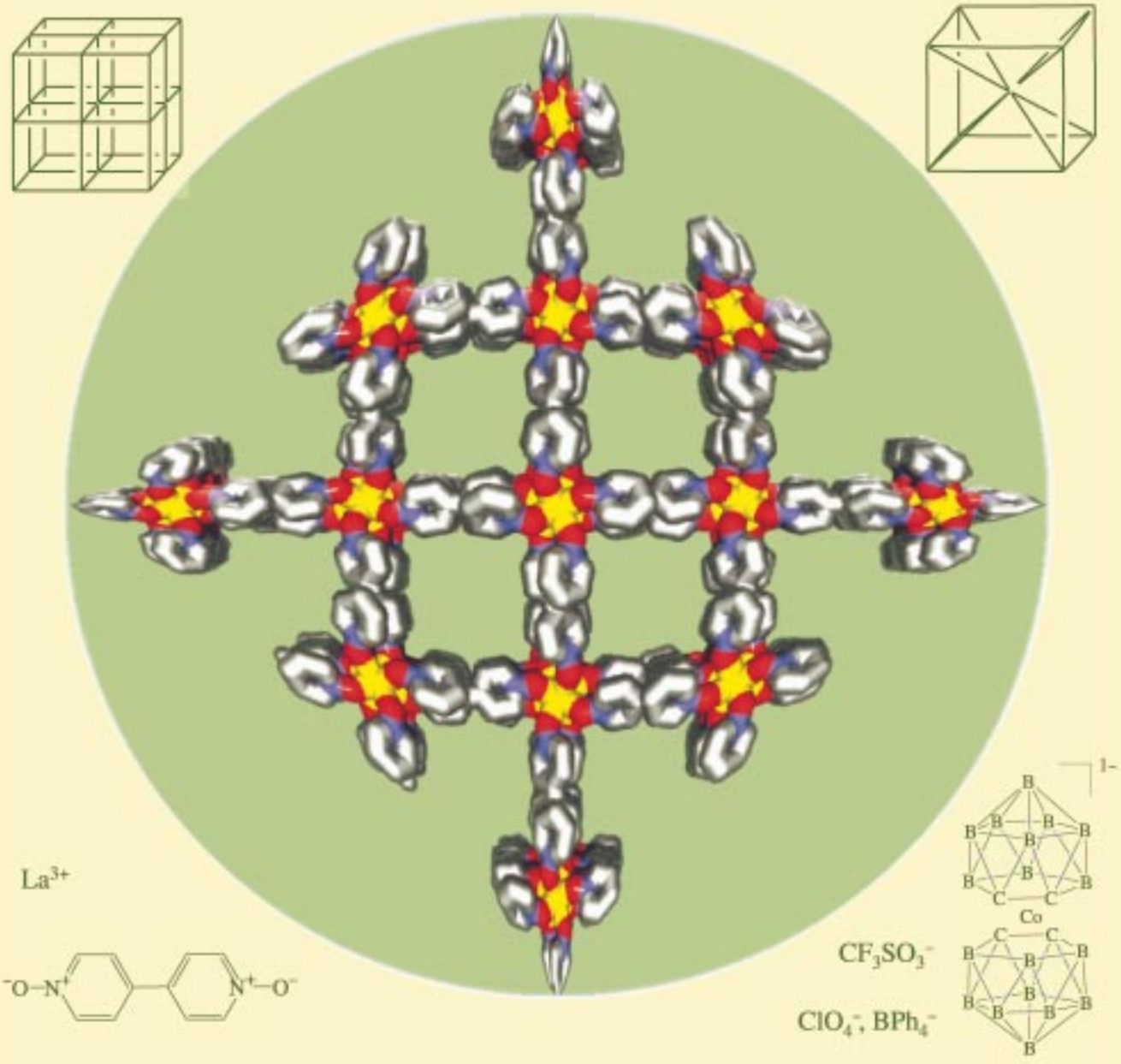
The sixfold connectivity of the NaCl crystal lattice is familiar to all chemists but is still rare for coordination framework polymers. Higher connectivities were previously unknown.

The diagram shows the first example of an eight-connected coordination network with CsCl-like topology.



By using the ligand 4,4′-bipyridine-*N*,*N*′-dioxide to bridge La^{III} centers, coordination networks of six-, seven-, and eight-connected topologies can be constructed. What is a seven-connected framework? Find out more on the following pages.

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Unprecedented Seven- and Eight-Connected Lanthanide Coordination Networks**

De-Liang Long, Alexander J. Blake, Neil R. Champness,* Claire Wilson, and Martin Schröder*

The classification by Wells[1] of framework materials according to their topological structures allows a general understanding of solid-state structures. Of the structural types depicted by Wells the majority are based upon three- and four-connected topologies which are commonly found in framework materials such as zeolites and, more recently, in coordination polymers.[2] Much of this latter work has focussed on d-block metal ions using three-,[3] four-,[4] or six-connected nodes,[5] and more recently, examples of five-connected structures have been reported.[5a, 6] Three-dimensional structures with high connectivity are familiar in the form of the NaCl lattice (6:6 coordination:connectivity) or CsCl (8:8 coordination:connectivity), but examples of six-connected structures are still rare for coordination framework polymers,[5] and connectivities higher than this are unknown. Due to their limited coordination numbers, it is difficult for polymeric structures with such high topological connectivites to be generated with d-block metal ions, and even six-connected nodes are uncommon with d-block metals due to steric hindrance for most commonly used heterocyclic N-donor ligands. Despite the tendency of lanthanide ions to adopt high coordination numbers, connectivities greater than six remain unknown for lanthanide coordination polymers.[7] We recently reported a general strategy for the construction of lanthanide coordination networks using 4,4′-bipyridine-*N*,*N*′-dioxide (L) as a bridging ligand and coordinating NO_3^- ions as terminal groups to give unusual three- and four-connected networks.[8] L not only presents a suitable donor atom for lanthanide ions, but its limited steric hindrance additionally offers the potential for higher coordination numbers and homoleptic coordination spheres. Thus, in the absence of competing ligands, the reaction of La^{III} cations with L is attractive for the synthesis of highly connected framework coordination polymers. Furthermore, we anticipated that by using noncoordinating and/or bulky anions such as $CF_3SO_3^-$, BPh_4^-, and $[Co(C_2H_{11}B_9)_2]^-$, lanthanide coordination networks with unusually high connectivity topologies could be prepared. We report herein three new coordination polymers with highly unusual three-dimensional network structures **1**–**3**, which adopt eight-, seven-, and six-connected lanthanum nodes, respectively.

$[La(L)_4]\cdot(CF_3SO_3)_3\cdot 4.2\,CH_3OH$ **1**

$[La(L)_4]\cdot(BPh_4)\cdot(ClO_4)_2\cdot 2.75\,CH_3OH$ **2**

$[La(L)_4]\cdot([Co(C_2H_{11}B_9)_2])_3\cdot 0.5\,CH_3OH$ **3**

Compound **1** was obtained by mixing methanolic solutions of $La(CF_3SO_3)_3$, 2,2′-bipyridine-*N*,*N*′-dioxide, and L. Complexes **2** and **3** were prepared by mixing methanolic solutions of a lanthanum salt, the sodium salt of the desired bulky anion, and L to afford a precipitate which dissolved with concomitant formation of crystals of the desired product over several days.

Single-crystal X-ray structural determinations confirm that compounds **1**,[9], **2**,[10] and **3**[11] have polymeric structures based on networks of *homoleptic* eight-coordinate La^{III} centers linked through L. In **1** the 4,4′-bipyridine-*N*,*N*′-dioxide ligands bridge to eight different neighboring metal centres (Figure 1a) forming a three-dimensional body-centered *cubic*, CsCl-like, framework structure (Figure 2a). This is the first example of this network topology observed for coordination polymers, and represents the highest connected topology of any known coordination network. The structure can be considered as being composed of (4,4) two-dimensional nets, parallel to the (100) plane, which intersect with further perpendicular (4,4) nets, parallel to the (010) plane (see Scheme 1a). The perpendicular nets are canted at such an angle that an eight-connected structure is generated. The

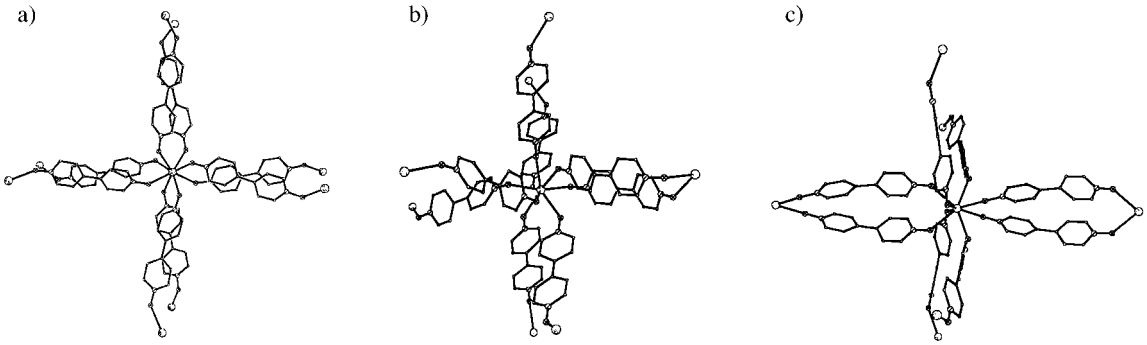

Figure 1. Views of the homoleptic eight-coordinate La^{III} centers in **1** (a), **2** (b), and **3** (c) illustrating the connections to eight, seven, and six nearest La^{III} neighbors, respectively.

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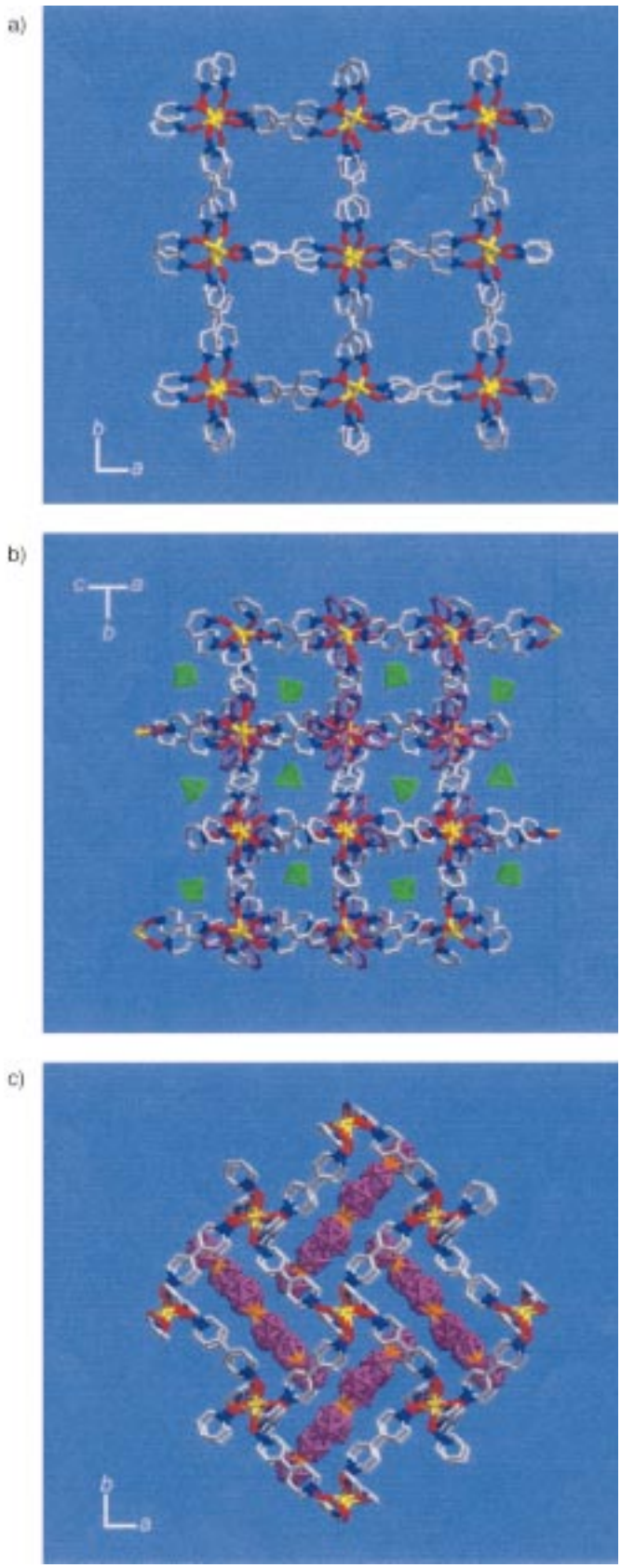

Figure 2. a) Square channels formed by the eight-connected coordination network in **1**. b) 3D structure of **2** showing cavities that accommodate BPh_4^- anions (purple) and channels accommodate ClO_4^- ions (green tetrahedrons). c) Cavities within the six-connected topology of compound **3** that accommodate the bulky $[Co(C_2H_{11}B_9)_2]^-$ ions. Methanol molecules are omitted for clarity.

framework is tetragonally distorted along the *c* axis as a result of the compressed square antiprismatic coordination geometry of the La^{III} cation, and comprises linked cuboids with dimensions of about $18 \times 18 \times 9$ Å. Channels of effective cross-section of about 9×9 Å run parallel to the *c* axis and are occupied by the $CF_3SO_3^-$ ions and MeOH solvent molecules.

The use of 2,2′-bipyridine-*N*,*N*′-dioxide in the preparation of **1** is crucial. When no 2,2′-bipyridine-*N*,*N*′-dioxide is added to the reaction of $La(CF_3SO_3)_3$ with L, a microcrystalline product is formed in only a few hours. X-ray powder diffraction studies confirm that this product adopts an unidentified phase different to that observed for **1**. The same reaction in the presence of 2,2′-bipyridine-*N*,*N*′-dioxide (La:2,2′-bipyridine-*N*,*N*′-dioxide ratio 1:1 or 1:2), produces **1**. Interestingly, the period of time prior to the first appearance of crystals increases as the La:2,2′-bipyridine-*N*,*N*′-dioxide ratio increases, while higher La:2,2′-bipyridine-*N*,*N*′-dioxide ratios (1:3 or 1:4) result in slowing of the crystallization process to such an extent that no solid can be isolated from the reaction mixture. 2,2′-Bipyridine-*N*,*N*′-dioxide reacts with La^{III} cations to form stable, highly symmetrical discrete species $[La(2,2'\text{-bipyridine-}N,N'\text{-dioxide})_4]^{3+}$, an example of cubic eight-coordination,[14] and thus, the presence of 2,2′-bipyridine-*N*,*N*′-dioxide may effect the crystal growth of **1** in two ways. First, it may decelerate the process of lanthanum coordination polymer formation by slowing the rate of reaction between La^{III} cations and L by forming intermediate La^{III}–2,2′-bipyridine-*N*,*N*′-dioxide species. Second, the highly symmetrical $[La(2,2'\text{-bipyridine-}N,N'\text{-dioxide})_4]^{3+}$ ions or related species may template the formation of the eight-coordinate geometry of the La^{III} centers observed in **1**, and thus induce the tetragonal structure observed in the final product, $\{[La(L)_4]^{3+}\}_\infty$.

Although the lanthanum centers in **2** adopt an eight-coordinate geometry, as observed in **1**, the infinite structure that is formed is quite different. Although eight bridging ligands L ligate each metal center, each La^{III} ion is bridged to *seven* nearest neighbors because a pair of ligands L form a "double-bridge" (Figure 1b). Although several bridging modes have been established for L,[15] this is the first observation of the "double-bridge" mode. The resultant three-dimensional (3D) structure can be described as consisting of (6,3) nets (parallel to the crystallographic $(10\bar{1})$ plane, the double-bridge being considered as one connection) interlinked by (4,4) nets (parallel to the crystallographic (010) plane) (Scheme 1b). Thus, the 3D structure that is formed adopts the unprecedented topology $4^{17}6^2$, which represents the first example of a seven-connected coordination network structure. The large cavities found in this structure (Figure 2b) are occupied by ClO_4^- and BPh_4^- counteranions and MeOH solvent molecules.

In **3**, each La^{III} center is ligated by eight molecules of L but is linked to only six nearest neighbors with two pairs of ligands L giving two "double-bridges" (Figure 1c). This affords a six-connected NaCl-like 3D structure (Scheme 1c). The network structure can be considered as two perpendicular (4,4) nets intersecting in a similar manner to that observed in **1**. However, in the case of **3** the (4,4) nets are not canted, in contrast to **1**, so that two "double-bridges" are common to

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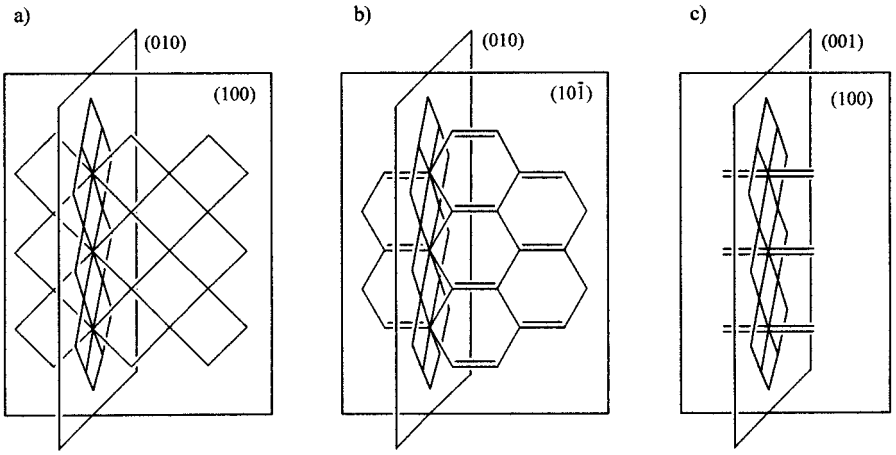

Scheme 1. Schematic representations of the topologies observed in **1** (a), **2** (b), and **3** (c) illustrating the intersecting canted (4,4) nets in **1**, (6,3) and (4,4) nets in **2** and (4,4) nets in **3**. "Double-bridges" are represented by pairs of parallel lines.

both nets to give a six-connected structure. The two "double-bridges" run parallel to the *c* axis, while the four remaining mono bridges propagate along the two diagonal directions of the *ab* face. The structure adopted is noncentrosymmetric, and the chiral cavities which are formed accommodate the $[Co(C_2H_{11}B_9)_2]^-$ ion and MeOH solvent molecules (Figure 2c).

Due to its large size, $[Co(C_2H_{11}B_9)_2]^-$ has been widely used as a counteranion in the extraction and separation of metal ions,[16a–d] but its use as a counteranion in the construction of coordination networks is extremely rare.[16e] As might be expected, our experiments indicate that this anion is preferentially crystallized upon coordination polymer formation over more commonly used anions. Thus, when either $LaCl_3$ or $La(NO_3)_3$ are used as starting materials in the presence of L and $[Co(C_2H_{11}B_9)_2]^-$, the same product, **3**, is obtained. In contrast, the reaction of $LaCl_3$ or $La(NO_3)_3$ with L in the presence of BPh_4^- ions affords different products depending on whether the nitrate or chloride is used as starting material.[17] $[Co(C_2H_{11}B_9)_2]^-$ also appears to have a significant effect in directing lanthanide coordination polymer formation, suprisingly affording the same 3D structures as **3** with either Eu^{III} or Ho^{III} ions,[18] despite the significant and usually influential contraction in cationic radius.[8]

We have confirmed that lanthanide ions can adopt high coordination numbers that can be employed for the construction of highly connected frameworks. The structures reported here are extremely unusual in that homoleptic La^{III} nodes have been used to form the first examples of eight- and seven-connected networks. The differences between the structures reported here highlight the importance of choice of anion upon framework topology, and the subtle balance between different topological structures formed by lanthanide coordination polymers. Our success in preparing the highly connected coordination frameworks of **1**–**3** confirm the potential for developing new structural families of solid-state materials using lanthanide-based coordination polymers.

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[9] a) Single-crystal X-ray experiments were performed on either a Nonius kappaCCD diffractometer (**1**) or a Bruker SMART1000 CCD diffractometer (**2**,**3**) both equipped with an Oxford Cryosystems open-flow cryostat (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). All structures were solved by direct methods[11] and all non-hydrogen atoms were located by using subsequent difference Fourier methods.[12] b) Crystals of **1** were grown by the following procedure: Lanthanum triflate hydrate (0.029 g, 5×10^{-5} mol), and 2,2′-bipyridine-*N*,*N*′-dioxide (0.010 g, 5×10^{-5} mol) were dissolved in MeOH (10 mL). After 24 h 4,4′-bipyridine-*N*,*N*′-dioxide hydrate (0.022 g, 1×10^{-4} mol) in MeOH (10 mL) was added. After about three days a crystalline product **1**, suitable for X-ray diffraction was formed. Crystal data for **1**, $C_{47.2}H_{48.8}F_9LaN_8O_{21.2}S_3$, $M_r = 1473.43$, tetragonal, $P\bar{4}c2$, $a = 25.9970(4)$, $c = 26.7847(6)$ Å, $V = 18102.3(6)$ Å^3, $T = 150(2)$ K, $Z = 12$, $\rho_{calcd} = 1.622$ Mg m^{-3}, $F(000) = 8923$, $\mu(Mo_{K\alpha}) = 0.920$ mm^{-1}. Crystal morphology: colorless block. Crystal dimensions: $0.20 \times 0.20 \times 0.11$ mm. A total of 19471 unique reflections were collected ($R_{int} = 0.325$), $\theta_{max} = 27.48°$. Semiempirical absorption correction from equivalents. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.199P)]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$. Goodness-of-fit on F^2 was 1.025, $R1$ (for 6414 reflections with $I > 2\sigma(I)$) = 0.132, $wR2 = 0.309$. Data/parameters 19471/650. Largest difference Fourier peak and hole 2.87 and -1.15 e Å^{-3}, respectively. c) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-154975 (**1**), CCDC-154976 (**2**), and CCDC-154977 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] Crystals of **2** were grown by the following procedure: Lanthanum perchlorate hydrate (0.022 g, 4×10^{-5} mol) and sodium tetraphenylborate (0.028 g, 8×10^{-5} mol) were dissolved in MeOH (15 mL). 4,4′-Bipyridine-*N*,*N*′-dioxide hydrate (0.033 g, 1.5×10^{-4} mol) in MeOH (10 mL) was added. The mixture produced a white precipitate, which transformed into pale yellow plate crystals over a period of about seven days. Crystal data for **2**, $C_{66.75}H_{63}BCl_2LaN_8O_{18.75}$, $M_r = 1497.87$, monoclinic, $P2_1/n$, $a = 13.2242(11)$, $b = 38.366(3)$, $c = 13.2515(11)$ Å, $\beta = 99.752(1)$, $V = 6626(2)$ Å^3, $T = 150(2)$ K, $Z = 4$, $\rho_{calcd} = 1.501$ Mg m^{-3}, $F(000) = 3062$, $\mu(Mo_{K\alpha}) = 0.805$ mm^{-1}. Crystal morphology: yellow triangular plate. Crystal dimensions: $0.17 \times 0.06 \times 0.04$ mm. A total of 12705 unique reflections were collected ($R_{int} = 0.095$), $\theta_{max} = 27.15°$. Semiempirical absorption correction from equivalents. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.261P)]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$. Goodness-of-fit on F^2 was 0.902, $R1$ (for 6541 reflections with $I > 2\sigma(I)$) = 0.062, $wR2 = 0.096$. Data/parameters 12705/861. Largest difference Fourier peak and hole 1.55 and -0.99 e Å^{-3}, respectively.[9c]

[11] Crystals of **3** were grown by the following procedure: Lanthanum chloride hydrate (0.012 g, 3×10^{-5} mol) and $Na[Co(C_2H_{11}B_9)_2]$ (0.035 g, 1×10^{-4} mol) were dissolved in MeOH (10 cm^3). 4,4′-Bipyridine-*N*,*N*′-dioxide hydrate (0.033 g, 1.5×10^{-4} mol) in MeOH (10 cm^3) was added, producing a white emulsion-like precipitate, from which large yellow plate crystals grew in about three days. Crystal data for **3**, $C_{52.5}H_{100}B_{54}Co_3LaN_8O_{8.5}$, $M_r = 1878.85$, orthorhombic, $P2_12_12$, $a = 17.5705(14)$, $b = 18.571(2)$, $c = 13.3355(11)$ Å, $V = 4351.4(10)$ Å^3, $T = 150(2)$ K, $Z = 2$, $\rho_{calcd} = 1.434$ Mg m^{-3}, $F(000) = 1894$, $\mu(Mo_{K\alpha}) = 1.098$ mm^{-1}. Crystal morphology: yellow plate. Crystal dimensions: $0.34 \times 0.12 \times 0.03$ mm. A total of 10175 unique reflections were collected ($R_{int} = 0.067$), $\theta_{max} = 28.69°$. Semiempirical absorption correction from equivalents. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0156P)]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$. Goodness-of-fit on F^2 was 0.919, $R1$ (for 7301 reflections with $I > 2\sigma(I)$) = 0.044, $wR2 = 0.061$. Data/parameters 10175/575. Flack parameter = 0.027(12). Largest difference Fourier peak and hole 0.98 and -0.71 e Å^{-3}, respectively.[9c]

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[18] For the europium analogue of **3**, elemental analysis calcd for $C_{52.5}H_{100}B_{54}Co_3EuN_8O_{8.5}$(%): C 33.33, H 5.33, N 5.92; found: C 32.75, H 5.16, N 5.78; cell dimensions: orthorhombic, $a = 17.4254(3)$, $b = 18.6346(3)$, $c = 13.2015(2)$ Å, $V = 4289.7(2)$ Å^3. For the holmium analogue of **3**, elemental analysis calcd for $C_{52.5}H_{100}B_{54}Co_3HoN_8O_{8.5}$(%): C 33.10, H 5.29, 5.88; found: C 32.76, H 5.65, N 6.05; cell dimensions: orthorhombic, $a = 17.363(7)$, $b = 18.715(5)$, $c = 13.184(5)$ Å, $V = 4284(2)$ Å^3.

Working Supramolecular Machines Trapped in Glass and Mounted on a Film Surface**

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Dedicated to Professor Siegfried Hünig on the occasion of his 80th birthday

The concept of a macroscopic machine can be realized[1] in solution at a supramolecular level in complexes where the self-assembly[2] of the components can be reversed upon quelling temporarily the molecular recognition that exists between the matching components. Thus, a supramolecular machine can be defined as an assembly of two or more molecular components designed to perform mechanical-like motions with respect to each other in response to some energy supply—for example, chemical, electrochemical, or photochemical—that can be switched on and off at will. One of the most highly investigated classes of supramolecular machines[1, 3] are those based on the complexes known as pseudorotaxanes.[4] The reason for this is that the dethreading and rethreading movements of a thread through the center of a ring are reminiscent of the action of a linear motor. Numerous artificial supramolecular machines,[1] based on pseudorotaxanes,[4] exist that can be induced to undergo co-conformational change[5] by chemical,[6] electrochemical,[7] and photochemical[8–10] means. They have been demonstrated[1] to operate efficiently in solution, albeit in an incoherent manner. In order to realize the full potential of these supermolecules in a machine-shop setting, they have to be organized at interfaces[11] or deposited on surfaces[12] so that they can be made to operate in unison. Herein we describe two solid-state supramolecular machines in action: one in which the machines are trapped physically in a rigid, nanoporous, optically transparent matrix, and the other in which

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