## Microsymposium

## Hybrid halogen bonded frameworks: topology variety and molecule sorption properties

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In depth understanding of intermolecular interactions that govern crystal packing in solids is a fundamental topic in presentday research due to its instrumental role in the design and synthesis of new materials. In particular, the use of metals in crystal engineering has developed entirely new classes of materials such as coordination polymers (CPs) and Metal Organic Frameworks (MOFs) [1]. The interest in these materials is related to their easy structural and functional tunability that allows for a plethora of applications in quite different fields, such as gas adsorption and separation, catalysis and molecular recognition [2].

Decorating the structure of ligands compounding CPs and MOFs with tailored functionalities is a pivotal strategy to control and tune their functional properties. Ligands bearing hydrogen bonding functionalities have widely used in this field, while moieties with halogen bonding (XB) donor groups have been poorly investigated. It's known that iodoperfluorinated moieties are very good halogen bonding donors and have been largely used as efficient building blocks in assembling functional materials under XB control [3]. The presence of a haloperfluorinated moiety in the ligand structure has a three-fold effect: (I) promotes the construction of the hybrid framework, (II) creates a fluorinated framework enhancing its thermal and chemical stability, and (III) exploits its halogen bonding donor capability in capture and release specific guest molecules.

In this communication, we report the exploitation of a cooperative approach between halogen bond, hydrogen bond and coordination bond for the assembly of hybrid metal organic materials. Specifically three new hybrid systems and their properties will be discussed: (I) a new XB donor-fluorinated-MOF containing unsaturated metal centres which shows a selective and reversible solvent absorption accompanied by solvatochromic effect, (II) a coordination polymer having a XB donor and an azobenzene unit (Figure) and (III) a fully organic framework sustained by XB and HB which shows a reversible uptake of guest molecules.

[1] Yaghi, O. M. et al. (2003) Nature 423, 705-714.

[2] Yoon, M. et al. (2010) Chem. Rev. 112, 1196-1231.

[3] Cavallo, G. et al (2016) Chem. Rev. 116, 2478-2601



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