NANOSIZE METALLODENDRIMERS

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Abstract: Building blocks have been designed for the non-covalent formation of nanosize assemblies. As non-covalent interactions coordination chemistry and hydrogen bonding have been used. The self-assembly process leads to spherical assemblies with diameters in the range of 100 to 400 nm, with standard deviations in the order of 10-15 %. The controlled assembly approach allows a precise controll of size and assemblies with molecular weights up to 10,000 Dalton have been realized. Finally, we have developed a strategy in which hydrogen bonding and coordination chemistry can be applied "orthogonally"

INTRODUCTION

There is an increasing demand to develop new methods to make structures with dimensions in the nanometer range. Grossly speaking two methods can be envisioned. One is the "nanophysical" approach in which structures are made starting from a bulk substrate. Lithography and etching techniques are frequently used, but the physical limits are constraining improvements. Alternatively, a "nanochemical" approach can be followed, in which the structures are built from "the atom up". An attractive feature of this approach is that in principle very precise control can be reached over the ultimate architecture. We have started an intensive program to develop new concepts to make well-defined structures of nano-size dimensions. We feel that one has to rely on assembly and self-assembly processes (Ref. 1), because the covalent build-up is too laborious and time intensive. Here, our recent results will be briefly described on the self-assembly and controlled assembly of metallodendrimers. The key component in our strategy is the use of (reversible) coordination

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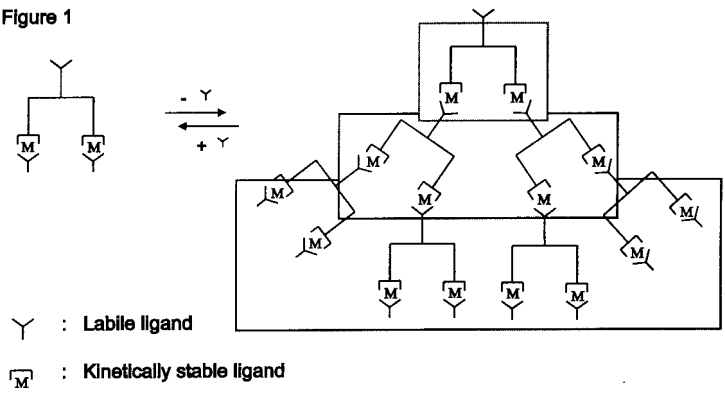
chemistry. Dendrimers are attracting a lot of interest these days, because they posses a unique architecture (spherical after a certain generation) and can in principle be made in monodispers form. They can be synthesized in a divergent or convergent way (Ref. 2). In the divergent approach building blocks are added generation after generation, starting from a polyfunctional core. In the convergent approach wedges, or dendrons, are made first, which are added in the final step to a polyfunctional core. Most dendrimers reported to date are organic in nature and made by the formation of covalent bonds.

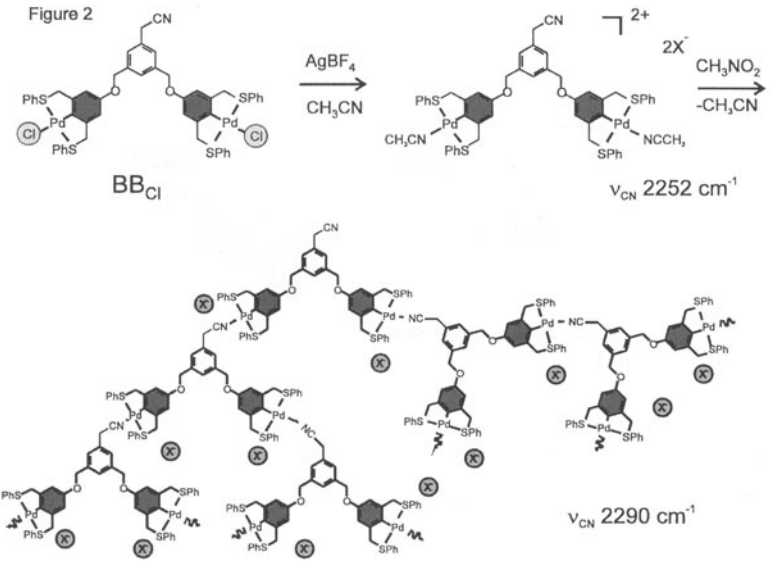
RESULTS AND DISCUSSION

Self-assembly Our first approach is schematically depicted in Figure 1. Two metal centers are bound kinetically inert to a "pincer" type ligand bridged via a spacer that contains a ligand that **cannot** intramolecularly bind to the metal centers. The fourth coordination position of the metal is occupied by a weakly bound ligand (e.g. acetonitrile). After removal of this weakly bound ligand, the ligand in the dinuclear building block will occupy the fourth position intermolecularly. This will create two reaction sites to which two building blocks can be added, etc.

Figure 1

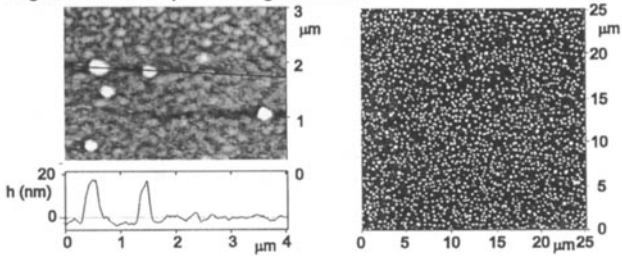


The building block that satisfies all demands is shown in Figure 2 (BB_{Cl}) (Ref. 3). It is made as the bis-chloride adduct, which is an overall neutral compound that can be easily purified by column chromatography. The chlorides can be quantitatively removed by reaction with two equivalents of $AgBF_4$ in acetonitrile.



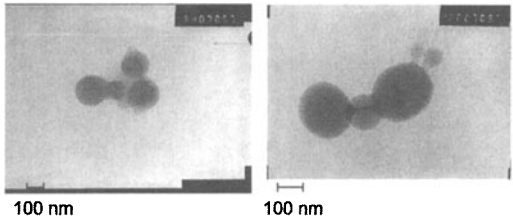
After removal of the two coordinated acetonitriles by gentle heating in nitromethane (polar but non-coordinative) the formation of large assemblies is induced. The ^{1}H NMR spectrum of this assembly shows broad peaks, which sharpens after the addition of small amounts of acetonitrile. Removal of the acetonitrile restored the original broad spectrum, showing that the assembly and disassembly is a completely reversible process. The size as determined by QELS (quasi-elastic light scattering) in nitromethane solution is 180 nm. The AFM picture after spreading the assembly on a glass or gold support is given in Figure 3. The mean size of the particles is 205 nm with a standard deviation in the order of 25-30 nm.

Figure 3: AFM of spheres on gold surface:



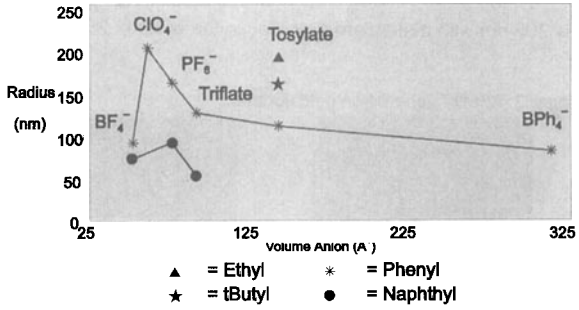
Finally, we have characterized the assemblies by TEM (Figure 4). The contrast is easily obtained without the need of shadowing, as a result of the presence of a large number of palladium ions. This is a direct proof of the concept shown in Figure 1.

Figure 4: TEM images



In order to control the size of the metallodendrimers a structural variation was carried out. The substituents on the sulfurs were varied from ethyl, to *tert*-butyl, to phenyl, and finally to naphthyl. Also the type of counter ion was changed (BF_4^-, ClO_4^-, triflate, tosylate, and BPh_4^-) (Ref 4). This simple structural variation allowed the formation of assemblies in the range of 50 to 200 nm (radius), with a relatively narrow size distribution (standard deviation in the order of 10 to 15 %). In general the larger the substituent and/or counter ion was, the smaller was the assembly (Figure 5). We do not have an explanation for the anomalous behavior of BF_4^-. The phosphorous analogue of BB_{Cl} and G_0 were also made, allowing the incorporation of Ni^{2+}, Pt^{2+}, and Pd^{2+}, but the assemblies proved to be very sensitive to oxidation (Ref. 5).

Figure 5: Sphere size vs. anion



Controlled Assembly In order to synthesize monodisperse assemblies of nanosize dimensions we have changed the strategy a little. In the divergent growth we start from the trifunctional core G_0, which is activated for further growth by removal of the three chloride ligands with $AgBF_4$. To this activated core three equivalents of the building block BB_{Cl} are added giving the first generation (G_1) (Figure 6a). This two-step sequence has been used up to G_5. Generations G_1 to G_4 could be characterized by ES-MS (Figure 6b), showing the molecular ion minus the loss of counter ions and chloride ligands (G_1). The fragmentation observed in the spectrum of G_2 is believed to have taken place in the mass spectrometer (Ref. 6).

Figure 6a

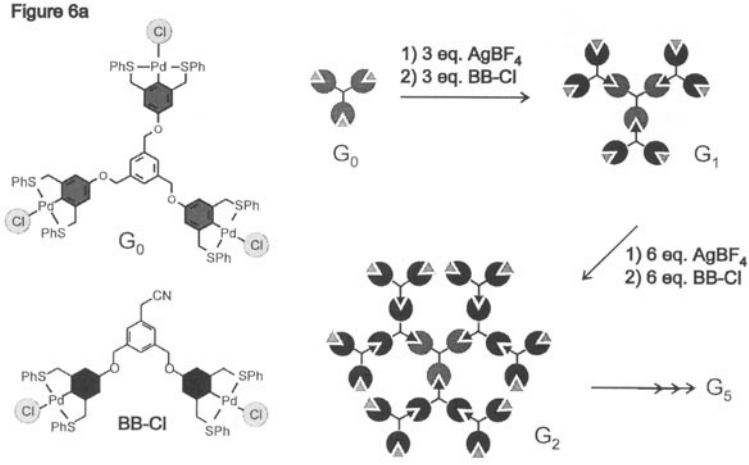
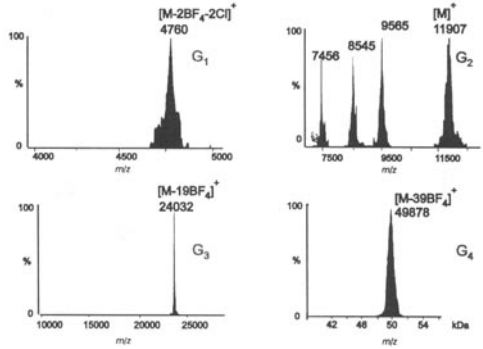
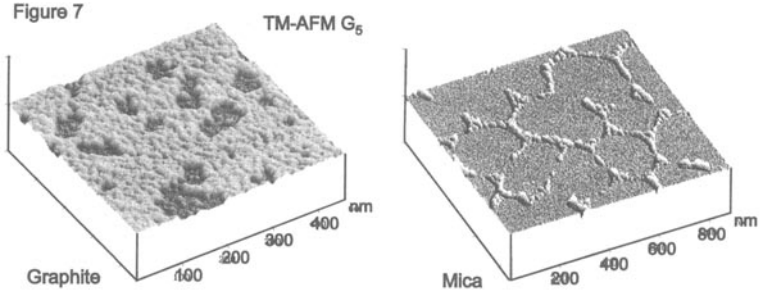


Figure 6b Electrospray Mass Spectra of G_1-G_4



Generation five could not be studied by ES-MS due to the too low resolution of the analyzer, but TM-AFM was successful (Figure 7). Figure 7 shows spherical aggregates with an approximate diameter of 15-20 nm and a height of 4.2 nm (Ref. 7).

Figure 7



Sofar, no true functionality is present in the assemblies. Porphyrins have a.o. interesting optical properties and therefore a porphyrin core and a porphyrin building block have been synthesized (Figure 8) (Ref. 8). With the controlled assembly, assemblies with 6 and 12 porphyrins, respectively, at the outer generation have been synthesized (Figure 9). Similarly, 4 or 8 porphyrins have been assembled around the tetrafunctional porphyrin core (Figure 9). The MALDI-TOF spectra of these assemblies show the molecular ion at 4961 and 11547 Dalton, respectively.

Figure 8

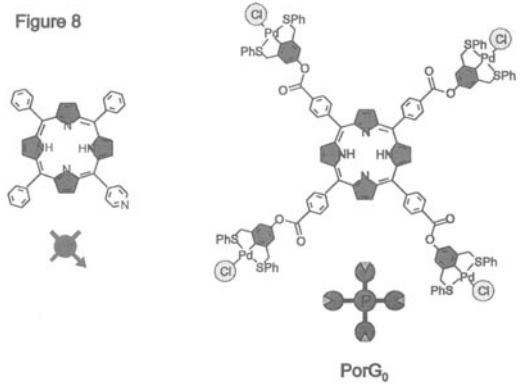
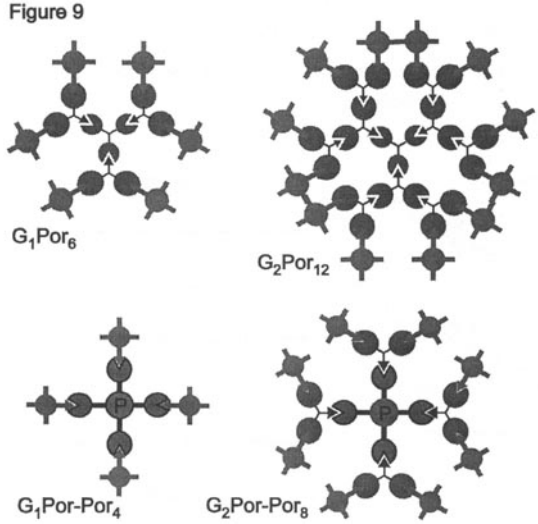
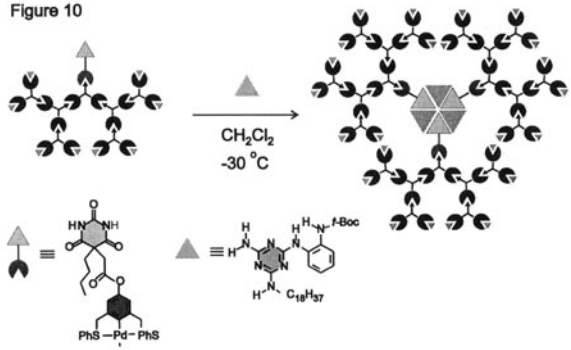


Figure 9



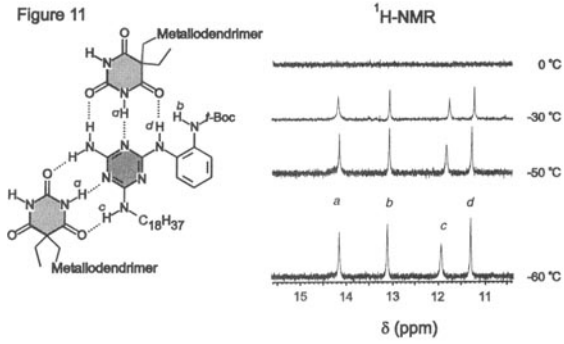
Rosettes In order to enlarge the scope of the assembly process we have combined the coordination chemistry with hydrogen bonding. Whitesides and co-workers have explored the hydrogen bonding of barbiturates and melamines extensively (Ref . 9). If melamines with large substituents on two of the amino groups are used the formation of a [3+3] hydrogen bonded species, a so-called *rosette*, is favored over non-cyclic species. We have synthesized a barbiturate with a pincer-palladium complex attached to it, to which up to three generations metallodendrimer were added with the controlled assembly approach (Ref. 10). Addition of a sterically demanding melamine derivative to a solution in CD_2Cl_2 of the barbiturate gave spontaneously the formation of rosettes (Figures 10 and 11).

Figure 10



The low temperature NMR spectra clearly showed the hydrogen-bonded protons at low field, which could all be assigned by 2D NOESY, COSY, and TOCSY experiments. The hydrogen bonding did not interfere with the coordination chemistry, making it an "orthogonal" tool in the development of new assembly strategies.

Figure 11



CONCLUSIONS

In this short resume three strategies are discussed to synthesize nanosize structures. The self-assembly approach allows the fast formation of spherical assemblies with diameters of 100 to 400 nm, with a relatively narrow size distribution. Monodisperse assemblies can be made with the controlled assembly approach, which comprises a simple two-step procedure. The third method exploits both coordination chemistry and hydrogen bonding, thus greatly enlarging the scope of these non-covalent strategies.

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