

Cadmium- and zinc-directed assembly of nano-sized, resorcarene-based host architectures which strongly bind C_{60} †

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Nano-sized molecular loops based on a trimer of resorcarene ligands assembled by six cadmium or zinc ions are shown to strongly bind the spherically shaped fullerene C_{60} in toluene and benzene solutions.

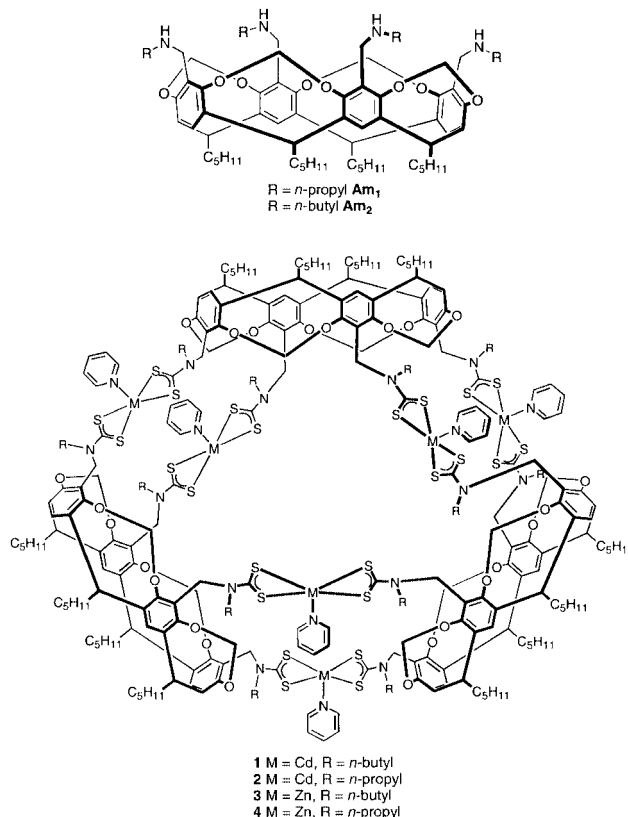
The chalice-shaped molecules, calixarenes, serve as excellent hosts for the binding of organic guest molecules through non-covalent interactions.¹ Pathways to multiple calixarene hosts employing self-assembly techniques that utilise numerous metal–ligand or hydrogen bonding interactions have been described recently.^{2,3} The potential to exploit these and other nano-sized hosts as molecular receptors or containers in which large or multiple substrate molecules can be bound, stored, transported or even reacted upon has generated much recent interest in both their synthesis and properties.⁴ Herein, we demonstrate the cadmium(II)- and zinc(II)-directed assembly of nano-sized host architectures based on a trimer of dithiocarbamate (dtc)-functionalised resorcarene ligands and show these loop-shaped hosts strongly bind buckminsterfullerene, C_{60} , in solution.

The C_4 symmetric resorcarenes are particularly suited for the generation of metal-assembled nano-hosts being easy to functionalise with a range of coordinating moieties. Reaction of tetra(bromomethyl)resorcarene with neat propylamine or butylamine yields tetrakis(alkylaminomethyl)resorcarenes **Am**₁, **Am**₂.† From these secondary amines, the dithiocarbamate cadmium(II) and zinc(II) resorcarene assemblies **1–4** were prepared in a one-pot synthesis from potassium hydroxide, carbon disulfide and metal(II) acetate and isolated as cream coloured powders. Recrystallisation from pyridine–water solutions afforded the pyridine adducts of the hexametallc hosts as pale yellow, prismatic crystals. All four compounds have been characterised by X-ray crystallography; three of the structures (**1**, **2** and **3**) are presented here (Fig. 1 and Table 1)‡ and **4** is described elsewhere.²

Metal complexes **1–4** are isomorphous and consist of three resorcarene cups linked by six divalent metal ions (all of which are crystallographically equivalent). The cup-shaped resorcarene ligands provide the corners of an equilateral molecular triangle whose sides are *ca.* 19–20 Å in length. In **1**, **2** and **3** the six metal(II) ions are five-coordinate with sulfur atoms of the bidentate dtc unit forming a square-plane [Cd–S 2.590(5)–2.635(5) Å **1**, 2.603(5)–2.641(5) Å **2**, Zn–S 2.444(4)–2.495(4) Å **3**]. Axial coordination *via* a pyridine molecule [Cd–N 2.35(2) Å **1**; 2.32(2) Å **2**, Zn–N 2.124(9) Å **3**] causes a pyramidal distortion which raises the metal ion slightly above the square plane [Cd 0.50 Å **1**, 0.49 Å **2**; Zn 0.53 Å **3**]. The trimeric loop-shaped assembly is formed by two parallel running sets of dtc–M(II)–dtc units on each side of the resorcarene bowl connecting to an adjacent resorcarene bowl.

Previously, calixarene and CTV macrocycles have been shown to bind fullerenes through favourable interactions between the π -electron system of the calixarene aromatics and the surface of the carbon sphere.^{5–7}

† Electronic supplementary information (ESI) available: synthetic, spectroscopic and crystallographic data for **1–4**. See <http://www.rsc.org/suppdata/cc/b0/b000481m/>



Purple solutions of C_{60} in toluene or benzene turn red–brown on addition of colourless hosts **1–4**. Such a colour change is

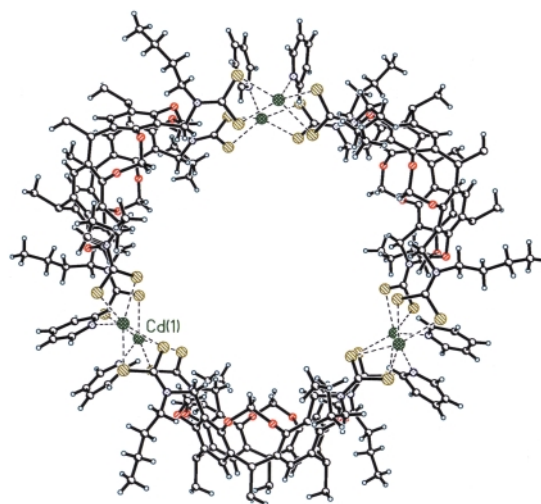


Fig. 1 View of the molecular structure of $Cd_6(L^1)_3$ **1**. For clarity, *n*-butyl chains at the bases of the resorcarenes have been removed.

Table 1 Structural parameters for hosts **1–4**

Host	M(II)	R	Intramolecular distances (Å)		Cavity dimensions (Å) ^c
			M...M(adj) ^a	M...M(opp) ^b	
1	Cd	Bu ⁿ	6.74	14.65	19.58
2	Cd	Pr ⁿ	6.73	14.72	19.59
3	Zn	Bu ⁿ	6.65	14.59	19.18
4	Zn	Pr ⁿ	6.61	14.69	19.13

^a Adjacent metal ions. ^b Opposite metal ions, *i.e.* across the cavity.

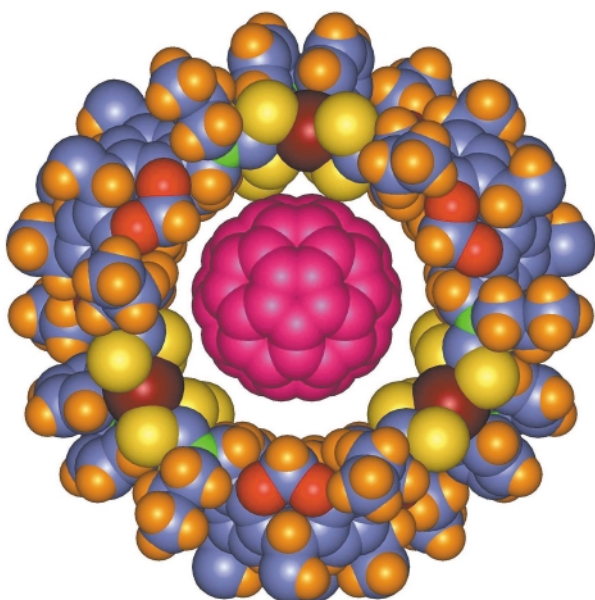
^c Dimensions of the cavity defined by carbon atoms close to the base of the resorcarene.

Table 2 Association constants (log K_{ass}) for host structures **1–4** and guest C₆₀ ($T = 295$ K)

Solvent	1	2	3	4
Benzene	4.7 ± 0.3	> 6 ^a	4.41 ± 0.03	4.07 ± 0.03
Toluene	4.3 ± 0.2	5.1 ± 0.1	3.70 ± 0.05	3.47 ± 0.03

^a Owing to the strength of binding a satisfactory convergence in the fitting program could not be reached.

indicative of a binding interaction between the host and the guest.⁸ To determine the stoichiometry of this interaction, UV–VIS absorption spectra of mixtures of known concentrations of host and guest species in toluene were examined using a method of continuous variance, commonly known as Job's method.⁹ Maxima in the curve of the Job's plot were observed at 1:1 concentration ratios of host and guest for all four compounds. The strength of binding was probed further by standard UV–VIS titration experiments of host and guest. Equivalents of host solutions **1–4** were added to a C₆₀ solution (in benzene or toluene) and the absorbance in the UV–VIS spectrum monitored. From this data, binding constants for the host–C₆₀ complexes in both toluene and benzene solutions were calculated using the computer programme Specfit. Table 2 shows all the host–guest stability constants are of substantial magnitudes and the binding is significantly stronger in benzene. It is noteworthy that the cadmium complexes **1** and **2** bind C₆₀ much more strongly than the zinc complexes **3** and **4**, although the cavity dimensions are very similar. The association constants determined for cadmium hosts **1** and **2** exceed those reported by

**Fig. 2** Space filling model of host–C₆₀ complex showing the proposed mode of fullerene binding by loop-shaped hosts **1–4**. For clarity, *n*-butyl chains at the base of the resorcarenes have been removed.

Fukazawa and coworkers who employed mono- and bis-calix[5]arene derivatives⁷ and are comparable in magnitude with a bisporphyrin system reported most recently by Tashiro *et al.*¹⁰

Space-filling CPK representations based on the crystal structures of **1–4** show that the cavity is circular with a diameter of *ca.* 16–17 Å and therefore suitable for the binding of spherically shaped molecules such as C₆₀ (Fig. 2). The interatomic distances and molecular dimensions in **1–4** are all very similar (Table 1). Thus, it is unlikely that the modest differences in host size and shape can reasonably account for the large variation in binding constants observed. Molecular models of C₆₀ inside hosts **1–4** indicate that a possible mode of receptor–guest binding is through the sulfur atoms of the dtc moieties;¹¹ the C₆₀ resting in a cup-shaped cavity formed by sixteen sulfur atoms and the resorcarene bowl. It is the position and electronic nature of these donor atoms, which, affected by the choice of metal ion, may dictate the strength of binding to the electron-deficient fullerene guest species. Studies are in progress to elucidate further details of these binding interactions.

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Notes and references

‡ Crystal data for complexes **1–3**: Cd₆(L¹)₃(py)₆·9H₂O·15EtOH **1**, C₂₈₈H₄₅₀Cd₆N₁₈O₄₈S₂₄, $M = 6376.5$, rhombohedral, space group $R\bar{3}c$, $Z = 6$, $a = 37.65(4)$, $c = 55.36(6)$ Å, $U = 67970$ Å³, $D_c = 0.935$ g cm⁻³, 6903 unique data. Cd₆(L²)₃(py)₆·27H₂O·6EtOH **2**, C₂₅₈H₄₀₈Cd₆N₁₈O₅₇S₂₄, $M = 6117.9$, rhombohedral, space group $R\bar{3}c$, $Z = 6$, $a = 37.52(4)$, $c = 56.04(6)$ Å, $U = 68312$ Å³, $D_c = 0.892$ g cm⁻³, 7089 unique data. Zn₆(L¹)₃(py)₆·10.5H₂O·9EtOH **3**, C₂₇₆H₄₁₇Cd₆N₁₈O_{43.5}S₂₄, $M = 5844.9$, rhombohedral, space group $R\bar{3}c$, $Z = 6$, $a = 37.23(4)$, $c = 55.63(6)$ Å, $U = 66769$ Å³, $D_c = 0.872$ g cm⁻³, 9055 unique data.

All the structures contained several molecules of disordered solvent and were refined on F^2 using SHELXL to R values for observed data of (R_1 , wR_2) 0.141, 0.204 for Cd **1**, 0.112, 0.243 for Cd **2**, and 0.141, 0.212 for Zn **3**.

CCDC 182/1537. See <http://www.rsc.org/suppdata/cc/b0/b000481m/> for crystallographic files in .cif format.

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- The model shown in Fig. 2 was generated on an SG workstation using Cerius² with the Universal Force Field.†

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