

# Università degli Studi di Salerno

*Dipartimento di Chimica e Biologia*

***Dottorato di Ricerca***

**“SCIENZA E TECNOLOGIE PER L’INDUSTRIA CHIMICA,  
FARMACEUTICA E ALIMENTARE”**

**-XI CICLO -Curriculum Chimica**

**2009-2012**

**Tesi di Dottorato**

## **Congegni Supramolecolari basati sul *Threading* di Calixareni**

***Dottorando***

**Carmen Talotta**

---

***Relatore***

**Prof. Placido Neri**

*Università degli Studi di Salerno*

***Co-Relatore***

**Dr. Corrada Geraci**

*CNR-Istituto di Chimica Biomolecolare-CT*

***Contro-Relatore***

**Prof. Alfonso Grassi**

*Università degli Studi di Salerno*

***Coordinatore***

**Prof. Gaetano Guerra**

*Università degli Studi di Salerno*

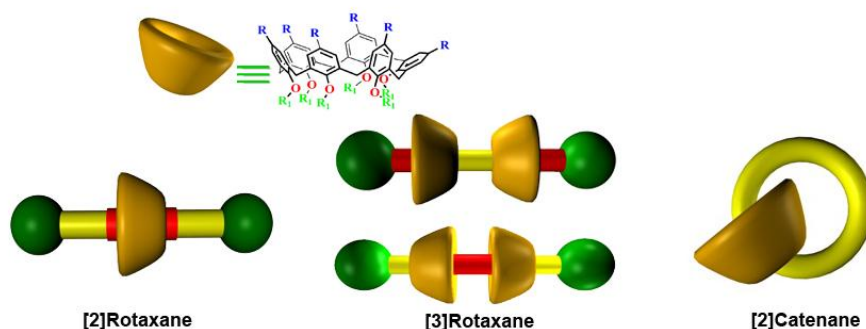
## Abstract

Recently, Neri et al<sup>1</sup> have introduced an efficient method to obtain endo-cavity complexation and *through-the-annulus* threading of large calixarenes exploiting the inducing effect of a weakly coordinating anion, tetrakis [3,5-bis (trifluoromethyl) phenyl]borate (TFPB<sup>-</sup>).

In this PhD thesis this approach has been used for the synthesis of [2]rotaxanes,<sup>2</sup> which showed an unprecedented inversion of the wheel orientation.

Subsequently, it was extended to the synthesis of pseudo[3]rotaxane systems in which two calix[6]arene macrocycles are threaded by a bis(benzylalkylammonium) axle.<sup>3</sup> Because of the three-dimensional nonsymmetrical nature of the calix[6]arene wheels, in these instances three sequence stereoisomers could be obtained, which were termed as head-to-head (H,H), head-to-tail (H,T) and tail-to-tail (T,T).

Taking advantage of these systems, it was possible to obtain the stereoprogrammed synthesis of the first examples of calixarene-based [3]rotaxane architectures. The base/acid treatment demonstrated that these systems act as molecular shuttles, which move on a nanometer scale level.<sup>4</sup>



The directionality of the threading and the observed high stereoselection have enabled the synthesis of directional calix[6]arene-based catenane. All these aspects represent interesting peculiar features of calixarene threading, which could be exploited for designing molecular machines with new properties or functions.

[<sup>1</sup>] a) Gaeta, C.; Troisi, F.; Neri, P. *Org. Lett.* **2010**, *12*, 2092. b) Gaeta, C.; Talotta, C.; Farina, F.; Camalli, M.; Campi, G.; Neri, P. *Chem.–Eur. J.* **2012**, *18*, 1219.

[<sup>2</sup>] Pierro, T.; Gaeta, C.; Talotta, C.; Casapullo, A.; Neri, P. *Org. Lett.* **2011**, *13*, 650.

[<sup>3</sup>] Talotta, C.; Gaeta, C.; Pierro, T.; Neri, P. *Org. Lett.* **2011**, *13*, 2098.

[<sup>4</sup>] Talotta, C.; Gaeta, C.; Neri, P. *Org. Lett.* **2012**, *14*, 3104.