Mesoporous chiral metal organic framework (CMOF) for asymmetrical photocatalyst

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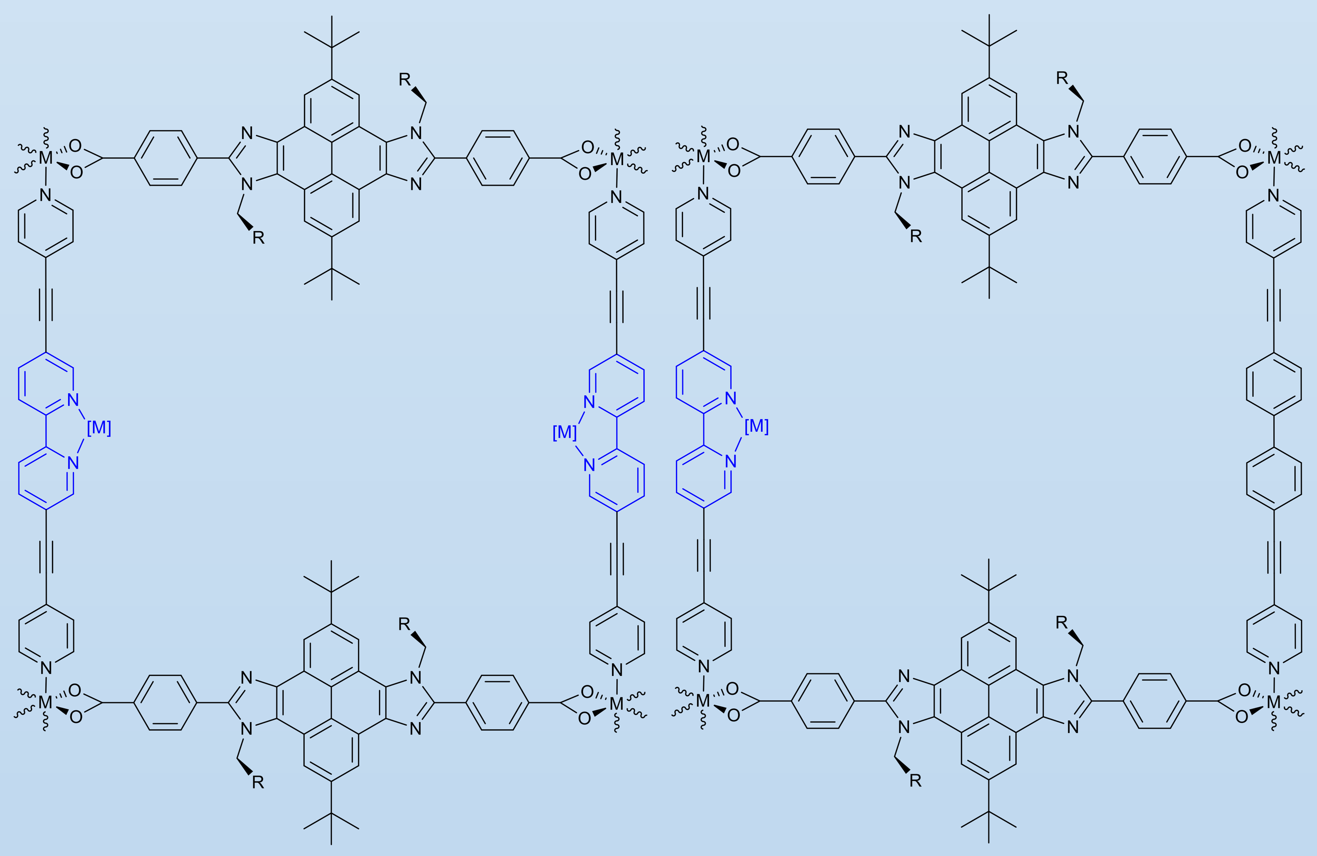
Introduction

Metal-organic framework (MOF) is a novel class of hybrid materials formed by metal or metal clusters and organic ligands. Each organic ligand will coordinate to two or more metal ions or clusters that act as nodes to form a rigid, stable and highly porous framework with pores of adjustable dimensions under the same topology.[1] In the field of catalysis, MOFs are generally designed to be the rigid backbone of a certain catalyst. In general, catalytic moieties are incorporated into the framework through node or linker functionalisation. By providing stable, separate and accessible active sites, many MOF catalysts was shown to effectively increase turnover rate and versatility in various catalytic reaction.[2] One could also introduce a chiral-induction center post-synthetically to the backbone to suit for asymmetrical catalyses. By introducing different type of chiral-induction centers, CMOFs could be tailor made to catalyze asymmetric syntheses.

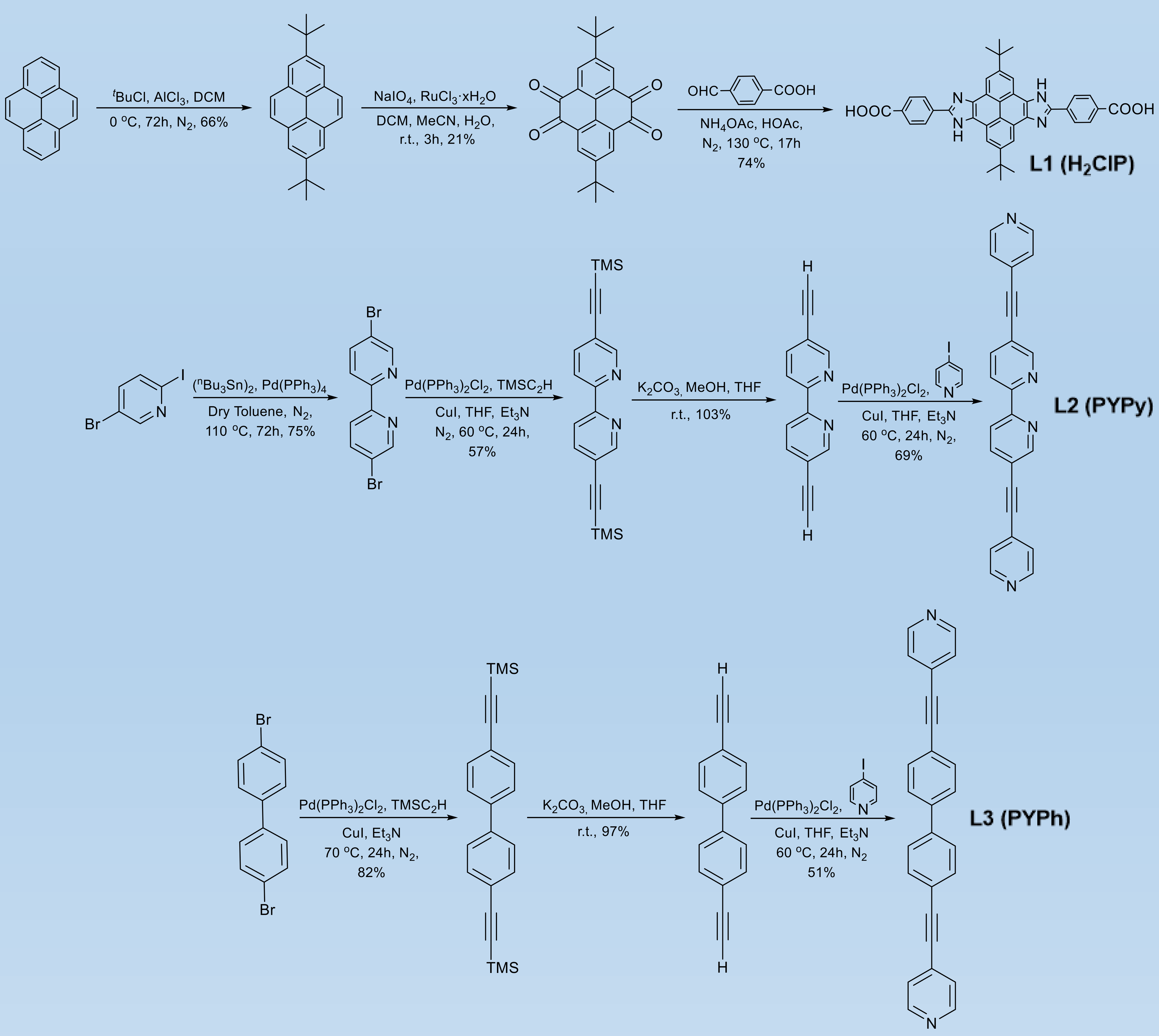
In this project, a series of pillar-layered CMOFs are designed and to be synthesized for catalyzing carbonyl asymmetric α-alkylation. The project was separated into multiple stages of work. As we had successfully synthesized the corresponding linkers, our current primary goal is to optimize single crystal MOF growth conditions.

Design, Synthesis and Characterization

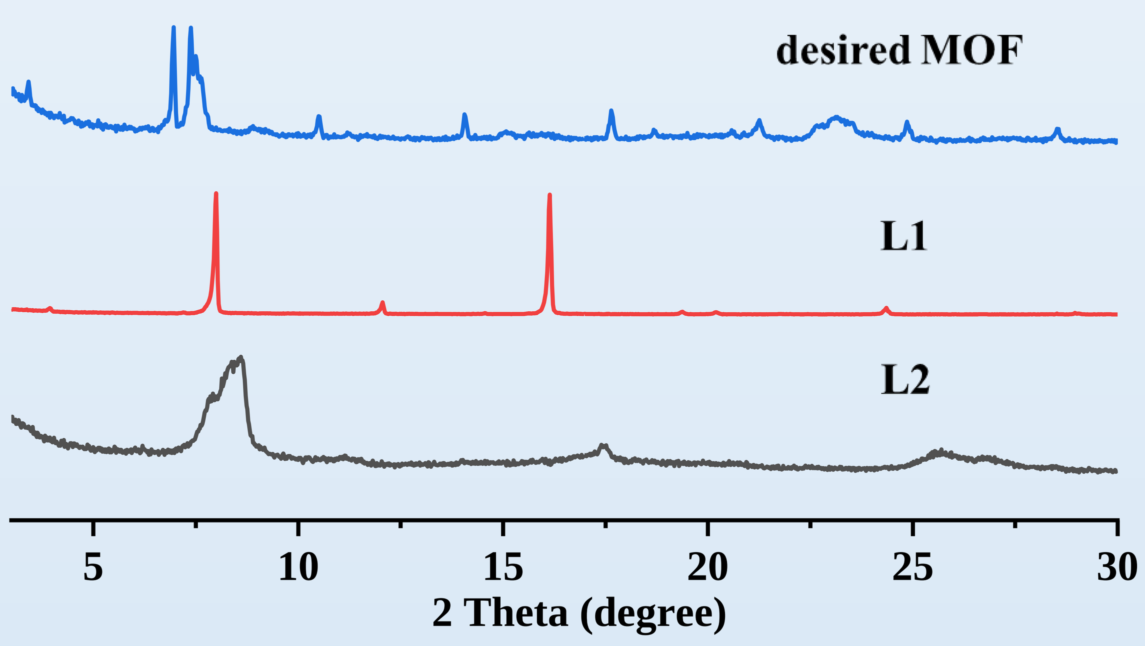
Pore designs (**Figure 1**):



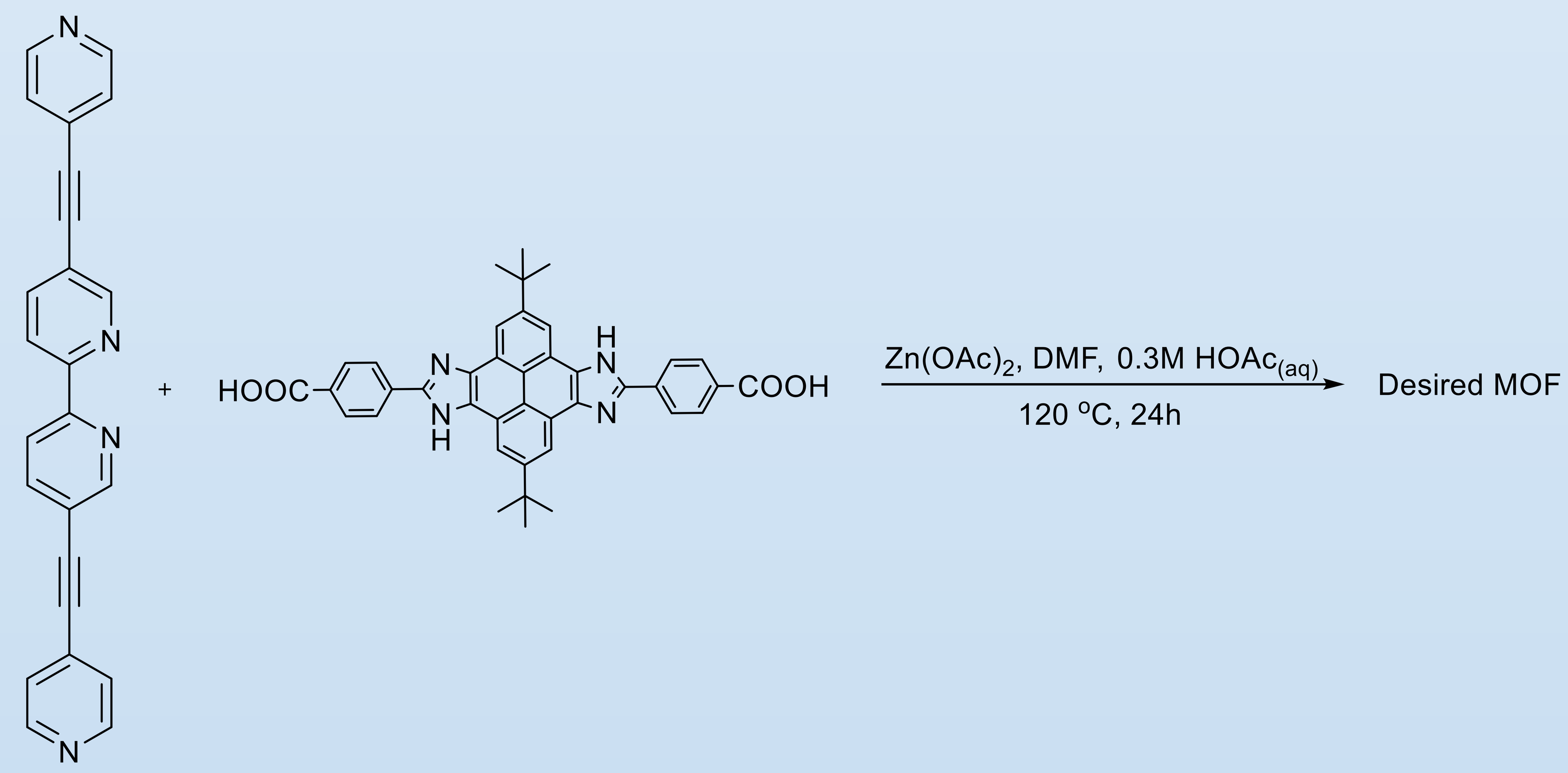
Synthetic Routes (**Figure 2**):



MOF Synthesis (**Table 1**) and PXRD spectrums (**Figure 3**):



- The MOF structure composed of only **L1** and **L2** was recently obtained with the following conditions:



- The PXRD spectrums confirmed that a novel crystalline structure had arisen from **L1** and **L2** only. However, we are still trying to resolve the crystalline data to certify pore structures and interlayer alignments. Once the pore structure and interlayer alignments are confirmed, the current MOF would be fully characterized.
- Reaction screening for **L3**-doped MOF is in progress.

Summary

- Layer linkers are cheaper in cost but less efficiently synthesized (10%) overall yield; Pillar linkers are more efficiently prepared but are also relatively expensive. However, we were able to achieve large scale synthesis (1-2 g) with decent purity.
- Viable MOF synthetic route was successfully obtained and confirmed by PXRD spectrums. The crystalline data obtained is being resolved for the full characterization of pore structure and interlayer alignment.

Outlook

- Continue seeking optimal single-crystal MOF growing conditions
- Explore post-synthetic attachment conditions for chiral-inducing moiety
- Simplify post-synthetic workup processes to reduce total time spent
- Explore dynamics between chiral-inducing moiety and photoactive metal centers
- Optimize photo-reactivity of the synthesized CMOF photocatalyst

References

1. Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 1230444.
2. Yang, D.; Gates, B. C. *ACS Catal.* **2019**, *9*, 1779.

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