Well-Defined Metallodendrimers by Site-Specific Complexation

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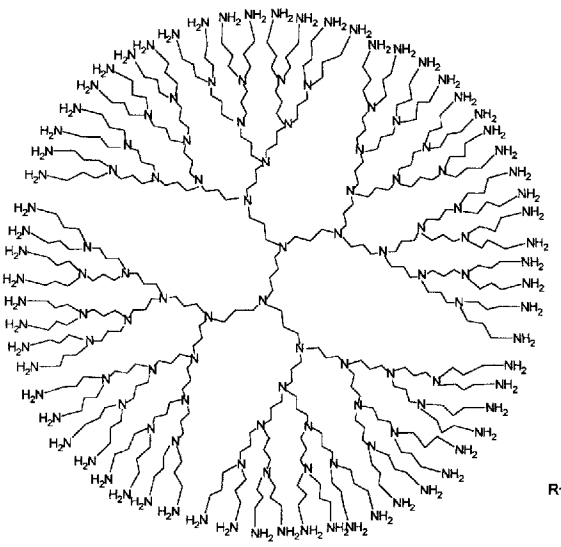
Strong multiple complexation of transition metal ions, Cu(II), Zn(II) and Ni(II) with different generations of well-defined poly(propylene imine) dendrimers as multi(tridentate) ligands has been used to construct nanoscopic assemblies of defined structure and size incorporating a distinct number of metal ions from 2 up to 32.

Metal-containing architectures of nanoscopic dimensions are thought to create new materials with promising electronic, magnetic or catalytic properties[1]. Polymers with metal-coordinating side groups[2,3] or amphiphilic assemblies[4] are most commonly used in this field. However, their three-dimensional architectures are less defined, due to the polydispersity of polymers and the dynamic character of amphiphilic assemblies. Recently, well-defined structures of dendritic macromolecules, like **1** (Scheme 1), have become available. These macromolecules emanate from a central core with a branching point at each monomer unit and possess a defined number of generations and end groups[5]. Therefore, dendrimers are well suited for nanoscopic materials, e.g. in the complexation of metals. Organometallic complexes have been used in the construction of assembly points of dendritic branches[6–9] and in end-group functionalization of dendrimers[10–12].



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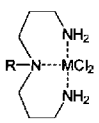

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It has been reported that the bis(3-aminopropyl)amine functionality acts as a strongly complexing tridentate coordinating site for various transition metals (**2**)[13–16]. Cu(II) complexes with bis(3-aminopropyl)amine are formed with high equilibrium constants of $K = 10^{14}$ M^{-1}[17]. Furthermore detailed insight into many complexes is obtained from single crystal X-ray data. Here we demonstrate that, with different generations of poly(propylene imine) dendrimers [DAB-*dendr*-$(NH_2)_n$; n = 4, 8, 16, 32, 64] as multifunctional ligands, it is possible to prepare metal-containing nanoscopic structures incorporating a well-defined number of up to 32 transition metal ions such as Cu(II), Zn(II), and Ni(II). Essential to this result is the combination of the high degree of definition attainable for poly(propylene imine) dendrimers and the metal-coordinating properties of the bis(3-aminopropyl)amine end groups.

Poly(propylene imine) dendrimers are synthesized in a stepwise manner from a central core, leading to a doubling of the end groups in every next generation up to 64 for the fifth generation (**1**)[18]. A high degree of definition of these structures has been established with electrospray mass spectroscopy, revealing a monodispersity of 1.0018 for the highest generation (**1**, n = 64)[19]. The addition of metal(II)chloride (MCl_2, with M = Cu, Zn, and Ni) in methanol to methanolic solutions of the dendrimers of different generations yielded the exclusive formation of the dendritic poly-bis(3-aminopropyl)amine–MCl_2 complexes. We have studied both the formation and the structure of these metallodendrimers with a number of different techniques.

Addition of $CuCl_2$ to different of generations poly(propylene imine) dendrimers in methanol results in the immediate formation of a deep blue color associated with a broad absorption band at 620 nm belonging to the copper d–d transition, typical for a five-coordinated Cu(II) species with a square-pyramidal or trigonal-bipyramidal ligand field[20]. Careful titration, while monitoring the band at 620 nm, reveals that multiple 1:2 complexes are formed (Figure 1). The constant slope in each titration curve demonstrates that the Cu(II) ions are strongly bound to the dendrimers, irrespective of the generation and the number of sites already occupied. The extinction coefficient of fully loaded Cu(II) poly(propylene imine) dendrimers of different generations increases linearly with the total number of end groups when

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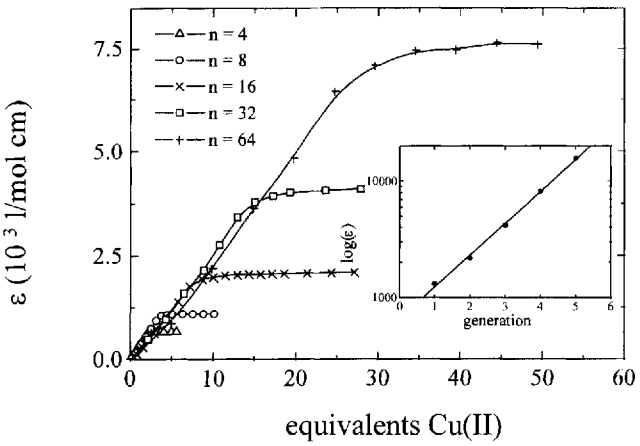
going from the first to the fifth generation (inset Figure 1). Multiple Cu(II) complexation for each generation results in molecules with 2.1 ± 0.1, 3.7 ± 0.2, 8.2 ± 0.3, 15.2 ± 0.5, and 30 ± 2 copper nuclei, respectively. These numbers are very close to $n/2$ for each generation and thus confirm the high definition of the poly(propylene imine) dendrimers. The exclusive interaction of Cu(II) with the bis(3-aminopropyl)amine end groups was further established using poly(propylene imine) dendrimers in which the primary amines had been converted into amides[21]. For amide end groups no complexation is observed, demonstrating the absence of interaction of Cu(II) with the inner tertiary amines.

Figure 1. Titration curves for DAB-*dendr*-$(NH_2)_n$ with $CuCl_2$ in methanol; inset shows the extinction coefficients for the fully occupied dendrimers of different generations



Characterization of the Cu(II) dendrimer complexes by ESR spectroscopy for all generations revealed an essentially isotropic four-line pattern (g_{iso} = 2.11) when less than one Cu(II) cation is present per dendrimer (Figure 2, for n = 4 as an example). When the number of Cu(II) ions per dendrimer exceeds one, a single broad signal is observed, caused by exchange interactions between the copper centers. Increasing the Cu(II)/NH_2 ratio to a value of 0.5, results in the emergence of the ESR signal of free $CuCl_2$ in MeOH (Figure 2), indicating that all coordinating sites are occupied in full agreement with the 1:2 complexation found in the UV/Vis titration experiment. The complex exhibits an ESR spectrum of axial symmetry at 130 K in a frozen MeOH matrix when using less than one Cu(II) ion per dendrimer, with $g_{\|}$ = 2.223, $g_{\perp}$ = 2.048, and $A_{\|}$ = 175 × 10^{-4} cm^{-1}, characteristic of a Cu(II) complex involving three nitrogen nuclei[22]. We propose a geometry between trigonal-bipyramidal and square-pyramidal for the dendrimer Cu(II) coordination complex, analogous to the X-ray structure of the copper(II) chloride complex with *N,N,N',N'*-tetrakis(3-aminopropyl)-1,5-diamino-3-oxapentane[14].

The Cu(II) complexes show one electrochemically irreversible reduction wave in aqueous solution when studied with cyclic voltammetry. E_{red} shifts to higher potentials when going to higher generations (Table 1). This shift is more pronounced for the two highest generations.

The Cu(II) complexes of the fifth generation dendrimer could be visualized by using transmission electron microscopy (TEM). The micrographs show the presence of spherical structures with a radius of 3 ± 1 nm (Figure 3). This value is comparable to the radius of gyration of the uncomplex dendrimer ligand of 1.4 nm[23]. We conclude that unimolecular nanoscopic structures are formed.

Figure 2. ESR spectra of DAB-*dendr*-$(NH_2)_4$ upon titration with $CuCl_2$ in methanol with (a) 0.4, (b) 1.1, (c) 1.9, and (d) 2.6 moles of $CuCl_2$ per mole DAB-*dendr*-$(NH_2)_4$

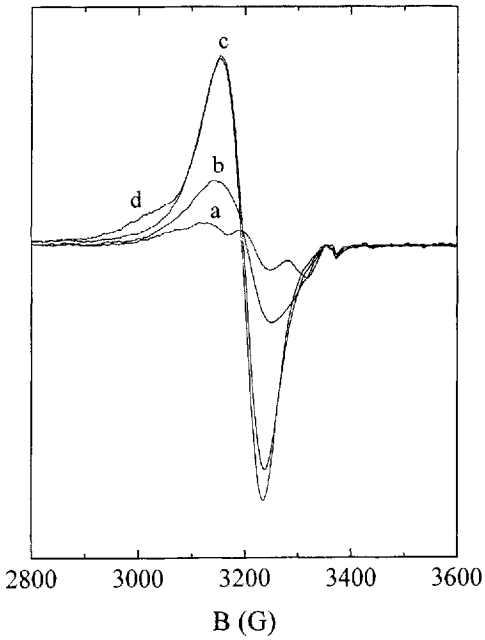
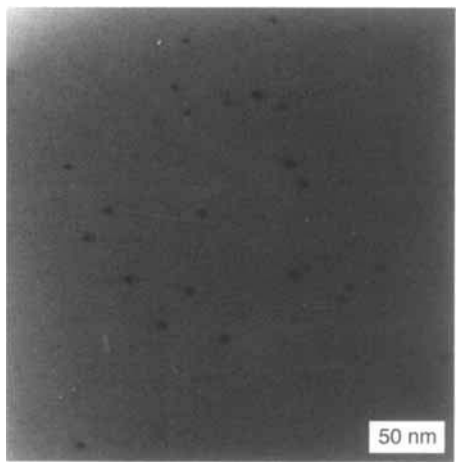


Table 1. Reduction potentials of different generations dendrimers fully occupied with $CuCl_2$

Generation	1	2	3	4	5
E_{Red}[a] (V)	−0.15	−0.15	−0.12	−0.04	0.05

[a] Measured in water with $NaClO_4$ as supporting electrolyte (0.1 M) vs. SSCE.

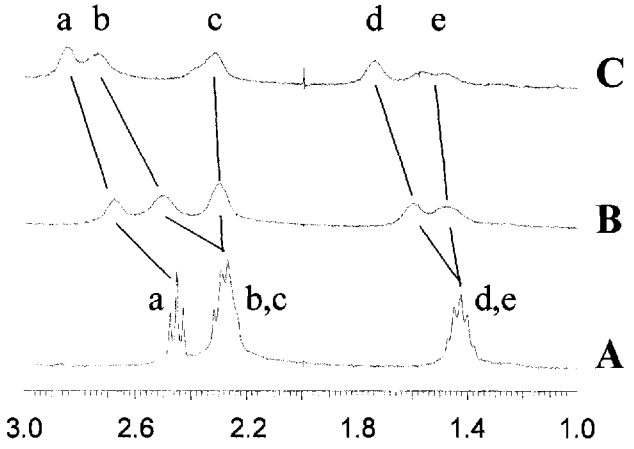
Figure 3. TEM micrograph of a 10^{-4} M aqueous solution of [Cu_{32}-DAB-*dendr*-$(NH_2)_{64}$]Cl_{64} (not stained); bar represents 50 nm



The formation of the complexes of the dendritic polyamines with $ZnCl_2$ in deuterated methanol can be followed by

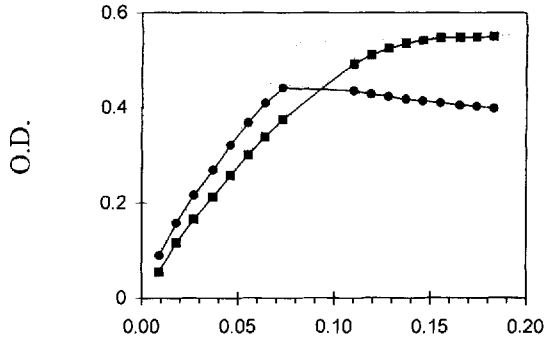
^{1}H-NMR spectroscopy by a down-field shift for the protons present in the outer tier (Figure 4). This indicates that complexation of Zn(II) occurs exclusively at the periphery of the dendrimers via the primary amines and the tertiary amines of the penultimate generation. No further shift of the proton resonances is observed when the Zn(II)/NH_2 ratio exceeds 0.5, supporting the proposed three-nitrogen coordinated Zn(II) cation, which is in agreement with X-ray data of a model compound[15].

Figure 4. ^{1}H-NMR spectra (δ scale) of DAB-*dendr*-$(NH_2)_{32}$ upon titration with $ZnCl_2$ in deuterated methanol at ratios of 0 (**A**), 8 (**B**), and 14 (**C**) moles $ZnCl_2$ per mole DAB-*dendr*-$(NH_2)_{32}$ (10^{-3} M solution); assingment: (**a**) protons α to primary amines; (**b**) protons γ to primary amines; (**c**) protons α to all tertiary amines except those in the outer tier; (**d**) protons β to primary amines; (**e**) protons β to all tertiary amines except those in the outer tier



Complexation of $NiCl_2$ with the poly(propylene imine) dendrimers revealed a somewhat different behavior as compared to $CuCl_2$ and $ZnCl_2$. Although the first generation dendrimer (n = 4) shows the same 1:2 ratio for complexation of Ni(II) to NH_2 end groups, all higher generations exhibit 1:4 complexation when the Ni(II) concentration is low compared to that of the polyamine. At higher Ni(II) concentrations, 1:2 complex is found between Ni(II) and the NH_2 end groups as evidenced from a reverse titration experiment in which aliquots of poly(propylene imine) dendrimer were added to a $NiCl_2$ solution (Figure 5). By monitoring the *d*–*d* absorption at 640 nm[20,24], a singularity is observed at a Ni(II)/NH_2 ratio of 1:2, while the absorption at 680 nm exhibits a singularity at a ratio of 1:4. Two different coordination spheres have also been found in complexes of Ni(II) with bis(3-aminopropyl)amine[17]. We propose that a low Ni(II)/NH_2 ratios, a site involving two bis(3-aminopropyl)amine end groups of the same dendrimer is formed, followed by a site with only one tridentate end group when the ratio of Ni(II) to dendrimer is increased (Scheme 2). The first complex is tentatively attributed to octahedrally coordinated Ni(II) as in bis[bis(3-aminopropyl)amine]nickel(II) perchlorate[16]. Apparently, the dendrimer can act as a multiple bis(tridentate) ligand, despite the restricted flexibility of the outer arms. For the lowest generation (n = 4) such a complex is not formed, possibly due to geometric constraints. In the second complex, Ni(II) is only coordinated by three nitrogen nuclei, probably in a similar fashion to Cu(II) and Zn(II).

Figure 5. Absorption of the *d*–*d* band of the Ni(II) complex at 640 nm (–•–) and 680 nm (–■–) recorded upon titration of Ni(II) with DAB-*dendr*-$(NH_2)_{32}$ in methanol (optical density corrected for dilution)



$$n/4\ Ni^{2+} + \text{DAB-}dendr\text{-}(NH_2)_n \rightleftharpoons [Ni_{n/4}(\text{DAB-}dendr\text{-}(NH_2)_n]^{n/2+}$$

$$n/4\ Ni^{2+} + [Ni_{n/4}(\text{DAB-}dendr\text{-}(NH_2)_n]^{n/2+} \rightleftharpoons [Ni_{n/2}(\text{DAB-}dendr\text{-}(NH_2)_n]^{n+}$$

n = 8, 16, 32, 64

In conclusion, we have shown that poly(propylene imine) dendrimers can be used as multiple polydentate ligands for Cu(II), Zn(II), and Ni(II). Complexation in methanol at room temperature takes place in a site-selective way in which the bis(3-aminopropyl)amine end group acts as very strong coordinating unit. The relatively high local concentration of metal centers at the periphery does not hamper the complexation proceeding to full conversion. The complexation has been used to construct metal-containing nanoscopic assemblies of defined structure and size incorporating a distinct number of transition metal ions up to 32, providing us with additional information on the high degree of perfection of these poly(propylene imine) dendrimers. The possibility of complexating other transition metals and the use of these metallodendrimers in catalysis are now under investigation.

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