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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 N₂ 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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