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MS.24.2

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Fluorocarbon control of crystal structures: NLO materials and supramolecular LCs

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Perfluorocarbon moieties are endowed with unique and useful aggregation features [1]. Perfluoroalkyl residues have a very poor affinity for both polar and non-polar moieties and this accounts for their tendency to form a separate phase in the liquid and to segregate into lamellar domains in the solid. Perfluoroaryl residues have a quadrupolar moment opposite to that of their hydrocarbon analogues and this accounts for the strong $\pi\cdots\pi$ staking interactions exemplified in the columns formed by hexafluorobenzene when interacting with benzene.

Electron distribution around covalent bonded halogens is highly asymmetric resulting in an electron rich belt perpendicular to the covalent bond and an electron poor cap (σ -hole) on its elongation. Both electron-poor and electron-rich sites can thus interact attractively with halogen derivatives and this occurs perpendicular to and on the elongation of the covalent bond, respectively. The interaction involving halogens and electron-rich sites is known as halogen bonding [2]. Due to the strong electron withdrawing properties of perfluorocarbon residues, the σ -hole on the heavier halogen in haloperfluorocarbons is particularly positive and the halogen bonding given by haloperfluorocarbons is a robust supramolecular synthon.

In this communication it will be described how the hierarchical organization of molecular components into heteromeric solid architectures can be designed and realized through a cooperative interplay of the strong halogen bonding given by heavier halogen of iodo- and bromoperfluorocarbons and the unique aggregation features of their perfluorocarbon skeleton. The correlation between the crystal structure of the supramolecular materials thus obtained and their functional properties will be discussed. For instance, it will be shown how the halogen bonding drives the formation of dimers and trimers when alkoxystilbazoles interact with mono- and diiodoperfluoroalkanes and -arenes. These oligomers further organize into 2D and 3D architectures under control of the segregation of perfluoroalkyl chains or the $\pi\cdots\pi$ staking interactions of the perfluoroaromatic residues [3]. While the single pure molecular components do not show any mesomorphic property, the obtained heteromeric architectures described above do show liquid crystalline properties which disappear on architecture disruption. Similar phenomena will be described for non-linear optical materials.

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Unprecedented chemical and thermal stability of MOFs with exposed metal Sites

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Natural and synthetic zeolites find worldwide applications in strategic industrial fields as adsorbents, desiccants and heterogeneous catalysts, due to their remarkable robustness and moderate surface area. Yet, their performances are somehow hampered by their framework stiffness, whose features cannot be easily tuned by self-assembly approaches. Metal-Organic Frameworks (MOFs) represent an authentic breakthrough in this context: a sagacious selection of metal nodes and organic spacers potentially allows the modulation of their key chemico-physical properties- surface area, pore size and decoration, guest affinity and catalytic activity. Nevertheless, MOFs current thermal and chemical stability cannot compete with that of zeolites, especially if *O*-donor spacers are adopted.

Following our long term tradition, this contribution describes how the *N*-donor ligand *sym*-tris(pyrazol-4-yl)benzene (H_3BTP) can be successfully coupled to transition metal ions to isolate MOFs of $M_3(BTP)_2$ formula (1_M , $M = Ni, Cu$; 2_M , $M = Zn, Co$).

As disclosed by XRPD, 1_M exhibit a sodalite-like framework with accessible metal sites, while 2_M possess a 3D architecture with hydrophobic surfaces and narrower channels. Desolvation of 1_M and 2_M reveals their permanent (micro)porosity, confirmed by BET surface areas in the range 930-1860 m²/g. Thermo-gravimetric and thermo-diffractometric analyses demonstrate the exceptional thermal stability of these materials, peaking to 510 °C in the case of 2_{Zn} . While 1_{Cu} and $2_{Co,Zn}$ undergo phase transitions to non porous 3D frameworks upon heating in boiling water, 1_{Ni} possesses an unprecedented robustness. Not only it is stable to heating in air up to 430 °C; more strikingly, it faces a number of harsh conditions mimicking those of industrial processes: as shown by juxtaposing XRPD and N_2 adsorption measurements, 1_{Ni} stands boiling water and boiling acidic or basic solutions for prolonged periods of time, preserving its structural features, crystallinity and surface area.

This stability definitely parallels that of zeolites. Combined with the presence of exposed metal sites- the preferred binding sites for adsorbates- it increases the potential of 1_{Ni} in key applications currently exploiting conventional porous inorganics.

Keywords: MOFs, XRPD, chemical inertness

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From molecules, via supramolecular assembly, to tunable physical properties

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What is the most likely outcome when a homogeneous solution containing different molecular solutes is allowed to evaporate to dryness? Unless a chemical reaction driven by the formation of covalent bonds takes place between the two solutes, one would, as a rule, expect the appearance of two separate molecular solids – the equivalent of a recrystallization. In the supramolecular laboratory, however, the very same process provides an opportunity to move in a completely different direction – a co-crystallization is a deliberate attempt at bringing together different molecular species within one periodic crystalline lattice without making or breaking covalent bonds. The goal of the former is a homomeric product, whereas the latter procedure strives for a heteromeric product and, in general, the odds are stacked firmly in favor of a homomeric product, so how do we go about developing reliable, effective, and versatile synthetic methods for the directed assembly of heteromeric co-crystals? This presentation will (a) outline practical strategies for modular and directed assembly of co-crystals [1], [2], [3] and (b) demonstrate how different physical properties of an active ingredient (such as a pharmaceutically relevant compound) can be altered through co-crystal synthesis [4]. Several co-crystals of a family of anti-cancer compound have been synthesized using a precise and well-defined hydrogen-bond based supramolecular approach which has produced structural consistency in the resulting solids. The melting points of the co-crystals correlate very well with the melting points of the individual acids, and the aqueous solubility can be changed in a predictable way compared to that of the individual drug. Consequently, co-crystals can offer new solid forms from which to choose an active ingredient were a particular physical property can be dialed-in, provided that the co-crystals show structural consistency and that systematic changes are made to the participating co-crystallizing agents.

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Probing mechanical anisotropy in molecular crystals using nanoindentation methods

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The control of mechanical properties of molecular solids is a particularly challenging aspect of crystal engineering and this is true especially in the case of pharmaceutically relevant substances. Since many organic compounds that are used in the pharmaceutical industry have to be crushed and ground during tableting, a correlative understanding of their hardness and toughness is important. With the recent advent of the nanoindentation technique, wherein loads and displacements can be measured with resolutions of 1 nN and 0.2 nm respectively, it is possible to evaluate the mechanical behavior of extremely small-scale systems such as thin films and small single crystals. We have employed the nanoindentation technique to relate the mechanical properties of saccharin single crystals with the underlying structure.¹ Indentations were performed on (100) and (011) faces to assess the mechanical anisotropy. The load-displacement

(*P-h*) curves indicate significant differences in the nature of plastic deformation. The *P-h* curves obtained on the (011) plane are smooth reflecting homogeneous plasticity. However discrete displacement bursts (pop-ins) are observed in the *P-h* curves obtained on the (100) plane suggesting a discrete deformation mechanism. The crystals of monoclinic form of sodium saccharinate (Na(sac).1.875 H₂O) was also studied using nanoindentation technique. The *P-h* curves obtained on two different facets of the crystals that the mechanical behavior of the crystals is indeed anisotropic. The structural origins of these fundamentally different deformation mechanisms have been analyzed in terms of the dimensionality of the hydrogen bonding networks. The study quantifies the relation between interaction anisotropy and mechanical properties such as plastic deformation and lack of continuous response to mechanical deformation. Notably, such a correlation between micro and macro level properties has the promise of designing organic crystals with pre-targeted properties. Further, nanoindentation of molecular crystals offers the scope to quantify the strengths of intermolecular interactions experimentally and to compare different types of interactions in a direct way.

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Removal of hydrocarbons from water by using organophilic zeolites

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Chlorinated volatile organic compounds (VOCs), such as 1,1-dichloroethylene (DCE) and aromatic hydrocarbons, BTX (benzene, toluene, and xylene) constitute a significant fraction of the hazardous air and water pollution [1]. Human beings are exposed to elevated levels of a wide spectrum of volatile organic carbons many of which have been found to be potentially carcinogenic. Research on hydrocarbon removal has been mainly focussed on single components from air matrix, whereas the studies involving aqueous dilute solutions are few. However, in most environmental applications, these pollutants are present in the form of mixtures in very dilute aqueous solution. Removal of organic contaminants from water and wastewater has been achieved using several treatment technologies, such as advanced oxidation processes, air stripping, reverse osmosis, ultrafiltration, and adsorption [2]. Recently, high-silica zeolites were shown to be more effective in removing certain organics from water than activated carbon [3]. In this work the efficiency of zeolite adsorbent materials for the removal of organic contaminant was tested in order to get a better understanding of the host-guest interactions occurring during adsorption processes.

In particular, evidences of 1,2-dichloroethane (DCE), methyl tert-butyl-ether (MTBE) and toluene (TOL) adsorption from dilute solutions into organophilic zeolites will be presented. A combined diffractometric, thermogravimetric and gas chromatographic study was used to: 1) investigate the adsorptive properties of hydrophobic synthetic zeolites; 2) characterise their structure after the adsorption of DCE, MTBE and TOL; 3) localise the organic species in the zeolite channel systems; 4) probe the interactions between organic molecules, water molecules and framework oxygen atoms.

The organophilic zeolites (FAU, MFI and MOR-type framework topology, respectively) were purchased in their protonated form by Tosoh Corporation (200 SiO₂/Al₂O₃ ratio). Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction -