Weak Intermolecular Interactions in the Solid State

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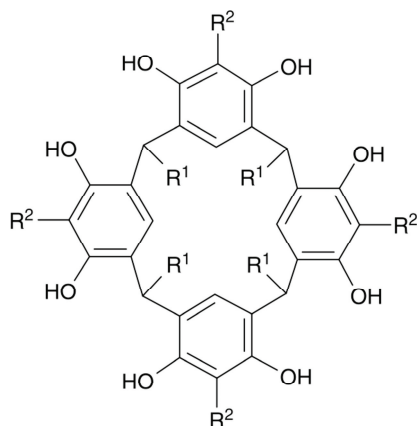*(E-mail: kari.t.rissanen@jyu.fi)*

Abstract. Contemporary research in Supramolecular Chemistry is focused on the studies of weak non-covalent intermolecular, *viz.* supramolecular interactions as the driving force in self-assembly and molecular recognition, especially important being the solid state studies by single crystal X-ray diffraction. Recent advances have been achieved in the studies on hydrogen and halogen bonded systems, $\pi\cdots\pi$, cation$\cdots\pi$, CH$\cdots$anion, anion$\cdots\pi$ interactions and metal ion coordination in molecular self-assembly and molecular recognition in various systems such a resorcinarenes, ditopic receptors, rotaxanes and L_6M_4 tetrahedra.

Keywords: hydrogen bonding, halogen bonding, X-ray structure, supramolecular chemistry

MOLECULAR ENCAPSULATION

For many years, self-assembling, reversibly hydrogen-bonded capsules have contributed a great deal to our current understanding of enzyme action. Considerable interest has been focused on the design and synthesis of biomimetic receptors. In order to achieve convergent arrangement of binding sites, many of these receptors have utilized the cone shape of the resorcinarenes and pyrogallarenes (Scheme 1) for a variety of applications. The easy large scale preparations of these compounds makes them very attractive building blocks in supramolecular chemistry.[1]

Resorcinarenes and pyrogallarenes have the ability to easily form molecular capsules *via* hydrogen bonded networks. Open inclusion complexes,[2] dimeric capsules,[3] hexamers,[4] larger supramolecular and tubular[5] assemblies linked together by hydrogen bonding with cavities aimed at trapping cationic and neutral guests. Recently anion complexation using resorcinarene based cavitand has been reported by us.[6] Ammonium cations have proven to be good guest candidates for resorcinarene complexation since they have the possibility to interact *via* cation$\cdots\pi$ and C–H$\cdots\pi$ interactions as well as advantageously fill the empty space in the hollow cavity of the resorcinarene host. Figure 1 depicts one
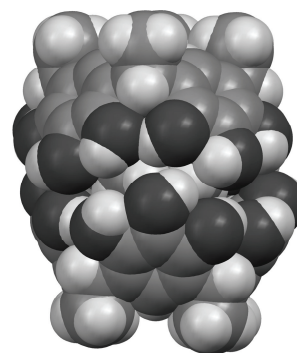
Scheme 1. Chemical structure of resorcinarene (R^2 = H) and pyrogallarene (R^2 = OH), R^1 = alkyl or aryl substituent.

Figure 1. The VDW presentation of the the X-ray structure of a pyrogallarene capsule[3g] with encapsulated tetramethyl ammonium (TMA) cation. The mediating MeOH removed for clarity.
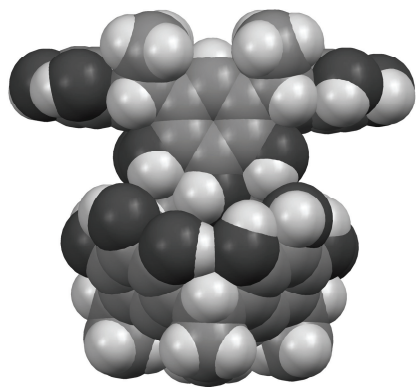
Figure 2. The VDW presentation of the X-ray structure of a asymmetric pyrogallarene capsule[3g] with encapsulatedethanol molecule. The lattice solvent molecules removed for clarity.

example of a dimer capsule formed in the solid state by two pyrogallarene in crown conformation encapsulating a small organic tetramethyl ammonium cation, the capsule halves are mediated, *viz.* connected *vis* several methanol molecules.

Generally the capsules are formed by assembly of two resorcinarenes or pyrogallarenes in crown conformation,[3,4] if strong hydrogen bonding between the capsule halves occur, an asymmetric, *viz.* containing two different conformation of the macrocycle can be observed as depicted in Figure 2.

Changing the crystallization conditions even slightly can effect a very large change in the self-assembly process and lead to completely different structures.[5] This was observed when resorcinarene was crystallized from *n*-propanol with dimethylDABCO dibromide as the quest. Figure 3 depicts the unprecentended nanotube structure, the included *n*-propanol can
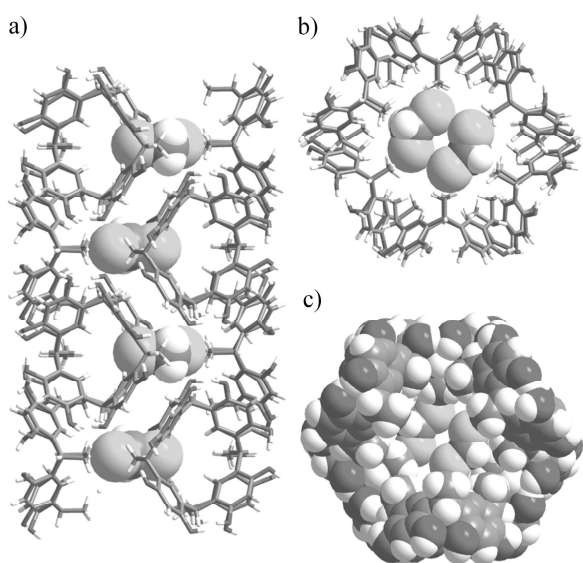

Figure 3. The X-ray structure of a resorcoinarene based nanotube[5b] with included dichloromethane molecules.

be exchanged to dichloromethane molecules upon soaking the nanotube crystals into CH$_2$Cl$_2$ solution.[5b]

Mass spectrometry[7] is an important tool to examine binding interactions of cations in the gas phase. It has the advantage of proving the complexation without solvent interference. Dimeric[2] and hexameric[3] capsules of resorcinarenes, pyrogallarenes and related compounds encapsulating small and large cations have been shown to prevail in the gas phase[7] without solvent mediation and have been predicted to be directly hydrogen bonded. Other cavitand and calixarene work has also been extensively reported.[8,9]
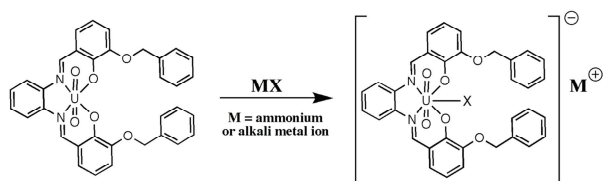
CATION···π INTERACTIONS

In recent years there has been a great interest in the design, synthesis, and investigation of ion pair binding receptors.[10] Since either of the charged partners of a ion pair is a likely site of recognition, a receptor specifically designed for effective ion pair complexation should consist of at least two subunits, each of which capable per se of binding to one of the partners of the ion pair (Scheme 2).

Several strategies have been devised to achieve recognition of the ionic subunits of the guest ion pair, most of which make use of crown ethers for cation recognition and hydrogen bond donors for anion recognition. We recently reported on the recognition of alkali metal halide ion pairs by uranylsalophen complexes bearing aromatic side arms (Scheme 3). Such receptors combine the strong binding of the hard Lewis acidic uranyl center to hard anions (F⁻, Cl⁻) with cation···π
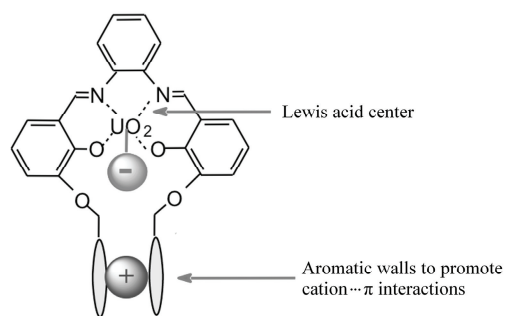
Scheme 2. Schematic structure of a possible ion pair, *viz.* ditopic receptor.

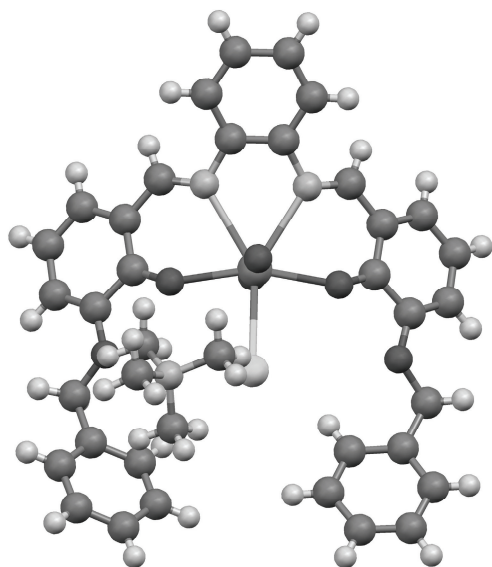**Scheme 3.** The ion pair recognition by a uranylsalophen complex.

Figure 4. The X-ray structure of the salophen complex[10d] presented in Scheme 3.

interactions between the flexible aromatic side arms and the alkali-metal countercation. Such a uranylsalophen ion pair complex is presented in Figure 4.

Consistent with the hard Lewis acid character of the uranyl, binding affinities for complexation of quarternary ammonium salts to uranylsalophen receptors in solution are higher the harder the anion. This is in agreement with the finding that in all of the isolated (ion pair)-receptor complexes, as well as the previously reported analogues with alkali-metal halides,[10b] the anion is firmly coordinated to the uranyl center in its equatorial plane. Less important, yet significant contri-
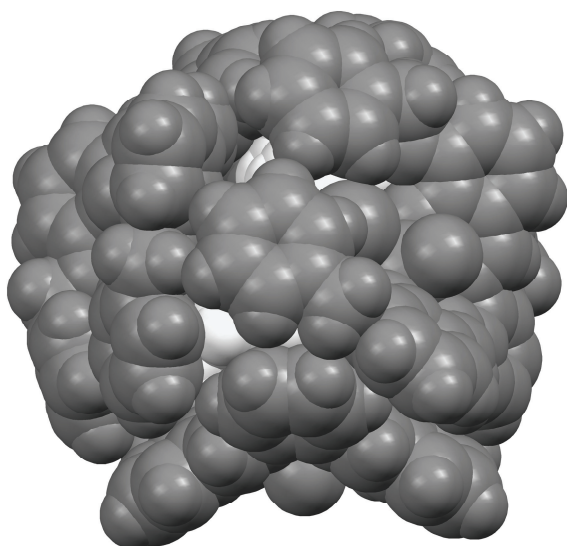

Figure 5. The VDW presentation of the X-ray structure of the tetrameric solid state assembly of the salophen complex[10d] presented in Scheme 3 and Figure 4. The salophen complex in grey color and the encapsulated TMA cations in white.

butions to complex stability in solution arise from cation$\cdots\pi$ and CH$\cdots\pi$ interactions of the quaternary ions with the aromatic pendants. More elaborate architectures are seen in the solid state compared with the simple receptor-anion-cation ternary complexes formed in the dilute solutions used in the ^{1}H NMR titrations. Thus, whereas simple ion pair recognition is achieved in so-lution, in the solid-state ion pair aggregates of varying composition and structure are basic elements in the formation of supramolecular assemblies with receptor molecules. A nice example of such higher order assembly was observed for the TMACl-uranylsalophen complex presented in Figure 4. The tetrameric $((TMA)Cl)_4$ cluster is found inside the cavity formed by the four salophen complexes. Figure 5 depicts the solid state tetrameric assembly of the ion pair complex.

ANION$\cdots\pi$ INTERACTIONS

Based on the fact that only recently it was commonly accepted that anion$\cdots\pi$ interactions are attractive non-covalent interactions if electron-deficient aromatics are present. The systematic studies of purely organic "receptors" without coordination of a metal ion to the aromatic unit have been rare and thus we focused our attention to this topic too. We attached a cationic moiety (ammonium, iminium, amidinium) to a pentafluoro-phenyl ring and introduced a halide as a counteranion. Suitable crystals for single crystal X-ray diffraction study were obtained by diffusion of HCl, HBr, or HI into an acetone or acetonitrile solution of pentafluoro-aniline.

The most interesting interactions were observed in the amidinium salt (Figure 6), where the anion is surrounded by four neighboring cations: two bind by NH hydrogen bonds (not shown in Figure 6) and one binds by "η_2"-type π-anion coordination (C–Br: 3.66, 3.73 Å). The interaction with the fourth cation (Figure 1c) takes place by a NH-hydrogen bond which fixes the anion on top of the aromatic system close to its center (C_{arom}–Hal) 3.65–3.83 Å. Halogen-centroid distances are ca. 3.48 Å with Hal-centroid aromatic plane angle of 85.7°. Our results show that anion π-interaction can occur in the crystals of salts with pentafluorophenyl substituted cations.
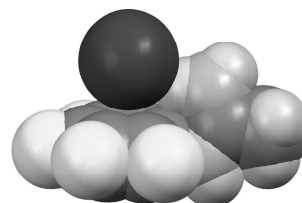

Figure 6. The VDW presentation of the X-ray structure[11a] of anion π-complex.

MOLECULAR Pac-Man

We have used piperazine[12] as functional or pre-functional spacers offering a straightforward route to functional piperazine cyclophanes of various sizes. Nitro group in an aromatic spacer do not render the *N*-alkylation during the synthesis and thus results in nitro functionalized piperazine cyclophanes. The synthetically feasible reduction of the nitro group to a more versatile amino group opens further possibilities for the functionalization of the cyclophanes. The spatial proximity of the hydrogen bond donating amino group and the tertiary amine as the hydrogen bond acceptor in piperazine moieties lead to unprecented intramolecular interactions which have a dominating effect to the overall conformation of the cyclophane. A completely circular hydrogen bonding in the piperazine containing tetramer leads to the folding of the cyclophane to a shell-like tertiary structure capable to enclosing an acetonitrile molecule inside the formed cavity in the crystalline state. As a result of the intramolecular hydrogen bonding observed in this compound new tertiary structures or spatial orientation of functional groups for large macrocycles can be designed and used to construct spatially directed functionalities or new properties due to the folding process.

HALOGEN BONDING

The basis for the understanding and use of halogen atoms as the recognition sites in self-organization processes was laid in 1960's and early 1970's by O. Hassel.[13b] A major breakthrough in the conceptualization of halogen bonding resulted in 1998 when G. Resnati rediscovered this interaction and further developed its use in solid state supramolecular chemistry
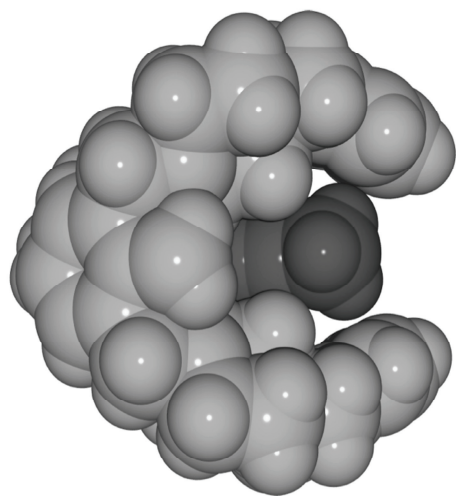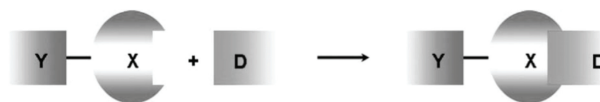

Figure 7. The VDW presentation of the X-ray structure[12l] of a molecular Pac-Man.

Scheme 4. Halogen bonding, Y = C or N, X=I, Br, Cl and D =N, O, S, I⁻, Br⁻ or Cl⁻.

together with his colleague P. Metrangolo. Based on a multitude of X-ray structural determinations of halogen bonded systems, they have developed the concept that halogen bonding is a strong, specific, and directional interaction[13b] that can in quite many cases overrule other intermolecular interactions, such as hydrogen bonding, $\pi \cdots \pi$, cation$\cdots \pi$ and C–H$\cdots \pi$ interactions. The nature of the halogen bond, determined as the interaction of a polarized halogen atom and electron donor atoms is schematically presented in the Scheme 4.

We have studied[13] various halogen bonding systems, one recent example the rational design of materials from the self-assembly of rigid macrocyclic building blocks. Piperazine cyclophanes[12] are structurally rigid rings, which delimit a nonpolar macrocyclic cavity large enough to accommodate small neutral guest molecules (Scheme 5).

In addition, the piperazine cyclophane ring bears multiple sp³ N atoms as potential bonding sites for halogen bonding (see Scheme 4). Whilst piperazine cyclophanes do not normally show the formation of channeled structures in the solid state, the single crystal X-ray structures of their 1:1 halogen-bonded complexes with 1,4-diiodotetrafluorobenzene (F4DIB) show the stacking of cyclophane rings into tubular structures[13d] (Figure 8).

As halogen bonding is most pronounced in perfluoroiodides we haveb looked for alternative new potential synthons for XB interactions and we focused our attention on iodonitrobenzenes, especially 1-iodo-3,5-dinitrobenzene, which due to the strongly electron withdrawing NO₂-groups, were expected to show strong polarization of the iodine atoms. Strong polarization leads to improvement of the strength and directionality of the halogen bonding. Strong halogen bond acceptor
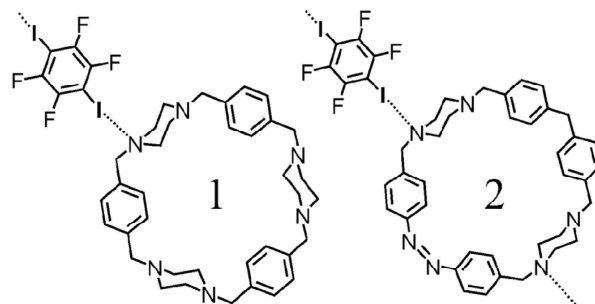
Scheme 5. The chemicals structures of the piperazine macrocycles and the halogen bonding between I and N atoms.
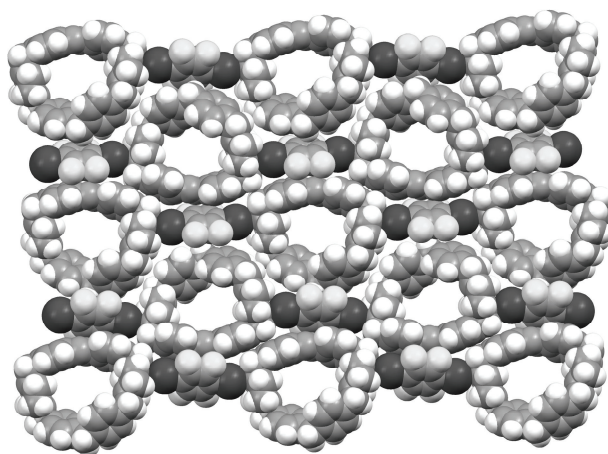
Figure 8. The VDW presentation of the halogen bonded porous crystal lattice[13d] of F4DIB and piperazine macrocycle. The solvent chloroform molecules omitted.

1,4-diazabicyclo[2.2.2]octane (DABCO) was used to diminish or overrule the weak halogen bonding acceptor character of the nitro group oxygens.[13e] The two polymorphic crystal structures of 1-iodo-3,5-dinitrobenzene-1,4-diazabicyclo-[2.2.2]octane reveal a new non-PFC based halogen bond synthon. The crystal structure determination of revealed the binding of two 1-iodo-3,5-dinitrobenzene molecules to DABCO *via* short N/I halogen bonds (Figure 9). Formation of the 2:1-complex was expected due to the employment of the monofunctional acceptor and bisfunctional donor in a 2:1 molar ratio. Contact distances of N27/I1 and N30/I14 are 2.77 and 2.73 Å (Figure 9), corresponding to 22 and 23 % reduction of the sum of the vdW radii, respectively.[13e]

METAL ION BASED SELF-ASSEMBLY

The metal ion based supramolecular self-asembly is a very topical research area, we have contributed a lot in this field,[14] below only a few examples are presented. The linear one-dimensional chains of metal ions has long been of interest in the context of conductive molecular wires. These chains conduct electricity through the delocalization of electrons between linearly arrayed metal centers, but have escaped technological utility
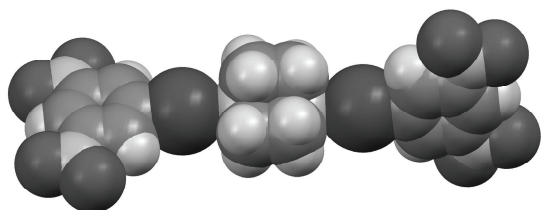

Figure 8. The VDW presentation of the X-ray structure of 2:1 1-iodo-3,5-dinitrobenzene-DABCO halogen bonded complex.[13e]
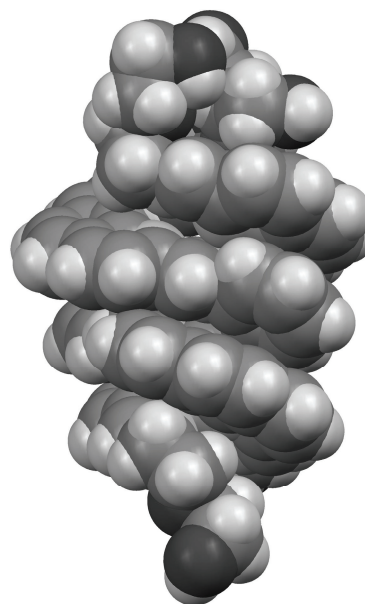

Figure 10. The VDW presentation of a helical self-assembled nanowire-like complex with four copper(I) ions.[14a]

because they are neither ductile, like metal wires, nor can conducting fibers be generated from solution or the melt, as with many polymers. More recently, oligomeric chains of metal atoms sandwiched between parallel ligand strands have been investigated as potential molecular wires. Recently we have demonstrated a self-assembly process for generating chains of copper(I) ions surrounded by helical ligand strands the lengths of which are not limited by the lengths of the precursor subcomponents. The ligand strands contain copper-bound imine (C=N) linkages that are generated from diamine and dialdehyde subcomponents by metal-ion templation. A pair of ligands twist around a linear array of four copper(I) template ions in a double-helical fashion (Figure 10).

As molecular nanowires also the hollow polyhedra prepared through metal–organic self-assembly within the wider context of container molecules has been a topic of great interest in recent years. These structures provide an inner phase of well-defined void space, within which the guest molecules have been encapsulated. Recently we described[14c] a new metal-organic cage complex that is capable of tightly binding a hydrophobic guest molecule in aqueous solution and in the solid state. Our anionic cage exhibited high selectivity for appropriately sized hydrocarbon guests (no affinity was detected for similarly sized alcohols or organic cations), and the constrictive nature of guest binding allowed a smaller guest to be selectively removed from the cage in vacuo while a larger one remained bound. Tetrahedral cage shown in Figure 11 was the unique product observed from the aqueous reaction of the 4,4'-diaminobiphenyl-2,2'-disulfonic acid and 2-formyl-
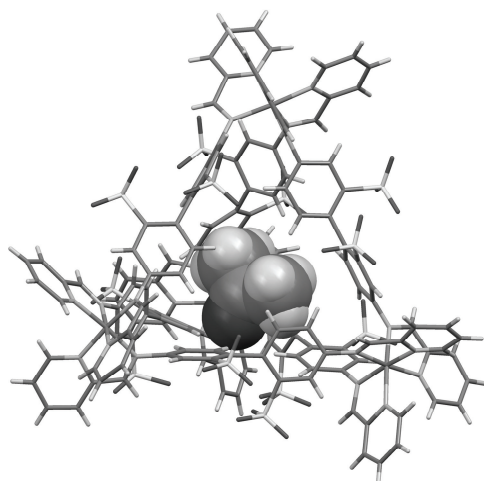
Figure 11. The X-ray stucture of the cage encapsulation an acetone molecule (VDW radii).[14c]

pyridine subcomponents with iron(II) metal ions and a base. Most recent study by us showed that even very pyroforic substances such as white phophorus (P$_4$) can be encarcerated inside the cavity rendering P$_4$ air-stable.[14e]

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SAŽETAK

Slabe molekulske interakcije unutar čvrstog stanja

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Suvremeno istraživanje na području supramolekulske kemije usmjereno je na studije slabih nekovalentnih interakcija kao pokretačke snage samo-strukturiranja i molekulskog prepoznavanja uz naglasak na važnost difrakcije X-zraka na monokristalu u studijama čvrstog stanja. Nedavni napredak postignut je u istraživanjima sustava koji sadrže vodikove i halogene veze, $\pi\cdots\pi$, kation$\cdots\pi$, CH$\cdots$anion i anion$\cdots\pi$ interakcija te koordiniranja iona metala u području samo-strukturiranja i molekulskog prepoznavanja sustava poput rezorcinarena, receptora sa dva mjesta za vezanje, rotaksana i L_6M_4 tetraedara.