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Review

Syntheses utilizing *n*-perfluoroalkyl iodides [R_FI, C_nF_{2n+1}-I] 2000–2010

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ABSTRACT

This review presents a comprehensive assessment of the synthetic utility of *n*-perfluoroalkyl iodides (R_FI, C_nF_{2n+1}-I, where $n = 2–14$) in the published literature from 2000 through 2010. R_FI is a versatile synthetic reagent widely utilized to introduce the perfluoroalkyl functionality and its unique functional characteristics into organic substances. Two distinct analysis tools were employed. First, Reaxys® was employed to examine the versatility and occurrences of R_FI in 1356 non-polymeric synthetic transformations. The most common R_FI synthetic conversions were (i) free-radical addition to carbon–carbon double or triple bonds, (ii) coupling to aryl halides, and (iii) Grignard, organolithium, or similar R_F anion addition to ketones and aldehydes. R_FI were also used as a chain transfer reagent in free-radical polymerization reactions of fluorinated and other unsaturated monomers. Second, a complementary Chemical Abstracts' STN AnaVist® search was employed to summarize the 779 publications describing reaction products that contained *n*-perfluoroalkyl chains (C_nF_{2n+1}-, where $n = 2–4$). The most common uses for materials into which R_FI was incorporated were surfactants, pesticides, electronic materials, pharmaceuticals, liquid crystals, dyes and optical materials, battery electrolytes, repellents, lubricants and polymerization catalysts.

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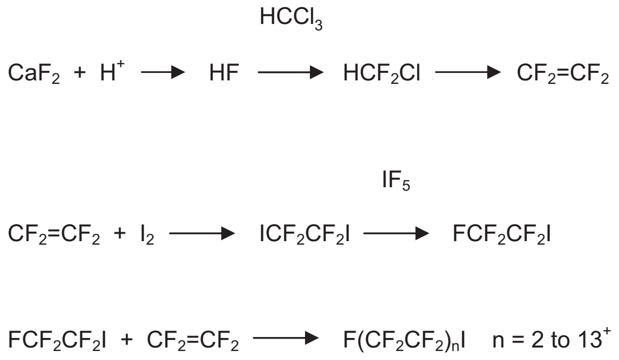
1. Introduction

More than a decade has past since Brace published three review articles on "Syntheses with Perfluoroalkyl Radicals from Perfluoroalkyl Iodides." These reviews spanned fifty years of R_FI chemistry, with an emphasis on the "practical synthetic methods" for R_F free-radical addition to alkenes or alkynes. In Part I, Brace [1] presented (i) the historical progress of the synthetic routes to R_FI, (ii) a description of the mechanism for the free-radical addition of R_FI to unsaturated compounds, (iii) general reaction conditions for the free-radical addition of R_FI to unsaturated compounds, and (iv) a survey of the range of unsaturated compounds successfully transformed by the free-radical addition of R_FI compounds. These unsaturated compounds included alkenes, alkynes, and unsaturated carboxylic acids, amines, alcohols, ethers and esters. Brace's first review also summarized the relative reactivity rates for the free-radical addition of R_FI to unsaturated compounds, comparing various R_FI and various unsaturated compounds (Scheme 1).



$$CaF_2 + H^+ \longrightarrow HF \xrightarrow{HCCl_3} HCF_2Cl \longrightarrow CF_2{=}CF_2$$

$$CF_2{=}CF_2 + I_2 \longrightarrow ICF_2CF_2I \xrightarrow{IF_5} FCF_2CF_2I$$

$$FCF_2CF_2I + CF_2{=}CF_2 \longrightarrow F(CF_2CF_2)_nI \quad n = 2 \text{ to } 13^+$$

Scheme 1. Industrial synthesis routes to perfluoroalkyl iodides, C_nF_{2n+1}, R_FI.

In his second review, Brace [2] focused on R_FI radical addition to non-conjugated dienes which yielded mono-adducts, bis-adducts, and cyclization products. As with other alkenes, the products of the addition of R_FI to dienes can undergo elimination of HI to give unsaturated compounds or reduction–hydrogenation to yield saturated compounds. In the free-radical addition of R_FI to cyclic and bicyclic alkenes, Brace concluded that temperature determined whether kinetic or thermodynamic influences dominated the outcome of the reaction, with a lesser effect for the steric consideration, i.e. that iodine and perfluoroalkyl groups are large, electronegative, and repel each other. In his third review, Brace [3] summarized the addition of R_FI radicals to norbornenes and unsaturated carboxylic acids, esters and anhydrides. While reaction stereochemistry was the focus of the research on R_FI free-radical addition to norbornenes, when R_FI was added to unsaturated carboxylic acids or similar derivatives, lactone formation was a common competing reaction. Brace concluded that the free-radical addition of R_FI to vinyl monomers exhibited "many different behaviors", including addition and polymerization.

More recently, in 2009 Morozov gave a brief overview of the chemistry of iodofluoroalkanes (including R_FI), highlighting their properties, syntheses and applications [4]. In addition, a table of physical characteristics of many R_FI and an extended discussion of the SbF_5 catalyst in the formation of iodofluoroalkanes were presented. In 2008, Zha briefly analyzed the production methods of $C_8F_{17}I$ using catalytic telomerization of TFE, with the goal of spurring domestic Chinese production of this critical intermediate for repellents and surfactants [5].

In the first decade of the 21st century (2000–2010), over 700 publications described research on the free-radical addition of R_FI to carbon–carbon double or triple bonds, including allenes, porphyrins and fullerenes; chemical families not extensively covered by Brace. The aim of this review is to present the past decade of research using R_FI. The review provides two distinct perspectives. First, the growing synthetic utility of R_FI to incorporate perfluoroalkyl groups into organic substances and polymers showing expanded (a) coupling of R_FI and aryl halides, (b) addition of R_F anions to ketones and aldehydes, (c) preparation of R_F organometallics, and (d) substitution of R_FI with sulfur nucleophiles. Second, while R_FI have a long history of synthetic utility, the unique chemical and physical properties of the perfluoroalkyl (R_F) are proving to be irreplaceable in modifying surface properties, eliminating pests, controlling catalyst solubility, altering magnetic, electronic, optical, dielectric or photochemical properties, facilitating molecular self-assembly in liquid crystals, ionic liquids or phospholipid bi-layers, providing lubricity, etc.

2. Search methods

2.1. The Reaxys® search

The Chemical Abstract Services Registration Numbers (CAS RN) for R_FI, linear, 1-perfluoroalkyl iodides, $C_nF_{2n+1}I$ where $n = 2–14$ and four perfluoroalkyl iodide mixtures, were used to search for publications where R_FI was indexed as one of the reactants (Table 1). These searches included papers, patents, talks and books published from January 1, 2000 through December 31, 2010. Perfluoroalkyl iodides with $n = 9$, 11, 13, 14 and the four perfluoroalkyl iodide mixtures were not found as reactants in these Reaxys® searches [6].

Reaxys® is a merging together of Elsevier's chemistry databases; CrossFire Beilstein, CrossFire Gmelin and Patent Chemistry Database. One functionality in Reaxys® allows the search output to be tabulated, showing reactants, reaction scheme,

Table 1
Perfluoroalkyl iodides searched in Reaxys®.

C_nF_{2n+1}-I	CASRN	Name	Formula
n			
2	354-64-3	n-Perfluoroethyl iodide	C_2F_5-I
3	754-34-7	n-Perfluoropropyl iodide	C_3F_7-I
4	423-39-2	n-Perfluorobutyl iodide	C_4F_9-I
5	638-79-9	n-Perfluoropentyl iodide	C_5F_{11}-I
6	355-43-1	n-Perfluorohexyl iodide	C_6F_{13}-I
7	355-58-0	n-Perfluoroheptyl iodide	C_7F_{15}-I
8	507-63-1	n-Perfluorooctyl iodide	C_8F_{17}-I
9	588-97-4	n-Perfluorononyl iodide	C_9F_{19}-I
10	423-62-1	n-Perfluorodecyl iodide	$C_{10}F_{21}$-I
11	307-50-6	n-Perfluoroundecyl iodide	$C_{11}F_{23}$-I
12	307-60-8	n-Perfluorododecyl iodide	$C_{12}F_{25}$-I
13	376-04-5	n-Perfluorotridecyl iodide	$C_{13}F_{27}$-I
14	307-63-1	n-Perfluorotetradecyl iodide	$C_{14}F_{29}$-I
Mixtures			
$n \geq 3$	25464-12-4	Ethene, 1,1,2,2-tetrafluoro-, telomer with trifluoroiodomethane	C_nF_{2n+1}-I, $n \geq 3$
$n \geq 4$	25398-32-7	Ethene, 1,1,2,2-tetrafluoro-, telomer with 1,1,1,2,2-pentafluoro-2-iodoethane	C_nF_{2n+1}-I, $n \geq 4$
$n \geq 4$	35830-66-1	Ethene, 1,1,2,2-tetrafluoro-, telomer with 1,1,1,2,2-pentafluoro-2-iodoethane	C_nF_{2n+1}-I, $n \geq 4$
$n \geq 4$	52257-95-1	Ethene, 1,1,2,2-tetrafluoro-, telomer with 1,1,1,2,2-pentafluoro-2-iodoethane	C_nF_{2n+1}-I, $n \geq 4$

and reaction classification for each reaction indexed. By limiting the Reaction Classification to "preparation", excluding "multi-step reactions" and reviewing the reactions indexed as "chemical behavior", 1356 reactions utilizing R_FI as the reactant were readily obtained. Many reactions were repeated in this list. Duplicates were not removed so more common synthetic reactions could be identified by their more frequent occurrence. For each reaction, the tabulated data in Reaxys® included reference cited, a description of the reaction product, a full text of the reaction, catalyst(s), yield and much more.

Reaxys® does not yet thoroughly cover the literature in an effective way for polymers and polymerization reactions. For example, in the addition reaction of R_FI to tetrafluoroethylene (TFE) to produce a longer chain R_FI, the R_FI was inconsistently indexed as either a 'reactant' or a 'product'. But in Reaction Classification, these synthetic transformations were indexed as "chemical behavior" instead of "preparation". The Reaction Classification of "chemical behavior" is normally reserved for thermal or photochemical degradation reactions of R_FI. Reviewing the reactions classified as "chemical behavior" was also necessary to identify those reactions where R_FI was undergoing a synthetic transformation. Another example of a gap in the Reaxys® database is seen in the living radical polymerization reaction of styrene in the presence of $C_6F_{13}I$ as a degenerative chain transfer agent [7]. For this reaction, the R_FI compound was indexed as a "reagent", a category normally reserved for reactions where the R_FI was merely an iodine transfer agent [8]. Furthermore, important journals for polymer research are not included in the Reaxys® database, for example, the journals of "Macromolecular Chemistry and Physics" and "Advances in Polymer Chemistry". These gaps in reviewing the syntheses utilizing R_FI in an addition reaction with TFE or as chain transfer reagents in free-radical polymerization reactions were overcome with a complementary CAS® STN® search strategy that gathered references containing the CAS RN of the R_FI compounds and the terms polymerization, chain transfer, and related terms.

2.2. CAS® STN® searches

As with the Reaxys® search strategy previously discussed, the same collection of CAS registry numbers (Table 1) for linear R_FI and perfluoroalkyl iodide mixtures were used as search terms within the STN file Chemical Abstracts Plus (CAPlus^{SM}) and limited to those indexed as reactants (/RCT). Chemical Abstracts Plus, otherwise known as CAPlus^{SM}, is a value-added database product from Chemical Abstract Service that offers the chemical research community unprecedented access to over 34 million records dating as far back as 1907. This collection of records has been amassed from monitoring over 10,000 journals and 61 patent issuing authorities while including industry-related conference proceedings, books, dissertations, technical disclosures and meeting abstracts.

Absent any publication date restrictions, a corpus of 1841 records was identified. All but two of the perfluoroalkyl iodide mixtures (CAS Nos. 35830-66-1 and 52257-95-1) were represented by at least one record while $C_6F_{13}I$, $C_8F_{17}I$ and C_4F_9I were the most highly represented with records of 756, 659 and 572 respectively. As will be discussed later in this review, this corpus was further refined using STN® AnaVist™ by selecting the Publication Year chart, creating a highlight set composing of the years 2000 thru 2010 and then visualizing a new subset. This ultimately resulted in a collection of 779 records and was the basis for the elucidation of product application cases for reaction products of R_FI compounds within that time period.

2.3. Reaxys® search results analysis on synthetic transformations

For the 1356 published synthetic transformation reactions of R_FI, examining the seventeen distributions of chain length in R_FI showed that the five even carbon numbered R_FI ($n = 2, 4, 6, 8, 10$) accounted for almost 92% of the reactions published (Fig. 1). These five R_FI received the most research interest due to their commercial availability from telomerization of perfluoroethyl iodide with TFE and therefore are practical, available reagents for research use. Odd carbon-number R_FI require synthesis beginning with the less readily available CF_3I or C_3F_7I. R_FI with carbon chain lengths C_{12} or greater were involved in little to no research activity due to their poor solubility and the insignificant difference in influence of the longer perfluoroalkyl chain compared to C_8F_{17} or $C_{10}F_{21}$ side chains on properties of interest such as surface tension [9].

3. Synthetic reactions with R_FI

3.1. Addition to carbon–carbon double and triple bonds

More than 55% of the R_FI synthetic transformations reported from 2000 to 2010 involved the addition of R_FI to carbon–carbon double or triple bonds. With nearly 750 reported reactions in the past eleven years, this synthetic transformation is a well established strategy for introducing perfluoroalkyl groups into chemical structures. In 1999, in the first of his three reviews, Brace

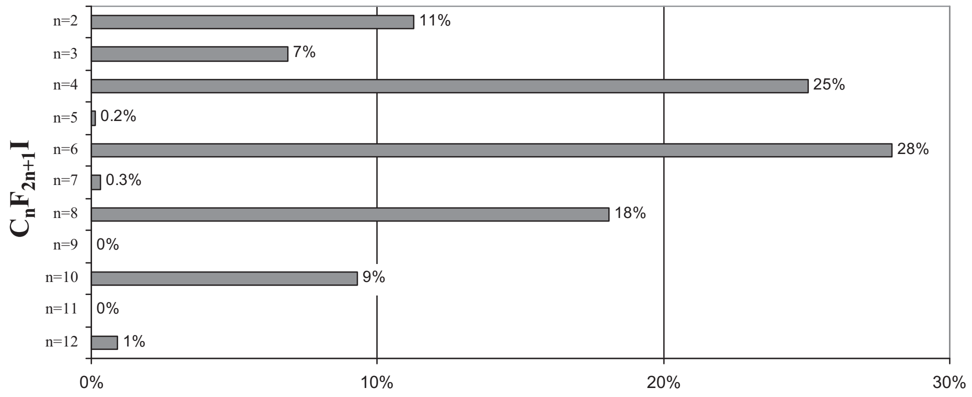


Fig. 1. Frequency of R_FI carbon chain length reported in publications, 2000–2010.

elaborated on the mechanism by which R_FI undergoes free-radical addition to an alkyne or an alkene; essentially the mechanism proposed by Kharasch for the addition of carbon tetrachloride or chloroform to olefins [10]; see Scheme 2. Formation of the R_F radical can occur by UV light, thermal initiation, or radical abstraction of iodine using peroxides, azonitriles, or redox systems. After irreversible Addition of the R_F radical to the alkyne or alkene, the intermediate can undergo either Transfer, Propagation, or Termination. Transfer gives the R_FI addition product, and another R_F radical for Addition. Propagation gives polymer chain formation when highly polarizable olefin/monomers are used, for example acrylamide, tetrafluoroethylene, or vinylidiene fluoride.

$$\text{Initiation:}\quad R_FI + R\bullet \longrightarrow RI + R_F\bullet$$

$$\text{Addition:}\quad R_F\bullet + C{=}C \longrightarrow R_F\text{-}C\text{-}C\bullet$$

$$\text{Transfer:}\quad R_FI + R_F\text{-}C\text{-}C\bullet \longrightarrow R_F\bullet + R_F\text{-}C\text{-}C\text{-}I$$

$$\text{Propagation:}\quad R_F\text{-}C\text{-}C\bullet + C{=}C \longrightarrow R_F\text{-}C\text{-}C\text{-}C\text{-}C\bullet$$

$$\text{Termination:}\quad R_F\bullet + R_F\text{-}C\text{-}C\bullet \longrightarrow R_F\text{-}C\text{-}C\text{-}R_F$$

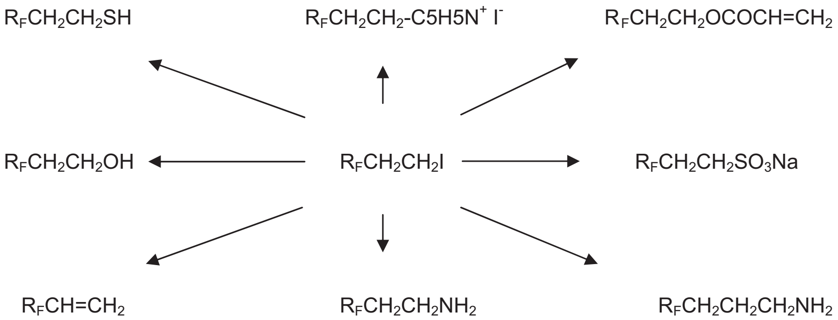
Scheme 2. General mechanism for R_FI addition to olefins.

As Brace showed, the addition of R_FI to ethylene has great commercial value due to the versatility of the intermediates available from the resulting perfluoroalkyl ethyl iodide, including primary alcohols, primary thiols, terminal olefins, and sulfonate salts; see Scheme 3. Igumnov added C_2F_5I, C_3F_7I, and $C_8F_{17}I$ to ethylene using copper acetate and hydrazine with corresponding perfluoroalkyl ethyl iodide yields of 100%, 60% and 100%, respectively [11]. Qing added $C_6F_{13}I$ to ethylene with sodium dithionate and base, obtaining $C_6F_{13}C_2H_4I$ in 95% yield [12]. Wlassics utilized a thermally initiated addition of $C_8F_{17}I$ to ethylene and obtained $C_8F_{17}C_2H_4I$ in 99% yield [13]. The commercial importance of the addition of R_FI to ethylene is further shown in patents describing these reactions filed by Allied-Signal [14] and DuPont [15].

The addition of R_FI to ethylene followed by hydrolysis to give perfluoroalkyl ethanol is a commercially valuable synthetic sequence, leading to a diverse array of surfactants and repellents. Other perfluoroalkyl primary alcohols have been synthesized as precursors to surfactants and repellents to compare the impact of the perfluoroalkyl group and the spacer between the R_F group and the polar linkage. The most common route to these other perfluoroalkyl primary alcohols is the free-radical addition of R_FI to ω-unsaturated primary alcohols, followed by dehalogenation of the iodohydrin. From 2000 through 2010, over 100 reactions were reported on the addition of R_FI to ω-unsaturated primary alcohols including allyl alcohol [16], 3-buten-1-ol [17], 4-penten-1-ol [18], 5-hexen-1-ol [19], 7-octen-1-ol [20], 9-decen-1-ol [21], 10-undecen-1-ol [22] and 16-heptadecen-1-ol and 21-docosen-1-ol [23]. The synthetic versatility of the addition of R_FI to unsaturated alcohols was also evident in the addition of R_FI to unsaturated cyclic alcohols [23], unsaturated branched alcohols [24] and phenols [25]. Among the more than seven hundred addition reactions of R_FI to carbon–carbon double or triple bonds reported since 2000, many represent interesting synthetic transformations beyond those thoroughly reviewed by Brace. A few representative examples are highlighted in the following sections.

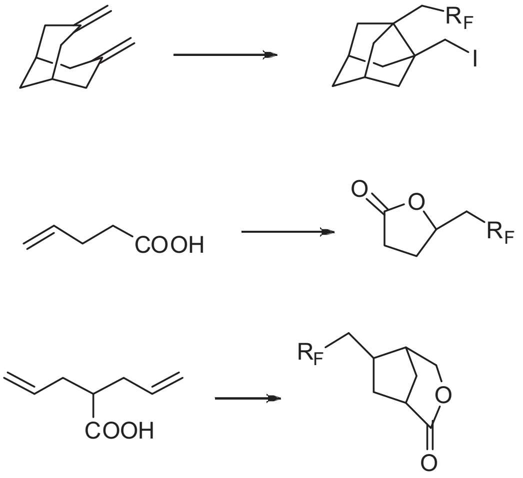
3.1.1. *Addition to carbon–carbon double bonds resulting in cyclization*

In the general mechanism described by Brace for the free-radical addition of R_FI to carbon–carbon double bonds, the Addition reaction product is a free-radical and the Transfer reaction product is an alkyl iodide. Both of these products can undergo intramolecular cyclization, the free-radical with a



Scheme 3. Diversity of fluorinated products from perfluoroalkyl ethyl iodide.

carbon–carbon double bond and the alkyl iodide with an internal nucleophile. A diverse variety of cyclization products due to R_FI addition to carbon–carbon double bonds have been reported. For example, Ponomarenko found that R_FI free-radical addition to 3,7-dimethylenebicyclo [3.3.1] nonane resulted in essentially quantitative tandem addition with cyclization to the corresponding noradamantanes [26]. Tsuchii studied the free-radical addition of R_FI to dienes, diynes, and enynes, which generally cyclized to form cyclopentanes, tetrahydrofurans, or pyrrolidines [27]. These cyclizations occurred under mild conditions (irradiation with near-UV light) in moderate to good yields (Scheme 4).



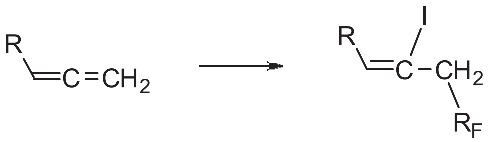
Scheme 4. R_FI addition to carbon–carbon double bonds resulting in cyclization.

Motoda developed a heterogeneous aqueous room temperature procedure for the palladium-catalyzed free-radical addition of R_FI to carbon–carbon double bonds. This report included the addition of R_FI to dienes, diallyl ethers and diallyl amines to afford cyclopentanes, tetrahydrofurans or pyrrolidines, respectively, in near quantitative yields [28]. Wu used sodium bisulfite or sodium sulfite in aqueous DMF to react perfluorohexyl iodide with 4-pentenoic acid. Free-radical addition to the carbon–carbon double bond, followed by nucleophilic substitution gave the γ-lactone in 43% yield [29].

Rubio found that the addition of R_FI to allyl alcohol or allyl amine (under basic conditions) gave a mixture of simple free-radical addition products (perfluoroalkyl allyl alcohol or perfluoroalkyl allyl amine, respectively) or tandem free-radical addition-cyclization products (perfluoroalkyl methyloxiranes and perfluoroalkyl methylaziridines, respectively) [30]. Yang accomplished tandem dual free-radical addition-lactonization of $C_6F_{13}I$ and 2-allyl-4-pentenoic acid in 92% yield [31]. Similar reactions with R_FI and 2-alkyl-2-allyl-4-pentenoic acids gave a mixture of the addition-lactonization bicyclic product and a cyclopentane resulting from dual free-radical addition.

3.1.2. Addition to allenes

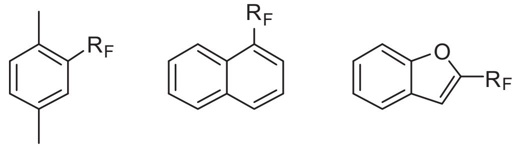
Ogawa reported that R_FI added in good yields to terminal allenes in the presence of Xe lamp, which was attributed to the absorption of R_FI in the 300–350 nm region [32]. Excellent regioselectivity was observed, but mixtures of stereoisomers were produced. Subsequent results strongly suggested that nonpolar solvents are most effective for this iodoperfluoroalkylation [33]. Similarly, Ma developed a $Na_2S_2O_4$-promoted, radical addition of R_FI with terminal allenes to give 1-perfluoroalkyl-2-alken-2-yl iodides in 52–69% yield [34] (Scheme 5).



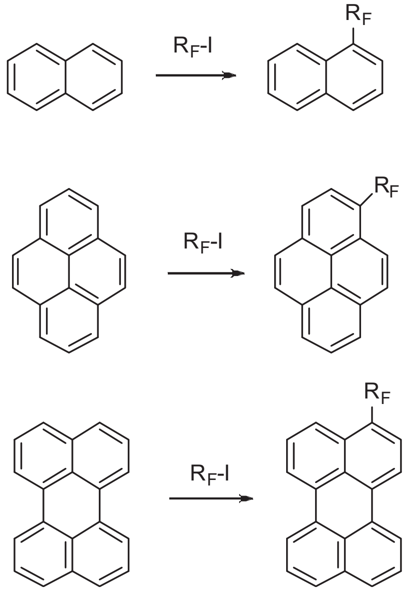
Scheme 5. R_FI addition to allenes. Yields 58–88%; R = t-butyl, n-butyl, n-hexyl, cyclohexyl; $R_FI = C_{10}F_{21}I$, C_4F_9I [33].

3.1.3. Addition/elimination on aromatic rings

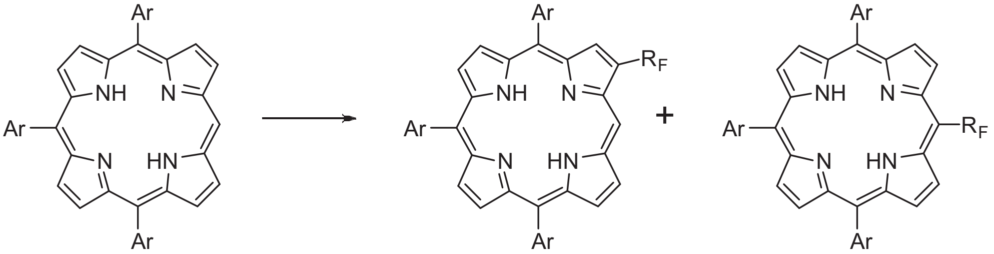
Perfluoroalkyl iodides (R_FI) undergo free-radical aromatic substitution reactions with a variety of aromatic and heteroaromatic ring systems. Iizuka found that benzene, p-dichlorobenzene, p-xylene, naphthalene, and benzofuran underwent mono-perfluoroalkylation with R_FI in the presence of TiO_2, $NaBF_4$, and UV light, with yields up to 44% [35]. In the mechanism proposed by Iizuka, the aromatic system traps the perfluoroalkyl radical, forming an arenium radical, which undergoes oxidation and proton elimination to give the perfluoroalkyl aromatic product. The resonance stability of the intermediate arenium radical accounts for the substitution pattern of the perfluoroalkyl group on the aromatic ring system. In preparing a series of insecticides, Onishi found that R_FI (C_2F_5I, C_3F_7I, C_4F_9I, $C_8F_{17}I$) gave mono-perfluoroalkylation for a variety of anilines. UV light, reducing agents, and phase transfer catalysts gave R_F derivatives for anilines including 2-methyl aniline, 2,6-dimethyl aniline, and 4-t-butyl aniline in yields from 18% to 94% [36]. Substitution occurred mostly para to amine group, though some ortho substitution occurred to a lesser extent. Li achieved mono-perfluoroalkylation of naphthalene, pyrene, and perylene with copper in yields of 65–75% [37] (Schemes 6 and 7).



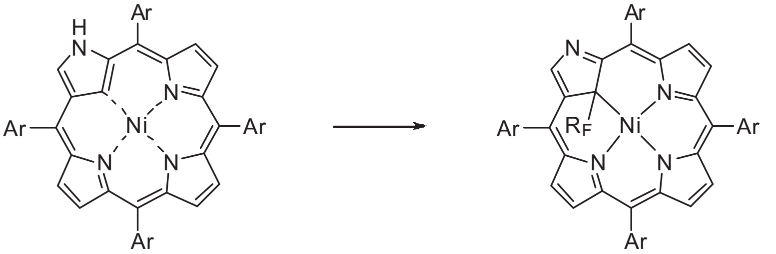
Scheme 6. R_F substituted aromatic rings synthesized by R_FI addition/elimination.



Scheme 7. R_FI addition/elimination to polyaromatic rings.



Scheme 8. R_FI addition/elimination to porphyrins.

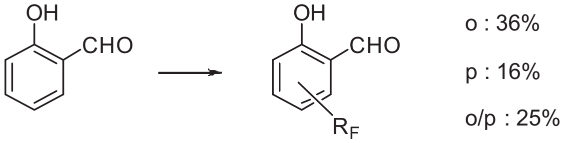


Scheme 9. R_FI addition/elimination to a nickel porphyrins complex [41].

3.1.4. Addition to porphyrins

Chen found that the free-radical addition of R_FI to tri-aryl porphyrins (followed by dehydrohalogenation) gave a mixture of mono-perfluoroalkyl adducts [38]. Similarly, Jin reported that the free-radical addition of R_FI to zinc di-aryl porphyrins (followed by dehydrohalogenation) gave a mixture of mono-perfluoroalkyl adducts [39]. Jin also reported that the free-radical addition of R_FI to tetra-substituted porphyrins (followed by dehydrohalogenation) gave only a single mono-perfluoroalkyl adduct [40]. Jiang synthesized N-confused porphyrins by treating nickel tetra-aryl porphyrins with R_FI followed by dehydrohalogenation [41] (Schemes 8 and 9).

Matsugi found that direct perfluoroalkylation of deactivated phenols occurred with R_FI (C_4F_9I, $C_6F_{13}I$, $C_8F_{17}I$, $C_{10}F_{21}I$) at room temperature in the presence of cesium carbonate and a free-radical initiator [42]. No oxygen-alkylation was observed, and electron withdrawing groups (aldehyde, nitro, nitrile) were required, to achieve successful carbon perfluoroalkylation when non-substituted phenol or alkyl phenols were used as substrates (Scheme 10).



Scheme 10. Aromatic carbon alkylation with R_FI. [41].

3.1.5. Addition to fullerenes

The introduction of perfluoroalkyl groups onto fullerenes is facilitated by (i) the stability of the perfluoroalkyl groups, (ii) the ease of formation of the perfluoroalkyl radical, and (iii) the reactivity of the perfluoroalkyl radical in addition–elimination reactions with carbon–carbon double bonds. The characterization of fullerenes is a challenging exercise, but the introduction of perfluoroalkyl groups to the carbon caged structure improves their solubility and facilitates traditional analytical methods. Generally, the fullerenes and R_FI are heated in an inert atmosphere. Depending on the temperature and dwell time, a variety of products were observed. Most of the recent research with R_FI advances the early work done with CF_3I. Kareev found that high-temperature reaction (~400 °C for ~3 h) of C_{60} and C_2F_5I produced two poly(perfluoroethyl) fullerenes: $C_{60}(C_2F_5)_6$ and $C_{60}(C_2F_5)_8$ [43]. Tamm's high-temperature reaction (~400 °C for 40–70 h) of C_{60} and C_2F_5I produced eight major poly(perfluoroethyl) fullerenes isomers: $C_{60}(C_2F_5)_6$ (one isomer), $C_{60}(C_2F_5)_8$ (five isomers), and $C_{60}(C_2F_5)_{10}$ (two isomers) which were isolated by chromatographic separation [44].

In subsequent research, Tamm treated a mixture of higher fullerenes C_{76} to C_{96} with excess C_2F_5I at 250 °C for 4–5 days. The resulting complex mixture contained the compositions $C_{60}(C_2F_5)_8$, $C_{60}(C_2F_5)_{10}$, $C_{70}(C_2F_5)_{10}$, $C_{60}(C_2F_5)_8$, $C_{84}(C_2F_5)_{12}$, $C_{76}(C_2F_5)_{10}$, $C_{76}(C_2F_5)_{12}$, $C_{78}(C_2F_5)_{10}$, and the main component $C_{84}(C_2F_5)_{12}$ [45]. Several isomers of each composition were identified. Tagmatarchis derivatized endohedral lanthanum metallofullerene with two C_8F_{17} groups by reacting the metallofullerene with R_FI under UV light. Only seven isomers of $La@C_{82}(C_8F_{17})_2$ were observed, isolated, and characterized. These seven isomers represent only a small portion of the large number of isomers possible due to the 44 chemically non-equivalent carbon atoms of the $La@C_{82}$ system [46].

3.2. Coupling reactions with aromatic halides

More than 15% of the synthetic transformations of R_FI reported from 2000 to 2010 involved coupling reactions with aromatic iodides and bromides. Generally, a copper-mediated cross-coupling is employed, in which the iodide to copper exchange takes place forming a copper(I) fluoroalkyl adduct (R_FCuI), which subsequently reacts with an aromatic halide to introduce the perfluoroalkyl chain into the aromatic system with good to excellent overall yield. This reaction has been described using a wide range of aromatic iodides [47], aromatic bromides [48], aromatic di-iodides [49] and aromatic di-bromides [50]. While much less common, aromatic chlorides also undergo coupling reactions with R_FI. Blom used a Grignard reagent to couple R_FI and chlorobenzene [51], and Wada used copper powder in DMSO to couple C_3F_7I and methyl 6-chloronicotinate enroute to "benzanilides with insecticidal activity" [52].

In aromatic systems with both bromide and iodide substituents, a competition exists in the coupling reaction of the aromatic halide with R_FI. Many researchers have demonstrated that the R_F substitution occurs exclusively with carbon–iodide bond cleavage to form the R_F–Ar–Br derivative. Bastero coupled $C_8F_{17}I$ and 4-bromophenyl iodide with copper and bi-pyridine to give 1-bromo-4-(perfluorooctyl)benzene in 79% yield [53]. Similarly, Hope coupled $C_6F_{13}I$ and ortho-, meta-, and para-bromophenyl iodide to give the three corresponding bromo perfluorohexylbenzenes [54] (Scheme 11).

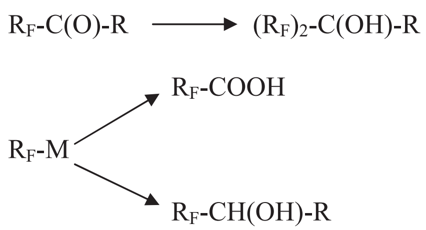
$$R_FI + X\text{-}Ar \rightarrow R_F\text{-}Ar \qquad X = Br, I, Cl$$

Scheme 11. R_FI coupling with aromatic halides.

The coupling reaction of R_FI with aromatic iodides and bromides occurs for a wide variety of aromatic and heteroaromatic systems, including pyrenes [55], pyridines [56], thiophenes [57], polythiophenes [58], pyrazoles [59], pyrroles [60], and triazoles [61]. This coupling reaction successfully occurs in the presence of many functional groups including amines [62], nitro groups [63], carboxylic acids [64], ketones [65], esters [66], sulfonamides [67], ethers [68], alcohols [69], nitriles [70], urethanes [71], phosphine oxides [72], aldehydes [73], phenols [74], anhydrides [75], alkynes [75], lactones [76] and imides [77].

3.3. R_F anions: Grignards, organolithium reagents, and TDEA

More than 14% of the synthetic transformations of R_FI reported from 2000 to 2010 involved the reaction of R_FI with inorganic reagents to form perfluoroalkyl anions, which subsequently underwent addition (for example to carbon–oxygen double bonds) or substitution (for example to borates). Of the nearly 200 reactions involving perfluoroalkyl anions published in the past eleven years, the vast majority utilized either organomagnesium (Grignard) or organolithium reagents, which reacted with carbonyl compounds with the expected results traditionally observed with alkyl organomagnesium or organolithium reagents. While certainly not exhaustive, here are a few representative examples. $C_6F_{13}MgI$ reacted with $^{13}CO_2$ to give the isotopically labelled perfluoroheptanoic acid [78]. $C_8F_{17}MgI$ reacted with 5-(2,2,5-trimethyl-1,3-dioxane) carbaldehyde to give the corresponding ketal alcohol [79]. C_3F_7Li reacted with 2,4-di-tert-butyl-2,4-cyclopentadien-1-one to give the corresponding cyclopentadien-1-ol [80]. C_4F_9MgI underwent addition to the ester methyl 1-naphthonate [81]. Kokotos published an extensive study on the synthetic utility of the addition reaction of R_FLi with various carboxylic acids, anhydrides, amides, esters, acid fluorides, carbonates, and aldehydes [82] (Scheme 12).



Scheme 12. R_F anion addition to ketones, CO_2 and aldehydes.

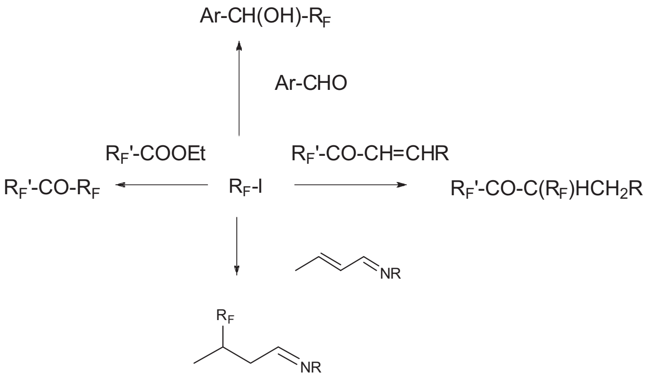
Perfluoroalkyl organomagnesium and organolithium reagents are utilized to prepare perfluoroalkyl borates and boranes. However, the controlled introduction of one or two R_F nucleophiles into a boron electrophile (ex. BCl_3 or BBr_3) cannot be achieved only by choosing the correct stoichiometry. Nishi reacted phenyl magnesium bromide with R_FI, then with boric acid trimethyl ester followed by fluorination to form ionic liquids (ILs) composed of perfluoroalkyltrifluoroborate ions [83]. In synthesizing perfluoroalkyltrifluoroborate salts as electrolytes, Zhou found that the choice of Grignard reagent and fluorinating agent, and the ratio of R_FI to borate ester greatly affected the yield and composition of the borate salt [84]. Abo-Amer prepared bis(perfluoroorgano) boron compounds by selecting a boron precursor with one good nucleofuge, i.e. $BCl(OCH_3)_2$ [85] (Scheme 13).

$$R_FMgI + B(OCH_3)_3 \rightarrow R_FBF_3(-)\ K(+) \qquad R_F = C_nF_{2n+1}, n=2,4,6$$

$$R_FLi \rightarrow Li\,[\,R_FBCl(OCH_3)_2\,] \rightarrow R_FB(OCH_3)_2 \rightarrow Li\,[\,(R_F)_2\text{-}B(OCH_3)_2\,]$$

Scheme 13. R_F Grignard and lithium addition to borates.

Beyond perfluoroalkyl magnesium or lithium reagents, other cations with perfluoroalkyl anions have been used effectively in synthetic transformations. Zeifman utilized activated aluminum to synthesize perfluoroketones by reduction of perfluorocarboxylic acid esters with R_F in about 40% yield [86]. Sato used diethyl zinc and rhodium catalysts to achieve α-fluoroalkylation of α,β-unsaturated ketones in good yields [87]. Examination of the reaction mechanism led Sato to conclude that a rhodium hydride complex was the critical intermediate, and that β substitution of the α,β-unsaturated ketone inhibits α-fluoroalkylation while facilitating addition of the perfluoroalkyl anion to the carbonyl carbon (Scheme 14).



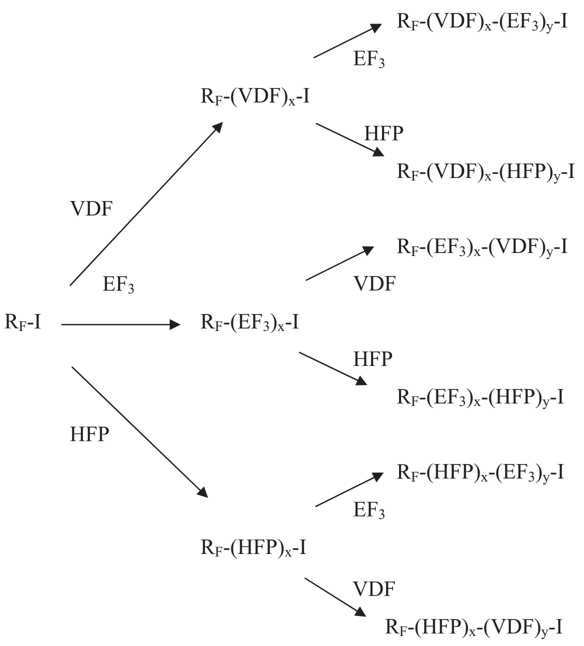
Scheme 14. Metal catalyzed R_FI addition.

Vasil'eva reported the pentacarbonyliron-promoted addition of C_4F_9I to 2-furaldehyde and various benzaldehydes followed the Barbier-like reaction pattern, giving the corresponding secondary alcohols, though the yields were generally low [88]. Subsequent research proposed an iron-carbonyl complex intermediate which explained the effect of the choice anion and aldehyde on the reaction yields [89]. Ueda prepared β-perfluoroalkyl oximes and hydrazones in good yields by treating the corresponding α,β-unsaturated imine derivatives with R_FI and triethyl borane [90]. While Ueda proposed a free-radical mechanism for this reaction, the net overall reaction is similar to a Michael-type addition of the perfluoroalkyl anion.

Mild nucleophilic perfluoroalkylation with R_FI has also been carried out using tetrakis(dimethylamino)ethylene (TDAE). Petrov found that nucleophilic substitution occurred with R_FI ($R_F = C_2F_5I$, C_3F_7I, C_4F_9I) and carboxylic acid chlorides, sulfonyl chlorides, chlorosilanes, and electron deficient carbonyl compounds, such as trifluoroacetophenone, cyclohexane carboxaldehyde, or propionaldehyde [91]. Pooput also reported that TDAE was an effective reagent for the nucleophilic addition of R_FI to aldehydes, ketones, and imines, and for the nucleophilic substitution of R_FI to disulfides and diselenides [92].

3.4. Addition to fluorinated olefins

While the most significant commercial route to R_FI remains the addition of R_FI to tetrafluoroethylene (TFE, $CF_2{=}CF_2$), recent inventions continued to improve the manufacturing of R_FI, with the objective of improving oligomers selectivity, reaction efficiency, and process safety. Many catalysts were described for optimizing the addition of R_FI to TFE, most notably copper [93], tin [94], nickel [95], and zinc [96], though many other transitions metals, their blends and their alloys were also reported [97]. Two Chinese patents described photothermal or photochemical methods for the syntheses of R_FI using a low pressure reactor (batch or continuous) with a mercury (254 nm) lamp [98]. High selectivity of R_FI was obtained in the addition of R_FI to TFE with the use of a fluorinated peroxide initiator; $R_FCOO–OOCR_F$ [99]. Depending on the specific R_FI starting materials and the goal composition of R_FI produced, inventions touted high temperature processes [100], medium temperature processes [101], or low temperature processes [102]. Inventions that mitigated the safety concerns due to the exothermic nature of the addition of R_FI to TFE and the explosive nature of TFE included a method for preparing R_FI through a vapor phase continuous catalytic process [103], and a process for preparing R_F at ambient pressure using a solid catalyst [104] (Scheme 15).



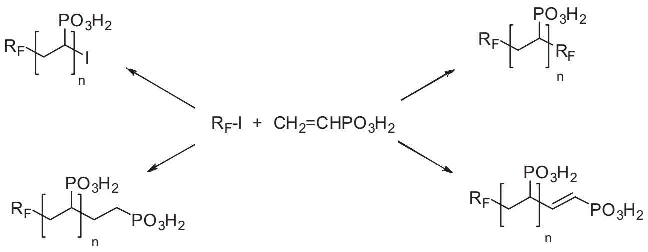
Scheme 15. R_FI addition to fluorinated olefins.

While the telomerization of vinylidiene fluoride, hexafluoropropene and other fluorinated olefins have been extensively investigated, recent publications have revealed further details of the polymerization mechanisms and kinetics, as well as improving the choice of catalysts, chain transfer agents, and monomer control to achieve synthetic objectives. Ameduri carried out the Iodine Transfer Polymerization (ITP) of vinylidiene fluoride with n-perfluorohexyl iodide as the chain transfer agent, and these polymerizations exhibited high efficiency and reactivity, a good control of average degree of polymer in number, and few defects of VDF chaining [105]. Ameduri reported on the controlled step-wise telomerization of vinylidene fluoride, hexafluoropropene and trifluoroethylene with R_FI [106]. These families of fluorinated polymers are valuable in many applications, especially as fluoroelastomers in the automotive, aerospace, and chemical industries. The monoadduct produced from vinylidene fluoride exclusively gave the $R_FCH_2CF_2I$ structure. The monoadduct produced from hexafluoropropene exclusively gave the $R_FCF_2CF(CF_3)I$ structure. But, the monoadduct produced from trifluoroethylene gave a mixture of R_FCFHCF_2I and R_FCF_2CHFI isomers.

3.5. R_FI as a chain transfer agent in free-radical polymerization

Boyer carried out the emulsion polymerization of vinylidene fluoride and α-trifluoromethacrylic acid with sodium thiosulfate using n-perfluorohexyl iodide as the chain transfer agent [107]. Ameduri made terpolymers with a monomer bearing an SF_5 group (perfluorosulfanylethylene, CF_2CFSF_5) with vinylidene fluoride and hexafluoropropylene, using n-perfluorohexyl iodide in the Iodine Transfer Polymerization (ITP) [108]. A similar monomer, pentafluorosulfanylethylene, did not terpolymerize under ITP conditions. Ameduri synthesized copolymers of vinylidene fluoride and perfluoromethyl vinyl ether as fluoroelastomers, using n-perfluorohexyl iodide as the chain transfer agent [109]. Ameduri synthesized poly(vinylidene fluoride)-poly(styrene) block copolymers by sequential iodine transfer copolymerization (ITP) of vinylidene fluoride and styrene in the presence of perfluoroalkyl iodides as chain transfer agents (CTAs) [110] (Scheme 16).

In the general mechanism described by Brace for the free-radical addition of R_FI to carbon–carbon double bonds, the Transfer and Propagation steps compete to form the alkyl iodide and the oligomers/polymer, respectively. When the rate of propagation greatly exceeds the rate of transfer, the R_FI becomes an initiator or a chain transfer agent (CTA) in the free-radical polymerization of the unsaturated monomer. As a CTA, the R_FI controls the molecular weight of the polymer and introduces a hydrophobic and oleophobic end group in the polymer chain; an important component of surfactants and repellents. David synthesized vinyl phosphoric acid oligomers using R_FI as the CTA, and found that the reaction was not a living polymerization, but followed a conventional radical telomerization [111]. Winnik showed that R_FI was an effective degenerative chain transfer (DCT) agent in the living/controlled free-radical dispersion polymerization of styrene [7]. Farcet used R_FI as DCT agent to prepare miniemulsions of styrene-butyl acrylate block copolymers [112] (Scheme 17).

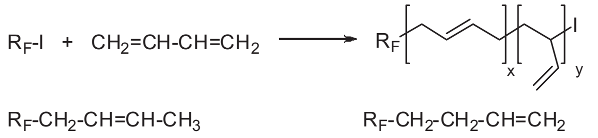


Scheme 17. R_FI free-radical transfer polymerization of vinyl phosphate [7].

$$PhCH_2CF_2—(—CH_2CF_2—)_n—I \xrightarrow{\text{styrene}} PhCH_2CF_2—(—CH_2CF_2—)_n—(—CH_2CHPh—)_m—I$$

Scheme 16. R_FI as a chain transfer agent in free-radical polymerization reactions. Synthesis of PVDF-b-polystyrene block copolymers [109].

Ameduri reported on the "Radical Telomerization of 1,3-Butadiene with Perfluoroalkyl Iodides", concluding that selection of the radical initiator, reaction temperature, reaction solvent, and initial molar ratios of the reactants controls the proportion of resulting mono-addition products (both 1,2 and 1,4 addition) and fluorinated oligomers [113]. Parker conducted an emulsion polymerization of styrene using perfluorohexyl iodide as a CTA [114]. Farcet used perfluorohexyl iodide as a CTA to prepare a gradient copolymer of poly(isobornyl acrylate)/methyl acrylate for cosmetic products [115] (Scheme 18).



Scheme 18. R_FI as a chain transfer agent in butadiene polymerization, with addition by-products.

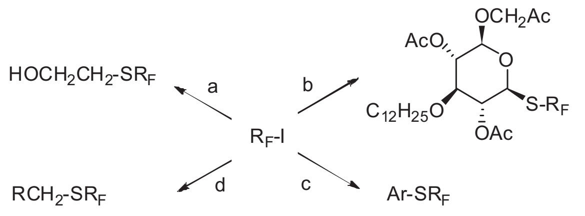
3.6. Sulfur chemistry

While the conversion of R_FI to perfluoroalkyl sulfonate salts (R_FSO_3Na) using sodium dithionite is well known, recent reports continue to optimize this synthetic transformation by varying the solvents, reaction temperature, bases, catalysts, etc. [116]. R_FSO_3Na are important intermediates to fluorinated sulfonyl chlorides, sulfonyl fluorides, sulfones, and sulfonamides (Scheme 19).

$$R_F\text{-I} \longrightarrow R_F\text{-}SO_2Na \longrightarrow R_F\text{-}SO_2Cl$$

Scheme 19. R_FI as a reagent for synthesis of perfluoroalkyl sulfonyl chlorides.[115].

Radical initiated substitution of iodide in R_FI with thiols is an effective alternative to the addition of R_FI to unsaturated compounds for introducing perfluoroalkyl chains into organic compounds. This substitution reaction is quite versatile for aromatic or aliphatic thiols, and for thiols containing a variety of other functional groups. Schwaebisch successfully made aromatic perfluoroalkyl thioethers, enroute to carbohydrate-containing liquid crystals [117]. Similarly, Schwaebisch made mixed alkyl-perfluoroalkyl substituted monosaccharide derivatives from R_FI [118]. Magnier reacted R_FI with mercaptoethanol, enroute to perfluoroalkyl vinyl sulfides, sulfoxides and sulfones [119] (Scheme 20).



a = $HOCH_2CH_2SH$; b = protected thiol sugar ; c = Ar-SH ; d = R_fCH_2SH

Scheme 20. R_FI reaction with mercaptans.

In Sizov's research, alkylation of 1,1-dihydropolyfluoroalkyl thiols with R_FI under the conditions for the formation of the sulfoxylate radical anion afforded the 1,1-dihydropolyfluoroalkyl sulfides in satisfactory yields of 37–48% [120].

3.7. Phosphorous chemistry

In 2009, Banger wrote a comprehensive review of the synthetic methods for preparing phosphorus(III) compounds with fluoroalkenyl, fluoroalkynyl and fluoroalkyl groups [121]. The most important synthetic routes to fluorinated phosphanes utilizing R_FI were (i) their reaction with sodium diphenyl phosphane, and (ii) their reaction with trimethylsilyl-containing phosphanes (Scheme 21).

$$R_F\text{-I} + Ph_2P\text{—}SnBu_3 \longrightarrow Ph_2P\text{—}R_F$$

$$R_F\text{-I} + Ph_2As\text{—}SnBu_3 \longrightarrow Ph_2As\text{—}R_F$$

$$R_F\text{-I} + PhSe\text{—}SnBu_3 \longrightarrow PhSe\text{—}R_F$$

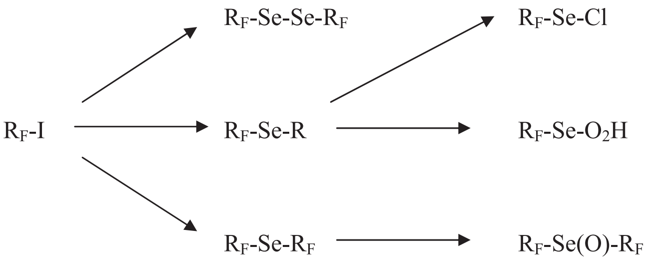
Scheme 21. Synthesis of R_F phosphines, arsines, selenides.

Brisdon described the reaction of R_FI with trimethylsilyl-containing phosphanes for primary, secondary, and tertiary with yields from 30% to 85% [122]. Lanteri expanded this synthetic approach by reporting the synthesis of perfluoroalkyl-phosphines, -arsines, and -selenides obtained by Pd-catalyzed cross-coupling reaction with organoheteroatom stannanes [123]. For R_FI of C_4F_9I, $C_6F_{13}I$, $C_8F_{17}I$, and $C_{10}F_{21}I$, the R_F phosphines were obtained in 15–48% yield, and the R_F arsines and R_F selenides were obtained in 47–90% yield.

3.8. Selenium chemistry

Organoselenium compounds have demonstrated antioxidant, antitumor, antimicrobial, and antiviral properties which are sparking an interest in synthetic methods to obtain perfluoroalkyl selenides. Cross-coupling reactions of selenium-stannanes were used to generate mixed alkyl, perfluoroalkyl selenides, especially with palladium catalysts. Bonaterra synthesized Ph-Se-R_F, for $R_F = C_8F_{17}$ and $C_{10}F_{21}$ in 70% and 90% yield respectively using n-$Bu_3SnSePh$ [124]. Magnier reacted R–Se–Se–R with R_FI to produce a variety of mixed alkyl, perfluoroalkyl selenides in yields from 28% to 80% [125]; the R_F groups ranged from C_1 to C_8, and the alkyl groups were phenyl, benzyl, and methyl.

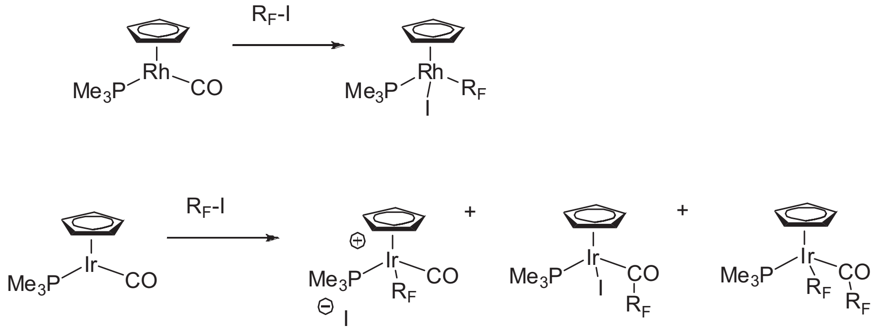
Gockel used a mixture of selenium and copper metals to convert R_FI to R_F–Se–R_F and R_F–Se–Se–R_F [126]. The di-perfluoroalkyl selenides were oxidized to the R_F–Se(O)–R_F with HOF. The mixed alkyl, perfluoroalkyl selenides also underwent oxidation to either the perfluoroalkyl selenium chloride or the perfluoroalkyl seleninic acid, which Crich used to catalyze the allylic oxidation of alkenes to enones [127] (Scheme 22).



Scheme 22. R_FI addition to selenium compounds.

3.9. Transition metal organometallics

Perfluoroalkyl transition metal compounds have been studied to improve the solubility of catalytically active transition metal complexes in fluorinated solvents. In the past ten years, research



Scheme 23. R_FI addition to organometallics.

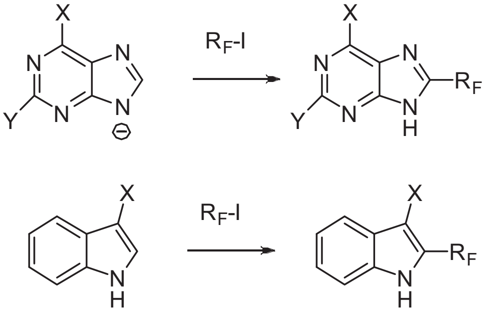
has been reported on the syntheses of R_F complexes of molybdenum (Mo), rhodium (Rh), palladium (Pd), tungsten (W), iridium (Ir), and platinum (Pt), which are generally formed by oxidative addition of R_FI to transition metal complexes.

The oxidative addition of C_2F_5I to the Pt(TMEDA)$(CH_3)_2$ afforded an octahedral Pt(IV) complex, trans-Pt(TMEDA)$(CH_3)_2(R_F)$I. Similarly, the reaction of Pd(TMEDA)$(CH_3)_2$ with C_2F_5I afforded a square planar Pd(II) complex Pd(TMEDA)$(CH_3)(R_F)$, presumably by oxidative addition followed by reductive elimination of CH_3I [128]. Hughes found that the molybdenum(II) and tungsten(II) complexes [M(cyclopentadienyl)$_2$L] (with M = Mo or W, L = C_2H_4 or CO) reacted with perfluoroalkyl iodides to give a variety of transition metal compounds, including complexes where the R_F group was bonded to the cyclopentadienyl ring, was bonded directly to the transition metal, or underwent addition to the ethylene ligand [129].

The choice of reaction solvent and temperature affected the distribution of reaction products when transition metal complexes reacted with R_FI. Bourgeois reported that reaction of C_3F_7I with Rh(cyclopentadienyl)(PMe_3)(CO) gave the expected product of oxidative addition, Rh(cyclopentadienyl)(C_3F_7)(I), and the low-temperature reaction of Ir(cyclopentadienyl)(CO)(PMe_3) with C_3F_7I gave the ionic complex Ir(cyclopentadienyl)(CO)$(PMe_3)(C_3F_7)^+$ I^-. However the room temperature reaction of the iridium complex with C_3F_7I gave a mixture of four products, including the ionic complex, a perfluoroalkyl complex, a perfluoroacyl complex and a perfluoroacyl(perfluoroalkyl) complex [130]. Hughes reported that the reaction of Pd(tetramethylethylenediamine)$(CH_3)_2$ with perfluoroalkyl iodides gave a mixture of products that depend markedly on the choice of solvent, presumably due to the solubility of these complexes and their subsequent reactivity [131] (Scheme 23).

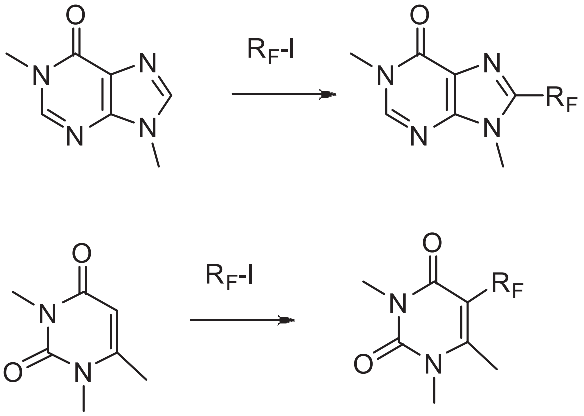
3.10. Other reactions

While about half of the synthesis reactions with perfluoroalkyl iodides are the free radical addition of R_FI to carbon–carbon double or triple bonds, a few synthetic reactions involved the addition of R_FI to carbon–nitrogen double or triple bonds. Medebielle synthesized analogs of known plant growth regulators using the indirect electrochemical induction of the $S_{Rn}1$ mechanism to obtain fluorinated purine and indole derivatives [132]. Similar reactivity for n-perfluorohexyl iodide and n-perfluorobutyl iodide with purine and indolyl anions was observed with yields ranging from 28% to 75% (Scheme 24).



Scheme 24. R_FI addition to purines and indoles.

Since 5-trifluoromethyl uracil is an intermediate for an anticancer and antiviral agent, Yamakawa developed a method for introducing a perfluoroalkyl group into a nucleobase, including uracils, cytosines, adenines, guanines, hypoxanthines, and xanthines [133]. A nucleobase was reacted with R_FI in the presence of a sulfoxide, a peroxide and an iron compound, undergoing addition and elimination of HI to produce the perfluoroalkyl-substituted nucleobase. While the patent claims for R_FI range CF_3I to $C_6F_{13}I$, most examples in the patent were for CF_3I. The few examples for $C_6F_{13}I$ gave relatively poor isolated yields of between 4% and 25% (Scheme 25).

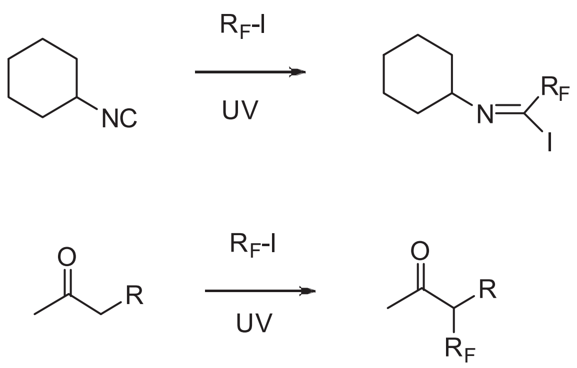


Scheme 25. R_FI addition to synthesize perfluoroalkyl-substituted nucleobases.

While the free radical addition reactions of R_FI to isocyanides was known, the analogous photoinitiated radical addition was reported by Tsuchii [33]. The reaction of cyclohexyl isocyanide with $C_{10}F_{21}I$ gave the iodo perfluorooctyl imine in 92% yield.

Photocatalysis was also used effectively to perfluoroalkylate octanal with good yield and high enantioselectivity. Nagib used an iridium photocatalyst and a commercial imidazolidinone catalyst to introduce the CF_3, C_2F_5, C_3F_7, and C_4F_9 perfluoroalkyl groups at C2 in octanol with yields of 79%, 73%, 69%, and 67%, respectively, and enantiomeric excesses of 99%, 93%, 99%, and 96%, respectively [134] (Scheme 26).

While the addition of R_FI to TFE is a well studied reaction to extend the carbon chain length of R_FI by two CF_2 groups, Oharu used fuming sulfuric acid to convert a perfluorohexyl iodide into a perfluorohexanoyl fluoride in 59% yield [135]. When the acid



Scheme 26. Photoinitiated R_FI addition.

fluoride was subsequently coupled to form fluorinated ethers, the resulting C_5F_{11} chain had been reduced by one carbon atom. This one-carbon reduction strategy for R_FI can be applied to other reactions of R_FCOF, for example, reactions with amines, amides and hydrazines.

4. Uses of perfluoroalkyl containing substances: CAS® STN® AnaVist® analysis

Application and use cases for R_FI reaction products were elucidated from a corpus of 779 records published between the years 2000 and 2010 using the product STN® Anavist™ from Chemical Abstracts Service. STN® Anavist™ is one of several tools available in the STN family of products and capable of in-depth analysis and visualization. It was specifically designed for a small selection of databases such as CAPlus, Derwent World Patent Index and several full-text patent files [136]. Using its comparative analysis features, STN® Anavist™ provides the means to quickly mine large document sets via a thematic mapping schema, field specific charts or two-dimensional matrices. These visual aids may highlight what otherwise may be trends left undetermined using traditional analysis methods. For this review, we focused on the use of the Technology Indicators chart to identify application and use cases described below.

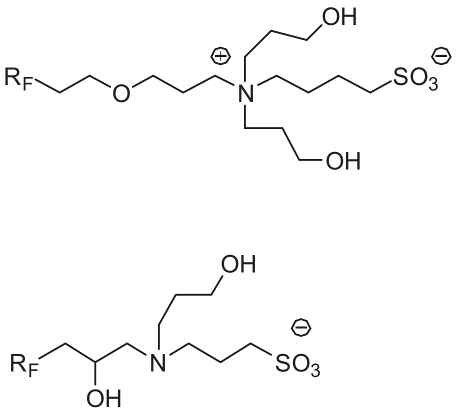
4.1. Surfactants

Fluorinated surfactants have been commercially available since the 1950s [137]. Because of their exceptionally low aqueous surface tension, foaming characteristics, and chemical and thermal stability, fluorinated surfactants are used in diverse applications including fire fighting foams, coatings, mining, electroplating, photographic emulsifiers, waxes, polishes, cleaners, mold release, ink jet printing, lithography, enhanced oil recovery, and emulsion polymerizations.

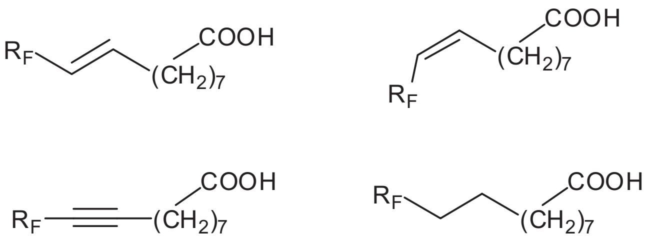
Maniero prepared perfluoroalkyl sulfonic acid (anioinic) and amino-sulfonic acid (betainic) surfactants for fire-fighting foams, which showed excellent amphipatic properties in highly saline aqueous environments [138] (Scheme 27).

Takai prepared perfluoroalkyl terminated fatty acids and found that these fluorinated fatty acids formed more stable monolayers with higher spreading pressures compared to their hydrocarbon analogs [139] (Scheme 28).

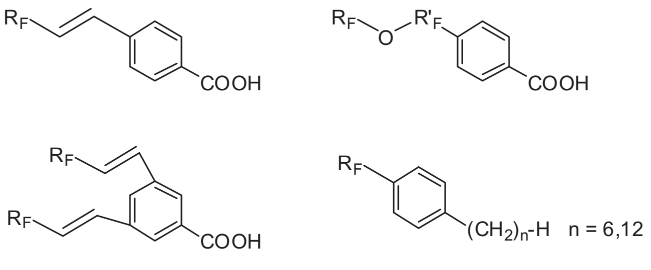
Grushin prepared mono- and di-perfluoroalkyl benzoates with potential as building blocks for advanced materials or as emulsifiers or surfactants in pharmaceutical or agrochemical applications [140] (Scheme 29).



Scheme 27. Betaine surfactants prepared from R_FI.

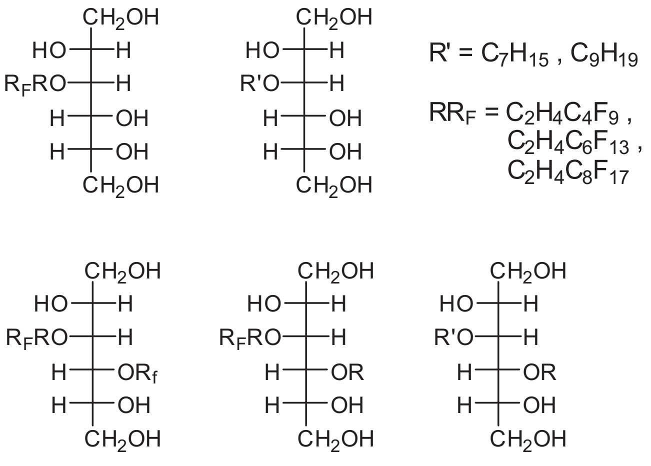


Scheme 28. Unsaturated carboxylic acid fluorinated surfactants.



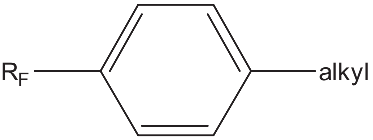
Scheme 29. Mono- and di-perfluoroalkyl benzenes.

Rogalska prepared a series of fluorinated, nonfluorinated, and hybrid nonionic surfactants derived from D-mannitol. Among the nine compounds studied only five (F4F4, H6H6, F6H6, F6F6 and F8F8) formed stable Langmuir monolayers when spread on a pure aqueous sub-phase. For compounds of an equal number of carbon atoms in the hydrophobic tails increasing substitution of hydrogen for fluorine atoms resulted in (i) increased time to attain the equilibrium of the adsorbed films at the air:water interface, and (ii) lower equilibrium surface tensions [141] (Scheme 30).



Scheme 30. d-Mannitol surfactants.

Kawase prepared an effective gemini surfactant with two perfluoroalkyl groups as hydrophobic components and two sulfonate groups as hydrophilic components [142]. Taylor prepared a variety of hybrid twin-tailed fluoroalkyl-alkyl surfactants which lowered surface tension, lowered interfacial tension, improved foaming, and increased leveling in coatings. Taylor's surfactants contained both alkyl and perfluoroalkyl hydrophobic components with either ethoxylate or phosphate hydrophilic groups [143]. Komoto found that perfluoroalkylbenzenes were effective surfactants for Lewis acid catalysis in supercritical carbon dioxide to carry out aldol, Mannich, and Friedel-Crafts type reactions [144] (Scheme 31).

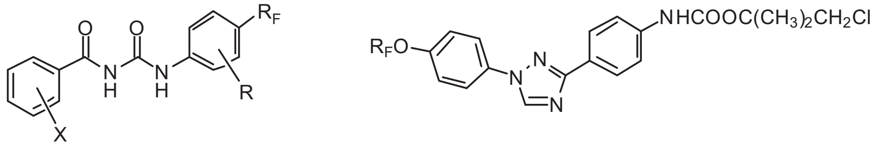


$R_F = C_4F_9, C_8F_{17}$ alkyl $= C_6H_{13}, C_{12}H_{25}$

Scheme 31. Hybrid twin-tailed fluoroalkyl-alkyl surfactants.

4.2. Pesticides

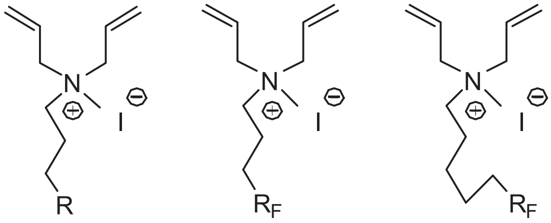
Incorporating perfluoroalkyl groups has been an effective synthetic tool for modifying and probing the reactivity of pesticides including insecticides, fungicides, herbicides, rodenticides, pediculicides, and biocides [145]. While fluorine or trifluoromethyl groups are more commonly used in fluorinated pesticides, the benefits of the perfluoroalkyl group are increasingly being reported. Lambert prepared perfluoroalkyl substituted benzoylurea compounds, which were effective pesticides [146]. Konobe prepared perfluoroalkyl heteroaryl-N-aryl carbamate compounds for controlling pests. While fluoro or trifluoromethyl groups were more common substitutents in Konobe's insecticides and acaricides, perfluoroethyl groups were also found to be effective [147] (Scheme 32).



Scheme 32. Urea and urethane pesticides containing R_F substituents.

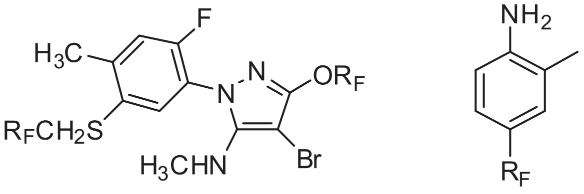
Sun carried out the synthesis and structure–activity relationship (SAR) of novel perfluoroalkyl-containing quaternary ammonium salts by examining their antibacterial activity against gram positive (*S. aureus*), gram negative (*Escherichia coli*) and fungi (*Candida albicans*) microorganisms on the basis of MIC (minimal inhibitory concentration) values and MBC (minimal bactericidal concentration) values [148]. The perfluoroalkyl-containing quaternary ammonium salts showed more effective antibacterial activities against gram-positive strain than their non perfluoroalkyl-containing counterpart, inferior antibacterial activity against the fungi strain, and none of these compounds showed effective antibacterial activities against gram-negative strain (Scheme 33).

Ohata prepared 3-alkoxy-1-phenylpyrazole derivatives as pest control agents containing one or more perfluoroalkyl chains that were effective insecticides, miticides, or nematicides [149]. Onishi prepared perfluoroalkylanilines as intermediates in the synthesis of agricultural and horticultural insecticides, which showed effective mortalities for Diamondback Moths and Common Cutworms [150] (Scheme 34).



$R = C_8H_{17}$ $R_F = C_6F_{13}, C_8F_{17}$

Scheme 33. Perfluoroalkyl and alkyl cationic surfactants.



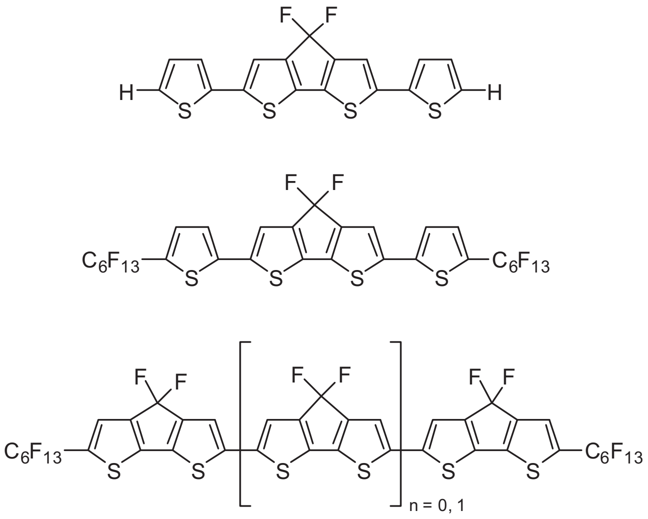
Scheme 34. Perfluoroalkyl substituted aniline and pyrazole insecticides.

4.3. Electronic materials

In organic electronic materials, both the electronegativity and the fluorous phase effect of perfluoroalkyl groups have been used to favorably control HOMO and LUMO energy levels and intermolecular organization. The strategic use of the perfluoroalkyl group in oligothiophenes, graphenes, and other poly-aromatic systems resulted in various semi-conductors and transistors.

Fluorinated oligothiophenes and polymers were shown to have low reduction potentials, low energy absorption bands, and other satisfactory electron transport properties useful as organic n-type semiconductors. These oligomers and polymers can be fabricated into thin-films and electronic devices [151]. Other n-type semiconductors and transistors have been made from bis(perfluorobutyl)pentacene [152] and perfluoroalkyl perylene bisimides [153]. Ie showed that the presence of perfluorohexyl groups at the α,ω-positions of the oligothiophene has influence on both oxidation and reduction peaks, and that the difluoromethylene bridge largely contributes to keeping planarity between the thiophene rings and lowering the LUMO level. The R_F-substituted quaterthiophene derivatives showed good n-type semiconducting behavior with field-effect electron mobilities [154] (Scheme 35).

In a series of papers, Marks has shown that substitution of a perfluoroalkyl for an alkyl substituent switches the majority carrier from holes to electrons in several oligothiophene series. Both α,ω- and β,β′-dihexyl substituted oligothiophenes (up to six thiophene units) are p-type semiconductors, while the analogous α,ω- and β,β′-diperfluorohexyl substituted oligothiophenes display n-type behavior. Substitution with strong electron



Scheme 35. R_F substituted oligothiophenes.

withdrawing perfluorohexyl groups increased the core ionization potential, enhanced volatility, and improved thermal stability in comparison to the dihexylsubstituted analogs [155]. Marks also synthesized and characterized of diperfluorooctyl-substituted phenylene-thiophene oligomers. These oligomers further demonstrated that transport characteristics of known p-type oligomers can be tuned by proper molecular functionalization, for example with R_F groups. As thin films, all of these fluorinated oligomers were n-type semiconductors [156]. Hong also found that R_F di-substituted thiophene-phenylene and thiophene-thiazole oligomers were effective semiconductors [157] (Scheme 36).

Modification of graphene with R_F groups allows control of the electronic structure by selective saturation of the π-bonds which opens a band gap, resulting in a semi-conducting or insulating form of graphene. This invention allows large-scale fabrication of electronic devices including interconnectors, dielectrics, and transistors [158] (Scheme 37).

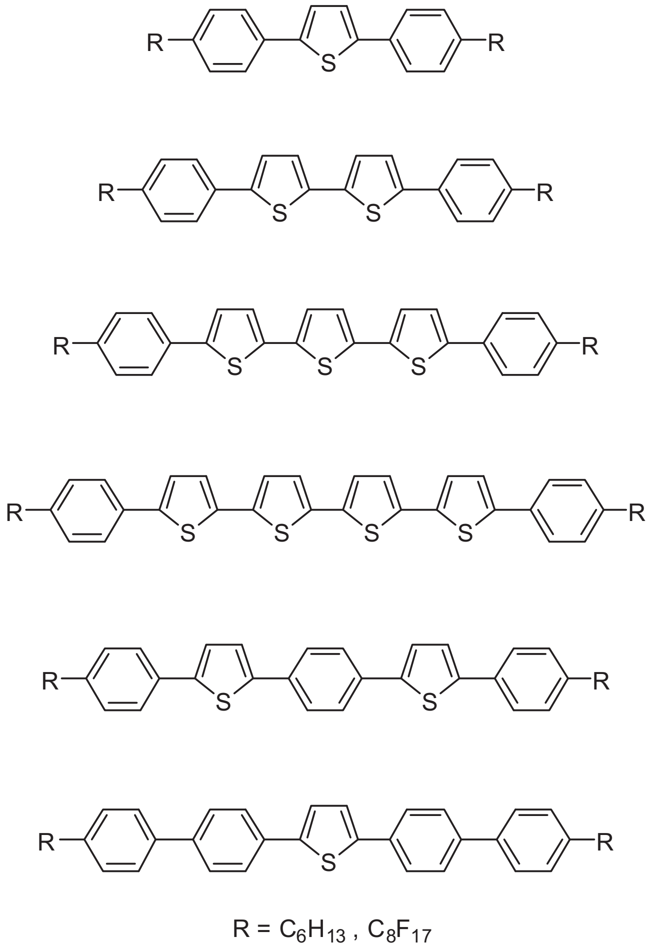
4.4. Pharmaceuticals

As with pesticides, the fluorine and trifluoromethyl groups have been effective substituents for modifying and probing the reactivity of biologically active agents. The perfluoroalkyl group has been increasingly valuable in biosurfactant applications and as substituents in steroid systems, though these systems are more often substituted with F or CF_3 than R_F.

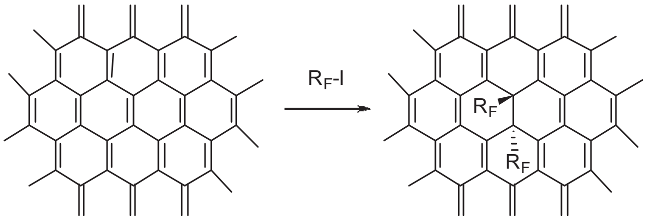
Fluorinated surfactants are valuable in a variety of biomedical applications, for example the administration of drugs. Li prepared a series of R_F substituted glucopyranoside surfactants, and found these materials for be excellent biosurfactants with low toxicities and low haemolytic activities, compared to their analogous hydrocarbon surfactants [159] (Scheme 38)

David prepared a series of perfluoroketone compounds for inhibition of phospholipase A2 activity, which has potential therapeutic uses for treating neural and inflammatory conditions [160]. Gaucheron synthesized and evaluated R_F substituted glycerophosphoethanolamines for in vitro cationic lipid-mediated gene delivery. These fluorinated biosurfactants demonstrated remarkably higher in vitro and in vivo transfection potency compared to conventional lipoplexes or even with PEI-based polyplexes [161] (Scheme 39).

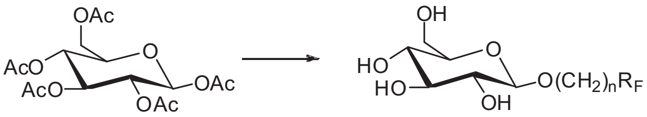
Gaucheron also designed and evaluated R_F substituted lipospermines as synthetic vectors for gene delivery. The efficiency of the fluorinated lipoplexes to transfect lung epithelial A549 cells was significantly higher than that of the analogous hydrocarbon lipoplexes [162] (Scheme 40).



Scheme 36. Alkyl and perfluoroalkyl substituted oligothiophenes.

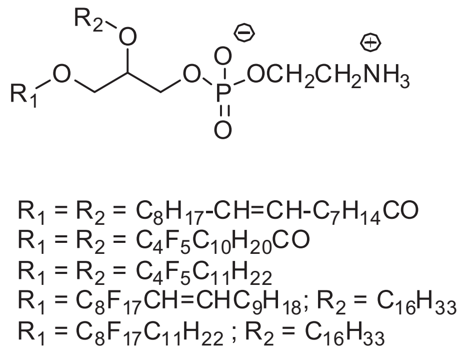


Scheme 37. R_F modified graphene.



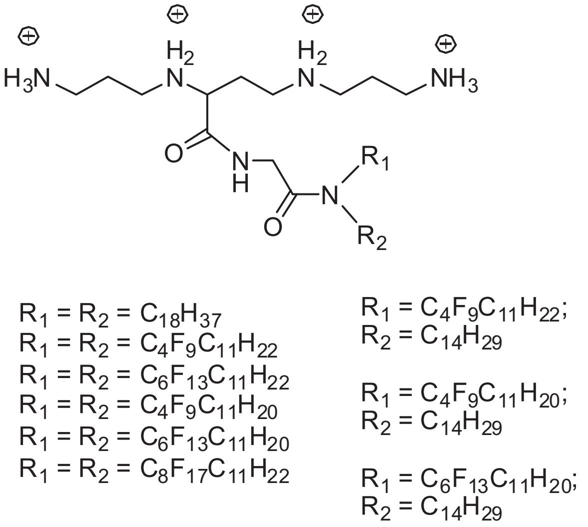
Scheme 38. Fluorinated surfactants for biomedical applications.

Malikayl prepared polyfluoroalkyl tryptophan tripeptides and showed that these materials were highly selective thrombin inhibitors which provided anticoagulant effects useful in the treatment of thrombin condition and in preventing the coagulation of stored blood products [163]. Eignerova synthesized a series of R_F substituted brassinosteroids, then found that their biological activity often reached the same range as their nonfluorinated analogs [164]. Jiang prepared a variety of R_F substituted



$R_1 = R_2 = C_8H_{17}\text{-}CH{=}CH\text{-}C_7H_{14}CO$
$R_1 = R_2 = C_4F_5C_{10}H_{20}CO$
$R_1 = R_2 = C_4F_5C_{11}H_{22}$
$R_1 = C_8F_{17}CH{=}CHC_9H_{18}$; $R_2 = C_{16}H_{33}$
$R_1 = C_8F_{17}C_{11}H_{22}$; $R_2 = C_{16}H_{33}$

Scheme 39. Alkyl and perfluoroalkyl substituted glycerophosphoethanolamines.



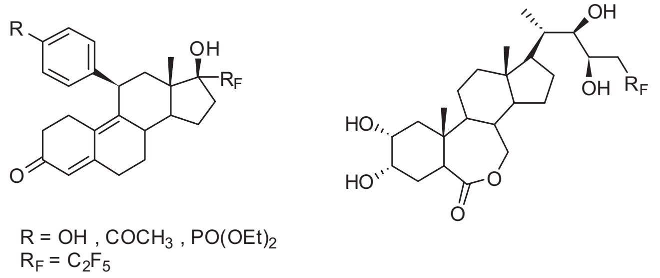
$R_1 = R_2 = C_{18}H_{37}$
$R_1 = R_2 = C_4F_9C_{11}H_{22}$
$R_1 = R_2 = C_6F_{13}C_{11}H_{22}$
$R_1 = R_2 = C_4F_9C_{11}H_{20}$
$R_1 = R_2 = C_6F_{13}C_{11}H_{20}$
$R_1 = R_2 = C_8F_{17}C_{11}H_{22}$

$R_1 = C_4F_9C_{11}H_{22}$; $R_2 = C_{14}H_{29}$

$R_1 = C_4F_9C_{11}H_{20}$; $R_2 = C_{14}H_{29}$

$R_1 = C_6F_{13}C_{11}H_{20}$; $R_2 = C_{14}H_{29}$

Scheme 40. Alkyl and perfluoroalkyl substituted lipoplexes.



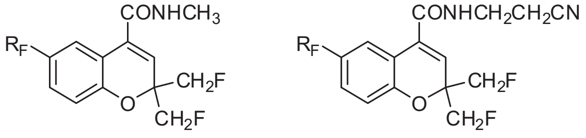
R = OH , $COCH_3$, $PO(OEt)_2$
$R_F = C_2F_5$

Scheme 41. Perfluoroalkyl substituted steroids.

11-phosphorus steroid derivatives useful as progesterone receptor modulators [165] (Scheme 41).

Cleve prepared a highly potent progesterone receptor antagonist by introduction of a C_2F_5 side chain at 17a into the D-ring of the steroidal skeleton. This R_F substituted steroid combines a pure anti-progestagenic endocrinological profile with high potency. An extensive structure–activity relationship study concluded that the favorable profile of potency and pharmacology for this R_F substituted steroid must be predominantly attributed to the pentafluoroethyl side chain [166].

Taka's research demonstrated that R_F substituted benzopyran-4-carboxamides were effective antihypertensive potassium channel openers (KCO), showing highly potent, slow and long-lasting antihypertensive effect and an improvement in lipid metabolism [167] (Scheme 42).



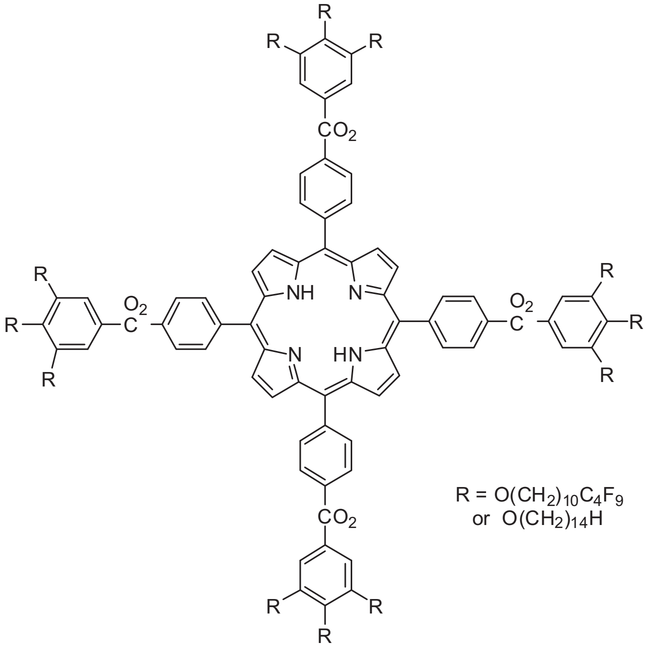
Scheme 42. R_F substituted benzopyrans.

4.5. Liquid crystals

The "fluorophobic effect" describes the tendency of fluorinated materials to self-organize, distinct from organic or aqueous/polar environments. Fluorinated materials are finding unique solutions to challenges in synthesis, catalysis, molecular recognition, and self-assembly due to the utilization of this "third phase" [168].

Broniatowski studied the liquid-crystalline phase behavior of perfluorooctyl-n-alkanes and perfluorodecyl-n-alkanes for C_8 through C_{16} alkanes. With shorter alkyl chains, smectic phases are observed at room temperature, but longer hydrogenated fragment are not capable of liquid-crystalline phase formation [169]. Gough developed liquid crystal compounds with a silane tail and a perfluoroalkyl terminal portion [170].

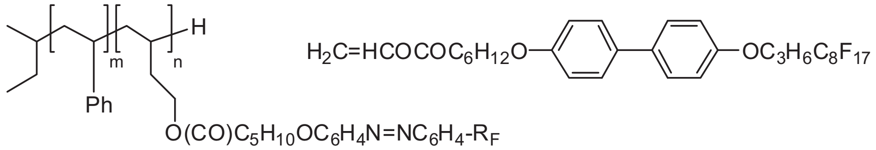
Percec demonstrated that the attachment of multiple R_F side-chains to electron-donor groups of a dendron facilitated the self-assembly in a p-stack located in the center of supramolecular helical pyramidal columns and also demonstrates the utility of the fluorophobic effect or fluorous phase in the self-assembly of liquid crystals [171]. Zhou synthesized a nanoscale discotic LC porphyrin with multiple R_F substitution. This fluorinated material exhibited an exceptionally enhanced uniform alignment and self-assembly, resulting in a controllable ordered nanostructure [172] (Scheme 43).



R = $O(CH_2)_{10}C_4F_9$
or $O(CH_2)_{14}H$

Scheme 43. Self-assembly of poly-R_F substituted porphyrin.

Zhang introduced R_F side chains in oligo(fluorene-co-bithiophene)s to increase their T_g and T_c, and encourage mesophase formation [173]. Ober prepared and studied a series of (co)polymers with R_F azobenzene pendant groups for their light-induced

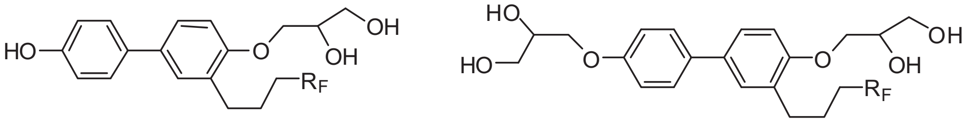


Scheme 44. Polymers with pendant R_F substituted azobenzene or biphenyl groups.

changes in surface properties and liquid crystal behavior [174] (Scheme 44).

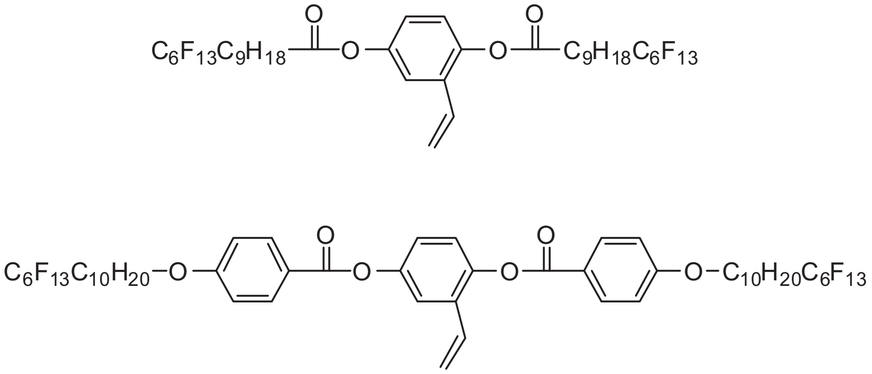
Viguier synthesized and researched acrylate monomers with R_F substituted biphenyl alkyl groups and their (co)polymers. An intermediate alkyl chain length was found to facilitate the formation of smectic A or smectic E enantiotropic mesophases. The bulk organization of the fluorinated side groups was diminished strongly for polymers in comparison with the corresponding fluorinated monomers [175].

Cheng synthesized two series of bolaamphiphilic triblockmolecules consisting of (i) a rigid biphenyl unit, (ii) polar dihydroxypropyloxy or a phenolic OH groups, and (iii) R_F side-chain, and found a complex dependence of the length of the R_F side-chain and the liquid crystalline phases [176] (Scheme 45).



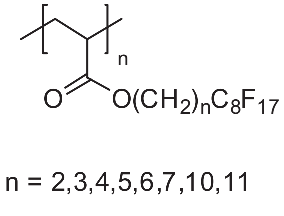
Scheme 45. R_F substituted biphenyls with liquid crystal behavior.

Ober synthesized monomeric vinyl hydroquinone cores with R_F side chains and their (co)polymerization behavior was examined. These semifluorinated mesogen-jacketed liquid-crystalline polymers formed stable hydrophobic surfaces and higher order smectic phases [177] (Scheme 46).



Scheme 46. Monomeric vinyl hydroquinones with R_F side chains.

Pees synthesized a series of ω-perfluorooctyl-alkyl polyacrylates and confirmed that the influence of the alkyl space on the isotropisation temperature followed an odd–even effect, which has already been observed in the case of non-fluorinated liquid crystalline polymers [178] (Scheme 47).



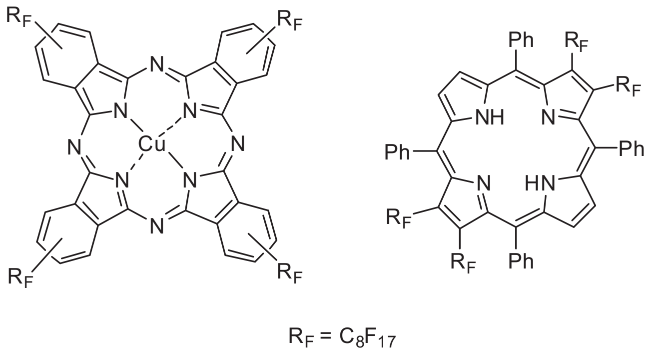
Scheme 47. ω-Perfluorooctyl-alkyl polyacrylates.

Gibbons used polyimides, poly (amic acids), and poly(amide esters) with R_F side chains as optical alignment layers in liquid crystal displays [179].

4.6. Dyes and optical materials

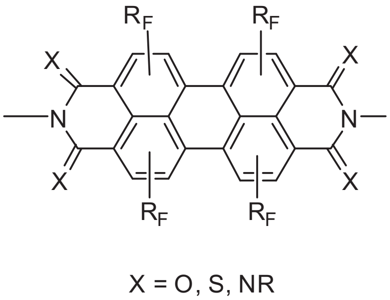
As with electronic materials, the perfluoroalkyl group allows manipulation of the HOMO and/or LUMO energies to provide effective dye properties, most importantly in electrophoretic dyes. An electrophoretic display (ex. electronic paper) forms visible images by rearranging charged pigment particles or electrophoretic dyes using an applied electric field. Research is also benefiting from perfluoroalkyl groups in the design of near-IR dyes. Gu prepared R_F polysubstituted porphyrins as electrophoretic dyes to improve the threshold characteristics, longevity, and image quality of electrophoretic displays [180]. (Scheme 48)

Moonen described R_F substituted phthalocyanines, naphthalocyanines, anthraquinones, perylenes, quinacridones, porphyrins, and naphthalimides as fluorinated dyes for use in electrophoretic



Scheme 48. R_F polysubstituted porphyrins as electrophoretic dyes.

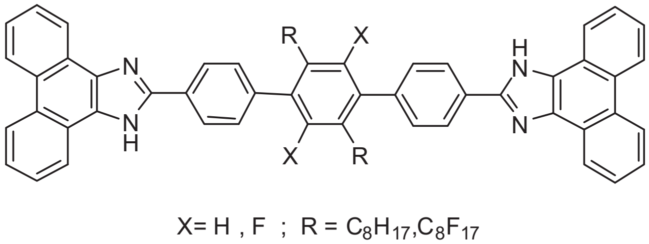
display devices [181]. Yang also prepared fluorinated heterocyclic phthalocyanines, naphthalocyanines, anthraquinones, perylenes, quinacridones, porphyrins, and naphthalimides for use in electrophoretic displays. These dyes exhibited good solubility in halogenated solvents and improved switching performance at low temperatures [182] (Scheme 49).



Scheme 49. Fluorinated dyes for use in electrophoretic display devices.

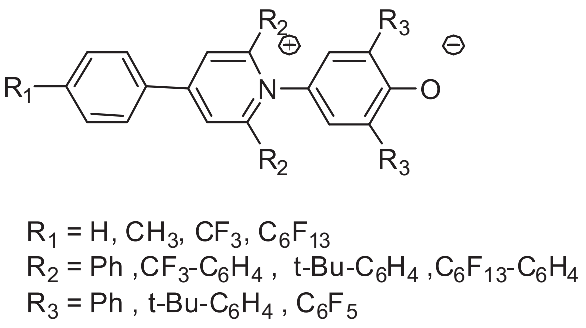
Hasegawa synthesized R_F substituted bis(2-tetrathiafulvalenylethynylphenyl)ethyne dyes which exhibited a transition between an open-chain anti and a helical syn conformation, with such conformational changes lead to unique electrochromic and on-off switching properties in the UV–visible-NIR spectra [183]. Tamura prepared p-phenylene diammonium salts with multiple R_F side chains as near IR-absorbing dyes with good heat resistance and hydrolytic stability [184].

Krebs reported an exceptional red shift in the fluorescence spectra of a bis(phenanthroimidazolyl)-p-terphenyl system when comparing C_8F_{17} side chains with C_8H_{17} substituents. The fluorescence spectra of the terphenyl system with R_F susbtituents also demonstrated a strong solvent effect [185] (Scheme 50).



Scheme 50. Terphenyl system with R_F susbtituents.

Reichardt synthesized pyridinium N-phenolate betaine dyes with R_F substituents to enlarge the supply of highly solvatochromic indicator dyes which were used to extend the E_T (30) scale of solvent polarity which is based on a UV–vis spectroscopically derived empirical scale of solvent polarity [186] (Scheme 51).



Scheme 51. Substituted betaine dyes.

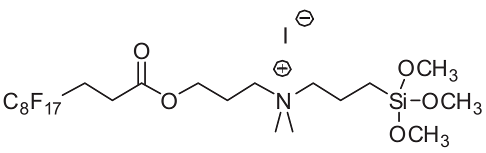
4.7. Battery electrolytes

As the use of secondary (rechargeable) batteries increases in transportation and grid storage, the demands of higher energy capacity and more power output are forcing higher voltage potentials in lithium ion batteries and competing technologies. As the system voltages increase, fluorinated materials become more necessary for electrolytes, additives, binders, and separators due to their oxidative stability. Gao described electrolytes for secondary lithium ion batteries containing 5- and 6-membered lactones or carbonates with R_F substituents. These R_F lactones provided good solubility for the electrolyte salt, effective fire resistance, and improved low temperature performance [187]. Meanwhile, Sato described the effectiveness of ionic liquids of Imidazolium fluoroethanesulfonylamides in secondary batteries, noting especially their good thermal stability and corrosion resistance [188].

4.8. Repellents

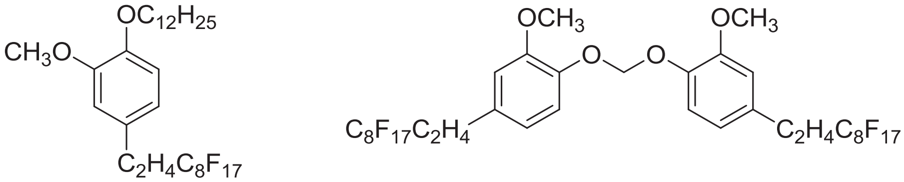
Fluorinated materials have provided a low surface energy coating to a diverse range of substrates for decades, repelling liquids and other contaminants on textiles, paper, leather, plastics, masonry, metal, and many other everyday materials. The fluorinated repellent industry has been transitioning to shorter perfluoroalkyl chains since about 2000 to eliminate the use of materials containing longer chained perfluoroalkyl groups.

Severac described (meth)acrylate copolymers with R_F side chains with a minimal proportion of hydrophilic monomers as an effective oil and water repellent for leather [189]. Guo described R_F (meth)acrylate (co)polymers as surfactants and as water and oil repellent treating reagents for textiles [190]. Yamamoto described a combination of R_F substituted urethanes and R_F containing (meth)acrylate (co)polymers as water and oil repellency and antifouling treatments for textiles, masonry, glass, paper, wood, leather, metal, and plastics [191]. Jiang showed that R_F-containing bisulfite adduct of a polyisocyanates imparted good durable press and water and oil repellent properties to cotton fabrics [192]. Kim prepared water repellent films from 3-(triethoxysilyl)propyl perfluoroalkyl urethanes, which showed good water contact angles and excellent long term stability [193]. Yu prepared a super-hydrophobic complex coating for cotton fabrics based on silica nanoparticles and a perfluorooctyl quaternary ammonium silane coupling agent. The silica nanoparticles in the coating gave a rougher surface and the perfluorooctyl quaternary ammonium silane coupling agent reduced the surface free energy [194] (Scheme 52).



Scheme 52. Perfluorooctyl quaternary ammonium silane.

Sato prepared water repellents for masonry, textiles, and painted surfaces from R_F derivatives of succinates [195]. Gerster modified the surfaces of synthetic polymers, especially nonwoven fabrics, with R_F substituted phenol derivatives to provide repellence, release, resistance, anti-adhesion, and similar properties against proteins and microorganism such as bacteria, fungi, and algae [196] (Scheme 53).

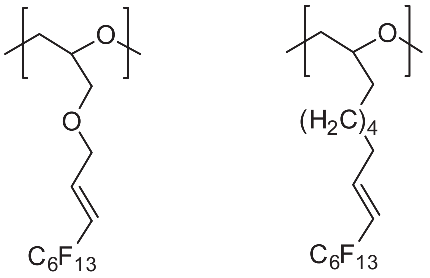


Scheme 53. R_F substituted phenol derivatives.

4.9. Lubricants

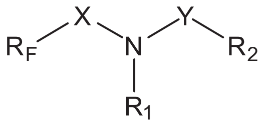
Perfluoropolyether oils and greases are exceptional lubricants in extreme conditions because of their (i) thermal, mechanical, and oxidative stability, (ii) broad operating temperature range, (iii) non-flammability, (iv) corrosion resistance, and (v) lubricity across a wide range of shear and pressure conditions. Lubricants with perfluoroalkyl groups are generally more effective as solid lubricants (i.e. low shear, high pressure conditions), though blends of traditional lubricants and fluorinated materials have demonstrated the lubricity benefits of both materials.

Bazhin prepared polyethers with pendant R_F groups as additives to industrial oil. While these compounds exhibited some modest repellency, the friction coefficients for industrial oil with additives of fluorinated polyethers was one-sixth of the industrial oil only [197] (Scheme 54).



Scheme 54. Polyethers lubricants with pendant R_F groups.

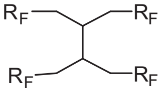
Mitsuhashi showed that R_F substituted amines were effective additives in synthetic lubricating grease for inhibiting the diffusion of the base oil [198] (Scheme 55).



R_F = C_1-C_4 perfluoroalkyl
R_1/R_2 = H or alkyl
X/Y = connecting groups

Scheme 55. Amine lubricants with pendant R_F groups.

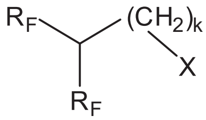
Gambaretto synthesized tetrakis(perfluoroalkyl)alkanes, and found that their high molecular weight, low vapor pressure, low melting point and low surface tension, provided a balance of properties as potential candidates for ski-waxes [199] (Scheme 56).



$R_F = C_6F_{13}$, C_8F_{17}

Scheme 56. Tetrakis(perfluoroalkyl)alkanes as waxes.

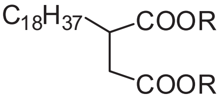
Kobayashi found that R_F branched alkyl compounds are effective lubricants for magnetic recording medium, e.g. magnetic tape. The fluorinated materials form very thin films, have excellent low-temp. performance, and durability [200] (Scheme 57).



R_F = C_2-C_{18} perfluoroalkyl
k = 2-12
X = OH, NH_2, $CONH_2$, OR

Scheme 57. Bis-R_F branched alkyl compounds, lubricants for magnetic recording medium.

Iwano showed that substituted succinate di-R_F esters were durable lubricants with dust resistance for magnetic recording medium, e.g. a helical-scan recording system using a magnetoresistance head [201]. Takahashi [202] and Sekino [203] also found fluorinated materials to be effective lubricants for magnetic recording materials (Scheme 58).



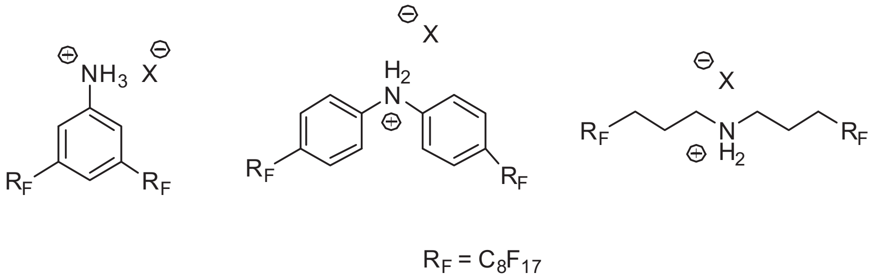
R = alkyl or R_F
alkyl = C_2-C_{10}
$R_F = C_7F_{15}$;C_8F_{17}

Scheme 58. Di-R_F esters as lubricants.

4.10. Catalysts

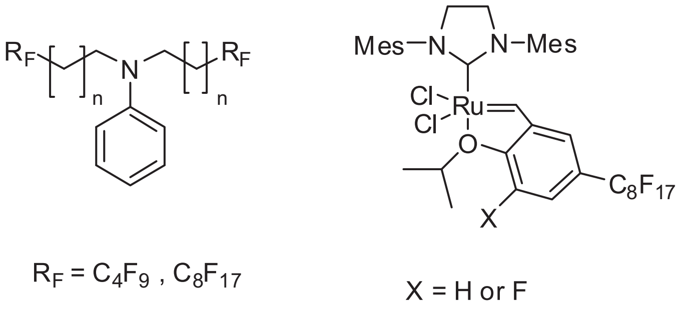
Perfluoroalkyl groups potentially provide many valuable benefits to catalysts. First, since fluorinated compounds can often be easily removed from an organic mixture by various methods (liquid–liquid extraction, solid phase extraction, precipitation), they can often be recovered and recycled with little to no loss of material or activity. Second, the electronegativity of the perfluoroalkyl group allows for polarization of a catalyst system to potentially enhance the catalysts effectiveness thus increasing reaction rates or furthering conversion rates. Third, perfluoroalkyl groups modify the solubility of a catalyst to provide homogeneous catalysis in fluorinated or organic solvents, with a particularly dramatic effect of temperature on solubility in common organic solvents. Many researchers have successfully exploited these benefits of the perfluoroalkyl group in their catalyst design.

Mercs reported the direct esterification of equimolar amounts of carboxylic acids and aliphatic alcohols under mild conditions in the presence of fluorinated ammonium triflates. High yield reactions were reported for either solid/liquid or fluorous biphasic conditions without the use of dehydrating agents and/or azeotropic removal of water for primary and secondary alcohols [50] (Scheme 59)



Scheme 59. Fluorinated ammonium triflate direct esterification catalysts.

Legros prepared two bis-R_F-4-(dimethylamino)pyridines (F-DMAP) and showed that their potential as catalysts in the acylation reaction of alcohols with anhydrides was similar to DMAP, though a method for conveniently recycling F-DMAP was not found. These acylation reactions catalyzed by F-DMAP typically had conversions of >98% [204] (Scheme 60).

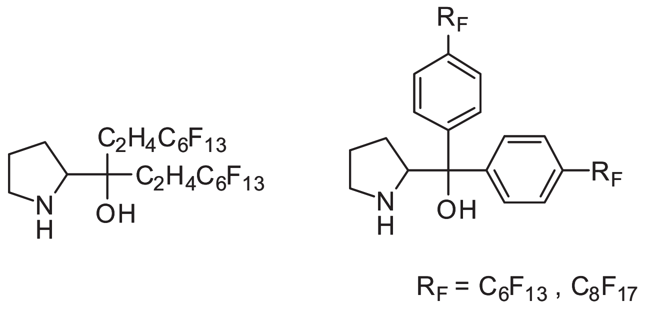


Scheme 60. R_F substituted catalysts for acylation and olefin metathesis.

Matsugi prepared and evaluated a fluorinated, recyclable, Grubbs–Hoveyda second-generation catalyst for olefin metathesis, which exhibited higher catalytic activity than the non-fluorinated analog. The fluorinated catalyst gave nearly quantitative olefin conversion for cyclization of three di-olefins and >95% catalyst recovery after 5 cycles in common organic solvents [205].

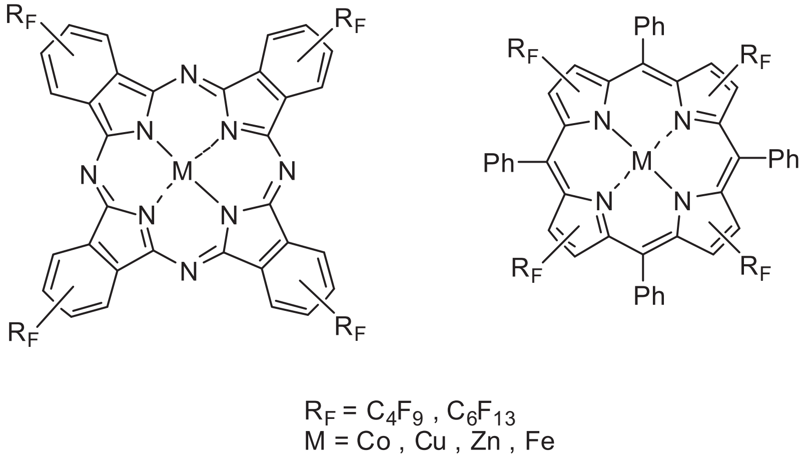
In the pursuit of green and sustainable chemistry, Qiu showed that perfluoroalkyl metallophthalocyanines can be used for the fluorous biphasic oxidation of ethyl benzene and benzyl alcohol with molecular oxygen with high selectivity and efficient catalyst recovery [206] (Scheme 61).

Cui reported an enantioselective asymmetric epoxidation for α,β-enones using easily accessible and recoverable fluorinated L-prolinols as catalysts with tert-butyl hydrogen peroxide as an oxidant with moderate yields and good enantiomeric excess [207] (Scheme 62).

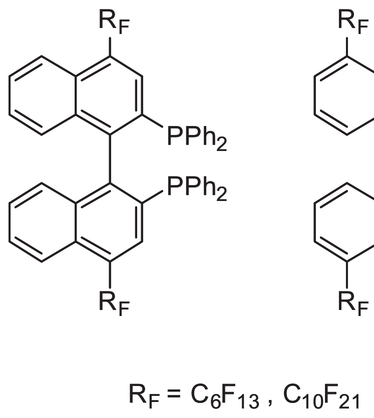


Scheme 62. R_F L-prolinols as enantioselective asymmetric epoxidation catalysts.

Liu reported fluorous biphasic catalytic oxidation of alkenes (to epoxides) and aldehydes (to carboxylic acids) with ambient air pressure in the presence of poly-perfluoroalkyl tetraphenyl porphyrin cobalt catalysts, with yields of 65–95% and excellent catalyst recovery [208]. Crich used perfluorooctyl seleninic acid to catalyze the allylic oxidation of alkenes to enones in moderate to good yield (41–65%) with excellent catalyst recovery by fluorous extraction (88–92%) [209]. Berthod used four chiral bis-perfluoralkyl BINAP ligands in the homogeneous asymmetric hydrogenation of ethyl acetoacetate in ethanol and in the asymmetric hydrogenation of methyl-2-acetamidoacrylate in supercritical carbon dioxide. Excellent conversion (essentially 100%) and



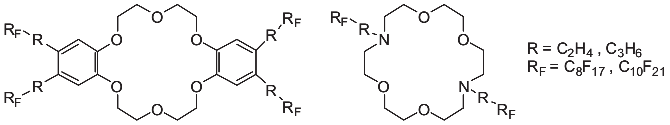
Scheme 61. R_F substituted porphyrins for "green" oxidation.



Scheme 63. bis-R_F BINAP ligands as asymmetric hydrogenation catalysts.

stereoselectivity (60–99% ee) were obtained in each reduction [210] (Scheme 63).

Pozzi demonstrated the fluorinated crown ethers are good phase-transfer catalysts, allowing solubilization of potassium salts in a non-coordinating, apolar perfluorocarbon solvent, which leads to efficient nucleophilic substitution and oxidation reactions. Catalyst recycle was accomplished by simply reusing the solution of fluorinated crown ether in perfluorocarbon solvent for subsequent reactions [211] (Scheme 64).



Scheme 64. Poly-R_F substituted crown ether catalysts.

Stuart synthesized a series of diaza 18-crown-6 ethers, and evaluated their properties and performance as phase transfer catalysts (PTC). Under solid–liquid phase-transfer conditions, the fluorinated macrocycles give similar, if not better, phase-transfer catalytic activity compared to the non-fluorinated analogous macrocycles in aliphatic and aromatic nucleophilic substitution reactions, with good to excellent yields and excellent catalyst recovery [212] (Scheme 64).

5. Summary and conclusions

The scientific literature of the past decade shows vibrant research that continues to expand and explore the synthetic utility of R_FI as a versatile synthon to accomplish facile incorporation of perfluoroalkyl groups into a host of substances with ever expanding potential commercial and scientific utility linked to the unique properties the perfluoroalkyl group imparts. New and expanded synthetic methodolgies for R_FI addition to carbon–carbon double and triple bonds, including allenes, porphyrins, and fullerines not previously explored have been reported as well as R_FI coupling to aryl halides and R_FI anion addition to ketones and aldehydes. Interesting new preparations of organometallics and substitution with sulfur nucleophiles also abound. Moreover, the potential uses of substances and materials into which perfluoroalkyl groups have been incorporated continues to grow as researchers seek to understand the attributes that this unique functionality can bring to a diverse range of applications from surfactants to pesticides to batteries to lubricants. Surely we will continue to read about new research utilizing R_FI in the future.

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