

Poster Presentations

[MS38-P09] Contact Ion Triplet Binding by Bis-Calix[6]arene Receptors.

Filip Topić,^c Steven Moerkerke,^b Stéphane Le Gac,^c Ivan Jabin,^b Kari Rissanen,^a

^aDepartment of Chemistry, Nanoscience Center, University of Jyväskylä, Finland,

^bLaboratoire de Chimie Organique, Université Libre de Bruxelles, Belgium,

^cInstitut des Sciences Chimiques de Rennes, Université de Rennes 1, France

E-mail: filip.f.topic@jyu.fi

The calix[6]arene macrocycle has emerged as an attractive scaffold for design of molecular receptors. Compared to the smaller calix[4]arene, increased macrocycle size results in a larger cavity and correspondingly greater conformational flexibility, offering more potential towards facile construction of receptors for small molecular species [1]. Linking of multiple calix[6]arene units offers a conceptually simple route to polytopic receptors [2]. We successfully prepared two tubular receptors by connecting two calix[6]arene macrocycles through three urea or thiourea moieties, respectively. Both receptors were shown to bind ion triplets consisting of alkylammonium cations and different anions, with the bis(*n*-alkylammonium) sulfates being bound particularly strongly [3,4]. Further insight into the binding process was gained through crystallographic investigation of the receptors and their complexes. Namely, the structure of the free bis-calix[6]thiourea receptor showed no self-association of thiourea moieties, while extensive disorder reflected the significant conformational flexibility of the free receptor. Moreover, the structure of the (EtNH₃)₂SO₄ complex with bis-calix[6]urea clearly demonstrated how the binding of the contact ion triplet is mediated by hydrogen bonds between the cations and the anion, urea linkers and the anion and finally, between the cations and the calix[6]arene moieties [4].

[1] Darbost, U., Rager, M.-N., Petit, S., Jabin, I. & Reinaud, (2005). *J. Am. Chem. Soc.* **127**, 8517-8525.

[2] Le Gac, S. & Jabin, I. (2008). *Chem. Eur. J.* **14**, 548-557.

[3] Moerkerke, S., Ménand, M. & Jabin, I. (2010). *Chem. Eur.* **16**, 11712-11719.

[4] Moerkerke, S., Le Gac, S., Topić, F., Rissanen, K. & Jabin, (2013). *Eur. J. Org. Chem.*, accepted for publication.

Keywords: receptor-ligand interactions; molecular recognition; ion binding