

s7.m24.o1 **Smart HBs in the Design of Crystals, Molecular Devices and Functional Materials.** Paola Gilli, Loretta Pretto and Gastone Gilli, *Department of Chemistry and Centre for Structural Diffractionometry, University of Ferrara, Via Borsari 46, 44100 Ferrara, Italy. E-mail: ggilli.chim@unife.it*

Keywords: Smart Hydrogen Bonds; Chemical Leitmotifs; Molecular Materials

Although HB is known since 1920, only recently it has been possible to develop a HB theory general enough to predict HB energies and geometries from the simple knowledge of the chemical formulae of the interacting molecules. Our main contribution to the solution of this problem are the five “*chemical leitmotifs*”, that is the only molecular patterns able to produce strong (four cases) and moderate (one case) HBs, which have been named as (+/-)CAHB, (-)CAHB, (+)CAHB, RAHB and PAHB (CAHB= Charge-Assisted, RAHB= Resonance-Assisted and PAHB= Polarization-Assisted HB).

The discovery of the five *chemical leitmotifs* has made it possible to single out strong HBs in complex molecular systems by simple inspection of their structural features, so discovering that (i) strong HBs are extremely rare in Nature, and (ii) when occurring, they exert a crucial role in the working mechanism of many complex chemical or biological systems.

We have called these strong HBs “*functional HBs*”, because they exert a functional role, or “*smart HBs*”, because they appear to behave in an intelligent way.

The range of phenomena whose mechanisms are controlled by a single strong HB (*smart HB*) is impressive and ranges from chemistry to biochemistry through molecular devices and functional materials, suggesting the possibility of taking advantage of smart HBs for the design of a variety of crystalline or polymeric materials displaying specific physical properties.

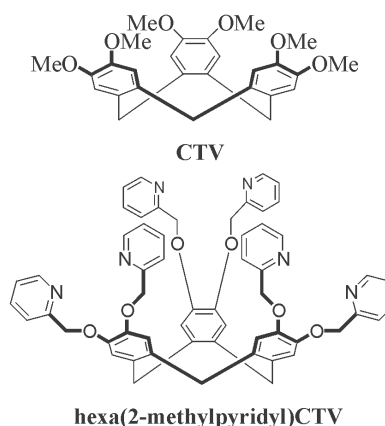
The lecture will focus on these possibilities, including: (1) crystal engineering of HB-controlled molecular or inorganic crystals; (2) bistate systems controlled by intramolecular or intermolecular RAHB-driven proton transfer (solid-state tautomeric processes); (3) order-disorder transitions in potentially ferro/antiferroelectric RAHB-controlled crystals; (4) ESPT (excited-state proton-transfer) as a reference mechanism of RAHB-driven light-switchable bistate systems; (5) role of CAHB (H₂O...H...OH₂)⁺ ions in the mechanisms of proton transmission in water and transmembrane channels.

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s7.m24.o2 **Rigid Molecular Hosts as Building Blocks for Network Structures.** Michael J. Hardie, Ruksanna Ahmad, Christopher Sumby, *School of Chemistry, University of Leeds, Leeds LS2 9JT, UK. E-mail: m.j.hardie@chem.leeds.ac.uk*

Keywords: Cyclotrimeratrylene; Hydrogen Bonding; Coordination Polymers

Cyclotrimeratrylene (CTV) is a rigid bowl-shaped molecule capable of acting as a molecular host for large guests such as fullerene and carborane.¹ Supramolecular assemblies of cyclotrimeratrylene show interactions beyond simple host-guest chemistry, with the dimethoxy moieties acting as hydrogen bond acceptors and/or chelating ligands. Complicated discrete or infinite network structures may result in the solid state. Examples include the highly complex hydrogen bonded structure of [Eu(H₂O)₉]_{1.5}(CTV)₆(CH₃CN)_{5.5}(H₂O)_{7.5}[Co(C₂B₉H₁₁)₂]_{4.5}² and the series of group-1 coordination polymers formed with halogenated mono-carboranes where both the anion and CTV act as ligands.³ [Na(H₂O)(CB₁₁H₆Br₆)(CF₃CH₂OH)] has a helical chain structure, while [Rb(CTV)(CB₁₁H₆Br₆)(H₂O)] and [Cs(CTV)(CB₁₁H₆Br₆)(CH₃CN)] shows a 2D coordination polymer of (6,3) topology. CTV is not a good ligand however, and does not allow for any degree of control over network topology. We are extending the CTV framework by adding functional groups capable of coordination to transition metals, for instance the hexa(2-methylpyridyl)CTV shown below. Hydrogen bonded network structures of CTV and coordination polymers with CTV or extended CTV will be discussed.



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