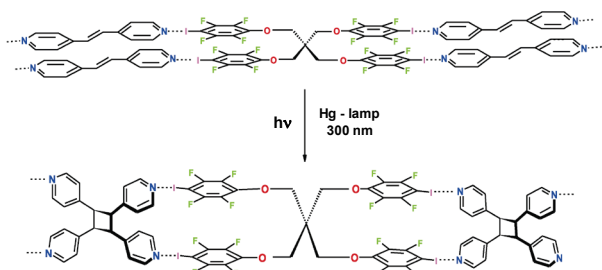


FA4-MS36-T01

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.
E-mail: pierangelo.metrangolo@polimi.it

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

FA4-MS36-T02

Confinement of 1,3-dimethylcyclobutadiene and intermediates in a crystalline matrix *. Y.-M. Legrand, A. van der Lee, M. Barboiu. *Institut Européen des Membranes*
Université de Montpellier II, France.

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.

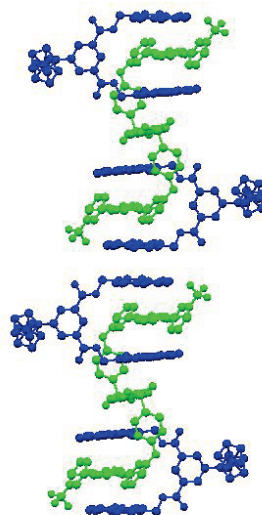
*Y.-M. Legrand, A. van der Lee, M. Barboiu ; accepted for publication in *Science* (2010)

FA4-MS36-T03

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.*
E-mail: c.j.cardin@rdg.ac.uk

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.



Recently we have refined in-house data on the elegant doubly-bound oligomer-tweezer ('zigzag') complex shown. The crystal structure provides the first unequivocal model for chain-folding and small-molecule binding in any synthetic polymer system. Moreover, the supramolecular geometry found in the solid state is remarkably consistent with extensive NMR studies of tweezer-binding in solution. The crystal contains very large solvent cavities and both model building and structure-refinement required very high quality diffraction data. The work was recently accepted for publication in *Nature Chemistry* [1].

[1] Sequence-selective assembly of tweezer molecules on linear templates enables frameshift-reading of sequence information, Z.Zhu, C.J. Cardin, Y. Gan and H.M. Colquhoun, *Nature Chemistry* 2010, (NCHEM 699).

FA4-MS36-T04

Copper Based Oxidation Catalysis. T.J. Muller, G. Steyl, A. Roodt. *Department of Chemistry, University of the Free State, Bloemfontein, 9300, South Africa.*
E-mail: Muller.Theunis@gmail.com

The aerobic oxidation of substituted phenols as a research topic plays an important role in synthesis and biological systems. The demand for value added derivatives of phenolic compounds is steadily growing in the world market, with benzoquinone derivatives constituting a key intermediate in the industrial production of Vitamin E [1]. The use of dioxygen as oxidant is environmentally friendly and available in bulk from the atmosphere. Dioxygen can be catalytically activated by first row transition metal complexes (Cu(II), Co(II) and Mn(IV)) [2]. The addition of co-catalysts (LiCl or MgCl₂) can significantly increase the reactivity of these catalysts during the oxidation cycle [3].

In the current study, model catalyst precursors containing O,O bidentate ligand systems such as tropolone and 2-methyl-3-hydroxy-4-pyrone derivatives, which form five-membered chelates, have been synthesized and structurally characterized and will be discussed. Different aspects of the dioxygen oxidation of selected organic substrates by these copper(II) catalysts, as well as a proposed mechanism for the process, will also be presented.

[1] Sun, H.; Harms, K.; Sundermeyer, J. *J. Am. Chem. Soc.*, 2004, 126, 9550. [2] Simandi, L.I. *Catalytic Activation of Dioxygen by Metal Complexes, Catalysis by Metal Complexes*, 1992, 13, 10. [3] Brenner, W. *German Patent Hoffman-La Roche*, 1972, 2(221), 624

Keywords: copper, oxidation, catalysis

FA4-MS36-T05

Influence of Substituents on PhonyH and its Associated Rh(I) Carbonyl Complexes. Gertruida J.S. Venter, Gideon Steyl, Andreas Roodt. *Department of Chemistry, University of the Free State, Bloemfontein, 9300, South Africa.*
E-mail: truidie@hotmail.com

X-PhonyH (X = aromatic substituents; PhonyH = 4-(phenylamino)pent-3-en-2-one) compounds belong to the group of enaminoketones. Since these contain nitrogen and oxygen

donor atoms as well as an alkene functionality, these electron-rich compounds are of interest in various areas, including application as liquid crystals [1], in fluorescence studies [2], the medical field [3,4] and with significant potential in homogeneous catalysis [5].

This study is therefore concerned with the synthesis of PhonyH derivatives as ligand system and the influence of halide substitution on such ligands with regard to rhodium(I) complex formation. A range of thirteen crystal structures of the (i) free ligands, (ii) complexes of the type [Rh^I(X-Phony)(CO)₂] (X-Phony = 4-(phenylamino)pent-3-en-2-onato derivatives), and (iii) [Rh^I(X-Phony)(CO)(PPh₃)] (substitution of a CO group in (ii) by PPh₃) complexes [6, 7] as catalyst precursors will be discussed. Furthermore, iodomethane oxidative addition, as key step in the catalytic cycles of olefin hydroformylation and methanol carbonylation and the influence of structure/ reactivity relationships therein, will be highlighted.

[1] Pyżuk, W.; Krówczynski, A.; Górecka, E. *Mol. Cryst. Liq. Cryst.* 1993, 237, 75-84. [2] Xia, M.; Wu, B.; Xiang, G. *J. Flu. Chem.* 2008, 129, 402-408. [3] Tan, H.Y.; Loke, W.K.; Tan, Y.T.; Nguyen, N.-T. *Lab Chip* 2008, 8, 885-891. [4] Fanshawe, W.J.; Crawley, L.S.; Safir, S.R.; Wiegand, G.E.; Cooley, E.C. *Substituted enaminoketones*, 1974, US3997530 (Patent). [5] Nair, V.A.; Suni, M.M.; Sreekumar, K. *Proc. Indian Acad. Sci. (Chem. Sci.)* 2002, 114, 481-486. [6] Venter, G.J.S.; Steyl, G.; Roodt, A. *Acta Cryst* 2009, E65, m1321-m1322. [7] Venter, G.J.S.; Steyl, G.; Roodt, A. *Acta Cryst* 2009, E65, m1606-m1607.

Keywords: rhodium, enaminoketone, dicarbonyl