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Encapsulation of Polyoxotungstate into Dendrimers by Ionic Bonding and Their Use As Oxidation Catalyst

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Abstract. A family of 36-armed dendrimers containing six internal amino groups was synthesized and used to incorporate polyoxometalates (POMs) into their structures by ionic bonding. Allyl-terminated dendrimer **17** (with oxidizable end groups) and methylphenyl-terminated dendrimer **18** (with non-oxidizable end groups) were used for these studies. It was found that the electrostatic incorporation of the tri-anionic POM $[PO_4\{WO(O_2)_2\}_4]^{3-}$ into the methylphenyl-terminated dendrimer **18**, in an acidic medium, leads to the dendritic POM hybrid **19**, bearing two POM units in its structure. In contrast, attempts to encapsulate POMs into allyl-terminated dendrimer **17** gave unsatisfactory results. Indeed, the epoxidation kinetics of the 36-olefinic terminated dendrimer **17** was too slow, and the expected 36-epoxy-dendritic POM framework **20** was not obtained. Lengthening the reaction up to six hours led to the decomposition of POM species. The solubility in organic solvents of the dendritic POM hybrid **19**, combined with its NMR and infrared data, indicate that POM units are clearly connected to the dendritic structure. The catalytic performance of this hybrid material in the oxidation of cyclooctene shows that the properties of POM are retained. The POM-encapsulated dendrimer **19** was found to be an effective catalyst in the oxidation of cyclooctene.

INTRODUCTION

Dendrimers and metallodendrimers are generating much attention for their potential applications in various areas.[1,2] The increasing use of these macromolecules in catalysis, pioneered by van Leeuwen and coworkers,[2b,d] is an emerging field, as the size of these macromolecules allows their easy recovery, an essential feature for reaction efficiency, economy, and environmental concern.[2] In this context, a variety of dendrimers, cores, branches, and end groups have been assembled and used in different domains such as supramolecular chemistry,[3] nanosciences,[1c] drug delivery,[4] and catalysis.[2,5] Polyoxometalates (POMs) are a large class of inorganic transition metal–oxygen clusters that are the source of fascinating architectures[6] and rich redox chemistry[7] upon which their catalytic activity in oxidation reactions is based.[8] However, dendritic polyoxometalate compounds are still under-represented.[9] A few heterogeneous[9a] and homogeneous[9b–h] dendritic POMs have been shown to be effective catalysts in oxidation reactions. Encapsulation of POMs within the cavities of dendrimers should combine the catalytic properties of POMs with the steric properties of dendrimers.[9] Although the incorporation of POMs into dendrimer cavities exhibits attractive perspectives in various areas, to the best of our knowledge, the work reported so far describes two families of dendritic POMs. The first family involves compounds with POM units located at the periphery of

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dendrimers,[9b,d,e,h,10] whereas the second family involves, hybrids in which a POM unit is encapsulated by surfactants or by dendrons (POM-cored compounds).[9c,f,g,11] Recently we have reported two series of dendritic POM hybrids, with a tetrakis(diperoxo-tungsto)phosphate $[PO_4\{WO(O_2)_2\}_4]^{3-}$ located respectively at the periphery of the dendrimer[9d,h] or at the core[9f,g]. The stability, solubility, and catalytic efficiency in the oxidation reaction, as well as recyclability, have been studied. We discovered that the stability of the anionic POM units, as well as their catalytic performance, was closely related to the structure of their dendritic counter cations. It was found that POM-cored dendrimers in which the POM unit is protected by the dendritic wedge were more stable and more efficient in oxidation reactions than their homologues functionalized at the periphery with POM units. The fact that POM units located at the periphery of dendrimers are exposed to the ambient environment probably accounted for their slow decomposition. Herein, we try to compensate by dendritic encapsulation, which should provide an effective protection to POMs by enhancing their stability against the ambient environment. Since the stability of POMs is one of the most important features of their properties, especially their catalytic properties, we describe the synthesis of dendrimers bearing six internal amino groups and their use to incorporate two tri-anionic POM $[PO_4\{WO(O_2)_2\}_4]^{3-}$ species into their structures. The remarkable consequence of the encapsulation of POMs into dendrimers is that stable dendritic POM hybrids bearing more than one POM unit in their structures, with retention of their properties, are now possible. The synthesis, isolation, and characterization of dendrimers encapsulating two POM units, as well as their use in the catalytic oxidation of cyclooctene, using hydrogen peroxide, have been investigated. The results obtained demonstrate that the encapsulation of POMs does not influence their catalytic properties.

EXPERIMENTAL

General Remarks

Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. Acetonitrile (CH_3CN) was stirred under argon overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride just before use. All other chemicals were used as received. The ^1H, ^{13}C, ^{31}P NMR spectra were recorded at 25 °C with a Brucker AC 250 FT spectrometer (^1H: 250.13, ^{13}C: 62.91 MHz) and a Brucker AC 200 FT spectrometer (^1H: 200.16, ^{13}C: 50.33, ^{31}P: 81.02 MHz). All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS). Elemental analyses were carried out at the Vernaison CNRS center. The infrared spectra were recorded in KBr pellets on an FT-IR Paragon 1000 Perkin-Elmer spectrometer. The matrix-assisted laser desorption (MALDI) mass spectra were recorded using a Perceptive Biosystems Voyager Elite (Framingham, MA) time-of-flight (TOF) mass spectrometer. Organic oxidation products were identified by ^1H and ^{13}C NMR using comparison of these spectra with those of authentic samples.

*Synthesis of Hexa-Amine Dendritic Core (**5**)*

*(a) 1,6-(1-chloroalkyl)phenyl (**1**)*

A mixture of 1 g (9.0 mmol) of hydroquinone, 6.2 g of K_2CO_3 (46.0 mmol), and 3.5 mL (24.0 mmol) of 1-chloro-6-iodopentane, in 20 mL of DMF, was stirred for 12 h at room temperature. The reaction mixture was then extracted with Et_2O (3 × 20 mL), and the resulting solution was washed with water and dried over sodium sulfate. The solvent was removed under vacuum, and the product was purified by chromatography on a silica-gel column with a 95:5 pentane/diethyl ether mixture to provide 2.5 g (80%) of **1** as a colorless oil.

^1H NMR ($CDCl_3$, 250 MHz): δ = 6.81 (s, 4H, Ar), 3.90 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, CH_2–O), 3.55 (t, $^3J_{H-H}$ = 6.9 Hz, 4H, CH_2–Cl), 1.80 (m, 8H, CH_2), 1.51 (m, 8H, CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 153.0 (C_q, Ar–O), 114.5 (CH, Ar), 69.0 (CH_2–O), 45.0 (Cl–CH_2), 33.4 (CH_2), 30.2 (CH_2), 29.3 (CH_2), 25.5 (CH_2).

Elemental analysis calcd (%) for $C_{18}H_{28}O_2Cl_2$ (347.32): C 62.25, H 8.13; found: C 62.46, H 8.04.

*(b) 1,6-(1-iodoalkyl)phenyl (**2**)*

A mixture of 1.8 g (4.9 mmol) of **1** and 3.7 g (24.4 mmol) of NaI in 20 mL of 2-butanone was stirred for 24 h at 80 °C. After removal of the solvent under vacuum, the residue was extracted with Et_2O (3 × 20 mL). The resulting solution was washed with an aqueous solution saturated with $Na_2S_2O_3$, dried over sodium sulfate, and then filtered. The solvent was removed under vacuum to provide 2.54 g (98%) of **2** as a colorless oil.

^1H NMR ($CDCl_3$, 250 MHz): δ = 6.81 (s, 4H, Ar), 3.89 (t, ^3J = 6.1 Hz, 4H, CH_2–O), 3.19 (t, $^3J_{H-H}$ = 6.7 Hz, 4H, CH_2–I), 1.88–1.76 (m, 8H, CH_2), 1.47 (m, 8H, CH_2).

$^{1,3}C$ NMR ($CDCl_3$, 63 MHz): δ = 153.01 (C_q, Ar–O), 115.4 (CH, Ar), 68.3 (CH_2–O), 33.4 (CH_2), 30.2 (CH_2), 29.1 (CH_2), 25.0 (CH_2), 7.0 (CH_2–I).

Elemental analysis calcd (%) for $C_{18}H_{28}O_2I_2$ (530.21): C 40.78, H 5.32; found: C 40.46, H 5.17.

*(c) Hexa-azide dendritic core (**4**)*

A mixture of 0.448 g (0.844 mmol) of **2**, 0.635 g (1.76 mmol) of tri-azidophenol **3**,[12] and 0.508 g (3.4 mmol) of K_2CO_3 in 10 mL of DMF was stirred for 15 h at room temperature. The reaction mixture was then extracted with Et_2O (3 × 10 mL), and the resulting solution was washed with water and dried over sodium sulfate. The solvent was removed under vacuum to provide 0.751 g (90%) of **4** as a colorless oil.

^1H NMR ($CDCl_3$, 250 MHz): δ = 7.18 (d, 4H, Ar), 6.83 (d, 4H, Ar), 6.82 (s, 4H, Ar), 3.91 (m, 8H, CH_2–O), 3.22 (t, $^3J_{H,H}$ = 6.4 Hz, 12H, CH_2–N_3), 1.79–1.34 (m, 40H, CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 157.1 (C_q, Ar–O), 137.2 (C_q, Ar), 127.7 (CH, Ar), 127.1 (CH, Ar), 114.2 (CH, Ar), 67.7

(CH_2–O), 51.9 (CH_2–N_3), 41.9 (C–CH_2), 33.4 (CH_2), 29.7 (CH_2), 29.3 (CH_2), 26.0 (CH_2), 23.2 (CH_2).

(*d) Hexa-amine dendritic core (**5**)*

A mixture of 0.752 g (0.760 mmol) of **4**, 1.43 g (5.56 mmol) of triphenylphosphene (PPh_3) and 0.1 mL (5.56 mmol) of H_2O, in 10 mL of THF, was stirred for 12 h at 40 °C. After removal of the solvent, the residue was extracted with CH_2Cl_2 (3 × 10 mL), and the resulting solution was concentrated. The product was precipitated by slow addition of pentane in the CH_2Cl_2 mixture. The solid was washed with pentane, and dried under vacuum providing 0.431 g (68%) of **5** as a colorless solid.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.25 (m, 4H, Ar), 6.83 (m, 4H, Ar), 6.81 (s, 4H, Ar), 3.91 (m, 8H, CH_2–O), 2.61 (t, $^3J_{H,H}$ = 5.6 Hz, 12H, CH_2–NH_2), 1.79–1.26 (m, 40H, CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 158.4 (C_q, Ar–O), 154.6 (C_q, Ar–O), 140.1 (C_q, Ar), 128.5 (CH, Ar), 116.5 (CH, Ar), 115.1 (CH, Ar), 69.5 (CH_2–O), 68.8 (CH_2–O), 43.1 (C–CH_2), 35.7 (CH_2), 30.5 (CH_2–NH_2), 30.4 (CH_2), 29.3 (CH_2), 27.6 (CH_2), 27.0 (CH_2).

MALDI-TOF mass spectrum: *m/z*: 834.3 $[M+H]^+$, calcd. 833.2.

Elemental analysis calcd (%) for $C_{50}H_{84}O_4N_6$ (833.25): C 72.07, H 10.16; found: C 72.63, H 9.89.

(e) 1-Chloroalkyl tri-allylphenyl dendron (7)

A mixture of 2.0 g (8.760 mmol) of triallylmethyl phenol **6**, 2.450 g (17.520 mmol) of K_2CO_3 and 1.6 mL (13.140 mmol) of 1-ch1oro-4-iodobutane, in 30 mL of DMF, was stirred for 48 h at room temperature. The reaction mixture was then extracted with Et_2O (3 × 30 mL), and the resulting solution was washed with water and dried over sodium sulfate. The solvent was removed under vacuum and the product was purified by chromatography on a silica-gel column with a 95:5 pentane/diethyl ether mixture to provide 2.709 g (97%) of **7** as a colorless oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.23 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar), 6.85 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar), 5.55 (m, 3H, CH_2 = CH), 5.02 (m, 6H, CH_2 = CH), 3.98 (t, $^3J_{H,H}$ = 5.8 Hz, 2H, CH_2–O), 3.57 (t, $^3J_{H,H}$ = 6.4 Hz, 2H, CH_2–Cl), 2.42 (d, $^3J_{H,H}$ = 7.3 Hz, 6H, CH_2 = CH–CH_2), 1.97 (m, 4H, CH_2–CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 156.70 (C_q, Ar–O), 143.54 (C_q, Ar), 134.56 (CH_2 = CH), 127.53 (CH, Ar), 117.41 (CH = CH_2), 113.69 (CH, Ar), 66.90 (CH_2–O), 44.85 (CH_2–Cl), 42.55 (C–CH_2), 41.83 (CH_2), 31.55 (CH_2), 29.38 (CH_2).

Elemental analysis calcd (%) for $C_{20}H_{27}OCl$ (318.88): C 75.33, H 8.53; found: C 75.27, H 8.50.

(f) 1-Iodoalkyl tri-allylphenyl dendron (8)

A mixture of 2.0 g (6.27 mmol) of **7** and 4.7 g (31.4 mmol) of NaI in 30 mL of 2-butanone was stirred for 24 h at 80 °C. After removal of the solvent under vacuum, the residue was extracted with Et_2O (3 × 30 mL). The resulting solution was washed with an aqueous solution saturated with $Na_2S_2O_3$, dried over sodium sulfate, and then filtered. The solvent was removed under vacuum to provide 2.47 g (96%) of **8** as a colorless oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.21 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar), 6.84 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar), 5.55 (m, 3H, CH_2 = CH), 5.02 (m, 6H, CH_2 = CH), 3.97 (t, $^3J_{H,H}$ = 5.8 Hz, 2H, CH_2–O), 3.27 (t, $^3J_{H,H}$ = 6.7 Hz, 2H; CH_2-I), 2.42 (d, $^3J_{H,H}$ = 7.3 Hz, 6H, CH_2 = CH–CH_2), 1.97 (m, 4H; CH_2–CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 156.62 (C_q, Ar–O), 143.45 (C_q, Ar), 134.56 (CH_2 = CH), 127.53 (CH, Ar), 117.41 (CH = CH_2), 113.69 (CH, Ar), 66.59 (CH_2–O), 42.55 (C_q–CH_2), 41.83 (CH_2), 31.58 (CH_2), 30.27 (CH_2), 6.56 (CH_2–I).

Elemental analysis calcd (%) for $C_{20}H_{27}OI$(410.33): C 58.54, H 6.63; found: C 58.40, H 6.60.

(g) Benzylalcohol tri-allylphenyl dendron (9)

A mixture of 0.928 g (7.475 mmol) of $HOCH_2$-*p*-C_6H_4OH, 2.066 g (14.950 mmol) of K_2CO_3 in 10 mL of DMF was stirred for 30 min at room temperature. 3.987 g (9.717 mmol) of dendron **8** was then added in the reaction mixture and the resulting solution stirred at 40 °C for 16 h. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the resulting solution washed with water and dried over sodium sulfate. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with a 7:3 pentane/ether mixture providing 2.461 g (81%) of **9** as a yellow oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.21 (2×d, 4H, Ar), 6.89 (2×d, 4H, Ar), 5.55 (m, 3H, CH_2 = CH), 5.02 (m, 6H, CH_2 = CH), 4.62 (s, broad, 2H, CH_2–OH), 4.04 (t, $^3J_{H,H}$ = 4.9 Hz, 2H, CH_2–O), 4.02 (t, $^3J_{H,H}$ = 4.9 Hz, 2H, CH_2–O), 2.42 (d, $^3J_{H,H}$ = 7.0 Hz, 6H, CH_2 = CH–CH_2), 1.98 (m, 4H, CH_2-CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 158.90 (C_q, Ar–O), 156.83 (C_q, Ar–O), 137. 83 (C_q, Ar), 137.83 (C_q, Ar), 134.68 (CH–CH_2), 132.96 (C_q, Ar), 128.92 (CH, Ar), 127.69 (CH, Ar), 117.53 (CH–CH_2), 114.77 (CH, Ar), 114.00 (CH, Ar), 67.92 (CH_2–O), 67.67 (CH_2–O), 65.15 (CH_2–OH), 42.76 (C_q–CH_2), 40.00 (CH_2), 29.13 (CH_2), 29.07 (CH_2), 22.86 (CH_2).

Elemental analysis calcd (%) for $C_{27}H_{34}O_3$ (406.56): C 79.77, H 8.43; found: C 80.54, H 8.58.

*(h) Benzylbromide tri-allylphenyl dendron (**10**)*

0.189 mL (2.016 mmol) of PBr_3 was added to a cooled mixture (0° C) of 2.460 mg (6.050 mmol) of dendron **9** in 20 mL of toluene. The resulting solution was stirred at room temperature for 4 h. After removal of the solvent, the residue was extracted with Et_2O, washed with water, and dried over sodium sulfate. The solvent was removed under vacuum providing 2.811 g (99%) of **10** as a yellow oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.23 (2×d, 4H, Ar), 6.84 (2×d, 4H, Ar), 5.55 (m, 3H, CH_2 = CH), 5.02 (m, 6H, CH_2 = CH), 4.50 (s, 2H, Br–CH_2), 4.04 (t, $^3J_{H,H}$ = 4.6 Hz, 2H, CH_2–O), 4.02 (t, $^3J_{H,H}$ = 4.6 Hz, 2H, CH_2–O), 2.43 (d, $^3J_{H,H}$ = 7.0 Hz, 6H, CH_2 = CH–CH_2), 1.97 (m, 4H, CH_2–CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 159.20 (C_q, Ar–O), 156.83 (C_q, Ar–O), 137. 83 (C_q, Ar), 137.83 (C_q, Ar), 134.57 (CH-CH_2), 130.33 (C_q, Ar), 127.53 (CH, Ar), 117.40 (CH, Ar), 114.77 (CH–CH_2), 114.62 (CH, Ar), 113.72 (CH, Ar), 67.72 (CH_2–O), 67.43 (CH_2–O), 42.76 (C_q–CH_2), 41.84 (CH_2), 34.13 (CH_2–Br), 29.01 (CH_2), 22.67 (CH_2).

Elemental analysis calcd (%) for $C_{27}H_{33}O_2Br$ (469.46): C 69.08, H 7.09; found: C 69.02, H 7.48.

*(i) Tri-methylbenzene phenol dendron (**12**)*

A mixture of 2.056 g (3.284 mmol) of protected tri-iodophenol dendron **11**, 4.108 g (29.556 mmol) of K_2CO_3, and 3.192 g (29.556 mmol) of *p*-cresol in 20 mL of DMF was

stirred at room temperature for 48 h. After addition of 2.282 g (16.420 mmol) of K_2CO_3 and 5 mL of H_2O, the reaction mixture was stirred at 40 °C for 12 h and extracted with Et_2O (3 × 20 mL). The resulting solution was washed with water and dried over sodium sulfate. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with a 6:4 pentane/ether mixture providing 1.524 g (84%) of **12** as a white solid.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.22 (d, 2H, Ar), 7.05 (d, 6H, Ar), 6.75 (m, 8H, Ar), 3.84 (t, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_2–O), 2.27 (s, 9H, CH_3), 1.83 (m, 6H, CH_2–CH_2); 1.59 (m, 6H, CH_2–CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 156.07 (C_q, Ar–O), 153.34 (C_q, Ar–O), 143. 18 (C_q, Ar), 138.71 (C_q, Ar), 127.73 (CH, Ar), 126.20 (CH, Ar), 114.99 (CH, Ar), 113.92 (CH, Ar), 68.34 (CH_2–O), 42.20 (C_q–CH_2), 33.79 (CH_2), 23.81 (CH_2), 20.68 (CH_3).

Elemental analysis calcd (%) for $C_{37}H_{44}O_4$ (552.75): C 80.40, H 8.02; found: C 79.87, H 8.72.

*(j) Chloroalkyl tri-methylphenyl dendron (**13**)*

A mixture of 2.700 g (4.884 mmol) of phenol **12**, 2.022 g (14.654 mmol) of K_2CO_3, and 1.2 mL (9.768 mmol) of 1-chloro-4-iodobutane in 20 mL of DMF was stirred at room temperature for 48 h. The reaction mixture was then extracted with Et_2O (3 × 30 mL), and the resulting solution was washed with water and dried over sodium sulfate. The solvent was removed under vacuum, and the product was purified by chromatography on a silica-gel column with a 99:1 pentane/diethyl ether mixture to provide 2.513 g (80%) of **13** as a colorless oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.28 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar), 7.08 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, Ar), 6.84 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar), 6.75 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, Ar), 3.99 (t, $^3J_{H,H}$ = 5.8 Hz, 2H, CH_2–O), 3.86 (t, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_2-O), 3.62 (t, $^3J_{H,H}$ = 6.1 Hz, 2H, CH_2-Cl), 2.28 (s, 9H, CH_3), 1.98 (m, 4H; CH_2–CH_2), 1.86 (m, 6H, CH_2–CH_2), 1.60 (m, 6H, CH_2–CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 155.06 (C_q, Ar–O), 154.94 (C_q, Ar–O), 136.74 (C_q, Ar), 128.01 (CH, Ar), 127.82 (CH, Ar), 125.68 (C_q, Ar), 112.51 (CH, Ar), 112.21 (C_q, Ar), 66.55 (CH_2–O), 66.00 (CH_2–O), 42.96 (Cl–CH_2), 40.24 (C_q–CH_2), 41.83 (CH_2), 31.88 (CH_2), 27.57 (CH_2), 24.98 (CH_2), 21.89 (CH_2), 18.63 (CH_3).

Elemental analysis calcd (%) for $C_{41}H_{51}ClO_4$ (643.3): C 76.55, H 7.99; found: C 76.18, H 8.09.

*(k) Iodoalkyl tri-methylphenyl dendron (**14**)*

A mixture of 2.500 g (3.886 mmol) of **13** and 2.900 g (19.400 mmol) of NaI in 30 mL of 2-butanone was stirred for 24 h at 80 °C. After removal of the solvent under vacuum, the residue was extracted with Et_2O (3 × 30 mL). The resulting solution was washed with an aqueous solution saturated with $Na_2S_2O_3$, dried over sodium sulfate, and then filtered. The solvent was removed under vacuum to provide 2.740 g (96%) of **14** as a colorless oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.23 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar), 7.03 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, Ar), 6.77 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar), 6.74 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, Ar), 3.95 (t, $^3J_{H,H}$ = 5.8 Hz, 2H, CH_2–O), 3.83 (t, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_2–O), 3.26 (t, $^3J_{H,H}$ = 6.1 Hz, 2H, CH_2–I), 2.26 (s, 9H, CH_3), 1.98 (m, 4H, CH_2–CH_2), 1.82 (m, 6H, CH_2–CH_2), 1.65 (m, 6H, CH_2–CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 155.08 (C_q, Ar–O), 154.94 (C_q, Ar–O), 137.50 (C_q, Ar), 128.70 (CH, Ar), 127.82 (CH, Ar), 126.40 (C_q, Ar), 113.20 (CH, Ar), 112.21 (C_q, Ar), 67.30 (CH_2–O), 65.40 (CH_2–O), 41.00 (C_q–CH_2), 32.60 (CH_2), 29.20 (CH_2), 22.60 (CH_2), 19.40 (CH_3), 5.40 (ICH_2).

Elemental analysis calcd (%) for $C_{41}H_{51}IO_4$ (734.7.3): C 67.02, H 7.00; found: C 67.75, H 7.48.

*(l) Benzylalcohol tri-methylphenyl dendron (**15**)*

A mixture of 0.232 g (1.860 mmol) of $HOCH_2$-*p*-C_6H_4OH, 0.513 g (3.720 mmol) of K_2CO_3 in 10 mL of DMF was stirred for 30 min at room temperature. 1.503 g (2.046 mmol) of dendron **14** was then added in the reaction mixture and the resulting solution stirred at 40 °C for 16 h. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the resulting solution washed with water and dried over sodium sulfate. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with a 7:3 pentane/ether mixture providing 1.045 g (70%) of **15** as a yellow oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.27 (m, 4H, Ar), 7.05 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, Ar), 6.87 (m, 4H, Ar), 6.75 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, Ar), 4.62 (s, 2H, CH_2–OH), 4.03 (m, 4H, CH_2–O), 3.85 (t, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_2–O), 2.27 (s, 9H, CH_3), 1.99 (m, 4H, CH_2–CH_2), 1.84 (m, 6H, CH_2–CH_2), 1.60 (m, 6H, CH_2–CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 158.39 (C_q, Ar–O), 156.70 (C_q, Ar–O), 138.29 (C_q, Ar), 132.98 (C_q, Ar), 130.65 (CH, Ar), 129.70 (CH, Ar), 128.74 (CH, Ar), 128.42 (CH, Ar), 127.32 (C_q, Ar), 115.18 (CH, Ar), 114.34 (CH, Ar), 114.18 (C_q, Ar), 68.19 (CH_2–O), 67.36 (CH_2–O), 67.14 (CH_2–O), 64.65 (CH_2–OH), 41.86 (C_q–CH_2), 33.53 (CH_2), 25.90 (CH_2), 23.54 (CH_2), 20.33 (CH_3).

Elemental analysis calcd (%) for $C_{54}H_{58}O_6$ (803.04): C 80.77, H 7.28; found: C 81.28, H 7.50.

*(m) Benzyl bromide tri-methylphenyl dendron (**16**)*

0.06 mL (0.600 mmol) of PBr_3 was added to a cooled mixture (0 °C) of 1.268 g (1.579 mmol) of dendron **15** in 15 mL of toluene. The resulting solution was stirred at room temperature for 4 h. After removal of the solvent, the residue was extracted with Et_2O, washed with water, and dried over sodium sulfate. The solvent was removed under vacuum providing 1.093 g (99%) of **15** as a yellow oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.30 (m, 4H, Ar), 7.05 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, Ar), 6.90 (m, 4H, Ar), 6.76 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, Ar), 4.45 (s, 2H, CH_2–Br), 3.94 (m, 4H, CH_2–O), 3.80 (t, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_2–O), 2.22 (s, 9H, CH_3), 1.91 (m, 4H; CH_2–CH_2), 1.79 (m, 6H; CH_2–CH_2), 1.63 (m, 6H; CH_2–CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 157.30 (C_q, Ar–O), 157.26 (C_q, Ar–O), 138.90 (C_q, Ar), 138.74 (C_q, Ar), 130.89 (C_q, Ar), 130.28 (CH, Ar), 130.18 (CH, Ar), 130.07 (CH, Ar), 127.93 (CH, Ar), 115.18 (C_q, Ar), 114.76 (CH, Ar), 114.48 (C_q, Ar), 68.80 (CH_2–O), 68.00 (CH_2–O), 67.69 (CH_2–O), 42.49 (C_q–CH_2), 34.52 (Br-CH_2), 34.14 (CH_2), 26.48 (CH_2), 24.14 (CH_2), 20.93 (CH_3).

Elemental analysis calcd (%) for $C_{54}H_{57}BrO_5$ (865.94): C 74.90, H 6.63; found: C 74.60, H 6.39.

*(n) 36-allyl-terminated hexa-amino dendrimer (**17**)*

A CH_2Cl_2 solution (10 mL) of 0.060 g (0.072 mmol) of hexa-amino dendritic core **5**, 0.609 g (1.296 mmol) of bromo benzyl dendron **10**, and 0.2 mL (1.252 mmol) of N,N-diisopropyl ethylamine, was stirred at room temperature for 48 h. After removal of the solvent, the residue was washed with CH_3CN (3 × 10 mL) to remove the excess of dendron **10** and dried under vaccum providing 277 mg (70%) of the corresponding 6-amino dendritic compound **17** as a white solid.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.71 (broad, 56H, Ar), 6.81 (broad, 56H, Ar), 5.54 (m_{broad}, 36H, CH_2 = CH), 5.00 (m_{broad}, 72H, CH_2 = CH), 3.98 (broad, 56H, CH_2–O), 3.35 (broad, 24H, N–CH_2), 2.42 (d_{broad}, 72H, CH_2 = CH–CH_2), 2.39 (broad, 12H, N–CH_2–CH_2), 1.94 (broad, 56H, CH_2–CH_2), 1.75–1.25 (32H, CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 159.82 (C_q, Ar–O), 156.55 (C_q, Ar–O), 137.44 (C_q, Ar), 136.69 (CH–CH_2), 132.61 (C_q, Ar), 130.17 (C_q, Ar), 129.15 (C_q, Ar), 127.39 (CH, Ar), 120.29 (C_q, Ar), 117.23 (CH–CH_2), 113.59 (CH, Ar), 67.33 (CH_2–O), 66.98 (CH_2–O), 56.75 (N–CH_2), 53.18 (N–CH_2), 42.41 (C_q–CH_2), 41.69 (CH_2), 36.61 (CH_2), 29.44 (CH_2), 29.20 (CH_2), 29.10 (CH_2), 25.82 (CH_2) 22.43 (CH_2).

MALDI-TOF mass spectrum: *m/z*: 5494.16 $[M]^+$, calcd. 5495.74.

Elemental analysis calcd (%) for $C_{374}H_{468}N_6O_{28}$ (5495.74): C 81.74, H 8.58; found: C 81.79, H 8.25.

*(o) 36-methylphenyl-terminated hexaamino dendrimer (**18**)*

277 mg (75%) of this compound was obtained as a white solid according to the procedure described above for **17**, but from **16** instead of **10**.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.21 (broad, Ar), 7.08 (broad, Ar), 6.83 (broad, Ar), 6.75 (broad, Ar), 4.00 (broad, 32H, CH_2–O, N–CH_2), 3.86 (broad, 72H, CH_2–O), 3.37 (broad, 12H, N–CH_2), 2.28 (s, CH_3), 1.94 (broad, CH_2), 1.83 (broad, CH_2), 1.59 (broad, CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 160.82 (C_q, Ar-O), 157.93 (C_q, Ar–O), 156.71 (C_q, Ar–O), 138.44 (C_q, Ar), 131.73 (C_q, Ar), 129.88 (C_q, Ar), 128.43 (C_q, Ar), 129.67 (CH, Ar), 127.52 (C_q, Ar), 114.36 (CH, Ar), 114.08 (CH, Ar), 68.41 (CH_2–O), 67.40 (CH_2–O), 62.99 (N–CH_2), 58.40 (N–CH_2), 42.08 (C_q–CH_2), 33.74 (CH_2), 26.22 (CH_2), 23.76 (CH_2), 20.53 (CH_3).

Elemental analysis calcd (%) for $C_{552}H_{680}N_6O_{64}$ (8423.47): C 78.71, H 8.14; found: C 78.66, H 7.50.

General Procedure for the Incorporation of POM Units in Dendritic Structures

10 mL of H_2O_2 (35% in water) was added to 0.160 mL of a water solution of 0.096 g (0.033 mmol) of the commercial heteropolyacid $H_3PW_{12}O_{40}$. The mixture was stirred at room temperature for 30 min. Then, 1.5 mL of a CH_2Cl_2 solution of 0.100 g (0.007 mmol) of the hexa-amine dendrimer was added, and the mixture was stirred for an additional 6 h for compound **20** and 1 h for the 36-methylphenyl POM dendrimer **19**. The CH_2Cl_2 layer was washed with 0.5 mL of water and dried over sodium sulfate. The product was obtained by removing the solvent under vacuum.

*36-methylphenyl terminated dendritic POM compound (**19**)*

0.093 g (85%) of the 36-methylphenyl terminated POM dendrimer **19** was obtained as a yellow solid according to the procedure described above.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.26 (broad, Ar), 7.19 (broad, Ar), 7.08 (broad, Ar), 6.83 (broad, Ar), 6.75 (broad, Ar), 4.30–4.00 (broad, N–CH_2), 3.85 (broad, CH_2–O), 2.28 (s, CH_3), 1.96 (broad, CH_2), 1.82 (broad, CH_2), 1.58 (broad, CH_2) 1.28 (broad, CH_2).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 156.76 (C_q, Ar–O), 156.68 (C_q, Ar–O), 138.48 (C_q, Ar), 138.38 (C_q, Ar), 131.96 (C_q, Ar), 129.67 (CH, Ar), 129.58 (C_q, Ar), 127.42 (C_q, Ar), 114.68 (CH, Ar), 114.21 (CH, Ar), 113.93 (CH, Ar), 68.29 (CH_2–O), 67.50 (CH_2–O), 67.00 (N–CH_2), 41.96 (C_q–CH_2), 33.61 (CH_2), 29.64 (CH_2), 25.88 (CH_2), 23.63 (CH_2), 20.40 (CH_3).

^{31}P NMR ($CDCl_3$, 81 MHz) δ_{ppm}: 3.46 (PO_4).

FTIR (KBr plates) ν_{cm-1}: 1090 and 1048 (P–O), 960 (W = O), 840 (O-O), 580 and 530 $W(O_2)_{s,as}$.

Elemental analysis calcd (%) for $C_{552}H_{686}N_6O_{112}P_2W_8$ (10730.23): C 61.79, H 6.44; found: C 62.46, H 6.21.

*Attempt of preparing the 36-epoxy-terminated dendritic POM compound (**20**)*

Following the procedure described above for **19**, all attempts to prepare the 36-epoxy-terminated dendrimer **20** failed because of the slow epoxidation kinetics for the 36 olefinic termini present in compound **17**. Lengthening the reaction time up to 6 h led to the decomposition of tri-anionic POM species, and a dendrimer bearing epoxi- and olefinic end groups was isolated from the reaction mixture.

RESULTS AND DISCUSSION

Synthesis and Characterization of Dendrimers with Internal Amino Groups

*(a) Formation of the hexa-amine dendritic core **5***

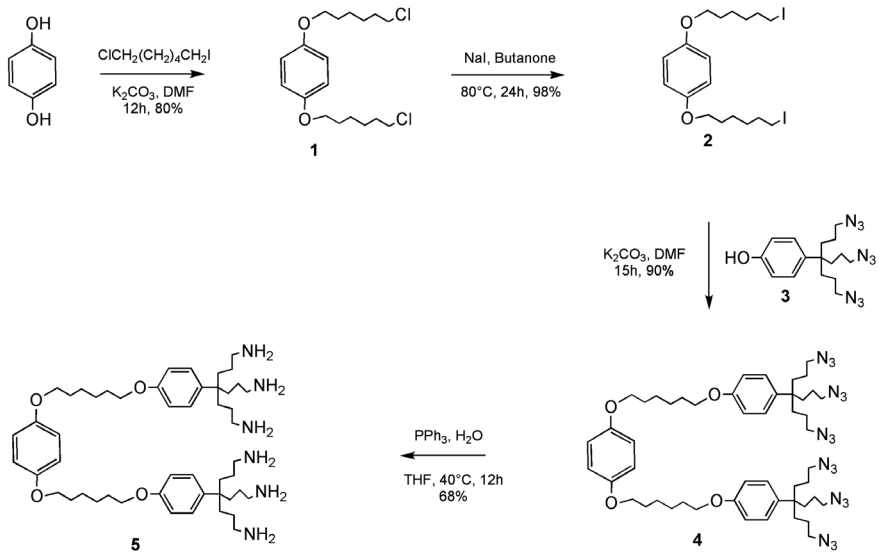
The synthetic strategy used to prepare the hexaamine dendritic core **5** is summarized in Scheme 1.

The reaction of 1-chloro-6-iodohexane (in excess) with hydroquinone leads to the corresponding chloro compound **1**. The latter in the presence of sodium iodide in butanone gives the iodo compound **2** in 98% yield. The hexa-azido compound **4** was then prepared in 90% yield by the coupling reaction of the tri-azido dendron **3**,[12] with the iodo compound **2**. The reaction was easily monitored in the ^{1}H NMR spectrum by the complete disappearance of the triplet at δ = 3.19 ppm, assigned to the CH_2I groups, and the appearance of a new triplet at δ = 3.91 ppm, attributed to the CH_2O groups. The synthesis of the hexa-amine dendritic core **5** was achieved by the reduction of the azido compound **4** with PPh_3 in the presence of water. The dendritic core **5** was obtained as a white solid in 68%. The complete disappearance of the triplet at δ = 3.22 ppm, assigned to the CH_2N_3 groups, and the appearance of a new triplet at δ = 2.56 ppm, attributed to the CH_2NH_2 groups in the ^{1}H NMR spectrum, as well as elemental analysis and the presence of a molecular peak in the MALDI-TOF mass spectrum (m/z: 834 $[M+H]^+$), clearly confirm the formation of the hexa-amine compound **5**.

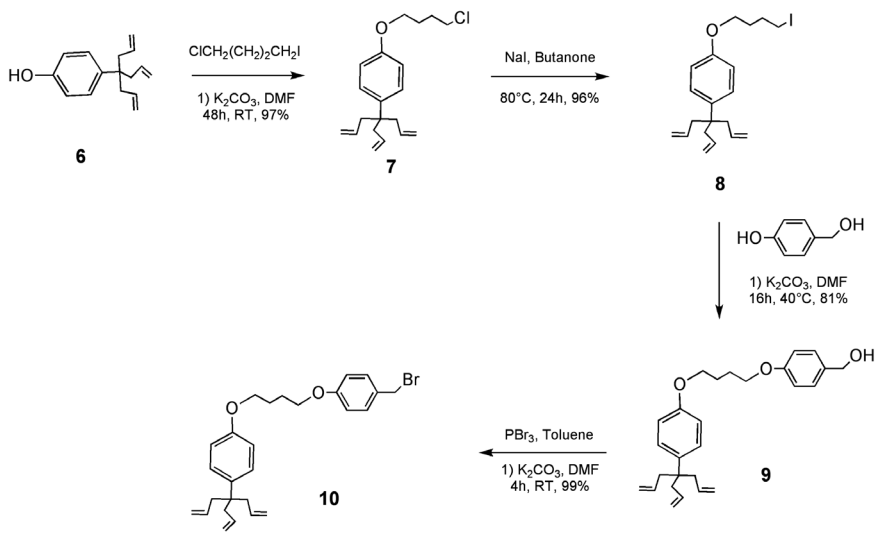
(b) Formation of the 36-armed dendrimers bearing 6-internal amino groups.

36-armed dendrimers bearing 6-internal amino groups have been successfully prepared in two steps. The first step involves the formation of benzylbromide dendrons, as summarized in Scheme 2 and Scheme 3, for allyl-terminated dendron **10** and methylphenyl-terminated dendron **16**, respectively. In the second step, the dendrons were then allowed to react with the hexamine dendritic core **5**, to give 36-armed dendrimers bearing 6-internal amino groups, as described in Scheme **4**. The dendron **10** was prepared from known tri-allylmethyl phenol **6**[13] (Scheme 2).

The alkylation of compound **6** with 1-chloro-4-iodobutane at room temperature, in the presence of K_2CO_3, led to the chlorobutane triallyl dendron **7** in 97% yield after chromatographic purification. The Cl/I exchange, by reaction of **7** with NaI in refluxing butanone, gives the corresponding iodoalkyl compound **8** in 96% yield. The reaction was monitored in the ^{1}H NMR spectrum by the disappearance of the triplet at δ = 3.57 ppm, assigned to the CH_2Cl group, and the appearance of a new triplet at δ = 3.27 ppm was attributed to the CH_2I group. In order to avoid the dehydrohalogenation reaction often observed during syntheses of dendrimers with halogenoalkyl, the iodoalkyl dendron **8** was functionalized at the focal point with $HOCH_2$-*p*-C_6H_4OH, in the presence of K_2CO_3. The bromation of the obtained benzyl alcohol dendron **9** with PBr_3 affords the *para*-substituted benzylbromide tri-allyl dendron **10** quantitatively. The synthesis of the benzyl bromide tri-methylphenyl dendron **16**

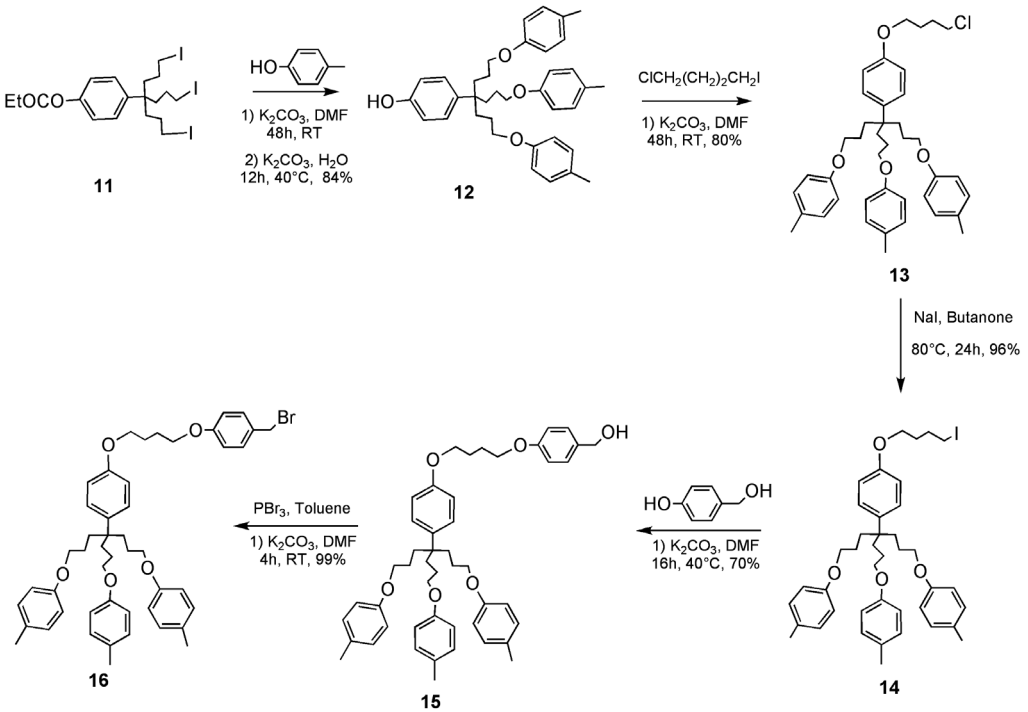


Scheme 1. Synthesis of the hexa-amine dendritic core **5**.

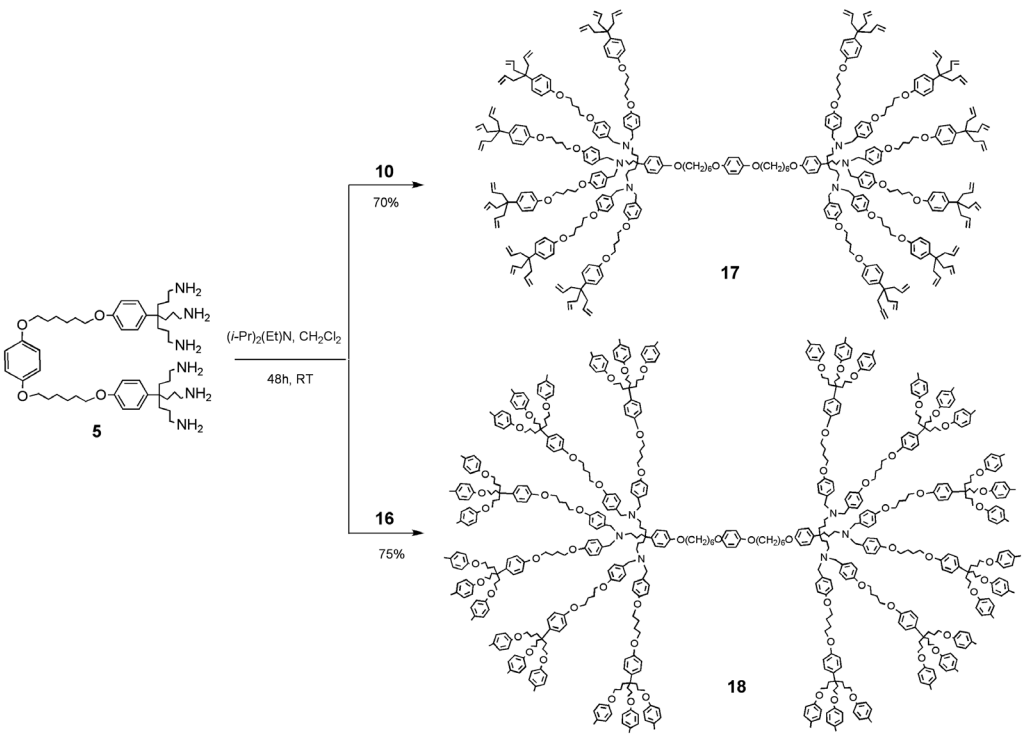


Scheme 2. Synthesis of the benzylbromide tri-allyl dendron **10**.

is summarized in Scheme 3, starting from the protected tri-iodo dendron **11**.[14] The later was allowed to react with *p*-cresol (in excess) in DMF in the presence of K_2CO_3 to give the tri-methylphenyl phenol dendron **12** in 84% yield. The reaction was monitored in the ^{1}H NMR spectrum by the complete disappearance of the triplet at δ = 3.23 ppm, assigned to the CH_2I groups, and the appearance of a new triplet at δ = 3.84 ppm, was assigned to



Scheme 3. Synthesis of the benzylbromide tri-methylphenyl dendron **16**.



Scheme 4. Synthesis of the 36-armed dendrimers **17** and **18**.

the CH_2O groups. The coupling reaction of **12** with two equivalent of 1-chloro-4-iodobutane at room temperature led to the chloro compound **13** in 80% yield. The corresponding iodobutyl derivative **14** was obtained in 96% yield from **13**, by Cl/I exchange reaction with NaI in butanone. The reaction of $HOCH_2$-*p*-C_6H_4OH with **14** and K_2CO_3 led to the benzyl alcohol **15**, which was allowed to react with PBr_3, to afford the *para*-substituted benzylbromide dendron **16** quantitatively.

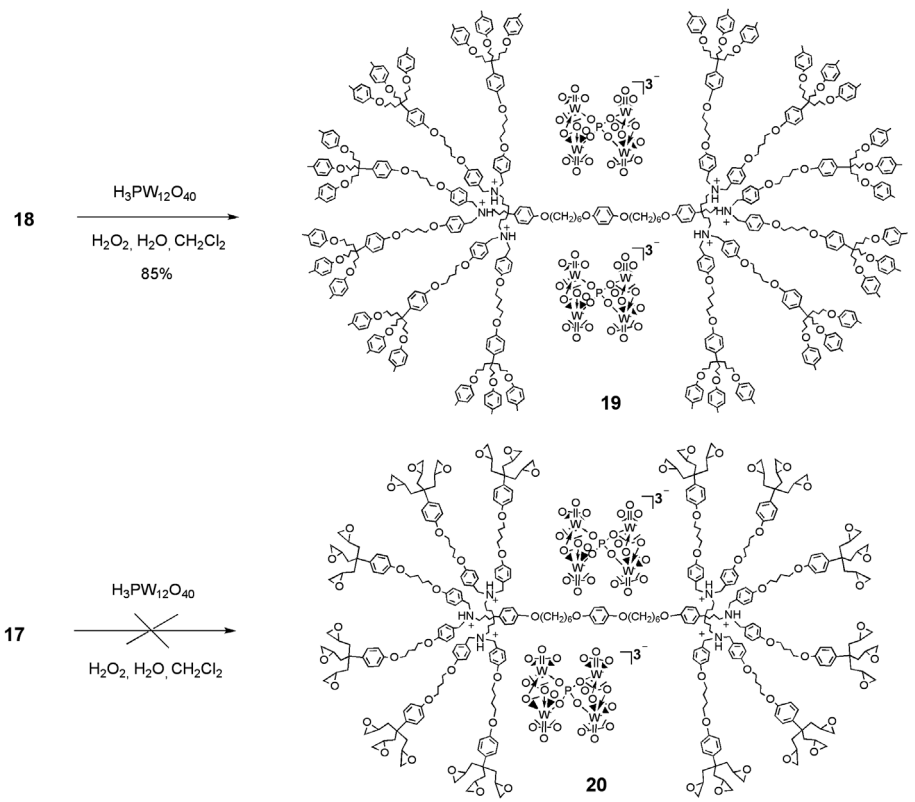
The second step in the synthesis of the 36-armed dendrimers involved the benzylation of the hexa-amino dendritic core **5** with dendron **10** and **16** respectively, as summarized in Scheme 4.

The reaction of hexa-amine dendritic core **5** with the benzylbromide tri-allyl dendron **10** and the benzylbromide tri-methylphenyl dendron **16**, respectively (3 equiv/amino group), leads to the corresponding 36-armed dendrimers **17** and **18** in 70 and 75% yield, respectively. The quaternarization of the amino group was not obtained. The molecular peak of the 36-allyl-terminated amino dendrimer **17** was observed in its MALDI-TOF mass spectrum (*m*/*z*: 5494.16 [M]+). The NMR characterization data of dendrimers **17** and **18** as well as their elemental analyses are consistent with the proposed structure (see Experimental section).

Electrostatic Encapsulation of POMs into Amino Dendrimers

The amino dendrimers **17** and **18** were used as hosts to encapsulate the Venturello tri-anionic species $[PO_4\{WO(O_2)_2\}_4]^{3-}$,[15] prepared by decomposition of the heteropoly acid $H_3PW_{12}O_{40}$ in the presence of H_2O_2.[16] The addition of amino dendrimer **18** in the above-mentioned acidic reaction medium leads to its corresponding organic–inorganic hybrid **19**, obtained by the electrostatic incorporation of POM units in the dendritic structure. The reaction of dendrimer **18** with an aqueous solution of heteropoly acid $H_3PW_{12}O_{40}$ and H_2O_2 yielded the 36-armed methylphenyl-terminated dendrimer **19**, which has two tri-anionic POM $[PO_4\{WO(O_2)_2\}_4]^{3-}$ encapsulated into its structure (Scheme 5). In this reaction, the internal dendritic amino groups are protonated in situ leading to the hexa-ammonium dendrimer, which reacts with the polyoxometalate, and incorporates two $PO_4\{WO(O_2)_2\}_4]^{3-}$ species into its structure. The dendritic chlorinated ammonium salt was also prepared by the protonation of amino groups of dendrimer **18** with dilute aqueous HCl, and used to incorporate the tri-anionic POM species into its structure by anion exchange between $3Cl^-$ and $PO_4\{WO(O_2)_2\}_4]^{3-}$, to yield compound **19**.

After the electrostatic encapsulation of POMs, the den-



Scheme 5. Synthesis of the 36-armed dendrimer **19** encapsulating two POM units.

dritic POM hybrid obtained was isolated from the organic layer. This result indicated that the hydrophilic environment of POMs had been successfully modified by the hydrophobic organic structure of the dendrimer. Only one signal was obtained in the ^{31}P NMR for **19** ($\delta = 3.46$ ppm). This value is comparable to those obtained for the Arquad salt of the $[PO_4\{WO(O_2)_2\}_4]^{3-}$ species ($\delta = 3.12$ ppm; Arquad = $[n\text{-}C_{18}H_{37}(75\%) + n\text{-}C_{16}H_{33}(25\%)]_2N(CH_3)_2]$), as well as dendritic POM hybrids previously reported by our group with the same POM species.[9d,f–h] The FTIR data also agreed with the literature values (see Experimental section). From these data, as well as the elemental analysis, we can conclude that compound **19** contains two tri-anionic $[PO_4\{WO(O_2)_2\}_4]^{3-}$ species incorporated in its dendritic structure. Moreover, the comparison of the ^{1}H NMR spectra of the free amino dendrimer **18** to that of its corresponding dendritic POM hybrid **19** shows the complete disappearance of the signal at $\delta = 3.35$ ppm assigned to CH_2N groups in **18**, and the appearance of a new broad singlet at $\delta = 4.20$ ppm attributed to the ammonium groups in **19**. The stability of the POM species, as well as the data described above, are consistent with the proposed structure for compound **19**. We have attempted to incorporate $[PO_4\{WO(O_2)_2\}_4]^{3-}$ into the 36-allyl-terminated amino dendrimer **17** by electrostatic bonding. Unfortunately, all our attempts to access the 36-epoxy-terminated dendrimer **20** (Scheme 5) failed because of the slow epoxidation of the 36 olefinic terminals in compound **17**. Lengthening the reaction time to 6 h led to the decomposition of tri-anionic POMs, leading to a dendrimer bearing a mixture of epoxi- and olefinic end groups, as observed in the NMR spectra. This result is a contrast to our previous work, in which the synthesis of POM core dendrimers using allyl-terminated ammonium dendrons and the tri-anionic POM $[PO_4\{WO(O_2)_2\}_4]^{3-}$ led to the corresponding epoxy-terminated POM-cored dendrimer. The trianionic species catalyzed the epoxidation of olefinic termini in a one-pot reaction and became the anionic core of ammonium dendrons. The result obtained in this paper with compound **17** is probably due to the high number of peripheral olefinic end groups to epoxidize by the POM species, which prevents their efficient incorporation into the dendrimer. To obtain a correct framework in which POMs are incorporated into dendrimers, amino dendrimers with non-oxidizable end groups are required. These results show the influence of the dendritic counter cation in the POM properties.

*Catalytic Oxidation Tests by Using the Dendritic POMs Hybrid **19***

The catalytic performance of **19** in the epoxidation of cyclooctene was accomplished by vigorous stirring of an aqueous/$CDCl_3$ biphasic mixture containing 250 equiv of cyclooctene, 800 equiv of hydrogen peroxide (35%), and 0.4 mol% of the catalyst, at 35 °C. The reaction kinetics was monitored over time by plotting the ratio between the intensity of the disappearing ^{1}H NMR signal of cyclooctene at 5.6 ppm vs. TMS and the rising peak of the epoxide at 2.9 ppm. Compound **19** oxidized cyclooctene with a quantitative conversion after 3 h, within the limits of ^{1}H NMR detection. The results obtained with POM-encapsulated dendrimer **19** in the oxidation of cyclooctene vs. 27-armed POM-cored dendrimers[9g] reveal that POM-encapsulated dendrimer **19** is more active. In our previous work, in similar reaction conditions, we have reported that 27-armed POM-cored dendrimers oxidized cyclooctene with 100% conversion after 5 h (see ref 9g for details) vs. 3 h for **19**. The relationship between the dendritic structure and the catalyst properties is complex, and the question as to what is responsible for this difference in activity between the three series of dendrimers is not easy to answer. Previously, we have found that POM-cored dendrimers (bearing only one POM unit) are more stable and highly effective catalysts in oxidation reactions than their counterparts bearing many POM units at their periphery. The results described here indicate that the microenvironment of the catalytic species in dendritic catalysts largely determines their properties.

CONCLUSION

The synthesis and characterization of two 36-armed dendrimers that bear six internal amino groups has been described. These compounds have been used to incorporate POMs into the dendrimer by ionic bonding in an acidic medium. The results obtained in the epoxidation of cyclooctene with the POM-encapsulated dendrimer hybrid reveal that, under the protection of the dendritic wedge, the catalytic properties of POMs are retained. Since structures of POMs are very sensitive to the environmental pH range, their incorporation into dendrimers retained their properties by protecting them against external acidic or basic attacks. POMs encapsulated in dendrimers represent very promising and multifunctional systems, since, on the one hand, they can be used as dual encapsulation and release systems; on the other hand, they consist of dendrimers, which are also important for a variety of applications (recovery, recyclability, etc); and finally they contain polyoxometalates that present other interesting properties (including catalysis). Interestingly, the encapsulation of POMs into the dendrimer increases their stability without affecting significantly their catalytic properties. The catalytic oxidation of more challenging substrates as well as catalyst recovery is being investigated in our group.

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