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Transformations within a Network of Cadmium Architectures**

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The transformation of molecules through sequential reactions is a central feature of metabolism, defining the flow of matter through a living organism.[1] These reactions are organized into pathways that can be unidirectional, cyclic, or branched, and that are interconnected at shared intermediates, forming the interlinked, highly complex networks of transformations that define an organism's metabolome.[2] Understanding how to manipulate dynamic structural interconversions through the application of external stimuli could not only shed light upon the basic principles that underpin many biological processes, but also be beneficial to the design and construction of biomimetic molecular machines.[3]

Many signals have been shown to be capable of altering the constitution of dynamic systems, switching one structure to another. They include light,[4] pH value,[5] chemical templates,[6] temperature,[7] solvent,[8] and a change in concentration.[9] The use of subcomponent self-assembly[10] to construct complex metal–organic architectures[11] provides pathways for these structures to dynamically reassemble by taking advantage of enthalpic or entropic driving forces.[2,12] Herein, we examine how a system of diverse self-assembled cadmium(II) complexes responds to a variety of chemical signals to produce an array of multinuclear architectures.

The system under study contains 4,4′-diformyl-3,3′-bipyridine (**A**), a variety of different amines, and cadmium triflate in acetonitrile solution. As shown in Figure 1, a change in the nature of the amine employed dramatically altered the product's structure: M_2L_3 triple helicate **1**, M_3L_3 triangular circular helicate **2**, M_4L tetrahedral cage **3**, or the remarkable $M_{12}L_{18}$ hexagonal prism **4**, were selectively formed when benzylamine (**B**), 2-dimethylaminoethylamine (**C**), tris(3-aminopropyl)amine (**D**), or anisidine **E**, respectively, were employed as subcomponents.

In the crystal structure of helicate **1** (Figure 2a), the three ligands and two metal ions are arranged so as to create the smallest structure possible by eliminating cavity space. This structure is stabilized by π–π stacking between the electron-rich terminal phenyl rings and the electron-poor pyridylimine groups of the helicate. The Cd–Cd distance is 8.154(2) Å, about 2 Å shorter than that in triangle **2** (10.402(2) Å, Figure 2b) and tetrahedron **3** (10.399(2)–10.789(2) Å), as a result of the greater twisting of the ligand in the helicate structure. The formation of analogous helicates with α-diimine ligands of similar size and any first-row transition metal ion has not been observed, owing to these ions' relatively small sizes and preferences for a more regular octahedral coordination geometry. These factors prevent three ligands from bridging two metal ions without forcing the ligands into an unfavorable conformation.[12a,13]

In amine **C**, the tertiary nitrogen at the γ position to the amino group serves as an additional donor, resulting in a bis-tridentate ligand, which favors the formation of triangular circular helicate **2**. The tetrahedron **3** (Figure 2c) is homochiral with approximate T point symmetry in solution and in

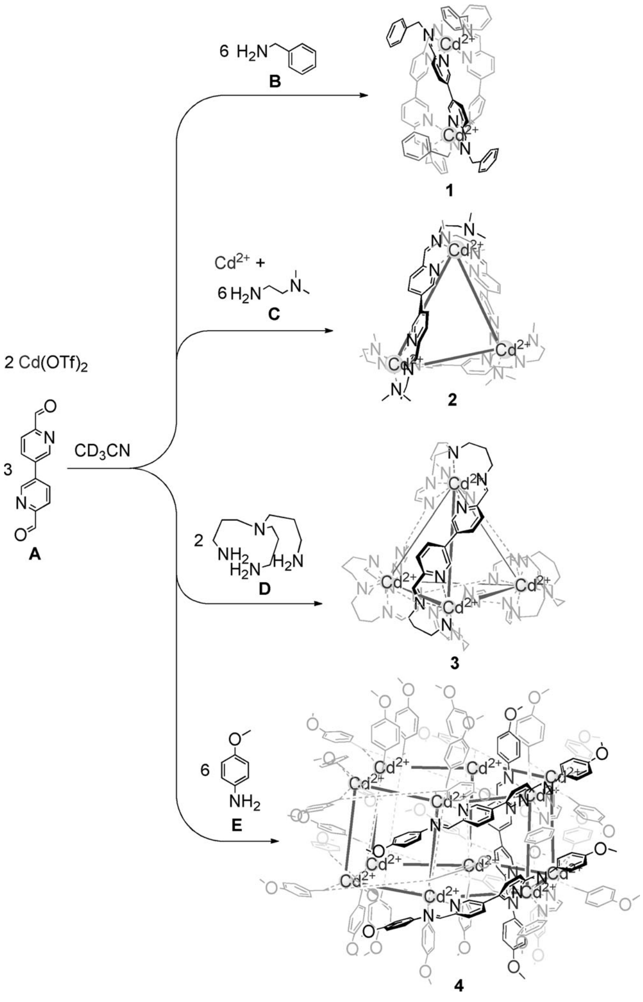

Figure 1. The diverse architectures generated from subcomponent self-assembly of dialdehyde **A** with amines **B**–**E** and cadmium triflate.

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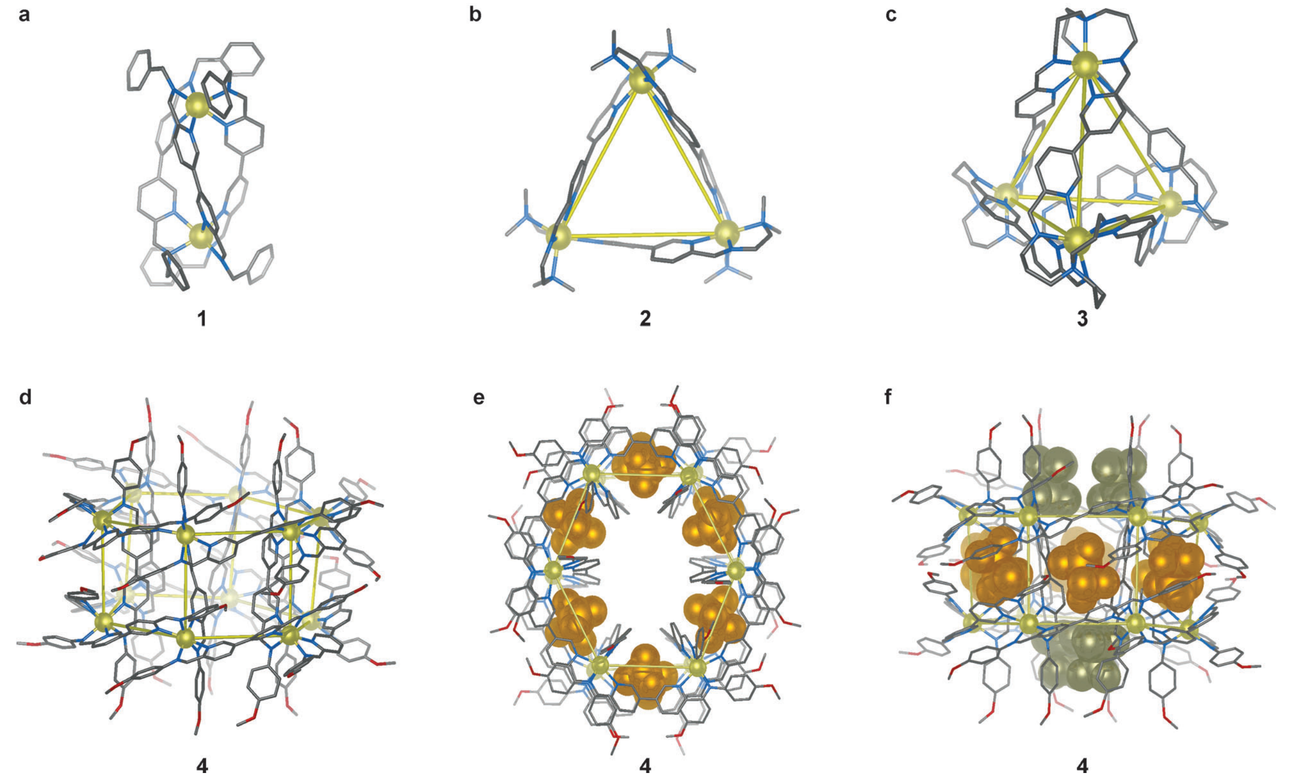

Figure 2. Crystal structures of complexes **1**–**4**.[27] For clarity, hydrogen atoms and solvent molecules are omitted. a) Helicate **1**; b) triangle **2**; c) tetrahedral cage **3**; d–f) hexagonal prism **4**: d) side view; e) top view illustrating the six peripheral pockets and the embedded triflate ions; f) side view showing the two triflate ions in each end of the central channel. Light-green spheres: Cd^{2+} ions.

the solid state. The structure of **3** may be described as a cryptate[14] where four tris(3-aminopropyl)amine residues cap the vertices of a tetrahedron and six residues of **A** form the edges. The Cd^{II} ions are coordinated by seven nitrogen donor atoms and adopt an approximately face-capped octahedral coordination geometry. The average bond lengths for Cd–N (3° amine) and Cd–N_{py} were found to be 2.5 Å, 0.2 Å longer than that for Cd–N (imine, 2.3 Å). The coordination of the tertiary amine, together with the geometrical requirements of the longer propylene spacers of **D**, appear to splay the ligand vectors of the bipyridine groups, thereby rendering the tetrahedral architecture of **3** more favorable than the triple-stranded cryptates formed with hexaimino cryptands constructed through [2+3] condensation of tris(2-aminoethyl)amine (tren) and dialdehydes.[15] Mass spectra of the product obtained when tren was used in place of **D** were consistent with a bicapped dimetallic structure similar to **1**.

Cage **3** encapsulates a volume of 196 $Å^3$,[16] 60 $Å^3$ larger than its Fe^{II} analogue constructed by using aniline.[12a] In the crystal structure, one acetonitrile molecule was found within the cavity with two others in van der Waals contact with the faces of the tetrahedron. In solution **3** was observed by NMR spectroscopy to bind triflate ions, with an association constant of $43\,\text{M}^{-1}$. Despite its cryptate structure, the affinity of **3** for triflate is approximately 10^3 times weaker than that of the analogous noncryptate cage constructed from Fe^{II} ions and anilines, but similar to what was observed for an iron(II) cage assembled from **A** and aliphatic amines.[13c] This observation suggests that the incorporation of aliphatic amine residues results in the formation of a more electron-rich binding pocket. The increased volume of the cadmium cage might also be too large for optimal triflate binding.[17]

When 4-methoxyaniline (**E**) was used as a subcomponent, a soluble product with complex NMR spectra was obtained. Vapor diffusion of diethyl ether into an acetonitrile solution of the reaction mixture led to the isolation of yellow crystals suitable for single-crystal X-ray diffraction. The structure obtained revealed a hexagonal prism **4** with formula $[Cd_{12}L_{18}](OTf)_{24}\cdot 30\,MeCN\cdot 30\,Et_2O$ (Figure 2 d–f). The structure's hexagonal symmetry is broken through elongation of one horizontal axis (Figure 2 e). Twelve ligands are arranged into a pair of circular helicate rings, which form the upper and lower hexagonal faces of **4**. These two rings are connected by six axial ligands on the structure's interior. The rings are stabilized by π–π interactions between the electron-rich anisidine residues and the electron-poor pyridyl rings. All Cd^{II} stereocenters have the same *mer* stereochemistry and handedness, and the same approximate local environment. One triflate anion is surrounded by four Cd^{II} ions, two axial and two equatorial ligands in each of the six peripheral pockets. The average calculated pocket volume is 141 $Å^3$.[16] The axial Cd–Cd distances (8.4 Å) are slightly shorter than the equatorial Cd–Cd distances (8.9 Å). In the solid state, no ordered species were found inside the channel of **4**, which has a volume of approximately 145 $Å^3$,[16] but two triflate ions were found at the top and bottom of each channel (Figure 2 f). Remarkably, the elaborate hexagonal prism structure of **4** is assembled from 72 building blocks (54 ligand subcomponents, 12 metal ions, and 6 structural anions) in a single reaction step.

Hexagonal prism **4** belongs to the same structural family as a $[Co_{10}L_{15}]$ D_5-symmetric pentagonal prism, which is assembled using **A**, toluidine, and $Co(ClO_4)_2$ under similar reaction conditions.[13d] The larger Cd^{II} ion is free of ligand field constraints and able to tolerate more structural distortion from an ideal octahedral geometry than Co^{II}, thereby allowing the formation of the larger hexagonal prism. The volume of each peripheral pocket is increased by around 80 % in going from the pentagonal to the hexagonal structure, allowing for the accommodation of the larger triflate anions. As with the pentagonal analogue,[13d] we infer that the triflate anions serve as peripheral templates within **4**, playing an important role in stabilizing the hexagonal-prismatic structure through coulombic and anion–π interactions[18] together with π stacking,[19] as has been observed in other similarly large and complex assemblies.[20]

Although we were not successful in numerous attempts to observe the parent ion of hexagonal prism **4** in ESI–MS—similarly highly-charged species that are held together by relatively weak coordinative interactions are reported to be difficult to successfully observe[21]—its formulation is confirmed by elemental analysis, and its complex NMR spectra in solution are consistent with the solid-state structure. Three separate sets of NMR measurements confirm the solution structure of **4**: First, the ^{1}H NMR spectrum shows three different ligand environments, consistent with idealized D_6 symmetry and the inequivalence of the three ligands at each *mer* Cd^{II} center. Second, the ^{19}F NMR spectrum shows peaks for both free and encapsulated triflate anions and a ^{1}H-^{19}F HOESY spectrum (Figure S18 in the Supporting Information) shows correlations between the encapsulated triflate and signals of the aromatic protons surrounding the peripheral pockets. Third, a ^{1}H DOSY experiment provided results consistent with the presence of a single complex with a hydrodynamic radius of 11.4 Å (Figure S19 in the Support-

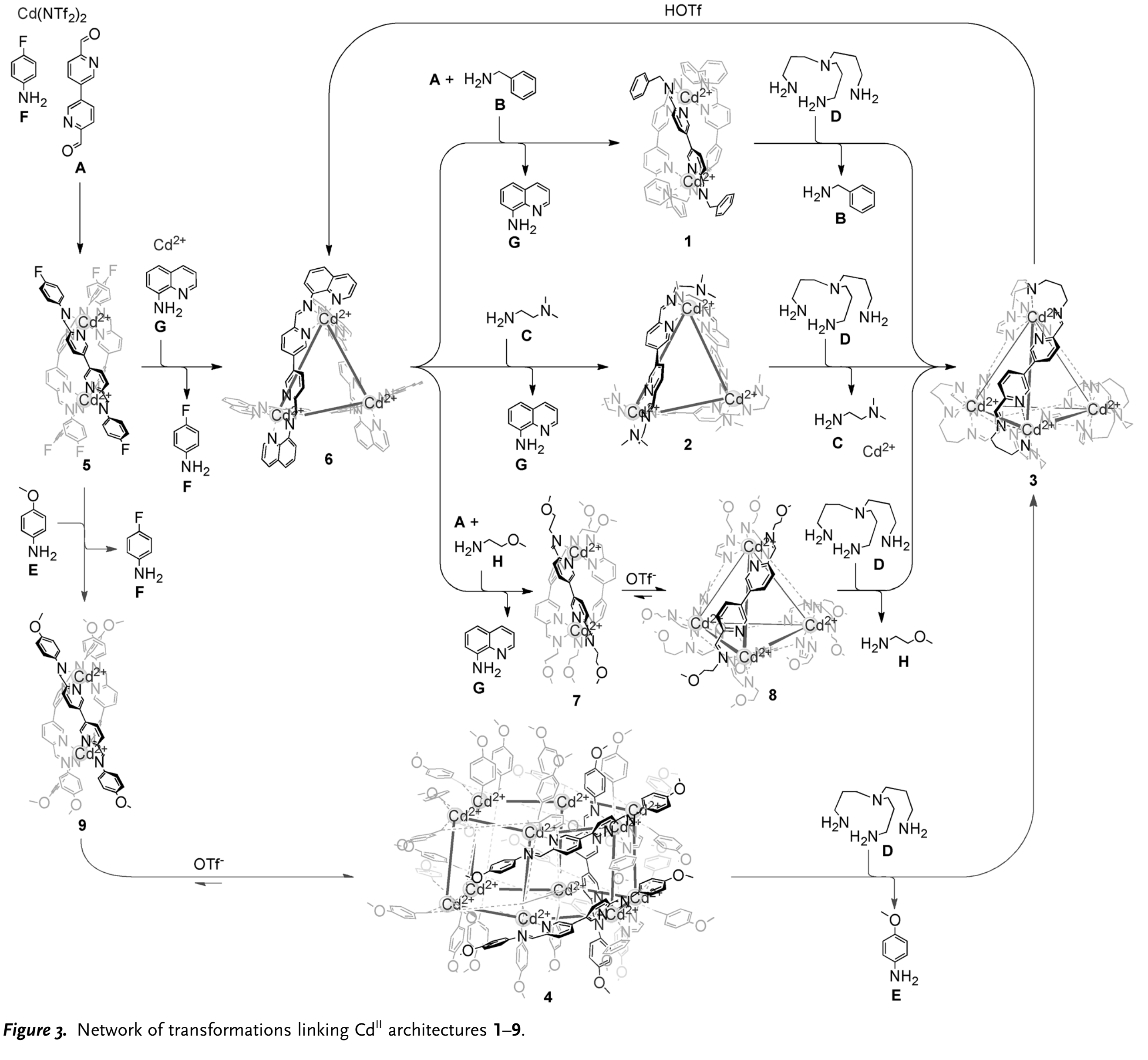

Figure 3. Network of transformations linking Cd^{II} architectures **1–9**.

ing Information), consistent with the radius of **4** of approximately 11.5 Å observed in the crystal.

The formation of these diverse, well-defined, complex structures revealed Cd^{II} to be a more versatile metal ion than Fe^{II} for subcomponent self-assembly: in the analogous reactions with iron(II) triflate, aliphatic amines **C** and **D** produced a complex mixture of products, and both **B** and **E** only yielded Fe_4L_6 tetrahedra.[12a] We attribute this difference to the larger size of the Cd^{II} ion (109 pm radius)[22] and the absence of crystal field stabilization effects (d^{10} electronic configuration) as compared to Fe^{II} (75 pm, d^6).[22] These factors allow Cd^{II} to adopt more distorted coordination geometries and achieve higher coordination numbers, allowing the development of greater structural diversity in self-assembled architectures.

As complexes **1**–**4** share common building blocks, they may be interconverted in response to the chemical stimuli provided through the addition of new subcomponents. Building upon earlier work on imine exchange,[10a,12,23] we were able to take advantage of the difference in electronic and steric properties of various amines, together with the chelate effect, to achieve the network of sequential transformations depicted in Figure 3.

In similar fashion to the synthesis of helicate **1** (Figure 1), the reaction between dialdehyde **A**, $Cd(NTf_2)_2$ and 4-fluoroaniline (**F**) produced a Cd_2L_3 triple helicate **5** as the only observed product by both NMR spectroscopy and ESI–MS (Figure 3). $Cd(NTf_2)_2$ was used to achieve better solubility. The addition of 8-aminoquinoline (**G**) along with additional $Cd(NTf_2)_2$ resulted in the transformation of helicate **5** to triangle **6** by the displacement of aniline **F** for **G**. The thermodynamic driving force was attributed to the chelate effect and the more electron-rich character of **G** as compared to **F**, as has been observed in other systems.[10a]

The introduction of a more nucleophilic aliphatic amine was observed to trigger further transformations of triangle **6**, which followed three distinct pathways depending on the structural features of the amine: **6** was observed to transform into triangle **2** when 2-dimethylaminoethylamine (**C**) was added, whereas the addition of benzylamine (**B**) or 2-methoxyethylamine (**H**) with additional **A** resulted in reversion to the triple helical motif of product **1** or **7**, respectively. Although the addition of sodium triflate (20 equiv) to helicate **1**, **5**, or **9** resulted in no reconfiguration of the system, NaOTf (20 equiv) was observed to convert helicate **7** predominantly (59 %) to tetrahedral cage **8**, as observed by ^{1}H NMR spectroscopy (Figure S44 in the Supporting Information). A similar equilibrium mixture of **7** and **8** (approximately 1:1.4) could be obtained through direct subcomponent self-assembly using $Cd(OTf)_2$ (see the Supporting Information).

Attempts at interconversion between complexes **1**, **2**, **7**, and **8** by imine exchange resulted in only complex mixtures, thus suggesting that these four structures are of similar stability. Helicate **1**, triangle **2**, or cage **8** could be converted into cage **3** through addition of tris(3-aminopropyl)amine (**D**). We infer that the chelate effect[24] drives this conversion, whereby the incorporation of one equivalent of tritopic **D** liberates three equivalents of monoamine or two equivalents of diamine.

The conversion sequence from helicate **5** to cage **3**, triggered by amine signals, established a hierarchy of thermodynamic stability among the various Cd^{II} architectures. This sequence reveals that, in general, a more nucleophilic amine generates a more thermodynamically favored product, and that the chelate effect plays an even more important role in determining thermodynamic stability.

When neat triflic acid (ca. 14 equiv) was added to the mixture obtained at the end of the sequence, containing cage **3**, amine **G**, and one of the amines **B**, **C**, or **H**, the most basic amine **D** was observed to be preferentially protonated. This protonation led to the destruction of cage **3** and the rearrangement of the other subcomponents to regenerate triangle **6**, incorporating **G** and **A**, with a yield of approximately 80 %, as revealed by ^{1}H NMR integration (Figure 4, Figures S45–47 in the Supporting Information).

Hexagonal prism **4** could be accessed from helicate **5** by using a two-step transformation (Figure 3, lower route): substitution of aniline **F** for more electron-rich **E** did not alter the structure of the complex, but produced a new helicate **9**. The addition of NaOTf (20 equiv) as a template converted **9** to **4** in a yield of 86 %. Hexagonal prism **4** could be transformed to cage **3** by adding amine **D**, after 12 h at 50 °C. The reconstitution of **4** into **3** involved breaking and reforming 36 imine linkages and the rearrangement of all *mer* Cd^{II} centers in **4** to the *fac* arrangements of **3**.

In summary, we have shown within a complex dynamic system how the application of different chemical signals may be used to interconvert a variety of complicated architectures through a network of selective transformations, including both divergent and convergent conversion sequences, as well as cyclical paths reminiscent of metabolic pathways.[25] Figure 3 shows the energetic hierarchy between different structures, and establishes which structure may be expected to be observed under a given set of conditions. Different functions associated with these diverse structures—such as guest binding within cages **3** or **8**, or the use of toroidal

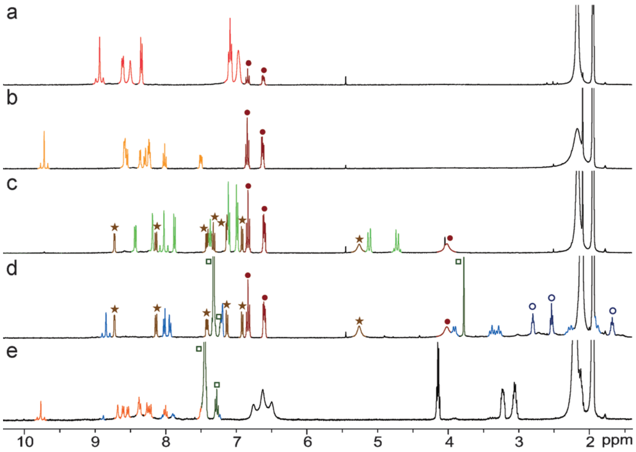

Figure 4. ^{1}H NMR spectra for a sequential one-pot transformation pathway among Cd^{II} complexes: a) helicate **5**; b) transformation from **5** to **6** following the addition of **G**; c) transformation from **6** to **1** following the addition of **B**; d) transformation from **1** to **3** following the addition of **D**; e) regeneration of **6** following the addition of triflic acid. The signals from free subcomponents **F**, **G**, **B**, and **D** are marked by a filled circle, star, square, and open circle, respectively.

structure **4** to establish a pore-like gateway through a membrane[26]—could thus be turned on and off under the control of chemical signals. Future work will focus on the exploration of such multiple functions within systems similar to the one outlined herein.

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[27] CCDC 885707, 885708, 885709, and 885710 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.