Synthesis of $\text{M}_4\text{L}_6$ metal organic cages via a chiral auxiliary strategy

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Metal organic cages are a promising class of discrete molecular containers that exhibit highly selective guest encapsulation for applications in molecular separations,[1] catalysis,[2] and the stabilisation of reactive species.[3] The rational design of organic ligand binding modes and corresponding metal coordination geometries leads to the predictable self-assembly of complex architectures such as $\text{M}_4\text{L}_6$ tetrahedra in this case. Here, we have designed $\text{M}_4\text{L}_6$ edge-linked tetrahedral cages with planar, $\text{C}_2$-symmetric bis(bidentate) 3,3’-bipyridine ligand backbones to provide the rigidity necessary for structure predictability. Together with octahedral transition metal nodes that define the vertices of the tetrahedron, these components self-assemble to enclose a central cavity that defines a distinct microenvironment. Metal organic cages exhibit highly selective encapsulation of guest molecules due to the well-defined size, shape and chemical environment within their internal cavities. Their high modularity enables metal organic cages to act as an excellent system for the separation of racemic mixtures.

Enantiopure coordination cages have presented a long-standing challenge to the field, as a mixture of diastereomers generally form upon self-assembly of achiral components around chiral metal centres, due to the lability of metal-ligand interactions. The aim of this study is to synthesise chiral metal organic cages for the enantioselective discrimination of guest molecules. Here, we employ chiral amino acid motifs on the capping positions of 3,3’-bipyridine based ligands to impart permanent chirality throughout the $\text{M}_4\text{L}_6$ tetrahedral cage (Figure 1). This synthetic route establishes predetermined chirality in the cage structure, unaffected by self-assembly through relatively labile coordination bonds. A chiral metal organic cage would successfully define a chiral space for the enantioselective encapsulation of guest molecules.

Figure 1. $[\text{Zn}_{\text{II}}^\text{II}]^8^+\text{cage modelled on Spartan ’14 (v1.1.8).}$ The equilibrium geometry at ground state was calculated with Hartree-Fock theory methods, performed using 3-21G in a vacuum. The tetrahedron is outlined in yellow for clarity. $\text{L} = 3,3'$-bipyridine ligand with methyl-protected L-tert-leucine auxiliaries.

