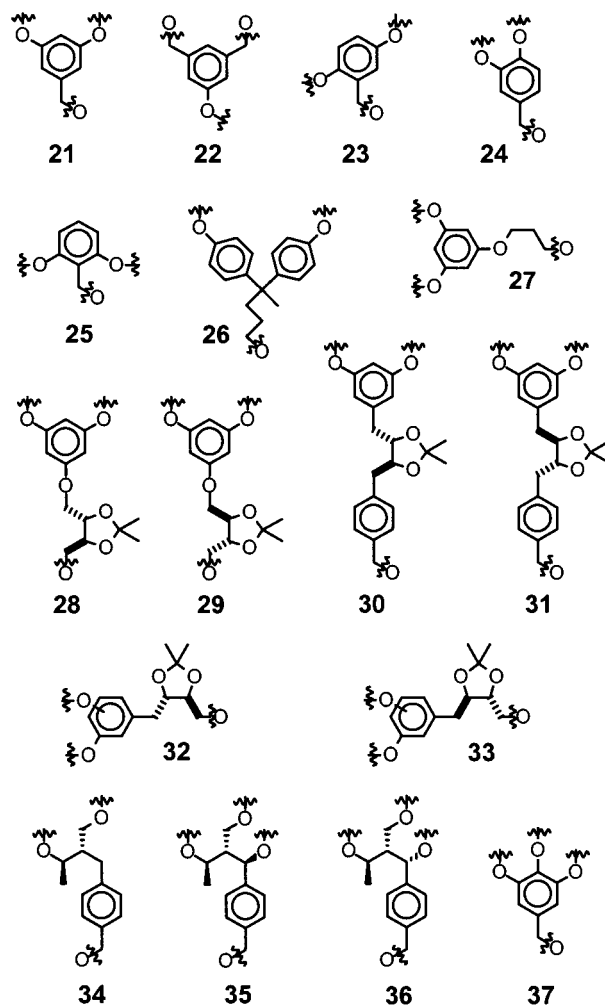


Figure 6.

repeat unit **21**. Tyler et al. reported the use of “reversed” monomer **22**, where the building block instead consists of two benzylic alcohols as the latent electrophiles, and one nucleophilic phenol.<sup>76,77</sup> Both the Fréchet-type dendrons and these “reversed” dendrons have proven to be of particular interest in light amplification<sup>45</sup> and light-harvesting systems,<sup>78–81</sup> because of their complementary behavior in energy transfer through their molecular frameworks. A number of structural variations have been reported on the original 3,5-branching geometry of repeat unit **21**, including 2,5-substitution,<sup>45</sup> **23**, 3,4-substitution,<sup>82–85</sup> **24**, and the “backfolded” system<sup>86</sup> which incorporates monomer **25**. As was the case with the “reversed” dendrons these structural variations lead to significant changes in properties of the resultant dendrons.<sup>45,82,86</sup> In addition, a range of different leaving groups (chloride, tosylate, and mesylate, as well as bromide) and masked focal functionalities (aldehyde and ester, as well as benzyl alcohol) has enabled further flexibility in the synthesis.

The poly(aryl ether) system can also be easily adapted to incorporate spacer groups. Wooley et al.

first reported the use of the 4,4-bis(4'-hydroxyphenyl)pentanol monomer **26** with identical Williamson coupling and bromination activation procedures, as a more extended, flexible repeat unit designed to reduce problematic steric interaction during the synthesis of large poly(aryl ether) dendrimers.<sup>87</sup> This goal was realized, as the new dendrons, in conjunction with the traditional poly(benzyl ether) dendrons, led to the first reported convergent synthesis of a seventh generation dendrimer. Chow et al. later reported the synthesis of similar poly(aryl ether) dendrons utilizing a 3-(3,5-dihydroxyphenoxy)propanol as a more extended repeat unit,<sup>88–90</sup> **27**. Because both of these poly(aryl ether) dendritic structures lack the benzylic ether functionality of the original synthesis, their stability to redox and acidic conditions is believed to be improved. For this reason, the Gorman and Chow groups have used these elongated dendritic structures extensively for the encapsulation of redox-active cores.<sup>91–95</sup>

To investigate the effect of chirality in dendrimers, a number of groups have incorporated chiral spacers into the poly(aryl ether) repeat unit. Chow et al.<sup>96–100</sup> modified their dihydroxyphenoxypropanol repeat unit **27** to include the acetonide protected diol spacers: (2*R*,3*R*)- or (2*S*,3*S*)-threitol, **28** and **29**. McGrath and co-workers incorporated similar chiral protected diols **30–33** into their studies,<sup>101–105</sup> whereas Seebach and co-workers<sup>106–109</sup> investigated the di- and tribranched chiral monomers **34–36**.

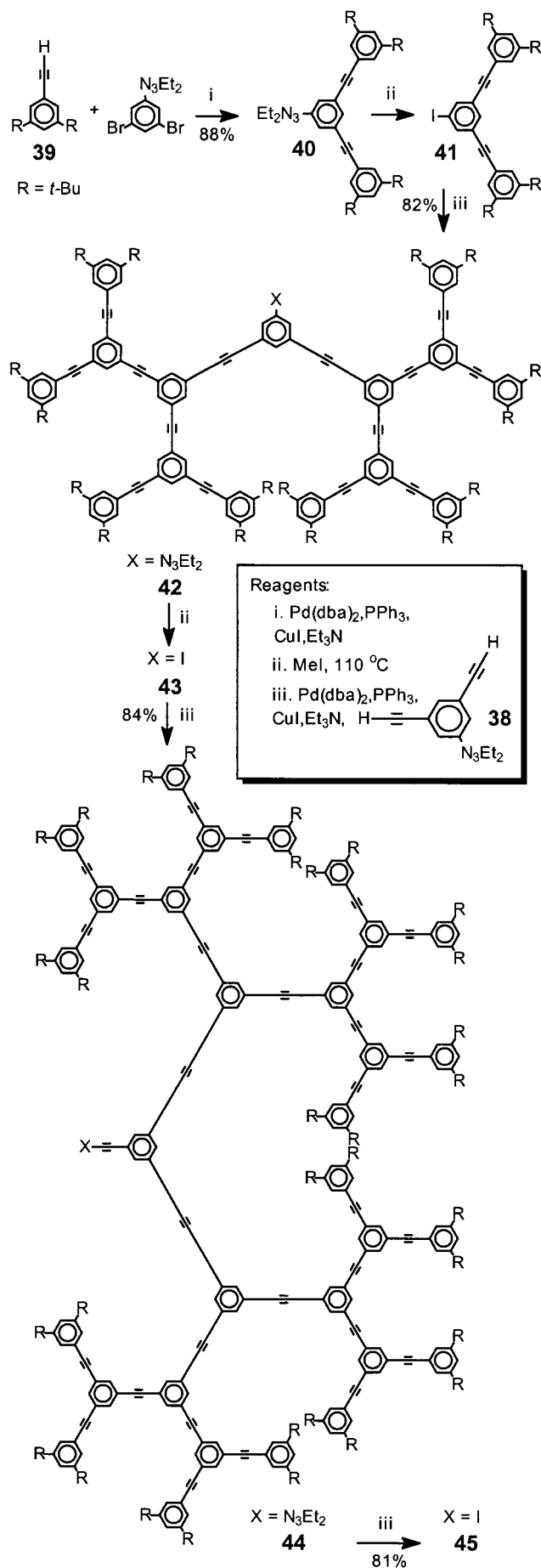
To expedite the synthesis of densely packed dendrons, Percec and co-workers<sup>110</sup> have utilized the triply branched monomer **37**, methyl 3,4,5-trihydroxybenzoate.<sup>84,85,111–113</sup> The materials were synthesized by coupling the phenolic groups of the monomer to 3 equiv of a benzylic chloride, followed by transformation of the focal ester functionality to a chloromethyl group, via LiAlH<sub>4</sub> reduction and SOCl<sub>2</sub> chlorination. This procedure could be repeated up to the fourth generation.

## 2. Poly(aryl alkyne) Dendrimers

Moore and co-workers have used aryl alkyne, or "phenylacetylene," building blocks to explore a variety of well-defined macromolecular architectures ranging from linear oligomers and complex macrocycles, to dendritic compounds.<sup>114</sup> Because of their poor intrinsic solubility, the poly(phenylacetylene) dendrons required solubilizing end groups. The 4-*tert*-butylphenyl peripheral units initially incorporated proved useful as solubilizing groups only to the third generation dendron; however, their replacement with the 3,5-di-*tert*-butylphenyl peripheral groups provided sufficient solubility to access fourth generation dendrons.<sup>115</sup> Initial modifications to enable the synthesis of larger dendrimers included the use of elongated monomer units designed to counteract steric hindrance.<sup>116</sup>

More recently, the synthesis has been optimized, to eliminate the necessity of extended monomer units by simply reversing the functionalities on the monomer while using a dialkyltriazene precursor for the focal iodo functionality.<sup>117</sup> The dendritic compounds (Scheme 3) were synthesized using the diethynyl

**Scheme 3**



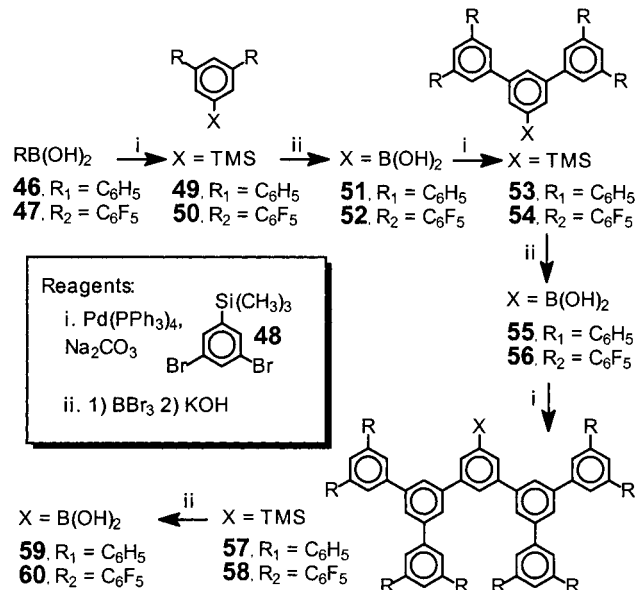


monomer **38** with a triazene protecting group. The terminal alkyne functionalities of the monomer are capable of two efficient palladium-catalyzed cross-couplings with the first generation aryl halide dendron **41**, producing the second generation dendron **42**. The nearly quantitative halogenation of the triazene group produces an aryl halide, **43**, activated toward further coupling with the monomer.<sup>117</sup> In addition to improving the yields significantly, this reversed approach enabled the synthesis of fifth generation dendrons, and allowed these compounds to be synthesized via a solid supported technique.<sup>117</sup> The notable features of these phenylacetylene dendritic structures are the rigid repeat units that lead to shape persistent dendrimers,<sup>118</sup> and the conjugated segments within the structure, which impart interesting photophysical properties.<sup>119–131</sup>

### 3. Poly(phenylene) Dendrimers

Two other convergent syntheses including that of a family poly(1,3,5-phenylene) dendrimers<sup>132,133</sup> were reported by Miller and Neenan shortly after that of the poly(benzyl ether) dendrimer.<sup>10</sup> Preparation of these polyphenylenes (Scheme 4) and their fluori-

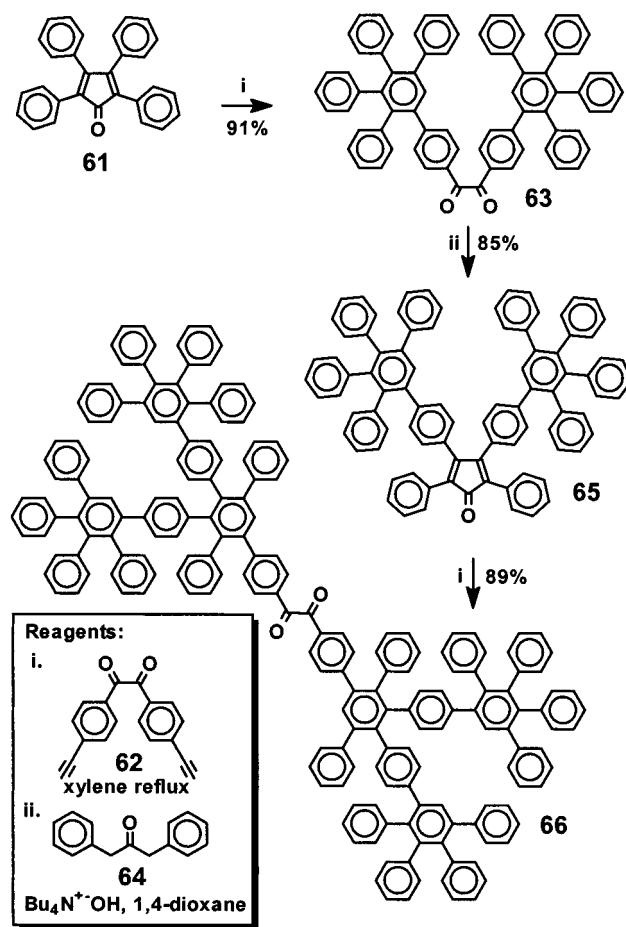
Scheme 4



nated analogues involved the Suzuki coupling of aryl boronic acids **46** or **47** with monomer **48**, 3,5-dibromo-1-(trimethylsilyl)benzene. Conversion of the trimethylsilyl (TMS) protecting group of products **49** and **50** to the boronic acid functionality in **51** and **52** enabled further coupling to the monomer. This procedure enabled the preparation of dendrons up to the third generation **57–60**. The rigid repeat units of these molecules lead to dendritic structures with well-defined shapes and diameters.

Recently, Müllen et al. have reported a convergent approach<sup>134</sup> to poly(phenylene) dendrimers (Scheme 5) similar to the divergent [4 + 2] cycloaddition route they had previously developed.<sup>135</sup> The process was initiated by a Diels–Alder reaction between tetra-substituted cyclopentadienone **61** and dialkynyl mono-

Scheme 5

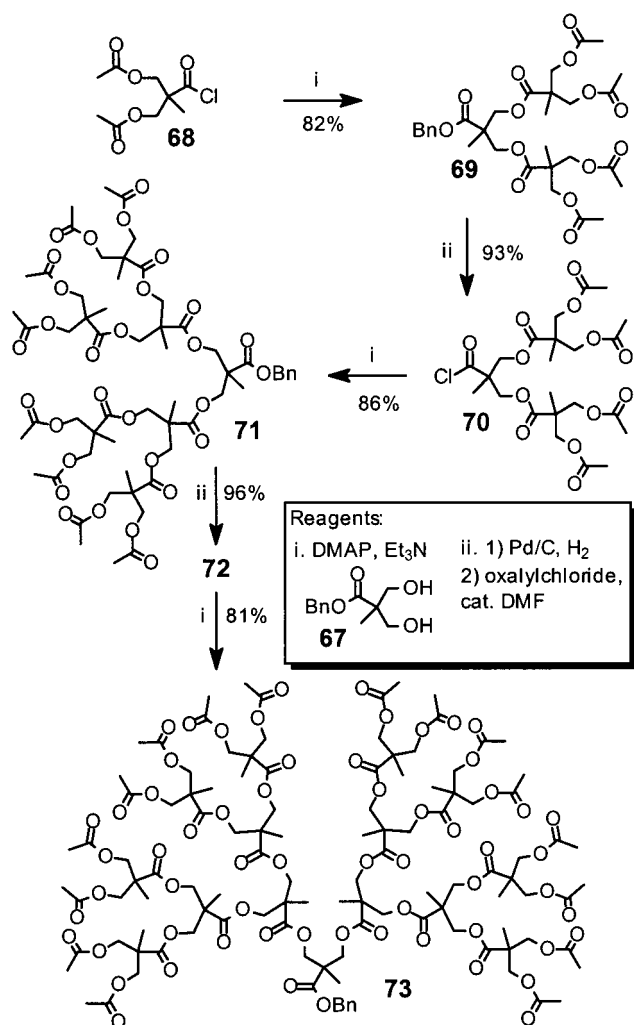


mer **62**, to yield the corresponding dione **63**. The Knoevenagel condensation of dione **63** and 1,3-diphenylacetone, **64**, then afforded the substituted cyclopentadienone **65**. This synthesis is of particular interest because it illustrates a potential steric complication involved in some convergent syntheses. Dendritic growth is not practical beyond the second generation, because the enormous steric interactions between the two poly(phenylene) wedges of **66** prevent them from adopting the conformation required for the subsequent Knoevenagel condensation. In contrast, the divergent synthesis using a Diels–Alder cycloaddition and a less conformationally demanding TMS deprotection step could be driven effectively to the fourth generation.

### 4. Poly(alkyl ester) Dendrimers

One of the more efficient convergent dendrimer syntheses was reported by Hult and co-workers (Scheme 6) utilizing a repeat unit based on 2,2-bis-(hydroxymethyl)propanoic acid.<sup>136</sup> The two alcohol moieties of the benzyl 2,2-bis(hydroxymethyl)propanoate monomer, **67**, could be coupled efficiently with an activated acid chloride end-group, **68**. Following removal of the focal benzyl ester by hydrolysis, the carboxylic acid could be transformed to the corresponding acid chloride **70**, in nearly quantitative yields using oxalyl chloride. The coupling-deprotection procedure was then repeated to the fourth generation dendron **73**. Although these poly-

## Scheme 6

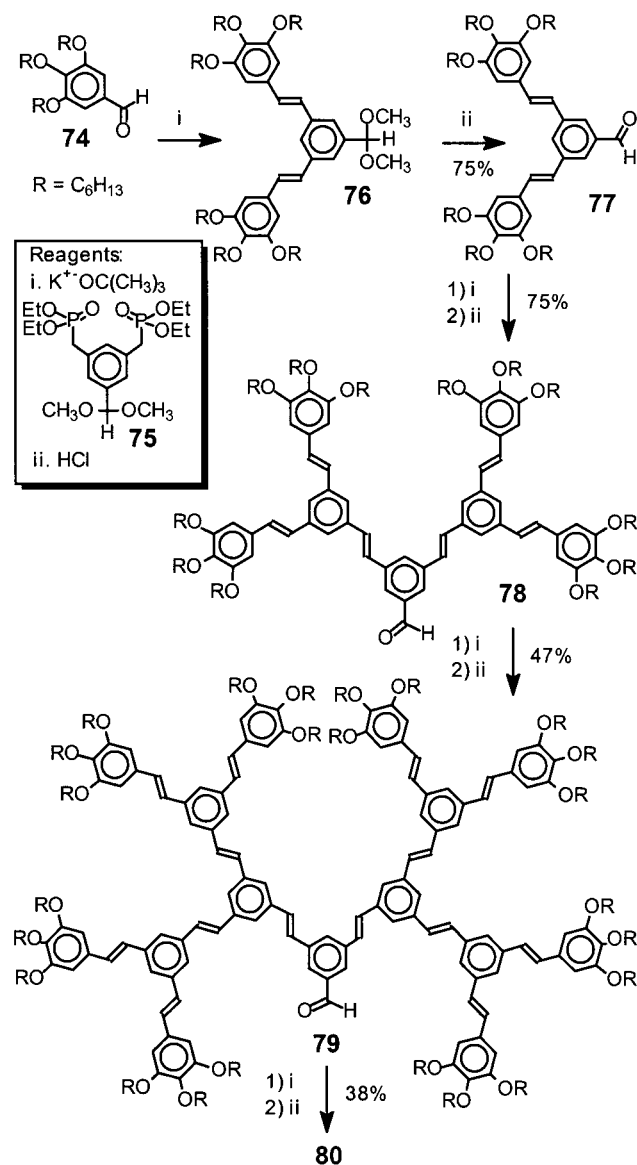


esters do not exhibit the chemical stability of other dendritic macromolecules based on ether or hydrocarbon linkages, the dendrons show rather high stability to acidic conditions because their ester functionalities are shielded from nucleophilic attack by the neighboring quaternary carbon. Recently, Ihre et al. reported a remarkably efficient<sup>137</sup> and versatile<sup>138</sup> divergent synthesis of analogous dendrimers.

## 5. Poly(aryl alkene) Dendrimers

The Meier and Burn groups both developed a convergent approach to conjugated poly(aryl alkene) dendrimers using coupling chemistry similar to the orthogonal synthesis first reported by Deb et al.<sup>139</sup> Meier and co-workers reported the synthesis of these compounds<sup>140–142</sup> using the Horner–Wadsworth–Emmons coupling of aldehyde **74** with the bis(phosphite) monomer **75**, (Scheme 7). The dimethoxyacetal focal point of product **76** could be readily hydrolyzed to regenerate the active aldehyde **77**. However, the synthesis suffered from low yields and prohibitively long reaction times above the fourth generation **80**. Burn and co-workers<sup>143,144</sup> reported the synthesis of an identical dendritic framework (Scheme 8), via the Heck coupling of a derivatized styrene **81** with the monomer 3,5-dibromobenzaldehyde, **82**,

## Scheme 7

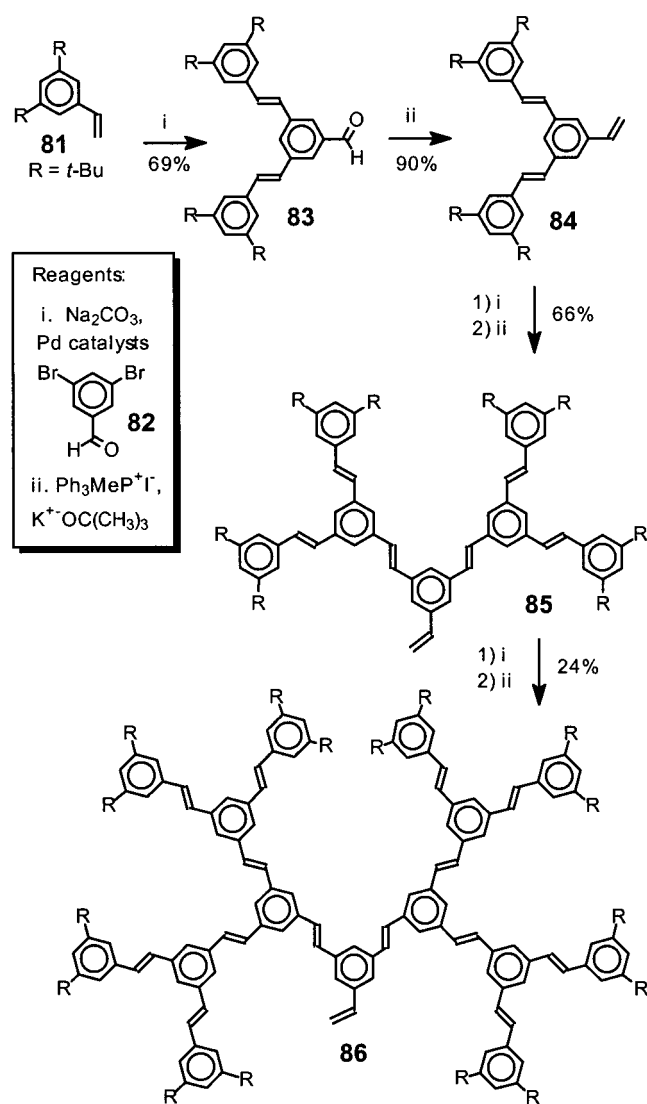


followed by a Wittig reaction with methyltriphenylphosphonium iodide to produce the activated dendritic styrene **84**. With this procedure, dendritic materials could be prepared up to the third generation **86**. Halim et al. have studied the photophysical properties of these materials, in particular their application toward light-emitting diode devices.<sup>145–148</sup>

## 6. Poly(alkyl ether) Dendrimers

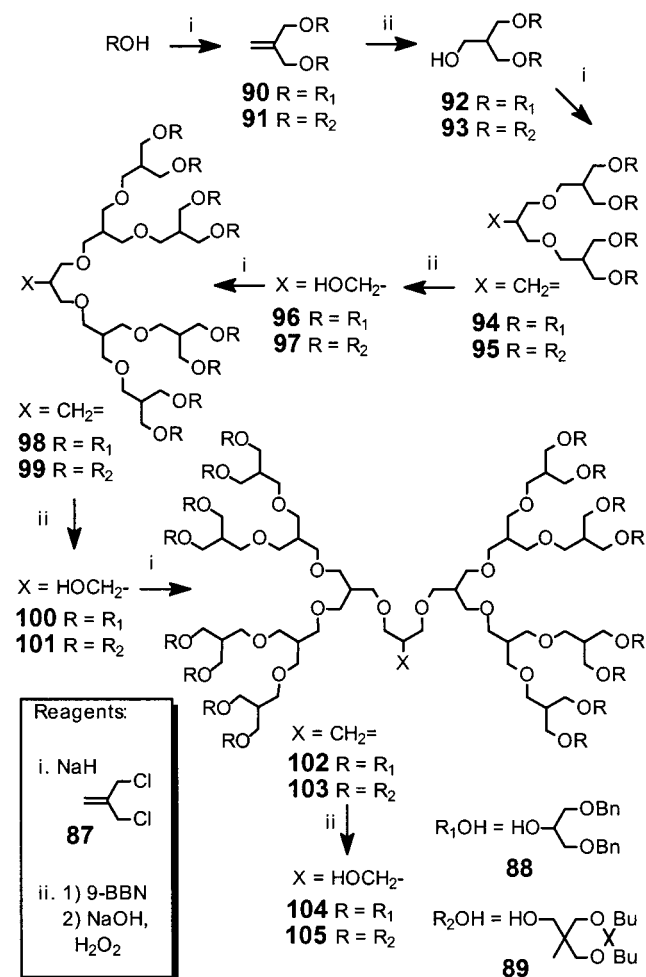
An aliphatic analogue of the poly(benzyl ether) dendrimer was recently developed by Fréchet and co-workers (Scheme 9). Based on monomer **87**, 3-chloro-2-chloromethyl-propene, the synthesis was initiated by coupling the end groups to the monomer using the Williamson ether coupling of a bis-protected triol, **88**, or **89**, with the allylic chloride functionalities of the monomer.<sup>149,150</sup> The double bond of the monomer serves three distinct functions: (i) it activates the allylic halide moieties for Williamson coupling, (ii) it prevents elimination side reactions, and (iii) it serves as a latent hydroxyl group for growth of the next generation. The double bond of the resulting

Scheme 8



product **90** or **91** was converted to the corresponding primary alcohol **92** or **93** via hydroboration/oxidation, thereby enabling further coupling. This procedure could be repeated in high yields (85% or greater for **88** and 69% or greater for **89**) through fifth generation dendrons **102**–**105**. Although the more demanding purification of these compounds will likely prevent them from supplanting the poly(benzyl ether) family for many applications, they offer a significantly more rugged backbone allowing a wider range of chemical modification. For example, the peripheral ketal and benzyl ether protecting groups can be quantitatively removed by acid-catalyzed hydrolysis or palladium-catalyzed hydrogenolysis exposing multiple peripheral hydroxyl groups capable of further modification by alkylation or esterification.<sup>40</sup> The poly(alkyl ether) dendrons were selected as solubilizing scaffolds for otherwise intractable oligothiophenes because they did not interfere with the N-bromosuccinimide bromination of the pendant oligothiophene or subsequent Stille couplings.<sup>151,152</sup> In addition, these compounds exhibit a significantly more polar backbone, similar to poly(ethylene glycol), which may prove useful in macromolecular catalysts or biomedical applications.

Scheme 9



## 7. Other Convergent Dendrimer Syntheses

A wide variety of other convergent syntheses have been developed for the preparation of dendritic poly(amides),<sup>132,153–160</sup> poly(esters),<sup>161,162</sup> poly(urethanes),<sup>163,164</sup> poly(carbonates),<sup>165</sup> poly(aryl ethers),<sup>166–169</sup> poly(arylamines),<sup>170–173</sup> poly(aryl ketones),<sup>174</sup> poly(aryl alkynes),<sup>175</sup> poly(aryl methanes),<sup>176</sup> poly(arylammonium) salts,<sup>177</sup> poly(ethers),<sup>178</sup> poly(ether imides),<sup>179</sup> poly(keto esters),<sup>180–182</sup> poly(amine ethers),<sup>183</sup> poly(amino esters),<sup>184</sup> poly(amide ethers),<sup>185–189</sup> poly(pyridyl amides),<sup>190</sup> poly(uracils),<sup>191</sup> poly(triazenes),<sup>192,193</sup> poly(saccharides),<sup>194</sup> poly(glycopeptides),<sup>195</sup> and poly(nucleic acids).<sup>196</sup> In addition, chiral dendrimers<sup>197,198</sup> including amide,<sup>199–201</sup> ether,<sup>96–108</sup> and ester<sup>202</sup> linkages, and organometallic dendrimers,<sup>203–207</sup> including silicon,<sup>208</sup> germanium,<sup>209</sup> palladium,<sup>210</sup> and platinum<sup>211–214</sup> containing repeat units have been reported. Syntheses that incorporate specific functional moieties within the monomer will be addressed in section 6.

## B. Accelerated Approaches

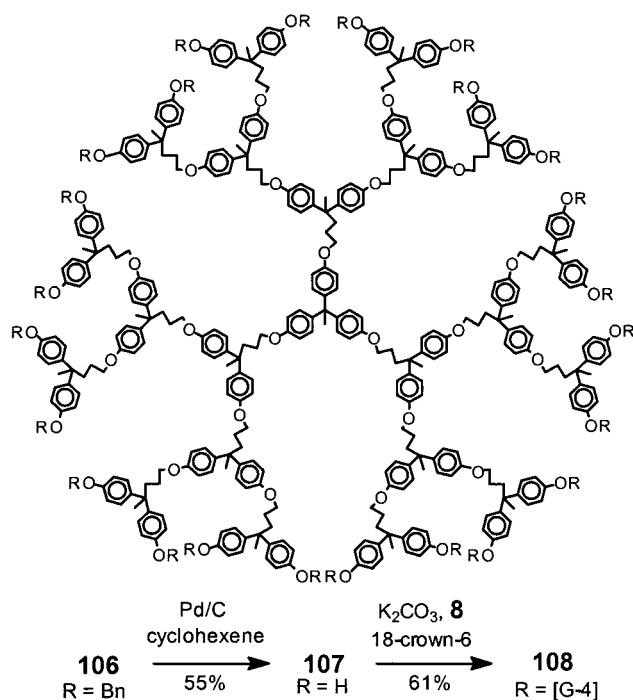
In response to the often tedious and purification intensive iterative dendrimer syntheses, many researchers have sought accelerated approaches that combine the convergent and divergent strategies.

These procedures generally maintain the versatility and product monodispersity offered by the traditional convergent method, but reduce the number of linear synthetic steps required to access larger dendritic materials.

### 1. Multigenerational Coupling: Hypercores, Hypermonomers, and Double Exponential Growth

Fréchet and co-workers developed the “hypercore” approach in order to improve the yields of sterically inhibited high-generation coupling reactions. The goal of this approach is to couple convergently synthesized dendrons to the periphery of a dendritic core that already contained layers of branching units. Using the standard convergent approach, first, second, and third generation dendrimers were constructed with 4,4-bis(4'-hydroxyphenyl)pentanol as the flexible repeat unit.<sup>87</sup> The benzyl ether periphery of these dendrimers could be removed via hydrogenolysis (Scheme 10) to expose 6, 12, or 24 phenolic

**Scheme 10**



groups. In a second stage of growth the dendritic polyols were utilized as multigenerational “hypercores” capable of coupling with the benzylic bromide functionalities of Fréchet-type dendrons. As a result, coupling of the third generation hypercore **107** with 24 fourth generation dendritic bromides **8** afforded the seventh generation dendrimers **108** in a 61% yield. This so-called “double stage convergent” approach not only provides access to dendrimers with chemically differentiated internal and external repeat units, but it also provides a more rapid and less demanding route to very large dendritic molecules. This approach has also been employed by Neenan and Miller, to enable the synthesis of a third generation poly(phenylene) dendrimer,<sup>133</sup> and by Xu et al. in the synthesis of a fourth generation phenylacetylene dendrimer.<sup>215</sup>

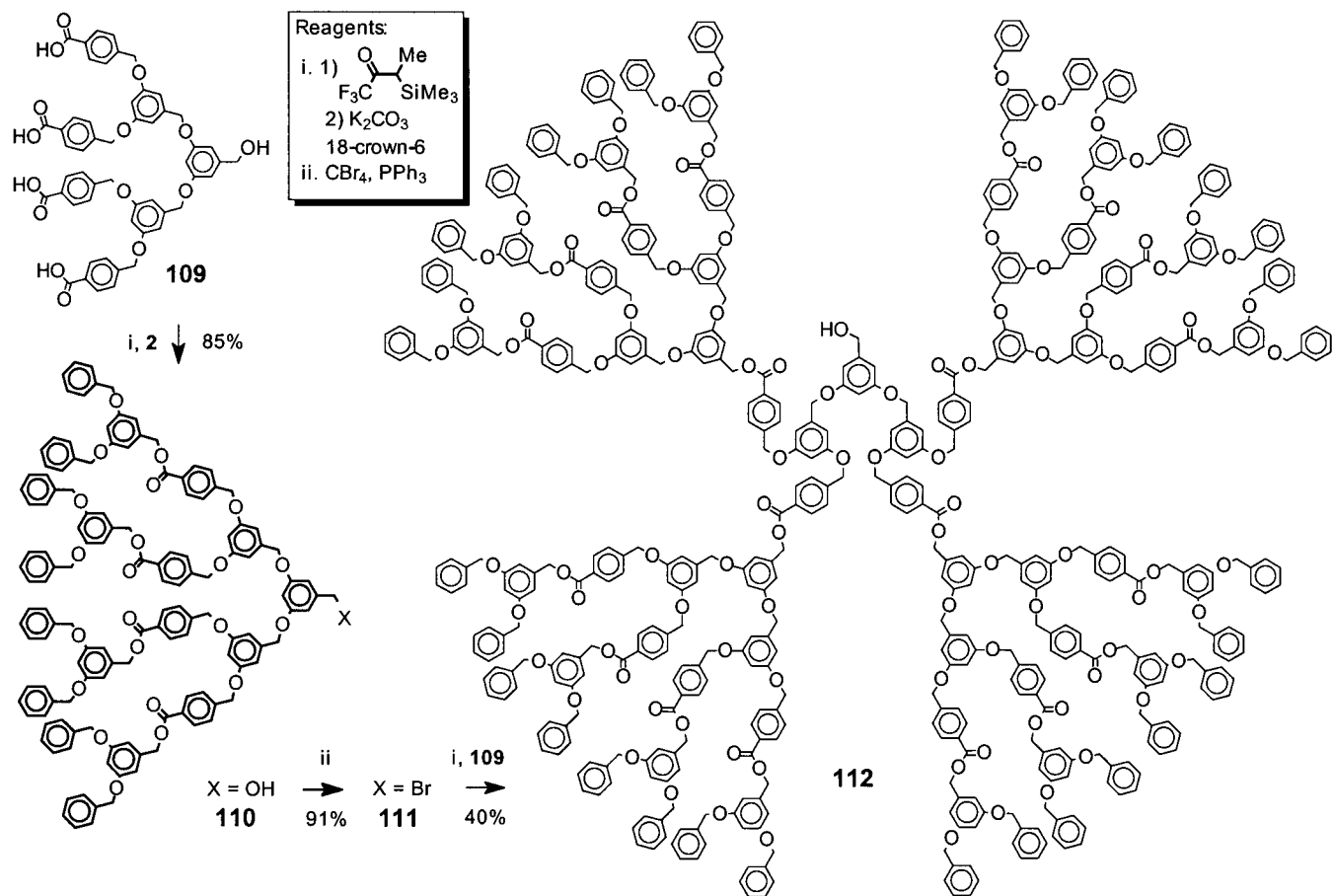
The “hypermonomer” approach, applies the concept of multistage growth to the monomer itself. Instead of assembling dendrons one generation at a time, hypermonomers contain two or more layers of branching units, enabling the addition of multiple generations during each coupling step. Although the coupling and activation steps may involve reactions identical to those used with traditional monomers, the number of individual coupling reactions per growth step increases exponentially with the generation of the hypermonomer, requiring the use of very efficient coupling chemistry.

Wooley et al. first demonstrated this approach (Scheme 11) by utilizing a second generation hypermonomer, **109**, consisting of two layers of branch points.<sup>216</sup> The carboxylic acid terminated hypermonomer allowed the facile synthesis of the fifth generation dendron **112** from the first generation benzyl bromide **2** in just three reaction steps. L’abbé and co-workers<sup>217,218</sup> later introduced silyl-protected second and third generation hypermonomers **113** and **114**, to enable the accelerated synthesis of the poly-(benzyl ether) dendrons initially reported by Hawker and Fréchet (Scheme 12). *tert*-Butyldiphenylsilyl protecting groups were selected for the periphery because they could withstand the conditions required for hypermonomer synthesis, yet could be readily cleaved with fluoride ions. The deprotection step is followed by an immediate in situ coupling to dendritic benzylic bromides to produce dendrons up to the fifth generation in greater than 80% yield.

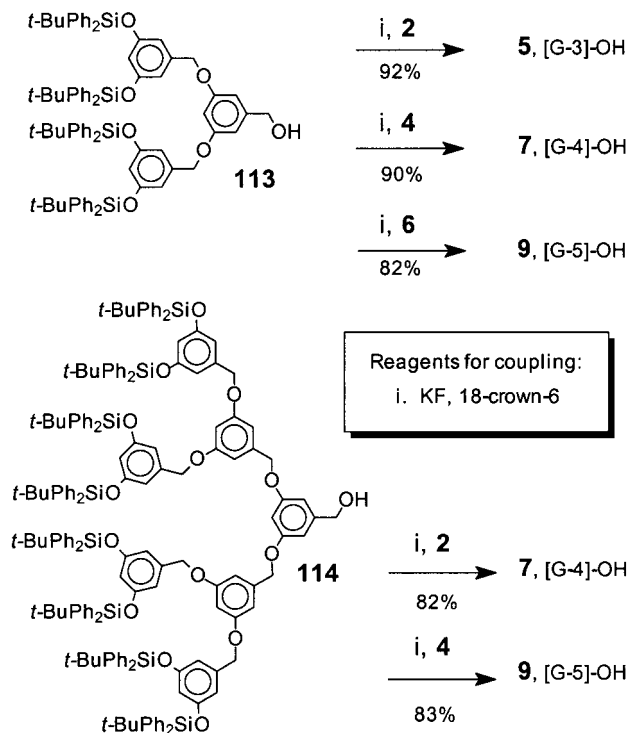
The final development in multigeneration growth was proposed by Moore and co-workers in 1995 and takes direct advantage of both divergent and convergent techniques.<sup>219</sup> Dubbed “double exponential dendrimer growth”, this procedure requires a monomer with orthogonally masked focal and peripheral functionalities. The first generation dendron can be modified either at the focal point, to obtain the activated dendron, or at the periphery, to yield the first generation monomer. Coupling of the monomer and activated dendron yields a second generation dendron, which may likewise be activated at either the focal point or the periphery. Coupling of the resultant activated second generation dendrons to the second generation hypermonomer affords a fourth generation dendron. Each successive repetition of these three steps (dendron activation, monomer activation, and coupling) leads to a doubling of the generation number.

To demonstrate this approach (Scheme 13), Moore and co-workers selected compound **115**, containing the orthogonal focal triazine protecting group and two TMS-protected alkynes, to initiate their synthesis. Conversion of its focal point to an iodo functionality afforded the activated first generation dendron **116**, while removal of the TMS protecting groups yielded the activated first generation monomer **117**. Coupling of monomer **116** with 2 equiv of dendron **117** yielded the second generation dendron **118**. Subsequent halogenation of its focal point or deprotection of its periphery yielded **119** and **120** respectively, the two reactants necessary to produce the fourth generation dendron **121**. Attempts to continue

## Scheme 11



## Scheme 12



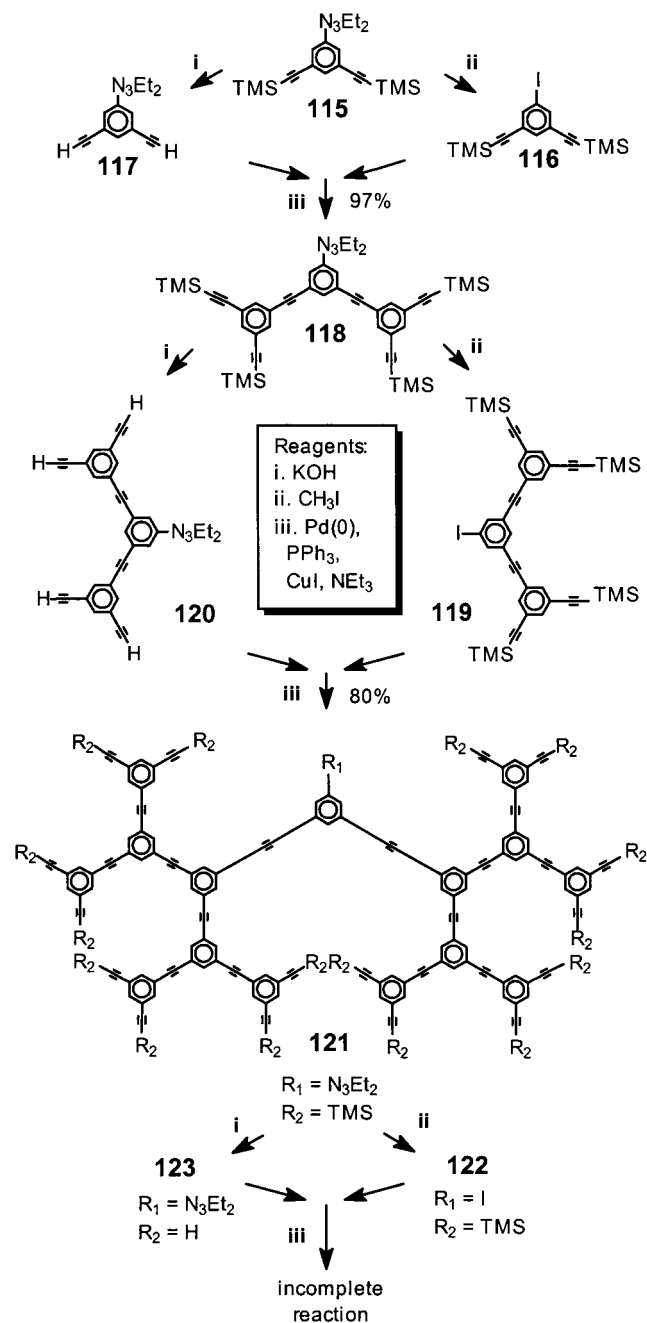
the synthesis to the eighth generation dendron proved problematic, however, as all 16 simultaneous couplings of **122** to **123** could not be completed.<sup>219</sup> Chi

et al. recently utilized this approach to synthesize a closely related poly(phenylacetylene) structure.<sup>220</sup>

Thre et al. utilized the double exponential growth approach (Scheme 14) to develop an efficient synthesis of aliphatic polyester dendrimers.<sup>221</sup> Similar to Moore's approach, the synthesis utilized orthogonal protecting groups for the focal and peripheral functionalities of the growing dendron. The 2,2-bis(hydroxymethyl)propanoic acid starting material was protected either with a cyclic acetonide group to mask the hydroxyl groups of **124**, or with a benzyl ester at its focal point, **125**. The two complementary dendrons **124** and **125** were coupled efficiently using DCC and catalytic amounts of DPTS to afford the second generation dendron **126**. The peripheral ketal of **126** could be hydrolyzed using an acidic polymer resin, to afford the second generation hypermonomer **127**. Alternatively, catalytic hydrogenolysis of dendron **126** produced the activated carboxylic acid dendron **128**. Finally, DCC coupling of **127** and **128** produced the fourth generation dendron **129**, in 91% yield.

These accelerated growth procedures have been used by a number of groups to synthesize dendritic poly(amides),<sup>222–224</sup> poly(esters),<sup>225</sup> poly(ether urethanes),<sup>226</sup> and chiral poly(ethers).<sup>227</sup> The orthogonality of the focal and peripheral protecting groups required for double exponential growth also enables facile modification at either the periphery or focal point. Although this approach is one of the most rapid methods yet reported for the synthesis of well-

Scheme 13

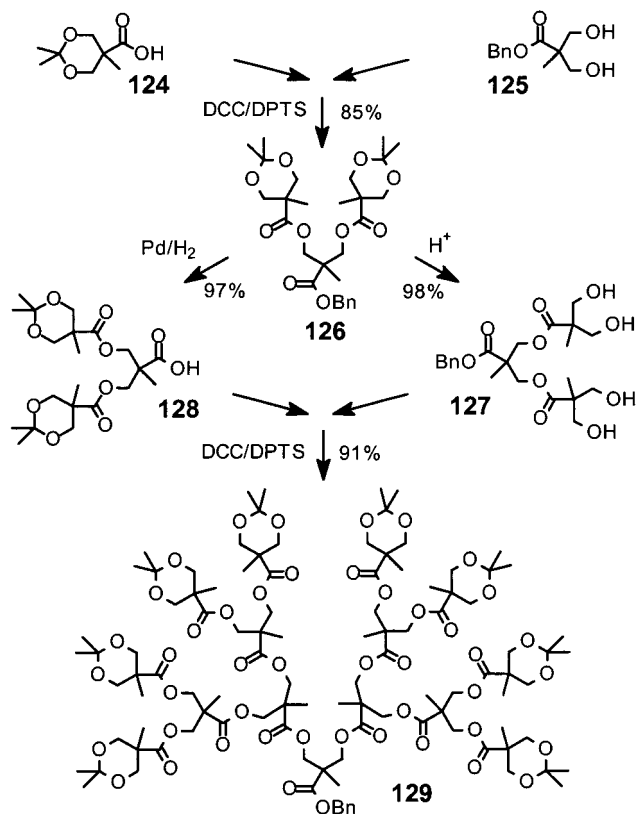


defined, large dendrimers, the number of coupling reactions required during each growth step increases exponentially each time the iteration is repeated, requiring high-yielding coupling chemistry. In this way, double exponential growth incorporates the advantages, and the disadvantages of both the convergent and divergent approaches.

## 2. Orthogonal Syntheses

The other accelerated approach for dendrimer synthesis, the orthogonal approach, involves convergent growth with two different monomers. The monomers, an AB<sub>2</sub> and a CD<sub>2</sub> must be carefully selected such that the focal functionalities of each individual monomer will only react with the periphery of the other monomer (B couples only with C and D only with A) thus removing the need for activation reactions. As

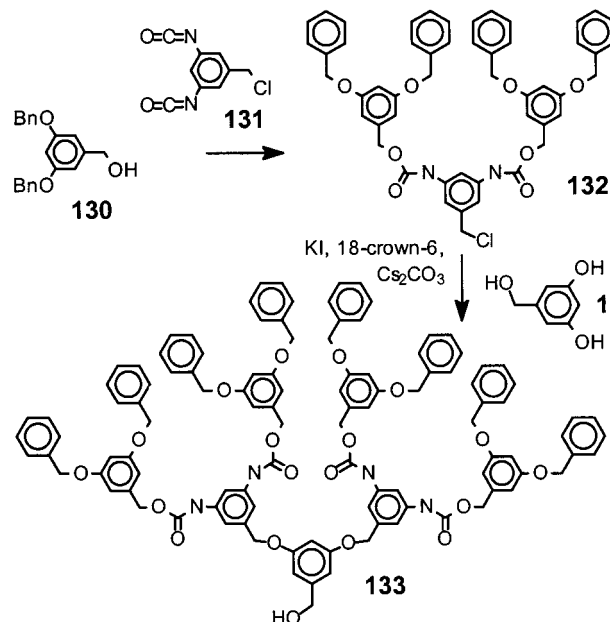
Scheme 14



a result of this synthetic design, each reaction in the synthesis adds a single generation to the dendron.

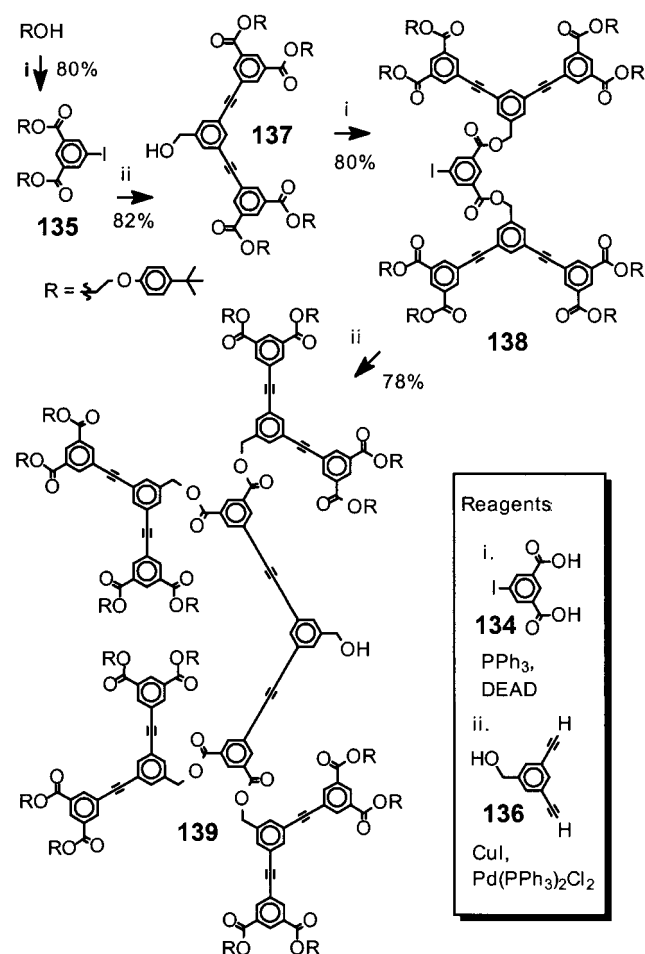
Spindler and Fréchet<sup>228</sup> reported the first orthogonal synthesis (Scheme 15) using the alternating

Scheme 15



monomers 3,5-diiocyanatobenzyl chloride, **131**, and 3,5-dihydroxybenzyl alcohol, **1**. Although this approach enabled a one-pot, two-step synthesis of the third generation poly(ether carbamate) dendron **133**, difficulties in purification prohibited further growth. Zimmerman and co-workers were the first to report

## Scheme 16



the orthogonal synthesis of high generation dendrimers,<sup>229</sup> producing dendrimers with alternating benzyl ester and alkynyl linkages (Scheme 16). The synthesis utilized the Mitsunobu esterification of the carboxylic acid end groups of monomer **134**, followed by the Sonogashira coupling of the resultant aryl iodide **135**, with the terminal alkyne units of a second monomer, **136**. The focal alcohol functionality of **137** is appropriately functionalized to continue iterative couplings to the diacid monomer **134** and the dialkyne monomer **136** yielding the fourth generation dendrimer **139**. Both coupling reactions afforded product in nearly 80% yield, through the fourth generation, demonstrating the efficiency of this route to high generation dendrons. To further accelerate the synthesis, the authors also investigated the use of the  $\text{AB}_4$  hypermonomers **140** and **141** (Figure 7),

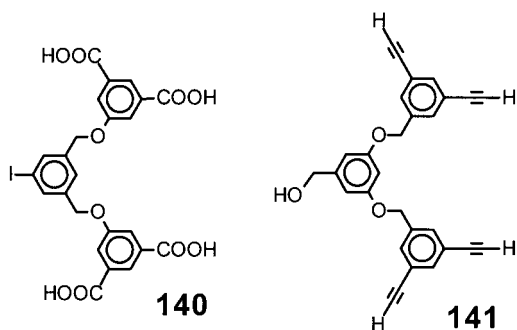
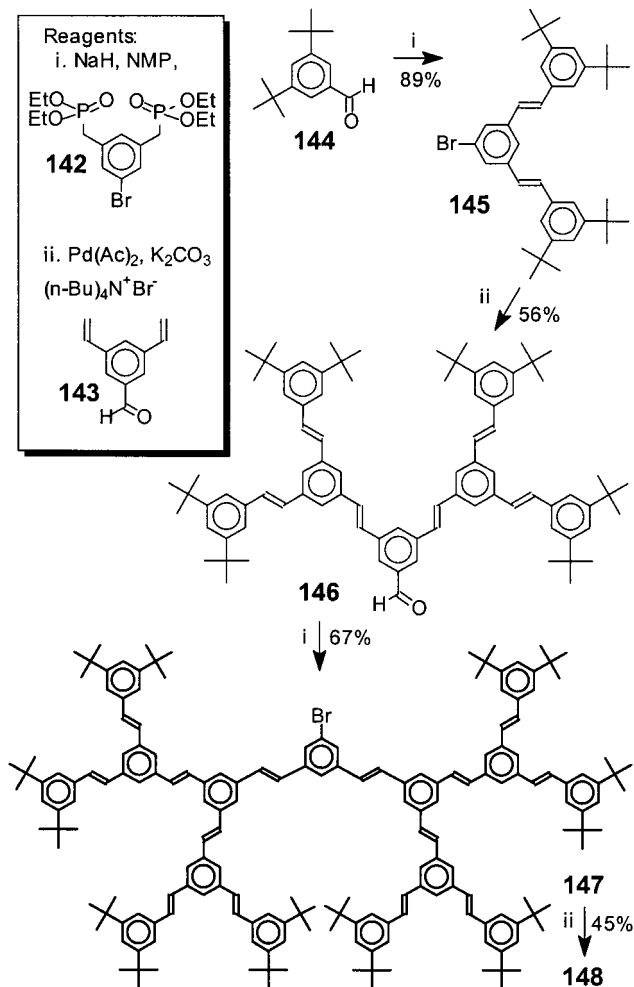


Figure 7.

utilizing the same two orthogonal coupling reactions. Although the yields for the higher generation reactions were reduced to less than 50%, a sixth generation dendrimer could be accessed in three synthetic steps with only two purifications.

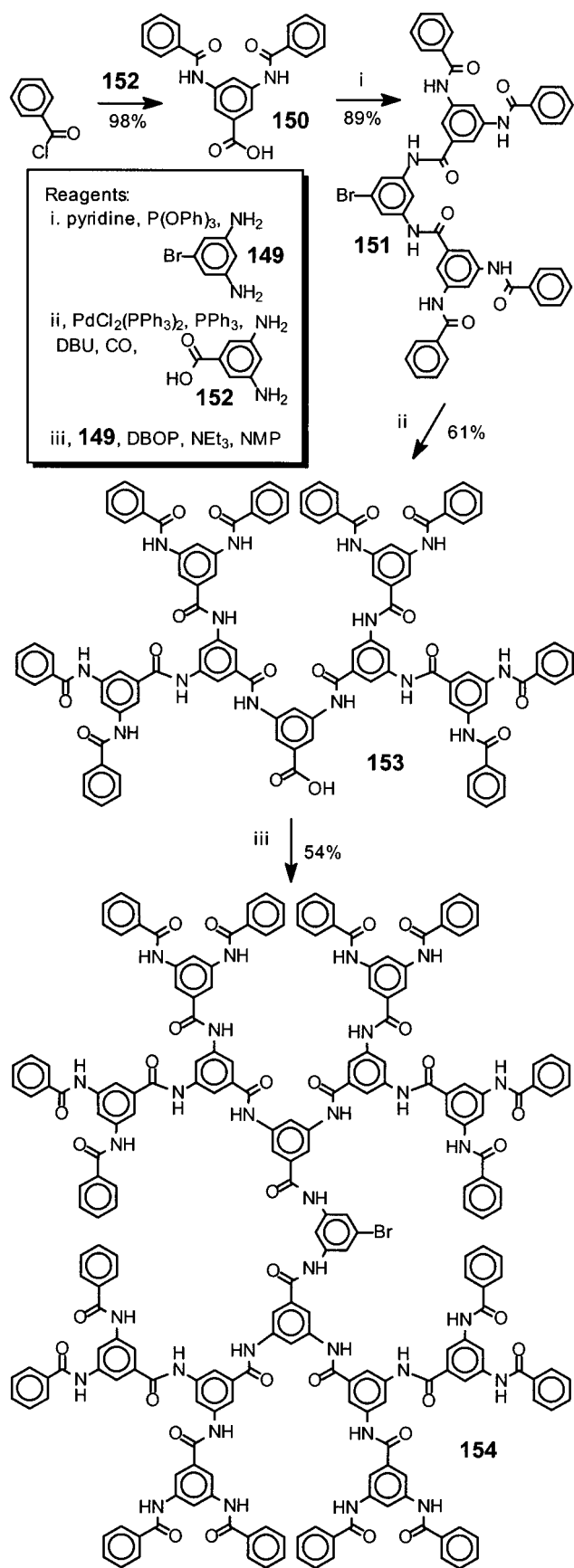
Yu and co-workers demonstrated the first orthogonal synthesis of chemically homogeneous dendrons (Scheme 17) with identical chemical connectivities,

## Scheme 17



alkenyl linkages, between each generation.<sup>139</sup> Combining the coupling strategies from the two previously discussed convergent approaches<sup>140–144</sup> their clever synthesis utilized a repetition of the Horner–Wadsworth–Emmons and the Heck coupling reactions. Monomers **142** and **143** could be used to access the fourth generation poly(aryl alkene) dendron **148** in an overall 15% yield in just four steps. Kakimoto and co-workers<sup>224</sup> also developed an orthogonal synthesis to poly(aryl amide) dendrimers (Scheme 18). Condensation of the monomer 3,5-diaminobromobenzene, **149**, and the carboxylic acid **150** yielded the dendritic bromide **151**. Dendrion **151** could then be activated by a palladium-catalyzed insertion of carbon monoxide, enabling reaction with the second monomer, **152**, to yield a dendritic carboxylic acid, **153**. All of the poly(aryl amide) dendrons exhibited solubility in THF and dimethylacetamide (DMAc),

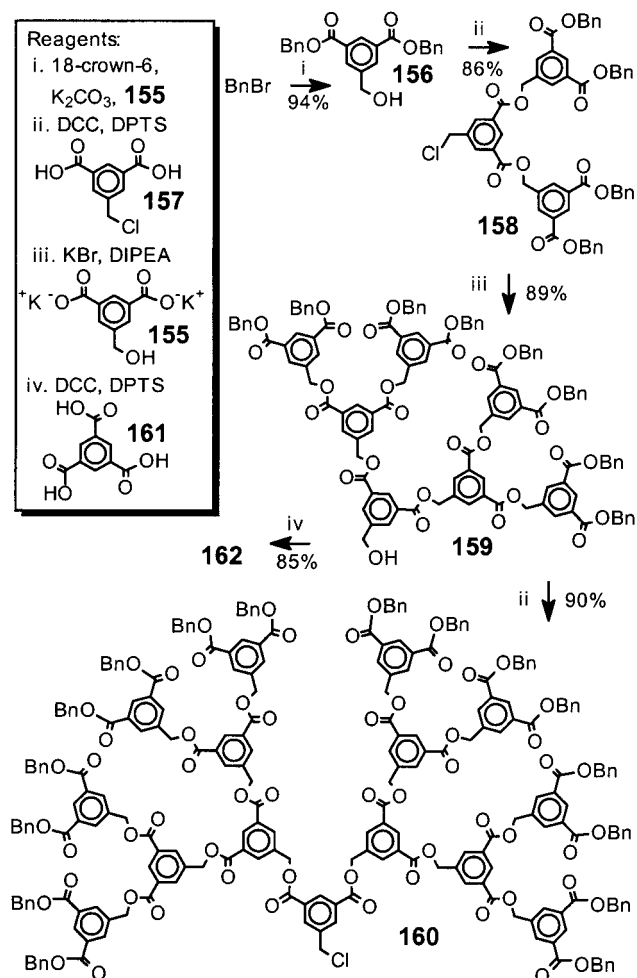
Scheme 18



but isolation of the third and fourth generation dendrons **153** and **154** required the use of preparative GPC.

The only chemically homogeneous orthogonal synthesis capable of efficiently producing high generation dendrimers (Scheme 19) was reported by Free-

Scheme 19



man and Fréchet.<sup>230</sup> Two complementary monomers **155** and **157** are used for this synthesis. Introducing benzyl ester end groups onto monomer **155** via nucleophilic displacement is followed by a DCC coupling with the second monomer to afford the second generation dendron **158**. The reactive benzylic chloride focal point of **158** allows its direct coupling with monomer **155**, and the process can be continued up to the fourth generation dendron **160**. The monomer sequence can also be readily reversed, by starting with the DCC coupling of benzyl alcohol to **157**, followed by the nucleophilic displacement reaction with monomer **155**. Both approaches afforded isolated yields of above 80% per coupling reaction through the fourth generation. The attachment of dendron **159** to the tricarboxylate core **161** produced the third generation dendrimer **162**, further demonstrating the high efficiency of the DCC-mediated esterification.

Although the orthogonal approach allows the rapid synthesis of dendrimers, and reduces the number of purification steps, few syntheses of this type have



been reported because of the complex synthetic parameters. In addition to requiring highly efficient coupling reactions, orthogonal syntheses require two pairs of coupling functionalities that are strictly orthogonal. This orthogonality also places a greater limitation on which functionalities may be incorporated into the dendritic structure without interfering with the synthesis.

### III. Modification of the Focal Functionality

The inward growth employed by the convergent synthesis is ideally suited for the attachment of diverse core moieties. In the divergent method, since the core is used to initiate dendritic growth, it must be stable to the subsequent activation and coupling conditions. The convergent synthesis, on the other hand, installs the core in the final step, enabling the incorporation of functionalities that may not withstand the conditions required for dendrimer growth. As a result, the convergent synthesis has been exploited for the construction of a wide variety of functional dendrimers.

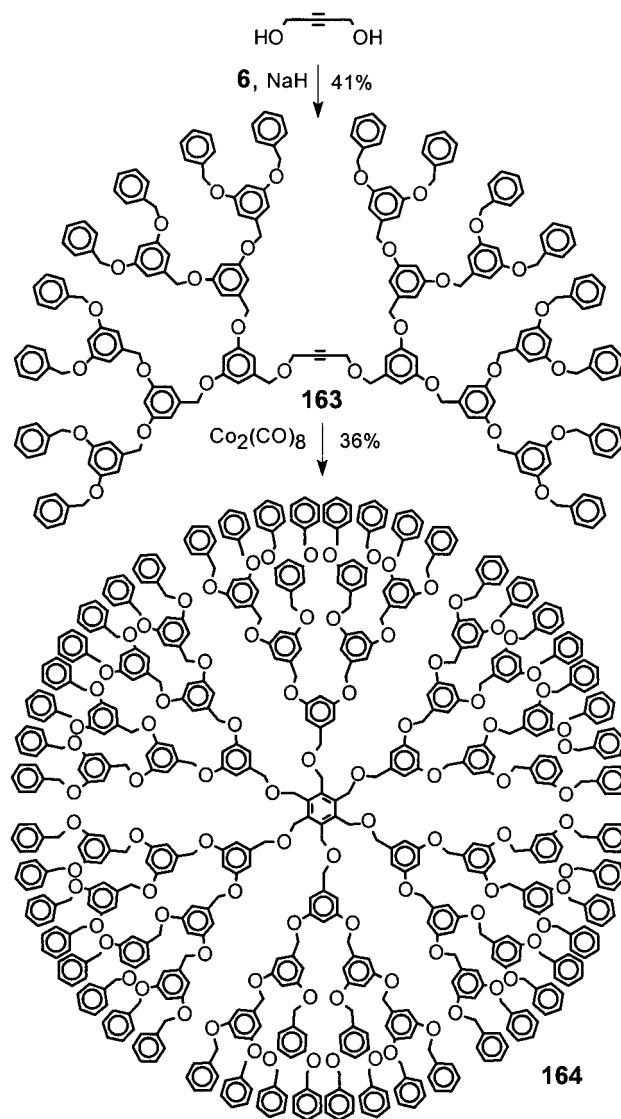
#### A. Traditional Covalently Bound Cores

For the purpose of this article, a traditional covalently bound core will be defined as a low molecular weight molecule with one or more functionalities capable of covalently coupling to the focal point of a dendron. This distinction is made to differentiate these cores from polymeric or self-assembled cores. The first dendrimer cores reported were simple di- or trifunctional molecules capable of coupling with dendrons utilizing identical chemistry as that repeated during dendron growth. For example, the earliest dendrimer cores (Scheme 2) include the trisphenolic core, **13**, reported by Hawker and Fréchet,<sup>10</sup> and the 1,3,5-triiodobenzene core reported by Moore and co-workers.<sup>231</sup>

Since then, a variety of methods for core attachment have been explored. Hecht and Fréchet<sup>232</sup> utilized the cobalt-catalyzed [2 + 2] cycloaddition (Scheme 20) of dendritically substituted alkynes **163** to produce a hexasubstituted benzene core dendrimer, **164**. Although the steric demand of higher generation substrates slowed the cyclization reaction, this approach successfully yielded highly functionalized, compact cores through the third generation. A similar cyclization approach has been reported by Van Wuytswinkel et al. utilizing the 1,3-dipolar cycloaddition reaction between a poly-azide core and dendritically di-substituted acetylene dicarboxylates.<sup>233</sup> Because of steric constraints, the reaction yields were significantly reduced with larger dendrons, preventing the preparation of the third generation dendrimer.

Within the past decade, a significant focus of dendrimer research has been the incorporation of "functional" core molecules that, by their very nature, contribute clearly to the properties of the dendrimers. A number of groups have investigated the feasibility of coupling dendrons to a buckminsterfullerene core.

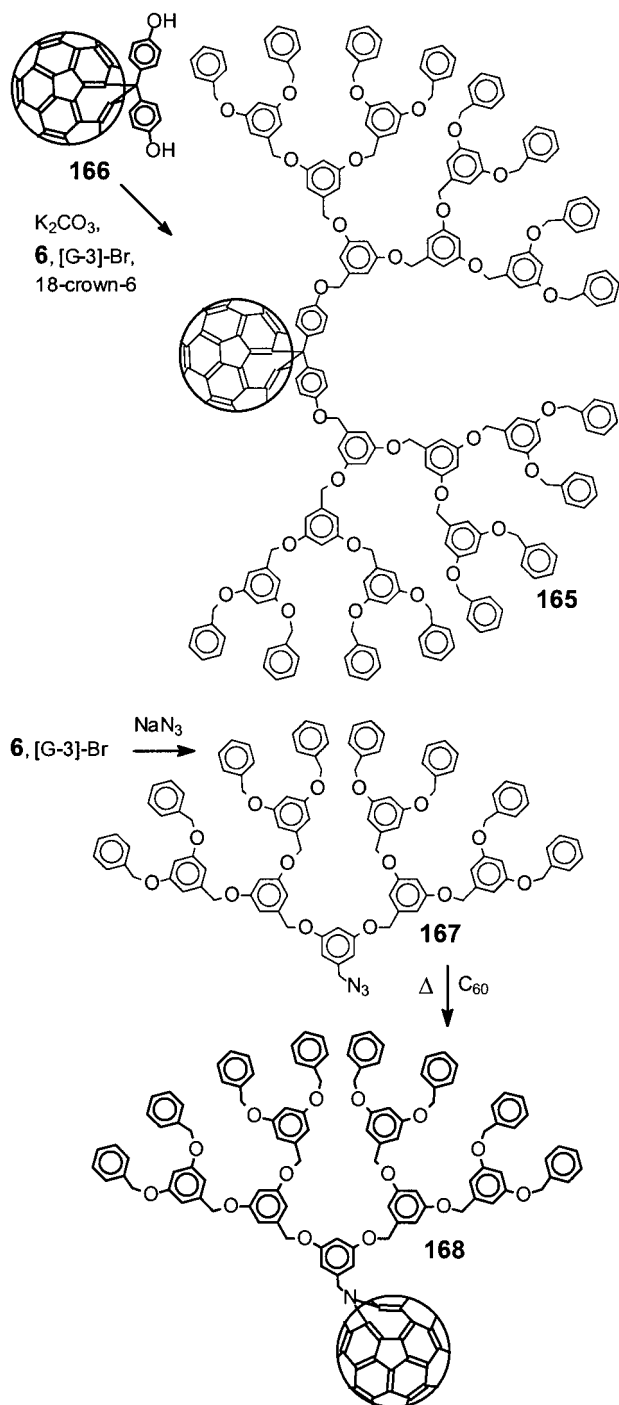
Scheme 20



Wooley et al.<sup>234</sup> reported the first dendrimer–fullerene hybrid, **165** (Scheme 21), via the alkylation of a prederivatized fullerene diphenol, **166**, with the dendritic bromide **6**. Because of purification problems related to impure fullerene starting material, Hawker et al. later investigated the direct cycloaddition<sup>235</sup> of a fourth generation azide-functionalized Fréchet-type dendron, **167**, with C<sub>60</sub>. This dendritic fullerene, **168**, could be easily isolated by flash chromatography and showed a significant increase in solubility over the parent fullerene. Avent et al. reported a similar cycloaddition of poly(phenylacetylene) dendrons bearing a focal tosylhydrazone functionality.<sup>236</sup>

More recently Hirsch and co-workers have pursued the controlled attachment of multiple dendrons to C<sub>60</sub> cores (Scheme 22) via the cyclopropanation of bis-dendritic malonates.<sup>237–239</sup> The versatility of the cyclopropanation coupling approach has been utilized by others to attach complex multifunctional dendrons.<sup>240</sup> Cyclopropanation could be achieved with less than a 2-fold excess of the bis-dendritic malonates per coupling site, enabling the attachment of six-third generation dendrons in 28% yield, or eight

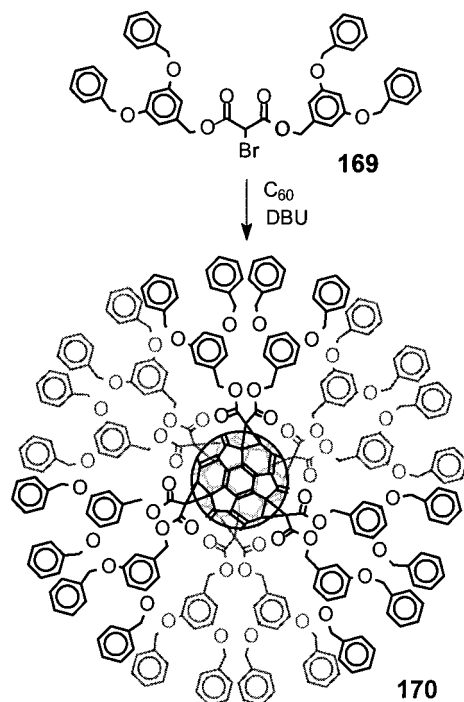
Scheme 21



second generation dendrons in a 73% yield.<sup>237</sup> Attachment of additional dendrons to the fullerene core appeared to be sterically disfavored,<sup>239</sup> as attempts to synthesize a fullerene with 12 first generation dendrons only proceeded in a 5.4% yield, **170**, and the analogous second generation molecule could not be synthesized.<sup>238</sup>

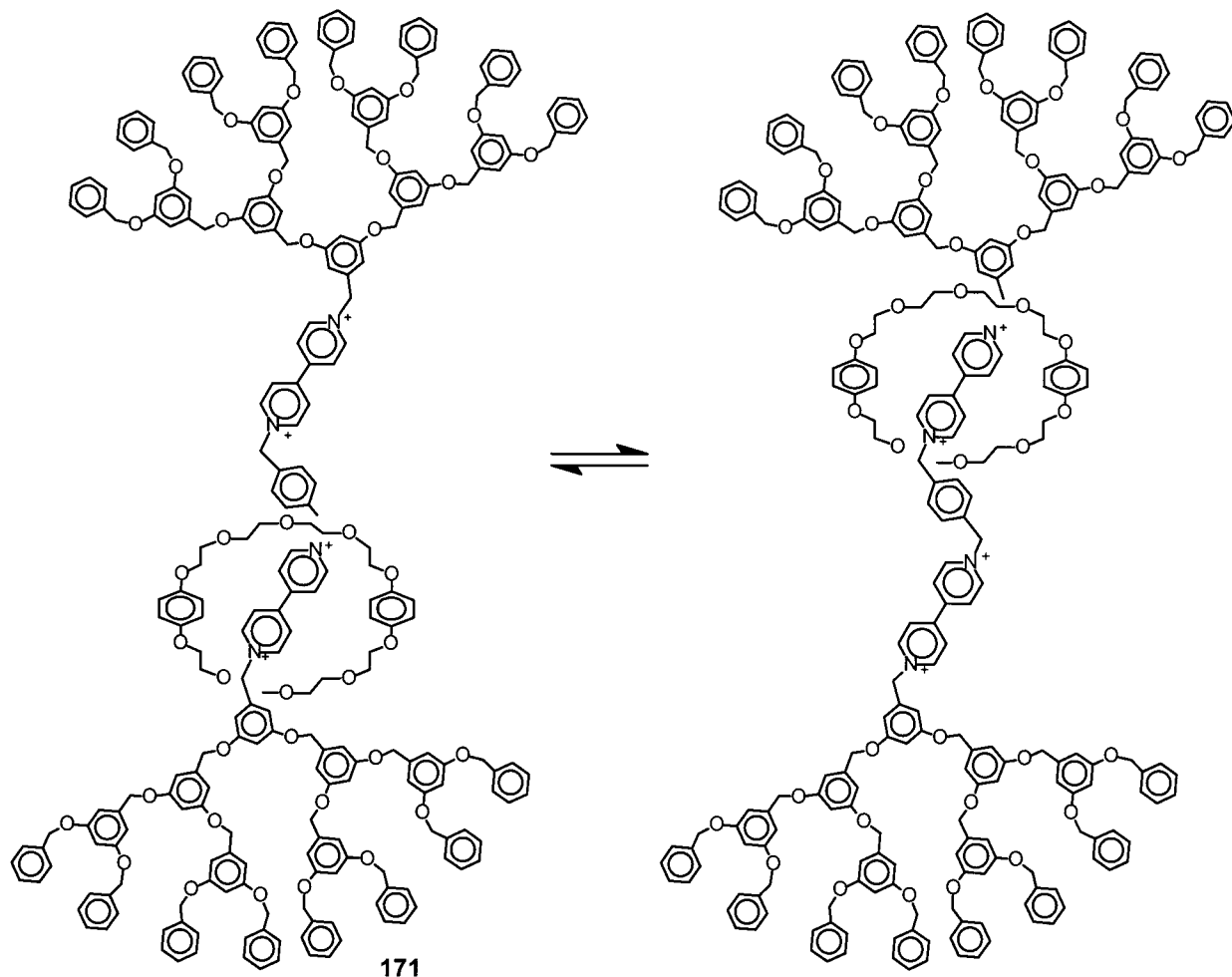
Dendrons have also been used as the capping moieties for rotaxane cores (Figure 8). Amabilino et al. reported the Williamson coupling of the third generation Fréchet-type dendrons **6** to cap polyether macrocycles threaded around linear bipyridinium oligomers.<sup>241</sup> When the linear component consisted of multiple viologen units, **171**, shuttling of the

Scheme 22



macrocycles could be observed between the different bipyridinium sites. Because the dendrons imparted enhanced solubility in organic solvents, the rate of shuttling as a function of solvent polarity could be determined and exhibited a dramatic increase in more polar solvents. Dendrimers have also been reported that incorporate a pseudo-rotaxane linkage between each of the dendrons and the core.<sup>242</sup> Gibson and co-workers assembled these pseudorotaxanes by threading Fréchet-type dendrons with a crown ether focal point onto a tris-ammonium salt core. Because these pseudorotaxanes lack one blocking group along the linear portion, the threading and dethreading equilibrium is subject to environmental conditions.

Porphyrins<sup>72,143,146,164,243–259</sup> and the closely related phthalocyanines<sup>260–267</sup> have been utilized extensively as dendrimer cores because of their interesting electrical, optical, and catalytic properties. Inoue and co-workers reported the first convergent synthesis of a porphyrin-core dendrimer<sup>248</sup> by attaching poly(aryl ether) dendrons onto the preformed porphyrin **172**. Fréchet and co-workers later compared the utility of this approach to the Lindsey condensation (Scheme 23) of dendritic aldehyde **173** and pyrrole.<sup>243</sup> The two methods offered complementary routes toward the synthesis of porphyrin-core dendrimer **174**, as the Lindsey condensation is acid catalyzed, while the Williamson route required prolonged reactions under basic conditions. Though the “Lindsey products” were easier to purify, the Williamson coupling appeared to be more suitable for the synthesis of larger dendrimers, since this approach was less sensitive to steric constraints. Similar complementary approaches have been reported for the synthesis of dendritic phthalocyanines.<sup>265,268</sup> The attachment of dendrons to the porphyrin and phthalocyanine cores enabled modification of their solubility,<sup>245,246,265,266</sup> improvement of their processibility,<sup>260,263,264</sup> and steric



**Figure 8.**

encapsulation of their reactive sites.<sup>253,254,259,263</sup> A substantial contribution to the field of dendritic porphyrins and phthalocyanines has also been made by the groups of Diederich<sup>269–272</sup> and Koboyashi<sup>268,273</sup> using the divergent approach.

In the following section, a variety of convergently prepared dendrimers will be discussed in the general context of their applications. Given the focus of this review, such a classification is quite appropriate since it is the application that dictates the design of the dendrimer and hence its synthesis.

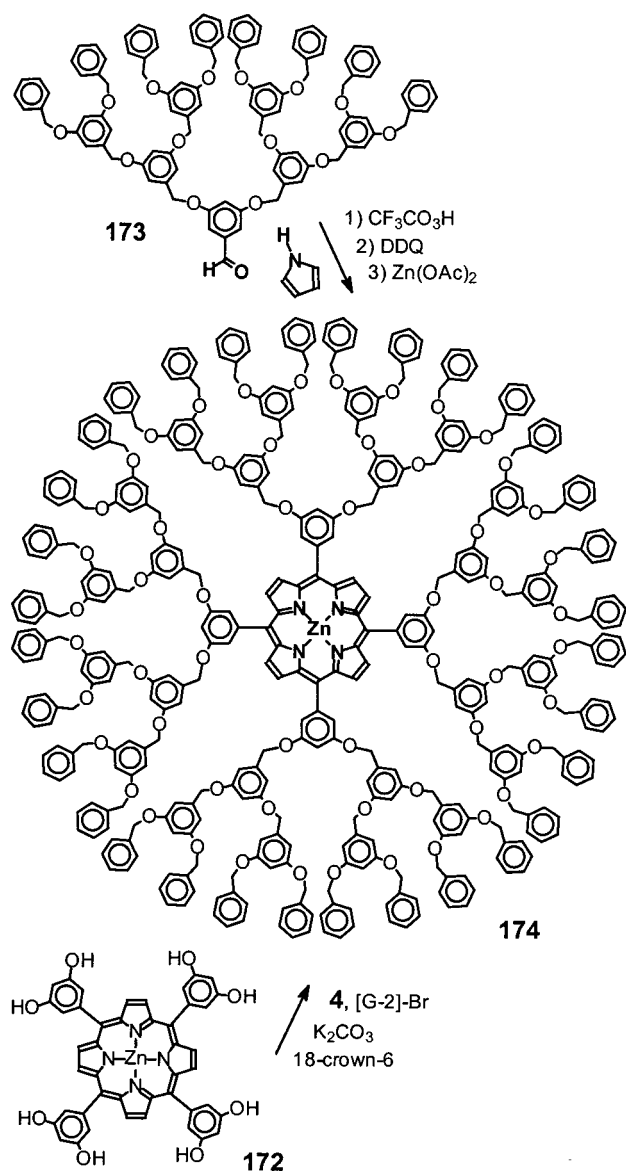
### 1. Environmentally Responsive Cores: Dendritic Probes

Because high generation dendrimers can sterically encapsulate the core from the external environment, the interior is expected to exhibit a unique microenvironment. The ability to tune this environment may eventually provide a synthetic mimic of enzymatic catalysis or biological binding events, but initial investigations have focused on the incorporation of responsive core moieties designed to help elucidate the complex nature of the dendritic molecules themselves. For example, Hawker et al. coupled the anion of 4-(*N*-methylamino)-1-nitrobenzene to Fréchet-type dendritic bromides (Figure 9) yielding **175**, a solvatochromic probe to elucidate the internal polarity of the dendrimer.<sup>274</sup> When measured in nonpolar sol-

vents, the solvatochromic shift in the absorption spectra appeared to change drastically between the third and fourth generations, confirming that only large dendrimers are capable of efficiently shielding their core from the exterior environment. Devadoss et al. reported a similar shift in the fluorescence spectra between the fourth and fifth generations, utilizing the characteristic charge transfer in poly(phenylacetylene) dendrimers having a 2,5-dimethoxyphenylethyne focal point.<sup>275</sup> In other studies, tryptophan cores were used to evaluate the nature of hydrogen bonding within the interior of the dendrimer,<sup>276</sup> rubicene cores were incorporated to determine the hydrodynamic volume of dendrimers in different solvents,<sup>277</sup> and paramagnetic,<sup>278</sup> or isotope labeled<sup>279</sup> cores were utilized in conjunction with nuclear magnetic resonance to probe dendritic conformation.

Vögtle and co-workers have also explored the steric demands and flexibility of the Fréchet-type dendrons by comparing the rate of rotaxane dethreading between the dendritic stoppers and traditional rigid stoppers.<sup>280</sup> The dendritic rotaxanes were prepared by Williamson ether coupling reaction between a bulky alkoxide and a dendritic bromide. Dethreading rates and computer modeling suggested that the steric requirements of the second generation dendron

## Scheme 23



exceeded those of a trityl group, whereas the third generation appeared to be larger than the *tert*-butyl trityl group.

## 2. Chiral Cores

The structural purity of convergent dendrimers has provided a unique opportunity to study chirality in synthetic macromolecules.<sup>197,198,281</sup> A wide variety of poly(aryl ether) dendrimers have been prepared with chiral cores, using the Williamson ether coupling reaction. The effect of dendritic substitution on the chiral properties of a core molecule depend primarily on the origin of its chirality. Dendritic analogues of the axially chiral molecule binaphthol **176** were prepared by the Williamson ether coupling of Fréchet-type dendritic bromides to the phenols of 1,1'-bi-2-naphthol (Figure 10). Increasing the size of dendritic substituents produces an increasingly negative value for the molar optical rotation.<sup>282–284</sup> Circular dichroism has determined that this effect results from an expansion of the dihedral angle

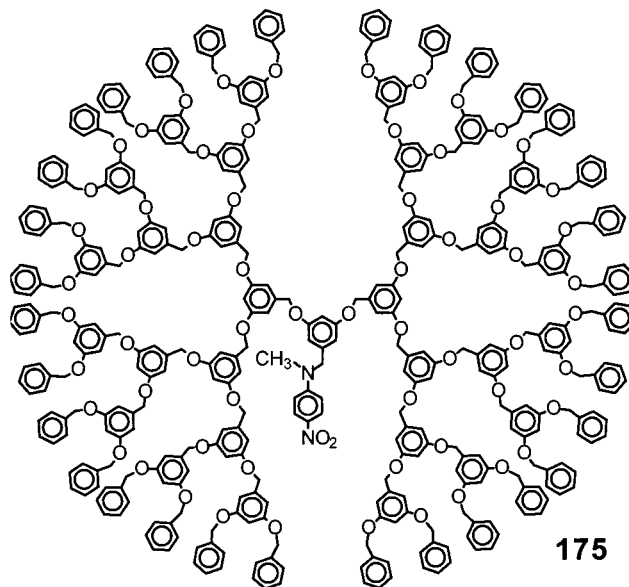


Figure 9.

between the naphthyl units caused by steric repulsion between the dendrons. The attachment of two Fréchet-type dendrons in the 6 and 6' positions<sup>285</sup> or four Moore-type dendrons to the 4, 4', 6, and 6' positions appeared to have a less drastic effect on the dihedral angle.<sup>286</sup> With the rigid spirobifluorene<sup>287</sup> core, less susceptible to sterically induced rotation, it was found that dendritic substitution had little effect on the optical rotation of these chiral molecules.

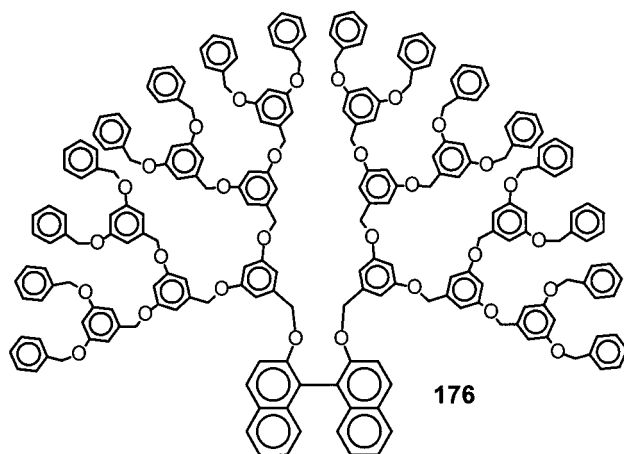
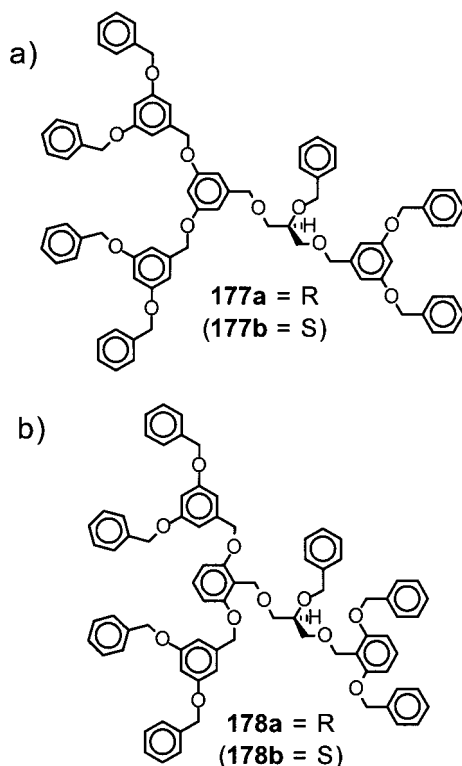


Figure 10.

The inclusion of Fréchet-type dendrons around stereogenic cores such as (3*R*,4*S*,5*R*)-3,5-dihydroxy-4-hydroxymethyl-2,2-dimethylhexane,<sup>288,289</sup> (1*R*,2*S*)-2-amino-1-phenyl-1,3-propanediol,<sup>290</sup> 2,5-anhydro-D-mannitol,<sup>291</sup> and TADDOL<sup>292</sup> produced the opposite effect. As the generation number of the attached dendrons increased, the molar optical rotation of these materials generally decreased. This trend is believed to result from perturbation of the chiral conformation by the bulky dendrons.<sup>86</sup>

Meijer and co-workers have prepared an interesting set of molecules with chirality that originates from dendrons of different generation radiating from an otherwise achiral pentaerythritol core.<sup>293–295</sup> Unfortunately, attempts to resolve the racemic products



**Figure 11.**

were unsuccessful, and the chirotopic properties of the materials could not be studied. However, the same group later reported the successful preparation (Figure 11) of the optically pure (*R*) and (*S*) enantiomers **177a** and **177b**, by Williamson coupling of Fréchet-type dendrons to a chiral glycerol derivative using a series of protection and deprotection steps.<sup>296</sup> These compounds were found to be “cryptochiral,” having no measurable chiral properties, presumably because of the flexibility of the molecule and the electronic similarity of the three poly(benzyl ether) dendritic substituents. When “backfolding” dendritic wedges were introduced in the preparation of **178a** and **178b**, the more rigid structure did exhibit optical activity.<sup>86</sup>

### 3. Host–Guest Core Binding Sites

The nature of dendritic architecture with its lack of congestion near the core and increased crowding near the chain-ends makes dendrimers attractive candidates for guest encapsulation. The coordination of fullerenes to Fréchet-type dendritic hosts has been achieved using cores consisting of an iridium complex,<sup>297</sup> cyclotrimeratrylene,<sup>298</sup> and a porphyrin.<sup>249</sup> The iridium-containing macromolecule was prepared by reacting two diphenyl phosphine derivatized dendrons with an iridium core. In all of these studies, the association constants appear to be higher for the larger dendrimers, presumably because the  $\pi$ – $\pi$  interactions between the dendrons and the bound fullerene slow the disassociation process. Shinkai and co-workers have provided support for this hypothesis by observing that Fréchet-type dendrimers can, by themselves, act as fullerene hosts.<sup>249,299</sup>

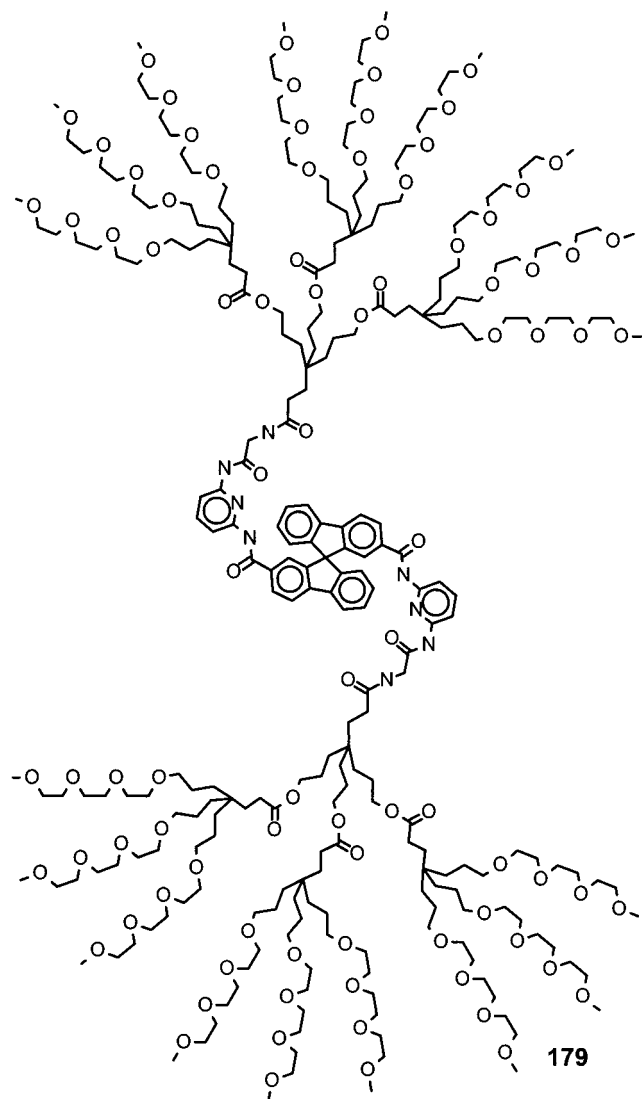
Zimmerman et al. have reported evidence that the binding constants between a dendritic naphthyridine

host and a benzamidine guest molecule are dependent upon both the size of the guest and the steric congestion of the host.<sup>300</sup> The macromolecular hosts were prepared by attaching the first through fourth generation dendrons of both the poly(phenylacetylene) and the poly(benzyl ether) families to a naphthyridine core via a Sonogashira coupling. In addition, two different benzamidine guests were investigated, a smaller one with a 3,5-*tert*-butylphenyl substituent and a larger one with a first generation poly(phenylacetylene) dendron attached. The difference in binding free energy values between the smaller guest and the eight different dendritic hosts was sufficiently small to conclude that the steric bulk of the dendrimer, up to the fourth generation, does not seriously impede access of small guests to the binding site. In contrast, the larger benzamidine guest exhibited an appreciable drop in binding free energy when interacting with the largest naphthyridine dendrimers.

The groups of Aida and Suslick have reported similar results with dendrimers having zinc porphyrin cores. Using computer modeling,<sup>250</sup> Aida determined that the porphyrin core of the dendrimers was accessible for the first three generations, partly accessible at the fourth and fully hindered at the fifth. Experimental measurements of the binding between dendritic zinc porphyrins and dendritic imidazoles confirmed the theoretical predictions, exhibiting a significant decrease in relative binding constants at the fifth generation.<sup>250</sup> Suslick observed similar results with aryl ester and aryl amide zinc porphyrin-core dendrimers, but noticed enhanced binding selectivities toward less hindered amines when incorporating backfolding benzyl ester dendritic wedges.<sup>251</sup>

Through fluorescence studies, Kaifer and co-workers documented a drastic decrease in binding efficiency between cyclodextrins and dansyl modified dendrons as the dendrimer size increases.<sup>301</sup> Yet, surprisingly, quantification of the binding efficiency with significantly larger anti-dansyl antibodies exhibited a less substantial decrease in binding stability between the first and third generations.

Diederich and co-workers have systematically investigated the effect of dendritic size on the stereoselective binding (Figure 12) between 9,9'-spiro[9*H*-fluorene] chiral cores and glucosides.<sup>287,302</sup> The dendrimers **179** were synthesized by reaction between the focal carboxylic acid functionality of the dendrons and glycine spacers attached to the spirobifluorene core. As the generation number of the dendritic host is increased from zero to two, the enantioselectivity of the macromolecular host appeared to be reduced while the diastereoselectivity was increased. A more recent study by Diederich and co-workers using Fréchet-type dendrons and derivatives of binaphthol as binding sites yielded less striking results.<sup>303</sup> This inconsistency is believed to result from the perturbation of the binding site by dendritic substitution. This result highlights the fact that although the steric bulk of the dendritic structure may not inhibit substrate access, it may adversely affect binding in other ways.

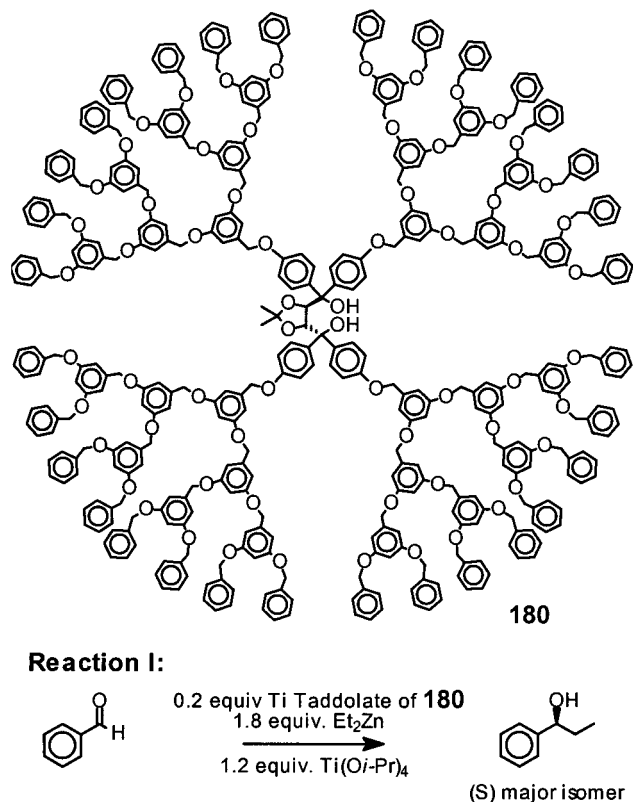
**Figure 12.**

Although the steric bulk of larger dendritic systems has been shown to suppress host–guest binding, the studies above suggest that smaller molecules can easily permeate into moderately sized dendritic structures—typically up to the fourth generation—and interact with the core moiety. This result provides encouraging evidence for substrate accessibility in appropriately designed dendrimers with catalytic cores.

#### 4. Core Catalytic Sites

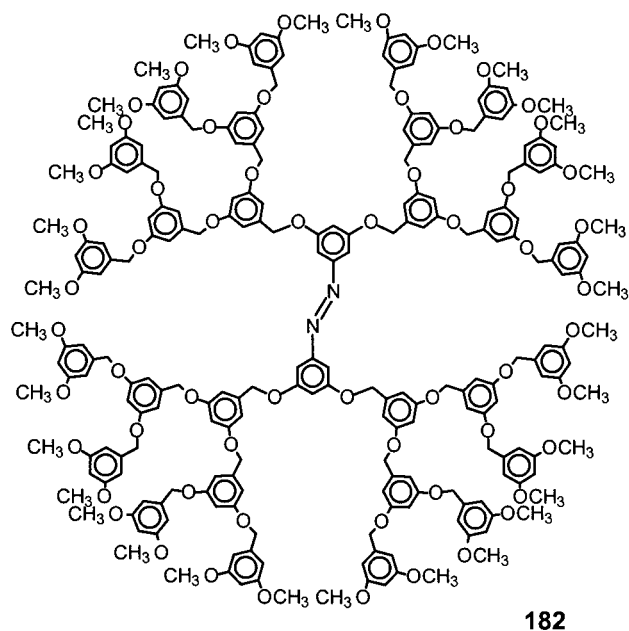
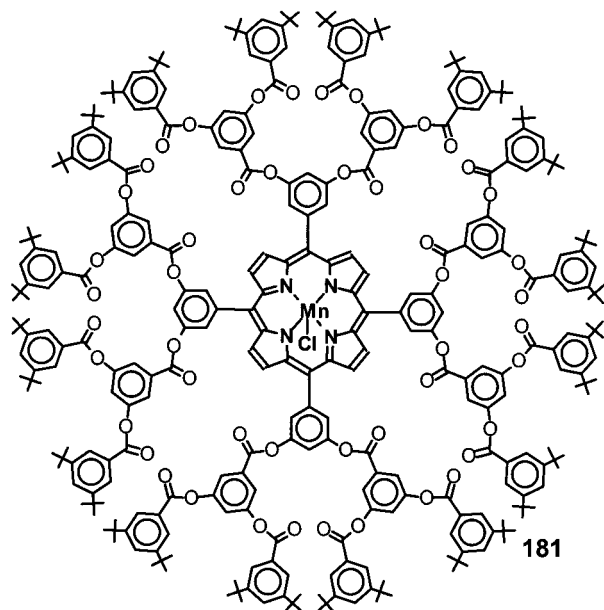
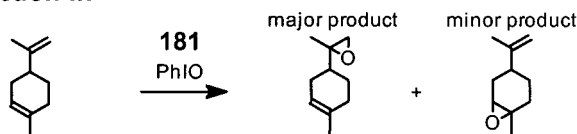
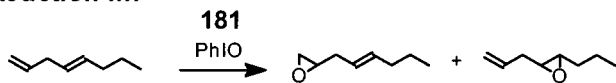
Convergent dendrimers, with their versatile three-dimensional scaffold, may be tailored to mimic, perhaps crudely, some elements of enzymatic structures. Numerous catalytic moieties, including manganese porphyrins,<sup>253,254</sup> bis(oxazoline) copper complexes,<sup>304,305</sup> tertiary amines,<sup>306</sup> binaphthol titanium complexes,<sup>285,307</sup> titanium taddolates,<sup>292,308</sup> thiazolium-cyclophanes,<sup>309</sup> and fullerene-bound bisoxazoline copper complexes,<sup>310</sup> have been incorporated at the core of dendritic molecules to determine the effect of dendritic encapsulation on their catalytic activity.

Not unexpectedly, a chiral TADDOL dendritic catalyst<sup>292</sup> demonstrated a slight reduction in enan-

**Figure 13.**

tioselectivity as the generation number of the dendrimer increased (Figure 13). These dendrimers were prepared by the Williamson ether coupling between the four phenolic groups of a TADDOL derivative and Fréchet-type dendritic bromides. During the nucleophilic addition of ethyl zinc to benzaldehyde, Seebach and co-workers showed a only a slight decrease from 99% stereoselectivity with the unsubstituted titanium taddolate ligand, to 94.5% with the fourth generation dendrimer **180**. Similar results were observed when using a binaphthol core.<sup>285</sup> Dendritic size did, however, exhibit a profound effect on the rate of the reaction. For both of the dendrimer-catalyzed chiral reactions, as well as achiral Diels–Alder<sup>310</sup> and Henry reactions,<sup>306</sup> rates of conversion fell sharply by the third or fourth generation, suggesting that the dendritic bulk was preventing substrate access to the active site.

Bhyrappa et al. have investigated the effect of dendritic substitution on the regioselectivity afforded by a porphyrin core during the epoxidation of substituted alkenes.<sup>253,254</sup> The attachment of first and second generation poly(aryl ester) dendrons to a manganese porphyrin core (Figure 14) through a DCC-mediated esterification yielded **181**. The dendritic substitution blocked the catalytic site from the top and bottom faces, thereby improving the oxidative stability of the catalysts and increasing catalyst lifetime. The reaction of the dendritic catalyst with unconjugated dienes, consisting of one more and one less hindered double bond, revealed that the second generation dendritic catalyst was significantly more regioselective than the parent porphyrin (2-fold for reaction II and nearly 4-fold for reaction III). However, the regioselectivities were not as high as those

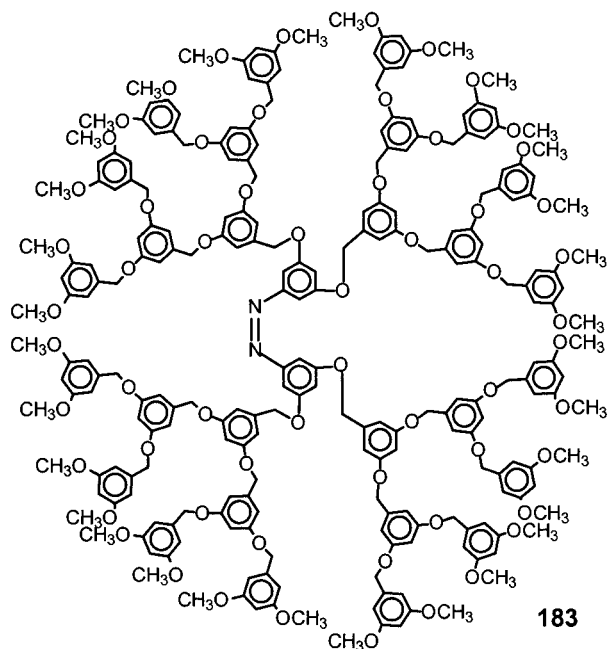
**Reaction II:****Reaction III:****Figure 14.**

reported for the bis(pocket porphyrin)<sup>311,312</sup> (5,10,15,-20-tetrakis(2',4',6'-triphenylphenylporphyrin)) that, according to computer modeling, exhibits an opening above and below the face of the porphyrin.

Because the increasing steric environment of high generation dendrimer reduces substrate accessibility, the larger dendritic system must be designed to address mass transport problems. In addition to providing some sterically induced regioselectivity, the dendritic scaffold appears capable of maintaining the stereoselectivity of analogous nondendritic systems. Currently, the most significant advantages of incorporating catalytic sites into dendritic structure are the ability to tune their solubility and facilitate catalyst recycling via precipitation or ultrafiltration.

### 5. Photochemically Responsive Cores

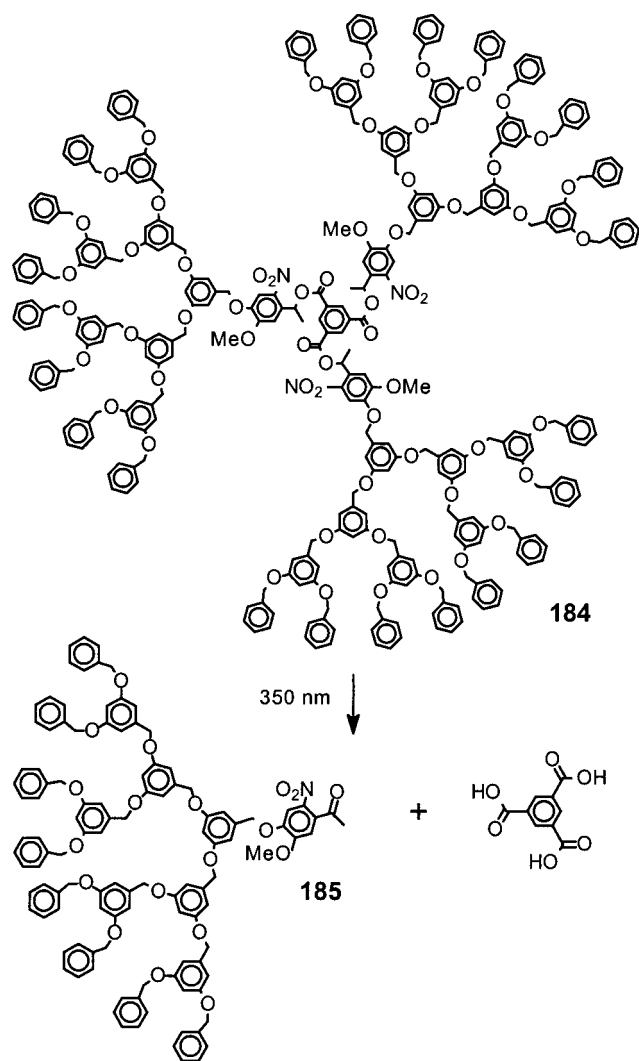
Molecules that can respond to external stimuli are of particular interest for macromolecular devices, and may potentially serve as molecular switches. A number of groups have examined the incorporation of photochemically responsive cores into dendritic structures. Azobenzene moieties, which are capable of undergoing a photochemical cis–trans isomerization, were first incorporated into the core of poly(aryl ether) dendrimers (Figure 15) via a Williamson ether coupling by Aida and co-workers<sup>313–315</sup> and shortly thereafter, by Junge and McGrath.<sup>316</sup> UV irradiation of the samples converted the more stable trans

**Figure 15.**

isomer **182** to the cis isomer **183**. It is interesting to note that the activation energy for this transformation is only marginally affected when the size of the dendron substituents is increased from the first to the fourth generation.<sup>317</sup> In addition, Jiang and Aida noted that IR irradiation could accelerate the conversion back to the trans conformation for sufficiently larger dendrimers. In detailed studies, they deduced that this process resulted from the absorption of multiple IR photons (1597 cm<sup>-1</sup>) by the aromatic rings of the dendritic framework, and subsequent transfer of the absorbed energy to the azobenzene core.<sup>313</sup>

In addition, Junge and McGrath have designed a trifunctional core moiety in which each dendron is attached via an azo linker, enabling three such isomerizations per macromolecule.<sup>318</sup> The physical properties of these dendrimers can be noticeably modified by this isomerization, and have been documented by a change of polarity during thin-layer chromatography and a change in hydrodynamic volume as measured by size exclusion chromatography.<sup>319</sup> McGrath also reported a photodegradable dendrimer, **184**, containing *o*-nitrobenzyl ester linkages (Scheme 24) that could be quantitatively cleaved by irradiation to strip the dendrons **185** from their core.<sup>320</sup>

Scheme 24



Photoresponsive dendrimers are of interest because the properties of these materials can be readily modified by an external stimulus. These initial studies have verified that the inclusion of photoactive moieties into dendritic systems does not adversely affect their photochemical response and can enable changes in the overall macromolecular structure.

#### 6. Fluorescent Cores

Dendrimers have also been attached to fluorescent cores in order to modify the properties of the dye. The

attachment of dendrons to oligothiophenes<sup>152,321–324</sup> improved the solubility of the oligothiophenes in organic solvents, whereas the placement of appropriate dendritic substituents on porphyrin chromophores yielded water solubility dyes.<sup>245,246,266</sup> In addition, the attachment of dendrons to chromophore cores can improve the processibility of the core<sup>151</sup> for incorporation in monolayers<sup>325</sup> and films.<sup>326</sup> However, by far the most useful advantage to dendritic chromophores is the site isolation<sup>28</sup> provided by large dendritic substituents. With sufficiently large dendritic shielding, intermolecular quenching between the encapsulated dyes can be significantly decreased leading to an enhanced luminescence efficiency,<sup>45,250,327,328</sup> and in some instances, the penetration of small molecule quenchers, such as triplet oxygen, can be reduced.<sup>329</sup> However, even in the case of fourth generation porphyrin core dendrimers, steric shielding may not be sufficient to prevent the penetration of small quenchers, such as vitamin K<sub>3</sub>. At least two groups have reported that the porphyrin at the core of a fourth generation poly(aryl ether) dendrimer was more efficiently quenched than the first generation analogue because the quencher was not only sufficiently small to penetrate the steric shielding, but also had a greater affinity for the dendritic structure than for the surrounding solvent.<sup>248,252</sup>

Dendrimers have also been used as scaffold for light-harvesting and light-emitting diode devices by controlling the spatial interaction between focal and peripheral functionalities, these will be discussed in detail in a later section.

#### 7. Redox-Active Cores

As with chromophores, the steric encapsulation of a dendrimer core can be utilized to prevent intermolecular interactions between redox active sites. A number of different redox active core moieties have been investigated, including, iron–sulfide clusters,<sup>93,94</sup> bis(terpyridine)iron(II) complexes,<sup>92</sup> tris(bipyridine)ruthenium(II) complexes,<sup>330</sup> zinc porphyrins,<sup>252</sup> oligothiophenevinylenes,<sup>331</sup> fullerenes,<sup>236,332</sup> ferrocenes,<sup>333–336</sup> oligothiophenes,<sup>322</sup> oligonaphthalenes,<sup>337</sup> and 4,4'-bipyridinium.<sup>338</sup>

Following the early cyclic voltammetry (CV) studies by Fréchet and co-workers with dendrimer-encapsulated fullerenes<sup>235</sup> **168** and Chow et al. with dendritic bis(terpyridine)iron(II) complexes **186** (Figure 16),<sup>92</sup> a number of groups have reported the insulating effect of dendritic structures on redox active sites.<sup>93,236,252,322,330–333,339</sup> Gorman et al. were the first to report the dendritic encapsulation (Figure 17) of inorganic clusters **187**. These molecules were synthesized by a ligand exchange reaction where alkanethiols on a (Fe<sub>4</sub>S<sub>4</sub>(S-*t*-Bu)<sub>4</sub>)<sup>2-</sup> cluster were replaced by dendritic aromatic thiols.<sup>93</sup> As demonstrated with other encapsulated redox sites, the irreversibility of electron transfer increases with dendrimer size because the active core moiety becomes more insulated from the electrodes and other redox sites. Comparison of the CV data of the poly(phenylacetylene) and the poly(benzyl ether) dendrimers suggested that more rigid poly(phenylacetylene) structure led to more efficient redox site encapsula-



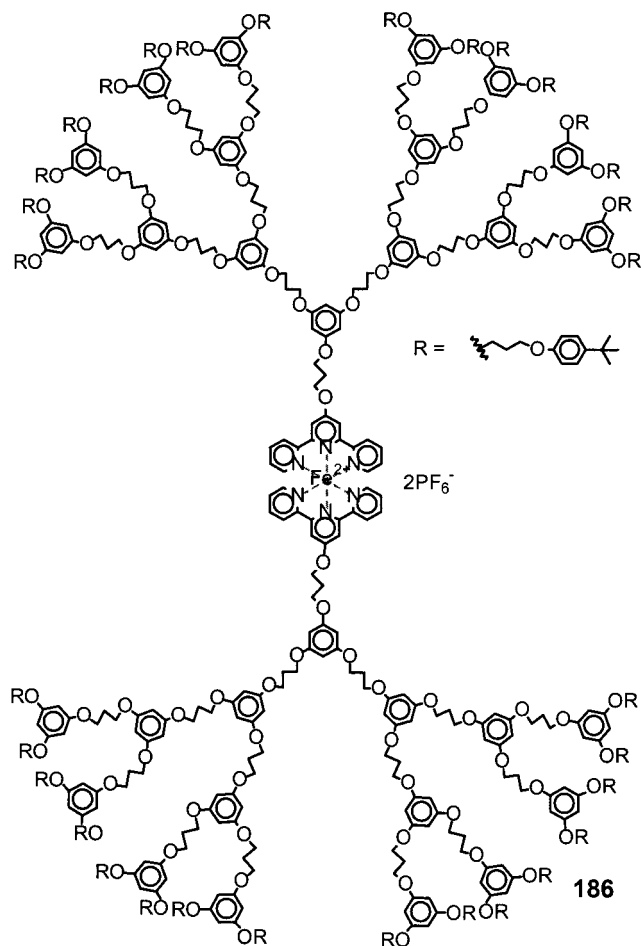


Figure 16.

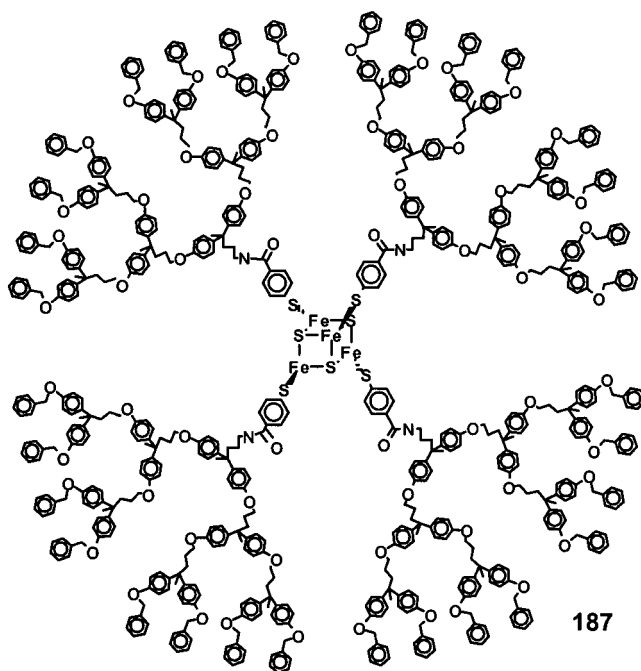


Figure 17.

tion.<sup>340</sup> Noteworthy redox active dendrimers prepared via the divergent approach have been reported by Diederich<sup>269–272</sup> and Newkome.<sup>341</sup>

Kaifer and co-workers designed an interesting molecular device that exhibits a pH dependency on

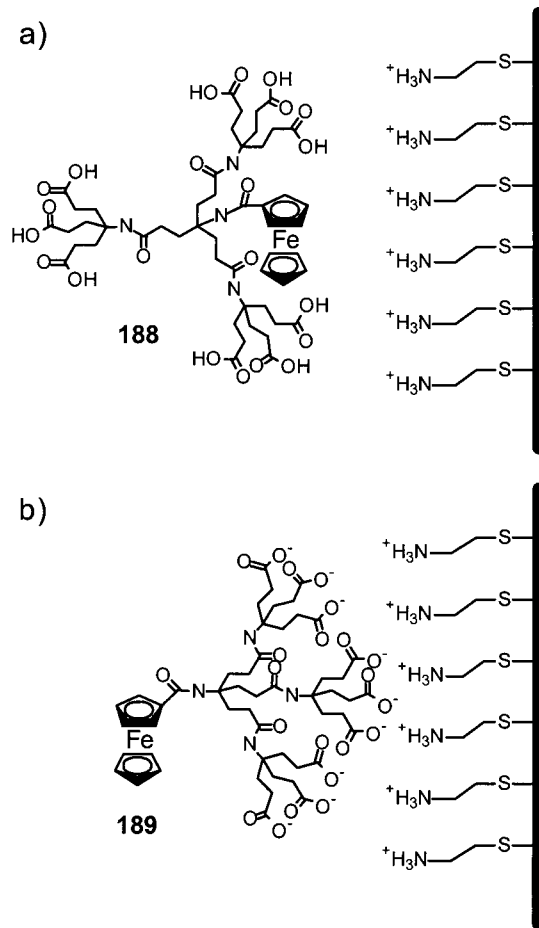


Figure 18.

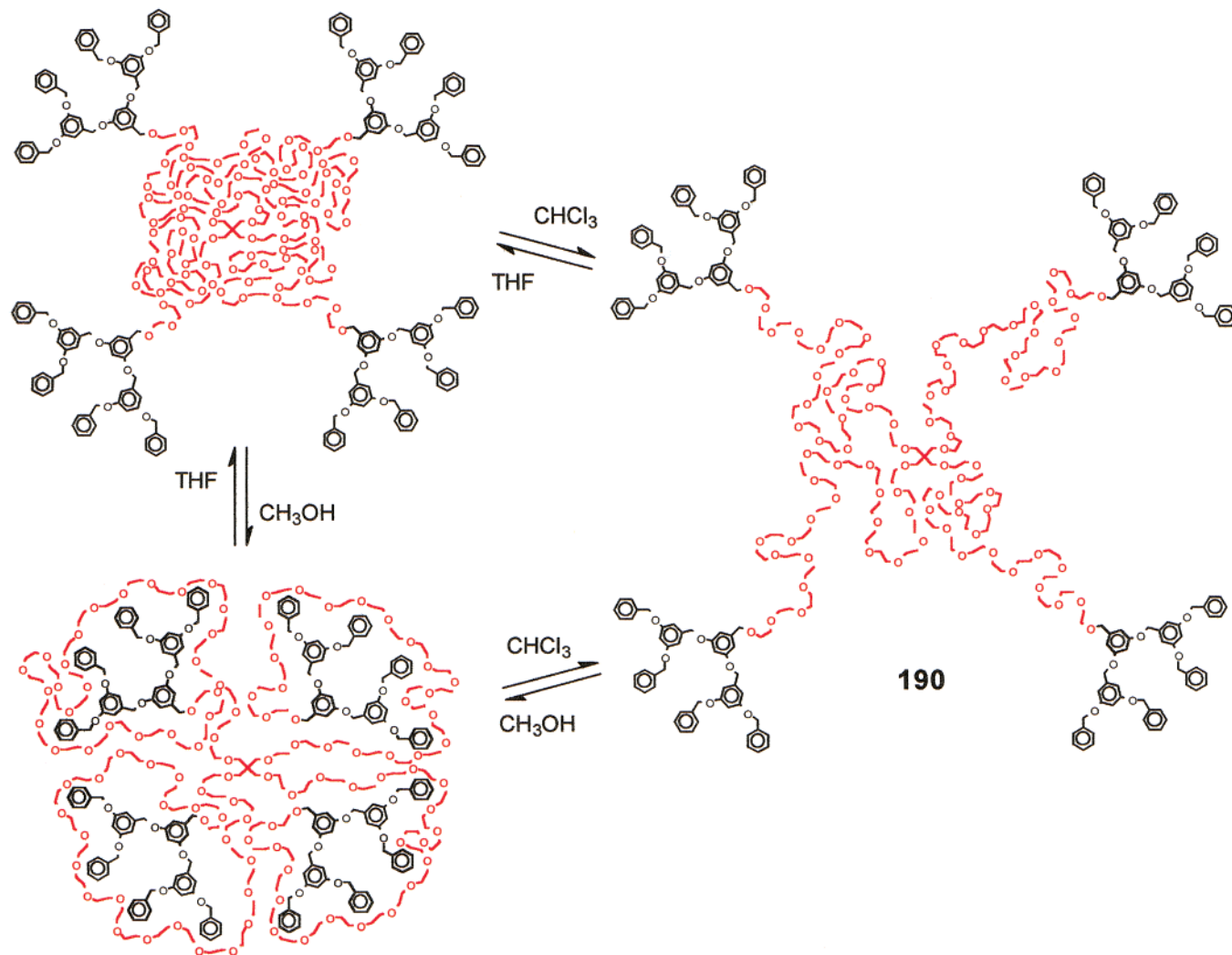
electron transfer.<sup>335</sup> They coupled a chlorocarbonyl-ferrocene core to first, second, or third generation amine functionalized convergently prepared Newkome-type dendrons,<sup>333</sup> and studied their conductivity on cystamine derivatized gold electrodes. At low pH, the peripheral carboxylic acid units of **188** were protonated, enabling the ferrocene units to freely interact with the electrodes, but at neutral pH, the carboxylates of **189** would bind to the ammonium surface of the electrode, insulating the ferrocene unit (Figure 18).

### 8. Other Core Functionalities

Other functional core moieties include: stable TEMPO-based radicals for controlled radical polymerization,<sup>342</sup> crown ethers,<sup>343,344</sup> hexacyclenes,<sup>170</sup> poly-(quarternary ammonium) cations,<sup>345</sup> ethylene thioates,<sup>346,347</sup> calixarenes,<sup>348–352</sup> cyclodextrins,<sup>178</sup> inorganic clusters,<sup>93–95,340,353,354</sup> dichalcogenides,<sup>355</sup> and silsesquioxanes.<sup>356</sup>

## B. Linear–Dendritic Copolymers

Because linear and dendritic polymers have very different physical properties and intermolecular interactions, copolymers of these two macromolecular architectures are expected to exhibit interesting behavior. Gitsov et al. first synthesized these polymeric hybrids by reacting one or both hydroxyl



**Figure 19.**

termini of poly(ethylene glycol) (PEG) chains with dendritic bromides.<sup>357,358</sup> Subsequent studies of PEG with one and two terminal dendrons, as well as a four armed-star PEG with four dendritic end groups, **190**,<sup>359,360</sup> revealed that these materials change conformation depending on their interactions with solvent (Figure 19). <sup>1</sup>H NMR verified that in nonpolar solvents the linear PEG chains collapse, enabling the nonpolar dendritic blocks to shield them from energetically unfavorable interactions with solvent. In polar solvents, the system minimizes its free energy by “inverting” so that the collapsed nonpolar dendrons are shielded from solvent allowing the surrounding PEG chains to form the interface between the molecule and the solvent.<sup>359,361,362</sup> In addition, these amphiphilic materials exhibited the ability to solubilize polyaromatic compounds, including fullerenes, without a critical micelle concentration (CMC).<sup>363</sup> Amphiphilic linear–dendritic block copolymers can also be utilized to modify surface properties. When used with a cellulose substrate or even a more hydrophobic poly(ethylene terephthalate) film, the PEG–poly(benzyl ether) dendron copolymers self-assemble at the surface, increasing its hydrophilicity.<sup>364</sup>

Linear–dendritic copolymers have also been synthesized by capping a “living” polystyrene dianion

with two poly(benzyl ether) benzyl bromides,<sup>365</sup> by atom transfer radical polymerization (ATRP) of styrene initiated by a dendritic benzyl bromide,<sup>366,367</sup> by a nitroxide mediated “living” radical polymerization,<sup>367,368</sup> and by ring opening polymerization of lactones with a dendritic alcohol.<sup>369,370</sup>

### C. Dendronized Linear Polymers

Dendronized, or dendritic-grafted linear polymers, are linear polymers that bear pendant dendrons along the repeat units. Although there have been a few reports of divergently prepared dendronized materials,<sup>138,371,372</sup> the majority of the research in this field has focused on the convergent approach. Recently, the convergent synthesis of these materials has been optimized, and their preparation has been reviewed extensively elsewhere.<sup>373–375</sup> The salient examples are, however, briefly mentioned below.

#### 1. Macromonomer Approach

The “macromonomer approach” refers to the polymerization of a monomer that is functionalized with a dendron. The first attempts to make these compounds via the convergent approach were reported by Hawker and Fréchet and utilized a fourth genera-

tion poly(benzyl ether) dendron having a styrene<sup>376</sup> or methacrylate<sup>362</sup> focal point functionality. Attempts to homopolymerize these materials led to the formation of oligomers in very low yields,<sup>362</sup> but these dendrons could be successfully copolymerized with styrene.<sup>376</sup>

In the last six years, a number of groups, most notably those of Schlüter and Percec, have developed the synthesis of dendritic grafted materials by utilizing a wide variety of polymerization techniques including: radical polymerization of methacrylates,<sup>84,377–382</sup> Suzuki polycondensation,<sup>383–385</sup> rhodium-catalyzed insertion,<sup>386</sup> ring-opening metathesis,<sup>387–389</sup> polyurethane condensation,<sup>390,391</sup> Heck coupling,<sup>392</sup> oxidative Hay coupling,<sup>393</sup> polyamide condensation,<sup>394,395</sup> polyimide condensation,<sup>395</sup> palladium-catalyzed polycondensation of poly(aryl alkynes),<sup>328</sup> Stille coupling of poly(thiophene),<sup>152</sup> and radical polymerization of styrenes.<sup>396–398</sup>

Because the steric bulk of the monomer shields the reactive functionality, higher generation macromonomers tend to produce materials with a low degree of polymerization, and only moderately controlled polydispersity. Examples with average degrees of polymerization above 100 repeat units usually involve small first or second generation dendrons.<sup>112,386,399,400</sup> Recently fourth generation dendrons have been incorporated into dendronized linear polymers, such as **192**, using a Suzuki polycondensation of macromonomer **191**, (Scheme 25), but with average degrees of polymerization near 10 and an average PDI of about 2.<sup>401,402</sup>

Scheme 25

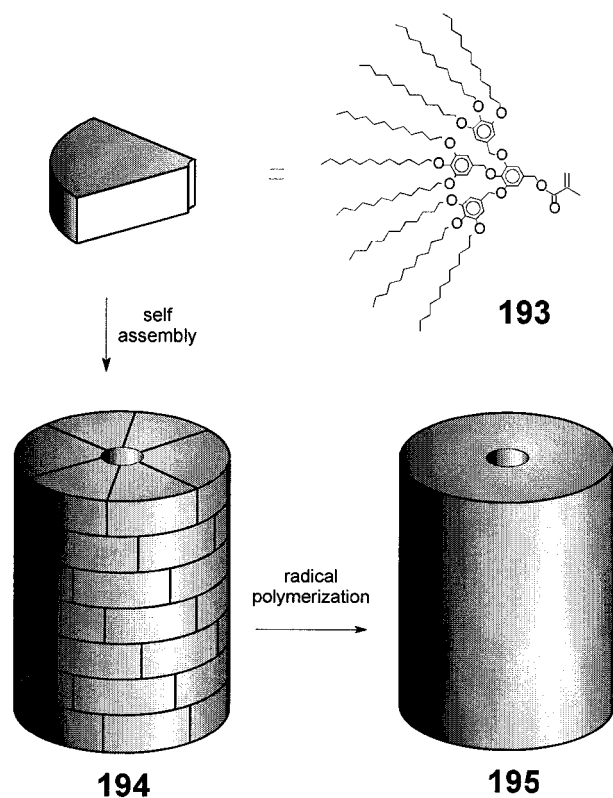
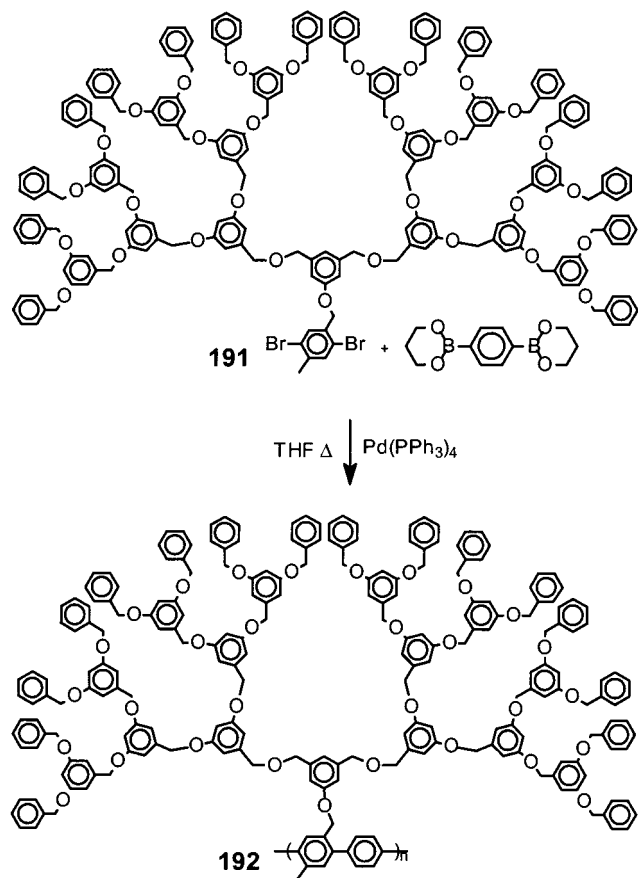


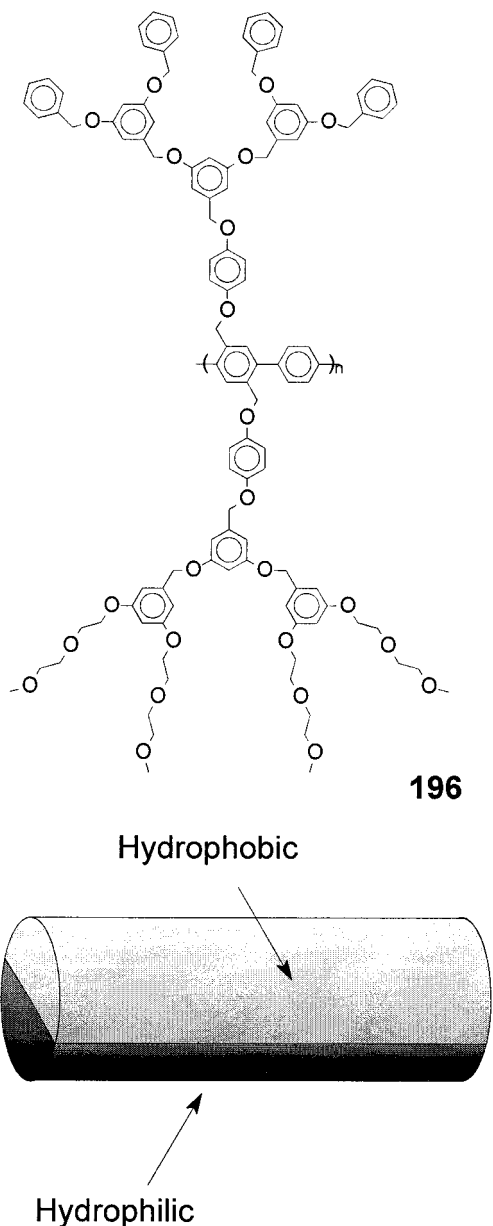
Figure 20.

Investigation with scanning force microscopy (SFM)<sup>385</sup> and small angle neutron scattering (SANS)<sup>397</sup> reveal that dendronized linear polymers exhibit a cylindrical conformation with a well-defined diameter, close to the predictions of molecular dynamics studies.<sup>403</sup> Schlüter's polymers exhibit a unique degree of structural control: as the degree of polymerization increases, the conformation of the polymers changes from a spherical to a tubular shape.<sup>403</sup>

Percec and co-workers developed a unique approach toward dendronized polymers,<sup>343,404</sup> making use of the tendencies of tapered dendrons with lipophilic chain ends **193** to self-assemble into columnar aggregates **194**. By incorporating styrene or methacrylate functionalities at the focal point (Figure 20), these dendritic macromonomers could be polymerized<sup>405</sup> after forming tubular aggregates.<sup>84,112,406–408</sup> Because of the proximity of the reactive monomer units in the shaft of the columnar aggregate, this approach exhibited an enhanced rate of polymerization.<sup>407</sup> During subsequent SFM studies, it was determined that as the size of the dendritic side chain increases, the steric bulk forces the molecule to adopt a more extended, rigidity conformation.<sup>408,409</sup>

Dendronized amphiphilic polymers have been synthesized with lengthwise segregation of the hydrophobic and hydrophilic domains (Figure 21). Bo et al. prepared these materials by polymerization of monomers that carried two domains of contrasting polarity,<sup>410,411</sup> affording polymers, such as **196**, capable of forming monolayers at the air/water interface.

In addition, luminescent linear backbones have been encapsulated in dendritic shells through this technique,<sup>152,328</sup> while the increased solubility im-



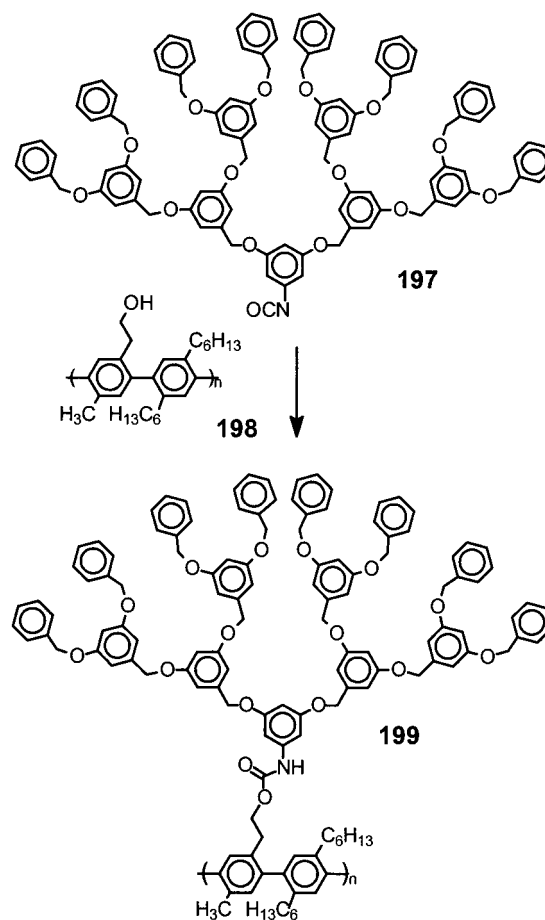
**Figure 21.**

parted by the dendrons has enabled the synthesis of elongated polymer chains.<sup>152</sup> Sato et al. reported poly(phenylene ethynylene) cores encapsulated with Fréchet-type dendrons that exhibited enhanced luminescence from both dendritic antenna effects and reduced intermolecular quenching through steric encapsulation.<sup>328</sup> Bao et al. also demonstrated that the encapsulation of poly(phenylenevinylene) cores with tris-branched poly(aryl ether) dendrons prevents the type of intermolecular  $\pi$ - $\pi$  stacking that frequently occurs with smaller side chains.<sup>392</sup>

## 2. "Coupling to" Approach

An alternative approach developed by Schlüter and co-workers involves the attachment of convergently prepared dendrons onto a preformed, functional linear polymer. This was first attempted by the Williamson ether couplings between dendritic bromides and pendant hydroxyl groups on poly([1.1.1]-propellane)<sup>412</sup> and poly(*p*-phenylene).<sup>413</sup> Nearly quan-

**Scheme 26**



titative coverage was obtained using the first and second generation Fréchet-type dendrons, while the more sterically demanding third generation dendron still achieved an impressive 70% coverage. A more efficient procedure (Scheme 26) involving the coupling of a third generation isocyanate functionalized dendron, **197**, with the pendant hydroxyl groups of the poly(*p*-phenylene) polymer **198**, led to a very high 92% coverage.<sup>384</sup>

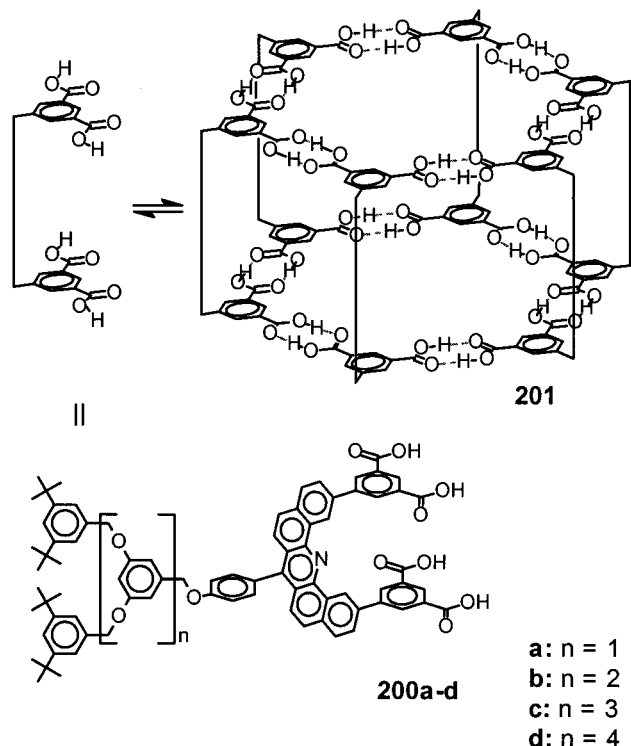
Hawker et al. recently reported the synthesis of a low polydispersity, partly dendronized polymer that carried a statistical distribution of dendrons on one-fifth of the repeat units.<sup>414</sup> A random copolymer containing 80% styrene and 20% of a styrenic monomer (*N*-oxysuccinimide 4-vinylbenzoate) bearing the activated ester was produced with polydispersities below 1.2 using the living free radical approach. Because of the relatively large statistical spacing between the activated esters, amine functionalized Fréchet-type dendrons could be coupled with a high degree of incorporation. For the first three generations, the coupling reaction appeared to be quantitative, but in the fourth and fifth generation materials, a small percentage of the activated ester remained unreacted.<sup>414</sup>

The two convergent approaches toward dendronized polymers offer complementary control over structural parameters. The macromonomer route ensures well-defined connectivity between the dendron and the polymer, but affords polymers with broad dispersity and generally low degrees of polymerization. In the

"coupling to" approach, on the other hand, the initial linear polymer may be prepared with a well-defined length and polydispersity, but the attachment of dendrons is prone to incomplete reaction.

#### D. Self-Assembly of Dendritic Cores

Self-assembled macromolecular structures are of particular interest because of their ability to reorganize in response to changes in their environment (concentration, solvent, pH, etc.)<sup>415,416</sup> Zimmerman and co-workers<sup>417,418</sup> first demonstrated the hydrogen-bond mediated self-assembly of dendritic cores (Figure 22) in 1996. The rigid bis(isophthalic acid)



**Figure 22.**

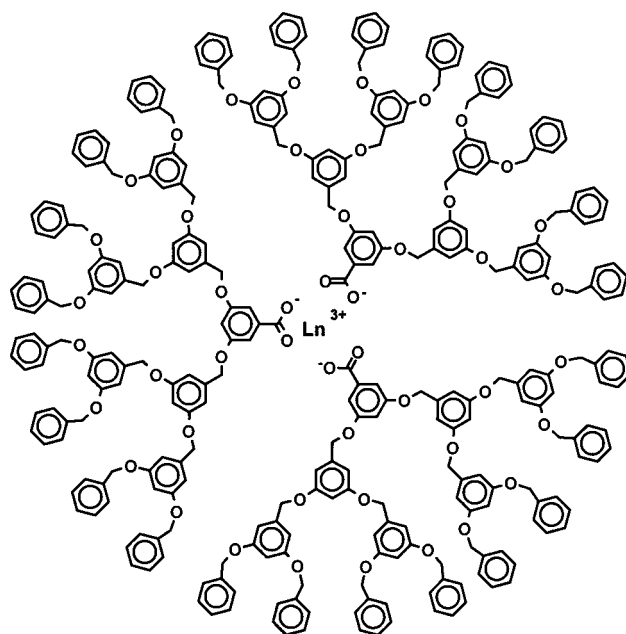
component **200** was designed to form a hexameric aggregate **201**. A number of Fréchet-type dendrons of different generations were attached to **200** to elucidate the aggregation behavior of the resulting compounds. Size exclusion chromatography studies revealed that the nature of aggregation was very dependent upon the size of the pendant dendrons, as the second through fourth generation compounds, **200b–d**, formed strongly associated hexamers, regardless of concentration, whereas the aggregation behavior of the first generation dendrimer, **190a**, appeared very sensitive to concentration. This approach has since been used to assemble dendritic hexamers,<sup>419</sup> trimers, and dimers<sup>420</sup> of hydrogen-bonded donor and acceptor moieties.

Shinkai and co-workers reported a spherical self-assembled system based upon a focal maltonolactone moiety.<sup>421</sup> The strong hydrogen bonding between focal saccharide moieties led to aggregation when placed in nonpolar solvents. Unlike previous examples, the number of dendrons aggregating was not due to a pre-designed core geometry or charge ratio and therefore was primarily influenced by the size of the

dendron attached. Dynamic light scattering data suggested that the sterically bulky high generation Fréchet-type dendrons produced small aggregates, while the smaller dendrons led to larger aggregates.<sup>422</sup>

Columnar aggregation was investigated by Aida and co-workers, who attached Fréchet-type dendrons to a *tert*-butoxycarbonyl-(L)-tyrosinyl-(L)-alanine focal group.<sup>423</sup> In moderately nonpolar organic solvents, hydrogen-bonding interactions between the peptide segments led to the formation of a gel for dendrons of the second and third generations. Cross-polarized microscopy and scanning electron microscopy revealed the presence of fibril bundles, on the order of 1  $\mu\text{m}$ . Such ordering was not seen in the parent peptide or the first generation dendron. The gel could be rapidly dissolved by addition of a small percentage of DMSO into the solvent.

Dendritic self-assembly has also been reported in a number of inorganic systems.<sup>45,92,327,329,353,424–426</sup> Seminal studies in this area were carried out by Balzani and co-workers utilizing the self-assembly of polypyridine-type ligands around transition metals.<sup>427–430</sup> These materials are considered beyond the scope of this review, as their preparation does not follow a strictly convergent methodology. However, more recently, convergent self-assembly utilizing polypyridine ligands around a transition metal core has been reported by the Chow,<sup>92</sup> Balzani, De Cola, and Vögtle groups.<sup>329</sup> Plevoets et al. designed a dendrimer consisting of three Fréchet-type dendrons bearing focal bipyridine units arranged around a ruthenium core.<sup>329,330</sup> In aerated solution the ruthenium core with higher generation dendrons exhibited longer luminescence lifetime because the dendritic wedges protected the core from dioxygen quenching. The self-assembly of Fréchet-type dendrons bearing a focal carboxylate group (Figure 23) around a series of lanthanide metals, **202–204**, was



**202**, Ln = Er; **203**, Ln = Eu; **204**, Ln = Tb

**Figure 23.**

reported by Kawa and Fréchet.<sup>45,327</sup> The product exhibited a generation dependent increase in luminescence, suggesting the larger dendrimers can more effectively isolate their lanthanide cores from each other, reducing the rate of self-quenching.<sup>45</sup> Enomoto et al. noted a similar dendritic stabilizing effect with bis( $\mu$ -oxo-bridged)copper complexes.<sup>353</sup> Triazacyclononanes with Fréchet-type dendron substituents were first metalated with copper and then oxygenated to form dimers. The half-lives of these compounds toward oxidative degradation were increased from 24 s for the second generation dendrimer to nearly an hour for the third.

The ability to construct and optimize self-assembled structures requires versatile substrates such as dendrons whose steric bulk, polarity and shape can be easily modified. Unfortunately relatively few systems are capable of producing large self-assembled structures with sufficient cohesive strength to withstand significant environmental changes.

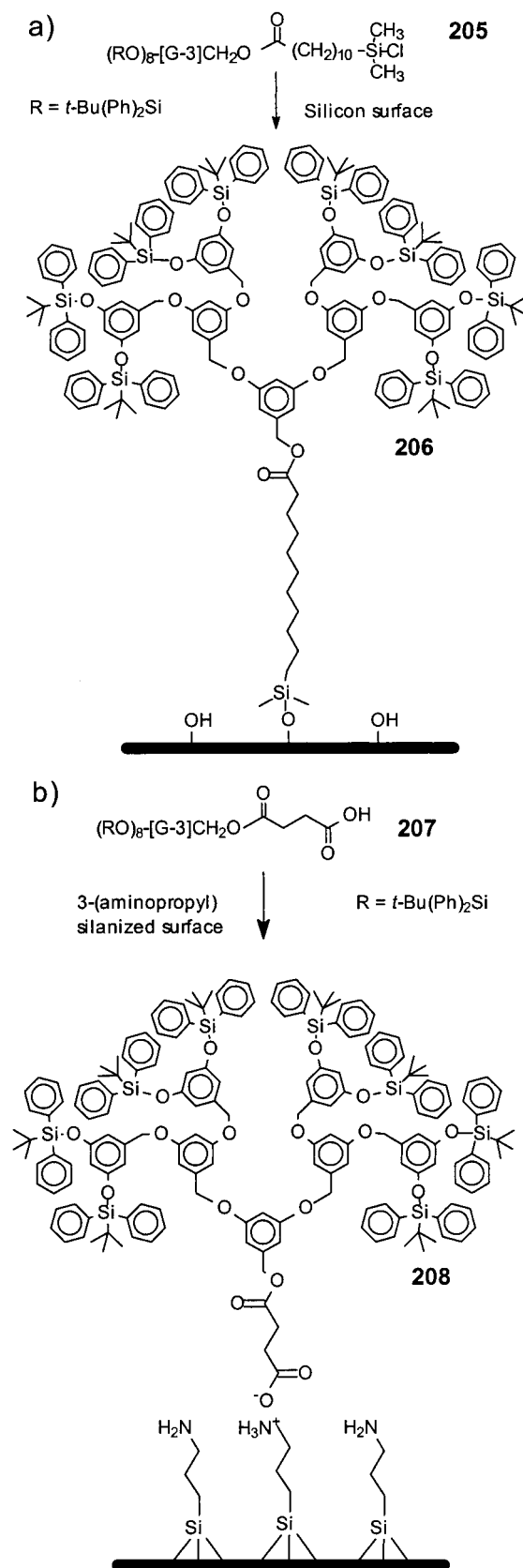
### E. Surface-Bound Dendrons

The control of surface chemistry has become increasingly important as numerous device and material properties are controlled by surfaces and interfaces. For example, surface patterning is the foundation of lithography, and its implications in fields such as microelectronics or microfluidics are profound.

The synthetic and functional versatility of dendrimers as well as their defined shape has made them attractive molecules for surface modification.<sup>431</sup> Gorman and co-workers first reported the attachment of dendrons to a solid surface. Using dendrons with a focal thiol substituent<sup>91</sup> they were able to assemble monolayers of first, second, or third generation dendrons on a gold surface.<sup>432</sup> Zhang and co-workers prepared similar monolayers of thiol substituted dendrons adsorbed onto silver and gold films and studied the modified surfaces in detail with scanning tunneling microscopy.<sup>433,434</sup> Light-harvesting dendritic antennas can also be self-assembled onto the surface of silicon wafers providing a synthetically less demanding approach toward constructing chromophore arrays for energy transfer applications.<sup>435</sup>

Recently, Tully et al. demonstrated that dendrons could be applied onto surfaces as single, uniform layers with potential for high-resolution nanolithography through molecular level addressing. Both covalent and ionic (Scheme 27) approaches were investigated for the attachment of poly(aryl ether) dendrons onto the surface of a silicon wafer. The covalent dendritic monolayers were attached via a silyl chloride functionalized linker, **205**, capable of reacting with the surface silanol groups of the wafer.<sup>436</sup> Ionically bound monolayers could also be prepared by treating an aminopropyl functionalized silicon surface with a dendron bearing a single carboxylic acid functionality at its focal point, **207**, while stronger surface attachment was achieved using dendrons bearing multiple carboxylate functionalities.<sup>437</sup> Both the covalently and the ionically bound dendritic monolayers could be patterned using scanning probe lithographic techniques, affording raised SiO<sub>2</sub> features in the patterned areas. The

**Scheme 27**



homogeneous thin dendrimer monolayer remaining in unpatterned areas of the wafer surface proved resistant to etching with aqueous HF, which removed the oxidized pattern and etched a positive tone trench into the underlying silicon. At present, this approach

to nanolithography is not limited by the properties of the dendritic materials but rather by the imaging tools available. Both the size of the tip, which far exceeds that of a dendrimer, and the very low throughput of the single-tip scanning probe instrument prevent this approach from realizing its ultimate single-molecule addressing potential.

#### IV. Modification of the Periphery

Modification of the dendritic periphery is of particular interest because this portion of the dendrimer acts as the primary interface with the external environment. As might be expected, the functionalities at the periphery dominate the solubility properties of the molecule as the generation of the dendrimer increases.<sup>35,40</sup> Although both NMR<sup>438</sup> and molecular dynamic<sup>439</sup> studies have suggested that the end groups of some dendritic systems are capable of "backfolding" toward the core, other studies clearly indicate that backfolding is not predominant in many dendritic systems.<sup>13,440</sup> Being related to free-energy that controls interactions between chain-ends, repeat unit, and general environment (solvent), backfolding can be controlled by changing the design of the dendrimer.<sup>13,440</sup> In fact, in a systematic comparison between analogous linear, hyperbranched, and dendritic polymers, Wooley et al. demonstrated that the chain ends of the poly(aryl ester) dendrimers were sufficiently accessible to be quantitatively modified, unlike the analogous functionalities of linear or hyperbranched structures.<sup>35</sup>

There are two possible approaches toward incorporation of functionality at the periphery: the attachment of the desired end group before initiating the dendritic synthesis, or modification of the existing peripheral groups after completion of the synthesis.

#### A. Introduction of End Groups Prior to Dendritic Growth

Because the convergent route begins with the attachment of the end groups to the monomer, initial incorporation of a functional end group involves only a few coupling reactions that can be easily driven to completion. However, these peripheral moieties must possess the appropriate stability and solubility to permit dendritic growth through the repetition of coupling and activation steps without side reaction or degradation of the end groups.

The first examples of convergent end group modification were carried out by initiating the poly(benzyl ether) synthesis with para-substituted benzyl bromide end groups.<sup>73,74</sup> A wide range of functional end groups proved compatible with the halogenation and Williamson coupling conditions required during iterative dendritic growth, including cyano,<sup>73,74,441,442</sup> bromo,<sup>74,443,444</sup> alkyl ester,<sup>41,442,445,446</sup> alkyl ether,<sup>43,110,447,448</sup> perfluoro alkyl ether,<sup>110,448–450</sup> and oligo(ethylene glycol) ether.<sup>46,451</sup> These simple variations enabled the solubility of the resulting dendrimers to be readily tuned. Fréchet-type dendrons have also been synthesized with end groups

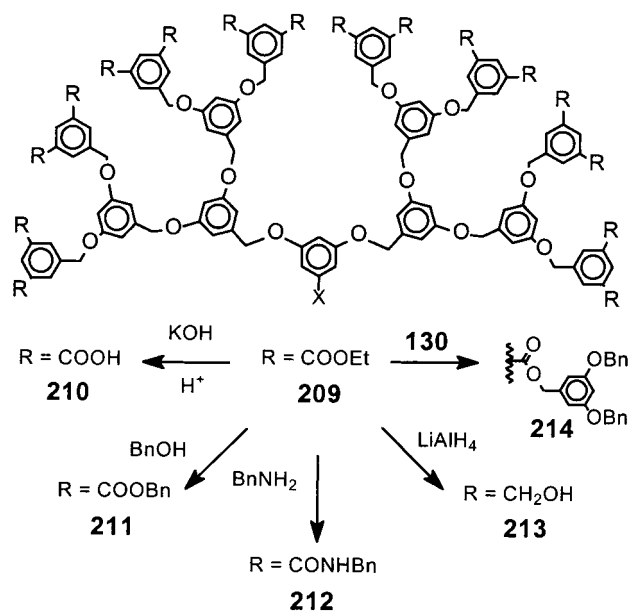
containing vinyl groups,<sup>308,452</sup> organoruthenium moieties,<sup>453–455</sup> ferrocenyl groups,<sup>456</sup> TADDOL catalytic sites,<sup>457</sup> concave pyridine units,<sup>458,459</sup> liquid crystalline end groups,<sup>240</sup> and chromophores.<sup>44,79–81,329,460,461</sup> Similar approaches have been employed to incorporate tri-arylamine,<sup>120</sup> oligo(ethylene glycol),<sup>462,463</sup> tetrathiafulvalene (TTF),<sup>464–466</sup> saccharide,<sup>467–469</sup> fullerene,<sup>426,470,471</sup> and ferrocene<sup>169,472</sup> moieties onto the periphery of other dendritic backbones.

#### B. Introduction of End Groups after Completion of Dendritic Growth

In the post modification route, the peripheral functionality is masked or remains unreactive during convergent growth, to be modified in a subsequent reaction. This approach allows the eventual incorporation of end groups that may be incompatible with the generation growth steps. However, these transformations suffer from the same complications as the divergent synthesis; in the case of larger dendrimers, the multiplicity of end group transformations requires the careful optimization of synthetic and purification techniques.

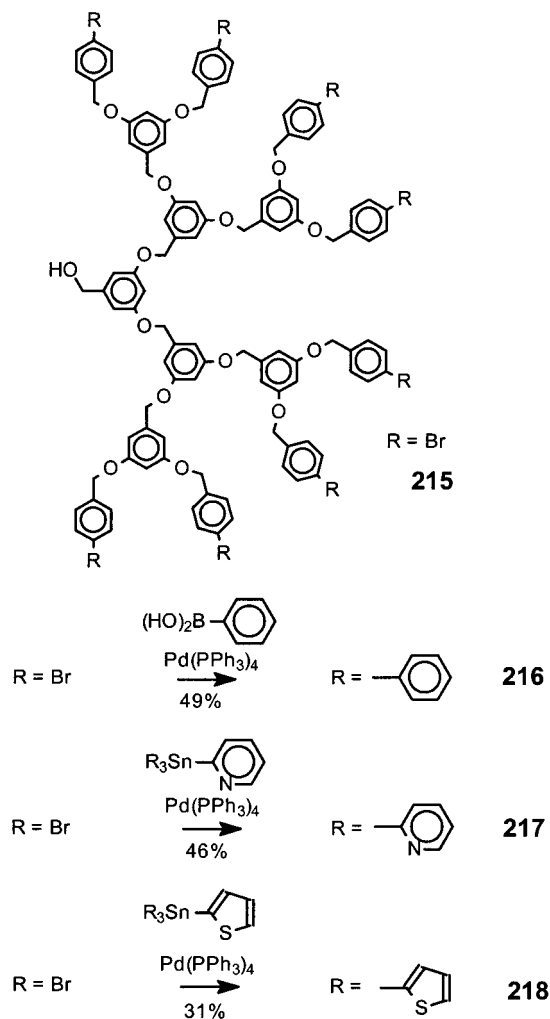
Numerous examples of postsynthetic modifications at the dendritic periphery have been explored. In early work, Hawker et al. investigated the hydrogenolysis and subsequent modification of benzyl-protected poly(aryl ester) dendrimers<sup>473</sup> and later the saponification of Fréchet-type dendrimers with *p*-methyl benzoate end groups to afford an anionic carboxylated periphery.<sup>41</sup> The isophthalate ester end groups proved to be especially versatile (Scheme 28)

Scheme 28



during the post modification of poly(benzyl ether) dendrimer **209**. Hydrolysis of the esters of **209** afforded poly-acid **210**,<sup>446</sup> while reduction produced the polyol **213**.<sup>366</sup> In addition, the isophthalate ester **209** could undergo transesterification or amidation reactions to yield **211** and **212**.<sup>446</sup> The efficiency of the transesterification reaction enabled the divergent

Scheme 29

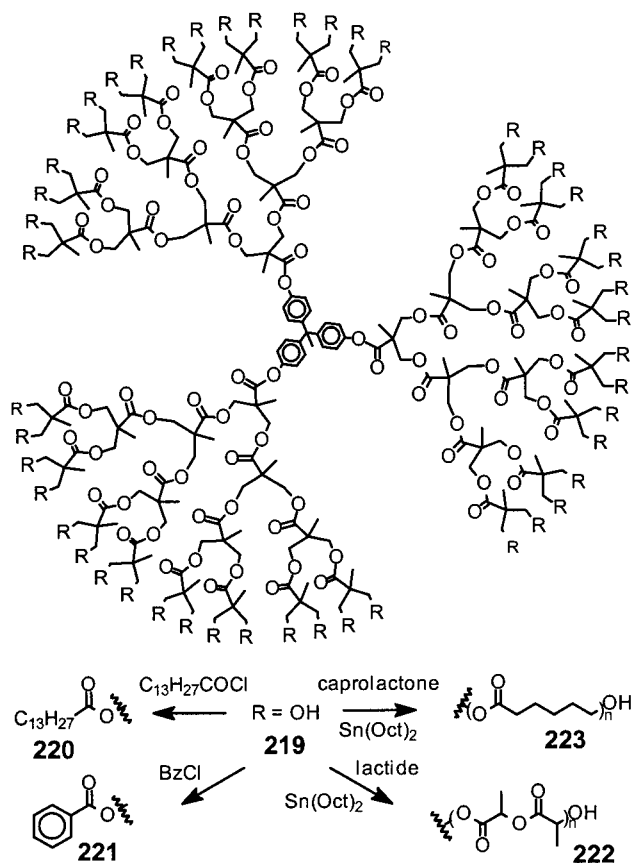


growth of an additional generation, **214**, by the attachment of first generation benzylic alcohols **130** to the periphery.

Groenendaal et al. have investigated the efficiency of palladium-catalyzed coupling reactions (Scheme 29) involving Fréchet-type dendrons with *p*-bromobenzyl end groups, **215**.<sup>444</sup> The yields for the Suzuki coupling of a phenyl group, **216**, and the Stille coupling of thienyl, **217**, and pyridinyl groups, **218**, remained consistently near 90% per coupling reaction. However, the multiplicity of end groups on the third generation dendron reduced the overall yield to below 50% demonstrating the importance of using highly efficient transformations during modification of the periphery. The poly(alkyl ether) dendrons reported by Grayson et al. could withstand a wide range of postsynthetic modification because of their chemically rugged backbone.<sup>40</sup> Quantitative hydrogenolysis of the benzyl ether end groups of **98** or hydrolysis of the ketal end groups of **99** yielded a poly-hydroxylated periphery that could be efficiently modified through a variety of high-yielding esterification or etherification reactions.

Because the double exponential growth approach requires orthogonal focal and peripheral functionalities, it is inherently suited for peripheral modification. Zanini and Roy reported the peripheral glycolation of poly(alkyl amide) dendrons by treating the

Scheme 30



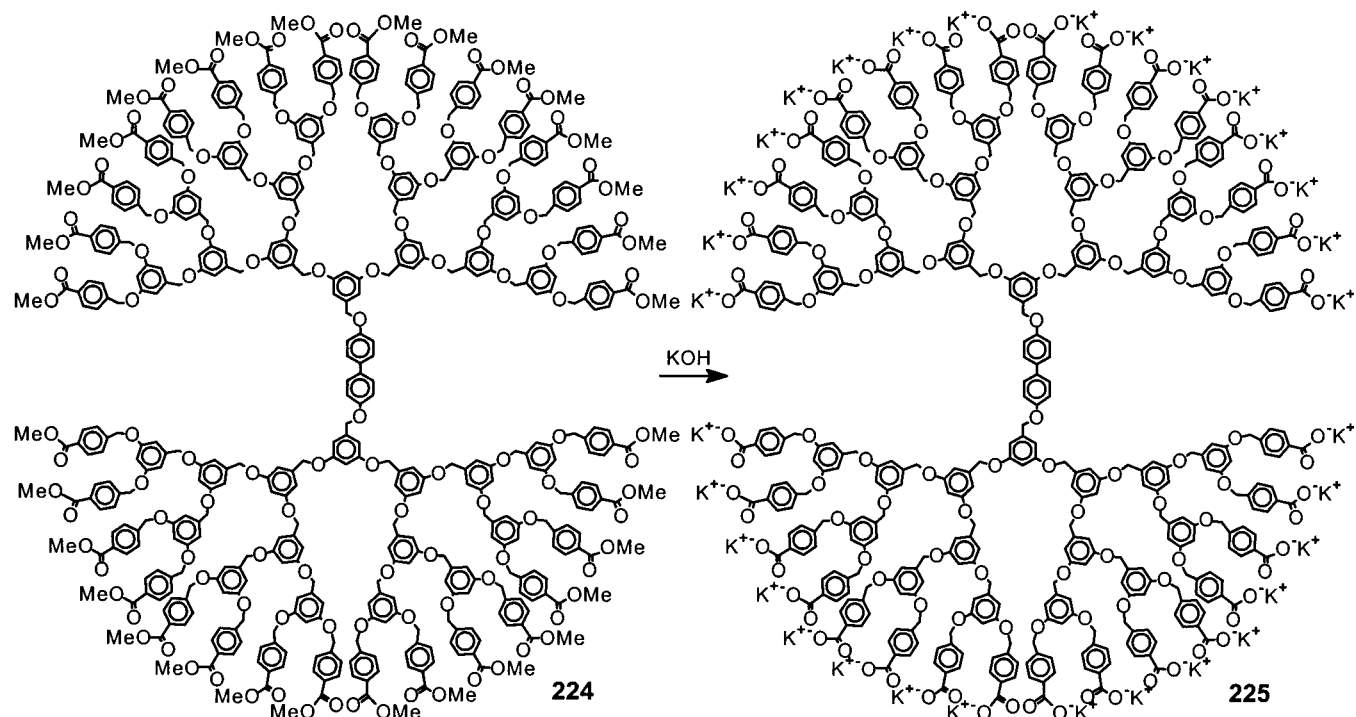
peripheral amine groups with chloroacetic anhydride and then coupling them to the desired sialic acid derivative.<sup>222</sup> Ihre et al. also demonstrated the facile peripheral functionalization (Scheme 30) of poly(alkyl ester) dendrimers prepared by both the double exponential growth and the single-stage convergent procedures. The poly-hydroxyl dendrimer **219** could be accessed by the hydrolysis of the acetonide protecting groups and esterified by reaction with the appropriate acid chloride<sup>221</sup> to afford a dendrimer with octanoate, palmitoate, **220**, benzoate, **221**, or even liquid crystalline peripheral units.<sup>474</sup> Hedrick and co-workers have also explored the assembly of star-polymer structures that incorporate both linear and dendritic polyester units into the polymeric architecture. Their investigation included the use of the hydroxyl-terminated dendrimers as initiators<sup>475–477</sup> for lactide, **222**, and caprolactone, **223**, ring opening polymerizations and the synthesis of dendrimers with a tertiary alkylbromide periphery for ATRP of methacrylate monomers,<sup>478</sup> as well as the incorporation of linear poly(ester) chains between dendritic branch points.<sup>479,480</sup> A similar approach was used by Hecht et al. to grow poly(caprolactone) from the multiple sites of a porphyrin core to insulate it from neighboring species.<sup>481,482</sup>

### C. Applications of Peripheral Modification

The simplest application of peripheral alteration is the modification of a dendrimer's solubility. For example, a number of groups have reported the use of terminal groups such as carboxylates<sup>41,265</sup> or oligo-



## Scheme 31



ethylene glycol chains<sup>261,262,303,334,483</sup> to impart water solubility on the corresponding dendrimers. Hawker et al. demonstrated the first convergent synthesis of dendritic unimolecular micelles,<sup>41</sup> using molecules with a spherical amphiphilic architecture (Scheme 31) analogous to that reported by Newkome in divergent systems.<sup>57</sup> Saponification of ester-terminated Fréchet-type dendrimer **224**, afforded a dendrimer with a polycarboxylate periphery and pH-dependent solubility.<sup>41</sup> The polycarboxylate **225** also exhibited micellelike solubilization of polycyclic aromatic hosts (e.g., pyrene). These structures have been dubbed “unimolecular micelles” because, unlike traditional micelles, their covalently bound structure is not subject to disaggregation below a certain concentration threshold. Piotti et al. later utilized these micellar properties to design efficient macromolecular nanoreactors **226** and **227** (Scheme 32), that used the polarity difference between the dendrimers’ interior and exterior to drive the reactants toward the internal catalytic sites while simultaneously expelling the products to prevent catalyst inhibition.<sup>43</sup>

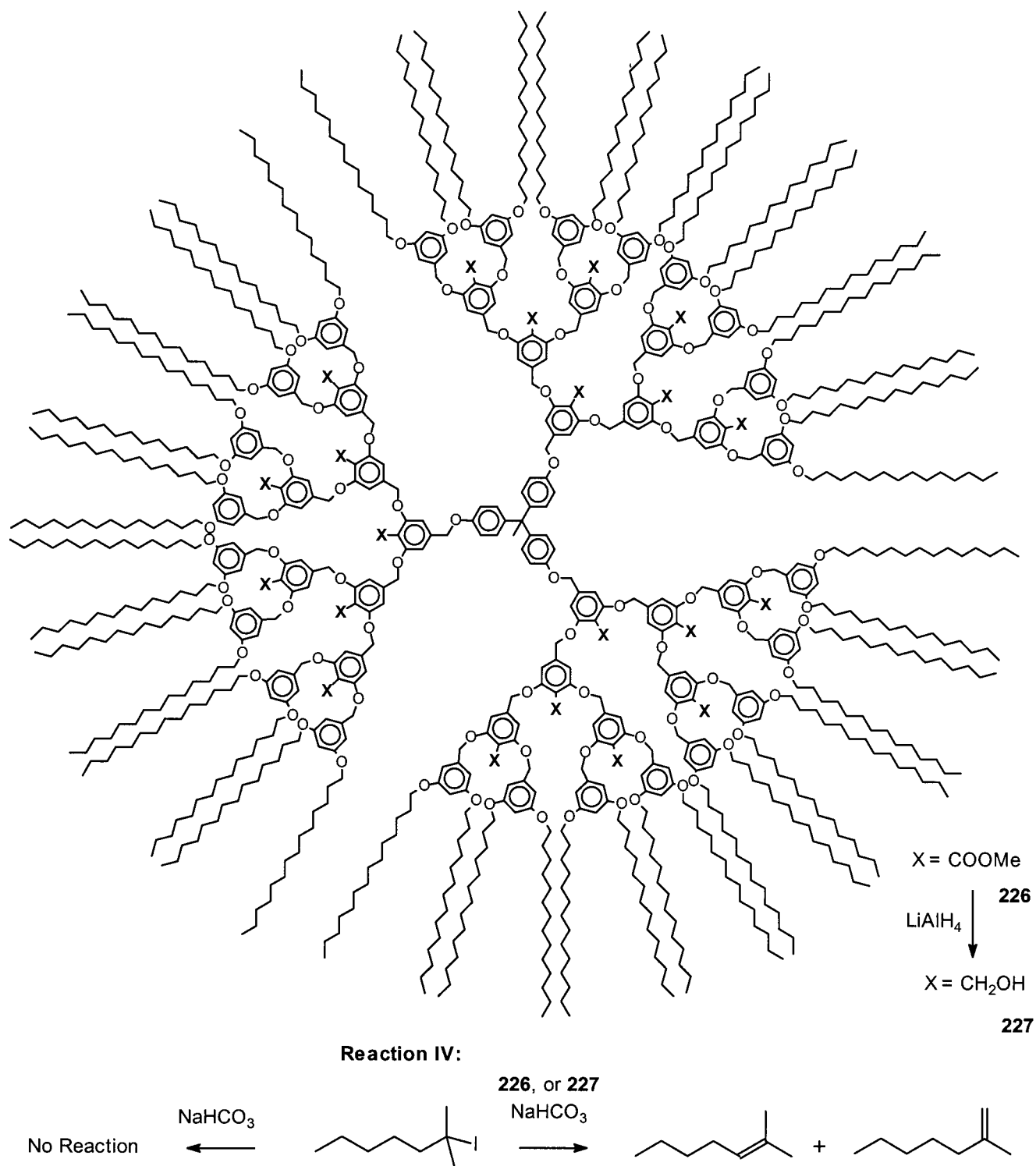
Because convergent dendrons exhibit a multiplicity of peripheral groups together with a single reactive focal point, providing for easy orthogonal functionalization and control of solubility, they represent an ideal scaffold for drug delivery applications.<sup>53</sup> Fréchet and co-workers recently investigated the incorporation of drug moieties by both encapsulation and covalent attachment. Liu et al. designed a water-soluble “unimolecular micelle” consisting of a dendritic polyether structure fitted with peripheral oligo(ethylene glycol) chains. The macromolecule could encapsulate 11 wt % of the model drug indomethacin and exhibited a slow sustained release of this drug when placed in an aqueous environ-

ment.<sup>46</sup> Kono et al. studied the concepts of covalent drug loading and targeting by attaching folate or methotrexate residues to Fréchet-type dendrons via diacylhydrazine linkages.<sup>484</sup> The water solubility of these materials could be improved by attachment of a poly(ethylene glycol) chain to the focal point of the dendron.

The ability to drastically alter dendritic solubility by modification of the end groups also makes convergent dendrons attractive materials for nanolithography. As photolithographic resolution approaches the size regime of linear polymers, the compact, “pixellike,” globular conformation of the dendrimer is expected to provide better resolution than longer linear polymer chains. Tully et al. have reported the preparation of *tert*-butyloxycarbonyloxy (*t*-BOC) protected dendrimers **228**, spun cast onto silicon wafers for use as dendritic photoresists (Scheme 33).<sup>485</sup> Imaging was achieved by activation of a photoacid generator where the polymeric film was exposed to e-beam lithography, leading to removal of the *t*-BOC protecting groups and producing the base-soluble poly-phenol dendrimer **229**. Developing with aqueous base removed the exposed regions of the resist, while development with organic solvents remove the unexposed polymer, enabling access to complementary images with feature sizes well below 100 nm.

Dendrimers can also serve as a scaffold for energy transfer between chromophores,<sup>44</sup> a useful step toward the goal of efficient light-harvesting and artificial photosynthesis. Although a number of studies have demonstrated the ability of dendritic repeat units to act as an antenna,<sup>119,257,428,429,486,487</sup> funneling energy toward the core, attachment of dye groups to the periphery of an “insulating” dendritic structure (Figure 24) has enabled Fréchet and co-workers to carry out a more systematic study of the energy

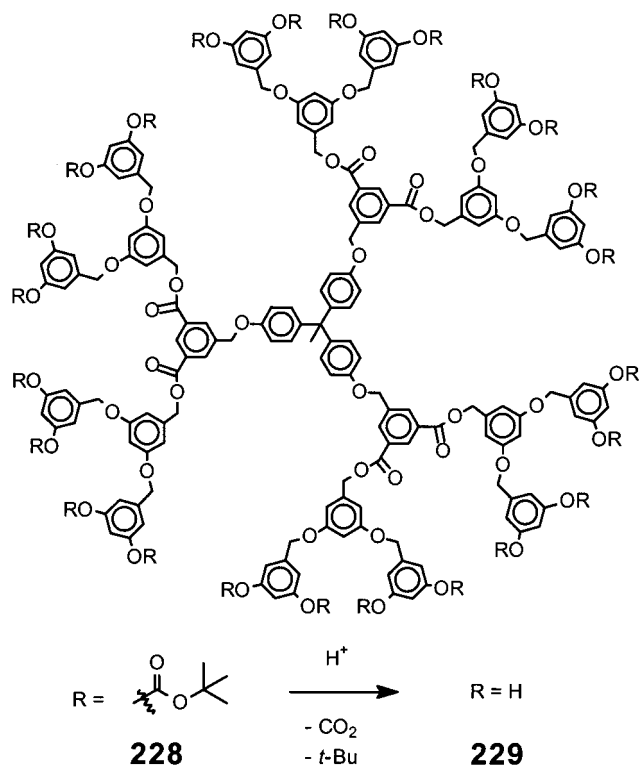
## Scheme 32



transfer in these dendritic systems.<sup>80,488,489</sup> The well-defined dendrimer architecture enables a multiplicity of donating chromophores at the periphery and an acceptor chromophore at the focal point to be fixed within the distance range required for efficient Förster energy transfer. In addition, the irradiation of multiple donating chromophores around a single acceptor amplifies the emission of the focal acceptor due to the highly efficient energy transfer that occurs within these molecules.<sup>488</sup> A variety of systems with different chromophores, including coumarin dyes **230**

and oligothiophenes have been investigated,<sup>81</sup> verifying the generality of this approach. In addition, Christoffels et al. have investigated the energy transfer between dye-labeled dendrons assembled onto a silicon substrate, and verified that the energy transfer and amplification phenomena could also be observed within monolayers.<sup>435</sup> Pioneering work by Moore and co-workers on a different approach utilizing a layered convergent structure<sup>119,486</sup> rather than end-functionalized dendrons is discussed in a later section.

## Scheme 33



Dendritic LEDs (light-emitting diodes) can also be prepared by attaching hole transporting triaryl-amines to the periphery of dendrimers bearing fluorescent cores.<sup>120,145–147,461</sup> Moore and co-workers<sup>120</sup>

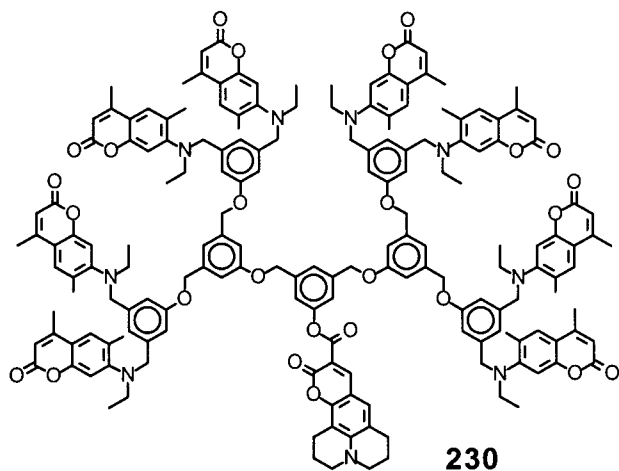


Figure 24.

first reported the design and synthesis of a dendritic LED (Figure 25) in 1996. The incorporation of triarylamine groups on the periphery **231** improved the hole injection process, lowering the onset voltage required to operate the devices. In separate work, Freeman et al. showed that if the dendrimers are designed to provide sufficient site isolation of their core, intermolecular energy transfer is inhibited enabling simultaneous emission from different core chromophores.<sup>461,490</sup> As a result, the color of emission from the device may be tuned by simply adjusting the ratio between different “site-isolated” dendritic chromophores.

The nature of dendritic self-assembly processes, and therefore the resulting overall architecture, can

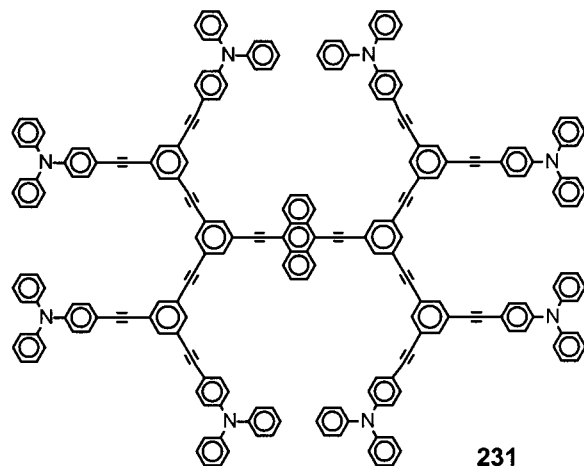


Figure 25.

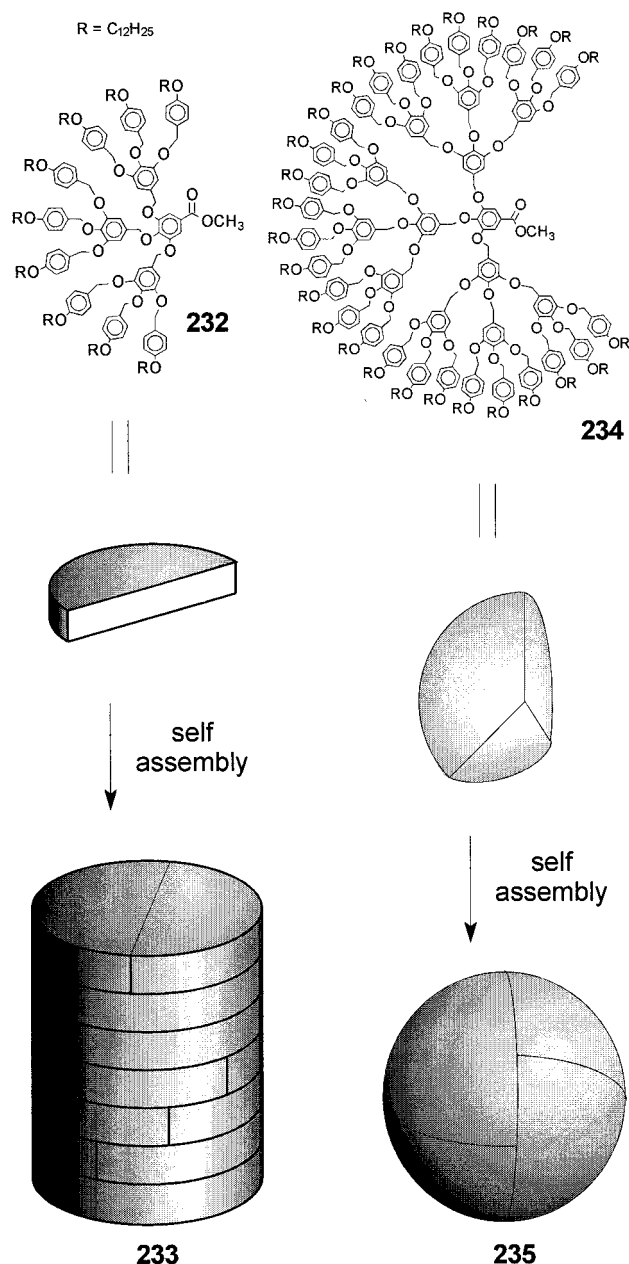


Figure 26.

also be tuned by modification of the periphery. After investigating the tubular self-assembly of first gen-

eration dendrons bearing lipophilic chains at the periphery,<sup>343,404,491</sup> Percec and co-workers systematically studied the effect of generation number on the self-assembly of dendrons.<sup>82,83,85,110–113,492,493</sup> X-ray diffraction of a representative system<sup>111</sup> (Figure 26) showed that the first and second generation dendrons exhibited disklike shapes **232** that self-assembled into cylindrical columns **233** while the third generation dendrons resembled a fragment of a sphere, **234**, and formed spherical aggregates **235**, within a cubic lattice.

The periphery of convergently synthesized dendrimers has also been modified to allow the assembly of monolayers,<sup>494</sup> to support dendritic catalysts,<sup>495</sup> to control the intermolecular assembly of porphyrin dendrimers,<sup>246</sup> to probe the effect of photoisomerization,<sup>319</sup> and to enable cross-linking of the periphery followed by removal of the core.<sup>496</sup> These studies in peripheral modification highlight the versatility of the convergent synthesis. In particular, the ability to selectively modify the periphery and focal functionalities of a dendron enables the design of complex macromolecules that involve the interaction between multiple functional components.

## V. Modification of Repeat Unit

The convergent approach also permits the incorporation of functional repeat units. Because the repeat units comprise the majority of the dendritic structure, they represent an ideal location for multiple functional moieties. In addition to the numerous examples of conjugated dendrimers previously discussed,<sup>115,116,119–122,124–130,132–134,140–148,497</sup> the convergent approach has been demonstrated as a viable route toward the preparation of dendrimers with a range of repeat units including: fullerene,<sup>498,499</sup> quaternary ammonium salt,<sup>177</sup> pyridine,<sup>382,500–502</sup> TTF,<sup>503–506</sup> triarylamine,<sup>171–173,507,508</sup> carbazole,<sup>509,510</sup> azobenzene,<sup>351,511–513</sup> liquid crystalline,<sup>514–516</sup> and chiral repeat units.<sup>96–108,199,202</sup>

### A. Incorporating Monomer with Functionality

Because of the sheer multiplicity of repeat units, the incorporation of functional moieties into the monomer can have a profound effect on macromolecular properties. For example, Nagasaki et al. reported the synthesis of photoresponsive dendrimers containing an azobenzene functionality in each repeat unit.<sup>351</sup> Exposure to UV light induced an isomerization of the azobenzene units, leading to a significant molecular contraction observed by both dynamic light scattering and size exclusion chromatography.<sup>350</sup> In the poly(TTF) dendrimers reported by Christensen et al., each of the 21 TTF units is capable of two single electron oxidations. All of the repeat units in the second generation dendrimer can be oxidized concurrently, affording a macromolecule exhibiting a 42<sup>+</sup> oxidation state.<sup>506</sup>

Modification of the repeat units can also provide conformational control in dendritic structures. Huang et al. reported the synthesis of a family of dendrons,

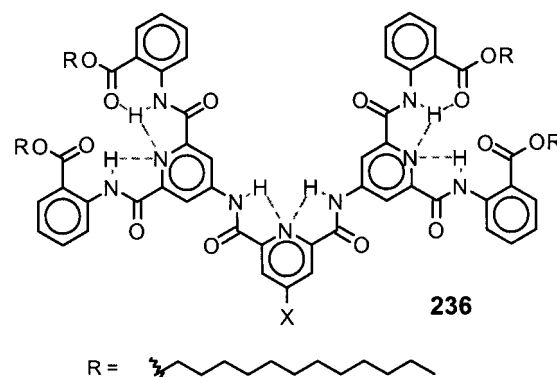


Figure 27.

**236**, that incorporate hydrogen bond donor and acceptor moieties within the repeat units (Figure 27) to rigidify dendritic structure.<sup>190,517</sup> <sup>1</sup>H NMR and IR characterization suggest that each of the expected hydrogen bonding interactions occurs in solution, affording a more conformationally rigid structure than the analogous Fréchet-type dendron. Pursuing the goal of controlled encapsulation and release of guest molecules, Tominaga et al. reported the synthesis of a dendron, **237**, with cross-linkable (Figure 28) uracil repeat units.<sup>518</sup> Upon irradiation at 280 nm,

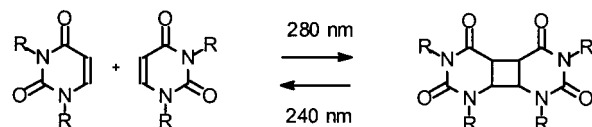
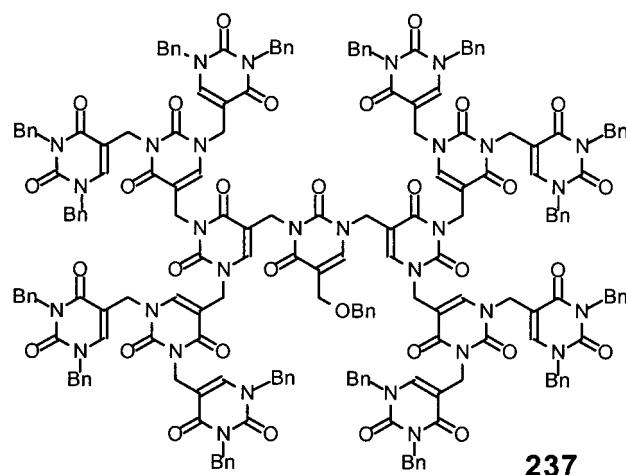


Figure 28.

the conformation could be “locked” through the incorporation of intramolecular cross-linking. The cyclization reaction could be readily reversed by irradiation at 240 nm reverting back to an “open” dendritic configuration. Recently, Thayumanavan and co-workers have synthesized dendrons based on an amphiphilic analogue of the Fréchet-type repeat unit that are expected to undergo drastic conformational transformations in response to changes in solvent polarity.<sup>519</sup>

Dendrimers containing chiral repeat units have also been investigated in the context of chiral recognition. While the coupling reaction between a tri-

functional chiral core and a dendron composed entirely of *S* repeat units, **35**, could be driven to completion, the coupling with the corresponding *R* enantiomer, **36**, could not proceed past the second coupling.<sup>107</sup>

## B. Postsynthetic Modification of Repeat Unit Functionality

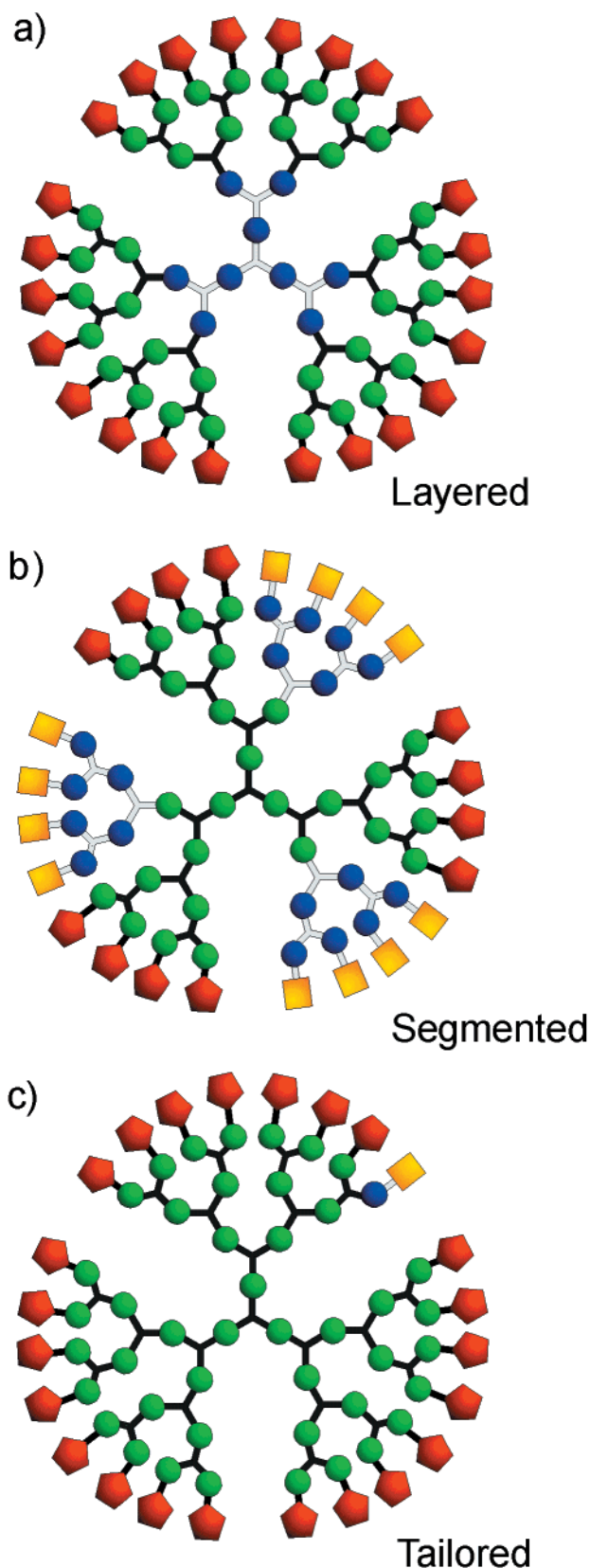
Postsynthetic transformations of dendritic repeat units have been largely ignored until recently. In early work, Lochmann et al. had investigated the deprotonation, metalation, and functionalization of generation four Fréchet-type dendrons with super-bases. The majority of the benzylic sites, as well as some aromatic sites, could be deprotonated and up to 34 atoms of potassium introduced without degradation of the dendrimer framework. Subsequent quenching and modification was carried out using D<sub>2</sub>O, carbon dioxide, or octadecylbromide.<sup>520</sup> At about the same time, Rajca et al. synthesized a dendritic polyradical by lithium metalation and iodine oxidation of a triarylmethyl alcohol repeat unit.<sup>176</sup> Matsuda et al. also reported the synthesis of a dendritic polycarbene from a poly(aryl ketone).<sup>174</sup> The ketone repeat unit was converted to the corresponding hydrazone, oxidized to the poly-azo compound, and then photolyzed to produce a polycarbene dendrimer. Although the later two dendrimers were prepared to study their magnetic properties, both proved to be unstable, likely due to flexibility in their structure that enabled cross-linking.

Recently Piotti et al. reported the modification of repeat units as a means of tuning the interior polarity of a dendrimer catalyst (Scheme 32). The relatively polar dendritic interior of **226** helped to catalyze the formation of the ionic intermediate in a unimolecular elimination reaction. (reaction IV) The product outflow is driven by a "free energy pump," resulting from the inverse micellar character of the dendrimer. Due to solvation effects, the relatively polar halide substrate is driven toward the dendritic interior from the nonpolar solvent pool, while the alkene product is readily expelled, giving rise to high turnover. If the ester group on the 4-position of each Fréchet-type repeat units of dendrimer **226** is reduced<sup>43</sup> to the alcohol **227**, the increased internal polarity leads to an increase in both conversion and turnover for the corresponding elimination reaction.

Since this study, the addition of repeat units capable of a postsynthetic transformation have been investigated. Bo et al. investigated the incorporation of an aryl bromide functionality on the Fréchet-type repeat unit, which could be modified by a Suzuki cross-coupling with an aryl boronic acid.<sup>521</sup> Freeman et al. explored the attachment of an allyl ether functionality on the same repeat unit,<sup>522</sup> while Schultz et al. incorporated an aromatic spacer with two allyl groups to enable internal cross-linking via olefin metathesis.<sup>523</sup>

## VI. Dendritic Copolymers

One of the primary advantages of the convergent synthesis is its unparalleled synthetic control that



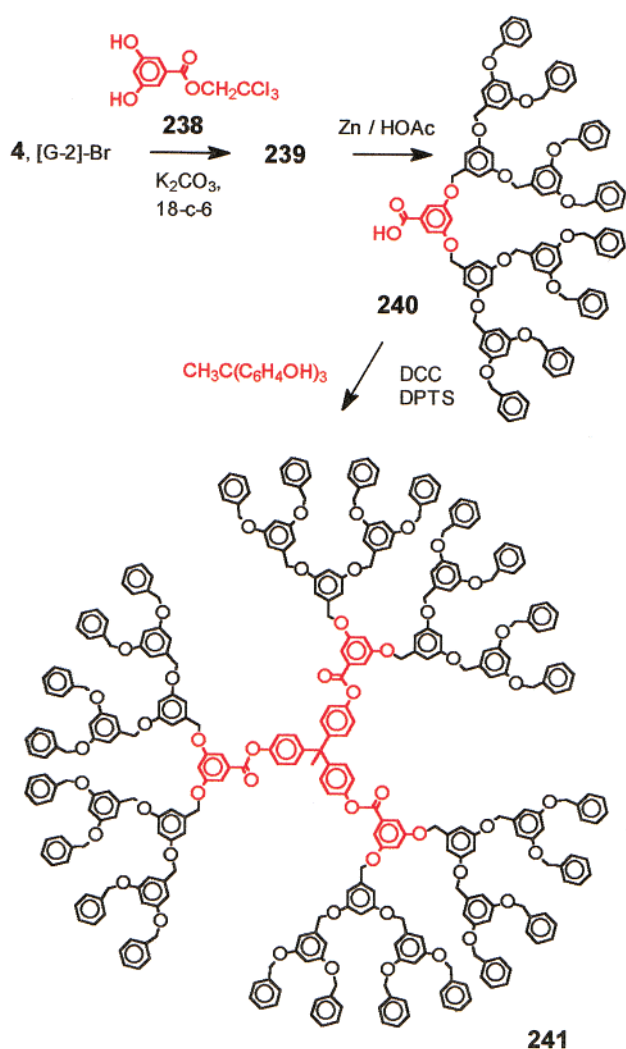
**Figure 29.**

enables the synthesis of well-defined dendritic copolymers. The wide range of possible dendritic copolymers can be divided into three basic structural categories (Figure 29): layered, segmented, and tailored copolymers.<sup>443</sup>

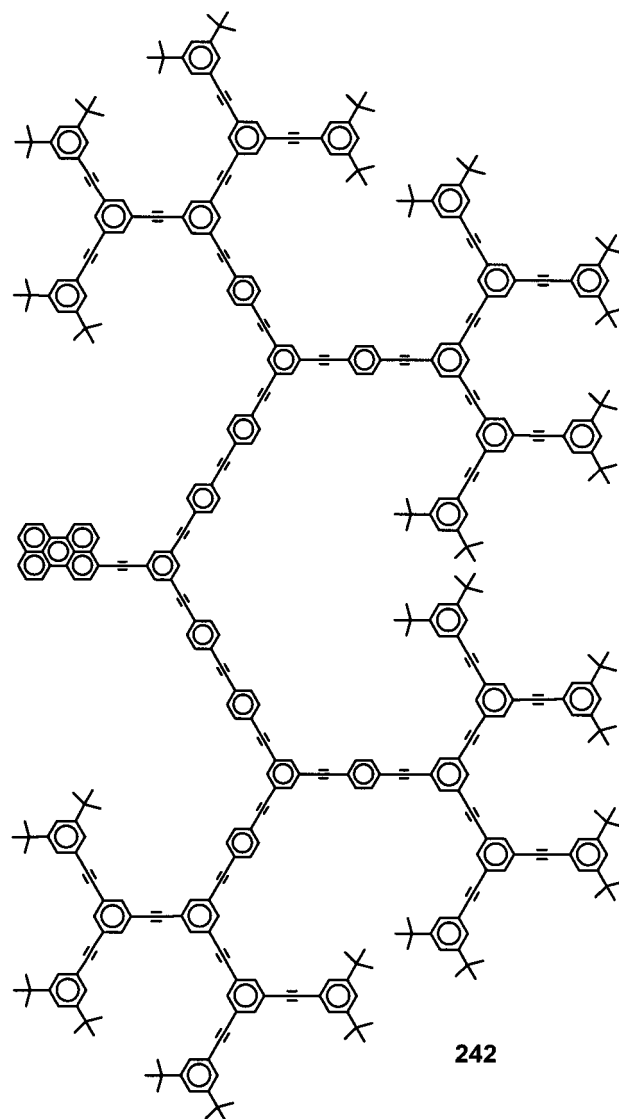
## A. Layered Copolymers

Layered copolymers contain two or more types of repeat units that are segregated in a layerwise fashion in the final dendritic product (Figure 29a). Since both the divergent and convergent syntheses progress by the stepwise addition of layers, both procedures can theoretically access these hybrid structures. However, with the notable exception of Balzani and co-workers, who have divergently prepared dendrimers containing concentric layers of transition metals connected through multidentate oligopyridine ligands,<sup>427,430</sup> and preliminary studies by Dvornic et al.,<sup>524</sup> layer copolymers have been predominantly investigated through the convergent growth approach. The first synthesis of a layered dendritic copolymer (Scheme 34) was reported by

**Scheme 34**



Hawker and Fréchet<sup>525</sup> via convergent attachment of preformed poly(benzyl ether) dendrons **4** to a poly-(benzyl ester) monomer, **238**. Continuation of the poly(benzyl ester) synthesis followed by coupling to a triphenolic core afforded the layered dendrimer **241**. The primary synthetic requirement for the two different monomers is that the outermost dendritic layers must be chemically inert to the coupling and



**Figure 30.**

activation conditions required during the dendritic growth of the inner repeat units.

The most noteworthy application of layered dendrimers to date has been their use in light-harvesting devices (Figure 30). Moore and co-workers reported an interesting gradient effect when using a poly(phenylacetylene) dendrimer, **242**, with repeat unit conjugation length that increases with generation from the periphery to the core.<sup>119,486</sup> As a result, the HOMO–LUMO gaps of the conjugated repeat units decrease from the exterior to the interior, causing a directional energy flow toward the core. A similar approach has been used by Morikawa et al. in the synthesis of graded poly(ether ketone) dendrons,<sup>181</sup> and van Manen et al. in the synthesis of layered metallodendrimers<sup>210</sup>

Dendritic layer copolymers have also been prepared via the hypercore approach,<sup>87</sup> and by divergent growth from the periphery of convergently prepared dendrimers,<sup>446</sup> or dendronized polymers.<sup>398</sup> This layered dendritic architecture has been used by a number of groups to probe the nature of chirality.

Mak and Chow<sup>99,100,526</sup> and Murer et al.<sup>107</sup> investigated the chiroptical properties of dendrimers consisting of alternating layers of chiral repeat units, whereas McGrath and co-workers examined a series of dendrons that contained a single chiral generational shell within an otherwise achiral fourth generation dendron.<sup>527</sup>

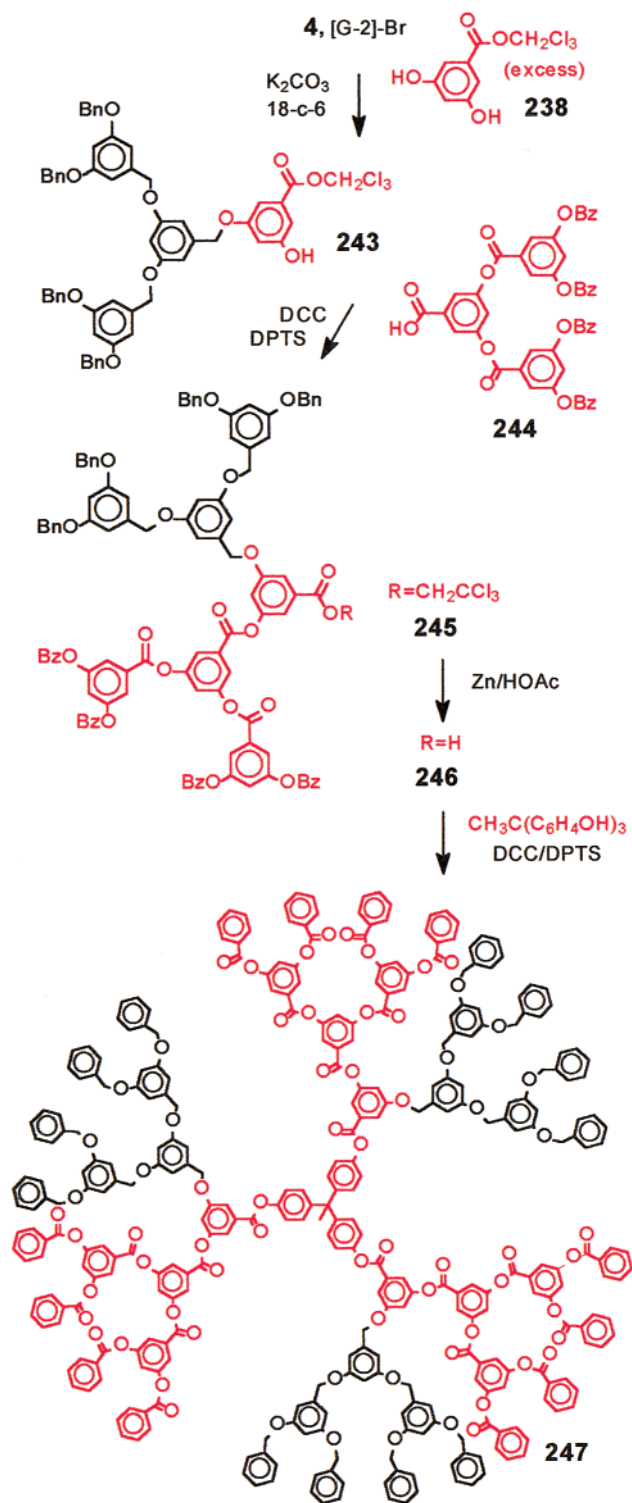
## B. Segmented Copolymers

Segmented copolymers are hybrids in which contrasting repeat units are segregated into wedge-shaped regions (Figure 29b). The convergent approach is ideally suited to create these structures because each growth reaction may be stopped after the first of two possible coupling reactions by using an excess of monomer. After isolating the singly coupled product, the remaining active functionality of the monomer may be coupled to a dendron with a chemically different backbone (Figure 5). This hybrid coupling strategy produces a dendron composed of two contrasting wedges. Because growth in the divergent synthesis proceeds outward from the core, it is difficult to control the multiple reactions of the surface groups with enough precision to access these architectures. Only through the application of protecting group chemistry have representative molecules of this type been accessed via the divergent methodology, but these approaches are not generally applicable.<sup>528–530</sup>

The first report of such architectures by Hawker and Fréchet, was again based on the poly(benzyl ether) and poly(benzyl ester) repeat units as contrasting dendritic components<sup>525</sup> (Scheme 35). The second generation Fréchet-type dendritic bromide **4** reacted with an excess of the poly(benzyl ester) monomer **238** to afford the singly coupled product **243**. The remaining phenol of **243** was coupled by a DCC-mediated esterification to the second generation poly(benzyl ester) carboxylic acid **244**, yielding the unsymmetrical hybrid dendron **245**. After activation of the focal point, three of these dendrons could be coupled to a trisphenolic core to yield dendrimer **247** with three pairs of hybrid ester–ether dendritic wedges. An analogous approach was utilized by Chow and co-workers during the preparation of dendritic copolymers with alternating D and L chiral segments.<sup>99,100,526</sup> Although the structures of the segmented block copolymers are often represented in two dimensions, implying  $C_n$  symmetry, the flexibility within the repeat units enables considerable conformational variations.

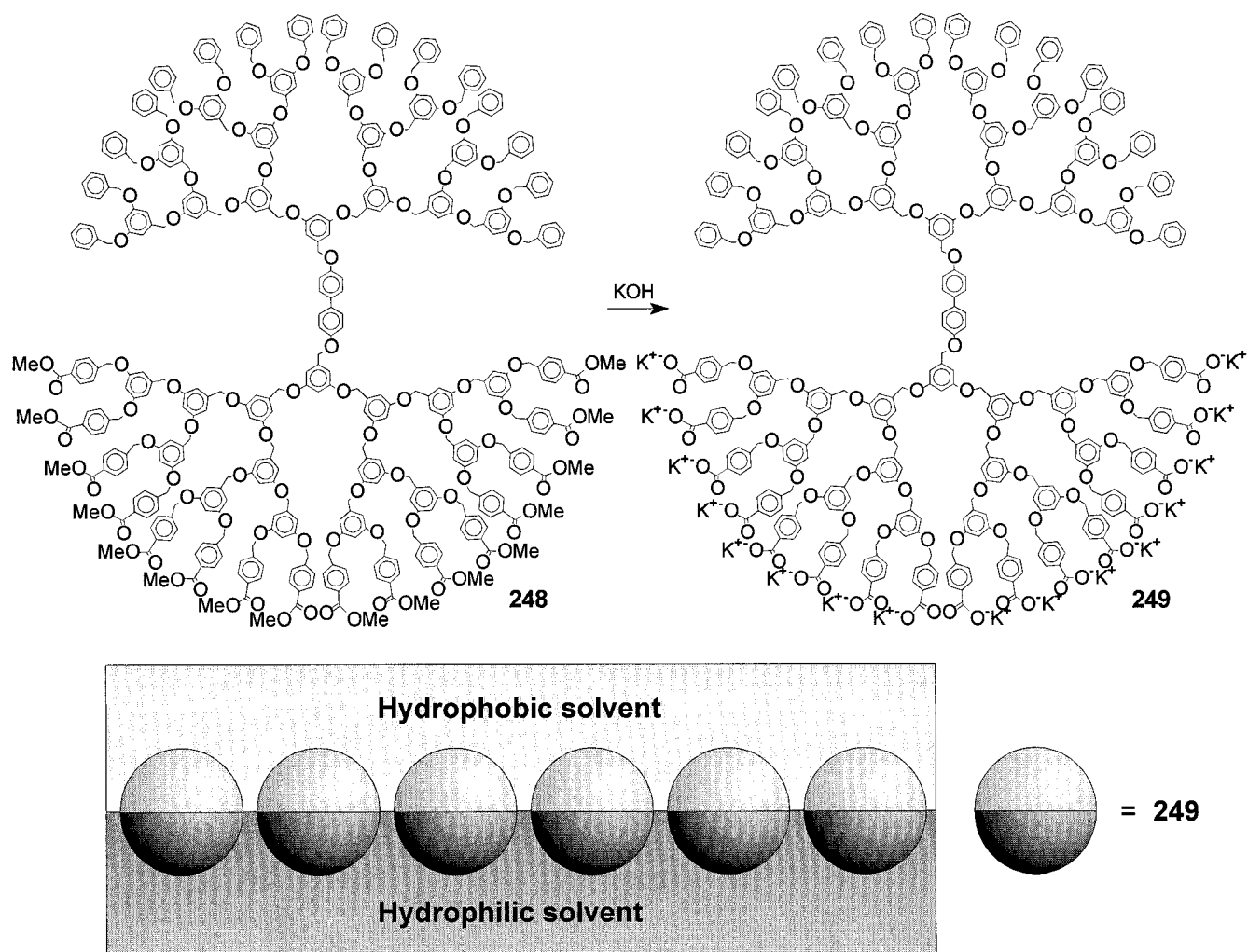
The synthesis of surface copolymers entails the same methodology as the segment copolymers, except the two contrasting dendrons differ only in the identity of their end groups.<sup>443</sup> This technique was developed to access hemispherically segregated surface copolymers. Wooley et al. described the preparation of dendrimers in which one of the hemispheres contained *p*-cyanophenyl electron-withdrawing groups, and the other traditional 3,5-bis(benzyloxy)phenyl electron-donating groups. The resulting dendrimer was shown to have a strong dipole due to its globular shape and the structural segregation of different end

Scheme 35



groups.<sup>441</sup> Dendrimers were also synthesized that contained benzyl ether end groups in one hemisphere and methyl esters in the other. Saponification of the esters produced the dendritic amphiphile **249** that demonstrated micellar properties (Scheme 36). Because of the well-segregated polar and nonpolar regions within the dendrimer, these structures are believed to orient themselves at the interface between hydrophilic and hydrophobic solvents.<sup>41</sup> Pesak and Moore used a similar approach to investigate the

Scheme 36



aggregation behavior of poly(phenylacetylene) dendrimers with a periphery made of lipophilic *tert*-butyl end groups, and blocks of 4, 8, 16, or 32 carboxylic acid groups,<sup>531</sup> and Bryce et al. used this approach to control the number of  $\pi$ -donor and  $\pi$ -acceptor groups on the periphery of polyester dendrimers.<sup>465</sup>

The chemically robust backbone of the poly(alkyl ether) dendrons enabled a unique opportunity to demonstrate the orthogonal functionalization of surface copolymers.<sup>40</sup> The benzyl and ketal protected dendrons reported by Grayson et al. were incorporated into two different copolymer architectures: a block and an alternating surface copolymer. The block copolymer (Scheme 37a) was synthesized by coupling a single allylic functionality of monomer **87** with the third generation ketal protected dendritic alcohol **97**. After isolation of **250**, displacement of the remaining allylic chloride by the third generation benzyl-protected dendron **96** afforded **251**. The fourth generation alternating copolymer (Scheme 37b) was prepared by using an identical hybrid coupling strategy to produce the second generation hybrid dendron **253** and then by repeating the activation and coupling steps until the fourth generation, **257**. Both copolymer structures exhibited a quantitative, selective deprotection of either the eight benzyl ethers

by palladium-catalyzed hydrogenation, **258**, or the four cyclic ketals by acid-catalyzed hydrolysis, **259** (Scheme 38). The periphery of these molecules could be selectively functionalized to replace the eight ketal-protected alcohols with oligoethylene glycol chains and the eight benzyl ethers with benzoate esters.<sup>40</sup>

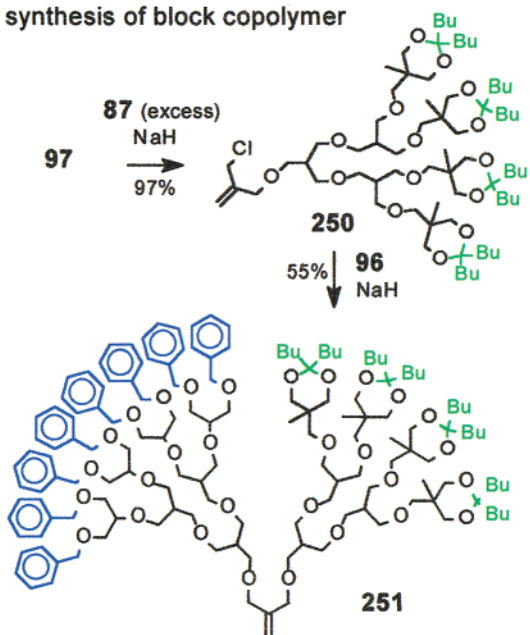
### C. Tailored Copolymers

Tailored copolymers can only be accessed by the convergent approach and utilize the hybrid coupling strategy during a series of coupling steps to control the exact number and placement of functional moieties within the dendritic structure (Figure 29c). Control over the peripheral functionalities is best exemplified by the synthesis of the fourth generation Fréchet-type dendron **260**, bearing a single *p*-cyano-benzyl group at the periphery<sup>73</sup> (Figure 31). This architecture is achieved (Scheme 39) by coupling one of the two phenolic groups of the monomer with benzyl bromide by using an excess of monomer **1**. After isolating **261**, the remaining phenolic group can be coupled with the *p*-cyanobenzyl bromide, yielding the hybrid dendron **262**. Activation of the focal functionality affords **263**, which can be coupled with

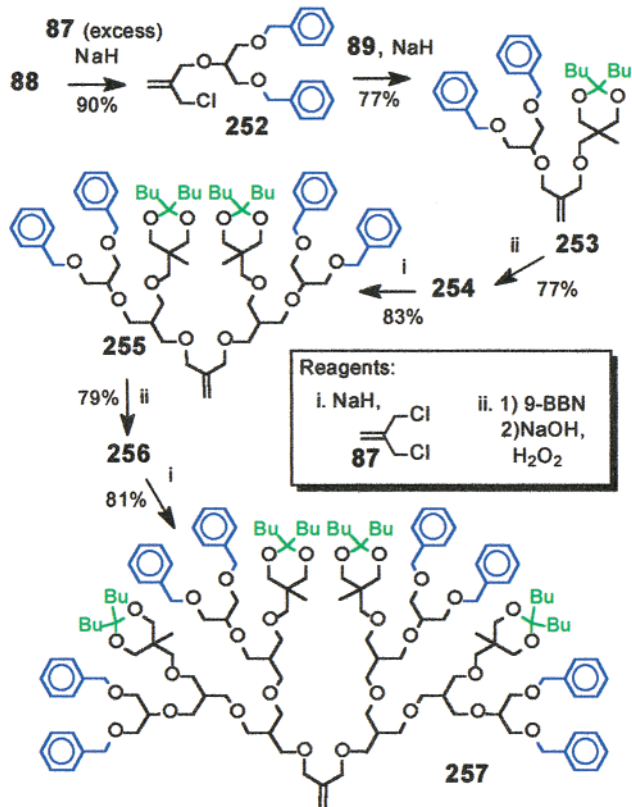


## Scheme 37

## a) synthesis of block copolymer



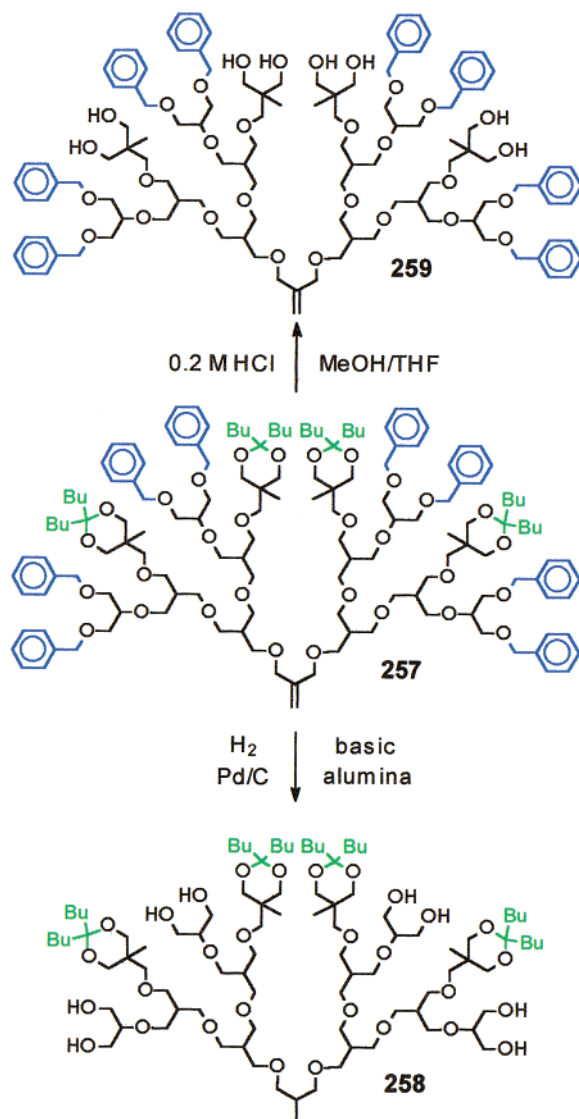
## b) synthesis of alternating copolymer



dendron **264** to produce the second generation dendron **265**, with a single peripheral nitrile group. Repetition of this process affords the fourth generation dendron **260**, bearing a single cyano substituent on its periphery. Though tedious, this procedure enables the synthesis of dendrons bearing any number of modified peripheral groups.

This technique can also be used to control the placement of a specific functionality on any repeat

## Scheme 38



unit within the interior of the dendrimer. Schlüter elegantly demonstrated this concept by preparing a third generation Fréchet-type dendrimer bearing a single *p*-bromo functionalized monomer unit at the first, second, or third generation branching points<sup>521</sup> (Scheme 40). These dendrons could then be incorporated into a dendrimer with two unfunctionalized

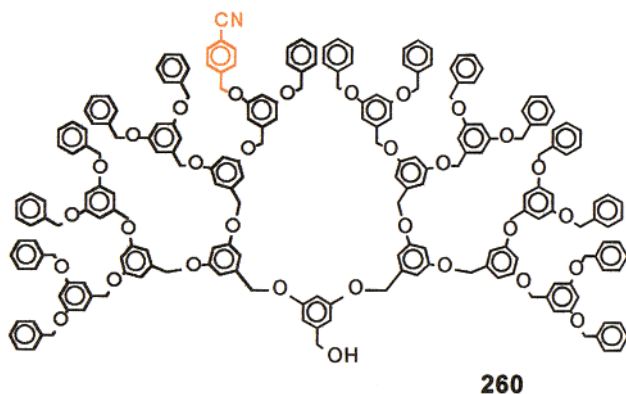
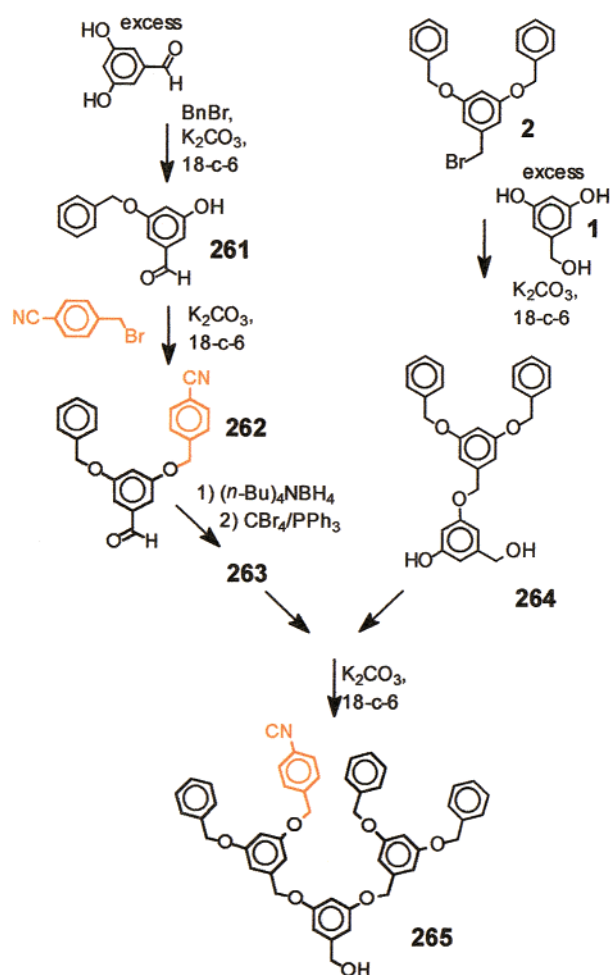


Figure 31.

Scheme 39



third generation dendrons. The single aryl bromide functionality of each dendrimer can be modified by a Suzuki cross-coupling reaction. The palladium-catalyzed coupling of *tert*-butylphenylboronic acid afforded the derivatized dendrimers in 88, 95, and 97% isolated yields for the dendrimers incorporating **267**, **269**, and **273**, respectively.

## VII. Conclusion

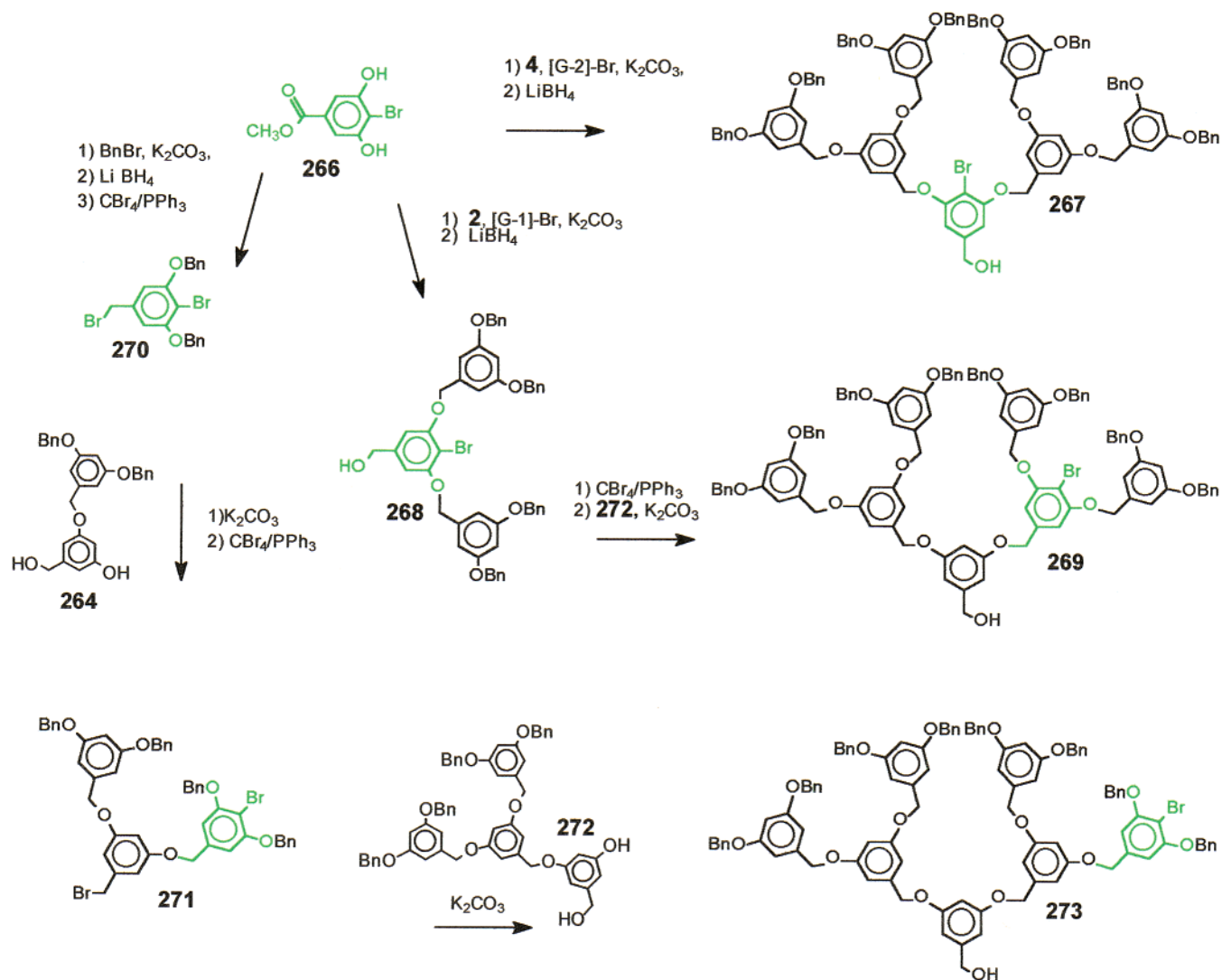
Many synthetic chemists appreciate the beauty of natural product synthesis where practical skill and creativity are cleverly combined to mimic nature's feats. The authors and many practitioners in the emerging field of nanotechnology derive much scientific fulfillment from designing targets such as molecular devices that are not specified by nature but for which function is the objective. Unlike natural product synthesis for which a very specific molecular target is provided by nature, the "materials" chemist makes use of elements of biomimetics, macroscopic analogies, and intuition to define the target. When nanometer scale assemblies are the target, this leads to unusual building blocks that today include elements such as fullerenes, clusters, nanocrystals, nanotubes, molecular wires, cage compounds, dendrons, dendrimers, etc. As a result of the countless

structural variations that can be implemented during their preparation, dendrimers are especially attractive to the materials chemist.

The convergent approach to dendrimer growth takes its place alongside the now well-established divergent synthesis providing an alternative approach from which the synthetic chemist can choose in order to construct a particular target molecule. Because of its modular design, great flexibility, and compatibility with the standard purification procedures of organic chemistry, the convergent approach offers a number of unique opportunities for the precise construction of nanoscale structures. Although high yield reactions always afford best results, the convergent synthesis is more tolerant of reactions that proceed in somewhat lower than ideal yields as only a few simultaneous reactions are required for growth of the convergent dendron and therefore a pure product can still be isolated and purified. This is clearly not the case with a divergent synthesis for which structural flaws resulting from lower yield reactions would quickly overwhelm the entire process and lead to a reaction mixture in which the desired product, if at all present, is only a minor component. Despite such realities, the fact remains that, in many instances, the presence of impurities that are structurally closely related to the desired product does not detract from the usefulness of dendrimers. Therefore the significance of the convergent approach will mirror its synthetic and functional versatility and not just its ability to afford some of the purest synthetic macromolecules known today. The presence of orthogonal functionalities at the focal point and the periphery of a dendron remains a very attractive feature for the molecule builder trying to assemble complex functional structures from a limited set of building blocks. There is no doubt that when issues of product availability—as translated into kilograms of materials—are taken into consideration, the divergent route will nearly always be superior to the convergent approach. When issues such as functional control, structural precision, building block versatility, the ability to perform custom encapsulation, and the like come to the fore, the convergent dendrimers will nearly always have an edge. Clearly, the synthetic requirements of the convergent method are such that all but the smaller dendrons can only be used for high added value applications or fundamental studies. With the convergent tool at their disposal, synthetic chemist can fashion large molecular assemblies that are structurally perfect and therefore provide ideal tools for fundamental studies. In many cases, when the ultimate properties of a molecule or material are known or when the mechanism of a phenomenon has been elucidated, it is possible to simplify the structure of the molecule or material. In such instances the convergently built molecules may well serve the role of model compounds or prototype leading to less perfect and simplified structures that perhaps perform a lesser function but benefit from increased accessibility.

In the age of nanotechnology, few nanoscale building blocks have the structural and functional versa-

## Scheme 40



tility exhibited by convergent dendrons. There is little doubt that these versatile building blocks that can be used to prepare not only highly symmetrical, but also anisotropic structures will continue to stimulate our creativity leading us to fundamental discoveries while seeding very real applications. For example, it may be expected that dendrimers will be used in a variety of energy harvesting and conversion functions, as nanoreactors or catalytic enzyme mimics, as highly targeted drugs capable of penetrating a variety of biological barriers, as carriers of genetic material, as shape-persistent or functional components for nanoscale electronics or microfluidics, as memory, storage, encoding, or logic devices, etc.

## VIII. Acknowledgments

Financial support of our work on convergent dendrimers by the National Science Foundation (DMR #9816166) and the US Department of Energy (Basic Energy Sciences, Polymer Program of the Center for Advanced Materials, Lawrence Berkeley National Laboratory) is gratefully acknowledged. The authors also thank Dr. Stefan Hecht and Prof. Alex Adronov for invaluable discussions.

## IX. Glossary

ATRP	atom transfer radical polymerization
9-BBN	9-borabicyclo[3.3.1]nonane
CMC	critical micelle concentration
CV	cyclic voltammetry
DBOP	(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester
DBU	diazabicyclo[5.4.0]-7-undecene
DCC	<i>N,N</i> -dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate
DIPEA	<i>N,N</i> -diisopropylethylamine
DMAc	dimethyl acetamide
DPTS	4-(dimethylamino)pyridinium <i>p</i> -toluenesulfonate
DSM	Dutch State Mines
GPC	gel permeation chromatography
LED	light-emitting diode
MALDI-TOF	matrix-assisted laser desorption ionization time-of-flight mass spectrometry
MS	time-of-flight mass spectrometry
MW	molecular weight
NMP	<i>N</i> -methyl-2-pyrrolidone
PAMAM	poly(amidoamine)
PEG	poly(ethylene glycol)
PPI	poly(propyleneimine)
SFM	scanning force microscopy

SANS	small angle neutron scattering
TADDOL	( <i>R,R</i> )- $\alpha,\alpha,\alpha',\alpha'$ -tetraaryl-1,3-dioxolane-4,5-dimethanol
<i>t</i> -BOC	<i>tert</i> -butyloxycarbonyloxy
TEMPO	2,2,6,6-tetramethyl-1-oxylpiperidine
TMS	trimethylsilyl
TTF	tetrathiafulvalene

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CR990116H

