

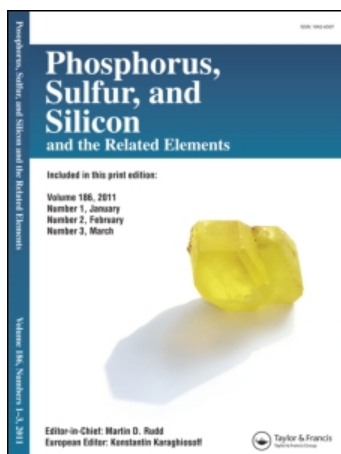
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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

A Multifunctional Molecular Assembly Associating Tetrathiafulvalene, Calixarene and Crown Ethers Units

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To cite this Article Blesa, M. -J. , Zhao, B. -T. , Allain, M. , Mercier, N. and Sallé, M.(2005) 'A Multifunctional Molecular Assembly Associating Tetrathiafulvalene, Calixarene and Crown Ethers Units', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 180: 5, 1475 — 1476

To link to this Article: DOI: 10.1080/10426500590913195

URL: <http://dx.doi.org/10.1080/10426500590913195>

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A Multifunctional Molecular Assembly Associating Tetrathiafulvalene, Calixarene and Crown Ethers Units

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INTRODUCTION

The calix[4]arene platform has been used extensively to prepare metal cation-selective ionophores, notably by association with a crown-ether unit. We have been engaged for some years in the design of various redox-responsive ligands¹ taking advantage of the well-established electrochemical behavior of the tetrathiafulvalene (TTF) unit.

RESULTS AND DISCUSION

The present study is related to the synthesis of an original series of three-membered assemblies: i) a calixarene platform promoting a three-dimensional-organization to optimize the binding process of a guest cation; ii) a crown ether binding part; and iii) an electroactive TTF unit to probe the complexation event.

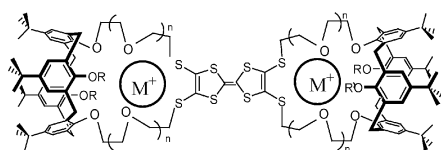
Received July 9, 2004; accepted October 5, 2004.

The 'Conseil Régional des Pays de la Loire' is gratefully acknowledged for postdoctoral fellowships (MJB and BTZ) as well as the 'Programa Europa XXI' CAI-DGA-CONSID+I (MJB). MS thanks the Institut Universitaire de France (IUF) for its financial support.

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Seven different receptors have been prepared. The 1,3-dialkylated systems (**L0-L2**) present a cone conformation promoted by intramolecular hydrogen binding interactions. The cone conformation is lost in the case of the R = Me substitution (**L3** and **L4**), for which a mixture of conformers is observed.² Conversely, for a longer R substituent, the cone conformation is maintained (**L5** and **L6**), thanks to the steric demand of R. The length (*n*) of the polyether spacer exerts a clear effect on the shape of the calixarene cavity (*i.e.*, a pinched or a regular cone, a flattened or a closed cone).

Na⁺ complexation by ligands **L3-L6** can be monitored by ¹H-NMR titration, because the metal complexation induces a rigidification of the molecular assembly, which evolves from a pinched cone conformation³ in the free state, to a symmetrical cone in the complex (two cations per one receptor).



R	n=0	n=1	n=2
-H	L0	L1	L2
-CH ₃		L3	L4
-CH ₂ CH ₂ OCH ₃		L5	L6

The binding efficiency of these receptors has been demonstrated by ¹H-NMR experiments, which demonstrate the conformational evolution upon complexation. Electrochemical studies (thin-layer cyclic voltammetry) are now in progress to validate the electrochemical recognition concept of these three-membered assemblies.

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