MULTI-VARIATE METAL ORGANIC NANOTUBES

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Through the incorporation of multiple different ligands that possess a plethora of functionalities, MV-MOFs exhibit properties exceeding those of their ligand-pure analogs. Due to the 3D topologies of MOFs, the ligands in a MV-MOF can be easily substituted while maintaining a homogeneous structure as the exterior of one pore is the interior of its neighbor (Figure 1, *left*). Notably, these concepts are not true for metal-organic nanotubes (MONTs), the 1-dimensional variant of a MOF.[1]

Unlike MOFs, individual MONTs aggregate into large crystalline bundles via relatively weak intertube interactions between ligands as opposed to the covalent bonds in MOFs, leaving small open spaces between the tubes.[2] Likewise, these intertube interactions in MV-MONTs can impact linking ligands on an adjacent tube and their crystalline packing in a manner that simply does not occur in 3D MOFs (Figure 1, *right*), which has severely limited the development of MV-MONTs.[3]

In this presentation, we showcase a successful strategy for the first multivariate ligand MONTs with different sized ligands. Dissimilar sized aryl groups on ligands were mixed together to yield crystalline MV-MONTs. Careful analysis of these crystals via SCXRD and PXRD (along with acid digestion) allows for absolute determination of composition. Some ligand pairings resulted in statistical mixtures for the MV-MONTs while others led to MONT phase separation. These combined results provide key insights into the possibilities — and limitations — of ligand multivariance in MONTs.

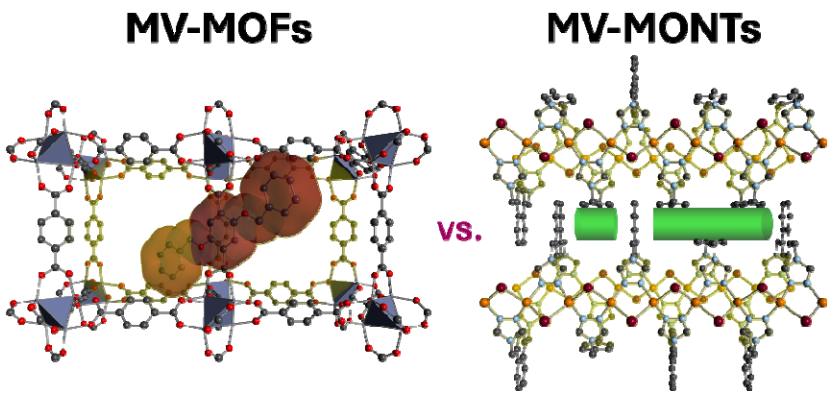

Figure 1. MOF and MONT pore space (yellow highlights throughout) and crystalline packing comparison for multivariant ligands. Multivariate MOFs can incorporate a wide variety of linking units (red highlight) without affecting the MOF packing as the ligand always resides within a pore (*left*). Multivariant MONTs, in contrast, require that the linking ligands interact in the packing space between the tubes (green highlight) which can alter the structure of the MONT (*right*).

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[1] Murdock, Christopher R.; Jenkins, David, M. *J. Am. Chem. Soc.*, **2014**, *136*, 10983-10988.

[2] Vailonis, Kristina M.; Gnanasekaran, Karthikeyan; Powers, Xian B.; Gianneschi, Nathan C.; Jenkins, David M. *J. Am. Chem. Soc.* **2019**, *141*, 10177-10182.

[3] Barrett, Jacob A.; Rosenmann, Nathan D.; Gnanasekaran, Karthikeyan; Carroll, Xian B.; Gianneschi, Nanthan C.; Jenkins, David M. *Chem. Sci.* **2023**, *14*, 1003-1009.