MS32 Molecular recognition and crystal engineering

Chairs: Dr. Berta Gómez-Lor, Prof. Delia Haynes

MS32-O1

The many lives of resorcinarene cavitands: from molecular recognition to crystal engineering

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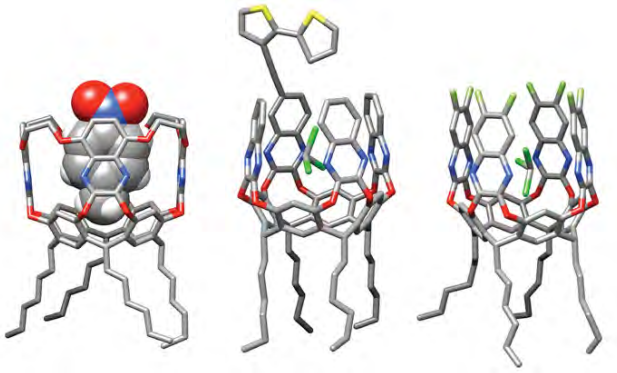
Since their first appearance on the chemistry scene thirty years ago [1], resorcinarene-based cavitands have been exploited both as receptors for molecular recognition and as building blocks for crystal engineering [2]. Their versatility primarily stems from the possibility of choosing different bridging groups to connect the phenolic hydroxyls of the resorcinarene scaffold. This allows the tuning of the shape, dimension and complexation properties of the cavity, which can thus interact with neutral and charged molecules through H-bonding, π···π stacking and CH···π interactions, but also form coordinative bonds with metal centers to create discrete complexes, cages or extended networks.

We present our recent investigations on various functionalised quinoxaline-bridged cavitands for molecular recognition (see figure below) and phosphonate cavitands as ligands for the formation of coordination compounds



References:

[1] Cram, D. J. (1983). Science, 219, 1177-1183
[2] Pinalli, R. et al. (2016). CrystEngComm. 18, 5788-5802.

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MS32-O2

Close contacts involving carbon and antimony: Tetrel bonded and pnictogen bonded systems by design

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In this communication we will describe the packing of some homomeric and heteromeric crystals wherein the composition and architecture is affected and/or determined by attractive interactions involving carbon and antimony atoms as electrophilic sites. Molecular modelling predicts that region(s) of depleted electron density are typically present on an atom opposite to the covalent bond(s) it is involved in. This is true for any element belonging to groups 14-18 of the periodic table [1] and the electrostatic potential at the depleted region(s) becomes positive when the atom is covalently bonded to strongly electron withdrawing residues [2]. We thus expected that the depleted regions on fluorinated carbon and antimony moieties might be positive enough to enable for the formation of attractive interactions with lone pair possessing atoms. We also expected that the resulting bonds might be strong enough to determine the crystal composition and architecture. Here we describe that various 5,5-difluorobarbituric derivatives form adducts were F–C···O=C intermolecular contacts can be as short as 90% of the sum of carbon and oxygen van der Waals radii. The C···O supramolecular synthon in these derivatives is robust enough to be observed also in 5,5-dichloro and 5,5-dibromo analogues, namely when halogens less electron withdrawing than fluorine are present (Fig. 1). As to fluorinated antimony derivatives, we report, for instance, that the tendency of antimony trifluoride to attractively interact with lone pair possessing atoms is so strong that in the tetrameric adducts formed on self-assembly with *p*-dipyridyl dioxide, two antimony atom gives two F–Sb···O close contacts with two different dioxide molecules. The described interactions are typically named tetrel bond and pnictogen bond [3], respectively. The reported results shown how their understanding is developed enough to enable for their successful use in the design of the intermolecular interactions of crystal lattices. The described structure may also suggest that tetrel bond and pnictogen bond are robust enough to become new, useful and general tools in crystal engineering.