

Exploring the effect of bulky 3D-linkers on MOF host-guest interactions

Lauren Macreadie^a

^a School of Chemistry, University of New South Wales, NSW, Australia
E-mail: l.macreadie@unsw.edu.au

Aromatic ligands, with polycarboxylate or multitopic functionalities, govern the synthetic chemists' toolbox when forming metal-organic frameworks (MOFs) due to their rigid nature, commercial availability, and their variable coordination modes. Conversely, despite their extensive success in creating a rich foundation for MOF development, restriction to solely phenyl interactions within adsorbates represents a possible limitation and reduced variation in the pore chemical environment of the materials.¹ Our research explores how aliphatic 3D-linkers in MOFs can influence the pore environment and overall structural properties of MOFs. Our team explores linkers such as cubane-1,4-dicarboxylic acid (H₂cdc), bicyclo[1.1.1]pentane-1,3-dicarboxylic acid (H₂pdc) and p-carborane-1,12-dicarboxylic acid (H₂pcarb). These linkers are structurally similar to benzene-1,4-dicarboxylic acid (H₂bdc) and therefore can be used to create analogues of well-known bdc MOF systems, to be used for direct host-guest behavioural comparisons. Using this approach, single and multicomponent MOFs have been synthesised, where the significant differences between these systems lie in the host-guest interactions between the MOF and gaseous and hydrocarbon guests.

I will give an overview of these host-guest interactions within 3DL-MOFs (3D-linker MOFs) and how they differ from their aromatic analogues. Through the incorporation of 3D-linkers into prominent MOF architectures, we demonstrate the striking effects a contoured, aliphatic pore environment has on gas and hydrocarbon adsorption, compared with its aromatic counterpart, and explore the potential separation capacities these frameworks may pose.^{1,2} 3DL-MOFs show enhanced selectivity and separation behaviour over their aromatic counterparts due to the highly contoured surface of the pore and the extra functionalities which protrude from the linker body into the MOF cavity. Furthermore, structural studies using neutron and synchrotron powder diffraction highlight the differences relating to negative thermal expansion behaviours between these MOF systems. These can be attributed to a multitude of properties relating to the linker, including influencing the pore size and shape, chemical environment and structural rigidity.

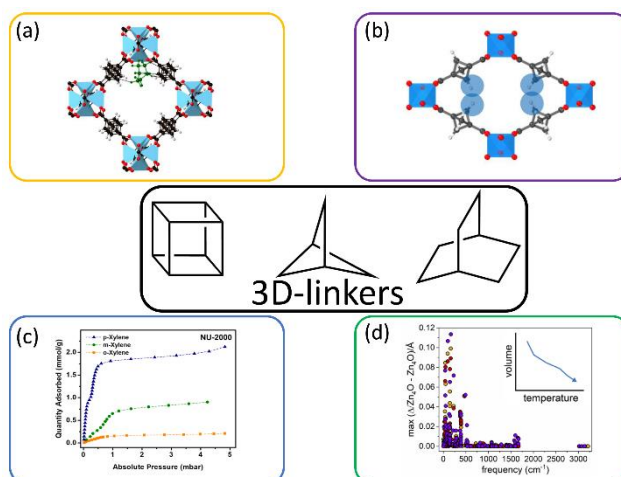


Figure 1. 3D-linkers have made impact in (a) selective host-guest chemistry, (b) enhancing MOF structural rigidity, (c) hydrocarbon separations, (d) structural sub-angstrom influences.

References

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- ² Macreadie, LK.; Babarao, R.; Setter, CJ.; Lee, SJ.; Qazvini, OT.; Seeber, AJ.; Tsanaksidis, J.; Telfer, SG; Batten, SR.; Hill, MR. *Angew. Chem. Int. Ed.*, **2020**, 59, 6090–6098.