

Self-assembly of hyperbranched spheres; correlation between monomeric synthon and sphere size

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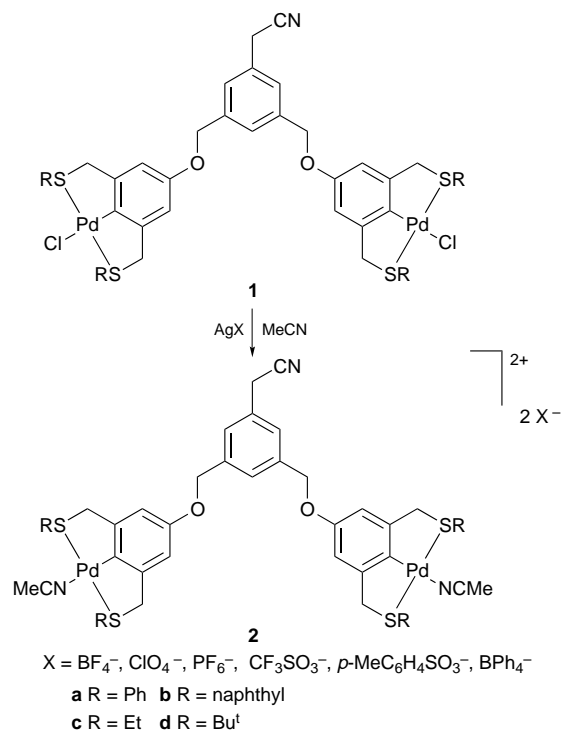
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Light-scattering experiments show that the size of self-assembled hyperbranched spheres can be varied from 100 to 400 nm, by variation of the building block structure and/or the counter anions.

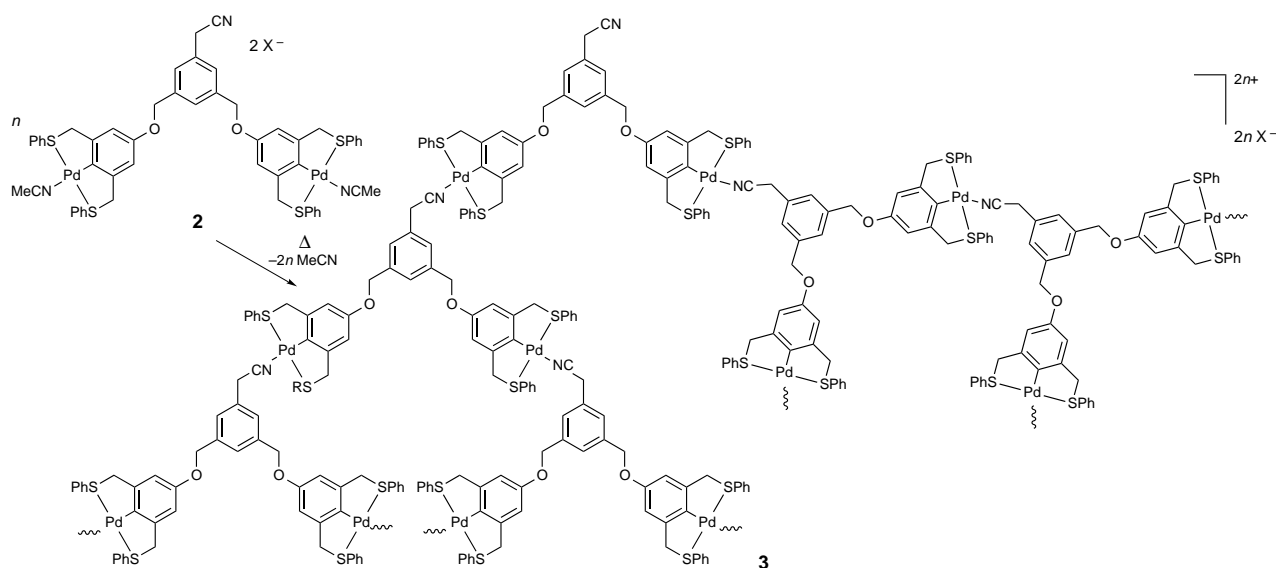
Recently, coordination chemistry has been exploited as a useful tool to form well-defined three-dimensional architectures *via* self-assembly. Transition metals can be used to control the geometry of architectures such as molecular squares,¹ helicates² and dendrimers.^{3,4} Previously, we have reported the stepwise, non-covalent synthesis of dendrimers of nanosize dimensions *via* assembly of bis-Pd 'pincer' complexes **1** (R = Ph).⁵

The same building blocks can be used for the self-assembly of **2** (X = BF₄⁻, R = Ph) into very large non-covalent structures. The size distribution of our self-assembled organopalladium spheres was remarkably narrow (AFM: mean size 200 nm, σ *ca.* 30 nm).⁶ These initial results prompted us to systematically study the influence of structural variations in the building block **1** and counter ions (X⁻) on the size of the spheres, because the bulkiness of the non-coordinating anions and thioether moieties are likely to determine the assembly process.

The different anions were introduced by reacting the Pd-Cl complex **1** with the appropriate silver salt in MeCN (Scheme 1).[†] AgCl precipitated immediately giving the corresponding acetonitrile complex **2**. We have synthesized phenyl thioether building blocks with BF₄⁻, ClO₄⁻, PF₆⁻, CF₃SO₃⁻, *p*-MeC₆H₄SO₃⁻ and BPh₄⁻ counteranions. For **2b** (R = naphthyl) the BF₄⁻, PF₆⁻ and CF₃SO₃⁻ systems were synthesized.



Scheme 1 Structural variation in the building blocks



Scheme 2 Schematic self-assembly of hyperbranched coordination polymers

Only the $p\text{-MeC}_6\text{H}_4\text{SO}_3^-$ could be isolated of the alkyl thioethers **2c**, **2d** because the Pd complexes were unstable with BF_4^- , PF_6^- and CF_3SO_3^- anions.

Removal of all acetonitrile by repeated evaporation and redissolving the residue in nitromethane results in the intermolecular coordination of the cyano groups of the building blocks to yield hyperbranched coordination polymers **3** (Scheme 2).[†]

The size of the resulting assemblies was determined by quasi-elastic light-scattering (QELS). In general, we observed that larger anions or bulkier thioethers, gave smaller spheres (Fig. 1). The naphthyl thioether with PF_6^- and CF_3SO_3^- anions shows a similar decrease in size as the phenyl analogues.[§] Comparing the entries for the PF_6^- , CF_3SO_3^- and $p\text{-MeC}_6\text{H}_4\text{SO}_3^-$ anions it is evident from Fig. 1 that with increasing size of the thioether groups smaller particles are formed.

In addition, AFM and TEM were used to study the shape of some of the assemblies. Spherical assemblies are clearly observed.[¶] From AFM data, sizes of 100 (± 20) nm for **3b** ($X^- = \text{BF}_4^-$) and of 110 (± 20) nm for **3b** ($X^- = \text{CF}_3\text{SO}_3^-$) were measured. This is in good agreement with the QELS data (140 and 104 nm, respectively). The TEM image shows assemblies of 225 nm for **3a** ($X^- = p\text{-MeC}_6\text{H}_4\text{SO}_3^-$), in good agreement with QELS data (220 nm).

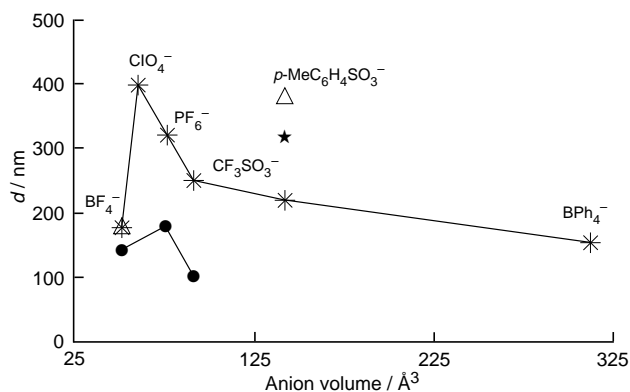


Fig. 1 Sphere size vs. anions as measured by QELS in MeNO_2 at room temp. ($\Delta = \text{Et}$, $* = \text{Ph}$, $\star = \text{Bu}$, $\bullet = \text{naphthyl}$)

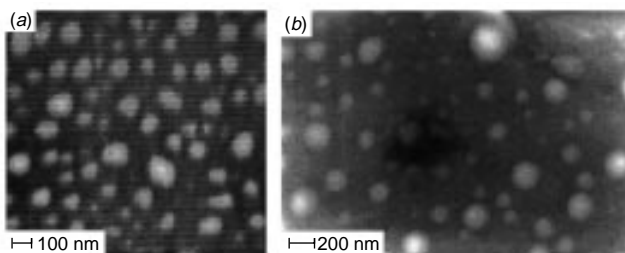


Fig. 2 (a) AFM image of **3b** ($X^- = \text{CF}_3\text{SO}_3^-$) and TEM image of **3a** ($X^- = p\text{-MeC}_6\text{H}_4\text{SO}_3^-$)

The observed size dependency can be rationalized by combining the size of the anion and the distribution of charge in the polyelectrolyte assembly. The assembly process stops when the anions inside the sphere can no longer compensate for the accumulating charges and start to occupy the surface. Consequently, the different sizes of the spheres are determined both by the size and the charge density of the anion and the structure of bis-Pd complex.

The hyperbranched structure with a dense outer surface is supported by disassembly experiments that give information on kinetic stability. When *ca.* 20 equiv. of acetonitrile was added to a nitromethane solution of the spheres, these disassembled slowly in the course of 15–30 min. This slow disassembly indicates that acetonitrile can not easily penetrate the outer shell of building blocks. With a larger nitrile, like benzonitrile, the disassembly process is hardly evident, even after heating to 70 °C for 15 min. These data are indicative that a branching architecture leads to a closely packed surface, as has been observed in dendrimer chemistry.⁷

Footnotes

[†] The Pd–Cl complexes were fully characterized by ^1H and ^{13}C NMR, FTIR, FAB–MS and elemental analysis. ^1H NMR shows a characteristic shift at δ 4.5 (br) for the CH_2S protons of the Pd-complex. Coordination of CN to the Pd-centres was evidenced by FTIR (2290 cm^{-1}).

[‡] ^1H NMR spectra in CD_3NO_2 of all assemblies show broad peaks, in agreement with large structures. Addition of CD_3CN sharpened the spectra, which means that the self-assembly and disassembly processes are completely reversible. The original broad spectrum is restored when the solution is evaporated completely and redissolved in acetonitrile-free nitromethane.

[§] The size of the anion was calculated using the option for Connolly Surfaces in CERIU2.⁸ For unknown reasons the BF_4^- anion behaves anomalously. The anion is, even inside the hyperbranched polymer, probably solvated and therefore appearing larger than the naked anion.

[¶] The size distribution could not always be derived from these data because of (extensive) clustering. In the case of **3b** ($X^- = \text{PF}_6^-$) only thin films were observed with AFM.

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