

Electrostatic self-assembly of *p*-sulfonatocalix[4]arene and pillar[*n*]pyridiniums into organic crystals

Kateryna Kravets¹, Mykola Kravets¹, Helena Butkiewicz¹, Volodymyr Sashuk¹, Oksana Danylyuk¹

¹Institute of Physical Chemistry Polish Academy of Sciences, kkravets@ichf.edu.pl, Poland

Macrocyclic host molecules are versatile building blocks in the supramolecular chemistry and crystal engineering. Depending on their structure and properties, macrocycles have found numerous applications in the host-guest systems, sensing, catalysis, design of porous materials, *etc.* We report here an aqueous self-assembly driven by complementarity in charge and shape between two families of oligocharged macrocyclic hosts - cationic pillar[*n*]pyridiniums and anionic *p*-sulfonatocalix[4]arene. *p*-Sulfonatocalix[4]arene with electron-rich basket-like cavity is well-known water-soluble supramolecular host, capable of forming various types of assemblies, such as bilayer clay-type structures, capsules, nanometer tubules, spheres or Russian-doll assemblies.[1] Pillar[*n*]pyridiniums are new family of water-soluble permanently charged cationic macrocycles of electron-deficient cavities, now available in two sizes – rigid square-shape tetramer and flexible roughly hexagonal hexamer. [2] These two types of macrocyclic hosts are complementary in terms of charge, shape and symmetry. Their self-assembly is guided mainly by the electrostatic attraction between anionic sulfonate groups of calix[4]arene and positive charge on the pyridinium rings of the cationic macrocycles. The crystallization in gel and liquid-liquid diffusion methods have been used to obtain suitable crystals build from mixed macrocycles for single crystal X-ray diffraction analysis. The structural aspects of the supramolecular architectures and main non-covalent interactions guiding the assembly will be discussed.

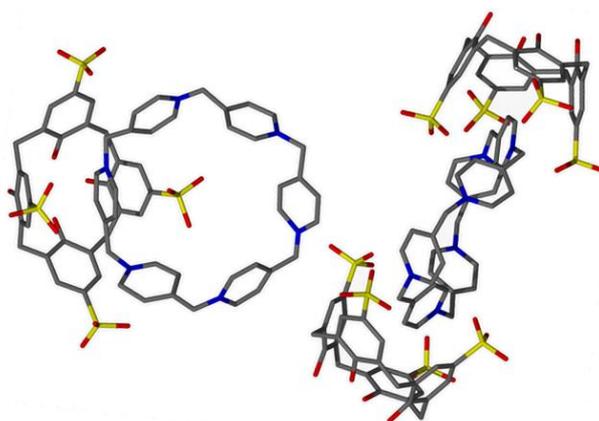


Fig. 1 Complex formed by *p*-sulfonatocalix[4]arene and pillar[6]pyridinium.

[1] Dalgarno S. J, Hardie M. J, Makha M, Raston C. L. Controlling the Conformation and Interplay of *p*-Sulfonatocalix[6]arene as Lanthanide Crown Ether Complexes. *J. Chem. Eur*, 9, 2834 (2003)

[2] Kosiorek S, Butkiewicz H, Danylyuk O, Sashuk V. Pillar[6]pyridinium: a hexagonally shaped molecular box that selectively recognizes multicharged anionic species. *J. Chem. Commun*, 54, 6316 (2018)

K.K. acknowledges support by the National Science Centre of Poland (grant Preludium BIS nr 2019/35/O/ST4/01865).