ChemComm
www.rsc.org/chemcomm

# A nanoscale dendrimer-based $Fe_{24}$ cluster: synthesis and molecular self-assembly

**Junfeng Geng,[a] Hongwei Li,[b] Wilhelm T. S. Huck[b] and Brian F. G. Johnson*[a]**

[a] *Department of Chemistry, Cambridge University, Lensfield Road, Cambridge, UK CB2 1EW. Fax: +44 (0)1223 336362; Tel: +44 (0)1223 763881; E-mail: bfgj1@cam.ac.uk*

[b] *Melville Laboratory, Chemistry Department, Cambridge University, Lensfield Road, Cambridge, UK CB2 1EW*

***Received (in Cambridge, UK) 24th May 2004, Accepted 1st July 2004***
***First published as an Advance Article on the web 2nd August 2004***

**We report the synthesis, characterisation and self-assembly of a nanoscopic $Fe_{24}$ cluster using an organic dendrimer as a molecular substrate for building up well-defined molecular nanostructures.**

The catalytic and magnetic properties of iron (Fe) nanoparticles have led to their use as nanoscale ferromagnets,[1] catalysts for hydrogenation and isomerization reactions[2] and catalytic seeds for growing carbon nanotubes.[3] Self-assembly of Fe or Fe-containing nanoparticles has been the subject of scientific investigation because of their importance in the development of high-density magnetic memory-storage devices[4] and surface-bound growth of nanotubes or nanowires.[5,6] The design and production of Fe nanoparticles with a controllable size and even a controllable molecular structure is therefore of significant appeal.

In this communication we report the synthesis of a nanoscale $Fe_{24}$ cluster built on an organic dendrimer host molecule. The ability to precisely control the size, atomic number and surface functionality of the nanoclusters distinguishes the synthesised molecules from Fe colloidal nanoparticles. In addition, in view of the general interest in the 'surface behaviour' of the particles, our effort has been extended to the investigation of various surface-driven self-assembly processes.

The starting material, DAB-dendr-$[N(CH_2PPh_2)_2]_8$ **1**, was prepared by double phosphinomethylation of each of the eight peripheral amino groups of a commercially available dendrimer, DAB-dendr-$[NH_2]_8$, through the use of $Ph_2PCH_2OH$ prepared *in situ* from $CH_2O$ and $HPPh_2$.[7] The completeness of the double phosphinomethylation is evident by the observation of the $^{31}P$ NMR spectrum of **1**, which shows a sharp single peak at $\delta = -27.8$ ppm. The compound DAB-dendr-$\{N(CH_2PPh_2)_2$-$[Fe_3(CO)_9]\}_8$, **2**, was prepared by binding eight $Fe_3(CO)_{12}$ cluster units onto the 8[P–N–P] tridentate terminals of compound **1**, thereby forming a nanoscale supercluster with each produced molecule containing 24 Fe atoms.

The reaction was monitored by infrared spectroscopy (IR) in the CO region. Following the progress of the reaction, a new set of bands at 1973 (s), 1937 (vs) and 1885 (m) $cm^{-1}$ appeared.† For comparison, the IR profile of the starting cluster and the purified product is shown in Fig. 1(a) and 1(b), respectively. Evidence for coordination of all the tridentate P atoms to clusters is provided by the observed single peak in the $^{31}P$ NMR spectrum.‡ The significant downfield shift, from $\delta = -27.8$ ppm for the non-coordinated phosphorus to $\delta = 59.5$ ppm in the coordinated product, results from the donation of electrons from the P atoms to the Fe centres. Elemental analysis is in agreement with that calculated for each dendrimer molecule containing eight $Fe_3(CO)_9$ units,§ and also assuming the replacement of three carbonyl ligands in the parent $Fe_3(CO)_{12}$ cluster by the amino nitrogen atom and the two phosphorus atoms of each dendritic terminal. A similar bonding mode was found in our previous studies using a $Ru_5C(CO)_{15}$ cluster.[8]

Molecular imaging of this dendrimer-based $Fe_{24}$ cluster has been achieved by deposition of the molecules on a Si substrate and by subsequent atomic force microscopy (AFM) (Fig. 2a).¶ The topographical height measurements for the majority of particles on the image give a dominant size of about 1.4 nm (Fig. 2b). The smaller number of bigger particles is believed to be aggregates of the single molecules. Given the fact that the dendrimer molecules

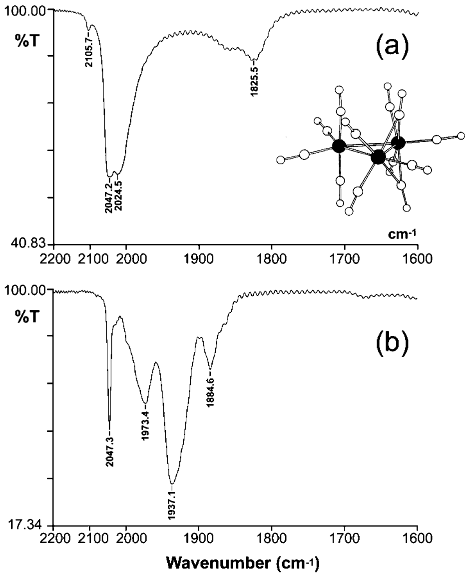


**Fig. 1** IR spectrum of the starting cluster $Fe_3(CO)_{12}$ (a), and of the product (b).

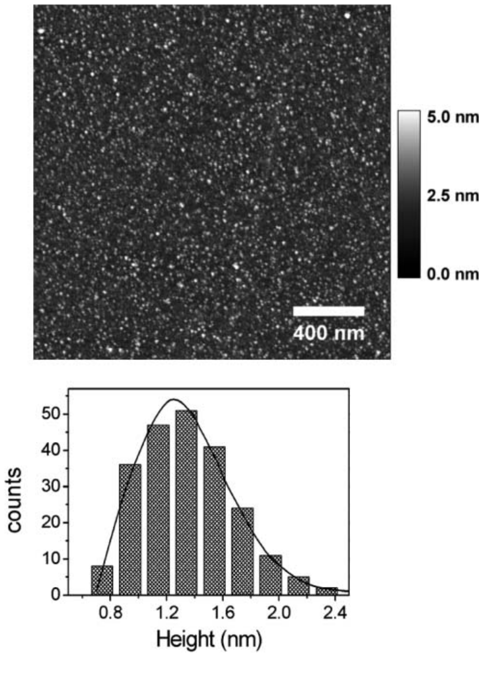


**Fig. 2** The image of the $Fe_{24}$ superclusters under the atomic force microscopy (AFM) (upper figure), and the corresponding topographical height measurements (lower figure).

DOI: 10.1039/b407717b

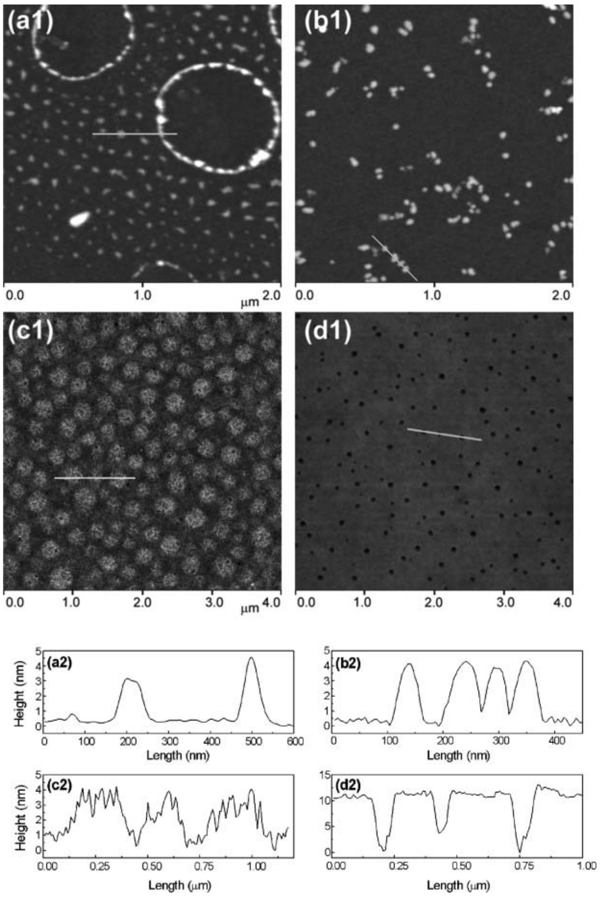
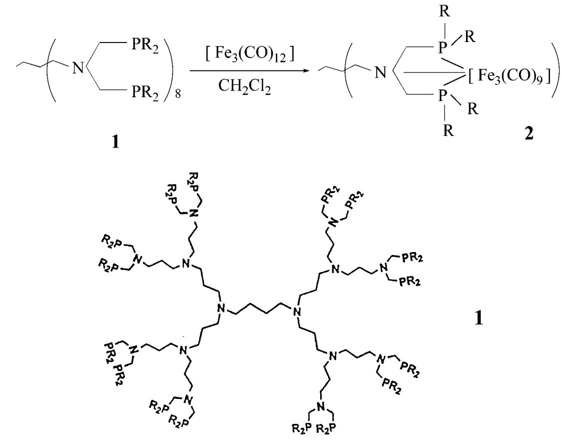


**Fig. 3** AFM images (a1–d1) showing the shapes or structures of the self-assemblies of the $Fe_{24}$ nanoclusters, and the topographical measurements (a2–d2) showing the typical size of the nanoparticles or nanoholes.

are soft and may flatten as a result of the surface adsorption, the measured height value for each molecule should be smaller than the real size (diameter). Based on our height analysis, and also taking the atomic numbers and the molecular structure into account, we estimate the real size of a single molecule to be at the scale of about 2–3 nm.

Interestingly, we find that depending on deposition conditions, these supermolecular clusters may self-assemble into various nanostructures on the Si substrate. A frequently seen structure is nanorings consisting of either single molecules or their aggregates (Fig. 3a). The rings are normally found after dipping the substrate into a dichloromethane solution of the clusters for a few minutes followed by a thorough rinse using pure dichloromethane and a blow-dry by a $N_2$ gun. Evaporation of the solvent may lead to formation of discrete nanoparticles with a typical size of about 4 nm (Fig. 3b). Cross-section measurements indicate that these nanoparticles possess similar characteristics to colloidal nanoparticles under AFM scanning, suggesting a "solid" feature possibly arising from a mechanism that involves the decarbonylation of the molecules and their subsequent agglomeration. If the dipped substrate is vertically taken out of the solution in a way such that the solution is allowed to naturally flow down along the surface, cluster islands may be formed (Fig. 3c). AFM scanning results show that each island is made up of several smaller particles, possibly the single molecules loosely assembled together. The width of these islands is approximately 100–200 nm, and the height 3–4 nm. It is also observed that when the dipping operation is replaced by a dropping one, a continuous film of molecules forms on which many scattered nanoscale holes are displayed (Fig. 3d). The diameter of the holes is typically in between 50 and 100 nm, and the hole-depth is about 5–10 nm. We believe that all these interesting nanostructures may arise from a combination effect that involves the immobilisation force exerted by the hydrogen-bonding between CO ligands of the clusters and OH groups on the substrate, together with the mobilisation action driven by thermal movement of the molecules and evaporation of the solvent. The controlled deposition of metal cluster–dendrimer complexes opens up new avenues for exploring their use as catalytic centres. Currently we are using similar complexes for the controlled growth of carbon nanotubes.



**Scheme 1** Synthesis of compound **2**. Reagents and conditions: $Fe_3(CO)_{12}$ 1.1 equiv. dendrimer **1** (the molecular structure is shown in this diagram), 1 equiv. $CH_2Cl_2$, rt, 22 h, in Ar, addition of hexene for precipitation of the product, purified by TLC techniques and dried in vacuum at 33 °C.

We thank Thomas Swan Lt. & Co. UK for financial support during the period in which this work was carried out.

## Notes and references

† The band of the starting cluster at 2024 $cm^{-1}$ no longer exists in the purified product presumably because of its transformation into the two new absorptions at lower wavenumbers (1973 and 1937 $cm^{-1}$) following coordination of the cluster units onto the chelating P–N–P ligands.

‡ A weak second peak in the $^{31}P$ NMR spectra for **2** was also observed at $\delta \approx 30$ ppm. This is believed to arise from a slow fluctuating process involving cluster rearrangement.

§ Elemental analysis (wt.%) for **2**: found: C 52.16, H 4.55, N 3.25, P 7.01; calcd for $C_{320}H_{272}N_{14}P_{16}O_{72}Fe_{24}$: C 52.64 , H 3.76, N 2.70, P 6.80.

¶ The employed Si substrates contain a thin native oxide layer. The substrates were first cleaned by a mixture of ethanol and acetone, then by water, in an ultrasonic bath, followed by $O_2$ plasma polishment for 10 minutes before use. AFM imaging was carried out using Tapping Mode.

1 I. M. L. Billas, J. A. Becker, A. Chatelain and W. A. de Heer, *Phys. Rev. Lett.*, 1993, **71**, 4067.
2 *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley-VCH, Weinheim, 1999, **vol. 2**.
3 M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1996.
4 S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.
5 R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787.
6 A. M. Morales and C. M. Lieber, *Science*, 1998, **279**, 208.
7 M. T. Reetz, G. Lohmer and R. Schwickardi, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1526.
8 N. Feeder, J. Geng, P. G. Goh, B. F. G. Johnson, C. M. Martin, D. S. Shephard and W. Zhou, *Angew. Chem., Int. Ed.*, 2000, **39**, 1661.