

# Megalo-Cavitands: Synthesis of Acridane[4]arenes and Formation of Large, Deep Cavitands for Selective C<sub>70</sub> Uptake

Jonathan Pfeuffer-Rooschütz, Salome Heim, Alessandro Prescimone, and Konrad Tiefenbacher\*

**Abstract:** Deep cavitands, concave molecular containers, represent an important supramolecular host class that has been explored for a variety of applications ranging from sensing, switching, purification and adsorption to catalysis. A major limitation in the field has been the cavitand volume that is restricted by the size of the structural platform utilized (diameter approx. 7 Å). We here report the synthesis of a novel, unprecedentedly large structural platform, named acridane[4]arene (diameter approx. 14 Å), suitable for the construction of cavitands with volumes of up to 814 Å<sup>3</sup>. These megalocavitands serve as size-selective hosts for fullerenes with mM to sub-μM binding affinity for C<sub>60</sub> and C<sub>70</sub>. Furthermore, the selective binding of fullerene C<sub>70</sub> in the presence of C<sub>60</sub> was demonstrated.

**D**eep Cavitands, concave molecular containers with one open end (Figure 1), represent an important host class in supramolecular chemistry.<sup>[1]</sup> The first member, cavitand **1** (Figure 1a), was reported by Cram in 1982.<sup>[2]</sup> Over the last 40 years, a multitude of cavitands has been synthesized and explored for a variety of applications ranging from sensing, switching, purification and adsorption to catalysis.<sup>[3,4]</sup> A large number of cavitands is based on resorcin[4]arene<sup>[5]</sup> as a structural platform that is extended by the installation of aromatic walls via nucleophilic aromatic substitution (see **1**,<sup>[2]</sup> **2**,<sup>[6]</sup> **3**,<sup>[7]</sup> **4**,<sup>[8]</sup> **6**,<sup>[9]</sup> **7**<sup>[10]</sup> in Figure 1 for examples). For such resorcin[4]arene-based deep cavitands two conformers exist, the C<sub>4v</sub> symmetric vase with axially oriented aromatic walls suitable for guest binding, and the C<sub>2v</sub> symmetric kite conformation featuring equatorially oriented aromatic walls enabling guest release and uptake.<sup>[3b,11]</sup> The Rebek group

reported that intramolecular hydrogen bonds can stabilize the vase conformation of cavitand **2**.<sup>[6]</sup> Furthermore, covalent linkages between the walls have been explored as an efficient way of preventing an opening of the vase conformation.<sup>[12]</sup> It has also been demonstrated that the introduction of triptycene moieties as walls enables a more encompassing binding of guest molecules; reducing their exchange rate within cavitands like **6**<sup>[9]</sup> and **7**.<sup>[3j,10,13]</sup>

The synthesis of enlarged cavitands has made tremendous progress and was enabled by the installation of larger, extended aromatic walls.<sup>[8,14]</sup> The resulting cavitands like **4**<sup>[8]</sup> and **5**<sup>[14b]</sup> feature large volumes of up to 400 Å<sup>3</sup> and suitable guests include even fullerene C<sub>60</sub> and calix[4]arenes. However, C<sub>60</sub> binding occurs only at the top of the aromatic walls and not within the deep cavity (see also Supporting Information, Chapter 5.4), resulting in fast guest exchange rates, and modest binding strength ( $K_a = 900 \text{ M}^{-1}$ ).<sup>[8]</sup> The size of the structural platform has prevented the formation of more voluminous cavitands that enable the binding of larger guests within the deep cavity. Besides resorcin[4]arene,<sup>[14]</sup> calix[4]arenes (for example **5** in Figure 1b),<sup>[15]</sup> calix[4]pyrroles,<sup>[16]</sup> tris-norbornadienes<sup>[17]</sup> or xanthene[3]arene (**8** in Figure 1d),<sup>[18]</sup> have been utilized as structural platforms. Xanthene[3]arene is different from the other structural platform as it features an extended aromatic building block; however, as it only forms a cyclic trimer, it does not lead to much more voluminous cavitands.

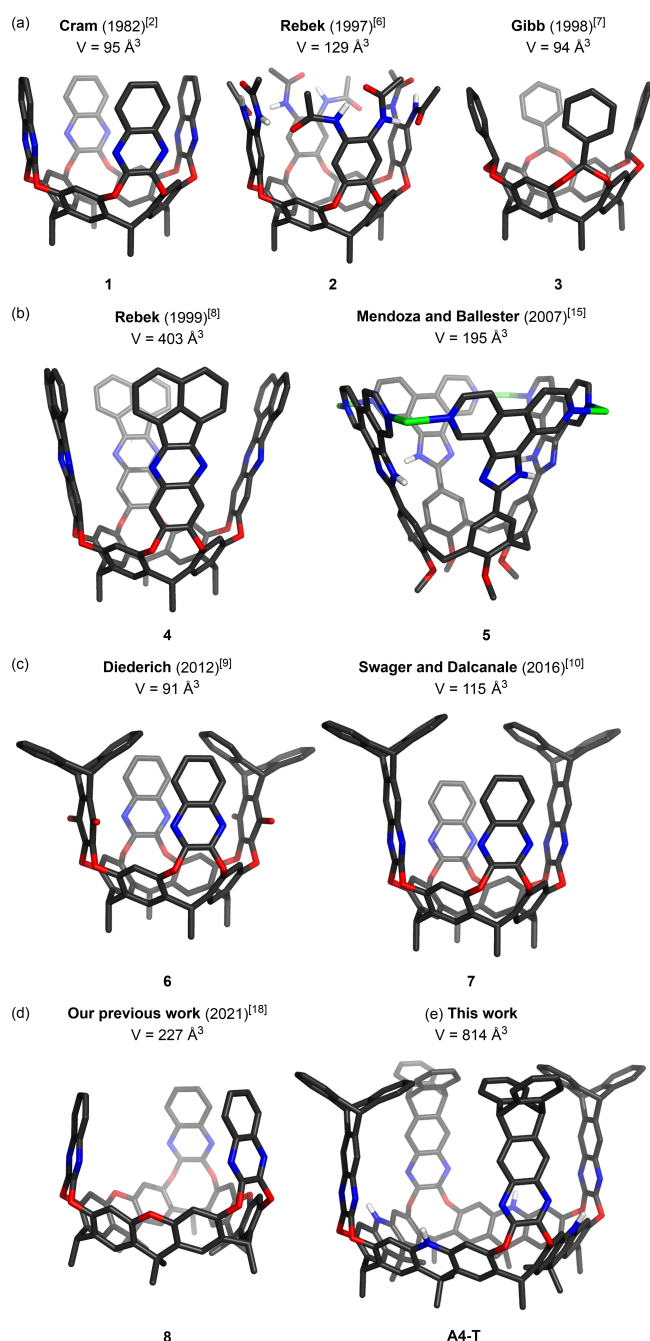
Inspired by the rich chemistry of cavitands, we aimed at expanding the size scope of cavitands by developing a novel structural platform. We here report the synthesis of “acridane[4]arene” macrocycles, which can be accessed in six steps and high yield. Furthermore, we demonstrate their utility by forming unusually large cavitands we propose to name “megalocavitands” (Figure 1e). They feature inner volumes of up to 814 Å<sup>3</sup>.

The synthesis of the key acridane building block **11** involves a simple five-step procedure, that is based on the existing literature on related acridanes (Scheme 1a).<sup>[19]</sup> Synthesis of precursor **10** was achieved by an Ullmann coupling of **9**, followed by esterification of the crude in good yield (65 % over two steps). Subsequently, Grignard-addition followed by Lewis acid-induced ring closure yielded the dimethoxyacridane (74 % over two steps), which was deprotected using BBr<sub>3</sub> to deliver the desired acridane **11** in excellent yield (96 %). Macrocyclization of **11** and dodecanal in the presence of catalytic amounts of triflic acid yielded the acridane[4]arene **12** in 83 % isolated yield after recrystallization from EtOAc. Interestingly, monitoring of the

[\*] J. Pfeuffer-Rooschütz, S. Heim, A. Prescimone, K. Tiefenbacher  
 Department of Chemistry, University of Basel  
 Mattenstrasse 24a, 4002 Basel (Switzerland)  
 E-mail: konrad.tiefenbacher@unibas.ch

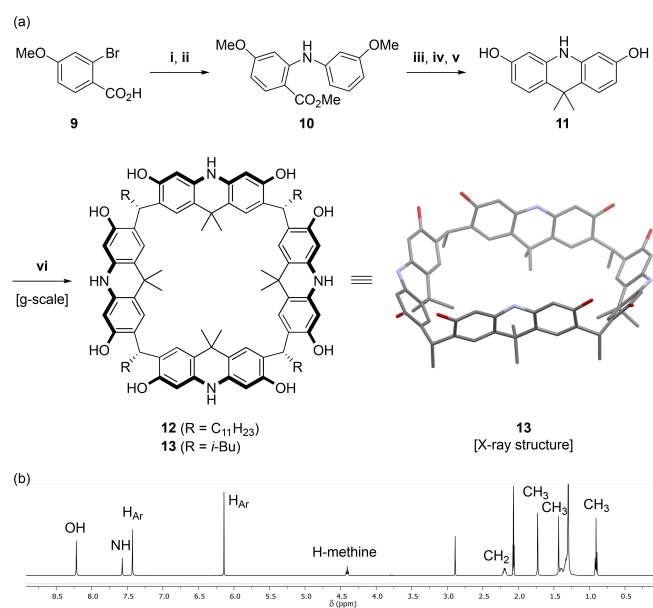
K. Tiefenbacher  
 Department of Biosystems Science and Engineering, ETH Zurich  
 Mattenstrasse 26, 4058 Basel (Switzerland)  
 E-mail: tkonrad@ethz.ch

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**Figure 1.** Selected Cavitands. Molecular models<sup>a</sup> of a) Early deep cavitands 1–3; b) large deep cavitands 4–5 capable of binding of large guests; c) deep cavitands 6–7 with reduced guest exchange rate; d) our previous xanthene[3]arene-based cavitant 8; e) this work: acridane[4]arene-based megalocavitand A4-T. <sup>a</sup> Cavity volumes were calculated using the SwissPdb Viewer v4.1 (see Supporting Information, Chapter 5.3); black = C, white = H, red = O, blue = N and green = Re.

reaction by <sup>1</sup>H NMR indicated the initial formation of several species, including the putative acridane[3]arene, that over time cleanly convert into the acridane[4]arene (see Supporting Information, Chapter 4). This observation suggests a reversible reaction mechanism including ring-opening and equilibration towards the thermodynamically most

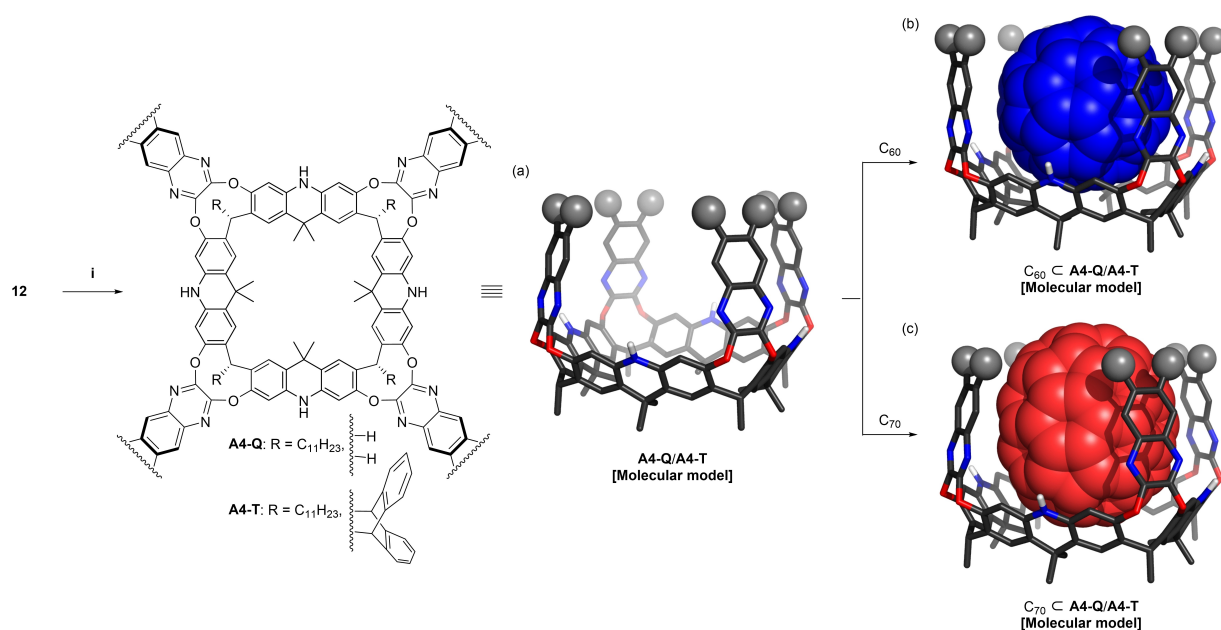


**Scheme 1.** a) Synthesis<sup>a</sup> of Acridane[4]arenes 12–13. b) <sup>1</sup>H NMR spectrum of 13 in acetone-d<sub>6</sub>. <sup>a</sup> Reagents and conditions: (i) 3-Methoxyaniline, CuI, Cs<sub>2</sub>CO<sub>3</sub>, DMF; (ii) MeI, Na<sub>2</sub>CO<sub>3</sub>, MW, 80–115 °C, DMF, 65% over two steps; (iii) MeMgBr, Et<sub>2</sub>O, THF; (iv) BF<sub>3</sub>·Et<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, 74% over two steps; (v) BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 96%; (vi) dodecanal, TfOH, CH<sub>2</sub>Cl<sub>2</sub>, 83% or isovaleraldehyde, TfOH, CH<sub>2</sub>Cl<sub>2</sub>, 53%.

stable product similar to the resorcin[4]arene formation.<sup>[20]</sup> The formation of the crown conformation is favored due to the hydrogen bond pattern of the free phenols and the preference of the R substituents for the axial orientation. Indeed, preliminary density functional theory (DFT) calculations indicate that A-4 is energetically favored over the A-3 (see Supporting Information, Chapter 5.1).

Acridane[4]arene 12 was characterized by <sup>1</sup>H-, <sup>13</sup>C-, and 2D NMR spectroscopy as well as ESI-HRMS measurements. Additionally, the crystalline acridane[4]arene derivative 13, featuring *i*-Bu instead of *n*-Undec feet was synthesized using isovaleraldehyde. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution of 13 in EtOAc at 4 °C. The crystal structure analysis of 13 (space group: *P* $\bar{1}$ ) confirms the crown conformation, which is however slightly deformed, likely due to packing effects. The <sup>1</sup>H NMR spectrum of 12, however, features only one set of sharp, well-defined signals (Scheme 1b), indicating the typical C<sub>4v</sub> symmetry of resorcin[4]arene in solution. Similar differences in the solid and solution state have been observed for related macrocycles.<sup>[21]</sup>

Cavitand formation was first explored with quinoxaline walls.<sup>[2]</sup> In analogy to the resorcin[4]arene-based cavitands, they were introduced by nucleophilic aromatic substitution to deliver cavitant A4-Q in good yields (56%, 93% yield per substitution, Scheme 2). With an internal cavity volume of 626 Å<sup>3</sup>, cavitant A4-Q represents, to our knowledge, the largest cavitant structure to date. We propose the name megalocavitands for cavitands derived from A4, as they feature an unprecedentedly voluminous deep cavity.



**Scheme 2.** Synthesis<sup>a</sup> of megalocavitands **A4-Q** and **A4-T** from the acridane[4]arene scaffold. Molecular models of a) megalocavitands **A4-Q/A4-T**; b) complex  $C_{60} \subset A4-Q/A4-T$ ; c) complex  $C_{70} \subset A4-Q/A4-T$ . <sup>a</sup> Reagents and conditions: (i) 2,3-Dichloroquinoxaline,  $Cs_2CO_3$ , DMF, 56% or 2,3-dichloroquinoxalinetriptycene **S5**,  $Cs_2CO_3$ , DMF, 21%.

Additionally, the even larger triptycene-quinoxaline walls<sup>[10]</sup> were introduced. The resulting cavitant **A4-T** was obtained in good yield considering that eight positions were functionalized (21%, 82% yield per substitution), and features an even larger internal cavity volume of 814 Å<sup>3</sup>. As the access to the cavity is hindered by the triptycene-roof, a reduced guest exchange rate is expected.

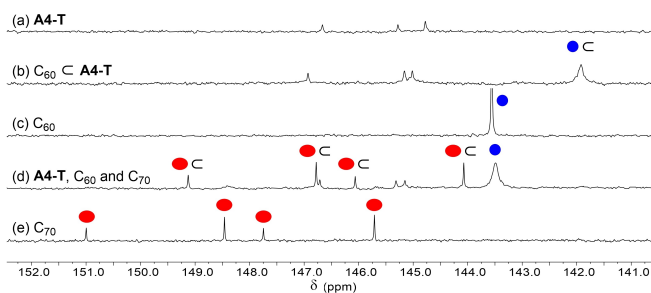
Megalocavitands **A4-Q** and **A4-T** were fully characterized by <sup>1</sup>H-, <sup>13</sup>C-, and 2D NMR spectroscopy as well as HRMS measurements. Both cavitands display good solubility in toluene, chloroform, and dichloromethane, but are insoluble in methanol. **A4-Q** is additionally well soluble in acetone and benzene, whereas **A4-T** is only sparingly soluble in these solvents.

Both cavitands possess an internal cavity suitable for the binding of fullerenes  $C_{60}$  and  $C_{70}$  according to molecular models (see Supporting Information, Chapter 5.2). Although currently alternative methods for fullerene separation or purification are used,<sup>[22]</sup> potential purification by supramolecular recognition has emerged as an attractive alternative.<sup>[23]</sup> However, only a few supramolecular systems are selective towards  $C_{70}$  and cavitant **4** (Figure 1b) is the only deep-cavitant that has been reported for fullerene binding.<sup>[23]</sup> Importantly, binding in **4** is limited to the top region of the cavitant, resulting in a reduced binding affinity ( $K_a = 900 \pm 250 M^{-1}$  for  $C_{60}$  in toluene). Host-guest interactions were investigated using <sup>13</sup>C NMR spectroscopy in toluene-*d*<sub>8</sub> (see Supporting Information, Chapter 3.1). It was observed that upon addition of a stoichiometric amount of megalocavitant **A4-Q** the  $C_{60}$  signal is shifted upfield by -0.84 ppm, while upon further addition of  $C_{60}$  the signal shifts back towards the free  $C_{60}$  signal. This initial upfield shift of the  $C_{60}$  signal indicates that  $C_{60}$  is bound inside the

cavitant in fast exchange on the <sup>13</sup>C NMR time scale. Interestingly for  $C_{70}$ , after similar uptake results were observed for the equimolar mixture of  $C_{70}$  and megalocavitant **A4-Q** (the five  $C_{70}$  signals were shifted between -1.24 and -1.66 ppm), further addition of  $C_{70}$  resulted in the observation of additional free  $C_{70}$  signals, indicating  $C_{70}$  binding in slow exchange on the <sup>13</sup>C NMR time scale. Similarly, both fullerenes,  $C_{60}$  and  $C_{70}$ , were bound by megalocavitant **A4-T** in slow exchange on the <sup>13</sup>C NMR time scale. Accordingly, three of the four host- $C_{60}/C_{70}$  complexes explored, displayed slow-exchange on the NMR time scale, and only  $C_{60}$  was complexed inside **A4-Q** in a fast exchange regime. In both cavitands, only one set of signals was observed for the bound  $C_{70}$  guest, indicating free rotation around the  $C_2$ -axis of  $C_{70}$ .

To further investigate the selectivity of fullerene binding, competition experiments with the megalocavitands **A4-Q** (see Supporting Information, Chapter 3.1.2) and **A4-T** (Figure 2) were performed. After initial stoichiometric uptake of fullerene  $C_{60}$  into **A4-T** (Figure 2b), it is completely exchanged upon the addition of an equimolar amount of  $C_{70}$  (Figure 2d). A similar result was obtained for the cavitant **A4-Q**. This preferential binding of the ellipsoidal  $C_{70}$  over the spherical  $C_{60}$  is likely due to a better shape fit, as seen in molecular models (see Supporting Information, Chapter 5.2).

Binding between the megalocavitands and fullerene guests ( $C_{70}$ ,  $C_{60}$ ,  $C_{60}(CO_2Me)_2$ ) was also followed via UV/Vis titration (see Supporting Information, Chapter 3.2). While all host-guest complexes showed high to very high binding constants, complexes with  $C_{70}$  stood out with sub- $\mu$ M binding affinities (Table 1). This correlates well with the NMR



**Figure 2.**  $^{13}\text{C}$  NMR spectra in toluene- $d_8$  of a) **A4-T** (2.00 mM), b) **A4-T** and  $\text{C}_{60}$  (both 2.00 mM), c)  $\text{C}_{60}$  (2.50 mM), d) **A4-T**,  $\text{C}_{60}$  and  $\text{C}_{70}$  (all 2.00 mM) and e)  $\text{C}_{70}$  (1.00 mM); (blue circle =  $\text{C}_{60}$ ; red ellipsoid =  $\text{C}_{70}$ ).

**Table 1:** Binding constants  $K_a$  of **A4-Q** and **A4-T** and the corresponding guest ( $\text{M}^{-1}$ ) determined by [a] UV/Vis titration in toluene, [b] NMR titration in toluene- $d_8$ .

Guest	<b>A4-Q</b> $K_a$ [ $\text{M}^{-1}$ ]	<b>A4-T</b> <sup>[b]</sup> $K_a$ [ $\text{M}^{-1}$ ]
$\text{C}_{70}$	$(4.88 \pm 1.66) \times 10^{6[\text{a}]}$	$(1.16 \pm 0.11) \times 10^{6[\text{a}]}$
$\text{C}_{60}$	$(2.61 \pm 0.06) \times 10^{3[\text{b}]}$	$(6.49 \pm 0.36) \times 10^{4[\text{a}]}$
$\text{C}_{60}\text{C}(\text{CO}_2\text{Me})_2$	$(1.11 \pm 0.03) \times 10^{3[\text{b}]}$	$(2.64 \pm 0.09) \times 10^{4[\text{a}]}$

experiments that indicated complete uptake of 1.0 equiv of guest.

In conclusion, we describe the efficient synthesis of a novel large structural platform, acridane[4]arenes **A4**, that is suitable for the construction of unprecedentedly large deep-cavitands **A4-Q** and **A4-T**. The acridane[4]arene **12** was synthesized in 6 steps with an overall yield of 38% and requires only three separations by column chromatography. As of yet, only a few suitable macrocycles for the construction of new deep-cavitands are available. Importantly, most used macrocycles so far are rather small with diameters of approximately 7 Å. In contrast, the synthesized acridane[4]arene features a diameter of 14 Å, which translates to large volumes of up to 814 Å<sup>3</sup> in the descendant megalocavitands. The megalocavitands serve as size-selective hosts for fullerenes with mM to sub- $\mu\text{M}$  binding affinity for  $\text{C}_{60}$  and  $\text{C}_{70}$ , respectively. Furthermore, the selective binding of fullerene  $\text{C}_{70}$  in the presence of  $\text{C}_{60}$  was demonstrated. While several  $\text{C}_{70}$  selective host systems have been reported, **A4-Q** and **A4-T** are the first cavitands to achieve this, further demonstrating their unprecedented size. We are convinced that the large volume and versatile structural variation potential of the reported megalocavitands will inspire the construction of future cavitand systems, far beyond what is reported in this communication. For instance, as the extended platform creates apertures at the sides of the cavitands (diameter approx. 6 Å), future work may aim at finding more suitable walls to obtain hosts with improved binding abilities for smaller guests. Furthermore, we expect the novel acridane[4]arene structural platform to be generally very useful as it represents a larger derivative of the resorcin[4]arene workhorse.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Calixarene • Deep Cavitands • Host–Guest Systems • Macrocycles • Supramolecular Chemistry

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