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Rational Design of Porous Coordination Polymers for Catalysis

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Over the past couple of decades, Porous Coordination Polymers (PCPs) have been extensively studied due to their variety of applications including gas storage, small molecule separations and sensors. Furthermore, heterogeneous catalysis using PCP's has recently become an area of considerable interest, as tuning the pore size can lead to selective catalysis in mixtures of reagents. However, these catalytically active PCP's often require post synthetic modification of an existing framework with a catalytically active metal.

A number of novel dicarboxylate ligands have been synthesised, which include an additional metal coordination site within the main body of the ligand itself, such as a diazabutadiene moiety. Having this additional coordination site allows for coordination of a catalytically active metal centre to the ligand, hence forming a metalloligand, before the synthesis of the coordination polymer.

With the intention of using this relatively unexplored route to rationally design PCP's, a range of metalloligands containing second row transition metal species have been developed. One such ligand, containing a Mo(CO)₄ fragment, has successful been utilised in the formation of a heterometallic molybdenum/cadmium PCP, with approximately 43% void volume. The Mo(CO)₄ fragments line the edges of 1D solvent channels within the structure and therefore should be accessible to substrates.

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