Polymers with Controlled Molecular Architecture: Control of Surface Functionality in the Synthesis of Dendritic Hyperbranched Macromolecules using the Convergent Approach

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The synthesis of unsymmetrically or non-uniformly surface-functionalized dendritic macromolecules using a stepwise convergent-growth approach is described. By stepwise alkylation of the monomer unit, 3,5-dihydroxybenzyl alcohol, with unsubstituted and substituted benzylic bromides, followed by activation of the group located at the focal point, dendritic 'wedges' can be obtained in which there is only a single substituent such as a cyano group at the periphery. Use of only substituted benzylic bromides in the first step of growth allows fully functionalized dendritic wedges to be obtained. Coupling to a polyfunctional core such as 1,1,1-tris-(4′-hydroxyphenyl)ethane can also be done in a stepwise manner with both mono or fully substituted and unsubstituted 'wedges' to give dendritic macromolecules containing one, two, or three cyano groups or sixteen or thirty-two bromine atoms at the periphery of the macromolecule. These hyperbranched dendritic polymers were purified by normal flash chromatography and fully characterized by a combination of spectroscopic and chromatographic techniques. By using variations of this general scheme both the number and placement of the functional groups at the periphery of the dendritic macromolecule can be accurately controlled to afford a large variety of functionalized hyperbranched moieties.

An increasingly important consideration in the synthesis of polymers is the accurate control of molecular architecture. This is a result of demands for speciality polymers with a range of new and improved properties[1] that may prove useful in a variety of technological applications. A large number of functional polymers as well as polymers with uncommon topologies have been developed; among these are the unusual class of dendritic macromolecules such as the 'Starburst' polymers.[2,3] These macromolecules are characterized by having a central polyfunctional core, from which arise successive layers of monomer units with a branch occurring at each monomer unit. This results in a nearly entanglement-free hyperbranched structure that may adopt a spherical shape, the periphery of which is made up of a large number of chain ends. A very extensive review[2] of the synthetic approaches to such dendritic structures has appeared. These approaches[2-7] all rely on the traditional divergent methodology exemplified by the 'Starburst' approach. This process involves the addition of an AB_x monomer, or equivalent, to a polyfunctional core molecule. Modification or activation of the resultant first-generation dendrimer is followed by exhaustive addition of a second layer of monomer units. Repetition of this addition–activation process allows growth to proceed outwards from the central core and results in an increasingly larger number of terminal, chain-end groups at the periphery of the macromolecule. As demonstrated in the literature,[2] this approach is very successful; however, by virtue of its divergent character, little or no control over the placement of just *one* or any limited number of reactive functionalities at the periphery of the dendritic macromolecule is possible.

We have demonstrated recently[8] a new 'convergent-growth' approach to dendritic macromolecules which is fundamentally different from the 'starburst' approach. On comparison, there are two significant differences. First, growth begins at what will become the periphery of the dendritic macromolecule, the final reaction being attachment of several large dendritic fragments or 'wedges' to a polyfunctional core. This is the reverse of the 'starburst' or divergent approach where growth starts from the core proceeding outwards. Second, each generation-growth step requires the same, limited number of reactions (in this case two) instead of an increasingly larger number of reactions for divergent growth. Owing to the greatly reduced number of possible side-products the 'convergent-growth' approach appears ideally suited for the preparation of hyperbranched macromolecules in which control over both the *number* and the *placement* of functional groups at the chain ends is achieved. We now report the first preparation of non-uniformly surface-functionalized dendritic macromolecules containing a predetermined and well defined number of functionalities at their periphery.

Results and Discussion

Dendritic Macromolecules with a Single or Limited Number of Surface Functionalities.—Strategy for the control of functionalities at chain ends. The limited number of reactions required for generation growth is the fundamental property of the 'convergent-growth' approach that allows the functionalities at the chain ends to be controlled. In the basic approach discussed herein, coupling of a single functional group at the 'focal point' of the growing macromolecule with two groups of the monomer is involved in every generation growth (Scheme 1). The starting material, **1**, contains what will eventually constitute the unsubstituted surface group 's' of the dendritic macromolecule as well as a reactive functional group 'f_r'; substrate **1** is then mono-coupled with monomer **2**, which contains two coupling sites 'c' and a protected functional group 'f_p'. This gives product **3**, having a free reactive group for further coupling. Coupling of product **3** with a substituted molecule **4**, containing the desired 'surface' functionality X, gives an unsymmetrical, monosubstituted, first-generation dendrimer **5**. Ultimately, functional group X will be located at the periphery or chain end of the final hyperbranched macromolecule. Activation of 'f_p' to 'f_r' gives intermediate **6**; this is coupled to the corresponding unsubstituted, mono-coupled dendrimer **7**, which is prepared in an analogous way to compound **3**. The second-generation dendritic 'wedge', **8**, is thus obtained and the process is continued by successive iterations, for example until

the dendritic 'wedge' **9** is obtained. Dendrimer **9** has a single reactive group 'f,' at its focal point and, more importantly, only one surface functional group X at the periphery. Coupling to a tetrafunctional core such as **10** yields the final dendritic macromolecule **11** which, in the illustration of Scheme 1, has exactly four of the exterior 64 surface groups substituted by the functionality X.

Synthesis of non-uniform dendritic wedges and their coupling to a core. Based on our previous work[8] directed towards symmetrical or uniformly functionalized dendritic molecules, the ability of the 'convergent-growth' approach to allow control over both the *number* and the *placement* of functional groups at the chain ends was investigated, with a number of dendritic polyether macromolecules containing one, two, or three functional groups at their periphery being chosen as synthetic targets.[9] To determine which functionalities were compatible with the reaction conditions employed for generation growth, *i.e.* K_2CO_3 and 18-crown-6 (18-C-6) in refluxing acetone for the coupling step, and CBr_4–PPh_3 in tetrahydrofuran (THF) for the focal-group-activation step, three candidates were chosen. These were the cyano, bromo, and methoxycarbonyl groups and therefore the corresponding substituted benzyl bromides were carried through these two sequential reactions to afford the corresponding first-generation bromides. As was established earlier,[8] the various generation dendritic macromolecules will be designated using the shorthand notation X_m-[G-n]-f, in which [G-n] refers to the generation number ($n = 0, 1, 2, \cdots$), f refers to the functional group at the focal point, X refers to the functional group at the periphery of the macromolecule, and m refers to the multiplicity of these groups. Similarly, the unsymmetrical monophenolic intermediates are designated as [G-*n*]-[M]-f, where [M] refers to the monoalkylated monomer unit containing one free phenolic group.

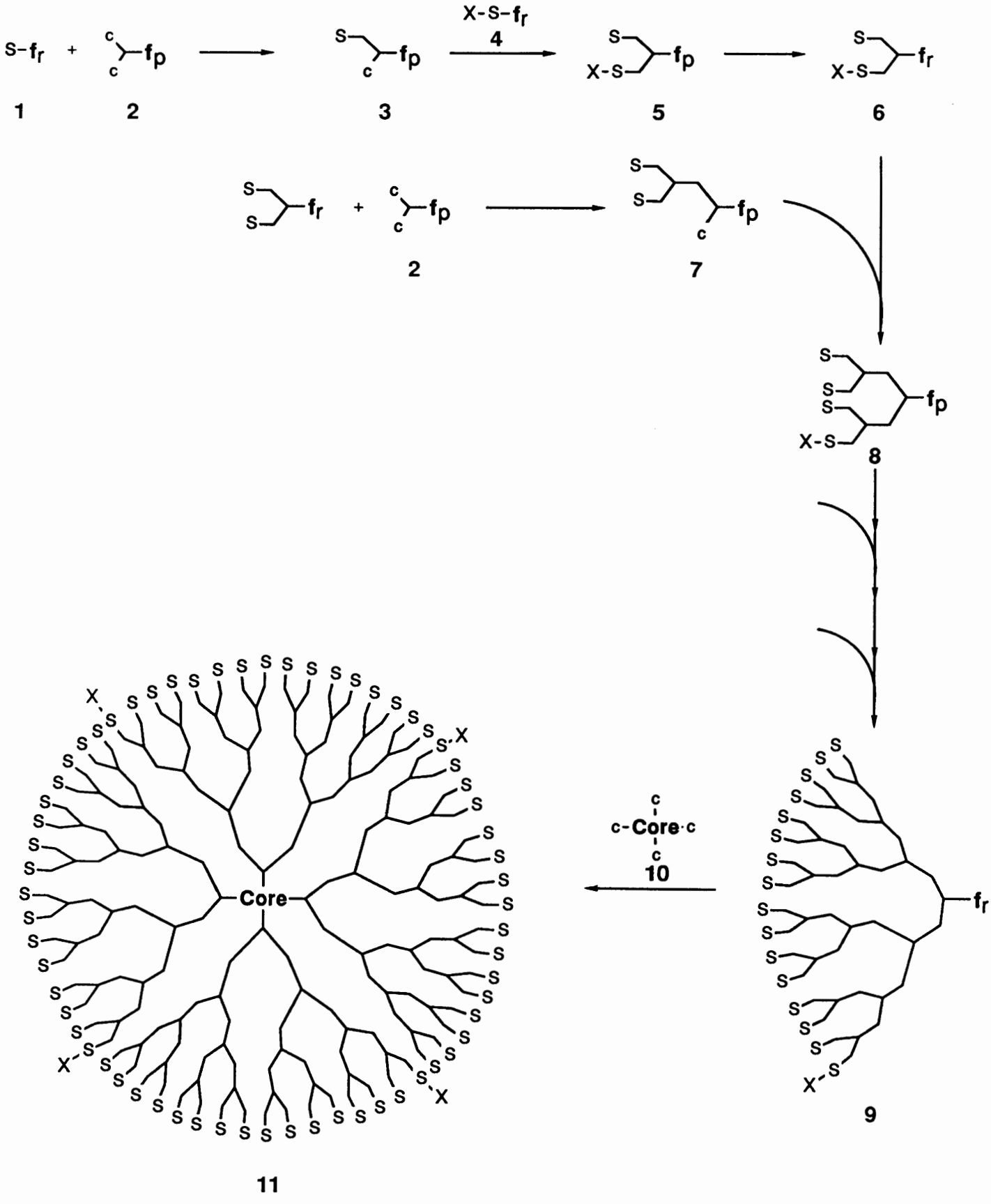
Reaction of benzyl bromide **12** with four mol equivalents of 3,5-dihydroxybenzyl alcohol **13** gave a mixture of products from which the desired monoalkylated phenol **14** was isolated in 54% yield. Purification of compound **14** was complicated by the presence of a significant amount of *C*-alkylated products of similar R_f-value (*e.g.* **15**, *ca.* 10%). Therefore a slightly modified monomer unit, 3,5-dihydroxybenzaldehyde **16**, was used instead of the alcohol **13** to eliminate this problem that caused a low yield of product **14** to be obtained. Monoalkylation of four mol equivalents of the aldehyde **16** with benzyl bromide led to a 72% yield of the desired phenol **17** with no detectable amount of *C*-alkylation [eqns. (1) and (2)]. Interestingly, reaction of the alcohol **13** with the 3,5-*dioxy*-substituted benzyl bromides, used below and in our previous work,[8] gave no detectable amounts of *C*-alkylated products. This finding suggests that activation of the bromomethyl group by the 3,5-dioxy substituents is sufficient to retard *C*-alkylation.

Alkylation of the monophenol **17** with one mol equivalent of 4-(bromomethyl)benzonitrile **18a**, 4-bromobenzyl bromide **18b**, or methyl 4(bromomethyl)benzoate **18c**, introduced the functional group to the periphery of the growing dendrimer and gave the first-generation, unsymmetrical aldehydes **19a–c**, X-[G-1]-CHO, in 86, 74, and 84% yield, respectively, after purification. Reduction of the aldehyde function in the presence of the 'X' functional groups could be accomplished with either $NaBH_4$ in refluxing methanol or tetrabutylammonium borohydride[10] in dichloromethane. The low solubility of compounds **19a–c** in refluxing methanol compared with their high solubility in dichloromethane at room temperature made the latter the reagent of choice. Reduction of aldehydes **19a–c** with Bu_4NBH_4 afforded the alcohols **20a–c**, X-[G-1]-OH, in 93, 84, and 91% yield, respectively. Conversion onto the corresponding bromides **21a–c**, X-[G-1]-Br, was by reaction with 1.25 mol equivalents of tetrabromomethane–triphenylphosphine, bromides **21a–c** being isolated in 85, 74, 88% yield, respectively (Scheme 2). All three functional groups investigated were stable to the reaction conditions required for generation growth. The cyano group was selected as the 'surface' functional group for the synthesis of the mono-, di-, and tri-substituted dendritic macromolecules for its potentially ready transformation into a variety of other useful functional groups (*e.g.*, CH_2NH_2,CO_2H, *etc.*).

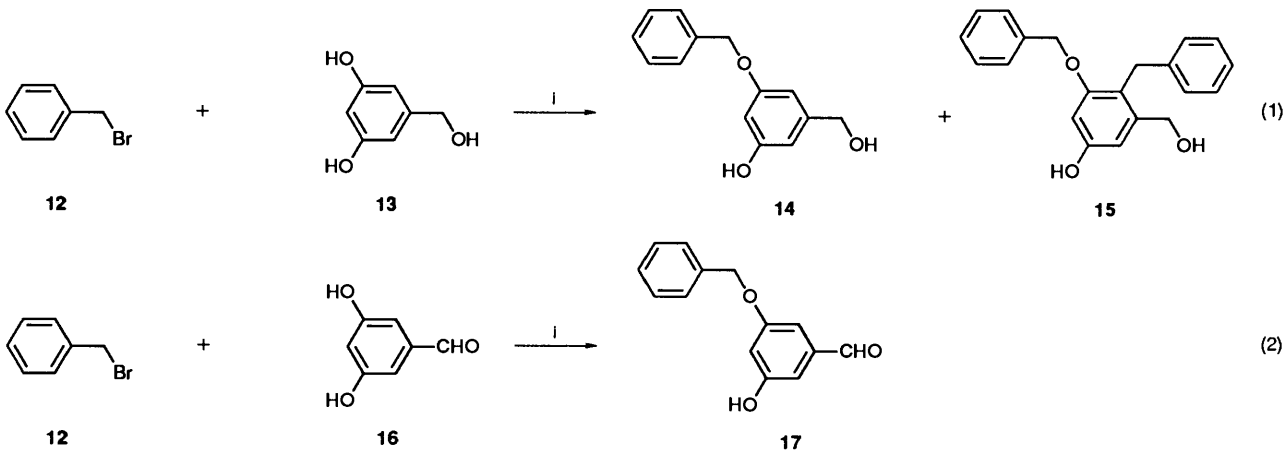
Proceeding to generation two, synthesis of the corresponding monophenolic compound **22** involved the reaction of the first-generation unsubstituted bromide, [G-1]-Br, with four mol equivalents of 3,5-dihydroxybenzyl alcohol **13**, compound **22** being isolated in 79% yield after purification. It must be noted that the alcohol **13** can now be used since all bromides from generation one, [G-1], onwards are 3,5-dioxy-substituted and therefore can lead to *O*-alkylation selectively. Coupling of the phenol **22** with the monocyano-substituted compound **21a** gave the second generation alcohol **23**, NC-[G-2]-OH, in 87% yield, which was brominated with CBr_4–PPh_3 to give bromide **24**, NC-[G-2]-Br. The corresponding monophenolic compound **25** was obtained in 71% yield from the reaction of the recorcinol **13** with [G-2]-Br. Alkylation of bromide **24** with the phenol **25** gave the third-generation, monocyano-substituted dendrimer **26**, NC-[G-3]-OH, in 85% yield, and activation of this with CBr_4–PPh_3 led to the bromide **27**, NC-[G-3]-Br, in 92% yield. The next-generation alcohol **29** was obtained from the reaction of the monophenol **28** with the monocyano-substituted bromide **27**, in 91% yield after purification. A slight excess of CBr_4–PPh_3 (2.50 mol equiv) was required to force the bromination reaction of compound **29** to completion, the bromide **30**, NC-[G-4]-Br, being isolated in 84% yield (Scheme 3). By virtue of our stepwise methodology, compound **30** has a single reactive functionality at its focal point and, more importantly, has only one of the exterior 16 phenyl rings substituted by a cyano functional group.

This stepwise methodology can also be extended to our final reaction, attachment to a polyfunctional core. As in our previous work,[8,9] 1,1,1-tris-(4′-hydroxyphenyl)ethane **31** [C]-$(OH)_3$, was used as the polyfunctional core due to its high solubility in the reaction medium. To obtain the unsymmetrically 'surface'-functionalized mono-or di-substituted macromolecules, triol **31** was initially alkylated with the corresponding unsubstituted fourth-generation bromide **32**, [G-4]-Br. Using standard alkylation conditions (K_2CO_3, 18-C-6, refluxing acetone), reaction of bromide **32** with ten mol equivalents of triol **31** gave a mixture of mono-, di-, and tri-alkylated core molecules. These could be readily separated and purified by flash chromatography due to the presence of two, one, and zero phenolic groups in the resulting products, respectively. Surprisingly, the monoalkylated core **33**, [G-4]-[C]-$(OH)_2$, was isolated in 33% yield after purification, the dialkylated core **34**, $[G\text{-}4]_2$-[C]-OH, in 41% yield, and the trialkylated core **35**, $[G\text{-}4]_3$-[C], in 10% yield [eqn. (3)]. This result is unexpected since a 30:1 ratio of phenolic to bromomethyl groups was used; it may reflect the enhanced reactivity of the more soluble mono-alkylated core.

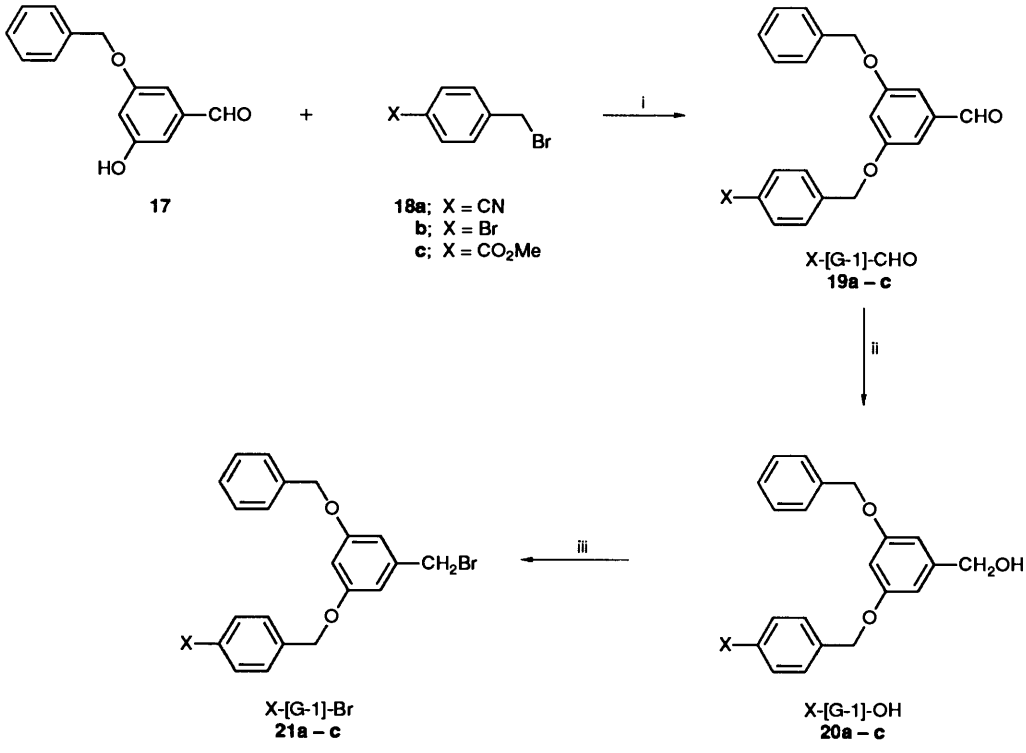
Alkylation of monophenol **34** with one mol equivalent of the substituted dendritic 'wedge' **30**, NC-[G-4]-Br, under standard conditions gave the dendritic macromolecule **36**, NC-[G-4]-[C]-$[G\text{-}4]_2$, in 80% yield. The periphery of compound **36**, has only one of the exterior 48 phenyl rings substituted by a cyano functional group. Similarly, reaction of the monoalkylated core **33** with two mol equivalents of **30** gave, in 72% yield after purification, the dendritic macromolecule **37**, $(NC\text{-}[G\text{-}4]])_2$-[C]-[G-4], which has two cyano functionalities at its periphery. A symmetrically but non-uniformly functionalized macromolecule was obtained when the core molecule **31** was alkylated exclusively with three mol equivalents of the substituted dendritic 'wedge' **30**, the product **38**, $(NC\text{-}[G\text{-}4])_3$-[C], being isolated in 77% yield after purification. The symmetry of compound **38** is due to each of the three wedges having a single cyano functionality [eqn. (4)].



Scheme 1



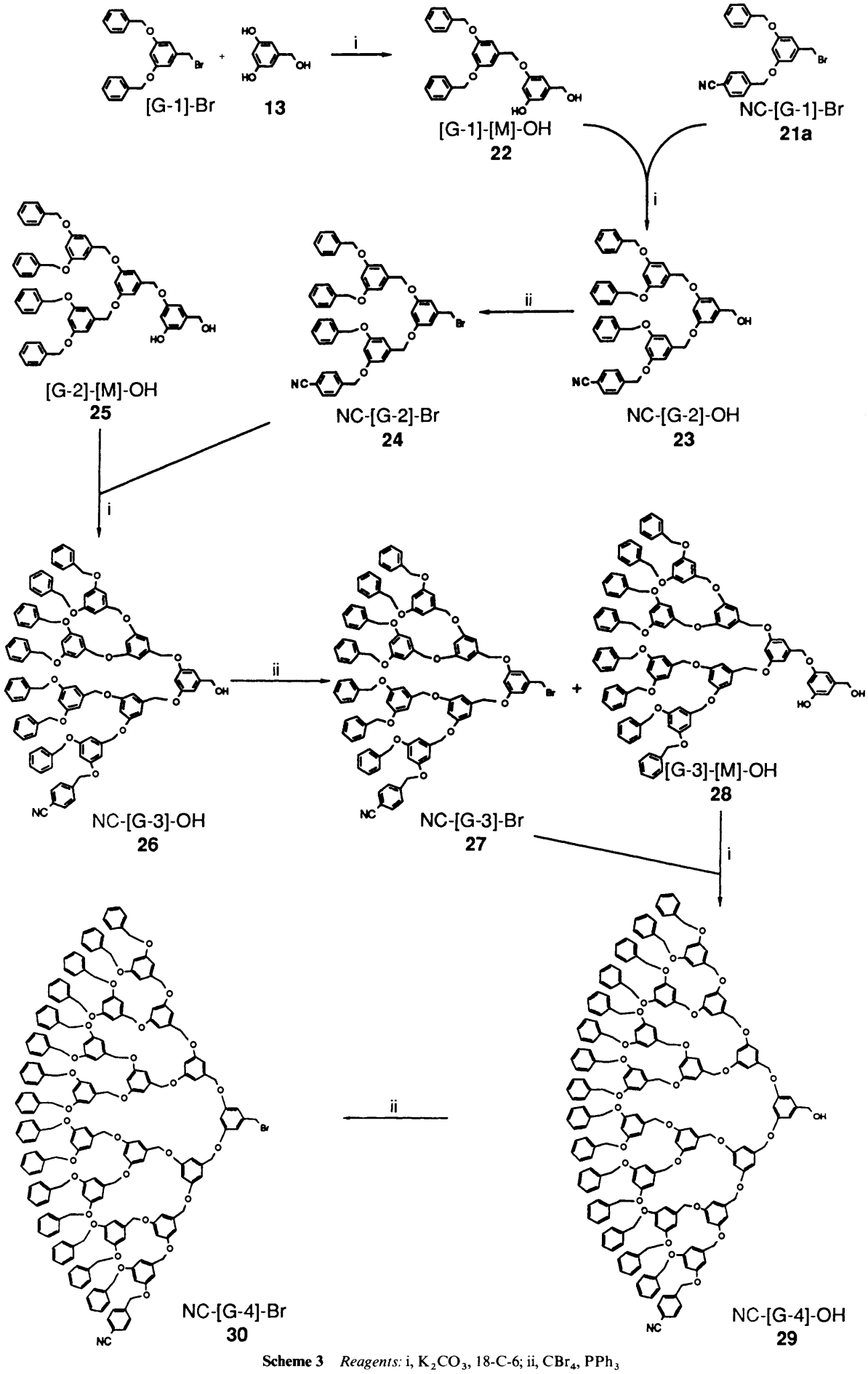
Reagents: i, K_2CO_3, 18-C-6



Scheme 2 *Reagents:* i, K_2CO_3, 18-C-6; ii, Bu_4BH_4; iii, CBr_4, PPh_3

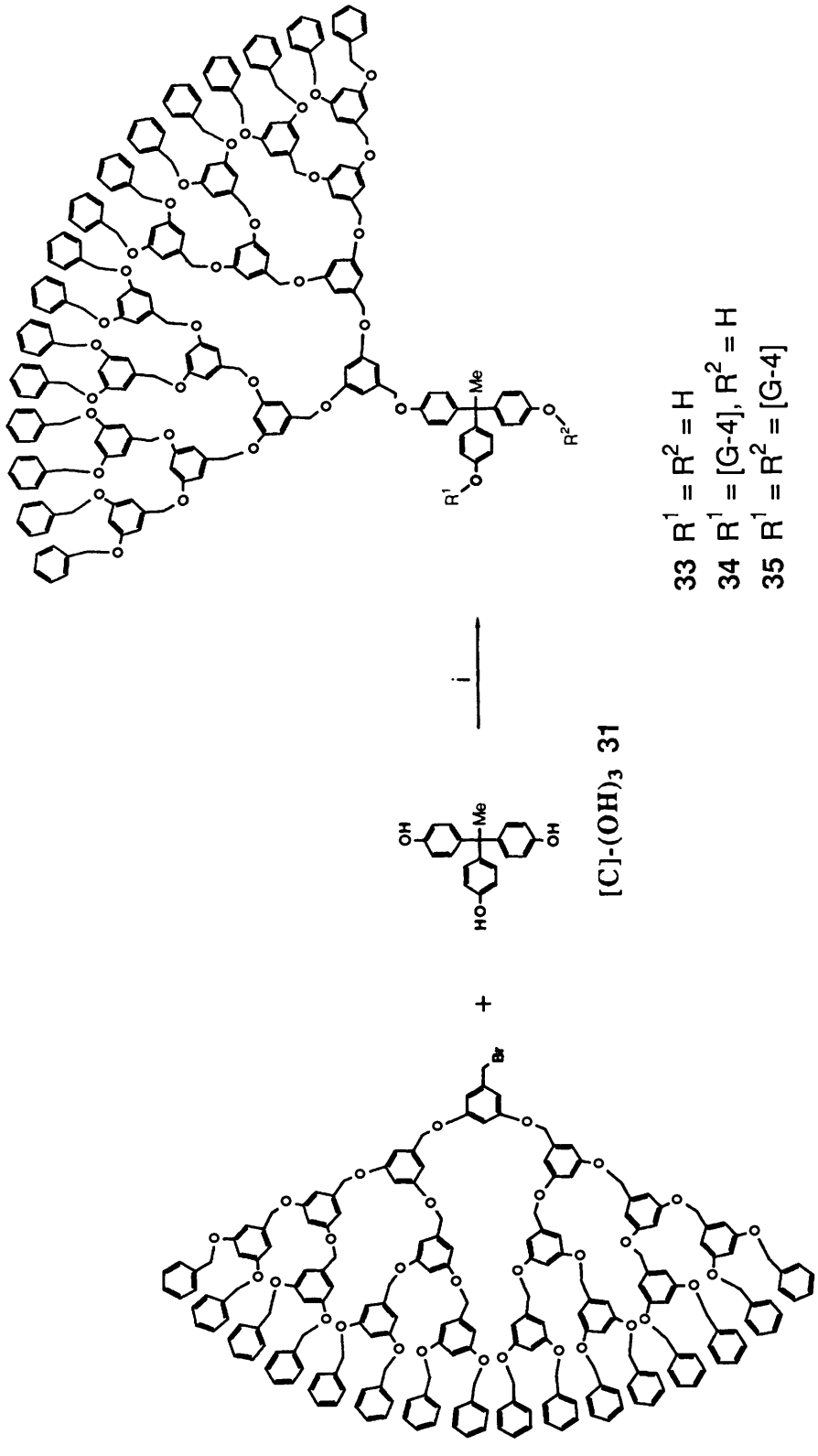
Block-type Dendritic Macromolecules with Different Surface Functionalities.—Strategy for control of chain-end functionalities. Typical block copolymers are characterized by segments of the polymer being composed of different monomer units. The high degree of control provided by the convergent-growth approach allows dendritic macromolecules of a block-type structure to be prepared. The key control step is attachment to the polyfunctional core. The basic approach described herein is the same as discussed above (Scheme 1). The starting material, **4**, contains what will eventually constitute the surface functional group 'X' of one block as well as a reactive functional group 'f_r'. Substrate **4** is then fully coupled with the monomer **2**, which contains two coupling groups 'c' as well as a protected functional group 'f_p.' Activation of 'f_p' to 'f_r' gives intermediate **39**, which is again coupled to the monomer unit **2**; this gives the second-generation dendritic 'wedge' **40**. Repetition of this two-step growth procedure leads, for example, to the dendritic 'wedge' **41**, the periphery of which is fully substituted by 16 surface functional groups X. The corresponding unsubstituted dendritic 'wedge' **42**, which in this case constitutes a different polymeric block, is partially coupled with a polyfunctional core, such as **10**, to give the tri-coupled core **43** which has a free coupling site 'c'. Coupling of core **43** with the fully substituted 'wedge' **41** yields the final dendritic macromolecule **44** which, in the illustration of Scheme 4, consists of two different blocks. In the above example, the blocks differ only by the presence of full peripheral substitution on one and the lack of substitution on the other. The internal structure of both blocks is the same; however, it should be noted that this need not be the case, the only requirement of the approach being that the different blocks or 'wedges' can be coupled successively to the same polyfunctional core.

Synthesis of block-type dendritic macromolecules. The surface functionality chosen to demonstrate the preparation of block-type dendritic macromolecules were bromoaromatic groups which, as was seen above, are compatible with the reaction conditions. Reaction of 4-bromobenzyl bromide **18b** (2.00 mol equiv.) with 3,5-dihydroxybenzyl alcohol **13** gave both the desired di-*O*-alkylated product **45**, Br_2-[G-1]-OH, as well as *C*-



Scheme 3 *Reagents:* i, K_2CO_3, 18-C-6; ii, CBr_4, PPh_3

(3)

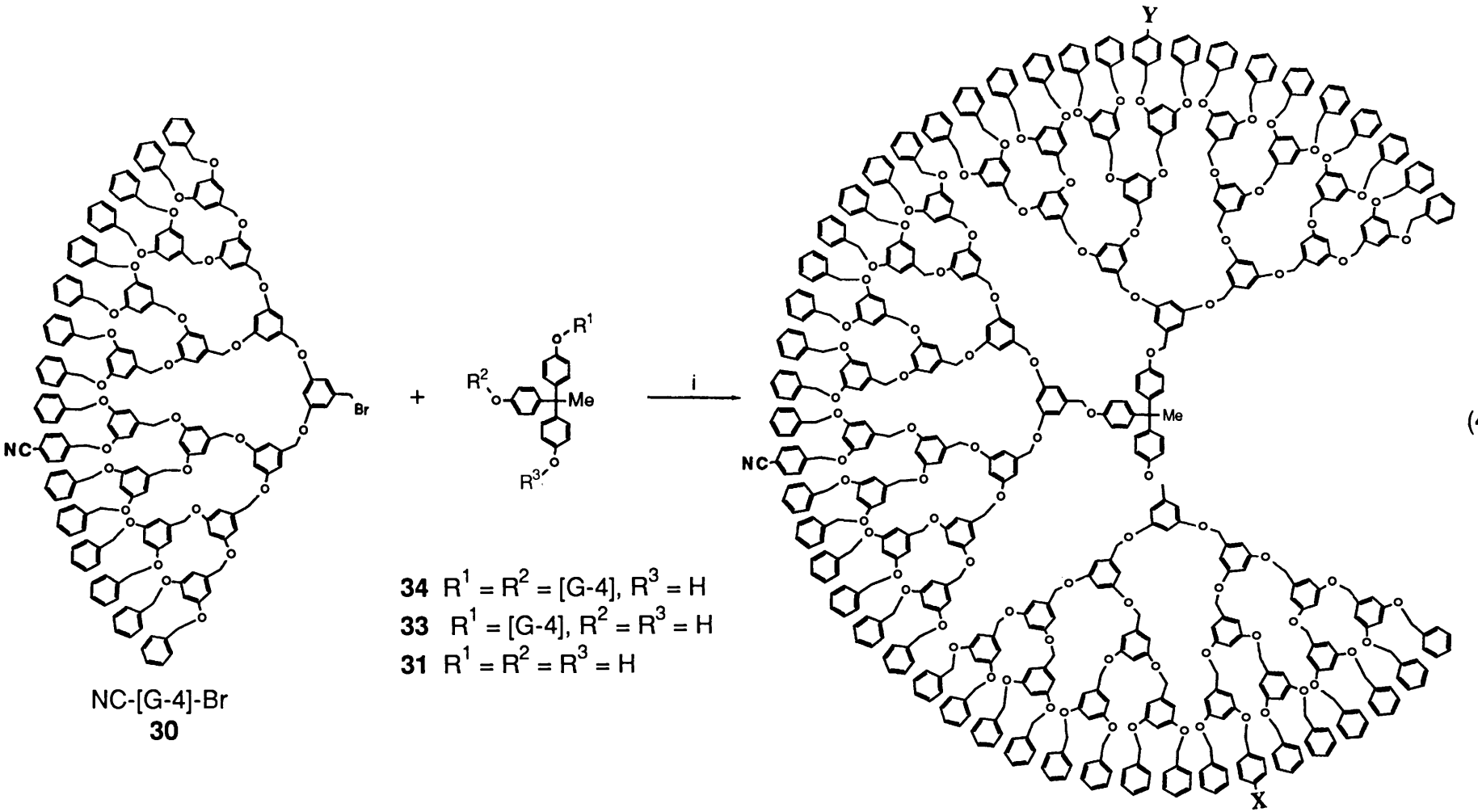


33 $R^1 = R^2 = H$
34 $R^1 = [G\text{-}4]$, $R^2 = H$
35 $R^1 = R^2 = [G\text{-}4]$

Reagents: i, K_2CO_3, 18-C-6

[C]-(OH)$_3$ 31

[G-4]-Br 32

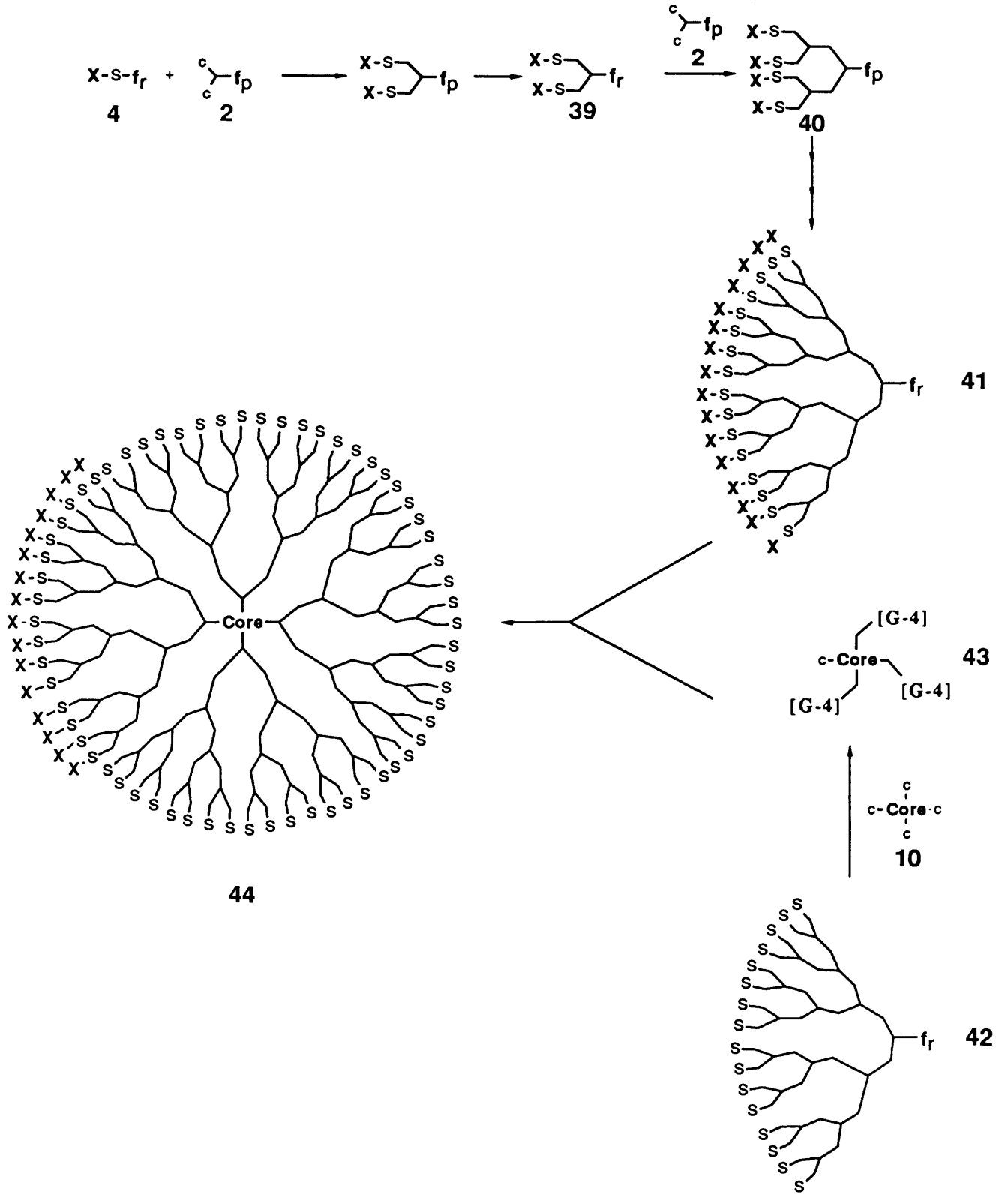


34 $R^1 = R^2 = [G\text{-}4]$, $R^3 = H$
33 $R^1 = [G\text{-}4]$, $R^2 = R^3 = H$
31 $R^1 = R^2 = R^3 = H$

(4)

NC-[G-4]-[C]-[G-4]$_2$	**36**	X = Y = H
(NC-[G-4])$_2$-[C]-[G-4]	**37**	X = H, Y = CN
(NC-[G-4])$_3$-[C]	**38**	X = Y = CN

Reagents: i, K_2CO_3, 18-C-6



Scheme 4

alkylated products. Unlike the above case, the purification of the alcohol **45** was not complicated by the presence of some undesired *C*-alkylated products and the purified yield of 76% was sufficient to render unnecessary the use of the aldehyde monomer **16**. Bromination of the alcohol **45** with CBr_4–PPh_3 (1.25 mol equiv), as above, gave the first-generation, fully substituted bromide **46**, Br_2-[G-1]-Br, in 87% yield after purification. Dialkylation of the triol **13** with **46** gave no detectable amount of *C*-alkylated products, as was expected, since the bromide is 3,5-dioxy-substituted. The alcohol **47**, Br_4-[G-2]-OH, was isolated in 88% yield. Activation of the alcohol **47** with CBr_4–PPh_3 (6.0 mol equiv) led to the bromide **48**, Br_4-[G-2]-Br, in 84% yield. The next-generation alcohol **49**, Br_8-[G-3]-OH, was obtained in 88% yield from the reaction of

bromide **48** with triol **13**; activation with CBr_4–PPh_3 then gave the third-generation bromide **50**, Br_8-[G-3]-Br, in 94% yield. Reaction of compound **50** with the monomer **13** in acetone gave no product, owing to the insolubility of the bromide **50** in refluxing acetone. Change of the solvent to 1,4-dioxane, with heating to 70 °C, gave the alcohol **51**, Br_{16}-[G-4]-OH, in 78% yield after purification. Again, an excess of CBr_4–PPh_3 (6.0 mol equiv) was required to force the bromination reaction to completion, the fully substituted, fourth-generation bromide **52**, Br_{16}-[G-4]-Br, being obtained in 90% yield (Scheme 5). The controlled nature of the convergent-growth approach allows us to prepare the bromide **52** in which each of the 16 exterior phenyl rings carries a single *para*-substituted bromine atom as substituent.

The final reaction, attachment to a polyfunctional core, was performed in a stepwise manner as above, using both the mono- and di-alkylated cores **33** and **34** respectively. Reaction of **34** with one equivalent of the fully brominated 'wedge' **55** was conducted in refluxing tetrahydrofuran due to the low reactivity of **52** in refluxing dioxane or acetone. Using potassium carbonate and 18-crown-6 in refluxing tetrahydrofuran, a mixture of **34** and **52** gave a 75% yield of the desired dendritic macromolecule **53**, Br_{16}-[G-4]-[C]-[G-4]$_2$. The periphery of **53** has two distinct regions, one where there are bromine atoms attached to the exterior phenyl rings and the second where the exterior phenyl rings are unsubstituted. The regions are of unequal size, there are twice as many peripheral phenyl rings unsubstituted as there are substituted. The reverse is true when **33** is alkylated with two equivalents of **52**, the block-type dendritic macromolecule **54**, (Br_{16}-[G-4]$_2$-[C]-[G-4]), being obtained in 86% yield after purification [eqn. (5)].

Characterization of the dendritic molecules. Since the products obtained above have essentially the same structure as the corresponding unsubstituted derivatives the methods used for determination of their purity and for characterization of both the focal point group and the bulk of the molecule were the same as those previously used.[8,9] The change in the resonance for the functionality at the focal point could again be followed by both ^1H and ^{13}C NMR spectroscopy. This, coupled to integration data for these groups, was also used to confirm the extent of coupling to either the core **31** or the monomer **13**, or to quantify the generation number. Size-exclusion chromatography (SEC) was also used to ascertain the purity of the products obtained. As was found for the unsubstituted dendrimers the molecular weight essentially doubled at each generation-growth step; in addition, on attachment to the core, the molecular-weight difference between mono-, di-, and tri-alkylated core molecules is substantial (*ca.* 3300 daltons). These significant differences between peaks for starting materials and products allows lower molecular weight impurities to be routinely detected at < 1% levels. Little or no difference in retention volume or polystyrene-equivalent molecular weight and polydispersity is observed on comparison of the substituted and unsubstituted dendrimers.

While we can routinely characterize and determine the purity of the substituted dendrimers, an additional difficulty lies in the accurate determination of the number of functional groups on the periphery of the macromolecule. ^1H NMR spectroscopy was instrumental in this analysis. Fig. 1 shows the the 300 MHz ^1H NMR spectra of the monocyano, **27**, NC-[G-3]-Br, unsubstituted, [G-3]-Br, and fully brominated **50**, Br_8-[G-3]-Br, third-generation benzylic bromides. A number of distinguishing features are apparent. The methylene region (δ 4.90–5.10) is more complex for compound **27**, as expected since the single cyano group at the periphery of the dendrimer disrupts the symmetry of the molecule. Also, an ABq (δ 7.46 and 7.61) is present in the spectrum of compound **27** at lower field than that for the exterior phenyl rings (δ 7.30–7.40). This unique resonance is due to a *para*-cyano-substituted phenyl ring, which is consistent with our structure. Conversely, for compound **50** no resonances are observed in the region δ 7.30–7.40 for unsubstituted phenyl rings; instead, only an ABq is observed at δ 7.24 and 7.45; this is consistent with an *p*-bromophenyl ring and indicates that all of the exterior phenyl rings carry a bromine atom. Integration data for these resonances, when compared with the other resonances in the spectrum, confirm that there is only one cyano functional group at the periphery of compound **27** and that there are eight bromo-substituted phenyl rings at the periphery of compound **50**.

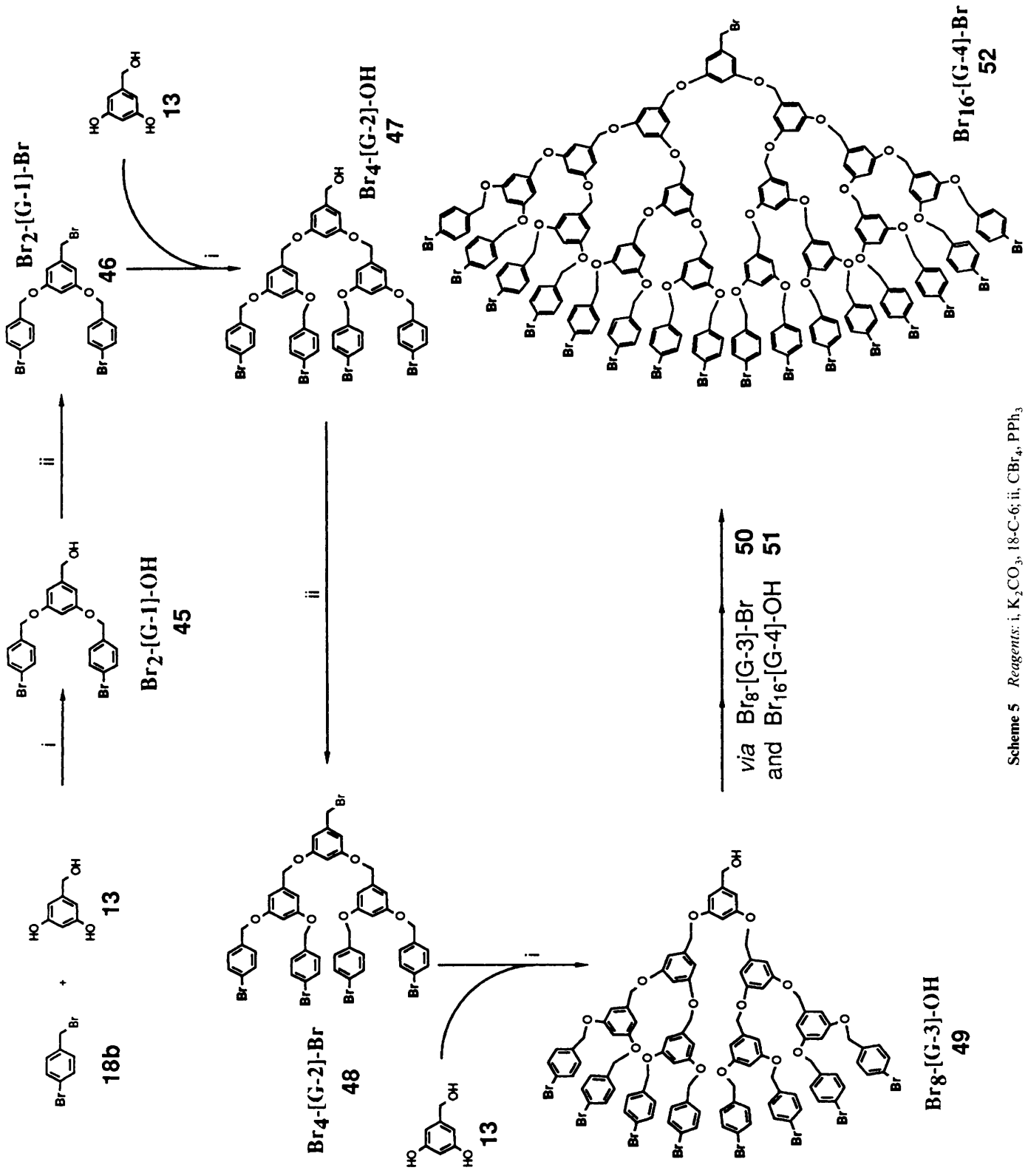
An interesting observation from ^1H NMR spectra is that the resonance for either the protons of the *para*-cyano- or the *para*-bromo-substituted phenyl rings shifts to higher field as the generation number of the dendritic 'wedge' increases. The difference between the hydroxymethyl and bromomethyl derivatives of the same generation number is negligible. On attachment of the respective fourth-generation bromides to the partially alkylated core molecules we see an even more pronounced shift to higher field, as is illustrated in Figs. 2 and 3. This behaviour is in agreement with the observation that the chemical shift of aromatic protons shifts to higher field as stacking of the aromatic rings increases.[11,12] Presumably, this is due to a combination of ring current and steric interactions. In our case as the number of exterior phenyl rings increases a corresponding increase in the steric and ring-current interactions between these phenyl rings at the periphery might result, leading to the observed upfield shift of the protons of the exterior phenyl rings. This property of dendritic macromolecules agrees with previous observations[2] which suggest that the dendrimers become progressively denser and more compact as molecular weight increases.

The bromo- and cyano-substituted phenyl rings also provides unique resonances in the ^{13}C NMR spectra, allowing the different series of compounds to be distinguished (Fig. 4). The resonance for the cyano group appears at δ_C 118.50–118.67 and decreases in height as the generation number increases, which is consistent with the reaction scheme.

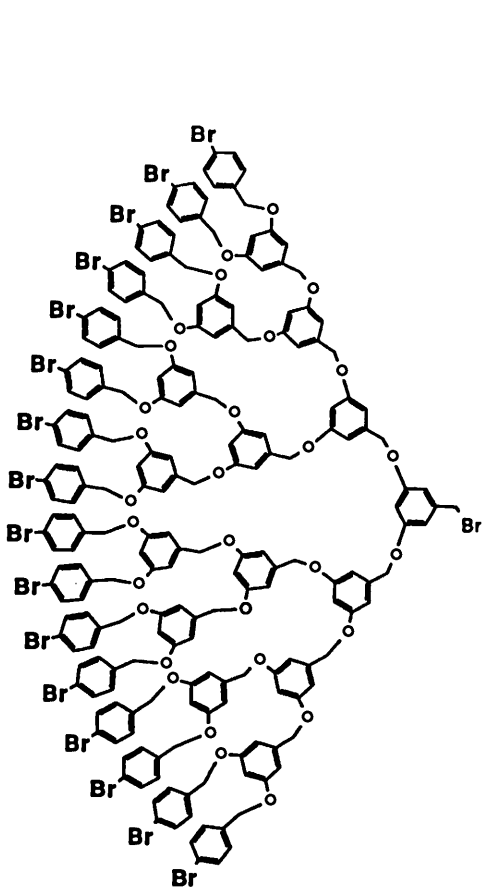
For the lower generation dendritic 'wedges' (less than fourth generation) the molecular ion was observable by either EI or FAB mass spectroscopy. For the cyano case any contamination by di-CN-substituted or unsubstituted impurities could easily be detected since they have molecular ions 25 daltons above or below that for the desired mono-CN-substituted products; poly-CN-substitution could similarly be observed. For example, compound **26**, NC-[G-3]-OH, which has a nominal molecular weight of 1617,* showed M^+ at 1617 and 1618 (*ca.* 1:1) ($C_{106}H_{91}NO_{15}$); no peaks were observed at *ca.* 1592, 1642, 1667, *etc.* Similarly, for the bromo case, peaks were not observed at lower molecular weights corresponding to only partial substitution of the exterior phenyl rings and the observed isotopic abundance patterns agreed with the theoretical patterns.

Unlike our previous work[8] IR spectroscopy proved useful, the C≡N stretch at 2230 cm^{-1} could readily be detected and the decrease in the area for this peak, when compared with the area for the C–H stretch at 3100–2900 cm^{-1}, correlated with that expected for generation growth. Similarly, the decrease in percentage nitrogen, as shown by elemental analysis, also confirmed the above results. Elemental analysis proved to be even more useful in the bromo case, the high relative percentage of Br declining as the generation number increased; for example $Br_{[2^n]}$-[G-*n*]-Br requires 44.30, 35.56, 31.44 and 29.42 percent bromine for generation numbers n = 1, 2, 3, and 4, respectively. In all cases the experimental value was within experimental error of the theoretical value.

* Calculated on the basis of C = 12.00, H = 1.00, O = 16.00

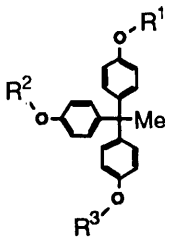


Scheme 5 *Reagents*: i, K_2CO_3, 18-C-6; ii, CBr_4, PPh_3



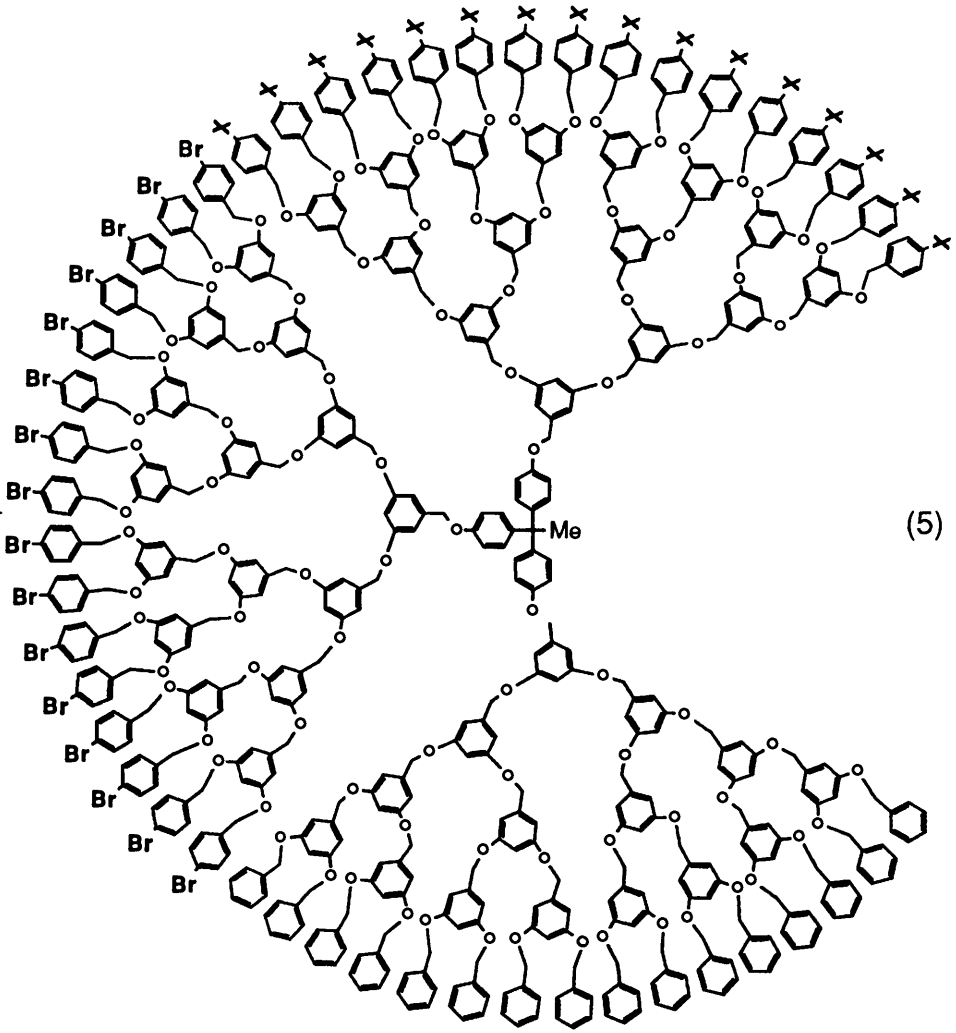
Br_{16}-[G-4]-Br
52

+



34 $R^1 = R^2 = [G\text{-}4]$, $R^3 = H$
33 $R^1 = [G\text{-}4]$, $R^2 = R^3 = H$

$\xrightarrow[\text{18-C-6}]{K_2CO_3}$



(5)

Br_{16}-[G-4]-[C]-[G-4]$_2$ **53** X = H
(Br_{16}-[G-4])$_2$-[C]-[G-4] **54** X = Br

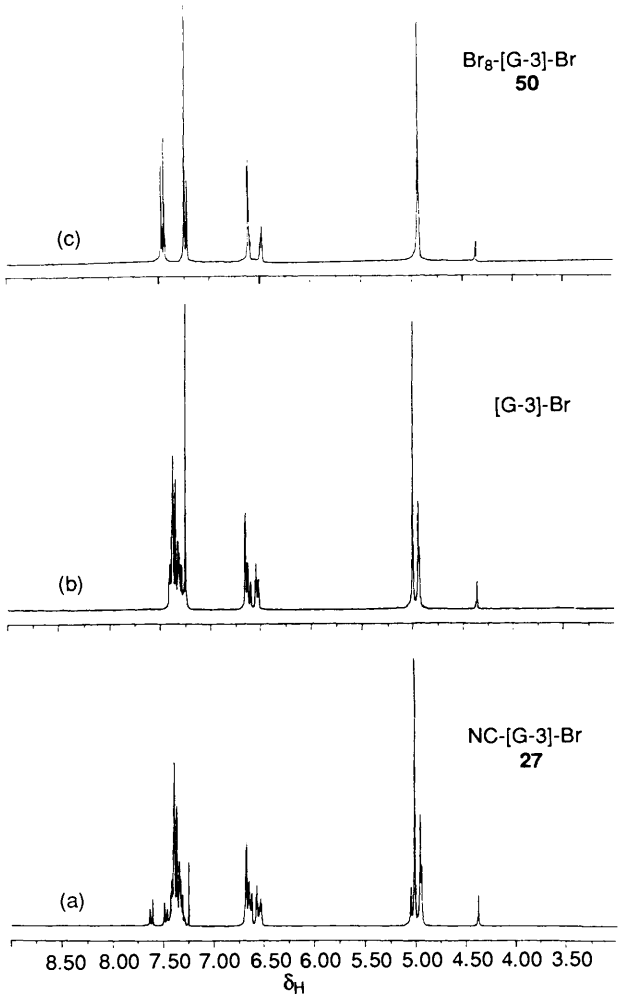


Fig. 1 300 MHz ^{1}H NMR spectra of compounds **27** (a), [G-3]-Br (b), and **50** (c)

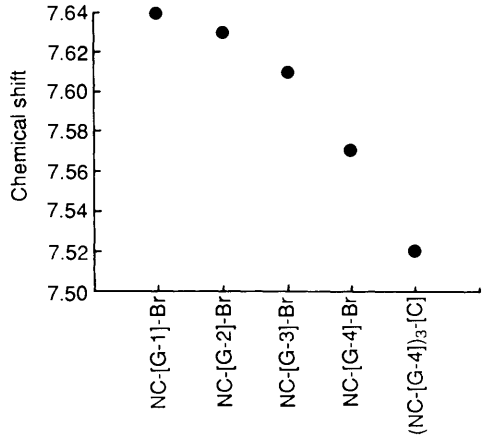


Fig. 2 Chemical shift of *ortho*-Hs of cyano-substituted phenyl ring *vs.* dendrimer size

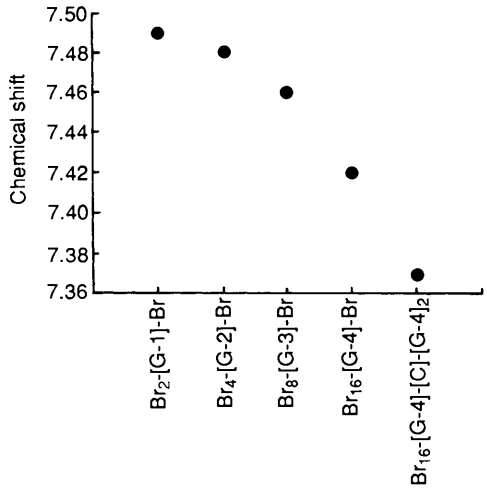


Fig. 3 Chemical shift of *ortho*-Hs of bromo-substituted phenyl ring *vs.* dendrimer size

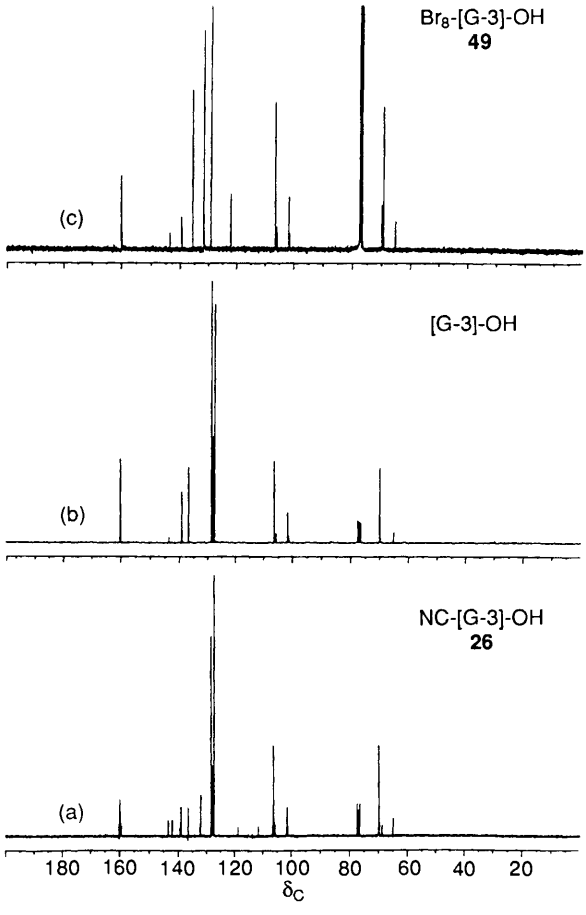


Fig. 4 75 MHz ^{13}C NMR spectra of compounds **26** (a), [G-3]-OH (b), and **49** (c)

Conclusions.—The concept of using a 'convergent' approach to the synthesis of dendritic macromolecules has a number of potential advantages: the small number of coupling reactions per generation-growth step gives greater control over the synthesis, the possibility of failure sequences is minimized, and the need for large excesses of reagents is avoided, which simplifies purification. We have demonstrated, *via* the synthesis of cyano-substituted dendritic macromolecules based on 3,5-dihydroxybenzyl alcohol **13**, that the 'convergent' approach offers unparalleled control over the number and placement of functional groups at the periphery. The three-step procedure, stepwise alkylation of the monomer unit with first unsubstituted and then substituted dendritic 'wedges' followed by conversion of the hydroxymethyl group into the corresponding bromomethyl group, was optimized and proved to be efficient, yields of > 60% being routinely obtained for each generation-growth step. Control over surface functionalization can also be achieved in the final reaction, attachment to the polyfunctional core. This allowed the synthesis of non-uniformly functionalized

dendritic macromolecules containing only one or two cyano groups, or one or two blocks of 16 bromo functionalities at their periphery, or a more symmetrical macromolecule where each wedge has a single cyano functionality at the periphery. Characterization of the consecutive dendritic wedges and macromolecules is both reliable, sensitive to impurities and defects, and allows the number of surface functionalities to be accurately determined. A combination of ^1H and ^{13}C NMR spectroscopy and SEC allowed every product to be fully characterized and the absence of starting materials or side-products to be demonstrated. SEC, using both polystyrene and the corresponding unsubstituted dendrimer samples of known molecular weight as standards, and mass spectra have provided confirmation of the nominal molecular weights for the higher and lower molecular weight products, respectively. Further work in progress in this laboratory will attempt to extend this approach to the preparation of unusual molecular dipoles or chiral moieties and explore the reactivity of the surface functional groups.

Experimental

General Directions.—M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Nicolet IR/44 spectrophotometer as thin films on NaCl disks. ^1H NMR spectra were recorded on solutions in $CDCl_3$ on a Bruker WM 300 (300 MHz) spectrometer, with the solvent proton signal as standard. *J*-Values are in Hz. ^{13}C NMR spectra were recorded at 75 MHz on a Bruker WM300 spectrometer, with $CDCl_3$ as the solvent and the solvent carbon signal as internal standard. Mass spectra were obtained on a Kratos MS890 using either EI or FAB ionization; the latter were run using 3-nitrobenzyl alcohol as the matrix.

Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254}(0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 mesh). SEC was carried out on a IBM LC/9560 Chromatograph connected to a Milton Roy refractoMonitor IV refractive index detector; data analysis was performed by a IBM system 9000 computer. Five 10 μm IBM GPC/SEC columns (300 × 7.7 mm) connected in series in order of decreasing pore size (IBM type B–F) were used with THF as solvent. The following abbreviations are used: Ar refers to aromatic rings derived from monomer **13**, Ph refers to aromatic rings derived from benzyl bromide, Ar′ refers to aromatic rings derived from the substituted benzyl groups, and Ar″ refers to aromatic rings derived from the core molecule **31**. Elemental analysis were performed by MHW Laboratories, Phoenix, Arizona.

3-Benzyloxy-5-hydroxybenzaldehyde **17**.—A mixture of benzyl bromide **12** (3.26 g, 2.26 cm^3, 19.1 mmol), 3,5-dihydroxybenzaldehyde[13] **16** (7.90 g, 57.2 mmol), potassium carbonate (2.80 g, 20.0 mmol), and 18-c-6 (530 mg, 2.0 mmol) in dry 1,4-dioxane (250 cm^3) was heated at reflux under nitrogen for 24 h. The mixture was then cooled and evaporated to dryness. The residue was partitioned between water and $CHCl_3$, the water layer was then extracted with diethyl ether (3 × 100 cm^3), and the extracts were evaporated to give unchanged substrate **16** (3.05 g). The chloroform phase was evaporated to dryness, and the residue was redissolved in ethyl acetate and extracted with 1 mol dm^{-3} NaOH (4 × 50 cm^3). The NaOH extracts were acidified with glacial acetic acid and extracted with $CHCl_3$ (4 × 50 cm^3). The combined extracts were dried, evaporated to dryness, and recrystallized from 1:1 toluene–heptane to give compound **17** as crystals; yield 72%; m.p. 91–93 °C (Found: C, 74.0; H, 5.3. $C_{14}H_{12}O_3$ requires C, 73.67; H, 5.62%); ν_{max}/cm^{-1} 3500–3300, 1705, 1220 and 805; δ_H 5.08 (2 H, s, PhCH_2O), 5.60 (1 H, br s, OH), 6.75 (1 H, t, *J* 2, ArH), 6.97 (1 H, d d, *J* 1 and 2, ArH), 7.07 (1 H, d d, *J* 1 and 2, ArH), 7.30–7.40 (5 H, m, PhH) and 9.87 (1 H, s, CHO); *m/z* (EI) 228.

General Procedure for Synthesis of Monosubstituted Aldehydes **19a–c**.—A mixture of the appropriate substituted benzyl bromide (1.05 mol equiv.), 3-benzyloxy-5-hydroxy-benzaldehyde **17** (1.00 mol equiv.), potassium carbonate (1.50 mol equiv.), and 18-c-6 (0.1 mol equiv.) in dry 1,4-dioxane was heated at reflux under nitrogen for 24 h. The mixture was then cooled and evaporated to dryness. The residue was partitioned between water and $CHCl_3$, the water layer was extracted with $CHCl_3$ (3 ×), and the combined organic layers were dried, and evaporated to dryness. The crude product was purified as outlined below.

NC-[G-1]-CHO **19a**. This was prepared from the monophenol **17** and 4-(bromomethyl)benzonitrile **18a**, and was purified by flash chromatography with 1:4 hexane–$CHCl_3$ as eluent to give *compound* **19a** as a foam; yield 86% (Found: C, 76.6; H, 5.25; N, 4.1. $C_{22}H_{19}NO_3$ requires C, 76.95; H, 4.99; N, 4.08%); ν_{max}/cm^{-1} 2230, 1700, 1600 and 1165; δ_H 5.09 and 5.14 (each 2 H, s, Ar′- and Ph-CH_2O), 6.84 (1 H, t, *J* 2, ArH), 7.07 and 7.13 (each 1 H, d d, *J* 1 and 2, ArH), 7.30–7.40 (5 H, m PhH), 7.52 and 7.67 (4 H, ABq, *J* 10, Ar′H) and 9.89 (1 H, s, CHO); δ_C 68.80, 69.96 (CH_2O), 106.24, 108.45 and 111.51 (arom C), 118.56 (CN), 127.33, 127.90, 128.46, 132.40, 136.40, 138.55, 142.03, 159.44 and 160.05 (arom C); *m/z* (EI) 343.

Br-[G-1]-CHO **19b**. This was prepared from the monophenol **17** and 4-bromobenzyl bromide **18b**, and was purified by flash chromatography with 1:4 hexane–$CHCl_3$ as eluent to give *compound* **19b** as a foam; yield 74% (Found: C, 63.6; H, 4.15. $C_{21}H_{17}BrO_3$ requires C, 63.49; H, 4.31%); ν_{max}/cm^{-1} 1700, 1600, 1290 and 1165; δ_H 5.01 and 5.08 (each 2 H, s, Ar′- and Ph-CH_2O), 6.84 (1 H, t, *J* 2, ArH), 7.08 and 7.12 (each 1 H, d d, *J* 1 and 2, ArH), 7.29 and 7.51 (4 H, ABq, *J* 8, ArH), 7.30–7.40 (5 H, m, PhH) and 9.88 (1 H, s, CHO); *m/z* (EI) 396 and 398 (*ca.* 1:1).

MeO_2C-[G-1]-CHO **19c**. This was prepared from the monophenol **17** and methyl 4-(bromomethyl)benzoate **18c**, and was purified by flash chromatography with 1:4 hexane–$CHCl_3$ as eluent to give *compound* **19b** as a foam; yield 84% (Found C, 73.1; H, 5.3. $C_{23}H_{20}O_5$ requires C, 73.39; H, 5.35%); ν_{max}/cm^{-1} 1720, 1700, 1610 and 1170; δ_H 3.89 (3 H, s, Me), 5.05 and 5.09 (each 2 H, s, Ar′- and Ph-CH_2O), 6.84 (1 H, t, *J* 2, ArH), 7.06 and 7.10 (each 1 H, d d, *J* 1 and 2, ArH), 7.30–7.40 (5 H, m, PhH), 7.47 and 8.05 (4 H, ABq, *J* 10, Ar′H) and 9.86 (1 H, s, CHO); δ_C 51.90 (Me), 69.49 and 70.26 (CH_2O), 107.96, 108.52, 126.83, 127.37, 128.06, 128.52, 129.78, 136.10, 138.43, 141.29, 159.96 and 160.32 (arom C), 166.49 (CO_2Me) and 191.34 (CHO); *m/z* (EI) 376.

General Procedure for Synthesis of Monosubstituted Alcohols **20a–c**.—To a solution of the aldehyde **19a–c** (1.00 mol equiv.) in dry CH_2Cl_2 was added tetrabutylammonium borohydride (0.50 mol equiv.) and the mixture was stirred at room temperature under nitrogen for 24 h. Water was added and the mixture was stirred for a further 30 min. The organic layer was removed, the aqueous layer was extracted with CH_2Cl_2 (3 ×), and the combined organic phases were dried and evaporated to dryness. The crude product was purified as outlined below.

NC-[G-1]-OH **20a**. This was prepared from the aldehyde **19a** and was purified by flash chromatography with CH_2Cl_2 as eluent to give *compound* **20a** as a foam; yield 93% (Found: C, 76.7; H, 5.7; N, 4.0. $C_{22}H_{19}NO_3$ requires C, 76.50; H, 5.54; N, 4.05%); ν_{max}/cm^{-1} 3400–3200, 2230, 1600 and 1165; δ_H 2.01 (1 H, t, *J* 6, CH_2OH), 4.61 (2 H, d, *J* 6, CH_2OH), 5.02 and 5.09 (each 2 H, s, Ar′- and Ph-CH_2O), 6.49 (1 H, t, *J* 2, ArH), 6.59 and 6.64 (each 1 H, d d, *J* 1 and 2, ArH), 7.30–740 (5 H, m, PhH) and 7.48 and 7.64 (4 H, ABq, *J* 8, Ar′H); δ_H 65.05 (CH_2OH), 68.96 and 70.15 (CH_2O), 101.37, 105.69, 106.13 and 111.70 (arom C),

118.64 (CN), 127.45, 127.51, 128.04, 128.60, 132.37, 136.74, 142.40, 143.76, 159.57 and 160.25 (arom C); *m/z* (EI) 345.

Br-[G-1]-OH **20b**. This was prepared from the aldehyde **19b** and was purified by flash chromatography with $CHCl_3$ as eluent to give *compound* **20b** foam; yield 84% (Found: C, 63.2; H, 5.05. $C_{21}H_{19}BrO_3$ requires C, 63.17; H, 5.05%); ν_{max}/cm^{-1} 3450–3250, 1600, 1290 and 1165; δ_H 1.80 (1 H, t, *J* 6, CH_2OH), 4.61 (2 H, d, *J* 6, CH_2OH), 4.96 and 5.02 (each 2 H, s, Ar′- and Ph-CH_2O), 6.51 (1 H, t, *J* 2, ArH), 6.58 and 6.62 (each 1 H, d d, *J* 1 and 2, ArH), 7.26 and 7.48 (4 H, ABq, *J* 8, ArH) and 7.30–7.40 (5 H, m, PhH); δ_C 65.22 (CH_2OH), 69.32 and 70.13 (CH_2O), 101.41, 105.79, 105.97, 121.88, 127.45, 127.99, 128.04, 128.57, 129.02, 131.70, 135.93, 136.63, 143.53, 159.90 and 160.22 (arom C); *m/z* (EI) 398 and 400 (*ca.* 1:1).

MeO_2C-[G-1]-OH **20c**. This was prepared from the aldehyde **19c** and was purified by flash chromatography with CH_2Cl_2 as eluent to give *compound* **20c** as a foam; yield 91% (Found: C, 73.3; H, 5.85. $C_{23}H_{22}O_5$ requires C, 73.00; H, 5.86%); ν_{max}/cm^{-1} 3400–3200, 1720, 1610 and 1170; δ_H 1.90 (1 H, t, CH_2OH), 3.89 (3 H, s, Me), 4.57 (2 H, d, *J* 6, CH_2OH), 4.98 and 5.00 (each 2 H, s, Ar′- and Ph-CH_2O), 6.51 (1 H, t, *J* 2, ArH), 6.60 and 6.63 (each 1 H, d d, *J* 1 and 2, ArH), 7.30–7.40 (5 H, m, PhH) and 7.43 and 8.02 (4 H, ABq, *J* 8, Ar′H); δ_C 51.87 (Me), 64.70 (CH_2OH), 69.10 and 69.87 (CH_2O), 101.10, 105.53, 105.77, 126.73, 127.25, 127.75, 128.35, 129.39, 129.62, 136.68, 142.01, 143.64, 159.60 and 159.96 (arom C) and 166.68 (CO_2Me); *m/z* (EI) 378.

General Procedure for Synthesis of First-generation Monosubstituted Bromides **21a–c**.—To a solution of the alcohol **20** (1.00 mol equiv.) in the minimum amount of dry THF were added tetrabromomethane (1.25 mol equiv.) and triphenylphosphine (1.25 mol equiv.) and the mixture was stirred at room temperature under nitrogen for 15 min. Water was added and the aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic extracts were dried, and evaporated to dryness. The crude product was purified as outlined below.

NC-[G-1]-Br **21a**. This was prepared from the alcohol **20a** and was purified by flash chromatography with 1:3 hexane–CH_2Cl_2 as eluent to give *compound* **21a** as a foam; yield 85% (Found: C, 65.1; H, 4.6; N, 3.3. $C_{22}H_{18}BrNO_2$ requires C, 64.71; H, 4.44; N, 3.43%); ν_{max}/cm^{-1} 2230, 1600 and 1165; δ_H 4.41 (2 H, s, CH_2Br), 5.03 and 5.08 (each 2 H, s, Ar′- and Ph-CH_2O), 6.51 (1 H, t, *J* 2, ArH), 6.61 and 6.66 (each 1 H, d d, *J* 1 and 2, ArH), 7.30–7.40 (5 H, m, PhH) and 7.51 and 7.66 (4 H, ABq, *J* 8, Ar′H); δ_C 33.20 (CH_2Br), 68.96 and 70.16 (CH_2O), 102.20, 108.08, 108.51 and 111.75 (arom C), 118.50 (CN), 127.40, 127.47, 128.02, 128.54, 132.29, 136.42, 139.96, 142.02, 159.39 and 160.08 (arom C); *m/z* (EI) 407 and 409 (*ca.* 1:1).

Br-[G-1]-Br **21b**. This was prepared from the alcohol **20b** and was purified by flash chromatography with 1:4 hexane–$CHCl_3$ as eluent to give *compound* **21b** as a foam; yield 74% (Found: C, 54.7; H, 4.15. $C_{21}H_{18}Br_2O_2$ requires C, 54.57; H, 3.93%); ν_{max}/cm^{-1} 1600, 1280 and 1170; δ_H 4.41 (2 H, s, CH_2Br), 4.97 and 5.03 (each 2 H, s, Ar′- and Ph-CH_2O), 6.53 (1 H, t, *J* 2, ArH), 6.62 and 6.66 (each 1 H, d d, *J* 1 and 2, ArH), 7.28 and 7.51 (4 H, ABq, *J* 8, ArH) and 7.30–7.40 (5 H, m, PhH); δ_C 33.37 (CH_2Br), 69.37 and 70.19 (CH_2O), 102.27, 108.20, 108.38, 121.94, 127.47, 128.04, 128.56, 129.04, 131.70, 135.93, 135.70, 136.60, 139.86, 159.79 and 160.10 (arom C); *m/z* (EI) 460, 462 and 464 (*ca.* 1:2:1).

MeO_2C-[G-1]-Br **21c**. This was prepared from the alcohol **20c** and was purified by flash chromatography with CH_2Cl_2 as eluent to give *compound* **21c** as a foam; yield 88% (Found: C, 63.0; H, 5.0. $C_{23}H_{21}BrO_4$ requires C, 62.60; H, 4.80%); ν_{max}/cm^{-1} 1720, 1610 and 1170; δ_H 3.92 (3 H, s, Me), 4.41 (2 H, s, CH_2Br), 5.02 and 5.08 (each 2 H, s, Ar′ and Ph-CH_2O), 6.54 (1 H, t, *J* 2, ArH), 6.63 and 6.66 (each 1 H, d d, *J* 1 and 2, ArH), 7.30–7.40 (5 H, m, PhH) and 7.48 and 8.06 (4 H, ABq, *J* 8, Ar′H); δ_C 33.31 (CH_2Br), 51.96 (Me), 69.35 and 70.09 (CH_2O), 102.18, 108.13, 108.34, 126.87, 127.40, 127.96, 128.49, 129.71, 129.77, 136.52, 139.83, 141.77, 159.67 and 160.03 (arom C) and 166.60 (CO_2Me); *m/z* (EI) 440 and 442 (*ca.* 1:1).

General Procedure for Synthesis of Monophenolic Dendrimers.—A mixture of the bromomethyl dendritic 'wedge' (1.00 mol equiv.), 3,5-dihydroxybenzyl alcohol **13** (4.00–5.00 mol equiv.), potassium carbonate (2.00 mol equiv.) and 18-c-6 (0.2 mol equiv.) in dry acetone was heated at reflux under nitrogen for 24 h. The mixture was cooled, evaporated to dryness, and partitioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 ×), and the combined organic layers were dried and evaporated to dryness. The crude product was purified as outlined below.

General Procedure for Synthesis of Monocyano-substituted Dendritic Alcohols NC-[G-n]-OH.—A mixture of the monocyano-substituted bromide (1.00 mol equiv.), the corresponding monophenolic derivative (1.00 mol equiv.), potassium carbonate (2.00 mol equiv.) and 18-c-6 (0.2 mol equiv.) in dry acetone was heated at reflux under nitrogen for 24 h. The mixture was cooled, evaporated to dryness, and partitioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 ×), and the combined organic layers were dried and evaporated to dryness. The crude product was purified as outlined below.

General Procedure for Synthesis of Substituted Dendritic Bromides X_m-[G-*n*]-Br.—To a solution of the alcohol X_m-[G-*n*]-OH (1.00 mol equiv.) in the minimum amount of dry THF were added tetrabromomethane (1.25 mol equiv.) and triphenylphosphine (1.25 mol equiv.) and the mixture was stirred at room temperature for 15 min. Water was added and the aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic extracts were dried and evaporated to dryness. The crude product was purified as outlined below.

[G-1]-[M]-OH **22**. This was prepared from [G-1]-Br, and was purified by flash chromatography with CH_2Cl_2 increasing to 1:3 Et_2O–CH_2Cl_2 as eluent to give *compound* **22** as foam; yield 79% (Found: C, 76.3; H, 5.85. $C_{28}H_{26}O_5$ requires C, 76.00; H, 5.92%), ν_{max}/cm^{-1} 3450–3250, 1605, 1430, 1290 and 1165; δ_H 1.80 (1 H, t, *J* 6, CH_2OH), 4.49 (2 H, d, *J* 6, CH_2OH), 4.86, 5.01 (2 H:4 H, each s, Ar- and Ph-CH_2O), 6.41, 6.44 and 6.48 (each 1 H, m, ArH), 6.62 (1 H, t, *J* 2, ArH), 6.72 (2 H, d, *J* 2, ArH) and 7.30–7.40 (10 H, m, PhH); δ_C 65.72 (CH_2OH), 69.60 and 69.95 (CH_2O), 101.51, 105.36, 106.34, 106.61, 127.45, 127.82, 128.42, 136.62, 139.14, 139.26, 142.98, 157.20 and 159.99 (arom C); *m/z* (FAB) 442.

NC-[G-2]-OH **23**. This was prepared from NC-[G-1]-Br **21a** and the monophenol **22**, and was purified by flash chromatography with CH_2Cl_2 increasing to 1:10 Et_2O–CH_2Cl_2 as eluent to give *compound* **23** as foam; yield 87% (Found: C, 78.1; H, 5.9; N, 1.75. $C_{50}H_{43}NO_7$ requires C, 78.00; H, 5.63; N, 1.82%); ν_{max}/cm^{-1} 3400–3200, 2230, 1600, 1440 and 1165; δ_H 1.87 (1 H, t, *J* 6, CH_2OH), 4.61 (2 H, d, *J* 6, CH_2OH), 4.96, 5.02 and 5.06 (4 H:6 H:2 H, each s, Ar-, Ph- and Ar′-CH_2O), 6.50, 6.53 and 6.58 (each 1 H, t, *J* 2, ArH), 6.60 (2 H, m, ArH), 6.64 and 6.69 (each 1 H, m, ArH), 6.68 (2 H, d, *J* 2 ArH), 7.30–7.40 (15 H, m, PhH) and 7.48 and 7.63 (4 H, ABq, *J* 8, Ar′H); δ_C 65.10 (CH_2OH), 68.85, 69.71, 69.85, 70.03 and 70.07 (CH_2O), 101.21, 101.42, 101.52, 105.60, 105.66, 106.11, 106.30, 106.56 and 111.57 (arom C), 118.66 (CN), 127.47, 127.50, 128.02, 128.55, 132.31, 136.54, 136.67, 139.19, 139.50, 142.19, 143.47, 159.46, 159.87, 159.96, 160.09 and 160.14 (arom C); *m/z* (FAB) 769.

NC-[G-2]-Br **24**. This was prepared from NC-[G-2]-OH **23**, and was purified by flash chromatography with 1:1 hexane–CH_2Cl_2 increasing to 1:4 hexane–CH_2Cl_2 as eluent to give *compound* **24** as a foam; yield 90% (Found: C, 71.8; H, 5.1; N, 1.7. $C_{50}H_{42}BrNO_6$ requires C, 72.11; H, 5.08; N, 1.68%); ν_{max}/cm^{-1}

2230, 1600, 1435 and 1165; δ_H 4.40 (2 H, s, CH_2Br), 4.96, 5.03 and 5.08 (4 H:6 H:2 H, each s, Ar; Ph- and Ar′-CH_2O), 6.48, 6.52 and 6.57 (each 1 H, t, *J* 2, ArH), 6.60–6.62 (3 H, m, ArH), 6.66 (2 H, d, *J* 2, ArH), 6.68 1 H, m, ArH), 7.30–7.40 (15 H, m, PhH) and 7.49 and 7.64 (4 H, ABq, *J* 8, Ar′H); δ_C 33.50 (CH_2Br), 68.74, 69.68, 69.82, 69.92 and 69.97 (CH_2O), 101.42, 101.50, 102.03, 106.07, 106.25, 106.50, 108.00, 108.08 and 111.47 (arom C), 118.59 (CN), 127.40, 127.50, 128.02, 128.49, 132.19, 136.47, 136.58, 138.88, 139.18, 139.67, 142.07, 159.38, 159.70, 159.79, 160.02 and 160.06 (arom C); *m/z* (FAB) 831 and 833.

[G-2]-[M]-OH **25**. This was prepared from [G-2]-Br and was purified by flash chromatography with CH_2Cl_2 increasing to 1:3 Et_2O–CH_2Cl_2 as eluent to give *compound* **25** as a foam; yield 71% (Found: C, 77.7; H, 5.95. $C_{56}H_{50}O_9$ requires C, 77.73; H, 5.81%); ν_{max}/cm^{-1} 3450–3250, 1600, 1290 and 1165; δ_H 1.85 (1 H, t, *J* 6, CH_2OH), 4.47 (2 H, d, *J* 6, CH_2OH), 4.83, 4.92 and 5.01 (2 H:4 H:8 H, each s, Ar- and Ph-CH_2O), 6.40, 6.44 and 6.49 (each 1 H, m, ArH), 6.58 (1 H, t, *J* 2, ArH), 6.62 (2 H, t, *J* 2, ArH), 6.68 and 6.72 (2 H:4 H, each d, *J* 2, ArH) and 7.30–7.40 (20 H, m, PhH); δ_C 65.72 (CH_2OH), 69.62, 69.76 and 69.91 (CH_2O), 101.46, 105.39, 106.33, 106.68, 127.45, 127.86, 128.42, 136.60, 139.10, 139.25, 142.98, 157.20, 159.80 and 159.94 (arom C); *m/z* (FAB) 866.

NC-[G-3]-OH **26**. This was prepared from NC-[G-2]-Br **24** and the corresponding monophenol **25**, and was purified by flash chromatography with CH_2Cl_2 increasing to 1:10 Et_2O–CH_2Cl_2 as eluent to give *compound* **26** as a foam; yield 85% (Found: C, 78.4; H, 5.9; N, 0.9. $C_{106}H_{91}NO_{15}$ requires C, 78.64; H, 5.67; N, 0.87%); ν_{max}/cm^{-1} 3400–3200, 2230, 1600, 1440, 1370 and 1165; δ_H 1.82 (1 H, t, *J* 6, CH_2OH), 4.58 (2 H, d, *J* 6, CH_2OH), 4.95, 5.01 and 5.04 (8 H:14 H:2 H, each s, Ar-, Ph-, and Ar′-CH_2O), 6.53–6.60 and 6.64–6.69 (21 H, m, ArH), 7.30–7.40 35 H, m, PhH), and 7.46 and 7.61 (4 H, ABq, *J* 8, Ar′H); δ_C 65.07 (CH_2OH), 68.82, 69.75, 69.82, 69.88, 70.01 and 70.05 (CH_2O), 101.14, 101.49, 101.56, 105.64, 106.10, 106.31, 106.57 and 111.54 (arom C), 188.66 (CN), 127.47, 127.50, 128.00, 128.51, 132.28, 136.53, 136.66, 139.14, 139.22, 139.30, 139.43, 142.17, 143.51, 159.44, 159.86, 159.96, 160.07 and 160.12 (arom C); *m/z* (FAB) 1617 and 1618 (*ca.* 1:1).

NC-[G-3]-Br **27**. This was prepared from NC-[G-3]-OH **26**, and was purified by flash chromatography with 1:1 hexane–CH_2Cl_2 increasing to 1:9 hexane–CH_2Cl_2 as eluent to give *compound* **27** as a foam; yield 92% (Found: C, 75.9; H, 5.2; N, 0.7. $C_{106}H_{90}BrNO_{15}$ requires C, 75.70; H, 5.39; N, 0.83%); ν_{max}/cm^{-1} 2230, 1600, 1455, 1365, 1170 and 1065; δ_H 4.38 (2 H, s, CH_2Br), 4.95, 4.96, 5.02 and 5.06 (4 H:8 H:14 H:2 H, each s, Ar-, Ph-, and Ar′-CH_2O), 6.52–6.58 and 6.62–6.69 (21 H, m, ArH), 7.29–7.43 (35 H, m, PhH) and 7.47 and 7.62 (4 H, ABq, *J* 8, Ar′H); δ_C 33.57 (CH_2Br), 68.87, 69.81, 69.94, 70.04 and 70.10 (CH_2O), 101.52, 101.58, 102.13, 106.14, 106.33, 106.39, 106.60, 108.14, 108.19 and 111.61 (arom C), 118.67 (CN), 127.50, 127.98, 128.56, 132.32, 136.55, 136.69, 138.97, 139.03, 139.11, 139.14, 139.43, 139.79, 142.19, 159.48, 159.88, 159.92, 160.02, 160.12 and 160.18 (arom C); *m/z* (FAB) 1679 and 1681 (*ca.* 1:1).

[G-3]-[M]-OH **28**. This was prepared from [G-3]-Br and was purified by flash chromatography with CH_2Cl_2 increasing to 1:3 Et_2O–CH_2Cl_2 as eluent compound **28** as a foam; yield 75% (Found: C, 78.2; H, 6.0. $C_{112}H_{98}O_{17}$ requires C, 78.39; H, 5.76%); ν_{max}/cm^{-1} 3450–3250, 1600, 1475, 1365 and 1165; δ_H 1.81 (1 H, t, *J* 6, CH_2OH), 4.46 (2 H, d, *J* 6, CH_2OH), 4.85, 4.92 and 4.99 (2 H:8 H:16 H, each s, Ar- and Ph-CH_2O), 6.20, 6.37 and 6.46 (each 1 H, m, ArH), 6.30 (1 H, t, *J* 2, ArH), 6.55 (3 H, m, ArH), 6.57 (4 H, t, *J* 2, ArH), 6.62, 6.65 and 6.68 (2 H:4 H:8 H, each d, *J* 2, ArH) and 7.30–7.40 (40 H, m, PhH); δ_C 64.87 (CH_2OH), 69.67, 69.88 and 70.00 (CH_2O), 101.46, 101.53, 105.34, 106.19, 106.35, 106.53, 127.51, 127.93, 128.50, 136.68, 139.14, 139.21, 139.39, 143.44, 157.17, 159.93 and 160.05 (arom C); *m/z* (FAB) 1714.

NC-[G-4]-OH **29**. This was prepared from NC-[G-3]-Br **27** and the corresponding monophenol **28**, and was purified by flash chromatography with CH_2Cl_2 increasing to 1:200 EtOAc–CH_2Cl_2 as eluent to give *compound* **29** as a foam; yield 91% (Found: C, 79.2; H, 5.8; N, 0.5. $C_{218}H_{187}NO_{31}$ requires C, 78.94; H, 5.68; N, 0.42%); ν_{max}/cm^{-1} 2230, 1600, 1440, 1370 and 1165; δ_H 1.76 (1 H, t, *J* 6, CH_2OH), 4.52 (2 H, d, *J* 6, CH_2OH), 4.91, 4.97 and 4.99 (16 H:30 H:2 H, each s, Ar-, Ar′- and Ph-CH_2O), 6.48–6.55 and 6.60–6.66 (45 H, m, ArH), 7.26–7.40 (75 H, m, PhH) and 7.43 and 7.58 (4 H, ABq, *J* 8, Ar′H); δ_C 65.07 (CH_2OH), 68.83, 69.77, 69.842, 69.90 and 70.01 (CH_2O), 101.13, 101.53, 105.73, 106.13, 106.33, 106.60 and 111.56 (arom C), 118.67 (CN), 127.50, 128.03, 128.51, 132.28, 136.57, 136.71, 139.13, 139.15, 139.18, 139.25, 139.32, 139.35, 139.44, 142.18, 143.51, 159.45, 159.89, 159.95, 160.00, 160.09 and 160.13 (arom C).

NC-[G-4]-Br **30**. This was prepared from NC-[G-4]-OH **29**, and was purified by flash chromatography with 1:3 hexane–CH_2Cl_2 increasing to 1:9 hexane–CH_2Cl_2 as eluent to give *compound* **30** as a foam; yield 84% (Found: C, 77.7; H, 5.75; N, 0.2. $C_{218}H_{186}BrNO_{30}$ requires C, 77.42; H, 5.54; N, 0.41%); ν_{max}/cm^{-1} 2230, 1600, 1455, 1365, 1170 and 1065; δ_H 4.33 (2 H, s, CH_2Br), 4.89, 4.92, 4.98 and 5.00 (4 H:24 H:30 H:2 H, each s, Ar-, Ar′- and Ph-CH_2O), 6.50–6.58 and 6.60–6.66 (45 H, m, ArH), 7.26–7.42 (75 H, m, PhH) and 7.44 and 7.60 (4 H, ABq, *J* 8, Ar′H); δ_C 33.56 (CH_2Br), 68.83, 69.78, 69.91 and 70.01 (CH_2O), 101.53, 102.10, 106.13, 106.33, 106.60, 108.22 and 111.57 (arom C), 118.67 (CN), 127.51, 128.00, 128.53, 132.28, 136.57, 136.71, 139.08, 139.12, 139.15, 139.22, 139.44, 139.73, 142.19, 159.47, 159.87, 159.90, 160.01, 160.09 and 160.15 (arom C).

Monoalkylated [G-4]-[C]-$(OH)_2$, **33**, *and Dialkylated* [G-4]$_2$-[C]-OH, **34**, *Core Molecules*.—A mixture of unsubstituted fourth-generation bromide [G-4]-Br **32** (1.50 g, 0.45 mmol), 1,1,1-tris-(4′-hydroxyphenyl)ethane [C]-$(OH)_3$ **31** (2.70 g, 8.80 mmol), potassium carbonate (1.50 g, 10.8 mmol) and 18-c-6 (50 mg, 0.19 mmol) in dry acetone (50 cm^3) was heated at reflux under nitrogen for 24 h. The reaction mixture was cooled, and evaporated to dryness, and the residue was partitioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 ×), and the combined organic layers were dried and evaporated to dryness. The crude product was purified by flash chromatography with 1:4 hexane–CH_2Cl_2 increasing to CH_2Cl_2 as eluent to give the *dialkylated core* **34** as a foam; yield 41% (Found: C, 79.3; H, 5.5. $C_{454}H_{390}O_{63}$ requires C, 79.56; H, 5.73%); ν_{max}/cm^{-1} 2950, 1600, 1455, 1365, 1170 and 1065; δ_H 2.08 (3 H, s, Me), 4.96 and 4.99 (124 H, each s, Ar- and Ph-CH_2O), 6.50–6.54 and 6.57–6.62 (92 H, m, Ar- and Ar″-H), 6.76 and 6.89 (8 H, ABq, *J* 8 Ar″H), 6.84 (2 H, B of ABq, *J* 8, Ar″H), and 7.26–7.41 (160 H, m, PhH); δ_C 30.86 (Me), 50.54 (*C*Me), 69.98 and 70.14 (CH_2O), 101.64, 106.20, 106.40, 111.67, 114.03, 127.54, 127.98, 128.56, 129.76, 136.79, 137.81, 139.22, 159.91, 160.06 and 160.17 (arom C).

Increasing the eluent polarity from CH_2Cl_2 to 1:50 Et_2O–CH_2Cl_2 gave the *monoalkylated core* **33** as a foam; yield 33% (Found: C, 79.7; H, 5.9. $C_{237}H_{204}O_{33}$ requires C, 79.51; H, 5.74%); ν_{max}/cm^{-1} 2950, 1600, 1455, 1365, 1170 and 1065; δ_H 2.06 (3 H, s, Me), 4.95 and 4.98 (62 H, each s, Ar- and Ph-CH_2O), 6.49–6.52 and 6.58–6.62 (49 H, m, Ar- and Ar″-H), 6.75 and 6.87 (4 H, ABq, *J* 8, Ar″H), 6.82 (4 H, B of ABq, *J* 8, Ar″H) and 7.26–7.37 (80 H, m, PhH); δ_C 30.82 (Me), 50.51 (*C*Me), 69.96 and 70.07 (CH_2O), 101.60, 106.13, 106.39, 111.63, 114.08, 127.53, 127.97, 128.54, 129.73, 136.74, 137.83, 139.18, 160.01, 160.04 and 160.11 (arom C).

Monocyano-substituted Dendritic Macromolecule: NC-[G-4]-[C]-[G-4]$_2$ **36**.—A mixture of NC-[G-4]-Br **30** (250 mg, 0.075

mmol), dialkylated core [G-4-$_2$][C]-OH **34** (500 mg, 0.075 mmol), potassium carbonate (207 mg, 1.50 mmol) and 18-c-6 (40 mg, 0.15 mmol) in dry acetone (20 cm^3) was heated at reflux under nitrogen for 24 h. The reaction mixture was cooled, and evaporated to dryness, and the residue was partitioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 ×), and the combined organic layers were dried and evaporated to dryness. The crude product was purified by flash chromatography with 1:4 hexane–CH_2Cl_2 increasing to CH_2Cl_2 as eluent to give the *monocyano dendrimer* **36** as a foam; yield 80% (Found: C, 79.35; H, 6.0; N, 0.4. $C_{672}H_{575}NO_{93}$ requires C, 79.61; H, 5.72; N, 0.14%); ν_{max}/cm^{-1} 2230, 1600, 1470, 1365, 1170 and 1060 δ_H 2.07 (3 H, s, Me), 4.91 (90 H, s, Ar-, Ar′- and Ph-CH_2O), 4.95 (96 H, s, PhCH_2O), 6.50–6.56 and 6.60–6.64 (135 H, m, ArH), 6.78 (6 H, d, *J* 9, core Ar″H), 6.94 (6 H, d, *J* 9, core Ar″H), 7.26–7.42 (238 H, m, PhH) and 7.52 (2 H, A of ABq, *J* 8, Ar′H); δ_C 30.76 (Me), 50.57 (*C*Me), 68.43, 69.75, 69.26, 69.84 and 69.95 (CH_2O), 101.50, 106.11, 106.30, 111.48 and 113.93 (arom C), 118.67 (CN), 127.48, 128.07, 128.49, 129.58, 132.22, 136.32, 136.57, 139.16, 139.44, 139.50, 141.97, 142.14, 156.68, 159.43, 159.87, 159.96 and 160.05 (arom C).

Dicyano-substituted Dendritic Macromolecule: (NC-[G-4])$_2$-[C]-[G-4] **37**.—A mixture of NC-[G-4]-Br **30** (250 mg, 0.075 mmol), monoalkylated core [G-4]-[C]-$(OH)_2$ **33** (132 mg, 0.037 mmol), potassium carbonate (207 mg, 1.50 mmol) and 18-c-6 (40 mg, 0.15 mmol) in dry acetone (15 cm^3) was heated at reflux under nitrogen for 24 h. The reaction mixture was cooled, and evaporated to dryness, and the residue was partitioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 ×), and the combined organic layers were dried and evaporated to dryness. The crude product was purified by flash chromatography with 1:4 hexane–CH_2Cl_2 increasing to CH_2Cl_2 as eluent to give the *dicyano-substituted dendrimer* **37** as a foam; yield 72% (Found: C, 79.8; H, 5.7; N, 0.2. $C_{673}H_{574}N_2O_{93}$ requires C, 79.53; H, 5.72; N, 0.28%); ν_{max}/cm^{-1} 2230, 1600, 1470, 1365, 1170 and 1060; δ_H 2.05 (3 H, s, Me), 4.92 (90 H, s, Ar-, Ar′- and Ph-CH_2O), 4.96 (96 H, s, PhCH_2O), 6.49–6.56 and 6.59–6.64 (135 H, m, ArH), 6.79 (6 H, d, *J* 9, core Ar″H), 6.94 (6 H, d, *J* 9, core Ar″H), 7.26–7.42 (238 H, m, PhH) and 7.53 (4 H, A of ABq, *J* 8, Ar′H); δ_C 30.79 (Me), 50.65 (*C*Me), 68.48, 68.75, 69.29, 69.87 and 69.94 (CH_2O), 101.50, 106.12, 106.32, 111.48 and 113.99 (arom C), 118.64, (CN), 127.50, 127.98, 128.50, 129.60, 132.25, 136.32, 136.64, 139.21, 139.46, 139.54, 142.01, 142.14, 156.73, 159.44, 159.85, 159.94 and 160.09 (arom C).

Tricyano-substituted Dendritic Macromolecule: (NC-[G-4])$_3$-[C] **38**.—A mixture of NC-[G-4]-Br **30** (250 mg, 0.075 mmol), 1,1,1-tris(4′-hydroxyphenyl)ethane [C]-$(OH)_3$ **31** (7.6 mg, 0.025 mmol), potassium carbonate (138 mg, 1.00 mmol) and 18-c-6 (26 mg, 0.10 mmol) in dry acetone (10 cm^3) was heated at reflux under nitrogen for 24 h. The reaction mixture was cooled and evaporated to dryness, and the residue was partitioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 ×) and the combined organic layers were dried and evaporated to dryness. The crude product was purified by flash chromatography with 1:4 hexane–CH_2Cl_2 increasing to CH_2Cl_2 as eluent to give the *tricyano-substituted dendrimer* **38** as a foam; yield 77% (Found: C, 79.7; H, 5.95; N, 0.5. $C_{674}H_{573}N_3O_{93}$ requires C, 79.58; H, 5.68; N, 0.41%); ν_{max}/cm^{-1} 2230, 1600, 1470, 1365, 1170 and 1060; δ_C 2.03 (3 H, s, Me), 4.89 (90 H, s, Ar-, Ar′-and Ph-CH_2O), 4.94 (96 H, s, PhCH_2O), 6.46–6.53 and 6.57–6.63 (135 H, m, ArH), 6.78 (6 H, d, *J* 9, core Ar″H), 6.93 (6 H, d, *J* 9, core Ar″H), 7.25–7.40 (238 H, m, PhH) and 7.52 (6 H, A of ABq, *J* 8, Ar′H); δ_C 30.70 (Me), 50.57 (*C*Me), 67.07, 68.77, 69.85 and 69.96 (CH_2O), 101.50, 106.12, 106.31, 106.57, 111.66 and 113.94 (arom C), 118.65 (CN), 127.49, 127.92, 128.50, 129.58, 132.23, 136.57, 136.71, 139.15, 139.23, 139.44, 139.51, 141.98, 142.15, 156.68, 159.43, 159.62, 159.87, 159.97 and 160.06 (arom C).

Block-type Bromo-substituted Dendritic Macromolecules

General Procedure for Synthesis of Polybromo Dendritic Alcohols Br[$_2n$]-[G-*n*]-OH.—A mixture of the bromo-substituted dendritic bromide Br[$_2(n-1)$]-[G-$(n-1)$]-Br (2.05 mol equiv.), 3,5-dihydroxybenzyl alcohol **13** (1.00 mol equiv.), potassium carbonate (2.00 mol equiv.) and 18-c-6 (0.2 mol equiv.) in dry acetone was heated at reflux under nitrogen for 48 h. The mixture was cooled and evaporated to dryness, and the residue was partitioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 ×), and the combined organic layers were dried and evaporated to dryness. The crude product was purified as outlined below to give the next-generation alcohol Br$_{[2n]}$-[G-*n*]-OH.

General Procedure for Synthesis of Polybromo Dendritic Bromides Br[$_2n$]-[G-*n*]-Br.—To a solution of the alcohol Br$_{[2n]}$-G-*n*]-OH (1.00 mol equiv.) in the minimum amount of dry THF were added tetrabromomethane (1.25 mol equiv.) and triphenylphosphine (1.25 mol equiv.) and the mixture was stirred at room temperature for 15 min. Water was added and the aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic extracts were dried and evaporated to dryness. The crude product was purified as outlined below.

Br_2-[G-1]-OH **45**. This was prepared using 4-bromobenzyl bromide **18b** and 3,5-dihydroxybenzyl alcohol **13** and was purified by flash chromatography with 1:19 EtOAc–CH_2Cl_2 as eluent to give *compound* **45** as a solid; yield 76%; m.p. 98–100 °C (Found: C, 52.9; H, 3.85; Br, 33.2. $C_{21}H_{18}Br_2O_3$ requires C, 52.75; H, 3.79, Br. 33.42%); ν_{max}/cm^{-1} 330, 2920, 2870, 1600, 1490, 1160, 1070, 1010, 830 and 805; δ_H 1.62 (1 H, t, *J* 6, CH_2O*H*), 4.62 (2 H, d, *J* 6, CH_2OH), 4.98 (4 H, s, Ar′CH_2O), 6.47 (1 H, t, *J* 2, ArH), 6.59 (2 H, d, *J* 2, ArH) and 7.28 and 7.50 (8 H, ABq, *J* 10, Ar′H); δ_C 65.21 (CH_2OH), 69.29 (CH_2O), 101.3, 105.8, 121.9, 129.0, 131.7, 135.8, 143.5 and 159.9 (arom C); *m/z* (EI) 476, 478 and 480 (*ca.* 1:2:1, M^+).

Br_2-[G-1]-Br **46**. This was prepared from Br_2-[G-1]-OH **45**, and was purified by flash chromatography with 1:3 hexane–CH_2Cl_2 as eluent and recrystallization from acetone–water to give *compound* **46** as crystals; yield 87%; m.p. 106–107 °C (Found: C, 46.7; H, 3.3; Br, 44.5. $C_{21}H_{17}Br_3O_2$ requires C, 46.62; H, 3.17; Br; 44.30%); ν_{max}/cm^{-1} 2925, 2870, 1600, 1490, 1160, 1070, 1015, 830 and 805; δ_H 4.39 (2 H, s, CH_2Br), 4.97 (4 H, s, Ar′CH_2O), 6.47 (1 H, t, *J* 2, ArH), 6.61 (2 H, d, *J* 2, ArH) and 7.28 and 7.50 (8 H, ABq, *J* 10, Ar′H); δ_C 33.32 (CH_2Br), 69.33 (CH_2O), 102.1, 108.2, 122.0, 129.0, 131.7, 135.5, 139.9 and 159.7 (arom C); *m/z* (EI) 538, 540, 542 and 544 (*ca.* 1:4:4:1, M^+).

Br_4-[G-2]-OH **47**. This was prepared using Br_2-[G-1]-Br **46** and 3,5-dihydroxybenzyl alcohol **13**, and was purified by flash chromatography with $CHCl_3$ as eluent to give *compound* **47** as a solid; yield 88%; m.p. 156–158 °C (Found: C, 55.65; H, 4.0; Br, 30.4. $C_{49}H_{40}Br_4O_7$ requires C, 55.50; H, 3.80; Br, 30.14%); ν_{max}/cm^{-1} 330, 2930, 2870, 1600, 1490, 1160, 1070, 1010, 830 and 805; δ_H 1.66 (1 H, t, *J* 6, CH_2O*H*), 4.61 (2 H, d, *J* 6, CH_2OH), 4.96 (4 H, s, ArCH_2O), 4.97 (8 H, s, Ar′CH_2O), 6.48 (3 H, m, ArH), 6.57 (2 H, d, *J* 2, ArH), 6.62 (4 H, d, *J* 2, ArH) and 7.25 and 7.48 (16 H, ABq, *J* 10, Ar′H); δ_C 64.97 (CH_2OH), 69.17 and 69.65 (Ar′- and Ar-*C*H_2O), 101.1, 101.4, 105.5, 106.3, 121.8, 129.0, 131.6, 135.7, 139.3, 143.5, 159.7 and 159.8 (arom C); *m/z* complex set of peaks at 1060 (M^+).

Br_4-[G-2]-Br **48**. This was prepared from Br_4-[G-2]-OH **47** and was purified by flash chromatography with 1:1 hexane–CH_2Cl_2 as eluent and recrystallization from acetone–water to give *compound* **48** as crystals; yield 84%; m.p. 152–154 °C

(Found: C, 52.45; H, 3.4; Br; 35.4. $C_{49}H_{39}Br_5O_6$ requires C, 52.39; H, 3.50; Br, 35.56%); ν_{max}/cm^{-1} 2925, 2870, 1600, 1490, 1160, 1070, 1010, 830 and 805; δ_H 4.40 (2 H, s, CH_2Br), 4.95 (4 H, s, $ArCH_2O$), 4.97 (8 H, s, $Ar'CH_2O$) 6.47 (1 H, t, *J* 2, ArH), 6.50 (2 H, t, *J* 2, ArH), 6.60 (2 H, d, *J* 2, ArH), 6.62 (4 H, d, *J* 2, ArH) and 7.26 and 7.48 (16 H, ABq, *J* 10, Ar'H); δ_C 33.56 (CH_2Br), 69.33 and 69.88 (Ar'- and Ar-CH_2O), 101.6, 102.2, 106.4, 108.2, 121.9, 129.1, 131.7, 135.7, 139.2, 139.8, 159.8 and 159.9 (arom C); *m/z* (EI) complex set of peaks centred at 1123 (M^+).

Br_8-[G-3]-OH **49**. This was prepared from Br_4-[G-2]-Br **48** and 3,5-dihydroxybenzyl alcohol **13**, and was purified by flash chromatography with $CHCl_3$ as eluent to give *compound* **49** as a glass; yield 88% (Found: C, 56.5; H, 3.7; Br, 28.8. $C_{105}H_{84}Br_8O_{15}$ requires C, 56.68; H, 3.81; Br, 28.73%); ν_{max}/cm^{-1} 3330, 2925, 2870, 1600, 1490, 1160, 1070, 1010, 830 and 805; δ_H 1.70 (1 H, t, *J* 6, CH_2OH), 4.58 (2 H, d, *J* 6, CH_2OH), 4.94 (28 H, s, Ar- and Ar'-CH_2O), 6.47 (7 H, m, ArH), 6.57 (2 H, d, *J* 2, ArH), 6.62 (12 H, m, ArH, ArH) and 7.24 and 7.46 (32 H, ABq, *J* 10, Ar'H); δ_C 65.20 (CH_2OH), 69.29, 69.83 and 69.88 (Ar'- and Ar-CH_2O), 101.3, 101.5, 101.6, 105.7, 106.3, 106.4, 121.9, 129.1, 131.7, 135.7, 139.31, 143.5, 159.8, 159.9 and 160 (arom C).

Br_8-[G-3]-Br **50**. This was prepared from Br_8-[G-3]-OH **49** with CBr_4 and PPh_3 being added in 3 additions (2.0 mol equiv.) every 10 min. The crude product was purified by flash chromatography with $CHCl_3$ as eluent and then precipitation into diethyl ether to give compound **50** as a glass; yield 94%; ν_{max}/cm^{-1} 2925, 2870, 1600, 1490, 1160, 1070, 1010, 830 and 805; δ_H 4.37 (2 H, s, CH_2Br), 4.94 (28 H, s, Ar- and Ar'-CH_2O), 6.47–6.49 (7 H, m, ArH), 6.60 (2 H, d, *J* 2, ArH), 6.61 (12 H, m, ArH) and 7.24 and 7.45 (32 H, ABq, *J* 10, Ar'H); δ_C 33.56 (CH_2Br), 69.31, 69.86 and 70.01 (Ar'- and Ar-CH_2O), 101.6, 102.2, 106.4, 108.2, 113.6, 121.9, 129.1, 131.7, 133.1, 135.7, 139.31, 159.9 and 160.0 (arom C).

Br_{16}-[G-4]-OH **51**. This was prepared from Br_8-[G-3]-Br **50** and 3,5-dihydroxybenzyl alcohol **13** in 1,4-dioxane at 70 °C, and was purified by flash chromatography with $CHCl_3$ as eluent to give *compound* **51**, as a glass; yield 78% (Found: C, 57.5; H, 4.0; Br, 28.0. $C_{217}H_{172}Br_{16}O_{31}$ requires C, 57.23; H, 3.81; Br, 28.07%); ν_{max}/cm^{-1} 2925, 2870, 1600, 1490, 1160, 1070, 1010, 830 and 805; δ_H 1.69 (1 H, t, *J* 6, CH_2OH), 4.51 (2 H, d, *J* 6, CH_2OH), 4.88 (60 H, s, Ar- and Ar'-CH_2O), 6.44–6.45 (14 H, m, ArH), 6.47 (1 H, t, *J* 2, ArH), 6.52 (2 H, d, *J* 2, ArH), 6.56–6.59 (28 H, m, ArH) and 7.19 and 7.42 (64 H, ABq, *J* 10, Ar'H); δ_C 65.12 (CH_2OH), 69.23, 69.79 and 69.90 (Ar'- and Ar-CH_2O), 101.5, 105.8, 106.2, 106.3, 121.9, 129.1, 131.7, 132.9, 135.7, 139.2, 139.3, 143.5, 159.8, 159.9 and 160.0 (arom C).

Br_{16}-[G-4]-Br **52**. This was prepared from Br_{16}-[G-4]-OH **51** with CBr_4 and PPh_3 being added in 4 additions (2.0 mol equiv.) every 10 min. The crude product was purified by flash chromatography with 1:50 hexane–$CHCl_3$ as eluent and precipitation into diethyl ether to give *compound* **52** as a glass; yield 90% (Found: C, 56.4; H, 4.1; Br, 29.2. $C_{217}H_{171}Br_{17}O_{30}$ requires C, 56.45; H, 3.67; Br, 29.42%); ν_{max}/cm^{-1} 2925, 2870, 1600, 1490, 1160, 1070, 1010, 830 and 805; δ_H 4.32 (2 H, s, CH_2Br), 4.88 (60 H, s, Ar- and Ar'-CH_2O), 6.43–6.45 (14 H, m, ArH), 6.48 (1 H, t, *J* 2, ArH), 6.55 (2 H, d, *J* 2, ArH), 6.56–6.59 (28 H, m, ArH) and 7.19 and 7.42 (64 H, ABq, *J* 10, Ar'H); δ_C 33.26 (CH_2Br), 69.17, 69.73 and 69.83 (Ar'- and Ar-CH_2O), 101.5, 102.0, 106.3, 108.2, 121.8, 129.0, 131.7, 135.7, 139.31, 139.33, 143.5, 159.8, 159.9 and 160 (arom C).

Br_{16}-[G-4]-[C]-$[G-4]_2$ **53**. A mixture of Br_{16}-[G-4]-Br **52** (250 mg, 0.075 mmol), dialkylated core $[G-4]_2$-[C]-OH **34** (500 mg, 0.075 mmol), potassium carbonate (207 mg, 1.50 mmol) and 18-c-6 (40 mg, 0.15 mmol) in dry THF (20 cm^3) was heated at reflux under nitrogen for 24 h. The reaction mixture was cooled and evaporated to dryness, and the residue was partitioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 ×), and the combined organic layers were dried and evaporated to dryness. The crude product was purified by flash chromatography with 1:4 hexane–CH_2Cl_2 increasing to CH_2Cl_2 as eluent to give the *dendrimer* **53** as a foam; yield 80% (Found: C, 70.45; H, 5.1; Br, 11.5. $C_{671}H_{560}Br_{16}O_{93}$ requires C, 70.76; H, 4.95; Br, 11.22%); ν_{max}/cm^{-1} 2950, 1610, 1460, 1370, 1170 and 1060; δ_H 2.05 (3 H, s, Me), 4.81 and 4.92 (186 H, each s, Ar-, Ar'- and Ph-CH_2O), 6.43–6.62 (135 H, m, ArH), 6.72 and 6.92 (12 H, ABq, *J* 9, core Ar″H), 7.13 and 7.37 (64 H, ABq, *J* 8, Ar'H) and 7.24–7.35 (160 H, m, PhH); δ_C 30.54 (Me), 50.68 (*C*Me), 69.18, 69.46, 69.80 and 69.97 (CH_2O), 101.54, 106.38, 111.39, 113.83, 121.72, 127.42, 127.96, 128.49, 131.52, 135.66, 136.73, 139.16, 139.27, 139.60, 142.05, 156.61, 159.73, 159.84, 159.95 and 160.05 (arom C).

$(Br_{16}$-[G-4]$)_2$-[C]-[G-4] **54**. A mixture of Br_{16}-[G-4]-Br **52** (250 mg, 0.075 mmol), monoalkylated core [G-4]-[C]-$(OH)_2$ **33** (132 mg, 0.037 mmol), potassium carbonate (207 mg, 1.50 mmol), and 18-c-6 (40 mg, 0.15 mmol) in dry THF (15 cm^3) was heated at reflux under nitrogen for 24 h. The reaction mixture was cooled, evaporated to dryness, and partitioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 ×), and the combined organic layers were dried and evaporated to dryness. The crude product was purified by flash chromatography with 1:4 hexane–CH_2Cl_2 increasing to CH_2Cl_2 as eluent to give the *dendrimer* **54** as a foam; yield 72% (Found: C, 63.8; H, 4.6; Br, 20.0. $C_{671}H_{544}Br_{32}O_{93}$ requires C, 63.70; H, 4.33; Br, 20.21%); ν_{max}/cm^{-1} 2945, 1600, 1460, 1375, 1170 and 1050; δ_H 2.04 (3 H, s, Me), 4.80 and 4.90 (186 H, each s, Ar-, Ar'- and Ph-CH_2O), 6.40–6.59 (135 H, m, ArH), 6.71 (6 H, d, *J* 9, core Ar″H), 6.87 (6 H, d, *J* 9, core Ar″H), 7.13 and 7.37 (128 H, ABq, *J* 8, ArH) and 7.24–7.35 (80 H, m, PhH); δ_C 30.64 (Me), 50.51 (*C*Me), 69.12, 69.70, 69.82 and 69.94 (CH_2O), 101.48, 106.33, 111.33, 113.99, 121.79, 127.47, 127.89, 128.47, 131.56, 135.63, 136.69, 139.14, 139.22, 139.28, 139.62, 141.99, 156.57, 159.76, 159.87, 159.94 and 160.04 (arom C).

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