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Spheroid Metallocavitands with Eight Calixarene-Shaped Receptors on the Surface

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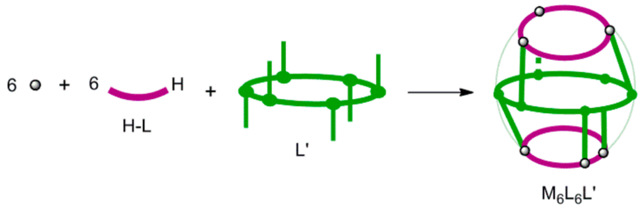
Ⓢ *Supporting Information*

ABSTRACT: Spheroid metallocavitands $[((Re(CO)_3L)_3)_2L']$ with a diameter of ~17 Å, possessing eight solvent-accessible calixarene-shaped receptors on the surface, were obtained from a $Re_2(CO)_{10}$, rigid NN donors (H-L), and flexible hexatopic N donors (L′) in a one-step process.

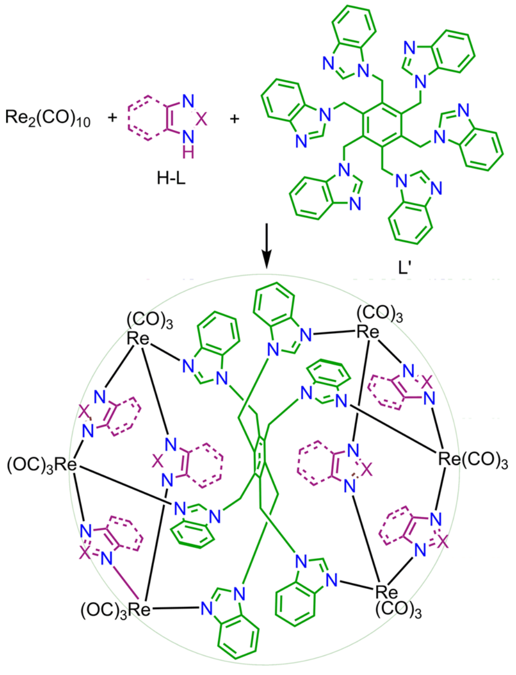
The design and synthesis of metallocavitands, i.e., multimetallic complexes where metal coordination is necessary for cavity formation,[1] using metal acceptors and organic donors have been getting continuous research interest because of their supramolecular phenomena such as host−guest encapsulation, catalysis, and unique regioselective reactivity.[1,2] Countable approaches are known for constructing various shapes and sizes of metallocavitands.[1−7] Among the synthetic principles, the *fac*-$Re(CO)_3$-core-directed method is one of the successful routes to neutral heteroleptic cavitands.[5,6] Up to now, much attention has been focused on modulating the inner cavities of the metallocavitands, decorating the framework with various functional groups, and making interlinked metallocavitands.[1−7] Because of their potentials in various fields, efforts are being directed toward the synthesis of new *fac*-$Re(CO)_3$-core-based cavitands with improved properties. One way to achieve this is to design a spheroid metallocavitand with several receptors on its exterior that is able to accommodate more guest molecules and could show cooperative or anticooperative guest inclusion.[8] Herein we report the first example of a rhenium(I)-based spheroid metallocavitand with eight calixarene-shaped receptors on the exterior. The self-assembly of cavitands was achieved from a $Re_2(CO)_{10}$, rigid NN donors, and flexible hexatopic N donors (Scheme 1).

Scheme 1. Synthetic Approach to a Spheroid Metallocavitand[a]



[a] ○ = *fac*-$Re(CO)_3$, H-L = rigid NN donors, and L′ = flexible hexatopic N donors.

Scheme 2. Synthesis of Spheroid Metallocavitands 1−3



1, X = CH; L = benzimidazolate
2, X = N; L = benzotriazolate
3, X = CH; L = imidazolate

The solvothermal treatment of a $Re_2(CO)_{10}$, NN donors [H-L = benzimidazole (H-benz), benzotriazole (H-btz), or imidazole (H-imz)], and 1,2,3,4,5,6-hexakis(benzimidazol-1-ylmethyl)benzene (L′) in a toluene/acetone solvent mixture resulted in the formation of metallacycles **1**−**3** [$\mathbf{1}\cdot(C_3H_6O)_4(C_7H_8)_2$, **1** = $[((Re(CO)_3benz)_3)_2L']$; $\mathbf{2}\cdot(C_3H_6O)_4$, **2** = $[((Re(CO)_3btz)_3)_2L']$; **3** = $[((Re(CO)_3imz)_3)_2L']$; Schemes 2 and S1 in the Supporting Information (SI)]. The products are air- and moisture-stable and sparingly soluble in organic solvents. The Fourier transform infrared spectrum of complex **1** showed three strong bands around 2025, 1938, and 1896 cm^{-1}, characteristic of a *fac*-$Re(CO)_3$ unit in an asymmetric environment.[5,6] The ^1H NMR spectrum of complex **1a** showed six doublets in the range of 5.4−3.9 ppm with geminal coupling constants (J = 14−16 Hz) for methylene $-CH_2-$ protons (Figures S1−S4 in the SI), indirectly supporting the formation of

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the complex. The upfield shift observed for $-CH_2-$ protons in **1a** may be due to the ring current effect from the adjacent benzimidazolyl and/or benzimidazolate units. The electrospray ionization mass spectra of **1**−**3** showed molecular-ion peaks (*m*/*z* 3183.1986 for $[\mathbf{1}]^+$, 3189.3008 for $[\mathbf{2} + H]^+$, and 2882.1041 for $[\mathbf{3}]^+$) that match the theoretical values (Figures S5−S7 in the SI). The X-ray photoelectron spectra of **1**−**3** confirmed the +1 oxidation state for rhenium ($4f_{7/2}$ and $4f_{5/2}$) in the complexes (Figure S8 in the SI).[9]

The results of single-crystal X-ray studies on crystals obtained in a toluene/acetone solvent mixture showed that complexes **1** and **2** adopt a M_6L_6L'-type spheroid structure with an outside diameter of ~17 Å (Figures 1 and 2). The complexes consist of six *fac*-$Re(CO)_3$ cores, six anionic bridging L units, and one neutral L′ ligand. The spheroids of **1** and **2** can also be viewed as a [2 + 1] assembly product of metallocalix[3]arene units[10] and a propeller-shaped or -sandwiched L′ unit. The alternatively arranged three *fac*-$Re(CO)_3$ cores and an anionic L make up the metallocalix[3]arene unit with cone conformation ((Re−benz−Re−benz−Re−benz); Re···Re = 6.349, 6.368, and 6.414 Å and N−Re−N = 87−90° for **1**). L′ in the complexes acts as a hexamonodentate N donor and takes a *syn,anti,syn,anti,syn,anti* conformation; i.e., three benzimidazolyl units are above the central benzene plane with a vertical head-to-head *syn* conformation, and three benzimidazolyl units are below it. A similar type of arrangement was observed in an acyclic ruthenium complex bearing a L′ ligand.[11] Two distinct solvent-accessible recognition sites are found on the exterior of complexes **1** and **2**. Two exocyclic metallocalix[3]arene units at the top and bottom of the spheroid **1** provide a convergent arrangement of a set of three *exo*-C−H bonds, which can act as H-bond donors (Figure 3). The presence of btz in **2** changes the metallocalix[3]arene functional units as H-bond acceptors and a metal-ligating tridentate binding pocket using three *exo*-N lone pairs (Figure 3).[10a,12,13] A similar type of enforced functional unit is found in M_3L_3L'' (L″ = tripodal N donors)-type metallacycles[10a] and heterocalix[3]triazines.[13] Complexes **1** and **2** possess six calix[4]arene-shaped cavities, which are made up of six benzimidazolate/benzotriazolate and six benzimidazolyl units, on the circular space. The alternatively arranged two neutral benzimidazolyl phenylene (bp) units and two anionic benzimidazolate phenylene (abp) or benzotriazolate units act as structural frameworks for calix[4]arene in **1** or **2**. The nonbonding distances between the upper rims are ~7.5 Å (bp···bp) and ~8.5 Å (abp···abp) in the calix[4]arene unit in **1**. In the crystal packing, spheroids **1** and **2** possess four acetone molecules on the exterior of the calixarene framework. It is worth mentioning that benzimidazole-based flexible ligands are used for making metallosupramolecules.[14]

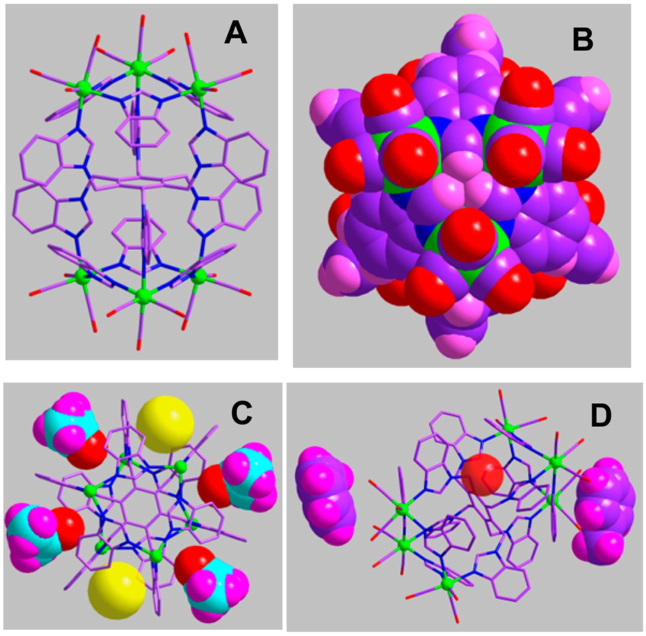

Figure 1. Molecular structures of **1**. For clarity, guest and lattice solvent molecules are omitted in parts A (side view) and B (top view); four guest acetone molecules are shown in the space-filling model, two empty calix[4]arene-shaped cavities are shown as dummy yellow balls, and toluene and CO groups are omitted in part C (top view). Molecular structure of **1a** (D, side view) with guest water (red ball) and lattice toluene molecules shown in the space-filling model. Color code: violet and turquoise, C; pink, H; blue, N; red, O; green, Re.

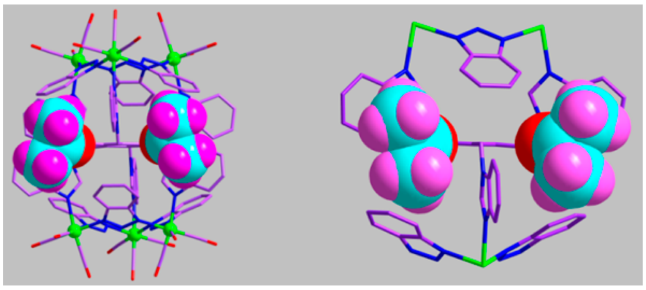

Figure 2. Molecular structure of **2** with two guest acetone molecules shown in the space-filling model (left). Two calixarene units with guest acetone molecules in **2** (right). Color code: violet and turquoise, C; pink, H; blue, N; red, O; green, Re.

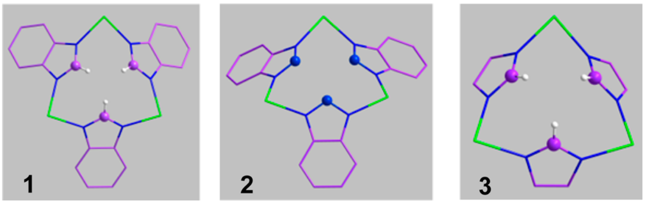

Figure 3. Metallacalix[3]arene units with three C−H bonds in **1** and **3** and three N donors in **2**. Color code: violet, C; white, H; blue, N; green, Re.

The acetone sits inside the cavity by directing the C═O unit inward and has contacts with the walls through the C−H···O bonds [C(48)−H···O(11)(acetone), *d* = 2.632 Å, *θ* = 149°; C(48)−H/C(43)−H···O(10)(acetone), *d* = 2.5667/2.6871 Å, *θ* = 144/127° in **1** (Figures 1 and S9 in the SI). The molecular structure of $\mathbf{1a}\cdot(H_2O)(C_7H_8)_2$, ($\mathbf{1a} = [((Re(CO)_3benz)_3)_2L']$), obtained from a crystal in toluene, possesses one guest water and two lattice toluene molecules (Figure 1D). The spheroid structure of **1a** is similar to that of molecule **1**. The water molecule occupied the inside of the calix[4]arene cavity in **1a**, similar to water in calix[4]arene molecules,[15] whereas the toluene molecules were outside the spheroid molecule and are stabilized by C−H···*π* interactions. However, the crystal structures of **1** and **1a** are different because of the different guest molecules and different orientations of the lattice solvent molecules (Tables S1 and S2 in the SI). The molecular structure of **3** (Figure 4), obtained from toluene/acetone solvent mixture,

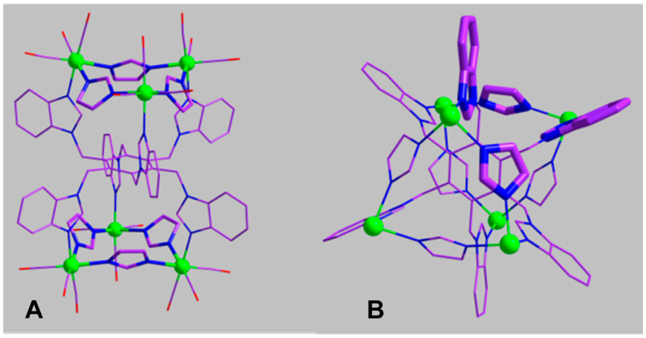

Figure 4. Molecular structures of **3** (A, side view; B, top view; metallocalix[3]arenes are highlighted in part A; one of the metallocalix[4]arenes is highlighted and carbonyl groups are omitted in part B; H atoms are removed for clarity in parts A and B). Color code: violet, C; blue, N; red, O; green, Re.

shows a structure closely similar to those of **1** and **2**. The size of the calix[4]arene cavity in **3** is decreased because of the small size of the imidazolate units (Figure 4). The molecules of **3** are packed in an ABAB pattern. Each spheroid **3** interacts with eight neighboring spheroids through the nonclassical hydrogen-bonding interactions [Re−C≡O(2)···H−C(19), d = 2.388 Å, θ = 166°; Re−C≡O(4)···H−C(3), d = 2.597 Å, θ = 138°; Figures S10 and S11 in the SI].

In conclusion, neutral heteroleptic hexanuclear rhenium-based spheroid metallocavitands with calixarene-shaped receptors on the exterior were self-assembled using two different organic ligands and $Re_2(CO)_{10}$ in a one-step approach. The solid-state structures of the complexes reveal that the *exo*-cavities on the circular space are able to act as receptors for small guest molecules including acetone and water molecules. The two exocyclic metallocalix[3]arene units in the spheroids could act as H-bond donors/H-bond acceptors and a metal-ligating unit.[13] The results also demonstrate that the depth of the cavitand size is tunable by changing the anionic linker. To the best of our knowledge, the complexes are the first *fac*-$Re(CO)_3$-based spheroid supramolecular coordination complexes.[16] The design approach, i.e., the bonding combination of orthogonal tritopic metal acceptors of a *fac*-$Re(CO)_3$ core, rigid angular anionic NN donors (120°), and neutral flexible bis-tripodal N donors, provides a way for assembling spherical molecules with solvent-accessible calixarene-shaped receptors on the exterior, which is very rare in the metal-based metallocavitands. The construction of a larger spheroid with receptors on the surface by replacing six benzimidazolyl units by six pyridyl-coordinating units in the hexatopic donor is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and CIF data for **1**−**3**. 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 interest.

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■ DEDICATION

This paper is dedicated to Dr. Mrinalini G. Walawalkar, Department of Chemistry, IIT- Bombay, India.

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