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Highly fluorinated molecular organised systems: strategy and concept

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This paper is dedicated to the memory of our friend Aimé Cambon.

Abstract

This paper presents recent efforts of our group in highly fluorinated organic synthesis which allow us to use the resulting compounds to elaborate molecular organised systems (MOSs). These MOSs can be considered either as organic materials such as artificial liposomes, oxygen carrier emulsions, liquid crystals, . . ., or as substrates for treatments of organic or inorganic materials, such as biocides or self-assembled monolayers (SAMs). In order to illustrate this work and the particular interests in the introduction of perfluorinated chains in these types of materials and compounds, recent results obtained in the fields of biotechnology, liquid crystals, self-assembled monolayers and polymers are presented.

Keywords: Highly fluorinated; Molecular organised system; Surfactant; Liposomes; Vesicles; Oxygen carrier; Self-assembled monolayer; Polymer; Varnishes; Liquid crystal

1. Introduction

For many years, the principal research direction of our group in the laboratory “Chimie des Matériaux Organiques et Métalliques” at the University of Nice-Sophia Antipolis concerns the synthesis of highly fluorinated functional compounds, and their use for the elaboration of molecular organised systems (MOSs). Whatever the type of MOSs to which the synthesised product is devoted, the structure of this substrate is elaborated always using the molecular design strategy in order to optimise the probability for fit between the prepared structure and its potential application.

The highly fluorinated compounds prepared can be classified according to four types of structures related to the MOSs applications

- surfactants used for vesicle preparation, oxygen carrier emulsions, biocides and additive agents in varnishes for optical materials;
- thermotropic liquid crystals as monomeric or polymeric forms for device applications;
- sulphur-containing molecules for self-assembled monolayers (SAMs) for the modification of metal surfaces;
- polyfunctionalised monomers for synthesis of fluorinated polymers with variable surface tension and hydrophobicity.

Some recent results are presented below to illustrate the different fields of application.

2. Synthesis and application of highly fluorinated surfactants

Perfluoroalkylated chains are considerably more hydrophobic than hydrocarbon chains, and their introduction in surfactants greatly intensifies their amphiphilic character, resulting in significantly enhanced hydrophobic interactions and surface activity. Therefore, fluorinated surfactants exhibit strong tendencies to collect at interfaces or to self-associate into supramolecular assemblies, in both cases avoiding the thermodynamically unfavourable contact between their highly fluorinated zone and water. It is well-known that fluorinated surfactants are generally both more effective and more efficient than their hydrogenated counterparts [1]. They display stronger surface

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[1] Up to the end of 1999, the laboratory “Chimie des Matériaux Organiques et Métalliques” was entitled “Laboratoire de Chimie Organique du Fluor”; it was managed by the late lamented Professor Aimé Cambon up to September 1998. Professor Serge Geribaldi is now the head of the laboratory.

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tension-lowering effects for lower surfactant concentrations. Moreover, because they are fluorophilic, fluorinated surfactants are best suited for emulsifying fluorocarbons and stabilising their emulsions. Surfactants largely determine the existence, particle size, stability, fluidity and other characteristics of emulsions and other organised dispersed systems such as vesicles or artificial liposomes. Although, a fluorinated surfactant does not guarantee emulsion stability, they are expected to facilitate the emulsification, to reduce the systems free energy, and to reduce the rate of molecular diffusion.

All these properties led us to synthesise series of neutral, anionic, cationic or amphoteric fluorinated surfactants for use in MOSs.

2.1. Surfactants and co-surfactants for formulations of surface active and gas-carrying systems for application in human healthcare

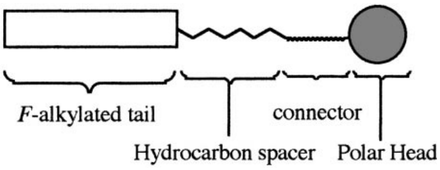
Inert perfluorocarbon liquids (PFC) have unique properties, most notably a relatively high respiratory gas-solubility, which make them highly attractive in medicine and biotechnology [2,3]. For instance, when emulsified using active systems, PFCs can be safely administered intravascularly. However, the viscosity of the emulsion depends, crucially, on both PFC concentration and composition.

The concept of using emulsions therapeutically is not new: fat emulsions are already commercialised as intravascular nutrients, clinical trials using the first-generation PFC emulsion Fluosol led to its approval by the US FDA in 1990 as an adjunct to coronary angioplasty adjuvant therapy and, more recently, improved emulsions (Oxygent®, Alliance Pharmaceutical Co.) have been evaluated as tissue oxygenation fluids in clinical trials in the United States [4].[2]

In 1994, a European consortium was created associating academic laboratories and industries in order to develop new formulations of PFCs for therapeutic and diagnostic applications [5]. The task allotted to our research group was to develop surfactants and co-surfactants to use in new PFCs emulsions.

Surfactants are crucial components of the fluorocarbon emulsions. Indeed, in view of their polarity and surface activity, the question of their biocompatibility is as acute as for the fluorocarbons themselves. Moreover, the surfactant largely determines the fate of the particles in the organism, for example intravascular persistence, phagocytosis, biodistribution and eventually the extent of their effects and side effects. In fact, ten criteria are required for a surfactant to be suitable for emulsions used as oxygen carriers. This surfactant must be (i) biocompatible; (ii) pure and well defined (monodisperse); (iii) prepared through selective, clean synthesis from reactants available commercially in a high state of purity; (iv) non toxic; (v) non haemolytic; (vi) totally excreted if it is not metabolised; (vii) or metabolised reasonably fast or excreted in the form of harmless metabolites; (viii) with as few biological side effects as possible; (ix) industrially cost efficient; (x) constitute families in which gradual variations in structure and properties can be achieved.

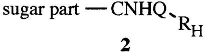
Since the emulsions used as oxygen carriers contain PFCs (core of the emulsion), water, and some other additives, and taking into account the general properties expressed above, it was clear that highly fluorinated or semifluorinated surfactants were molecules of choice for this application. So, tailor-made highly fluorinated surfactants with particular molecular size, structure, shape, charge, hydrophilic, lipophilic and fluorophilic character, nature of the head and so on have been prepared by our group. With this aim in view, we have first synthesised versatile intermediates allowing a modular structural design of the different part of the surfactant molecule (nature of the chain(s), connector, spacer, hydrophilic head(s)...). Several families of such surfactants have first been investigated, for which the general formula could be



This first approach has been rapidly adjusted. Indeed, several tails (two fluorinated or one fluorinated and one hydrocarbon) have been introduced; the hydrocarbon spacer has been situated before or after the connector; various polar heads which are non ionic, monopodal, multisite or polypodal have also been introduced. Thus, a first class of classical highly fluorinated surfactants has been synthesised including sugar derivatives, **1** or **2** [6–8], polyol derivatives with an urea or a thiourea **3** [6], a carbonate **4** [6,9], an ester **5** [10,11] or an amide group **6** [12] as connector.

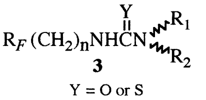

$\text{sugar part}-\overset{O}{\overset{\|}{C}}NH(CH_2)_nQR_F$

1

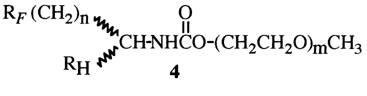

$\text{sugar part}-\overset{O}{\overset{\|}{C}}NHQ\begin{matrix}(CH_2)_nR_F\\R_H\end{matrix}$

2

Q = nothing, or an heteroatom or a function
R_F = perfluoroalkylated chain, mainly C_4F_9, C_6F_{13}, C_8F_{17}
R_H = alkylated chain

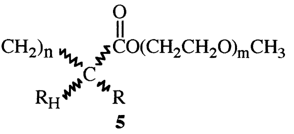

$R_F(CH_2)_nNH\overset{Y}{\overset{\|}{C}}N\begin{matrix}R_1\\R_2\end{matrix}$

3

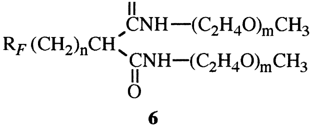

$\begin{matrix}R_F(CH_2)_n\\R_H\end{matrix}CH\text{-}NH\overset{O}{\overset{\|}{C}}O\text{-}(CH_2CH_2O)_mCH_3$

4

Y = O or S
R_1,R_2 = H or polyhydroxylated chain


$R_F(CH_2)_n\overset{}{C}(R_H)(R)\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_mCH_3$

5


$R_F(CH_2)_nCH\begin{matrix}\overset{O}{\overset{\|}{C}}NH-(C_2H_4O)_mCH_3\\\underset{O}{\underset{\|}{C}}NH-(C_2H_4O)_mCH_3\end{matrix}$

6

R = H or $\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_mCH_3$

A second class of highly fluorinated surfactants we have named "tensioactive dowels" has also been prepared in

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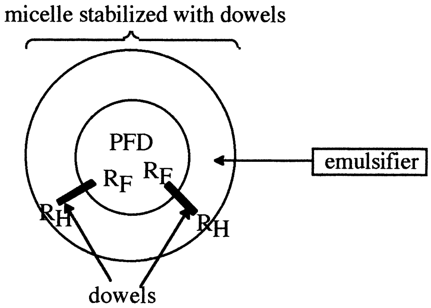
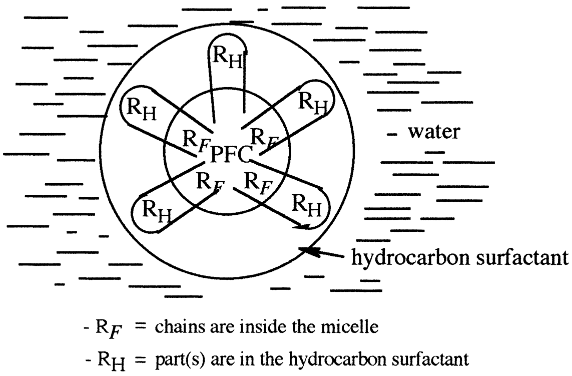
[2] http://www.bloodlink.bc.ca/oxygent.htm.

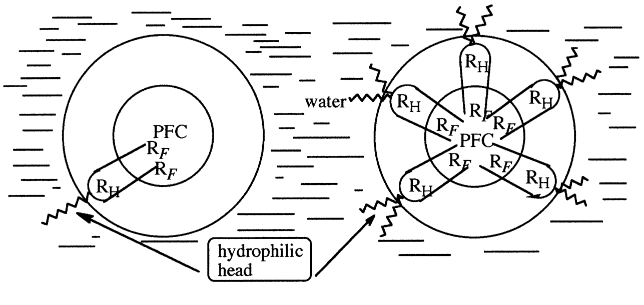
order to increase the stabilisation of perfluorocarbon emulsions. Indeed, it is well-known that coalescence and molecular diffusion destroy emulsions which are thermodynamically unstable. Some progress has been achieved concerning stabilisation of perfluorocarbon emulsions, and several methods have been tested. One of these consists in addition of a fluorocarboned/hydrocarbon co-surfactant (such as perfluoroalkylalkanes: $C_mH_{2m+1}-C_nF_{2n+1}$ or alkenes $C_mH_{2m+1}-CH{=}CH-C_nF_{2n+1}$) to the emulsion. Such compounds act as molecular dowels between the highly fluorinated oxygen carrier and the hydrocarbon emulsifier (pluronics for instance), as shown in the following scheme:



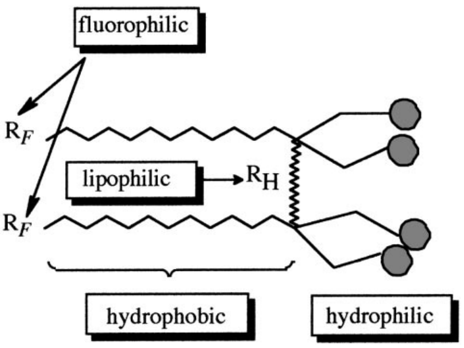
This concept was developed for the first time by Meinert et al. for emulsions using pluronics as surfactants, and a strong stabilising effect was observed [13]. Therefore, from this concept, it is possible to imagine several types of stabilisation of micelles. For instance



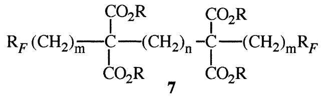
or



In order to stabilise micelles obtained from the oxygen carrier and hydrocarbon surfactant such as pluronics or yolk zphospholipids, we have adopted this last concept and prepared dowels with the structure

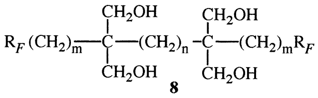


The compounds synthesised may be classified in two groups, alkyl esters **7** [14,15], and alcohols **8**.



$$R_F(CH_2)_m-C(CO_2R)_2-(CH_2)_n-C(CO_2R)_2-(CH_2)_mR_F$$

7



$$R_F(CH_2)_m-C(CH_2OH)_2-(CH_2)_n-C(CH_2OH)_2-(CH_2)_mR_F$$

8

All these new fluorinated and semifluorinated surfactants were used to prepare new emulsions of PFCs [16–18]. These emulsions are steam-sterilisable and stable at room temperature for over 1 year. Some emulsions were assessed as perfusates for isolated mammalian organs, where in vitro vital functions were markedly improved; some of the novel fluoro-surfactants inhibited aggregation of human platelets in vitro in a dose-dependent manner [19–21], or presented immunomodulator effects [22]. They could be used in the following medical fields:

- protection of ischemic tissues against insufficient oxygen supply;
- protection of vessels, tissues and organs against inflammatory damage;
- protection against vascular re-occlusion after reperfusion;
- protection of ischemic tissues against insufficient nutrition;
- preservation of organs for transplantation purposes;
- enhanced understanding of the cellular biology and management of ischemic injury and reperfusion damage;
- improvement of appropriate in vitro systems as standards for preliminary biocompatibility tests for injectable biomaterials, in accord with the current directives;
- development of a new class of potentially multifunctional oxygen-delivering therapeutic agents.

2.2. *Surfactants for liposome technology*

Liposomes can be characterised as associated colloids, built up of amphoteric lipid molecules that self-assemble in aqueous media into spherical, self-closed structures. Liposomes can be composed of either extracted and purified, naturally occurring lipids or many synthetic products. In this last case, the artificial liposomes are named vesicles. Liposomes arouse great interest in various fields, and more particularly in the pharmaceutical and medical fields as carriers of drugs [23,24], vaccines [25], enzymes or genetic material [26]. In general, conventional liposomes exhibit poor stability during storage, use and transit if used in medical fields. Several studies were performed to improve the liposomes' stability: for instance, addition of cholesterol [27] or water-soluble cryoprotectants such as sucrose [28], polymerisation of lipids containing polymerizable groups [29], attachment of natural or synthetic polymers to the liposomes' outer surface [30] and introduction of fluorocarbon segments in the double-chain lipids structure [31,32]. Among these methods, the last one seems very promising because the perfluoroalkyl groups of lipids result in an increase of hydrophobic interactions and in the formation of a hydrophobic, lipophobic and fluorophilic rigid area within bilayers. The stability of perfluoroalkylated lipids-based liposomes is confirmed by an increase in their critical phase transition temperature [33]. Moreover, physico-chemical studies of properties of bilayer membrane of fluoroalkylcarbon surfactant amphiphiles showed that the increase of the bilayer fluorophilicity implies a decrease of its permeability [34]. Thanks to the high stability and chemical inertness of their components, F-alkylated liposomal structures should be able to exhibit a strong power of drugs retention between the administration site and the considered target. Their relative impermeability should also be able to considerably reduce the toxicity of drugs. Our aim in this field is to finalise simple strategies of synthesis to easily obtain new perfluoroalkylated lipids having a modular structure and to test their ability to form membrane bilayers. Table 1 collects the different structures of synthetic perfluoroalkylated lipids, **9–25**, from which we obtain stable

Table 1
Molecular structures of some perfluoroalkylated lipids synthesised by the group [33–45]

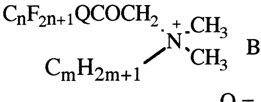
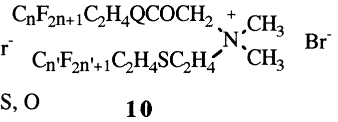
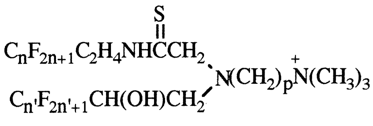
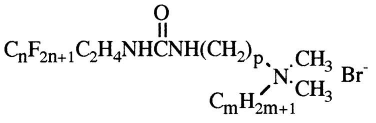
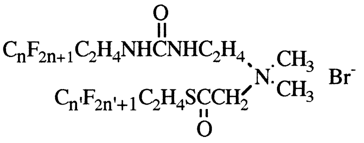
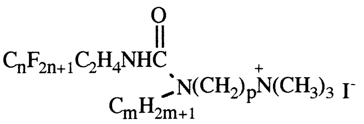
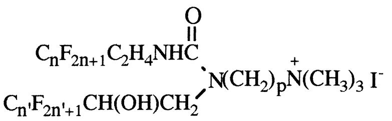
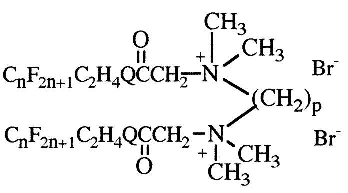
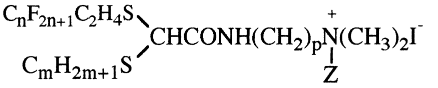
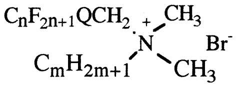
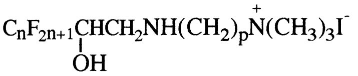
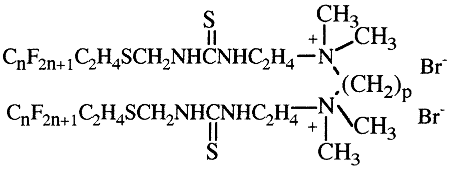
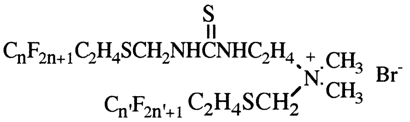
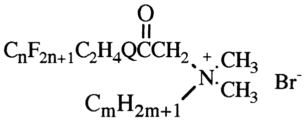
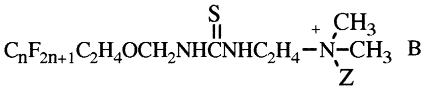
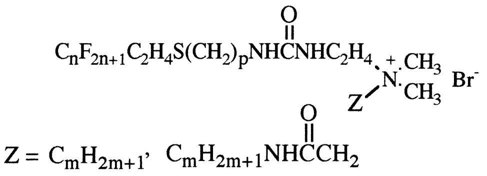
Molecular structure	*n*	*n′*	*m*	*p*	Reference
 **9** Q = S, O  **10**	4, 6, 8	4, 6, 8	7–10, 12		[36]
 **11**	6	8		2, 3	[37]
 **12**	6		12	2	[38]
 **13**	6	6			[38]
 **14**	6		12	2	[38]
 **15**	6	8		3	[38]
 **16**	6			2–4, 6	[39]

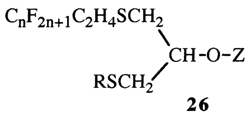
Table 1 (*Continued*)

Molecular structure	*n*	*n*′	*m*	*p*	Reference
 $\mathrm{(C_nF_{2n+1}C_2H_4S)(C_mH_{2m+1}S)CHCONH(CH_2)_p\overset{+}{N}Z(CH_3)_2I^-}$ **17**	6		8	3	[40]
 $\mathrm{(C_nF_{2n+1}C_2H_4S)(C_{n'}F_{2n'+1}C_2H_4S)CHCONH(CH_2)_p\overset{+}{N}Z(CH_3)_2Br^-}$ **18** $\mathrm{Z = CH_3, CH_2CH{=}CH_2}$	6	6		3	[40]
 $\mathrm{(C_nF_{2n+1}QCH_2)(C_mH_{2m+1})\overset{+}{N}(CH_3)_2\,Br^-}$ Q = NHCO, SCO, OCO **19**	6		12		[41]
 $\mathrm{C_nF_{2n+1}CH(OH)CH_2NH(CH_2)_p\overset{+}{N}(CH_3)_3I^-}$ **20**	6, 8			3	[41]
 $\mathrm{[C_nF_{2n+1}C_2H_4SCH_2NHC(S)NHC_2H_4\overset{+}{N}(CH_3)_2]_2(CH_2)_p\ 2Br^-}$ **21**	6			3	[42]
 $\mathrm{(C_nF_{2n+1}C_2H_4SCH_2NHC(S)NHC_2H_4)(C_{n'}F_{2n'+1}C_2H_4SCH_2)\overset{+}{N}(CH_3)_2\,Br^-}$ **22**	6	6			[42]
 $\mathrm{(C_nF_{2n+1}C_2H_4QC(O)CH_2)(C_mH_{2m+1})\overset{+}{N}(CH_3)_2\,Br^-}$ Q = NH, O, S **23**	4, 6, 8		12, 14, 16, 18		[43]
 $\mathrm{C_nF_{2n+1}C_2H_4OCH_2NHC(S)NHC_2H_4\overset{+}{N}Z(CH_3)_2\,Br^-}$ **24** $\mathrm{Z = CH_2CH{=}CH_2, CH_2C_6H_5, C_mH_{2m+1}, C_{n'}F_{2n'+1}C_2H_4NHCOCH_2}$	6, 8	6	10, 12		[44]
 $\mathrm{C_nF_{2n+1}C_2H_4S(CH_2)_pNHC(O)NHC_2H_4\overset{+}{N}Z(CH_3)_2\,Br^-}$ **25** $\mathrm{Z = C_mH_{2m+1}, C_mH_{2m+1}NHC(O)CH_2}$	4, 6, 8		6, 8, 12, 16	1, 3	[45]

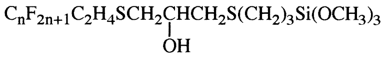
liposomes. The diversity of the synthesised substrates allows us to select the principal structural parameters which are important to assure liposome formation, as well as to study the liposomes' properties (stability, fluidity, rigidity, permeability) as a function of structural variations (number and length of alkyl and perfluoroalkyl chains, nature of connector linking the perfluoroalkyl tail to the polar head, number of polar heads, length of spacer). For instance in the case of mixed chain lipids of series **25**, homogeneous unilamellar liposomes are observed [35]; but if the hydrocarbon tail is too short, micelles or rods are observed. In the case of fully perfluorinated double-chain lipids, bent liposomes are obtained.

2.3. Surfactants as additive agents for varnishes of lens materials

Polycarbonate is a special material that can be used to make spectacle lenses. It is very impact-resistant and hence is extremely unlikely to break. This makes it ideal for use when safety is important. For instance, children's glasses, for people with good vision in one eye where protection is vitally important or for people who wear their glasses while playing sports. Many safety glasses are also made with polycarbonate lenses, especially if used in an area where people are exposed to high speed projectiles. Like the other types of plastic lenses, including high index and traditional plastic material, polycarbonate lenses have built-in scratch-resistant coatings. In this field, our aim was to find fluorinated additives to polysiloxane type thermohardener varnishes of polycarbonate lenses. For confidentiality reasons, our work performed with industrial partners cannot be published at this time. Simply, we have synthesised two series of fluorinated amphiphiles, **26** and **27**.



26



$C_nF_{2n+1}C_2H_4SCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2S(CH_2)_3Si(OCH_3)_3$

27

n = 4, 6

$Z = CH_2CH{=}CH_2$, $COCH{=}CH_2$, $(CH_2)_3S(CH_2)_3Si(OCH_3)_3$

$R = C_{n'}F_{2n'+1}C_2H_4$, C_mH_{2m+1}, C_6H_5 with n' = 4, 6, 8; m = 6, 8, 12

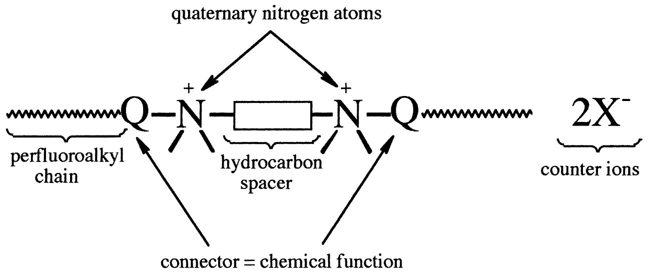
The addition of compound **26** at 1‰ concentration into polysiloxane type varnishes during their formulation leads to varnishes with very good adhesive and optical properties. The presence of the hydroxylic function in series **27** allows access to the different polymerisable and copolymerisable sites. Compounds **27** also add very well to polysiloxane type varnishes, and they increase the hardness and the brilliancy of the lenses [46].

2.4. *Surfactants as biocide compounds*

The presence of micro-organisms in water require the development of process ability to exterminate them. The well-known means used on a large scale for water purification are chlorination and ozonation processes. However, the toxic and economic aspects of these processes give some new alternatives for a soft and efficient destruction of such micro-organisms. This question is all the more important because this soft destruction is the single kind adaptable to small scale installations. For these overall applications downstream from the usual processes of water treatment, the destruction of these micro-organisms in such an ecosystem requires the use of biocide molecules.

Numerous chemical structures can exhibit biocidal properties, as for instance isothiazolines [47] (Kathon^{TM}), which are biocides used for water treatment. Some other compounds exhibit biocidal properties such as betaine from which are included tego series (dodecyldiaminoethylglycine ampholyte derivatives) and anionic surfactants such as carboxylic, sulfinic, sulphuric, phosphoric or phosphinic acids derivatives [48]. The aim of our work is to improve the biocidal properties of compounds well-known from the beginning of the last century: the quaternary ammoniums [49]. It has been known for years, that certain quaternary ammonium compounds have biocide properties. However, the emergence of bacteria-resistance phenomena facing antibiotics of different nature [50] including quaternary ammoniums [51] implies the synthesis of new compounds. In the case of quaternary ammoniums which we take into account, numerous studies are ascribed to the improvement of the performance of these compounds by the introduction of new molecular parameters [52–56]. Our strategy is based on fluorine. In fact, it appears that a surfactant structure plays an important role in the biocidal activity of quaternary ammoniums. On the other hand it is well-known that the introduction of fluorine and more particularly a highly fluorinated part confers to the system intrinsic properties such as chemical inertness, thermal stability, low surface tension, ... which can affect in a favourable manner, the biocidal activity.

So, we have decided to investigate several molecular parameters in order to improve the biocide activity of quaternary ammonium compounds with highly fluorinated parts. Four series of quaternary ammoniums with the same perfluoroalkyl chain length were synthesised and noted Quaterfluo^{TM} A*y*, B*y*, C*y* or D*y*, which differ in the length (*y*) of the hydrocarbon spacer and the nature of the chemical function in the shape (A, B, C or D). The general structure of these compounds is



By variation of structural parameters such as spacer or connector, we would like to establish a structure-activity relationship and to target the critical parameters efficient against biocidal activity. Our molecules were tested on Gram+ and Gram− bacterias (*Staphylococcus aureus* and *Pseudomonas aeruginosa*, respectively), yeast (*Candida albicans*), and fungi (*Aspergillus niger*) which relate to the water treatment.

It appears that one of these series (called A) and particularly compound Quaterfluo^{TM}A2, shows very interesting performance against a wide spectra of micro-organisms: Gram+ and Gram− bacteria and fungi. Quaterfluo^{TM}A2 is three to six times more efficient than BAC50 (benzalkonium chloride) which is taken as a reference, on *S. aureus*, *P. aeruginosa* and *A. niger*.

Quaterfluo^{TM}A2 is less efficient than BAC50, on the yeast Candida Albicans, but its MIC (minimal inhibitory concentration) is still interesting if we consider the global performances of A2.

The speed of kill test on *P. aeruginosa* with Quaterfluo^{TM}A2 at 5 ppm concentration showed performances very similar to Kathon WT^{TM} taken as a reference. Concerning the eradication efficiency, Quaterfluo^{TM}A2 has a better speed of kill if we consider that A2 has a molecular weight (about three times) more favourable than Kathon WT^{TM}.

From biocidal evaluation, Quaterfluo^{TM}A series and particularly Quaterfluo^{TM}A2 show very interesting performances on a wide spectra of micro-organisms: Gram+ and Gram− bacteria and fungi. These results are really significant and give short-term prospects for their use as new biocide materials for biofilm and disinfectant applications. From the structure-activity relationship [57], it is possible now to induce a variation of some molecular parameters in order to optimise these biocidal structures. This kind of molecules could become an interesting alternative to the classical compounds used for the water treatment for which bacteria resistance is now observed [50,51].

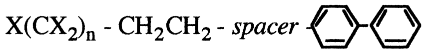
3. Synthesis of thermotropic liquid crystals

The introduction of a fluorinated tail into a molecule does not necessarily lead to an improvement in liquid crystal activity. The strategy and the concept of new liquid crystal (LC) materials must proceed to an increase of efficiency of the material. This is all the more true within highly fluorinated series: since fluorine-containing molecules are generally more expensive than non fluorinated homologous ones, a clear advantage needs to be gained to justify the inclusion of fluorine in commercial applications. Molecular design allows the careful choice of the kind of moiety which will be most suitable for the amplification of the potentialities of the perfluorinated tail. The introduction of such tails leads to consideration of a more systematic approach in the liquid crystal field based on the molecular design of amphiphile structure. The introduction of fluorine and more particularly a highly fluorinated tail is in connection with the quest for more efficient material. In such an approach we studied, to start with the intrinsic impact of the fluorinated tails on the mesomorphic behaviour of biphenyl derivatives in order to determine what kind of parameter can intensify the liquid crystal behaviour. Then we applied these results to materials which can present a technological interest such as short molecular weight ferroeletric liquid crystals (SMWFLC) or side chain liquid crystal polymers (SCLCP).

3.1. Fluorinated liquid crystal hypothesis

The concept of molecular shape has often been considered as a necessary parameter for obtaining anistropic properties. However, the introduction of sufficiently incompatible moieties allows us to induce a liquid crystalline potentiality. Fluorine and more particularly a highly fluorinated tail could be one of these incompatible parameters [58]. Among the used LC phases, smectic phases are the subject of intensive work on these LC displays to the detriment of the nematic phase. On the other hand, the introduction of perfluorinated tails within LC materials can prove a useful short-term prospect as interesting alternatives to avoid the defaults or instabilities shown in hydrocarbon series. In fact, one of the most important points for potential use as LC materials is the wide temperature range of mesomorphism, with enantiotropy and reproducibility during the phase transition phenomena, but also chemical stability. The perfluorinated species are chemically stable, and possess low viscosity, and can in suitable cases, dope the instability of the resulting mesomorphic phases.

Such substitution (fluorine instead of hydrogen) in the flexible extremities of mesogens, such as a partial or total fluorination of one of the end chains of classical rod-like molecules, leads to asymetric mostly smectogen [59–65] compounds (**28**–**31**). Some peculiar properties were recorded (cf. Fig. 1). It is worth noting that the nature of the spacer, binding the perfluorinated tail to the rigid core, can govern and exacerbate [66–69] the potential smectogenic character of the F-alkyl tail according to compounds **30b**–**38**.



spacer= -SC(O)-; -NH=CH-

28,29 X = H; n = 4,6,8 Cr → LC → I

30,31 X = F; n = 4,6,8 Cr → I

3.2. Application to SMWFLC

The discovery of ferroelectricity in the chiral smectic C (SC*) phase by R. Meyer in 1975 and the proposal of

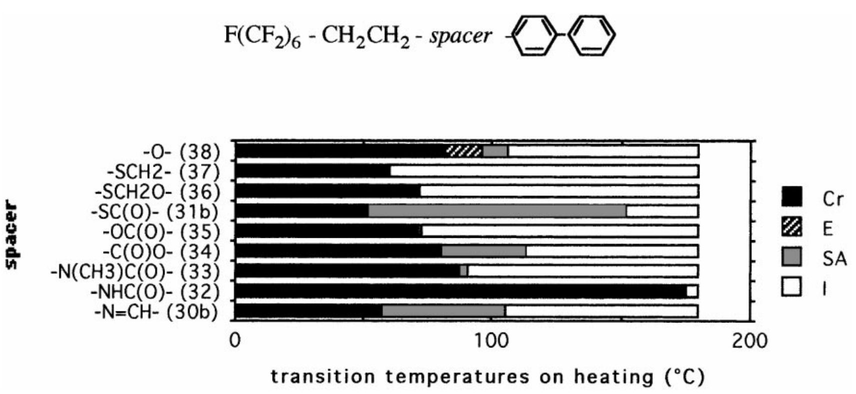
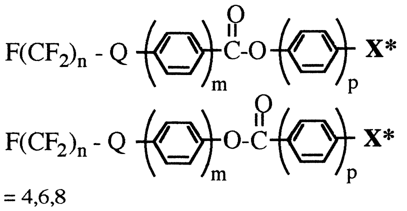


Fig. 1. Comparison of the span of the mesophase against the nature of the spacer (Cr: crystal; E, SA: smectic phases; I: isotrope).

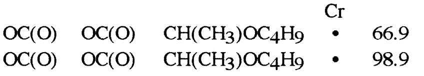
electro-optical devices using ferroelectric liquid crystals by Clark and Lagerwall in 1980, have generated a great deal of interest in academic and industrial research laboratories. Since then, extensive studies have been done on ferroelectric liquid crystal materials and their application. For applications requiring very high intrinsic speed in repetitive operation, ferroelectric liquid crystal technology offers the possibility to make large area, high resolution screens without the need for the transistors or other active elements usually used in classical nematic liquid crystals. To study the correlation between molecular structure and mesomorphic properties so as to prepare desirable materials, various molecular designs have been made, and a great number of ferroelectric liquid crystals have been synthesised. It was initially found that these materials require at least two aromatic rings in the core and two terminal chains at the end, one of which contains one chiral group, even if the formal presence of a chiral centre can be avoided in some cases [70–72]. The previous studies lead to the highlighting of the great smectogenic character of the perfluorinated tail as compared with their hydrocarbon homologues. Thus, association of a F-alkylated moiety with a chiral unit via a mesogen appears to offer a further attractive alternative. In this aim, we have prepared and studied series of compounds containing a semiperfluoroalkylated tail, two or three aromatic rings and an aliphatic chiral tail on the other extremity (structures **39** and **40**)

39
40



n = 4,6,8
m=1,2 and p =0,1
X* = OR*, C(O)OR*, OC(O)R*, ...

The studies carried out on these compounds (optical microscopy, differential scanning calorimetry, RX, dielectric measurements, . . .) lead us to conclude that the influence of the fluorinated tail is the same as that observed for the biphenyl derivatives, i.e. the lengthening of the perfluorinated tail increases both the melting and the clearing temperatures. We can also point out that all of these compounds exhibit a smectic behaviour over a wide temperature range [73] as described for **41–46**.



	n	x	A	R*	temperature transitions (°C)				
					Cr		LC		I
41	4	OC(O)	OC(O)	$CH(CH_3)OC_4H_9$	•	66.9	•	104.7	•
42	6	OC(O)	OC(O)	$CH(CH_3)OC_4H_9$	•	98.9	•	162.8	•
43	8	OC(O)	OC(O)	$CH(CH_3)OC_4H_9$	•	105.2	•	190.4	•
44	6	OC(O)	O	$CH_2CH(CH_3)Et$	•	84.7	•	182.2	•
45	6	_	OC(O)	$CH(CH_3)OC_4H_9$	•	89.7	•	125.8	•
46	6	-	O	$CH_2CH(CH_3)Et$	•	78.9	•	130.5	•

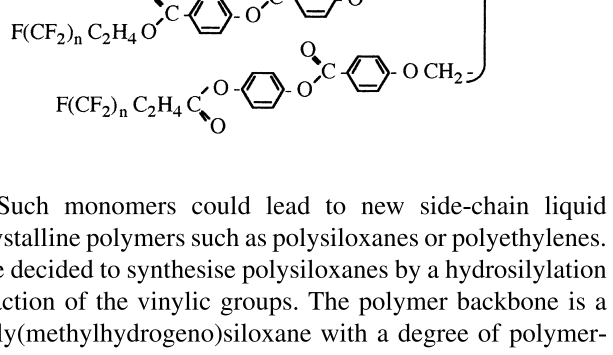
(Cr: crystal, LC: liquid crystal; I: isotropic phase)

A thorough physical investigation, by X-ray and electro-optic measurements allows us to use these compounds in high frequency information transfer systems such as optical fibres, but also as dopants in smectic mixtures and to decrease the anchoring phenomena in confined systems.

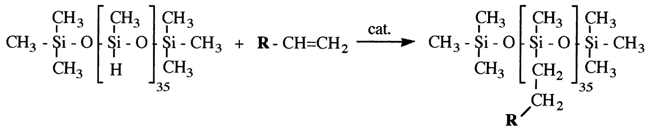
3.3. Application to SCLCP

Liquid crystalline polymers are devised in two classes: main chain polymers when the mesogenic groups and the spacers alternating from the basic polymer thread, found so far to be mainly nematic. Side-chain liquid crystalline polymers (SCLCPs), which are of both theoretical and practical interest because they combine the anisotropy of a liquid crystal with intrinsic properties of the polymer backbone, such as mechanical properties and glassy state. These polymers behave as the low mass liquid crystal and form the corresponding nematic, smectic and cholesteric mesophase. In such SCLCPs, siloxane polymer is often used as a backbone, because of its low glass transition temperature and great flexibility. Thus, such substances show usefulness for applications in electro-optic devices such as alphanumeric displays, high definition TV displays, projection systems and their ability to provide thin films can be applied over very large areas. Obviously, a spacer between the polymer backbone and the mesogenic unit must be present. Thus, the synthesis of molecular rod-like liquid crystals which exhibit conventional calamitic mesophases and the presence of an unsaturated moiety are required. These facts suggest the synthesis of new structures containing a fluorinated "flexible" chain attached to a mesogenic moiety (compounds **47–50**)

47
48
49
50



Such monomers could lead to new side-chain liquid crystalline polymers such as polysiloxanes or polyethylenes. We decided to synthesise polysiloxanes by a hydrosilylation reaction of the vinylic groups. The polymer backbone is a poly(methylhydrogeno)siloxane with a degree of polymerisation of 35 that can give a homogeneous population of polysiloxane molecules. These polymers are prepared as below (where R values are described above).

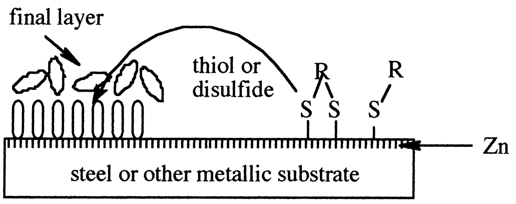


$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{H}{\overset{CH_3}{Si}}-O\right]_{35}-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 + R-CH=CH_2 \xrightarrow{cat.} CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_2CH_2R}{\overset{CH_3}{Si}}-O\right]_{35}-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

The overall liquid crystal evaluation from the monomers or polymers allows us to highlight [74,75] the considerable impact of the molecular parameter on the liquid crystal range. The knowledge of the peculiar nature of material performances generates a strategy for the molecular design which could become a new alternative for the usual formulations. Such considerations can be applied for obtaining a stable lyotropic cubic phase [58].

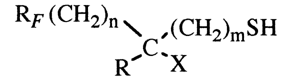
4. Synthesis of thiol derivatives and application for self-assembled monolayers (SAMs)

The concept of SAMs of organic compounds on solid substrates has been known for 17 years [76,77]. Functional organic compounds such as thiols [78–80], disulfides [76], and thioethers [81] are known to naturally bind gold and form dense layers more or less organised according to the experimental conditions, the surface composition and deposition conditions. Concerning fluorinated thiols or disulphides, much work on SAMs has been performed on Au (1 1 1) [82–90]. Efforts to modify other metal surfaces with thiols have also been reported [91], but to our knowledge nothing similar has been reported on zinc. Yet, zinc is known to play a major role as a protective layer for steel and other metallic substrates due to its high corrosion resistance in atmospheric and other environments [92,93]. To further enhance this corrosion resistance of the zinc layer and promote adhesion of organic coatings or adhesives, a thin conversion coating is formed by reacting the metal with an aqueous solution of chromic acid, chromate salts, and mineral acid. However, an important drawback of this otherwise successful approach is the high toxicity of the hexavalent chromium [94]. In this context chromate-free substitution surface conversion treatments must be researched with the double objective of the formation of a stable interfacial film and a suitable coupling effect between the metallic substrate and the final organic layers (finish lacquer or paint layers). Thus, we decided to use the concept of SAMs of fluorinated thiols and disulfides to achieve this aim, as shown in scheme below



Bilayer of thiol or disulfide molecules bound to the metallic substrate with the finish lacquer or paint layers

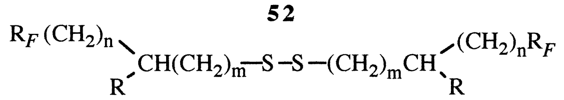
This work constitutes a collaboration between our group and the LISE laboratory at Namur [95]. It requires the synthesis of tailor-made partially fluorinated thiols **51** or **52** and disulphides **53** using original synthetic methods synthesised in our laboratory [96]. Preliminary results obtained for SAMs on zinc are promising but call for improvements and additional characterisations [97–99].



51

$HS(CH_2)_n(CF_2)_p(CH_2)_nSH$

52



53

$R = H$ or R_H or $R_F(CH_2)_p$ $X = H$ or $(CH_2)_mSH$

5. Polyfunctional monomers for synthesis of fluorinated polymers

Considerable attention has also been devoted to the preparation of fluorine-containing polymers because of their properties and high temperature performances. Indeed, fluorine-containing polymers are well-known to have specific properties such as high chemical and thermal stability, low dielectric constant, low surface energy and low water uptake. Based on the obvious attractive potential, the introduction of fluorine atom into condensation polymers has been studied in order to improve further their properties [100]. So, polymers containing fluorinated moieties comprise an important class of materials. A number of applications are known [101,102], e.g. as low dielectric constant polymers in the electronic industry [103], low surface coating [104], anti-fouling agent, etc.

In this aim, we have prepared some highly fluorinated monomers which are devoted to the following applications:

- Surface coating for preparation of materials exhibiting variations of their hydrophobic properties. Indeed, one of the most successful strategies for lowering the surface tension of a film is to incorporate fluorine into the polymer molecule comprising the coating. The fluorine can be incorporated as a side chain polymer using a fluorinated diol (**55**) to prepare for example a polyurethane. Surface tension reduction is also possible for copolymers prepared by incorporation of fluorinated monomers (**56**, **57**) and by chemical grafting of perfluoroalkyl groups onto polymers. We have decided to elaborate and to evaluate properties of some fluorine-containing condensation polymers including aromatic polyesters and polyimides.

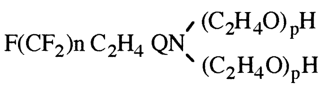
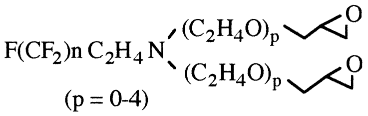
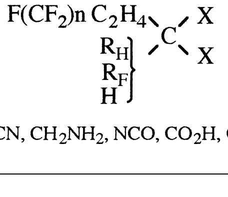
- Biomedical applications like hydrogels for contact lens. In fact, for such an application the polymer material must satisfy a number of requirements [105], it must be optically transparent, possess chemical and thermal stability and be biologically compatible with the ocular environment. In addition to the compatibility with the contact lens manufacturing technique, the material must be permeable to atmospheric oxygen due to a lack of blood vessels within the corneal framework.

The main motivations arise from anchoring processes from the overall applications described previously in this paper. The strategies envisioned lead to materials from polyfunctional monomers having the following molecular parameters:

- a perfluorinated tail or bisegmented tails (one hydrocarbon and one perfluorinated);
- a hydrophilic core;
- at least, a bifunctionality in the alpha–alpha or alpha–omega positions.

On the basis of the above studies reported so far, we have designed and synthesised a series of novel monomers reported in Table 2 [106–114]. We found these compounds to have good solubility and excellent thermal stability. In order to get more insight into the effect of the fluoroalkylene unit on the properties of the resulting polymer, we have synthesised two new families of semifluoroalkylene-containing aromatic polyamines from aromatic diamines and the key monomer **56**. In addition we have systematically studied the influence of the fluorine content on the thermal behaviour and surface wettability.

Table 2
Molecular structures of fluorinated monomers prepared

Molecular structure	Compound no.	Reference
$A - (CF_2)_n - A$ ($A = CH{=}CH_2$ or $C_2H_4NH_2$)	**54**	[106]
 $F(CF_2)nC_2H_4QN\begin{smallmatrix}(C_2H_4O)_pH\\(C_2H_4O)_pH\end{smallmatrix}$ ($Q = -, SCH_2, OCH_2; p = 0\text{-}4$)	**55**	[107–109]
 ($p = 0\text{-}4$)	**56**	[110,111]
 ($X = CN, CH_2NH_2, NCO, CO_2H, CH_2OH$)	**57**	[112–114]

6. Conclusion

The molecular design strategy applied to elaboration of molecular organised systems leads to materials which usually exhibit remarkable properties as compared to hydrocarbon homologues. So, we have described, through some examples which constitute the research axis of our group, the development of new molecules which leads to new high potential materials. Through European contracts and close association with industrial partners, it is possible to elaborate materials which present synergistic properties of surface and interface. These can be found in each application cited, as for instance blood substitutes, self-assembled monolayers, liquid crystals for device applications, and so on, where the improvement of the technological point of view depends on the control or the careful modification of the substrate interface.

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