

Chiral dendrimer encapsulated Pd and Rh nanoparticles

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Received (in Cambridge, UK) 22nd January 2008, Accepted 18th February 2008

First published as an Advance Article on the web 17th March 2008

DOI: 10.1039/b801215f

The synthesis of a series of chiral PAMAM dendrimers and the formation of chiral dendrimer encapsulated metal nanoparticles are described.

Expression of chirality is a common feature in materials of both synthetic and natural origin. Homochirality of molecular building blocks such as D-sugars and L-amino acids in macromolecular structures like DNA and proteins accounts for many of the fascinating functions of biological systems. Chirality in artificial and naturally occurring macromolecular systems has been studied extensively raising the question of the origin of chirality in biological macromolecules.^{1,2}

Chirality in metal nanoparticles is a sparsely explored phenomenon mainly due to the lack of reliable preparative procedures. DNA templated synthesis of Ag nanoparticles has been accomplished using both single stranded DNA and double stranded DNA.³ In an elegant study, Schaaff and Whetten have isolated a series of gold–glutathione cluster compounds using gel electrophoresis on polyacrylamide.⁴ The gold clusters were characterised by mass spectrometry and CD and showed a large dependence in the chirality on the molecular weights of the clusters. Au⁰ and Pd⁰ nanoparticles stabilised by (S)-BINAP and (R)-BINAP have also been prepared and the chirality of the Pd⁰ particles has been utilised in the enantioselective hydrosilylation of olefins.⁵ Similarly CdS quantum dots have been prepared using a D-penicillamine stabiliser and the resulting particles also proved chiral.⁶ Chiral mesoporous silica and chiral metal clusters prepared in the presence of a virus-based structure have also been described recently.⁷ The chiral nature of the stabilised metal particles in the above mentioned studies could in principle be a result of several different factors.⁵ Either the metal particle itself has crystallised in a low symmetry (chiral) space group, or alternatively the chiral organic stabiliser has transferred its chirality to the metal particle either by imprinting of the metal surface directly or through-space influences on the electronic structure of the metal particle.

Since Meijer and co-workers described the dendritic box in 1994, many studies using molecular encapsulation in dendrimers have been disclosed, inspiring the use of dendrimers as scaffolds for uses ranging from light-harvesting structures to drug-delivery systems.^{8–10} Encapsulation of molecular species

inside dendrimers provides a fascinating route to well-defined objects of nanometre dimensions depending on the size of the dendrimer.¹¹ These metal particles have potential uses in optical devices, catalysis and drug-delivery to name a few. Dendrimer encapsulated metal particles of well-defined sizes have been reported for a number of different metals including Pd, Pt, Au, Ag, Ni and Cu.^{12–14} The preparation of dendrimer encapsulated metal nanoparticles follows the general protocol for preparation explored in depth by Crooks and co-workers. In brief, a metal salt is absorbed by the dendrimer and the dendrimer encapsulated metal particle is formed by *in situ* reduction of the metal salt by an external reducing agent (Fig. 1).¹¹ Dendrimer encapsulated metal particles in catalysis have been a popular research target and recyclable systems have been prepared for a number of reactions such as hydrogenation of olefins,¹⁵ the Suzuki reaction,¹⁶ the Stille reaction¹⁷ and the Heck reaction.¹⁸

Here we describe the use of a chiral poly(amido amine) (PAMAM) dendrimer as a molecular scaffold for the encapsulation of Pd and Rh metal particles. The resulting chiral particles have a mean diameter of 1.7 nm. We describe for the first time a PAMAM dendrimer that has chirality both at the core of the dendrimer and throughout the internal structure. The surface of the chiral dendrimers is achiral and hydrophobic in nature. These features allow for the formation of

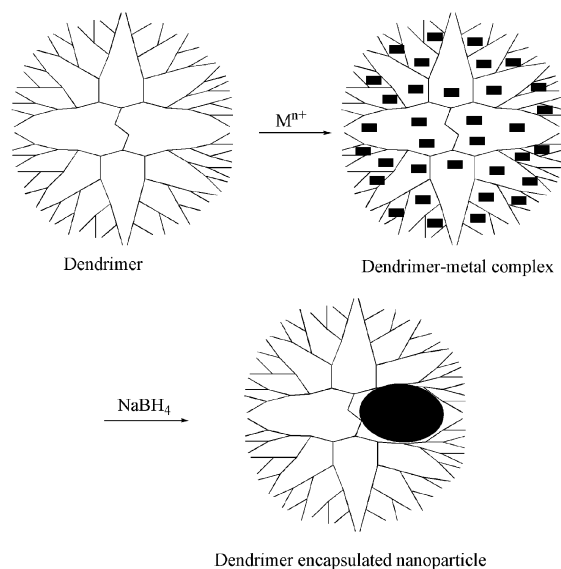


Fig. 1 Synthetic scheme for encapsulation of metal particles inside dendrimers.

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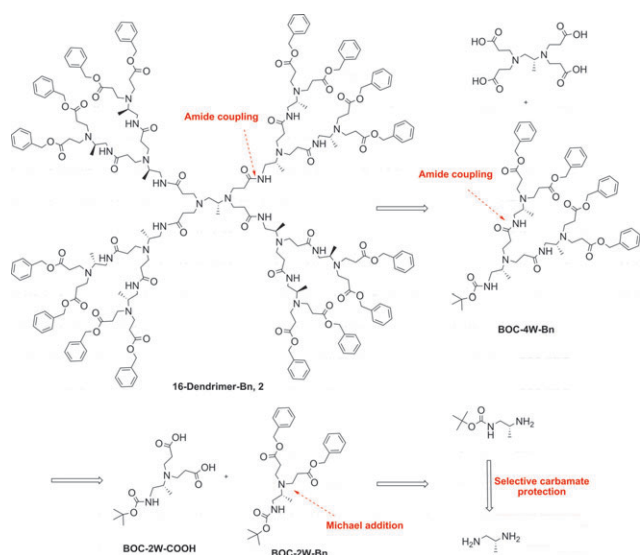


Fig. 2 Retrosynthesis of chiral PAMAM dendrons and dendrimers.

dendrimer–metal complexes inside the dendrimers while at the same time enhancing the solubility of these complexes in organic solvents. As a consequence of these features, reduction of the complexed metal atoms inside the chiral dendrimers results in monodisperse dendrimer encapsulated metal nanoparticles.

The chiral PAMAM dendrimers were synthesised using a protocol developed for the convergent synthesis of racemic (internally branched) PAMAM dendrimers (Fig. 2).¹⁹ In brief, selective BOC protection of (–)-1,2-diaminopropane followed by a double conjugated addition of the free amino group in neat benzyl acrylate gave the protected 2-wedge (BOC-2W-Bn). Synthetically, the BOC amino protection group and the benzyl ester protection groups are orthogonal and separate removal of the protection groups and coupling of these with an amide coupling reagent (PyBOP) gave the 4-wedge (BOC-4W-Bn). Boc deprotection of BOC-4W-Bn and coupling to the benzyl-protected 2-wedge gave the 8-wedge (BOC-8W-Bn). The core of the dendrimer (**4**) was synthesised by conjugate addition of (–)-1,2-diaminopropane in neat benzyl acrylate. The benzyl ester groups were removed by catalytic hydrogenation over Pd/C to give the tetracarboxylic acid. The dendrimers were assembled by BOC deprotection of the three dendrons and amide coupling (using PyBOP as the coupling reagent) to the tetracarboxylic acid core to give the series of chiral PAMAM dendrimers (**1–3**) (Fig. 3).

Pd and Rh encapsulated metal particles were prepared according to the procedure outlined in Fig. 1 with the chiral PAMAM-32 dendrimer as the template.† Mixing 20 equivalents of Pd(OAc)₂ or RhCl₃·3.5H₂O dissolved in 1 : 3 methanol : chloroform with the dendrimer (**1**) resulted in a pale yellow Pd²⁺–dendrimer complex or a pale red Rh³⁺–dendrimer complex, respectively. These were reduced by addition of NaBH₄ in 1 : 3 methanol : chloroform to give pale brown solutions of dendrimer encapsulated Pd⁰ or Rh⁰ metal particles (Pd@PAMAM-32 and Rh@PAMAM-32). The solution of metal particles was extracted with water, dried and evaporated to dryness. The resulting solids were freely soluble in

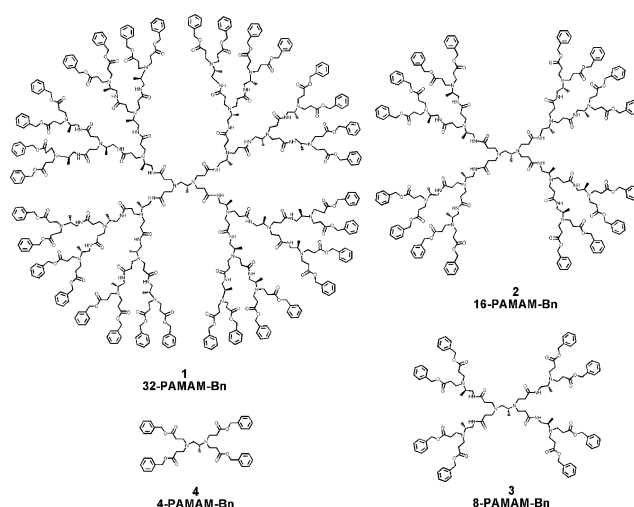


Fig. 3 Structure of the series of chiral PAMAM dendrimers (**1–4**).

dichloromethane but insoluble in alcohol. The metal particles were conveniently stored in the solid state and retained their solubility and monodispersity as tested over a period of several months.

In Fig. 4, the UV-Vis spectra of the chiral dendrimer PAMAM-32, the Pd@PAMAM-32 nanoparticles and the Rh@PAMAM-32 nanoparticles in dichloromethane solutions are shown. The UV-Vis spectra of the Rh@PAMAM-32 and the Pd@PAMAM-32 metal nanoparticles exhibit broad absorption bands in the high energy part of the visible region (up to ~500 nm) (Fig. 4).^{20,21} These bands are ascribed to the electronic structure of the nanoparticles and are thus not proof of specific interactions with the dendrimer. The appearance of the spectrum of the chiral dendrimer PAMAM-32 is illustrative of the general appearance of all spectra of the dendrons and dendrimers shown in Fig. 2 and 3.

In Fig. 5, the CD spectra of the chiral dendrimer PAMAM-32, the Pd@PAMAM-32 nanoparticles and the Rh@PAMAM-32 nanoparticles in dichloromethane solutions are shown.²² The CD spectra (Fig. 5) shows that the UV-Vis bands arising from the electronic structure of the metal particles exhibit different absorptions dependent upon the circular polarisation of the light, that is a Cotton effect. This clearly illustrates that while the interaction between the nanoparticles and the dendrimer cannot be determined directly

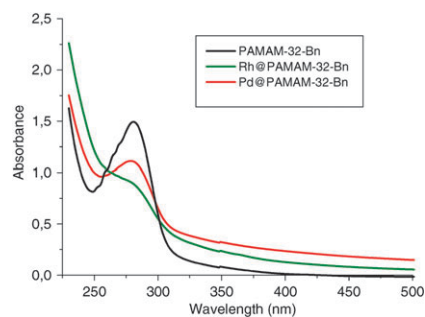


Fig. 4 UV-Vis spectra of the chiral PAMAM-32-Bn dendrimer (**1**) in CH₂Cl₂, the chiral Pd@PAMAM-32 nanoparticles and the Rh@PAMAM-32 nanoparticles.

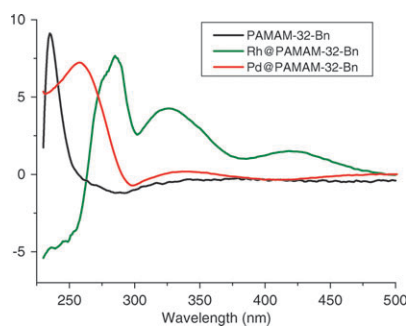


Fig. 5 CD spectra of the chiral PAMAM-32-Bn dendrimer (**1**) in CH_2Cl_2 , the chiral Pd@PAMAM-32-Bn nanoparticles and the Rh@PAMAM-32-Bn nanoparticles.

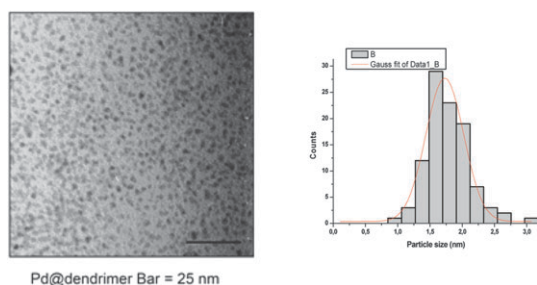


Fig. 6 TEM picture of Pd@PAMAM-32-Bn nanoparticles.

from the UV-Vis spectra it can be seen from the CD-spectra. The absorptions are not only indicative of the interactions between the dendrimer and the nanoparticles but also of the chiral electronic structure of the dendrimer encapsulated metal particles. As a control experiment the Pd metal particles were prepared using a racemic PAMAM dendrimer as the template and this material was indeed CD silent.

Transmission electron microscopy (TEM) was performed on the dendrimer encapsulated metal particles drop cast from a dilute dichloromethane solution on Cu grids and revealed the highly monodisperse nature of the dendrimer encapsulated nanoparticles. The Pd@PAMAM-32 particles have a mean diameter of 1.7 nm as measured from 100 metal particles (Fig. 6). This is in good agreement with the size expected based on data reported for dendrimer templated metal particles in PAMAM dendrimers, and indicates that the metal is indeed encapsulated inside the dendrimer and not merely stabilized by the organic material.¹¹

In conclusion, we have shown, in an unprecedented clean and simple way, that dendrimer encapsulated metal particles can be formed inside chiral PAMAM dendrimers. The chirality of the dendritic scaffold is transferred to the electronic transition of the metal particles and a Cotton effect from the metal nanoparticle UV-Vis bands appears. The coordination of the nanoparticles to the inside of the dendrimer, and not, as in the examples above, by the binding of chiral building blocks to the exterior of a particle, is indicated by the observed CD-signal in a system where the surface groups on the dendrimer

are achiral. This represents an entirely new concept within the field of chiral nanoparticles. The chirality transferred from the dendrimer to the metal particles and the low polydispersity of the particles makes this procedure attractive for the construction of chiral catalysts and chiral materials in general.

Notes and references

† Dendrimer encapsulated metal particles, general procedure: dendrimer **1** (10 mg, 0.00113 mmol) was dissolved in CHCl_3 (0.2 mL) and MeOH (0.1 mL) and the appropriate metal salt (0.0226 mmol, 20 eq.) was added dissolved in CHCl_3 (0.2 mL) and MeOH (0.1 mL). This mixture was stirred for 30 minutes. Then NaBH_4 (1.8 mg, 0.0452 mmol, 40 eq.) dissolved in CHCl_3 (0.2 mL) and MeOH (0.1 mL) was added and the mixture was stirred for 30 minutes. Water was added (3 mL) and the phases were separated. The organic phase was dried (Na_2SO_4), filtered through paper and evaporated to dryness. TEM, UV-Vis and CD were performed on solutions made in spectroscopy grade CH_2Cl_2 .

Instruments: TEM was recorded on a Philips CM-20 electron microscope operated at 200 kV. UV-Vis spectroscopy (Varian CARY 5E) and CD spectroscopy (JEOL J-710 spectropolarimeter) were recorded in the laboratories at the Department of Inorganic Chemistry, University of Copenhagen.

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