Multifunctional organic-inorganic hybrid films deposited by the Langmuir-Blodgett technique

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Chapter 7

Thin Film Deposition of Perovskite-Based Ferromagnetic Organic-Inorganic Hybrid

Perovskite-based organic-inorganic hybrids prepared through layer-by-layer deposition hold great potential for many applications in electronics, optoelectronics and as components of biosensors. However, many of these applications require thin films grown with complete control over structure and thickness – a major challenge that needs to be addressed. The work presented in this chapter is an effort towards this goal and concerns the construction at ambient conditions of heterostructures that consist of a framework of alternating perovskite and organic layers. The Langmuir-Blodgett technique used to assemble these structures provides the intrinsic control over the molecular organization and film thickness down to the molecular level. These CuCl₄-based LB films showed long range ferromagnetic ordering below 10 K. The easy axis of the magnetic spins lies in the out-of-plane direction - contrary to what was found for similar organic-inorganic hybrids in bulk form. Moreover, these films exhibit polar interfaces between the perovskite and the organic layers and are hence different from the traditional Van der Waals interaction-based intercalated compounds.

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*This chapter is based on N. Akhtar, A. O. Polyakov, A. Aqeel, H. Amenitsch, P. Rudolf and T. T. M. Palstra, “Thin Film Deposition of Perovskite-Based Ferromagnetic Organic-Inorganic hybrid”, in preparation for submission.
7.1. Introduction

Organic-inorganic hybrid materials have attracted significant attention due to their versatility for combining various functionalities such as multiferroicity, semiconducting and exotic magnetic properties\textsuperscript{1-6}. Such materials enable the integration of desirable properties of individual components into one single composite and have the additional advantage of low cost processing, which is important for technological applications\textsuperscript{7-11}. In particular, self-assembling heterostructures with well-defined smooth interfaces hold great promise for integrated device systems. The work presented here derived inspiration from the report on multiferroicity in $\text{CuCl}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$ hybrid crystals\textsuperscript{2}; these crystals have a layered structure with polar interfaces where the interaction between the $\text{CuCl}_4^{2-}$ octahedra and $\text{NH}_3^+$ group has a crucial effect on properties of material. The challenge addressed by this project was to produce these materials in the form of thin films to make them potentially available for industrial applications\textsuperscript{12-13}.

The copper-based hybrid family was taken as a bulk-form prototype for the film synthesis. The hybrid structure in the bulk compound is formed by self-assembly with solvent evaporation\textsuperscript{14}. Organic and inorganic parts are connected via hydrogen bonds between the $\text{NH}_3^+$ group and the chloride part of $\text{CuCl}_4^{2-}$ octahedra. In the case of thin films, one can expect the same arrangement. In his pioneering efforts, Mitzi has demonstrated various techniques for the successful deposition of organic-inorganic thin films via sol-gel, Langmuir-Blodgett (LB) and solution processing\textsuperscript{15}. Among these techniques, the Langmuir-Blodgett technique which takes advantage of the soluble nature of the precursors for these hybrid materials provides an excellent control down to the molecular level through simple tuning of external parameters during growth. This technique can be used to grow not only organic supramolecular architectures on surfaces but also ultrathin inorganic structures\textsuperscript{16}, for example H. Sugai \textit{et al.} used LB deposition to synthesize $\text{PbTiO}_3$ ultrathin films with stearic acid, Pb salts, and Ti salt as starting precursors\textsuperscript{17}. Contrary to pulsed laser deposition (PLD) or molecular beam epitaxy (MBE), where light organic molecules will easily decompose as a result of high temperature processing, the LB technique provides safe synthesis conditions for the organic material. In fact, it implies layer-by-layer synthesis from the solvent-air interface, and thus simply requires amphiphilic organic molecules with terminal cationic groups which, when spread on the $\text{CuCl}_2$ salt containing water surface, lead to hybrid formation at the interface. Moreover, it allows to tune the electrical and magnetic properties by modifying the interlayer spacing in the multilayer film. The distance between the inorganic sheets can be changed by changing the length of the organic ligands.
7.2. LB film preparation

Octadecyl amine (>99 %) was purchased from Fluka. Copper chloride (CuCl\(_2\); 99.999 %), methyl ammonium chloride (MA), and other chemical reagents of analytical grade were purchased from Sigma-Aldrich and used as received. To prepare octadecyl ammonium chloride (ODA\(\text{H}^+\)Cl\(^-\)), concentrated hydrochloric acid was slowly added to a stoichiometric octodecyl amine solution in ethanol. After reaction, the end product was filtered and re-crystallized with ethanol and chloroform. The subphase employed in the experiments was an aqueous solution of CuCl\(_2\) (1.0×10\(^{-3}\) mol/L) and MA (1.0×10\(^{-3}\) mol/L). Ultra-pure ion free water having a resistivity of greater than 18 M\(\Omega\)-cm was used for the preparation of subphase. Surface pressure-molecular area (\(\Pi\)-a) isotherm measurements and deposition experiments were performed using a NIMA Technology thermostated LB trough. The temperature was kept at 21 \(^\circ\)C during these experiments. Langmuir films were obtained by spreading a chloroform-methanol (9:1) solution of ODA\(\text{H}^+\)Cl\(^-\) (0.15 mg/ml) onto the subphase. After a one hour waiting time to allow for solvent evaporation, the molecules were compressed at a rate of 30 cm\(^2\) min\(^{-1}\) by a movable barrier until a desired surface pressure was reached and this pressure was kept constant during the whole deposition process. The compressed Langmuir film was allowed to stabilize for 30 min time before deposition. LB films were deposited by vertical dipping of hydrophobic substrates into the subphase at a dipping speed of 5 mm/min. A Langmuir film was deposited each time the substrate moved across the air-water interface. Hence, one dipping cycle (dipping down and taking up the substrate from the subphase) gives two hybrid layers.

7.3. Results and discussion

7.3.1. Characterization of the Langmuir film and deposition

A first step towards the optimization of the quality of a film deposited by the Langmuir-Blodgett technique is to study the properties of Langmuir film assembled at the air-water interface. Pressure-area isotherms recorded during the compression of the Langmuir film indicate on whether a film is formed from the available molecular building blocks and yield crucial information on the molecular packing and the stability of the film. Brewster angle microscopy (BAM) on the other hand provides direct real time visualization of the homogeneity and the morphology, as well as highlight phase changes in the floating film at water surface.
Figure 7.1 displays the surface pressure-area per molecule (\(\Pi-a\)) isotherm of ODAH\(^+\)Cl\(^-\) on CuCl\(_2\)-MA subphase along with BAM images taken at various stages during continuous compression. While \(\Pi-a\) isotherms recorded in a Langmuir trough usually start at \(\Pi=0\), here isotherm started at an initial surface pressure of \(\sim 2\) mN/m. Such a high initial surface pressure in the ODAH\(^+\)Cl\(^-\) isotherm has also been observed for a PbCl\(_2\)-MA subphase, as reported by L. Xu \textit{et al.}\(^{18}\), and results from the electrostatic repulsion between ODAH\(^+\) and positive metal ions.

The isotherm of ODAH\(^+\)Cl\(^-\) layer on pure water gives a lift-off area of \(\sim 30\) Å\(^2\)\(^{18}\). In the presence of CuCl\(_2\)-MA in the water resulted in a higher lift-off area of \(\sim 50\) Å\(^2\). The surface pressure showed a smooth rise upon compression in the expanded regime of the Langmuir film (\(\Pi < 16\) mN/m) and a uniform film was observed at \(\Pi \sim 10\) mN/m as shown by the BAM image. At \(\Pi = 16\) mN/m, where the isotherm changed slope, a phase transition was observed in the BAM images associated with a change in conformation of ODAH\(^+\) molecules at water surface. Presumably the ODAH\(^+\) molecules tend to lie down on the water surface at lower pressures (\(\Pi < 16\) mN/m) but stand up when the pressure is increased and give rise to a higher reflectivity in the BAM images.

The steeper slope of the isotherm in the region \(\Pi > 16\) mN/m supports this hypothesis since it indicates that the new phase is more rigid and densely packed. The Langmuir film could not be compressed beyond a molecular area of 20 Å\(^2\) and collapsed at \(\Pi \sim 38\) mN/m. The isotherm behaviour suggests the compression has induced the formation of a rigid CuCl\(_x\)-based sheet underneath the ODAH\(^+\) molecular layer through electrostatic interaction. As sketched in the model of the Langmuir film in Figure 7.2, we propose that this CuCl\(_x\)-based layer is composed of Cl octahedra encaging the central Cu ions. Such a perovskite-like inorganic-organic superlattice structure has been reported for lead chloride\(^{18\text{-}19}\). The CuCl\(_6^{2-}\) octahedra are formed by 4 Cl\(^-\) atoms coming from the neighbouring atoms in the same plane, plus one from the methylammonium chloride (MA) in the subphase and one from the amphiphilic ODAH\(^+\)Cl\(^-\) molecule. In such an arrangement the resulting hybrid structure has two types of organic spacers, – ODAH\(^+\) and MA, as drawn in the top left panel of Figure 7.2. When a hydrophobic substrate is dipped into the trough, the hydrophobic tails of octadecyl ammonium chloride interact with it during the downstoke, while during the upstroke the methyl ammonium chloride spacers interact and a Y-type LB film structure is formed at the end of the cycle.
Figure 7.1. Π-a isotherm of ODAH$^+$Cl$^-$ on an aqueous CuCl$_2$-MA subphase and Brewster angle micrographs taken at various stages during the continuous compression.

An additional indication that such a stable and therefore easily transferable Langmuir film has actually formed comes from the transfer characteristics plotted in figure 7.3, which testify to the successful transfer of the Langmuir layer onto a substrate. The dashed line in the top panel of figure 7.3 shows the displacement of the substrate as a function of time which corresponds to dipping into the subphase; four dip cycles are clearly identified. The solid black curve represents the trough area covered by the ODAH$^+$-CuCl$_x$ recorded as a function of deposition time. When the substrate moves into the subphase during each dip, the trough area reduces due to the transfer of part of the Langmuir film from the subphase surface to the substrate. The transfer ratio is 1 if the decrease in area is equal to the substrate surface area. In the present case, the transfer ratio was unity for the downward stroke and 0.98±0.02 for the upward stroke, suggesting Y-type deposition$^{20}$. The grey curve in the bottom panel of figure 7.3 displays the surface pressure during the deposition process; it is seen to remain perfectly stable as desired in good deposition conditions.
Figure 7.2. Schematics of the ordered Langmuir film floating at the subphase surface, built up from octadecyl ammonium chloride (ODAH\textsuperscript{+}Cl\textsuperscript{−}), CuCl\textsubscript{2} and methyl ammonium chloride (MA), and its transfer to a hydrophobic substrate during one dipping cycle at stable surface pressure.
Figure 7.3. Deposition of an 8-layer-thick $CuCl_4$-based hybrid LB film at stable surface pressure of $\sim 30$ mN/m (grey curve). Upper panel: the dashed curve shows the displacement of the substrate as a function of time which corresponds to dipping into the subphase; the black curve represents the trough area covered by the Langmuir film. The trough area is seen to decrease in each dipping cycle as a result of the transfer of the Langmuir film from the trough to the substrate. Lower panel: the grey curve denotes the surface pressure which is constant during the whole deposition.

### 7.3.2. Scanning electron microscopy (SEM)

To visualize the LB film on the surface, a scanning electron microscopy (SEM; JSM-7000F; Jeol) analysis was performed on a 3-layer thick $CuCl_4$-based hybrid LB film deposited on a hydrophobic Au surface. The SEM micrographs presented in figure 7.4 showed the presence of patches (dark areas in the images) with a diameter of 3-5 μm and well defined boundaries. Between the patches the deposited film seems to be less ordered or amorphous.
7.3.3. X-ray photoelectron spectroscopy data acquisition and analysis

X-ray photoelectron spectroscopy (XPS) measurements were performed on a bulk hybrid with molecular formula $(C_6H_5CH_2CH_2NH_3)_2CuCl_4$ in powder form and on a 16-layer thick $CuCl_4$-based hybrid LB film. Both samples are layered materials where the charged sheets of $CuCl_4^{2-}$ are bonded with the $NH_3^+$ group of the organic molecules at the inorganic/organic interface. We expect the crystal structure of the $CuCl_4$ layer in the LB film to be akin to that of the bulk hybrid and therefore the photoemission lines of N, Cu, and Cl to be similar. The survey spectrum of the $CuCl_4$-based hybrid LB film shown in figure 7.5 featured the photoemission lines of all expected elements, namely C, N, Cu, and Cl. This confirms the incorporation of the inorganic component along with the organic ones in the film structure. To investigate the bonding of the constituent elements in the material, detailed scans of the Cu 2p, Cl 2p, and N 1s core level regions were collected and analysed. The photoemission spectra of Cu 2p$_{3/2}$ core level region for $CuCl_4$-based powder hybrid and $CuCl_4$-based hybrid LB film are presented in figure 7.6. Both spectra showed broad shoulder at the high binding energy side of the main peak. This is a signature of Cu being in the +2 oxidation state and arises due to multiplet splitting. The Cu 2p$_{3/2}$ spectrum for the bulk hybrid was fitted with a single component peaked at a binding energy (BE) of 934.4 eV which corresponds to Cu-Cl bonds within the octahedra; the broad shoulder was fitted with two peaks in this case.
Figure 7.5. X-ray photoemission survey spectra of a $CuCl_4$-based bulk hybrid in powder form (a) and of a 16-layer-thick $CuCl_4$-based hybrid LB film (b).

Figure 7.6. X-ray photoemission spectra of the Cu 2p$_{3/2}$ core level region of a $CuCl_4$-based bulk hybrid (left panel) in powder form and of a 16-layer-thick $CuCl_4$-based hybrid LB film (right panel) and fits to the experimental lines (see text for details).
Fitting the Cu 2p$_{3/2}$ line of the CuCl$_4$-based hybrid LB film revealed the presence of an additional low energy component at a BE of 932.9 eV next to the one at 934.6 eV. This low energy component also originates from Cu$^{2+}$ ions as is evident from the corresponding multiplet structure appearing at 941.5 eV. The multiplet structure was fitted with one broad peak due to the limited signal to noise ratio in hybrid LB films. Similarly, the multiplet structure of the component at a binding energy of 934.6 eV was fitted with a single broad peak centred at 943.6 eV. The ratio of main component peak area to that of corresponding satellite peak remains same for bulk hybrid and hybrid LB film.

A detailed scan of Cl 2p core level region for the CuCl$_4$-based bulk hybrid is shown in figure 7.7; the spectrum is fitted with one component peaked at 198.2 eV binding energy and that corresponds to Cl-Cu bond in the octahedron. However, an additional peak appears in the Cl 2p line of the hybrid LB film at 199.4 eV. The presence of two types of components in the Cu 2p$_{3/2}$ and Cl 2p spectra points to two phases in the film structure. About ~70% of the LB film has an inorganic layer structure similar to that of the CuCl$_4$-based powder hybrid. The second phase still has Cu$^{2+}$ and Cl$^-$ as the inorganic part but the bonding geometry must be different from the octahedral one since the lower binding energy of the additional component in the Cu 2p$_{3/2}$ spectrum indicates a lower co-ordination. If we estimate the Cu$^{2+}$ to Cl$^-$ ratio for two phases from the intensities of the components in the photoemission spectra normalized by the sensitivity factors of each element including analyser transmission, we find Cu$^{2+}$ : Cl$^-$ = 1 : 4 for the octahedral co-ordination and Cu$^{3+}$ : Cl$^-$ = 1 : 3 for the 2$^{nd}$ phase. Table 1 lists the binding energies of all fitted components of the Cu 2p$_{3/2}$, Cl 2p and N 1s XPS lines and the corresponding contribution to the total peak area in percentage. Figure 7.7 also shows the N 1s spectra for both samples. The spectrum of the bulk hybrid consists of a single line assigned to the H$_3$N$^+$-C bond of the organic molecule. In the spectrum of the CuCl$_4$-based hybrid LB film, an additional component at lower binding energy (400.3 eV) specifies that ~21% of the nitrogen is de-protonated. This suggests that the presence of the organic molecules with a de-protonated amine group results in the formation of the 2$^{nd}$ phase in the CuCl$_4$-based hybrid LB film.
Figure 7.7. X-ray photoemission spectra of the Cl 2p (top panels) and N 1s (bottom panel) core level region of a CuCl₄-based bulk hybrid in powder form and a 16-layer-thick CuCl₄-based hybrid LB film. Fits to the experimental lines are also shown (see text for details).
Table 1. Binding energies (B.E.) of photoemission peaks and corresponding peak areas obtained from fitting of the experimental data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu 2p$_{3/2}$</th>
<th>Cl 2p</th>
<th>N 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.E. (eV)</td>
<td>Peak area (%)</td>
<td>B.E. (eV)</td>
</tr>
<tr>
<td>CuCl$_4$-based bulk hybrid</td>
<td>934.4</td>
<td>100</td>
<td>198.2</td>
</tr>
<tr>
<td>CuCl$_4$-based hybrid LB film</td>
<td>934.6</td>
<td>71</td>
<td>198.3</td>
</tr>
<tr>
<td></td>
<td>933.0</td>
<td>29</td>
<td>199.4</td>
</tr>
</tbody>
</table>

7.3.4. X-ray diffraction analysis of multilayer LB films

X-ray diffraction (XRD) is one of the key techniques used to investigate crystalline/layered materials. To gain insight into the structural properties of CuCl$_4$-based hybrid LB films, in-plane diffraction patterns and rocking curves (θ-scan) at the 001 peak position in the out of plane geometry were collected with an X-ray energy of 8 keV at the SAXS beamline of the Elettra synchrotron (Trieste).

As suggested by the Π-a isotherms discussed above and verified by XRD (not shown) CuCl$_4$-based hybrid LB films deposited at Π < 20 mN/m were amorphous. Crystal formation was detected in films deposited at 20 mN/m and the crystallinity improved when the Langmuir film was further compressed during deposition. Figure 7.8 displays the specular X-ray reflectivity of an 8-layer-thick CuCl$_4$-based hybrid LB films deposited at Π = 25 mN/m and of two films deposited at Π = 30 mN/m, one 8-layer-thick, the other 16-layer-thick. The X-ray diffraction patterns for films prepared at Π = 30 mN/m showed diffraction peaks as well as a Kiessig fringes, best seen in the magnified scan in the right panel, which are a clear evidence for a well-ordered layered structure. The position of the (00l) diffraction peak gives the length of smallest repeat unit (d) in the film growth direction, whereas the Kiessig fringes result from the interference of X-rays reflected from two interfaces as a consequence of the angle-dependent phase shift. Their period is determined by the thickness of the film. A layered material with n repeat units shows n-2 Kiessig fringes between two diffraction peaks in the X-ray reflectivity spectrum$^{22}$. 

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Figure 7.8. X-ray specular reflectivity patterns of multilayer $CuCl_4$-based hybrid LB films. The solid lines in the left panel show the corresponding fits (see text for details). The magnified view of the data relative to a 16-layer-thick $CuCl_4$-based hybrid LB film deposited at a surface pressure of 30 mN/m (right panel) shows Kiessig fringes as indicated by arrows along with diffraction peaks.

The length of smallest periodic unit perpendicular to the film surface ($d$) was calculated from the position of the diffraction peaks using the Bragg formula. To determine the peak position precisely, the diffraction pattern was fitted with a linear combination of Gaussian and Lorentzian line shapes with a 75-25% ratio. The background taken in the fitting procedure was a polynomial function of 4th order. The value for $d$ found for both 8-layer-thick and the 16-layer-thick $CuCl_4$-based hybrid LB film deposited at $\Pi = 30$ mN/m was 54.5±0.4 Å, which demonstrates that the crystal structure is independent of the number of layers. Total thickness of these $CuCl_4$-based hybrid LB films as calculated from Kiessig fringes was 219 Å for the 8-layer-thick film and 436 Å for the 16-layer-thick one. Calculations, based on the X-ray single diffraction studies of the bulk $CuCl_4(CH_3CH_2NH_3)_2$ hybrid$^{23}$ have determined a Cu-Cl out-of-plane distance of 2.3038 Å. Taking into account these values and the length of ODAH$^+$ molecule$^{24}$, the $d$ value based on our model is about 62 Å. The smaller value of the experimental $d$ calculated from the diffraction peak positions can be explained as due to tilting or interdigitation of the long ODA ligands.

Figure 7.9 displays the rocking curve ($\theta$-scan) measured at the (001) peak position in the out-of-plane orientation. A Gaussian fit of the rocking curve indicates that the individual layers are stacked almost parallel to each other with an average misalignment angle of 0.039±0.001° as visualized in the sketch in figure 7.9. The in-plane XRD pattern of the 16-
layer-thick $CuCl_4$-based hybrid LB film presented figure 7.10 showed one diffraction peak which confirms the in-plane crystallinity in the hybrid LB film.

Figure 7.9. Left panel: Rocking curve measured at the (001) diffraction peak position of a 16-layer-thick $CuCl_4$-based hybrid LB film deposited at a surface pressure of 30 mN/m. The red solid line represents the Gaussian fit to the data. Right panel: Sketch of the layer stacking in the film growth direction.

Figure 7.10. In-plane diffraction pattern of a 16-layer-thick $CuCl_4$-based hybrid LB film.
7.3.5. Magnetic characterization

To ascertain whether the LB films are ferromagnetic like the $CuCl_4(C_6H_5CH_2CH_2NH_3)_2$ hybrid crystals, magnetization measurements were performed on a 1184-layer-thick $CuCl_4$-based hybrid LB film; the elevated film thickness was necessary in order to obtain a satisfactory signal/noise ratio. The top panel in figure 7.11 depicts the in-plane zero-field-cooled (ZFC) and field-cooled (FC) measurements giving evidence for a ferromagnetic state below 10 K. For the FC measurements, the $CuCl_4$-based hybrid LB film was cooled in a magnetic field of 1 T applied parallel to film plane and then measured in a 0.03 T field parallel to film plane. Splitting of the ZFC and FC curves was observed at temperatures below 6 K. The high temperature region above 10 K can be fitted by the Curie-Weiss law with a Curie constant of $\sim 0.43$, which is close to that observed in bulk hybrids. The change of slope of the FC curve at 4 K points to (super-)paramagnetic inclusions most likely due to the less ordered/amorphous phase in the sample. The bottom left panel of figure 7.11 illustrates how the in-plane magnetization in the $CuCl_4$-based hybrid LB film depends on the applied field at 3K. The central part of this curve is amplified in the inset and shows a clear hysteresis loop with a coercive field ($H_c$) of 245 Oe, which again confirms ferromagnetic exchange interactions. Carrying out analogous measurements at various temperatures in the range 3-25 K, we could establish the temperature dependence of the coercive field presented in the bottom right panel of figure 7.11. No hysteresis loop opening could be detected at $T \geq 12$ K. The coercive field $H_c$ increases abruptly upon cooling below 5 K. The $CuCl_4(C_6H_6CH_2CH_2NH_3)_2$ bulk hybrid did not show any magnetic memory in the ordered state.

As it was mentioned before, the main advantage of tuning the interlayer distance between inorganic layers is the possibility to change the magnetic anisotropy of the sample. To verify whether the 1184-layer-thick $CuCl_4$-based hybrid LB film presents such an anisotropy, out-of-plane magnetization measurements were performed. The top left panel of Figure 7.12 shows the out-of-plane FC magnetization measurement carried out by cooling the film in a 1 T field and measuring in a 0.03 T field, as well as the ZFC measurement performed in a 0.03 T field (H applied perpendicular to film plane). Both measurements again confirmed an ordering temperature $T_c$ of 10 K. However, the maximum value of the magnetization was higher than that for the in-plane measurements.
Figure 7.11. In-plane magnetic measurements for a 1184-layer-thick $CuCl_x$-based hybrid LB film; top left panel: zero-field-cooled (ZFC) obtained by cooling the film without applied magnetic field and measuring at 0.1 T and field-cooled (FC) obtained by cooling the film in 1 T and measuring at 0.1 T; top right panel: sketch of the measurement geometry; bottom left panel: magnetization ($M$) vs applied field ($H$) loop at 3 K with an inset presenting a magnified view clearly showing a hysteresis with non-zero coercivity; bottom right panel: temperature dependence of the coercive field.

Unlike the $CuCl_2(C_6H_5CH_2CH_2NH_3)_2$ bulk hybrid, where the easy axis of the magnetic spins lies parallel to the film plane, in the hybrid film the easy axis is therefore along the growth direction. The out-of-plane magnetization measured as a function of magnetic field applied perpendicular to film plane also exhibited magnetic memory at low magnetic fields. The inset in bottom panel of figure 7.12 displays the magnified view of the $M$ vs $H$ loop at low magnetic fields, clearly showing a $H_C$ of 245 Oe. These studies suggest that by varying the organic ligand and/or transition metal salt in the synthesis through Langmuir Blodgett deposition, promising properties like high $T_c$ ferromagnetism, ferroelectricity and spin-polarized conduction can be achieved.
7.4. Conclusion and perspectives

CuCl$_4$-based hybrid LB films synthesized through Langmuir-Blodgett deposition showed ferromagnetic ordering below 10 K. Such LB films appear to be a perfect candidate for applications in electronics, due to their robust magnetic properties. By using a different inorganic part in the LB synthesis, like FeCl-(phenylethylaammonium)$_2$ which orders
antiferromagnetically below 102 K\textsuperscript{25}, higher ordering temperatures should be achievable. Taking advantage of the flexibility of the Langmuir Blodgett technique, organic ligands with different length can be used to tune the distance between inorganic layers to tailor the magnetic properties. Moreover, with a well-chosen organic ligand one may also introduce other functional properties such as ferroelectricity\textsuperscript{2}. Spintronics applications call for conductive thin films and this also seems within reach in these LB films since Arkenbout and coworkers\textsuperscript{25,27} have shown subliming TTF onto the surface of CuCl\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}NH\textsubscript{3})\textsubscript{2} yields a conductive interface with an activation energy of 0.17 eV. Therefore one can conclude that organic-inorganic hybrid LB films with smooth and flat surfaces like the ones presented here are highly promising as active layer in high quality soluble electronic devices.

References

Chapter 7


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