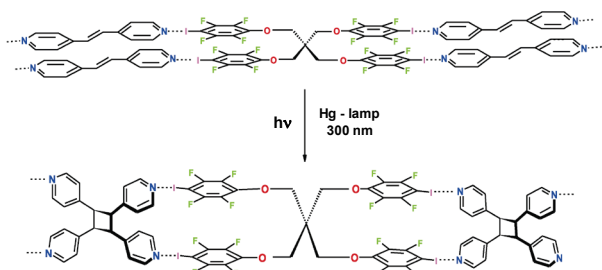


FA4-MS36-T01

Solid-State Reactivity in Halogen-Bonded Co-Crystals. Pierangelo Metrangolo^{a,b}, Serena Biella^{a,b}, Gabriella Cavallo^a, Tullio Pilati^c, Giuseppe Resnati^{a,b,c}, Giancarlo Terraneo^{a,b}. ^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.
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Halogen bonding (XB) [1] defines any noncovalent interaction directed towards the positive region of the electrostatic potential surface of halogen atoms [2]. XB has increasingly facilitated the assembly of diverse host-guest solids [3]. In this contribution, we show the application of this rather new intermolecular interaction in the control of solid-state reactivity in the context of co-crystals. Examples ranging from templated [2+2] photoreactions [4] to gas-to-solid reactions will be presented. In particular, it will be shown that a well-known class of organic salts, bis(trimethylammonium) alkane diiodides, can reversibly encapsulate I₂ [5] and a series of α,ω -diiodoperfluoroalkanes [6] directly from the vapour phase, yielding the same product formed from solution despite a lack of porosity of the starting lattice structure.



[1] P. Metrangolo, G. Resnati, *Science* 2008, 321, 918-919. [2] An IUPAC Task Group set up to examine the definition of halogen bonding has not yet reported, so that given here should be taken as temporary (see www.iupac.org/web/ins/2009-032-1-100 and www.halogenbonding.eu). [3] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, *Angew. Chem. Int. Ed.* 2008, 47, 6114 – 6127. [4] T. Caronna, R. Liantonio, T. A. Logothetis, P. Metrangolo, T. Pilati, Giuseppe Resnati, *J. Am. Chem. Soc.* 2004, 126, 4500-4501. [5] A. Abate, M. Brischetto, G. Cavallo, M. Lahtinen, P. Metrangolo, T. Pilati, S. Radice, G. Resnati, K. Rissanen, G. Terraneo, *Chem. Commun.* 2010, 46, 2724-2726 (Front Cover). [6] P. Metrangolo, Y. Carcenac, M. Lahtinen, T. Pilati, K. Rissanen, A. Vij, G. Resnati, *Science* 2009, 323, 1461-1464.

Keywords: Halogen Bonding, Solid State Reactivity, Templated Photoreaction

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Confinement of 1,3-dimethylcyclobutadiene and intermediates in a crystalline matrix *. Y.-M. Legrand, A. van der Lee, M. Barboiu. *Institut Européen des Membranes*
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Cyclobutadiene is a notable exception in organic chemistry, partly because its ring has 4 π electrons and thus does not

follow Hückel's rule, although it has alternating single and double bonds. Numerous attempts have been reported to stabilize and isolate its structure and to measure its properties, most often in extreme temperature conditions. In this study we show how 1,3-dimethylcyclobutadiene can be prepared, isolated and confined in a calixarene bowl which is capped by guanidine molecules. The atomic structure of 1,3-dimethylcyclobutadiene and several other derivatives trapped in calixarene macrocycles have been determined by X-ray diffraction at low temperature.

*Y.-M. Legrand, A. van der Lee, M. Barboiu ; accepted for publication in *Science* (2010)

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Tweezers and zigzags – models for sequence specific tweezer-polymer interactions. Christine Cardin, Yu Gan, Zhixue Zhu, Howard Colquhoun. *Department of Chemistry, university of Reading, Whiteknights, Reading, RG6 6AD, UK.*
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Intense current interest in the design of multi-component, nanoscale molecular assemblies has led to the exploitation of many types of intermolecular interaction, including π -stacking between aromatic donor and acceptor sites. This type of interaction has recently enabled the fabrication of nanoscale devices including light- and redox-driven switches and molecular logic-gates. In view of the relatively labile nature of the N-benzylpyridinium linkage on which much research into π -stacked molecular assemblies has so far depended, Professor Colquhoun has recently developed a new class of supramolecular materials based on aromatic poly(imide-sulfone) chemistry. Linear and macrocyclic materials of this type display extreme thermochemical stability and readily form π -stacked donor-acceptor complexes with polycyclic hydrocarbons such as pyrene.

Most importantly, sequence-selective complexation of the imide residues in aromatic co-polyimides by a pyrene-based molecular tweezer enables monomer-sequence information to be read by the tweezer and reported through sequence-dependent ¹H NMR complexation shifts. These very significant discoveries in molecular information-processing have been crucially dependent on single-crystal X-ray analyses of tweezer-complexes with linear and cyclic oligo-imides. Tweezer-chain binding has thus been shown to arise not only from π - π stacking interactions but also from N-H...O and C-H...O hydrogen bonding, and from polymer chain-folding. Crystallographic data of this type are of the utmost importance for predictive computational modelling of tweezer-polymer interactions.

