Molecular Sensors

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Metal-Tunable Nanocages as Artificial Chemosensors**

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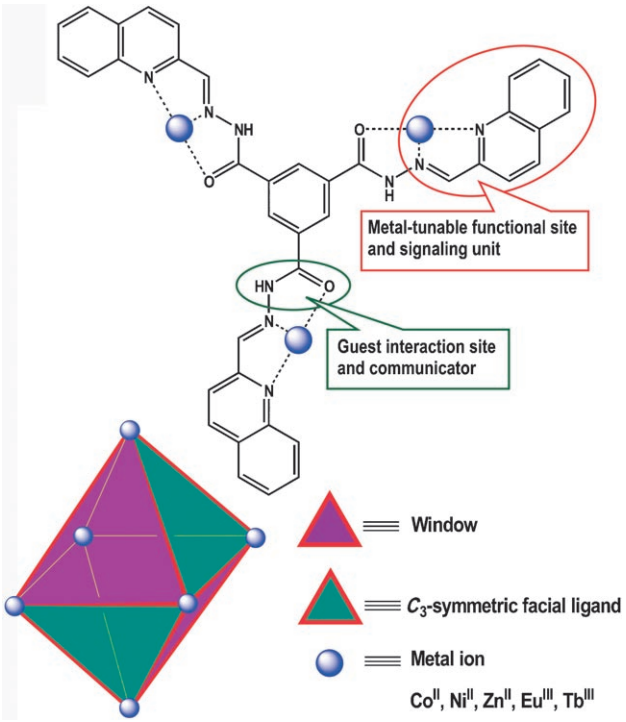
Supramolecular assembly of predesigned organic and inorganic building blocks is an excellent tool for constructing well-defined nanosized molecular cavities. The nanocages can encapsulate and stabilize guest substrates, and chemical transformations can be catalyzed within these "microreactor" cagelike structures.[1] Recently, synthetic strategies for constructing functional coordination cages with various structures and novel inclusion properties have been well established.[2,3] Substantial developments have been made in the creation of Werner-type capsules that can be used for sensing special guests with selective signal responses.[4] In this case, the major challenge goes beyond achieving a size- or shape-selective dynamic molecular recognition and includes detecting and amplifying guest-bonding events to produce a measurable output. Thus, a proper communication system that is able to transduce the recognition information into an easy-to-measure signal must be included in the overall molecular design.[5]

By combining three quinoline groups into a disk-shape molecule—by *meta* substitution of a central benzene ring—we developed a new strategy for the preparation of octahedral nanocages, which can be used as artificial chemosensors (Scheme 1, $H_3\mathbf{L^1}$). Each quinoline group acts as both chromophore and fluorophore, thus serving as an N_2O tridentate coordinating site for the amide groups, which are introduced as trigger sites to achieve efficient guest interactions and a consequently good signal response.[6] Since the formation of donor-type hydrogen bonds with the amide groups may perturb the electronic distribution on the conjugated backbone of the ligand, such host–guest interactions can affect the charge transfer associated with the quinoline units and lead to significant changes in the optical properties.[7,8]

Tridentate coordinated units are efficient building blocks that can be used to fix the orientation of ligands coordinated to a transition-metal center at an angle of exactly 90°.[9] Our preparation strategy, which is based on using a C_3-symmetric facial ligand that comprises three such tridentate coordinating sites, forces various metal ions to form metal-variable isostructural octahedral nanocages with considerable stabilities. This method allows us to finely tune the metal ions and ligand chromophore units to obtain highly selective and sensitive responses toward particular guest molecules. By appropriately modulating the quinoline groups to pyridine groups, the synthetic strategy can be further extended to lanthanide ions, which exhibit a low stereochemical preference. Interesting metal-dependent luminescent properties are expected for these isostructural coordination architectures.



Scheme 1. Structure of the ligand $H_3\mathbf{L^1}$ and constitutive/constructional fragments of the functional octahedral cages. For ligand $H_3\mathbf{L^1}$ (quinoline derivative), the metal ions used are Co^{II} and Zn^{II}. For ligand $H_3\mathbf{L^2}$ (pyridine derivative), the metal ions used are Ni^{II}, Eu^{III}, and Tb^{III}.

The ligand $H_3\mathbf{L^1}$ was easily obtained by Schiff base reaction of 2-quinoline carboxaldehyde with 1,3,5-tricarbohydrazine benzene in ethanol. Adding a solution of cobalt(II) or zinc(II) perchlorate in methanol to a chloroform/methanol solution of the ligand $H_3\mathbf{L^1}$ led to high-yield formation of the Co^{II} compound **1** and the Zn^{II} compound **2**.[10] Crystal-structure analyses reveal that compounds **1** and **2** are isostructural (Figure 1). Both of them crystallize in the

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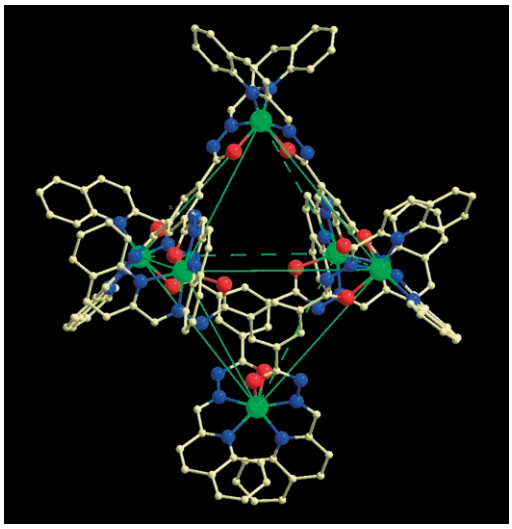

Figure 1. Molecular structure of the octahedral cage in the isostructural compounds **1** and **2**. Hydrogen atoms, anions, and solvent molecules are omitted for clarity. The metal, oxygen, nitrogen, and carbon atoms are green, red, blue, and gray, respectively.

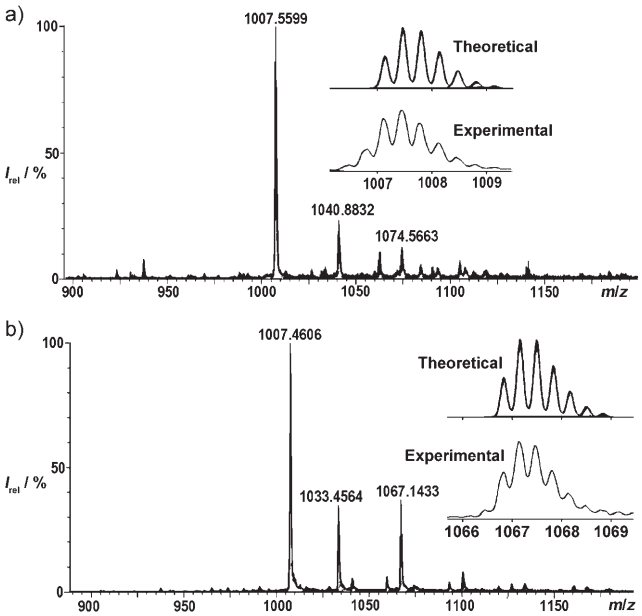

Figure 2. ESI-MS of compound **1** in a) methanol solution and b) methanol–DMSO solution upon addition of glucosamine. The inserts show the measured and simulated isotopic patterns at *m*/*z* 1007.6 (a) and *m*/*z* 1067.1 (b).

space group $R\bar{3}$. Each octahedral cationic cage $[M_6(H_9\mathbf{L}^1_4)]^{9+}$ has an ideal C_3 symmetry, with one of the four ligands located on the crystallographic threefold axis. The pseudo S_4 symmetry is achieved by alternatively arranging the four planar ligands onto the eight triangle faces of the octahedron defined by the six metal ions. The three rigidly separated N_2O tridentate chelators of each ligand coordinate with three different metal centers, while six metal centers occupy the vertical positions of the octahedron, each of them coordinating with two planar tridentate N_2O chelators to form a *mer* configuration. These $[M_4L_6]$ cages are closely related to the hexanuclear palladium octahedron structures reported by Fujita and co-workers.[11] The separation between two metal ions bridged by one ligand is of about 9.77 Å, whereas the distance between two diagonally opposing metal ions is about 13.8 Å (the average inner volume has been estimated to be about 440 Å^3). The presence of nine disordered perchlorate anions for each cationic cage suggests that only three amide groups in the four ligands lost their protons during coordination. These amide groups—located within the positively charged cages—provide static, geometric, coordinative, and functional properties to the cagelike capsules, which are important for the recognition of monosaccharide derivatives, such as glucosamine.[12,13]

The electrospray ionization mass spectrometry (ESI-MS) data demonstrate that compounds **1** and **2** are substantially stable in solution (see the Supporting Information). As shown in Figure 2a, compound **1** exhibits an intense peak at *m*/*z* $\approx$1007.56 and two moderate peaks at *m*/*z* values of 1040.88 and 1074.56, with the isotopic distribution patterns being separated by a distance of (0.33 $\pm$ 0.01) Dalton. These signals can be assigned to the positively charged species $[Co_6(H_3\mathbf{L}^1_4)]^{3+}$, $[Co_6(H_4\mathbf{L}^1_4)(ClO_4)]^{3+}$, and $[Co_6(H_5\mathbf{L}^1_4)(ClO_4)_2]^{3+}$.

In the case of a solution of compound **1** in the presence of an equimolar amount of glucosamine (NH_2-Glu; Figure 2b), an exact comparison of the most interesting experimental peak (which is observed at *m*/*z* 1067.14) with the simulation results obtained on the basis of natural isotopic abundances reveals that this trivalently charged species can be reasonable assigned to $[Co_6(H_3\mathbf{L}^1_4)\supset(NH_2\text{-Glu})]^{3+}$, thus providing evidence of a 1:1 stoichiometric host–guest complexation. The peak at *m*/*z* 1033.46, on the other hand, can be safely assigned to the species $[Co_6(H_3\mathbf{L}^1_4)(DMSO)]^{3+}$ (DMSO = dimethyl sulfoxide). Upon addition of glucose, instead of glucosamine, no host–guest complex species were detected in the ESI-MS spectra under the same experimental conditions, which suggests a selective recognition of compound **1** by glucosamine in solution.

The inclusion phenomenon was further characterized by means of UV/Vis measurements (Figure 3a). Both the cobalt(II) (**1**) and the zinc(II) (**2**) compounds exhibited clear ligand-based charge-transfer bands[14] (at about 280 and 415 nm) in an acetonitrile solution (5×10^{-6} M). The addition of glucosamine caused a significant increase in the absorbance intensity at 415 nm and clear decrease at 340 nm. The presence of sharp isosbestic points at 300, 315, and 380 nm indicates that only two species coexist in equilibrium. The individual profile (see the Supporting Information) of the band at 415 nm (increasing) also demonstrates the occurrence of 1:1 stoichiometric host–guest complexations with association constants ($\log K_{ass}$) of 5.52 $\pm$ 0.02 and 4.97 $\pm$ 0.02 for compounds **1** and **2**, respectively. The addition of glucose does not cause any obvious spectroscopic changes, which suggests that the affinities of compounds **1** and **2** for glucosamine are better than for glucose.

Furthermore, the coordination of zinc(II), blocks photoinduced electron transfer (PET) between the quinoline and the amide groups in the ligand, which causes a fluorescence

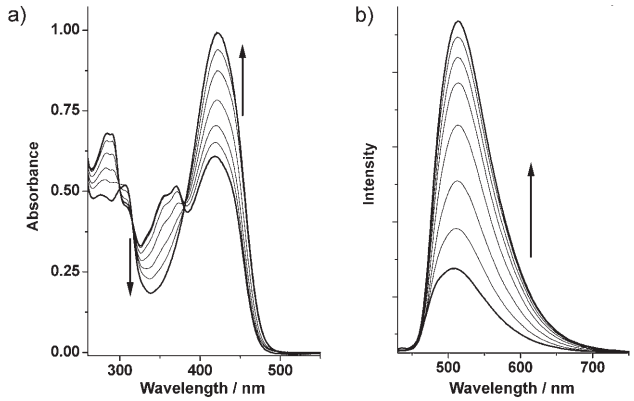

Figure 3. Spectra of compound **2** in acetonitrile: a) UV/Vis spectra (at a concentration of 5.0×10^{-6} M) and b) fluorescence spectra (at a concentration of 5.0×10^{-6} M, excitation at 380 nm), upon addition of a standard solution of glucosamine.

enhancement and, at the same time, opens a photoinduced-charge-transfer (PCT) channel.[7a,15] The metal-tunable emission band of compound **2** in acetonitrile (1×10^{-5} M, excitation at 380 nm) appears at about 530 nm (see the Supporting Information), and the addition of glucosamine causes a significant enhancement of the luminescence (Figure 3b). It is clear that the amide group is an efficient binding–signaling transductor, which can convert the recognition information into both UV/Vis and luminescent responses. From a mechanistic viewpoint, the formation of a donor-type hydrogen bond between the amide groups and the guest molecule could favor electronic delocalization and lower the highest occupied molecular orbital (HOMO) energy of the electronic donors, which would lead to a further blocking of the PET processes that take place between the amide and the quinoline groups and to a significant enhancement of the metal-tunable luminescence signal.[16]

The host–guest complexation of the d^{10} Zn^{II} compound (**2**) with glucosamine was also examined by means of ^{1}H NMR spectroscopic titration (see Figure 4). The observed downfield shifting of the glucosamine signals suggest the inclusion of this molecule into the positively charged cage,[17] and the presence

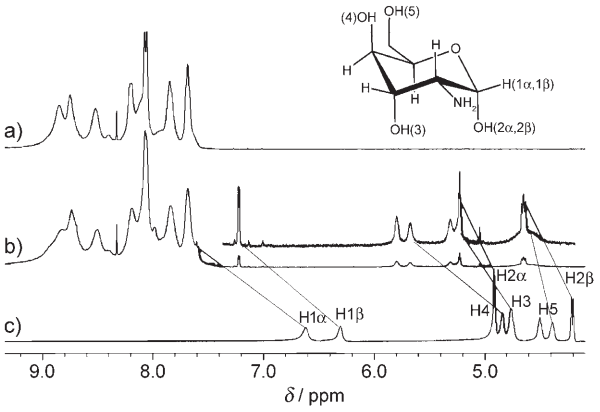

Figure 4. ^{1}H NMR spectra in [D$_6$]DMSO of a) compound **2**, b) compound **2** in the presence of an equimolar amount of glucosamine, c) free glucosamine.

of a new peak at about 16.2 ppm could be an indicator of the formation of hydrogen bonds with the amide groups, which act as donors (see the Supporting Information).

To control the assembly of lanthanide ions and obtain highly ordered architectures, the ligands must be highly predisposed and the lanthanide ions must be modified using auxiliary ligands to prevent further connections.[18] Using pyridine—instead of quinoline—moieties gave the ligand $H_3\mathbf{L^2}$, which retained the N_2O tridentate units for the assembly of octahedral structures. This ligand can introduce lanthanide ions with high coordination numbers into highly symmetric architectures by decreasing the spatial restriction around the metal center. Treating the ligand $H_3\mathbf{L^2}$ with nickel(II) tetrafluoroborate gave the nickel(II) compound **3**, which crystallizes in the highly symmetric space group $Fd\bar{3}$, with the octahedral cationic cage $[Ni_6(H_9\mathbf{L^2}_4)]^{9+}$ exhibiting an ideally octahedral symmetry.[19]

Using $Eu(NO_3)_3\cdot6H_2O$ in the synthetic procedure gave compound **4**. Single-crystal structural characterization demonstrated the formation of a lanthanide-based octahedral cage (Figure 5).[19] The $[Eu_6(H_3\mathbf{L^2})_4(NO_3)_{12}]^{6+}$ cage crystallizes

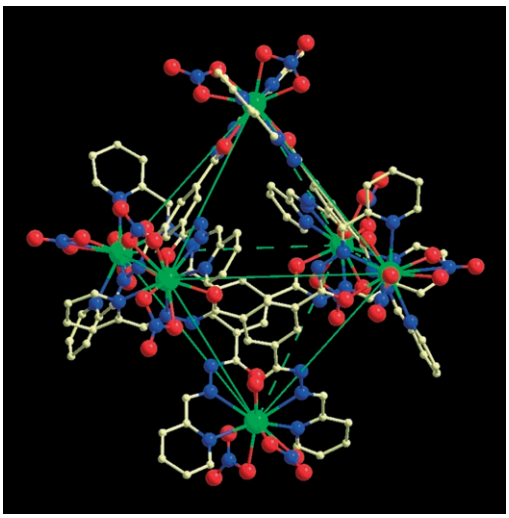

Figure 5. Structure of the octahedral cage $[Eu_6(H_3\mathbf{L^2})_4(NO_3)_{12}]^{6+}$ (of compound **4**). Hydrogen atoms are omitted for clarity. The metal, oxygen, nitrogen, and carbon atoms are green, red, blue, and gray, respectively.

in the highly symmetric space group $R\bar{3}$ and exhibits crystallographic threefold symmetry, with one of the four ligands positioned on a threefold axis. Two Eu^{III} ions bridged by one ligand are separated by a distance of about 10.5 Å, and each metal center is coordinated by two N_2O tridentate chelating units and two bidentate coordinating nitrate anions. Replacing $Eu(NO_3)_3\cdot6H_2O$ with $Tb(NO_3)_3\cdot6H_2O$ gave compound **5.** The octahedral cage $[Tb_6(H_9\mathbf{L^2}_4)(NO_3)_9]^{6+}$ in this compound also exhibits a crystallographic threefold symmetry, but it crystallizes in the space group $P\bar{3}c1$.[19] Each cage in the crystal connects three neighbors through intermolecular interactions, thereby featuring a two-dimensional (6,3) sheet. Adjacent sheets stack to form 1D nanochannels (see the Supporting Information).

Solid-state emission spectroscopy data demonstrate the presence of a strong intrinsic red luminescence signal for compound **4**, which can be attributed to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transitions.[20] The analogue compound **5** exhibits green luminescence (see the Supporting Materials). Clearly, this synthetic strategy is an efficient way to obtain metal-tunable molecular cages, thereby preserving the integrity of the whole structure. Although the poor solubility of the lanthanide compounds in most organic solvents prevents us from studying the host–guest interactions present in this case, changing the anion could improve their solubility and thus their sensing properties.

In summary, we report a new strategy for preparing metal-tunable octahedral nanocages with potential applications in molecular sensing. The introduction of an amide group does not only provide a guest-accessible functional site but also offers an efficient communicator that is able to convert the recognition information into an optical signal. Our strategy can be extended to other metal-tunable Werner-type capsules composed of lanthanide ions (which exhibit a low stereochemical preference), and could therefore be used to fabricate size- or shape-selective dynamic molecular chemosensors with various responses and metal-triggered functions.

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[10] Crystal data: **1**: $[Co_6(C_{156}H_{105}N_{36}O_{12})]\cdot 9\,ClO_4\cdot 5\,CHCl_3\cdot 25\,CH_3OH\cdot H_2O$, hexagonal, $R\bar{3}$, $a = 26.360(1)$ Å, $c = 61.768(2)$ Å, $V = 37171(1)$ Å^3, $T = 180(2)$ K, $R_1 = 0.0797$, and $wR_2 = 0.2268$ for 6509 reflections with $I \geq 2\sigma(I)$. **2**: $[Zn_6(C_{156}H_{105}N_{36}O_{12})]\cdot 9\,ClO_4\cdot 2\,HCCl_3\cdot 16\,CH_3OH\cdot H_2O$, hexagonal, $R\bar{3}$, $a = 25.907(1)$ Å, $c = 61.528(1)$ Å, $V = 35764(1)$ Å^3, $T = 180(2)$ K, $R_1 = 0.0770$, and $wR_2 = 0.2028$ for 4708 reflections with $I \geq 2\sigma(I)$. CCDC 656405 (**1**) and 656404 (**2**) 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.

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[19] Crystal data: **3**: $[Ni_6(C_{108}H_{81}N_{36}O_{12})]\cdot 9\,BF_4\cdot 0.5\,CHCl_3\cdot 14.5\,CH_3OH\cdot H_2O$, cubic, $Fd\bar{3}$, $a = 42.364(1)$ Å, $V = 76029(1)$ Å^3, $T = 180(2)$ K, $R_1 = 0.0789$, and $wR_2 = 0.2167$ for 1471 reflections with $I \geq 2\sigma(I)$. **4**: $[Eu_6(C_{108}H_{84}N_{36}O_{12})(NO_3)_{12}]\cdot 6\,NO_3\cdot 8\,CHCl_3\cdot 7\,H_2O$, hexagonal, $R\bar{3}$, $a = 28.796(1)$ Å, $c = 44.685(2)$ Å, $V = 32089(2)$ Å^3, $T = 180(2)$ K, $R_1 = 0.0763$, and $wR_2 = 0.2039$ for 4547 reflections with $I \geq 2\sigma(I)$. **5**: $[Tb_6(C_{108}H_{81}N_{36}O_{12})(NO_3)_9(H_2O)]\cdot 6\,NO_3\cdot 6\,CHCl_3\cdot 5\,CH_3OH\cdot 2\,H_2O$, trigonal, $P\bar{3}c1$, $a = 28.858(4)$ Å, $c = 38.894(8)$ Å, $V = 28052(8)$ Å^3, $T = 180(2)$ K, $R_1 = 0.0779$, and $wR_2 = 0.2438$ for 4586 reflections with $I \geq 2\sigma(I)$. CCDC 656406 (**3**), 656407 (**4**), and 656408 (**5**) 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.

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