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New Thin Materials for Electronics

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New Thin Materials for Electronics

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Abstract

The work described in this report is from an Early Career LDRD to develop and investigate novel thin film organic conductors with drastically improved electronic properties over the current state of the art. In collaboration with the Molecular Foundry at Lawrence Berkeley National Laboratory a Langmuir-Blodgett trough (LB) was built from scavenged parts and added to a scanning Raman microscope at LBNL. First order thin peptoid film samples were fabricated for testing Raman and photoluminescence imaging techniques. Tests showed that a single peptoid sheet can be successfully imaged using confocal Raman spectroscopy and a peptoid sheet can be successfully imaged using near-field photoluminescence at a resolution less than 70 nm. These results have helped position Sandia for advances in this area of MOF film creation.

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CONTENTS

1. Introduction.....	7
2. Background.....	9
3. Approach/Experimental	11
3.1. Film Fabrication.....	11
3.2. Characterization of Bonding, Structure, and Composition	12
3.3. Nucleation and Growth.....	13
3.4. Nucleation and Growth-Future Efforts	13
4. Results.....	15
5. Summary	19
6. References.....	21
Appendix A: Publications and Presentations	23
Distribution	25

FIGURES

Figure 1. Schematic of idealized MOF films versus the current state of the art MOF thin films that are poly-crystalline and have no crystallite-to-crystallite order. 9

Figure 2. Example MOF structure (top, MOF-508) and thin film growth methodology (bottom): a) Zinc ions are dissolved in water, and organic linker molecules (benzene dicarboxylic acid) are dispersed onto the surface of the LB trough at low (gas-like) concentration; b) the surface of the LB trough is compressed inducing monolayer thin film formation. This film is removed by surface contact with a desired substrate; c) the LB formed MOF monolayer on the substrate, this is the XY plane shown in schematic at top; d-e) for growth in the Z direction, a secondary linker (4,4' bipyridine) is added to the substrate f) followed by washing and addition of the initial metal salt XY linker. By repeating these steps it is possible to form crystalline thin films with controllable thickness and functionality (by altering the chemistry of the Z-linker). 11

Figure 3. Schematic diagrams of characterizational techniques used. Confocal Raman/PL (left) has been performed with high NA objectives with back-collection. Near field experiments (center) have been performed in the forward collection mode through both apertured tips (~50 nm resolution) and plasmonic enhancement tips (~10 nm resolution) for PL. It should be noted that these experiments require transparent substrates. STXM (right) is performed at the synchrotron beam line 5.3.2 at the advanced light source. X-rays are focused through a zone plate onto a sample and transmitted photons are detected by phosphor screen and photomultiplier tube..... 12

Figure 4. Peptoid sheets shown with photoluminescence imaging (top) and the monomer units which make up these lipid bi-layer-like structures (bottom). 16

Figure 5. Peptoid Raman image of a single peptoid sheet. At each point a full Raman spectrum has been collected. All that is shown is the intensity of the benzene breathing mode. 17

NOMENCLATURE

LB	Langmuir-Blodgett
MOF	Metal-Organic Framework
PL	Photoluminescence
STXM	Scanning Transmission X-ray Microscopy

1. INTRODUCTION

The work described in this report is from an Early Career LDRD to develop and investigate novel thin film organic conductors with drastically improved electronic properties over the current state of the art. While the technique for film fabrication and the resulting materials are fundamentally different from current crystalline thin-films, many of the underlying questions remain the same: What is the nature of nucleation and how does it affect overall growth? How do defects form and propagate through the film? It is conceivable to propose mechanisms similar to those in ionic crystal growth such as catalytic nucleation, and lattice vacancies. By leveraging the unique crystallinity of metal-organic frameworks (MOFs) and a novel Langmuir-Blodgett deposition technique it was proposed that large area crystalline organic films for electronic applications could be generated on any substrate. The proposed research was based on developing a synthetic methodology for the growth of large area crystalline thin films of MOFs, currently impossible, and a set of imaging and spectroscopic tools including confocal and near-field Raman imaging, atomic force microscopy, electron microscopy, and scanning transmission X-ray microscopy, revealing ultra-high resolution chemical information critical to a complete understanding of film growth kinetics.

In collaboration with the Molecular Foundry at Lawrence Berkeley National Laboratory a Langmuir-Blodgett trough (LB) was built from scavenged parts and added to a scanning Raman microscope at LBNL. First order thin peptoid film samples were fabricated for testing Raman and photoluminescence imaging techniques. Tests showed that a single peptoid sheet can be successfully imaged using confocal Raman spectroscopy and a peptoid sheet can be successfully imaged using near-field photoluminescence at a resolution less than 70 nm. These results have helped position Sandia for advances in this area of MOF film creation.

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2. BACKGROUND

Electrically conducting organics, including polymers,¹ and crystalline small molecule,² are the great hope for inexpensive, flexible electronics. However, conduction in these materials is dominated by hopping mechanisms, limiting the efficiency of resulting devices. Metal Organic Framework films (MOFs) have the benefit of highly crystalline structure with large lattice parameters and highly tunable chemistry. These may help increase the distance per hop traveled by charge carriers, making them good candidates for improved organic electronic materials.

The first major hurdle to successful employment of MOF electronic materials is forming large area crystalline films. It is currently impossible to do this. As shown schematically in Figure 1, the desired film is continuous and has uniform crystalline orientation. The reality of MOF film growth is shown on the right of the figure. They are polycrystalline, with no crystal alignment, which will not work well as electronic materials.³ Ultimately, the desired MOF films would have directed one dimensional conductivity. Laterally, the films will be insulating. This is ideal for many electronic applications in which directed charge transport improves efficiency drastically. This requires that the crystalline films have uniform crystal orientation. In this work, I develop both a synthetic methodology for growth and a set of spectroscopic and microscopic tools for the complete analysis of such films.

Figure 1. Schematic of idealized MOF films versus the current state of the art MOF thin films that are poly-crystalline and have no crystallite-to-crystallite order.

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3. APPROACH/EXPERIMENTAL

3.1. Film Fabrication

2D MOF films are grown on a Langmuir-Blodgett (LB) trough as shown schematically in Figure 2. This basic idea of MOF growth at the air/water interface has been demonstrated recently.^{4,5} The insoluble organic precursors are placed at the interface and metal salts are dissolved into the water phase (Figure 2a). After sufficient time has passed for the metal-organic paddlewheel bonds to form into a uniform film, the LB trough is compressed forcing individual islands into a continuous sheet (Figure 2b). The chemistry of this growth process is similar to that of MOF-508, however, the Z-axis ligand (bipyridine) is replaced by pyridine. This restricts growth into the 2D plane.

Figure 2. Example MOF structure (top, MOF-508) and thin film growth methodology (bottom): a) Zinc ions are dissolved in water, and organic linker molecules (benzene dicarboxylic acid) are dispersed onto the surface of the LB trough at low (gas-like) concentration; b) the surface of the LB trough is compressed inducing monolayer thin film formation. This film is removed by surface contact with a desired substrate; c) the LB formed MOF monolayer on the substrate, this is the XY plane shown in schematic at top; d-e) for growth in the Z direction, a secondary linker (4,4' bipyridine) is added to the substrate f) followed by washing and addition of the initial metal salt XY linker. By repeating these steps it is possible to form crystalline thin films with controllable thickness and functionality (by altering the chemistry of the Z-linker).

By monitoring surface pressure it is possible to determine when a complete sheet has formed and the reaction is complete. Termed a Langmuir isotherm, this technique is the basic method of characterization for LB deposition. This sheet is directly lifted off the interface using virtually any substrate (Figure 2c).

Further advancements involve varying organic linker molecules such as those used in MOF-508 as shown in Figure 1 (in the XY plane), metal salts, and reaction conditions. For the duration of these experiments, similar chemistries have been used to those in the work of Makiura et al and MOF-508 to ensure the growth of 2D planes and minimize variability from experiment to experiment.

3.2. Characterization of Bonding, Structure, and Composition

There are three main techniques employed in the characterization of MOF thin films. These are shown in Figure 3. Confocal Raman and photoluminescence (PL) imaging are the most basic techniques, and with ~ 250 nm spatial resolution provide an overview of film structure and defects. Raman is the more powerful of the two techniques giving chemical information on bonding and structure. The main limitation here is sensitivity. Raman has been used to show the potential of single monolayer imaging both with confocal diffraction limited techniques, as well as with near-field sub-diffraction limited photoluminescence imaging on a similar material, peptoid sheets. This will be described later.

Figure 3. Schematic diagrams of characterizational techniques used. Confocal Raman/PL (left) has been performed with high NA objectives with back-collection. Near field experiments (center) have been performed in the forward collection mode through both apertured tips (~ 50 nm resolution) and plasmonic enhancement tips (~ 10 nm

resolution) for PL. It should be noted that these experiments require transparent substrates. STXM (right) is performed at the synchrotron beam line 5.3.2 at the advanced light source. X-rays are focused through a zone plate onto a sample and transmitted photons are detected by phosphor screen and photomultiplier tube.

3.3. Nucleation and Growth

MOFs in general are a young research topic. Little is understood about how bulk MOF crystals nucleate or the kinetics of their growth. Studying growth kinetics on the LB trough can yield valuable information in both this study of thin film growth and in the general field. The LB growth method has a distinct advantage over the bulk solution phase with regard to the study of growth kinetics. Reactions can be “frozen” at any point during the reaction in their present state by removal of the film without compression (Figures 2b and 2c). In this way I have monitored the appearance of seed particles as well as individual island formation and growth. Time series have been taken where reactions are “frozen” at fixed time points and imaged using the above characterization techniques. I have been able to monitor the growth of the film and generate a kinetic trace including seed formation, initial nucleation, and island growth. This will be a major figure of merit and a meaningful result with implications for both thin film growth and MOF growth in general. This information will direct future work in this project.

3.4. Nucleation and Growth-Future Efforts

The most likely scenario of growth involves the formation of islands, as mentioned above. This will ultimately be determined explicitly in these kinetic studies and will be the operating assumption at this point. In order to form the continuous film, the LB trough is compressed and the islands coalesce into a monolithic film. There are several interesting questions involving this mechanism that we will be able to answer. First, what is the reaction between individual islands? Is the compression a reversible process, or once it is compressed, can the islands diffuse apart again? This is critical to understanding how to form continuous crystalline films. If the islands do not bond upon compression, each junction will be a defect. This will be determined by performing repeated Langmuir isotherms after the reaction is complete. If the compression is reversible, there will be a normal pressure increase on the first compression as the islands are forced together, but there will be no interaction on the second compression until the pressure bars reach the already formed film. Alternatively, each compression will yield identical Langmuir isotherms – showing a lack of interaction and reaction between the islands. Second, will the islands orient to each other to form a continuous, single crystalline film, or will it be polycrystalline? This will be determined this using the high resolution imaging techniques mentioned above. Specifically, AFM will allow lattice orientation to be observed as well as crystallite size. If the film does not form as a single crystal vacuum thermal annealing to “heal” the film will be explored to induce 2D crystalline order. Finally, when the islands coalesce, there will be small voids left behind. Is it possible to “heal” these voids and reduce defects? Post-film formation exposure to reagents will be used and imaging before and after will show if this is effective.

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4. RESULTS

The key to MOF film formation is having Langmuir-Blodgett (LB) trough capabilities. This has been accomplished with a five-month refurbishment of an unused LB trough at LBNL that included writing a new software code to control existing hardware over the long reaction times necessary for these experiments. To monitor MOF film growth on the Langmuir-Blodgett surface, the LB trough was modified to work with an existing Witec/Raman/PL imaging system. This provides the capability to monitor emissions from MOF constituents on the surface. However, it was not entirely clear that Raman imaging could be used to study films as thin as 3 nm.

Because MOF thin film growth effort begins very slowly, existing peptoid sheets were used as surrogates to test system capabilities. These are lipid bi-layer like structures composed of engineered peptoid monolayers, as shown in Figure 4.^{7,8} The reason this trial experiment is necessary is that it is not entirely clear that it is even possible to measure, by Raman imaging, materials this thin (~3 nm). The test results show that it is possible to not only measure Raman of individual peptoid sheets, but also successfully perform full hyperspectral Raman imaging. We can observe signature Raman modes from the substituent molecules, and even see regional variation in those signatures indicating some level of structural inhomogeneity. This is shown in Figure 5 for a Raman image of the benzene breathing mode band of a single peptoid sheet. At each point a full Raman spectrum was collected. All that is shown here is the intensity of the benzene breathing mode.

Figure 4. Peptoid sheets shown with photoluminescence imaging (top) and the monomer units which make up these lipid bi-layer-like structures (bottom).

Figure 5. Peptoid Raman image of a single peptoid sheet. At each point a full Raman spectrum has been collected. All that is shown is the intensity of the benzene breathing mode.

These are the first results to demonstrate confocal Raman imaging of single Peptoid sheet. They are also the first to demonstrate near-field PL imaging of Peptoid sheet at less than 70 nm resolution. In addition to Raman imaging, preliminary tests also demonstrate the super-resolution imaging of a peptoid sheet with an integrated dye molecule. This work seems to indicate that there are crystalline domains present within the sheets, something predicted, but never observed. This will be pursued in future studies.

MOF thin films present great potential for revolutionizing solid state bulk- and nano-scale device physics. This work has helped position Sandia for advance in this area of MOF film creation. The interactions with LBNL also led to award of two user projects at the Molecular Foundry at LBNL led by current Sandia staff and the appointment of a current Sandia staff to the Molecular Foundry User Executive Committee.

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5. SUMMARY

In collaboration with the Molecular Foundry at Lawrence Berkeley National Laboratory, a Langmuir-Blodgett trough (LB) was built and added to a scanning Raman microscope at LBNL. Thin peptoid film samples were fabricated for testing Raman and photoluminescence imaging techniques. Tests showed that a single peptoid sheet can be successfully imaged using confocal Raman spectroscopy, and a peptoid sheet can be successfully imaged using near-field photoluminescence at a resolution less than 70 nm. These results have positioned Sandia for advance in this area of MOF film creation. The interactions with LBNL also led to award of two user projects at the Molecular Foundry at LBNL led by current Sandia staff and the appointment of a current Sandia staff to the Molecular Foundry User Executive Committee.

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APPENDIX A: PUBLICATIONS AND PRESENTATIONS

1. Work was presented at: the 8th confocal Raman imaging symposium, in Ulm Germany as an invited speaker, at an invited seminar at Bielefeld University in Germany, and an invited seminar at the Molecular Foundry, Lawrence Berkeley National lab.
2. Article in progress on thin film growth and imaging of MOF films. Once the data collection is complete this work will be submitted.
3. Currently working on a publication on hyperspectral and near-field imaging of peptoid sheets.
4. Generated a MOF review article with Mark Allendorf and Vitalie Stavila [Allendorf, M. D.; Schwartzberg, A. M.; Stavila, V.; Talin, A. A., A roadmap to implementing metal-organic frameworks in electronic devices: challenges and critical directions. **Chemistry, A European Journal** 17, 11372-11388 (2011)].

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