

MS32-P13**Playing hopscotch with pyridine@p-tert-butylcalix[6]arene crystal structures**Maura Malinska¹

1. Faculty of Chemistry, University of Warsaw, Warsaw, Poland

email: mmalinska@chem.uw.edu.pl

Calix[n]arenes have applications in the areas of host-guest chemistry, ion and molecular recognition, enzyme mimics, catalysis, interaction with biomolecules, ion extraction, and selective ion transport.[1] However, crystallisation of these systems is still challenging owing to their conformational flexibility. Therefore, crystallisation conditions (supersaturation, temperature, additives) were screened to obtain crystal structures with varying architecture such as channels and spherical voids with different conformations of the host. The molecular recognition and self-assembly between host p-tert-butylcalix[6]arene and guest pyridine led to kinetic trapping and crystallisation of the intermediate complexes, which were characterised by X-ray diffraction. The crystalline kinetic complex underwent slow spontaneous dissolution and subsequently recrystallises as thermodynamic inclusion complexes. Single-crystal X-ray diffraction revealed these first formed crystals to be the 15:1, 6:1 association complexes. These two crystal structures can transform into four different crystal structures depending on crystallisation conditions, forming 1:1, 1:1, 3:1, and 6:1 pyridine and p-tert-butylcalix[6]arene complexes. The crystal structure of the host-guest system can be tuned by the supersaturation changes and hydrogen-bonding properties of used additives to form crystal structures with designed architecture.

References:

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Keywords: host-guest, crystallisation, complexes**MS32-P14****Self-assembly and gelation capability of N-Boc-protected tyrosine-based retropeptides**Mario Cetina¹, Josipa Matić², Debdeep Maity², Zoran Džolić²

1. Department of Applied Chemistry, Faculty of Textile Technology, University of Zagreb, Zagreb, Croatia

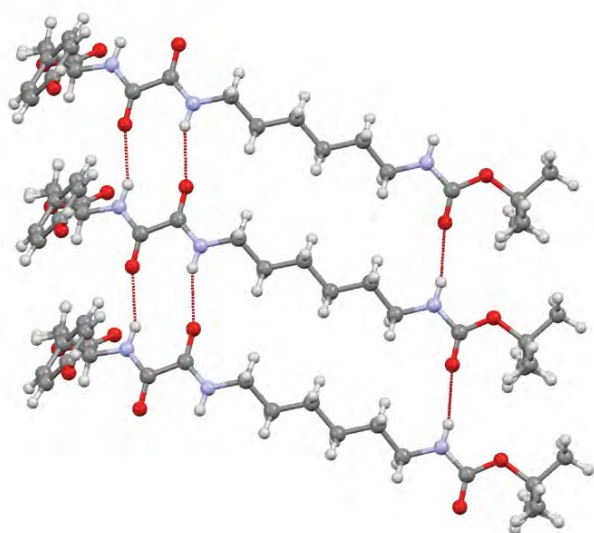
2. Division of Organic Chemistry and Biochemistry, Ruder Bošković Institute, Zagreb, Croatia

email: mario.cetina@tff.hr

Gelators are compounds capable of solidifying various solvents and water. It has been shown that gel fibres are formed by the predominantly unidirectional self-assembly of gelator molecules through different types of intermolecular interactions. When the aggregates are sufficiently long, they entangle into a three-dimensional network capable of immobilizing the solvent. Considerable attention in supramolecular chemistry and materials science have received low molecular weight gelators (LMWGs). Potential for chemical variation among LMWGs is practically unlimited. The use of co-gelators, additives or solvent mixtures allows adjustment of the physical properties of gels for a range of applications, including template synthesis of nanoparticles and nanostructures, catalysis, drug delivery etc. One of the property of LMWGs is increasing possibility that a fully supramolecular approach can be achieved. Particularly attractive systems are those that can act as logic gates, with switchable behaviour that varies depending on the combination of thermal, optical and mechanical inputs [1-3].

Herein we present our recent investigation on gelation properties of oxalamide derivatives of tyrosine with *tert*-butyloxycarbonyl protecting group, by means of single-crystal X-ray analysis, scanning electron microscopy, transmission electron microscopy and atomic force microscopy. These derivatives differ in the length of the aliphatic chain (containing 2, 3, 5 or 6 methylene units) between *tert*-butyloxycarbonyl and oxalamide groups. Gelation property in these compounds is governed by strong intermolecular N-H...O hydrogen bonds between oxalamide groups and amide groups of the neighbouring molecules which form one-dimensional chain (see Figure). Such self-assembly appears to be one of the prerequisites for gelation behaviour of the compounds. Disposition of chains leads to the formation of channels with molecules of the crystallization solvent trapped within them.

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Keywords: self-assembly, gelators, oxalamides

MS32-P15

Supramolecular analysis of intramolecular H-bonds in (P,N) chelates and (P,C) palladacycles: towards understanding the mechanism of asymmetric induction *via* crystal engineering

Attila Benyei¹, Gergely Farkas², József Bakos²

1. Department of Physical Chemistry, University of Debrecen, 1 Egyetem tér., Debrecen, Hungary
 2. Department of Organic Chemistry, University of Pannonia, 10 Egyetem u., Veszprém, Hungary

email: benyei.attila@science.unideb.hu

(P,N) chelates and (P,C) palladacycles [1] are very important complexes, especially in catalytic research. A set of pentane-2,4-diyl based chiral aminoalkylphosphine ligands Ph PCH(CH₂)CH₂CH(CH₂)NHR and their palladium complexes were prepared (as an example, see Figure). Single crystal X-ray diffraction; solution phase 1D and 2D NMR studies and theoretical calculations [2] were applied to verify the results and outcome of crystal engineering and to support catalytic studies. According to our latest results, mild oxidation of the complexes bearing suitable R substituents resulted in intramolecular C-H activation and concomitant formation of (P,C) coordinated palladacycles. Intramolecular H-bond between the coordinated chloride as acceptor and methylene/NH proton seems to play crucial role in stabilizing the conformation of the ring and fixing the stereogenic nitrogen atom, hence in transmission of chiral information in enantioselective catalysis. This opens the possibility to engineer suitable structures for enantioselective catalytic reactions of various substrates. Palladium was replaced with other metals having square planar coordination geometry and their structures were also studied.

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Keywords: supramolecular chemistry, hydrogen bond, enantioselective catalysis