

# Symmetry-Mismatched SBU Transformation in MOFs: Postsynthetic Metal Exchange from Zn to Fe and Its Effects on Gas Adsorption and Dye Selectivity

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**ABSTRACT:** This research explores the alteration of metal–organic frameworks (MOFs) using a method called postsynthetic metal exchange. We focus on the shift from a Zn-based MOF containing a  $[\text{Zn}_4\text{O}(\text{COO})_6]$  secondary building unit (SBU) of octahedral site symmetry (ANT-1(Zn)) to a Fe-based one with a  $[\text{Fe}_3^{\text{III}}\text{O}(\text{COO})_6]^+$  SBU of trigonal prismatic site symmetry (ANT-1(Fe)). The symmetry-mismatched SBU transformation cleverly maintains the MOF's overall structure by adjusting the conformation of the flexible 1,3,5-benzenetribenzoate linker to alleviate the framework strain. The process triggers a decrease in the framework volume and pore size alongside a change in the framework's charge. These alterations influence the MOF's ability to adsorb gas and dye. During the transformation, core–shell MOFs (ANT-1(Zn@Fe)) are formed as intermediate products, demonstrating unique gas sorption traits and adjusted dye adsorption preferences due to the structural modifications at the core–shell interface. Heteronuclear clusters, located at the framework interfaces, enhance the heat of  $\text{CO}_2$  adsorption. Furthermore, they also influence the selectivity of the dye size. This research provides valuable insights into fabricating novel MOFs with unique properties by modifying the SBU of a MOF with flexible organic linkers from one site symmetry to another.

**KEYWORDS:** metal–organic framework, postsynthetic metal exchange, secondary building unit transformation, single-crystal-to-single-crystal transformation, core–shell MOF

