Gavino Chessa* and Alberto Scrivanti

Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta, 2137, 30123 Venezia, Italy

Received August 18, 1997

The synthesis of dendritic polypyridines is described. The dendrimers were prepared by a divergent approach using diethyl 4-hydroxypyridine-2,6-dicarboxylate **1** and 4-hydroxy-2,6-bis(acetoxymethyl)pyridine **6** as building blocks. The transformation of the surface functionalities of the second generation dendrimer led to imperfections which did not allow us to further increase the size of the macromolecule.

J. Heterocyclic Chem., **34**, 1851 (1997).

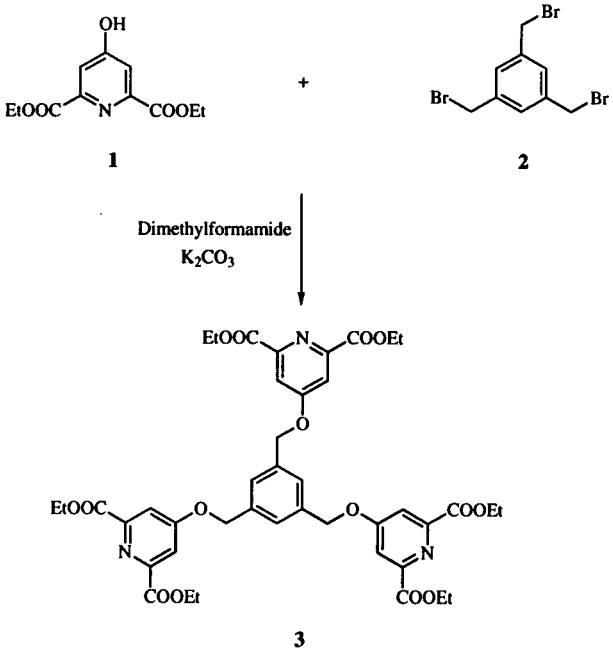
Introduction and Discussion.

The aim to produce materials with new functional properties has prompted many research groups to be concerned with the chemistry of hyperbranched polymers and dendrimers. Hyperbranched polymers [1,2] are usually prepared by one-pot polycondensation of AB_x monomers. This procedure leads to polydisperse macromolecules whose structures are not perfectly branched. At variance, dendrimers are monodisperse high molecular weight macromolecules which are perfectly branched. There are two fundamentally different methodologies to prepare dendrimers: the divergent approach in which the synthesis is begun at the centre of the macromolecule [3,4] and the convergent approach in which the synthesis is begun at the "periphery" of the macromolecule [5,6]. Using these synthetic strategies several dendritic structures have been synthesized and characterized [7-10].

Recently, we have reported the first example of a dendrimer having a pyridine based skeleton, which was prepared by a convergent approach [11]. Although the convergent methodology we adopted allowed us to successfully prepare up to third generation dendrimers, we were concerned that, with dendritic wedges of fourth or higher generation, problems would arise in the sterically congested final step of a convergent synthesis. Since the divergent approach has the advantage of eliminating this problem we decided to study its applicability to the synthesis of dendritic polypyridines. The aim of the synthetic work described here was the preparation of polypyridines of fourth or higher generation and a comparison of the effectiveness of the two synthetic approaches. In this paper, we report the results of such study.

The synthetic strategy we envisioned involves the following steps (Scheme 1): i) Coupling of diethyl 4-hydroxypyridine-2,6-dicarboxylate **1** [11] to 1,3,5-tris(bromomethyl)benzene **2** [12] to give the first generation dendritic molecule **3**; ii) Reduction of the ethoxycarbonyl moieties to hydroxymethyl groups; iii) Activation of the hydroxymethyl groups by transformation into chloromethyl groups; iv) Coupling of the chloromethyl dendritic intermediate to more of monomer **1** to give the second generation dendritic molecule.

Scheme 1

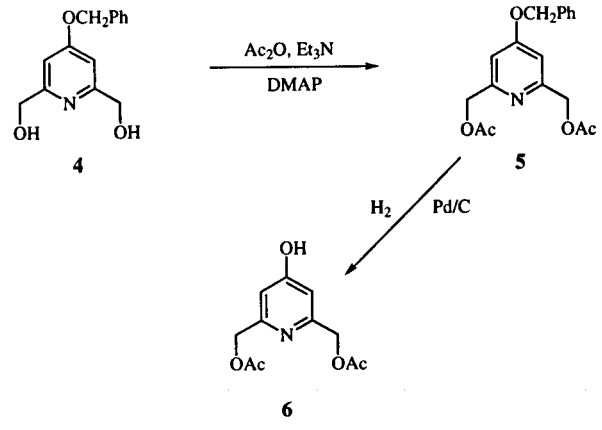


At this stage, repetition of the activation step sequence (ii, iii) and coupling (iv) would give the next generation dendrimer.

The coupling of diester **1** with tribromide **2** in *N,N*-dimethylformamide in the presence of anhydrous potassium carbonate gave the hexaester **3**. Unfortunately, reduction of **3** by sodium borohydride was unsuccessful because of difficulties in isolation of the product which is scarcely soluble in common organic solvents. To circumvent this problem, a new monomer unit 4-hydroxy-2,6-bis(acetoxymethyl)pyridine **6** was prepared (Scheme 2). Treatment of the hydroxy precursor **4** with acetic anhydride in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine gave compound **5**.

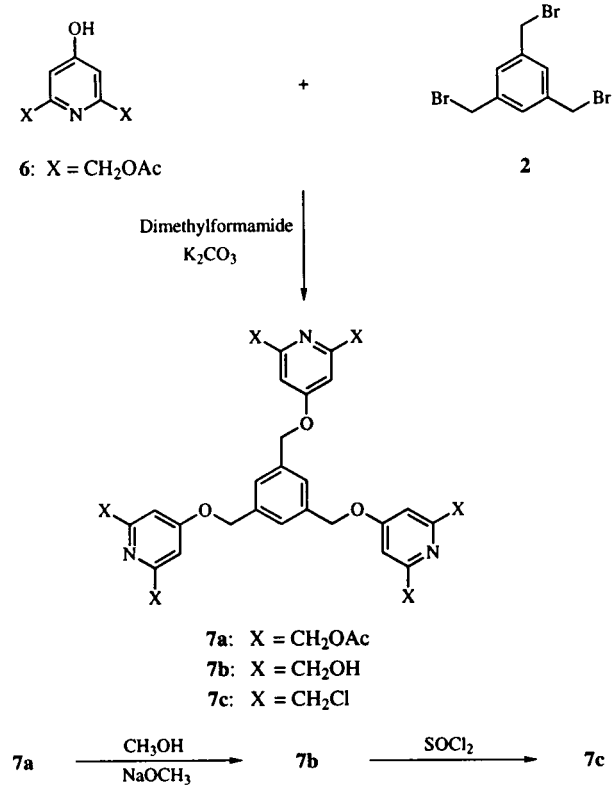
The conversion of **4** into **5** was confirmed by nmr spectroscopy. In particular, in the ^1H nmr spectrum of **5** no signal attributable to hydroxyl groups is present, and the acetate moieties appear as a singlet at δ 2.15, whereas in the ^{13}C nmr spectrum they appear at δ 20.9 and 170.5.

Scheme 2



Removal of the benzyl protecting group from acetate **5** by palladium-on-carbon catalyzed hydrogenolysis gave the desired building block **6**. It is worth noting that under hydrogenolysis conditions the formation of side products due to the transformation of the acetoxymethyl moieties to methyl groups was also observed. Indeed, upon exhaustive hydrogenolysis compound **5** is completely converted into 4-hydroxy-2,6-dimethylpyridine, which was isolated and characterized by nmr spectroscopy. However, the choice of suitable reaction conditions considerably reduces the formation of this side product and allows us to obtain compound **6** in high yield. The tribromide **2** was then coupled with monomer **6** in *N,N*-dimethylformamide/potassium carbonate to provide the hexaacetate **7a** (Scheme 3).

Scheme 3



The ^{1}H nmr spectrum of **7a** exhibits singlets at δ 2.14 (18H), 5.16 (18H), 6.88 (6H) and 7.48 (3H). Therefore it appears that the methylene groups are accidentally equivalent. At the variance, in the ^{13}C nmr spectrum of **7a** two well separated resonances at δ 66.6 and 69.4 in an approximate 2:1 integration ratio are found for the pyridyl and the aryl methylene groups, respectively.

Transesterification of acetate **7a** with sodium methoxide in methanol gave compound **7b** which was treated with thionyl chloride furnishing the hexachloride **7c** (Scheme 3). The structure of **7c** was easily confirmed by its ^{1}H nmr spectrum which showed four singlets at δ 4.61, 5.20, 7.04, and 7.50 for the pyridyl methylene, aryl methylene, pyridyl and aryl protons, respectively.

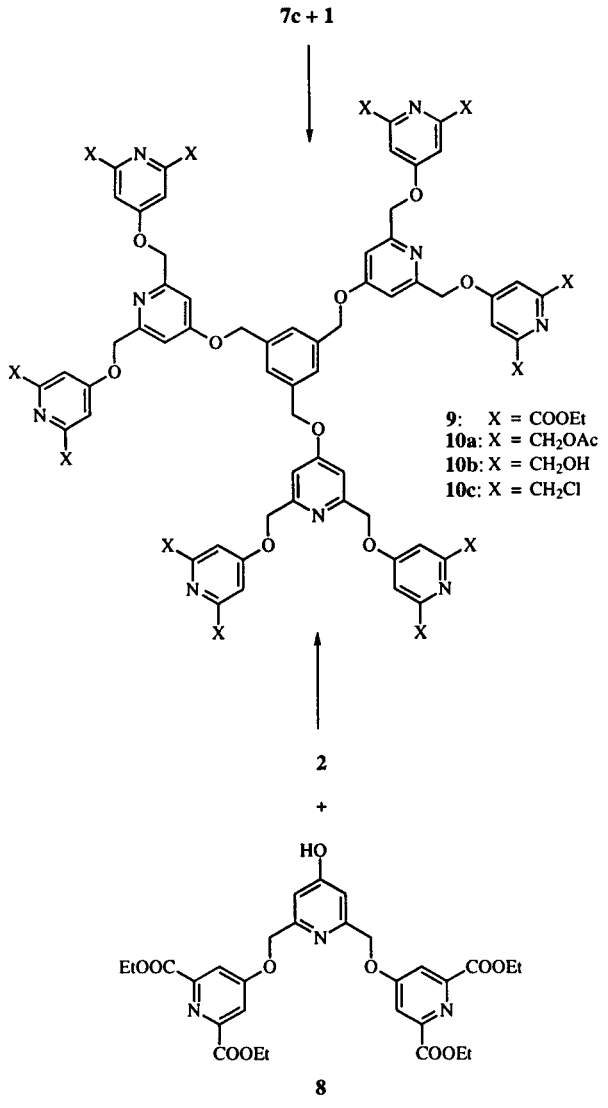
Treatment of chloride **7c** with a slight excess of diester **1**, under the usual coupling conditions, allowed us to obtain the second generation ester **9** in 78% yield after chromatographic purification (Scheme 4).

For comparative purposes, dodecaester **9** was also prepared by a convergent strategy, *i.e.* by coupling tribromide **2** with the dendritic fragment **8** synthesized as previously reported [11]. No difference between dodecaesters **9** was found in ir, nmr, mass spectra and elemental analysis.

To further increase the dendritic structure the hexachloride **7c** was coupled with monomer **6** to give the dodecaacetate **10a** (Scheme 4), whose structure was confirmed by nmr spectroscopy. Significantly, in the ^{1}H nmr spectrum of **10a**, the signal of chloromethyl groups is not longer recognizable, instead the acetate resonance is present as a singlet at δ 2.11. Correspondingly, two peaks at δ 20.8 and 170.4 were found in the ^{13}C nmr spectrum. In keeping with the proposed structure for **10a** three separate singlets in the appropriate integration ratios were found for the three different methylene groups in both ^{1}H nmr and ^{13}C nmr spectra.

Transesterification of **10a** gave the corresponding polyalcohol **10b**. The ^{1}H nmr and ^{13}C nmr data for **10b** agree with its structure: in particular no resonance attributable to the acetate groups is present and the hydroxymethyl moieties give rise to a doublet at δ 4.45 (CH_2) which couples with a triplet at δ 5.37 (OH). It should be mentioned that although the spectroscopic data completely agree with the structure proposed for **10b** its elemental analysis was outside acceptable standards. The difficulty to obtain correct elemental analyses with some dendrimers has been noticed by other authors [13,14], and it has been attributed either to hygroscopic characteristics of those dendrimers or an enhanced ability to confine solvent molecules and other impurities within the dendritic structure with an increase in molecular weight. However, the mass

Scheme 4



$$\mathbf{7c} + \mathbf{6} \xrightarrow[K_2CO_3]{\text{Dimethylformamide}} \mathbf{10a} \xrightarrow[NaOCH_3]{CH_3OH} \mathbf{10b} \xrightarrow{SOCl_2} \mathbf{10c}$$

spectrum (MALDI- TOF) of **10b** showed only one major peak (M + Na^+) at 1424 confirming the expected mass.

Treatment of the polyalcohol **10b** with thionyl chloride produced the dodecachloride **10c**. Purification of this compound by flash chromatography afforded a product which showed a ^1H nmr spectrum in keeping with the proposed structure. However, tlc analysis revealed that **10c** was still contaminated by impurities having R_f-values very similar to that of the desired product.

Since neither the ^1H nmr nor the ^{13}C nmr spectrum of compound **10b** displayed signals that could be attributed to either unreacted acetate groups or impurities it is probably that the formation of side products occurs only during the conversion of the hydroxymethyl groups into chloromethyl functionalities. This prompted us to investigate an alternative route to get **10c**. Thus we treated the polyacetate **10a** with hydrogen bromide (33% solution in acetic acid). The reaction was monitored by ^1H nmr spectroscopy: after 3 days at room temperature the ^1H nmr of the isolated product indicated an approximate 80% conversion of the acetate groups into bromomethyl moieties.

The complete conversion required one week, but after this period of time, the ^1H nmr spectrum of the crude product exhibited, alongside the resonances attributable to the bromomethyl derivative, undesired signals in the methylene and aromatic regions. Once again tlc analysis showed that the product was contaminated with impurities having R_f-values very similar to that of the main product.

Thus, it was not possible to extend the synthesis to the third generation dendritic structure which was previously obtained by a convergent growth approach [11].

In conclusion, we have succeeded in preparing dendritic polypyridines up to the second generation by a divergent approach. However we were unable to further increase the dendrimer size since the preparation of the intermediate **10c** occurred with the formation of side products which proved to be difficult to separate from the desired major product. These synthetic problems associated with the divergent approach, usually, are overcome by purification procedures. In the present case this was unsuccessful.

Thus, with regard to the dendrimers which we have been able to prepare up to now, the steric congestion around the functional group located at the focal point of the dendritic wedges appears to be a less limiting factor than the problems arising from side reactions occurring at the terminal groups.

EXPERIMENTAL

General Comments.

Melting points were measured in capillary tubes with a Buchi 535 apparatus and are uncorrected. For compounds **9** and **10** definite melting points could not be determined. Elemental analyses were performed by the Microanalytical Laboratory of the University of Padua. The ir spectra (potassium bromide pellets) were obtained on a Bio-Rad Digilab FTS-40 spectrophotometer. The ^1H nmr (200 MHz) and ^{13}C nmr (50 MHz) spectra were obtained in deuteriochloroform solutions, unless otherwise indicated, on a Bruker AC 200 spectrometer using the solvent signal as internal standard. All mass spectra of dendrimers were measured by Matrix Assisted Laser Desorption Ionization Mass Spectrometry (MALDI-ms) carried out on a REFLEX™ Time of flight instrument (Bruker-Franzen Analytik) equipped with a scout ion source (nitrogen laser λ = 337 nm; laser energy = 50 μJ; acceleration voltage = 30 KV). 2,5-Dihydroxybenzoic acid was used as a matrix deposited in solution with the sample.

Analytical tlc was performed on commercial (Merck) plates with silica gel GF_{254} (0.25 mm thick). Flash chromatographic separations were performed on ICN silica 60 A (200-400 mesh). *N,N*-dimethylformamide was purified by distillation from calcium hydride and stored over 4A° molecular sieves. Thionyl chloride was distilled before use. Other solvents and reagents were used without further purification. The systematic nomenclature for cascade molecules proposed by Newkome is used [15].

6-Cascade:benzene[3-1,3,5]:(4-methoxypyridin-2,6-yl):ethyl carboxylate (**3**).

A mixture of diethyl 4-hydroxypyridine-2,6-dicarboxylate **1** (2.37 g, 9.9 mmoles) and anhydrous potassium carbonate (1.24 g, 9 mmoles) in dry *N,N*-dimethylformamide (30 ml) was stirred at 25° *in vacuo* for 30 minutes, then 1,3,5-tris(bromomethyl)benzene **2** (1.07 g, 3 mmoles) was added and the reaction mixture was allowed to react at 70-80° for 24 hours under an atmosphere of argon. The mixture was evaporated *in vacuo* and the residue was partitioned between dichloromethane and water. The organic layer was washed with 1% aqueous acetic acid, water and dried (sodium sulfate). The residue obtained, after removal of the solvent, was recrystallized from ethanol and dried *in vacuo* at 50° to give 2.21 g (88%) of **3** as a white solid, mp 166-167°; ir: ν 1742 (C=O), 1719 (C=O), 1594; 1340, 1249, cm^{-1}; ^1H nmr: δ 1.44 (t, J = 7.1 Hz, 18H, OCH_2CH_3), 4.47 (q, 12H, OCH_2CH_3), 5.28 (s, 6H, $PhCH_2$), 7.55 (s, 3H, PhH), 7.88 (s, 6H, pyH-3,5); ^{13}C nmr: δ 14.2, 62.4, 70.0, 114.4, 126.9, 136.4, 150.4, 164.5, 166.3; ms: m/z 855 ($M + Na^+$).

Anal. Calcd. for $C_{42}H_{45}N_3O_{15}$: C, 60.65; H, 5.45, N, 5.05. Found: C, 60.49; H, 5.49, N, 4.98.

4-Benzyloxy-2,6-bis(hydroxymethyl)pyridine (**4**).

This compound was prepared from diethyl 4-benzyloxypyridine-2,6-dicarboxylate [11] (15.06 g, 50 mmoles) and sodium borohydride (9.45 g, 250 mmoles) as previously described [16]. The organic product was isolated by extraction with 15% ethanol in chloroform. After evaporation of the solvent the residue was recrystallized from dichloromethane to give 10.32 g (84%) of **4** as a white crystalline solid, mp 106-107° (lit [16] 106-107°).

4-Benzyloxy-2,6-bis(acetoxymethyl)pyridine (**5**).

To a suspension of 4-benzyloxy-2,6-bis(hydroxymethyl)pyridine **4** (3.67 g, 15 mmoles) in acetic anhydride (10 ml) was added triethylamine (4.5 ml, 32 mmoles) and 4-dimethylaminopyridine (183 mg, 1.5 mmoles). In a short period of time, the starting product dissolved. After 2 hours at room temperature the reaction mixture was cautiously decomposed by adding methanol, then concentrated *in vacuo* to give a residue which was treated with water and extracted with dichloromethane. The organic extract was washed with 10% aqueous sodium carbonate and water, dried (sodium sulfate) and then evaporated to give an oil, which solidified on standing. The crude product was recrystallized from diethyl ether-hexane (1:1) to give 4.47 g (90%) of a crystalline solid, mp 68-69°; ir: ν 1738 (C=O), 1608, 1578, 1384, 1361, 1249, 1225, cm^{-1}; ^1H nmr: δ 2.15 (s, 6H, CH_3), 5.13 (s, 2H, $PhCH_2$), 5.16 (s, 4H, $pyCH_2$), 6.87 (s, 2H, pyH-3,5), 7.41 (s, 5H, PhH); ^{13}C nmr: δ 20.9, 66.6, 70.1, 107.5, 127.6, 128.5, 128.7, 135.4, 157.4, 166.2, 170.5.

Anal. Calcd. for $C_{18}H_{19}NO_5$: C, 65.65; H, 5.82; N, 4.26. Found: C, 65.66; H, 5.82, N, 4.17.

4-Hydroxy-2,6-bis(acetoxymethyl)pyridine (**6**).

A stirred solution of benzyl ether protected diacetate **5** (3.29 g, 10 mmoles) in dichloromethane (50 ml) with 10% palladium-charcoal (800 mg) was hydrogenated at 0° for 45 minutes. The reaction mixture was filtered through Celite and the solvent was evaporated *in vacuo* to give an oil, which solidified on standing. After purification, by flash chromatography eluting with ethyl acetate, the product was precipitated from dichloromethane with hexane to give 2.13 g (89%) of **6** as a white solid, mp 116.5-117°; ir: ν 1748 (C=O), 1738 (C=O), 1634, 1358, 1225 cm^{-1}; ^1H nmr: δ 2.09 (s, 6H, CH_3), 5.02 (s, 4H, $pyCH_2$), 6.58 (s, 2H, pyH-3,5), 11.83 (bs, 1H, OH); ^{13}C nmr: δ 20.6, 63.9, 112.9, 150.9, 170.7, 174.3.

Anal. Calcd. for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48; N, 5.85. Found: C, 55.19; H, 5.51; N, 5.80.

6-Cascade:benzene[3-1,3,5]:(4-methoxypyridin-2,6-yl):acetoxymethyl (**7a**).

1,3,5-Tris(bromomethyl)benzene **2** (714 mg, 2 mmoles) was treated with acetate **6** (1.51 g, 6.3 mmoles) and anhydrous potassium carbonate (829 mg, 6 mmoles) in dry *N,N*-dimethylformamide (30 ml) as described above for **3**. After evaporation of the solvent *in vacuo*, the residue was partitioned between dichloromethane and water. The organic extract was washed with brine, dried (sodium sulfate) and evaporated to give an oil which was flash chromatographed eluting with ethyl acetate/dichloromethane (8:2). The product was then precipitated from dichloromethane with hexane to give 1.39 g (84%) of a white solid, mp, 117-118°; ir: ν 1741 (C=O), 1603, 1236 cm^{-1}; ^1H nmr: δ 2.14 (s, 18H, CH_3), 5.16 (s, 18H, $pyCH_2$ and $PhCH_2$), 6.88 (s, 6H, pyH-3,5), 7.48 (s, 3H, PhH); ^{13}C nmr: δ 20.9, 66.6, 69.4, 107.5, 126.6, 136.9, 157.6, 166.0, 170.5; ms: m/z 855 ($M + Na^+$).

Anal. Calcd. for $C_{42}H_{45}N_3O_{15}$: C, 60.65; H, 5.45; N, 5.05. Found: C, 60.52; H, 5.47, N, 5.01.

6-Cascade:benzene[3-1,3,5]:(4-methoxypyridin-2,6-yl)^2:hydroxymethane (**7b**).

A mixture of hexaacetate **7a** (832 mg, 1 mmole), sodium methoxide (14 mg, 0.61 mmole) and methanol (120 ml) was heated to reflux for 2 hours. On cooling (25°) 568 mg (98%) of hexaalcohol **7b** separated as a white crystalline solid, mp 191-191.5°; ir: ν 3300 (OH) cm^{-1}; ^1H nmr (dimethyl-d_6 sulfoxide): δ 4.46 (s, 12H $pyCH_2$), 5.24 (s, 6H, $PhCH_2$), 5.37 (bs, 6H, OH, deuterium oxide-exchangeable), 6.96 (s, 6H, pyH-3,5), 7.55 (s, 3H, PhH); ^{13}C nmr (dimethyl-d_6 sulfoxide): δ 64.2, 69.0, 104.9, 126.8, 137.3, 163.3, 165.9.

Anal. Calcd. for $C_{30}H_{33}N_3O_9 \cdot 1.5H_2O$: C, 59.40; H, 5.98; N, 6.93. Found. C, 59.03; H, 5.97, N, 6.81.

6-Cascade:benzene[3-1,3,5]:(4-methoxypyridin-2,6-yl):chloromethane (**7c**).

Hexaalcohol **7a** (580 mg, 1 mmole) was added to thionyl chloride (25 ml) cooled at 0° and the mixture was heated at 60° for 6 hours. The excess thionyl chloride was removed, ice-cold water was added and the resultant solution was neutralized with 10% aqueous sodium carbonate and filtered. The precipitate was dried and purified by flash chromatography eluting with dichloromethane/ethyl acetate (9:1). The product was then precipitated from dichloromethane with hexane to give 630 mg (91%) of a white solid, mp 156-157°; ir: ν 1596, 1348 cm^{-1}; ^1H nmr: δ 4.61 (s, 12H, $pyCH_2$), 5.20 (s, 6H, $PhCH_2$), 7.04 (s, 6H, pyH-3,5),

7.50 (s, 3H, PhH); ^{13}C nmr: δ 46.4, 69.5, 108.7, 126.5, 136.8, 158.1, 166.3.

Anal. Calcd. for $C_{30}H_{27}Cl_6N_3O_3$: C, 52.20; H, 3.94; N, 6.09. Found: C, 52.26; H, 3.90; N, 6.10.

12-Cascade:benzene[3-1,3,5]:(4-methoxypyridin-2,6-yl)^2:ethyl carboxylate (**9**).

Divergent Method.

Hexachloride **7c** (345 mg, 0.5 mmole) was treated with diester **1** (789 mg, 3.3 mmoles) in dry *N,N*-dimethylformamide (20 ml) in the presence of anhydrous potassium carbonate (495 mg, 3 mmoles) as above described for **3**. After purification by flash chromatography eluting sequentially with 1% methanol in dichloromethane and 2% methanol in dichloromethane, the product was precipitated from dichloromethane with diethyl ether and finally dried *in vacuo* at 50° to give 749 mg (78%) of a white solid; ir: ν 1722 (C=O), 1596, 1343, 1249, cm^{-1}; ^1H nmr: δ 1.40 (t, 36H, J = 7.1 Hz, OCH_2CH_3), 4.42 (q, 24H, OCH_2CH_3), 5.14 (s, 6H, $PhCH_2$), 5.28 (s, 12H, $pyCH_2$), 7.04 (s, 6H, pyH-3,5), 7.44 (s, 3H, PhH), 7.85 (s, 12H, pyH-3,5); ^{13}C nmr: δ 14.1, 62.3, 69.6, 70.7, 107.5, 114.4, 126.5, 136.6, 150.3, 156.8, 164.4, 166.1, 166.4; ms: m/z 1930 (M + Na$^+$).

Anal. Calcd. for $C_{96}H_{99}N_9O_{33}\cdot 1H_2O$: C, 59.90; H, 5.29; N, 6.55. Found: C, 60.08; H, 5.28; N, 6.46.

Convergent Method.

Tribromide **2** (179 mg, 0.5 mmole) was treated with the dendritic fragment **8** [11] (986 mg, 1.65 mmoles) in dry *N,N*-dimethylformamide (20 ml) with anhydrous potassium carbonate (207 mg, 1.5 mmoles) by the procedure used for **3**. The purification as described above in the divergent method gave 618 mg (64%) of **9** as a white solid; ir: ν 1718 (C=O), 1596, 1343, 1249, cm^{-1}; ^1H nmr: δ 1.40 (t, 36H, J = 7.1 Hz, OCH_2CH_3), 4.43 (q, 24H, J = 7.1 Hz, OCH_2CH_3), 5.15 (s, 6H, $PhCH_2$), 5.29 (s, 12H, $pyCH_2$), 7.05 (s, 6H, pyH-3,5), 7.45 (s, 3H, PhH), 7.86 (s, 12H, pyH-3,5); ^{13}C nmr: δ 14.1, 62.4, 69.6, 70.7, 107.5, 114.5, 126.6, 136.6, 150.3, 156.8, 164.4, 166.1, 166.4 ms: m/z 1930 (M + Na$^+$).

Anal. Calcd. for $C_{96}H_{99}N_9O_{33}\cdot 1H_2O$: C, 59.90; H, 5.29; N, 6.55. Found: C, 60.19; H, 5.32; N, 6.47.

12-Cascade:benzene[3-1,3,5]:(4-methoxypyridin-2,6-yl)^2:acetoxymethyl (**10a**).

Hexachloride **7c** (483 mg, 0.7 mmole) was treated with acetate **6** (1.05 g, 4.41 mmoles) in dry *N,N*-dimethylformamide (30 ml) and with potassium carbonate (581 mg, 4.2 mmoles) as described above for **7a**. Purification by flash chromatography eluting with 4% methanol in dichloromethane furnished an oil which was precipitated from dichloromethane with diethyl ether to give 1.2 g (90%) of a white solid; ir: ν 1740 (C=O), 1604, 1579, 1228 cm^{-1}; ^1H nmr: δ 2.11 (s, 36H, CH_3), 5.13 (s, 24H, $pyCH_2$), 5.15 (s, 6H, $PhCH_2$), 5.19 (s, 12H, $pyCH_2$), 6.87 (s, 12H, pyH-3,5), 7.05 (s, 6H, pyH-3,5), 7.51 (s, 3H, PhH); ^{13}C nmr: δ 20.8, 66.5, 69.6, 70.2, 107.2, 107.4, 127.0, 136.6, 157.5, 157.6, 165.7, 166.4, 170.4; ms: m/z 1930 (M + Na$^+$).

Anal. Calcd. for $C_{96}H_{99}N_9O_{33}$: C, 60.47; H, 5.23; N, 6.61. Found: C, 60.23; H, 5.28; N, 6.46.

12-Cascade:benzene[3-1,3,5]:(4-methoxypyridin-2,6-yl)^2:hydroxymethane (**10b**).

To a boiling solution of acetate **10a** (477 mg, 0.25 mmole) in methanol (50 ml) was added a solution of sodium methoxide (12 mg, 0.5 mmole) in methanol (10 ml). The reaction mixture was refluxed for 6 hours during which time a solid precipitated. After cooling (25°) the solid material was filtered and dried *in vacuo* at 50° to give 348 mg (99%) of **10a**; ir: ν 3300 (OH) cm^{-1}; ^1H nmr (dimethyl-d_6 sulfoxide): δ 4.45 (d, J = 2.8 Hz, 24H, $pyCH_2$), 5.21 (s, 12H, $pyCH_2$), 5.24 (s, 6H, $PhCH_2$), 5.37 (t, 12H, OH, deuterium oxide-exchangeable), 6.96 (s, 12H, pyH-3,5), 7.13 (s, 6H, pyH-3,5), 7.55 (s, 3H, PhH); ^{13}C nmr (dimethyl-d_6 sulfoxide): δ 64.1, 69.5, 69.9, 104.9, 107.7, 127.5, 136.8, 157.8, 163.3, 165.7, 166.1; ms: m/z 1424 (M + Na$^+$).

Anal. Calcd. for $C_{72}H_{75}N_9O_{21}\cdot 1H_2O$: C, 60.88; H, 5.46; N, 8.88. Found: C, 54.99; H, 5.47; N, 8.70.

Acknowledgements.

We thank the MURST (Ministero per l'Università e la Ricerca Scientifica e Tecnologica) for financial support, Dr. P. Traldi and R. Serraglia for mass spectra.

REFERENCES AND NOTES

[1] Y. H. Kim and O. W. Webster, *J. Am. Chem. Soc.*, **112**, 4592 (1990).

[2] J. M. J. Fréchet and C. J. Hawker, *React. Funct. Polym.*, **26**, 127 (1995).

[3] D. A. Tomalia, A. M. Naylor and W. A. Goddard III, *Angew. Chem., Int. Ed. Engl.*, **29**, 138 (1990).

[4a] G. R. Newkome, Z. Yao, G. R. Baker and V. K. Gupta, *J. Org. Chem*, **50**, 2003 (1985); [b] G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, P. S. Russo and M. J. Saunders, *J. Am. Chem. Soc.*, **108**, 849 (1986).

[5a] C. J. Hawker and J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.*, 1010 (1990); [b] C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **112**, 7638 (1990); [c] C. J. Hawker and J. M. J. Fréchet, *Macromolecules*, **23**, 4726 (1990).

[6] T. M. Miller and T. X. Neenan, *Chem. Mater.*, **2**, 346 (1990).

[7] H. Mekelburger, W. Jaworek and F. Vogtle, *Angew. Chem., Int. Ed. Engl.*, **31**, 1571 (1992).

[8] G. R. Newkome, C. N. Moorefield and G. R. Baker, *Aldrichimica Acta*, **25** (2), 31 (1992).

[9] D. A. Tomalia, *Aldrichimica Acta*, **26** (4), 91 (1993).

[10] G. R. Newkome, C. N. Moorefield, F. Vogtle, Dendritic Molecules: Concepts, Synthesis, Perspectives, VCH, Germany, 1996, pp 49-222.

[11] G. Chessa and A. Scrivanti, *J. Chem. Soc., Perkin Trans. 1*, 307 (1996).

[12] F. Vogtle, M. Zuber and R. G. Lichtenthaler, *Chem. Ber.*, **106**, 717 (1973).

[13] G. R. Newkome, R. K. Behera, C. N. Moorefield and G. R. Baker, *J. Org. Chem.*, **56**, 7162 (1991).

[14] M. Jorgensen, K. Bechgaard, T. Bjornholm, P. Sommer-Larsen, L. G. Hansen and K. Schaumburg, *J. Org. Chem.*, **59**, 5877 (1994).

[15] G. R. Newkome, G. R. Baker, J. K. Young and J. G. Traynham, *J. Polym. Sci. Part A: Polym. Chem.*, **31**, 641 (1993).

[16] G. Chessa, G. Marangoni and B. Pitteri, *React. Polym.*, **12**, 219 (1990).