J|A|C|S
ARTICLES
Published on Web 09/18/2004

Dendrimer Interior Functional Group Conversion and Dendrimer Metamorphosis−New Approaches to the Synthesis of Oligo(dibenzyl sulfone) and Oligo(phenylenevinylene) Dendrimers

Hak-Fun Chow,* Man-Kit Ng, Chi-Wing Leung, and Guo-Xin Wang

Contribution from the Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong SAR

Received June 11, 2004; E-mail: hfchow@cuhk.edu.hk

Abstract: A series of [G1] to [G3]-oligo(dibenzylsulfide) dendrimers containing up to 21 interior dibenzylsulfide moieties was prepared as starting materials toward the syntheses of two new series of oligo(dibenzyl sulfone) and oligo(phenylenevinylene) dendrimers using two different dendrimer-to-dendrimer conversion strategies. The first strategy entailed the interior functionalization of the [G1] to [G3]-oligo(dibenzylsulfide)s to the corresponding [G1] to [G3]-oligo(dibenzyl sulfone)s via hydrogen peroxide oxidation. Successful conversions of up to 21 interior dibenzylsulfide moieties to the corresponding dibenzyl sulfone groups were demonstrated. The second involved the skeletal rearrangements, also named as dendrimer metamorphosis, of the [G1] and [G2]-oligo(dibenzyl sulfone) dendritic backbones to the corresponding [G1] and [G2]-oligo(phenylenevinylene)s dendrimers via the Ramberg−Bäcklund (RB) reaction. Up to nine RB rearrangements on a dendrimer skeleton were realized and the conversion efficiency of each single RB rearrangement reaction was found to be 96%.

Introduction

Dendritic macromolecules are now playing an important role with emerging interest in synthetic chemistry, biomedical technology, and material science.[1] This unique structural motif allows the orderly placement of a large number of functional groups in close proximity inside a hyperbranched polymer framework. As a result, such functionalities may act in a synergistic manner and produce the so-called 'dendritic effects'[2] that are of prime interest in functional dendrimer chemistry.

Despite rapid advances in the potential applications of dendrimers, their synthesis are still confined to the divergent[3] or the convergent[4] synthetic strategies that were devised more than 10 years ago. Hence there is still an urgent need for newer methods for dendrimer constructions. In the divergent method, the dendritic framework is constructed from the interior core toward the periphery. On the other hand, dendrimer is assembled from the periphery toward the central core in the convergent protocol. Both strategies rely on functional group transformations occur either on the dendrimer surface or on the dendron focal point. On the other hand, direct syntheses of dendritic macromolecules involving dendrimer-to-dendrimer transformations (i.e. post-dendrimerization modifications) are less known. Under this synthetic strategy, the full dendritic framework is first secured either by the divergent or convergent method. The dendritic backbone (i.e. branch and/or branching juncture) is then subsequently modified to afford the desired target dendrimer. Hence, dendrimer-to-dendrimer transformations invariably invoke functional group conversions in the interior of the dendrimer, which present a formidable challenge to both polymer and synthetic chemistry.[5] Nonetheless, dendrimer-to-dendrimer conversion is a powerful strategy because new dendrimers can be made in those cases where the required branching building blocks are difficult to prepare or do not possess enough reactivity to be used in the iterative synthetic constructions. A review of the literature showed that most dendrimer-to-dendrimer conversions reported to date involved solely interior functional group transformations.[5] On the other hand, dendrimer-to-dendrimer transformations utilizing dendrimer backbone rearrangements have not been disclosed in the literature. Herein we report a new synthesis of oligo(phenylenevinylene) dendrimers **1** via multiple dendrimer backbone rearrangements of oligo(dibenzyl sulfone) dendrimers **2** by the Ramberg−Bäcklund (RB) reaction (Figure 1).[6] We use the term 'dendrimer metamorphosis' to describe such an extensive

(1) For recent reviews on dendrimer chemistry, see: (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons. Concepts, Syntheses, Applications*; Wiley-VCH: Weinheim, Germany, 2001. (b) Stiriba, S.-E.; Frey, H.; Haag, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 1329−1334. (c) Fréchet, J. M. J. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 3713−3725. (d) Boas, U.; Heegaard, P. M. H. *Chem. Soc. Rev.* **2004**, *33*, 43−63.

(2) Chow, H.-F.; Leung, C.-F.; Wang, G.-X.; Yang, Y.-Y. *C. R. Chimie* **2003**, *6*, 735−745.

(3) (a) Buhleier, E.; Wehner, W.; Vögtle, F. *Synthesis* **1978**, 155−158. (b) Tomalia, D. A.; Baker, H.; Dewald, J. R.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117−132. (c) Newkome, G. R.; Baker, G. R. *Org. Prep. Proced. Int.* **1986**, *18*, 117−144.

(4) (a) Hawker, C.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010−1013. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638−7647.

(5) For a review, see Hecht, S. *J. Polym. Sc. Part A: Polym. Chem.* **2003**, *41*, 1047−1058.

(6) For a recent review, see Taylor, R. J. K.; Casy, G. *Org. React.* **2003**, *59*, 357−475.

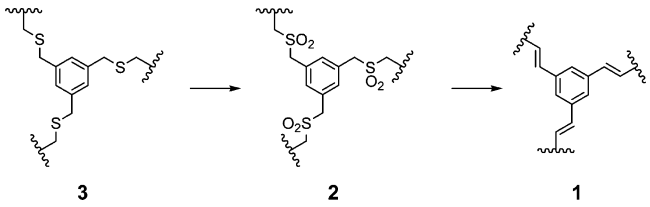
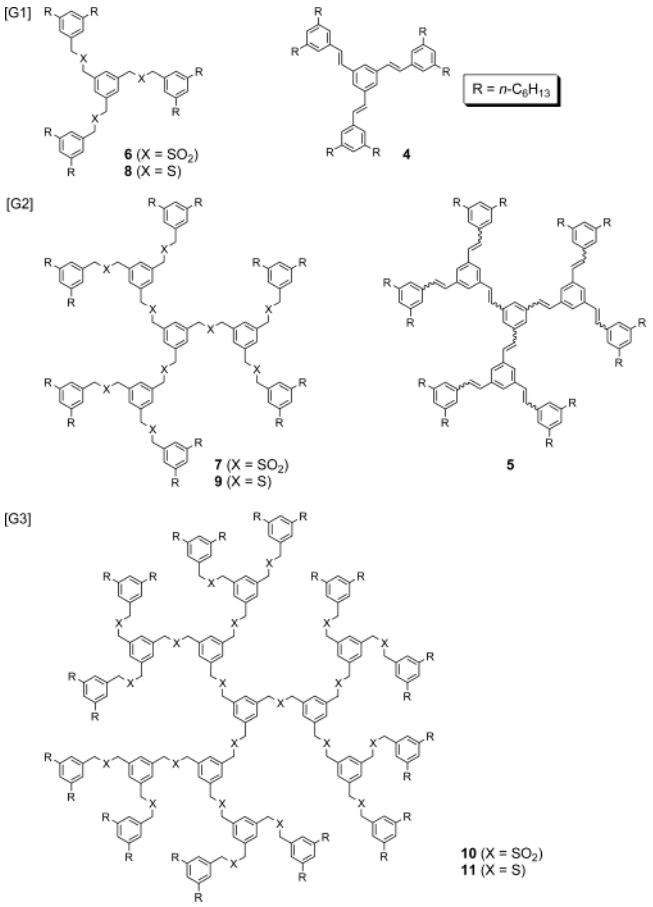


Figure 1. Interior functional group conversion from an oligo(dibenzylsulfide) dendrimer **3** to an oligo(dibenzyl sulfone) dendrimer **2** and dendrimer metamorphosis of an oligo(dibenzyl sulfone) dendrimer **2** to an oligo(phenylenevinylene) dendrimer **1**.

backbone rearrangement on a dendritic molecule since a new type of dendrimer with a completely different backbone structure is generated by this new strategy. We also show here that the oligo(dibenzyl sulfone) dendrimers **2** can be prepared from oligo(dibenzylsulfide) dendrimers **3** through dendrimer-to-dendrimer conversions involving interior functional group transformations. The scope and limitations of the dendrimer interior functional group conversion and dendrimer metamorphosis are also discussed. These strategies are of particular interest to the future synthetic design of dendrimers, post-dendrimerization modifications and interior functionalizations of dendrimers.

Oligo(phenylenevinylene) dendrimers[7] and their derivatives had been shown to possess interesting liquid crystalline,[8] photophysical,[8b,d,9−13] electrochemical,[9c,d,10a−c,e] and electroluminescence properties.[9a,d] The stilbene skeleton was established either by the Heck reaction between an aryl halide with a vinylbenzene derivative,[9a,b,10d,11,13] or by the Horner−Wadsworth−Emmons coupling between an aromatic aldehyde with a benzylphosphonate.[8,9,10c−e,12−14] With the exceptions of those reported by Martín[10c] and Mongin,[12] the C═C bonds generated from the above reactions were solely of (*E*)-configuration.

We previously demonstrated that the modified RB reaction (KOH/Al_2O_3, CBr_2F_2, *t*-BuOH) reported by Chan[15] could be used to construct highly conjugated systems such as enediyne,[16] 1,3,5-hexatrienes,[17] and 1,3,5,7-octatetraenes[18] with good (*E*)-stereoselectivity from various sulfone precursors. This modified procedure had been reported to suppress the formation of a dihalocarbene-olefin adduct that was frequently formed as a side product in the Meyers RB protocol.[19] We disclose here that both the [G1]-tri(phenylenevinylene) **4** and [G2]-nona(phenylenevinylene) **5** dendrimers can readily be prepared from the corresponding [G1]-tri(sulfone) **6** and [G2]-nona(sulfone) **7** derivatives, respectively, via dendrimer metamorphosis. It should be noted that three and nine molecular rearrangements are involved in the transformation reactions of the [G1] and [G2] dendrimers, respectively. To the best of our knowledge, multiple RB rearrangements on a single molecule involving these many processes have not been reported before. Unfortunately, despite many attempts, we were unable to extend this dendrimer metamorphosis strategy to the [G3]-series due to steric shielding and heterogeneous nature of the RB reaction conditions. The [G1] to [G3]-oligo(sulfone) dendrimers **6**, **7**, and **10**, in turn, were readily prepared by sulfide oxidation[20] under homogeneous reaction conditions from the corresponding [G1] to [G3]-oligo(sulfide) dendrimers **8**, **9**, and **11**, respectively, via functional group conversions occurred in the interior domain.



Results and Discussion

Synthesis of [G1] to [G3]-Oligo(dibenzylsulfide) Dendrimers. The [G1] to [G3]-oligo(sulfide) dendrimers **8**, **9**, and **11** consist of four structural components: the surface sector, the linker, the branching unit, and the central core. An *n*-hexyl group was chosen as the surface unit, which was required to improve the solubility property of the dendrimers and to facilitate their structural characterizations. The linker used was a $-CH_2SCH_2-$

(7) For a reveiw on oligo(phenylenevinylene) dendrimers, see Meier, H.; Lehmann, M. In *Encyclopedia of Nanoscience and Nanotechnology, Vol. 10*; Nalwa, H. S., Ed.; American Scientific Publishers: California, 2004; pp 95−106.

(8) (a) Meier, H.; Lehmann, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 643−645. (b) Lehmann, M.; Schartel, B.; Hennecke, M.; Meier, H. *Tetrahedron* **1999**, *55*, 13377−13394. (c) Meier, H.; Lehmann, M.; Kolb, U. *Chem. Eur. J.* **2000**, *6*, 2462−2469. (d) Lehmann, M.; Fischbach, I.; Spiess, H. W.; Meier, H. *J. Am. Chem. Soc.* **2004**, *126*, 772−784.

(9) (a) Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. *Adv. Mater.* **1999**, *11*, 371−374. (b) Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **1999**, *32*, 5985−5993. (c) Pålsson, L.-O.; Beavington, R.; Frampton, M. J.; Lupton, J. M.; Magennis, S. W.; Markham, J. P. J.; Pillow, J. N. G.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **2002**, *35*, 7891−7901. (d) Beavington, R.; Frampton, M. J.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2003**, *13*, 211−218.

(10) (a) Díez-Barra, E.; García-Martínez, J. C.; Rodríguez-López, J.; Gómez, R.; Segura, J. L.; Martín, N. *Org. Lett.* **2000**, *2*, 3651−3653. (b) Langa, F.; Gómez-Escalonilla, M. J.; Díez-Barra, E.; García-Martínez, J. C.; de la Hoz, A.; Rodríguez-López, J.; González-Cortés, A.; López-Arza, V. *Tetrahedron Lett.* **2001**, *42*, 3435−3438. (c) Segura, J. L.; Gómez, R.; Martín, N.; Guldi, D. M. *Org. Lett.* **2001**, *3*, 2645−2648. (d) Díez-Barra, E.; García-Martínez, J. C.; Merino, S.; del Rey, R.; Rodríguez-López, J.; Sánchez-Verdú, P.; Tejeda, J. *J. Org. Chem.* **2001**, *66*, 5664−5670. (e) Díez-Barra, E.; García-Martínez, J. C.; del Rey, R.; Rodríguez-López, J.; Giacalone, F.; Segura, J. L.; Martín, N. *J. Org. Chem.* **2003**, *68*, 3178−3183.

(11) Sengupta, S.; Sadhukhan, S. K.; Singh, R. S.; Pal, N. *Tetrahedron Lett.* **2002**, *43*, 1117−1121.

(12) Mongin, O.; Brunel, J.; Porrès, L.; Blanchard-Desce, M. *Tetrahedron Lett.* **2003**, *44*, 2813−2816.

(13) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9079−9080.

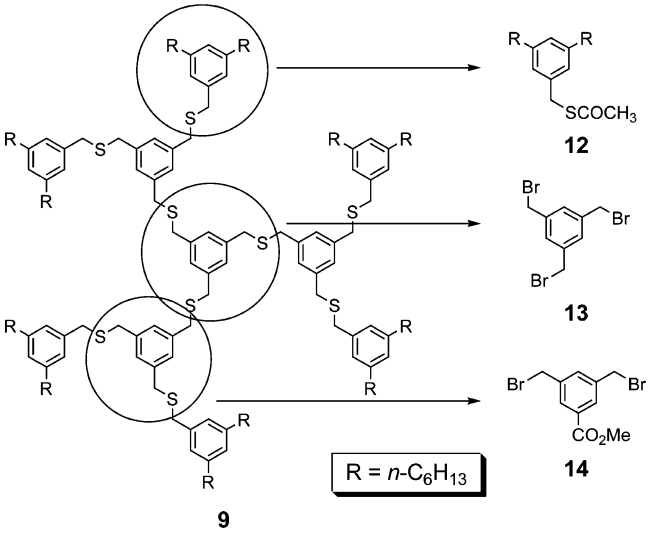


Figure 2. Retrosynthetic analysis of the [G2]-oligo(dibenzylsulfide) dendrimer **9**.

unit, which was already endowed with the structural element for its future transformation to the stilbene functionality. Both the branching juncture and the central core employed were a 1,3,5-phenylene unit. A retrosynthetic analysis on the [G2]-oligo(dibenzylsulfide) dendrimer **9** suggested that such dendrimers could be assembled from three basic components: 3,5-di-(*n*-hexyl)benzylthiolacetate **12** as the surface unit, 1,3,5-tris(bromomethyl)benzene **13**[14] as the central core, and methyl 3,5-bis(bromomethyl)benzoate **14**[21] as the branching propagating unit (Figure 2).

The convergent synthetic approach was used to assemble the target oligo(sulfide) dendrimers. Hence, Sonogashira coupling[22] between 1-hexyne (4 equiv) and commercially available methyl 3,5-dibromobenzoate afforded the bis(acetylene) adduct **15** as a yellow oil in 85% yield (Scheme 1). The triple bonds were then hydrogenated in the presence of 10% Pd/C in absolute EtOH at 25 °C to give the di-*n*-hexyl substituted benzoate **16** (95%) as an oil. The methyl ester **16** was subsequently reduced by lithium aluminum hydride (LAH) in THF to give the corresponding benzyl alcohol **17** in 95% yield. Finally, reaction of the alcohol **17** with thiolacetic acid in the presence of triphenylphosphine (PPh_3) and diisopropyl azodicarboxylate (DIAD) produced the benzylthiolacetate **12** in 87% yield. The structure and purity of all the dendrons described above were confirmed by ^{1}H and ^{13}C NMR, mass spectroscopy, and elemental analyses.

For the synthesis of the [G1]-tri(sulfide) **8**, the acetyl group of the thiolacetate **12** was removed in the presence of sodium methoxide in a mixture of THF and MeOH to give the corresponding thiol **18**. The choice of the solvent was crucial for the success of this reaction. In the absence of MeOH, the rate of acetyl cleavage was too slow as sodium methoxide was only slightly soluble in THF. On the other hand, the thiolacetate **12** was not soluble in pure MeOH and hence a mixture of MeOH and THF was required to facilitate the transformation. Thin layer chromatographic (TLC) analysis of the reaction mixture indicated the coupling reaction was very fast, and was completed in 3 min at 25 °C. Strict exclusion of oxygen during the coupling reaction was also important as the thiol **18** was highly susceptible to self-oxidation to give a disulfide that was difficult to separate from the target [G1]-tri(sulfide) **8**. Therefore the thiol **18** was generated in situ and immediately coupled to the trifunctional core **13** to give the target [G1]-tri(sulfide) **8** in 83% as colorless oil after chromatography.

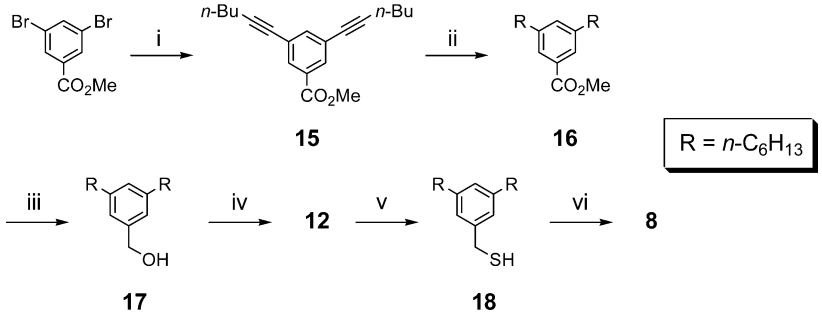
To obtain the [G2]-series of compounds, the thiol **18** (2 equiv) was reacted with methyl 3,5-bis(bromomethyl)benzoate **14** to give the [G2]-methyl ester dendron **19** in 92% yield (Scheme 2). The methyl ester **19** was reduced to the corresponding benzyl alcohol **20** by LAH followed by functional group conversion (CH_3COSH/PPh_3/DIAD) to produce the [G2]-thiolacetate **21** in an overall 77% yield. Finally, 3 equiv of the thiolacetate **21** was linked to the trifunctional core **13** to furnish the [G2]-nona-(sulfide) dendrimer **9** in 78% yield after chromatographic purification.

The syntheses of the various [G3]-dendrons and [G3]-heneicos(sulfide) dendrimer **11** were similarly accomplished by using the same synthesis sequence. Hence, coupling of the [G2]-thiolacetate **21** (2.0 equiv) with the branching unit **14** in the presence of sodium methoxide gave the desired [G3]-ester dendron **22** in 78% yield (Scheme 3). Reduction of the ester **22** with LAH then afforded the [G3]-benzyl alcohol **23** in 87% yield. The alcohol **23** was then converted to the corresponding thiolacetate **24** in 76% yield under the Mitsunobu conditions (CH_3COSH/PPh_3/DIAD). Anchorage of the [G2]-thiolacetate **24** to the central core **13**, however, turned out to be relatively slow (~1 h) and this could be due to steric inhibition at the focal point thiol functionality. Nonetheless, the desired [G3]-heneicos-(sulfide) **11** could be obtained in 66% yield after chromatographic purification.

The structural identities of the various [G2] and [G3]-dendrons as well as the target oligo(sulfide)s **8**, **9**, and **11** were determined by ^{1}H, ^{13}C NMR, and mass spectroscopy. The layer architecture of the oligo(sulfide) dendrimers can be clearly revealed from their ^{1}H NMR spectra. Hence the aromatic protons of the central core appeared as a singlet at around $\sim\delta$ 7.1 for all three generations of dendrimer, while those of the surface aromatic branching units were located as two sets of singlet at $\sim\delta$ 6.9. On the other hand, the proton signals of the aromatic branching units situated in the intermediate layer(s) were found to situate between δ 7.17 and 7.07 (Table 1). While the relative integration values obtained from ^{1}H NMR spectroscopy is very useful in ascertaining the structure of the lower generation [G1]- and [G2]-series of compounds, it alone cannot provide conclusive evidence for those of the higher generation [G3] compounds as the relative integration of the central core aromatic protons now became relatively small to be measured accurately. Hence, MS and SEC data were also obtained to confirm their structure and homogeneity. Using MALDI-TOF MS analysis, the mo-

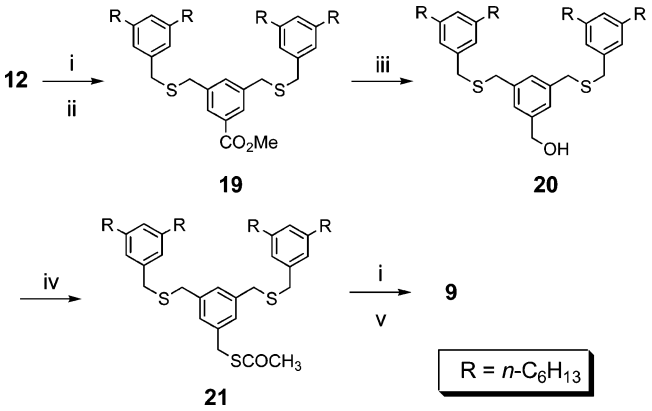
(14) Díez-Barra, E.; García-Martínez, J. C.; Rodríguez-López, J. *Tetrahedron Lett.* **1999**, *40*, 8181−8184.
(15) Chan, T.-L.; Fong, S.; Li, Y.; Man, T.-O.; Poon, C.-D. *J. Chem. Soc., Chem. Commun.* **1994**, 1771−1772.
(16) Cao, X.-P.; Chan, T.-L.; Chow, H.-F. *Tetrahedron Lett.* **1996**, *37*, 1049−1052.
(17) Cao, X.-P.; Chan, T.-L.; Chow, H.-F.; Tu, J. *J. Chem. Soc., Chem. Commun.* **1995**, 1297−1299.
(18) Cao, X.-P. *Tetrahedron* **2002**, *58*, 1301−1307.
(19) Meyers, C. Y.; Malte, A. M.; Matthews, W. S. *J. Am. Chem. Soc.* **1969**, *91*, 7510−7512.
(20) The direct oxidation of linear poly(sulfide) polymers to their corresponding poly(sulfone) polymers had been reported in the literature, see Marvel, C. S.; Weil, E. D. *J. Am. Chem. Soc.* **1954**, *76*, 61−69.
(21) Markovac, A.; LaMontagne, M. P. *J. Med. Chem.* **1980**, *23*, 1198−1201.
(22) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−630.

Scheme 1. Synthesis of Surface Unit **12** and [G1]-Tri(sulfide) Dendrimer **8**[a]



[a] (i) 1-hexyne (4 equiv), $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, C_6H_6, 80 °C, 48 h; (ii) H_2, 10% Pd/C, EtOH, 25 °C, 18 h; (iii) $LiAlH_4$, THF, 0−25 °C, 1 h; (iv) CH_3COSH, DIAD, PPh_3, THF, 0−25 °C, 2 h; (v) NaOMe, MeOH, THF, 25 °C, 5 min; (vi) 1,3,5-tris(bromomethyl)benzene (0.3 equiv), MeOH, THF, 25 °C, 1 h.

Scheme 2. Synthesis of [G2]-Dendrons and [G2]-Nona(sulfide) Dendrimer **9**[a]



[a] (i) NaOMe, MeOH, THF, 25 °C, 5 min; (ii) methyl 3,5-bis(bromomethyl)benzoate **14** (0.5 equiv), MeOH, THF, 25 °C, 1 h; (iii) $LiAlH_4$, THF, 0−25 °C, 1 h; (iv) CH_3COSH, DIAD, PPh_3, THF, 0−25 °C, 2 h; (v) 1,3,5-tris(bromomethyl)benzene (0.3 equiv), MeOH, THF, 25 °C, 1 h.

lecular peaks found for the [G1], [G2], and [G3]-oligo(sulfide)s were at 1097.5 ($M + Ag^+$), 2421.3 ($M + Ag^+$), and 5064.4 ($M + Ag^+$), respectively. Their SEC chromatograms also revealed the presence of one major peak with a polydispersity index of less than 1.04.

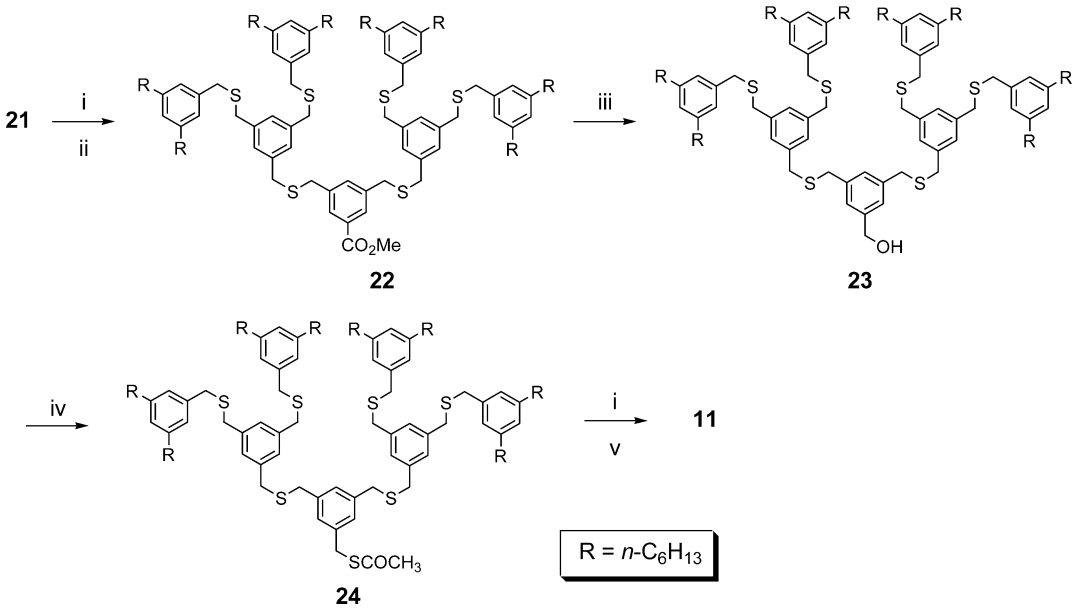
Interior Functional Group Transformations−Oligo (dibenzylsulfide) to Oligo(dibenzoyl sulfone) Dendrimers. The [G1] to [G3] oligo(sulfide) dendrimers **8**, **9**, and **11** were then converted to the corresponding oligo(sulfone)s **6**, **7**, and **10**, respectively, by oxidation reactions of all the sulfide functionalities located in the interior domain. Initial trials on the [G1]-tri(sulfide) **8** employing oxone[23] as the oxidizing agent either in MeOH or in CH_2Cl_2 were unsuccessful. The reaction time was long (>48 h) and the conversion was poor. It was later found that the use of 35% H_2O_2 in a boiling mixture of acetic acid and CH_2Cl_2 proved to be highly effective in converting all the sulfides to the corresponding sulfone moieties (Scheme 4). Apart from the [G1]-tri(sulfone) **6**, the higher generation [G2] and [G3]-oligo(sulfone)s obtained are highly crystalline materials and have poor solubility[24] except in large amount of chlorinated solvents or THF. The addition of CH_2Cl_2 was essential in promoting the complete oxidation of the oligo(sulfide)s. In the absence of CH_2Cl_2, the partially oxidized species containing both sulfoxide and sulfone oxidation states tended to precipitate from the reaction medium and further oxidation of the remaining sulfoxide moieties would stop to proceed. By using this procedure, the [G1] **8**, [G2] **9**, and [G3]-oligo(sulfide)s **11** could be successfully converted to the [G1]-tri(sulfone) **6** (95%), [G2]-nona(sulfone) **7** (64%), and [G3]-heneicos(sulfone) **10** (51%), respectively.

The ^1H NMR spectroscopic data of the oligo(sulfone)s revealed one interesting feature of these species in solution (Table 2). Upon oxidation, the ^1H aromatic signals due the central core and the surface aromatic rings were slightly downfield shifted (∼0.2 ppm). On the other hand, the corresponding signals originated from the intermediate branching aromatic ring(s) experienced a significantly large downfield shift of ∼0.7 ppm. However, there was little difference between the chemical shifts of the core and intermediate branching aromatic protons in the corresponding oligo(sulfide) series. We speculated that the presence of many strong sulfone-oxygen dipoles favored the oligo(sulfone)s to adopt a conformation wherein the aromatic rings in the intermediate layer were experiencing a strong deshielding effect from another aromatic moieties. Furthermore, the ^1H benzylic signals adjacent to the sulfone moieties in all three generations of oligo(sulfone) were downfield shifted to ∼δ 4.1−4.3. We could not detect any products due to partial oxidation to the sulfoxide state as no signals was found in the region (∼δ 3.9) normally ascribed to benzylic signals adjacent to a dibenzylsulfoxide skeleton. Due to the relatively poor solubility of the [G3]-heneicos(sulfone) **10** in $CDCl_3$, the aliphatic ^1H NMR signals were partly masked by the residue water signal in the solvent. Therefore, accurate integration values in this region could not be obtained but its layered structure could be clearly revealed by examining the ^1H NMR signals in the aromatic region. Furthermore, the conversion of all the sulfide moieties to the corresponding sulfone groups could be confirmed from MALDI-TOF MS analysis. In all cases, the molecular ion found was due to the $(M + Ag)^+$ species. We could not identify any mass peaks with *m*/*z* value of $(M - 16)^+$, $(M - 32)^+$, or $(M - 48)^+$ that were due to the incompletely oxidized sulfoxide species (Figure 3). The structural purity of the [G1] to [G3]-oligo(sulfone)s was also examined by SEC analysis. In all cases, a major peak was identified in the SEC chromatogram although it was slightly broaden as compared to that of the corresponding oligo(sulfide) analogue.

Dendrimer Metamorphosis−Synthesis of Oligo(phenylenevinylene) Dendrimers. The [G1]-tri(sulfone) **6** was then

(23) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 1287−1290.
(24) Linear poly(sulfone)s were reported to be highly crystalline and possess poor solubility, see: (a) Macro, C.; Bello, A.; Pereña, J. M.; Fatou, J. G. *Macromolecules* **1983**, *16*, 95−99. (b) Lee, J.-C.; Litt, M. H.; Rogers, C. E. *Macromolecules* **1997**, *30*, 3766−3774.

Scheme 3. Synthesis of [G3]-Dendrons and [G3]-Heneicos(sulfide) Dendrimer **11**[a]



[a] (i) NaOMe, MeOH, THF, 25 °C, 5 min; (ii) methyl 3,5-bis(bromomethyl)benzoate (0.5 equiv), MeOH, THF, 25 °C, 1 h; (iii) $LiAlH_4$, THF, 0−25 °C, 1 h; (iv) CH_3COSH, DIAD, PPh_3, THF, 0−25 °C, 2 h; (v) 1,3,5-tris(bromomethyl)benzene (0.3 equiv), MeOH, THF, 25 °C, 1 h.

Table 1. Selected ^{1}H NMR Chemical Shift Values of Oligo(sulfide) Dendrimers **8**, **9**, and **11**[a,b]

dendrimer	core Ar*H*	intermediate Ar*H*	surface Ar*H*	$-CH_2SCH_2-$
[G1]-tri(sulfide) **8**	7.13 (3)	−	6.93 (6), 6.88 (3)	3.59 (6), 3.57 (6)
[G2]-nona(sulfide) **9**	7.11 (3)	7.17 (9)	6.95 (12), 6.90 (6)	3.60 (18), 3.58 (18)
[G3]-heneicos(sulfide) **11**	7.12 (3)	7.16 (9), 7.13 (12), 7.07 (6)	6.91 (24), 6.86 (12)	3.58 (12), 3.56 (48), 3.54 (24)

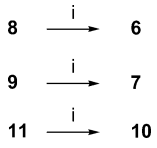
[a] In $CDCl_3$. [b] Number in parentheses indicates number of protons.

Table 2. Selected ^{1}H NMR Chemical Shift Values of Oligo(sulfone) Dendrimers **6**, **7**, and **10**[a,b]

dendrimer	core Ar*H*	intermediate Ar*H*	surface Ar*H*	$-CH_2SO_2CH_2-$
[G1]-tri(sulfone) **6**	7.38 (3)	−	7.04 (9)	4.16 (6), 4.08 (6)
[G2]-nona(sulfone) **7**	7.35 (3)	7.83 (6), 7.81 (3)	7.07 (12), 7.04 (6)	4.31 (12), 4.28 (6), 4.19 (18)
[G3]-heneicos(sulfone) **10**	7.32 (3)	7.86 (3), 7.71 (6), 7.69 (12), 7.32 (6)	7.04 (24), 7.01 (12)	4.42 (6), 4.37 (6), 4.23 (24), 4.19 (24), 4.16 (24)

[a] In $CDCl_3$. [b] Number in parentheses indicates number of protons.

Scheme 4. Interior Functional Group Conversions[a]



[a] (i) 35% H_2O_2, HOAc, CH_2Cl_2, 40 °C, 6 h.

subjected the RB rearrangement reaction using Chan's modified conditions (KOH/Al_2O_3, CBr_2F_2) in *t*-BuOH.[15] However, the reaction was too slow and sluggish. After several experimentations, it was found that a mixture of THF and *t*-BuOH was a better solvent system for the reaction as the oligo(sulfone) dendrimers were found to have slightly better solubility (Scheme 5). Under the new conditions, rearrangements of all three sulfone moieties proceeded smoothly even at −45 °C. The reaction was found to complete in 10 min and the all (*E*)-[G1]-tri(phenylenevinylene) dendrimer **4** could be isolated in 91% yield. The (*E*)-configuration of the newly formed double bonds was confirmed by the large coupling constant ($J = 16.5$ Hz) between the olefinic protons in its ^{1}H NMR spectrum. There were no other isomeric products found according to ^{1}H NMR analysis. The high (*E*)-stereoselectivity of the modified RB reaction was consistent with those observed for primary dibenzylic sulfones reported earlier.[15]

Reaction of the [G2]-nona(sulfone) **7** under similar conditions afforded the corresponding [G2]-nona(phenylenevinylene) dendrimer **5** (72% yield) at −45 °C. To our surprise, the C=C bonds formed are of both (*E*)- and (*Z*)-configurations. Hence, the (*E*)-stereoselectivity of the RB reaction decreased in the case of the G2 dendrimer. Nonetheless, the all (*E*)-[G2]-nona(phenylenevinylene) isomer **5** could be isolated as the major product in 48% yield after careful silica gel chromatography. The (*E*)- and (*Z*)-percentage distributions of the remaining mixture (24%) of isomers could not be ascertained from ^{1}H NMR spectroscopy. Since there are nine independent RB rearrangements on this molecule, the conversion efficiency of each RB rearrangement is therefore 96%. This value is and has to be extremely high in order to produce the target dendrimer in good yields, as one single failure out of the nine rearrangements would completely ruin the dendrimer metamorphosis process. Both the pure all (*E*)-isomer **5** and the geometrical mixtures could be separately converted to the same saturated [G2]-nona(phenyleneethylene) dendrimer **25** in 78% and 82% yield, respectively, by catalytic hydrogenation (10% Pd/C, CH_2Cl_2, EtOH).

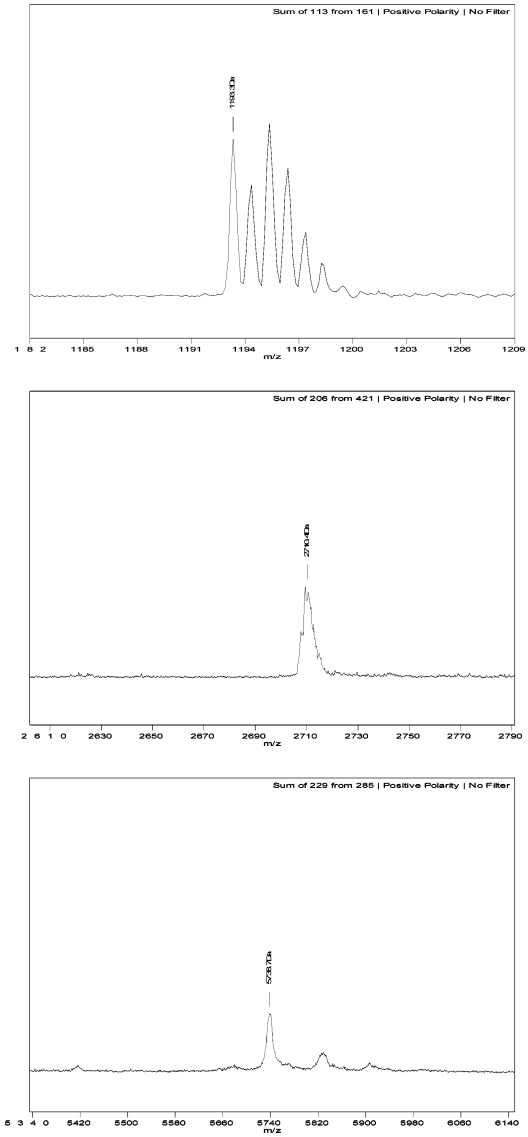
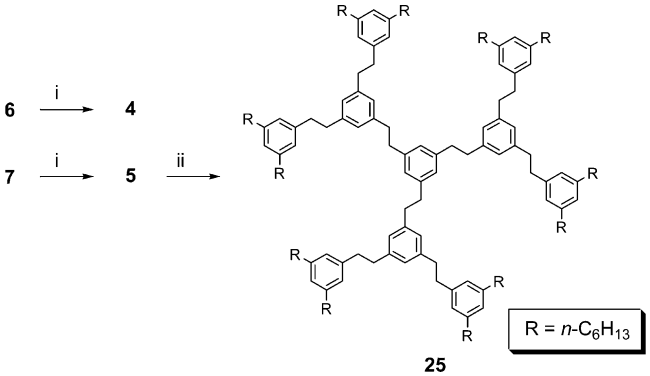


Figure 3. MALDI-TOF mass spectra of oligo(sulfone) dendrimers [G1] **6** (top), [G2] **7** (middle), and [G3] **10** (bottom).

Scheme 5. Dendrimer Metamorphosis[a]



[a] (i) KOH/Al_2O_3, CBr_2F_2, THF, *t*-BuOH, −45 °C, 10 min; (ii) H_2, 10% Pd/C, CH_2Cl_2, EtOH, 25 °C, 48 h.

Rearrangement of the [G3]-heneicos(sulfone) **10** under similar reaction conditions, however, failed to produce the target [G3]-heneicos(phenylenevinylene). TLC analysis of the crude reaction suggested the formation of many inseparable reaction products. Further examination by ^{1}H NMR spectroscopy revealed the presence of residual benzylic protons at ~δ 4.1−4.3, indicating that some of the sulfone groups remained unreacted. The ^{1}H NMR signals in the aromatic and olefinic regions (δ 7.8−6.7) were very broad and complex, suggesting the C═C bonds formed were of both (*E*)- and (*Z*)-configurations. Hence, the products were a mixture of partially converted RB reaction products that still contained some unreacted dibenzylic sulfone moieties. However, no further transformations took place even when the crude product was re-subjected to the same RB rearrangement conditions. Despite numerous attempts by changing the reagents, the reaction solvents and temperature, a complex mixture of similar ^{1}H NMR signal profile was always formed.

We believed the failure to effect the dendrimer metamorphosis with the [G3]-heneicos(sulfone) **10** was attributed to both steric shielding and the heterogeneous reaction conditions. Since potassium hydroxide was impregnated on alumina and had a limited solubility in THF/*t*-BuOH, therefore the interior sulfone moieties may have difficulty in undergoing deprotonation to initiate the first step of the RB rearrangement. Furthermore, once the sulfone moieties near the dendrimer surface have been converted into the corresponding stilbene functionalities, the dendrimer skeleton will become more compact as the dendrimer branch has now changed from a three-atom to a two-atom spacer. This could lead to the encapsulation of the interior sulfone moieties and prevented them from reactions. It should be pointed out that the rearrangement reactions involving all 21 sulfone moieties were very similar to those reactions in the divergent dendrimer synthetic approach; both of which required a large number of reactions to take place on a molecular species. The results of Meijer's work on the synthesis of poly(propylene imine) dendrimers had already illustrated that even with highly optimized reaction conditions, the production of defect-free products was impossible to achieve by the divergent synthetic procedure.[25] An additional complicated factor in our situation was that the rearrangement reactions had to take place not on the periphery, but inside the interior of the dendrimer, and was therefore sterically more demanding than the divergent growth on a dendrimer surface.

Experimental Section

Materials and General Methods. Melting points were determined on an Electrothermal IA9000 apparatus and were uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Brüker Avance DPX300 spectrometer (^{1}H: 300 MHz; ^{13}C: 75.5 MHz) in $CDCl_3$. Mass spectra were obtained on a HP 5989 mass spectrometer by electron ionization (EI) or a home-built time-lag focusing matrix-assisted laser desorption ionization (MALDI) mass spectrometer. Saturated $AgNO_3$/EtOH was added as the cationization reagent. The reported molecular mass (*m*/*z*) values were the most abundant monoisotopic mass. UV spectra were recorded on a Hitachi U-3300 spectrophotomer at 27 °C using spectroscopic grade $CHCl_3$ as the solvent. SEC (Waters Styragel HR4, HR3, HR2, and HR1 columns in series) measurements were carried out in THF at 40 °C on a Waters HPLC 510 pump equipped with a Waters 486 tunable UV absorbance detector. Elemental analyses were carried out either at MEDAC Ltd., UK, or at Shanghai Institute of Organic Chemistry, China. All reagents were purchased from commercial suppliers (Acros or Aldrich) and used without further purification. All reactions were performed under N_2 atmosphere unless otherwise noted. Thin-layer chromatography (TLC) was performed on

(25) Hummelen, J. C.; van Dongen, J. L. J.; Meijer, E. W. *Chem. Eur. J.* **1997**, *3*, 1489−1493.

silica gel sheets 60 F_{254} (E. Merck). Flash chromatography was performed on silica gel (Macherey Nagel Kieselgel 60M 230−400 mesh).

Methyl 3,5-Di-(hex-1-ynyl)benzoate (15). A mixture of methyl 3,5-dibromobenzoate (7.35 g, 25 mmol), 1-hexyne (11.0 mL, 100 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.40 g, 2.0 mmol), copper(I) iodide (0.19 g, 1.0 mmol), and triethylamine (20 mL) in dry benzene (80 mL) was heated at 80 °C for 48 h. The mixture was filtered through a short pad of silica gel and washed with ethyl acetate (200 mL). The solvent was concentrated in vacuo and the residue chromatographed on silica gel (hexane/CH_2Cl_2 = 8/1) to give compound **15** (6.30 g, 85%) as a yellow oil; R_f 0.25 (hexane/CH_2Cl_2 = 8/1); ^{1}H NMR: 7.92 (d, J = 1.5 Hz, 2 H), 7.56 (t, J = 1.5 Hz, 1 H), 3.89 (s, 3 H), 2.39 (t, J = 6.6 Hz, 4 H), 1.60−1.40 (m, 8 H), 0.94 (t, J = 7.2 Hz, 6 H); ^{13}C NMR: 166.0, 138.4, 131.4, 130.3, 124.6, 91.8, 79.1, 52.2, 30.6, 21.9, 19.0, 13.6; MS (EI, *m*/*z*): 296 (M^+, 64%). Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.98; H, 7.98.

Methyl 3,5-Di-(*n*-hexyl)benzoate (16). A mixture of compound **15** (6.30 g, 21 mmol) and 10% Pd/C (1.0 g) in absolute EtOH (60 mL) was stirred under hydrogen at atmospheric pressure at 25 °C. After 18 h, the mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo and the residue chromatographed on silica gel (hexane/EtOAc = 15/1) to give compound **16** (6.13 g, 95%) as a colorless oil; R_f 0.57 (hexane/EtOAc = 10/1); ^{1}H NMR: 7.68 (s, 2 H), 7.18 (s, 1 H), 3.90 (s, 3 H), 2.62 (t, J = 8.2 Hz, 4 H), 1.70−1.55 (m, 4 H), 1.40−1.25 (m, 12 H), 0.88 (t, J = 6.6 Hz, 6 H); ^{13}C NMR: 167.4, 143.0, 133.2, 129.9, 126.8, 51.8, 35.7, 31.6, 31.3, 28.9, 22.5, 14.0; MS (EI, *m*/*z*): 305 ($M + H^+$, 100%). Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.95; H, 10.47.

General Procedure for the Synthesis of Benzyl Alcohols [Gn]-CH_2OH (n = 1−3). Powdered lithium aluminum hydride (1.1 mol. equiv) was added in small portions to a solution the dendritic methyl ester [Gn]-CO_2Me (1.0 mol. equiv) in dry THF at 0 °C. The mixture was allowed to stir at 25 °C. The reaction progress was monitored by TLC until all the starting material disappeared (∼1 h). The excess hydride was quenched by the addition of ice water. The product was extracted with ethyl acetate and dried ($MgSO_4$). The organic solvent was filtered and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/EtOAc = 15/1) to give the target compound.

[G1]-CH_2OH (17). Starting from [G1]-CO_2Me **16** (6.00 g, 19.7 mmol), compound [G1]-CH_2OH **17** (5.18 g, 95%) was obtained as a colorless oil; R_f 0.31 (hexane/EtOAc = 6/1); ^{1}H NMR: 7.02 (s, 2 H), 6.96 (s, 1 H), 4.63 (d, J = 5.7 Hz, 2 H), 2.61 (t, J = 7.5 Hz, 4 H), 2.13 (t, J = 5.7 Hz, 1 H), 1.70−1.55 (m, 4 H), 1.45−1.27 (m, 12 H), 0.93 (t, J = 6.6 Hz, 6 H); ^{13}C NMR: 143.1, 140.7, 127.8, 124.3, 65.4, 35.9, 31.7, 31.5, 29.1, 22.6, 14.1; MS (EI, *m*/*z*): 276 (M^+, 58%). Anal. Calcd for $C_{19}H_{32}O$: C, 82.55; H, 11.67. Found: C, 82.48; H, 11.56.

[G2]-CH_2OH (20). Starting from [G2]-CO_2Me **19** (4.84 g, 6.5 mmol), compound [G2]-CH_2OH **20** (4.42 g, 93%) was obtained as a colorless oil; R_f 0.25 (hexane/EtOAc = 6/1); ^{1}H NMR: 7.17 (s, 3 H), 6.93 (s, 4 H), 6.89 (s, 2 H), 4.67 (s, 2 H), 3.61 (s, 4 H), 3.59 (s, 4 H), 2.57 (t, J = 7.8 Hz, 8 H), 1.70 (s, 1 H), 1.68−1.52 (m, 8 H), 1.42−1.23 (m, 24 H), 0.90 (t, J = 6.6 Hz, 12 H); ^{13}C NMR: 143.0, 141.3, 138.9, 137.5, 128.9, 127.3, 126.4, 126.1, 65.1, 35.91, 35.86, 35.6, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time: 34.11 min; MS (MALDI-TOF, *m*/*z*): 823.4 ($M + Ag^+$). Anal. Calcd for $C_{47}H_{72}OS_2$: C, 78.71; H, 10.12. Found: C, 78.62; H, 10.47.

[G3]-CH_2OH (23). Starting from [G3]-CO_2Me **22** (2.77 g, 1.7 mmol), compound [G3]-CH_2OH **23** (2.58 g, 87%) was obtained as a colorless oil; R_f 0.22 (hexane/EtOAc = 6/1); ^{1}H NMR: 7.23 (s, 1 H), 7.14 (s, 6 H), 7.12 (s, 2 H), 6.95 (s, 8 H), 6.91 (s, 4 H), 4.63 (s, 2 H), 3.61 (s, 8 H), 3.60 (s, 16 H), 2.58 (t, J = 7.8 Hz, 16 H), 1.92 (s, 1 H), 1.70−1.54 (m, 16 H), 1.42−1.25 (m, 48 H), 0.91 (t, J = 6.7 Hz, 24 H); ^{13}C NMR: 143.0, 141.5, 138.7, 138.6, 138.4, 137.5, 128.8, 128.4, 128.3, 127.3, 126.4, 126.3, 64.8, 35.8, 35.5, 35.4, 35.3, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time: 32.15 min. Anal. Calcd for $C_{103}H_{152}OS_6$: C, 77.38; H, 9.58. Found: C, 77.65; H, 9.43.

General Procedure for the Synthesis of Dendritic Thiolacetates [Gn]-CH_2SAc (n = 1−3). DIAD (2.0 mol. equiv) was added to a solution of triphenylphosphine (2.0 mol. equiv) in dry THF at 0 °C. After 10 min, a solution of the dendritic alcohol [Gn]-CH_2OH (1.0 mol. equiv) and thiolacetic acid (2.0 mol. equiv) in dry THF was then added and the reaction mixture was stirred at 25 °C for 2 h. Hexane was added to precipitate the triphenylphosphine oxide formed. The reaction mixture was filtered through a short pad of silica gel and the filtrate was concentrated in vacuo. The crude product was purified by silica gel chromatography (hexane/EtOAc = 30/1) to afford the desired product.

[G1]-CH_2SAc (12). Starting from [G1]-CH_2OH **17** (5.10 g, 18.4 mmol), [G1]-CH_2SAc **12** (5.86 g, 87%) was obtained as a colorless oil; R_f 0.75 (hexane/EtOAc = 10/1); ^{1}H NMR: 6.93 (s, 2 H), 6.90 (s, 1 H), 4.11 (s, 2 H), 2.57 (t, J = 7.7 Hz, 4 H), 2.37 (s, 3 H), 1.68−1.50 (m, 4 H), 1.40−1.25 (m, 12 H), 0.92 (t, J = 6.5 Hz, 6 H); ^{13}C NMR: 195.2, 143.2, 137.0, 127.6, 126.1, 35.8, 33.5, 31.7, 31.4, 30.2, 29.0, 22.6, 14.1; MS (EI, *m*/*z*): 335 (M^+, 22%). Anal. Calcd for $C_{21}H_{34}OS$: C, 75.39; H, 10.24. Found: C, 75.49; H, 10.48.

[G2]-CH_2SAc (21). Starting from [G2]-CH_2OH **20** (4.40 g, 6.1 mmol), [G2]-CH_2SAc **21** (3.97 g, 83%) was obtained as a colorless oil; R_f 0.70 (hexane/EtOAc = 10/1); ^{1}H NMR: 7.15 (s, 1 H), 7.10 (s, 2 H), 6.94 (s, 4 H), 6.90 (s, 2 H), 4.11 (s, 2 H), 3.58 (s, 8 H), 2.58 (t, J = 7.7 Hz, 8 H), 2.37 (s, 3 H), 1.70−1.55 (m, 8 H), 1.40−1.25 (m, 24 H), 0.90 (t, J = 6.6 Hz, 12 H); ^{13}C NMR: 194.8, 143.0, 139.0, 137.7, 137.6, 128.6, 128.0, 127.3, 126.4, 35.9, 35.8, 35.4, 33.3, 31.7, 31.5, 30.3, 29.1, 22.6, 14.1; SEC retention time: 34.14 min; MS (MALDI-TOF, *m*/*z*): 881.4 ($M + Ag^+$). Anal. Calcd for $C_{49}H_{74}OS_3$: C, 75.91; H, 9.62. Found: C, 75.86; H, 9.86.

[G3]-CH_2SAc (24). Starting from [G3]-CH_2OH **23** (2.50 g, 1.56 mmol), the [G3]-CH_2SAc **24** (1.96 g, 76%) was obtained as a colorless oil; R_f 0.71 (hexane/EtOAc = 10/1); ^{1}H NMR: 7.16 (s, 1 H), 7.12 (s, 4 H), 7.10 (s, 2 H), 7.08 (s, 2 H), 6.92 (s, 8 H), 6.87 (s, 4 H), 4.08 (s, 2 H), 3.59 (s, 8 H), 3.57 (s, 8 H), 3.56 (s, 4 H), 3.54 (s, 4 H), 2.55 (t, J = 7.8 Hz, 16 H), 2.32 (s, 3 H), 1.68−1.50 (m, 16 H), 1.40−1.22 (m, 48 H), 0.88 (t, J = 6.6 Hz, 24 H); ^{13}C NMR: 194.9, 143.0, 138.81, 138.76, 138.4, 138.0, 137.5, 128.7, 128.5, 128.4, 128.2, 127.3, 126.4, 35.9, 35.8, 35.5, 35.4, 35.3, 33.2, 31.7, 31.5, 30.3, 29.1, 22.6, 14.1; SEC retention time: 32.08 min; MS (MALDI-TOF, *m*/*z*): 1761.5 ($M + Ag^+$). Anal. Calcd for $C_{105}H_{154}OS_7$: C, 76.12; H, 9.37. Found: C, 75.76; H, 9.33.

General Procedure for the Synthesis of Dendritic Methyl Ester [Gn]-CO_2Me (n = 2 and 3). Powdered sodium methoxide (2.4 mol. equiv) was added in one portion to a stirred solution of the thiolacetate [Gn]-CH_2SAc (2.2 mol. equiv) in THF/CH_3OH (v/v = 1/1) at 25 °C. After 5 min, methyl 3,5-bis(bromomethyl)benzoate **14** (1.0 mol. equiv) in dry THF was added and the mixture was stirred for 1 h. The mixture was concentrated and the residue was extracted with EtOAc. The extracts were dried ($MgSO_4$), filtered and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography (hexane/EtOAc = 30/1) to give the target compound.

[G2]-CO_2Me (19). Starting from [G1]-CH_2SAc **12** (5.80 g, 17.3 mmol), [G2]-CO_2Me **19** (5.30 g, 92%) was isolated as a colorless oil; R_f 0.52 (hexane/EtOAc = 10/1); ^{1}H NMR: 7.86 (s, 2 H), 7.46 (s, 1 H), 6.93 (s, 4 H), 6.90 (s, 2 H), 3.94 (s, 3 H), 3.63 (s, 4 H), 3.57 (s, 4 H), 2.57 (t, J = 7.1 Hz, 8 H), 1.70−1.52 (m, 8 H), 1.42−1.25 (m, 24 H), 0.90 (t, J = 6.6 Hz, 12 H); ^{13}C NMR: 166.6, 143.0, 139.1, 137.3, 134.0, 130.4, 128.7, 127.3, 126.3, 52.0, 35.8, 35.7, 35.1, 31.7, 31.4, 29.0, 22.6, 14.1; SEC retention time: 34.21 min; MS (MALDI-TOF, *m*/*z*): 851.2 ($M + Ag^+$). Anal. Calcd for $C_{48}H_{72}O_2S_2$: C, 77.36; H, 9.74. Found: C, 77.21; H, 9.96.

[G3]-CO_2Me (22). Starting from [G2]-CH_2SAc **21** (3.80 g, 4.9 mmol), [G3]-CO_2Me **22** (2.82 g, 78%) was obtained as a colorless oil; R_f 0.49 (hexane/EtOAc = 10/1); ^{1}H NMR: 7.83 (s, 2 H), 7.46 (s, 1

H), 7.10 (s, 6 H), 6.91 (s, 8 H), 6.86 (s, 4 H), 3.87 (s, 3 H), 3.59 (s, 4 H), 3.58 (s, 8 H), 3.55 (s, 12 H), 2.54 (t, $J = 7.2$ Hz, 16 H), 1.67−1.48 (m, 16 H), 1.40−1.20 (m, 48 H), 0.87 (t, $J = 6.6$ Hz, 24 H); ^{13}C NMR: 166.6, 143.0, 138.9, 138.8, 138.1, 137.5, 134.2, 130.5, 128.9, 128.5, 128.3, 127.3, 126.4, 52.1, 35.9, 35.8, 35.5, 35.1, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time: 32.10 min; MS (MALDI-TOF, *m*/*z*): 1734.4 ($M + Ag^+$). Anal. Calcd for $C_{104}H_{152}O_2S_6$: C, 76.79; H, 9.42. Found: C, 77.04; H, 9.50.

General Procedure for the Synthesis of [Gn]-Oligo(sulfide) Dendrimers ($n = 1-3$). Powdered sodium methoxide (1.1 mol. equiv) was added in one portion to a stirred solution of the thiolacetate [Gn]-CH_2SAc (1.0 mol. equiv) in THF/CH_3OH (1/1) at 25 °C. After 5 min, a solution of 1,3,5-tris(bromomethyl)benzene **13** (0.3 mol. equiv) in dry THF was added and the mixture was stirred at 25 °C for 1 h. The mixture was concentrated under reduced pressure and the residue was diluted with water and extracted with EtOAc. The combined extracts were dried ($MgSO_4$), filtered and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography (hexane/EtOAc = 20/1) to give the target compound.

[G1]-Tri(sulfide) (8). Starting from [G1]-CH_2SAc **12** (2.00 g, 6.0 mmol), [G1]-tri(sulfide) **8** (1.48 g, 83%) was isolated as a colorless oil; R_f 0.76 (hexane/EtOAc = 15/1); ^{1}H NMR: 7.13 (s, 3 H), 6.93 (s, 6 H), 6.88 (s, 3 H), 3.59 (s, 6 H), 3.57 (s, 6 H), 2.58 (t, $J = 7.8$ Hz, 12 H), 1.70−1.50 (m, 12 H), 1.40−1.25 (m, 36 H), 0.91 (t, $J = 6.6$ Hz, 18 H); ^{13}C NMR: 143.0, 138.7, 137.5, 128.3, 127.3, 126.4, 35.9, 35.7, 35.5, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time: 33.05 min; MS (MALDI-TOF, *m*/*z*): 1097.5 ($M + Ag^+$). Anal. Calcd for $C_{66}H_{102}S_3$: C, 79.94; H, 10.37. Found: C, 79.66; H, 10.14.

[G2]-Nona(sulfide) (9). Starting from [G2]-CH_2SAc **21** (1.50 g, 1.94 mmol), [G2]-nona(sulfide) **9** (1.05 g, 78%) was obtained as a colorless oil; R_f 0.69 (hexane/EtOAc = 15/1); ^{1}H NMR: 7.17 (s, 9 H), 7.11 (s, 3 H), 6.95 (s, 12 H), 6.90 (s, 6 H), 3.60 (s, 18 H), 3.58 (s, 18 H), 2.57 (t, $J = 7.8$ Hz, 24 H), 1.70−1.52 (m, 24 H), 1.42−1.23 (m, 72 H), 0.90 (t, $J = 6.6$ Hz, 36 H); ^{13}C NMR: 143.0, 138.7, 138.5, 138.4, 137.5, 128.5, 128.4, 128.3, 127.3, 126.4, 35.9, 35.54, 35.46, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time: 31.03 min; MS (MALDI-TOF, *m*/*z*): 2421.3 ($M + Ag^+$). Anal. Calcd for $C_{150}H_{222}S_9$: C, 77.86; H, 9.67. Found: C, 77.60; H, 9.51.

[G3]-Heneicos(sulfide) (11). Starting from [G3]-CH_2SAc **24** (0.20 g, 0.12 mmol), [G3]-heneicos(sulfide) **11** (0.12 g, 66%) was obtained as a colorless oil; R_f 0.67 (hexane/EtOAc = 15/1); ^{1}H NMR: 7.16 (s, 9 H), 7.13 (s, 12 H), 7.12 (s, 3 H), 7.07 (s, 6 H), 6.91 (s, 24 H), 6.86 (s, 12 H), 3.58 (s, 12 H), 3.56 (s, 48 H), 3.54 (s, 24 H), 2.53 (t, $J = 7.7$ Hz, 48 H), 1.70−1.50 (m, 48 H), 1.40−1.20 (m, 144 H), 0.87 (t, $J = 6.6$ Hz, 72 H); ^{13}C NMR: 143.0, 138.7, 138.63, 138.60, 138.53, 138.47, 137.5, 128.6, 128.5, 128.3, 127.3, 126.4, 35.9, 35.7, 35.6, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time: 29.52 min; MS (MALDI-TOF, *m*/*z*): 5064.4 ($M + Ag^+$). Anal. Calcd for $C_{318}H_{462}S_{21}$: C, 77.03; H, 9.39. Found: C, 77.04; H, 9.58

General Procedure for the Synthesis of [Gn]-Oligo(sulfone) Dendrimers from [Gn]-Oligo(sulfide) Dendrimers ($n = 1-3$). A mixture of the [Gn]-oligo(sulfide) dendrimer and 35% hydrogen peroxide (10 mol. equiv per sulfide) in CH_2Cl_2/HOAc (10/1) was refluxed for 6 h. The solvent was removed under reduced pressure and the residue was precipitated with ice water. The solid was collected, redissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$ solution. The organic solvents were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude product was purified as described in the following text.

[G1]-Tri(sulfone) (6). Starting from [G1]-tri(sulfide) **8** (1.30 g, 1.3 mmol) and after purification of the crude product by silica gel chromatography (CH_2Cl_2/EtOAc = 30/1), [G1]-tri(sulfone) **6** (1.35 g, 95%) was obtained as a white solid; mp 103−105 °C; ^{1}H NMR: 7.38 (s, 3 H), 7.04 (s, 9 H), 4.16 (s, 6 H), 4.08 (s, 6 H), 2.59 (t, $J = 7.7$ Hz, 12 H), 1.70−1.50 (m, 12 H), 1.40−1.22 (m, 36 H), 0.88 (t, $J = 6.6$ Hz, 18 H); ^{13}C NMR: 143.9, 134.1, 129.5, 128.7, 128.1, 127.0, 59.2, 56.8, 35.8, 31.7, 31.4, 29.1, 22.6, 14.1; SEC retention time: 32.70 min; MS (MALDI-TOF, *m*/*z*): 1193.3 ($M + Ag^+$). Anal. Calcd for $C_{66}H_{102}O_6S_3$: C, 72.88; H, 10.14. Found: C, 73.01; H, 9.41.

[G2]-Nona(sulfone) (7). Starting from [G2]-nona(sulfide) **9** (1.00 g, 0.43 mmol), the crude product was purified by dissolving in CH_2Cl_2 and precipitated by the addition of MeOH to afford the title compound **7** (0.72 g, 64%) as a white solid; mp 181−183 °C; ^{1}H NMR: 7.83 (s, 6 H), 7.81 (s, 3 H), 7.35 (s, 3 H), 7.07 (s, 12 H), 7.04 (s, 6 H), 4.31 (s, 12 H), 4.28 (s, 6 H), 4.19 (s, 18 H), 2.59 (t, $J = 7.7$ Hz, 24 H), 1.68−1.48 (m, 24 H), 1.40−1.20 (m, 72 H), 0.87 (t, $J = 6.7$ Hz, 36 H); ^{13}C NMR ($CDCl_3$): 143.9, 134.7, 134.5, 130.1, 129.5, 129.3, 128.5, 128.1, 127.2, 60.1, 56.9, 56.3, 55.6, 35.7, 31.7, 31.4, 29.0, 22.6, 14.1; SEC retention time: 31.09 min; MS (MALDI-TOF, *m*/*z*): 2710.4 ($M + Ag^+$). Anal. Calcd for $C_{150}H_{222}O_{18}S_9$: C, 69.24; H, 8.60. Found: C, 68.97; H, 8.71.

[G3]-Heneicos(sulfone) (10). Starting from [G3]-heneicos(sulfide) **11** (120 mg, 0.02 mmol), the crude product was purified by dissolving in CH_2Cl_2 and precipitated by addition of MeOH to give the title compound **10** (70 mg, 51%) as a white solid; mp 188−190 °C; ^{1}H NMR: 7.86 (s, 3 H), 7.71 (s, 6 H), 7.69 (s, 12 H), 7.32 (s, 9 H), 7.04 (s, 24 H), 7.01 (s, 12 H), 4.42 (s, 6 H), 4.37 (s, 6 H), 4.23 (s, 24 H), 4.19 (s, 24 H), 4.16 (s, 24 H), 2.56 (t, $J = 7.8$, 48 H), 1.68−1.48 (m, 48 H), 1.40−1.20 (m, 144 H), 0.86 (t, $J = 6.7$ Hz, 72 H); ^{13}C NMR: 143.84, 143.77, 143.7, 134.5, 134.3, 129.9, 129.7, 129.6, 129.4, 129.3, 128.8, 128.2, 127.1, 59.6, 56.9, 56.6, 56.2, 35.7, 31.9, 31.7, 31.4, 29.7, 29.3, 29.2, 29.0, 22.6, 14.1; SEC retention time: 29.57 min; MS (MALDI-TOF, *m*/*z*): 5738.7 ($M + Ag^+$). Anal. Calcd for $C_{318}H_{462}O_{42}S_{21}$: C, 67.84; H, 8.27; Found: C, 67.48; H, 8.37.

General Procedure for the Synthesis of [Gn]-Oligo(phenylenevinylene) Dendrimers by the Ramberg−Bäcklund Rearrangement of [Gn]-Oligo(sulfone) Dendrimers ($n = 1$ and 2). Finely divided KOH/Al_2O_3 was added to a rapidly stirred solution of the [Gn]-oligo(sulfone) dendrimer in THF/*t*-BuOH/CBr_2F_2 (1/1/1) at −45 °C. After 10 min, the mixture was filtered through a pad of Celite and washed with CH_2Cl_2. The filtrate was evaporated under reduced pressure to give the crude product that was further purified by silica gel chromatography (hexane/CH_2Cl_2 = 50/1).

[G1]-Tri(phenylenevinylene) Dendrimer (4). Starting from [G1]-tri(sulfone) **6** (1.20 g, 1.1 mmol), the desired [G1]-tri(phenylenevinylene) dendrimer **4** was obtained (0.89 g, 91%) as a white solid: mp 61−63 °C; R_f 0.77 (hexane/CH_2Cl_2 = 8/1); ^{1}H NMR: 7.57 (s, 3 H), 7.22 (s, 6 H), 7.20 (d, $J = 16.5$ Hz, 3 H), 7.16 (d, $J = 16.5$ Hz, 3 H), 6.95 (s, 3 H), 2.64 (t, $J = 7.8$ Hz, 12 H), 1.75−1.60 (m, 12 H), 1.47−1.30 (m, 36 H), 0.92 (t, $J = 6.6$ Hz, 18 H); ^{13}C NMR: 143.2, 138.2, 137.0, 129.6, 128.3, 127.9, 124.1, 123.7, 36.0, 31.8, 31.5, 29.1, 22.6, 14.1; UV (λ_{max}, log ϵ): 320 nm (5.6); SEC retention time: 32.69 min; MS (MALDI-TOF, *m*/*z*): 889.2 ($M + H^+$). Anal. Calcd for $C_{66}H_{96}$: C, 89.12; H, 10.88. Found: C, 89.06; H, 10.79.

[G2]-Nona(phenylenevinylene) Dendrimer (5). Starting from [G2]-nona(sulfone) **7** (0.70 g, 0.27 mmol), a mixture of (*E*)- and (*Z*)-configurated [G2]-nona(phenylenevinylene) dendrimers (0.39 g, 72%) was isolated as an oil. The all (*E*)-isomer **5** (0.26 g, 48%) could be isolated as an oil by careful silica gel chromatography; R_f 0.30 (hexane/CH_2Cl_2 = 8/1); ^{1}H NMR: 7.67 (s, 3 H), 7.62 (s, 9 H), 7.30 (s, 6 H), 7.22 (s, 12 H), 7.17 (d, $J = 16.5$ Hz, 6 H), 7.18 (d, $J = 16.5$ Hz, 6 H), 6.95 (s, 6 H), 2.63 (t, $J = 7.7$ Hz, 24 H), 1.70−1.55 (m, 24 H), 1.47−1.25 (m, 72 H), 0.90 (t, $J = 6.6$ Hz, 36 H); ^{13}C NMR: 143.3, 138.3, 138.1, 137.8, 137.0, 129.7, 129.2, 128.8, 128.4, 127.8, 124.1, 123.9, 36.0, 31.8, 31.5, 29.1, 22.6, 14.1; UV (λ_{max}, log ϵ): 322 nm (5.9); SEC retention time: 30.63 min; MS (MALDI-TOF, *m*/*z*): 2007.1 (M^+). Anal. Calcd for $C_{150}H_{204}$: C, 89.76; H, 10.24. Found: C, 89.40; H, 10.19.

[G2]-Nona(phenyleneethylene) Dendrimer (25). A geometrical mixture of the [G2]-nona(phenylenevinylene) dendrimer **5** (0.20 g, 0.10 mmol) in CH_2Cl_2/EtOH (v/v = 1/1) and 10% Pd/C was stirred under hydrogen at atmosphere pressure at 25 °C. After 48 h, the mixture was

filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/CH_2Cl_2 = 30/1) to give the target compound **30** (0.17 g, 82%) as a colorless oil; R_f 0.42 (hexane/CH_2Cl_2 = 8/1); ^{1}H NMR: 7.00 (s, 3 H), 6.95 (s, 6 H), 6.93 (s, 3 H), 6.87 (s, 18 H), 2.90 (s, 12 H), 2.86 (s, 24 H), 2.56 (t, J = 7.8 Hz, 24 H), 1.68−1.53 (m, 24 H), 1.40−1.20 (m, 72 H), 0.89 (t, J = 6.8 Hz, 36 H); ^{13}C NMR: 142.9, 142.3, 142.2, 142.1, 141.8, 126.2, 126.13, 126.08, 125.8, 38.33, 38.25, 36.0, 31.7, 31.6, 29.2, 22.6, 14.1; SEC retention time: 31.21 min; MS (MALDI-TOF, m/z): 2134.4 ($M + Ag^+$). Anal. Calcd for $C_{150}H_{222}$: C, 88.95; H, 11.05. Found: C, 89.00; H, 10.78. The all (*E*)-[G2]-nona-(phenylenevinylene) dendrimer **5** could also be similarly converted to same compound **25** in 78% yield.

Conclusions

We report a new synthesis of oligo(sulfone) and oligo-(phenylenevinylene) dendrimers by the combined use of dendrimer interior functional group conversion and dendrimer metamorphosis strategies. Hence, the [G1] to [G3]-oligo(sulfide) dendrimers containing up to 21 sulfide moieties could be converted into the corresponding [G1] to [G3]-oligo(sulfone) dendrimers in good yields and purities. All the interior sulfide functionalities could be transformed into the sulfone moieties under homogeneous oxidative reaction conditions. The dendrimer interior functionalization method is best suited for the preparation of such oligo(dibenzyl sulfone) dendrimers as they are not readily accessible by either the divergent or convergent strategies. We also show here that the [G1] and [G2]-oligo-(sulfone)s could be transformed into the corresponding [G1] and [G2]-oligo(phenylenevinylene)s. An unprecedented molecular backbone transformation involving nine RB rearrangement reactions on a [G2] dendritic species was realized and the conversion efficiency of each RB rearrangement was 96%. Due to steric shielding of the reaction sites and the heterogeneous reaction conditions, such dendrimer metamorphosis failed to realize in the case of the [G3]-heneicos(phenylenevinylene) dendrimer. Nonetheless, we believe this dendrimer metamorphosis methodology could serve as an alternative dendrimer synthesis strategy when both the dendrimer steric environment and the reaction conditions are favorable.

Acknowledgment. This paper is dedicated to Dr. Tze-Lock Chan. We thank Prof. L. Li for mass spectral measurements, the Physical Science Panel, CUHK (Account No. 2060145), and an anonymous donor to the Chemistry Department for the financial support.

Supporting Information Available: Selected ^{1}H and ^{13}C NMR, mass spectra, and SEC chromatograms of all dendrons and dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

JA046557M