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Syntheses of polyamine- and polynitrile dendrimers from a nona-arm core up to 144-nitrile using Vögtle's iteration

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Summary — The Michael reaction of acrylonitrile applied to a nonol core **3** yielded a nona-nitrile **4** which was used as the starting point for an iterative divergent synthesis of polynitrile and polyamine dendrimers using the seminal Vögtle strategy. The nona-nitrile **4** was reduced to the nona-amine **5** using BH_3·THF in refluxing THF or BH_3·Me_2S in THF at 20 °C followed by methanolysis of the borane adduct. The second iterative step was unchanged and consisted in the Michael reaction of the nona-amine **5** with acrylonitrile to give the octadeca-nitrile **7**. This iterative sequence was applied up to the 144-CN dendrimer.

poly-amine dendrimer / polynitrile / nitrile reduction

Résumé — Synthèses de dendrimères polyamines et polynitriles à partir d'un cœur nonabranché jusqu'à 144 nitriles en utilisant l'itération de Vögtle. La réaction de Michaël de l'acrylonitrile appliquée au cœur nonol **3** a conduit à un nona-nitrile **4** utilisé comme point de départ pour la synthèse itérative divergente de dendrimères polynitriles et polyamines selon la méthode originale de Vögtle. Le nona-nitrile **4** a été réduit en nona-amine **5** par BH_3·THF à reflux ou BH_3·Me_2S dans le THF à 20 °C, puis l'adduit amine-borane a été méthanolysé. La seconde étape de l'itération n'a pas été modifiée et a consisté à faire réagir la nona-amine **5** avec l'acrylonitrile suivant une réaction de Michaël pour donner l'octadéca-nitrile **7**. Cette synthèse itérative a été poursuivie jusqu'au dendrimère 144-CN.

dendrimère polyamine / polynitrile / reduction de nitrile

Introduction

Nanomolecules such as dendrimers which can reach sizes of biomolecules are forming a relatively new part of supramolecular chemistry [1, 2]. Yet, in 1998, the 20th anniversary of the publication of the first dendritic iteration by Vögtle [3] is being celebrated. Since that time, the field of dendrimer chemistry has grown considerably [4–8] and promised applications in materials science [4, 7] and molecular biology [8]. The specific topology of dendrimers had led to the finding of dendritic effects in molecular recognition [9] and redox catalysis has been applied to catalysts branched to the termini of nanoscale stars without significant loss of catalytic activity [10].

The strategy by Vögtle consisted in the Michael reaction of a diamine with acrylonitrile producing a tetra-nitrile followed by the reduction of the nitrile to the tetra-amine (scheme 1). This latter step has recently been improved by Vögtle's group [11] and others [12, 13]. The maximum number of branches has remained around hundred and defects were observed by ^{13}C NMR. It was believed that these defects were due to steric saturation of the periphery of the dendrimer due to the high number of branches. In delineating our synthetic scheme, we reasoned that a relatively large core with many branches could allow us to rapidly reach a high number of branches. The $CpFe^+$-induced polyallylation of polymethylbenzene derivatives is a clean, selective and powerful way to reach a relatively large number of branches in one reaction [14].

For instance, the nona-allylation of (CpFe mesitylene)$^+PF_6^-$ **1** gives the nona-allyl compound **2**, and regiospecific hydroboration using a large borane followed by oxidation using H_2O_2 cleanly gives the nonol **3** [15] (scheme 2). This known compound could then serve as a starting material for dendritic syntheses. The first step consists in lengthening the branches to provide more space for the development of the dendritic generations. This was attempted using the Michael addition of acrylonitrile to the alcohol branches which had already been used by Newkome in the case of a tripod

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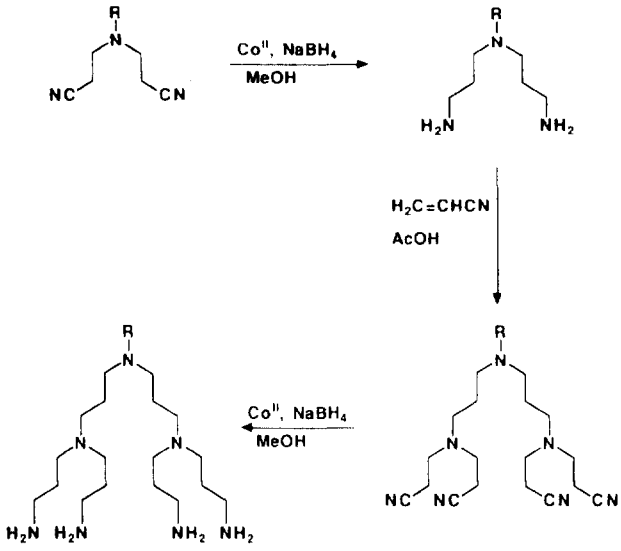
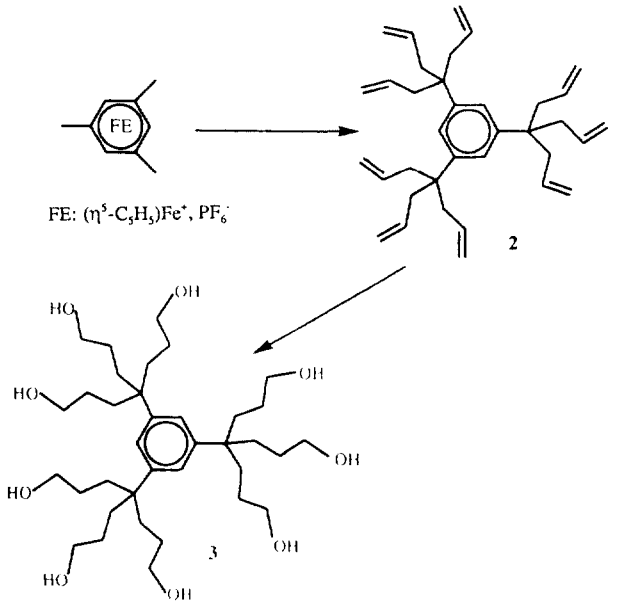


Scheme 1



Scheme 2

[16]. We were interested in the syntheses of polyamine dendrimers to make polyamidometallocene dendrimers [9, 17] for molecular recognition whose preliminary results have been communicated [9, 18]. Tomalia [5, 19], Caminade et Majoral [6, 20], Labarre [21], Regen [22], Fréchet [23], Shinkai [24] and Kim [25] have also published syntheses of dendrimers with terminal amine or hydrazine groups using other synthetic schemes.

Results and discussion

The Michael reaction of acrylonitrile with the nonol ***3*** *and nitrile reduction*

This Michael reaction was carried out, as reported by Newkome [16] in a tripodal series, in dioxane with 10% KOH and the nona-nitrile obtained (eq 1) was purified by column chromatography and characterized by ^1H and ^{13}C NMR, its molecular peak in the mass spectrum and elemental analysis.

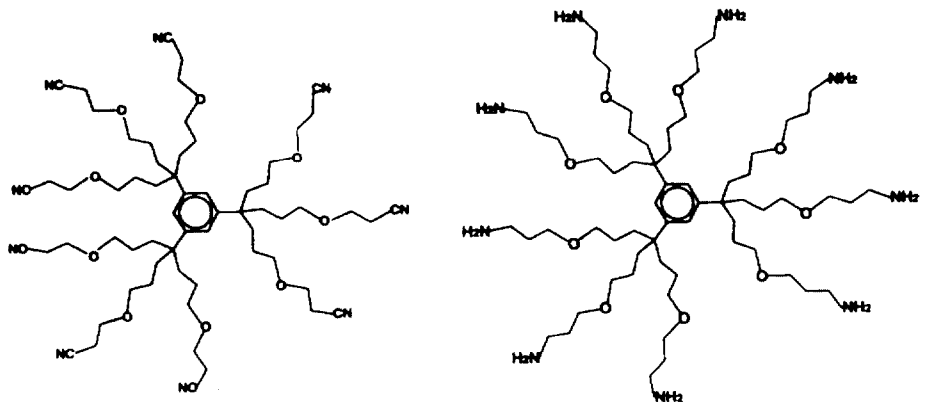
$$\text{dendri-OH} \xrightarrow[\substack{\text{dioxane}\\ \text{KOH, 10\%}}]{CH_2CH{=}CN} \text{dendri-OCH}_2\text{CH}_2\text{CN} \qquad (1)$$

Nitrile reduction

Attempted reduction of the nona-nitrile **4** using Raney Ni and elevated temperature and pressure previously reported [12, 13] was repeated several times on the same sample to reach completion, but only up to 90% reduction could be obtained. Under more drastic conditions, the material was destroyed and gave weak, paramagnetic NMR signals, possibly due to the incorporation of magnetic metal species into the dendrimer. Obviously, heterogeneous catalysis depends very much on the state of the metal particles which are used (pretreatment, rate of stirring, etc). It is unfortunate that such a reaction system is just too slow under ordinary laboratory conditions. We anticipated that these problems would become even worse as generation numbers would increase, and switched to other solutions. $LiAlH_4$ and other classic anionic hydrides led to C–O cleavage, however. Finally, reduction was found successful using either excess BH_3·THF at reflux [26] or excess BH_3·Me_2S in THF [27] at 20 °C (eq 2, fig 1). This second method may prevent retro-Michael processes.

$$\text{ROCH}_2\text{CH}_2\text{CN} \xrightarrow[\text{THF, 20 °C}]{\text{excess } BH_3\cdot Me_2S} \text{ROCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \qquad (2)$$

Hydrolysis of the amine-borane adduct is not convenient because it is very difficult to separate **5** from $B(OH)_3$. Methanolysis is much more convenient as $B(OMe)_3$ is easily removed. The nona-amine **5** is well soluble in water and methanol and less soluble in THF or DMSO. It was characterized by ^1H and ^{13}C NMR in D_2O showing that reduction was complete. In ^1H NMR, the triplet at $\delta = 2.55$ ppm due to the CH_2 near the cyano group disappears whereas a new triplet appears at $\delta = 2.74$ ppm due to the CH_2 near the amino group. The molecular peak at 1156 is observed in the MALDI-TOF mass spectrum. When the methanolysis is not complete, additional peaks separated by 72 units above the molecular peak appear. They correspond to $-NHB(OCH_3)$ branches which have not been methanolized. The elemental analyses are not correct and show the presence of large amounts of water, as the polyamines are very hygroscopic. Protonation of the nona-amine by addition of an aqueous solution of HCl or HPF_6 to a methanolic solution of the nona-amine gives the nona-ammonium salts **6** as white powders after removing the solvents under vacuum (eq 3). These salts are less hygroscopic than the nona-amine, easier to handle and can be more conveniently and directly used in reactions with acyl chlorides to synthesize the polyamides [9, 17]. They were also characterized by NMR in D_2O.



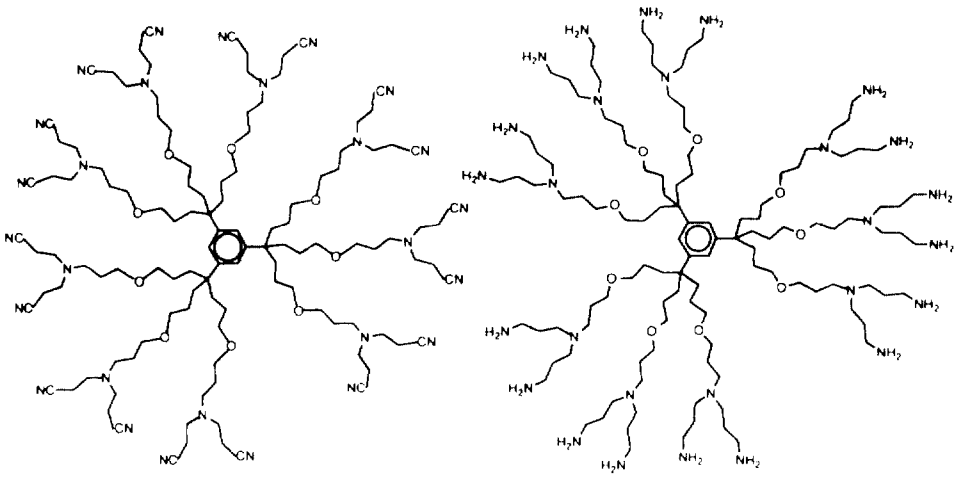
9-CN

4

9-NH_2

5

Fig 1



18-CN

7

18-NH_2

8

Fig 2

$$\underset{\mathbf{5}}{\text{9-NH}_2} \xrightarrow{\text{aqueous HCl or HPF}_6} \underset{\mathbf{6}}{\text{9-NR}_4^+\ X^-} \qquad X = \text{Cl or } PF_6 \qquad (3)$$

Iteration

The reaction of 9-NH_2 with acrylonitrile in water at 80 °C gives 18-CN. In ^{1}H NMR, the α protons of the tertiary amine can be distinguished. The 18 core protons give a broad triplet at δ = 2.58 ppm and the 36 acrylonitrile α protons give a broad triplet at δ = 2.81 ppm. The molecular peak in the MALDI TOF mass spectrum is found at m/z = 2220 for MAg^+ and 2135 for MNa^+. Reduction of 18-CN was carried out as indicated above for the reduction of 9-CN. The iteration chemistry consisting in the sequence of these two reactions was carried out similarly up to the 144-nitrile (fig 2, scheme 3).

Reaction times were not optimized, but arbitrarily prolonged as the generation number increased. The polynitrile dendrimers are viscous oils, well soluble in organic solvents such as THF, dichloromethane and chloroform and were purified by chromatography at each generation including 144-CN. They were characterized by ^{1}H and ^{13}C NMR and infrared spectroscopy (no retro-Michael) and by correct elemental analysis. On the other hand, the polyamines become less and less soluble as the generation number increases, which makes their characterization by ^{13}C NMR more and more difficult. Finally, this decrease of solubility from one generation to the next one, in particular from 36-NH_2 to 72-NH_2 and the low solubility of 72-NH_2 led us to the conclusion that 144-NH_2 would be completely insoluble and impossible to characterize. The NMR data

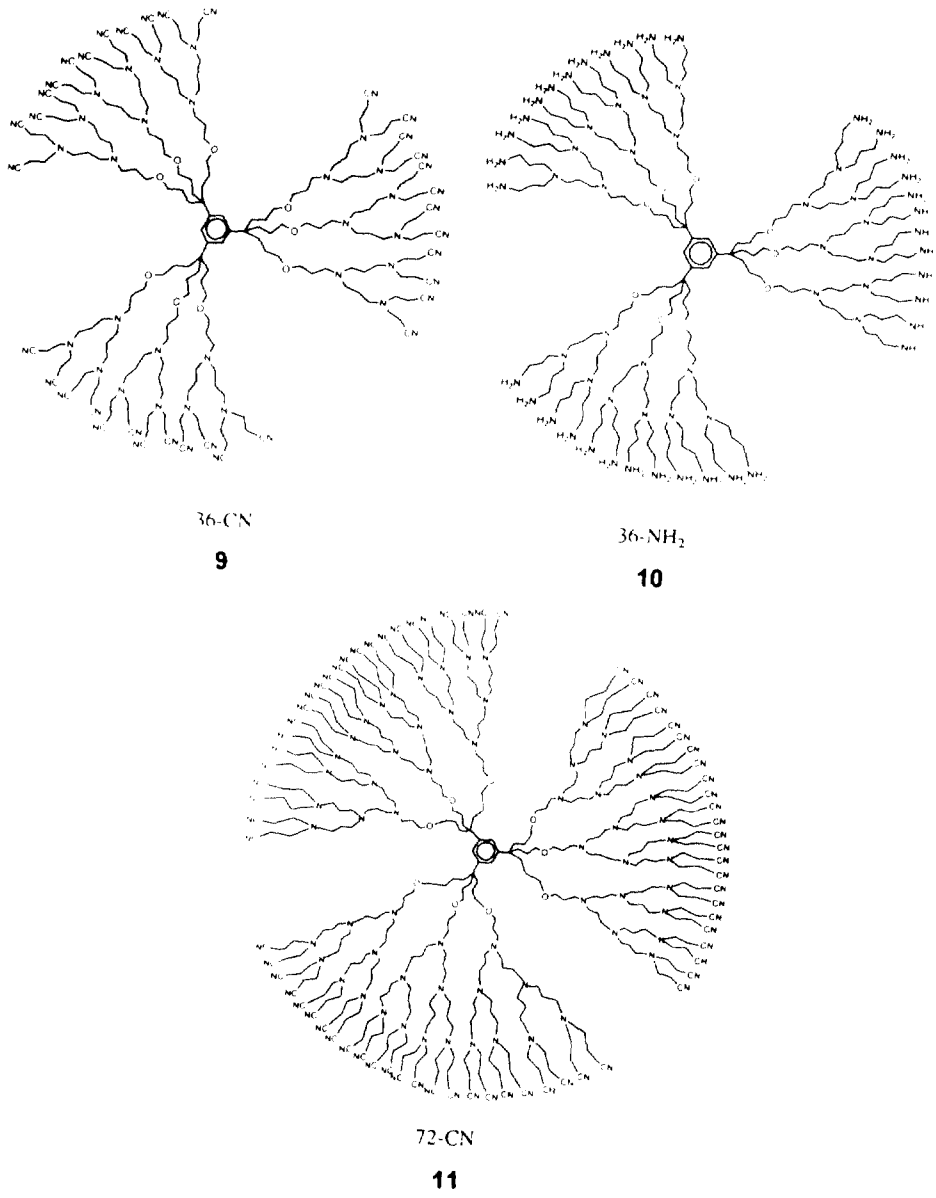
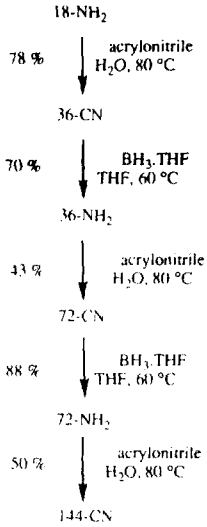


Fig 3



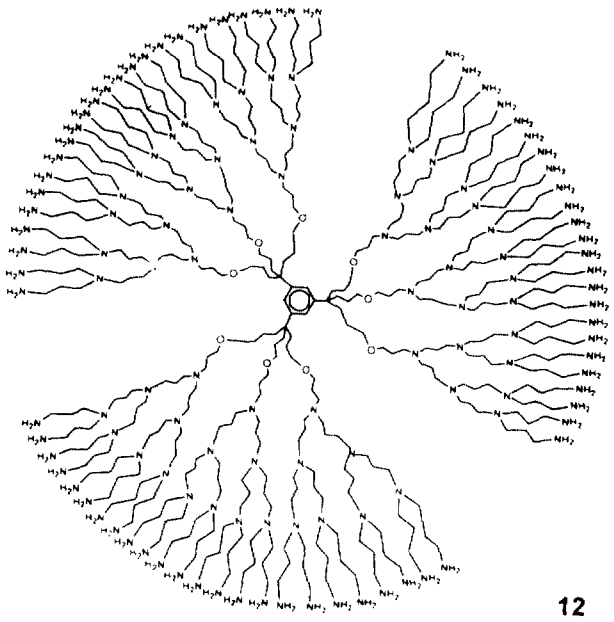
Scheme 3

always showed complete reduction up to 72-NH_2, however. Thus, purification was effected essentially at the polynitrile level for each generation (figs 3 and 4).

Concluding remarks

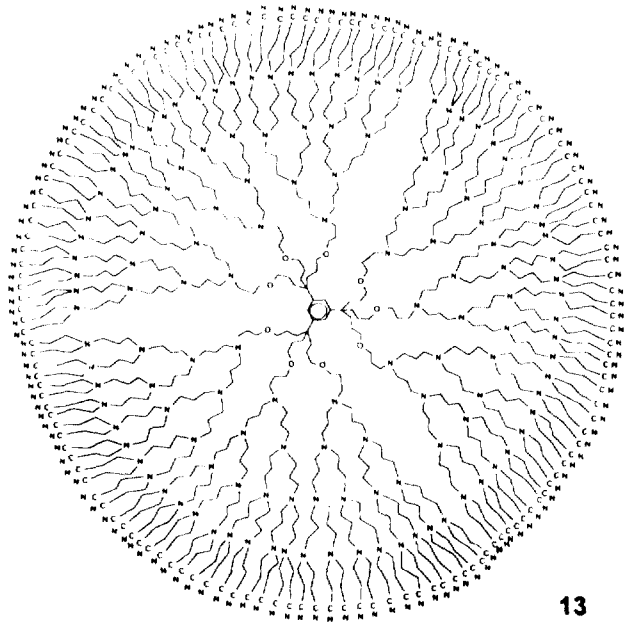
• The $CpFe^+$-induced nona-allylation of mesitylene, followed by regiospecific hydroboration and oxidation of the nona-borane to the nonol (scheme 1) provided an easy access to a large muti-arm core for an efficient dendritic construction. The lengthening of the arms by Michael reaction of the nonol with acrylonitrile was a key factor to bring more space around the branches for the dendritic construction. Indeed, analogous synthesis performed after the present work without this lengthening indicated that the 18-amine obtained in that way was insoluble [28].

• Using a modification of the Vögtle' strategy concerning the nitrile reduction step, dendrimers with up



12

72-NH_2



13

144-CN

Fig 4

to 144-nitrile branches could be synthesized, which is the largest number of branches obtained using this strategy. A key step is the reduction of the nitriles. Mass spectral studies showed that retro-Michael reactions occurred in more or less important amounts, depending on the nature of the hydride (anionic hydrides are the worst) and reaction conditions used. With BH_3·THF, these side reactions were not detectable by ^{13}C NMR, although mass spectra showed minite cleavage of the O–C bond according to this retro-Michael reaction. Finally, these side reactions could be suppressed by lowering the temperature to 20 °C in the case of BH_3·Me_2S.

The dendrimers were purified by chromatography and analytically characterized at the polynitrile level.

• Although syntheses of higher dendrimers has not been attempted, it is likely that we are very close to the limit because the polyamines are more and more insoluble as the generation increases. The 72-NH_2 dendrimers had little solubility in water (^1H and ^{13}C NMR could still be recorded, but with great difficulty for ^{13}C), and it is likely that the 144-NH_2 dendrimer would have been too insoluble to carry out characterization and further chemistry. Thus the lengthening of the arm using the acrylonitrile fragment pushed the limit of insolubility from 18-NH_2 to 144-NH_2. It is probable that the insolubility at the limit is due to a combination of steric saturation at the periphery [29] and H-bonding of the terminal amine groups.

• This series of dendrimers has been useful for synthesizing polyamidometallocene dendrimers which proved very efficient as sensors with dendritic effects for molecular recognition.

Experimental section

General data

FeCp(mesitylene) (PF_6) **1** [30] and the nona-allyl **2** and nonol **3** [15] precursors were synthesized according to published procedures. Before use, the solvents were purified as follows: pentane, ether and dimethoxyethane were dried over sodium with sodium benzophenone ketyl as the indicator; methanol was distilled over magnesium wires; dichloromethane and dimethylformamide were dried over calcium hydride and stored under nitrogen. All reactions were performed under a nitrogen atmosphere. All the other reagents were purchased commercially as reagent-grade chemicals and used without further purification. Column chromatography was performed using 60 mesh silica gel or activated alumina II–III. ^1H and ^{13}C NMR spectra were recorded on Bruker WM-200, AC-250 or DPX-400 spectrometers. MALDI-TOF mass spectral studies were performed on a Voyager Elite time-of-flight mass spectrometer (Perseptive Biosystems, Framingham, USA). One microliter of a solution in acetone of the matrix (2,5-dihydroxybenzoic acid) and analyte at concentrations of 0.1 M and 0.1 mM respectively was deposited on the target for MALDI analysis.

Numbering of the C (and attached H) atoms throughout the NMR data: unsubstituted aromatic C^1H; substituted aromatic C^2; Ph-C^3-C^4-C^5-C^6-OC^7-C^8-C^9-N-C^{10}-C^{11}-C^{12}-N-C^{13}-C^{14}-C^{15}-N-C^{16}-C^{17}-C^{18}-N-C^{19}-C^{20}-C^{21}; s: singlet; d: doublet; t: triplet; q: quintuplet; m: broad, unresolved multiplet.

9-CN, **4**

In a Schlenk tube containing 9-OH (1 g, 1.56 mmol), KOH (9 mg, 0,15 mmol), dioxane (0.7 mL) and, dropwise, acrylonitrile (0.57 g, 10.8 mmol, 1.1 equiv per branch) were added. The reaction mixture was left for 2 days at room temperature, then 100 mL dichloromethane was added, the organic phase was washed with water, dried over sodium sulfate and the solvent was removed under vacuum. The beige oil obtained was chromatographed over a column of neutral activated alumina using dichloromethane.

Anal calc for $C_{63}H_{93}O_9N_9$ (1120.50 g·mol^{-1}): C 68.47; H 8.38; found: C 68.82; H 8.23.

Mass spectrum (MALDI TOF): m/z: 1144 (MNa^+) and 1160 (MK^+).

^{1}H NMR ($CDCl_3$, δ ppm): 1.27 (d, CH_2, H^{4-5}, 36H); 2.52 (t, CH_2CN, H^8, 18H); 3.34 (t, CH_2O, H^7, 18H); 6.99 (s, CH, H^1, 3H).

^{13}C NMR ($CDCl_3$, δ ppm, 62.9 MHz): 16.94 (CH_2, C^8); 23.94 (CH_2, C^5); 33.57 (CH_2, C^4); 42.74 (Cq, C^3); 65.16 (CH_2, C^7); 71.77 (CH_2, C^6); 118.30 (CN, C^9); 122.01 (CH, C^1); 145.62 (Cq, C^2).

IR (NaCl plates): 2 910 cm^{-1}: $\nu_{as}CH_2$; 2 840 cm^{-1}: ν_sCH_2; 2 240 cm^{-1}: νCN (nitrile); 1 600 cm^{-1}: νC=C (Ar); 1 465 cm^{-1}: νCH_2; 1 100 cm^{-1}: νCO (ether).

Polynitriles: 18-CN **7**, *36-CN* **9**, *72-CN* **11** *and 144-CN* **13**

• *General procedure*

To the polyamine in 15 mL water, acrylonitrile (4 equiv per branch) was added. The reaction mixture was refluxed (80 °C) for a time which depended on the generation, then the solvent was removed under vacuum and 100 mL dichloromethane was added. The organic phase was washed with water, dried over sodium sulfate and the solvent was removed under vacuum. The crude oil was chromatographed over an alumina column (activity II–III) using an eluent whose nature depended on the generation number. The chromatographed light yellow oil was washed with pentane.

18-CN, **7** (1.24 g, 68%) was obtained from 9-NH_2, **6** (1 g, 0.865 mmol) and acrylonitrile (2 mL, 31.14 mmol). The reaction time was 12 h and the eluent was dichloromethane/methanol: 80:20.

Anal calc for $C_{117}H_{183}O_9N_{27}$, $6H_2O$ (2111.9 g mol^{-1}): C 63.30; H 8.85; found: C 63.14; H 8.50.

MALDI TOF mass spectrum: MNa^+: 2135.6; MH^+: 2113.6.

^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 1.28–1.63 (d, CH_2, H^{4-5}, 36H); 1.66 (t, CH_2, H^8, 18H); 2.47 (t, CH_2CN, H^{11}, 36H); 2.59 (t, CH_2N, H^9, 18H); 2.81 (t, CH_2N, H^{10}, 36H); 3.42 (tt, CH_2O, H^6, 18H); 3.66 (t, CH_2O, H^7, 18H); 6.98 (s, CH, H^1, 3H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ ppm: 17.04 (CH_2, C^{11}); 24.22 (CH_2, C^5); 27.67 (CH_2, C^8); 33.95 (C_H2, C^4); 42.78 (Cq, C^3); 49.69 (CH_2, C^{10}); 49.78 (CH_2, C^9); 67.82 (CH_2, C^7); 71.66 (CH_2, C^6); 118.92 (CN, C^{12}); 121.81 (CH, C^1); 145.61 (Cq, C^2).

IR (NaCl plates): 2 910 cm^{-1}: $\nu_{as}CH_2$; 2 840 cm^{-1}: ν_sCH_2; 2 240 cm^{-1}: νCN (nitrile); 1 600 cm^{-1}: νC=C (Ar); 1 465 cm^{-1}: νCH_2; 1 140 cm^{-1}: νCN (amine); 1 110 cm^{-1}: νCO (ether).

36-CN, **9** (0.73 g, 78%) was obtained from 18-NH_2, **8** (0.50 g, 0.229 mmol) and acrylonitrile (1.09 mL; 16.48 mmol). The reaction time was 72 h and the eluent was dichloromethane/methanol: 80:20.

Anal calc for $C_{225}H_{363}O_9N_{63}$ (4094.8 g mol^{-1}): C 64.94, H 8.80; found: C 64.97; H 8.70.

^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 1.23–1.60 (d, H^{4-5}, 36H); 1.61 (m, H^{8-11}, (18 + 36)H); 2.48 (t, H^{14}, 72H); 2.51 (m, $H^{9-10-12}$, (18 + 36 + 36)H); 2.82 (t, H^{13}, 72H); 3.36 (m, H^6, 18H); 3.50 (m, H^7, 18H); 7.01 (s, H^1, 3H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ ppm: 14.95 (CH_2, C^{14}); 24.47 (CH_2, C^5); 24.88 (CH_2, C^{11}); 26.98 (CH_2, C^8); 33.69 (CH_2, C^4); 42.90 (Cq, C^3) ; 49.55 (CH_2, C^{13}); 50.43 (CH_2, C^9); 51.36 (CH_2, C^{12}); 51.57 (CH_2, C^{10}); 68.85 (CH_2, C^7); 71.36 (CH_2, C^6); 119.03 (CN, C^{15}); 121.96 (CH, C^1); 145.82 (Cq, C^2).

IR (NaCl plates): 2 920 cm^{-1}: $\nu_{as}CH_2$; 2 860 cm^{-1}: ν_sCH_2; 2 250 cm^{-1}: νCN (nitrile); 1 600 cm^{-1}: νC=C (Ar).

72-CN, **11** (0.163 g, 43%) was obtained from 36-NH_2, **10** (0.200 g, 0.047 mmol) and acrylonitrile (0.29 mL, 6.79 mmol). The reaction time was 5 days and the eluent was dichloromethane/methanol: 20:80.

Anal calc for $C_{441}H_{723}O_9N_{135}$ (8060.6 g mol^{-1}): C 64.58; H 8.88; found: C 64.30; H 9.03.

^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 1.20–1.61 (d, CH_2, H^{4-5}, 36H); 1.54 (m, CH_2, $H^{8-11-14}$, (18 + 36 + 72)H); 2.43 (t, CH_2CN, H^{17}, 144H); 2.49 (m, CH_2N, $H^{9-10-12-13-15}$, (18 + 36 + 36 + 72 + 72)H); 2.78 (t, CH_2N, H^{16}, 144H); 3.31 (m, CH_2O, H^{6-7}, (18 + 18)H); 6.88 (s, CH, H^1, 3H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ ppm: 16.88 (CH_2, C^{17}); 24.30 (CH_2, C^{11}); 24.95 (CH_2, C^{14}); 24.47 (CH_2, C^5); 26.98 (CH_2, C^8); 33.69 (CH_2, C^4); 42.90 (Cq, C^3); 49.52 (CH_2, C^{16}); 51.37 (CH_2, C^{15}); 51.52 (CH_2, C^{13}); 51.58 (CH_2, C^9); 51.98 (CH_2, C^{10}); 52.17 (CH_2, C^{12}); 70.33 (CH_2, C^7); 73.15 (CH_2, C^6); 118.85 (Cq, CN, C^{18}); 121.29 (CH, C^1); 146.29 (Cq, C^2).

IR (NaCl plates): 2 940 cm^{-1}: $\nu_{as}CH_2$; 2 840 cm^{-1}: ν_sCH_2; 2 240 cm^{-1}: νCN(nitrile); 1 460 cm^{-1}: νCH_2.

144-CN, **13** (0.99 g, 50%) was obtained from 72-NH_2, **12** (0.10 g, 0.012 mmol) and acrylonitrile (0.15 mL, 3.45 mmol). The reaction time was 7 days and the eluent was methanol.

Anal calc for $C_{873}H_{2019}O_9N_{279}$, 1 equiv Na_2SO_4 (16572.5 g mol^{-1}): C 62.72; H 9.18; found: C 62.79; H 9.36.

^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 1.19–1.61 (d, CH_2, H^{4-5}, 36H); 1.54 (m, CH_2, $H^{8-11-14-17}$, (18 + 36 + 72 + 144)H); 2.43 (t, CH_2CN, H^{20}, 288H); 2.49 (m, CH_2N, $H^{9-10-12-13-15-16-18}$, (18 + 36 + 36 + 72 + 72 + 144 + 144)H); 2.78 (t, CH_2N, H^{19}, 288H); 3.31 (m, CH_2O, H^{6-7}, (18 + 18)H); 6.88 (s, CH, H^1, 3H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ ppm: 16.87 (CH_2, C^{20}); 22.56 (CH_2, C^{11}); 24.30 (CH_2, C^{11}); 24.39 (CH_2, C^{14}); 24.47 (CH_2, C^5); 25.02 (CH_2, C^{17}); 26.98 (CH_2, C^8); 29.22 (CH_2, C^{14}); 33.69 (CH_2, C^4); 42.90 (Cq, C^3); 49.55 (CH_2, C^{19}); 50.66 (CH_2, C^{12}); 51.18 (CH_2, C^{13}); 51.41 (CH_2, C^{18}); 51.58 (CH_2, C^9); 51.95 (CH_2, C^{16}); 51.98 (CH_2, C^{10}); 52.17 (CH_2, C^{12}); 52.22 (CH_2, C^{10}); 52.66 (CH_2, C^{15}); 70.33 (CH_2, C^7); 73.15 (CH_2, C^6); 118.80 (Cq, CN, C^{21}); 121.29 (CH, C^1); 146.29 (Cq, C^2).

IR (NaCl plates): 2 940 cm^{-1}: $\nu_{as}CH_2$; 2 840 cm^{-1}: ν_sCH_2; 2 240 cm^{-1}: νCN(nitrile); 1 460 cm^{-1}: νCH_2.

Polyamines: 9-NH_2 **5**, *18-NH_2* **8**, *36-NH_2* **10**, *72-NH_2* **12**

• *General procedure*

Method A: to a solution of polynitrile in 20 mL of freshly distilled THF under N_2, BH_3·THF (M in THF, 20 equiv per nitrile group) was added using a syringe and the reaction mixture was refluxed for 10 days. After cooling to 0 °C, methanol (75 mL) was added dropwise and the reaction mixture was stirred for one day at room temperature. After removing the volatiles under vacuum, a white solid was obtained. It was washed three times with ether and refluxed with ether. After filtration, a very hygroscopic white powder was obtained. The C and H elemental analyses gave experimental values which were much lower than theoretical ones, consistent with large water contents (also seen in the ^{1}H NMR spectra), but the structures were confirmed by the ^{1}H and ^{13}C NMR spectra and by elemental analyses of the polynitriles with twice more branches obtained from these amines.

Method B: to a solution of nona-nitrile (720 mg, 0.64 mmol) in 2.5 mL of fresly distilled THF under N_2, BH_3·Me_2S (2.9 mL, 10 M in THF, 29 mmol, 5 equiv per nitrile group) was added using a syringe and the reaction mixture was stirred at room temperature until gelification. Then, 2.9 mL of BH_3·Me_2S in THF were again added three times over one

day while stirring was continued. The reaction mixture was then methanolized as in method A and analogous treatment yielded 69% of **5** (510 mg, 0.44 mmol).

9-NH_2, ***5*** (1.053 g, 64%) was also obtained from 9-CN, **4** (1.5 g, 1.34 mmol) and BH_3·THF (120 mL, M in THF, 120 mmol) according to method A.

MALDI TOF mass spectrum: MH^+: 1157.65 (method B).

^{1}H NMR (D_2O, 250 MHz) δ ppm: 1.37–1.81 (d, H^{4-5}, 36H); 1.84 (q, H^8, 18H); 2.92 (t, H^9, 18H); 3.37 (t, H^7, 18H); 3.48 (t, H^6, 18H); 7.09 (s, H^1, 3H).

^{13}C NMR (D_2O, 62.9 MHz) δ ppm: 26.78 (CH_2, C^5); 30.39 (CH_2, C^8); 36.53 (CH_2, C^4); 40.76 (CH_2, C^9); 46.05 (Cq, C^3); 70.99 (CH_2, C^7); 75.05 (CH_2, C^6); 125.70 (CH, C^1); 149.47 (Cq, C^2).

18-NH_2, ***8*** (0.621 g, 60%) was obtained from 18-CN, **7** (1.00 g, 0.473 mmol) and BH_3·THF (85 mL, M in THF, 85 mmol).

^{1}H NMR (D_2O, 250 MHz) δ ppm: 1.32–1.8 (d, H^{4-5}, 36H); 1.76 (m, CH_2, H^{8-11}, (18 + 36)H); 2.56 (m, CH_2, H^{9-10}, (18 + 36)H); 2.96 (t, CH_2, H^{12}, 36H); 3.40 (m, CH_2 H^{6-7}, 36H); 6.92 (s, CH, H^1, 3H).

^{13}C NMR (D_2O, 62.9 MHz) δ ppm: 26.94 (CH_2, C_5); 27.71 (CH_2, C^{11}); 29.03 (CH_2, C^8); 36.96 (CH_2, C^4); 41.66 (CH_2, C^{12}); 46.12 (Cq, C^3); 53.73 (CH_2, C^9); 53.85 (CH_2, C^{10}); 72.30 (CH_2, C^7); 75.02 (CH_2, C^6); 125.26 (CH, C^1); 148.62 (Cq, C^2).

36-NH_2, ***10*** (0.362 g, 70%) was obtained from 36-CN, **9** (0.50 g, 0.122 mmol) and BH_3·THF (44 mL, M in THF, 44 mmol).

^{1}H NMR (D_2O, 250 MHz) δ ppm: 1.4–1.80 (m, H^{4-5}, 36H); 1.72 (m, $H^{14-11-8}$, (72 + 36 + 18)H); 2.56 (m, $H^{13-12-10-9}$, (72 + 36 + 36 + 18)H); 2.8 (m, H^{15}, 72H); 3.4 (m, H^{6-7}, 36H); 7.16 (s, H^1, 3H).

^{13}C NMR (D_2O, 62.9 MHz) δ ppm: 26.28 (CH_2, C^5); 27.16 (CH_2, C^8); 28.92 (CH_2, C^{11}); 29.80 (CH_2, C^{14}); 36.84 (CH_2, C^4); 42.12 (CH_2, C^{15}); 45.64 (Cq, C^3); 49.16 (CH_2, C^{10}); 53.56 (CH_2, C^{12}); 53.73 (CH_2, C^9); 54.44 (CH_2, C^{13}); 72.04 (CH_2, C^7); 74.68 (CH_2, C^6); 134.52 (CH, C^1); 149.48 (Cq, C^2).

72-NH_2, ***12*** (0.136 g, 88%) was obtained from 72-CN, **11** (0.15 g, 0.0186 mmol) and BH_3·THF (13.4 mL, M in THF, 13.4 mmol).

^{1}H NMR (D_2O, 250 MHz) δ ppm: 1.367–1.807 (m, H^{4-5}, 36H); 1.842 (q, H^8, 18H); 2.922 (t, H^9, 18H); 3.368 (t, H^7, 18H); 3.477 (t, H^6, 18H); 7.091 (s, H^2, 3H).

^{13}C NMR (D_2O, 62.9 MHz) δ ppm: 26.938 (CH_2, C^5); 27.708 (CH_2, C^{11}); 29.033 (CH_2, C^8); 36.963 (CH_2, C^4); 41.657 (CH_2, C^{12}); 46.117 (Cq, C^3); 53.732 (CH_2, C^9); 53.850 (CH_2, C^{10}); 72.302 (CH_2, C^7); 75.022 (CH_2, C^6); 125.698 (CH, C^1); 151.54 (Cq, C^2).

9-NH_3 $(PF_6)_9$, ***6***

To a colorless solution of 9-NH_2, **5** (200 mg, 0.17 mmol) in methanol, aqueous HPF_6 (0.59 mL, 4.67 mmol) was added at room temperature. The solution was left for 12 h at room temperature, then the solvents were removed under vacuum. The white residue was washed twice with ether, giving a white powder (0.336 g, 0.14 mmol; 80%) for $C_{63}H_{138}O_9N_9P_9P_{54}$ (2470.5 g mol^{-1}).

^{1}H NMR (D_2O, 200 MHz) δ ppm: 1.30 (m, 18H, H^5); 1.74 (m, 18H, H^4); 1.95 (m, 18H, H^8); 3.10 (t, J = 7.29 Hz, H^9); 3.47 (t, 18H, H^7); 3.58 (t, J = 6.03 Hz, 18H, H^6); 7.18 (s, 3H, H^1).

^{13}C NMR (D_2O, 200 MHz) δ ppm: 23.18 (C^5), 26.58 (C^8), 36.58 (C^4), 37.32 (C^9), 42.47 (C^3), 67.36 (C^7), 71.45 (C^6), 122.10 (C^1), 145.90 (C^2).

IR (KCl, cm^{-1}): 3 400 ν(N–H), 1 100 ν(O–C–O), 840 $\nu(PF_6^-)$.

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References

1 a) Lehn JM, *Supramolecular Chemistry. Concepts and Perspectives*, VCH, Weinheim, 1995
b) Lehn JM, *La Chimie Supramoléculaire. Concepts et Perspectives*, De Boerck Université, Paris, 1997

2 Vögtle F, *Supramolecular Chemistry*, 2nd ed, Wiley, Chichester, 1993

3 a) Bühlein E, Wehner W, Vögtle F, *Synthesis* (1978) 155
b) Vögtle F, Weber E, *Angew Chem Int Ed Engl* (1979) 18, 753

4 Newkome GR, Moorefield CN, Vögtle F, *Dendritic Molecules. Concepts, Syntheses and Perspectives*, VCH, Weinheim, 1996

5 a) Tomalia DA, Naylor NA, Goddart II WA, *Angew Chem Int Ed Engl* (1990) 29, 138
b) Tomalia DA, Dupont DA, *Top Curr Chem* (1993) 165, 193

6 a) Caminade AM, Majoral JP, *Main Group Chemistry News* (1995) 3, 14
b) Launay M, Caminade AM, Majoral JP, *J Am Chem Soc* (1995) 117, 3282

7 Ardoin N, Astruc D, *Bull Soc Chim Fr* (1995) 132, 875

8 Astruc D, *CR Acad Sci* (1996) 322, Série II b, 757

9 Valério C, Fillaut JL, Ruiz J, Guittard J, Blais JC, Astruc D, *J Am Chem Soc* (1997) 119, 2588

10 Rigaut S, Delville MH, Astruc D, *J Am Chem Soc* (1997) 119, 11132

11 Moors R, Vögtle F, *Chem Ber* (1993) 126, 2133

12 Wörner C, Mülhaupt R, *Angew Chem Int Ed Engl* (1993) 32, 1306

13 de Brabander-van der Berg EMM, Meijer EW, *Angew Chem Int Ed Engl* (1993) 32, 1308

14 For a review on $CpFe^+$-induced aromatic chemistry, see Astruc D, *Top Curr Chem* (1991) 160, 47

15 Moulines F, Djakovitch L, Boese R, Gloaguen B, Thiel W, Fillaut JL, Delville MH, Astruc D, *Angew Chem Int Ed Engl* (1993) 32, 1075

16 Newkome GR, Yao ZQ, Baker GR, Gupta VK, Russo PS, Saunders MJ, *J Am Chem Soc* (1986) 108, 849

17 Alonso E, Valério C, Ruiz J, Astruc D, *New J Chem* (1997) 21, 1139

18 Astruc D, Valério C, Fillaut JL, Ruiz J, Hamon JR, Varret F, *Supramolecular Magnetism*, Kahn O, Ed, NATO ASAI Series, Kluwer, Dordrecht, 1996, p 107

19 a) Tomalia DA, Baker H, Dewald J, Hall M, Kallos G, Martin S, Roeck J, Ryder J, Smith P, *Polymer J* (1985) 17, 117
b) Ottaviani MF, Bossmann S, Turro NJ, Tomalia DA, *J Am Chem Soc* (1994) 116, 661

20 Launay N, Galliot C, Caminade AM, Majoral J, *Bull Soc Chim Fr* (1995) 132, 1149

21 Sournies F, Crasnier F, Graffeuil M, Faucher JP, Lahana R, Labarre MC, Labarre JF, *Angew Chem Int Ed Engl* (1995) 34, 578

22 Watanabe S, Regen SL, *J Am Chem Soc* (1994) 116, 8855

23 Hawker CJ, Fréchet JMJ, *J Am Chem Soc* (1990) 112, 7638

24 James TD, Shinmori H, Takeuchi M, Shinkai S, *J Chem Soc Chem Commun* (1996) 705

25 Kim YH, *J Am Chem Soc* (1992) 114, 4947

26 Brown HC, Heim P, *J Am Chem Soc* (1964) 86, 3566

27 a) Brown HC, Choi Y, Narasimhan, *Synthesis* (1981) 605
b) Id, *J Org Chem* (1982) 47, 3153

28 a) Rigaut S, Delville MH, Astruc D, unpublished results
b) Rigaut S, Thesis, University Bordeaux I, 1997

29 De Gennes PG, Hervet H, *J Phys Lett* (1983) 44, L-351

30 a) Nesmeyanov AN, Vol'kenau NA, Bolesova IN, *Tetrahedron Lett* (1963) 25, 1725
b) Astruc D, Hamon JR, Lacoste M, Desbois MH, Román E, *Organometallic Synthesis*, King RB (Ed), Vol IV, 1988, p 172