

Preview

MOFs the movie: Molecule to nuclei evolution during metal-organic framework formation

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The chemical and structural diversity of Metal-Organic Frameworks (MOFs) makes them an exciting class of materials as a scientific playground to potentially address a variety of applications, yet this diversity poses a daunting challenge to fully understanding their fundamental principles. Scientists from Netherlands and Belgium have captured MOFs in motion through a complementary set of simple yet informative *in situ* spectroscopy to promote an in-depth visualization of the nucleation growth process. Not only does this work elucidate guiding theories for MOF synthesis, but it also paints a picture of complex nucleation dynamics for those seeking to strengthen their foundational knowledge.

Observing a material formation process in real-time is perhaps the most straightforward way to fundamentally understand the reaction mechanism and eventually tune the synthetic process toward desired structures/properties. The research in metal-organic frameworks (MOFs) can be particularly benefited with such fundamental understanding due to the abundant choices in the reactants-metals, organic ligands, and reaction conditions. While most of previous characterization works on MOF synthesis and formation focus on the nucleation step and post-nucleation growth,^{1–4} researchers from Netherlands and Belgium have elucidated the coordination chemistry during the pre-nucleation stage (Figure 1) using classic characterizations tools accompanied with computational modeling.⁵

The authors chose ZIF-67 as the model system to probe what happens in the pre-nucleation stage. When $\text{Co}(\text{NO}_3)_2$ and 2-methyl-imidazole (2-mlm) are mixed, the linker ligand 2-mlm immediately substitutes the pristine solvating ligands OR ($R = \text{H}, \text{HMe}, \text{H}_2$) due to the stronger orbital interaction be-

tween imidazole and Co^{2+} versus OR. When Co^{2+} binds to the bulkier imidazole ligands, the steric hindrance forces the formation of complexes with reduced coordination number, generating a pool of $\text{Co}(\text{2-mlm})_{4-x}(\text{OR})_{x+y}$ species ($y = 0$ for tetrahedral, $y = 1$ for trigonal bipyramidal, $y = 2$ for octahedral). Along with the coordination geometry evolving from centrosymmetric O_h (octahedral) to non-centrosymmetric T_d (tetrahedral), the d-d transition on Co^{2+} with d^7 configuration becomes spin-allowed, and the visible absorption spectra red-shifts to lower energy and intensifies. This permits *in situ* monitoring of the coordination environment evolution of the complex species during MOF formation. At the pre-equilibrium stage before nucleation occurs, the Co-complex pool contains a variety of species with varying coordination numbers, symmetries, and types of ligands (2-mlm to OR ratios). These monomers serve as precursors or pre-nucleation building units for ZIF nucleation.

Inspired by zeolite nucleation process, multiple mechanisms have been previ-

ously proposed for MOF nucleation:⁶ amorphous gel formation and re-crystallization, pre-nucleation building units formation and assembly, and oriented particle-to-particle attachment. These mechanisms differ in their nucleus formation pathways and states/structures. ZIF nucleation was previously suggested via amorphous gel formation.^{3,7,8} However, the driving force and the reaction mechanism at molecular scale for such a process remained unclear. To this end, the authors used electrospray-ionization mass-spectrometry (EIS-MS) to determine the presence of an overwhelming majority of monomeric coordination units compared to oligomeric units are observed, which rules out the nuclei formation via the oligomer-to-oligomer attachment mechanism. Furthermore, the authors pinpoint the underlying molecular mechanism of amorphous intermediates formation; the 2-mlm-poor coordination species with unmatched symmetry and chemical composition in the complex-pool add to the oligomeric pre-nuclei, resulting in configurationally-disordered thermoset type polymers in a higher energetic state that then reconstruct to thermodynamically more stable crystalline structure. Supporting absorption spectra and LCF study reveals the continuous consumption of O_h type complexes through ligand addition and their conversion to $\text{Co}(\text{2-mlm})_4$ (T_d) building units for ZIF-67 particle formation.

The MOF formation typically does not follow basic stoichiometry, and varying ligand-to-metal (L/M) ratio typically has trivial impact the structure of final product. However, the authors point out that tuning the L/M in ZIF-67

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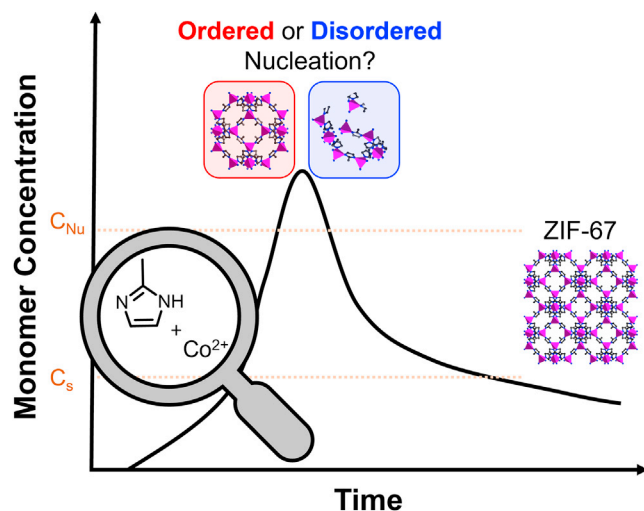


Figure 1. The nucleation path toward ZIF-67 formation

synthesis significantly affects the nucleation kinetics and species distribution. Increasing the L/M ration from 1-40 accelerates the ZIF-67 formation as well as causes the formation of more oligomeric nuclei and thus smaller average ZIF-67 particles due to the fixed number of Co^{2+} in the solution. As the formation of stable oligomeric nuclei requires bridging individual monomeric complexes through 2-mlm, increasing L/M ration pushes the equilibrium toward formation of 2-mlm rich complexes for faster oligomerization. It is interesting that the formation of the 2-mlm rich complex $\text{Co}(2\text{-mlm})_3\text{OR}$ ceases at high L/M ratio; although $\text{Co}(2\text{-mlm})_4$ contribution intensifies,

the nucleus and particle formation were hindered. Supplementary to the authors' rationalization that this arises from the inability of mutual bridging between $\text{Co}(2\text{-mlm})_4$ complexes, we provide our understanding from a fundamental coordination chemistry point of view below.

It is worth noting that imidazole species are not solely ligands but also strong bases with pK_b values around 7. To bridge Co^{2+} species into three-dimensional frameworks, 2-mlm must experience a deprotonation process and form imidazolate (Figure 2). As the pK_a of imidazole is high, a spontaneous deprotonation process is expected to be

slow even though coordinating to Co^{2+} is likely to increase the acidity of the proton on 2-mlm and facilitate the deprotonation process to some extent. When increasing the L/M ratio, the equilibrium does not only shift toward the formation of monomeric 2-mlm rich Co complexes, but the excess amount of imidazole can also simultaneously serve as a base to promote the formation of imidazolate species (Figure 2). This potentially accelerates the bridging process, giving rise to stable oligomeric nucleus in a short reaction period. The bridging process can happen through multiple pathways, for instances, through mutual ligand exchange by replacing either another 2-mlm or a OR ligand from adjacent Co-monomeric complexes. As the Co-OR bond is thermodynamically weaker than Co-2-mlm bond, kicking out a Co-OR from Co-complexes will be kinetically faster to form stable oligomeric species. At lower L/M ratio, where there is sufficient Co-OR containing complexes (i.e., $\text{Co}(2\text{-mlm})_3\text{OR}$), the increased amount of 2-mlm will serve as base to facilitate the deprotonation process to bridge monomeric growth species to stable oligomeric nuclei. In scenarios of abundant 2-mlm, $\text{Co}(2\text{-mlm})_4$ becomes predominant and the mutual substitution between 2-mlm ligands on colliding complexes will be much slower as the Co-2-mlm bond is strong and 2-mlm itself is bulky. As a result, at the initial stage of increasing L/M ratio, the nucleation rate increases until the L/M ratio saturates the rate. Regardless of the underlying mechanism, the observation from the authors provides an additional, simple knob to tune the size of MOF particles via a modulator-free approach.

This work fills the gap between conventional coordination chemistry in homogeneous system and heterogeneous formation of solid-state MOFs by providing a clear vision of how the molecular coordination chemistry evolves during the nucleation stage to promote

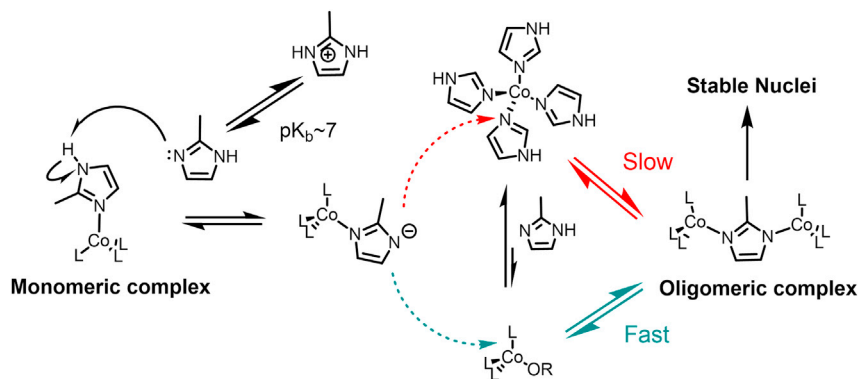


Figure 2. Illustration of possible roles of excess ligand 2-mlm during the formation of stable oligomeric nuclei

MOF particle growth. The fundamental knowledge can be transferred to other MOF systems to understand and control their syntheses. More importantly, this work directly and clearly bridges textbook coordination science knowledge with frontier research activities, offering an accessible nucleation point for beginners entering the MOF field.

1. Stavitski, E., Goesten, M., Juan-Alcañiz, J., Martinez-Joaristi, A., Serra-Crespo, P., Petukhov, A.V., Gascon, J., and Kapteijn, F. (2011). Kinetic control of metal-organic framework crystallization investigated by time-resolved in situ X-ray scattering. *Angew. Chem. Int. Ed. Engl.* *50*, 9624–9628.
2. Millange, F., Medina, M.I., Guillou, N., Férey, G., Golden, K.M., and Walton, R.I. (2010). Time-resolved in situ diffraction study of the solvothermal crystallization of some prototypical metal-organic frameworks. *Angew. Chem. Int. Ed. Engl.* *49*, 763–766.
3. Cravillon, J., Schröder, C.A., Nayuk, R., Gummel, J., Huber, K., and Wiebcke, M. (2011). Fast nucleation and growth of ZIF-8 nanocrystals monitored by time-resolved in situ small-angle and wide-angle X-ray scattering. *Angew. Chem. Int. Ed. Engl.* *50*, 8067–8071.
4. Xing, J., Schweighauser, L., Okada, S., Harano, K., and Nakamura, E. (2019). Atomistic structures and dynamics of prenucleation clusters in MOF-2 and MOF-5 syntheses. *Nat. Commun.* *10*, 3608.
5. Filez, M., Caratelli, C., Rivera-Torrente, M., Muniz-Miranda, F., Hoek, M., Altelaar, M., Heck, A.J.R., Speybroeck, V.V., and Weckhuysen, B.M. (2021). Elucidation of the pre-nucleation phase directing metal-organic framework formation. *Cell Reports Physical Science* *2*. <https://doi.org/10.1016/j.xcrp.2021.100680>.
6. Liu, X., Chee, S.W., Raj, S., Sawczyk, M., Král, P., and Mirsaidov, U. (2021). Three-step nucleation of metal-organic framework nanocrystals. *Proc. Natl. Acad. Sci. USA* *118*, 2008880118.
7. Van Vleet, M.J., Weng, T., Li, X., and Schmidt, J.R. (2018). In Situ, Time-Resolved, and Mechanistic Studies of Metal-Organic Framework Nucleation and Growth. *Chem. Rev.* *118*, 3681–3721.
8. Terban, M.W., Banerjee, D., Ghose, S., Medasani, B., Shukla, A., Legg, B.A., Zhou, Y., Zhu, Z., Sushko, M.L., De Yoreo, J.J., et al. (2018). Early stage structural development of prototypical zeolitic imidazolate framework (ZIF) in solution. *Nanoscale* *10*, 4291–4300.