MAMANE VICTOR

RESEARCH

Halogen and Chalcogen Bond in Catalysis

Halogen and Chalcogen Bond in HPLC on Chiral Stationary Phase

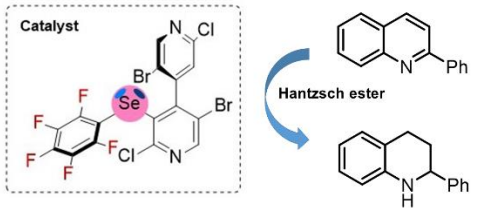
Methods in Heterocyclic Chemistry

Carbon Nanotube Functionalization

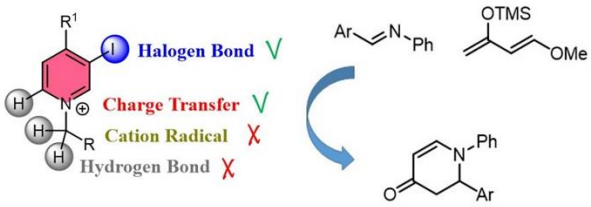
Halogen and Chalcogen Bond in Catalysis

We study the σ-hole interactions in solution and we develop new chiral halogen and chalcogen bond donors for application in (asymmetric) catalysis.

Halogen and Chalcogen Bond Donors Based on Axially Chiral 4,4'-bipyridine Scaffold

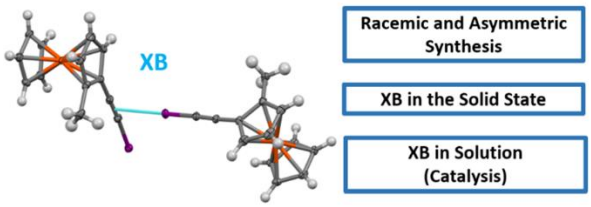


Molecules 2019

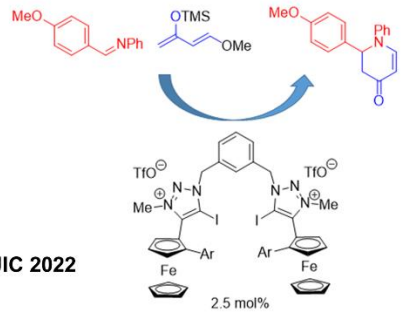


Adv. Synth. Catal. 2021

Halogen Bond Donors Based on Planar Chiral Ferrocenyl Scaffold

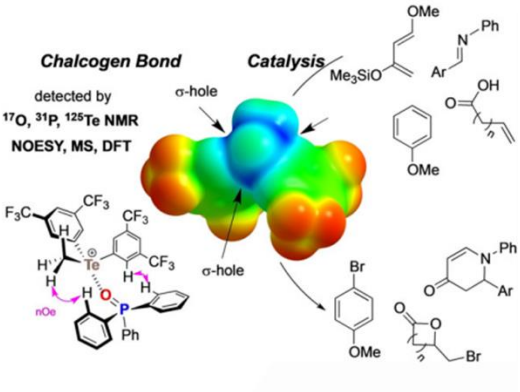


Organometallics 2020

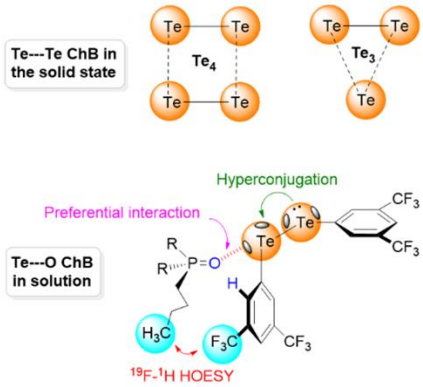


Eur JIC 2022

Chalcogen Bond Donors Based on Tellurium



Angew. Chem. Int. Ed. 2021



Chem. Eur. J. 2022

Selected publications:

1) Weiss, R.; Aubert, E.; Peluso, P.; Cossu, S.; Pale, P.; Mamane, V. Chiral Chalcogen Bond Donors Based on the 4,4'-Bipyridine Scaffold. *Molecules* **2019**, *24*, 4484.

2) Mamane, V.; Peluso, V.; Aubert, E.; Weiss, R.; Wenger, E.; Cossu, S. Pale, P. Disubstituted Ferrocenyl Iodo- and Chalcogenoalkynes as Chiral Halogen and Chalcogen Bond Donors. *Organometallics* **2020**, *39*, 3936.

3) Weiss, R.; Aubert, E.; Pale, P.; Mamane, V. Chalcogen-Bonding Catalysis with Telluronium Cations. *Angew. Chem. Int. Ed.* **2021**, *60*, 19281.

4) Weiss, R.; Golisano, T.; Pale, P.; Mamane, V. Insight into the Modes of Activation of Pyridinium and Bipyridinium Salts in Non-Covalent Organocatalysis. *Adv. Synth. Catal.* **2021**, *363*, 4779.

5) Aubert, E., Doudouh, A., Wenger, E.; Sechi, B.; Peluso, P.; Pale, P.; Mamane, V. Chiral Ferrocenyl–Iodotriazoles and –Iodotriazoliums as Halogen Bond Donors. Synthesis, Solid State Analysis and Catalytic Properties. *Eur. J. Inorg. Chem.* **2022**, *2022*, e202100927.

6) Weiss, R.; Aubert, E.; Groslambert, L.; Pale, P.; Mamane, V. Chalcogen Bonding with Diaryl Ditellurides: Evidence from Solid State and Solution Studies. *Chem. Eur. J.* **2022**, *28*, e202200395.

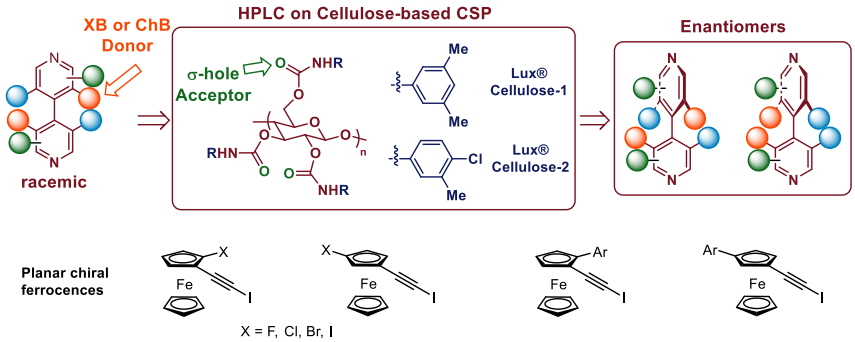
7) Peluso, P.; Mamane, V. Stereoselective Processes Based on σ-Hole Interactions. *Molecules* **2022**, *27*, 4625.

8) Pale, P.; Mamane, V. Chalcogen Bonds: How to Characterize Them in Solution? *ChemPhysChem* **2023**, *24*, e202200481 (Concept Article).

9) Groslambert, L.; Padilla-Hernandez, A.; Weiss, R.; Pale, P.; Mamane, V. Chalcogen-Bond Catalysis: Telluronium-Catalyzed [4+2]-Cyclocondensation of (in situ Generated) Aryl Imines with Alkenes. *Chem. Eur. J.* **2023**, 10.1002/chem.202203372.

Halogen and Chalcogen Bond in HPLC on Chiral Stationary Phase

In collaboration with P. Peluso, we have demonstrated that stereoselective XBs and ChBs are able to control enantioseparation of polyhalogenated atropisomeric 4,4'-bipyridines and planar chiral ferrocenyl iodoalkynes by HPLC on cellulose-based chiral stationary phases (CSPs).



Selected publications:

1) Peluso, P.; Mamane, V.; Aubert, E.; Cossu, S. Insights into the impact of shape and electronic properties on the enantioseparation of polyhalogenated 4,4'-bipyridines on polysaccharide-type selectors. Evidence of stereoselective halogen bonding interactions. *J. Chromatogr. A* **2014**, *1345*, 182.

2) Peluso, P.; Mamane, V.; Cossu, S. Liquid chromatography enantioseparations of halogenated compounds on polysaccharide-based chiral stationary phases: role of halogen substituents in molecular recognition. *Chirality* **2015**, *27*, 667.

3) Peluso, P.; Mamane, V.; Aubert, E.; Dessì, A.; Dallocchio, R.; Dore, A.; Pale, P.; Cossu, S. Insights into halogen bond-driven enantioseparations. *J. Chromatogr. A* **2016**, *1467*, 228.

4) Peluso, P.; Mamane, V.; Dallocchio, R.; Dessì, A.; Villano, R.; Sanna, D.; Aubert, E.; Pale, P.; Cossu, S. Polysaccharide-based chiral stationary phases as halogen bond acceptors: a novel strategy for detection of stereoselective σ-hole bonds in solution. *J. Sep. Sci.* **2018**, *41*, 1247.

5) Dallocchio, R.; Dessì, A.; Solinas, M.; Arras, A.; Cossu, S.; Aubert, E.; Mamane, V.; Peluso, P. Halogen bond in high-performance liquid chromatography enantioseparations: Description, features and modelling. *J. Chromatogr. A* **2018**, *1563*, 71.

6) Peluso, P.; Gatti, C.; Dessì, A.; Dallocchio, R.; Weiss, R.; Aubert, E.; Pale, P.; Cossu, S.; Mamane, V. Enantioseparation of fluorinated 3-arylthio-4,4'-bipyridines: Insights into chalcogen and π-hole bonds in high-performance liquid chromatography. *J. Chromatogr. A* **2018**, *1567*, 119.

7) Peluso, P.; Mamane, V.; Dessì, A.; Dallocchio, R.; Aubert, E.; Gatti, C.; Mangelings, D.; Cossu, S. Halogen bond in separation science: a critical analysis across experimental and theoretical results. *J. Chromatogr. A* **2020**, *1616*, 460788.

8) Peluso, P.; Mamane, V.; Dallocchio, R.; Dessì, A.; Cossu, S. Noncovalent interactions in high-performance liquid chromatography enantioseparations on polysaccharide-based chiral selectors. *J. Chromatogr. A* **2020**, *1623*, 461202.

8) Gatti, C.; Dessì, A.; Dallocchio, R.; Mamane, V.; Cossu, S.; Weiss, R.; Pale, P.; Aubert, E.; Peluso, P. Factors Impacting σ- and π-Hole Regions as Revealed by the Electrostatic Potential and Its Source Function Reconstruction: The Case of 4,4′-Bipyridine Derivatives. *Molecules* **2020**, *25*, 4409.

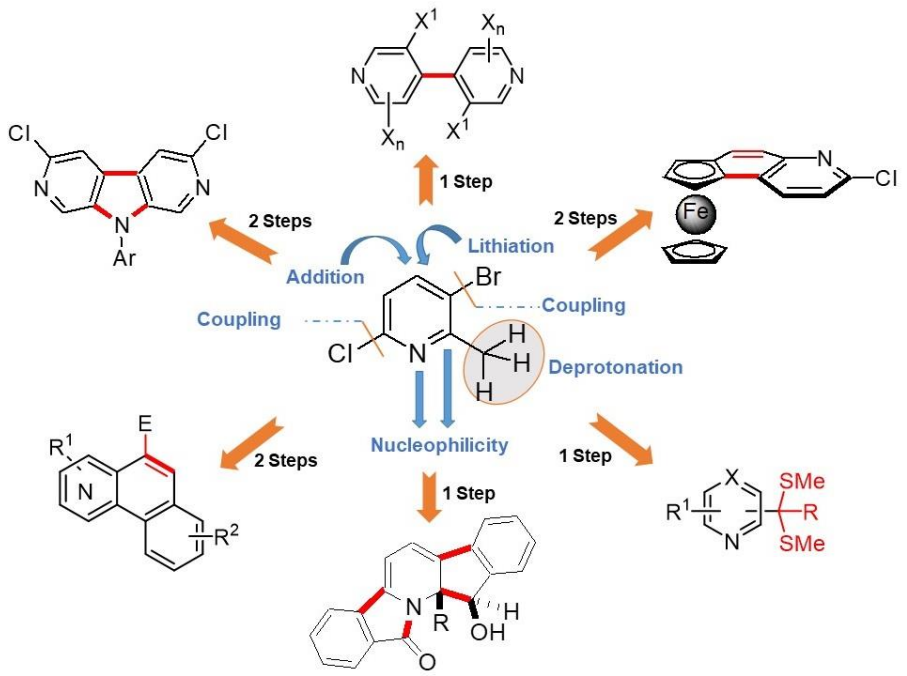
9) Peluso, P.; Dessì, A.; Dallocchio, R.; Sechi, B.; Gatti, C.; Chankvetadze, B.; Mamane V.; Weiss, R.; Pale, P.; Aubert, E.; Cossu, S. Enantioseparation of 5,5'-dibromo-2,2'-dichloro-3-selanyl-4,4'-bipyridines on polysaccharide-based chiral stationary phases: exploring chalcogen bonds in liquid-phase chromatography. *Molecules* **2021**, *26*, 221.

10) Dallocchio, R.; Sechi, B.; Dessì, A.; Chankvetadze, B.; Cossu, S.; Mamane V.; Weiss, R.; Pale, P.; Peluso, P. Enantioseparations of polyhalogenated 4,4'-bipyridines on polysaccharide-based chiral stationary phases and molecular dynamics simulations of selector–selectand interactions. *Electrophoresis* **2021**, *42*, 1853.

11) Peluso, P.; Dallocchio, R.; Dessì, A.; Sechi, B.; Chankvetadze, B.; Cossu, S.; Mamane, V.; Aubert, E.; Rozzo, C.; Palmieri, G.; Spissu, Y. Exploring interaction modes between polysaccharide-based selectors and biologically active 4,4'-bipyridines by experimental and computational analysis. *J. Chromatogr. Open* **2022**, *2*, 100030.
12) Dessì, A.; Sechi, B.; Dallocchio, R.; Chankvetadze, B.; Pérez-Baeza, M.; Cossu, S.; Mamane, V.; Pale, P.; Peluso, P. Comparative enantioseparation of planar chiral ferrocenes on polysaccharide-based chiral stationary phases. *Chirality* **2022**, *34*, 609-619.
13) Sechi, B.; Dessi, A.; Gatti, C.; Dallocchio, R.; Chankvetadze, B.; Cossu, S.; Mamane, V.; Pale, P.; Peluso, P. Unravelling functions of halogen substituents in the enantioseparation of halogenated planar chiral ferrocenes on polysaccharide-based chiral stationary phases: experimental and electrostatic potential analyses. *J. Chromatogr. A* **2022**, *1673*, 463097.
14) Dallocchio, R; Dessì, A.; Sechi, B.; Chankvetadze, B.; Jibuti, G.; Cossu, S.; Mamane, V.; Peluso, P. Enantioseparation of planar chiral ferrocenes on cellulose-based chiral stationary phases: Benzoate versus carbamate pendant groups. *Electrophoresis* **2023**, *44*, 203.
15) Peluso, P.; Mamane, V. Ferrocene derivatives with planar chirality and their enantioseparation by liquid-phase techniques. *Electrophoresis* **2023**, *44*, 158.

Methods in Heterocyclic Chemistry

New methods based on pyridine functionalization were developed for accessing complex heterocyclic systems with specific properties: catalysis, chirality, coordination, fluorescence.



Selected publications:

1) Mamane, V.; Fort, Y. Convenient access to new chiral ferroceno-(iso)quinolines. *J. Org. Chem.* **2005**, *70*, 8220.

2) Mamane, V.; Aubert, E.; Fort, Y. The methyl group as a source of structural diversity in heterocyclic chemistry: side-chain functionalization of picolines and related heterocycles. *J. Org. Chem.* **2007**, *72*, 7294.

3) Mamane, V.; Louërat, F.; Iehl, J.; Abboud, M.; Fort, Y. A general and efficient method for the synthesis of benzo-(iso)quinoline derivatives. *Tetrahedron* **2008**, *64*, 10699.

4) Abboud, M.; Mamane, V.; Aubert, E.; Lecomte, C.; Fort, Y. Synthesis of polyhalogenated 4,4'-bipyridines via a simple dimerization procedure. *J. Org. Chem.* **2010**, *75*, 3224.

5) Chamas, Z.; Dietz, O.; Aubert, E.; Fort, Y.; Mamane, V. Synthesis of new pentacyclic chromophores through a highly regio- and diastereoselective cascade process. *Org. Biomol. Chem.* **2010**, *8*, 4815.

6) Abboud, M.; Aubert, E.; Mamane, V. Double N-arylation reaction of polyhalogenated 4,4’-bipyridines. expedious synthesis of functionalized 2,7-diazacarbazoles. *Beilsten J. Org. Chem.* **2012**, *8*, 253.

7) Mamane, V.; Aubert, E.; Peluso, P.; Cossu, S. Synthesis, resolution, and absolute configuration of chiral 4,4′-bipyridines. *J. Org. Chem.* **2012**, *77*, 2579.

8) Chamas, Z.; Marchi, E.; Modelli, A.; Fort, Y.; Ceroni, P.; Mamane, V. Highly fluorescent, π-extended indenopyrido[2,1-a]isoindolone derivatives prepared by a palladium-catalysed cascade reaction. *Eur. J. Org. Chem.* **2013**, 2316.

9) Mamane, V.; Aubert, E.; Peluso, P.; Cossu, S. Lithiation of prochiral 2,2'-dichloro-5,5'-dibromo-4,4'-bipyridine as a tool for the synthesis of chiral polyhalogenated 4,4'-bipyridines. *J. Org. Chem.* **2013**, *78*, 7683.

10) Mamane, V.; Chamas, Z.; Aubert, E.; Fort, Y. Ag_2O mediated N-demethylation and oxidative opening of indenopyrido[2,1-*a*]isoindolones. Efficient access to polysubstituted 1-azafluorenones. *RSC Adv.* **2013**, *3*, 19110.

11) Chamas, Z.; Marchi, E.; Presson, B.; Aubert, E.; Fort, Y.; Ceroni, P.; Mamane, V. Synthesis and solid-state fluorescence properties of pentacyclic 7-substituted-indeno[1’,2’:4,5]pyrido[2,1-*a*]isoindol-5-ones. *RSC Adv.* **2015**, *5*, 2715.

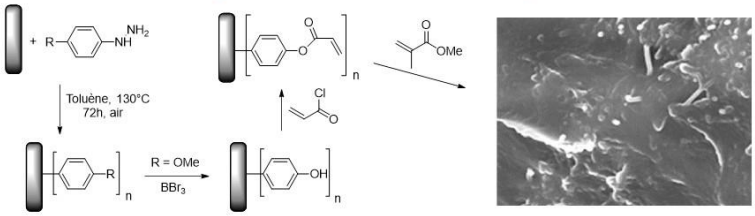
12) Mamane, V.; Peluso, P.; Aubert, E.; Cossu, S.; Pale, P. Chiral hexahalogenated 4,4′-bipyridines. *J. Org. Chem.* **2016**, *81*, 4576.

13) Aubert, E.; Abboud, M.; Doudouh, A.; Durand, P.; Peluso, P.; Ligresti, A.; Vigolo, B.; Cossu, S.; Pale, P.; Mamane, V. Silver(I) coordination polymers with 3,3’,5,5’-tetrasubstituted 4,4’-bipyridine ligands: towards new porous chiral materials. *RSC Adv.* **2017**, *7*, 7358.

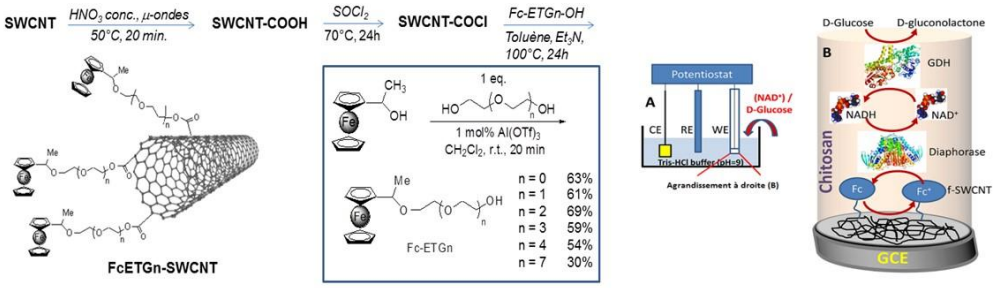
Carbon Nanotube Functionalization

In order to take advantage of mechanical and electrical conductivity properties of carbon nanotubes (CNTs), new methods for their covalent functionalization have been developed.

Aryl Radical Addition on CNTs and Polymerization



Smooth Oxydation of CNTs, their Functionalizaton by Ferrocene and Preparation of Bio-electrochemical Device



Selected publications:

1) Dossot, M.; Gardien, F.; Mamane, V.; Fort, Y.; Liu, J.; Vigolo, B.; Humbert, B.; McRae, E. Optical parameter to reveal the interplay between covalent functionalization and the state of aggregation of single-walled carbon nanotubes. *J. Phys. Chem. C.* **2007**; *111*, 12199.

2) Vigolo, B.; Mamane, V.; Valsaque, F.; Le, T. N. H; Thabit, J.; Ghanbaja, J.; Aranda, L.; Fort, Y.; McRae, E. Three-step procedure to chemically modify single-walled carbon nanotubes for nanocomposites processing. *Carbon* **2009**, *47*, 411.

3) Lejosne, J.; Mercier, G.; Mamane, V.; Fort, Y.; Marêché, J.-F.; McRae, E.; Valsaque, F.; Vigolo, B. Low degree of functionalization of single-walled carbon nanotubes probed by highly sensitive characterization techniques. *Carbon* **2011**, *49*, 3010.

4) Wang, Z.; Etienne, M.; Pöller, S.; Schuhmann, W.; Kohring, G.-W.; Mamane, V.; Walcarius, A. Dehydrogenase-based reagentless biosensors: electrochemically assisted deposition of sol-gel thin films on functionalized carbon nanotubes. *Electroanal*. **2012**, *24*, 376.

5) Allali, N.; Mamane, V. $Al(OTf)_3$ as a new efficient catalyst for the direct nucleophilic substitution of ferrocenyl alcohol substrates. Convenient preparation of ferrocenyl-PEG compounds. *Tetrahedron Lett.* **2012**, *53*, 2604.

6) Urbanova, V.; Allali, N.; Ghach, W.; Mamane, V.; Etienne, M.; Dossot, M.; Walcarius, A. Functionalized carbon nanotubes for bioelectrochemical applications: Critical influence of the linker. *J. Electroanal. Chem.* **2013**, *707*, 129.

7) Mamane, V.; Mercier, G.; Abdul Shukor, J.; Gleize, J.; Azizan, A.; Fort, Y.; Vigolo, B. Chemi- vs physisorption in the radical functionalization of single-walled carbon nanotubes under microwaves. *Beilstein J. Nanotechnol.* **2014**, *5*, 537.

8) Devaux, X.; Vigolo, B.; McRae, E.; Valsaque, F.; Allali, N.; Mamane, V.; Fort, Y.; Soldatov, A. V.; Dossot, M.; Tsareva, S. Y. Covalent functionalization of HiPco single-walled carbon nanotubes: differences in the oxidizing action of H_2SO_4 and HNO_3 during a soft oxidation process. *ChemPhysChem* **2015**, *16*, 2692.

9) Battie, Y.; Dossot, M.; Allali, N.; Mamane, V.; En Naciri, A.; Broch, L.; Soldatov, A. V. Mild covalent functionalization of single-walled carbon nanotubes highlighted by spectroscopic ellipsometry. *Carbon* **2016**, *96*, 557.

10) Allali, N.; Urbanova, V.; Etienne, M.; Devaux, X.; Mallet, M.; Vigolo, B.; Adjizian, J.-J.; Ewels, C.P.; Oberg, S.; Soldatov, A.V.; McRae, E.; Fort, Y.; Dossot, M.; Mamane, V. Accurate control of the covalent functionalization of singlewalled carbon nanotubes for the electro-enzymatically controlled oxidation of biomolecules. *Beilstein J. Nano.* **2018**, *9*, 2750.