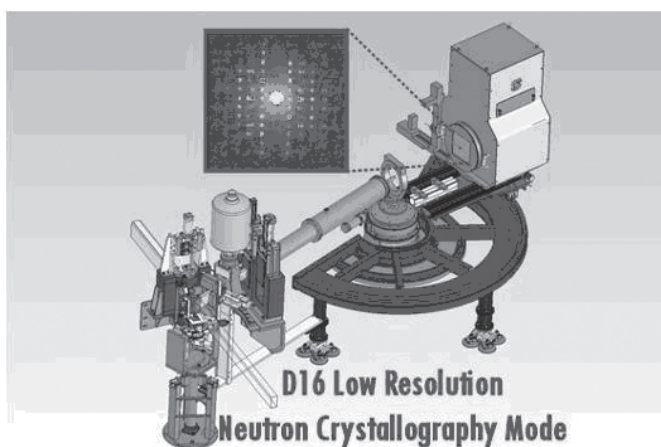


complex technique requiring prohibitive crystal volumes and long data collection times. The technique came of age as a result of developments in many areas from sample preparation to instrumentation [5], alongside developments in complementary structural methods.

The particular case of low resolution neutron crystallography will be presented in the context of the upgrading of the monochromatic D16 neutron beamline at the Institut Laue Langevin (ILL). Similar experiments were previously carried out on the DB21 beamline at the ILL, where the neutron flux and detector sensitivity were poorer. A low resolution crystallography mode is under commissioning on D16 where users will use cold neutrons to collect neutron diffraction data on crystals of 0.01mm³ or smaller. The role of the technique in the modern structural biology scenario will be demonstrated: typical applications and sample environment will be described, namely for membrane proteins where contrast variation is used to study areas in contact with the membrane *in vivo*. Obtaining suitable crystals of membrane proteins is still a challenge and information on the packing of detergent and membrane proteins in the crystal will be a significant contribution to filling an historical gap between crystallography and membrane proteins.



[1] S.C.M. Teixeira, G. Zaccai, et al., *Chemical Phys.* **2008**, *345*, 133-151. [2] M.P. Blakeley, S.C.M. Teixeira, I. Petit-Haertlein, I. Hazemann, A. Mitschler, M. Haertlein, E. Howard, A.D. Podjarny, *Acta Cryst.* **2010**, *D66*, 1198-1205. [3] M.P. Blakeley, P. Langan, N. Niimura, A. Podjarny, *Curr. Opin. Struct. Biol.* **2008**, *18(5)*, 593-600. [4] A. Podjarny, A. Mitschler, I. Hazemann, T. Petrova, F. Ruiz, M. Blakeley, M.T. Dauvergne, F. Meilleur, M. Van Zandt, S. Ginell, A. Joachimiak, D. Myles, *Acta Cryst.* **2004**, *A60*, s155. [5] T. Gutberlet, U. Heinemann, M. Steiner, *Acta Cryst.* **2001**, *D57*, 349-354.

Keywords: neutron, contrast-variation, crystallography

MS.87.1

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Handedness of two-fold helices and chiral space-groups

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We have not so far discussed about right- or left-handedness of enantiomeric assemblies with two-fold helices. In fact, a two-fold helical axis with 180 degrees rotation and translation has only a symbol 2_1 , while a distinguishable three-fold helical axis has two symbols; 3_1 for a right-handed helix and 3_2 for a left-handed helix. In daily life, one can use right- or left-handed stairs. When one walks upstairs, turns to the left on staircase landing, and further go upstairs, the stairs can

be recognized to be right-handed. The reverse right-turn yields left-handed stairs.

We investigated supramolecular chirality for 1D assemblies of benzene molecules. Benzene molecules form right-handed 2_1 helical assembly with side-to-side contact in channels of inclusion crystals of cholic acid [1]. It was confirmed that polymorphic crystals of benzene itself have 2_1 helical assemblies with two and three kinds of molecular contacts for $P2_1/c$ and $Pbca$, respectively. Moreover, we analyzed 1D hydrogen bonding networks of primary ammonium carboxylates. The networks have 2_1 helical connection among nitrogen and oxygen [2].

We termed such enantiomeric relation of the two-fold helices as supramolecular tilt chirality [3], [4]. This handedness definition has consistency with the helical discrimination for polymeric materials such as DNA and proteins. It is no doubt that a large amount of organic crystals consist of molecular assemblies with right- or left-handed helices, likewise biopolymers. The Cambridge Structural Database involves over 500,000 data till 2011. Among them, over seventy percent have space groups with two-fold helices. Moreover, it was found that supramolecular chirality lies in each step of hierarchical structures, such as helical molecular assemblies, bundles of the helices, complimentary helical assemblies of host and guest components.

In the crystallographic theory, the concept of both point groups and space groups in mathematics is described as assemblies of points, where materials are approximated as a single point. The theory based on one-point approximation is surely correct in the case of atoms and ions with spherical symmetry, but is not considered to be always correct in the case of molecules, particularly, organic molecules with various shapes. These molecules require multi-point approximation methods instead of the one-point method. Now we know that a two- and three-point approximation method enables us to discriminate right- or left-handedness of 2_1 helical assemblies.

Among 65 chiral space-groups, only eleven groups are split into the enantiomeric pairs, while the remaining 43 groups are not split into the pairs. This mainly comes from the crystallographic theory that two-fold rotations have no handedness. We checked handedness of space-groups involving 2_1 -, 4_2 -, 6_3 -helices, two-, three-, four-, six-rotations as well as asymmetric $P1$ group with multipoint approximation methods. As a result, the 43 chiral space-groups were found to be split into the enantiomeric pairs.

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Keywords: organic crystal, helical structure, space groups

MS.87.2

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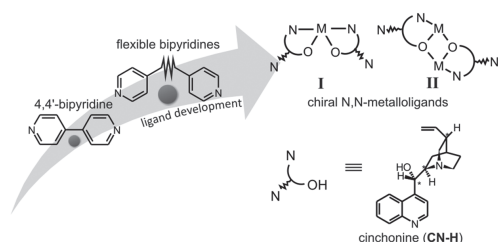
Molecular building block approach to chiral coordination polymers and noncovalent porous materials

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Among the vast library of building blocks simple achiral bipyridines are the most commonly used linkers for constructing metal-organic frameworks (MOFs), but their chiral derivatisation have encountered difficulties. Therefore, developing versatile strategies for facile generation of chiral bipyridine-type ligands is the key challenge for

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

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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.

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[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

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