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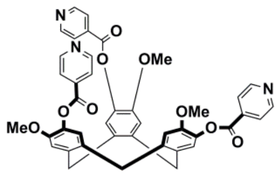
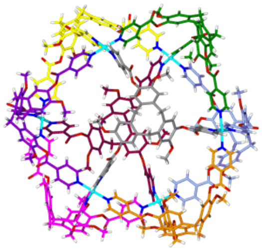
Metallo-supramolecular assemblies with cavitand ligands

Nanometre-sized polyhedral or prismatic chemical architectures can self-assembly from combinations of transition metal cations and multifunctional ligands. Likewise supramolecular materials such as coordination polymers may be formed by similar reactions. These assemblies are often hollow or porous and provide a confined chemical space where other molecules can be bound. Hence many of these systems are being developed as *nano-scale vessels* or *crystalline sponges* for chemical entrapment, signalling and sensors, and even as tiny reaction vessels.

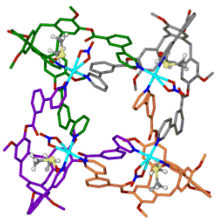
We use the cavitand host molecule cyclotriveratrylene (CTV) as a platform as its relatively rigid pyramidal shape lends itself to the formation of cage-like or porous species. We have developed a library of CTV-type ligands and have used these to generate a series of discrete metallo-cages with a spiked or "star-burst" shape,[1-5] and coordination polymer or other network materials.[6-8] Particular highlights are: the family of Pd_6L_8 stella octangula assemblies all > 3 nm in diameter;[2] and examples of highly unusual topological complexity in triply interpenetrating [2]catenanes,[3] in the "Solomon's cube" a self-entangled Pd_4L_4 assembly, and in a remarkable chain-mail assembly of M_6L_6 metallacycles with infinite Borromean-ring motifs, both of the later were hitherto unreported in chemistry.[4] We have recently developed a series of smaller metallo-cryptophanes with bis-carbene co-ligands (see figure) which hold particular promise for host-guest binding behaviour, and act as crystalline sponges in the solid state, as do coordination polymers of networked metallo-cryptophanes.[5,6]



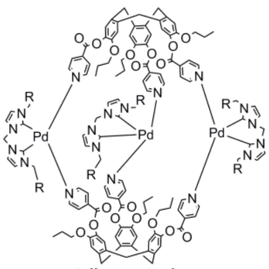
A ligand-functionalised cavitand



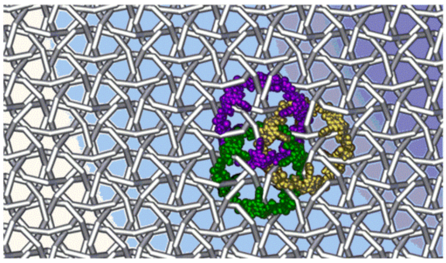
stella octangula $[Pd_6L_8]^{12+}$



Solomon's cube $[Pd_4L_4(NO_3)_2(H_2O)_2]^{6+}$



metallo-cryptophane



Chain-mail of Borromean-ring motifs

Different projects are available in this area, for example in: (i) development of functional metallo-cryptophanes for applications such as molecular recognition, chemical sensors or catalysis; (ii) development of new types of chemical topologies and metallo-cages and an investigation of their host-guest chemistries; (iii) development of stimuli-responsive metallo- and organic cages which can change shape or composition with a physical or chemical trigger; (iv) crystalline sponge behaviour of cage and networked-cage materials.

Project work will involve *multi-step organic synthesis* of ligands; *synthetic coordination chemistry*; investigations of the *self-assembly behaviour* of metallo-cages, and their solution characterisation using mass spectrometry and NMR; all aspects of *single crystal X-Ray structure determination*; and studies of the *host-guest chemistry* of the cages by techniques such as NMR, ITC, gas binding etc. Other characterisation methods that we employ include IR, fluorescence spectroscopy, thermal techniques (DSC, TGA) and electron microscopy where appropriate.

References

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