# Cation- and Anion-Exchanges Induce Multiple Distinct Rearrangements within Metallosupramolecular Architectures

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S *Supporting Information*

ABSTRACT: Different anionic templates act to give rise to four distinct Cd^{II}-based architectures: a Cd_2L_3 helicate, a Cd_8L_{12} distorted cuboid, a $Cd_{10}L_{15}$ pentagonal prism, and a $Cd_{12}L_{18}$ hexagonal prism, which respond to both anionic and cationic components. Interconversions between architectures are driven by the addition of anions that bind more strongly within a given product framework. The addition of Fe^{II} prompted metal exchange and transformation to a Fe_4L_6 tetrahedron or a $Fe_{10}L_{15}$ pentagonal prism, depending on the anionic templates present. The equilibrium between the $Cd_{12}L_{18}$ prism and the Cd_2L_3 triple helicate displayed concentration dependence, with higher concentrations favoring the prism. The $Cd_{12}L_{18}$ structure serves as an intermediate en route to a hexafluoroarsenate-templated $Cd_{10}L_{15}$ complex, whereby the structural features of the hexagonal prism preorganize the system to form the structurally related pentagonal prism. In addition to the interconversion pathways investigated, we also report the single-crystal X-ray structure of bifluoride encapsulated within a $Cd_{10}L_{15}$ complex and report solution state data for *J*-coupling through a $CH\cdots F^-$ hydrogen bond indicating the strength of these interactions in solution.
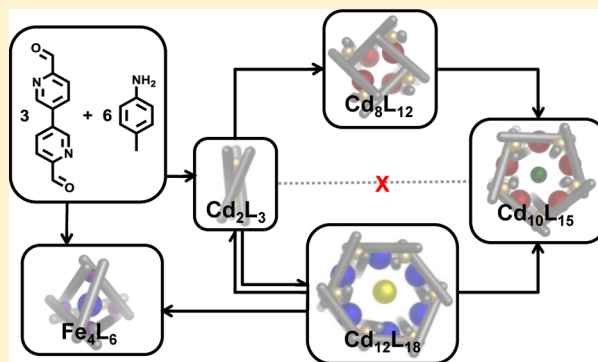
INTRODUCTION

Structures made through self-assembly are capable of reassembling, through rearrangement of the reversibly formed linkages that hold building blocks together.[1−13] Such rearrangements may be prompted through the addition of new building blocks, which shift the thermodynamic landscape[14−18] or open new pathways for transformation.[14,15,19−27] Reassembly may affect a structurally dependent property[9,28−34] or signal an analyte's presence.[16,35] Self-assembling structures capable of reassembling in different ways upon the addition of distinct chemical species, may also be used within a chemical network;[36−38] however, most such architectures reassemble upon the addition of either an anion[20,39−49] or a metal-cation[50−57] but not both. The present work builds upon these foundations to develop systems that undergo both anion- and cation-driven structural transformations, in addition to responding to changes in concentration.[14,58−61] Furthermore, a singular pathway-dependent reaction[62,63] was identified, the outcome of which depended not only on the interplay between the actions of different added chemical components but also the order of addition of these components.

RESULTS AND DISCUSSION

The combination of ligand **L**, generated from the in situ condensation of *p*-toluidine (**A**) and 6,6′-diformyl-3,3′-bipyridine (**B**) around cadmium(II) and anionic templates led to the formation of one of four discrete architectures: Cd_2L_3

triple helicate Cd-**1**, Cd_8L_{12} cuboid Cd-**2**, $Cd_{10}L_{15}$ pentagonal prism Cd-**3** or $Cd_{12}L_{18}$ hexagonal prism Cd-**4** (Figure 1). Two different types of structure-directing anionic templates were used. We define these as either primary templates, whose action was alone sufficient to generate a final architecture, or secondary templates, which acted in concert with another templating anion to generate a structure.[7,10,19,27,63−67] The diversity of the observed structures reflects the adaptable coordination sphere of cadmium(II), which has a large ionic radius (0.95 Å)[68] and is free of ligand field constraints.[10,21]

The simplest cadmium(II) complex isolated was the Cd_2L_3 triple helicate, Cd-**1**, which was generated when bis-(trifluoromethanesulfonyl)imide (triflimide or NTf_2^-) was the sole anion present. The structure was confirmed through ^1H NMR, which indicated one magnetic environment per ligand proton, ESI-MS and elemental analysis, which were consistent with the Cd_2L_3 formulation. Our assignment is also in agreement with the previously reported Cd_2L_3 crystal structure formed with **B** and benzylamine.[21] The helicate structure forms solely as a result of the combination of the geometric and stereochemical information provided by the metal and organic components, as no significant void space exists within the structure to accommodate an internal anionic template.
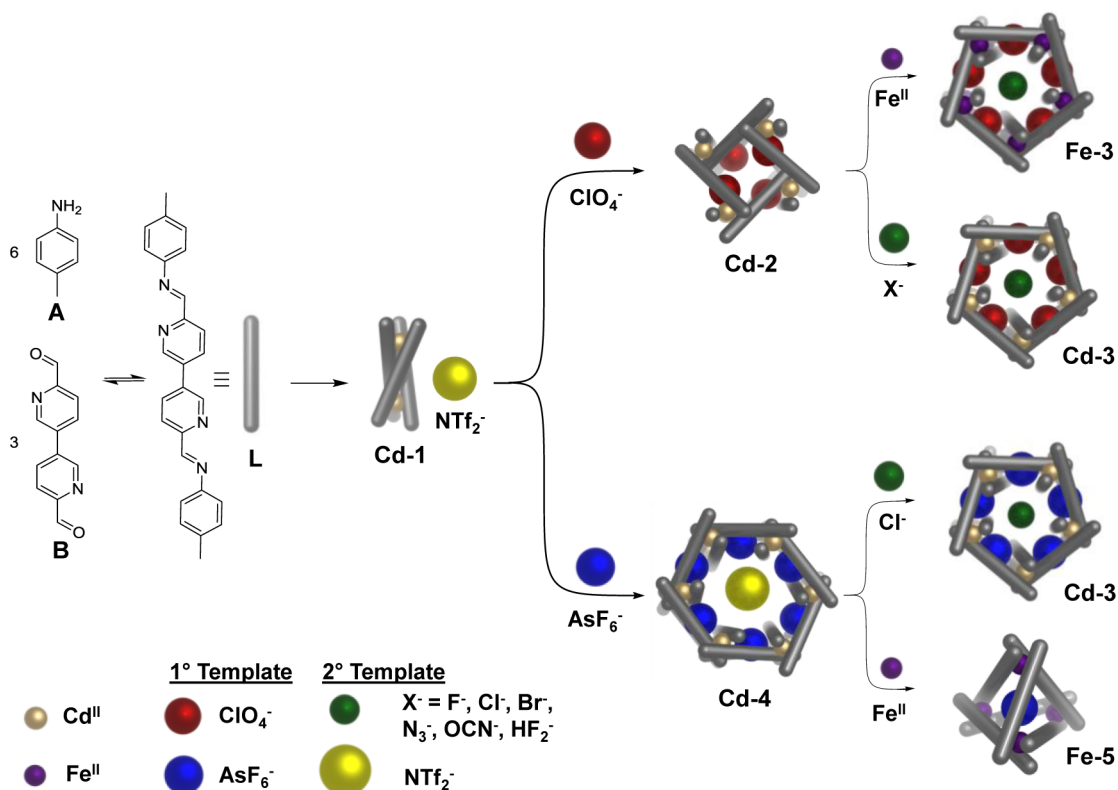
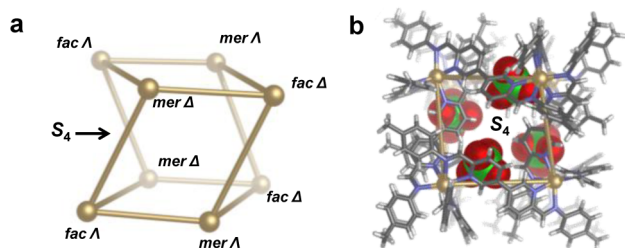**Figure 1.** Structure interconversion pathways: Cd-**1** was generated from $Cd(NTf_2)_2$ and the subcomponents *p*-toluidine (**A**) and 3,3′-diformyl-6,6′-bipyridine (**B**); Cd-**2** was generated through addition of $LiClO_4$ (1 equiv) to a solution of Cd-**1** or when $Cd(ClO_4)_2 \cdot 6H_2O$ was employed in the self-assembly reaction; Cd-**2** → Cd-**3** followed the addition of a secondary template anion, F^- (0.7 equiv), Cl^- (0.4 equiv), Br^- (0.6 equiv), N_3^- (1 equiv), F_2H^- (1.7 equiv), or OCN^- (0.7 equiv); Cd-**1** → Cd-**4** followed the addition of AsF_6^- or PF_6^- at 70 mM **L** concentration; Cd-**4** → Cd-**3** followed the addition of the secondary template anion Cl^- (0.2 equiv); Cd-**2** → Fe-**3** followed the addition of $Fe(ClO_4)_2$ (1.1 equiv); Cd-**4** → Fe-**5** followed the addition of $Fe(NTf_2)_2$ (2.0 equiv). All equivalents reported relative to **L**.

Anion-Driven Structural Transformations. Addition of the primary template anion perchlorate to an acetonitrile solution of Cd-**1** resulted in the formation of a product Cd-**2** having a significantly more complex ^1H NMR profile than Cd-**1**. Six magnetically distinct environments per ligand proton were observed for the new complex, consistent with previously identified M_8L_{12} architectures.[10] The single-crystal X-ray structure of Cd-**2** (Figure 2) confirmed the formation of a structural analogue to the previously reported Ni_8L_{12} complex.[10]

The distorted cuboid, Cd-**2**, links together through the combination of alternating stereochemical configurations (Figure 2a): Each facially coordinated (fac) metal center is linked to three meridionally coordinated (mer) ones, and vice versa. Each metal center of Λ handedness is linked to one other Λ metal center and two Δ metal centers, with the inverse being true of Λ metal centers. These configurations lend the assembly approximate S_4 point symmetry. Four axial (ax) ligands, defined as those that lie parallel to the principal S_4 axis, bridge between faces on the outside of the structure, and the remaining eight equatorial (eq) ligands comprise two 2 × 2 grids that generate the square faces of the architecture.[10] The two grids lie parallel to each other and are linked by the axial ligands, giving rise to the overall cubic architecture.

Four internally bound perchlorate anions were observed to template the formation of the Cd_8L_{12} complex Cd-**2**. Our previous work indicated only the smaller NO_3^- and BF_4^- anions, to have been accommodated within this framework when composed of first-row transition metals Ni^{II} and Co^{II}.[10] We infer the increased M−M distances in the cadmium(II) complex (ax 8.44 Å; eq 10.06 Å) relative to the nickel(II) complex (ax 8.07 Å; eq 9.35 Å) to facilitate binding of the larger perchlorate anions.

Characterization of Cd-**2**, as well as its larger congeners Cd-**3** and Cd-**4** discussed below, proved challenging under standard ESI-MS conditions. These labile multinuclear complexes fragmented readily in the gas phase and were either observed at very low intensity, or not at all, when using the mildest ionization conditions. The parent ions were observed at much higher intensity following the addition of 20% by volume of methanol to an acetonitrile solution (1 mM) of the complexes. We posit this effect to be due to methanol's stronger, more stabilizing interactions with both the cationic and anionic

Figure 2. X-ray crystal structure of Cd-**2**. (a) Side on view with the stereochemical configurations of metal centers labeled; (b) top down view highlighting the S_4 symmetry of the complex and the position of the four internally bound perchlorate anions.

constituents of these complexes, relative to acetonitrile, as reflected in methanol's stronger hydrogen-bond-accepting and -donating ability.[69] This technique may present an alternative to Coldspray Ionization-MS.[70−72] No evidence for structural rearrangement was observed in the ^{1}H NMR profile of a solution of Cd-**2** in 20% v/v CD_3OD/CD_3CN at room temperature over 2 h; longer timeframes did however result in degradation of the sample.

Subsequent addition of a range of small spherical or linear anions (F^-, Cl^-, Br^-, N_3^-, OCN^-, or HF_2^-) as secondary templates to an acetonitrile solution of Cd-**2** generated a series of $Cd_{10}L_{15}$ complexes, Cd-**3**. ESI mass spectra indicated that in each case the $Cd_{10}L_{15}$ complex was associated with a single secondary template anion and the remainder of the charge was balanced by perchlorate anions, supporting the hypothesis that the secondary template anion is bound within the singular central binding pocket observed in such structures.[9] In the absence of perchlorate, transformation to Cd-**3** was not observed, and significant precipitation occurred. The addition of any of the larger anions I^-, SCN^-, or $SeCN^-$ to Cd-**2** also resulted in precipitation.

With the exception of fluoride, the addition of each of the secondary template anions to Cd-**2** generated a single Cd-**3** complex as observed by ^{1}H NMR. A clear trend in the ^{1}H NMR chemical shifts of the internally directed, 4,4′-bipyridine protons of the axial ligands was observed for this series of guests with the most electronegative centrally bound guests effecting the largest downfield shift (Figure S5).[73−76]

Addition of KF (0.7 equiv) to an acetonitrile solution of Cd-**2** generated a complex ^{1}H NMR profile consistent with the formation of two discrete $Cd_{10}L_{15}$ species. A $^1H-^{19}F\{^1H\}$ HOESY spectrum (Figure 3) of the reaction mixture confirmed
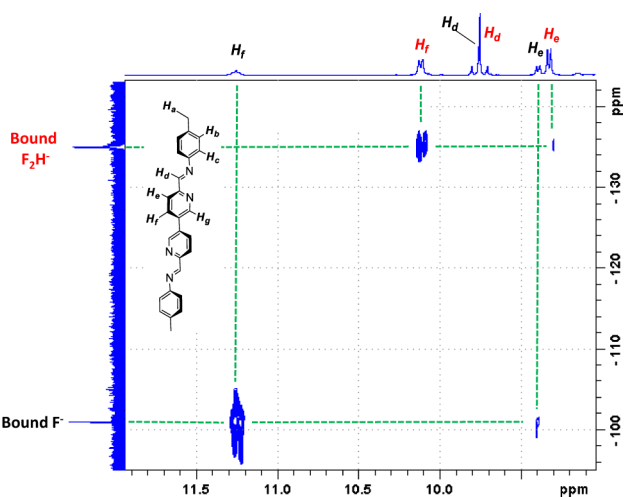

Figure 3. Partial $^1H-^{19}F\{^1H\}$ HOESY spectrum (400 MHz, 298 K, CD_3CN), indicating NOE interactions between ^{19}F and ^1H signals, and thus physical proximity between the nuclei; resonances labeled in black are assigned to $F^- \subset$ Cd-**3**, resonances labeled in red correspond to $HF_2^- \subset$ Cd-**3**.

that each of the complexes associated with a chemically distinct fluoride-containing species. As a proportion of fluoride will exist as bifluoride under the conditions of the experiment,[77,78] and its linear geometry and small size make it an ideal candidate for inclusion within the central binding pocket of the $Cd_{10}L_{15}$ architecture, we inferred HF_2^- to be acting as a secondary anion. The observation of a triplet in the ^{1}H NMR spectrum

(18.90 ppm, J = 128 Hz) of the reaction mixture along with a corresponding doublet in the ^{19}F spectrum, is consistent with the expected fluorine-to-proton coupling within bifluoride.[79,80]

High resolution ESI-MS of the product mixture confirmed that the $F^- \subset$ Cd-**3** complex had been formed alongside the bifluoride analogue.[77,81,82] Furthermore, addition of KHF_2 (1.7 equiv) to an acetonitrile solution of Cd-**2** generated a ^{1}H NMR spectrum containing only the resonances assigned to $HF_2^- \subset$ Cd-**3** and not $F^- \subset$ Cd-**3**, further supporting our assignments of these complexes.

The X-ray structure of $HF_2^- \subset$ Cd-**3** (Figure 4) was solved from a crystal grown through slow diffusion of diethyl ether
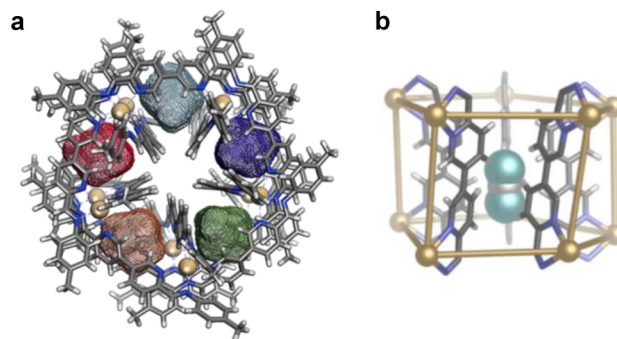
Figure 4. (a) Top down view of the X-ray structure of $HF_2^- \subset$ Cd-**3** with all anions removed and the five peripheral binding pockets represented using shaded mesh. (b) Cutaway view of the central binding pocket, with the equatorial ligands removed for clarity, indicating the asymmetrically bound central bifluoride anion, only one position of which is shown for clarity.

into a mixture of F^- and HF_2^- adducts of Cd-**3**. The connectivity of the $Cd_{10}L_{15}$ complex is the same as that reported for the first-row metal complexes of this type.[9,10]

The electron density in the central binding pocket was found to be a good match for a bifluoride anion bound asymmetrically in the center of the complex; one fluorine atom is located close to the center of the complex while the second fluorine was modeled as disordered over two locations, above and below the center. The encapsulated bifluoride is stabilized by hydrogen bonding to the bipyridyl protons with $CH\cdots F^-$ contacts in the range 2.29−2.50 Å. The NMR spectra of this complex showed no evidence for asymmetric binding in the solution state down to 263 K, suggesting that in solution the bifluoride anion is either bound symmetrically at the center of the molecule or able to move between two positions within the central channel of the cavity with a low activation barrier.

The pentagonal prism consists of two Cd_5L_5 circular helicates bridged by five axial ligands, which bridge on the inside of the structure, in contrast to the externally situated ligands of Cd-**2**. Embedded within the structure of Cd-**3** are five roughly spherical anion binding pockets, the average volume of which is 100 Å[3]. This volume is larger than those measured for the first row transition metal analogues,[9,10] confirming that as the metal ionic radius increases, so does the volume of the peripheral binding pockets.

When the ionic radius of the metal ion in each of the known perchlorate-templated $M_{10}L_{15}$ complexes was plotted against the average volume of the peripheral binding pockets, calculated using VOIDOO[83] on single-crystal X-ray structures, a high-quality linear correlation was observed (Figure 5).
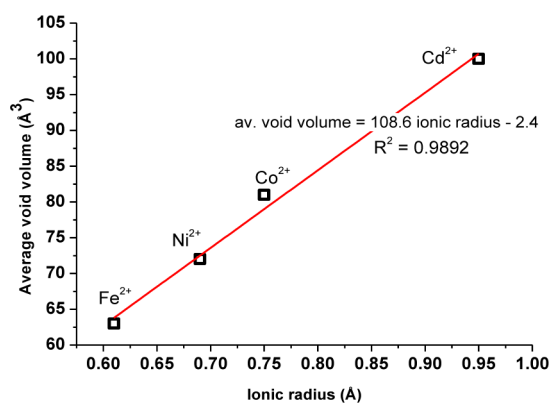
Figure 5. Correlation between the ionic radius of the metal ion and the average volume of the peripheral binding pockets, as calculated by VOIDOO[83] from single-crystal X-ray structures for a series of perchlorate templated $M_{10}L_{15}$ complexes; Fe^{II}, Ni^{II}, Co^{II}, and Cd^{II}.[9,10]

As the template used in each case was the same, ClO_4^-, the quality of the fit of this anion within the binding pocket must change as the volume increases with increasing metal template radius. We infer that the looser, less thermodynamically favored fit of perchlorate within the larger peripheral binding pockets of Cd-**3** underlies the tendency for the more compact Cd_8L_{12} Cd-**2** structure to form preferentially in the absence of a secondary, central template, and for the architecture of Cd-**3** to form with the larger template AsF_6^- (discussed below). These phenomena are not observed in the cases of the smaller metals Fe^{II}, Ni^{II}, Co^{II}, and Zn^{II}.[10]

The requirement of both peripheral anionic templates and a central anionic template to generate the $Cd_{10}L_{15}$ architecture is distinctly different from that of the first row transition metal Co^{II}. $Co_{10}L_{15}$ complexes (of the form Co-**3**) do not require a central anionic template, although the binding of small anions within their central binding pockets occurs with very high affinity.[9]

Upon addition of KF to Cd-**2**, the ^1H NMR resonance of the internally directed 4- and 4′-bipyridyl protons of the axial ligands were transformed from a doublet into an apparent triplet. A ^{19}F NMR spectrum (Figure S11) of the mixture confirmed that the centrally bound fluoride anion, which appears as a multiplet, underwent J-coupling with the centrally directed bipyridine protons. The apparent triplet observed at 11.25 ppm in the ^1H NMR spectrum is, therefore, the result of the overlap of two doublets with different coupling constants: $^1H-^1H$ coupling between the adjacent 4,4′- and 5,5′-bipyridine protons, and $^1H-^{19}F$ coupling between the centrally bound fluoride anion and the ten inward facing 4,4′-bipyridine protons. The observation of $^1H-^{19}F$ J-coupling through a hydrogen bonded fluoride anion has been observed in a few notable cases.[79,84−86] In each of these, a single-crystal X-ray structure confirms a highly organized spherical arrangement of donor atoms. In the $Cd_{10}L_{15}$ complex a single fluoride anion would be expected to be bound very tightly in the central binding pocket, surrounded by an almost spherical arrangement of ten inward-facing CH groups. The measured crystallographic CH···F^- distances of 2.29−2.50 Å reported for $HF_2^- \subset$ Cd-**3** are expected to be comparable to the distances within $F^- \subset$ Cd-**3** and are shorter than the hydrogen-bond lengths reported by Bowman-James and co-workers (2.84−2.88 Å).[79] The CH···F^- hydrogen bond distances therefore fall within the range where J-coupling is known to propagate through a hydrogen bond.

This observation thus provides further evidence for the strength of CH···F^- hydrogen bonds in solution,[87−90] weighing against the argument that considers CH···X^- hydrogen bonds to be too weak to impact processes occurring in solution.[91]

Upon addition of $KAsF_6$ (0.7 equiv) to an acetonitrile solution of Cd-**1** (35 mM in [**L**]) the ^1H NMR and ^{19}F NMR profiles of the helicate and anion, respectively, were observed to broaden. ESI mass spectra of the resultant mixture were consistent with the presence of a mixture of Cd_2L_3 species with varying numbers of NTf_2^- and AsF_6^- counterions. Slow diffusion of diethyl ether or ethyl acetate into this reaction mixture yielded a polycrystalline material, which upon dissolution displayed a different ^1H NMR profile from that of Cd-**1**.

The ^1H NMR spectrum of the new complex, Cd-**4**, displayed three magnetically distinct environments per ligand proton but differed markedly from the spectra of Cd-**3**, and also from spectra of the reported $M_{10}L_{15}$ complexes Fe-**3** and Zn-**3**.[10] Solutions of Cd-**4** were also observed to be unstable at concentrations below 70 mM in [**L**]; upon redissolution at lower concentrations the crystalline Cd-**4** complex was observed to convert to the Cd-**1** helicate.

When preparation was performed at higher concentration (70 mM in [**L**]), ^1H NMR spectra reproducibly indicated formation of a mixture of Cd-**1** and Cd-**4**, confirming the concentration-dependent stability of Cd-**4**.

X-ray quality single-crystals were obtained following the slow diffusion of diethyl ether into an acetonitrile solution over 3 days, at which point the vial was sealed and allowed to stand undisturbed for one month at room temperature. The slow crystallization process is necessary to obtain suitable crystals; if the vial was not sealed after 3 days polycrystalline material was repeatedly obtained.

The single-crystal structure of hexagonal-prismatic Cd-**4** shares many common features with the $Cd_{10}L_{15}$ architecture, Cd-**3** (Figure 6). Like the pentagonal-prismatic Cd-**3** complexes discussed above, the solution data of Cd-**4** indicate three distinct chemical environments per ligand proton, which we assign to two environments on the equatorial ligands and one environment for the axial ligands, which bridge from the top to the bottom of the structure on the inside of the prism. All of the metal centers again display mer coordination stereochemistry and each structure is homochiral, containing all Λ or all Δ metal centers. The single-crystal X-ray structure is consistent with our previously reported triflate-templated $Cd_{12}L_{18}$ complex,[21] while differing from the $Cd_{12}L_{18}$ complex reported by Kwong and co-workers,[5] which is generated through combination of alternating mer and fac ligand arrangements and Λ and Δ metal centers.

High resolution ESI-MS data of Cd-**4** (Figure S15) confirm the presence of Cd-**4**, indicating the presence of a $Cd_{12}L_{18}^{24+}$ cation associated with a mixture of NTf_2^- and AsF_6^- counterions. In the single-crystal X-ray structure, six AsF_6^- anions are observed to bind within the peripheral binding pockets and a single NTf_2^- anion is bound within the central channel. A $^1H-^{19}F\{^1H\}$ HOESY spectrum (Figure S16) of the reaction mixture shows correlations between the axial imine, 4,4′-bipyridine and 5,5′-bipyridine ^1H resonances and the ^{19}F signal for NTf_2^-, consistent with encapsulation of this anion in solution.

Comparable solid and solution-state data were obtained for the hexafluorophosphate-templated $Cd_{12}L_{18}$ complex generated upon addition of KPF_6 to a solution of Cd-**1** (70 mM in [**L**]).
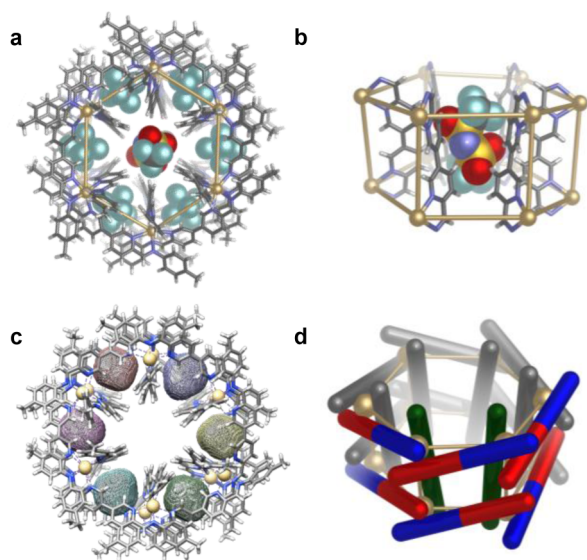
Figure 6. Single-crystal X-ray structure of the $Cd_{12}L_{18}$ complex Cd-**4**; (a) top-down view with peripheral AsF_6^- anions and a central NTf_2^- anion shown in space-filling mode; (b) side-on view of the central channel of Cd-**4** showing the centrally bound triflimide anion in space filling mode; (c) top down view with all anions removed and the void pockets shown using shaded mesh; (d) side-on view of Cd-**4** with the three magnetically distinct ligand environments colored in red, blue, and green. In all views the nonencapsulated anions, solvent molecules and disorder are omitted for clarity.

The single-crystal X-ray structure (Figure S26) shows six PF_6^- anions bound within the peripheral binding pockets and a single NTf_2^- anion within the central channel.

The addition of NaCl (0.2 equiv) prompted the transformation of hexafluoroarsenate-templated Cd-**4** into hexafluoroarsenate-templated Cd-**3**. NMR and ESI-MS analyses of a mixture of Cd-**1** and Cd-**4** (70 mM in [**L**]) following NaCl addition provided results consistent with the formation of a $Cd_{10}L_{15}$ Cd-**3** pentagonal-prismatic structure with five AsF_6^- anions in the peripheral binding pockets and a single Cl^- anion in the central binding pocket. The common structural features of Cd-**4** and Cd-**3** (prismatic architecture, *mer* coordination) appear to preorganize the subunits of Cd-**4** to form Cd-**3**.

The Cd-**3** complex generated by this route did not show the same instability at lower concentrations exhibited by its Cd-**4** precursor; we infer this additional stabilization to be conferred by tight binding to chloride. Intriguingly, the Cd-**3** complex was not observed following addition of AsF_6^- and Cl^- to an acetonitrile solution of Cd-**1**: Cd-**4** appeared to be a necessary intermediate for the formation of this complex.[62,63]

Metal-Driven Structural Transformations. Transmetalation processes which allow formation of architectures not available through direct self-assembly processes have been investigated by a number of researchers,[52,53,57,92] however, to the best of our knowledge three-dimensional structural rearrangements driven by metal-ion exchange have yet to be reported. We therefore probed the differing templation effects of a smaller metal ion through the addition of Fe^{II} to Cd-**2** and a mixture of Cd-**1** and Cd-**4**.

The well-understood architectural preferences displayed by ligand **L** with a range of metals and anions[10] suggested that thermodynamically driven structural interconversion would be possible, taking advantage of energy differences in metal-N bond strengths as a driving force.[93] The larger ionic radius of

cadmium(II) results in longer $Cd^{II}-N$ bonds which are significantly more labile than their iron(II) counterparts. We inferred that the difference in energy between these metal–nitrogen bonds would be significant enough to allow replacement of Cd^{II} by Fe^{II} in solution. Upon this displacement, the supramolecular complex underwent rearrangement to generate the most stable Fe^{II}-containing structure dictated by the templating anions present.

Addition of 1.6 equiv of Fe^{II} per Cd^{II} to perchlorate-containing Cd-**3** generated a $Fe_{10}L_{15}$ pentagonal prism Fe-**3**, perchlorate being an optimal template for this architecture. Similarly, the addition of excess Fe^{II} to a mixture of Cd-**1** and Cd-**4** generated a Fe_4L_6 tetrahedron (Fe-**5**) incorporating a centrally bound AsF_6^- anion. Both solution state data and the single-crystal X-ray structure (Figure S27) of $AsF_6^- \subset$ Fe-**5** indicate that a single AsF_6^- anion is bound within the central cavity of the tetrahedron. No transformations were observed after heating a sample of $AsF_6^- \subset$ Fe-**5** at 343 K for 1 week, indicating that AsF_6^- is not a suitable template for the M-**4** structural type when Fe^{II} is used as the metal template.

The transformations described above demonstrate the utility of metal exchange in accomplishing complex three-dimensional structural interconversions.

CONCLUSIONS

The system reported herein is thus responsive to four distinct chemical events: (1) primary anion templation, (2) secondary anion templation, (3) metal ion exchange, and (4) changes in concentration. Furthermore, we have shown that different combinations of these events prompt distinct structural rearrangements. Architectures generated upon rearrangement display distinctly different properties from the initial complexes, facilitating the liberation or sequestration of different cations and anions. Such behavior may allow for anions, such as HF_2^-, to persist in environments where they would not typically be stable. Additionally, the open tubular structural features common to Cd-**3** and Cd-**4** are suggestive of their ability to act as synthetic anion channels, which may be capable of not only stabilizing anions but also selectively gating only those species which could fit through their central cavities.

EXPERIMENTAL SECTION

General. Unless otherwise specified, all starting materials were purchased from commercial sources and used as supplied. Cadmium-(II) triflimide was synthesized following a literature procedure;[21] this salt was stored and manipulated in an inert-atmosphere glovebox. 6,6′-Diformyl-3,3′-bipyridine was synthesized following a modified synthetic protocol detailed in the Supporting Information. NMR spectra were recorded on a Bruker DRX-400, Bruker Avance 500 Cryo and Bruker 500 TCI-ATM Cryo. ^{1}H chemical shifts (δ) are reported in parts per million (ppm) and are reported relative to the solvent residual peak CD_3CN at $\delta = 1.94$ ppm. Low resolution electrospray ionization mass spectra (ESI-MS) were obtained on a Micromass Quattro LC and high resolution mass spectra acquired using a Thermofisher LTQ Orbitrap XL.

Synthesis of Cd-1. $Cd(NTf_2)_2$ (21.1 mg, 0.03 mmol), 6,6′-diformyl-3,3′-bipyridine (10.0 mg, 0.05 mmol), and *p*-toluidine (10.1 mg, 0.09 mmol) were added to a Schlenk flask containing 3.0 mL of CH_3CN. The Schlenk flask was sealed and then heated for 24 h at 343 K. Cd-**1** was then precipitated as a pale yellow microcrystalline powder by the addition of diisopropyl ether (34.0 mg, 86%). ^{1}H NMR (400 MHz, 298 K, CD_3CN): $\delta = 8.92$ (s, imine; d, $J^{113Cd-1H} = 43.6$ Hz, 10H, imine), 8.58 (dd, $J = 2.0$, 7.9 Hz, 6H, 4,4′-bipyridine), 8.48 (d, $J = 1.6$ Hz, 6H, 2,2′-bipyridine), 8.31 (d, $J = 8.0$ Hz, 6H, 5,5′-bipyridine), 7.09 (d, $J = 8.1$ Hz, 6H, 2-aniline), 6.83 (d, $J = 8.2$ Hz, 6H, 3-aniline), 2.35

(s, 18H, methyl); ^{13}C NMR (126 MHz, 298 K, CD$_3$CN): δ = 163.8, 149.8, 148.2, 145.7, 142.4, 140.5, 139.2, 132.4, 131.1, 123.1, 21.0; ^{19}F NMR (376 MHz, 298 K, CD$_3$CN): δ = −80.1 (NTf$_2^-$); ESI-MS: m/z: $\{[Cd\text{-}1]\}^{4+}$ = 348.9, $\{[Cd\text{-}1] + NTf_2^-\}^{3+}$ = 558.8, $\{[Cd\text{-}1] + 2NTf_2^-\}^{2+}$ = 977.7; Elemental analysis (%) calcd for C$_{86}$H$_{66}$Cd$_2$F$_{24}$N$_{16}$O$_{16}$S$_8$: C 41.04, H 2.64, N 8.90; found: C 40.95, H 2.61, N 8.69.

Synthesis of Cd-2. Cd(ClO$_4$)$_2$·6H$_2$O (2.6 mg, 0.01 mmol), 6,6′-diformyl-3,3′-bipyridine (2.0 mg, 0.01 mmol), and p-toluidine (2.0 mg, 0.02 mmol) were loaded into a J-Young NMR tube and dissolved in CD$_3$CN (0.6 mL). The NMR tube was sealed, sonicated, and then heated for 24 h at 343 K yielding Cd-**2** as the major product. ^1H NMR (500 MHz, 298 K, CD$_3$CN): δ = 9.38 (s, imine; d, $J^{113Cd\text{-}1H}$ = 42.4. Hz, 4H, imine), 9.31 (d, J = 2.4 Hz, 4H, 2,2′-bipyridine), 9.14 (m, 12H, 2,2′-bipyridine, 2 × 2,2′-bipyridine), 8.90 (s, 4H, imine), 8.80 (d, J = 1.7 Hz, 4H, 2,2′-bipyridine), 8.68 (s, 4H, imine), 8.66 (s, 4H, imine), 8.63 (d, J = 8.6 Hz, 4H, 5,5′-bipyridine), 8.60 (d, J = 9.2 Hz, 4H, 5,5′-bipyridine), 8.53 (dd, J = 2.0, 8.1 Hz, 4H, 4,4′-bipyridine), 8.49 (dd, J = 2.0, 8.0 Hz, 4H, 5,5′-bipyridine), 8.47 (s, 4H, imine), 8.34 (d, J = 1.9 Hz, 4H, 2,2′-bipyridine), 8.20 (s, imine; d, J = 41.6 Hz, 4H, imine), 8.18 (d, J = 1.8 Hz, 4H, 2,2′-bipyridine), 8.09 (m, 8H, 2 × 5,5′-bipyridine), 7.83 (dd, J = 1.9, 8.1 Hz, 4H, 4,4′-bipyridine), 7.75 (d, J = 1.7 Hz, 4H, 2,2′-bipyridine), 7.72 (d, J = 8.0 Hz, 4H, 5,5′-bipyridine), 7.55 (d, J = 8.1 Hz, 4H, 5,5′-bipyridine), 7.44 (m, 12H, 4,4′-bipyridine, 2-aniline), 7.23 (d, J = 8.2 Hz, 8H, 3-aniline), 7.20 (d, J = 8.6 Hz, 8H, 3-aniline), 7.05 (d, J = 8.3 Hz, 8H, 3-aniline), 6.93 (m, 8H, 3-aniline), 6.85 (d, J = 8.2 Hz, 8H, 3-aniline), 6.75 (d, J = 8.3 Hz, 8H, 2-aniline), 6.73 (d, J = 8.3 Hz, 8H, 2-aniline), 6.51 (d, J = 8.6 Hz, 8H, 2,aniline), 6.45 (d, J = 8.1 Hz, 8H, 2-aniline), 6.44 (d, J = 7.9 Hz, 8H, 2-aniline), 6.00 (d, J = 8.1 Hz, 8H, 2-aniline), 2.39 (s, 12H, methyl), 2.24 (s, 12H, methyl), 2.23 (s, 12H, methyl), 2.22 (s, 12H, methyl), 2.21 (s, 12H, methyl), 2.20 (s, 12H, methyl);^{13}C NMR (126 MHz, 298 K, CD$_3$CN): δ = 164.3, 162.3, 162.1, 162.0, 161.4, 160.5, 152.3, 151.0, 150.1, 149.1, 148.6, 148.4, 148.2, 147.9, 147.6, 146.9, 146.0, 145.3, 144.7, 144.6, 144.5, 144.5, 144.3, 143.6, 141.9, 141.8, 141.6, 141.5, 140.8, 140.7, 140.6, 140.4, 140.4, 140.2, 140.2, 140.0, 139.7, 138.6, 137.9, 136.9, 136.7, 135.9, 132.8, 132.8, 131.9, 131.6, 131.4, 131.4, 131.2, 131.0, 130.8, 130.5, 130.5, 130.2, 21.8, 21.2, 21.2, 21.2, 21.0, 20.5; $^{19}F\{^1H\}$ (376 MHz, 298 K, CD$_3$CN): δ = −80.1 (NTf$_2^-$); ESI-MS: m/z: $\{[Cd\text{-}2]+8ClO_4^-\}^{8+}$ = 797.7, $\{[Cd\text{-}2]+9ClO_4^-\}^{7+}$ = 925.2, $\{[Cd\text{-}2]+10ClO_4^-\}^{6+}$ = 1096.1, $\{[Cd\text{-}2]+11ClO_4^-\}^{5+}$ = 1335.1, $\{[Cd2]+12ClO_4^-\}^{4+}$ = 1693.7. Elemental analysis (%) calcd for C$_{312}$H$_{264}$Cd$_8$Cl$_{16}$N$_{48}$O$_{64}$·14H$_2$O: C 50.45, H 3.96, N 9.05; found: C 50.27, H 3.73, N 8.83.

Preparation of Cd-3 from Cd-2. A stock solution of Cd-**2** in CD$_3$CN was prepared. Cd(ClO$_4$)$_2$·6H$_2$O (20.8 mg, 0.05 mmol), 6,6′-diformyl-3,3′-bipyridine (16.0 mg, 0.08 mmol), and p-toluidine (16.2 mg, 0.15 mmol) were loaded into a Schlenk tube and dissolved in CD$_3$CN (4.8 mL). The tube was sealed, sonicated for 1 h, and heated at 343 K for 24 h. Upon cooling 0.6 mL aliquots of the solution (2.0 mg, 0.01 mmol of 6,6′-diformyl-3,3′-bipyridine) were transferred to J-Young NMR tubes. The respective guest (0.4−1.7 equiv) was added to each tube, the tubes were sealed, sonicated, and heated at 343 K for 24 h at which point the host and host−guest complexes were observed to have equilibrated.

Synthesis of Cd-4. Cd(NTf$_2$)$_2$ (12.7 mg, 0.02 mmol), 6,6′-diformyl-3,3′-bipyridine (6.0 mg, 0.02 mmol), and p-toluidine (6.1 mg, 0.04 mmol) were loaded into a J-Young NMR tube and dissolved in CD$_3$CN (0.4 mL) yielding Cd-**1** as the sole product as observed by ^1H NMR. KAsF$_6$ (3.75 mg, 0.02 mmol) was added to the sample and the NMR tube was sealed, sonicated and then heated for 24 h at 343 K yielding Cd-**4** as the major product. ^1H NMR (500 MHz, 298 K, CD$_3$CN): δ = 9.60 (s, imine; d, $J^{113Cd\text{-}1H}$ = 40.2 Hz, 10H, imine), 9.12 (d, J = 8.3 Hz, 10H, 4,4′-bipyridine), 8.75 (s,10H, 2,2′-bipyridine), 8.62 (d, J = 9.0 Hz,10H, 5,5′-bipyridine), 8.48 (s, 10H, imine), 8.06 (s, 20H, 2 × 2,2′-bipyridine), 7.97 (d, J = 7.6 Hz, 10H, 4,4′-bipyridine), 7.84 (d, J = 6.8 Hz, 10H, 4,4′-bipyridine), 7.67 (d, J = 8.0 Hz, 10H, 5,5′-bipyridine), 7.38 (d, J = 8.9 Hz, 20H, 2-aniline), 7.12 (d, J = 9.0 Hz, 20H, 3-aniline), 7.02 (d, J = 7.9 Hz, 10H, 5,5′-bipyridine), 6.92 (s, imine; d, $J^{113\text{-}1H}$ = 29.3 Hz, 10H, imine), 6.73 (d, J = 8.0 Hz, 20H, 3-

aniline), 6.69 (d, J = 6.1 Hz, 20H, 3-aniline), 6.43 (d, J = 7.0 Hz, 20H, 2-aniline), 6.31 (d, J = 7.7 Hz, 20H, 2-aniline), 2.49 (s, 30H, methyl), 2.35 (s, 30H, methyl), 2.23 (s, 30H, methyl); ^{13}C NMR (126 MHz, 298 K, CD$_3$CN): δ = 161.1, 160.7, 159.5, 149.8, 149.8, 148.8, 148.2, 147.8, 146.8, 145.7, 144.2, 142.9, 142.6, 142.3, 141.1, 140.8, 140.6, 140.0, 139.2, 138.0, 137.4, 131.9, 131.7, 131.5, 131.3, 131.1, 130.1, 123.4, 123.1, 122.6, 21.8, 21.0, 21.0; $^{19}F\{^1H\}$ (376 MHz, 298−260 K, CD$_3$CN): δ = −64.7 (br. m, free and bound AsF$_6^-$), −80.5 (NTf$_2^-$); High resolution ESI-MS: m/z: $\{[Cd\text{-}4] + 3NTf_2^- + 12AsF_6^-\}^{9+}$ = 1275.505, $\{[Cd\text{-}4] + 4NTf_2^- + 11AsF_6^-\}^{9+}$ = 1285.642, $\{[Cd\text{-}4] + 5NTf_2^- + 10AsF_6^-\}^{9+}$ = 1295.780, $\{[Cd\text{-}4] + 6NTf_2^- + 9AsF_6^-\}^{9+}$ = 1306.437, $\{[Cd\text{-}4] + 2NTf_2^- + 14AsF_6^-\}^{8+}$ = 1449.233, $\{[Cd\text{-}4] + 3NTf_2^- + 13AsF_6^-\}^{8+}$ = 1460.482, $\{[Cd\text{-}4] + 4NTf_2^- + 12AsF_6^-\}^{8+}$ = 1470.606, $\{[Cd\text{-}4] + 5NTf_2^- + 11AsF_6^-\}^{8+}$ = 1481.980, $\{[Cd\text{-}4] + 6NTf_2^- + 10AsF_6^-\}^{8+}$ = 1493.604, $\{[Cd\text{-}4] + 7NTf_2^- + 9AsF_6^-\}^{8+}$ = 1504.979, $\{[Cd\text{-}4] + 8NTf_2^- + 8AsF_6^-\}^{8+}$ = 1516.103, $\{[Cd\text{-}4] + 9NTf_2^- + 7AsF_6^-\}^{8+}$ = 1527.852$\{[Cd\text{-}4] + 2NTf_2^- + 15AsF_6^-\}^{7+}$ = 1680.875, $\{[Cd\text{-}4] + 3NTf_2^- + 14AsF_6^-\}^{7+}$ = 1693.909, $\{[Cd\text{-}4] + 4NTf_2^- + 13AsF_6^-\}^{7+}$ = 1708.676, $\{[Cd\text{-}4] + 5NTf_2^- + 12AsF_6^-\}^{7+}$ = 1720.960, $\{[Cd\text{-}4] + 6NTf_2^- + 11AsF_6^-\}^{7+}$ = 1733.817, $\{[Cd\text{-}4] + 7NTf_2^- + 10AsF_6^-\}^{7+}$ = 1746.817, $\{[Cd\text{-}4] + 8NTf_2^- + 9AsF_6^-\}^{7+}$ = 1759.818, $\{[Cd\text{-}4] + 9NTf_2^- + 8AsF_6^-\}^{7+}$ = 1773.100,$\{[Cd\text{-}4] + 10NTf_2^- + 7AsF_6^-\}^{7+}$ = 1786.247. Peaks attributed to AsF$_6^-$ templated Cl$^-$ ⊂ Cd-**3** complex were also observed in the high resolution mass spectrum of Cd-**4**.

Preparation of Cd-3 from Cd-4. A solution of Cd-**4** was prepared as described above. Addition of NaCl (0.2 mg, 0.01 mmol) to Cd-**4** (6.0 mg 6,6′-diformyl-3,3′-bipyridine) followed by sonication and heating the sample at 323 K for 24 h yielded the desired Cd-**3** structure alongside minor Cd-**1** impurities. Slow diffusion of diethyl ether into a mixture of Cd-**1** and Cd-**3** yielded pure Cd-**3** as a polycrystalline solid. Unlike Cd-**4**, Cd-**3** was stable at low concentrations and once isolated did not convert to Cd-**1**. ^1H NMR (500 MHz, 298 K, CD$_3$CN): δ = 10.85 (d, J = 9.1 Hz, 10H, 4,4′-bipyridine), 9.72 (s, imine; d, $J^{113Cd\text{-}1H}$ = 40.9 Hz, 10H, imine), 8.83 (d, J = 8.8 Hz, 10H, 5,5′-bipyridine), 8.50 (s, 10H, 2,2′-bipyridine), 8.44 (s, imine; d, $J^{113Cd\text{-}1H}$ = 38.8 Hz, 10H, imine), 8.21 (d, J = 7.8 Hz, 10H, 4,4′-bipyridine), 8.12 (s, 10H, 2,2′-bipyridine), 8.06 (d, J = 7.9 Hz, 10H, 4,4′-bipyridine), 7.98 (s, 10H, 2,2′-bipyridine), 7.63 (d, J = 7.9 Hz, 10H, 5,5′-bipyridine), 7.51 (d, J = 8.8 Hz, 20H, 2-aniline), 7.16 (d, J = 8.9 Hz, 20H, 3-aniline), 7.05 (d, J = 8.0 Hz, 10H, 5,5′-bipyridine), 6.88 (d, J = 8.0 Hz, 20H, 3-aniline), 6.80 (m, 30H, 3-aniline, imine), 6.58 (d, J = 8.0 Hz, 20H, 2-aniline), 6.46 (d, J = 7.7 Hz 20H, 2-aniline), 2.52 (s, 30H, methyl), 2.26 (s, 30H, methyl), 2.23 (s, 30H, methyl); ^{13}C NMR (126 MHz, 298 K, CD$_3$CN): δ = 160.7, 159.9, 158.3, 151.4, 148.8, 147.9, 146.8, 146.7, 143.6, 142.8, 142.7, 142.6, 142.1, 142.1, 141.9, 141.07, 140.6, 139.0, 138.5, 138.4, 131.7, 131.5, 131.1, 131.0, 130.9, 130.4, 123.6, 122.9, 122.6, 21.6, 21.0, 20.9; ESI-MS: m/z: $\{[Cl^- ⊂ Cd\text{-}3] + 9AsF_6^-\}^{10+}$ = 872.3, $\{[Cl^- ⊂ Cd\text{-}3] + NTf_2^- + 8AsF_6^-\}^{10+}$ = 880.8, $\{[Cl^- ⊂ Cd\text{-}3] + 2NTf_2^- + 7AsF_6^-\}^{10+}$ = 890.0, $\{[Cl^- ⊂ Cd\text{-}3] + 10AsF_6^-\}^{9+}$ = 989.9, $\{[Cl^- ⊂ Cd\text{-}3] + NTf_2^- + 9AsF_6^-\}^{9+}$ = 999.8, $\{[Cl^- ⊂ Cd\text{-}3] + 2NTf_2^- + 8AsF_6^-\}^{9+}$ = 1010.3, $\{[Cl^- ⊂ Cd\text{-}3] + 3NTf_2^- + 7AsF_6^-\}^{9+}$ = 1020.0, $\{[Cl^- ⊂ Cd\text{-}3] + 11AsF_6^-\}^{8+}$ = 1137.1, $\{[Cl^- ⊂ Cd\text{-}3] + NTf_2^- + 10AsF_6^-\}^{8+}$ = 1148.6, $\{[Cl^- ⊂ Cd\text{-}3] + 2NTf_2^- + 9AsF_6^-\}^{8+}$ = 1159.8, $\{[Cl^- ⊂ Cd\text{-}3] + 3NTf_2^- + 8AsF_6^-\}^{8+}$ = 1171.0, $\{[Cl^- ⊂ Cd\text{-}3] + 12AsF_6^-\}^{7+}$ = 1326.8, $\{[Cl^- ⊂ Cd\text{-}3] + NTf_2^- + 11AsF_6^-\}^{7+}$ = 1338.6, $\{[Cl^- ⊂ Cd\text{-}3] + 2NTf_2^- + 10AsF_6^-\}^{7+}$ = 1352.4, $\{[Cl^- ⊂ Cd\text{-}3] + 3NTf_2^- + 9AsF_6^-\}^{7+}$ = 1366.0, $\{[Cl^- ⊂ Cd\text{-}3] + 4NTf_2^- + 8AsF_6^-\}^{7+}$ = 1378.5, $\{[Cl^- ⊂ Cd\text{-}3] + 5NTf_2^- + 7AsF_6^-\}^{7+}$ = 1391.3, $\{[Cl^- ⊂ Cd\text{-}3] + NTf_2^- + 12AsF_6^-\}^{6+}$ = 1593.2, $\{[Cl^- ⊂ Cd\text{-}3] + 2NTf_2^- + 11AsF_6^-\}^{6+}$ = 1608.7, $\{[Cl^- ⊂ Cd\text{-}3] + 3NTf_2^- + 10AsF_6^-\}^{6+}$ = 1625.1, $\{[Cl^- ⊂ Cd\text{-}3] + 4NTf_2^- + 9AsF_6^-\}^{6+}$ = 1639.8, $\{[Cl^- ⊂ Cd\text{-}3] + 5NTf_2^- + 8AsF_6^-\}^{6+}$ = 11655.2.

Preparation of Fe-5 from a Mixture of Cd-1 and Cd-4. 6,6′-Diformyl-3,3′-bipyridine (6.0 mg, 0.02 mmol), p-toluidine (6.1 mg, 0.04 mmol), and Cd(NTf$_2$)$_2$ (12.7 mg, 0.02 mmol) were stirred in CD$_3$CN (0.4 mL) at room temperature for 24 h yielding Cd-**1** as the sole product (Figure S21a). Conversion of Cd-**1** to a mixture of Cd-**1** and Cd-**4** (Figure S21b) was achieved upon addition of KAsF$_6$ (3.4

mg, 0.01 mmol) to the solution of Cd-**1** Fe(NTf$_2$)$_2$·3H$_2$O (14.6 mg, 0.03 mmol) was then added to the solution which was degassed and sealed under nitrogen. The sample was heated at 343 K for 48 h, after which time no evidence for either Cd-**1** or Cd-**4** remained. Finally the sample was purified through two precipitation cycles with diethyl ether (Figure S21d). ^{1}H NMR and ESI-MS data of the final product were consistent with data reported for Fe-**5** generated directly from subcomponents. ^{1}H NMR (400 MHz, 298 K, CD$_3$CN): δ = 8.96 (s, 12H, imine), 8.50 (d, J = 7.8 Hz, 12H, 5,5′-bipyridine), 8.11 (d, J = 7.7 Hz, 12H, 4,4′-bipyridine), 7.03 (d, J = 7.6 Hz, 24H, 3-aniline), 6.88 (s, 12H, 2,2′-bipyridine), 5.46 (d, J = 7.6 Hz, 24H, 2-aniline), 2.33 (s, 36H, methyl); HR ESI-MS: m/z: {[Fe-**5**] + NTf$_2^-$ + AsF$_6^-$}$^{6+}$ = 505.90, {[Fe-**5**] + NTf$_2^-$ + 2AsF$_6^-$}$^{5+}$ = 644.73, {[Fe-**5**] + 2NTf$_2^-$ + AsF$_6^-$}$^{5+}$ = 663.12, {[Fe-**5**] + NTf$_2^-$ + 3AsF$_6^-$}$^{4+}$ = 853.23, {[Fe-**5**] + 2NTf$_2^-$ + 2AsF$_6^-$}$^{4+}$ = 876.1, {[Fe-**5**] + 3NTf$_2^-$ + AsF$_6^-$}$^{4+}$ = 898.80, {[Fe-**5**] + NTf$_2^-$ + 4AsF$_6^-$}$^{3+}$ = 1200.59, {[Fe-**5**] + 2NTf$_2^-$ + 3AsF$_6^-$}$^{3+}$ = 1230.89, {[Fe-**5**] + 3NTf$_2^-$ + 2AsF$_6^-$}$^{3+}$ = 1261.40, {[Fe-**5**] + 4NTf$_2^-$ + AsF$_6^-$}$^{3+}$ = 1291.72.

Preparation of Fe-3 from Cd-2. 6,6′-Diformyl-3,3′-bipyridine (4.0 mg, 0.02 mmol), p-toluidine (4.0 mg, 0.04 mmol), and Cd(ClO$_4$)$_2$·6H$_2$O (5.2 mg, 0.01 mmol) were sonicated in CD$_3$CN (0.6 mL) for 2 h yielding Cd-**2** as the major product (Figure S25a). Fe(ClO$_4$)$_4$·xH$_2$O (5.1 mg, 0.02 mmol) was then added to the solution which was degassed and sealed under nitrogen. The sample was heated at 343 K for 14 days, after which time no evidence for Cd-**2** remained. Finally the sample was purified through three precipitation cycles with diethyl ether (Figure S25d). ^{1}H NMR and ESI-MS data of the final product were consistent with data previously reported for Fe-**3** (Figure S25e); no evidence for the Fe-**5** complex, ClO$_4^-$ ⊂ Fe$_4$L$_6$, was observed in the final reaction mixture. ^{1}H NMR (400 MHz, 298 K, CD$_3$CN): δ = 10.88 (d, J = 9.4 Hz, 10H, 4,4′-bipyridine), 9.53 (d, J = 8.7 Hz, 10H, 5,5′-bipyridine), 9.48 (s, 10H, imine), 8.70 (s, 10H, imine), 8.36 (s, 10H, 2,2′-bipyridine), 7.99 (s, 10H, 2,2′-bipyridine), 7.94 (d, J = 7.9 Hz, 10H, 4,4′-bipyridine), 7.85 (d, J = 8.0 Hz, 10H, 5,5′-bipyridine), 7.63 (d, J = 7.9 Hz, 10H, 4,4′-bipyridine), 7.47 (m, 20H, 5,5′-bipyridine, imine), 7.13 (s, 10H, 2,2′-bipyridine), 7.00 (d, J = 8.4 Hz, 30H, 3-aniline), 6.80 (d, J = 7.9 Hz, 30H, 3-aniline), 6.43 (d, J = 8.4 Hz, 30H, 2-aniline), 6.03 (d, J = 8.0 Hz, 30H, 2-aniline), 2.54 (s, 30H, methyl), 2.25 (s, 30H, methyl), 2.15 (s, 30H, methyl); HR ESI-MS: m/z: {[Cl$^-$ ⊂ Fe-**3**]+10ClO$_4^-$}$^{9+}$ = 827.18, {[Cl$^-$ ⊂ Fe-**3**]+11ClO$_4^-$}$^{8+}$ = 943.01, {[Cl$^-$ ⊂ Fe-**3**]+12ClO$_4^-$}$^{7+}$ = 1091.92, {[Cl$^-$ ⊂ Fe-**3**]+13ClO$_4^-$}$^{6+}$ = 1290.58, {[Cl$^-$ ⊂ Fe-**2**]+14ClO$_4^-$}$^{5+}$ = 1568.68.

Further details and experimental data can be found in the Supporting Information.

ASSOCIATED CONTENT

ⓢ Supporting Information

Full experimental procedures, NMR and ESI-MS spectra, details of the calculation of the volumes and CIFs. Crystallographic data have also been deposited with the CCDC (numbers 994962−994966). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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