

Monomer Sorting and Parallel Polymerization in Bichannel MOFs

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Organic polymers have, up to this point, been largely left out of the conversation in favor of rigid inorganic species when it comes to engineering materials at the sub-nanometer scale. This is because their entangled and disordered nature in the bulk phase has traditionally limited the scale of nanostructural features they can retain, with the noted exception of assemblies on surfaces. In light of this, our group has found success in developing templated polymerization methods whereby the nanopores of metal-organic frameworks (MOFs) are used as reaction vessels for polymerization. The properties of these nanopores are reflected by the polymers made inside them, enacting rational design at the sub-nanoscale such as two-dimensional pores producing polymer nanosheets of unimolecular thickness¹ and one-dimensional pores bearing immobilized monomers controlling the compositional sequence of individual monomer units in copolymers.²

In this work, we used a type of MOF bearing two distinct one-dimensional pores (a “Bichannel MOF”) and were able to further evolve our method by achieving self-sorting of two different monomers into two respective pore types, where they could be separately polymerized in adjacent pores (“parallel polymerization”) (Figure 1). The MOF focused on here, [Cu(5-methylisophthalate)]_n, has hydrophilic and hydrophobic pores arranged in alternating fashion, and thus sorts vinyl monomers based on their polarity. Polymers which would normally undergo phase separation in the bulk state are therefore formed intercalated with each other on a single-chain level by way of the sub-nanometer alternation pattern of channels in the MOF crystal.

Further, crosslinking through the MOF walls was investigated using divinylated ligands as part of the MOF structure. The two-polymer assemblies formed are unprecedented array structures where two types of polymer chain alternate on the molecular level, and are anticipated as next-generation functional materials.

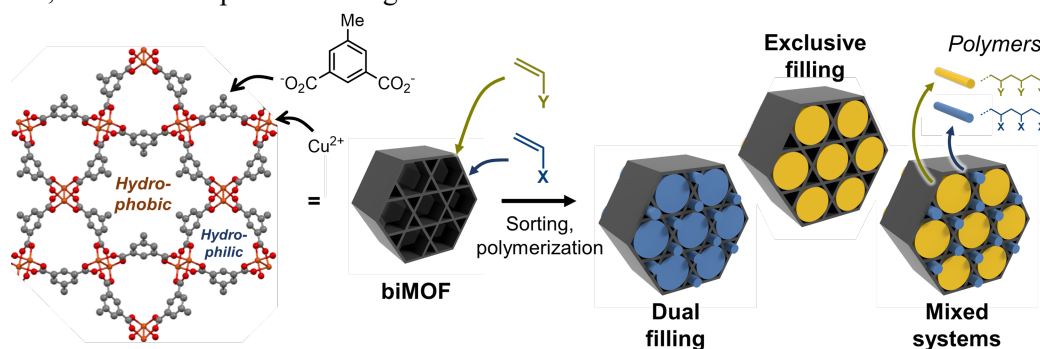


Figure 1. Schematic of the monomer sorting and parallel polymerization in a bichannel MOF.

1) Hosono, N. et al. *Nat. Commun.* **2020**, *11*, 3573. 2) Mochizuki, S. et al. *Nat. Commun.* **2018**, *9*, 329.