Convergent and Divergent Noncovalent Synthesis of Metallodendrimers

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Received November 25, 1997. Revised Manuscript Received March 29, 1998

Abstract: A new building block is constructed with one pyridine and two kinetically inert complexed Pd(II) ions, for the controlled assembly of metallodendrimers following either a *convergent* or a *divergent* route. The double pincer ligand **8** was cyclopalladated with $Pd[CH_3CN]_4(BF_4)_2$ and subsequently converted into the neutral bis-palladium chloride complex **3**. The pyridine moiety of **3**, that is covalently attached to the spacer bridging the two pincer complexes, coordinates to activated palladium centers. Via a combination of pyridine- (**3**) and cyano-based (**2**) building blocks, dendrons up to generation three were assembled and characterized with ^{1}H NMR and FT-IR spectroscopy and MALDI-TOF mass spectrometry. These dendrons can coordinate through a cyano ligand to an activated nucleus **1** forming *convergently* assembled metallodendrimers. Alternatively, building blocks **3** were used in the *divergent* assembly of more stable metallodendrimers, because of the stronger coordination of pyridine compared to cyano ligands. The formation of metallodendrimers is evidenced by IR and ^{1}H NMR spectroscopy and electro spray and MALDI-TOF mass spectrometry.

Introduction

Nanochemistry is a rapidly expanding field that is concerned with the synthesis, characterization, and properties of structures of nanosize dimensions.[1] The use of conventional "covalent" chemistry requires increasingly laborious multistep syntheses. Therefore, supramolecular chemistry has exploited self-assembly to synthesize large, finite structures using a range of noncovalent interactions.[2] There are two main approaches which are to a certain extent inspired by nature. One exploits the formation of hydrogen bonds between complementary units.[3] The other is the use of (reversible) coordination chemistry as the driving force in the assembly process. Sauvage and co-workers were the first to synthesize catenanes and knots using Cu^+ ions as the assemblers.[4] The use of metal ions has also led to the formation of double and triple helices, grids, and ladders.[5] Another type of structures that can be constructed via coordination chemistry are metallocages and capsules.[6] Last but not least, the square planar coordination around Pd^{2+} and Pt^{2+} has been extensively exploited by Fujita and Stang and their co-workers in the formation of metallosquares and large metallorings.[7] We have used coordination chemistry to synthesize metallodendrimers.

Dendrimers are attractive nanosize model compounds because of their globular architecture and their highly functionalized surface.[8] These hyperbranched compounds are synthesized in a repetitive reaction sequence of nearly quantitative reactions. The synthetic route can either be *divergent*,[9] starting from the nucleus toward the surface, or *convergent*,[10] where "dendrons" or "wedges" are covalently linked to a polyfunctional nucleus. Compared to dendrimers that are fully organic in nature, the number of metallodendrimers is still limited.[11] Metallodendrimers can have a metal in the core, in every generation, or only at the outside.

Recently, we have developed a noncovalent, divergent synthesis toward nanosize metallodendrimers.[12] The "controlled assembly" (Figure 1) is based on the activation of nucleus **1** (Chart 1), containing three Pd−Cl pincer complexes, by removing the chloride ion with $AgBF_4$. Subsequent addition of 3 equiv of nitrile-containing building blocks **2** yields a first

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S0002-7863(97)04031-6 CCC: $15.00
Published on Web 06/12/1998

Scheme 1

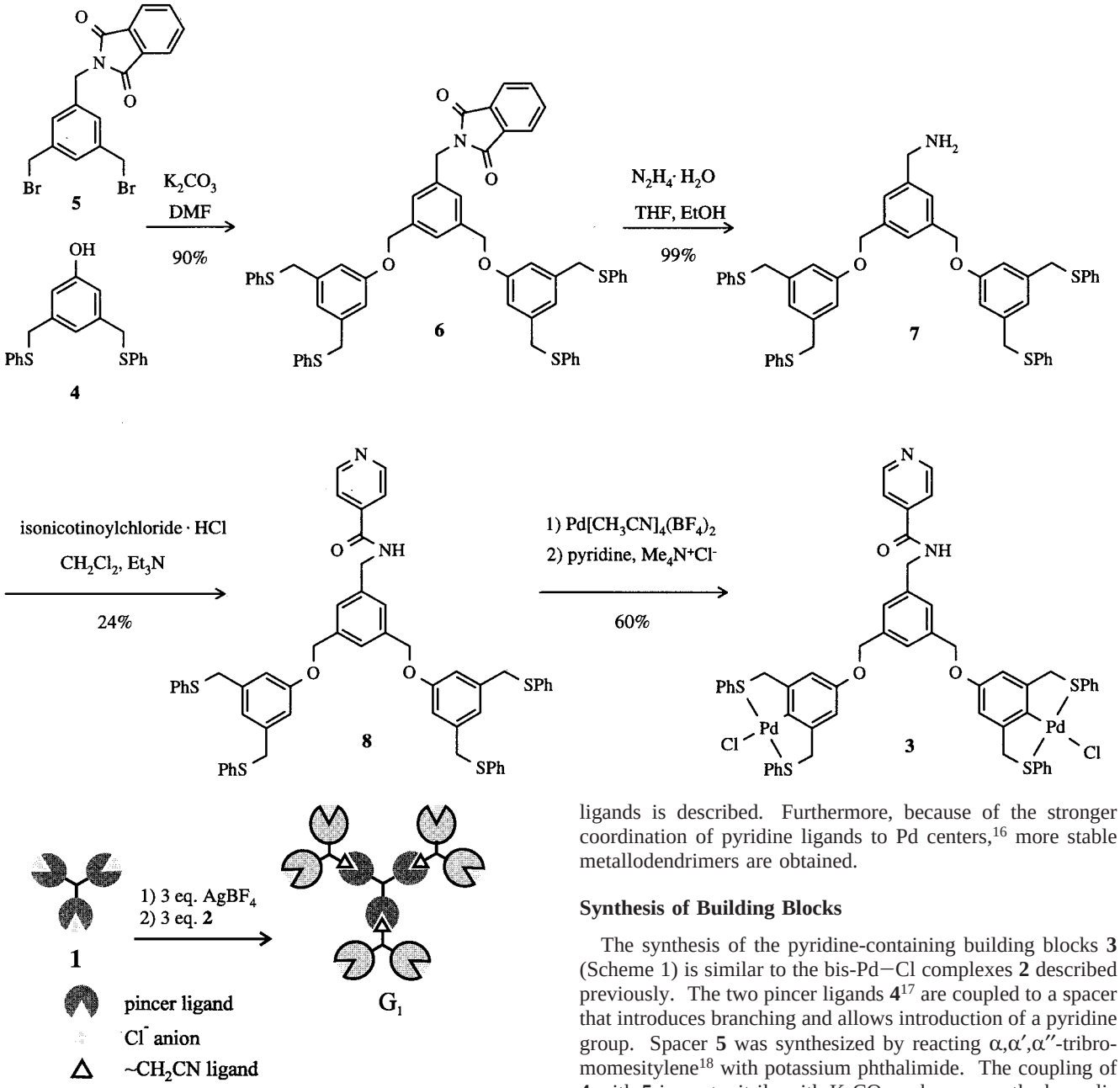

Figure 1. Schematic representation of the controlled assembly of a first generation metallodendrimer.

generation metallodendrimer by coordination of the nitrile ligands to the palladium centers. Using controlled assembly we were able to synthesize metallodendrimers up to generation five.[12,13]

In this article we describe the combination of two different ligands to construct metallodendrimers not only via a *divergent* but also via a *convergent* route. To our knowledge only the approach of Balzani and co-workers also allows a divergent and convergent built up of the metallodendrimers.[14] A number of different metallodendrimers containing transition metals in *every* generation have been reported in the literature.[15] The synthesis of building blocks **3** with pyridine instead of nitrile ligands is described. Furthermore, because of the stronger coordination of pyridine ligands to Pd centers,[16] more stable metallodendrimers are obtained.

Synthesis of Building Blocks

The synthesis of the pyridine-containing building blocks **3** (Scheme 1) is similar to the bis-Pd−Cl complexes **2** described previously. The two pincer ligands **4**[17] are coupled to a spacer that introduces branching and allows introduction of a pyridine group. Spacer **5** was synthesized by reacting α,α′,α″-tribromomesitylene[18] with potassium phthalimide. The coupling of **4** with **5** in acetonitrile with K_2CO_3 as base gave the benzylic ether **6** in 70% yield. Subsequently, the phthalimido group of

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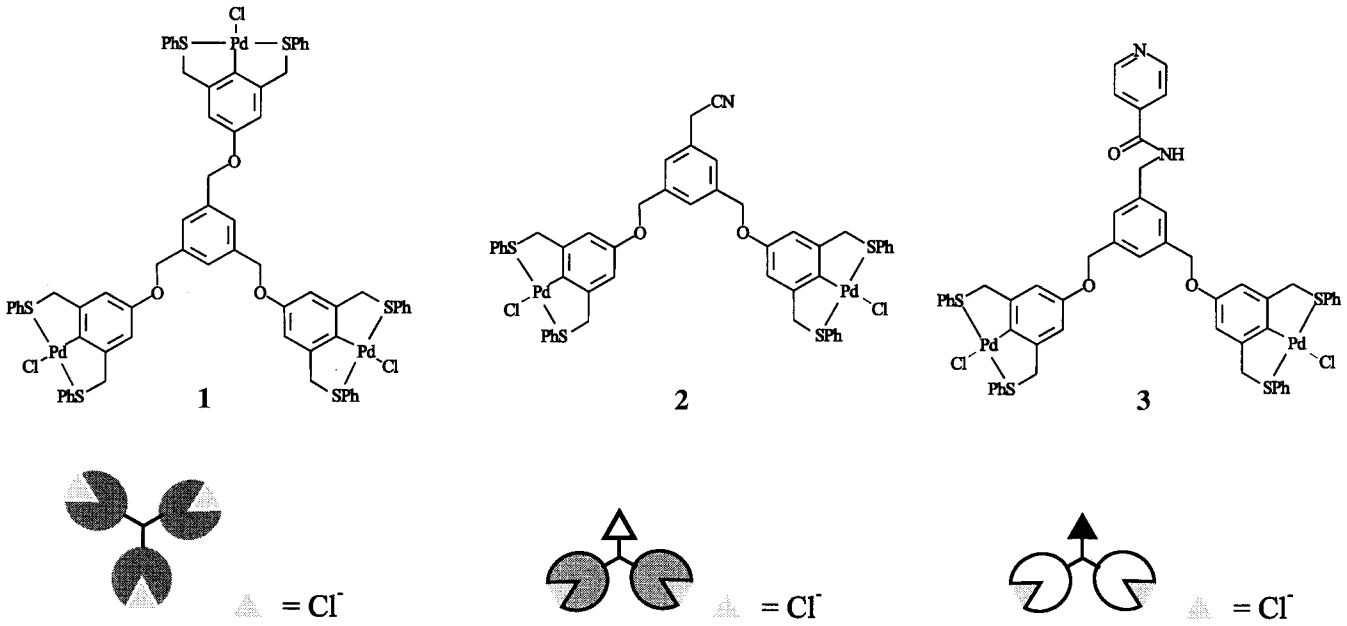
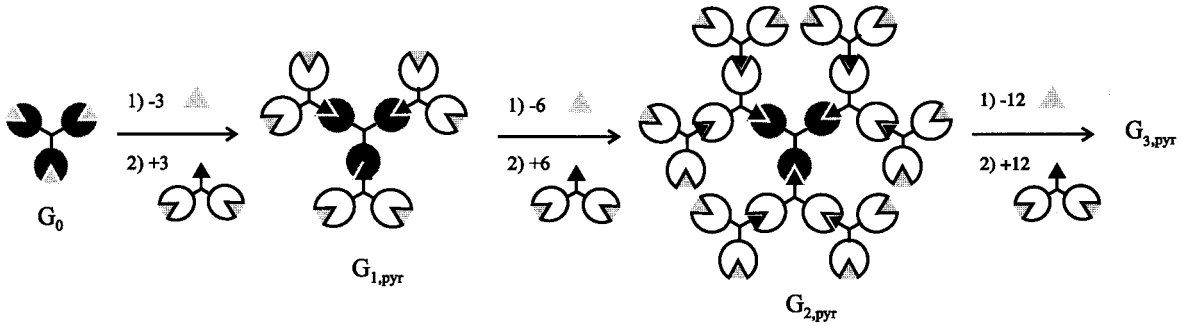
Chart 1



Scheme 2



6 was reduced quantitatively to the amine **7** using hydrazine monohydrate.

The pyridine moiety was introduced in high yields by reacting amine **7** with isonicotinoyl chloride. The cyclopalladation of **8** was quantitative using $Pd[CH_3CN]_4(BF_4)_2$ in CH_3CN. The ^1H NMR spectrum of the complex shows a broad signal at δ 4.6 ppm for the CH_2S protons in the five-membered palladium-containing rings. No signal at δ 6.76 ppm corresponding to the two aromatic protons *ortho* to both thiomethyl groups of the starting material is observed, indicating complete cyclometalation. The cyclopalladation reaction generates 2 equiv of HBF_4, and consequently the pyridine moiety is protonated. The last step is the introduction of a strongly coordinating chloride anion to obtain the overall neutral Pd−Cl complexes. The reaction with brine failed to introduce the chloride ligand because insoluble products were formed immediately upon addition of water. The synthesis of **3** was achieved by adding a few drops of pyridine to an acetonitrile−dichloromethane solution of the cationic complex,[19] before introducing the chloride via $Me_4N^+Cl^-$. After column chromatography and trituration with MeOH, the pure building block **3** was obtained in 60% yield.

(19) The pyridine ligand is deprotonated in aqueous environments and probably forms a (hyperbranched) polymer by coordinating to the activated Pd centers. The addition of pyridine causes the polymers to break down. See for similar hyperbranched polymers: Huck, W. T. S.; van Veggel, F. C. J. M.; Kropman, B. L.; Blank, D. H. A.; Keim, E. G.; Smithers, M. M. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 8293−8294. Huck, W. T. S.; Snellink-Ruël, B. A.; van Veggel, F. C. J. M.; Lichtenbelt, J. W. Th.; Reinhoudt, D. N. *Chem. Commun.* **1997**, 9−10.

Three different building blocks, **1**,[17] **2**,[12] and **3** (Chart 1), are available to assemble dendritic structures. Because of the large size of these assemblies it is convenient to introduce schematic representations for the building blocks. Dendrimers composed entirely of **3** are all given the suffix "pyr" (e.g., $\mathbf{G_{1,pyr}}$). The absence of this suffix indicates the exclusive use of cyano-containing building blocks.

Divergent Assembly

The three Pd−Cl centers of **1** were "activated" with 3 equiv of $AgBF_4$. Subsequently, 3 equiv of **3** were added, and a first generation dendrimer $\mathbf{G_{1,pyr}}$ was formed. Via a repetition of the activation and assembly step, generations two ($\mathbf{G_{2,pyr}}$) and three ($\mathbf{G_{3,pyr}}$) were assembled (Scheme 2).

^1H NMR spectroscopy provides valuable information on the formation of the metallodendrimers. The ^1H NMR spectra of **3**, $\mathbf{G_{1,pyr}}$, $\mathbf{G_{2,pyr}}$, and $\mathbf{G_{3,pyr}}$ are shown in Figure 2. The metallodendrimers are not soluble in most organic solvents. The ^1H NMR spectra of $\mathbf{G_{1,pyr}}$ and $\mathbf{G_{2,pyr}}$ were recorded in a mixture of CD_2Cl_2 and CD_3NO_2 at 35 °C. The ^1H NMR spectrum of $\mathbf{G_{3,pyr}}$ was measured in CD_3NO_2 at 80 °C.

The ^1H NMR data unequivocally show that the pyridine groups are coordinated to the Pd center as the signal for the α-pyridine protons shifts upfield from δ 8.69 to δ 8.30 ppm. The shift of the β-pyridine protons is not significant. Another indication for the coordination of pyridine to the Pd centers is the broadening of the signals for the α-pyridine protons in the dendrimers. This is probably due to hindered rotation of the pyridine ligands with respect to the plane of coordination.

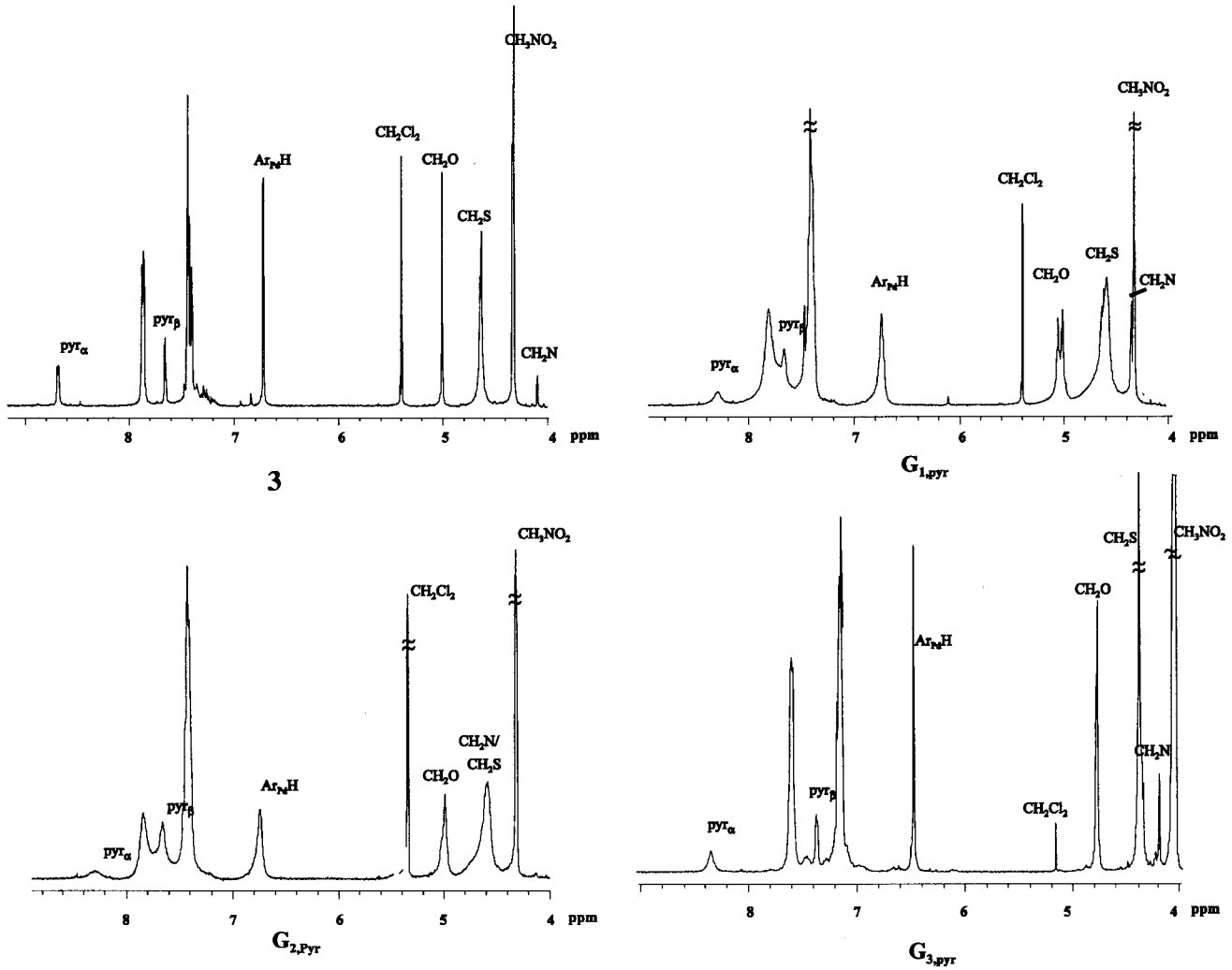


Figure 2. Part of the 400 MHz ^{1}H NMR spectra of **3**, $\mathbf{G_{1,pyr}}$, $\mathbf{G_{2,pyr}}$, and $\mathbf{G_{3,pyr}}$.

Two different signals ($\Delta\delta$ 0.05 ppm) for the CH_2O protons are present in the spectrum of $\mathbf{G_{1,pyr}}$. In the ^{1}H NMR spectrum of $\mathbf{G_{2,pyr}}$, the second signal is present as a shoulder, and in the case of $\mathbf{G_{3,pyr}}$, two sharp singlets can clearly be seen upon magnification. One signal corresponds to the CH_2O protons of the chloride protected Pd complexes on the surface and the other to the Pd−pyridine complexes. The ratio of the peaks is roughly equal to the theoretically expected ratio. This difference in shift is caused by the large electronic effect of the pyridine ligand on the pincer ligand system especially on the *para*-position. The ratios of the intensities of the signals around δ 6.7 ppm for the aromatic protons of the palladated ring ($Ar_{Pd}H$) and around δ 7.6 for the β-pyridine protons are in agreement with the values expected for $\mathbf{G_{1,pyr}}$ to $\mathbf{G_{3,pyr}}$. This shows that the assembly of these metallodendrimers is a quantitative process.

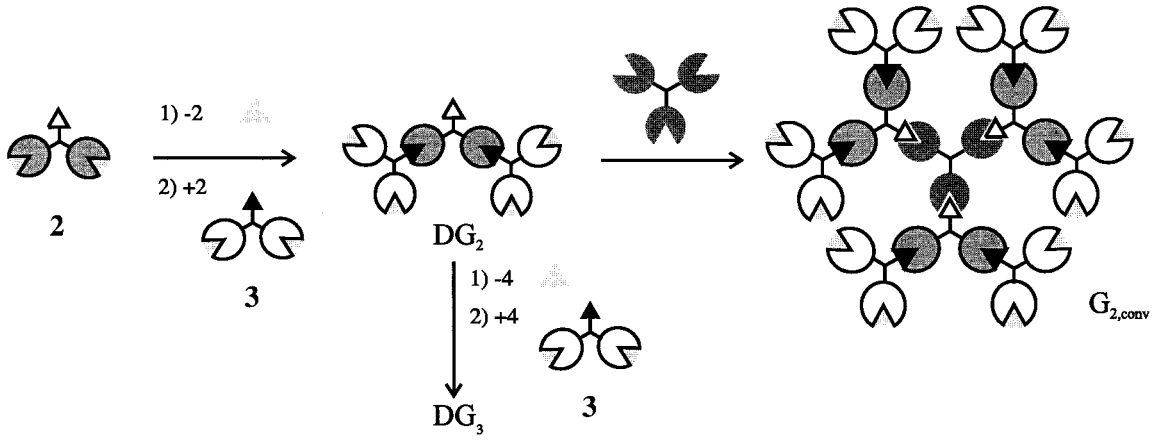
The ES-MS spectrum of $\mathbf{G_{1,pyr}}$ shows the formation of the metallodendrimer. In the spectrum a signal is present at *m*/*z* 1679.9 corresponding to $[\mathbf{G_{1,pyr}} - 3BF_4]^{3+}$. The loss of anions has been observed for other metallodendrimers and is precedented in the literature.[12,20] Other signals that are present in the ES-MS spectrum at *m*/*z* 1161.0 and 1516.4 correspond to $[\mathbf{3} - Cl]^+$ and $[\mathbf{1} - Cl]^+$. The signal for the building blocks originates most likely from disassembly of $\mathbf{G_{1,pyr}}$ in the mass spectrometer. ES-MS experiments with other generations did not give signals at high *m*/*z* values. The low solubility of the assemblies might render ionization of separate metallodendrimers difficult. The MALDI-TOF spectra of $\mathbf{G_{1,pyr}}$ and $\mathbf{G_{2,pyr}}$ show peaks at 5205.7 and 12684, respectively, which are assigned to $[M - BF_4]^+$.

As mentioned above, dendrimers $\mathbf{G_{1,pyr}}$-$\mathbf{G_{3,pyr}}$ are poorly soluble in nitromethane in contrast to the dendrimers $\mathbf{G_1}$-$\mathbf{G_3}$ described previously.[12] To increase the solubility different noncoordinating anions were introduced. By activating the Pd−Cl complexes silver tosylate, analogous metallodendrimers with more lipophilic anions were obtained. Unfortunately, initial experiments did not seem to yield more soluble assemblies.

Subsequently, the coordination strength of the Pd−pyridine bond was compared with the Pd−cyano bond. The Pd−Cl centers of **1** were activated with $AgBF_4$. To this activated core 3 equiv of **3** and 3 equiv of **2** were added simultaneously. The ^{1}H NMR spectrum shows that only $\mathbf{G_{1,pyr}}$ is formed. Hence, it can be concluded that **2** does not coordinate in competition with **3**. In principle this can still be a kinetic effect. Therefore, titration experiments were carried out to study the stability of the Pd−cyano and Pd−pyridine bond in the presence of the competing ligands. Solutions of $\mathbf{G_{1,pyr}}$ were prepared containing 0, 1, 3, 6, and 12 equiv of benzylcyanide, respectively. ^{1}H NMR measurements of these mixtures indicated that only coordinated pyridine was present, since only one signal for the α-pyridine protons at δ 8.30 ppm was visible. This means that the $-CH_2CN$ ligand cannot displace coordinated pyridine. An

(20) Leize, E.; van Dorsselaer, A.; Krämer, R.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 990−993.

Scheme 3



analogous experiment was carried out with a mixture of $\mathbf{G_1}$ containing 0, 1, 3, 6, and 12 equiv of isonicotinoyl benzylamide, an analogue of **3**. ^{1}H NMR measurements showed a very fast substitution of the $-CH_2CN$ ligand by the pyridine, since in all cases only the signals of coordinated pyridine were present.

Convergent Assembly

The pyridine ligand in **3** coordinates much stronger to activated palladium centers than the nitrile ligand in **2**, which makes a *convergent* approach possible. The convergent route starts with the synthesis of "dendrons" or "dendritic wedges" which can be coupled to a polyfunctional nucleus to form the dendrimer structure. A dendritic wedge ($\mathbf{DG_2}$) was constructed via controlled assembly as shown in Scheme 3. Activation of **2** with $AgBF_4$ and subsequent addition of 2 equiv of **3** gave $\mathbf{DG_2}$ after coordination of the pyridine ligands. The IR spectrum of this wedge only shows a signal at 2252 cm^{-1} for the noncoordinated cyano groups.[21] The ^{1}H NMR spectrum of $\mathbf{DG_2}$ confirms the coordination of the pyridine moieties as only one signal at δ 8.30 ppm is present for the α-pyridine protons. As was observed for $\mathbf{G_{1,pyr}}$ two signals for the CH_2O protons are present at δ 5.07 and δ 5.03 ppm; one for the Pd complex with the pyridine ligand and one for the Pd−Cl complex. The MALDI-TOF MS spectrum (Figure 3) shows a signal at *m*/*z* 3498.2, corresponding to $[\mathbf{DG_2} - BF_4]^+$, (calcd 3502.8).

Upon the addition of 3 equiv of $\mathbf{DG_2}$ to the activated nucleus **1**, a second generation dendrimer was constructed via the convergent assembly route (Scheme 3). The IR spectrum confirms the connection to the nucleus via coordination of the $\sim CH_2CN$ ligands as the characteristic signal at 2290 cm^{-1} is visible.[21] The ^{1}H NMR spectrum of $\mathbf{G_{2,conv}}$ shows the signals for the pyridine, the $\sim CH_2CN$ ligands, and the CH_2O protons in the correct ratios.[22]

To show the possibility of constructing larger wedges, the four Pd centers of the previously described dendron $\mathbf{DG_2}$ were deprotected and 4 equiv of **3** were added. The ^{1}H NMR spectrum shows the coordination of the pyridine ligands. In the IR spectrum a signal at 2252 cm^{-1} corresponding to noncoordinated cyano ligands is present. The MALDI-TOF MS spectrum (Figure 3) clearly shows the formation of wedge $\mathbf{DG_3}$. The signal at *m*/*z* 8490.3 corresponds to $[\mathbf{DG_3} - BF_4]^+$, (calcd 8490.7).

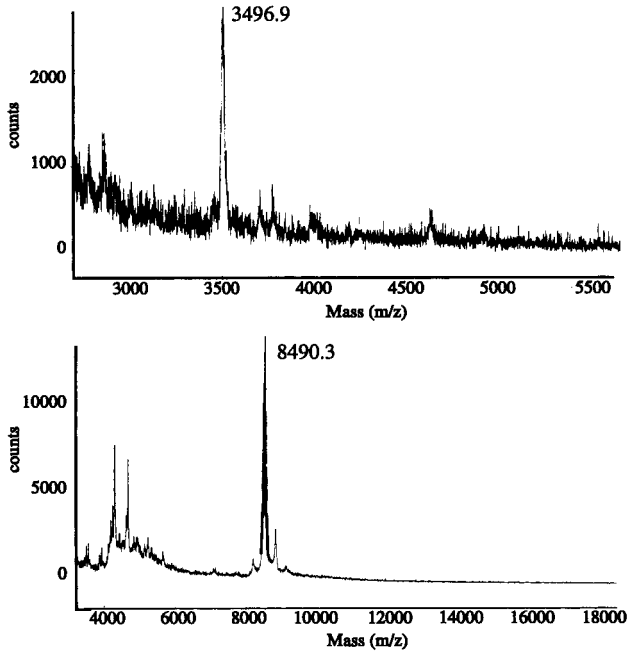


Figure 3. MALDI-TOF spectra of $\mathbf{DG_2}$ (top) and $\mathbf{DG_3}$ (bottom).

Conclusions

The combination of pyridine- with cyano-based building blocks allowed the assembly of dendrons up to the third generation. It has been possible to attach these dendrons to an activated nucleus. This is an example of the assembly of metallodendrimers via a *convergent* route. This is a substantial broadening of the scope of the controlled assembly process which also allows the *divergent* assembly of metallodendrimers. The pyridine-based building blocks will be used to introduce functionality in large, noncovalent assemblies.

Experimental Section

Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless indicated otherwise) with Me_4Si as internal standard on a Bruker AC 250 spectrometer. FAB-MS spectra were recorded with a Finnigan MAT 90 spectrometer using *m*-NBA as a matrix. THF was freshly distilled from Na/benzophenone, hexane (referring to petroleum ether with bp 60−80 °C), and CH_2Cl_2 from

(21) Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1−23.

(22) The MALDI-TOF spectrum of $G_{2,conv}$, obtained from a mixture of polypropylene glycol and the UV matrix indole-acrylic acid, shows a small, but significant signal at an *m*/*z* value of 12 194, that can be assigned to $[M - BF_4]^+$. However, also weak signals at higher *m*/*z* ratios are observed. This might be an effect of the matrix and/or applied technique, which is currently under investigation.

K_2CO_3. Nitromethane was washed with 1 N HCl and water and distilled from $CaCl_2$. NaH was a 50% dispersion in mineral oil and was used after washing with hexane. Other chemicals were of reagent grade and were used as received. Column chromatography was performed with silica gel 60H (0.005−0.040 mm) from Merck. $Pd[CH_3CN]_4(BF_4)_2$[23] and compound **4**[17] were prepared according to literature procedures.

Electrospray ionization mass spectrometry (ES-MS) was carried out using a Micromass Platform quadrupole mass spectrometer, coupled to a Micromass Masslynx data system. The samples were introduced into the source by constant infusion or direct injection via a valve-loop system. Constant infusions were made by loading the samples (dissolved in nitromethane or chloroform) into a 10 mL gastight SGE syringe. The sample was presented to the source at a rate of 10 μL/min of nitromethane or chloroform solution via a Cole Palmer Model 74900 syringe pump. Loop injection was accomplished by using a Rheodyne 7125 injector valve with a 10 μL loop.

Matrix Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) mass spectrometry was carried out using a PerSeptive Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer. A 337 nm UV Nitrogen laser producing 3 ns pulses was used in the linear and reflectron mode. The samples were prepared by mixing 10 μL of a 50% nitromethane/chloroform solution of the sample with 20 μL of a solution of 3 mg/L 2-(4-hydroxyphenylazo)benzoic acid (matrix 1) or a mixture of 2,5-dihydroxybenzoic acid and 2-(4-hydroxyphenylazo)-benzoic acid (ratio 2:1, matrix 2) in nitromethane. Of this solution 1 μL was loaded on the gold sample plate, giving approximately 100 μg of sample.

α,α′-Dibromo-α″-phthalimidomesitylene (5). A mixture of α,α′,α″-tribromomesitylene (8.0 g, 22.42 mmol) and potassium phthalimide (4.63 g, 25.0 mmol) in DMF (100 mL) was stirred for 10 h at 40 °C. DMF was evaporated and CH_2Cl_2 (100 mL) was added. Subsequently, the organic layer was washed with a saturated aqueous solution of $NH_4{+}Cl^-$ (250 mL), 1 N HCl (100 mL), $NaHCO_3$ (100 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. Purification by column chromatography (silica, eluent: CH_2Cl_2/hexane 90/10) gave **5** as a white solid (4.41 g, 47%). Mp 181−183 °C; ^{1}H NMR δ 7.88−7.83 (m, 2H), 7.75−7.70 (m, 2H), 7.38 (s, 2H), 7.35 (s, 1H), 5.2 (s, 1H), 4.82 (s, 2H), 4.43 (s, 4H); ^{13}C NMR δ 168.1, 139.0, 137.8, 134.1, 131.8, 129.8, 129.3, 123.5, 40.1, 32.4; EI-MS *m*/*z*: 420.932 (M^+, calcd 420.931). Anal. Calcd for $C_{17}H_{13}O_2NBr_2 \cdot 0.5CH_2Cl_2$: C, 46.05; H, 3.00; N, 2.98. Found: C, 45.81; H, 2.95; N, 2.78.

α,α′-Bis-(3,5-bis(phenylthiamethyl)phenyloxy)-α″-phthalimidomesitylene (6). After a mixture of **4** (1.23 g, 3.64 mmol) and K_2CO_3 (0.60 g, 4.34 mmol) in CH_3CN (75 mL) had been stirred for 1 h, compound **5** (0.78 g, 1.82 mmol) was added. The suspension was stirred overnight at room temperature. After evaporation of DMF CH_2Cl_2 (100 mL) was added to the remaining solid. Subsequently, the organic layer was washed with a saturated solution of $NH_4{+}Cl^-$ (250 mL) and water (50 mL). After drying over $MgSO_4$, the solvent was evaporated, and compound **6** was obtained as a white foam after column chromatography (silica gel, eluent: CH_2Cl_2) (1.20 g, 70%). ^{1}H NMR δ 7.73−7.68 (m, 2H), 7.58−7.53 (m, 2H), 7.33 (s, 2H), 7.27 (s, 1H), 7.19−7.01 (m, 20H), 6.75 (s, 2H), 6.68 (s, 4H), 4.79 (s, 4H), 4.76 (s, 2H), 3.91 (s, 8H); ^{13}C NMR δ 167.9, 158.8, 139.2, 137.8, 137.0, 136.2, 134.1, 132.1, 130.0, 128.9, 127.4, 126.4, 126.2, 123.4, 122.0, 114.1, 69.6, 41.4, 39.0; FAB-MS *m*/*z* 937.2 (M^+, calcd 937.2). Anal. Calcd for $C_{57}H_{47}O_4S_4N \cdot 2H_2O$: C, 70.27; H, 5.28; N, 1.44. Found: C, 70.1; H, 5.20; N, 1.51.

α,α′-Bis-(3,5-bis(phenylthiamethyl)phenyloxy)-α″-aminomesitylene (7). To a solution of **6** (1.13 g, 1.21 mmol) in THF (25 mL) and ethanol (25 mL) was added hydrazine monohydrate (13 mL, 0.3 mol). The mixture was stirred overnight at 50 °C. The reaction was quenched using 1 N HCl (50 mL) and subsequently extracted with CH_2Cl_2 (100 mL). The organic layer was washed with $NaHCO_3$ (100 mL) and brine (100 mL), followed by drying over $MgSO_4$ and evaporation to dryness. Compound **7** was obtained as a slightly yellow oil (0.96 g, 99%). ^{1}H NMR δ 7.19−7.00 (m, 23H), 6.74 (s, 2H), 6.71 (s, 4H), 4.80 (s, 4H), 3.90 (s, 8H), 3.76 (s, 2H); ^{13}C NMR δ 158.9, 143.5, 139.2, 137.5, 136.2, 129.9, 128.9, 126.4, 126.0, 125.3, 122.1, 114.1, 69.8, 46.1, 39.0; EI-MS *m*/*z*: 807.231 (M^+, calcd for $C_{49}H_{45}O_2S_4N$: 807.233).

α,α′-Bis-(3,5-bis(phenylthiamethyl)phenyloxy)-α″-(4-pyridinecarboxamido)mesitylene (8). Isonicotinoyl chloride hydrochloride (115 mg, 0.65 mmol) was added to a solution of **7** (260 mg, 0.32 mmol) and Et_3N (0.18 mL, 1.29 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred overnight at room temperature and subsequently washed with 1 N HCl (100 mL), $NaHCO_3$ (100 mL), and brine (100 mL). After drying over Na_2SO_4 the solvent was evaporated under reduced pressure. Column chromatography (silica gel, eluent: CH_2Cl_2:MeOH 99:1) was used to purify the product and after drying under vacuum compound **8** was obtained as a white solid: (0.23 g, 79%). Mp 115−117 °C; ^{1}H NMR δ 8.65 (d, 2H, J = 6.0 Hz), 7.49 (d, 2H, J = 6.0 Hz), 7.30 (s, 1H), 7.26 (s, 2H), 7.20−7.07 (m, 20H), 6.76 (s, 2H), 6.73 (s, 4H), 4.88 (s, 4H), 4.59 (d, 2H, J = 6.4 Hz), 3.94 (s, 8H); ^{13}C NMR δ 165.4, 158.7, 150.6, 141.2, 139.3, 138.3, 138.0, 136.2, 129.8, 128.9, 126.7, 126.4, 126.1, 122.2, 120.9, 114.0, 69.5, 44.0, 38.9; FAB-MS 913.3 (M^+, calcd 913.2). Anal. Calcd for $C_{55}H_{48}O_3N_2S_4 \cdot H_2O$: C, 70.94; H, 5.41; N, 3.01. Found: C, 70.73; H, 5.26; N, 2.97.

Bis-Palladium Chloride Complex 3. Ligand **8** (70.0 mg, 0.077 mmol) was dissolved in a mixture of CH_2Cl_2 (25 mL) and CH_3CN (75 mL), and $Pd[CH_3CN]_4(BF_4)_2$ (68.2 mg, 0.15 mmol) was added. After stirring for 1 h at room temperature the solvents were evaporated, and the cationic complex was used without further purification to prepare **3**. The bis-palladium complex was dissolved in a mixture of CH_2Cl_2 (25 mL) and CH_3CN (25 mL). After the addition of some droplets of pyridine, tetramethylammonium chloride (4.0 g, 36 mmol) was added whereupon the solution was stirred vigorously overnight at room temperature. The mixture was filtered to remove excess tetramethylammonium chloride. The solution was evaporated to dryness and subjected to column chromatography (silica gel, eluent CH_2Cl_2/MeOH gradient 99:1 to 97:3) to give **3** as a yellow solid (56.0 mg, 61%). Mp 158−160 °C. ^{1}H NMR 8,54 (d, 2H, J = 6.0 Hz), 7.74−7.71 (m, 8H), 7.65 (d, 2H, J = 6.0 Hz), 7.42−7.22 (m, 15H), 6.56 (s, 4H), 4.87 (s, 4H), 4.55 (d, 2H, J = 6.4 Hz), 4.43 (s, 8H), 3.48 (s, 3H); ^{13}C NMR δ 165.4, 156.6, 151.3, 150.4, 150.1, 140.9, 139.4, 137.5, 132.2, 131.3, 129.9, 129.7, 127.2, 121.3, 109.1, 69.8, 51.7, 43.8; FAB-MS 1194.2 (M^+, calcd 1193.8). Anal. Calcd for $C_{55}H_{46}O_3S_4N_2Cl_2Pd_2 \cdot CH_3OH$: C, 54.82; H, 4.11; N, 2.28. Found: C, 54.25; H, 4.09; N, 2.20.

To make comparison with the dendritic structures possible, **3** was also measured in a 1:1 solution of CD_2Cl_2 and CD_3NO_2. This resulted in the following spectrum: ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3NO_2 = 1:1, 35 °C): δ 8.69 (d, 2H, J = 6.0 Hz), 7.91−7.82 (m, 8H), 7.65 (d, 2H, J = 6.0 Hz), 7.45−7.39 (m, 15H), 6.72 (s, 4H), 5.00 (s, 4H), 4.65 (bs, 10H).

$G_{1,pyr}$. To a solution of **1** (10.0 mg, 6.44 μmol) in CH_2Cl_2 (5 mL) was added 119.9 μL (19.32 μmol) of a freshly prepared stock solution of $AgBF_4$ in water (0.1611 μM). The mixture was stirred for 5 min, and the color changed from bright to pale yellow. Subsequently, **3** (23.0 mg, 19.3 μmol) was added, and the mixture was stirred for 5 min after which all solvent was evaporated in vacuo. To remove all water from the sample the residue was dissolved in dry nitromethane (5 mL) and evaporated to dryness again under reduced pressure (three times). Finally, dry nitromethane (5 mL) was added, and the suspension was filtered through Hyflo/cotton to remove AgCl. After evaporation of the solvent, **G_1** was obtained as a yellow solid (30.7 mg, 90%). Mp 168−172 °C; ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3NO_2 = 1:1, 35 °C) δ 8.30 (bs, 6H), 7.75 (bs, 36H), 7.67 (bs, 6H), 7.50−7.32 (m, 66H), 6.73 (s, 18H), 5.08 (s, 12H), 5.02 (s, 6H), 4.75−4.55 (m, 42H); ES-MS *m*/*z* 1676.9 [$(M-3BF_4)^{3+}$, calcd 1677.9]; MALDI-TOF MS (matrix 2) *m*/*z* 5205.7 [$(\mathbf{G}_{1,pyr} - BF_4)^+$, calcd 5204.0].[24] Anal. Calcd for $C_{234}H_{195}O_{12}S_{18}N_6Pd_9B_3F_{12} \cdot 3CH_3NO_2$: C, 54.10; H, 3.91; N, 2.40. Found: C, 54.50; H, 3.83; N, 2.36.

$G_{2,pyr}$. To a solution of **1** (5.0 mg, 3.22 μmol) in CH_2Cl_2 (5 mL) was added 60.0 μL (9.66 μmol) of a freshly prepared stock solution of $AgBF_4$ (0.1611 μM). The mixture was stirred for 5 min, and

(23) Sen, A.; Ta−Wang, L. *J. Am. Chem. Soc.* **1981**, *103*, 4627−4629.

(24) Due to a too low resolution the isotope pattern was not observed. However, the calculated isotope pattern with the experimental resolution was in good agreement with the measured signals.

subsequently **3** (11.5 mg, 9.65 μmol) was added. The mixture was evaporated to dryness, and the residue dissolved in nitromethane (5 mL). After assembly of $\mathbf{G_{1,pyr}}$ all solvent was evaporated; the residue dissolved in dry nitromethane and evaporated to dryness again (three times). Crude $\mathbf{G_{1,pyr}}$ was dissolved in nitromethane (5 mL), and $AgBF_4$ (119.9 μL, 19.32 μmol) was added again. After stirring for 5 min **3** (23.0 mg, 19.3 μmol) was added to assemble $\mathbf{G_2}$. The solvent was evaporated after which the residue was dissolved in dry nitromethane and evaporated to dryness again (three times). After filtration through Hyflo/cotton $\mathbf{G_{2,pyr}}$ was obtained as a yellow solid (40.8 mg, 95%). Mp 165−167 °C; ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3NO_2 = 1:1, 35 °C) δ 8.26 (bs, 18H), 7.77 (bs, 84H), 7.67 (bs, 18H), 7.50−7.33 (m, 156H), 6.75 (s, 42H), 5.03 (bs, 42H), 4.71−4.53 (bs, 102H); MALDI-TOF MS (matrix 2) *m*/*z* 12684 [$(\mathbf{G_{2,pyr}} - BF_4)^+$, calcd 12682].[24] Anal. Calcd for $C_{564}H_{471}O_{30}S_{42}N_{18}Cl_{12}Pd_{21}B_9F_{36}\cdot 2CH_3NO_2$: C, 52.74; H, 3.73; N, 2.17. Found: C, 52.54; H, 3.83; N, 2.50.

$\mathbf{G_{3,pyr}}$. similar procedure as for $\mathbf{G_{2,pyr}}$; dark yellow solid; mp 164−167 °C. ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3NO_2 = 1:1, 35 °C) δ 8.56 (bs, 42H), δ 7.82 (bs, 180H), 7.66 (bs, 42H), 7.48−7.35 (m, 336H), 6.73 (s, 90H), 5.03 (bs, 90H), 4.71−4.58 (bs, 222H). Anal. Calcd for $C_{1224}H_{1023}O_{66}S_{90}N_{42}Cl_{24}Pd_{45}B_{21}F_{84}\cdot 4CH_3NO_2$: C, 52.73; H, 3.73; N, 2.30. Found: C, 52.84; H, 3.72; N, 2.69.

Dendron $\mathbf{DG_2}$. Cyano building block **2** (7.50 mg, 6.82 μmol) was dissolved in a 1:1:1 mixture of CH_2Cl_2, CH_3NO_2, and CH_3CN (10 mL). $AgBF_4$ (2.66 mg, 13.64 μmol) was added, and the mixture was stirred for 15 min before pyridine building block **3** (16.3 mg, 13.63 μmol) was added. After stirring for 5 min the solution was evaporated to dryness under reduced pressure. The crude product was subsequently dissolved in a 1:1 mixture of CH_2Cl_2 and CH_3NO_2 and evaporated. This was repeated two times. After dissolving the wedge again in CH_2Cl_2 and CH_3NO_2 the solution was filtered over Hyflo, followed by evaporation of the solvents and drying under high vacuum. $\mathbf{DG_2}$ was obtained as a yellow solid. Mp 142−146 °C. ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3NO_2 = 1:1, 35 °C) δ 8.32 (bs, 4H), 7.85 (bs, 24H), 7.67 (bs, 4H), 7.50−7.32 (m, 45H), 6.78 (s, 4H), 6.75 (s, 8H), 5.07 (s, 8H) 5.03 (s, 4H), 4.75−4.53 (m, 28H), 3.86 (s, 2H); IR (KBr) 2252 cm^{-1} (C≡N). MALDI-TOF MS (matrix 1) *m*/*z* 3498.2 [$(\mathbf{DG_2} - BF_4)^+$, calcd 3502.8]. Anal. Calcd for $C_{160}H_{133}O_8S_{12}N_5Pd_6Cl_4B_2F_8\cdot 2CH_3NO_2$: C, 52.84; H, 3.80; N, 2.66. Found: C, 52.44; H, 3.80; N, 2.91.

$\mathbf{G_{2,con}}$. To a solution of **1** (3.58 mg, 2.31 μmol) in a 1:1 mixture of CH_2Cl_2 and CH_3NO_2 (15 mL) was added $AgBF_4$ (1.35 mg, 6.93 μmol). After stirring for 15 min $\mathbf{DG_2}$ (24.85 mg, 6.93 μmol) was added. The dendrimer $\mathbf{G_{2,con}}$ was obtained after standard workup (solvation and evaporation (3×), filtration over Hyflo) as a yellow solid.[22] Mp 144−148 °C. ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3NO_2=1:1, 35 °C) δ 8.30 (bs, 12H), 7.82 (bs, 84H), 7.64 (bs, 12H), 7.48−7.30 (m, 156H), 6.73 (s, 42H), 5.07 (s, 30H), 5.03 (s, 12H), 4.68−4.53 (m, 96H), 3.86 (s, 6H); IR (KBr) 2290 cm^{-1} (C≡N). Anal. Calcd for $C_{549}H_{456}O_{27}S_{42}N_{15}Cl_{12}Pd_{21}B_9F_{36}\cdot 2CH_3NO_2$: C, 52.37; H, 3.68; N, 1.88. Found: C, 52.25; H, 3.77; N, 2.10.

Dendron $\mathbf{DG_3}$. Wedge $\mathbf{DG_2}$ (9.32 mg, 2.59 μmol) was dissolved in a 1:1:1 mixture of CH_2Cl_2, CH_3NO_2, and CH_3CN (15 mL). Deprotection with $AgBF_4$ (2.02 mg, 10.38 μmol), after 15 min followed by the addition of **3** (12.40 mg, 10.38 μmol). After standard workup (solvation in CH_2Cl_2/CH_3NO_2 and evaporation (3×) subsequent filtration over Hyflo) $\mathbf{DG_3}$ was obtained as a yellow/brown solid. Mp 138−140 °C: ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3NO_2 = 1:1, 35 °C) δ 8.04 (bs, 12H), 7.86 (bs, 56H), 7.64 (d, 12H, J = 6.0 Hz), 7.46−7.35 (m, 105H), 6.73 (s, 28H), 5.02 (s, 28H), 4.61 (bs, 68H), 3.82 (s, 2H); IR (KBr) 2250 cm^{-1} (C≡N). MALDI-TOF MS (matrix 1) *m*/*z* 8490.3 [$(\mathbf{DG_3} - BF_4)^+$, calcd 8490.7]. Anal. Calcd for $C_{380}H_{317}O_{20}S_{28}N_{13}Cl_8Pd_{14}B_6F_{24}\cdot 5CH_3NO_2$: C, 52.06; H, 3.77; N, 2.84. Found: C, 51.84; H, 3.48; N, 2.73.

Acknowledgment. We thank the Dutch Foundation for Chemical Research (SON) for financial support.

JA974031E