# Bidirectional Regulation of Halide Binding in a Hetero-metallic Supramolecular Cube



William J. Ramsay, Tanya K. Ronson, Jack K. Clegg, and Jonathan R. Nitschke wr234@cam.ac.uk, jrn34@cam.ac.uk

University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW

### Introduction

The construction of organo-metallic supramolecular structures often relies on coordination driven self-assembly via metal-ligand interactions. We take advantage of a subset of this design strategy, which involves the stabilisation of a covalent imine bond through dative bond coordination to a metal ion, to create many synthetic capsules<sup>1</sup>. A stellated octahedron can be formed through a one pot synthesis of 62 building blocks, illustrating the power of integrative self-sorting in a bimetallic system (Scheme 1)<sup>2</sup>, and in a similar self-assembly process, a porphyrin-faced cube can be synthesised (Scheme 2)<sup>3</sup>.



Scheme 1. The two-step synthesis (i) of a hetero-metallic cube *via* a square-planar Pt<sup>II</sup> intermediate and the one-pot synthesis (ii) of starting from free subcomponents and metal ions.

Scheme 2. The design and synthesis of a porphyrin-faced cube through sub-component self-assembly.

# Hetero-metallic Cube

Based on our previous investigations of metallo-supramolecular hosts, we predicted that the combination of a  $C_{a}$ -symmetric tetrakis-bidentate ligand derived from a molyddenum 'paddle wheel' complex<sup>4</sup> with  $C_{3}$ -symmetric iron(II) tris(pyridylimine) centres would result in the formation of a cationic cubic structure with the coordinatively unsaturated molyddenum centres located on the faces of the architecture. The reaction between 2-formylpyridine (24 equiv.), tetrakis(para-aminobenzoato)dimolyddenum (6 equiv.) and iron(II) trifluoromethanesulfonate (triflate, 8 equiv.) produced cage 1 as the uniquely observed product (Scheme 3).



Scheme 3. Iron(II) triflate, 2-formylpyridine, and *tetrakis(para-aminobenzoato)*dimolybdenum selfassemble to form a cubic structure in acetonitrile.

#### Synthesis and Characterisation

Mass spectrometry, microanalysis and NMR were all consistent with the formation of the highly symmetric face-capped cubic architecture. Slow vapour diffusion of diethyl ether into an acetonitrile solution of 1 produced small crystals suitable for X-ray diffraction experiments; the approximately *O*symmetric solid state structure (Figure 1a-c) was consistent with the high-symmetry spectra recorded in solution.



**Figure 1. a**, Schematic view of the X-ray crystal structure of 1, modelled as a space filling diagram, and b, along the  $S_6$ -axis (axially coordinating species, non-coordinated anions and solvent molecules removed for clarity). c, X-ray crystallographic analysis revealed four triflate anions coordinated to exterior sites (modelled above, right, left, and behind the structure). X-ray crystal structures: C, grey; O, red; N, blue; Fe, purple; H, white; Mo, orange; S, yellow; F, light blue.

#### **Conclusion and Future Outlook**

We have demonstrated that lining the cavity of a supramolecular architecture with well-defined binding sites allows guests to directly modulate each others' binding affinities through steric and electronic interactions. Future work will include investigations of larger analogues of 1, able to host more extensive collections of interacting guests, as well as the use of guest affinity modulation to specifically 'pick up' and 'drop off' substrates in well-defined chemical contexts, as might be useful in anion transport or nuclear waste processing. The use of functional chemical systems to accomplish tasks that no single chemical species can achieve takes inspiration from the intricate functionality exhibited by biological systems.

#### **Host-Guest Complexes**

The high positive charge (+16) of the framework and the observation of triflate coordination at the molybdenum sites encouraged investigation of 1 as an anion receptor. Titrations with UV-Vis spectroscopy indicated 1:1 interactions between 1 and fluoride, chloride, bromide and iodide; a larger anionic guest, trifluoroacetate (CF<sub>3</sub>CO<sub>2</sub><sup>-7</sup>, 5), wa also determined to form a host-guest complex.

We also discovered neutral molecules coordinated preferentially to the interior of the structure, most notably ammonia (NH<sub>3</sub>, **2**, Figure 2), trimethylamine (NMe<sub>3</sub>, **3**), and trimethylphosphine oxide (OPMe<sub>3</sub>, **4**). Figure 2. The X-ray crystal structure of 2 with twelve equivalents of NH<sub>3</sub> (shown as space filling representations) saturated all

molybdenum coordination sites

# **Tuning Halide Binding**

When the association of the strongest coordinating halide (iodide) was investigated in the presence of different ligating species in 1, it was determined that a balance of steric effects, charge, and favourable chemical interactions from the primary coordinating species provided a method to regulate iodide affinity (Figure 3).



Figure 3 (association constants are all  $\times 10^3$  M<sup>-1</sup>). a, Iodide was found to have the highest affinity of the halides for 1. b, when NH<sub>3</sub> was bound within 2, iodide affinity increased by an order of magnitude (f). The more weakly-binding NMe<sub>3</sub> (c) brought about increased iodide affinity (g) and the more strongly-binding OPMe<sub>2</sub> (d) produced the weakest increase in iodide binding strength (h). The presence of excess trifluoroacetate (e) competitively inhibited iodide binding (i).

# References and Acknowledgments

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