

### *The halogen bond in crystal chemistry and beyond*

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According to the recommendation recently issued by an IUPAC Committee, the halogen bond is the net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity [1]. Two distinctive features of the halogen bond are its directionality and the tunability of its strength. There is in fact a remarkable tendency of nucleophilic species to enter the elongation of the carbon-halogen covalent bond as this is the region of the halogen where the electrostatic potential is most positive. The strength of halogen bonds increases with the polarizability of the halogen atom, namely moving from fluorine to chlorine, to bromine, to iodine and with the electron withdrawing ability of groups neighboring the halogen.

Thanks to these two features described above, the halogen bond impacts in all fields where molecular recognition and self-assembly processes have a role. In this lecture it will be discussed how haloperfluorocarbon residues are particularly good halogen bond donors and how halogen bond driven self-assembly processes allow for the preparation of two-, three-, and four-component co-crystals by design. The obtained systems may contain zero-dimensional adducts or one-, two-, or three-dimensional networks. A nice control of the metric and topology of the crystalline solids can be obtained. It will be described, for instance, how a library of halogen bonded Borromean networks was obtained by design [2].

It will be presented how the XB is robust enough from the structural point of view to control the packing of molecular materials in the solid and their organization in the liquid and it will be shown how the interaction can be used to turn on, to turn off, and/or to tune useful functional properties [3]. For instance, the formation of supramolecular gels and liquid crystals will be described and the effectiveness of the interaction in driving the self-assembly and performances of light-responsive supramolecular polymers will be considered [3].

Finally, we will discuss how the halogen bond is robust enough from the conceptual point of view to enable for the collective understanding of the general ability of various groups in the Periodic Table, in addition to halogens, to form attractive interactions with nucleophiles. The mindset developed in relation to the halogen bond studies favored the rationalization that the elements of the chalcogen, pnictogen, and tetrel groups can all form attractive interactions with nucleophiles as the result of an overlooked anisotropic distribution of the electron density around the atoms. Some crystals where tetrel and chalcogen bonds control the lattice will be briefly presented.

[1] Desiraju, G. R., Ho, P. S., Kloo, L., Legon, A. C., Marquardt, R., Metrangolo, P., Politzer, P., Resnati, G. and Rissanen, K. (2013) *Pure Appl. Chem.* 85, 1711-1713.

[2] Kumar, V., Pilati, T., Terraneo, G., Meyer, F., Metrangolo, P., Resnati, G. (2017) *Chem. Sci* 8, DOI: 10.1039/C6SC04478F.

[3] Cavallo, G., Metrangolo, P., Milani, R., Pilati, T., Priimagi, T., Resnati, G. and Terraneo, G. (2016) *Chem. Rev.* 116, 2476-2601.

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