

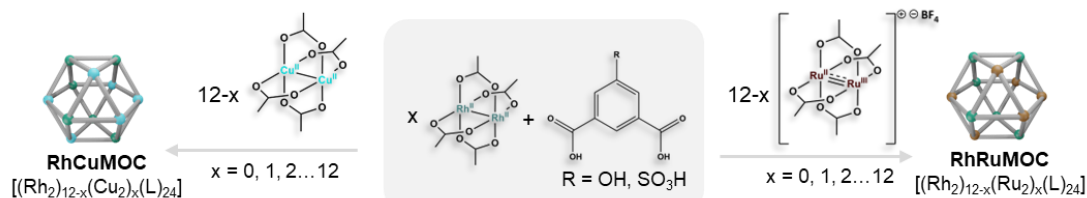
Heterometallic Metal-Organic Cages: Characterising the Complexity of a Confined System

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New or improved performance of heterometallic materials is the benchmark for observation of how mixed metals may interact in a unitary system. As a higher quantity of different metal elements gets incorporated, the system gets exponentially complex. This manifests a question of how such an enriched system can be structurally characterized. Indeed, the recent emergence of high-entropy materials often forsakes a more in-depth investigation of system heterogeneity in favor of quantification of the enhanced material performance.¹ To overcome this challenge, the discrete metal-containing nanocage architecture serves as a platform to probe the heterometallic interaction. Unlike in clusters or alloys, the metal constituents in metal-organic cages (MOCs) are spatially fixed within their structure by ligand design,² allowing us to examine their arrangement, relation, and consequential molecular properties.

In this work, we demonstrate the synthesis of heterobimetallic cuboctahedral cages from the mixture of dirhodium and diruthenium M_2 -paddlewheel secondary building units (SBUs) constrained by functionalized 1,3-benzendicarboxylate organic linkers ($[(Rh_2)_{12-x}(Ru_2)_x(L)_{24}]$, $x = 0, 1, 2 \dots 12$). Here, the variation in the metal composition gives way to an inspection of performance tunability *via* the electrochemical measurements. In an analogous system, the chemically mixed rhodium/copper MOC ($[(Rh_2)_{12-x}(Cu_2)_x(L)_{24}]$) also demonstrates the cooperative effect of metal-mixing *via* an increase in hydro- and thermo-stabilities. Cryospray ionization mass spectroscopy further identified the populational distribution within a single bulk product; a hint of system heterogeneity that was later also observed in the Brunauer–Emmett–Teller surface identification (BETSI). Thusly, we have unraveled the first thread of the heterometallic system complexity through observation of heterogeneity across the molecular-, meso-, and macro-scale.



- 1) Peng, Jian, et al. *Angew. Chem. Int. Ed.* **2022**, 34 (4), 319-330.
- 2) Eddaoudi, M., et al. *J. Am. Chem. Soc.* **2001**, 123 (18), 4368-4369.