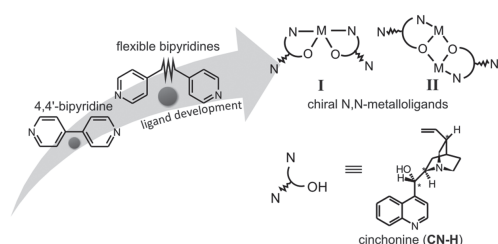


advancing the field of homochiral MOFs. Biomolecules have emerged recently as particularly attractive building blocks for constructing MOFs. Following this direction, we turned our attention toward *Cinchona* alkaloids and our work aims to develop a novel attractive route to chiral bipyridine-type linkers 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

Nikoletta B. Báthori and Luigi R. Nassimbeni, *Department of Chemistry, Cape Peninsula University of Technology, Cape Town (South Africa)*. E-mail: bathorin@cput.ac.za

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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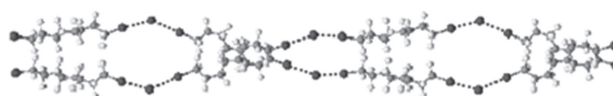
Chirality in halogen-bonded supramolecular architectures

Giancarlo Terraneo,^{a,b} Serena Biella,^{a,b} Pierangelo Metrangolo,^{a,b} Tullio Pilati,^c Giuseppe Resnati,^{a,b,c} *INFMLab - D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, I-20131 Milan (Italy)*. ^bCNST-IIT@POLIMI, *Politecnico di Milano, Via G. Pascoli 70/3, I-20133 Milan (Italy)*. ^cC.N.R. - I.S.T.M., *University of Milan, Via C. Golgi 19, I-20133 Milan (Italy)*. E-mail: giancarlo.terraneo@polimi.it

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,