Repetitive Synthesis of Bulky Dendrimers – A Reversibly Photoactive Dendrimer with Six Azobenzene Side Chains

Hans-Bernhard Mekelburger[a], **Kari Rissanen**[b], and **Fritz Vögtle***[a]

Institut für Organische Chemie und Biochemie der Universität Bonn[a],
Gerhard-Domagk-Straße 1, W-5300 Bonn 1, Germany

Department of Chemistry, University of Jyväskylä[b],
PL 35, SF-40351 Jyväskylä, Finland

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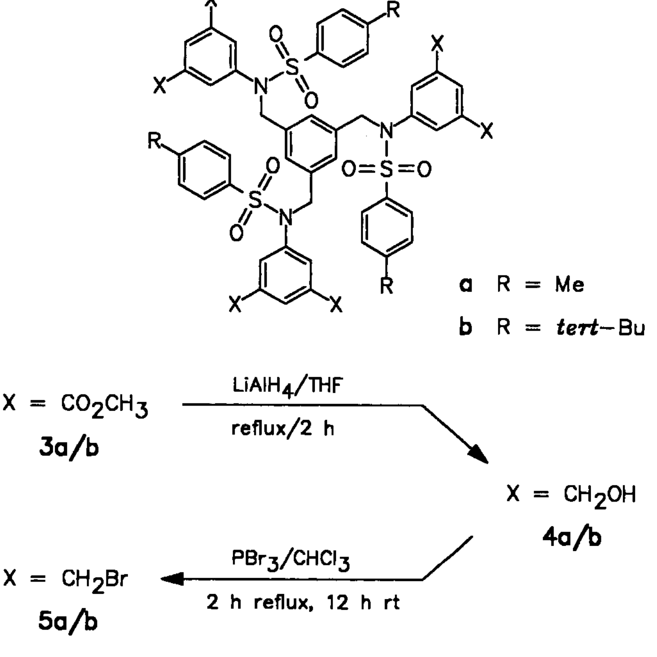
Dendrimers with bulky repeating units containing up to 43 benzene rings (in **9**) have been obtained by using a repetitive divergent synthetic strategy (three generations). The new functional dendrimer **13** containing six azobenzene units at the periphery was synthesized allowing a reversible switching of the shape and size of the molecule upon irradiation. An X-ray structure analysis of the dendritic molecule **3a** shows the inclusion of acetonitrile.

Since our first synthesis of multi-branched cascade molecules in 1978[1] dendrimers have gained widespread attention in organic, supramolecular, and polymer chemistry[2]. The research groups of Denkewalter[3], Newkome[4–7], Tomalia[8–11], Masamune[12], and others used the divergent synthetic method, whereas Fréchet[13–16], Neenan[17], Shinkai[18], and Moore[19] employed the convergent methodology. Recently we described a synthetic scheme of a new family of monodisperse dendritic molecules using large and bulky repeating units[20]. Due to obvious disadvantages of the current nomenclature system with regard to length of names and their missing relation to the structure Newkome proposed a new systematic nomenclature for cascade molecules[21] which is used below.

1. Synthetic Strategy

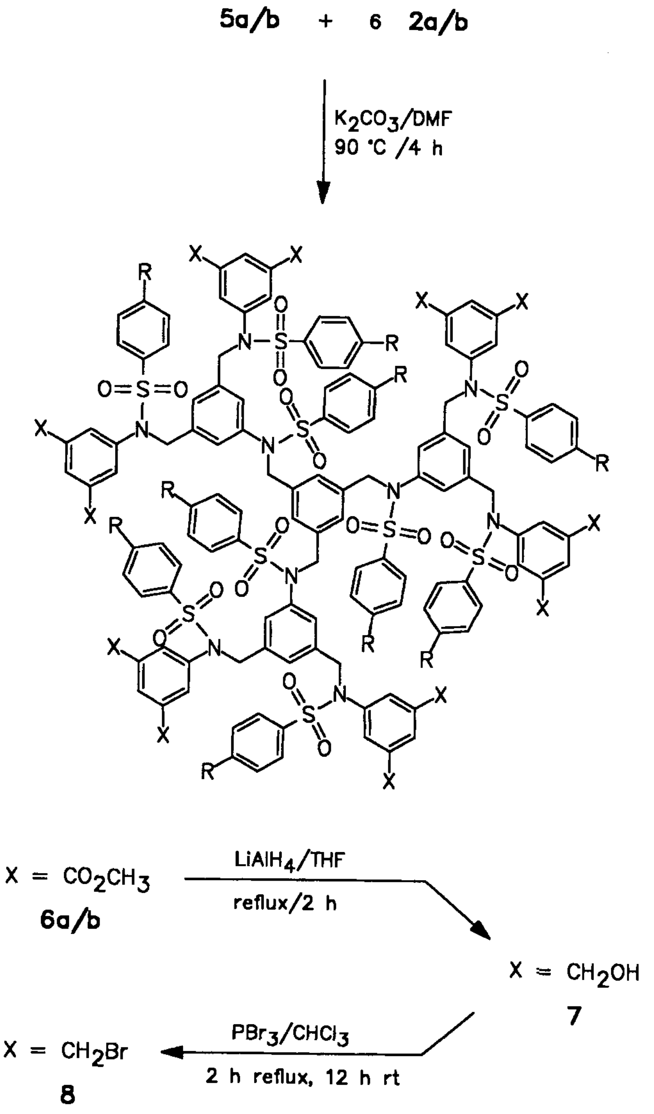
In this paper we report on the extension of our repetitive synthetic concept using modified monomers to give a "functional dendrimer", a reversibly photoactive molecule functionalized with six azobenzene units at the periphery. After divergent synthesis the monomeric units are connected in a more or less rigid fashion, yet the dendrimers of all generations (with one exception) are still very soluble in common organic solvents. These dendrimers were designed to incorporate a balanced mixture of aromatic and aliphatic parts. This is not only advantageous for the characterization of these products by ^{1}H- and ^{13}C-NMR spectroscopy but also for the solubility in organic solvents.

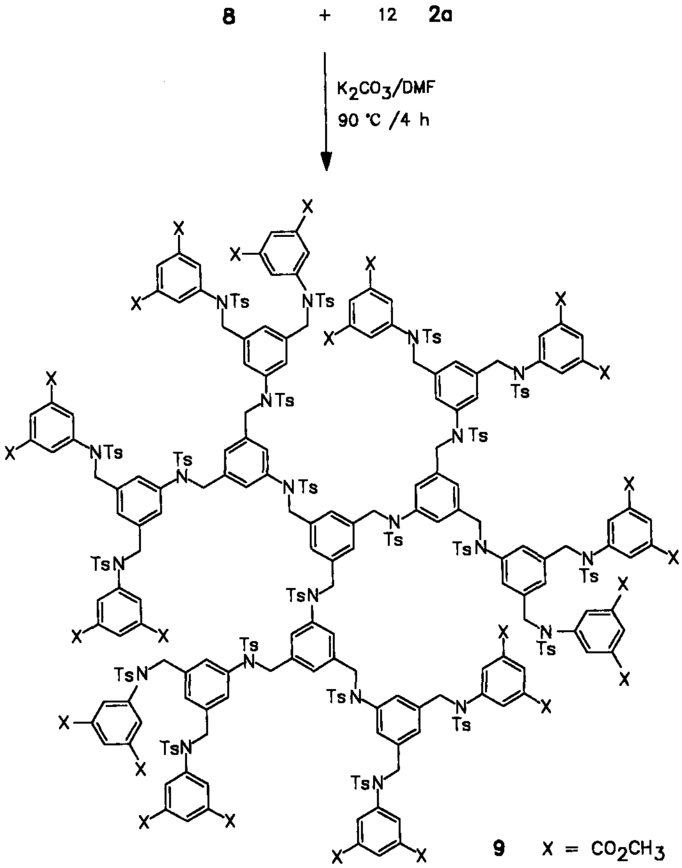
The building blocks can be prepared in a single step from commercially available starting materials. The core 1,3,5-tris(bromomethyl)benzene (**1**), was synthesized by *N*-bromosuccinimide (NBS) bromination[22] and the dimethyl 5-aminoisophthalate was tosylated to afford building block **2a**[23]. The reaction of **1** with three equivalents of **2a** in DMF using K_2CO_3 as base gave the hexaester **3a** in 81% yield[23]. After reduction of **3a** with $LiAlH_4$ in THF, alcohol **4a** was obtained in a moderate yield of 49% after recrystallization. This is probably due to the low solubility of **4a** in THF; however, attempts to carry out the reduction in ether failed. After transformation of hexaalcohol **4a** with PBr_3 to give hexabromide **5a** in 55% yield, one cycle of the repetitive strategy was completed.



In the beginning we pursued another route in order to transform the ester functionalities into bromomethyl groups. After reduction of ester **3a** with $LiAlH_4$ the reaction was quenched with acetic anhydride instead of water, yielding a hexaacetate. This compound was treated with a 33% solution of HBr in glacial acetic acid at room temperature. However, not only was the acetate transformed into the bromide, but also the tosyl groups were cleaved and thus two hydrogen atoms of each of the terminal benzene rings were replaced by two bromine atoms. This prompted us to look for the alternative route described above.

The reaction of hexabromide **5a** with six equivalents of **2a** gave dodecaester **6a** in 43% yield after chromatographic purification. Subsequent reduction to alcohol **7** was achieved almost quantitatively, again followed by bromination in 62% yield to **8**. The yield of the second reduction increased considerably due to the better solubility of dodecaalcohol **7** compared to hexaalcohol **4a**. The third-generation dendrimer **9** with 24 ester groups was prepared analogously (33% yield after column chromatographic purification), but now twelve equivalents of the building block **2a** were needed.





9 X = CO_2CH_3

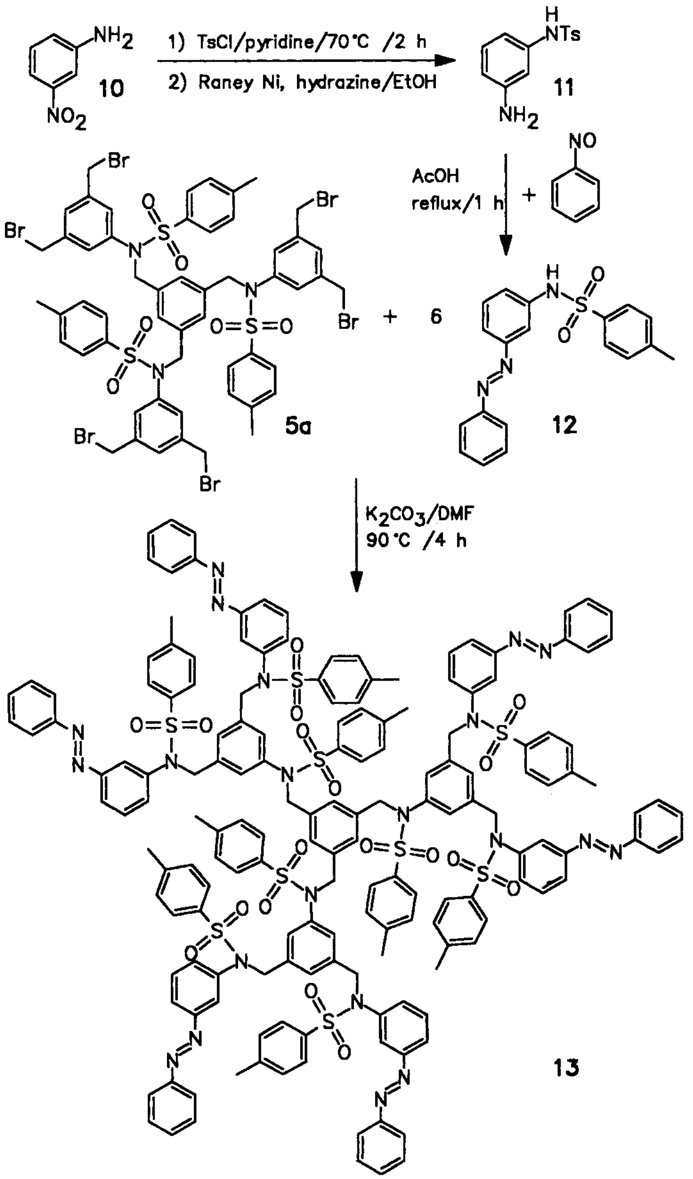
In order to increase the solubility of the first-generation alcohol we exchanged the tosyl groups for 4-*tert*-butylphenylsulfonyl (*t*Bus) groups. This alternative synthesis was carried out up to dodecaester **6b** with comparable yields. But the yield of alcohol **4b** increased to 78%. This can be attributed to its excellent solubility (e.g. in $CHCl_3$ and ethanol), whereas the alcohol **4a** is only soluble in hot ethanol.

In our efforts to obtain a dendrimer functionalized with azobenzene units we had to prepare the azobenzene derivative **12**. Starting with 3-nitroaniline (**10**), we obtained N-tosyl-1,3-phenylendiamine (**11**) in 62% overall yield after tosylation and reduction of the nitro group with Raney nickel and hydrazine[24,25]. Treatment of **11** with nitrosobenzene gave the desired orange compound **12** in a yield of 43% after chromatographic purification of the dark reaction mixture[25]. Finally, the reaction of hexabromide **5a** with six equivalents of 3-(tosylamino)azobenzene (**12**) in DMF led to the desired dendrimer **13** in 40% yield.

2. Properties of the Dendrimer 13

As one can imagine, the azobenzene-funtionalized dendrimer **13** is photoactive. Irradiation of a solution of the *all-E* isomer **13** with e.g. daylight or a fluorescent tube induces partial isomerization to the *Z* form. After heating a solution of **13** in DME to reflux in the dark for some hours complete reisomerization to the thermodynamically more stable *all-E* isomer has taken place.

Irradiation of **13** (*all-E*) at 313 nm for 5 min leads to a photostationary equilibrium (PSE I) where the azobenzene units are switched largely to the *Z* form as demonstrated by UV/Vis absorption spectroscopy (Figure 1). Subsequent irradiation at 436 nm for 3 min leads to another photostationary equilibrium (PSE II) where most of the azobenzene units are reisomerized to the *E* form. Further cycles of this irradiation experiment show the same PSE as at the beginning. This demonstrates that **13**, a molecule containing 25 benzene rings and six azobenzene moieties, constitutes a photofunctional dendrimer which upon irradiation changes with respect to the shape and size of its void regions. How many of the six azobenzene units in a definite molecule isomerize after irradiation remains unknown; only the average number of isomerizing groups could be determined. However, the hexaazobenzene derivative **13** obviously belongs to a new type of functionalized dendrimers which are reactive e.g. towards ions[26], small molecules, or light due to their respective functional groups.



All products obtained as colourless solids were identified by ^{1}H- and ^{13}C-NMR spectroscopy. Especially the change of functional groups could be recognized in the spectra. All product structures except that for **9** were also confirmed by FAB mass spectrometry. Besides the $[M^+ + H]$ peak the $[M^+ - Ts]$ peak is observed. Due to instrumental and technological limitations, the molecular ion of the third-generation ester **9** could not be detected. A molecular mass determination of the dendritic esters **3a**, **6a**, and **9** by osmometry showed a somewhat lower mass than calculated[27]. This deviation increased with growing size of the dendrimers. However, when a narrow-dispersity polystyrene standard ($M = 3770$; $M_w/M_n < 1.04$) instead of benzil ($M = 210$) was used for calibration the deviation was smaller. One of the reasons for this observation may be the fact that solvent residues are "captured" in the pores of the dendrimers (Figure 2), as could be demonstrated by the X-ray structure analysis of **3a** (see below). Even after drying **9** under reduced pressure for several days solvent molecules such as DMF and ethyl acetate could be detected by mass spectrometry. Another reason might be the progressively denser and more compact structure of dendrimers with increasing molecular mass compared to polystyrenes[2,8,9,14].

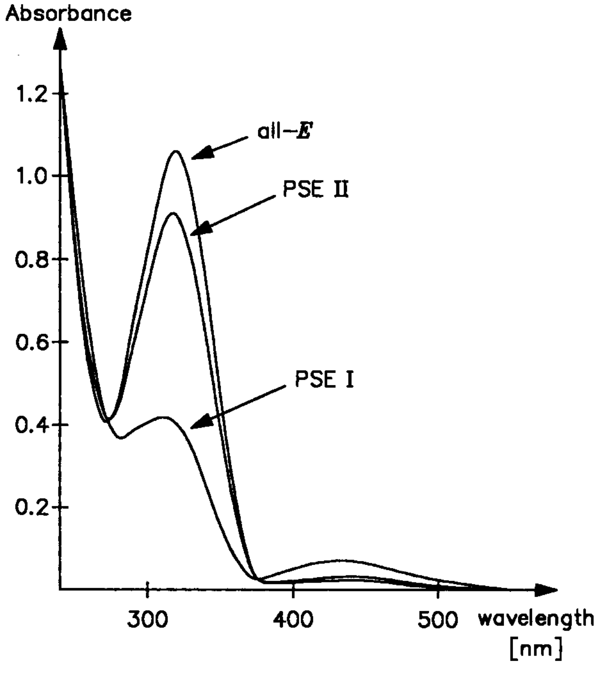


Figure 1. UV/Vis spectrum of the azobenzene-functionalized dendrimer **13** in CH_2Cl_2

A molecular mass of 6910 d (as for **9**) is huge for a dendrimer of the third generation. Also the size of these new dendrimers grows in large increments as the number of generations increases (Figure 2). Thus, the order of magnitude considered for nanostructures[28] can be reached after few generations.

Application of this synthetic strategy may be further extended to larger core units and to core units with a higher degree of branching but also to other functional dendrimers giving them new supramolecular properties.

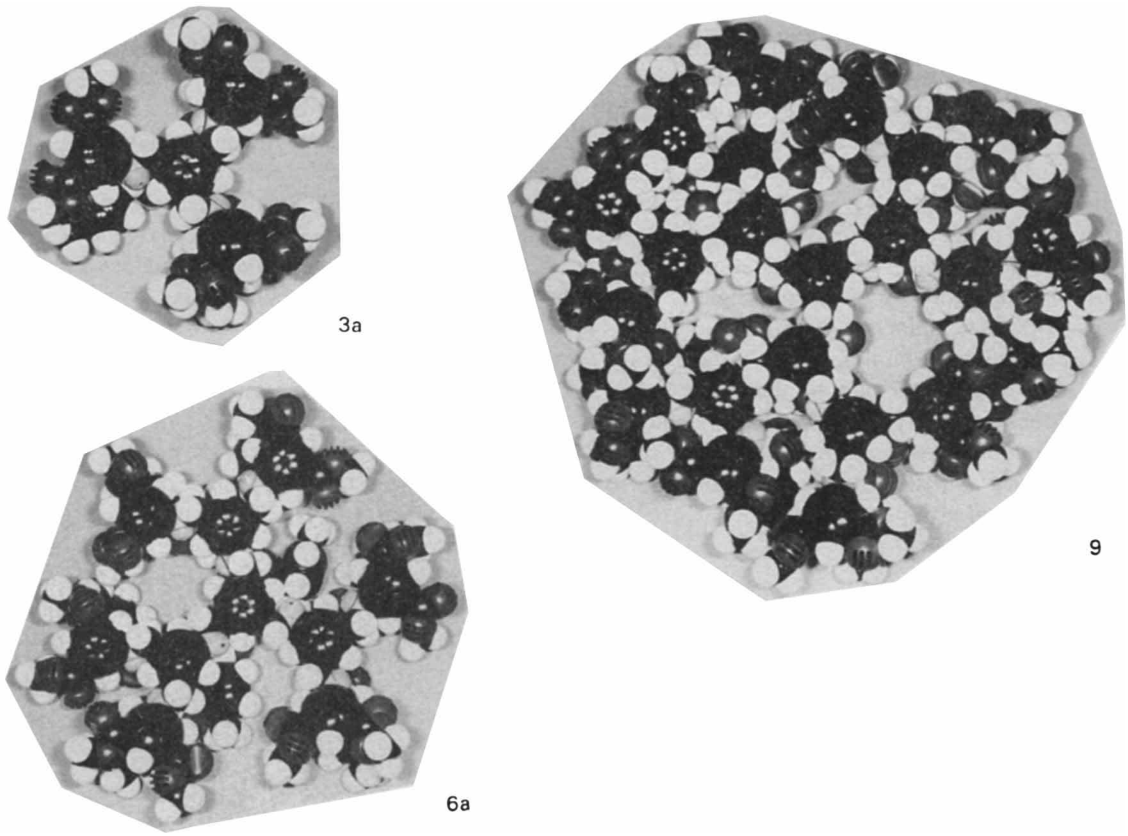


Figure 2. Comparison of the CPK models of the dendritic esters **3a** (1st generation), **6a** (2nd generation), and **9** (3rd generation). They show the growing size of the esters and the increasing quantity of pores and cavities with increasing number of generations

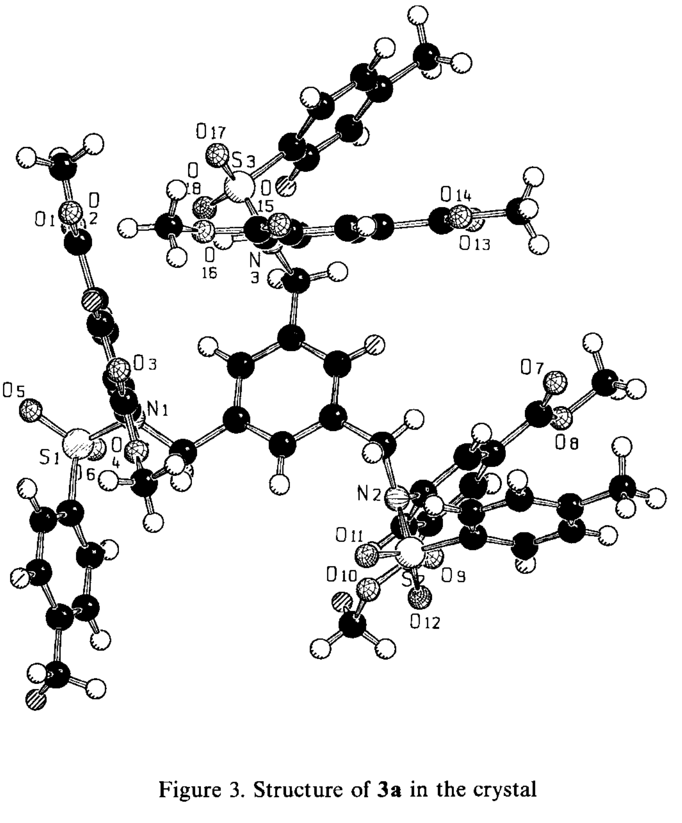


Figure 3. Structure of **3a** in the crystal

3. X-ray Structure Analysis of Dendrimer 3a

Our efforts to obtain single crystals of a dendritic molecule were rewarded by the hexaester **3a**. Application of the vapour diffusion method using $CHCl_3$/methylcyclohexane or $CHCl_3$/acetone gave no acceptable crystals. Recrystallization from pure acetone resulted in single crystals, but the *R* value of the X-ray analysis was not satisfying. Finally, we were able to grow suitable crystals which were recrystallized from acetonitrile. They had to be measured in a capillary tube because they decomposed immediately when taken out of solution.

The X-ray structure analysis shows that the dendrimer **3a** (Figure 3) adopts a configuration where two of the three isophthaloyl groups point upwards and the third one downwards when shown from the central benzene ring plane. The molecules of **3a** are packed in the unit cell in an octopus-like manner, the tosyl and isophthaloyl groups of the adjacent molecules are interlocking like tentacles to create differently sized and shaped cavities (Figure 4). These cavities are occupied alternately by the solvent molecules acetonitrile and water in an imperfectly ordered fashion leading to occupational disorder of the solvent molecules.

To our knowledge an X-ray structure analysis of a dendritic molecule has not been reported yet. This is probably due to the fractal nature of dendrimers[29] and their ability to adopt a multitude of different conformations which pre-

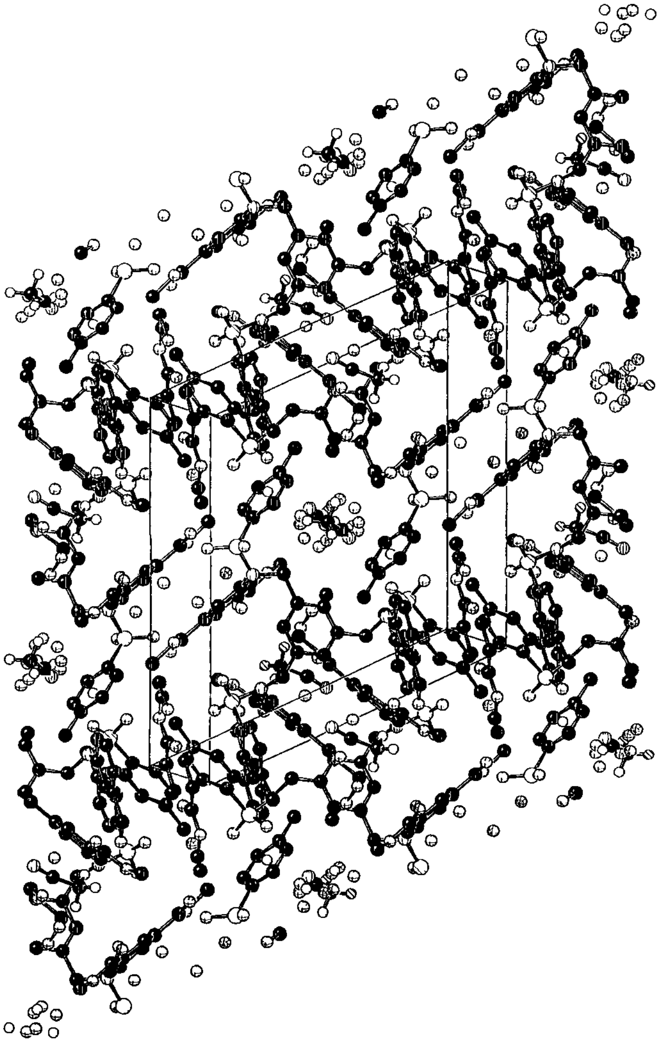


Figure 4. Packing of **3a** showing the disordered solvent molecules

vents the formation of extended areas of structural order. Although we were successful with the first-generation dendrimer **3a**, we have not been able to get crystals of higher-generation dendrimers until now.

We thank Dipl.-Chem. *M. Bauer* for his helpful suggestions and Dipl.-Phys. *U. Wolff* for performing the irradiation experiments and measuring the UV/Vis spectra.

Experimental

Melting points: Kofler-Mikroskop-Heiztisch, uncorrected. — ^{1}H and ^{13}C NMR: Bruker WM-250 (250 MHz/62.9 MHz), WH-90 (90 MHz/22.6 MHz), AC-400 (400 MHz/100.6 MHz). — MS: A.E.I. MS-50 (70 eV). — FAB-MS: Kratos Concept 1 H (in *m*NBA). — UV/Vis: Shimadzu UV-1200A. — Column chromatography: Merck silica gel 60 (40—63 µm). — TLC: Merck silica gel plates (60 F_{254}). — Organic solvents were purified by standard procedures. — The new nomenclature system for cascade molecules proposed by Newkome[21] is applied.

6-Cascade: benzene[3-1,3,5]: [5-(N-tosyl-1-azaethyl)-1,3-phenylene]: methyl Carboxylate (**3a**): In an argon-flushed flask a solution of 7.14 g (0.02 mol) of **1** and 21.80 g (0.06 mol) of **2a** in 300 ml of dry DMF was added within 30 min to a suspension of 20.73 g (0.15 mol) of K_2CO_3 in 120 ml of dry DMF. The reaction mixture was heated to 90°C for 4 h. The cooled mixture was filtered to remove the salts, and most of the solvent was evaporated under reduced pressure. The product precipitated from the concentrated solution and was collected by filtration. Recrystallization from toluene/methylcyclohexane (4:1) yielded 19.50 g (81%) of white crystals, m.p. 193—194°C. — ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.43$ (s, 9H), 3.88 (s, 18H), 4.52 (s, 6H), 6.95 (s, 3H), 7.27 (d, 6H, $J = 8.1$ Hz), 7.42 (d, 6H, $J = 8.1$ Hz), 7.75 (d, 6H), 8.46 (t, 3H). — ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.45$ (CH_3), 52.41 (CH_3), 53.51 (CH_2), 127.52 (CH), 127.55 (CH), 129.61 (CH), 129.73 (CH), 131.35 (C), 133.03 (CH), 134.40 (C), 136.26 (C), 139.63 (C), 144.17 (C), 165.08 (C). — MS (FAB, *m*NBA), *m/z* (%): 1204.2 (82) [M^+ + H], 1172.2 (100) [M^+ − OCH_3], 1048.2 (84) [M^+ − Ts].

$C_{60}H_{57}N_3O_{18}S_3$ (1204.3)
Calcd. C 59.84 H 4.77 N 3.49 S 7.99
Found C 59.88 H 4.80 N 3.42 S 7.80

6-Cascade: benzene[3-1,3,5]: {5-[N-(4-tert-butylphenylsulfonyl)-1-azaethyl]-1,3-phenylene}: methyl Carboxylate (**3b**): The procedure used for the synthesis of **3a** was applied to 3.57 g (0.01 mol) of **1**. The product was subjected to column chromatography on silica gel (eluent: $CHCl_3$/ethyl acetate, 20:1, v/v, $R_f = 0.35$). Yield: 9.84 g (74%), m.p. 111—113°C. — ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.35$ (s, 27H), 3.88 (s, 18H), 4.56 (s, 6H), 7.01 (s, 3H), 7.45 (d, 6H, $J = 8.5$ Hz), 7.49 (d, 6H, $J = 8.5$ Hz), 7.73 (d, 6H), 8.49 (t, 3H). — ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 31.01$ (CH_3), 35.21 (C), 52.48 (CH_3), 53.71 (CH_2), 126.15 (CH), 127.49 (CH), 127.69 (CH), 129.80 (CH), 131.43 (C), 133.23 (CH), 134.29 (C), 136.38 (C), 139.72 (C), 157.14 (C), 165.15 (C). — MS (FAB, *m*NBA), *m/z* (%): 1330.3 (38) [M^+ + H], 1298.3 (100) [M^+ − OCH_3], 1132.2 (86) [M^+ − *t*Bus].

$C_{69}H_{75}N_3O_{18}S_3$ (1330.5)
Calcd. C 62.29 H 5.68 N 3.16
Found C 61.91 H 5.67 N 3.34

6-Cascade: benzene[3-1,3,5]: [5-(N-tosyl-1-azaethyl)-1,3-phenylene]: methanol (**4a**): To a suspension of 7.60 g (0.2 mol) of $LiAlH_4$ in 1000 ml of dry THF 24.10 g (0.02 mol) of solid **3a** was added in several portions. The mixture was heated at reflux for 2 h and, after cooling, cautiously hydrolyzed by dropwise addition of water. The solvent was evaporated under reduced pressure, and diluted HCl was added to the residue. After the mixture had been cooled again the liquid was decanted and the crude oily product recrystallized from ethanol to yield 10.15 g (49%) of a white solid, m.p. 210—211°C. — ^{1}H NMR (250 MHz, DMSO): $\delta = 2.41$ (s, 9H), 4.37 (s, 12H), 4.60 (s, 6H), 4.83 (s, 6 OH), 6.85 (d, 6H), 7.07 (s, 3H), 7.20 (t, 3H), 7.39 (d, 6H, $J = 8.25$ Hz), 7.51 (d, 6H, $J = 8.25$ Hz). — ^{13}C NMR (62.9 MHz, DMSO): $\delta = 21.09$ (CH_3), 53.57 (CH_2), 62.41 (CH_2), 123.72 (CH), 124.50 (CH), 125.78 (CH), 127.50 (CH), 129.75 (CH), 135.18 (C), 136.99 (C), 138.85 (C), 143.25 (C), 143.57 (C). — MS (FAB, *m*NBA), *m/z* (%): 1036.6 (100) [M^+ + H], 880.5 (73) [M^+ − Ts].

6-Cascade: benzene[3-1,3,5]: {5-[N-(4-tert-butylphenylsulfonyl)-1-azaethyl]-1,3-phenylene}: methanol (**4b**): The procedure used for the synthesis of **4a** was applied to 5.32 g (4 mmol) of **3b**. The aqueous acidic solution was extracted with $CHCl_3$. The organic phase was washed with water, dried with Na_2SO_4, and the solvent was removed. Yield: 3.60 g (78%), m.p. 143—145°C. — ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.31$ (s, 27H), 4.28 (s, 12H), 4.50 (s, 6H), 6.56 (d, 6H), 6.96 (s, 3H), 7.12 (t, 3H), 7.46 (br. s, 6 + 6H). — ^{13}C NMR (22.6 MHz, $CDCl_3$): $\delta = 31.14$ (CH_3), 35.28 (C), 54.15 (CH_2), 63.99 (CH_2), 124.91 (CH), 125.94 (CH), 126.11 (CH), 127.56 (CH), 135.17 (C), 136.75 (C), 139.05 (C), 142.42 (C), 157.05 (C). — MS

(FAB, *m*NBA), *m/z* (%): 1162.2 (26) [M$^+$ + H], 964.2 (70) [M$^+$ − *t*Bus].

6-Cascade: benzene[3-1,3,5]:[5-(N-tosyl-1-azaethyl)-1,3-phenylene]: bromomethane (**5a**): In an argon-flushed apparatus a solution of 5.8 ml (0.06 mol) of PBr_3 in 30 ml of dry $CHCl_3$ was added within 30 min to a suspension of 10.36 g (0.01 mol) of **4a** in 250 ml of dry $CHCl_3$. The mixture was refluxed for 2 h and stirred at ambient temp. for another 12 h. After hydrolysis with water the aqueous and organic phases were separated, and the aqueous phase was washed with $CHCl_3$. The organic phases were combined, washed with water, and dried with Na_2SO_4. The solvent was removed and the crude product subjected to column chromatography on silica gel (eluent: $CHCl_3$, $R_f = 0.25$) to afford 7.76 g (55%) of **5a**, m.p. 76−77°C. − ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.44$ (s, 9H), 4.29 (s, 12H), 4.48 (s, 6H), 6.81 (d, 6H), 6.92 (s, 3H), 7.25 (d, 6H, $J = 8.4$ Hz), 7.29 (t, 3H), 7.45 (d, 6H, $J = 8.4$ Hz). − ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.70$ (CH_3), 32.23 (CH_2), 54.11 (CH_2), 127.75 (CH + CH), 128.90 (CH), 129.36 (CH), 129.86 (CH), 134.77 (C), 136.44 (C), 139.23 (C), 139.97 (C), 144.09 (C). − MS (FAB, *m*NBA), *m/z* (%): 1413.7 (37) [M$^+$ + H], 1257.7 (24) [M$^+$ − Ts].

6-Cascade: benzene[3-1,3,5]:{5-[N-(4-tert-butylphenylsulfonyl)-1-azaethyl]-1,3-phenylene}: bromomethane (**5b**): The procedure used for the synthesis of **5a** was applied to 1.08 g (0.93 mmol) of **4b**. Yield: 0.81 g (57%), m.p. 89−91°C. − ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 1.33$ (s, 27H), 4.27 (s, 12H), 4.50 (s, 6H), 6.79 (d, 6H), 6.94 (s, 3H), 7.21 (t, 3H), 7.47 (br. s, 6 + 6H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 31.08$ (CH_3), 32.13 (CH_2), 35.18 (C), 54.08 (CH_2), 126.14 (CH), 127.48 (CH), 127.55 (CH), 128.78 (CH), 129.37 (CH), 134.42 (C), 136.38 (C), 139.09 (C), 139.84 (C), 156.89 (C). − MS (FAB, *m*NBA), *m/z* (%): 1539.9 (38) [M$^+$ + H], 1341.8 (35) [M$^+$ − *t*Bus].

12-Cascade: benzene[3-1,3,5]:[5-(N-tosyl-1-azaethyl)-1,3-phenylene]^2: methyl Carboxylate (**6a**): In an argon-flushed flask a solution of 14.14 g (0.01 mol) of **5a** and 21.80 g (0.06 mol) of **2a** in 250 ml of dry DMF was added within 30 min to a suspension of 20.73 g (0.15 mol) of K_2CO_3 in 150 ml of dry DMF. The reaction mixture was heated to 90°C for 4 h. The cooled mixture was poured into cold diluted HCl with stirring. The precipitate was filtered off, washed with water and dissolved in $CHCl_3$. The organic phase was washed with water again and dried with Na_2SO_4. The solvent was removed and the crude product subjected to column chromatography on silica gel (eluent: $CHCl_3$/ethyl acetate, 5:1, v/v, $R_f = 0.45$) to afford 13.36 g (43%) of white crystals, m.p. 111−113°C. − ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.34$ (s, 18H), 2.38 (s, 9H), 3.78 (s, 36H), 4.36 (s, 6H), 4.50 (s, 12H), 6.78 (s, 6H), 6.80 (s, 3H), 6.95 (s, 3H), 7.13−7.20 (m, 24H), 7.38 (d, 12H, $J = 8.1$ Hz), 7.70 (d, 12H), 8.45 (t, 6H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.42$ (CH_3), 52.35 (CH_3), 53.67 (CH_2), 54.06 (CH_2), 126.20 (CH), 127.15 (CH), 127.24 (CH), 127.57 (CH), 128.00 (CH), 129.54 (CH), 129.63 (CH), 129.70 (CH), 131.39 (C), 133.28 (CH), 134.45 (C), 134.86 (C), 136.76 (C), 137.01 (C), 139.91 (C), 140.12 (C), 143.75 (C), 144.02 (C), 165.06 (C). − MS (FAB, *m*NBA), *m/z* (%): 3108.6 (17) [M$^+$ + H], 2952.6 (100) [M$^+$ − Ts].

$C_{156}H_{147}N_9O_{42}S_9$ (3108.5) Calcd. N 4.06 S 9.28
Found N 4.01 S 8.92

12-Cascade: benzene[3-1,3,5]:{5-[N-(4-tert-butylphenylsulfonyl)-1-azaethyl]-1,3-phenylene}^{2}: methyl Carboxylate (**6b**): The procedure used for the synthesis of **6a** was applied to 0.42 g (0.27 mmol) of **5b**. The crude product was subjected to column chromatography on silica gel (eluent: $CHCl_3$/ethyl acetate, 10:1, v/v, $R_f = 0.71$). Yield: 0.21 g (22%), m.p. 133−134°C. − ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.27$ (s, 54H), 1.34 (s, 27H), 3.76 (s, 36H), 4.40 (s, 6H), 4.57 (s, 12H), 6.88 (s, 6 + 3H), 7.03 (s, 3H), 7.31 (d, 6H, $J = 8.55$ Hz), 7.39 (d, 12H, $J = 8.7$ Hz), 7.45 (d, 12H, $J = 8.7$ Hz), 7.51 (d, 6H, $J = 8.55$ Hz), 7.70 (d, 12H), 8.47 (t, 6H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 31.04$ (CH_3), 31.09 (CH_3), 35.19 (C), 35.24 (C), 52.41 (CH_3), 53.92 (CH_2), 54.30 (CH_2), 126.00 (CH), 126.14 (CH + CH), 127.33 (CH + CH), 127.59 (CH), 128.21 (CH), 129.82 (CH), 131.51 (C), 133.50 (CH), 134.53 (C), 135.17 (C), 137.02 (C), 137.23 (C), 140.00 (C), 156.85 (C), 157.01 (C), 165.16 (C). − MS (FAB, *m*NBA), *m/z* (%): 3509.9 (90) [M$^+$ + Na], 3290.0 (100) [M$^+$ − *t*Bus].

12-Cascade: benzene[3-1,3,5]:[5-(N-tosyl-1-azaethyl)-1,3-phenylene]^2: methanol (**7**): To a suspension of 2.28 g (60 mmol) of $LiAlH_4$ in 300 ml of dry THF 9.32 g (3 mmol) of solid **6a** was added in several portions. The mixture was heated at reflux for 3 h and, after cooling, cautiously hydrolyzed by dropwise addition of water. The solvent was evaporated under reduced pressure, and diluted HCl was added to the residue. After the mixture had been cooled again the product was filtered off, washed with water, and dried to yield 8.24 g (99%) of a white solid, m.p. 135−137°C. − ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.35$ (s, 18H), 2.45 (s, 9H), 4.27 (s, 24H), 4.46 (s, 12 + 6H), 6.50−6.80 (m, 18H), 6.95−7.10 (m, 12H), 7.16 (d, 12H, $J = 8.5$ Hz), 7.22−7.35 (m, 12H), 7.42 (d, 12H, $J = 8.5$ Hz). − ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.47$ (CH_3), 21.58 (CH_3), 53.76 (CH_2), 54.25 (CH_2), 63.89 (CH_2), 124.92 (CH), 125.91 (CH), 127.36 (CH), 127.55 (CH + CH), 128.11 (CH), 129.60 (CH + CH), 129.93 (CH), 134.37 (C), 134.98 (C), 136.93 (C), 137.50 (C), 138.68 (C), 139.31 (C), 142.46 (C), 143.85 (C), 144.38 (C). − MS (FAB, *m*NBA), *m/z* (%): 2778.8 (44) [M$^+$ + Li], 2616.8 (100) [M$^+$ − Ts].

12-Cascade: benzene[3-1,3,5]:[5-(N-tosyl-1-azaethyl)-1,3-phenylene]^2: bromomethane (**8**): In an argon-flushed apparatus a solution of 1.6 ml (16.2 mmol) of PBr_3 in 20 ml of dry $CHCl_3$ was added within 30 min to a suspension of 5.00 g (1.8 mmol) of **7** in 80 ml of dry $CHCl_3$. The mixture was refluxed for 2 h and stirred at ambient temp. for another 12 h. After hydrolysis with water the aqueous and organic phases were separated, and the aqueous phase was washed with $CHCl_3$. The organic phases were combined, washed with water, and dried with Na_2SO_4. The solvent was removed and the crude product subjected to column chromatography on silica gel (eluent: $CHCl_3$, $R_f = 0.12$) to afford 3.94 g (62%) of **8**, m.p. 129−131°C. − ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.30-2.45$ (m, 27H), 4.20−4.30 (m, 24H), 4.42 (s, 6H), 4.48 (s, 12H), 6.70−7.05 (m, 30H), 7.15−7.35 (m, 24H), 7.40 (d, 12H, $J = 8.5$ Hz). − ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.54$ (CH_3), 21.66 (CH_3), 32.23 (CH_2), 53.64 (CH_2), 54.25 (CH_2), 127.67 (CH + CH), 128.80 (CH), 129.27 (CH), 129.38 (CH), 129.77 (CH + CH), 130.21 (CH), 130.91 (CH), 134.37 (C), 134.79 (C), 136.49 (C), 137.12 (C), 139.19 (C), 139.82 (C + C), 143.93 (C). − MS (FAB, *m*NBA), *m/z* (%): 3527.0 (17) [M$^+$ + H], 3371.3 (62) [M$^+$ − Ts].

24-Cascade: benzene[3-1,3,5].[5-(N-tosyl-1-azaethyl)-1,3-phenylene]^3: methyl Carboxylate (**9**): In an argon-flushed flask a solution of 3.53 g (1 mmol) of **8** and 4.36 g (12 mmol) of **2a** in 200 ml of dry DMF was added within 30 min to a suspension of 4.15 g (30 mmol) of K_2CO_3 in 200 ml of dry DMF. The reaction mixture was heated to 90°C for 4 h. The cooled mixture was poured into cold diluted HCl with stirring. The precipitate was filtered off, washed with water and dissolved in $CHCl_3$. The organic solution was washed with water again and dried with Na_2SO_4. The solvent was removed and the crude product subjected to column chromatography on silica gel (eluent: $CHCl_3$/ethyl acetate, 5:1, v/v, $R_f = 0.30$) to afford 2.28 g (33%) of white crystals, m.p. 137−139°C. − ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.35$ (s, 63H), 3.78 (s, 72H), 4.3−4.6 (m, 42H), 6.6−7.1 (m, 30H), 7.1−7.25 (d, 60H), 7.35−7.45 (d, 24H), 7.72 (d, 24H), 8.45 (t, 12H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.52$ (CH_3), 52.42 (CH_3), 53.81 (CH_2), 53.90 (CH_2), 54.05 (CH_2), 127.41 (CH), 127.68 (CH), 129.80 (CH), 131.47 (C), 133.39 (CH), 134.58 (C), 137.24 (C), 140.06 (C), 144.09 (C), 165.15 (C).

$C_{348}H_{327}N_{21}O_{90}S_{21}$ (6916.8) Calcd. N 4.25 S 9.73
Found N 4.40 S 8.95

3-(Tosylamino)azobenzene (**12**): In an argon-flushed flask a solution of 7.87 g (0.03 mol) of **11** and 3.21 g (0.03 mol) of nitrosobenzene in 40 ml of glacial acetic acid was refluxed for 1 h. After cooling to room temp. the black mixture was poured into 400 ml of water, treated with 30 ml of diluted HCl and extracted with 100 ml of $CHCl_3$. The organic phase was washed with diluted HCl (2 × 50 ml), dried with Na_2SO_4, and the solvent was removed under reduced pressure. The black residue was subjected to column chromatography on silica gel with CH_2Cl_2/methanol (60:1, v/v, $R_f = 0.37$) to yield 4.50 g (43%) of an orange solid, m.p. 117–118°C. – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.33$ (s, 3H), 7.22 (d, 2H, $J = 8.2$ Hz), 7.27 (m, 1H), 7.37 (dd, 1H, $J = 8.0$ Hz), 7.45–7.53 (m, 3H), 7.62–7.66 (m, 2H), 7.74 (d, 2H, $J = 8.2$ Hz), 7.84–7.90 (m, 2H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.50$ (CH_3), 114.91 (CH), 119.75 (CH), 122.95 (CH), 123.08 (CH), 127.31 (CH), 129.08 (CH), 129.76 (CH), 129.89 (CH), 131.32 (CH), 135.82 (C), 137.57 (C), 144.10 (C), 152.33 (C), 153.24 (C). – MS (70 eV), m/z (%): 351 (100) [M^+], 246 (71) [$M^+ - PhN_2$].

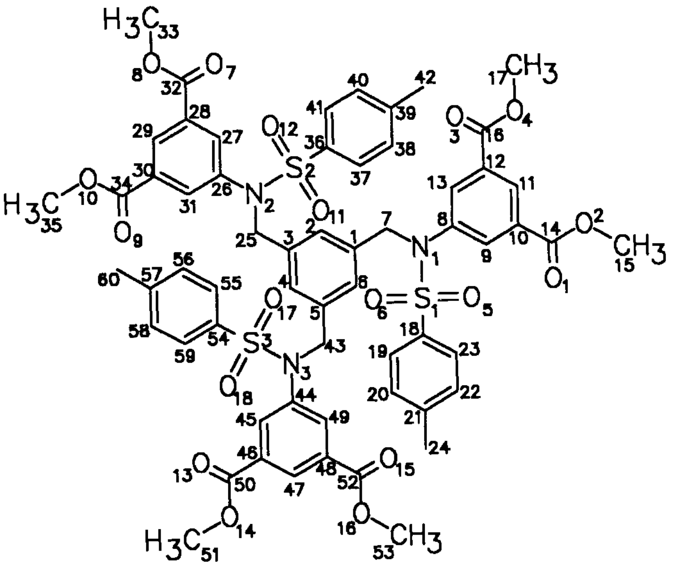
$C_{19}H_{17}N_3O_2S$ Calcd. 351.1042 Found 351.1049 (MS)

6-Cascade: benzene[3-1,3,5]: [5-(N-tosyl-1-azaethyl)-1,3-phenylene]: 3-(N-tosyl-1-azaethyl)azobenzene (**13**): In an argon-flushed flask a solution of 0.99 g (0.7 mmol) of **5a** and 1.48 g (4.2 mmol) of **12** in 15 ml of dry DMF was added within 5 min to a suspension of 1.16 g (8.4 mmol) of K_2CO_3 in 10 ml of dry DMF. The reaction mixture was heated to 90°C for 4 h and, after cooling to room temp., poured into 60 ml of diluted HCl with stirring. The precipitate was filtered off, washed with water and a small amount of cold ethanol, and dried. Yield: 0.85 g (40%), m.p. 78–80°C. – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.21$ (s, 9H), 2.32 (s, 18H), 4.39 (s, 6H), 4.54 (s, 12H), 6.75–6.9 (m, 15H), 6.95–7.2 (m, 33H), 7.4–7.5 (m, 36H), 7.65 (d, 6H), 7.82 (m, 12H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.40$ (CH_3), 21.48 (CH_3), 53.78 (CH_2), 53.96 (CH_2), 121.77 (CH), 122.97 (CH), 123.03 (CH), 126.27 (CH), 127.28 (CH), 127.58 (CH), 127.74 (CH), 127.91 (CH), 129.05 (CH), 129.33 (CH), 129.50 (CH), 129.61 (CH), 131.13 (CH), 131.22 (CH), 134.85 (C), 134.92 (C), 136.78 (C), 137.18 (C), 139.56 (C), 139.86 (C), 143.50 (C), 143.65 (C), 152.32 (C), 152.76 (C). – MS (FAB, *m*NBA), m/z (%): 3036.8 (73) [$M^+ + H$], 2881.1 (100) [$M^+ - TsH$].

$C_{168}H_{147}N_{21}O_{18}S_9 \cdot 3\,H_2O$ (3090.7)
Calcd. C 65.29 H 4.99 N 9.52
Found C 65.26 H 5.30 N 9.45

Irradiation Experiment with **13**: A solution of **13** (*all-E*) in CH_2Cl_2 ($c = 1.05 \cdot 10^{-5}$ mol l^{-1}) was prepared in the dark and 4 ml of the solution filled into a quartz cuvette. The sample was irradiated at 313 nm for 5 min, and a UV/Vis spectrum was recorded immediately. Then the sample was irradiated at 436 nm for 3 min, and again a UV/Vis spectrum was recorded immediately. Irradiations at 313 and 436 nm were repeated, each time followed by UV/Vis spectroscopy.

X-Ray Crystal Structure Analysis of **3a**: Recrystallization from acetonitrile gave colourless crystals which had to be measured in a capillary tube because of decomposition when taken out of solution. Crystal data: $C_{60}H_{57}N_3O_{18}S_3 \cdot CH_3CN$ (two disordered molecules) · 3.25 H_2O (disordered at 11 positions), $M_{tot} = 1303.90$, crystal 0.40 × 0.50 × 0.50 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.173(6)$, $b = 15.633(2)$, $c = 17.513(2)$ Å, $\alpha = 115.26(1)$, $\beta = 90.14(2)$, $\tau = 103.81(2)°$, $V = 3597(2)$ Å^3, $Z = 2$, $D_c = 1.204$ g cm^{-3}, $F(000) = 1368$, $T = 296 \pm 1$ K. Data collection and reduction: Enraf Nonius CAD4 diffractometer using graphite-monochromatized Mo-K_α radiation [λ(Mo-K_α) = 0.7107 Å], $\omega/2\Theta$ scan mode (scan width in degrees: 0.50 + 0.35 tanΘ) to $2\Theta = 46°$ (h: $0 \rightarrow 16$, k: $-7 \rightarrow 17$, l: $-9 \rightarrow 19$), 10502 collected reflexions, 10053 independent reflexions ($R_{int} = 0.006$), refinement with 5521 reflexions with $I > 3\sigma I$, empirical absorption correction[30] [μ(Mo-K_α) = 0.165 mm^{-1}] of the data with minimum and maximum correction coefficients of 0.758 and 1.094, respectively. Structure solution and refinement: The structure was solved by direct methods and subjected to block-matrix refinement [x, y, z of S(1)–C(60) as first block, U's of S(1)–C(60) as second block, x, y, z, and U's of N(61)–O(77) as third block, scale and DU[iso] as forth block]. All non-disordered non-H atoms were refined anisotropically and the disordered isotropically. Refinement with only the fully occupied atoms [S(1)–C(60)] gave an R value of 0.132, and the residual electron density did not show any clearly defined solvent molecules (max. peak 1.63 e Å^{-3}). Based on the recrystallization solvent (CH_3CN with traces of water) and distances of the peaks the residual electron density was treated as disordered CH_3CN and H_2O molecules. (This resulted in a marked decrease in the R values and also improved the residual electron density map.) Due to the rather large thermal movement of one of the ester methyl groups [C(17)] it had to be refined as riding atom [the x, y, z, and U's were riding along with the corresponding parameters of O(4)]. Some geometrical restraints had to be imposed during the refinements to prevent anomalous bond distances and angles in the disordered CH_3CN molecules (1.150 and 1.500 Å with sigma 0.001 Å for C≡N and C–C bonds and 180° with sigma 0.1° for the N–C–C angle). The occupancies of the disordered atoms were assigned on the basis of molecular geometry, difference Fourier calculations, and "reasonable" temperature factors. The hydrogen atoms for the non-disordered atoms and disordered CH_3CN molecules were calculated to their idealized positions (C–H distance 1.00 Å) and included with fixed isotropic factors ($U = 0.08$ Å^2) in the final structure factor calculations but were not refined. The hydrogens of the disordered water molecules could not be located by means of difference Fourier map or calculated and were therefore ignored during the refinements. F_o/parameter ratio = 6.78. The final R value for 814 para-



3a

Figure 5. Scheme of the dendrimer **3a** with numbering scheme

Table 1. Fractional atomic coordinates (with e.s.d.'s in parentheses) and equivalent isotropic temperature factors U_{iso} [Å^2] of non-H atoms of **3a**. The equivalent isotropic temperature factors were calculated according to $U_{iso} = [U(11) \cdot U(22) \cdot U(33)]^{1/3}$

Atom	x/a	y/b	z/c	U(iso)	
S(1)	0.2256(1)	0.7573(1)	0.51768(8)	0.0814	
S(2)	0.3219(1)	0.1972(1)	0.1706(1)	0.0844	
S(3)	0.2206(1)	0.7715(1)	0.1043(1)	0.0880	
O(1)	0.4986(3)	1.0335(4)	0.3528(3)	0.1202	
O(2)	0.3491(3)	0.9920(3)	0.3545(3)	0.1086	
O(3)	0.6775(4)	0.8419(7)	0.4170(6)	0.1849	
O(4)	0.6076(4)	0.7282(6)	0.4571(5)	0.1588	
O(5)	0.2598(3)	0.8617(3)	0.5540(2)	0.0948	
O(6)	0.1299(3)	0.7136(4)	0.4975(3)	0.1073	
O(7)	0.0946(4)	0.1153(5)	−0.1565(3)	0.1396	
O(8)	−0.0450(3)	0.0492(3)	−0.1413(3)	0.1042	
O(9)	−0.1404(3)	0.0853(4)	0.1327(4)	0.1306	
O(10)	−0.0357(3)	0.1611(4)	0.2449(3)	0.1081	
O(11)	0.3966(3)	0.2680(4)	0.2316(3)	0.1084	
O(12)	0.2582(3)	0.1299(4)	0.1917(3)	0.1038	
O(13)	0.3367(3)	0.4288(3)	−0.1702(3)	0.1145	
O(14)	0.4880(3)	0.4744(3)	−0.1532(2)	0.0931	
O(15)	0.6650(3)	0.7538(4)	0.0940(3)	0.1088	
O(16)	0.5921(3)	0.8424(3)	0.1967(2)	0.0979	
O(17)	0.3005(3)	0.8453(3)	0.1111(3)	0.1013	
O(18)	0.1579(4)	0.7912(3)	0.1654(3)	0.1154	
N(1)	0.2706(3)	0.7122(3)	0.4274(2)	0.0755	
N(2)	0.2630(3)	0.2591(3)	0.1458(3)	0.0724	
N(3)	0.2566(3)	0.6814(3)	0.1074(3)	0.0710	
C(1)	0.2548(4)	0.5597(3)	0.2929(3)	0.0677	
C(2)	0.2832(3)	0.4752(3)	0.2537(3)	0.0682	
C(3)	0.2801(3)	0.4282(3)	0.1659(3)	0.0614	
C(4)	0.2479(3)	0.4666(3)	0.1171(3)	0.0622	
C(5)	0.2205(3)	0.5530(3)	0.1557(3)	0.0631	
C(6)	0.2249(3)	0.5988(3)	0.2437(3)	0.0680	
C(7)	0.2547(4)	0.6050(4)	0.3886(3)	0.0854	
C(8)	0.3559(4)	0.7706(4)	0.4199(3)	0.0682	
C(9)	0.3523(4)	0.8449(4)	0.3976(3)	0.0718	
C(10)	0.4321(4)	0.9034(4)	0.3889(3)	0.0739	
C(11)	0.5158(4)	0.8871(4)	0.4018(3)	0.0856	
C(12)	0.5193(4)	0.8128(5)	0.4229(3)	0.0878	
C(13)	0.4388(4)	0.7549(4)	0.4326(3)	0.0809	
C(14)	0.4325(4)	0.9836(4)	0.3635(4)	0.0871	
C(15)	0.3419(6)	1.0609(6)	0.3212(6)	0.1279	
C(16)	0.6070(6)	0.7932(7)	0.4331(5)	0.1273	
C(17)	0.6924(3)	0.7046(3)	0.4745(2)	0.2747	
C(18)	0.2669(3)	0.7118(4)	0.5827(3)	0.0709	
C(19)	0.2137(4)	0.6307(4)	0.5874(3)	0.0870	
C(20)	0.2483(5)	0.5924(4)	0.6351(4)	0.0961	
C(21)	0.3375(5)	0.6348(5)	0.6781(4)	0.0944	
C(22)	0.3879(4)	0.7167(4)	0.6723(4)	0.0939	
C(23)	0.3552(4)	0.7561(4)	0.6260(3)	0.0823	
C(24)	0.3732(6)	0.5917(6)	0.7288(5)	0.1291	
C(25)	0.3147(3)	0.3380(4)	0.1250(3)	0.0724	
C(26)	0.1709(3)	0.2092(3)	0.1039(3)	0.0643	
C(27)	0.1496(3)	0.1775(4)	0.0179(3)	0.0709	
C(28)	0.0605(4)	0.1315(3)	−0.0195(3)	0.0733	
C(29)	−0.0075(3)	0.1163(4)	0.0279(4)	0.0766	
C(30)	0.0128(3)	0.1468(4)	0.1142(4)	0.0754	
C(31)	0.1020(3)	0.1948(3)	0.1530(3)	0.0710	
C(32)	0.0405(4)	0.0991(5)	−0.1130(4)	0.0971	
C(33)	−0.0735(5)	0.0157(6)	−0.2295(5)	0.1170	
C(34)	−0.0628(4)	0.1272(5)	0.1632(5)	0.1000	
C(35)	−0.1084(7)	0.1374(7)	0.2927(6)	0.1464	
C(36)	0.3684(3)	0.1318(4)	0.0782(3)	0.0737	
C(37)	0.4541(4)	0.1716(4)	0.0645(4)	0.0812	
C(38)	0.4881(4)	0.1221(4)	−0.0089(4)	0.0895	
C(39)	0.4386(4)	0.0336(4)	−0.0704(4)	0.0868	
C(40)	0.3540(5)	−0.0047(4)	−0.0575(5)	0.1044	
C(41)	0.3167(4)	0.0418(4)	0.0170(5)	0.0978	
C(42)	0.4774(6)	−0.0192(6)	−0.1528(5)	0.1227	
C(43)	0.1855(3)	0.5951(4)	0.1034(3)	0.0741	
C(44)	0.3386(3)	0.6626(3)	0.0691(3)	0.0646	
C(45)	0.3333(3)	0.5850(3)	−0.0100(3)	0.0698	
C(46)	0.4138(3)	0.5658(3)	−0.0423(3)	0.0665	
C(47)	0.4972(3)	0.6248(4)	0.0026(3)	0.0706	
C(48)	0.5023(3)	0.7039(4)	0.0809(3)	0.0697	
C(49)	0.4225(3)	0.7220(3)	0.1148(3)	0.0677	
C(50)	0.4068(4)	0.4824(4)	−0.1286(3)	0.0808	
C(51)	0.4897(5)	0.3955(5)	−0.2347(4)	0.0996	
C(52)	0.5960(4)	0.7678(4)	0.1236(3)	0.0813	
C(53)	0.6795(5)	0.9126(6)	0.2395(5)	0.1203	
C(54)	0.1590(4)	0.7235(4)	0.0034(4)	0.0809	
C(55)	0.2041(4)	0.7279(5)	−0.0636(4)	0.0948	
C(56)	0.1547(5)	0.6848(6)	−0.1433(4)	0.1093	
C(57)	0.0637(4)	0.6385(5)	−0.1572(5)	0.1006	
C(58)	0.0210(4)	0.6370(5)	−0.0891(5)	0.1025	
C(59)	0.0674(4)	0.6792(5)	−0.0092(5)	0.0972	
C(60)	0.0133(6)	0.5932(6)	−0.2456(6)	0.1407	
					Occ.
N(61)	0.911(2)	0.589(2)	0.109(2)	0.20(1)	0.50
C(62)	0.885(2)	0.653(2)	0.156(1)	0.16(1)	0.50
C(63)	0.844(2)	0.732(2)	0.214(2)	0.16(1)	0.50
N(64)	0.206(2)	0.369(2)	0.396(2)	0.22(1)	0.50
C(65)	0.138(2)	0.389(1)	0.415(2)	0.18(1)	0.50
C(66)	0.053(2)	0.415(3)	0.451(3)	0.22(2)	0.50
O(67)	0.141(3)	0.342(4)	0.420(3)	0.14(1)	0.25
O(68)	0.440(4)	0.496(5)	0.450(4)	0.32(3)	0.50
O(69)	0.895(3)	0.636(3)	0.337(3)	0.17(1)	0.50
O(70)	0.850(2)	0.650(2)	0.104(2)	0.24(1)	0.25
O(71)	0.504(2)	0.516(2)	0.502(2)	0.29(2)	0.25
O(72)	0.088(4)	0.326(4)	0.455(3)	0.20(2)	0.25
O(73)	0.002(6)	0.702(6)	0.322(5)	0.30(3)	0.25
O(74)	0.396(6)	0.374(7)	0.438(5)	0.32(3)	0.25
O(75)	0.079(4)	0.066(4)	0.452(3)	0.21(2)	0.25
O(76)	0.453(8)	0.524(8)	0.448(7)	0.21(5)	0.25
O(77)	0.859(4)	0.014(5)	0.499(4)	0.25(2)	0.25

meters was $R = 0.075$ and $R_w = 0.069$; $w = w' \cdot [1.0 - (\Delta F/6 \cdot \sigma F)^2]^2$, where w' = Chebychev polynomial for F_c with five coefficients (4.32, −4.44, 0.0135, −3.03, −2.31). Convergence, max. shift/error < 0.12. A final difference map displayed no electron density higher than 0.47 e Å^{-3}. The programs SHELXS[31], CRYSTALS[32], and SCHAKAL[33] were used. Fractional atomic coordinates and the equivalent isotropic temperature factors are listed in Table 1; atom numbering is shown in Figures 3 and 5[34].

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[1] E. Buhleier, W. Wehner, F. Vögtle, *Synthesis* **1978**, 155–158.

[2] D. A. Tomalia, A. M. Naylor, W. A. Goddard III, *Angew. Chem.* **1990**, *102*, 119–157; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138–175.

[3] R. G. Denkewalter, J. Kolc, W. J. Lukasavage, U. S. Patent 4.289.872, 1981; *Chem. Abstr.* **1985**, *102*, 79324q.

[4] G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, *J. Org. Chem.* **1985**, *50*, 2003–2004.

[5] G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, P. S. Russo, M. J. Saunders, *J. Am. Chem. Soc.* **1986**, *108*, 849–850.

[6] G. R. Newkome, G. R. Baker, M. J. Saunders, P. S. Russo, V. K. Gupta, Z. Yao, J. E. Miller, K. Bouillion, *J. Chem. Soc., Chem. Commun.* **1986**, 752–753.

[7] G. R. Newkome, A. Nayak, R. K. Behara, C. N. Moorefield, G. R. Baker, *J. Org. Chem.* **1992**, *57*, 358–362.

[8] D. A. Tomalia, H. Baker, J. R. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polym. J.* **1985**, *17*, 117–132.

[9] D. A. Tomalia, H. Baker, J. R. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Macromolecules* **1986**, *19*, 2466–2468.

[10] A. B. Padias, H. K. Hall Jr., D. A. Tomalia, J. R. McConnell, *J. Org. Chem.* **1987**, *52*, 5305–5312.

[11] D. A. Tomalia, D. M. Hedstrand, M. S. Ferritto, *Macromolecules* **1991**, *24*, 1435.

[12] H. Uchida, Y. Kabe, K. Yoshino, A. Kawamata, T. Tsumuraya, S. Masamune, *J. Am. Chem. Soc.* **1990**, *112*, 7077–7079.

[13] C. Hawker, J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.* **1990**, 1010–1013.

[14] C. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647.

[15] K. L. Wooley, C. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4252–4261.

[16] I. Gitsov, K. L. Wooley, J. M. J. Fréchet, *Angew. Chem.* **1992**, *104*, 1282–1285; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1200.

[17] T. M. Miller, T. X. Neenan, R. Zayas, H. E. Blair, *J. Am. Chem. Soc.* **1992**, *114*, 1018–1025.

[18] T. Nagasaki, M. Ukon, S. Arimori, S. Shinkai, *J. Chem. Soc., Chem. Commun.* **1992**, 608–610.

[19] Z. Xu, J. S. Moore, *Angew. Chem.* **1993**, *105*, 261–264; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 246–248.

[20] H.-B. Mekelburger, F. Vögtle, *Supramolecular Chemistry*, in press.

[21] G. R. Newkome, G. R. Baker and J. K. Young introduced a new systematic nomenclature for cascade molecules; we thank G. N. for his personal communication previous to publication.

[22] F. Vögtle, M. Zuber, R. G. Lichtenthaler, *Chem. Ber.* **1973**, *106*, 717–718.

[23] Cf. H.-W. Losensky, H. Spelthann, A. Ehlen, F. Vögtle, J. Bargon, *Angew. Chem.* **1988**, *100*, 1225–1227; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1189.

[24] G. T. Morgan, F. M. G. Micklethwait, *J. Chem. Soc.* **1906**, *89*, 1289–1300.

[25] M. Bauer, F. Vögtle, *Chem. Ber.* **1992**, *125*, 1675–1686.

[26] T. Nagasaki, M. Ukon, S. Arimori, S. Shinkai, *J. Chem. Soc., Chem. Commun.* **1992**, 608–610.

[27] $M = 1021$ (calc. 1204.32) for **3a**, $M = 2367$ (calc. 3108.45) for **6a**, $M = 3903$ (calc. 6916.76) for **9**, calibrated with benzil; $M = 4780$ for **9**, calibrated with a polystyrene standard ($M = 3770$).

[28] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319.

[29] D. Farin, D. Avnir, *Angew. Chem.* **1991**, *103*, 1409–1410; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1379–1380.

[30] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A*, **1983**, *39*, 158–166.

[31] G. M. Sheldrick in *Crystallographic Computing 3* (Ed.: G. M. Sheldrick, C. Krüger, R. Goddard), Oxford University Press, Oxford, **1985**, S. 175–186.

[32] D. Watkin, B. Carruthers, P. W. Betteridge, *CRYSTALS*, Chemical Crystallography Laboratory, Oxford, **1990**.

[33] E. Keller, *SCHAKAL88*, Kristallographisches Institut der Universität Freiburg, Freiburg, **1988**.

[34] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56749, the names of the authors, and the journal citation.

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