



## Preface

## Fluorine chemistry in France

France is certainly one of the countries in the world, maybe with Britain, the US and Germany, where fluorine chemistry has the strongest roots. There are at least three reasons: strong emphasis on scientific innovation, tendency of fundamental chemical research to systematization, sensitivity to industrial achievements.

The first organic fluoride  $\text{CH}_3\text{F}$  had already been prepared in 1835 by Jean-Baptiste Dumas. Thirty years later Frémy obtained for the first time pure HF by thermal decomposition of  $\text{KHF}_2$  despite major technical difficulties related to corrosion and toxicity (Louyet died as a consequence of an HF accident). Henri Moissan, who manifested an avowed personal vocation for inorganic chemistry at a time organic research was strongly developing and heavily encouraged by current scientific studies, found out in analyzing the previous failures to obtain elemental fluorine that any trace of water must be avoided in an eventual preparation process. He recommended low temperature high intensity electrolysis as the most appropriate isolation technique. After vain attempts with  $\text{PF}_3$  and  $\text{AsF}_3$  leading to electrolyte oxidations, he succeeded in July 1886 at the age of 34 in preparing pure fluorine by electrolysis of KF-containing HF at  $-50^\circ\text{C}$  and characterizing the evolving anode gas by silicon combustion. Moissan used the obtained fluorine for many inorganic and organic syntheses in order to characterize the exceptionally high reactivity of the new element. In 1906 he was rewarded with the first Nobel Prize in inorganic chemistry at a time his main activity turned already towards high temperature syntheses.

French fluorine chemistry is strongly related to the position of the element in the Mendeleiev classification, where fluorine can be considered as a corner-stone.

It is the most electronegative halogen. Its size is only a little smaller than that of oxygen, but the M–O distance is often slightly shorter than the M–F one due to stronger  $\pi$ -bonding. Such a similarity favors indeed easy O–F substitutions in crystallized and vitreous oxyfluorides, provided charge compensation has been assured.

The resulting low polarizability accounts for weaker magnetic interactions: it has been shown for instance that fluorine substitution reduces strongly the Curie temperature of  $\text{Fe}_3\text{O}_{4-x}\text{F}_x$  or  $\text{Fe}_{3-x}\text{Ni}_x\text{O}_{4-x}\text{F}_x$  spinels. The molecular field model of Néel applies better to fluorides than to oxides, as second order interactions may be neglected. The ferroelectric Curie point when of displacive nature diminishes

drastically also, e.g. in fluorine-substituted  $\text{Sr}_2\text{KNb}_4\text{TiO}_{14}\text{F}$  whose high permittivity is practically temperature and frequency independent over a large temperature range.

Electronic localization is favored in fluorides such as TKWB-type  $\text{K}_3\text{Fe}_3\text{F}_{15}$  ordered  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  distribution and induces spontaneous polarization (J. Ravez). Fluorine substitution reduces similarly the electronic conductivity in metal–non metal transition oxides such as  $\text{Na}_x\text{WO}_{3-y}\text{F}_y$  or  $\text{VO}_{2-x}\text{F}_x$ , despite higher number of d-electron carriers involved (J.P. Doumerc).

Strong electronegativity of fluorine results in large energy gaps despite the small covalent contribution to chemical bonding (e.g.  $\text{MgF}_2$  has a gap of 12 eV). Absorption spectra are shifted to the blue due to a weak nephelauxetic effect. Easy electron transfers to the conduction band either from the valence band or from electron hole-combination centers account for wide utilization of fluorides, e.g. in ionizing radiation or nuclear particle scintillators or as photostimulable phosphors for medical X-ray imaging (C. Fouassier).

Lower covalency often increases the cationic coordination number in oxyfluorides. For big cations Coulomb energies can be very close for different coordination polyhedra. Such proximities have led to the discovery of heavy element fluoride glasses by Jacques Lucas in Rennes in the 1970s with large application possibilities for protective coating as well as low attenuation fibers or photon multipliers. On the contrary light cation glasses thanks to long lifetimes in the excited levels have been used as host materials for high power UV-lasers (J. Portier).

The strong ionic character of fluorine bonding in crystallized fluorides explains the existence of many structural families based on relatively simple geometrical arrangements. The first systematic architecture was probably set up by Robert de Pape in Bordeaux and later in Le Mans where he has prepared the first fluoride bronzes  $\text{K}_x\text{FeF}_3$ . Recently Gérard Ferey has elaborated several families of large tunnel porous fluorides by eliminating the weakly bound guest  $\text{H}_2\text{O}$ -molecules: applications as sieves and catalysts are expected.

Transition element oxidation states exceeding those of oxides have been achieved thanks to high electronegativity of fluorine (J. Grannec). There is, however, an evolution from high pressure syntheses to metathetical reactions in low temperature superacidic HF under the influence of Neil Bartlett in Berkeley: such reactions induced by  $\text{F}^-$  acceptors

like  $\text{SbF}_5$  allowed for instance the isolation of thermodynamically unstable (but kinetically stable) binary fluorides such as  $\text{NiF}_4$  or  $\text{AgF}_3$ .

The weak binding energy of the  $\text{F}_2$ -molecule accounts for the practical absence of  $\text{F}^-$ -anion vacancies in binary fluorides, whereas non-stoichiometry is the rule for 3d-oxides. On the contrary charge compensation may lead to easy formation of  $\text{F}^-$ -vacancies in ternary fluorides and strong fluoride ion conductivity (J.M. Réau). Defect clustering allows worthwhile spectral "hole burning" applications for high density data recording.

Alain Tressaud has shown from many examples that high oxidation states 4d- and 5d-fluorides are easily intercalated between graphite layers without altering the  $\text{sp}^2$ -hybridization of the carbon atom thanks to electron transfer to the guest molecules.

I have been the editor of *Inorganic Solid Fluorides: chemistry and physics* (Academic Press) in 1985, a contributive volume developing the main synthesis methods, the structural classification and the various physical or mechanical properties of the inorganic fluorides in terms of their chemical features. This international review book has been luckily updated recently by A. Tressaud in cooperation with B. Zemva and T. Nakajima in *Advanced Inorganic Fluorides* (Elsevier).

French fluorine solid state chemistry is strongly orientated towards systematic studies, this privileged development field being the border region with solid state physics and much emphasis being given to possible industrial applications.

Organic fluorine chemistry has received a new impetus in France in the last 30 years, raising the formation of many new university research groups. Synthesis of novel sulphur-fluorine molecules has been achieved for instance on a large scale in the CNRS research center of Thiais and later at Versailles University (Claude Wakselman).

France has actively participated in the recent development of functional fluorinated polymers or copolymers. Due to presence of fluorine such materials enjoy indeed a remarkable thermostability, an outstanding chemical inertia (excellent resistance to flammability for instance), low dielectric constants and easy heat dissipation. The applications are

numerous, involving building protection, fire-fighting foams and even space and aerospace applications (for instance low-temperature reservoirs). Those researches have been strongly promoted in the French industry by a great pioneer: Robert Lichtenberger. They are presently being developed in a systematic way by a dynamic research group at the Montpellier chemical engineering school (B. Ameduri and B. Boutevin) and the RHODIA Company (S. Ratton). Easy  $^{19}\text{F}$  NMR characterization contributes to the rigor of the structural determinations.

At the International Fluorine Chemistry Centenary Symposium held in Paris in 1986 for celebrating the work of Moissan, a Henri Moissan Fluorine Research Prize has been created by the French organizers with the available funds, in order to reward every 3 years the most innovative achievements in fluorine chemistry after an international vote preceding the coming international meeting. All awardees — except one French — have been so far British or American.

It is my great pleasure to acknowledge the auspicious initiative of the Journal of Fluorine Chemistry to set up this special issue on fluorine chemistry in France under the joint responsibility of Alain Tressaud and Claude Wakselman. The association of publications devoted to quite different research problems brings a relevant flavor of the diversity of the problems and illustrates the well established French target of a systematic and prospective approach which appears in a quite relevant way in most fields concerned.

Many thanks to the guest editors and to the concerned authors!

Paul Hagenmuller\*  
*University of Sciences & Technologies  
Bordeaux, France*

Received 11 September 2000

\* Tel.: +33-5-568-46325; fax: +33-5-568-46324  
*E-mail address:* hagenmuller@icmcb.u-bordeaux.fr  
(P. Hagenmuller)