

Molecularly thin films of metallodendrimers

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ABSTRACT: A non-covalent synthesis route to assemble metallodendrimers was extended to the fifth generation. Generation four (**G**₄) was characterized by electrospray mass spectrometry. Thin films of generation five (**G**₅) metallodendrimers were studied by tapping mode scanning force microscopy. Both on graphite and on mica spherical particles with a diameter of *ca* 15 nm were observed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: metallodendrimers; molecularly thin films

INTRODUCTION

The miniaturization of devices is still an ongoing challenge in nanotechnology.¹ At the nanometer scale, materials may exhibit new electronic or optical properties. Nanophysical (lithographic) fabrication methods generally yield two-dimensional, silicon-based structures between 50 and 100 nm. Nanochemistry follows a 'bottom up' approach and may be used to synthesize nanostructures of more complex shapes, able to perform a specific function. The covalent synthesis of such large structures becomes cumbersome because of the large number of subsequent steps. However, non-covalent synthesis might provide new and efficient routes for the construction and functionalization of nanosize structures.² Dendrimers are nanoparticles with a highly branched architecture leading to spherical shapes combined with high molecular weights.³ We have previously reported the non-covalent assembly of metallodendrimers up to generation three (**G**₃).⁴ This work has now been extended to the assembly of generations four and five (**G**₄ and **G**₅, respectively) to study the macromolecular (probably globular) shape of such nanosize structures.

To assemble nanosize structures *via* non-covalent interactions we designed the building blocks depicted in Scheme 1. These building blocks contain branched spacers that should favor dendritic growth with metal

centers embedded in so-called pincer complexes. The insertion of the metal in the aromatic C—H bonds gives kinetically stable complexes with S donor atoms. The fourth coordination site at the Pd center is occupied by a strongly, but reversibly, coordinated Cl[−] ligand.

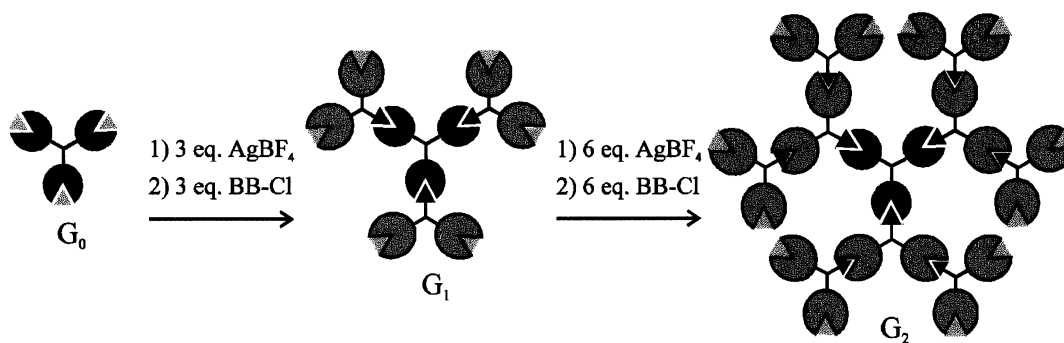
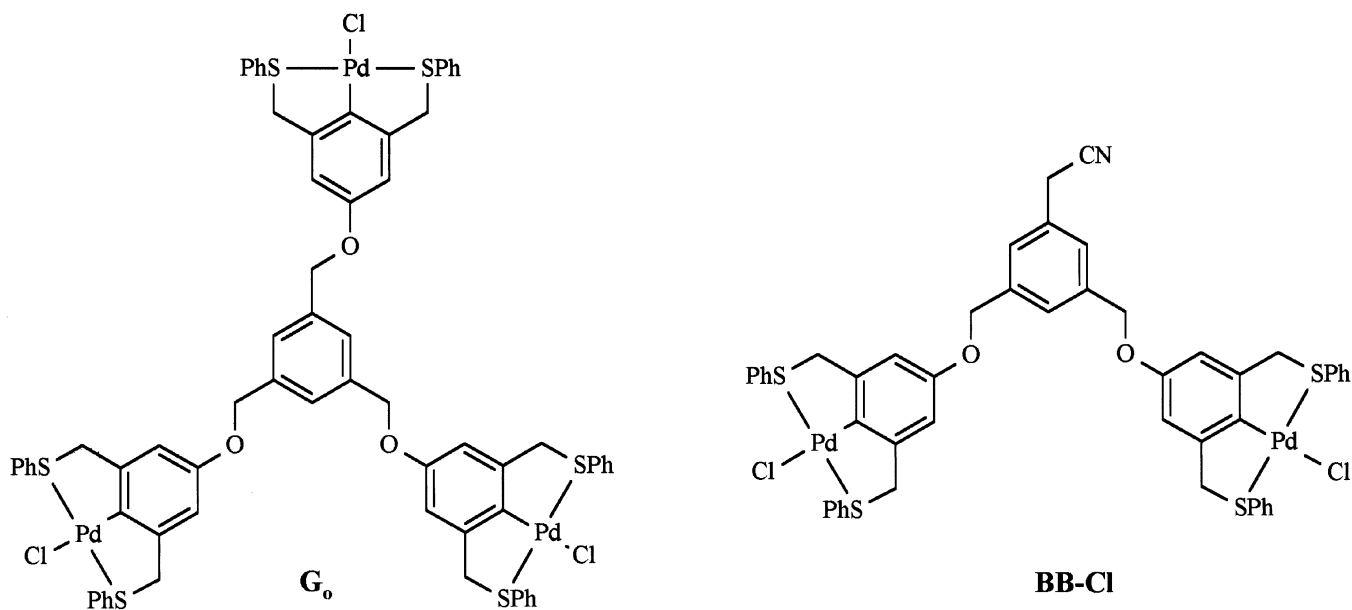
Nucleus **G**₀ can be 'activated' by removing the Cl[−] ligands with AgBF₄. Building block **BB-Cl** contains a CH₂CN group that can coordinate to the activated Pd centers of **G**₀. The assembly of activated **G**₀ and three **BB-Cl** building blocks yields a first-generation metallodendrimer. This controlled assembly procedure can be repeated to assemble larger structures. Scheme 2 shows the assembly of a second-generation metallodendrimer.

The same sequence of repetitive activation and addition steps yielded **G**₂ to **G**₅ *via* a one-pot procedure. Here we report the assembly of **G**₄ and **G**₅. The ¹H NMR spectra of **G**₄ and **G**₅ in CD₃NO₂ are remarkably simple because of the high symmetry of the nucleus and the similarity of the building blocks. The ¹H NMR spectra of both compounds show some broadening of peaks compared with the lower generations, indicating a high molecular weight and/or a decrease in rotational freedom of the dendritic arms. In the IR spectrum the coordination of the cyano group is confirmed by the characteristic shift of the C≡N stretch vibration from 2252 cm^{−1} for free **BB-Cl** to 2290 cm^{−1} upon coordination.⁵ The molecular weight of metallodendrimer **G**₄ was determined using Electrospray mass spectrometry (ESMS). The highest molecular weight thus obtained was 49878 Da (Fig. 1) corresponding to **G**₄⁺39BF₄[−]. The spectrum is broadened because of the natural isotope distribution of the Pd-containing metallodendrimers. The resolution of the mass spectrometer was unfortunately not high enough to resolve the signals of **G**₅ and its mass therefore could not be determined. An attempt was made to determine the

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size of G_5 in nitromethane solution also with QELS. Extensive clustering was observed at millimolar concentrations. The size of the particles decreased considerably after diluting the sample. At very low concentrations (10^{-6} M) the average diameter remained more or less constant at 10 ± 2 nm. However, the intensity of this signal was weak and therefore no definite conclusions can

be drawn. GPC did not give satisfactory results, as the metallo dendrimers in general interact too strongly with the column material.

As commonly observed, the molecular weight for dendrimer G_4 lacks a number of anions (G_4 contains 45 BF_4^- anions). Apparently there is a preferential loss of a number of anions. The loss of counter ions has been reported.⁶ In some cases cationic complexes have been prepared in order to allow measurements of ES mass spectra.⁷

Molecular mechanics (MM) calculations were performed for G_3 using the universal force field⁸ implemented in Cerius.^{2,9} Higher generations consist of too many atoms and could not be minimized. The size of G_3 in the gas phase, as determined by MM, is 7–8 nm in diameter. Extrapolating the MM results, a diameter of ca 10 nm is expected for G_5 .

To obtain experimental results on the size of the metallo dendrimers, tapping mode scanning force microscopy (TM-SFM) studies were carried out. Molecularly thin films were prepared by spin-casting solutions (0.2–

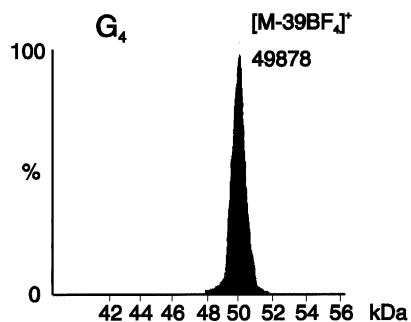


Figure 1. Deconvoluted ESMS spectrum of G_4

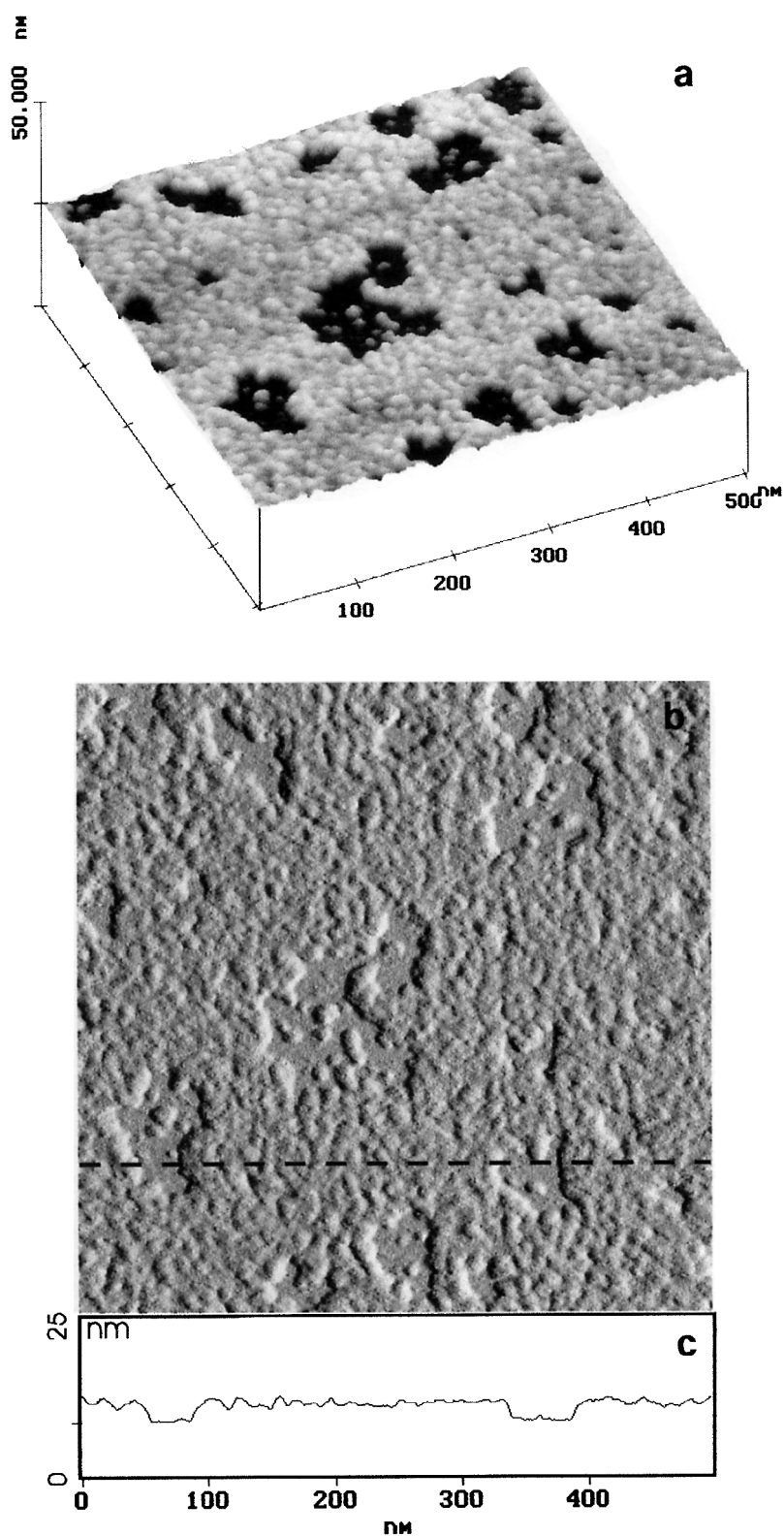


Figure 2. Tapping scanning force micrographs of a non-closed molecular film of G_5 which was prepared by spincasting a dilute solution (0.2 mg ml^{-1}) of G_5 in nitromethane on freshly cleaved HOPG. (c) Amplitude signal; (b) height image (light areas correspond to elevated structures); (a) stereoscopic projection of (b)

1.2 mg ml^{-1}) of G_5 on a freshly cleaved graphite [highly oriented pyrolytic graphite (HOPG)] or mica surface. The

tapping mode was used in order to minimize lateral shear deformations caused by interactions with the tip. The

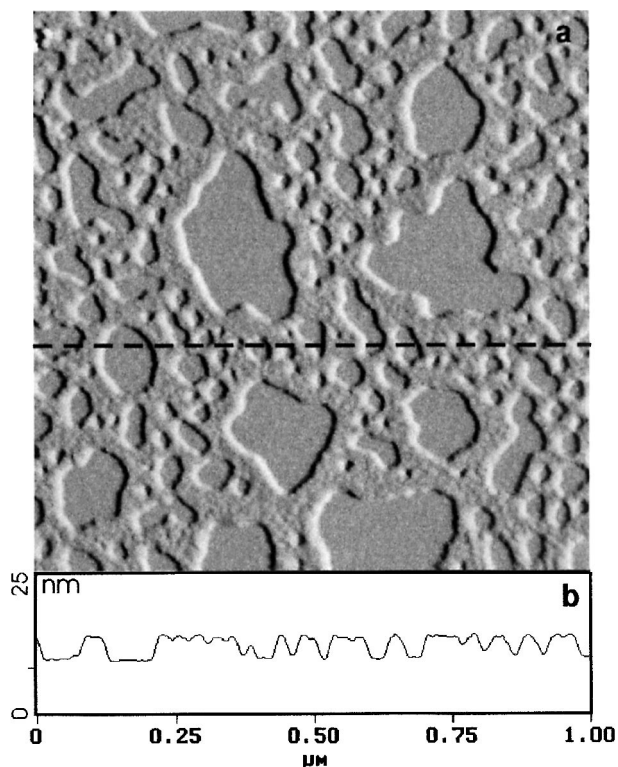


Figure 3. Tapping scanning force micrograph of a film of G_5 which was prepared by spincoating a 1 mg ml^{-1} solution in nitroethane onto freshly cleaved mica. Top: height image (light areas correspond to elevated structures); Bottom: amplitude signal

images in Fig. 2 show a not fully closed monolayer on the rather apolar surface of graphite. The dark areas are holes in this layer and show bare graphite. The film has a granular structure where the individual grains have a diameter of *ca* 15–20 nm as determined from the lateral periodicity. When the surface was scanned with minimum force, a height of 4.2 nm was measured for the film. When the force was increased the apparent height decreased to 2.8 nm as the SFM tip compressed the soft metallodendrimers. (Generally, the observed height of organic dendrimers in SFM measurements deviates from the theoretical value.¹⁰)

A different pattern was observed on mica. Different adsorption preferences between the hydrophobic surface, the nitromethane solvent and the metallodendrimers resulted in the dewetting patterns shown in Fig. 3(b). Even at high concentrations no closed films were formed. Lower concentrations resulted in patterns where separate spheres are clearly visible [Fig. 4(a) and 4(b)]. This is in contrast to films on a graphite surface which fully covered the graphite at higher concentrations. As on graphite, the films cast on mica showed a globular fine structure. The particles depicted in Figs 2(b) and 4(b) had the same size, i.e. 15–20 nm in diameter and at a minimum normal force about 5 nm in height.

To compare the results of the SFM measurements we

estimated the diameter of G_5 , with a molecular weight of 108 kDa, as 7 nm using the equations

$$V = \frac{4}{3}\pi r^3 \quad (1)$$

$$\rho = \frac{M}{V} \quad (2)$$

where $\rho \approx 1.1 \text{ g mL}^{-1}$ and $M = 108.548 \text{ g mol}^{-1}$.

The diameter of the structures observed by SFM is twice as large as the calculated value. This can be explained by considering that the spherical metallodendrimers will flatten out on the surface. The hard core diameter of 7 nm for spherical assemblies of G_5 doubles to *ca* 15 nm for the half-spheres on the surface and the height is decreased as reported above. The apparent distortion compared with a globular shape might be exaggerated owing to the convolution of the surface structure with the tip shape.¹² Assuming spherical geometry of the molecules with a radius $r = 3.5 \text{ nm}$ and a maximum radius $R = 8 \text{ nm}$ for the tip apex, the measured diameter could be as large as $D = 4 \sqrt{Rr} \approx 21 \text{ nm}$.

CONCLUSIONS

By using a non-covalent synthesis route, metallodendrimers up to G_5 were assembled with molecular weights of over 100 000 Da and with an approximate size of 7 nm in diameter. TM-SFM studies on thin films cast on a graphite or mica surface showed the presence of spherical assemblies in the expected size range. Further research will be concentrated on the introduction of functionality (*e.g.* porphyrins, redox or catalytically active centers) in these nanosize structures.

EXPERIMENTAL

All chemicals used were of reagent grade and were used as received. The syntheses of $BB\text{-Cl}^{11}$ and of G_0 , G_1 , G_2 and G_3 have been described previously.⁴ The instrument used for SFM was a Nanoscope III operated in the tapping mode. The force measurements were performed with Si probes at their fundamental resonance frequency of about 300 kHz. The radius of the probe apex was less than 10 nm. Nitromethane was washed with 1 M HCl and water and distilled from CaCl_2 . Nitromethane solutions with concentrations between 0.2 and 1.2 mg ml^{-1} were spin-cast on clean surfaces at 1000 rpm.

ESMS 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–chloro-

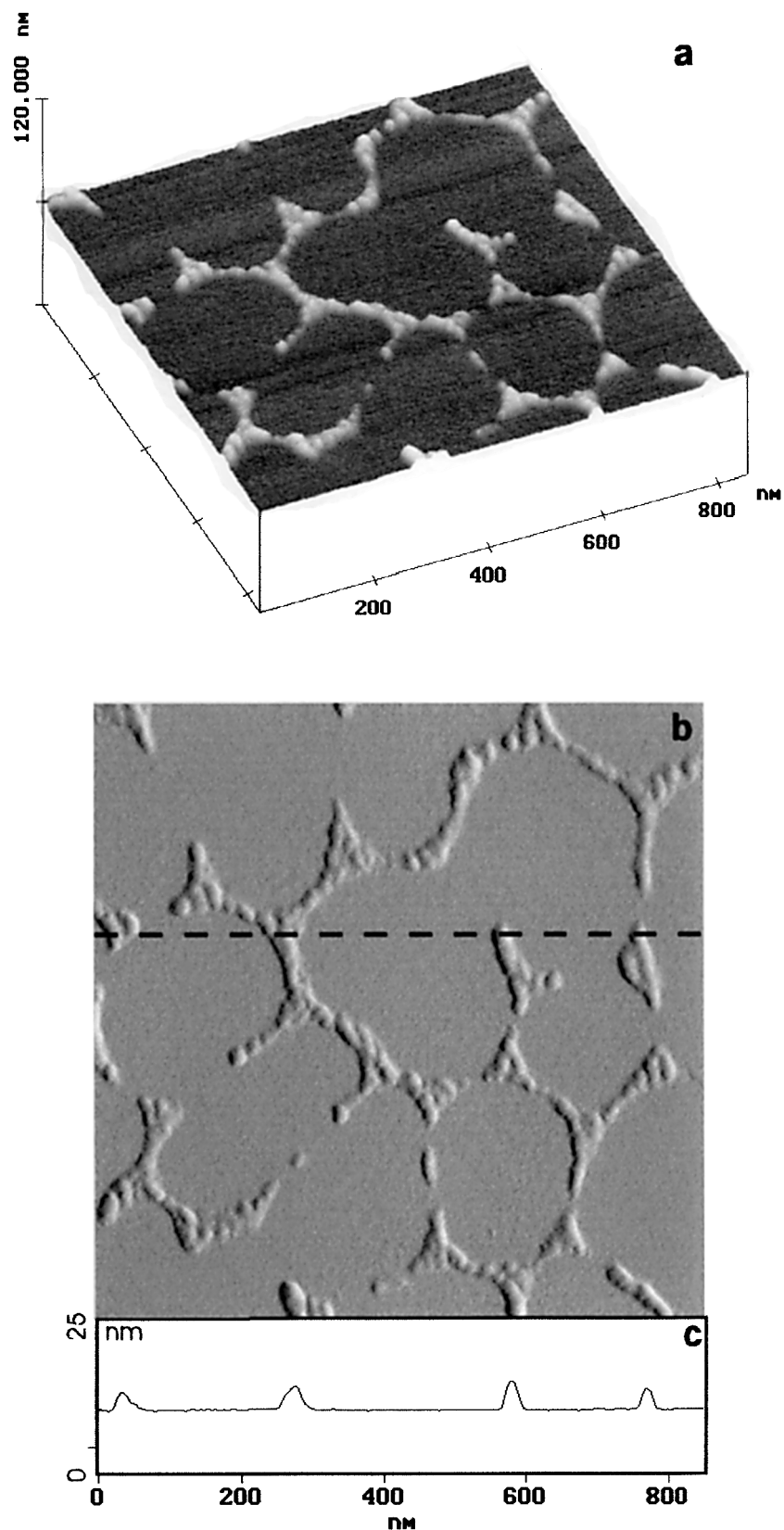


Figure 4. Tapping scanning force micrographs of G_5 spin cast from a 0.2 mg ml^{-1} solution in nitromethane on freshly cleaved mica. (c) Amplitude signal; (b) height image (light areas correspond to elevated structures); (a) stereoscopic projection of (b)

form) into a 10 ml gas-tight SGE syringe. The sample was presented to the source at a rate of $10 \mu\text{l min}^{-1}$ of nitromethane–chloroform solution *via* a Cole Palmer Model 74900 syringe pump. Loop injection was accomplished by using a Rheodyne Model 7125 injection valve with a $10 \mu\text{l}$ loop.

General procedure for the controlled assembly of metallodendrimers. To solution of **G**₀ (2.50 mg, $1.61 \mu\text{mol}$) in CH_2Cl_2 (5 ml) were added $30.0 \mu\text{l}$ ($4.83 \mu\text{mol}$) of a freshly prepared stock solution of AgBF_4 (0.1611 M). The mixture was stirred for 5 min and subsequently **BB-CI** (5.30 mg, $4.83 \mu\text{mol}$) was added. The mixture was evaporated to dryness and the residue dissolved in nitromethane (5 ml). To assemble **G**₁ all the solvent was evaporated under reduced pressure. The residue was dissolved in nitromethane and evaporated to dryness again. Crude **G**₁ was dissolved in nitromethane (5 ml) and AgBF_4 ($59.4 \mu\text{l}$, $9.56 \mu\text{mol}$) was added. After stirring for 5 min. **BB-CI** (10.6 mg, $9.6 \mu\text{mol}$) was added to assemble **G**₂. Repeating this procedure (activation with AgBF_4 and addition of new building blocks) two or three more times, **G**₄ and **G**₅ were assembled in a one-pot procedure. After filtration through Hyflo/cotton to remove AgCl , nitromethane was evaporated and **G**₄ was obtained as a yellow solid (76.8 mg, 90%). M.p. $154\text{--}156^\circ\text{C}$. $^1\text{H NMR}$ (CD_3NO_2), δ 7.77–7.68 (m, 372 H, SPh), 7.56–7.44 (m, 696 H, SPh + ArH), 6.8 (s, 186 H, $\text{Ar}_{\text{Pd}}\text{H}$), 5.0 (s, 186 H, CH_2O), 4.5 (bs, 372 H, CH_2S), 3.9 (s, 90 H, CH_2CN); ESMS, m/z 49 878 ($[\text{G}_4^{39}\text{BF}_4]^+$, calculated 49 905); IR (KBr), 2290 cm^{-1} ($\text{C}\equiv\text{N}$). Analysis: calculated for $\text{C}_{2319}\text{H}_{1902}\text{B}_{45}\text{N}_{45}\text{O}_{93}\text{F}_{180}\text{S}_{186}\text{Cl}_{48}\text{Pd}_{93}\cdot 25\text{CH}_3\text{NO}_2$, C 51.30, H 3.63, N 1.79, Cl 3.10; Found, C 50.44; H 3.54; N 1.82, Cl 2.87%.

After filtration through Hyflo/cotton to remove AgCl , nitromethane was evaporated and **G**₅ was obtained as a yellow solid (140.2 mg, 85%), m.p. $149\text{--}151^\circ\text{C}$, which was characterized only by $^1\text{H NMR}$ and IR spectroscopy. $^1\text{H NMR}$ (CD_3NO_2), δ 7.77–7.68 (m, 756 H, SPh), 7.56–7.44 (m, 1416 H, SPh + ArH), 6.8 (s, 378 H, $\text{Ar}_{\text{Pd}}\text{H}$), 5.0

(s, 378 H, CH_2O), 4.5 (bs, 756 H, CH_2S), 3.9 (s, 186 H, CH_2CN); IR (KBr), 2289 cm^{-1} ($\text{C}\equiv\text{N}$).

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