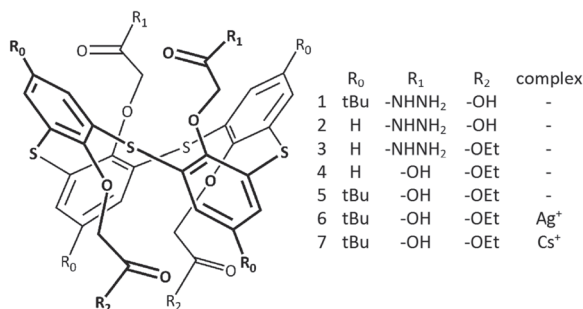


MS25-P5 New bifunctional thiacalix[4]arenes as potential heteroditopic receptors. Bulat M. Gabidullin, Aidar T. Gubaidullin, Sergey N. Podyachev, Svetlana N. Sudakova. A.E. Arbusov Institute of Organic and Physical Chemistry, Kazan, Russia.
E-mail: gabidullin@iopc.ru

Calix[n]arenes in 1,3-alternate conformation, bearing different functional groups on their lower rim, are of interest as potential heteroditopic receptors, i.e. having two unequal binding centres. Heterometallic complexes have numerous applications in catalysis, reveal unique magnetic and luminescent properties and are commonly used as keystones for the creation of redox-responsive switches.

Structure of five new bifunctional thiacalix[n]arenes, substituted by carboxyl, ester, and/or hydrazide groups on the lower rim, as well as two homometallic complexes with Ag^+ and Cs^+ is presented. Conformation and pattern of inter- and intramolecular interactions in crystal are analyzed with respect to their probable effect on binding abilities. For example, hydrozide groups of calixarenes **1**, **2**, **3** tend to participate in intramolecular hydrogen bonding with each other, closing the cavity, whereas carboxyl groups form preorganized cavity in all studied compounds. Another aspect of our work was to investigate solvate molecules' arrangement in the crystals and examine their influence on the crystal stability. For instance, in compound **7**, which is extremely unstable being exposed to air, methanol molecules are highly disordered and form channels of large volume (30%), so their evaporation leads to a crystal collapse.



Keywords: heterotopic, bifunctional, thiacalixarene

MS25-P6 Metal-organic coordination networks with *meso*-tetra(3-carboxyphenyl) porphyrin, Israel Goldberg, Sophia Lipstman, School of Chemistry, Tel Aviv University, Tel Aviv, Israel.
E-mail: goldberg@post.tau.ac.il

Our group has focused in recent years on “bottom-up” formulations of porphyrin-based supramolecular solids from suitably functionalized building blocks, utilizing robust coordination metal-ion linkers and hydrogen bonding synthons between the porphyrin scaffolds. The chemical and structural diversity of porphyrins allows us to reasonably control their self-assembly process and to alter systematically the composition, topology and porosity of the supramolecular arrays that form. Here we explore the utility of *meso*-tetra(3-carboxyphenyl)porphyrin (T^3CPP) in the construction of supramolecular assemblies via different molecular recognition synthons. The conformational flexibility of the T^3CPP building block, namely the possibility of the four 3-carboxyphenyl arms to align in different orientations with respect to the rigid porphyrin plane, further diversifies its supramolecular reactivity. Until now two main conformers have been observed in structures of this porphyrin unit [1, 2]. The “chair-like” mode with two *cis*-related carboxyphenyl substituents oriented in one direction with respect to the porphyrin macrocycle, while the other carboxyphenyl pair is oriented towards the opposite side. It will be shown that the chair-like T^3CPP involves in stable 2D and 3D layered wavy metal-organic coordination networks both with d-shell as well as f-shell transition-metal ions. Another mode represents a “table-like” structure with all carboxyphenyl functions pointing in the same direction (not observed earlier). This conformation is perfectly suited to form chains of ‘molecular boxes’ sustained by inter-coordination of two porphyrin units to each other via their carboxylate sites through metal-ion connectors, and then sideways coordination to neighbouring pairs. The third conformer, with alternating orientations of adjacent carboxyphenyl groups along the porphyrin macrocycle, represents tetrahedral functionality which may lead to open coordination polymers of diamondoid topology when reacted with metal centres/clusters of complimentary binding preference (as previously observed with the 3-pyridyl porphyrin analogue [3, 4]). The presented results illustrate new types of coordination architectures, and provide further challenge for the design of attractive porphyrin-based (possibly porous) framework solids.

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Keywords: porphyrin assemblies; coordination networks; framework solids