# Synthesis and complexing ability of a new type of molecular clips based on diaza-18-crown-6 or diamino-dibenzo-18-crown-6 with pendant p-tert-butylcalix[4]arenes.

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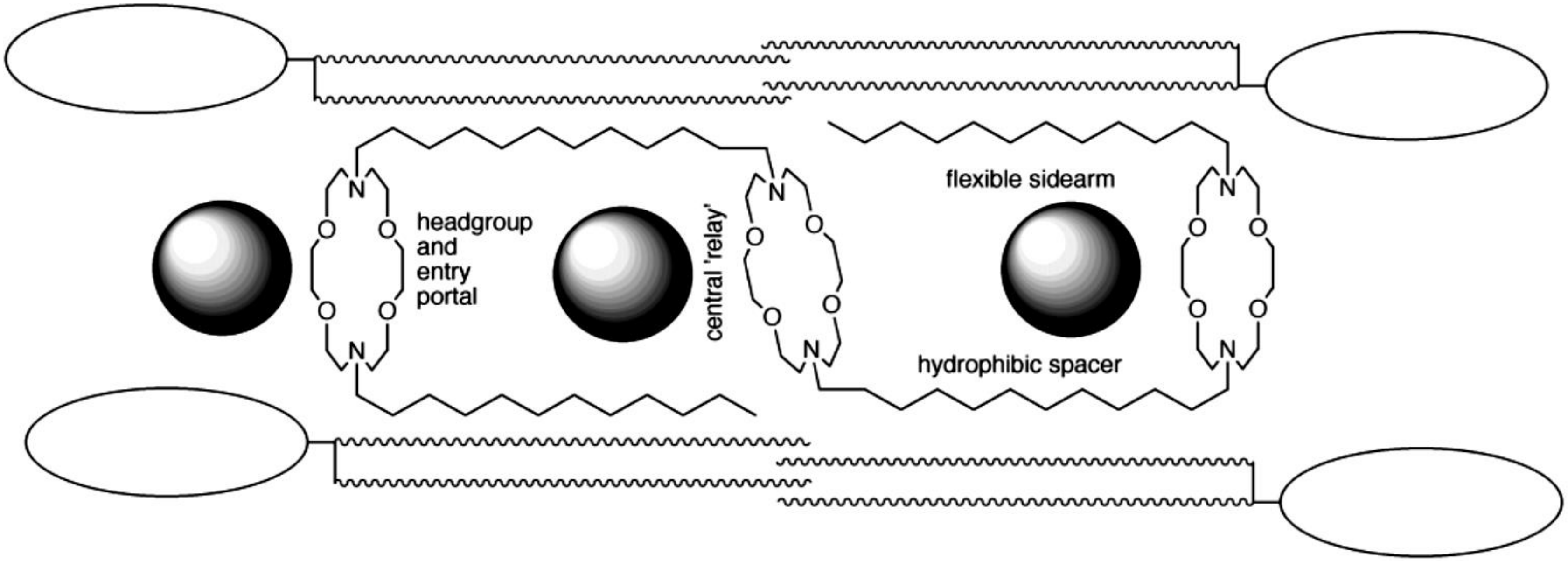
**A convenient method to obtaining a new type of molecular clips based on diazacrown or diamino-dibenzocrown ethers with two calixarene molecules attached to a central fragment using an amide bonds has been developed. The synthesis and complexing properties of two first members of this series - N,N'-bis(p-tert-butylcalix[4]arene-methoxycarbonyl)diaza-18-crown-6 (1) and N,N'-bis( p-tert-butylcalix[4]arene-methoxycarbonyl)-diamino-dibenzo-18-crown-6 (2) were demonstrated in this work. The complexing properties of the obtained compounds were evaluated through spectrophotometric titration method. A clip based on diaza-18-crown-6 forms 1:1 complexes with sodium, potassium and cesium cations (lg$K_{Cs}$ < 3) in the alkali metal series. At the same time, a clip 1 demonstrates exceptional selectivity toward barium in the alkaline earth metal series. The study of complex formation processes involving transition metal cations indicates that clip 1 forms the complexes 1 : 1 (L : M) with cobalt, cadmium and lead cations, but with copper and iron cations this compound interacts with formation of 2 : 1 (L : M) complexes. A different behavior is typical for clip 2 based on diamido-dibenzo-18. With sodium cation 2 forms complexes 1 : 2 (L : M), the complex with the cesium cations is characterized by a high lg$K$ value (> 7), in the series of alkaline earth metals the formation of mononuclear complexes with relatively high stability constants (lg$K$ 3.88 − 4.94) is observed for barium, strontium and calcium cations. On the contrary, clip 2 forms with the magnesium cations a binuclear complex with lg$K_{12}$ 5.75. The same compound in the series of transition metals interacts with cations of copper, iron and cadmium to form 1:1 complexes with low values of stability constants.**

# Starting point

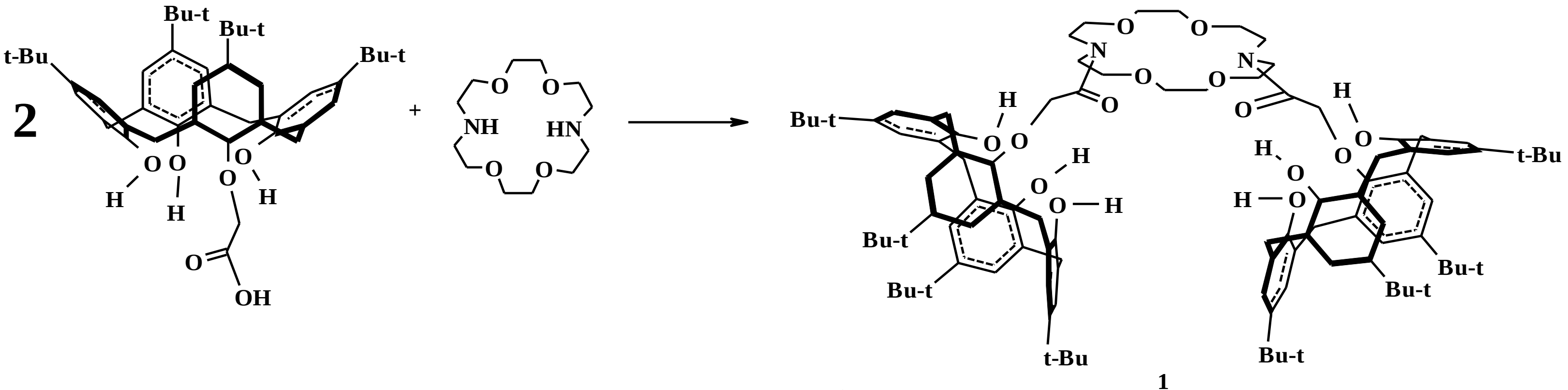
In terms of the design of structures, so-called “hydrophiles” can be said to embody the concept of three macrocycles, where the central macrocyclic ligand serves to pass the cation from one macrocyclic “portal” to another. The hydrophobic sidearms connecting the macrocycles are modified to regulate the length of the channel depending on the nature of the membrane.

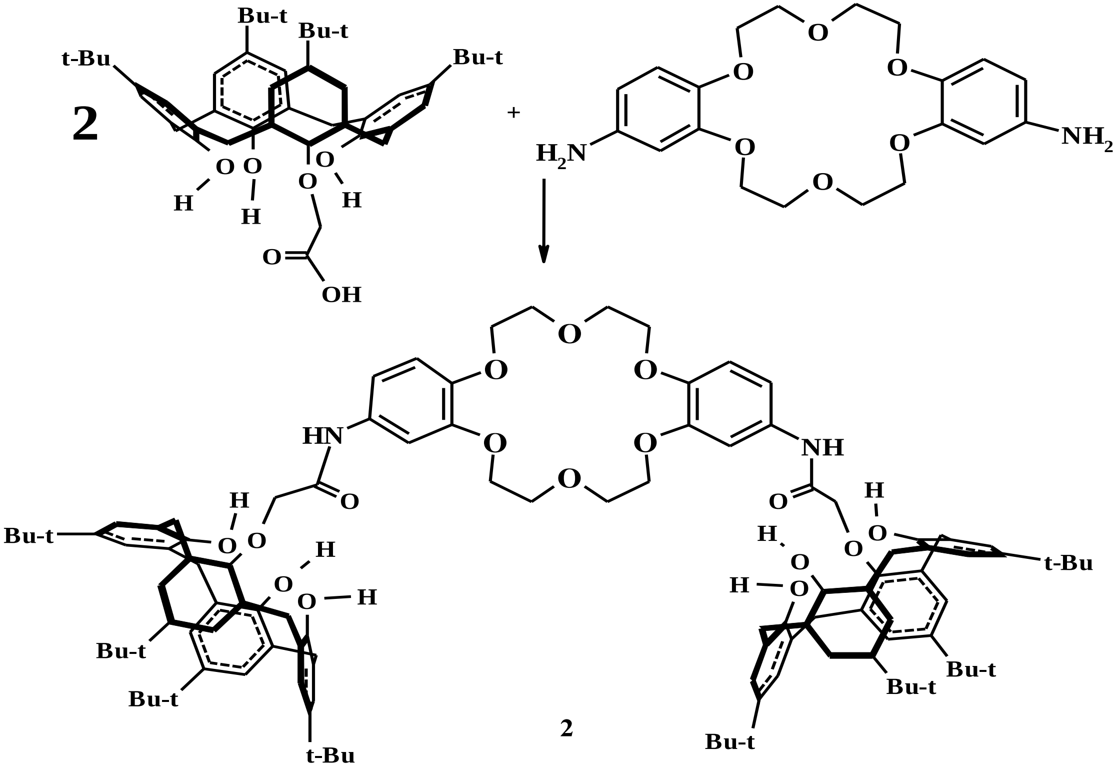


An idealized representation of the tunnel form of tris(macrocycle) based on the linking of three molecules of diaza-18-crown-6

Gokel, G.W. Hydraphiles: design, synthesis and analysis of a family of synthetic, cation-conducting channels. *Chem. Commun*. **2000**, *1*, 1-9.

The idea that inspired our research into creating molecular clips based on calixarenes and crown ethers is to have the calixarenes act as twin-headed amphiphiles, with difunctionalized crown ether as the central moiety. Diazacrown ethers or diamino-dibenzocrown ethers can be used as such central molecules.





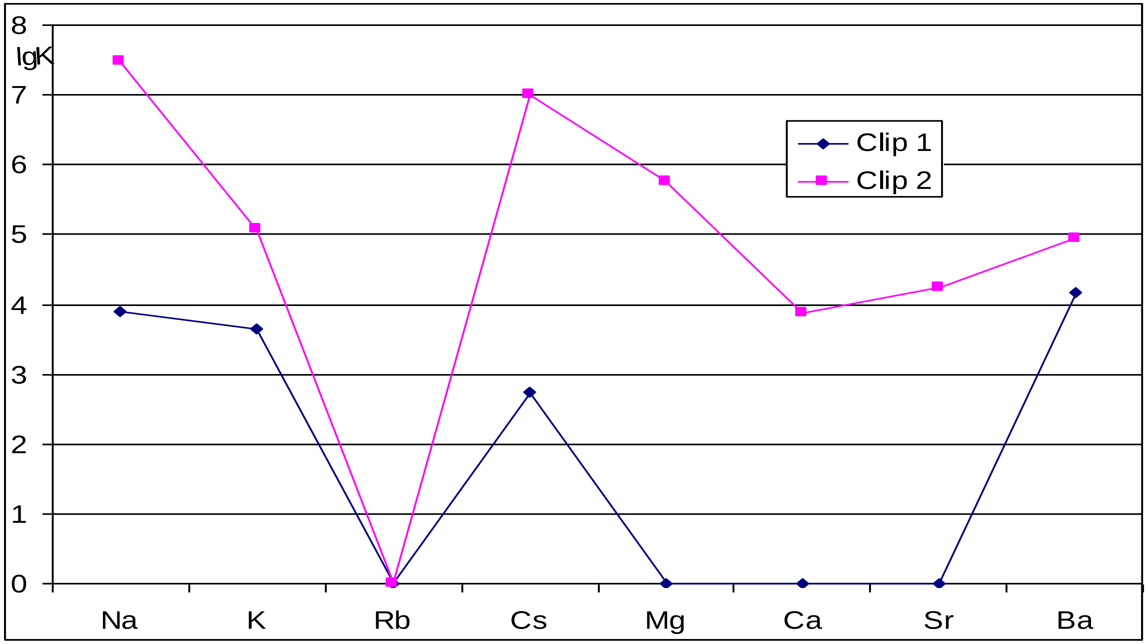
Synthesis of clip **1**: EDC, THF, r.t., 5h, yield - 50%.

Synthesis of clip **2**: EDC, CH$_3$CN, r.t., 3h, yield - 75%.

**Table 1.** Stability constants (lg$K_n$) of the complexes of clips **1** and **2** with alkali and alkaline earth metal cations in MeOH

| **Comp.** | **Cation** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **lg*K*** | **$Na^+$** | **$K^+$** | **$Cs^+$** | **$Mg^{2+}$** | **$Ca^{2+}$** | **$Sr^{2+}$** | **$Ba^{2+}$** |
| **1** | **lg$K_{11}$** | **3.9** | **3.66** | **2.74** | **-*** | **-** | **-** | **4.16** |
| **2** | **lg$K_{11}$** | **2.0** | **5.07** | **7.1** | **1.75** | **3.88** | **4.25** | **4.94** |
| | **lg$K_{12}$** | **7.47** | | | **5.75** | | | |

* The changes in spectrum were too small and it was impossible to calculate the binding constant.



Dependence of the stability of the complexes and the selectivity of the ligands on the nature of the cation of the s-element.
In case clip **2**, data lg$K_{12}$ for complexes with $Na^+$ and $Mg^{2+}$ are given

**Table 2.** Stability constants (lg$K_n$) of the complexes of clips **1** and **2** with transition metal cations and lead in MeOH

| Comp. | Cation (ionic rad.) | | | | | |
|---|---|---|---|---|---|---|
| | | Fe$^{3+}$ (1.28) | Co$^{2+}$ (1.48) | Cu$^{2+}$ (1.44) | Cd$^{2+}$ (1.94) | Pb$^{2+}$ (2.40) |
| 1 | lg$K_{11}$ | 1.57 | 2.4 | 0.41 | 4.40 | 5.23 |
| | lg$K_{21}$ | 7.33 | | 7.03 | | |
| 2 | lg$K_{11}$ | 1.98 | -* | 2.20 | 3.12 | - |

* The changes in spectrum were too small and it was impossible to calculate the binding constant.

Thus, we have obtained new examples of molecular clips based on crown ethers difunctionalized at nitrogen atoms, in which calixarene molecules act as pendant headgroups. We compared the complexing abilities of the novel members of these series based on diaza-18-crown-6 ether and diamido-dibenzo-18-crown ether. The exceptional selectivity of N,N’-bis(calixarenecarbonyl)diaza-18-crown-6 towards barium cations in the series of alkaline earth metals and the possibility to forming binuclear monoligand complexes with sodium and magnesium cations with the participation of N,N’-bis(calixarene)diamido-dibenzo-18-crown-6 have been demonstrated.