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

Lei Zhang, a Camelia I. Onet, a Rodolphe Clérac, b c Mathieu Rouzières, bc Bartosz Marzec, a Markus Boese, c Munuswamy Venkatesan d and Wolfgang Schmitt a

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.3 However, this approach has only been standing DFFs obtained by this method have molecularly smooth surfaces and more importantly are characterised by good thermal 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 whilst 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 d4 MnIII Jahn–Teller sites provide such kinetically labile positions (high water exchange rates >107 s−1 at 298 K), allowing the introduction of various ligand moieties.5b,c A tert-butylphosphonate-stabilized {Mn13} complex, [(MnII 0.5MnIII 0.5) MnIII 12(µ4-O)(µ4-OH)4(µ-CH3O)4(tert-butyl-PO4)10(CH3OH)8]0.5Cl− (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-phenylpropyl)-pyridine (ppp) moieties to give a double-tiered cluster amphiphile [(MnII 0.5MnIII 0.5)MnIII 12(µ4-O)(µ4-OH)4(µ-CH3O)4(tert-butyl-PO4)10(CH3OH)8]([Cl]0.5(PPP)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 MnCl2·4H2O and KMnO4 in the presence of tert-butylphosphonic acid, Et3N or 4-(3-phenylpropyl)-pyridine in methanol produced red crystals of [(MnII 0.3MnIII 0.7)MnIII 12(µ4-O)(µ4-OH)4(µ-CH3O)4(tert-butyl-PO4)10(CH3OH)8]Cl0.5·6CH3OH ([1]Cl0.5·6CH3OH) and (H2O)1.5[(MnII 0.5MnIII 0.5)MnIII 12(µ4-O)(µ4-OH)4(µ-CH3O)4(tert-butyl-PO4)10(CH3OH)8]([PPP]2)·8CH3OH ([(H2O)1.5·2]·8CH3OH, respectively. Single crystal X-ray diffraction analysis revealed that both complexes contain isostructural {Mn13} core structures which are stabilized by organophosphonate, methanol, chloride or 4-(3-phenylpropyl)-pyridine ligand moieties. The structure of the {Mn13} 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 {Mn12} structure in which a central Mn ion is located on an inversion centre and is connected to six adjacent MnIII ions via six µ4-O2− ligands. A single MnIII centre, a dinuclear...
The {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_{3}O 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. 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, which are characterised by dominant antiferromagnetic interactions between the Mn spin centres leading to S ≠ 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. 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
form extended DFFs that cover every hole that has been in contact with its solution at these applied optimized concentrations.

The produced films are homogeneous 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 \([\text{Mn}_{13}]\) cores can be directly visualized by high-resolution TEM. The size of the clearly identifiable dark dots compares well with the dimensions of the \([\text{Mn}_{11}]\) 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 their surfaces without collapsing. Fig. 2b–d show a DFF-covered standing, unsupported films withstand the deposition of metal films 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$_3$N$_4$ 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 \([\text{Mn}_{13}]\) 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