

β -cyclodextrins make a dimer facing bigger rims to each other. Inside the dimer, two l-menthols are included with their molecular axes in the same direction.

Keywords: inclusion complex, β -cyclodextrin, l-menthol

MS38.P05

Acta Cryst. (2011) A67, C487

Self-assembly of metal trischelates to afford extended structures for porous applications

Tia Jacobs, Michael J. Hardie, School of Chemistry, University of Leeds, Leeds, (United Kingdom). E-mail: t.jacobs@leeds.ac.uk

The search for porous materials and design principles to achieve this aim is ever increasing. These materials have a variety of potential applications such as catalysis, gas separation and storage. Problems that exist in the assembly of porous materials are the tendency of molecules to pack closely in the solid state, thereby obliterating free space. In recent years the use of polymeric metal-coordination compounds for porous applications has increased with the realisation that judicious choice of metal centre and rigid bridging ligand can afford two- and three-dimensional solids that feature the desired characteristics [1, 2, 3]

Work will be presented where octahedral trischelate complexes based on functionalised 2,2'-bipyridine ligands are linked into two- and three-dimensional networks using a variety of supramolecular interactions. The stability of these crystalline materials toward evacuation and solvent-loss will be shown, as well as their permeability to gasses as proven by gas sorption.

[1] S.R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1461-1494. [2] B. Moulton, M.J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629-1658. [3] S.L. James, *Chem. Soc. Rev.* **2003**, *32*, 276-288.

Keywords: self-assembly, supramolecular, bipyridine

MS38.P06

Acta Cryst. (2011) A67, C487

Novel coordination polymers based on rigid and flexible organic ligands and Cu(II) ions

Ana Belén Lago, Rosa Carballo, Emilia Garcia-Martínez, Sabina Rodríguez-Hermida, Ezequiel M. Vázquez-López. Departamento de Química Inorgánica, Facultad de Química, Edificio de Ciencias Experimentales, Universidad de Vigo. E-36310 Vigo, Galicia. (Spain). E-mail: ablago@uvigo.es

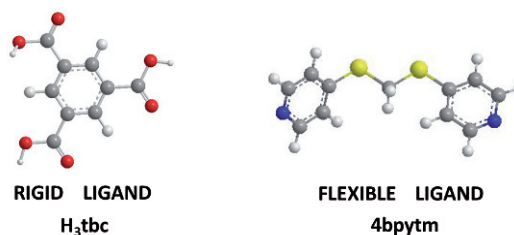
Dynamic polymers based on monomeric components connected through either labile noncovalent interactions or reversible covalent bonds, are the subject of intense investigation. [1] A special class is formed by coordination polymers, where the control of the polymerization is made through metal-ion coordination bonds. In addition, the presence of noncovalent interactions along the polymeric backbone results in that the material could exhibit reversible polymerization/depolymerization properties. [2] Many of the architectures reported to date are based upon rigid linear linker ligands, with less efforts focusing on the use of ligands showing conformational flexibility. The use of flexible ligands can lead to the formation of interesting architectures without loss of control in the self-assembly process.

We have performed an investigation on the formation of copper(II) coordination compounds based on the use of the 1,3,5-benzenetricarboxylic acid (H_3btc) and the spacer with conformational

flexibility, bis(4-pyridylthio)methane (4bpytm). As result of this study two new coordination polymers are prepared and characterized: $^1_\infty[Cu(H_2btc)_2(4bpytm)]$ (**1**) and $^2_\infty[Cu(Hbtc)(4bpytm)_2] \cdot H_2O$ (**2**). Both compounds are obtained as a mixture by a solvothermal procedure. The optimization of the synthetic route allowed the isolation of the pure phases in a high yield.

The 1D covalent network (**1**) is achieved by the bridging role of 4bpytm ligand between the copper(II) ions, with the biprotonated H_2btc^- ligand acting as terminal ligand. 4bpytm produce also chains in (**2**) that are further pillered by the monoprotinated ligand $Hbtc^-$ to form high robust layers. An interesting feature is that in both compounds exist different open sites per copper atom that form coordinatively unsaturated metal centres (UMCs) that can strongly interact with guest molecules. The use of a ligand with carboxylate groups partially protonated makes that the corresponding supramolecular associations are organized by the effect of different OH...O hydrogen bonds.

Acknowledgments: A.B.L. thanks to Xunta de Galicia for a postdoctoral-fellowship "Ángeles Alvaríño". Financial support from Xunta de Galicia (Spain) (research project 10TMT314002PR) is gratefully acknowledged.



[1] C.F. Chow, S. Fujii, J.M. Lehn. *Angewandte Chemie* **2007**, *46*, 5007-5010.

[2] J.B. Beck, J.M. Ineman, S.J. Rowan. *Macromolecules* **2005**, *38*, 5060-5068.

Keywords: copper complexes, crystal structures, metallosupramolecular chemistry.

MS39.P01

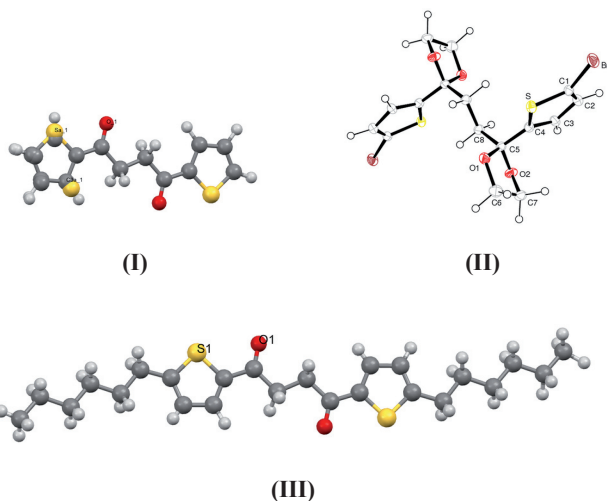
Acta Cryst. (2011) A67, C487-C488

Structural studies and electron density analysis of thiophene based compounds

Maqsood Ahmed,^a Sajida Noureen,^b Philippe C. Gros,^b Benoit Guillot,^a Christian Jelsch,^a Claude Lecomte,^a ^aUMR CNRS 7036(CRM²), Laboratoire de Cristallographie, Résonance Magnétique et Modélisation, ^bUMR CNRS 7565 (SOR), Synthèse Organométallique et Réactivité, Faculté des Sciences et Technologies - UHP, BP 239, 54506 Vandœuvre-lès-Nancy cedex, (France). E-mail: maqsood.ahmed@crm2.uhp-nancy.fr

As the galloping energy demands of the world combined with the environmental concerns call for looking alternate and cleaner sources of energy, much attention is being diverted to the renewable sources of energy, including the solar energy. Dye sensitized solar cells (DSSCs) are proving to be a potential alternate for the conventionally used semiconductor based solar cells [1]. They offer many advantages such as tuneable electronic properties, especially the band gap, by chemical modifications and substitutions. In this context, thiophenes and their substituted homologues have attracted much attention of the scientific community as the starting materials for the synthesis of organic dyes and metal organic complexes worth applicable in DSSCs. It is considered that the backbone retains its π -conjugated coplanar conformation if the long alkyl chain is substituted at a suitable

position [2]. In this type of molecules, it is observed, however, that the thiophene ring often shows a disorder [3] even at low temperature, if the adjacent environment allows for free rotation around a single bond. Thus the structural analysis is extremely important for substitution and chain extension at the required position to obtain the required electrochemical efficiency. The experimental analysis of the electronic environment is also desirable to obtain the optimum efficiency of the target molecule. In the meeting, three different representative cases of thiophene based compounds will be presented. The case of *1,4-bis(2-thienyl) butane-1,4-dione* (I), for which the modelling is done for the disordered thienyl group. Secondly, the case of *2, 2'-(1, 2-ethanediyl) bis [2-(5-bromo-2-thienyl)-1, 3-Dioxolane* (II), for which the electron density parameters have been transferred from the ELMAM2 database [4] and lastly, the case of *1,4-bis(5-hexyl-2-thienyl) butane-1,4-dione* (III), whose experimental electron density analysis is underway using MoPro software [5].



[1] M. Grätzel, *Nature*. **2001**, *414*, 338. [2] C. Roux, J.-Y. Bergeron, M. Leclerc, *Macromo. Chem.* **1993**, *194*, 868-877. [3] S. Wang, F. Brisse, F.B. Gariéy, A.D. Bouillud, M. Leclerc, *Acta. Cryst.* **1998**, *C54*, 553-555. [4] S. Domagala, P.M. Munshi, M. Ahmed, B. Guillot, C. Jelsch, *Acta. Cryst.* **2011**, *B67*, 63-78. [5] C. elsch, B. Guillot, A. Lagoutte, C. Lecomte, *J. Appl. Cryst.* **2005**, *38*, 38-54.

Keywords: solar cells, thiophenes, electron density

MS39.P02

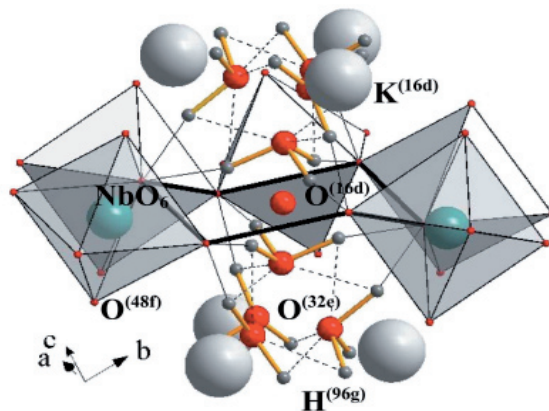
Acta Cryst. (2011) **A67**, C488

The exotic ions arrangement in the pyrochlore -type framework of protonic conductor $K_{0.88}Nb_2O_7.58H_{4.28}$ for intermediate temperature PSOFCS

Smirnova Olga, *Institute for Chemical Research, Kyoto University (Japan)*. E-mail: smirnova@msk.kuicr.kyoto-u.ac.jp

According to single-crystal, synchrotron powder X-ray diffraction and neutron powder diffraction studies, the novel pyrochlore-type compound contains the water molecules located in 32e sites, the hydroxide ions and potassium ions are located in 16d sites with a significant amount of 'free' protons in 96g sites corresponding to the structural formula $K_{0.88}(OH)_{0.54}H_{1.66}(H_2O)_{1.04}Nb_2O_6$. The total weight loss at temperatures up to 773 K is limited to about 8%, suggesting the oxygen escape from 48f sites can be excluded and 'free' protons must be kept in the structure. The bulk conductivity in ambient air reaches the plateau at $10^{-2} S \cdot cm^{-1}$ for 623 K. Owing to the wide stability range and resistance to water solubility, the compound can be considered as a

candidate to fill the gap for intermediate temperature solid-oxide fuel-cell applications materials. Even more hydrogen-containing materials are prepared with ion exchange for protons.



The protonic sites in hydrothermally grown $K_{0.88}Nb_2O_7.58H_{4.28}$ as extracted from neutron powder diffraction data.

[1] O. Smirnova, N. Kumada, T. Takei, Y. Yonesaki, M. Yashima, N. Kinomura. *Acta Cryst.* **2010**, *B66*, 594-602.

Keywords: protonic conductor, intermediate temperature SOFCs, powder diffraction

MS39.P03

Acta Cryst. (2011) **A67**, C488-C489

Rationalising the molecular origins of dyes used in dye sensitized solar cells

Kian Sing Low^a, Jacqueline Cole,^{a,b} ^a*Cavendish Laboratory, J.J Thomson Avenue, Cambridge, CB3 0HE, (UK)*. ^b*Departments of Chemistry and Physics, University of New Brunswick, P. O. Box 4400, Fredericton, New Brunswick E3B5A3, Canada*. E-mail: k1356@cam.ac.uk

The dye sensitized solar cell (DSC) has been at the forefront of worldwide research since the pioneering work of O'Regan and Grätzel [1] showing that these devices can achieve a power conversion efficiency of over 11%. One of the key aspects controlling the performance of the DSC is the molecular nature of the dye used. However, even after two decades of study, one of the first ever produced dyes for DSC's (N719) still provides record efficiencies. This is puzzling as the DSC field is so driven by economics and Ruthenium, which is contained in N719, is a rare transition metal making it relatively expensive.

We have used X-ray diffraction and accompanying statistical analysis to compare three Ruthenium based dyes and one Iron based dye which are structurally similar to N719 in order to elucidate why it is still one of the best performing dyes to date. Iron and Ruthenium lie in the same group of the periodic table. Consequently the Iron based dye has been considered as a cheaper alternative to Ruthenium based dyes despite affording reduced efficiency.

Our X-ray diffraction studies concentrate on a Ruthenium dye and an Iron dye that have the same principal molecular structure but different counter ions. We also looked at the structural differences of the previously mentioned Ruthenium dye with and without carboxylate groups attached. These structures were all compared to that of N719 both structurally and spectroscopically.

The Cambridge Structural Database (CSD) was then employed