

# 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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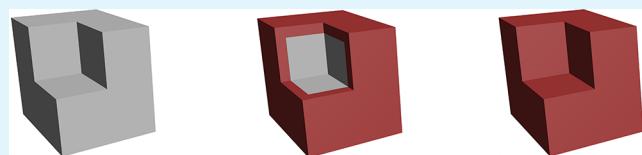
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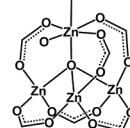
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**ABSTRACT:** This research explores the alteration of metal-organic frameworks (MOFs) using a method called postsynthetic metal exchange. We focus on the shift from a Zn-based MOF containing a  $[\text{Zn}_4\text{O}(\text{COO})_6]$  secondary building 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, 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.



ANT-1(Zn) → ANT-1(Zn@Fe) → ANT-1(Fe)



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

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.