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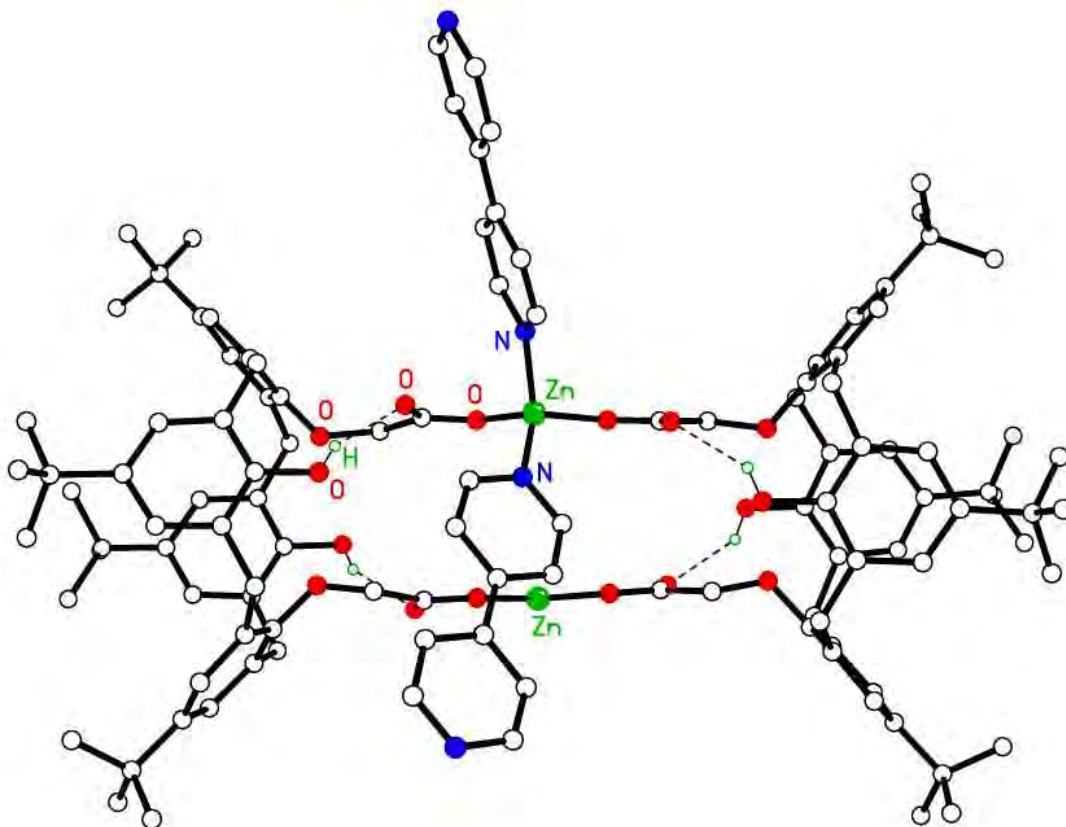
Pillared 2-D MOFs Based on a Lower-Rim Acid-Appended Calix[4]arene.

M. Elsegood¹, L. Horsburgh¹, C. Redshaw², O. Rowe³, S. Teat⁴

¹Loughborough University, Chemistry Department, Loughborough, UK, ²University of Hull, Department of Chemistry, Hull, UK, ³University of East Anglia, School of Chemistry, Norwich, UK, ⁴Berkeley National Laboratory, Advanced Light Source, Berkeley, USA

Calixarenes have been the focus of intense research study of both their organic and metal-coordinated chemistry over the past twenty or so years. Calixarenes generally have intrinsic cavities in their cone or partial cone structures, often filled with coordinated or non-coordinated solvent of crystallization, or filled with substituents from neighboring calixarene molecules. Much of this research has generated molecular, or zero-dimensional compounds, rather than oligomeric or polymeric materials. The shape and size of the calixarene molecules and complexes has led to their use in separation science, catalysis, imaging, etc. Over the same time period, studies on metal-organic frameworks (MOFs) have also been prominent, driven mainly by the ambition to store gases like hydrogen or trap CO₂. Metal ions form nodes and bond to organic spacers which generate a rigid or flexible poly-dimensional framework with pores. This research contribution marries the two fields and incorporates calixarene molecules, with their inherent pores, into MOFs. Solvothermal reactions of the lower-rim functionalized diacid calix[4]arene 25,27-bis(methoxycarboxylic acid)-26,28-dihydroxy-4-tert-butylcalix[4]arene (LH₂) with Zn(NO₃)₂·6H₂O and the dipyridyl ligands 4,4'-bipyridyl (4,4'-bipy), 1,2-di(4-pyridyl)ethylene (DPE) or 4,4'-azopyridyl (4,4'-azopy) afforded a series of 2-D structures of the formulae {[Zn(4,4'-bipy)(L)]·2½DEF}_n (1, Fig. 1.), {[Zn₂(L)(DPE)]·DEF}_n (2) and {[Zn(OH₂)₂(L)(4,4'-azopy)]·DEF}_n (3) (DEF = diethylformamide). Figure 1. {[Zn(4,4'-bipy)(L)]·2½DEF}_n (1)

[1] C. Redshaw, O. Rowe, M. Elsegood, et al., *Cryst. Growth Des.*, 2014, 14, 270-277.



Keywords: Metal-Organic Frameworks, Calixarene, zinc coordination chemistry