Tandem catalysis: One-pot reactions are of compelling interest in the development of sustainable synthetic practices due to a decrease in the number of work-up procedures that significantly increases the efficiency of the overall process. Tandem catalysis, an important subclass of one-pot reactions, has several inherent advantages over multistep syntheses, including faster reaction time, reduced catalyst and purification costs, atom economy, environmental friendliness, and applicability to diversity-oriented high-throughput synthesis and combinatorial chemistry.

Research objective: The goal of the present project is to explore new aspects of MOF preparation using molecular epitaxial growth and to study the resulting MOF films in tandem catalysis. This approach has the potential to allow exquisite control over MOF structures through a layer-by-layer (LBL) methodology. Our aim is to exploit MOF structures to create useful multi-functional catalysts that are incompatible in analogous homogeneous systems and, indeed, unprecedented in chemical catalysis. The possibilities include: a) useful multi-catalyst architectures that are difficult to access through conventional routes, b) powerful combinations of seemingly incompatible catalysts.

Technical Approach: LBL “liquid-phase molecular epitaxial” growth of MOFs stands in intriguing contrast to conventional solvothermal synthetic protocols. Appropriately tailored surfaces are exposed to desired MOF components (e.g. metal ion, metalloligands I and II) sequentially and independently (Figure 1).[1] Since the solution phase never contains more than one component, this approach to synthesis is inherently self-limiting at the level of one molecular (or ionic) layer per exposure step. Because it entails growth from a surface, the approach is related, conceptually at least, to the well-established solid-phase synthesis of complex biopolymers, such as polypeptides and DNA. The proposed substrate-supported highly oriented MOFs could be reliably synthesized in an automated fashion as described in Figure 1.

Demonstration of catalytic tandem reactions with MOFs grown via LBL: Flexibility in the design of MOFs facilitates the engineering of catalytic sites in the material, as ligands with functional moieties, such as metalloporphyrins, could be readily incorporated into the MOF thin films via liquid-phase epitaxy.[2] In the tandem catalytic systems that we investigated, two different catalysts were carefully incorporated into the MOF using a systematic LBL approach. As proof of concept, we have investigated and successfully demonstrated two different catalytic tandem reactions using MOFs. Target catalytic reactions were investigated using the bulk MOFs; once optimized reaction conditions were obtained with the bulk materials, the MOFs were prepared as thin films and these films were investigated as catalysts.

I. Olefin epoxidation followed by CO₂ insertion to form cyclic carbonates: Epoxides are useful intermediates in organic synthesis and significant research efforts have been directed toward selective catalytic epoxidations. Monoxygenase can selectively oxidize a wide range of alkanes and alkenes and is of fundamental importance for detoxification in the human body. A variety of metalloporphyrins, e.g. Mn(III)-porphyrins[3] and Fe(III)-porphyrins,[4] in combination with single-oxygen donor species have been studied as model oxidation catalysts for monoxygenases.

![Figure 1. Layer-by-layer approach for the growth of MOFs on a SAM-functionalized substrate. The approach involves repeated cycles of immersion in solutions of the metal precursor and solutions of organic complexes I and II. Between steps, the material is rinsed with solvent.](image-url)
Carbon dioxide has the potential to become an inexpensive and abundant C₃ feedstock if efficient methods for its transformation into value-added products can be discovered. Additionally, utilization of CO₂ as a C₃ feedstock could have an important impact on global carbon management. Thus, carbon dioxide fixation remains a challenging and important synthetic goal.

As a first target for tandem catalysis, we investigated olefin epoxidation followed by CO₂ capture to form cyclic carbonates (Fig. 2b). Robust Porphyrinic Materials (RPM)⁵ were chosen for our proposed tandem olefin epoxidation-CO₂ insertion reaction. RPMs are a class of non-interpenetrated, pillared-paddlewheel MOFs which were recently reported by our group (Fig. 2a). RPMs are site-isolated, bi-functionalized MOFs with a high degree of porosity and large three directional channels. Before preparing thin films of RPMs, we synthesized bulk RPM material in order to establish and optimize the reactions conditions. The catalyst could also be easily recovered and reused which is highly desirable in terms of cost and sustainability, Fig. 2b.

As the catalyst for the first step of the tandem reaction – olefin epoxidation – we targeted a Mn-porphyrin as Mn-porphyrins in combination with single-oxygen donors (SOD) are known to act as oxidation catalysts similar to monooxygenases. For the CO₂ insertion step, a Zn-porphyrin was utilized as a Lewis acid to incorporate CO₂ into an epoxide via a non-concerted cycloaddition reaction. Production of cyclic carbonates via CO₂ insertion into an epoxide is one of the most successful examples of CO₂ fixation and could potentially be a more environmentally friendly route for the industrial preparation of carbonates, which currently involves highly toxic and corrosive phosgene and diols.⁵ With the ZnMn-RPM in hand, we first investigated epoxidation and CO₂ capture with styrene using 1-((tert-butylsulfonyl)-2-iodosylobenzene as the SOD. Under optimized conditions, we obtained the desired carbonate product in good yield with high selectivity for the desired product (Scheme 1).

Notably, when styrene was oxidized with the ZnMn-RPM without CO₂, overoxidation and/or oxidative cleavage was observed as indicated by the formation of the side products phenyl acetaldehyde and benzaldehyde in yields up to 30%. In contrast, under our optimized tandem catalytic reaction conditions, we did not observe the formation of 2-phenyl acetaldehyde and benzaldehyde was observed in only trace amounts, which suggests that the Mn- and Zn-porphyrins are indeed acting in tandem, as the reactive intermediate (epoxide) is captured by the second catalyst before the formation of any undesirable side-products can occur.

II. Olefin epoxidation followed ring opening by nucleophiles: After successfully demonstrating tandem catalysis for olefin epoxidation and carbon dioxide insertion, we next investigated olefin epoxidation.

Figure 2. a) crystallographically derived representation of a unit cell of ZnMn-RPM. b) a schematic representation of tandem olefin epoxidation followed by CO₂ capture to form cyclic carbonates via ZnMn-RPM. FG = functional group

Scheme 1. Schematic representation of tandem catalysis of ZnMn-RPM for the synthesis of cyclic carbonate.
followed by nucleophilic attack and epoxide ring opening in a tandem catalytic reaction again using ZnMn-RPM (Scheme 2).

We found that the heterogeneous MOF catalyst ZnMn-RPM could be recovered by simple filtration and could be reused for Without a loss in activity. The PXRD studies showed no change in the crystallinity of the ZnMn-RPM indicating the MOF remains stable after at least two catalytic cycles.

**Preparation of MOF thin films via liquid-phase molecular epitaxy:** Having demonstrated the concept of tandem catalysis with bulk phase MOFs, we next prepared MOF thin films using the LBL approach and then investigated the catalytic activity of the thin films for the above-mentioned tandem reactions.

Our synthetic strategy for the preparation of epitaxially grown thin film MOFs was based on the LBL growth of MOF RPM on a coated silicon substrate. The silicon was first functionalized with an N-terminated self-assembled monolayer (SAM) before deposition of the MOF. 3-aminopropyl trimethoxysilane (3-APTMS) was selected as the substrate for SAM because it leads to terminal amine groups on the surface, thus mimicking the ligands normally used in solvothermal synthesis.

After modification of the substrate surface with the SAM, the MOF was grown LBL using repetitive cycles of individual dipping steps. In the first step, the modified substrate was exposed to zinc acetate in ethanol, which leads to zinc ion coordination to the surface amine groups. After rinsing with ethanol, the substrate is then exposed to a zinc-TCPP (TCPP = tetra(4-carboxyphenyl)porphyrin) solution, followed by another rinsing step, and exposure to meso-5,15-dipyridyl-10,20-bis(pentafluorophenyl))porphyrinatomanganese, followed by a final rinsing cycle. By subsequently repeating and alternating immersion of the substrate in the metal ion solution or the organometallic ligand solution, three-dimensional MOFs are grown epitaxially in LBL fashion. Importantly, our group has substantial experience with LBL MOF synthesis chemistry.

Our group has several automated instruments for epitaxial growth of MOFs. The computer programmable injection systems on these instruments ensure a high degree of reproducibility; additionally, each adsorption and desorption (washing) step can be directly observed.
Films were studied using Scanning Electron Microscopy (SEM). The cross sectional view clearly shows the decorated silicon with a RPM thin film. The thickness of a 22 layer film was determined to be 48.7±2nm nm (Figure 3, top), which gives a growth rate of 22 Å/cycle that exactly corresponds to the expected zinc-zinc distance between each 2D sheet. This data strongly suggests that only one layer grows per cycle (Figure 3, bottom). The thickness of the film was further evaluated with ellipsometry and profilometry which gave values about 48nm and 49nm, respectively, consistent with the data obtained by SEM. The surface of the film was also studied using Atomic Force Microscopy (AFM) and as can be seen from Figure 4, the surface is very smooth with a roughness of only one to two layers.

The Zn:Mn ratio of the film was investigated with Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS) and the ratios were found to be 2.97 : 1 by TOF-SIMS and : 2.8 : 1 by XPS which are consistent with the theoretical value as 3:1.

Finally, we utilized the RPM thin film for the tandem reactions previously investigated with bulk MOF RPM (vide supra). As shown in Scheme 3 and 4, the RPM thin film successfully catalyzed the reactions. We are still working on developing optimized reaction conditions for these reactions.

Our future plan: Catalytic alkane metathesis by tandem alkane dehydrogenation–olefin metathesis:
We have thus far demonstrated that bulk and thin film MOF materials perform in tandem catalytic reactions. Based on these results, we will next pursue growth of porous films containing desirable, but inherently incompatible catalysts (i.e. incompatible under typical homogeneous solution reaction conditions). As a starting point, we will consider Brookhart and Goldman’s[7] proposed tandem transfer-hydrogenation/olefin metathesis for net alkane metathesis (Scheme 5). Their initial plan was to use Ir-pincer and Grubbs’ olefin metathesis catalysts (easy to handle), but this particular catalyst pairing did not work. Their solution was to use a Schrock catalyst (very hard to work with) for the olefin metathesis cycle. The mutual incompatibility of the initially desired catalyst pair comes from having iridium, in oxidation state (I), systematically abstracting two chlorides from RuCl₂(PR₃)₂(CHPh), thereby destroying

![Scheme 3. Schematic representation of tandem catalysis of ZnMn-RPM thin film.](image1)

![Figure 4. 2D and 3D AFM image of the RPM thin film with 22 layers.](image2)

![Scheme 4. Schematic representation of tandem catalysis of ZnMn-RPM thin film for the synthesis of alpha-hydroxy ethers.](image3)
both catalysts very efficiently. The alternative metathesis catalyst, a Schrock catalyst, is functional but is much more chemically challenging to handle.

The development of a LBL method for site-isolation of Grubbs second-generation catalysts from the incompatible catalysts (Ir-pincer) will be a good illustration of the utility of multifunctional layer-by-layer MOF synthesis. Choice of topology for the catalytic alkane metathesis by tandem alkane dehydrogenation–olefin metathesis: As a starting point, we will use paddlewheel MOF nodes, since they will offer higher stability and tunability compared to many alternatives. We will start with the synthesis of Ir-pincer 1 as the dehydrogenating catalyst and Grubbs II catalyst 2 for the olefin metathesis. The well-known tetraacid linker 3 (developed at Northwestern and sold by Aldrich) will be utilized to form pillared paddlewheel MOFs based on mixed-ligand Zn(II) coordination to carboxylates and dipyridyls. The tetraacid ligand will form a 2D sheet within the xy-plane, which can be pillared by a dipyridyl ligand (Scheme 6). This will allow for diverse functionalities to be incorporated into new functional MOFs. In parallel to preparing the above-mentioned MOFs from metallo-porphyrins/salens, we will prepare 1 and 2 (3 is commercially available) and the corresponding MOF for the alkane metathesis and optimization conditions.

Publications: We are in the process of finishing up control experiments and writing up these results.

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References:


