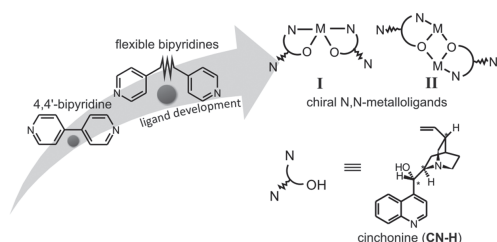


advancing the field of homochiral MOFs. Biomolecules have emerged recently as particularly attractive building blocks for constructing MOFs. Following this direction, we turned our attention toward *Cinchona* alkaloids and our work aims to develop a novel attractive route to chiral bipyridine-type linkers based on N,N-ditopic metalloligands with the backbone of these readily accessible biomolecules.

We will demonstrate that mono- or dinuclear chiral *N,N*-ditopic metalloligands derived from *Cinchona* alkaloids, the metallotectons of the type **I** and **II** (Scheme 1), exhibit intrinsic molecular shape-derived properties for noncovalent interactions-driven self-assembly into chiral microporous supramolecular architectures prone to racemate separation or selective gas sorption [1], [2]. We also recognized and successfully employed their second assembly mode, wherein they act as *N,N*-ditopic metalloligands for metal-containing nodes giving rise to novel heterometallic coordination polymers with helical or zig-zag chain topologies [3], [4].



Scheme 1 Strategy for developing novel chiral *N,N*-ditopic linkers

[1] T. Kaczorowski, I. Justyniak, T. Lipińska, J. Lipkowski, J. Lewiński, *J. Am. Chem. Soc.* **2009**, *131*, 5393-5395. [2] J. Lewiński, T. Kaczorowski, D. Prochowicz, T. Lipińska, I. Justyniak, Z. Kaszkur, J. Lipkowski, *Angew. Chem. Int. Ed.* **2010**, *49*, 7035-7039. [3] J. Lewiński, T. Kaczorowski, I. Justyniak, D. Prochowicz, *Chem. Commun.* **2011**, 950-952. [4] I. Justyniak, D. Prochowicz, J. Lewiński, *Chem. Eur. J.* **2011**, submitted.

**Keywords:** cinchona alkaloids, metalloligands, structure

## MS.87.3

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### Chiral discrimination in the solid state

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The methods of enantiomeric resolution have been studied extensively, and involve the process of spontaneous resolution by crystallisation, diastereomer formation, enzymatic transformations and chromatographic methods. However, to our knowledge, no detailed study of the correlation between structure in the solid state and enantiomeric resolution has been carried out. We have taken a different approach to the question of enantiomeric resolution in order to understand the mechanism of the molecular recognition that drives the differentiation of the resolving agent for one particular enantiomer.

A series of supramolecular systems was analyzed to investigate the mechanism of chiral discrimination in the solid state. We have set up a series of competition experiments where the resolving agent was exposed to mixtures of enantiomers, and the mole fraction of the starting mixture were varied systematically. The ensuing solutions were allowed to crystallise and the mole fraction of the entrapped enantiomer were measured by analysing the crystal structure. This is an extension of the technique employed to measure the selectivity profile of a given host compound (H) towards a pair of guests A and B, whereby the host, H is dissolved in a series of solutions where the mole fraction  $X_A$  varies in steps from 0 to 1. The resulting crystals are analysed, yielding mole fractions of  $X_A$  as  $Z_A$ . The selectivity coefficient at each point is then defined as

$$K_{A:B} = (K_{B:A})^{-1} = Z_A/Z_B * X_B/X_A \text{ where } (X_A + X_B = 1)$$

and is a measure of the discrimination of the host for a given guest. In our case the two guests were replaced by (*R*)- and (*S*)-enantiomers. One obtains more information regarding the resolution process when the selectivity is relatively poor and the targeted (*R*)- and (*S*)-enantiomers are both entrapped in the same crystal, although in different proportions. In this manner, one can assess the forces that impinge on both guests as they are entrapped in the crystal structure and the resultant conformation changes that occur in the host in order to best accommodate these guests.

Thus we characterized a series of related inclusion compounds [1] and diastereomeric salts [2], using selected resolving agents. Investigation of the resultant structures was carried out and the main characteristics of structural changes during the discrimination process were summarized and elucidated.

[1] N.B. Báthori, L.R. Nassimbeni, *Cryst. Growth & Des.* **2010**, *10*, 1782-1787.

[2] N.B. Báthori, L.R. Nassimbeni, *Chem. Commun.* **2011**, 47, 2670-2672.

**Keywords:** chiral, diastereomer, inclusion

## MS.87.4

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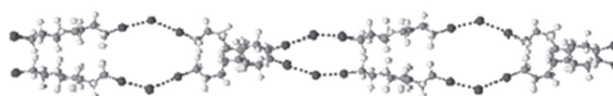
### Chirality in halogen-bonded supramolecular architectures

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Halogen bonding (XB), namely any noncovalent interactions directed towards the positive region of the electrostatic potential surface of halogen atoms [1], has proven its efficiency and reliability in the design and construction of self-assembly processes in supramolecular chemistry, crystal engineering, and materials science [2]. New aggregation processes can be realised with the novelty coming from either the molecular identity of single modules that are assembled or from the way the modules are arranged in the supramolecular architectures.

In this contribution, we will discuss the conformational enantiomorphism of perfluoroalkyl chains and display that perfluoroalkanes have an enantiophobic preference towards selection of molecular chirality in halogen-bonded architectures. Is this intrinsic preference responsible for the supramolecular chirality observed in the reported structures?

Examples of the halogen bonding ability to control spontaneous resolution phenomena in hybrid perfluorocarbon-hydrocarbon architectures will be reported where the involved modules are long-chain iodoperfluoroalkanes or diiodoperfluoroalkanes interacting with different halogen bonding acceptors [3, 4].



### Supramolecular Homochiral XB Double Helices

[1] www.iupac.org/web/ins/2009-032-1-100 and www.halogenbonding.eu. [2] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo *Angew. Chem. Int. Ed.* **2008**, *47*, 6114-6127. [3] H. Neukirch, E. Guido, R. Liantonio, P. Metrangolo,

T. Pilati, G. Resnati *Chem. Commun.* **2005**, 1534–1536. [4] A. Casnati, R. Liantonio, P. Metrangolo, G. Resnati, R. Ungaro, F. Ugozzoli *Angew. Chem. Int. Ed.* **2006**, *45*, 1915–1918.

**Keywords:** halogen bonding, spontaneous resolution, supramolecular architectures

## MS.87.5

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### Precise absolute structure determination for light-atom structures

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In an absolute structure determination one absolute structure is refined competitively against the inverted alternative. The result is expressed by the Flack parameter  $x(u)$ , which for absolute configuration determination can be interpreted as the mole fraction of the alternative enantiomer in the crystal [1]. The physical range of  $x$  is 0 to 1; Flack and Bernardinelli have shown that even if the bulk material is known to be enantiopure the standard uncertainty ( $u$ ) should be less than 0.1 before any firm conclusions can be drawn [2].

The likely success of an absolute structure determination can be gauged using the *Friedif* parameter [3]. If *Friedif* has a value of about 80 or more routine absolute structure determination should present little problem. Light atom structures may have values of *Friedif* of 30 or less even for Cu-K  $\alpha$  radiation, and Flack and Bernardinelli's criterion has proved to be extremely demanding for such cases. Two refinement strategies will be described which can improve the  $u$  to 0.1 or less for such structures.

One method is based on the quantity

$$D(\mathbf{h}) = \frac{I(\mathbf{h}) - I(-\mathbf{h})}{I(\mathbf{h}) + I(-\mathbf{h})} = (1 - 2x) \frac{F^2(\mathbf{h}) - F^2(-\mathbf{h})}{F^2(\mathbf{h}) + F^2(-\mathbf{h})}$$

The term based on  $I(\mathbf{h})$  and  $I(-\mathbf{h})$  and its standard uncertainty can be calculated from a single crystal X-ray diffraction data set. The term based on  $F^2(\mathbf{h})$  and  $F^2(-\mathbf{h})$  can be calculated from the model. It is therefore possible to write out a set of restraints based on observed and calculated values of  $D(\mathbf{h})$  and apply these in an absolute structure refinement. Systematic errors in the intensities, such as absorption, tend to cancel out (in an average way) so that measured values of  $D(\mathbf{h})$  should be more accurate than the values of the measured intensities.

The second method is based on *leverage analysis*, which yields quantities which measure the influence that observations have on the precision of a specific parameter. [4] A weighting scheme has been developed where data which strongly influence the Flack parameter are systematically up-weighted.

Both methods yield significantly more precise values of the Flack parameter than conventional refinement. For example when a data set was collected for L-alanine (*Friedif* = 34) with Cu-K  $\alpha$  radiation at 100 K, conventional refinement yielded a Flack parameter equal to 0.12(21), whereas the restrained refinement yielded a value of 0.00(8). A refinement based on the leveraged weighting scheme yielded  $x = -0.02(5)$ . In the case of a hydrocarbon with *Friedif* = 9 a value of  $x = 0.07(10)$  was obtained.

Both methods carry the advantage that the Flack parameter is allowed to refine along with all the other parameters, so that its standard uncertainty reflects correlations present in the refinement.

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*J. Appl. Cryst.* **2000**, *33*, 1143–1148. [3] H.D. Flack, U. Shmueli, *Acta Cryst.*, **2007**, *A63*, 257–265. [4] E. Prince, *Mathematical Techniques in Crystallography and Materials Science*. Springer **2004**.

**Keywords:** chirality, flack parameter, refinement

## MS.88.1

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### Anion-deficient perovskites modulated by periodic translational interfaces

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Although the perovskite-related structures have already been investigated extensively for many years, some blank spots in this field have still not been unraveled. Here I present a new family of anion-deficient perovskite-based compounds containing an easily polarizable A cation with a sterically active lone electron pair, where the parent structure is periodically modulated by translational interfaces with properties similar to those of crystallographic shear (CS) planes [1, 2]. The oxygen content in the anion-deficient perovskites  $(\text{Pb,Bi})_{1-x}\text{Fe}_{1+x}\text{O}_{3-y}$  can be varied over a wide range through a long-range-ordered arrangement of the (CS) planes, resulting in incommensurately modulated structures. Based on the results of electron diffraction, high-resolution scanning transmission electron microscopy and neutron powder diffraction a superspace model was constructed describing a periodic arrangement of the CS planes of any arbitrary orientation. The superspace description is based on compositionally-dependent constructions of discontinuous atomic domains for the layer sequences of two basic low-index CS planes subsequently “merging” them in appropriate ratio into a single superspace model for the CS planes of desired orientation. The refinement of displacive modulation parameters revealed the antiferroelectric nature of the structure related to antiparallel orientation of the lone electron pair domains on  $\text{Pb}^{2+}$  and  $\text{Bi}^{3+}$  at both sides of the CS planes.

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**Keywords:** perovskite, incommensurately modulated, ferrite

## MS.88.2

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### Minerals in superspace

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Modulated structures are frequently observed in mineral systems. Their existence is usually restricted to certain pressure/temperature conditions and often depends on the composition. Thus minerals of the same group may show modulations if they are from one type location, while they have normal structures, if they are from a different location, where the formation conditions were different.

Some examples of minerals exhibiting modulated structures are: framework aluminosilicates (e.g. plagioclase, nepheline, sodalites), silica polymorphs (e.g. quartz, tridymite), layered aluminosilicates (e.g. melilites, antigorite, fersnoite), iron oxides and sulfides (pyrrhotite,