Self-Assembly

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A Supramolecular Sorting Hat: Stereocontrol in Metal–Ligand Self-Assembly by Complementary Hydrogen Bonding**

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Abstract: *A combination of self-complementary hydrogen bonding and metal–ligand interactions allows stereocontrol in the self-assembly of prochiral ligand scaffolds. A unique, non-tetrahedral M_4L_6 structure is observed upon multicomponent self-assembly of 2,7-diaminofluorenol with 2-formylpyridine and $Fe(ClO_4)_2$. The stereochemical outcome of the assembly is controlled by self-complementary hydrogen bonding between both individual ligands and a suitably sized counterion as template. This hydrogen-bonding-mediated stereoselective metal–ligand assembly allows the controlled formation of nonsymmetric discrete cage structures from previously unexploited ligand scaffolds.*

The central tenet in strategically planning the construction of molecular polyhedra by metal–ligand self-assembly is to maximize the symmetry and rigidity of the constituent ligands.[1] To apply a greater scope of function to self-assembled cages, however, ligands with appended functional groups are required. Functionalized highly symmetric ligands are accessible,[2] but there are few simple scaffolds that are capable of both self-assembly and function, especially with regard to their reactivity once assembled.[3] If less symmetrical ligands could be employed in self-assembly, a toolbox of functionalized species for use in the creation of biomimetic self-assembled architectures would be achievable.[4] One roadblock to this goal is that many methods of metal–mediated self-assembly involve octahedral metals as structural vertices, and this introduces the problem of metal-centered isomerism.[5] For example, symmetrical linear iminopyridine ligands such as **1** form Fe_4L_6 tetrahedra that consist of four *fac* metal centers. The relative stereochemistry is controlled: short, rigid ligands form only one isomer upon assembly, and longer, more flexible ligands form a mixture of three isomers, where both Δ and Λ configurations are observed at the four metal centers, leading to cages of *T*, S_4, and C_3 symmetry.[5a] This isomerism can be controlled in certain circumstances,[6] but the use of nonlinear ligands that can display multiple orientations upon assembly introduces daunting complexity to the analysis of a system. Here we describe a solution to this problem through the introduction of a second controlling element that favors the formation of self-assembled constructs: complementary hydrogen bonds.

Hydrogen bonding is well-precedented as a strategy of multicomponent self-assembly,[7] but the combination of both hydrogen bonding and metal–ligand interactions as integral components in controlling self-assembly is rare. A limited number of polygons[8] and larger aggregates[9] have been formed, and self-assembled cages are known that use hydrogen bonding to aid guest binding.[10] Other contributions such as steric hindrance[11] and guest templation can dramatically alter the outcome of the self-assembly process,[10] but the use of hydrogen bonds to control and alter the stereochemical outcome of complex metal-mediated self-assembly is unexplored. Here we describe the formation and anion-binding properties of a novel polyhedral structural motif that forms through both metal–ligand- and hydrogen-bond-mediated self-assembly.

Using hydrogen bonding as a control element necessarily limits the scope of the metal–ligand contacts used to mediate assembly: cage complexes that are only soluble in water or DMSO cannot exploit weak H bonds due to solvent competition. Fortunately, the assembly of 2-iminopyridine ligands with Fe^{II} centers occurs readily in aprotic solvents such as acetonitrile. We recently reported the formation of a self-assembled M_2L_3 *meso*-helicate complex derived from diamino-dibenzosuberol that contained alcohol groups on the interior of the assembly.[12] The bent suberol scaffold formed an assembly of M_2L_3 stoichiometry with controlled stereochemistry. An M_2L_3 assembly is quite simple in structure, and with only a small cavity, stereocontrol is relatively easy. On the other hand, formation of an M_4L_6 assembly is vastly more complex if a more nonsymmetrical ligand such as **2** is used. In this case, one could imagine more than 100 different isomers if a truly tetrahedral M_4L_6 structure occurred (Figure 1; see the Supporting Information (SI) for a more detailed analysis). These isomers arise from the possibility of metal-centered isomerism (individual *fac* and *mer* possibilities lead to fac_4, fac_3•mer_1 isomers, etc.) as well as Δ or Λ stereoisomerism. In addition, further isomerism is possible by orientation of the CHOH ligand face "in" and "out" of the cage, as well as by the introduction of possible diastereomers at the CH–OH center upon self-assembly into a chiral environment. Obviously, not all of the possible isomers would form, but a highly complex, essentially unassignable mixture of numerous cages could be expected upon self-assembly.

To answer the question of whether simple alcohols could provide control of the assembly by self-complementary hydrogen bonding, the dianiline precursor **A** was targeted, allowing the analysis of the assembly properties of ligand **2** (Figure 2, see SI for synthetic procedures). Selective bis-

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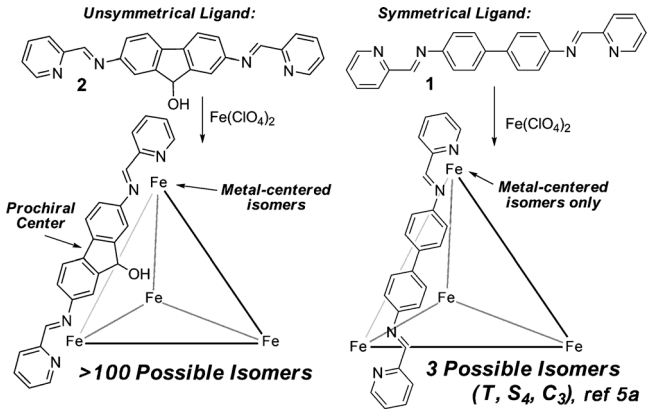

Figure 1. Possibilities for the metal-mediated assembly of both symmetrical[5a] and desymmetrized Fe^{II}-iminopyridine cages $[Fe_4{\cdot}L_6]^{8+}$.

nitration[13] of fluorenone gave the 2,7-dinitro compound in 41% yield, followed by exhaustive reduction with Raney nickel and hydrazine to give **A** in 61% yield.[14] Multicomponent self-assembly of **A** was performed by treatment with 2-formylpyridine and iron(II)perchlorate. After heating in CH_3CN at 60°C for 3 h, a deep purple solution was formed, which upon treatment with diethyl ether led to the precipitation of a purple solid. The resulting complex was soluble in CD_3CN and could be analyzed by NMR spectroscopy. The ^1H NMR spectrum of the assembly is shown in Figure 2a, and although complex, the peaks are sharp and correspond to a cage assembly rather than to nondiscrete aggregates. The peaks displayed a single diffusion constant in a DOSY NMR experiment, indicating that only one stoichiometry of assembly is formed, and the presence of an M_4L_6 complex was observed by ESI-MS. The NMR spectrum did not appreciably change upon varying the temperature from 75°C to −40°C.

X-ray quality crystals of $[Fe_4{\cdot}\mathbf{2}_6]^{8+}$ were obtained by slow evaporation from a saturated solution in CD_3CN, and the solid-state structure was determined by X-ray diffraction analysis (Figure 2b,c). The solution of the structure was challenging: the crystals were rotationally twinned and contained seven highly disordered perchlorate counterions, not to mention numerous disordered solvent molecules. The structure of the M_4L_6 cage complex is quite unusual; a true tetrahedral arrangement is not formed and the observed cage assembly bears a striking resemblance to a wizard's hat. This analogy is strengthened by the presence of a single perchlorate ion at the base of the cage: the assembly rests atop of it. The complex displays two different types of ligand positioning: the "base" ligands are on the outside of the structure, whereas the "axial" ligands occupy the interior. The four Fe^{II} centers show different stereochemical arrangements (as opposed to the identical arrangements common in standard tetrahedra):[15] the iron center at the "peak" displays a Λ-*fac* orientation, whereas the other three centers at the base display the rarely observed Δ-*mer* configuration.[16] The three ligands at the lower base of the assembly are oriented so that the alcoholic groups point upwards toward the "peak", whereas the three vertical ligands are positioned inside the base, and their alcohol units point toward the central cavity.

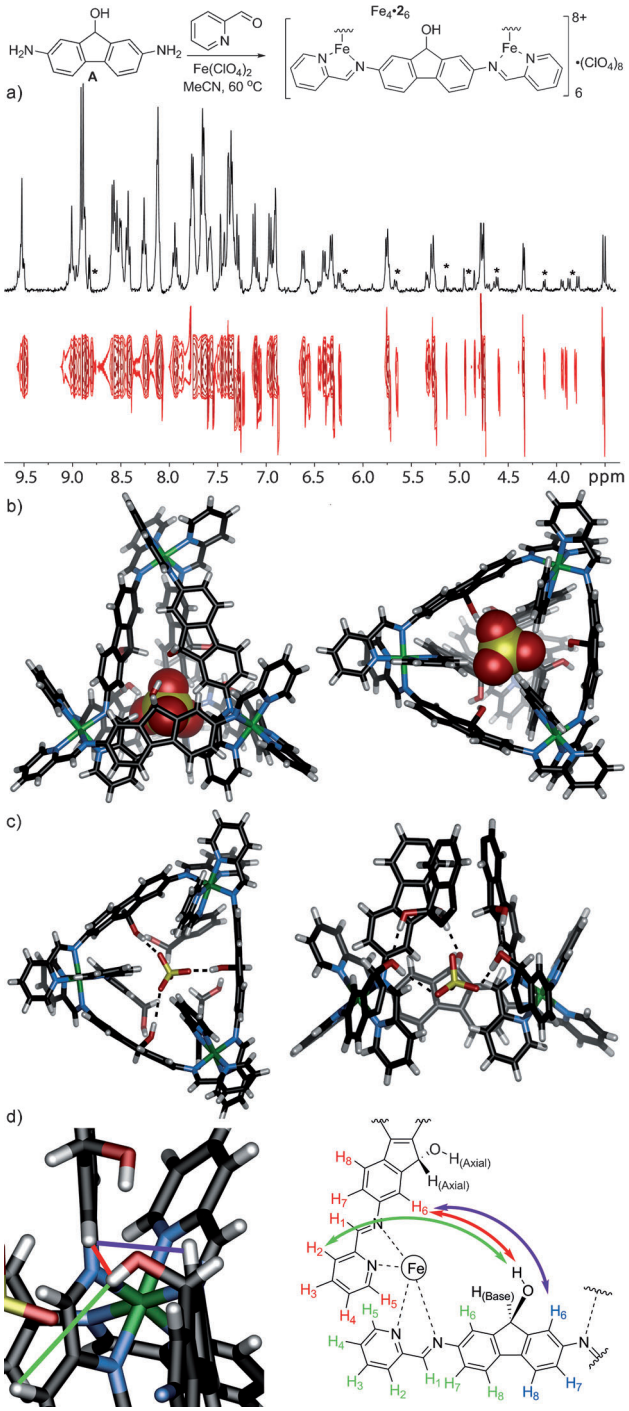

Figure 2. Characterization of $[Fe_4{\cdot}\mathbf{2}_6]^{8+}$: a) ^1H NMR and 2D DOSY spectra of $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6]^{7+}$ (CD_3CN, 400 MHz, 298 K; $\Delta = 100$ ms, $\delta = 2.6$ μs, diffusion coefficient $= 4.8\times10^{-10}$ m^2s^{-1}). * = minor peaks from other isomers. b) Crystal structure of the $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6]^{7+}$ cage showing the presence of both Λ-*fac* and Δ-*mer* iron(II) centers and the bound perchlorate guest. c) Cropped views of the X-ray crystal structure of $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6]^{7+}$ showing: hydrogen bonding between ligand alcohols and the bound perchlorate and hydrogen bonds between different ligand alcohol groups. d) NOE contacts observed by NOESY analysis of the solution-phase structure (see SI for full assignment).

The structure displays pseudo-C_3 symmetry: whereas at first glance the structure appears to possess a C_3 rotation access

through the Λ-*fac* Fe center, the three Fe–Fe distances in the base are not identical in the solid-state structure.

Not only is the stereochemistry at the metal centers controlled, but also that of the prochiral ligands. In the chiral environment of the assembly, the CHOH group in the center of the fluorenol ligands becomes prochiral, and each ligand could orient the hydroxy group either "in" or "out" of the cage core. This does not occur in this assembly: each OH group is oriented toward the center of the prism structure, and this provides an explanation for the stereoselectivity of the assembly.

The cavity of the prism is not particularly large, and the internally pointing OH groups are capable of self-complementary hydrogen bonding with other OH groups on adjacent ligands. In addition, the single bound perchlorate ion on the interior of the cavity exerts a templating effect through hydrogen bonding with the alcohols at the base.

Figure 2c shows the two different types of H bonding present in the structure: the view from below shows three of the oxygen atoms from the bound ClO_4^- ion hydrogen bonding with the OH groups at the base of the cage. The H–O distances are 2.2 Å and the perchlorate ion fully occupies the base of the assembly. The hydrogen-bonding network is not merely an anion templation effect: the axial ligands are in close proximity to each other, and additional hydrogen bonds are present between OH groups on the axial and base ligands, rather than to the bound perchlorate. This combination of both self-complementary and templating hydrogen bonds can only occur in the conformation shown by $[Fe_4{\cdot}\mathbf{2}_6]^{8+}$. Other conformations would point the OH groups away from the center of the cage, preventing favorable hydrogen bonds. In the case of a truly tetrahedral arrangement, the resultant cavity would be too large to allow templation by small anions. While the majority of the energy of formation upon self-assembly comes from favorable M–L interactions in the Fe-iminopyridine units, the discrimination between different isomers comes from favorable hydrogen bonding.

Whereas only one isomer was observed in the solid state, this could conceivably be an artifact of favorable crystallization of the major product. At first glance, the complex NMR spectrum may suggest the presence of an equal distribution of multiple isomers formed upon assembly of ligand **2**, but further analysis indicates otherwise. Even though the ^{1}H NMR spectrum of $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6]^{7+}$ is complex, it can be assigned. The nonsymmetric nature of the assembly leads to most of the ligand protons occupying different magnetic environments and the significant majority of peaks in Figure 2a correspond to individual protons in one assembly. 2D NMR experiments (COSY, TOCSY, HSQC, and NOESY) were performed to allow the assignment. The full solution-phase assignment is described in the Supporting Information, but the notable NOE contacts corroborating the solid-state structure are shown in Figure 2d. There are some minor peaks in the ^{1}H NMR spectrum corresponding to other minor isomers (these peaks are denoted by * in Figure 2a), indicating that the assembly is not 100% selective, but most of the sample upon self-assembly exists as the single diastereomer shown in Figure 2. It is challenging to determine the structure of these minor isomers, but they display the same diffusion coefficient as the parent complex, and most likely belong to different orientations of the CH–OH groups in the ligands of $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6]^{7+}$. Even so, considering the daunting number of isomer possibilities for this complex assembly and the weak nature of the directing hydrogen bond contacts, this selectivity is remarkable.

It is noteworthy that the ClO_4^- ion does not completely fill the cage interior; although it occupies the base of the cage, the peak appears unfilled. Cocrystallized solvent molecules of acetonitrile were highly disordered in the solid-state structure, and were not observed in the cavity. In solution, however, there is evidence from diffusion analysis for a weak association of the acetonitrile solvent with the cage (see SI). The 2D DOSY NMR spectrum of $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6]^{7+}$ shows two diffusion constants for acetonitrile: one corresponding to the bulk solvent and one that codiffuses with the cage, suggesting either co-encapsulation of solvent with the anion, or at least a strong interaction between the assembly and a small number of solvent molecules.

The presence of a bound perchlorate in the cavity is unsurprising, considering that polycationic cages are well-precedented to show strong anion binding, especially in the solid state.[17] The structure of the perchlorate anion allows a strong templating effect, as it is perfectly positioned to interact with the internal alcohol functions. Other counterions were not as effective, however. When **A** was treated with $Fe(OTf)_2$ and 2-formylpyridine, a discrete complex was not observed in solution. In contrast, a broad, undefined spectrum was observed upon ^{1}H NMR analysis in CD_3CN (Figure 3b).

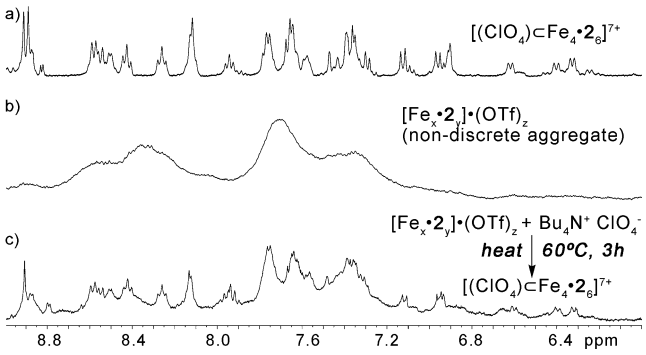

Figure 3. ^{1}H NMR spectra showing anion-templation studies of $[Fe_4{\cdot}\mathbf{2}_6]^{8+}$ (CD_3CN, 400 MHz, 298 K): a) $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6](ClO_4)_7$; b) $[Fe_x{\cdot}\mathbf{2}_y](OTf)_z$; c) $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6](OTf)_7$.

The triflate anion is evidently too weak a hydrogen-bond acceptor to template the cage formation and no discrete assembly is observed. When this undefined aggregate (hereinafter referred to as $[Fe_x{\cdot}\mathbf{2}_y]{\cdot}(OTf)_z$ for simplicity) was treated with Bu_4NClO_4 at room temperature, no change to the nondiscrete aggregate was observed. This aggregate displays similar solubility properties to $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6]^{7+}$, and has the characteristic purple color of an Fe^{II}-iminopyridine complex, so is most likely a mixture of nondiscrete oligomeric aggregates. Upon heating $[Fe_x{\cdot}\mathbf{2}_y]{\cdot}(OTf)_z$ in the presence of Bu_4NClO_4 in CD_3CN with ultrasonication for 3 h, the undefined oligomeric aggregates reverted to the discrete cage $[(ClO_4){\subset}Fe_4{\cdot}\mathbf{2}_6]^{7+}$ (Figure 3c).

If the self-assembly process was performed in a protic solvent such as ethanol, rather than acetonitrile, no discrete cage was formed. Ligand **A** was heated in EtOH with 2-formylpyridine and $Fe(ClO_4)_2$, followed by removal of EtOH in vacuo. Redissolution in CD_3CN and subsequent NMR analysis showed only broad, undefined peaks similar to those of the $[Fe_x\cdot\mathbf{2}_y]\cdot(OTf)_z$ oligomers. This oligomer contains ClO_4^- ions, however, and upon heating in CD_3CN, the discrete cage could be reformed (see SI for spectra). The self-assembly process, though slow, is reversible, and the addition of suitable templating anions allows the formation of the cage assembly from either starting materials or an oligomeric "unformed" aggregate. If the hydrogen-bonding network is interrupted by either a poorly hydrogen-bonding counterion, or a protic assembly medium, the discrete cage is not formed, but the "misfolding" can be easily corrected by conversion to conditions favorable to hydrogen-bonding control.

The scope of anions that are suitable templates for the assembly was explored by treating the oligomeric aggregate $[Fe_x\cdot\mathbf{2}_y]\cdot(OTf)_z$ with different organic-soluble salts as described above for the perchlorate displacement. $[Fe_x\cdot\mathbf{2}_y]\cdot(OTf)_z$ was heated with ultrasonication in acetonitrile with various $Bu_4N^+X^-$ salts and the presence of discrete assemblies was studied by ^1H NMR analysis. As would be expected from the crystal structure of $[(ClO_4)\subset Fe_4\cdot\mathbf{2}_6]^{7+}$, only select anions are suitable templates for assembly, determined by the size and shape of the anion as well as H-bond-acceptor ability. Oxoanions such as perchlorate, nitrate, and hydrogen sulfate all lead to successful templation. These oxygen-containing anions display the correct size and geometry to both fit inside the cavity of $[Fe_4\cdot\mathbf{2}_6]^{8+}$ and provide hydrogen-bond-donor groups that can interact with the internally oriented OH groups of the ligand. Whereas the tetrahedral ClO_4^- shows hydrogen bonding with at least four OH groups, anions with fewer donors such as nitrate are tolerated as well. The lone-pair donors need not be oxygen-based: treatment of $[Fe_x\cdot\mathbf{2}_y]\cdot(OTf)_z$ with the BF_4^- anion resulted in templated cage formation. Interestingly, although one could imagine triflate providing suitable H-bond-acceptor sites for binding, it is not an effective template, nor are longer oxoanions such as $S_2O_4^{2-}$. The much larger $Ph_3SiF_2^-$ and PF_6^- anions are also too large to fit inside of the cage, and no templation is observed. All halide anions are ineffective templates as well, as they are either too small to effectively engage in the requisite hydrogen bonding or cause decomposition of the cage upon heating. Also, oxidizing anions were incompatible: periodate and nitrite led to decomposition of the cages and precipitation of an insoluble brown solid. The ^1H NMR spectra of these other $[anion\subset Fe_4\cdot\mathbf{2}_6]$ assemblies all show slightly different chemical shifts to those of $[(ClO_4)\subset Fe_4\cdot\mathbf{2}_6]^{7+}$, as would be expected from the nonsymmetric nature of the assembly and the close interactions between ligand and template. The differences are minor, however, and correspond to the same overall assembly structure.

Although the presence of a single equivalent of anion template is sufficient to promote the formation of the desired cage, the anion is not irreversibly bound in the cavity. Whereas the ^1H NMR spectrum of both $[(ClO_4)\subset Fe_4\cdot\mathbf{2}_6]^{7+}$ and $[Fe_x\cdot\mathbf{2}_y]\cdot(OTf)_z$ was too complex for an accurate analysis of the anion exchange, the binding of BF_4^- could be monitored by ^{19}F NMR spectroscopy. The BF_4-bound cage $[(BF_4)\subset Fe_4\cdot\mathbf{2}_6](OTf)_7$ was formed by heating the $[Fe_x\cdot\mathbf{2}_y]\cdot(OTf)_z$ aggregate with one equivalent of Bu_4NBF_4. The anion-exchange process was then evaluated by titrating excess Bu_4NBF_4 into that solution. Fast anion exchange was observed, as evidenced by a shift in the ^{19}F resonance toward that of free BF_4^-.

The association constant between the BF_4^- anion and the $[(BF_4)\subset Fe_4\cdot\mathbf{2}_6](OTf)_7$ species was determined to be $430\pm7\,M^{-1}$ based on a titration experiment tracked by ^{19}F NMR spectroscopy. The low association constant is likely due to competition between the anion and the weakly hydrogen-bonding acetonitrile solvent. When a similar experiment was performed on the $[(ClO_4)\subset Fe_4\cdot\mathbf{2}_6](ClO_4)_7$ assembly using the BF_4^- anion, an even lower association constant was observed ($15\pm2\,M^{-1}$). In addition to competing with acetonitrile, the tetrafluoroborate is now competing with the perchlorate anion, which can also bind inside the cage. The cage is kinetically stable throughout the exchange: although templation is required for its formation, the template can dissociate from the cage without disrupting the structure. This is unsurprising: as the cage rests atop the templating anion, complete encapsulation does not occur, and there is a low barrier to anion exchange.

In conclusion, we have shown that the presence of hydrogen-bonding groups, even those as weak as alcohols can have profound implications on the stereochemistry of the self-assembly in metal–organic cage complexes. Intramolecular hydrogen bonding can template the formation of a non-tetrahedral M_4L_6 self-assembled cage structure, and the orientation of the hydrogen bonds sorts the assembly process, favoring one diastereomer over multiple other possibilities, while conferring selectivity for suitable anion templates. We are currently exploiting these assemblies for controlled biomimetic reactivity and the discovery of unprecedented supramolecular architectures.

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