

Calix[4]pyrrole Discovered to Form Supramolecular Self-Assemblies with Cations and Anions—Cover Article in *Angewandte Chemie*

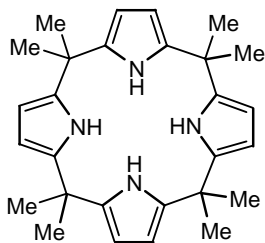
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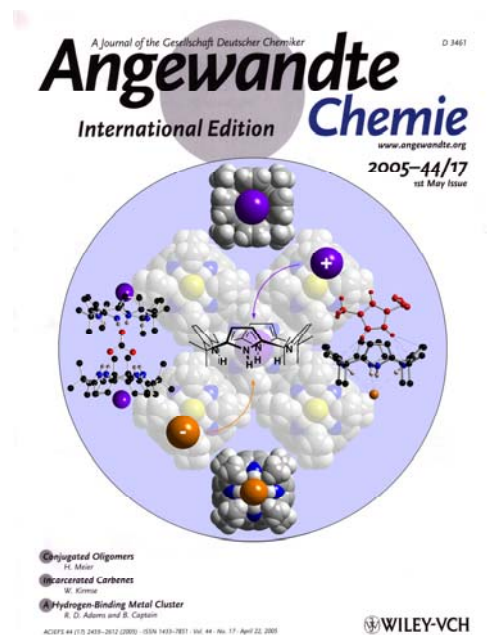
The discovery of ion-pair receptors that achieve a higher level of control over recognition than that obtainable from simple ion binding has intrigued researchers in the supramolecular chemistry field over the last decade. As described in our paper featured on the May 1 cover of *Angewandte Chemie*, the simple *meso*-octamethylcalix[4]pyrrole (**C4P**) molecule possesses the remarkable ability to simultaneously host both a cation and anion in elegant solid-state self-assemblies, providing a model for behavior in liquid-liquid separation systems. Previous studies from our laboratories have demonstrated that the binding of halide anions by cooperative hydrogen bonding involving the four pyrrole N–H groups of **C4P** organizes the receptor into a bowl- or cup-like shape. Prompted by anomalous behavior observed in liquid-liquid extractions of cesium halide salts by **C4P**, we were led to consider that the electron-rich bowl-like cavity so



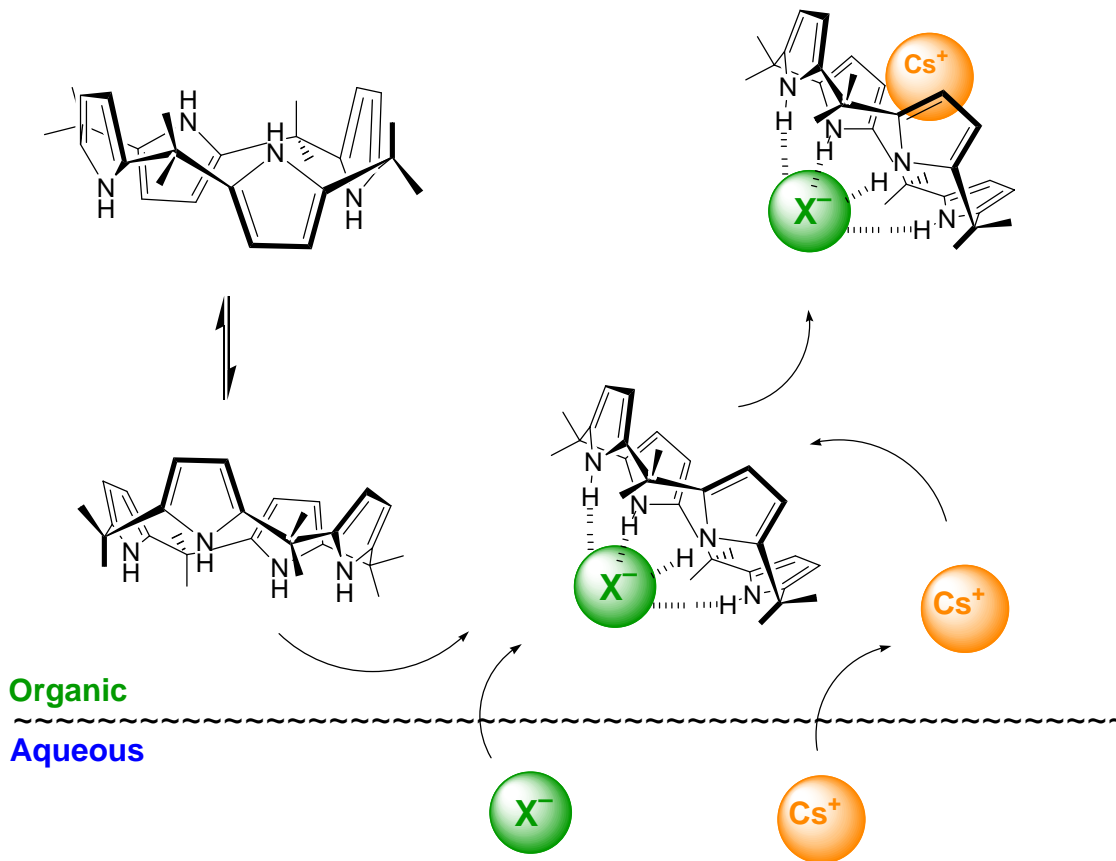
meso-Octamethylcalix[4]pyrrole

formed might serve as a receptor for electropositive species. Subsequent crystallographic analysis of the anion recognition behavior of **C4P** in the presence of two large cations, namely Cs⁺ and imidazolium, in both cases confirmed the hypothesized cation-anion binding. This advance in the understanding of ion-pair recognition and of the behavior of the versatile calixpyrrole family may be significant for developing novel separation systems or for directing the self-assembly of novel solid-state materials.

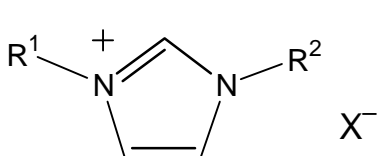
This study has been published in *Angewandte Chemie* **2005**, *44*(17), 2537–2542 under a collaboration involving Oak Ridge National Laboratory (FWP ERKCC08), University of Texas at Austin (Grant DE-FG02-04ER63741), and the University of Southampton.



Additional Graphics and Supporting Information

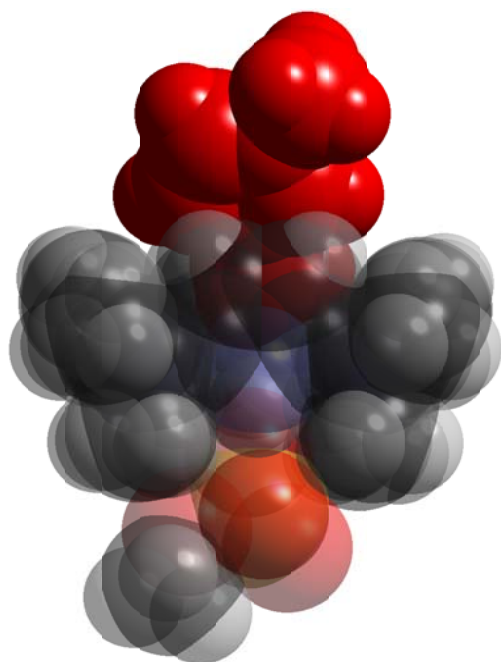


meso-Octamethylcalix[4]pyrrole prefers to exist in a shape not in itself suited for efficient binding of either cation or anion, but it is capable of rearranging itself to bind small halide ions X^- , effecting an extraction of a salt. The resulting electron-rich bowl-like cavity formed by the calixpyrrole is thought to be able to attract electropositive species to within its electron-rich cavity to form an ion-pair complex in solution. Exciting possibilities for chemical modification of the bowl-like walls will allow the basic recognition and extraction properties of the system to be further enhanced. For instance, fluorinated calixpyrroles have been produced that are much more effective extractants than the parent calixpyrrole systems.



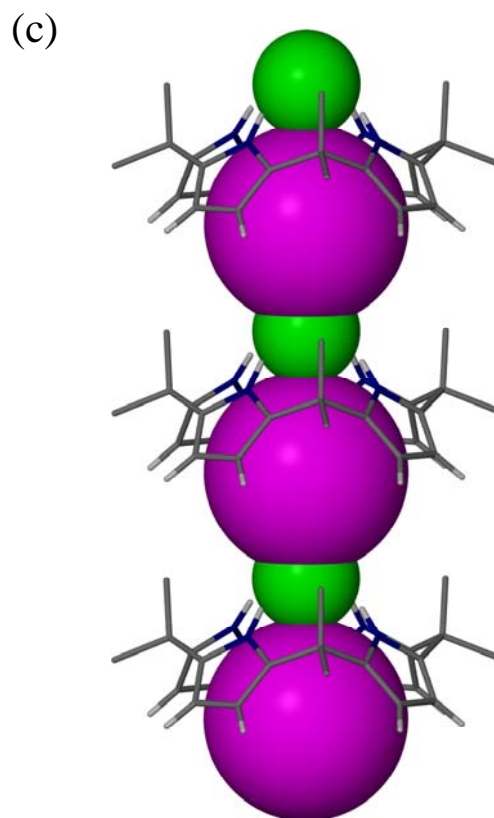
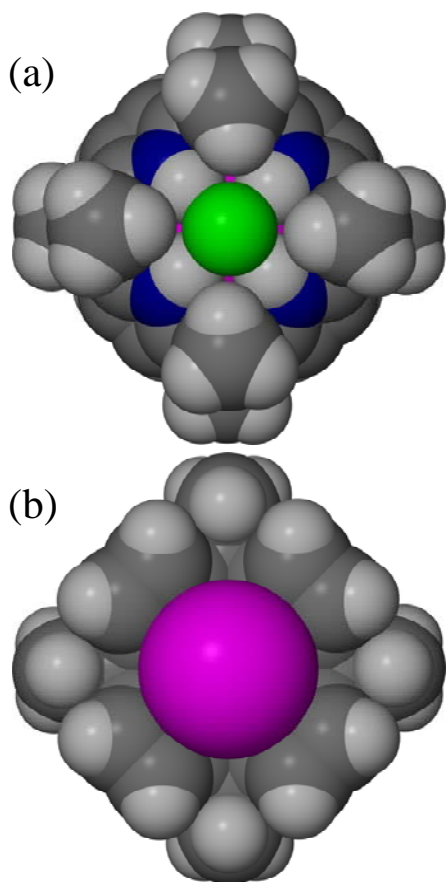
- 1 $R^1 = nBu$, $R^2 = Me$, $X^- = Cl^-$
- 2 $R^1 = nBu$, $R^2 = Me$, $X^- = Br^-$
- 3 $R^1 = Et$, $R^2 = Me$, $X^- = Br^-$
- 4 $R^1 = R^2 = Me$, $X^- = MeSO_4^-$

Gale and co-workers showed that both the anionic and cationic components of imidazolium salts (compounds used as environmentally friendly 'ionic liquid' solvents)



are also complexed by *meso*-octamethylcalix[4]pyrrole. The anionic components of salts **1-4** bind to the pyrrole N–H hydrogen bond array enforcing a cone conformation in the macrocycle. This allows the imidazolium cation to bind to the cup-shaped cavity formed by the four pyrrole rings. The crystal structure of the complex of salt **4** is shown at left. The calix[4]pyrrole **C4P** and methylsulfate anion are rendered transparent to illustrate the inclusion of the red imidazolium cation in the cup. Preliminary solution studies suggest that a similar arrangement occurs in solution.

Below is the crystal structure of **C4P**·CsF, showing a) the binding of F⁻ by the four N–H groups (N is blue, H is light gray, C is dark gray, and F⁻ is green), b) Cs⁺ in the cup (Cs⁺ is magenta), and c) linear chain formed by the **C4P**·CsF units in the crystal.



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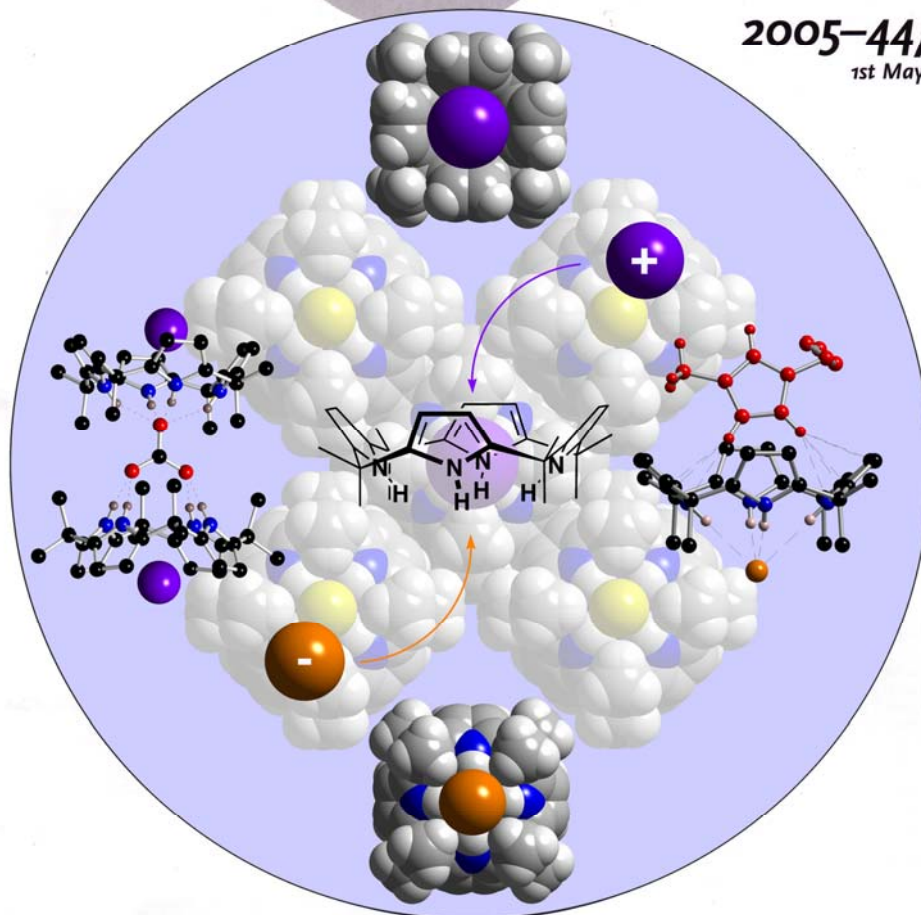
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Conjugated Oligomers

H. Meier

Incarcerated Carbenes

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