Self-Organized Honeycomb Structures of Mn₁₂ Single-Molecule Magnets

Hang Sun,[†] Wen Li,[†] Lance Wollenberg,[§] Bao Li,[†] Lixin Wu,^{*,†} Fengyan Li,[‡] and Lin Xu[‡]

State Key Laboratory of Supramolecular Structure and Materials, Department of Chemistry, Jilin University, Changchun 130012, People's Republic of China, Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China, and Pharmaceutical and Pharmacological Sciences, West Virginia University, P.O. Box 9530, Morgantown, West Virginia 26506

Received: July 10, 2009; Revised Manuscript Received: September 11, 2009

In this paper, Mn_{12} -based ordered honeycomb structures were successfully constructed from a simple solution casting process at high relative humidity through the modification of fatty acids to Mn_{12} clusters. Mn_{12} -fatty acid complexes maintain typical features of a single-molecule magnet as confirmed by IR spectra and magnetization hysteresis studies. Investigation of the effects of concentration, velocity of humid airflow, solvent, substrate, and alkyl chain length of the Mn_{12} complex on the morphology of the honeycomb structures demonstrated wide generality and high reproducibility of the formation of Mn_{12} -based self-organized honeycomb-patterned films. Both two-dimensional and three-dimensional honeycomb-patterned films maintain a paramagnetic response at room temperature, and thus give rise to a spatially distributed magnetic pattern on the substrate, which can be imaged by magnetic force microscopy. Importantly, the single-molecule magnetic property of the Mn_{12} complex at low temperature is well maintained in the honeycomb-patterned film, which represents a promising outlook for high-density information storage and quantum computing applications.

Introduction

Controlled condensation of water vapor on the cooling surface of volatile polymer solutions leads to patterned structures of arrayed water droplets.¹ A process generally referred to as "breath figures" has attracted much interest in the past few years, providing a simple approach to generating patterned structures with periodicity, in a size range of 50 nm to 20 μ m.² By using this method, a variety of polymer materials have been successfully employed for the fabrication of honeycomb structures exhibiting various functionalities such as superhydrophobic surfaces, microlens arrays, cell culture substrates, and patterned templates.³ Normally, stabilization of the condensed water droplets is essential for the patterned structure to achieve high regularity, which seriously limits the materials applied for this method.^{2b} Therefore, to integrate diverse functions into patterned structures, development of new materials is essential, with recent attention concentrated on the functional patterns of nanomaterials with unique optical, magnetic, and biological properties.⁴ For example, both honeycomb and ringlike structures were reported by surface modified Au nanoparticles and quantum dots.5

Single-molecule magnets (SMMs), the nanoscale magnetic clusters of a sharply defined size, exhibit large spin ground states with high axial magnetic anisotropy, resulting in an energy barrier for spin reversal.⁶ Interesting magnetic properties of SMMs, such as out-of-phase ac magnetic susceptibility signals and stepwise magnetization hysteresis loops, offer a potential access to ultimate high-density information storage and quantum-computing applications.⁷ To achieve a true molecular device based on SMMs, spatially and geometrically controlled patterns

of SMMs on a given surface are essential.⁸ The Mn₁₂ family $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]$ (R = substituted group) consists of a structure containing a basic cluster of four Mn(IV) and eight Mn(III) centers coordinated by an outer shell of 16 peripheral carboxylate groups, representing a typical SMM system which has been widely studied for the deposition of Mn₁₂ complexes to substrates.9 For example, Mn₁₂ clusters were reported to anchor on different surfaces such as Au(111) and Si(100) through ionic or covalent interactions, and a Si/SiO₂ surface through photolithography or lithographically controlled wetting methods.¹⁰ However, Gatteschi and co-workers found that functionalized Mn₁₂ complexes deposited on gold surfaces by covalent interaction lose their SMM behavior by using X-ray absorption spectroscopy and X-ray magnetic circular dichroism methods, even though the molecules seem to be structurally undamaged.¹¹ By using a substituted Mn₁₂ complex comprised of aromatic biphenyl moieties, self-organized magnetic rings were readily obtained through directed formation by condensed water droplets.¹² However, it is difficult to control the size and arrangement of the ring structures unless premodification to the substrate is carried out. By varying the peripheral carboxylate ligands, the Mn₁₂ complex becomes wettable and stable at the interface between the water droplets and the organic solution, at which point the ordered honeycomb structure based on the Mn₁₂ complex could be generated through arrayed water droplets as the template.

Following previous studies on surface patterning of functional hybrid complexes,¹³ we herein designed and synthesized a type of Mn_{12} -fatty acid complex, and demonstrated the self-organization of the Mn_{12} complexes into highly ordered honeycomb structures over different surfaces by simple solution casting of Mn_{12} -fatty acid complexes at high relative humidity. This strategy exhibits several advantages for the self-organization of Mn_{12} clusters including the following: (1) The modifica-

^{*} To whom correspondence should be addressed. E-mail: wulx@jlu.edu.cn. [†] Jilin University.

[§] West Virginia University.

^{*} Northeast Normal University.

SCHEME 1: Chemical Structure of Fatty Acids Applied To Modify the Mn_{12} Clusters: Stearic Acid (St), Hexadecanoic Acid (He), and Tetradecanoic Acid (Te)



tion of fatty acids provides the Mn_{12} cluster an amphiphilic property in organic solvents. (2) Long alkyl chains of fatty acids enhance the stability of the Mn_{12} cluster when in contact with water, in contrast to the rapid decomposition of simple clusters.^{9f} (3) Modification of Mn_{12} clusters facilitates good organization and typical SMM features in surface patterning. We investigated the effects of complex concentration, velocity of humid airflow, solvent type, substrate composition, and the alkyl chain length of the Mn_{12} complex on the morphology of the honeycombpatterned films. Furthermore, we tested the magnetic properties of the Mn_{12} -based self-organized honeycomb-patterned film. Subsequently, the results presented here provide a novel approach for the development of Mn_{12} clusters into patterned structures.

Experimental Section

Materials. [Mn₁₂O₁₂(O₂CCH₃)₁₆(H₂O)₄]•8H₂O (Mn₁₂Ac) was freshly prepared according to literature procedures.^{9a} Stearic acid, hexadecanoic acid, and tetradecanoic acid were purchased from Tianjin Guangfu Chemical Works and used as received.

Preparation of Mn₁₂–Fatty Acid Complexes. Mn₁₂–fatty acid complexes were prepared through a modified procedure as reported in the literature,⁹ by a substitution reaction in the presence of the desired fatty acid as well as the precursor Mn₁₂Ac, to produce the Mn₁₂-stearic acid complex. A mixture of $Mn_{12}Ac$ (0.10 g, 0.05 mmol) and stearic acid (0.49 g, 1.5 mmol) was added to 50 mL of a 1:1 (v/v) solution of dichloromethane and toluene and was stirred for 24 h at 45 °C. Then, the mixture was concentrated to remove resulting acetic acid. The resulting solid and additional stearic acid (0.33 g, 1.0 mmol) were dissolved in 50 mL of a 1:1 (v/v) solution of dichloromethane and toluene, stirred for 24 h at 45 °C, and then concentrated to remove resulting acetic acid. To fully substitute the acetate ligands, this procedure was repeated three times. The resulting brown solid was dissolved in hot methanol, filtered, and washed with hot methanol (total 100 mL) to remove uncomplexed stearic acid. The brown powder was further dried under vacuum until its weight remained constant, giving the product of Mn₁₂-stearic acid complex (Mn₁₂St). Following similar procedures, Mn_{12} -hexadecanoic acid complex (Mn_{12} He) and Mn₁₂-tetradecanoic acid complex (Mn₁₂Te) were prepared (Scheme 1). All three complexes were characterized by IR spectra (Figure S1 in the Supporting Information), elemental analysis, and thermogravimetric analysis (TGA) (Figure S2 in the Supporting Information) as follows.

IR (KBr, cm⁻¹) for $Mn_{12}St$: $\nu = 2920$, 2850, 1583, 1569, 1531, 1468, 1455, 1443, 1429, 1380, 1317, 1261, 1098, 1025, 868, 804, 721, 705, 673, 641, 610, 568, 558. Anal. Calcd for $Mn_{12}St$ ($C_{208}H_{402}O_{45}Mn_{12}$, 4282.65): C, 58.33; H, 9.45. Found: C, 57.99; H, 8.99. The TGA (temperature range 30–150 °C) corresponds to the loss of crystallized water (0.52%), and the

calculated number of crystallized water is ca. 1. Combining the TGA and elemental analysis, $Mn_{12}St$ should correspond to the formula $Mn_{12}O_{12}(C_{17}H_{35}COO)_{11}(CH_3COO)_5H_2O$. TGA measurement was used to verify the mass ratio of $[Mn_{12}O_{12}]$ core and peripheral stearic ligands correctly. This technique serves to decompose the organic component at 600 °C, and all the inorganic residuals consist of a mixture of Mn_2O_3 and MnO_2 with equal molar ratio (assuming the valence of Mn is invariable). TGA analysis demonstrates 22.84 wt % remaining after heating the sample to 600 °C. This experimental value obtained from TGA is in perfect agreement with the calculated value of 22.87 wt % from the given structural formula above.

IR (KBr, cm⁻¹) for Mn₁₂He: $\nu = 3524$, 2919, 2850, 1713, 1583, 1531, 1503, 1468, 1455, 1443, 1414, 1380, 1321, 1254, 1178, 1113, 721, 674, 640, 613, 568, 552, 523. Anal. Calcd for Mn₁₂He (C₂₂₈H₄₄₄O₄₆Mn₁₂, 4581.19): C, 59.78; H, 9.77. Found: C, 59.63; H, 9.80. The TGA (temperature range 30–150 °C) corresponds to the loss of crystallized water (0.88%), and the calculated number of crystallized water is about 2. Combining the TGA and elemental analysis, Mn₁₂He corresponds to the formula Mn₁₂O₁₂(C₁₅H₃₁COO)₁₄(CH₃COO)₂(H₂O)₂. TGA measurement was used to verify the mass ratio of the [Mn₁₂O₁₂] core and peripheral hexadecanoic ligands. Analysis of these results demonstrates 20.24 wt % remaining after heating the sample to 600 °C. This experimental result obtained from TGA is in reasonable agreement with the calculated value of 21.38 wt % from the given structural formula noted above.

IR (KBr, cm⁻¹) for Mn₁₂Te: $\nu = 2922$, 2852, 1710, 1574, 1541, 1443, 1377, 1316, 1263, 1116, 1088, 1028, 959, 721, 610. Anal. Calcd for Mn₁₂Te (C₂₁₂H₄₂₀O₅₀Mn₁₂, 4428.83): C, 57.49; H, 9.56. Found: C, 57.43; H, 9.60. The TGA (temperature range 30–150 °C) corresponds to the loss of crystallized water (2.68%), and the calculated number of crystallized water is about 6. Combining the TGA and elemental analysis, Mn₁₂Te should correspond to the formula Mn₁₂O₁₂(C₁₃H₂₇COO)₁₅(CH₃COO) (H₂O)₆. TGA measurement was used to verify the mass ratio of the [Mn₁₂O₁₂] core and peripheral tetradecanoic ligands. Analysis of these results demonstrates 20.93 wt % remaining after heating the sample to 600 °C. The experimental result obtained from TGA is in reasonable agreement with the calculated value of 22.11 wt % from the given structural formula.

Preparation of Honeycomb-Patterned Thin Films. Typically, honeycomb-patterned thin films were prepared by direct casting 20 µL of Mn₁₂-fatty acid complex in chloroform solution (1.5 mg/mL) onto the glass substrate under a moist airflow. The humid conditions were achieved by bubbling nitrogen gas through a water-filled conical flask. The nitrogen gas saturated with water vapor (temperature 25 °C) was exported through a glass nozzle onto the surface of the sample solution vertically. The velocity of humid airflow was controlled at 200-400 mL/min, which was monitored by a flow meter to ensure reproducibility. The internal diameter of the glass nozzle used to apply moist airflow is 0.6 cm, and the distance between the solution surface and the nozzle is ca. 1.2 cm. White thin films covering an area of ca. 1 cm² were left remaining after the complete evaporation of the solvent and water within 30-60 s. The control experiments without humid airflow have been conducted under ambient atmosphere (relative humidity 20-30%) and no porous structures were obtained, resulting in unpatterned flat films deposited on the surface.

Measurements. Fourier transform infrared (FT-IR) spectral measurements were completed on a Bruker IFS66 V FT-IR spectrometer equipped with a DGTS detector (32 scans), using

KBr pellets, and the spectra were recorded with a resolution of 4 cm⁻¹. Element analysis (C, H, N) was carried out on a Flash EA1112 analyzer from ThermoQuest Italia SPA Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer TG/ DTA-7 instrument, and the heating rate was set at $10 \,^{\circ}\text{C min}^{-1}$. The optical photographs were taken with an Olympus BX-51 optical microscope (OM). Scanning electron microscopic (SEM) images were collected on a JEOL JSM-6700F field emission scanning electron microscope. Magnetization hysteresis data were collected at 2 K, between +5 and -5 T, cooling the samples at zero field with a magnetometer (Quantum Design MPMSXL-5) equipped with a SQUID sensor. The powder sample of Mn₁₂St complex and the crystal sample of Mn₁₂Ac complex were measured directly. The honeycomb-patterned film of Mn₁₂St complex was removed from the substrate and collected for measuring. Each sample is first cooled to 1.8 K in zero field, then a 100 G field is applied and magnetization is measured as the temperature is increased to 10 K to give the zero-field-cooled (ZFC) data. This is then followed by cooling the sample from 2.0 to 10.0 K with the 100 G field maintained to give the field-cooled (FC) data. Atomic force microscopy (AFM) and magnetic force microscopy (MFM) measurements were carried out on a commercial instrument (Digital Instrument, Nanoscope III, Dimension 3000TM) at room temperature in air. The AFM images were obtained in tapping mode using phosphorus or antimony (n) doped Si tips. For MFM measurement, cobalt-coated tips were used operating in the lift mode. Each image was confirmed by measurements with three films in at least five different well-separated 20 \times 20 μ m² sites.

Results and Discussion

Characterization of Mn₁₂-Fatty Acid Complexes. Mn₁₂fatty acid complexes were prepared by a substitution reaction in the presence of the desired fatty acid along with the precursor Mn₁₂Ac through a modified procedure as reported in the literature.⁹ However, not all the acetate ligands of the Mn₁₂ cluster are substituted by the desired fatty acids after four successive attempts of the substitution reaction. There are only 11 stearic ligands in Mn₁₂St, 14 hexadecanoic ligands in Mn₁₂He, and 15 tetradecanoic ligands in Mn₁₂Te, as confirmed by elemental analysis and TGA. The number of coordinated fatty acids does not increase in seven sequential substitution reactions repeated for all three complexes. Considering the decreased solubility of the Mn₁₂ cluster in the reaction solution after the modification with fatty acids, as well as the similar coordination constants of acetic acid and fatty acid to Mn, the partial substitution of acetate ligands by fatty acids in Mn₁₂ clusters is reasonable. The number of coordinated fatty acids in Mn₁₂ clusters decreases with increasing alkyl chain length of fatty acids since the solubility of Mn₁₂-fatty acid complexes decreases with increasing alkyl chain length. As there are eight axial and eight equatorial ligand positions in Mn₁₂ clusters,^{9a,14} under the present case, we could not identify the positions of the acetate ligands in the Mn_{12} cluster that were not substituted by fatty acids, because all three Mn₁₂-fatty acid complexes are too difficult to crystallize.

Importantly, all three Mn_{12} -fatty acid complexes maintain their cluster structures by comparing typical vibration absorptions of $[Mn_{12}O_{12}]$ clusters to those $Mn_{12}Ac$ complexes reported in the literature, as exemplified by $Mn_{12}St$ (Figure S1 in the Supporting Information). $Mn_{12}Ac$ shows intense vibration absorptions at 1561 and 1450 cm⁻¹, which are assigned to the characteristic vibrations of Mn_{12} clusters.⁹ For the $Mn_{12}St$ complex, similar intense vibration absorptions appear at 1569



Figure 1. Magnetization hysteresis loops of the $Mn_{12}Ac$ complex (black circles), the $Mn_{12}St$ complex (red squares), and its honeycomb-patterned film (blue triangles) at 2 K.

and 1455 cm⁻¹, demonstrating the basic cluster structure of $[Mn_{12}O_{12}]$ is invariable during the process of ligand exchange. The bands at 2920 and 2850 cm⁻¹, which are assigned to the antisymmetric and symmetric stretching vibrations of the methylene group, respectively, indicate that the alkyl chain conformation of $Mn_{12}St$ is well-ordered.¹⁵ The other two complexes, $Mn_{12}He$ and $Mn_{12}Te$, also show characteristic vibration bands similar to those of the $Mn_{12}St$ complex. Similar to $Mn_{12}St$, $Mn_{12}He$ complexes display antisymmetric and symmetric stretching vibrations of the methylene group at 2919 and 2850 cm⁻¹, indicative of ordered alkyl chains, whereas the vibrations appear at 2922 and 2852 cm⁻¹ for $Mn_{12}Te$, implying relatively disordered alkyl chains.

To further verify that the magnetic properties of Mn₁₂ clusters can be maintained in Mn₁₂-fatty acid complexes, herein we utilize the Mn₁₂St complexes as an example to perform the magnetization hysteresis study by comparison with the $Mn_{12}Ac$ complex. The magnetization hysteresis loops for the Mn₁₂St complex in the powder state and the $Mn_{12}Ac$ complex in its crystal state have been measured at 2 K as shown in Figure 1. The samples were first magnetically saturated in a + 5 T field, and then the field was swept down to -5 T and cycled back to +5 T. The field-dependent magnetization of Mn₁₂Ac complex shows a rapid increase at low field to reach a value of 11.38 $\mu_{\rm B}$ at 0.9 T. Upon increasing the field intensity, the magnetization increases smoothly and reaches 14.94 $\mu_{\rm B}$ at the highest field of the experiment (5 T). However, saturation is not reached in a 5 T field. This is in contrast to the situation found in a single crystal of Mn₁₂Ac complexes, and reflects the fact that the Mn₁₂Ac complex is not well oriented with respect to the applied field in our case.9c,16 Mn12St complex also shows a magnetization unsaturation at a high magnetic field, suggesting that the Mn₁₂St complex is randomly oriented with respect to the applied field, which is consistent with its powder state. Furthermore, the magnetization of the Mn₁₂St complex is lower than that of the Mn₁₂Ac complex at the highest field of 5 T, which could be ascribed to a different spin ground state of the molecules after the substitution of St ligands in the Mn₁₂Ac complex. Previous work has shown that carboxylic ligands have an important influence on the spin ground state of the Mn₁₂ cluster, and this may result in what we have observed in our experiment.¹⁷ Mn₁₂Ac complex clearly shows a hysteresis with a coercive field of 0.84 T. As for the Mn₁₂St complex, the coercive field decreases to 0.4 T due to the partial substitution of acetate ligands by diamagnetic fatty acids, and the hysteresis clearly confirms the magnetic anisotropy in the Mn₁₂St complex. The hysteresis loop for the Mn₁₂St complex does not show steplike features, indicative of quantum tunneling of magnetization (QTM) between the energy states of the molecule, in contrast to what is observed for the crystal of the Mn₁₂Ac complex.¹⁶



Figure 2. Honeycomb structure images prepared from 1.5 mg/mL Mn_{12} St complex chloroform solution: (a) SEM image of top surface, (b) local magnification of (a), (c) SEM image of cross section, and (d) AFM image.

The absence of well-defined QTM steps can be primarily explained by the different molecular environments and the distribution of magnetization relaxation barriers existing in the randomly oriented powder sample. Similar hysteresis loops without QTM steps are a common feature of large SMMs, where disordered solvents, counterions, and ligands result in the inefficient packing of molecules.¹⁸ It is known that the shape of the hysteresis loop is always sensitive to the morphology of the sample and the remaining solvates. Here, the diamagnetic stearic ligands, the unsymmetrical microenvironment of the Mn₁₂ cluster derived from the partial substitution of stearic acids to acetate ligands in the Mn₁₂St complex, and the powder morphology of the Mn₁₂St complex all have an important influence on the magnetization of the Mn₁₂ cluster. All of these possible factors are accounted for the observed differences of magnetization hysteresis loops between the random oriented powder sample of the Mn₁₂St complex and the crystal of the $Mn_{12}Ac$ complex. Furthermore, we performed the zero-fieldcooled (ZFC) and field-cooled (FC) susceptibility measurements to estimate the blocking temperatures of the Mn₁₂Ac complex and the Mn₁₂St complex, respectively (Figure S3 in the Supporting Information). The divergence of the ZFC and the FC susceptibilities below about 3.1 K for Mn₁₂Ac complex indicates the occurrence of irreversibility of magnetization. Thus, the blocking temperature for the Mn₁₂Ac complex is about 3.1 K, whereas for the Mn₁₂St complex the blocking temperature decreases to about 2.0 K. Thus, for the Mn₁₂Ac complex and the Mn₁₂St complex, the blocking temperature decreases with decreasing the saturation of the magnetization.

Ordered Honeycomb Structures of Mn_{12} –Fatty Acid Complexes. The honeycomb structures of Mn_{12} –fatty acid complexes are constructed by casting their chloroform solutions onto glass substrates under a moist airflow across the solution surface. The films exhibit bright iridescent colors when viewed with reflected light, indicating a periodic refractive index of variation with the film thickness. Figure 2 shows representative SEM and AFM images of the honeycomb-patterned film casting from 1.5 mg/mL Mn_{12} St chloroform solution under a humid airflow of 200 mL/min. The top view of the SEM image reveals the regular, spherical pores covering a large area. A close examination through the magnified SEM image shows that the holes are uniform and well-ordered. From the image of the cross section, we can clearly see that the holes are monolayered and reach the surface of the substrate. Through use of AFM performed in tapping mode, ordered micrometer-sized porous structures can be seen, typically at a depth of 0.5 μ m, with a uniform diameter of 1.6 μ m and an interval of 1.5 μ m between adjacent holes. The Mn₁₂St honeycomb-patterned film shows similar characteristic vibration absorptions of the [Mn₁₂O₁₂] cluster and the methylene group with its bulk compound (Figure S1 in the Supporting Information).

The honeycomb-patterned films were successfully fabricated over a wide concentration range from 1.5 to 5.0 mg/mL Mn₁₂St solution. However, the holes tend to be multilayered in the honeycomb-patterned film with increasing concentration of the Mn₁₂St complex in chloroform. Specifically, the SEM and AFM images of the honeycomb-patterned film casting from 5.0 mg/ mL Mn₁₂St solution are shown in Figure 3. From the top view of the SEM image, the pores in the second layer can be seen clearly through the surface layer. SEM image of the cross section indicates that the holes are multilayered, but do not reach the bottom of the film. Tapping mode AFM images further confirm the ordered micrometer-sized porous structures with a porous sublayer, where the average diameter of the surface holes is ca. 1.2 μ m separated by ca. 1.3 μ m, which is smaller than those in the case of 1.5 mg/mL complex solutions. By comparison of honeycomb-patterned films prepared from 1.5 and 5.0 mg/mL complex solutions, we can see that the concentration of the complex solution has an impact on both the size and arrangement of the pores. An increase in the concentration of the complex solution usually results in the multilayered structure accompanied by a decrease in the pore size;¹⁹ thus we could adjust the structure of the honeycomb-patterned film to some extent by changing the concentration of the complex solution. No honeycomb morphology has been observed on the films prepared under ambient atmosphere with relative humidity below 30%, further confirming that the honeycomb structure formation is driven by the water droplets condensing on the surface of the evaporating solution.

To examine the generality of this supramolecular selforganized method for the construction of Mn₁₂St honeycomb structures, we investigated the effects of the velocity of humid airflow, as well as solvent type and substrate composition, on the morphology of the honeycomb structures. As seen from the comparison of Figure 2 and Figure S4 in the Supporting Information, the average size of the holes in the honeycombpatterned film increases from 1.6 to 1.9 μ m, and the wall contracts from 1.5 to 1.2 μ m, with increasing velocity of humid airflow from 200 to 300 mL/min. By further increasing velocity of humid airflow to 400 mL/min, the average size of the holes increases to 2.2 μ m with the walls contracting to 0.5 μ m. Furthermore, at this higher velocity of humid airflow, holes in the honeycomb-patterned film show a relatively large size distribution, and some visible defects appear. A high velocity of humid airflow increases the evaporation rate of solvent, and thus reduces the opportunities for the condensation and growth of water droplets.²⁰ At the same time, a high velocity of humid airflow also brings additional moisture and can result in contradictory effects. Here, the increase in velocity of humid airflow seemed to aid in the condensation and swelling of the water droplets on the casting solution even with an increased evaporation rate of solvent. Additionally, the extremely high velocity of humid airflow results in the unavoidable coalescence of the condensed water droplets and the increased instability of the evaporating solution, both of which result in the disorder and defects observed in the honeycomb-patterned film.



Figure 3. Honeycomb structure images prepared from 5.0 mg/mL $Mn_{12}St$ complex chloroform solution: (a) SEM image of top surface, (b) SEM image of cross section, and (c) AFM image.

TABLE 1: Vapor Pressure and Molecular Weight of the Used Solvents (20 $^{\circ}\mathrm{C})$

	dichloromethane	carbon disulfide	chloroform	benzene
vapor pressure (kPa)	46.50	39.24	21.28	10.67
molecular weight	84.93	76.14	119.38	78.11

Films prepared from dichloromethane, carbon disulfide, and benzene solutions also show honeycomb structures, but the holes are less regular than those formed from chloroform (Figure S5 in the Supporting Information). Micropores in the film castings from dichloromethane and carbon disulfide are smaller than those formed from chloroform, while the film casting from benzene shows a larger-sized honeycomb structure. The major differences between the solvents applied are their differential evaporation rates. The evaporation rate of the solvent depends mostly on the vapor pressure above the solvent as well as the molecular weight of the solvent (Table 1). Typically, higher vapor pressure and lower molecular weight lead to faster evaporation rates.²¹ With vapor pressure decreasing, solvent volatility is lessened, allowing water droplets more time to coalesce and grow larger on the surface of the solution, consequently forming larger pores. Rapid evaporation of solvent leads to the instability of the solution surface, and the honeycomb-patterned film may be solidified well before the arrangement of the condensed water droplets. On the other hand, slow evaporation of solvent may lead to unavoidable coalescence, which decreases the order of the honeycomb-patterned films. As a result, the proper evaporation rate of the solvent is essential for the formation of ordered honeycomb-patterned films. In addition to glass, mica and silicon were used as the substrates for the preparation of Mn₁₂St honeycomb-patterned films (Figure S6 in the Supporting Information).²² An ordered honeycomb-patterned surface was observed on mica, similar to that on glass. However, on the less hydrophilic silicon substrate, disordered holes with a relatively broad size distribution were observed. The ordered honeycomb-patterned films are easily prepared on hydrophilic substrates because of the favorable spreading of the complex solution, as well as the steady absorbance of the condensed water droplets onto the hydrophilic substrates to assist in molding patterned structures.

Moreover, we have also tried Mn_{12} complexes with shorter alkyl chains, $Mn_{12}He$ and $Mn_{12}Te$, to fabricate honeycomb structures (Figure S7 in the Supporting Information). Films formed from solutions of 1.5 and 5.0 mg/mL $Mn_{12}He$ in chloroform exhibit a type of honeycomb-patterned morphology; however, pores in these honeycomb-patterned films do not show an ordered hexagonal packing. In the case of $Mn_{12}Te$, failure to form uniformed honeycomb structures is demonstrated, and only large disordered holes with a relatively broad size distribution are observed in the casting field at the 1.5 and 5.0 mg/mL concentrations. The porous films of both $Mn_{12}He$ and $Mn_{12}Te$ complexes show the same spectral features of their corresponding bulk compounds, respectively (Figure S1 in the Supporting Information). The results show that the Mn_{12} -fatty acid complexes with the shorter alkyl chains are unfavorable for the construction of ordered honeycomb structures, which is consistent with our previous studies on surfactant-encapsulated polyoxometalate complexes and DNA-surfactant complexes.¹² Furthermore, we have also tried to prepare Mn_{12} -eicosanoic acid complex for honeycomb pattern formation, but the obtained complex shows low solubility in chloroform, dichloromethane, benzene, etc., and thus cannot form films by solvent casting techniques. Therefore, it is difficult to give an example of honeycomb-patterned films fabricated from Mn_{12} complexes with more hydrophobic fatty acid ligands to establish the trend for the formation of ordered honeycomb-patterned films.

Honeycomb-patterned films based on polymers and nanoparticle materials by using ordered condensed water droplets as template have been extensively investigated.^{2a,23} Considering the consistency of our results with those of polymer systems and modified nanoparticles, a similar mechanism for the formation of ordered honeycomb-patterned films of Mn₁₂-fatty acid complexes is proposed: (1) When the moist airflow passes across a volatile solution of Mn₁₂-fatty acid complex, the rapid evaporation of the solvent induces a cooling of the solution surface, allowing water vapor to condense into droplets on the solution surface. (2) The water droplets grow with time by molecular condensation until they reach a self-limiting narrow size distribution, while convective currents on the surface and short-range lateral capillary forces among the water droplets drive the droplets into hexagonally packed arrays. Coalescence of the water droplets is inhibited by Mn₁₂-fatty acid complexes adsorbed and precipitated at the interface between the chloroformcontaining solution and the water droplets. Additionally, this mechanism provides a reasonable explanation for the formation of multilayered films. It is proposed that water droplets will continually sink into the solution at which point they will condense and arrange themselves upon a previously fashioned monolayer of water droplets, creating a structure similar to that observed in Figure 3b. (3) After complete evaporation of the solvent and the encapsulated water droplets, hexagonally arranged pores are imprinted in the film of the Mn₁₂-fatty acid complex. Based on experimental results presented here, it is obvious that the size and regularity of the pores can be controlled by changing any experimental parameters that affect the above three steps, such as humidity, solvent, temperature, and casting volume.

Magnetic Property of Ordered Honeycomb Structure. MFM, a microscopy technique utilizing a magnetic tip, is a powerful tool to study magnetic properties of patterned structures, allowing the combination of topographic imaging of an object with the mapping of local distribution of magnetic moments. Mn₁₂ clusters are paramagnetic without a preferential



Figure 4. MFM images of $Mn_{12}St$ honeycomb-patterned film: (a) topography, (b) corresponding phase-contrast image at 300 nm lift height, and (c) cross section along the line indicated in (a).

ordering of their magnetic moments at room temperature. Nevertheless, application of a magnetic tip will magnetize Mn₁₂ clusters at room temperature, and this collection of magnetic moments of Mn₁₂ clusters is powerful enough to generate a detectable magnetic contrast with the diamagnetic surroundings in MFM images.²⁴ Figure 4 shows the MFM image of the honeycomb-patterned surface casting from 1.5 mg/mL Mn₁₂St chloroform solution at room temperature. The image was recorded in two scans over the same area. On the first scan, the topography was recorded using "tapping mode", and a similar pattern to that shown in Figure 2d, albeit with a lower resolution due to the use of a thicker cobalt-coated tip, was observed (Figure 4a). Furthermore, from the cross section of the MFM topography image, it can be seen that the walls of the holes are not vertical but sloped with respect to the substrate (Figure 4c), which is common in breath figure patterned films and consistent with the shape of the water droplets.2b Subsequently, the tip was retracted to a selected lift scan height in the range of 50-300 nm, at which height the interatomic van der Waals force is virtually nonexistent and only long-range magnetic force persists. The MFM image shown in Figure 4b with a cobaltcoated tip at 300 nm clearly indicates a magnetic gradient response corresponding to the molecular position found by topographic imaging. The regions with deposited Mn₁₂St complex show a lighter phase than the uncovered areas, indicating that the deposited material is magnetically active and interacts in an attractive manner with the magnetized tip. It is noted that the inner edge of the holes also demonstrates a magnetic signal from the Mn₁₂St complex in MFM phasecontrast image because the walls of the holes are sloped. Only the center of the hole, which is exposed substrate, shows a different magnetic contrast than the Mn₁₂St complex. Combining the topography and phase-contrast results from the MFM image, ca. 62% of the total area of the honeycomb film is covered by $Mn_{12}St$ complex with a typical thickness of 0.5 μ m. This observation confirms the formation of a spatially distributed magnetic pattern and thus confirms the role of magnetic $Mn_{12}St$ complexes in the formation of the honeycomb-patterned surface.

Significantly, the typical magnetic properties of Mn_{12} singlemolecule magnets are maintained in the Mn_{12} St honeycombpatterned film as confirmed by the magnetization hysteresis study at 2 K. The magnetization hysteresis loop for the Mn_{12} St ordered honeycomb-patterned film shows both similar loop features and the same coercive field of 0.4 T with those randomly oriented Mn_{12} powder samples as seen in Figure 1. Furthermore, the Mn_{12} St honeycomb-patterned film shows similar magnetization at the highest field of 5 T and the blocking temperature. Thus, the solvent casting process under humid conditions shows little influence on the single-molecule magnetic property of the complex. Mn_{12} St honeycomb-patterned surfaces demonstrating typical single-molecule magnetic properties show a promising perspective as magnetic quantum bits for information storage or quantum computing.

Conclusions

The modification of fatty acids not only brings the Mn_{12} clusters an amphiphilic property, allowing themselves to stabilize the condensed water droplets, but also protects the Mn₁₂ clusters from decomposition when in contact with water and helps maintain the features of SMMs, thus forming ordered magnetic patterns on substrates. Both two-dimensional and threedimensional honeycomb structures were obtained by adjusting the concentration of the complex solution. The ordered honeycomb structures are easily formed on the hydrophilic substrates. The pore size of the honeycomb-patterned film can be scaled down by decreasing the velocity of the humid airflow or increasing the concentration of the complex solution and the vapor pressure of the solvents. The proper hydrophobicity of the fatty acid in the Mn₁₂ complex was confirmed to be a prerequisite for the formation of ordered honeycomb-patterned films. Specifically, highly ordered honeycomb-patterned surfaces, with monolayered, closely packed, hexagonally patterned holes were formed on glass substrates from a solution containing 1.5 mg/mL Mn₁₂St in chloroform. Mn₁₂-based honeycomb structures exhibit a paramagnetic response at room temperature, and thus give rise to a spatially distributed magnetic pattern on the substrate, which can be characterized by MFM. Importantly, the single-molecule magnetic property of the Mn₁₂ complex at low temperature is well maintained in the honeycomb-patterned film, which can be effectively used as a permanent information storage medium with magnetic readout, representing a promising perspective for high-density information storage and quantum computing applications.

Acknowledgment. The authors acknowledge financial support from the National Basic Research Program (2007CB808003), National Natural Science Foundation of China (20731160002, 20973082, 50973042, 20703019), National Science Foundation International Research Experience for Students (OISE-0824860), PCSIRT of Ministry of Education of China (IRT0422), 111 Project (B06009), for supporting the visit and helpful discussion from Prof. Bin Hu at the University of Tennessee, Open Project of State Key Laboratory of Polymer Physics and Chemistry of CAS, and West Virginia Graduate Student Fellowships in Science, Technology, Engineering and Mathematics (STEM).

Supporting Information Available: FT-IR spectra and TGA thermograms of Mn_{12} —fatty acid complexes. SEM images and optical micrographs of the honeycomb-patterned films prepared under different conditions: velocity of humid airflow; substrate; solvent; length of alkyl chain in Mn_{12} cluster. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(a) Widawski, G.; Rawiso, M.; Francois, B. *Nature* **1994**, *369*, 387–389.
 (b) Francois, B.; Pitois, O.; Francois, J. *Adv. Mater.* **1995**, *7*, 1041–1044.

(2) (a) Srinivasarao, M.; Collings, D.; Philips, A.; Patel, S. Science **2001**, 292, 79–82. (b) Bunz, U. H. F. Adv. Mater. **2006**, *18*, 973–989.

(3) (a) Yabu, H.; Takebayashi, M.; Tanaka, M.; Shimomura, M. *Langmuir* **2005**, *21*, 3235–3237. (b) Yabu, H.; Shimomura, M. *Chem. Mater.* **2005**, *17*, 5231–5234. (c) Yabu, H.; Shimomura, M. *Langmuir* **2005**, *21*, 1709–1711. (d) Nishikawa, T.; Nishida, J.; Ookura, R.; Nishimura, S.-I.; Wada, S.; Karino, T.; Shimomura, M. *Mater. Sci. Eng. C* **1999**, *8–9*, 495–500. (e) de Boer, B.; Stalmach, U.; Nijland, H.; Hadziioannou, G. Adv. Mater. **2000**, *12*, 1581–1583.

(4) (a) Leroueil, P. R.; Hong, S.; Mecke, A.; Baker, J. R.; Orr, B. G.; Holl, M. M. B. *Acc. Chem. Res.* **2007**, *40*, 335–342. (b) Penner, R. M. *Acc. Chem. Res.* **2000**, *33*, 78–86. (c) Yu, X.; Cao, C.; An, X. *Chem. Mater.* **2008**, *20*, 1936–1940.

(5) (a) Khanal, B. P.; Zubarev, E. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 2195–2198. (b) Zhang, L.; Si, H.; Zhang, H. *J. Mater. Chem.* **2008**, *18*, 2660–2665. (c) Li, J.; Peng, J.; Huang, W.; Wu, Y.; Fu, J.; Cong, Y.; Xue, L.; Han, Y. *Langmuir* **2005**, *21*, 2017–2021. (d) Böker, A.; Lin, Y.; Chiapperini, K.; Horowitz, R.; Thompson, M.; Carreon, V.; Xu, T.; Abetz, C.; Skaff, H.; Dinsmore, A. D.; Emrick, T.; Russell, T. P. Nat. Mater. **2004**, *3*, 302–306.

(6) (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141–143. (b) Sessoli, R.; Tsai, H.-K.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804–1816.

(7) (a) Krusin-Elbaum, L.; Shibauchi, T.; Argyle, B.; Gignac, L.; Weller, D. *Nature* **2001**, *410*, 444–446. (b) Chudnovsky, E. M.; Tejada, J. *Macroscopic Quantum Tunneling of the Magnetic Moment*; Cambridge University Press: Cambridge, 1998. (c) Del Barco, E.; Vernier, N.; Hernandez, J. M.; Tejada, J.; Chudnovsky, E. M.; Molins, E.; Bellesa, G. *Europhys. Lett.* **1999**, *47*, 722–728. (d) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *40*, 789–793. (e) Coronado, E.; Gatteschi, D. J. Mater. Chem. **2006**, *16*, 2513–2515.

(8) Gómez-Segura, J.; Veciana, J.; Ruiz-Molina, D. Chem. Commun. 2007, 3699–3707.

(9) (a) Lis, T. Acta Crystallogr. **1980**, B36, 2042–2046. (b) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. MRS Bull. **2000**, 25, 66–71. (c) Gatteschi, D.; Sessoli, R. Angew. Chem., Int. Ed. **2003**, 42, 268–297. (d) Aubin, S. M. J.; Sun, Z.; Eppley, H. J.; Rumberger, E. M.; Guzei, I. A.; Folting, K.; Gantzel, P. K.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. Polyhedron **2001**, 20, 1139–1145. (e) Terazzi, E.; Bourgogne, C.; Welter, R.; Gallani, J.-L.; Guillon, D.; Rogez, G.; Donnio, B. Angew. Chem., Int. Ed. **2008**, 47, 490–495. (f) Rogez, G.; Donnio, B.; Terazzi, E.; Gallani, J.-L.; Kappler, J.-P.; Bucher, J.-P.; Drillon, M. Adv. Mater. **2009**, 21, 1–11.

(10) (a) Nait Abdi, A.; Bucher, J. P.; Rabu, P.; Toulemonde, O.; Drillon,
M.; Gerbier, P. J. Appl. Phys. 2004, 95, 7345–7347. (b) Steckel, J. S.;
Persky, N. S.; Martinez, C. R.; Barnes, C. L.; Fry, E. A.; Kulkarni, J.;
Burgess, J. D.; Pacheco, R. B.; Stoll, S. L. Nano Lett. 2004, 4, 399–402.
(c) Condorelli, G. G.; Motta, A.; Fragalà, I. L.; Giannazzo, F.; Raineri, C.;
Caneschi, A.; Gatteschi, D. Angew. Chem., Int. Ed. 2004, 43, 4081–4084.

(d) Kim, K.; Seo, D. M.; Means, J.; Meenakshi, V.; Teizer, W.; Zhao, H.; Dunbar, K. R. *Appl. Phys. Lett.* **2004**, *85*, 3872–3874. (e) Cavallini, M.; Biscarini, F.; Gómez-Segura, J.; Ruiz-Molina, D.; Veciana, J. *Nano Lett.* **2003**, *3*, 1527–1530.

(11) Mannini, M.; Sainctavit, P.; Sessoli, R.; dit Moulin, C. C.; Pineider, F.; Arrio, M.-A.; Cornia, A.; Gatteschi, D. *Chem. – Eur. J.* **2008**, *14*, 7530–7535.

(12) Gómez-Segura, J.; Kazakova, O.; Davies, J.; Josephs-Franks, P.; Veciana, J.; Ruiz-Molina, D. *Chem. Commun.* **2005**, 5615–5617.

(13) (a) Bu, W.; Li, H.; Sun, H.; Yin, S.; Wu, L. J. Am. Chem. Soc.
2005, 127, 8016–8017. (b) Sun, H.; Li, H.; Bu, W.; Xu, M.; Wu, L. J. Phys. Chem. B 2006, 110, 24847–24854. (c) Sun, H.; Li, H.; Wu, L. Polymer 2009, 50, 2113–2122. (d) Sun, H.; Li, W.; Wu, L. Langmuir 2009, 25, 10466–10472.

(14) Soler, M.; Artus, P.; Folting, K.; Huffman, J. C.; Hendrickson,
 D. V.; Christou, G. Inorg. Chem. 2001, 40, 4902–4912.

(15) MacPhail, R. A.; Strauss, H. L.; Snyder, R. G.; Elliger, C. A. J. Phys. Chem. 1984, 88, 334–341.

(16) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145–147.

(17) (a) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. J. Am. Chem. Soc. **1993**, *115*, 1804–1816. (b) Coronado, E.; Forment-Aliaga, A.; Gaita-Ariño, A.; Giménez-Saiz, C.; Romero, F. M.; Wernsdorfer, W. Angew. Chem., Int. Ed. **2004**, *43*, 6152–6156.

(18) (a) Stamatatos, T. C.; Abboud, K. A.; Wernsdorfer, W.; Christou, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 884–888. (b) Coronado, E.; Feliz, M.; Forment-Aliaga, A.; Gómez-García, C. J.; Llusar, R.; Romero, F. M. *Inorg. Chem.* **2001**, *40*, 6084–6085. (c) Clemente-León, M.; Coronado, E.; Forment-Aliaga, A.; Romero, F. M. C. R. Chim. **2003**, *6*, 683–688.

(19) (a) Tian, Y.; Liu, S.; Ding, H.; Wang, L.; Liu, B.; Shi, Y. *Macromol. Chem. Phys.* **2006**, 207, 1998–2005. (b) Cheng, C.; Tian, Y.; Shi, Y.; Tang, R.; Xi, Fu *Macromol. Rapid Commun.* **2005**, *26*, 1266–1272.

(20) Wong, K. H.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. Polymer 2007, 48, 4950–4965.

(21) (a) Peng, J.; Han, Y.; Yang, Y.; Li, B. *Polymer* **2004**, *45*, 447–452. (b) Tian, Y.; Ding, H.; Jiao, Q.; Shi, Y. *Macromol. Chem. Phys.* **2006**, 207, 545–553.

(22) Cheng, C.; Tian, Y.; Shi, Y.; Tang, R.; Xi, F. *Langmuir* **2005**, *21*, 6576–6581.

(23) (a) Pitois, O.; Francois, B. *Eur. Phys. J. B* 1999, 8, 225–231. (b) Maruyama, N.; Koito, T.; Nishida, J.; Sawadaishi, T.; Cieren, X.; Ijiro, K.; Karthaus, O.; Shimomura, M. *Thin Solid Films* 1998, *327–329*, 854–856.
(c) Karthaus, O.; Maruyama, N.; Cieren, X.; Shimomura, M.; Hasegawa, H.; Hashimoto, T. *Langmuir* 2000, *16*, 6071–6076.

(24) Nishide, H.; Ozawa, T.; Miyasaka, M.; Tsuchida, E. J. Am. Chem. Soc. 2001, 123, 5942–5946.

JP906520J