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Synthetic Receptors

Bidirectional Regulation of Halide Binding in a Heterometallic Supramolecular Cube**

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Biological receptors are capable of selectively and multiply binding a range of signal molecules, such as hormones and neurotransmitters, as parts of communication networks in complex biomolecular systems.[1] Although synthetic receptors are growing in sophistication, the design of receptors with tuneable guest affinities is a key technical barrier towards more accurate emulation of natural systems, and thus remains a challenge in host–guest chemistry.

Supramolecular chemistry has brought greater insight into the functioning of complex natural signaling systems, which has in turn allowed preliminary progress to be made in the design of synthetic mimics of these systems' complex functions.[2] This design process requires an understanding of the factors that govern the strength of binding between a chemical signal and its receptor. Anions are examples of chemical signals in biomolecular systems, and many biological functions rely upon the transport, transformation, and recognition of a wide range of negatively charged species.[3] Anion transport proteins in mammalian cells regulate electrical activity, pH value, volume, and the flow of osmolites and metabolites; these activities are important in immunology, cell migration, cell proliferation, and differentiation.[4] There has been significant progress in the development of supramolecular anion receptors with applications in the transport,[5] sensing,[6] and extraction[7] of anions. Metal–organic capsules,[8] in particular, have shown great affinity and selectivity in anion binding.[9] Although many synthetic hosts[10] can selectively encapsulate anions, there are few systems in which the binding affinity of anionic guests can be tuned without significant synthetic modification to the host framework.[11] Taking inspiration from these anion binding capsules and our own previous investigations into metallosupramolecular hosts,[12] we found that the combination of a C_4-symmetric tetrakis-bidentate ligand derived from a molybdenum(II) 'paddle wheel' complex[13] with C_3-symmetric iron(II) tris(pyridylimine) centers resulted in the formation of a cationic cubic structure (Figure 1). The coordinatively unsaturated molybdenum centers located on each face of the cube were envisioned to serve as binding sites for coordinating species.

The reaction between 2-formylpyridine (24 equiv), tetrakis(*para*-aminobenzoato)dimolybdenum(II) (6 equiv, Section 1.2 in the Supporting Information), and iron(II) trifluoromethanesulfonate (triflate, 8 equiv) produced cage **1** as the single product (Figure 1a). Mass spectrometry, microanalysis, and NMR spectroscopy results were all consistent with the formation of a highly symmetric face-capped cubic architecture (Section 1.3 in the Supporting Information). The ^{1}H NMR spectrum displayed distinct signals for each of the phenyl protons of the ligand owing to restricted rotation, with separate signals corresponding to those that face into the cavity (*endo*, H^2 and H^4) and those that face outward (*exo*, H^1 and H^3); this inequivalence is consistent with what has been observed in analogous structures.[12b]

Slow vapor diffusion of diethyl ether into an acetonitrile solution of **1** produced small crystals suitable for X-ray diffraction experiments at Diamond Light Source.[14] The approximately *O*-symmetric solid state structure (Figure 1b–d) is consistent with the high symmetry spectra recorded in solution.

The eight tris(pyridylimine)iron(II) vertices in **1** have facial coordination and have the same Δ or Λ stereochemistry; both enantiomers are present in the crystal lattice. The cube faces consist of six dimolybdenum(II) paddle wheels, and enclose a void space of 559 Å^3 (Figure S8 in the Supporting Information). X-ray analysis identified four triflate anions and two water molecules coordinated to the externally oriented molybdenum centers (Figure 1d), as well as three disordered acetonitrile molecules within the cavity. The distance between the interior molybdenum centers of the faces averages 11.3 Å, and the Fe^{II} metal–metal distance diagonally across the faces averages 18.7 Å. The broad triflate signal in the ^{19}F NMR spectrum in acetonitrile solution at $\delta = -78.2$ ppm (free triflate is observed at $\delta = -79.5$ ppm, Figure S3 in the Supporting Information) indicates fast exchange between molybdenum-bound and free triflate ligands on the NMR time scale. The high positive charge (+16) of the framework and the observation of triflate anion coordination at the molybdenum sites encouraged further investigation of **1** as an anion receptor.

The addition of tetra-*n*-butylammonium fluoride, chloride, bromide, or iodide caused the broad ^{19}F NMR signal for

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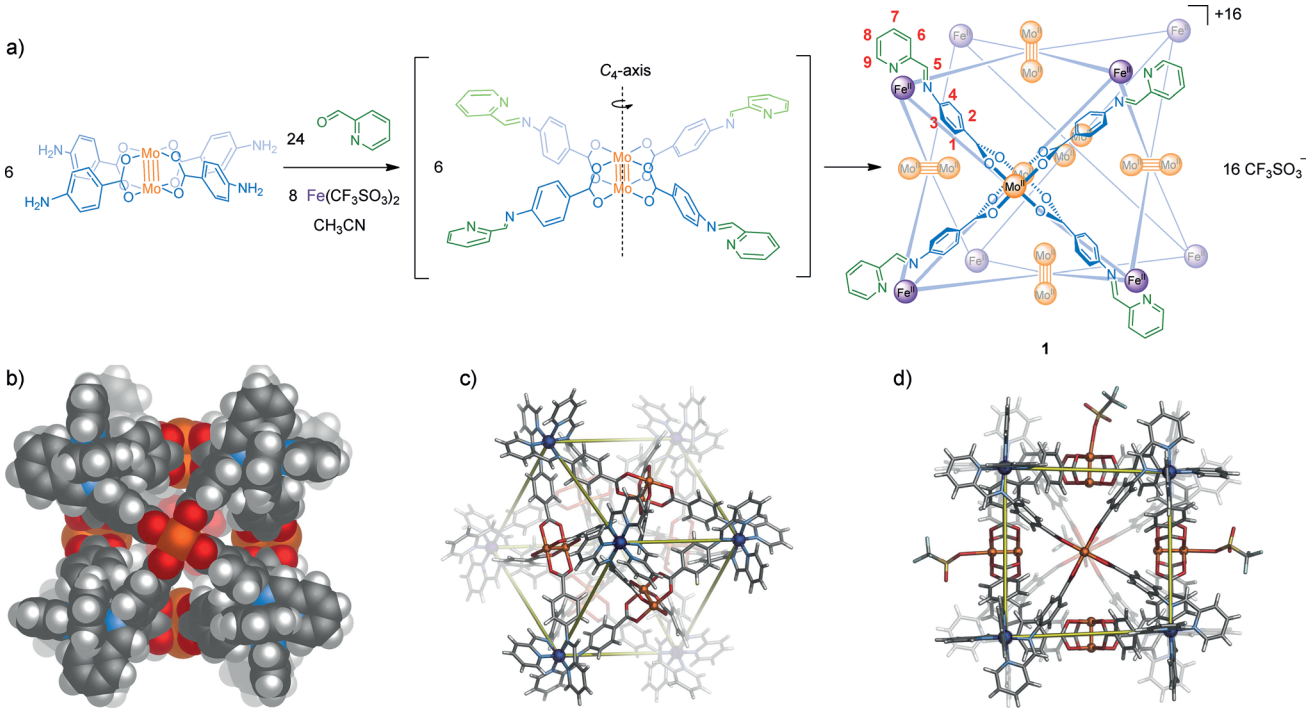

Figure 1. a) Iron(II) triflate, 2-formylpyridine, and tetrakis(*para*-aminobenzoato)dimolybdenum(II) self-assembled to form cubic structure **1** in acetonitrile (^{1}H NMR atom numbering scheme shown in red); b) space-filling representation of the X-ray crystal structure of **1**, perpendicular to a face, and c) framework representation along the cube's body diagonal (axially coordinating species, noncoordinated anions, and solvent molecules are removed for clarity); d) X-ray crystallographic analysis revealed four triflate anions coordinated to exterior molybdenum sites (shown on three sides and behind the structure). X-ray crystal structures: C gray, O red, N blue, Fe purple, H white, Mo orange, S yellow, F light blue (Section 2.1 in the Supporting Information for an ORTEP drawing of **1**). The edges of the cubic framework are highlighted by yellow lines.

triflate in **1** to sharpen and move to a chemical shift associated with free triflate in solution (Section 3 in the Supporting Information). This observation is consistent with displacement of the weakly bound triflate counterions by more strongly coordinating halides. UV/Vis spectroscopy allowed the quantification of the strengths of the halides' interactions with **1**.[15] Titration experiments resulted in reproducible decreases in the intensity of the metal-to-ligand charge-transfer (MLCT) band at 435 nm. This band is derived from the electronic coupling of the metal–metal δ-bonding orbital with the carboxylate π system of the aminobenzoate ligand.[16] Job's plots identified the stoichiometry of binding to be 1:1 in all cases and the titration data were therefore modeled with 1:1 binding isotherms. The isosbestic points in the fluoride, chloride, and bromide titrations shifted upon the addition of excess halide (>10 equiv), consistent with further, weaker binding events at higher guest concentration; these higher halide concentrations were not considered during binding constant calculations. Owing to Coulumbic repulsion, it is unlikely that two halide anions occupy the guest cavity simultaneously, and it is inferred that the shift in isosbestic point at higher halide concentrations is a result of exterior binding or precipitation of the host–guest complex. The association constants for fluoride, chloride, bromide, and iodide (relative to the displacement of triflate) were thus determined to be $(4.9\pm0.6)\times10^3$, $(5.0\pm1.4)\times10^3$, $(1.7\pm0.4)\times10^4$, and $(3.8\pm0.4)\times10^4$ L Mol^{-1}, respectively. The observation that iodide bound most strongly to **1** is consistent with the preference of the molybdenum centers for soft, polarizable axial ligands.[17] Titrations carried out for bromide and iodide, monitored by using ^{1}H NMR spectroscopy, indicated fast halide exchange on the NMR time scale. Binding induced a downfield shift in the interior proton signal (H^2, Figures S43 and S47), consistent with anion binding within the cube's interior cavity; the fluoride and chloride titrations could not be monitored by NMR spectroscopy. In all cases, the ^{1}H NMR spectra of **1** remained symmetric, thus suggesting that the encapsulated guest rapidly underwent exchange between equivalent binding sites on the NMR timescale.

In addition to halide encapsulation in **1**, we discovered that neutral molecules, such as ammonia, coordinated to the molybdenum centers. The crystal structure of the NH_3 adduct (**2**)[14] of the cubic host (Figure 2) was consistent with the ligation of twelve NH_3 molecules to the molybdenum centers when **1** crystallized in the presence of excess NH_3 (15 equiv). Elemental analysis, however, suggested that only six equivalents remained after the crystals had been dried under nitrogen; we infer that the outward-facing NH_3 ligands had been lost preferentially. Solution investigations yielded an intrinsic binding constant, K_{int}, of $(6.5\pm0.8)\times10^3$ L Mol^{-1} for the coordination of one equivalent of NH_3 to a single interior axial position. It was determined that the fraction of axial sites bound to ammonia in solution was consistent with predominant formation of a 1:1 complex under the experimental conditions employed in determining the halide association

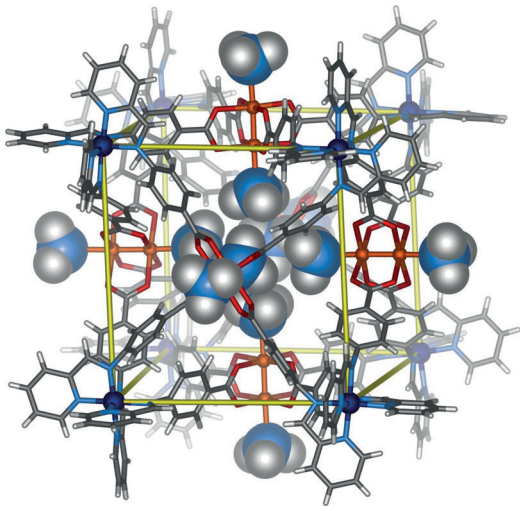

Figure 2. The X-ray crystal structure of **2** with twelve equivalents of ammonia (shown as space-filling representations) saturating the molybdenum coordination sites. Colors as in Figure 1 (anions not shown for clarity).

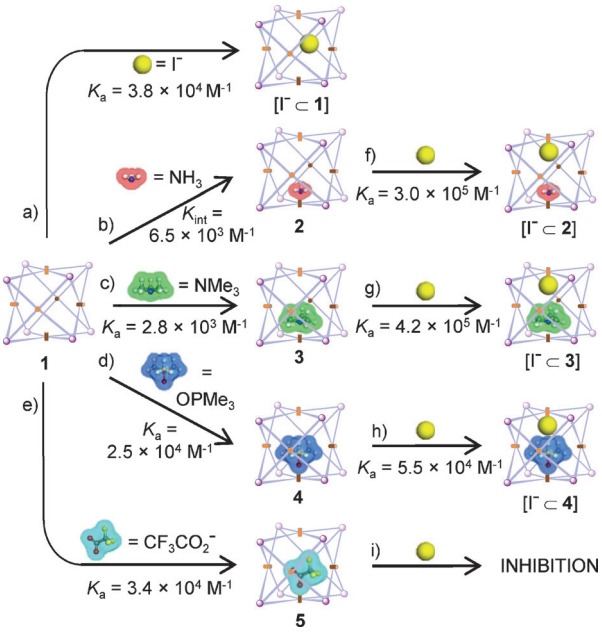

Figure 3. Iodide was found to have the highest affinity of the halides for **1** (a); when NH_3 was bound within **2** (b), iodide affinity increased eightfold (f). The more weakly binding NMe_3 (c) brought about a further increase in iodide affinity (g) and the more strongly binding $OPMe_3$ (d) produced the smallest increase in iodide binding strength (h). The presence of excess trifluoroacetate (e) competitively inhibited iodide binding (i).

with **2** (see below and Section 1.4 in the Supporting Information). The Mo–Mo bond lengths in **2** (2.098(3)–2.116(3) Å) were slightly longer than those in **1** (2.063(1)–2.076(1) Å), consistent with the presence of more-strongly bound axial ligands in the case of **2** than **1**.[18]

In addition to ammonia, trimethylamine (NMe_3), trimethylphosphine oxide ($OPMe_3$), and the ammonium salt of trifluoroacetate ($CF_3CO_2^-$) were investigated as guests for **1**, and their binding constants were determined (Figure 3).

We then investigated the binding of the most strongly coordinating halide (iodide) to **1** in the presence of these additional ligands.

The ammonia adduct **2** bound iodide eight times more strongly than **1** (Section 4.4 in the Supporting Information); **2** exhibited similar twofold, twelvefold and sixfold increases in binding affinity over **1** for fluoride, chloride and bromide, respectively (Sections 4.1, 4.2, and 4.3 in the Supporting Information). In each case, 1:1 halide binding was confirmed by a Job's plot. The downfield shifts of the inward-facing cage proton, H^2, in the ^{1}H NMR titrations were consistent in each case with interior binding. The addition of 12 equivalents of iodide resulted in a 0.03 ppm downfield shift of the H^2 signal (Figure 4), which was greater than that observed in the case of outward-facing H^1 (0.01 ppm), a result that suggests a stronger interior interaction; still larger changes in the chemical shift of H^2 (0.05 ppm) were recorded in the chloride and bromide titrations (Figures S55 and S59, respectively). These observations of a preferred interior binding mode are consistent with the higher effective molarity of binding sites inside the host's cavity. Although the magnitudes of these chemical shifts are small, they are in the region of previously reported host–guest interactions.[19] The small magnitudes of these shifts are attributed to the rapid exchange of halide between equivalent binding sites, each one of which exhibits 1/6 of the chemical shift perturbation induced by a 'static' halide. The outward-facing protons' chemical shift perturbation is attributed to a weaker interaction with the excess iodide present in solution, which did not perturb the observed 1:1 binding stoichiometry (Figure S49).

When NMe_3 ($K_a = (2.8 \pm 0.9) \times 10^3$ L Mol^{-1}) was bound to **1**, forming **3**, (Section 1.5 in the Supporting Information), the binding constant for iodide was measured to be $(4.2 \pm 0.2) \times 10^5$ L Mol^{-1}, an elevenfold increase from that of **1** (Section 5 in the Supporting Information), and slightly greater than then the iodide affinity of **2**. The coordination of one equivalent of $OPMe_3$ ($K_a = (2.5 \pm 0.6) \times 10^4$ M^{-1}) to **1**, forming **4**, (Section 1.6 in the Supporting Information) resulted in a substantially weaker binding constant for iodide ($(5.5 \pm 0.4) \times 10^4$ L Mol^{-1}, Section 6 in the Supporting Information). The presence of $CF_3CO_2^-$ in **5** (Section 1.7 in the Supporting Information) inhibited or 'down-regulated' the coordination of iodide (Section 7 in the Supporting Information).

We infer that in all ternary host–guest complexes incorporating neutral ligands, the neutral ligand's displacement of a weakly coordinating triflate anion from the host framework enhanced the halide binding affinity as a result of an increase in favorable Coulomb forces between the host and halide. Steric effects also play a role, for it appears that the simultaneous encapsulation of triflate and a halide is unfavorable, whereas the smaller neutral ligand and halide association presents a complementary host–guest arrangement. In the case of NH_3-containing **2**, the stabilization of the iodide adduct might also derive from favorable hydrogen-bonding interactions between the two guests.[20] As C–H···I interactions involving NMe_3 in **3** would be weaker than the N–H···I hydrogen bonds in **2**,[21] the stronger iodide associa-

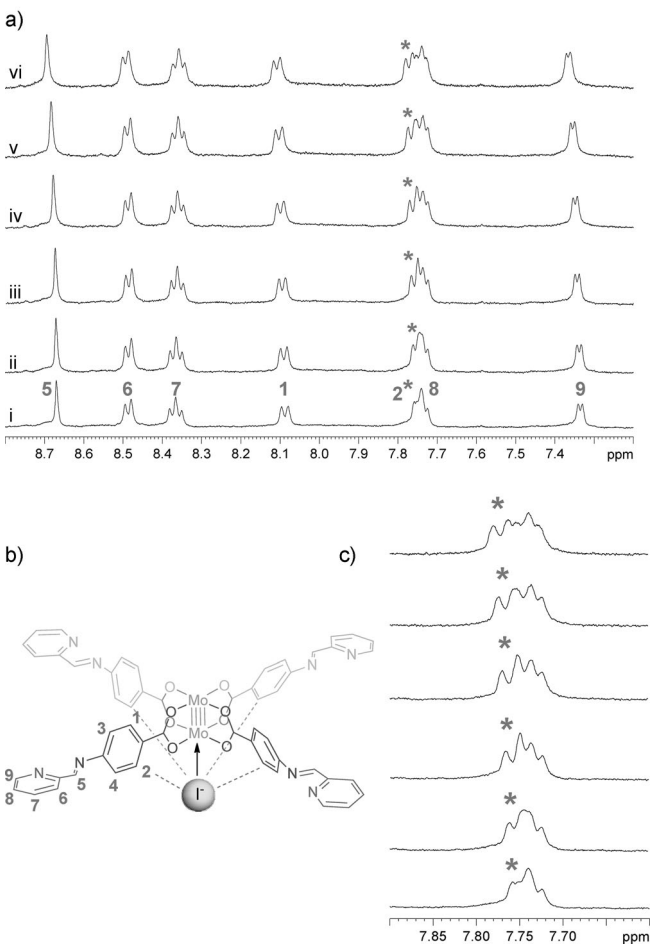

Figure 4. a) Relevant sections of ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of the titration of nBu$_4$NI against **2**: the signal arising from the proton closest to the interior molybdenum site (H^2; red asterisk) was observed to shift downfield in the ^{1}H NMR spectrum of **2** during titration following the addition of i) 0.0 equiv, ii) 0.7 equiv, iii) 2.2 equiv, iv) 3.8 equiv, v) 6.3 equiv, and vi) 12.1 equiv of iodide; b) partial ligand structure of **2** showing the inferred binding mode and atom numbering scheme; c) expansion of the ^{1}H NMR region between $\delta = 7.6$ and 7.9 ppm, showing changes to the signal of H^2.

tion constant in this case might be attributed to a more complementary guest packing arrangement within the host cavity as a result of the larger NMe_3 ligand. The even larger $OPMe_3$ ligand may engender unfavorable steric interactions with iodide, thus diminishing the enhancement of binding affinity relative to the other neutral ligands. Although the titration of iodide in the presence of $CF_3CO_2^-$ in **5** did not lead to any decrease in the MLCT bands in the UV/Vis spectrum, ^{1}H NMR titration identified very minor shifts ($\Delta\delta =$ 0.01 ppm) of the interior and exterior proton signals when a large excess of iodide was added; this observation is consistent with competition between anionic species with similar binding constants. In excess, the trifluoroacetate anion is thus observed to inhibit the binding of iodide. The balancing of steric effects, charge, and favorable chemical interactions between bound species thus provided a method to regulate iodide affinity.

Our approach thus provides an alternative to the use of allosteric effects[22] to modulate binding: the lining of the cavity of **1** with well-defined binding sites allows guests to directly influence each other's binding affinities through steric and electronic interactions. This approach is inherently simple; to tune guest binding, many receptors must undergo synthetic alteration, which can be complex and laborious. By taking advantage of the multivalent guest binding possibilities of structure **1**, we can modulate guest binding affinity without covalent modification of the structure. The chemical functionality of the neutral guest could be further tailored to engender specific interactions with a specific anion. Future work will include investigations of larger analogues of **1**, able to host more extensive collections of larger 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.[23]

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