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Lanthanide-Hinged Calixarene Bicapsules: Discrete Hexanuclear Ln^{III}/Phenanthroline/*p*-Sulfonatocalix[4]arene Oligomers (Ln = Gd, Tb)

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The dumbbell-like calixarene bicapsule in two novel Ln^{III}–C4AS compounds was found to be a hexanuclear Ln^{III}/phenanthroline/*p*-sulfonatocalix[4]arene oligomer. The magnetic and luminescent properties of these compounds were examined.

Introduction

Recently the water-soluble sulfonated calix[*n*]arenes (*n* = 4–8) have been attracting considerable attention in supramolecular and coordination chemistry.[1] Amongst them, the smallest, *p*-sulfonatocalix[4]arene(C4AS),[2] has been the most-widely studied mainly because of its cone conformation and ease of synthesis. Various inclusion and/or coordination complexes of *p*-sulfonatocalix[4]arene have been reported with main group, transition metal, and lanthanide species, and with additional organic supramolecular building components.[3] It is noted that most of the reported structures exhibit pairs of calixarenes arranged into molecular capsules in which crown ethers or other related disc-shaped molecules are encapsulated.[4–9] Many reports deal with the isolated molecular capsules or "Russian dolls", and a few contain 1D/2D capsule polymers bridged by sodium or lanthanide ions. 2D capsule layers are described in the supramolecular complexes of C4AS and (*S*)-tyrosine or (*R*,*S*)-phenylalanine, in which the "upper" and "lower" calixarenes in one capsule are bridged by sodium ions [in the case of (*S*)-tyrosine] or unconnected [in the case of (*R*,*S*)-phenylalanine].[5] The (*S*)-serine and C4AS system is more complex because the introduction of additional sodium or cesium leads to the formation of bridged 2D capsule layers (with a fourfold excess of sodium chloride) or 1D capsule chains (with a twofold excess of cesium bromide).[6] Another exception is the lanthanide and C4AS system. 1D coordination capsule chains bridged by sodium cations form in the scandium and C4AS system in the absence of [18]-crown-6, whereas a 2D capsule-layer structure is found in which an 'up' and a 'down' calixarene unit from two neighboring Sc-coordinated calixarene sheets form a structure to encapsulate the crown-ether molecule.[7] Similar 2D capsule layers were also observed in the Ln–C4AS system (Ln = Ce, Nd, Sm, and Eu) in the presence of a [2.2.2]cryptand.[8] However, in the Nd–C4AS system with 1-aza-15-crown-5, four neodymium metals coordinate to the sulfonate groups of both the upper and lower calixarenes of each capsule such that the closed capsules are bridged into 2D hinged capsule layers.[9] Here we present a novel calixarene capsule oligomer, "hinged bicapsule", which will aid in the understanding of the transformation from isolated capsules to 1D/2D capsule polymers or even to 3D coordination metal–calixarene frameworks.

Results and Discussion

The isostructural compounds $[Ln_3(C_{12}H_8N_2)_4(C_{28}H_{19}S_4O_{16})(C_{28}H_{20}S_4O_{16})(H_2O)_n]$ {Ln = Gd (**1**) and Tb (**2**), *n* = 26.5 and 27.5 for **1** and **2**, respectively} were synthesized by the hydrothermal method. Both compounds crystallize in the triclinic system with space group $P\bar{1}$. The striking feature of both structures is the lanthanide-hinged calixarene bicapsules, i.e. hexanuclear Ln_6(phenanthroline)$_6$(C4AS)$_4$ units. The calixarene bicapsules are interconnected by π-stacking interactions to form 2D wavelike layers that are further connected to form a 3D extended structure by C–H···π interactions and additional molecular interactions.

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The solvent water molecules are located in the interstices and generate H-bonding interactions between each other and with the bonded water molecules or sulfonate groups.

In the structures, there are three crystallographic positions for the metal cations with three differently bonded phenanthroline molecules (Figures 1 and S1). All three Ln sites are coordinated by eight atoms but they have different coordination environments, i.e. Ln1 is coordinated to one phenanthroline molecule and three sulfonate groups from three different calixarenes, while Ln2 and Ln3 are coordinated to one phenanthroline molecule, five water molecules, and one sulfonate group. We note that the phenanthroline molecules bonded to Ln1 and Ln2 perch over the cavities of the calixarenes, while that bonded to Ln3 is located outside. There are two crystallographic calixarene molecules with different coordination environments, one bonded to Ln1 and Ln3 by two adjacent sulfonate groups and the other bonded to Ln1 and Ln2 by two opposite sulfonate groups. Both calixarene molecules adopt a pinched-cone conformation. These two calixarene molecules bridged by Ln1 are located face-to-face to form a capsule or a C-shaped subunit that is similar to a single-bridged double calixarene. After an inversion operation through the symmetry center, another capsule is generated and a bicapsule forms with two Ln1 atoms that hinge all the four calixarene units (Figure 1).

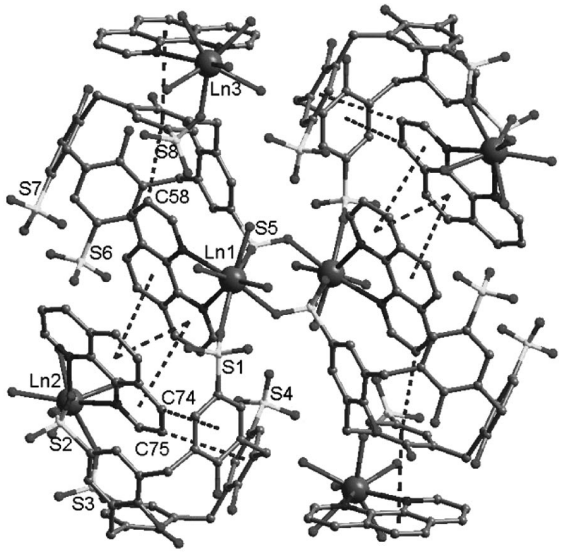

Figure 1. A bicapsule formed by a hexanuclear Ln unit showing the π···π and C–H···π interactions (dotted lines). All hydrogen atoms are omitted for clarity.

Within a bicapsule unit, the phenanthroline molecules bonded to Ln1 and Ln2 are encapsulated in the cavity of the capsule with π···π stacking interactions between each other (Cg···Cg, 3.580–3.984 Å) and C–H···π interactions between the phenanthroline molecules and aromatic rings of the calixarenes [C74–H74···π (C21–C25, C1) 3.678 Å, 170° in **1** and 3.642 Å, 172° in **2**; C75–H75···π (C15–C19, C28) 3.613 Å, 135° in **1** and 3.596 Å, 136° in **2**; C58–H58···π (C43–C47, C56) 3.453 Å, 141° in **1** and 3.440 Å, 142° in **2**] (Figure S2). The phenanthroline molecules bonded to Ln3 also form π···π stacking interactions with the calixarene (π_{phen}···$\pi_{calixarene}$ [(C43–C47, C56), 3.614 (**1**) and 3.599 Å (**2**)]. By comparing the sulfonate groups bonded to the metal atoms, one can see that there are two kinds of sulfonate groups – one in which S5 is bonded to the metal atoms and the other in which S1, S3, and S8 is bonded to one metal atom. Two Ln1 atoms and two sulfonate groups with S5 atoms form an 8-atom ring that hinges two adjacent capsules to form a dumbbell-like bicapsule. The bicapsules are then connected into linear chains by the π···π stacking interactions between the outside phenanthroline and aromatic rings of C4AS (Cg···Cg, 3.901–4.085 Å), which are further interconnected with each other by other π···π stacking interactions between the aromatic rings of C4AS [(C3–C7, C26) 3.885 (**1**) and 3.870 (**2**) Å] to form a wavelike layer (Figure 2). The 3D supramolecular structure is constructed by the bridging of isolated phenanthroline molecules and the

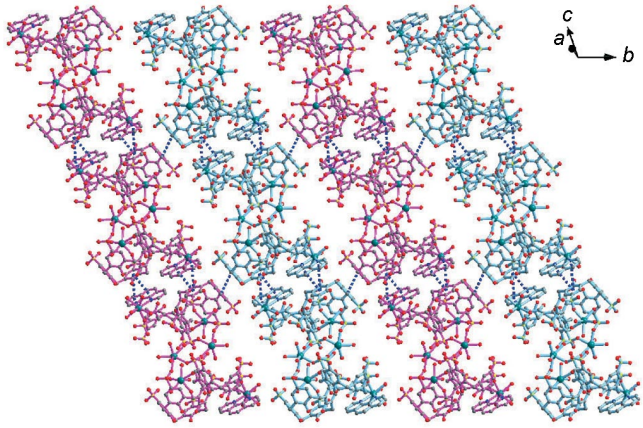

Figure 2. A wavelike layer showing the adjacent 1D chains in purple/grey and cyan/grey.

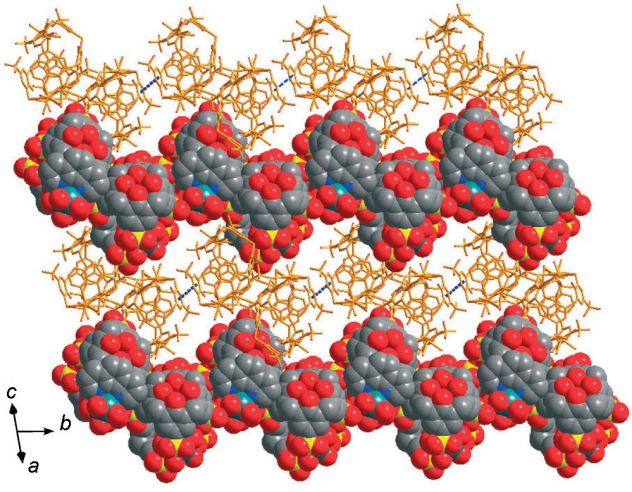

Figure 3. View of the extended structure showing the wavelike layers. The adjacent layers are illustrated in wireframe and spacefill styles. The blue dotted lines show the π···π stacking interactions between the 1D chains. All hydrogen atoms and isolated oxygen atoms are omitted for clarity.

wavelike layer (Cg···Cg, 3.717–4.081 Å), and by the hydrogen bond between the phenanthroline group and sulfonate oxygen atoms (C97–H97···O16, 3.257 Å, 169° in **1** and 3.341 Å, 167° in **2**), as well as by other molecular interactions (Figure 3 and Figures S2–S5).

The magnetic susceptibility of compound **1** was measured in the temperature range 2–300 K. Figure 4 shows the temperature dependence of the magnetic susceptibility in the form of $\chi_M T$ vs. T for **1**. Upon cooling, the $\chi_M T$ value slightly decreases from 8.04 to 7.52 $cm^3 mol^{-1} K$ at 2 K, which suggests weak antiferromagnetic interaction between the Gd^{III} ions. According to the crystal structure of **1** described above, two Gd1 atoms generated through a symmetry centre are the nearest neighbors. However, the distance Gd1–Gd1 is 6.075 Å, and this large separation allows us to consider that all the Gd atoms are magnetically isolated. The weak antiferromagnetic behavior of **1** may be attributed to the superexchange between the metal centers.[10]

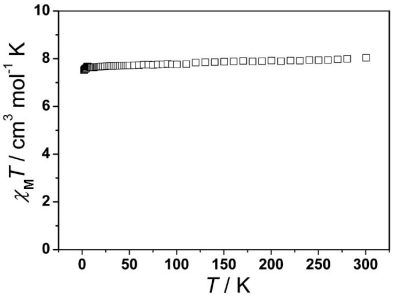

Figure 4. Thermal dependence of $\chi_M T$ for **1** at 0.1 T, which is indicative of weak antiferromagnetic interaction between the gadolinium(III) ions.

The solid-state luminescence behavior of compound **2** was investigated at room temperature (Figure 5). Upon excitation at 303 nm, the obtained spectrum exhibits four characteristic emission bands centered at 619, 583, 543, and 489 nm, which originate from $^5D_4 \rightarrow {}^7F_J$ (J = 3, 4, 5, 6) transitions of the Tb^{3+} ion, respectively. The $^5D_4 \rightarrow {}^7F_5$ transition at 543 nm (green) is most prominent. The strong luminescence of compound **2** indicates efficient energy transfer processes from the C4AS ligand to the Tb^{3+} ion. This indicates clearly that, on the one hand, the calixarene behaves as a good antenna chromophore for UV and near-UV light because of its large π-conjugate system that expands over the entire molecule, and on the other hand, the pinched-cone conformation of the calixarene leads to a higher energy level of the ligand-based excited state than the Tb^{III}* level, which prevents energy back-transfer processes from Tb^{III} to the calixarene ligand.[11]

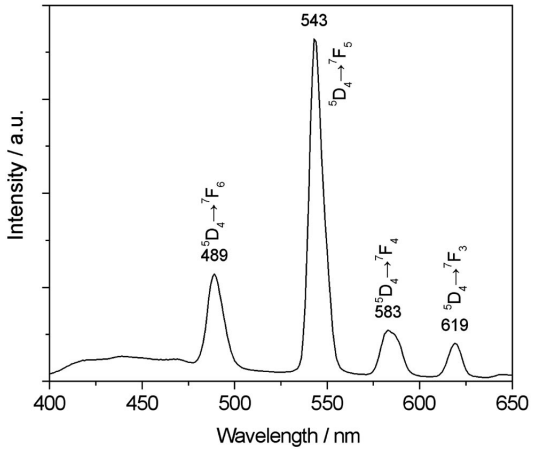

Figure 5. Room-temperature solid-state emission spectrum of **2** (303 nm) showing the characteristic emission bands of Tb^{3+}.

Conclusions

In conclusion, two novel Ln^{III}–C4AS compounds have been synthesized containing the rarely reported Ln^{III}-hinged calixarene bicapsules, which further interconnect to form 2D wavelike layers by π···π stacking interactions and then a 3D extended structure by hydrogen bonding and π···π stacking interactions. The Gd-containing sample exhibits a very weak antiferromagnetic interaction between the Gd^{3+} ions, and the Tb-containing shows characteristic Tb-centered luminescence, which indicates efficient energy transfer from the calixarene unit to the Tb^{3+} ion. This work also presents an example for the fourfold coordination calixarene oligomers, which should aid in the understanding of the formation of 1D/2D capsule polymers and also the 3D coordination metal–calixarene networks.

Experimental Section

Syntheses of 1 and 2: A suspension of the sodium salt of *p*-sulfonatocalix[4]arene (100 mg), $LnCl_3 \cdot 6H_2O$ (60 mg, Ln = Gd and Tb), and 1,10-phenanthroline (40 mg) in water (10 mL) was transferred into a Teflon-lined autoclave (20 mL) and heated to 130 °C over 90 min. The autoclave was kept at 130 °C for 4 d and then slowly cooled to 30 °C at about 4 °C h^{-1}. The final pH value was about 4. Yellow single crystal blocks were collected for the X-ray diffraction determination and other measurements. Yield: ca. 10% with respect to calixarene.

Variable-temperature magnetic susceptibility measurements, zero-field ac magnetic susceptibility measurements, and the field dependence of magnetization of **1** were performed on an Oxford Maglab 2000 System or a Quantum Design MPMS-XL5 SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables). The photoluminescence emission spectra of **2** were recorded with a Hitachi F-4500 spectrophotometer equipped with a 150-W xenon lamp as the excitation source. The X-ray intensity data for compounds **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) operated at 2.0 kW (50 kV, 40 mA). The crystal structures were solved by means of direct methods and refined by employing full-matrix least-squares on F^2 (SHELXTL-97). All the non-hydrogen atoms were refined anisotropically, with the exception of the water oxygen atoms which were refined without hydrogen atoms. CCDC-664263 (**1**) and -664264 (**2**) contains 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.

Crystal Data for 1: $C_{104}H_{124.07}Gd_3N_8O_{58.53}S_8$, M = 3150.97 g mol^{-1}, triclinic, $P\bar{1}$, a = 17.8825(9) Å, b = 19.8403(10) Å, c = 19.8596(10) Å, α = 110.4380(10)°, β = 102.6290(10)°, γ = 93.9080(10)°, V = 6361.8(6) Å^3, Z = 2, $D_{calcd.}$ = 1.613 g cm^{-3}, μ = 1.776 mm^{-1}, T = 150(2) K, θ_{max} = 25.0°, F(000) = 3064, crystal dimensions 0.12 × 0.18 × 0.20 mm, reflections collected/unique 35294/22083 (R_{int} = 0.029), final R_1 = 0.0641, wR_2 = 0.1854 [$I > 2\sigma(I)$], GooF = 1.04.

Crystal Data for 2: $C_{104}H_{126.01}N_8O_{59.51}S_8Tb_3$, M = 3173.46 g mol^{-1}, triclinic, $P\bar{1}$, a = 17.8726(8) Å, b = 19.8395(9) Å, c = 19.8406(9) Å, α = 110.5210(10)°, β = 102.7430(10)°, γ = 93.7980(10)°, V = 6346.6(5) Å^3, Z = 2, $D_{calcd.}$ = 1.661 g cm^{-3}, μ = 1.885 mm^{-1}, T = 150(2) K, θ_{max} = 25.0°, F(000) = 3210, crystal dimensions 0.12 × 0.17 × 0.30 mm, reflections collected/unique 43002/22085 (R_{int} = 0.027), final R_1 = 0.0552, wR_2 = 0.1627 [$I > 2\sigma(I)$], GooF = 1.06.

Supporting Information (see footnote on the first page of this article): Figures showing structural details and other magnetic data for **1** are presented.

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