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Gels, Borromeates and Self-Assembled Nanostructures from Competing Interactions to Ureas. Jonathan W. Steed. Department of Chemistry, Durham University, South Road, Durham DH1 3LE. E-mail: jon.steed@durham.ac.uk

A series of pyridyl-appended bis(urea) ligands form supramolecular gels in the presence of metal ions (metallogels), particularly copper(II) and silver(I). The gels have been chracterised by rheometry and SEM, and the effect of the metal ions on gel strength and morphology examined. The metal-induced gelation is linked to the competition between urea-urea and urea-pyridyl hydrogen bonding interactions. Crystals grown from these gels reveal a wealth of structural information about these systems that can be related to gel structure using powder X-ray diffraction data of their xerogels. Exotic species such as Borromean weaves and metallomacrocycles are all formed as alternatives to gelation.

[1] Angew. Chem., Int. Ed., 2008, 47, 5761–5764. [2] Chem. Soc. Rev., in press.

Keywords: gel, Borromean, urea

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Halogen bonds: mechanosynthesis, unusual acceptors and metal-organic materials. <u>Tomislav</u> <u>Friščić</u>, William Jones. *Department of Chemistry*, *University of Cambridge, United Kingdom*. E-mail: <u>tf253@cam.ac.uk</u>, <u>wj10@cam.ac.uk</u>

The past decade has witnessed an explosive growth of interest of chemists, materials scientists and biochemists in halogen bonds. As a result of such intensive research, halogen bonding is now becoming recognised as a versatile design element in crystal engineering. The presentation will provide a brief overview of the current status of halogen bonding in crystal engineering, and highlight several halogen-bonded systems that are being studied in our laboratory. We will describe the application of halogen bonding and isostructurality for the construction of cocrystal-based materials with controllable properties,[1] with particular attention given to systems involving halogen bond acceptors that are not compatible with hydrogen bonding, such as sulfur groups. The application of solid-state mechanochemistry for the synthesis of halogenbonded architectures will be described,[2] and we will illustrate how the study of mechanochemical cocrystallisation using halogen bonds led to a better understanding of the mechanosynthesis of hydrogen-bonded cocrystals. Finally, the presentation will address our efforts towards the development of designs to construct halogen-bonded metal-organic materials.



[1] Cinčić, D., Friščić, T., Jones W., *Chem. Eur. J.*, 2008, 14, 747. [2] Cinčić, D., Friščić, T., Jones W., *J. Am. Chem. Soc.* 2008, 130, 7524.

Keywords: halogen bonding, cocrystals, metal-organic compounds

FA4-MS30-T03

Halogen Bonding: A New Supramolecular Synthon in Anion Coordination Chemistry. <u>Giancarlo</u> <u>Terraneo</u>^{a,b}, Serena Biella^{a,b}, Pierangelo Metrangolo^{a,b}, Tullio Pilati^e, Giuseppe Resnati^{a,b,c}. ^aNFMLab -D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy. ^bCNST -IIT@POLIMI, Politecnico di Milano, Via G. Pascoli 70/3, 20133 Milan, Italy. ^cC.N.R. - I.S.T.M., University of Milan, Via C. Golgi 19, 20133 Milan, Italy. E-mail: <u>giancarlo.terraneo@polimi.it</u>

The halogen bonding (XB), namely the noncovalent interactions wherein halogen atoms function as electrophilic species [1], can be considered as a first choice intermolecular interaction for effective design of self-assembly processes, crystal engineering, and materials science [2]. The particular effectiveness of the interaction in self-assembly processes involving neutral species has received broad attention, on the contrary anion coordination and anion-templated assembly under XB control is a much less developed field [3]. In this contribution, we report some examples of anion binding driven by halogen bonding wherein halide anions act as halogen bonding acceptors. We will present how XB directs the self-assembly of anions forming discrete adducts and 1D, 2D, or 3D supramolecular networks. We will also describe how oxyanions, by far the most numerous class of anions in organic chemistry, can be used as new building block in crystal engineering based on halogen bonding. Some specific examples will be discussed in order to outline some general principles for the design of effective and selective receptors based on XB.



[1] Metrangolo P., Resnati G., *Science*, 2008, 321, 918. [2]. Metrangolo P., Meyer F., Pilati T., Resnati G., Terraneo G., *Angew*.