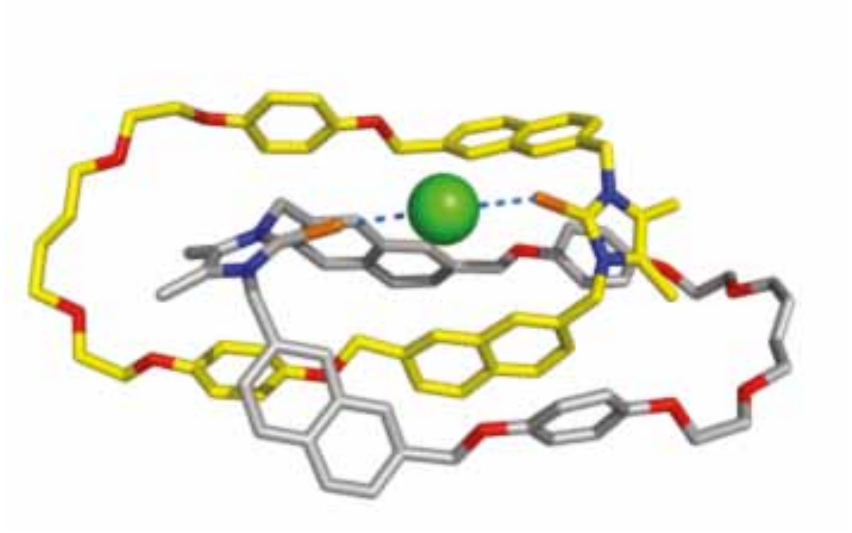
HALOGEN-BONDING IN ANION RECOGNITION

P. J. Costa[1], **V. Félix**[1] **and P. D. Beer**[2]



(1) Department of Chemistry & CICECO & Department of Health Sciences, University of Aveiro
(2) University of Oxford

Halogen bonding (XB) is the attractive intermolecular interaction between an electron deficient positively polarized halogen atom and a Lewis base. Usually, anion recognition in solution takes advantage of the ubiquitous hydrogen bonding, but XB is rapidly also becoming an established field in its own right. An extensive collaboration between our group and Prof. Paul Beer (University of Oxford) resulted in the development and application of XBs in the field of anion recognition.

In the first work [1] anion templation was used to prepare the first XB catenane, which bind and sense selectively chloride and bromide in CH3CN solution. Molecular dynamics (MD) simulations were performed in explicit CH3CN using the structure of the XB catenane bound to chloride and, among other analyses, a representative snapshot was extracted (Fig. 1). Two simultaneous halogen bonds are established between the bromine atoms of both macrocycles and the chloride anion. A π–π stacking interaction between one hydroquinone and a naphthalene group was also observed throughout the course of MD simulation, corroborating the experimental data.

In the second work, a new family of fluorescent XB macrocyclic halo-imidazolium receptors was described [2] showing that the bromo- and iodo- receptors bind selectively iodide and bromide, respectively, in the competitive CD3OD/D2O (9:1) aqueous solvent mixture, sensing these anions exclusively via a fluorescence response. The remarkable affinity of both receptors towards bromide was investigated by means of Density Functional Theory (DFT) calculations and MD simulations. The DFT optimized structure of the iodo-imidazolium receptor binding bromide is depicted in Fig. 2 and show that indeed the receptor is able to bind bromide with great affinity and relatively short C-I···Br– distances (3.192 Å). The subsequent MD simulations showed that those two simultaneous XBs were stable in explicit CH3OH/H2O mixtures, helping to complement the experimental characterization.

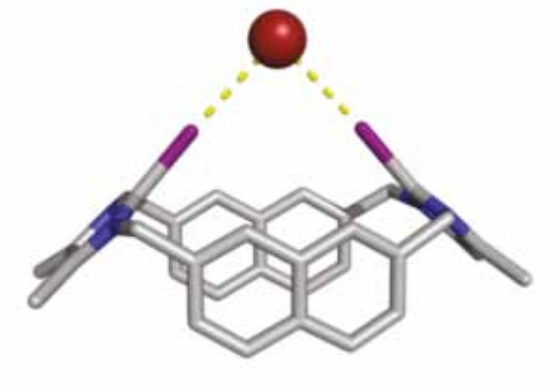


FIGURE 1
Representative co-conformation of the XB catenane bound to chloride in CH3CN solution. The two C-Br···Cl– halogen bonds are drawn as light blue dashed lines.

FIGURE 2
DFT optimized structure of the iodo-imidazolium receptor binding bromide, showing the corresponding halogen bonding interactions as yellow dashed lines