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# Photomagnetic nanorods of the $Mo(CN)_8Cu_2$ coordination network†

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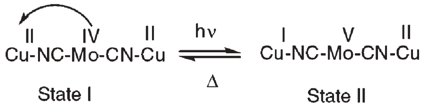
*Received (in Cambridge, UK) 30th September 2004, Accepted 3rd November 2004*
*First published as an Advance Article on the web 16th December 2004*
**DOI: 10.1039/b415157g**

**Nanorods of the photomagnetic coordination network $Mo(CN)_8Cu_2$ coated with polyvinylpyrrolidone were prepared and exhibit an enhanced effect upon irradiation when compared to the bulk.**

Despite the wide variety of properties afforded by transition metal coordination networks, little attention has been devoted to the study of nanoscopic objects made of such systems. High surface to volume ratio in nanoscopic coordination systems, where charge transfer or spin change occurs upon an external stimulus, may have a crucial influence on their physical properties. Moreover, mastering the preparation of nanoparticles of coordination compounds can be an original and challenging way to understand cooperativity in photomagnetic and spin transition systems.

Prussian Blue analogues can be considered as the archetypes of coordination systems that have a three-dimensional (3D) structure *i.e.* coordination bonds in the three directions of space. Nanoparticles of such systems were first stabilised within reverse micelles by Moulik and coworkers who reported aggregates of $Cu_2Fe(CN)_6$[1] and then mainly by Mann and co-workers, who managed to image nanoparticles from 12 to 50 nm organised into superlattices.[2] However, isolation of the nanoparticles from the microemulsion was not described, hence preventing any magnetic characterisation. We recently succeeded in isolating nanoparticles around 3 nm for the ferromagnet $Ni[Cr(CN)_6]_{2/3}$ by introducing a pyridine derivative which coordinates to the inorganic core and brings solubility.[3] We have shown that such dispersible particles may be incorporated in a polyvinylpyrrolidone (PVP) matrix which allows the characterization of their superparamagnetic behaviour. The use of PVP to stabilise metallic nanoparticles[4] has been extended to Prussian Blue by Kitagawa and coworkers,[5] leading to nanoparticles protected by PVP chains with a size ranging from 12 to 27 nm. Another approach is to synthesize the nanoparticles within a silica xerogel, as was recently reported for the photomagnetic $CoFe(CN)_6$ Prussian Blue analogue.[6] In the field of photomagnetism, it is of special interest to process the compounds as films in order to ensure better penetration of light and complete transformation of the compound. One interesting system exhibiting a photomagnetic effect is the coordination network $Mo(CN)_8Cu_2$ which has a 3D structure close to compounds of the same family reported recently.[7] Upon irradiation, an electron transfers from one diamagnetic $Mo^{IV}$ centre to a $Cu^{II}$ site creating ferromagnetically coupled $Mo^{V}$–CN–$Cu^{II}$ units within the compound.[8,9] (see Scheme 1).



**Scheme 1** Photoinduced electron transfer process in $Mo(CN)_8Cu_2$.

In this communication, we report the preparation of anisotropically shaped nanoparticles of $Mo(CN)_8Cu_2$ and their photomagnetic behaviour when processed as films. We used the PVP polymer as already reported in order to control the growth of the 3D system and prepare the nanosized particles.[5]

A 2 mM aqueous solution containing $CuSO_4$ and PVP K30 was prepared in a ratio of $[pyr]/[Cu^{2+}] = 100$ (where pyr stands for the pyrrolidone monomer). Adding an equivalent volume of a 2 mM $K_4Mo(CN)_8$ aqueous solution resulted in an immediate colour change to purple due to the intervalence band characteristic of the electronic delocalisation between the $Mo^{IV}$ and $Cu^{II}$ sites.[10] The mixture remained clear during the whole process, and 3 volumes of acetone were added after 1 h stirring at room temperature to precipitate the particles and to avoid the presence of an excess of free PVP. The resulting solid was centrifuged and then dispersed in EtOH. Films could be prepared by slow evaporation of the solvent and were directly used in the irradiation experiments. The IR spectrum revealed the asymmetric vibration of bridging cyanides at 2164 $cm^{-1}$. The presence of the polymeric chains was evidenced by the C=O broad peak at 1654 $cm^{-1}$ and C–H vibrations between 2890 and 2960 $cm^{-1}$. The UV-visible spectrum of the particles dispersed in EtOH shows the presence of the intervalence band at 529 nm. Elemental analysis performed on the sample gives the following composition: $Cu_2Mo(CN)_8(pyr)_7 \cdot 11H_2O$.‡ The X-ray powder diffraction diagram of the ground film is similar to that of the bulk compound.§ Scanning Transmission Electronic Microscopy (STEM) using dark field enabled us to image the nanoparticles as strongly anisotropic objects (Fig. 1) with a width/length average ratio of 0.19 ($\sigma = 0.07$). The statistics performed on 350 particles revealed a relatively constant width of 11.3 nm ($\sigma = 3.3$ nm) and a length of 70.3 nm ($\sigma = 28.8$ nm).¶

TEM imaging performed on the bulk compound revealed the presence of filamentous objects with a large size distribution up to one micrometer (not shown here). The role of PVP is thus mainly the stabilization of the objects on a nanometric scale with a relatively narrow size distribution as compared to the bulk.

The magnetic studies were performed on a film of nanoparticles before and after light irradiation at 406–415 nm. Because the energy barrier for recovering the initial state (State I on Scheme 1)

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† Electronic supplementary information (ESI) available: XRPD diagrams for the bulk and the ground film of $Mo(CN)_8Cu_2$. See http://www.rsc.org/suppdata/cc/b4/b415157g/

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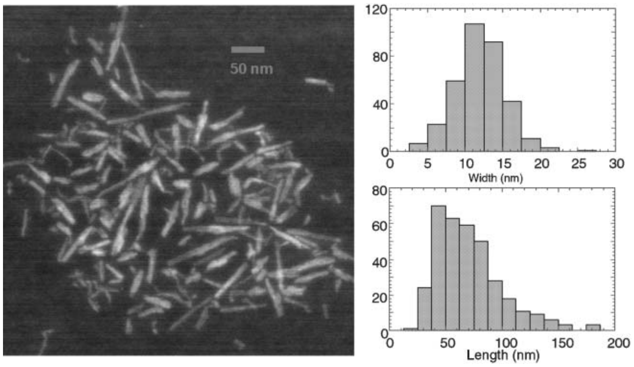

**Fig. 1** Dark field STEM image of the nanorods of $Mo(CN)_8Cu_2$ and distributions of length and width of the nanorods.

is around 200 K, the metastable photoinduced state (State II) is trapped and can be studied below this temperature.

After irradiation, the $\chi T = f(T)$ plot reveals the appearance of a ferromagnetic interaction between the paramagnetic $Mo^V$ and the residual $Cu^{II}$ centres (Fig. 2). The maximum in the $\chi T$ plot may be due to interparticle interaction or to the presence of appreciable magnetic anisotropy within the rod shaped nanoparticles. After thermal treatment at $T = 300$ K, the paramagnetic behaviour is recovered. The bulk compound shows similar behaviour but the maximum of the $\chi T$ is much lower than that of the nanoparticles.[8] ||

Magnetisation (*M*) *vs.* field (*H*) studies performed at 5 K on the film of nanoparticles show that after irradiation saturation of the magnetization is reached (1.91 μB) with a value at 5 Tesla close to the expected one (2 μB) for a $Cu^IMo^{IV}Cu^{II}$ entity (Fig. 3a). The $M = f(H)$ plots before irradiation and after thermal treatment are almost identical, thus showing that the photomagnetic effect is fully reversible. The $M = f(H)$ behaviour was measured at $T = 4$ K after irradiation on the bulk and the film of nanoparticles (Fig. 3b). The different curvature of the two curves suggests that the photomagnetic effect on the bulk compound is not as efficient as in the case of the nanoparticles. It is possible to reproduce the magnetisation plot of the bulk by considering a contribution of 75% from the magnetisation of the nanoparticles and 25% from the magnetisation corresponding to the sum of the Brillouin functions of two $S = 1/2$ states (Fig. 3b). This leads to the conclusion that only 75% of the electron transfer process occurs upon irradiation for the bulk compound as compared to the nanoparticles.**

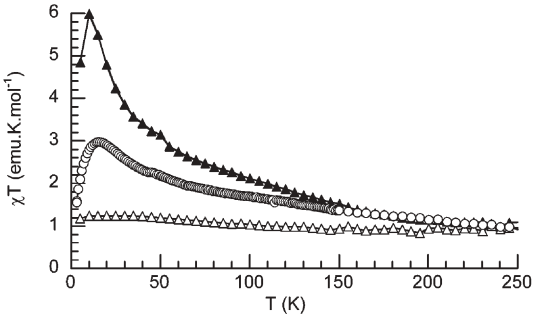

**Fig. 2** $\chi T = f(T)$ observed after irradiation of the bulk (○), of the film of nanorods (▲) and after thermal relaxation (●).

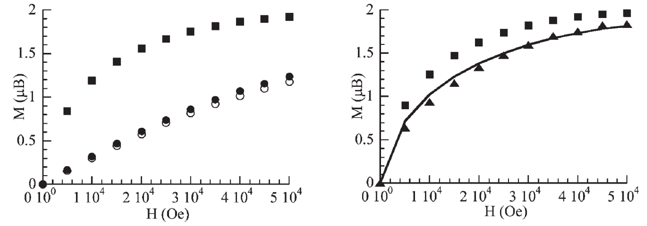

**Fig. 3** (left) $M = f(H)$ plots on the nanoparticles film, (○) before irradiation, (■) after irradiation and (●) after thermal relaxation at $T = 5$ K; (right) $M = f(H)$ at $T = 4$ K of the film (■) and the bulk (▲); (—) magnetisation curve corresponding to 75% of the nanoparticles $M = f(H)$ curve and 25% of the Brillouin function for two $S = 1/2$ spin states.

In this communication, we show that it is possible to prepare nanorods made of a photomagnetic coordination compound coated with the PVP polymer enabling a straightforward preparation of films and handling in solution. The photomagnetic effect is more efficient in the case of the nanoparticles as compared to the bulk. This effect is related to better light penetration due to film processing. Preparation of nanoparticles with different sizes is underway in order to get more insight into the effect of size reduction on the efficiency of the photomagnetic effect in the $MoCu_2$ coordination compound.

We thank the CNRS (Centre National de la Recherche Scientifique), the French programme Nanoscience (ACI SupNanoMol NR0142), and the European Community for financial support (Contract MRTN-CT-2003-504880/RTN Network "QuEMolNa").

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## Notes and references

‡ Elemental analysis: % exp C 42.67, H 6.08, N 14.93, Cu 9.03, Mo 6.82; % calc. for $Cu_2Mo(CN)_8(C_6H_9NO)_7\cdot 11H_2O$ C 42.85, H 6.07, N 14.75, Cu 9.00, Mo 6.72.

§ The bulk compound was prepared as already reported.[11] The broad peaks are due to overlapping of many diffraction peaks so that the average size of the crystallites could not be extracted from the XRPD diagram.

¶ STEM experiments were done using a dedicated cold FEG STEM VG HB05. High angle annular dark field images were recorded using a collection angle above 60 mrad and an acquisition time of around 15 s per image. The obtained contrast was sufficient to threshold the particle contours. Geometrical parameters for each isolated particle were then obtained using DM 3.4 Gatan software. EELS experiments (not shown) have also confirmed the presence of C, N and Cu in the nanorods.

|| Photomagnetic experiments were carried out with a Quantum Design MPMS-5S magnetometer working in the dc mode. The measurements were performed in the 5–300 K range with a magnetic field of 5000 Oe for $\chi T$ and at 4 and 5 K up to 5 Tesla for magnetisation. The photomagnetic experiments were performed with a $Kr^+$ laser coupled through an optical fiber directed into the SQUID cavity. A small piece ($\approx 0.3$ $cm^2$) of the film

was laid down on a sample holder. The diamagnetic contribution and the weight were estimated by comparing the magnetisation curves (at different temperatures) before irradiation with those recorded for the powdered sample in a routine experiment (20 mg of sample loaded into gel caps). These comparisons give $m$ = 0.26 mg and diamagnetic correction = $-4\ 10^{-2}$ emu mol$^{-1}$. The film was irradiated continuously using the multiline 406–415 nm under a magnetic field of 5 kOe at 10 K, till the magnetization saturation was obtained (15 h). The output power laser light was 60 mW/cm$^2$, which corresponds to the effective power received by the sample measured to $\approx 3$ mW/cm$^2$. The experiments on the bulk were carried out on a sample of thoroughly ground powder put on a tape in the same conditions of the film of nanoparticles ($m$ = 0.12 mg and diamagnetic correction = $-2\ 10^{-4}$ emu mol$^{-1}$).

** Since the process is fully reversible for the bulk compound and the film of nanoparticles, no defect formation occurs upon irradiation.

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