New macrocycles for selective binding of ions

K. Sleziakova[a] and V. Sindelar[a]

[a] *Department of Chemistry and Research Centre for Toxic Compounds in the Environment, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic.*
E-mail: 177422@mail.muni.cz

Bambusurils (BUs) represent a relatively novel class of host molecules that are formed via templated ring-closure reaction between 2,4-disubstituted glycoluril and formaldehyde.[1,2] Resulting cyclic products, BU[4] and BU[6], are arranged in flexible structure comprising internal cavity with different sizes. Exclusively, the interior of BU[6] favors the binding of inorganic anions with remarkably high affinities reaching 10^7 M^{-1} for iodide and perchlorate even in such competitive environment as water.[3]

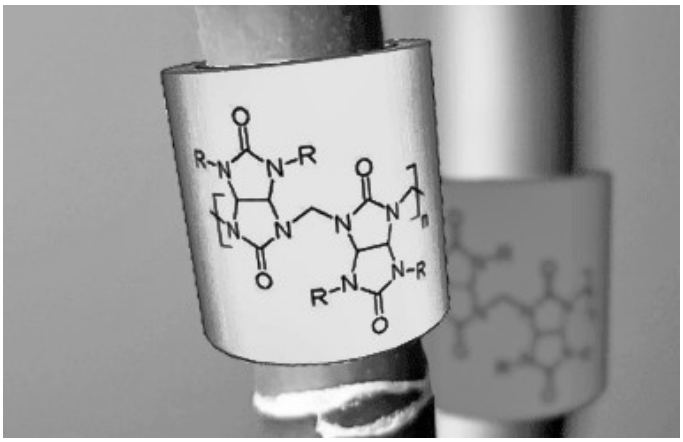

Figure 1. Substituted bambusuril, R = carboxybenzyl or polyethyleneglycol group.

In order to gain broader insight into strong interaction between BU and anion, we studied the binding properties of neutral and charged BUs in more detail. Firstly, we report supramolecular study of $(COOHBn)_{12}BU[6]$. Acidic carboxybenzyl groups become negatively charged in basic pH. As a consequence, $(COO^-Bn)_{12}BU[6]$ simultaneously accommodates anion inside the cavity and cations at the negatively charged carboxybenzyl groups. Moreover, binding of anion by $COO^-Bn_{12}BU[6]$ can be modulated either positively or negatively in the presence of certain salts. Secondly, we present neutral BU with polyethyleneglycol chains ($PEG_{12}BU[6]$), that is highly soluble in almost all solvents ranging from toluene to water. This has given us the opportunity to compare the behavior of $PEG_{12}BU[6]$ in different environments. This study has brought us to conclusion, that besides hydrogen bonding between C-H groups of BU[6] and anion, there is evidence of significant solvophobic effects stabilizing the anion inside BU[6].

Acknowledgments
Support for this work was provided by the Czech Science Foundation (13-15576S) and the Czech Ministry of Education (projects LM2011028 and LO1214).

[1] J. Svec, M. Necas and V. Sindelar, *Angew. Chem. Int. Ed.*, 2010, **49**, 2378–2381.
[2] V. Havel, J. Svec, M. Wimmerova, M. Dusek, M. Pojarova and V. Sindelar, *Org. Lett.*, 2011, **13**, 4000–4003.
[3] M. A. Yawer, V. Havel and V. Sindelar, *Angew. Chem. Int. Ed.*, 2015, **54**, 276–279.