

Tunable Host-Guest Interactions in Photo-Functional Metal-Organic Frameworks

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This work was focused on the synthesis and characterization of zwitterionic metal-organic frameworks (ZW MOFs) as a new means to rationally design stimulus-responsive materials for small-molecule separation and storage applications. In 2016-2017, we explored the fundamentals of design strategies to access new polytopic ZW ligands. This work enabled us to systematically synthesize and characterize a broad range of new ZW MOFs (*Dalton Trans.* **2017**, *CrystEngComm* **2016**) with the highlight of reporting the first photo-responsive example for small-molecule separation (*Chem. Mater.* **2016**). In the 2017-2018 period we investigated new frontiers in this field, namely, the first rational design of pore size and functionality through reticulation of ZW MOFs. Details of this work are presented in the following paragraph.

The isoreticular expansion and functionalization of charged-polarized porosity has been systematically explored by the rational design of eleven isostructural zwitterionic ZW-MOFs. This extended series of general structural composition $\{[M_3F(L1)_3(L2)_{1.5}] \cdot \text{guests}\}_n$ was prepared by employing the solvothermal reaction of Co and Ni tetrafluoroborates with a binary ligand system composed of zwitterionic pyridinium derivatives (L1) and traditional functionalized ditopic carboxylate auxiliary ligands (L2). Single-crystal structure analyses revealed cubic crystal symmetry ($I-43m$, $a = 31\text{-}36 \text{ \AA}$) with a 3D pore system of significant void space (73-81%). The pore system features three types of pores being systematically tunable in size ranging from 17.4-18.8 Å (pore I), 8.2-12.8 Å (pore II), and 4.8-10.4 Å (pore III) respectively by the choice of auxiliary ligands (Figure 1). All members of this series have non-interpenetrating structures and exhibit robust architectures, as evidenced by their permanent porosity and high thermal stability (up to 300°C). The structural integrity and specific surface areas could be systematically optimized using supercritical CO₂ exchange methods for framework activation resulting in BET surface areas ranging from 1250 to 2250 m²/g. Most interestingly, as structural landmark, we found the pore surfaces lined with charge gradients employed by the pyridinium-ligands. This key feature results in significant adsorption of carbon dioxide and methane which is attributed to polarization effects. The novel and intrinsic value of this design approach lies in the ability to control and direct the reticulation of pyridinium building blocks into extended networks in which specific properties can be targeted. Given the unique structural attributes of the herein studied isoreticular MOF series, including their thermal stability and adsorption properties, it is expected that this work will contribute to inspire the development of new structural design strategies for the discovery of specifically underexplored zwitterionic MOFs. This work is currently under review in *Chem. Mater.*

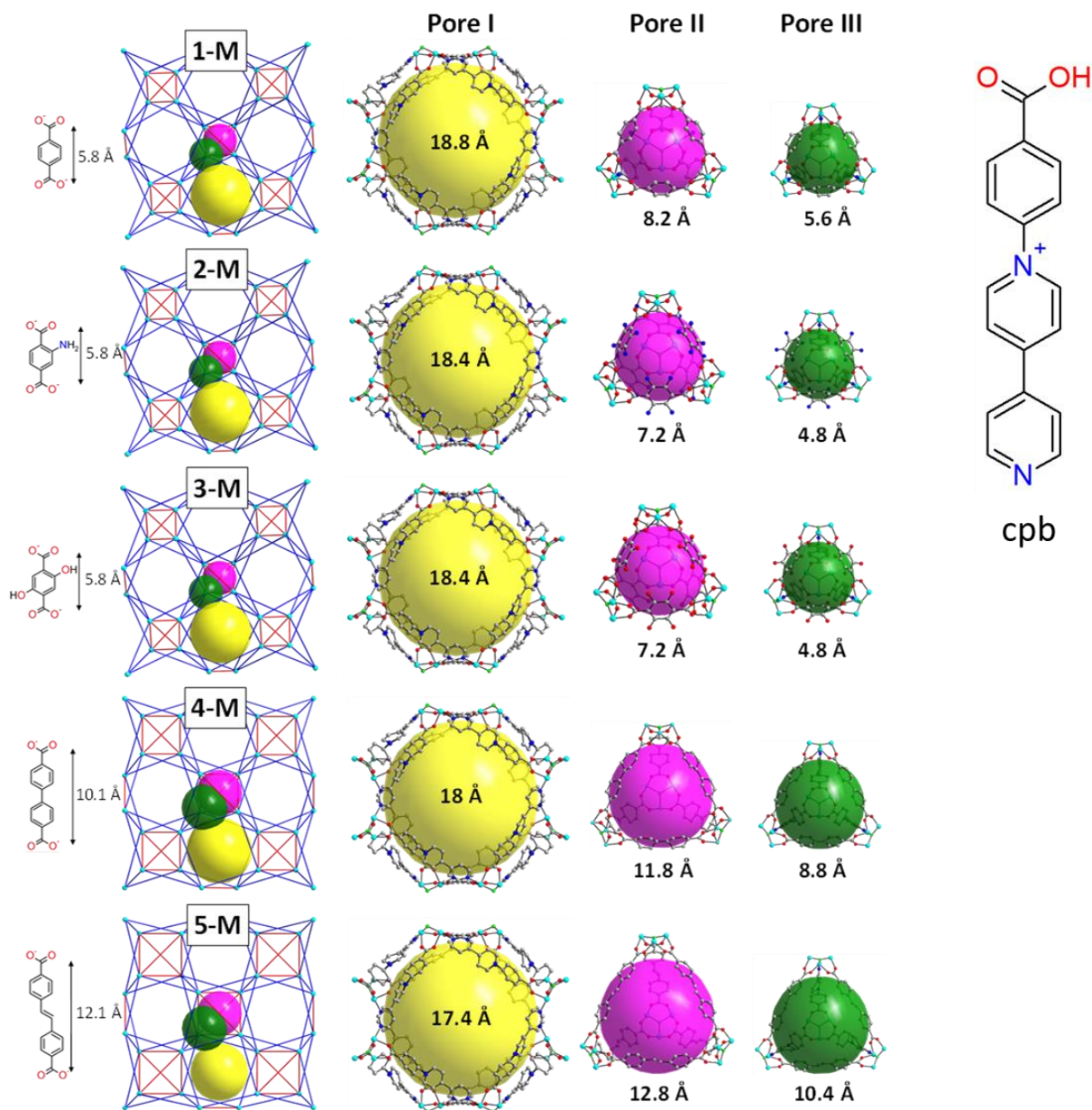


Figure 1. Schematic representation of crystal structures of isoreticular series along with their respective pore structures, pore dimensions, and Lewis structures of modulating auxiliary ligands. All structures shown are composed of the ZW ligand cpb (right).

Impact. The results obtained from this DNI seed grant set the stage to receive my NSF CAREER award entitled "Zwitterionic Metal-Organic Frameworks with Multi-Stimulus-Responsive Properties" in 2018. Also, my first graduate student working on this grant for her final two years secured a permanent position as Scientific Instrumentation Specialist at the University of Toledo, while two of my undergraduate students working on this grant received excellent permanent positions as project engineers in industry.