

PhD subject: Halogen & chalcogen bonding in molecular crystals

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Organic halogen atoms, at least the most polarizable ones (Br, I) exhibit a non-spherical distribution of the electronic density, with an electropositive area in the prolongation of the C–Hal bond, called σ -hole. This zone can potentially interact with any Lewis base (B) to form adducts formulated C–I \cdots B, reminiscent of the hydrogen bonded systems such as O(N)–H \cdots B. This intermolecular interaction, called halogen bonding, is very directional and allows for the formation of complex supramolecular crystalline structures, with numerous applications in *crystal engineering*, anion recognition and anion transport, or molecular conductors, in organocatalysis.

During this PhD thesis, we want to explore the ability of molecules with N–I groups to efficiently act as halogen bond donors, particularly toward the elaboration of polar structures with potentially *ferroelectric properties*. The ability to transfer the iodine atom from one site to the other is also considered. This work will be further extended to similar systems based on chalcogen atoms also blessed with such a sigma-hole, toward *anion recognition* properties

This PhD thesis implies therefore a solid background in organic chemistry for synthesis of halogen(chalcogen) bond donors, an interest for the solid state, involving crystal growth of halogen (chalcogen)-bonded adducts, structural studies of these adducts by single crystal X-ray diffraction, together with solid state NMR and theoretical analysis of the electron density, the latter in collaboration with colleagues in Rennes and Nancy.

We offer (i) a comprehensive, interdisciplinary research in molecular crystal engineering associating organic synthesis, crystal growth, crystallography, solid state NMR, theoretical approaches, (ii) supportive mentoring by at least two complementary advisors, (iii) exchange with PhD students of the participating laboratories in Rennes and Nancy, and (iv) insertion in the Rennes doctoral school (300 PhD students in chemistry and physics).

Financial support is based on an ANR contract administrated by CNRS. Net salary amounts to 1400 €/month, on a 36 months basis, to start in September 2018.

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Recent illustrative references:

- 1) Cocrystal or Salt: Solid State-Controlled Iodine Shift in Crystalline Halogen-Bonded Systems
O. Makhotkina, J. Lieffrig, O. Jeannin, M. Fourmigué, E. Aubert, E. Espinosa
Cryst. Growth Des. **2015**, *15*, 3464
- 2) Organic selenocyanates as strong and directional chalcogen bond donors for crystal engineering
H.-T. Huynh, O. Jeannin, M. Fourmigué
Chem. Commun. **2017**, *53*, 8467–8469
- 3) La liaison halogène. *L'Actualité Chimique*, Fév. 2018, pp 11–18.