A facile "bottom-up" approach to prepare free-standing nano-films based on manganese coordination clusters†

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We present herein a novel method to prepare free-standing Dried Foam Films (DFFs) whereby individual polynuclear manganese complexes cover quantitatively the holes of micro-grids; the fabricated, homogeneous films have a cross-sectional thickness of only *ca.* 5 nm and are characterised by high mechanical stability.

Thin, molecule-based films and two-dimensional (2D) materials of nanometre thickness can give rise to unique intrinsic attributes that are exploitable in optical, electronic, spintronic and other magnetic devices.[1] The concept of dried foam films (DFFs) pioneered by Ichinose and co-workers provides a highly applicable technique for the preparation of free-standing nano-films.[2] DFFs can form upon immersing a porous substrate into solutions of surfactants. Subsequent evaporation of entrapped solvent molecules after drying promotes the formation of stable bi-layer films that unsupportedly extend over several micrometres. The free-standing DFFs obtained by this method have molecularly smooth surfaces and more importantly are characterised by good thermal and mechanical stability.[3] However, this approach has only been applied to films consisting of simple commercially available, organic surfactants. Inspired by this preceding work, we decided to explore the application of this method for the fabrication of DFFs comprising of complex molecular entities, in particular nanoscopic, functional Mn coordination complexes.[4]

To develop this synthetic concept one requires a suitable Mn cluster system that can selectively be functionalized to tune its amphiphilicity whist the core structure promotes interesting physical properties. During our research into hybrid organic–inorganic

materials we found that kinetically labile coordination sites that point in defined directions of space can be used to selectively functionalize complexes.[5] Tetragonally elongated d^4 Mn^{III} Jahn–Teller sites provide such kinetically labile positions (high water exchange rates $>10^7$ s^{-1} at 298 K), allowing the introduction of various ligand moieties.[5b,c,6] A *tert*-butylphosphonate-stabilized {Mn_{13}} complex, [($Mn^{II}_{0.5}Mn^{III}_{0.5}$)$Mn^{III}_{12}(\mu_4$-O)$_6(\mu$-OH)$_2(\mu$-CH$_3$O)$_4$(*tert*-butyl-PO$_3$)$_{10}$(CH$_3$OH)$_6$]$^{0.5+}$ (**1**), containing six active coordination sites provides such structural characteristics. These six Jahn–Teller sites are susceptible to ligand exchange reactions and can selectively be used to link the clusters into coordination polymers and open-framework materials.[5b] Here we further demonstrate that the sites can also be employed to tune the amphiphilicity through introduction of hydrophobic 4-(3-phenyl-propyl)-pyridine (ppp) moieties to give a double-tailed cluster amphiphile [($Mn^{II}_{0.5}Mn^{III}_{0.5}$)$Mn^{III}_{12}(\mu_4$-O)$_6(\mu$-OH)$_2(\mu$-CH$_3$O)$_4$(*tert*-butyl-PO$_3$)$_{10}$(CH$_3$OH)$_2$(Cl$_2$)(ppp)$_2$]$^{1.5-}$ (**2**). We successfully prepared, extended free-standing, stable DFFs through self-assembly of this complex surfactant. The obtained materials were characterised by single-crystal X-ray diffraction, mass spectrometry, magnetic susceptibility measurements and electron microscopy, including helium ion, scanning and transmission electron microscopy (HIM, SEM and TEM).

The comproportionation reactions between MnCl$_2$·4H$_2$O and KMnO$_4$ in the presence of *tert*-butylphosphonic acid, Et$_3$N or 4-(3-phenylpropyl)-pyridine in methanol produced red crystals of [($Mn^{II}_{0.5}Mn^{III}_{0.5}$)$Mn^{III}_{12}(\mu_4$-O)$_6(\mu$-OH)$_2(\mu$-CH$_3$O)$_4$(*tert*-butyl-PO$_3$)$_{10}$(CH$_3$OH)$_6$]Cl$_{0.5}$·6CH$_3$OH ([**1**]Cl$_{0.5}$·6CH$_3$OH) and (H$_3$O)$_{1.5}$[($Mn^{II}_{0.5}Mn^{III}_{0.5}$)$Mn^{III}_{12}(\mu_4$-O)$_6(\mu$-OH)$_2(\mu$-CH$_3$O)$_4$(*tert*-butyl-PO$_3$)$_{10}$(CH$_3$OH)$_2$(Cl$_2$)(ppp)$_2$]·8CH$_3$OH ((H$_3$O)$_{1.5}$[**2**]·8CH$_3$OH), respectively. Single crystal X-ray diffraction analysis revealed that both complexes contain isostructural {Mn_{13}} core structures which are stabilized by organophosphonate, methanol, chloride or 4-(3-phenylpropyl)-pyridine ligand moieties. The structure of the {Mn_{13}} cluster core in **1** and **2** (Fig. 1) can be visualised as divided into distinct subunits. The central unit consists of a typical hexagonal '*brucite*'-type {Mn_7} structure in which a central Mn ion is located on an inversion centre and is connected to six adjacent Mn^{III} ions *via* six μ_4-O^{2-} ligands. A single Mn^{III} centre, a dinuclear

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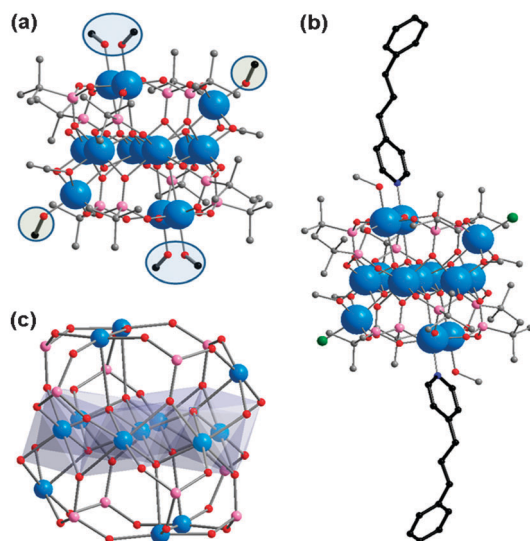
Fig. 1 Crystal structure of (a) **1** and (b) **2**, highlighting the Jahn–Teller sites, which can be used for the selective functionalization. (c) The structure of the $\{Mn_{13}\}$ cluster core. Color code: Mn—light blue, O—red, P—pink, N—blue, C—black or grey.

$\{Mn–(OH)–Mn\}$ moiety, and their symmetry equivalents are located above and below this hexagonal $\{Mn_7\}$ plane and are connected to it *via* oxo-ligands, deprotonated phosphonate ligands and two μ-CH_3O^- ligands. Bond valence sum (BVS) calculations confirm that the outer 12 Mn centres in **1** and **2** adopt +III oxidation states while the central Mn atoms in **1** and **2** have BVS values of 2.696 and 2.605, clearly suggesting a partial occupancy of these positions involving Mn^{II} and Mn^{III} ions at a nearly 50:50% ratio.[5b] Six of the outer Mn^{III} sites contain kinetically labile monodentate ligands in Jahn–Teller sites imparting functionality to the $\{Mn_{13}\}$ cores. In **1**, all of these six sites

are occupied by methanol molecules, whereas in **2**, they are occupied by two chloride, two methanol and two 4-(3-phenylpropyl)-pyridine molecules. Related oxo-cluster topologies that contain the 'brucite'-type $\{Mn_7\}$ core observed here have previously been reported highlighting that these arrangements of the Mn centres can give rise to remarkable magnetic properties,[5b,7] which are characterised by dominant antiferromagnetic interactions between the Mn spin centres leading to $S \neq 0$ spin ground states.†

The investigated $\{Mn_{13}\}$ system provides distinctive sites, which allow functionalization on the outer periphery. Introduction of hydrophobic moieties, such as 4-(3-phenylpropyl)-pyridine residues, that point in distinct directions of space allows one to tune the amphiphilicity of the complexes which can be compared to the surfactant-like polyoxometalates developed by Cronin and Liu.[8] This feature is a key requirement for such complex molecular entities to be used for the fabrication of free-standing films. The approach applied here results in cluster-based double-tailed surfactant **2**, whose structural characteristics give rise to the formation of hierarchical assemblies that self-organize over extended areas and thus we decided to use this complex as a building block to fabricate DFFs.

The solution stability of **2** was confirmed by electrospray-ionization mass spectrometry (ESI-MS) analysis. Perforated 2000-mesh copper grids, with square holes of 10 µm × 10 µm, were used as substrates for the preparation of DFFs and immersed in the methanolic solutions of **2**. The porous substrates were then carefully lifted into the air and allowed to stand for two hours at room temperature. Upon evaporation of solvent, the surfactant-like molecules of **2** self-assembled into free-standing thin films. The obtained dried foam films were initially investigated by helium ion and scanning electron microscopy (HIM & SEM) (Fig. 2). Our investigations demonstrate that **2** has the ability to
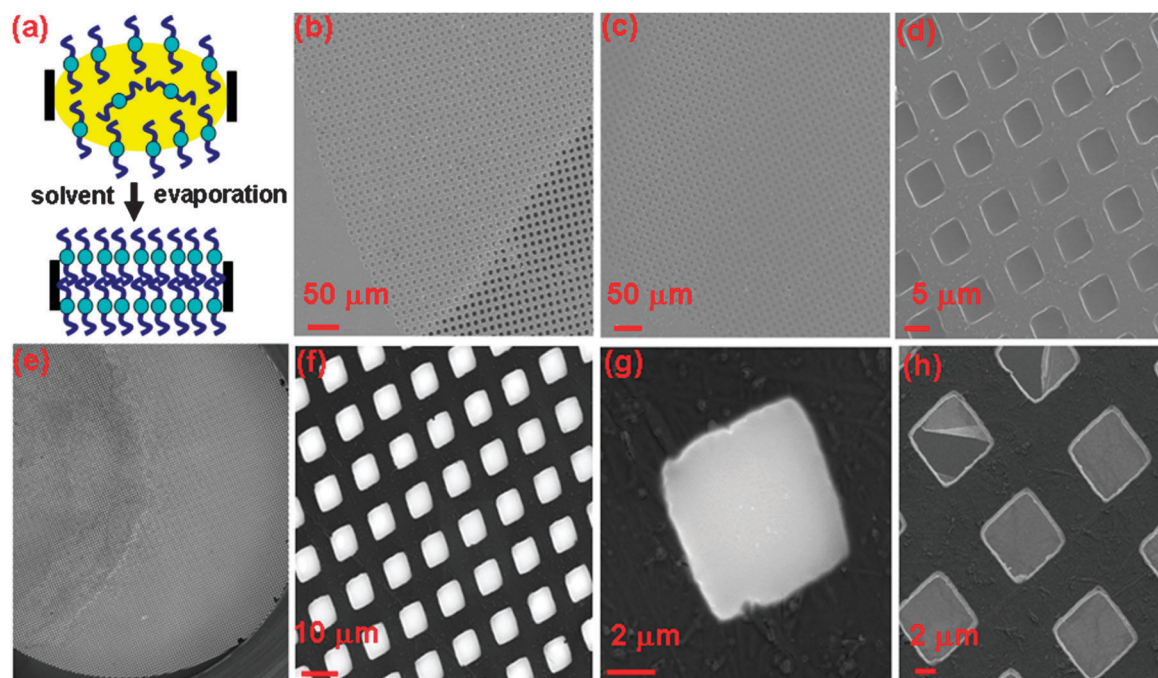

Fig. 2 (a) A schematic diagram of the DFF formation based on double-tailed cluster amphiphiles; (b)–(d) helium-ion micrographs (HIM) of the DFFs based on **2** (coated by Pt); (e)–(g) SEM micrographs of the DFFs based on **2** (without coating); (h) SEM micrograph of DFFs prepared using a lower concentrated solution of **2** (without coating).
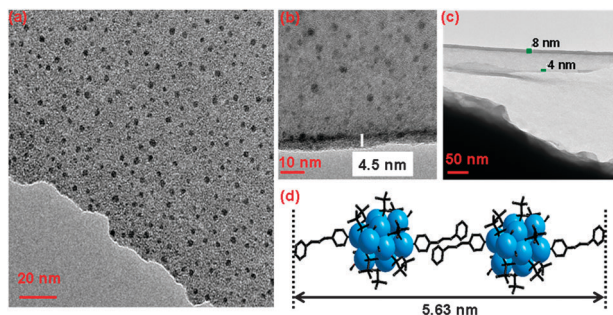
Fig. 3 (a)–(c) TEM images of DFFs formed by **2**; (d) the packing of two molecular entities in the crystal structure of **2**, indicating comparable distances to the thickness of the DFFs.

form extended DFFs that cover every hole that has been in contact with its solution at these applied optimized concentrations.

The produced films are homogenous and are characterized by smooth surfaces and quantitative hole coverages. In the SEM images, shown in Fig. 2e–g, the films are light and can be easily distinguished from the grids and empty holes (both dark). To investigate the thickness, the pre-formed DFFs were purposely broken (cutting of a covered grid or application of stress to the grid) and imaged by transmission electron microscopy (TEM). Based on this analysis, as shown in Fig. 3, the thickness of the films can be estimated to be *ca.* 5 nm (± 1 nm). EDX analysis confirms that the films are composed of C, O, P, Cl, Mn, and the atomic ratio of Mn/P = 1.27 is in good agreement with the expected value of 1.30 in **2**. IR spectra further confirm that the DFFs are composed of the described polynuclear entities of **2**. In addition, individual $\{Mn_{13}\}$ cores can be directly visualized by high-resolution TEM. The size of the clearly identifiable dark dots compares well with the dimensions of the $\{Mn_{13}\}$ cluster as determined by X-ray crystallography. Considering these structural analyses and the fact that the length of a single molecule of **2** does not exceed 3 nm, one can conclude that the observed assembly process results in a bilayer arrangement of single complexes. This observation is in agreement with the proposed formation mechanism of DFFs highlighted in Fig. 2a. It is remarkable that these molecule-based, free-standing films are stable under these electron microscopic conditions and do not undergo severe electron beam-induced transformations. We further noted the remarkable mechanical stability of the obtained DFFs. The free-standing, unsupported films withstand the deposition of metal films on their surfaces without collapsing. Fig. 2b–d show a DFF-covered substrate after an *ca.* 5 nm Pt layer has been deposited on its surface using physical vapour deposition.

It is further noteworthy that metal-coated DFFs can further be processed by He-ion beams. The ability to modify or cut certain parts of the coated films was demonstrated by the introduction of individual holes with cross-sectional diameters of *ca.* 10–20 nm that form when the desired areas are treated with a focused He ion beam (see ESI†).

The mechanical stability and the processability are key requirements for these materials to be applied for the preparation of electronic devices whereby, for instance, Mn-based films could be used as tunnel barrier in magnetic tunnel junctions or spin-valve systems. It is feasible to assume that commonly applied 'wafer-flip' methods allow the deposition of stacks of metallic layers

on both sides of the Mn-based DFFs to give for instance magnetic read-out devices. Under this purview it is important to note that the approach is not restricted to copper grids with square cavities. Moreover, the method can for instance be applied to highly insulating Si_3N_4 grids composed of spherical holes (see ESI†).

The synthetic approach applied to Mn cluster-based DFFs is highly sensitive to the solvent system, concentration of the solution and the amphiphilicity of the coordination cluster. Optimized MeOH solutions of **2** result in homogeneous DFFs with almost quantitative hole coverages, whilst MeCN solutions give inhomogeneous and non-uniform assemblies that cover parts of the holes. Lower concentrations produce DFFs with significantly lower coverages and incomplete films.

In summary, we have demonstrated that the DFF concept is not restricted to simple organic surfactants but can also be applied to complex systems containing nanoscopic coordination clusters thus allowing the fabrication of functional films that may reveal interesting magnetic properties. The chemical amenability of a $\{Mn_{13}\}$ compound that results from kinetically labile Jahn–Teller sites allows the selective introduction of hydrophobic side chains to give manganese cluster-based surfactants with desired amphiphilicity. Their assembly results in thin, homogeneous, free-standing DFFs built from individual molecular entities that cover quantitatively the holes of micro-grids. Their surprisingly high mechanical stability allows the deposition of metals on their surfaces. This feature in combination with the processability may provide new avenues for the fabrication of magneto-electronic devices. The elucidation of the electronic and magnetic properties of the obtained films will be the subject of our future investigations.

Notes and references

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