Chemical and Structural Complexity in functional Multi-metal Metal-Organic Frameworks

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Metal–organic frameworks (MOFs) offer an exceptional platform for the design of functional materials, as their modular synthesis enables the incorporation of different metal elements into well defined crystalline architectures. In particular, multimetal MOFs provide access to increased chemical and structural complexity, opening opportunities to tune reactivity, stability, redox behaviour, and catalytic performance. However, achieving control over the incorporation of multiple metals remains a significant synthetic challenge, since crystallisation pathways, kinetics, and structural constraints often determine whether the final materials display homogeneous distributions, segregation phenomena, or defective arrangements.

Our research addresses these questions through the development of synthetic strategies for the controlled preparation of multimetal framework materials and through the use of advanced diffraction methods to resolve their structures across different length scales. We have explored rare earth multivariate MOFs [1], in which the identity and proportion of the metal precursors strongly influence crystallisation and cation distribution, as well as new approaches based on heterometallic molecular clusters acting as messenger building units (*m*BUs),[2] and multimetal routes that enable the incorporation of previously inaccessible elements such as iridium into framework secondary building units.[3] These studies show how synthetic design can be used to expand the accessible chemical space of framework solids and generate materials with enhanced compositional complexity and functional response.[4]

Within this context, powder diffraction plays a central role, not only in phase identification and structure solution, but also in understanding the structural consequences of multimetal incorporation and subsequent solid state transformation. The combination of X ray and neutron powder diffraction with total scattering and pair distribution function analysis provides access to both average and local structural information, enabling the determination of cation distributions, defect formation, and oxygen vacancy generation in complex materials. In rare-earth based systems and their calcination derived oxides, this approach reveals statistically homogeneous cation mixing, absence of compositional segregation, and a systematic increase in oxygen vacancies upon lanthanide substitution.[5] Overall, these results show that the rational development of functional materials with tailored complexity and properties relies on the combined use of synthetic control and complementary techniques able to probe structure across different length scales.

[1] R. L. Vasile et al., Chem. Mater. (2022). 34, 7029-7041
[2] C. López-García et al. Small Struct. (2025). 6, 2400581.
[3] R. L. Vasile et al., J. Amer. Chem. Soc. (2024). 146, 25824-25831.
[4] C. Martínez-Gómez et al., Submitted (2026). DOI: 10.2139/ssrn.5885581
[5] K. Wilson et al. Submitted (2026)