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Bridging organic, molecular, macromolecular, supramolecular and biological sciences to create functions *via* fluorine chemistry and fluorinated reagents

Perspective

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After a brief introduction highlighting the challenges of fluorine chemistry and the latest developments in the field, this Perspective will discuss how a combination of fluorine and fluorous chemistry together with fluorinated reagents helped to bridge between organic, molecular, macromolecular, supramolecular and biological sciences to create functions in the laboratory of the corresponding author. The reactivity of fluoride as a leaving group is best illustrated by S_NAr reactions when it helped to demonstrate single electron transfer-mediated side reactions and through molecular design replaced activated aryl fluorides with aryl chlorides in the synthesis of poly(etherketone)s. Subsequently it was demonstrated how Ni(II) sigma complexes provided an orthogonal approach to the Suzuki-type cross-coupling of arylfluorides, other halides and all aryl C–O based electrophiles. Fluorinated reagents facilitated cylotrimetrization vs cyclotetramerization of bis(methoxy)benzyl chloride and alcohol and the synthesis of the simplest molecular liquid crystals. Triflic acid, methyl triflate facilitated the most tolerant living polymerizations including of cyclic siloxanes, functional vinyl ethers and oxazolines to generate self-organizable dendronized polymers while fluorine, trifluoromethyl and trifluoromethoxy groups facilitated disassembly and reassembly of liquid crystal polyethers and poly(*p*-phenylenes). Fluorinated stereocenters accessed the first heterochiral

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recognition in side-chain liquid crystal poly(vinyl ether)s and their model compounds. Alkali metal triflates mediated self-organization of supramolecular nonfluorinated and fluorinated self-assembling minidendrons, dendrons, dendrimers and self-organizable dendronized polymers. The role of fluorinated alkyl groups and of alkali metal triflates in the self-assembly, disassembly and isomorphic replacement analysis, of supramolecular helical columns, of the assembly of helical cogwheel coat and of spherical supramolecular dendrimers forming Frank-Kasper periodic and quasiperiodic arrays was highlighted. A brief discussion of fluorinated amino acids, peptides and peptoids and their potential role in the self-assembly and functions resulted from dendritic dipeptides followed by a discussion of semifluorinated amphiphilic Janus dendrimers as models of biological membranes, including for cell fusion and fission, concludes this Perspective.

1 Introduction

Fluorine, the most electronegative element and the smallest after hydrogen is the 13th most abundant from the crust of Earth. It exists mostly as fluorite also known as fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$). HF is the only hydrogen halide that is liquid (bp 19.5 °C), non-ionizable and the weakest (HF pKa 3.17; HCl pKa –6.3; HBr pKa –8.7; HI pKa –9.3) of all hydrohalic acids. The combination of highest electronegativity and small size makes C–F the strongest bond of all organic chemical bonds. The fluoride anion is the most basic halide and the least efficient leaving group in S_N1 and S_N2 reactions. The strength of C–F bond transforms both aliphatic and aromatic perfluorinated molecules into thermally stable compounds [1–11]. Perfluorinated linear paraffins adopt a helical conformation that is induced by the electrostatic repulsion of fluorine atoms in the relative 1,3-positions making them lipophilic but insoluble in their hydrogenated homologues at low temperature. This particularity led to the development of the field of fluorous chemistry [12]. Perfluorinated aromatic hydrocarbons are electron acceptors. Fluorinated carboxylic and sulfonic acids and alcohols have lower pKa values than the corresponding hydrogenated homologues. The pKa of CF_3SO_3H is –15 which makes it the classic superacid while that of CH_3SO_3H is –7. The strongly basic fluoride is an efficient hydrogen bond acceptor and therefore, due to its strong solvation it is a very poor nucleophile. HF was obtained in 1764 by reacting CaF_2 with H_2SO_4 under heat. However, since HF does not conduct electricity its electrolysis to F_2 was successful only in 1886. This experiment led in 1906 to the Nobel Prize in Chemistry to Henry Moissan. The unusual high reactivity of HF and F_2 limited access to the synthesis of organofluorine compounds and polymers to industrial companies only, particularly DuPont. While we never dared to work with fluorine or HF in our laboratory, we were fascinated by the fact that fluorine self-organizes at very low temperature the $Pm\bar{3}n$ or A15 Frank-Kasper phase [13,14] that we discovered in supramolecular dendrimers in 1997 [15] and elaborated its fundamental principles after the discovery. The refrigerant Freon-12 (CCl_2F_2) and the accidental discovery of Teflon by Roy J. Plunkett employed mostly in non-stick cookware, the development of amorphous Teflon, Teflon AF, Cytop [16] some semifluorinated polymers such us polyvinylidene fluoride, polyvinyl fluoride, Nafion and surfactants, dental care products, pharmaceuticals and agrochemicals are only few of the fluorinated and semifluorinated compounds that increased the standard of our life during the 20th century. The early part of 21th century witnessed a tremendous development of organofluorine chemistry in academic laboratories [17–33] bypassing even the need to employ HF in the synthesis of fluorinated organic compounds. This development changed fluorine chemistry from an industrially limited method to an academic accessible methodology. Our laboratory never had been involved in a research program devoted to fluorine chemistry. One reason was that during early 1980th to early 2010th I (VP) was a consultant to Central Research from the Experimental Station of DuPont including the organofluorine research group and therefore, in this way potential conflicts of interest with DuPont were avoided. However, due to its numerous functions fluorinated reagents and compounds have been employed for many years in our laboratory to solve some fundamental problems of organic, molecular, macromolecular, supramolecular and biological sciences, unrelated to DuPont research and technological interests. Consequently, VP was repeatedly invited to present plenary and invited lectures at international conferences on Fluorine and Fluorous Chemistry, without ever having the time to contribute the content of his lecture to the particular Symposium publications. Therefore, the decision was made to dedicate this Invited Perspective to provide a survey of our laboratory contributions to the creation of functions via fluorinated structures in all topics of research mentioned above. A brief introduction to the concept discussed before employing fluorine and fluorination was made to justify each topic of research. Future perspectives and new experiments will be also briefly mentioned.

2 Some contributions to organofluorine chemistry

2.1 What transforms fluoride from the least efficient leaving group in S_N1 and S_N2 to the most efficient in S_NAr reactions?

Due to the smallest size and highest electronegativity of fluorine, fluoride is the least efficient leaving group in stepwise S_N1 and concerted S_N2 reactions. In both cases the breaking of the C-X bond occurs in the rate-determining step, although usually S_N2 is usually a concerted one step reaction. However, the same fluoride becomes the best leaving group in S_NAr reactions. What makes fluoride the best leaving group in S_NAr reactions and why the other halides, that are the most efficient in S_N1 and S_N2 reactions, are the least efficient in S_NAr reactions? S_NAr is an addition-elimination reaction (Fig. 1) although recently concerted examples were reported [25]. In the first addition

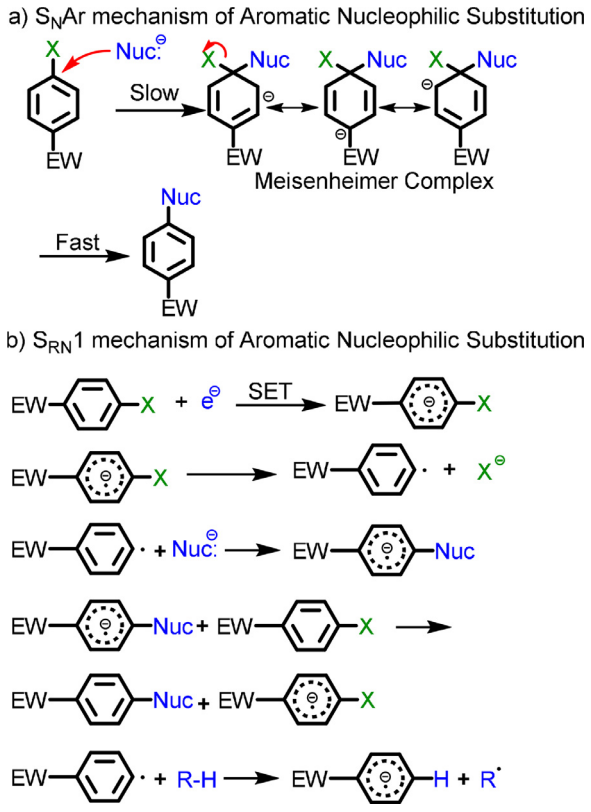


Fig. 1

(a) Aromatic nucleophilic substitution mechanism (S_NAr); (b) radical-nucleophilic aromatic substitution ($S_{RN}1$) and the reductive elimination mechanism. The Figure was redrawn from references 35–38.

step of this aromatic nucleophilic substitution the nucleophile attacks the *ipso* position of the leaving group and transforms the aromatic compound into a non-aromatic intermediate named the Meisenheimer complex. The first step is the rate-limiting step of S_NAr. During the second step the Meisenheimer complex becomes aromatic and the leaving group is eliminated (Fig. 1). Therefore, the nature of the halogen forming the C–X bond is not so important in the second step as it is in the first step. The addition of the nucleophile is the slow step of this reaction since it breaks aromaticity while the elimination of the leaving group is the fast step during which the aromaticity is regained in an exothermic reaction. The Meisenheimer complex is stabilized by the presence of strong electron-withdrawing groups in the *ortho*- and *para*-positions of the leaving group. Therefore, the rate determining step of S_NAr is increased by the presence of strong electron-withdrawing groups including by the electronegativity of the leaving group. Two commercial polymers were produced by this aromatic nucleophilic substitution. The amorphous aromatic poly(ether sulfone) (PES) was produced in the 1980th by Union Carbide from the reaction of 4,4′-dichlorodiphenylsulfone with bisphenol-A while the crystalline aromatic poly(ether ketone) (PEK) was commercialized by Hoechst from the reaction of 4,4′-difluorobenzophenone (DFB) with hydroquinone. The presence of fluorine in the structure of DFB made the price of PEK almost prohibitive although its physical properties were extraordinary. I (VP) was a consultant for Hoechst during that time. During one of my visits in the late 1980 the vice-president of research of Hoechst, Professor Harald Cherdron, who also co-authored one of the best textbooks of Practical Macromolecular Organic Chemistry [34] asked me (VP) if I could think of a way to replace fluorine with the less expensive chlorine during the synthesis of PEK. My answer was, yes I believe I could, but it would take some mechanistic work to understand the difference between the reaction of DFB and and of 4,4′-dichlorobenzophenone (DCB) with the same nucleophiles. My graduate student Robert S. Clough was immediately assigned to this project for his PhD thesis. A first communication published in 1991 [35] demonstrated that PEK synthesized from DCB contained both chlorobenzophenone and benzophenone chain ends. A single electron transfer (SET) mechanism was suggested by us to complete with the S_NAr mechanism. SET from the nucleophile acting as an electron-donor to the halobenzophenone-end group would provide a radical anion of the aryl halide. When the halide was chlorine it could leave as a good leaving group producing an aryl radical that ultimately will become a benzophenone chain end (Fig. 1). This reductive elimination reaction did not occur with DFB since the fluoride was an inefficient leaving group under these conditions. This reaction did not occur during the synthesis of PES from 4,4′-dichlorodiphenylsulfone and bisphenol-A. Two reasons were most probably responsible for this difference. The sulfone was a better electron-withdrawing group than the keto group and therefore, could stabilize the Maisenheimer complex better than the keto group. The phenolate of bisphenol A was less electron donating that the phenolate of completely deprotonated hydroquinone. Replacing 4,4′-dichlorodiphenyl sulfone with 4,4′-diiododiphenyl sulfone in the synthesis of PES while maintaining bisphenol A did not generate the reductive dehalogenation while replacing bisphenol A with hydroquinone induced the reductive elimination [36,37]. Bis(aryl chloride)s containing several keto groups and bisphenols containing ether bonds were immediately designed, synthesized and employed in the synthesis of PEK with high molar mass without undergoing any reductive elimination. Even DCB could be used to make very high molar mass PEK in the presence of less electron-donor bisphenols than hydroquinone [38]. These results were obtained during the Christmas Eve of 1993. I called my contact from Hoechst, Dr. Arnold Schneller, at home to announce our great success and both our success and his reply were very disappointing to all of us. Hoechst decided to shut down the production of PEK one day earlier. This process was not a reversible process, but it provided the best demonstration of the outcome of not solving scientific problems in time. Solving scientific problems is also a race as it was in the classic case of solving the structure of the double helix of DNA [39,40].

2.2 Orthogonal and quantitative Ni-catalyzed homo- and cross-coupling of aryl halides, fluorinated sulfonates and fluorides including with indefinitely air-stable sigma-Ni^{II} precatalysts

In 1992 our laboratory started to develop synthetic methodologies based on Ni-catalyzed homocoupling of aryltriflates and arylenebistriflates derived from hydroquinones and from other derivatives for the synthesis of complex functional biphenyls and soluble poly(paraphenylene)s by exploring the

constitutional isomerism as a tool to decrease crystallinity [41–43]. Several years later, in 1995, the aryl mesylates evolved into 4-fluorobenzenesulfonates [44], tosylates and mesylates [45]. During the same year aryl triflates, fluorosulfonates, tosylates, phenyl sulfonates and even mesylates were shown by our laboratory to undergo Ni-catalyzed Suzuki-Miyaura-like cross-coupling with arylboronic acids [46]. At that time Pd-catalysis could not yet mediate cross-couplings of aryl sulfonates including mesylates. Simple methodologies for the synthesis of complex functional biphenyls including fluorinated biphenyl resulted from regiospecific homocoupling of aryl mesylates [47]. The generality of Ni-catalyzed cross-coupling of aryl mesylates was demonstrated with carbanion synthons like organotin (Stille-type cross-coupling) -magnesium and -zinc. Very efficient Ni-catalyzed cyanation of aryl mesylates were all demonstrated in 1995 [48]. In the next step more active Ni-catalysts including based on the mixed-ligand effect were elaborated [49]. Borylation of functional aryl iodides, bromides, chlorides and tosylates including with neopentylborane generated in-situ was subsequently elaborated [50–55]. Cross-coupling of aryl sulfamates [56] followed. The first activated sigma Ni(II) precatalyst was elaboratyed in 2012 [57] simultaneous with more elaborated cross-coupling rections [58,59]. The literature on this topic was reviewed in 2011 [60]. In 2014 a library of air-stable sigma complexes of Ni(II) precatalysts was developed by our laboratory [61]. These catalysts facilitated the cross-coupling of aryl fluorides (Fig. 2) with aryl boronic esters and the orthogonal cross-coupling of aryl fluorides with aryl iodides, bromides, chlorides and mesylates [62]. Finally, our air-stable sigma Ni(II) precatalyst was shown to be the only catalyst providing quantitative cross-coupling of all six C–O based electrophiles, aryl mesylates, sulfamates, carboxylic esters, carbonates, carbamates and methyl ethers with aryl boronic esters demonstrating the highest efficacy and generality than of any other previously reported catalyst [63]. This generality of Ni-catalysis and of its air-stable catalyst have been demonstrated in the synthesis of libraries of very complex and multifunctional building blocks to be discussed later.

2.3 Selective electrophilic cyclotrimerization and cyclotetramerization of 3,4-bis(methyloxy)benzyl derivatives with fluorinating acids and salts

The products distribution during the electrophilic cyclooligomerizations of 3,4-bis(methyloxy)benzyl chloride, 3,4-bis(methoxy)benzyl alcohol, N-veratrylethanilamine-N-tosylate and 1,2-bis(methoxy)benzene with formaldehyde and with paraformaldehyde using a large diversity of conditions was investigated in order to discover reaction conditions for the large-scale synthesis of the cyclotriveratrylene (CTV) and cyclotetraveratrylene (CTTV) [64]. CTV and CTTV are precursors for the synthesis of building blocks that self-organize pyramidal and columnar hexagonal thermotropic liquid crystals. CTV, the kinetic cyclization product, was discovered to be formed almost exclusively when 3,4-bis(methoxy)benzyl chloride was reacted with stoichiometric amount of $AgBF_4$ in methylene chloride (Fig. 3). CTV also forms in large conversion when 3,4-bis(methoxy)benzyl alcohol was reacted with CF_3SO_3H in bulk. The thermodynamic product CTTV forms under high conversion by the electrophilic oligomerization of 3,4-bis(methyloxy)benzyl alcohol with excess of CF_3COOH in methylene chloride (Fig. 3). Nonnucleophilic counter-anions based on the electronegative fluorine were employed in all these experiments. These methodologies were employed to produce in a very simple way libraries of CTTV-based columnar liquid crystals [65] and libraries of self-organizable dendronized CTTV exhibiting a diversity of columnar and Frank-Kasper assemblies [66]. The synthesis of CTTV by this methodology was expanded to prepare the fist hyperbranched polymer containing CTTV columnar assemblies [67].

2.4 A systematic approach to the synthesis of the simplest class of thermotropic liquid crystals containing a single benzene unit by fluorination and of other liquid crystals and derived functions

Rod-like thermotropic liquid crystals require a minimum of two aromatic units incorporated either in a biphenyl or phenylbenzoate fragment containing an alkyl group that determines their melting temperature and a functional group preferentially –CN that provides a dipole moment [68]. When the alkyl group was replaced with a semifluorinated alkyl group attached to benzene it was demonstrated that the largest diversity of functional groups $–NO_2$, –CN, $–CO_2CH_3$, $–CH_2OH$, $–CO_2H$, and $–COCH_3$ could be attached in the *para*-position of the semifluorinated alkyl group from benzene to generate the simplest class of liquid crystal displaying S_A and S_C phases. The thermal stability of the LC phase increases with the increase of the length of the perfluorinated fragment attached to the alkoxy group. A ratio of the perhydrogenated $[(CH_2)_m]$/perfluorinated $[F(CF_2)_n]$ segment lengths of m/n smaller than 1 favors the formation of the liquid crystalline phases when $n + m = 10$ and 12. Additional substitution in the 2-position of the benzene ring with a methyl group decreases the thermal stability of the liquid crystal phase [69]. The structure of these liquid crystal phases was determined by X-ray diffraction [70]. We expect that using fluorine as a substituent in the 2-position may provide a new class of liquid crystals with very broad thermal stability. This statement is supported by the incorporation of fluorine in two new classes of substituted diphenylacetylene and phenylethyny(diphenylacetylene) liquid crystals [71–75].

Cyclotrimerization of some of these substituted acetylenes form the simplest disc-like molecules that self-assemble into columnar liquid crystals [76]. Some unprecedented functions were designed from the focal conic texture of semifluorinated liquid crystal S_A structures [77–79]. They include toroidal microchannels and molecularly designed superhydrophobic surfaces. Recently semifluorinated discotic triphenylene based liquid crystals were developed [80]. They display columnar hexagonal liquid crystal phases in the range of short alkyl groups that up to very recently, with the exception of one supramolecular example [81] formed only helical columnar crystals [82–84]. This is a very important advance in the design of columnar liquid crystals.

2.5 Helical conformation of linear perfluorinated alkanes and of Teflon

The small increase in size from hydrogen to fluorine is sufficient to transform the zig-zac conformation of polyethylene into a helical

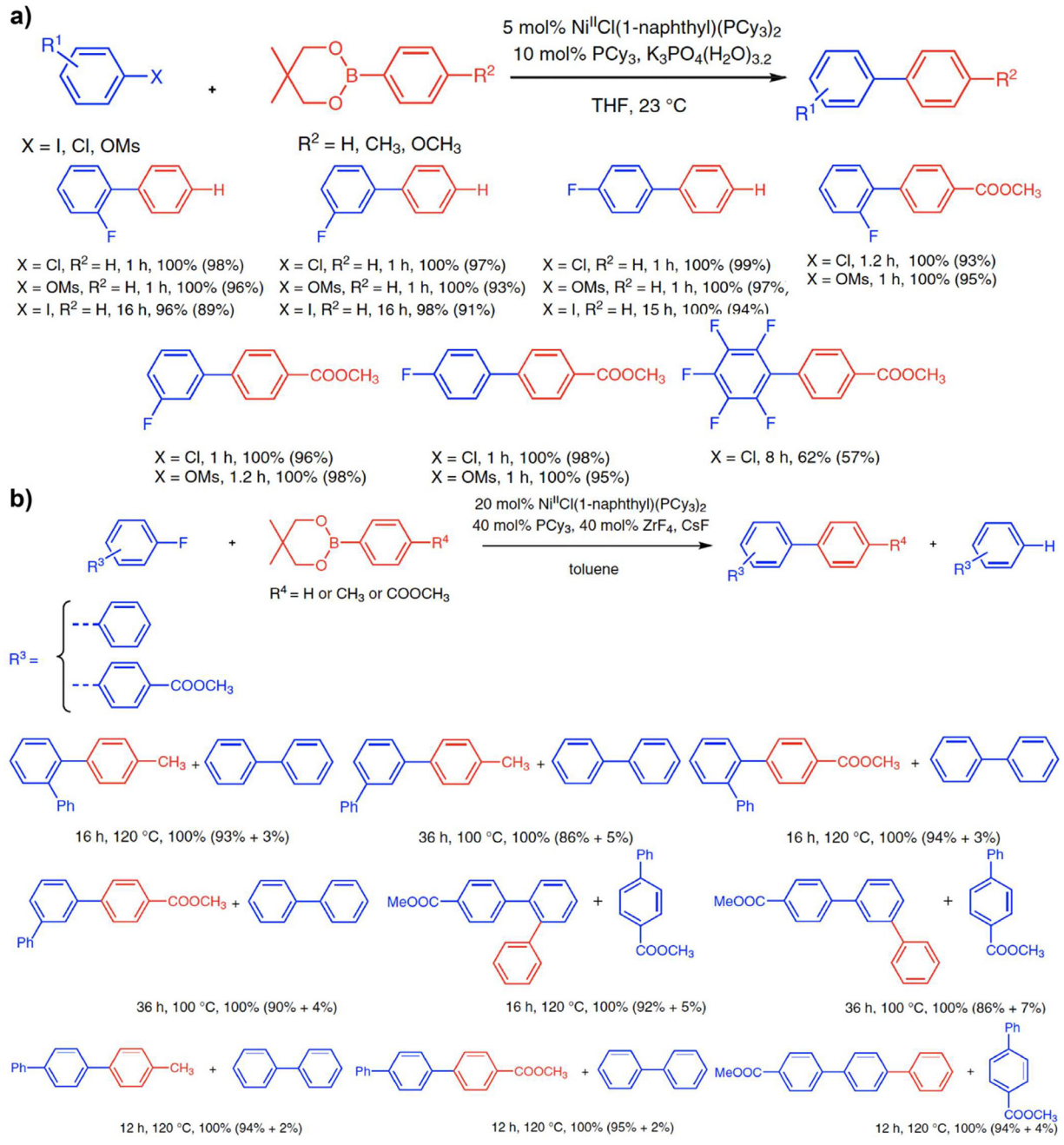


Fig. 2

(a) Cross-coupling of *ortho, meta*, and *para* electron-deficient aryl halides and aryl mesylates with electron-rich and neutral aryl neopentylglycolboronates catalyzed by NiIICl(1-naphthyl)(PCy$_3$)$_2$/PCy$_3$ in anhydrous THF at 23 °C. (b) Cross-coupling of aryl fluorides with aryl neopentylglycolboronates catalyzed by NiIICl(1-naphthyl)(PCy$_3$)$_2$/PCy$_3$/ZrF$_4$ in toluene at 100 and 120 °C. Adapted with permission [62]. Copyright 2016, Georg Thieme Verlag.

conformation for poly(tetrafluoroethylene) (Teflon) [85–87]. ^{19}F-NMR [88] and vibrational circular dichroism spectroscopies [89] demonstrated that the helicity from the crystal state is persistent in solution even at very short linear perfluoroalkanes containing 6 to 8 carbons. Attachment of a stereogenic center at the end of the perfluoroalkane select the handedness of the helix (Fig. 4). Therefore, perfluoroalkanes are the simplest and the most basic chiral helix that can be exploited in many fundamental and practical applications. This helicity is induced by the electrostatic repulsions of the fluorine atoms from the 1,3-positions of the linear structure.

3 Fluorine in polymer synthesis

3.1 Synthesis of poly(methylsiloxane)s with different molecular weight and of poly(methysiloxane-co-dimethylsiloxane)s with different molecular weight and composition by cationic ring opening polymerization initiated with CF_3SO_3H

Poly(methylsiloxane)s with different molecular weight and poly(methylsiloxane-co-dimethylsiloxane)s with different molecular weight and composition were synthesized by cationic ring opening polymerization of 1,3,5,7-tetramethylcyclotetrasiloxane (D4′) and by copolymerization of

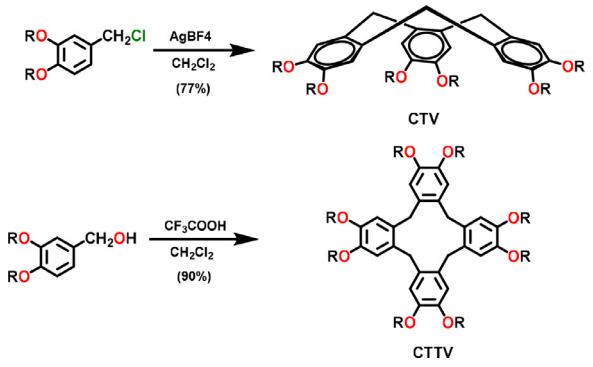


Fig. 3

Synthesis of CTTV and CTV by employing fluorinated reagents.

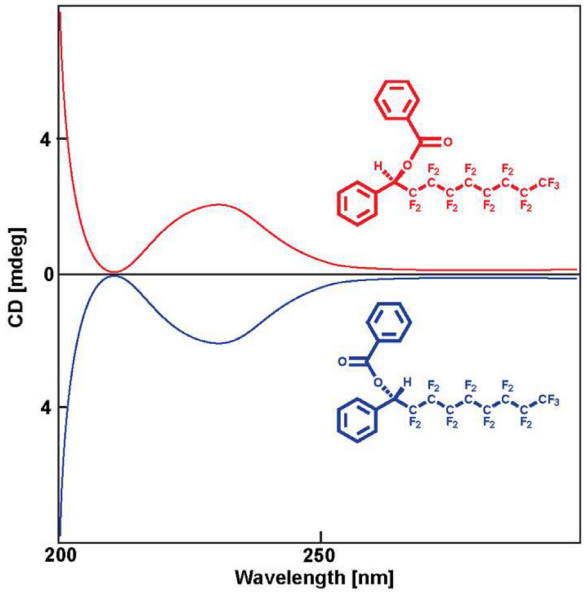


Fig. 4

Circular dichroism (CD) spectra of the enantiomeric perfluorinated compounds. Adapted and modified from reference 89.

D' with 1,3,5,7-octamethylcyclotetrasiloxane (D4) intitiated with CF_3SO_3H. The molecular weight of the polymers was controlled in both cases by using the proper amount of hexamethyldisiloxane (MM) as chain terminator. Polymerization were carried out in bulk at room temperature for 24 h in order to reach equilibrium and therefore, to generate a random distribution of the two monomer repeat units in the resulting copolymer (Fig. 5) [90]. Details of the mechanism of polymerization and copolymerization as well as of the equilibrium random composition were discussed in the original publication [90]. Again, the nonnucleophilic counteranion responsible for these polymerizations was generated with the help of fluorine. These homopolymers and copolymers were functionalized by hydrosilylation with mesogenic groups containing terminal olefins. They generated well defined side-chain liquid crystalline polymers employed in fundamental studied involving molecular engineering of phase transition and the design of biphasic highly decoupled side-chain liquid crystal polymers [90–105]. Alternatively, they were functionalized with self-assembling dendrons containing terminal olefins to produce self-organizable dendronized polymers [106–117].

3.2 Synthesis of side-chain liquid crystals and other functional polymers by living group transfer polymerization catalyzed by hydrofluoride, HF_2^-

Living group transfer polymerization of acrylates was discovered at DuPont Experimental Station by Owen Webster [118–120]. Our laboratory employed it for the living polymerization of a diversity of liquid crystalline monomers and of bifunctional monomers to elucidate fundamental concepts in the field of side-chain liquid crystal polymers and also to create reactive polymers [121,122]. GTP remains one of the most efficient living polymerizations that produces extremely well-defined polymers from functional monomers while tolerating a large diversity of functional groups.

3.3 Living polymerization of substituted polyphenylacetylenes mediated by the ortho-substituent effect

Cis-stereoisomers of polyphenylacetylene (PPA) exhibit a helical conformation that impacted dramatically the fundamental and applied fields of helical polymers [123–131]. The simplest way to induce the living polymerization of substituted phenyl acetylene is by placing substituents in the *ortho*-position of the triple bond from the monomer (Fig. 6) [132]. This methodology was not yet investigated in details and we consider that fluorinated substituents like CF_3, OCF_3, SCF_3 and even larger must be studied in view of the *ortho*-substituent effect to produce both living polymerization regardless of the polymerization method and also affect chain conformation and conjugation [132,133].

3.4 Living cationic polymerization of vinyl ethers containing functional mesogenic groups and self-assembling dendrons initiated with $CF_3SO_3H/(CH_3)_2S$

Webster group from Experimental Station at DuPont elaborated the living cationic polymerization of isobutyl vinyl ether initiated by CF_3SO_3H in the presence of $(CH_3)_2S$ and other dialkyl sulfides at -40 to -15 °C [134] (Fig. 7). Triflic acid adds to the vinyl ether and the resulting carbocation enters immediately into an equilibrium with the sulfide that is more nucleophilic that the triflate counteranion forming the unreactive sulfonium. The equilibrium between sulfonium and carbocationic species is shifted towards sulfonium and thus provides a very small concentration of carbocationic propagating species. This process reduces the concentration of chain transfer reactions yielding a polymer with well-defined molecular weight that is determined by the ratio between vinyl ether and triflic acid initiator. This methodology provides polymers with very narrow polydispersity and the fluorinated nonnucleophilic counteranion is responsible for this process. I (VP) was involved as a consultat in the development of this methodology. In 1986 we discovered side-chain liquid crystal poly(vinyl ether)s [135]. In 1991 we demonstrated that liquid crystal vinyl ethers that contain additional nucleophilic sites in addition to the $(CH_3)_2S$ nucleophile and many functional groups including crown-ethers and semifluorinated spacers undergo an even more efficient living cationic polymerization than isobutyl vinyl ether at 0 °C rather than at -40 to -15 °C as reported by DuPont laboratory [37,136–165]. When onium salts were

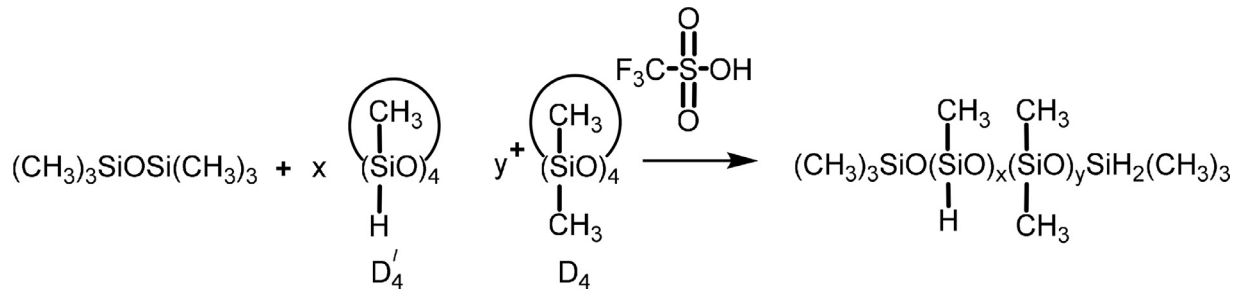


Fig. 5

Synthesis of poly(methylsiloxane-co-dimethylsiloxane)s. Adapted and modified from reference 90.

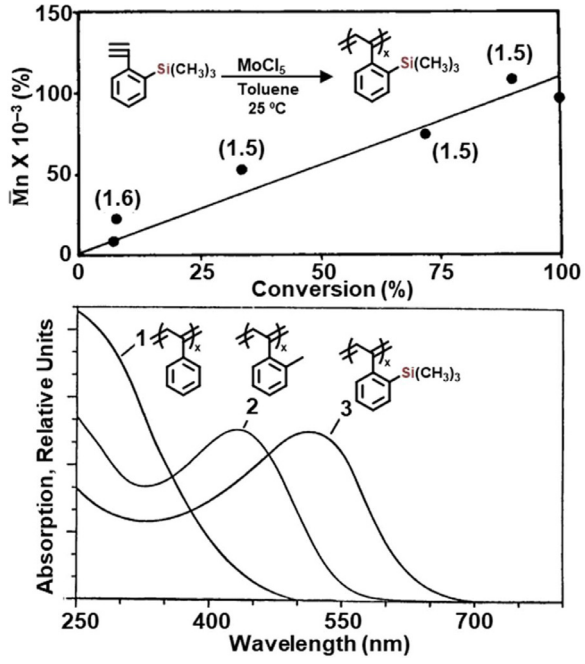


Fig. 6

The dependence of number-average molecular weight versus conversion for the $MoCl_5$ initiated polymerization of *ortho*-trimethylsilylphenylacetylene (top). Data between parentheses represent M_w/M_n. Ultraviolet spectra (solution in CCl_4) for the purified polyphenylacetylene, poly(*ortho*-methylphenylacetylene, and poly(*ortho*-trimethylsilylphenylacetylene)prepared in toluene (bottom). This figure was adapted and modified from reference 132.

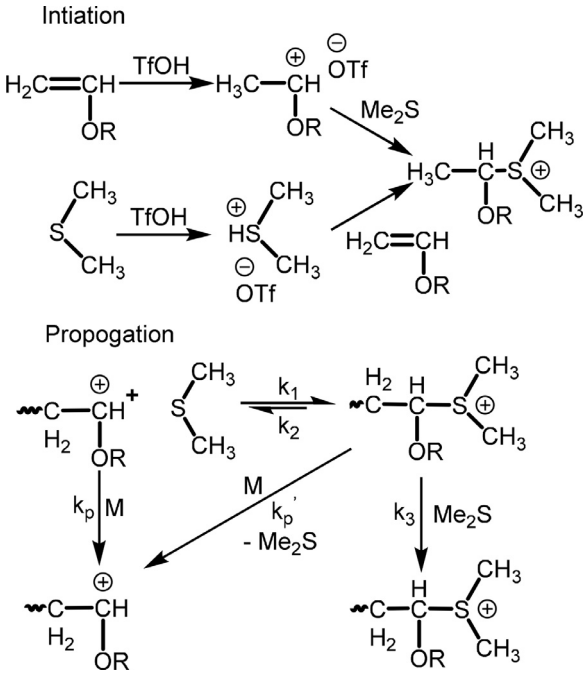


Fig. 7

Mechanism of living cationic polymerization of isobutyl vinyl ether. This figure was redrawn from reference 134.

used as precursors of the cationic polymerization of vinyl ethers polymers with broader polydispersities were obtained both under thermal and UV mediated conditions [166,167]. Together with theoretical thermodynamic schemes [168] this work allowed to elucidate the most fundamental principles of side-chain liquid crystal polymers [169,170]. No better living polymerization method was developed in the meantime. In parallel with these experiments, the living polymerization of vinyl ethers containing self-assembling dendrons was elaborated by the same catalytic system to provide extremely well defined self-organizable dendronized polymers [171,172]. Living cationic polymerization of vinyl ethers containing perfluorinated alkyl groups was also accomplished [173]. Amorphous, crystalline and liquid crystalline poly(vinyl ether)s were accomplished by this methodology.

3.5 Chiral molecular recognition including between fluorinated enantiomers and diastereomers in chiral side-chain liquid crystal poly(vinyl ether)s synthesized by living cationic polymerization initiated with $CF_3SO_3H/(CH_3)_2S$

This series of experiments could not have been performed before the living cationic polymerization of mesogenic vinyl ethers initiated with $CF_3SO_3H/(CH_3)_2S$ discussed in the previous subchapter was discovered. This research started with the synthesis and living polymerization if vinyl ethers containing chiral mesogenic units that were of great interest for the design of chiral S_C^* phases. Methodologies for the synthesis of enantiomers and diastereomers containing a stereogenic center with functional groups including fluorine were elaborated [148,153,165,174–179]. Reactive liquid crystalline polymers that can be crosslinked after alignment [180] and monolayers of these polymers on the surface of water were also investigated [181]. These first series of experiments provided the methodologies required to investigate for the first time heterochiral interactions between molecular, macromolecular and copolymer pairs containig R and

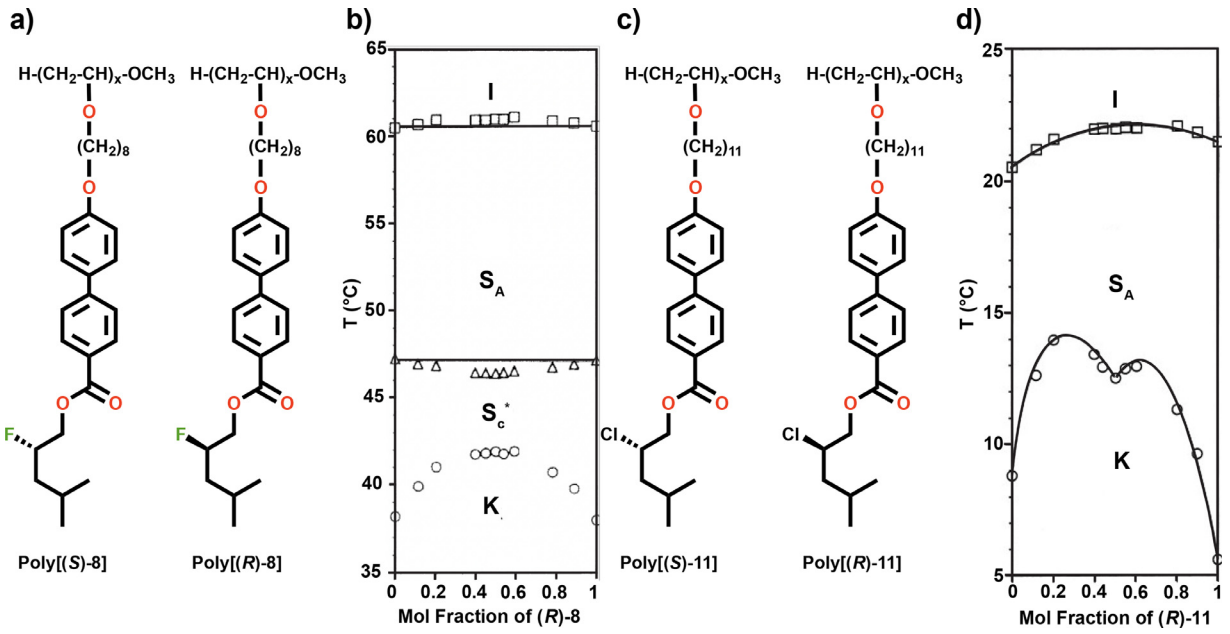


Fig. 8

(a) composition of the binary mixtures of poly[(R)-11] with poly[(S)-11]. This figure wad adapted and modified from references 182 and 189. Copyright 1994 & 1999, American Chemical Society.

S enantiomers and diastereomers. Investigation of this molecular recognition process requires comparison of polymer homologous series of enantiomers and diastereomers as a function of degree of polymerization. Due to the polydispersity effect these experiments cannot be performed with a single molecular weight sample or pair of samples even at very narrow polydispersity. Therefore, the demonstration of strictly identical phase transitions for enantiomers requires first to demonstrate strictly identical phase transition dependences as a function of molecular weight. Only after that comparison of different ratios between enantiomers and diastereomers as polymer mixtures and as copolymers can pe performed. These very demanding experiments could be performed only with the help of this living polymerization and copolymerizetion [182–190].

Fluorinated stereocenters and fluorinated aromatic part of the mesogen were very important for these series of experiments. Hetereochiral interactions were detected as a positive deviation from the linear dependence of a phase transition temperatures as a function of composition (Fig. 8). These interactions are very important since less than 100 % enantiomeric purities are affecting their physical properties. Other fascinating properties incorporated by low molar mass fluorination in liquid crystals were reviewed and will not be discussed here [191]. Heterochiral interactions were discovered in between fluorinated, and chlorinated enantiomers that are frequently used in the design of liquid crystals for displays applications.

3.6 Synthesis of side-chain liquid crystal polymers containing semifluorinated spacers and cyclopolymerization to incorporate crown-ethers in the main-chain by living cationic polymerization and cyclopolymerization initiated with $CF_3SO_3H/(CH_3)_2S$

Vinyl ethers containing a semifluorinated spacers between the vinyl group and the mesogenic group as well as divinyl

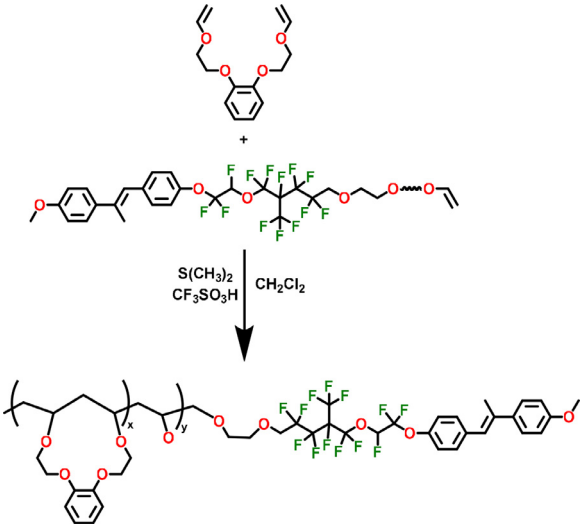


Fig. 9

Living cationic copolymerization accompanied by cyclization of l,2-bis(2-etheny1oxyethoxy)benzene (DVE) with 11-[(4′-cyano-4-biphenyl)oxy] undecanyl vinylether (CVE) and 3-[2-(1,2,2-trifluoroethoxy-2-(4-methoxy-4′-((Y- methylsti1bene)oxy))-1-(trifluoromethyl)trifluoroethoxy]-1-[2-(ethenyloxy)ethoxy]-2,2,3,3-tetrafluoropropane (MVE). This figure was redrawn from reference 193.

ethers which can incorporate crown ethers in the main chain by cyclopolymerization were both designed and employed in living polymerizations and copolymerizations mediated with $CF_3SO_3H/(CH_3)_2S$ (Fig. 9) [192,193].

It is remarkable that this initiating system tolerates so much functionality during its living polymerization process. The incorporation of crown ethers in liquid crystals is important since it provides access to molecular recognition directed phase

transitions and functionalization. This topic will be demonstrated and discussed in details in a different subchapter.

3.7 Synthesis of side-chain-liquid crystal polymers and self-organizable dendronized polymers by living cationic ring opening polymerization of cyclic imino ethers initiated with CF_3SO_3Me (MeOTf)

The cationic polymerization of cyclic imino ethers, the most common being 2-substituted-2-oxazolines, were discovered independently in four different laboratories [194–197]. Methods for the living cationic ring opening polymerization including methodologies to accomplish high molecular weight polymers were elaborated and reviewed [198–200].

Cyclic iminoethers were employed in the synthesis of numerous functional polymers and block copolymers that we will not be discussed here. However, we will provide only two examples that cannot be made easily by other methods [201,202]. In 1987 our laboratory discovered the synthesis of side-chain liquid crystal polymers by the living cationic ring-opening polymerizatioin of cyclic imino ethers containing mesogenic groups [203]. In the year 2000 our laboratory initiated a program for the convenient synthesis of the simplest class of dendronized polymers by attaching minidendrons as side groups to cyclic imino ethers and to other monomers that undergo living ring opening polymerization by other methods [204–206].

A diversity of electrophilic initiators including methyl and benzyl halides and tosylates was used for the living polymerization of functional cyclic iminoethers. Our preferred initiator is however methyl triflate since it provides very fast initiation and chain end functionalization with many nucleophiles (Fig. 10a). This combination of cyclic imino ether functionalized with minidendrons and methyl triflate initiator allowed a detailed structure-phase behavior degree of polymerization correlation to be elaborated for visualizable self-organizable dendronized polymers exhibiting columnar hexagonal phases [206] as the one developed with living cationic polymerization of liquid crystalline poly(vinyl ether)s and dendronized poly(vinyl ether)s. 3,4-Dialkoxysubstituted phenyl poly(oxazoline)s with n-octyl, n-decyl, n-dodecyl and n-tridecyl generated only columnar hexagonal mesophases regardless of their degree of polymerization [206]. Increasing the alkyl chain length to n-tetradecyl and n-pentadecyl generated dendronized polymers exhibiting $Pm\bar{3}n$ known also as Frank-Kasper A15 phase at low degrees of polymerization, followed by a columnar hexagonal phase at high degrees of polymerization [207]. This degree of polymerization dependence of phase behavior transiting from spherical dendronized polymers to columnar hexagonal resemble the similar trend observed with higher generation dendronized polymers prepared by conventional radical polymerization [208,209].

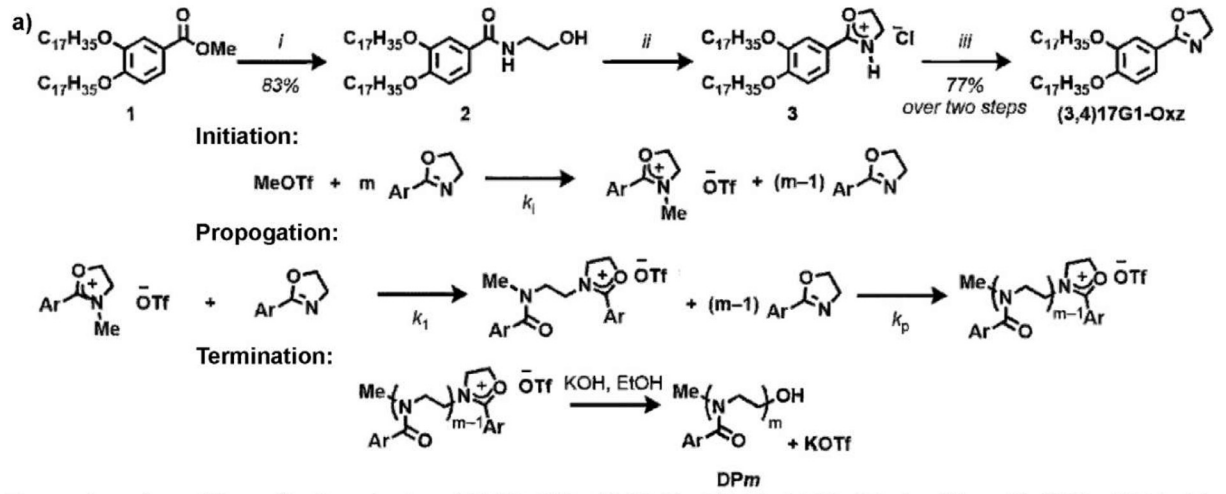
However, the living polymerization of dendronized oxazolines allowed the precise mapping of the phase behavior as a function of the degree of polymerization and it was employed to demonstrate the limitations of living polymerization methodologies in the design and construction of 3D structures based on single polymer chains [207]. Attaching three n-dodecyl alkyl groups in the 3,4,5-positions of the dendron changed the $Pm\bar{3}n$ or A15 cubic phase of the polyoxazoline into a body centered cubic (BCC) phase [211]. Semifluorination of the *n*-dodecyl groups of the 3,4,5-dendron generated only columnar forming dendronized poly(oxazoline)s [212]. Changing back to 3,4-disubstituted phenyl dendrons, this time containing *n*-hexadecyl alkyl groups, provided a dendronized poly(oxazoline) displaying $Pm\bar{3}n$ or A15 phase at very low degree of polymerization, tetragonal $P4_2/mnm$ or sigma Frank-Kasper phase [213] between degrees of polymerization 10 and 50 and columnar hexagonal *P6mm* at higher degree of polymerization than 75 [214]. Increasing the *n*-alkyloxy group of the 3,4-disubstituted dendronized poly(oxazoline) from *n*-hexadecyl to *n*-heptadecyloxy groups provides an extraordinarily complex system which displays within only five monomer repeat units liquid crystal liquid quasicrystal (Fig. 10b) [215]. A15 and sigma Frank-Kasper phases [210]. These experiments demonstrated the extraordinary capability of minidendritic poly(oxazoline)s to map the phase behavior of the dendronized polymers. No other living polymerizations except of vinyl ethers and of oxazolines, both mediated by fluorinated initiators giving nonnucleopihilic counter-anions, and discussed in this subchapter and in the previous subchapters could contribute with the same level of precision and functionality tolerance to solve these fundamental problems of supramolecular polymer chemistry. These two living polymerizations are complementary to each other. The vinyl ether polymerization proceeds efficiently at 0 °C while that of oxazolines at high temperatures that allowed polymerization to exceed the size of the supramolecular spheres forming cubic phases since in the isotropic disordered state where spheres are most probably random coil or extended propagating chains.

3.8 Synthesis of side-chain liquid crystal poly(vinyl ether) copolymers with poly(vinyl ether)s containg semifluorinated side groups initiated with $CF_3SO_3H/(CH_3)_2S$

This methodology allowed also the synthesis of the first AB semifluorinated block copolymer containing side-chain liquid crystal polymer segments (Fig. 11) [216]. They exhibit a microphase separated morphology, that was not determined at that time. Fluorinated initiators for living radical polymerization were used to synthesize end-functionalized polystyrene and polybuthylmethacrylate containing perfluorocarbon chain ends. Upon mixing their perfluorinated fragments interact with each other providing a new approach to block copolymer-like self-assembly of fluorocarbon end-functionalized polystyrene and polybutylmethacrylate [217].

3.9 Sequence-defined including alternating multicomponent semifluorinated polyethylene oligomers synthesized by single electron-transfer (SET) self-organize a columnar hexagonal mesophase

A simple methodology by the SET-mediated synthesis of multi-alternating semifluorinated polyethylene oligomers was developed (Fig. 12) [218,219]. This block alternating block copolymer structure was designed to self-organize columnar hexagonal mesophase and it did.



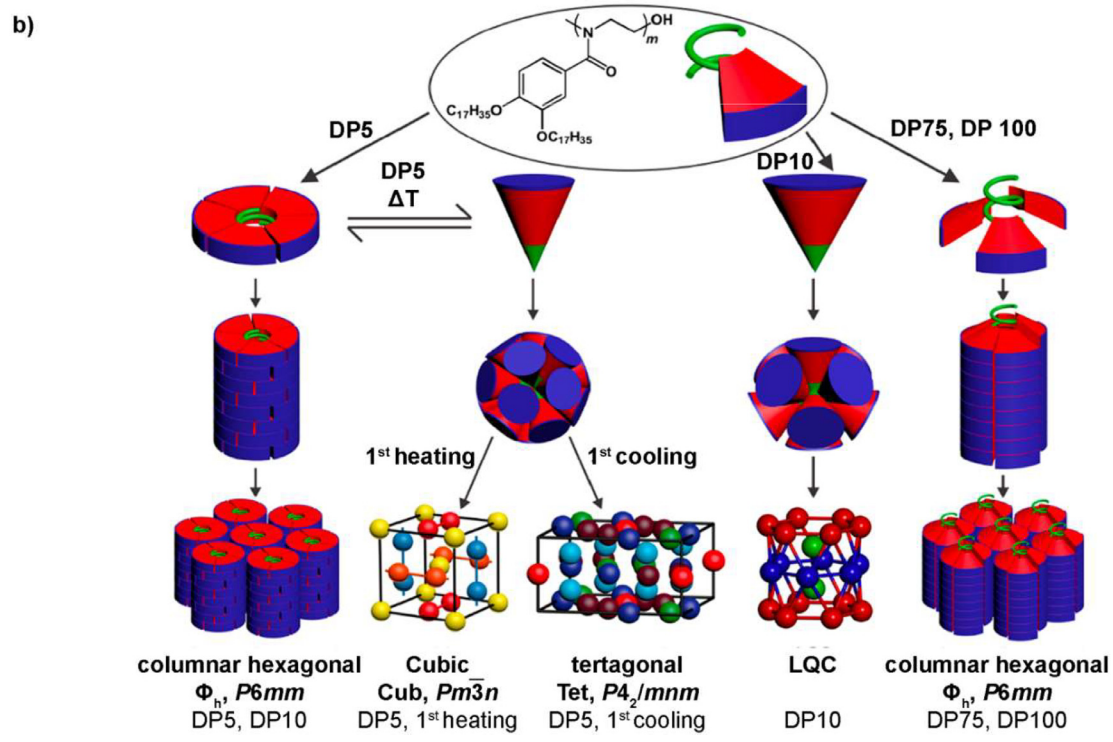


Fig. 10

(a) Synthesis and mechanism of living cationic ring opening polymerization of (3,4)17G1-Oxz. Summary of periodic and quasiperiodic arrays self-organized from assemblies of poly[(3,4)17G1-Oxz]. This figure was adapted and modified from reference 210. Copyright 2018©, American Chemical Society.

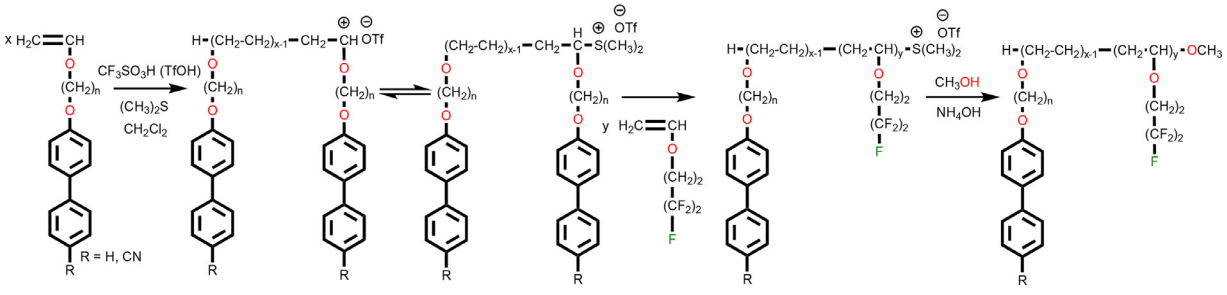


Fig. 11

Synthesis of the block copolymer of 2-(4-blphenyloxy)ethyl vinyl ether with 1H, 1H, 2H, 2H-perfluorodecyl vinyl ether. This figure was redrawn from rerence 64.

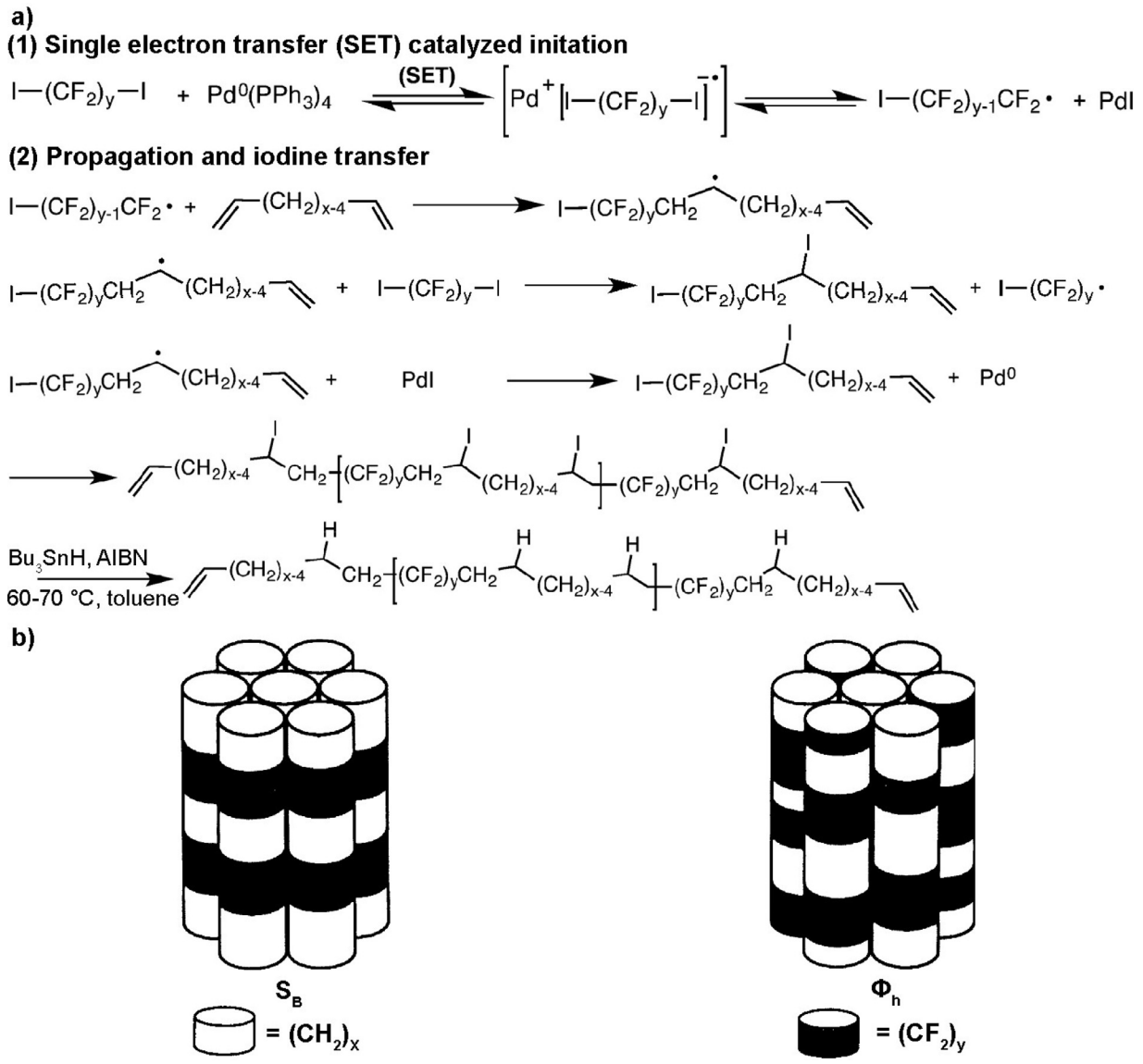


Fig. 12

(a) Mechanism of Pd(0)-Catalyzed SET copolymerization of α,ω-diiodoperfluoroalkanes with α,ω-dienes to sequence-controlled smifluorinated oligomers (b); schematic representation of the S_B phase and the hexagonal columnar (Φ_h) Phase. This figure was adapted and modified from references 218 and 219. Copyright © 1997, American Chemical Society Copyright © 2014, American Chemical Society.

3.10 Fluorinated reagents monomers and solvents in living radical polymerizations

The participating reagents of all living polymerization methodologies, including INIFERTERS such as dithiocarbamates, xanthates, tetraphenylethanes, alkoxyamines, nitroxides, chain transfer agents for RAFT, initiators, ligants and solvents for ATRP and for SET-LRP, initiators for iodine transfer polymerization, etc., were fluorinated in order to functionalize the chain end of the resulting polymers and to improve polymerization conditions in different solvents including fluorinated solvents and for different monomers including fluorinated monomers. A review covering this topic up to 2002 in a very well-organized way is available [220]. More recent related reviews but more specialized are also available [221–231]. This is a large field of research that is outside the scope of this perspective and with the exception of several experiments on SET-LRP that were elaborated in our laboratory will not be discussed here. A method for the synthesis of perfluorosulfonyl chloride and bromide and their use as initiators in living radical polymerization catalyzed by CuCl was investigated (Fig. 13) [232].

Arylsulfonyl halide were introduced as initiators in metal catalyzed living radical polymerization by our laboratory in 1995 [233–246].

Perfluorosulfonyl halides act as intitiators via a different mechanism from alkyl halides and arylsulfonyl halides [247,248]]. Aryl and alkyl sulfonyl halides act as initiators by the addition of their sulfonyl radicals to the double bond of the monomer while perfluoroalkylsulfonyl halides generate the sulfonyl radical by metal catalysis, extrude the SO_2, and subsequently the resulting perfluoalkyl radical adds

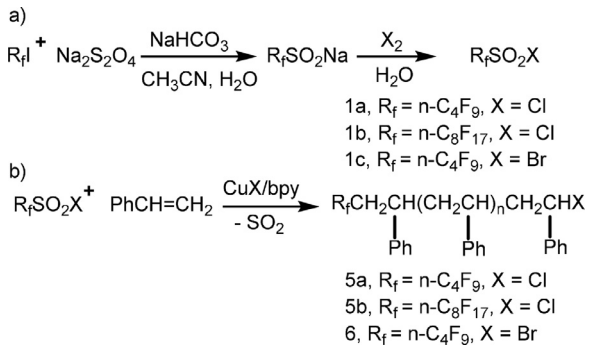


Fig. 13

(a) Synthesis of perflurosulfonyl halides; (b) metal catalyzed living radiocal polymerization of styrene initiated with perflurosulfonyl halides. This figure was adapted and redrawn from reference 232. Copyright © 2000, John Wiley & Sons, Inc.

as an initiator to the monomer (Fig. 13). Metal catalyzed living radical polymerization initiated with perfluorosulfonyl halides was carried out with styrene to demonstrate this mechanism of initiation [232]. Interestingly perfluoroalkyl sulfonyl halides could also be used in copolymerization of tetrafluoroethylene with hexafluoropropylene [232]. This last experimental was performed at the Experimental Station of DuPont. Fuorinated alcohols including 2,2,2-trifluoroethanol (TFE) and 2,2,3,3-tetrafluoropropanol (TFP) were used as solvents in single-electron-transfer living radical polymerization (SET-LRP) [249–259] of hydrogenated hydrophilic, hydrophobic and amphiphilic acrylates and methacrylates [260–263]. They are generating the highest molar mass polymers from this class obtained so far by any methodology for some of them [264] as well as in the polymerization of selected examples of fluorinated acrylates and methacrylates such as 1H,1H,2H,2H-perfluorooctyl acrylate, 2,2,3,3,4,4-heptafluorobutyl acrylate and 1H,1H,5H-octafluoropentyl methacylate, 1,1,1,3,3,3-hexafluoroisopropyl acrylate (HFIPA), 1,1,13,3,3-Hexafluoroisopropyl methacrylate (HFIPM), pentafluorophenyl acrylate (PFPA) and pentafluorophenyl methacrylate (PFPM) [265]. Both TFE and TFP are excellent solvent for the disproportionation of Cu(I)X into Cu(0) and Cu(II)X_2. Hexafluoroisopropanol (HFIP) is not a disproportionating solvent. However, its mixtures with water provide also an excellent solvent for SET-LRP [266]. Improved activity of TFE and TFP in mixtures with water was also observed [267]. These experiments allowed the design of novel reactive semifluorinated polyacrylate and polymethacrylates as well as reaction condition for the transesterification and transamidation of their side groups [268].

SET-LRP experiments are most conveniently performed with Cu-wire as a catalyst. Cu-wires are covered with Cu-oxides predominantly Cu_2O that although is reactive and was employed itself as a catalyst [236,249,250,269–273] exhibit lower activity than Cu(0). At the same time the surface of Cu(0) wire is not homogeneous since not all faces of the Cu(0) face centered cubic unit cell of the Cu(0) crystal exhibit identical reactivity in SET-reactions and therefore, even in the absence of oxidation different Cu-wires exhibit different reactivity [274]. Reduction

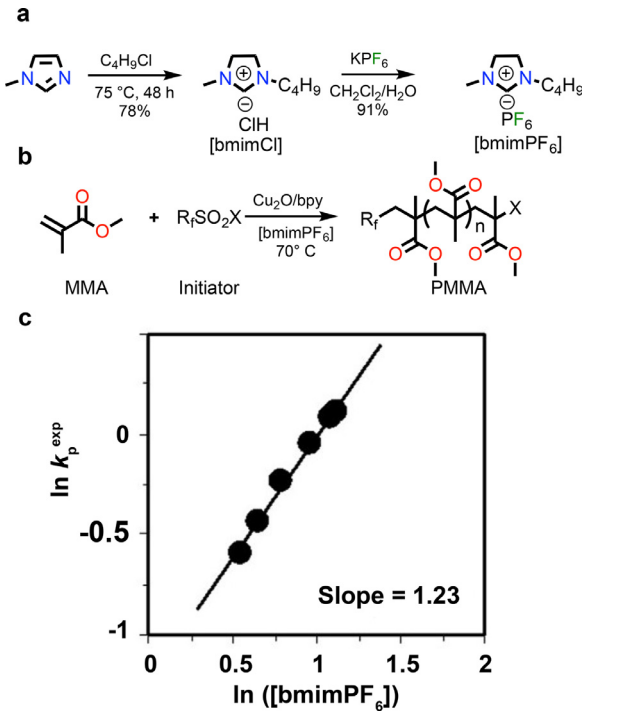


Fig. 14

(a) Two-step synthesis of [bmimPF$_6$]; (b) living radical polymerization of MMA initiated from PDSC and catalyzed by Cu_2O/bpy at 70 °C; (c) determination of the external order of reaction of the rate constant of propagation on the concentration of ionic liquid for the LRP of MMA initiated from PDSC and catalyzed by Cu_2O/bpy at 70 °C. This Figure was adapted and modified from reference 285. Copyright © 2005, John Wiley & Sons, Inc.

of Cu_2O with hydrazine [275], strong acid dissolution [276] or even the use of acetic acid as a solvent [277] do not undergo the induction period (IP). Therefore, it is not surprising the SET-LRP of methacrylic acid is not accompanied by IP [278]. No IP was observed during SET-LRP in TFE and TFP [279]. This self-activating mechanism of fluorinated alcohols was quite surprising since the pKa of TFE is 12.46 while that of TFP is 13.05. However, these pKa values seem to be sufficient to activate the surface of Cu(0)-wire during the SET-LRP process. A synergistic and cooperative effect was observed for mixtures of TFE and TFP with DMSO [264].

This effect is similar to that observed in other mixtures of solvents [280], but in addition to the increased in rate of polymerization, it produces the highest molar mass poly(2-ethylhexyl acrylate) with perfectly controlled chain ends by SET-LRP or by any other method. Originally the mechanism of this cooperative and synergistic effect was not explained. At this point we have at least a hypothesis for it. Recently it has been demonstrated that DMSO has a very unusual capability to stabilize Cu(0) nanoparticles during disproportionation of Cu(I)X into Cu(0) and Cu(II)X_2 exhibiting a catalytic effect [281–283]. Most probably, mixtures of DMSO with other solvents including fluorinated alcohols may exhibit the same catalytic process at a certain composition [280]. A catalytic effect of the ionic liquid 1-butyl-3-methylimidaziolinium hexafluorophosphate was observed during the metal catalyzed living radical polymerization initiated with arenesulfonyl halides (Fig. 14) [284]. These

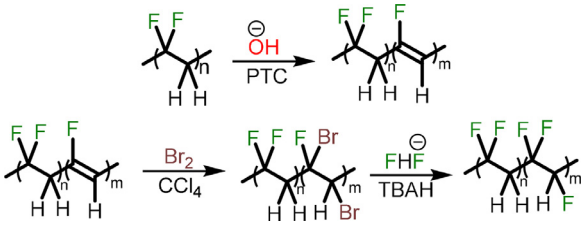


Fig. 15

Synthesis of poly(vinylidene fluoride-co-trifluoroethylene) block copolymers. This figure was redrawn from reference 286. Copyright © 1997, John Wiley & Sons, Inc.

experiments with fluorinated reagents provided an important contribution to the field of living polymerization including, new solvents for SET-LRP, extremely good control of the living polymerization of hydrophilic, hydrophobic, amphiphilic and fluorinated monomers with excellent molecular weight dependence to extremely high molecular weights and perfect chain ends functionality, self-activation activity of the catalyst by the fluorinated solvents, new reactive polymers by simple methodologies, synergistic effect of the fluorinated alcohols with DMSO, catalytic effect of solvent, to name just a few. Considering the reduced number of experiments performed on this topic, this number of accomplishments is remarkable.

3.11 Synthesis of poly(vinylidene fluoride-co-trifluoroethylene) by phase transfer catalyzed modification of polyvinylidene fluoride

Poly(vinylidene fluoride-co-trifluoroethylene) is of great interest for its piezo and pyroelectric properties but the synthesis of this copolymer is limited to the conventional radical copolymerization that provides a statistical copolymer [286]. In order to expand the synthetic methodologies of this synthesis we developed an new concept that involved a phase transfer catalyzed dehydrofluorination of poly(vinylidene fluoride) followed by halogenation of the resulting double bonds and exchange of the added chloride or bromide with fluoride via KF or KHF_2. The first step was accomplished in solution (DMF or DMSO) with potassium *tert*-butoxide or NaOH and tetrabutylammonium hydrogen sulfate (TBAH) as phase transfer catalyst. This step was also carried out in heterogeneous state with powder, single crystals or films of polymer, aqueous NaOH and TBAH. Although both chlorination and bromination of the resulting polymer double bonds were carried out, as expected the most successful intermediate for the next step was the brominated compound.

The strongly basic character of the fluoride made the third step difficult particularly with the chlorinated copolymer. However, the brominated material was successfully functionalized by replacing the bromide with fluoride and thus creating a block copolymer of poly(vinylidene fluoride-b-trifluoroethylene) (Fig. 15) [286,287]. The brominated or chlorinated intermediates from this process (Fig. 15) can be used for graft-copolymerization by a related mechanism as the one used in the case of PVC [288]. Experiments on this line must be performed.

3.12 Living phase-transfer catalyzed (PTC) and single-electron transfer (SET) mediated polyetherifications

Single electron transfer (SET)-mediated polymerizations proceeding via radical-ions both radical-anion and radical-cation species and phase-transfer catalyzed (PTC) polyetherifications were shown during the mid 1980th to deviate from the conventional condensation polymerizations proceeding with equal reactivity of growing species regardless of the degree of polymerization. In both cases reactivity of the growing species increases as the degree of polymerization increases thus providing the first examples of living-like condensation polymerizations (Fig. 16) [37,176,285,286,289–323]. This became an entirely new field of research [324,325].

Mechanistic explanations were provided for all polymerization systems but they will not be discussed here. It is just important to mention that these polymerizations generated narrow molecular weight distribution polymers with well-defined chain-ends that were employed in the synthesis of block copolymers and for the elucidation of some fundamental aspects that will be discussed later.

3.13 Expanding architectural complexity with liquid crystal polyethers and liquid crystal polyethers based on conformational isomerism including with fluoro and trifluoromethyl substitution

The discovery of liquid crystal polyethers by PTC polyetherification (Fig. 17) [292,294–298,299,300,326] and the ability to prepare them with different molecular weight and identical chain ends allowed a large diversity of fundamental problems from this field to be solved and almost at the same time facilitated the discovery of an additional new concept, liquid crystal polyethers based on conformational isomerism. [298,327–343]. Fluorine, and trifluorophenyl substituted liquid crystal polymers based on conformational isomerism played an important role in these fundamental studies [344–346]. Liquid crystal polyethers based on conformational isomerism were equipped with constitutional isomerism [347–352].

This combination of conformational and constitutional isomerism allowed the discovery of nematic liquid crystalline dendrimers [352–354], liquid-crystalline main-chain elastomers [355], the molecular design of nematic, smectic and columnar phases of main chain LC polyethers [356], and macrocyclic liquid crystals [160,161,357–371]. This work demonstrated that macrocyclics and not linear is the most suitable conformation providing the most stable liquid crystal phases thus infirming a concept promoted for over 100 years [372–374]. This led to the design of the first example of main-chain and side-chain liquid crystal polymers based on macrocyclic mesogenic groups [370,375–377].

4 Fluorine and fluorinated reagents in self-assembly, disassembly, reassembly and self-organization

4.1 Self-organization mediated by alkali metal triflates

Alkali metal salts of triflic acid or alkali metal triflates have excellent solubility in fragments of polyethylene glycol known as podants, crown ethers and cryptands. This is due to the weak interaction between the nonnucleophilic and nonbasic triflate anion and the metal cation. Starting in 1987 we reported the

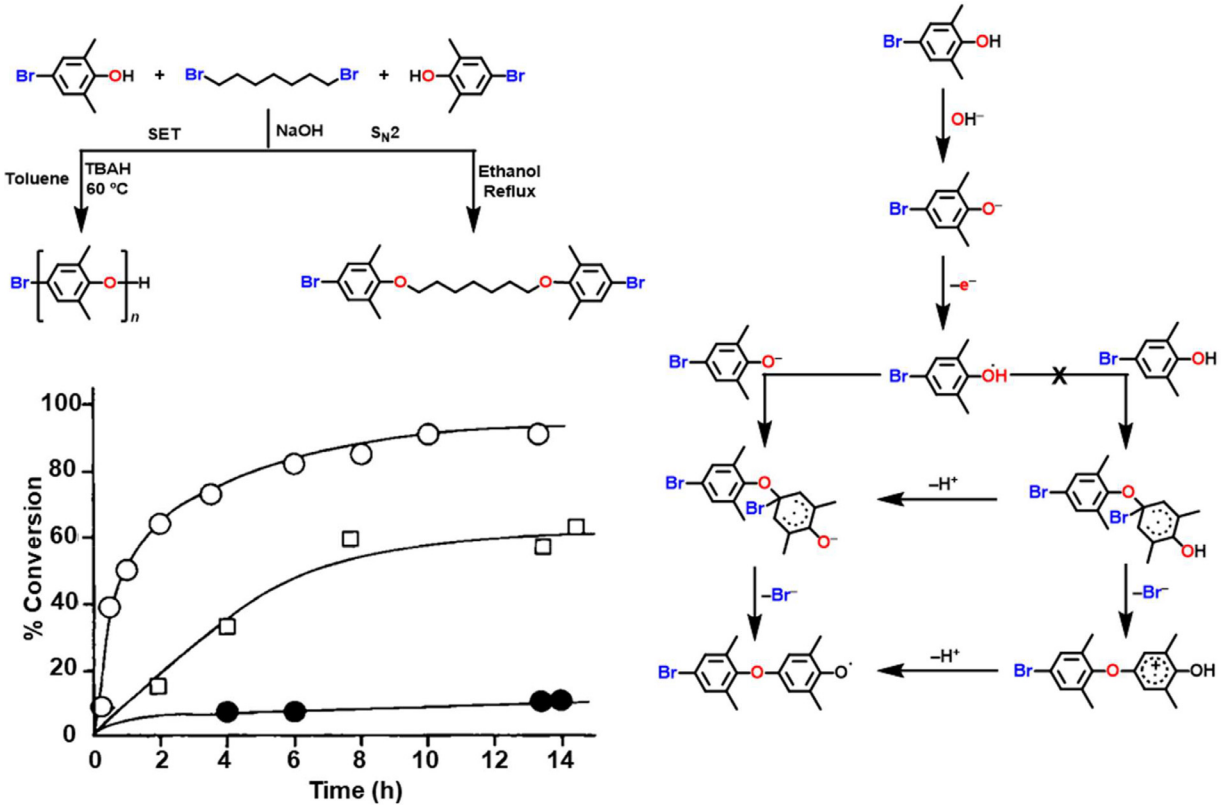


Fig. 16

SET polymerization mechanism demonstrating phenol or phenolate addition to the phenoxy radical. Plots of percent conversion versus reaction time for the polymerization of BDMP under different reaction conditions:(a) 6N aqueous NaOH and air, ○; (b) 6N aqueous NaOH and nitrogen, ●.; (c) 3N aqueous NaOH and air, □. This Figure was adapted and redrawn from reference 303.

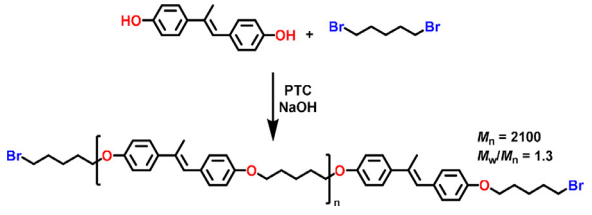


Fig. 17

Polymerization of polyethers of mesogenic bisphenols. This figure was redrawn from reference 326. Copyright © 1984 John Wiley & Sons, Inc.

co-assembly of alkali metal triflates with oligoethylene fragment of liquid crystal polyethers that acted as recognition sited for the metal salts [378] to mediate phase transitions of the corresponding liquid crystal polymers. Side-chain liquid crystal polymers containing crown ethers in the side-groups were also employed in these complexation experiments [379]. We named this process molecular recognition directed phase transitions in liquid crystalline polymers. Lower order phases such as nematic will increase their thermal stability while higher order like smectic and crystalline would decrease their stability transforming a polymer containing crystal and liquid crystal multiple phases into a polymer exhibiting only a very broad temperature range for its nematic phase [379]. Libraries of liquid crystal polymers containing crown ethers were elaborated and subjected to these experiments [141,380–384]. New concepts in mesomorphic polyelectrolytes were generated by the synthesis of side-chain liquid crystalline polymers containing end-on [385] and side-on [385] fixed mesogenic groups and oligooxyethylene spacers.

Once we elaborated the principles of molecular recognition directed phase transitions in liquid crystals by complexation with alkali metal triflates we expanded the same very simple methodology to molecular recognition directed self-assembly of supramolecular columns and helical columns from dendrons or minidendrons containing crown ethers or oligooxyethylene fragments at their apex (Fig. 18) [386–390]. When dendrons were attached to oligooxyethylene glycols they were also functionalized with polymerizable groups and polymerized. The resulting polymers have a backbone jacketed with a dendritic coat assembling a columnar structure. When dendronized crown ethers or oligooxyethylenes are only crystalline, complexation induces a columnar assembly that exhibits a columnar hexagonal liquid crystal whose characterization by X-ray allowed to construct the supramolecular model of the assembly. Therefore, either non-self-assembling dendronized crown ethers or oligooxyethylenes form already a supramolecular assembly, or if they do not, complexation with metal triflates induces the self-assembly and self-organization process. In the case the building blocks self-organized in a columnar hexagonal

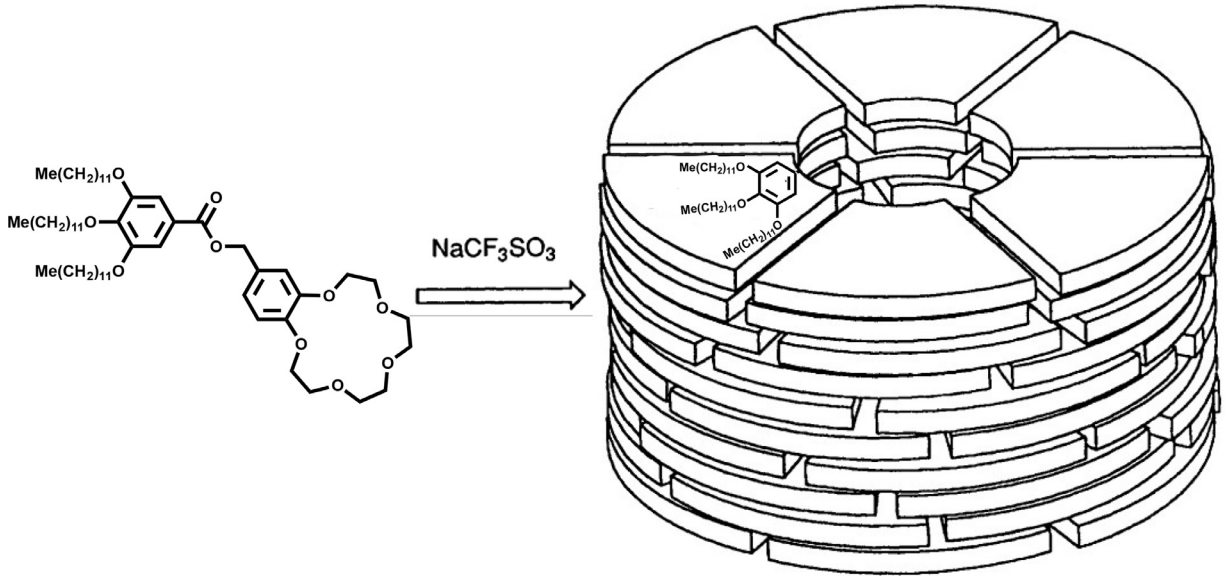


Fig. 18

Schematic representation of the self-assembly of the tapered endo-receptor (2,4,7,10,13-pentaoxacyclopentadecan-2-ylmethyl 3,4,5-tris(dodecy1oxy)benzoate) minidendron, into a tubular molecular architecture upon complexation with $NaCF_3SO_2$. This figure was adapted and redrawn with permission from reference 390. Copyright © 1994, Royal Society of Chemistry.

liquid crystal, complexation with metal triflates enhances the stability of the resulting assembly. A comparison of the role of complexation by comparison with the equivalent contribution of H-bonding and of a polymer backbone was possible for the first time. This comparison was published in a brief review article and it will not be repeated here [391]. However, what we would like to mention here is that the center of all these supramolecular columns consists of an ionically conducting channel whose ionic conductivity is determined by the state of the assembly [386]. These materials are of great interest as polyelectrolytes for batteries. Alkali metal triflates is a new but very general self-assembly and self-organization concept [212,392–398] that produces supramolecular assemblies or polymers resembling Tobacco Mosaic Virus [171,399] with numerous applications and even more complex design capabilities [400,401].

4.2 Supramolecular organizations mediated by phenyl-perfluorophenyl stacking interractions

Phenyl-perfluorophenyl stacking interractions is a new concept that mediates self-assembly by a very simple and elegant methodology [402–410]. This very simple methodology was used to mediate phase transitions in liquid crystals and in polymers as well as to construct new macromolecular architectures. This concept, that is inspired from biology, is so simple and powerful that not even a figure is needed to imagine its infinite capabilities.

4.3 Fluorocarbons and fluorinated amphiphiles in drug delivery and biomedical research

Fluorinated hydrocarbons and fluorinated amphiphiles are not enzymatically degraded. However, due to their lipophilicity they are easily eliminated from the organism. They have numerous biomedical applications including for *in vivo* oxygen transport as blood substitutes in diagnosis and in drug delivery. Numerous review articles on this topic are available and we are not going to expand this topic more than just to refresh our readers about their utility [411–422].

4.4 Disassembly poly(p-phenylene) crystal structure by substitution with –CF_3 and –OCF_3

Poly(paraphenylene) is an insoluble polymer that decomposes before melting. Therefore, transforming it into a soluble polymer via minimum chemical modification of its repeat unit is of interest for many fundamental questions accompanied by potential technologic applications. Incorporation of large substituents in a regioirregular placement is one method to accomplish this goal [41–44,51,423–425].

A method elaborated in our laboratory [47] provided access for the first time to a comparison of the regioregular and regioirregular poly(*p*-phenylene)s by employing the Ni(0)-catalyzed homocoupling of arylene bismesylates developed in our laboratory [426]. A diversity of substituents were employed in these experiments, between many of them being *o*-, *m*- and *p*-fluorobenzoketone. Surprisingly fluorine was again the most active substituent employed to disassemble the 3D order of poly(*p*-phenylene). The next series of experiments was with –CF_3 and –OCF_3 substituents. Regioregular and regioirregular poly(*p*-phenylene)s containing these substituents allowed the synthesis of the highest molecular weight and, soluble and completely free of crystallization poly(*p*-phenylene)s (Fig. 19) [427].

This polymer had excellent physical properties and it almost ended up being a commercial product from DuPont. For reasons that we prefer to keep confidential it was not commercialized. However, it demonstrated the power of –CF_3 and specially of –OCF_3 as substituents to disassemble 3D structure of poly(p-phenylene) and most probably of many other crystalline polymers.

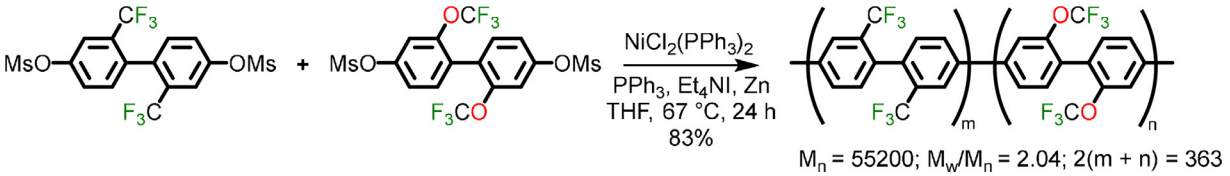


Fig. 19

Ni(0)-Catalyzed copolymerization of 2,2ᶜdisubstituted-4,4ᶜbis[(methylsulfonyl)oxy]biphenyls. This figure was redrawn from reference 427. Copyright © 1996, American Chemical Society.

4.5 Extraordinary amplification of the self-assembly of dendrons and dendronized polymers and the induction of their spontaneous homeotropic alignment by semifluorination

Self-assembly and self-organization of dendrons, minidendrons and dendronized polymers as well as of minidendronized polymers was discovered in our laboratory in the late 1980th. The first supramolecular structure discovered by these experiments was columnar that most frequently self-organizes a columnar hexagonal periodic array [74,171,172,205,253,391,399,401,428–463]. Libraries of self-assembling dendrons and dendronized polymers were subsequently elaborated to discover the fundamental principles for the self-organization of columnar hexagonal and helical columnar hexagonal periodic arrays [208,209,400,464–473]. Placing interacting functional groups at the apex of the self-assembling dendron or polymer backbones increase the tendency of self-assembly and self-organization. When the apex contains an oligooxyethylene frangment attached or not to a polymer backbone or a crown ether, complexation with alkali metal triflates already discussed in subchapter 4.1, also help the self-organization process. Semifluorination of dendrimers started as early as in 1992 [474–477] and continued for almost all classes of conventional dendrimers. An excellent review article on this topic is available [478]. However, most of this work was dedicated to potential applications [479–486] and will not be discussed again here. Systematic investigations on self-assembly, disassembly, reassembly and self-organization were performed in our laboratory and will be briefly mentioned here. Semifluorination of the alkyl groups from the periphery of the dendron, minidendron and dendronized polymers provides, by comparison with all apex functionalities, an extraordinary amplification of the self-assembly and self-organization both for the dendrons and for the dendronized polymers [455,487]. Replacement of four out of a total of twelve carbons with perfluorinated fragments eliminates the crystallization of the building block and induces the self-organization of a columnar hexagonal phase. Increasing the number of fluorinated carbons from four to six and to eight out of the total of twelve carbons continues to increase the thermal stability of the columnar assembly. This trend was observed with minidendrons, first generation dendrons and with the corresponding dendronized polymers. This semifluorination concept was also applied to dendronized crown ethers [392]. Two different crown ethers were employed in these experiments. The contribution of fluorination was compared in this case with the contribution of complexation with alkali metal triflates. In addition to the extraordinary increase of self-assembly, semifluorination provided access to an extraordinarily simple method for the self-organization of the resulting supramolecular columns with their long axis perpendicular to an untreated optical microscope glass slide. This alignment is known as homeotropic alignment and is a very complex process in the area of columnar hexagonal or of any other 1D and 2D liquid crystals and self-organizations [392]. A final experiment exploring the capabilities of fluorination was reported in 2022. It demonstrated not only the increase in self-assembly and self-organization but also it showed a dramatic increase in the order of the supramolecular assembly via fluorination [488]. These experiments demonstrated definitively the extraordinary capability of semifluorination to both accelerate and increase the order during self-assembly and self-organization. The spontaneous homeotropic alignment allowed for the first time the direct visualization of the supramolecular columns assembled both from minidendrons and from first generation dendrons organized perpendicular and parallel to the glass surface and also the determination of the physical properties of these supramolecular columns (Fig. 20) [450]. The homeotropic alignment of semifluorinated dendrons was observerved also in other laboratoris [489,490] demonstrating the generality of this concept. Semifluorination of dendrons and minidendrons allowed the elaboration of several new concepts in the field or self-assembly and self-organization. They will be discussed in the following subchapters.

4.6 Fluorination mediates self-assembly, co-assembly and self-organization of helical self-repairing electronically active periodic arrays derived from conjugated-minidendrons

Semifluorinated self-assembling minidendrons were equipped at their apex with libraries of electron-acceptor and electron-donor groups [491]. Both the minidendrons containing electron-acceptor and electron-donor groups self-assemble in supramolecular helical columns with the acceptor and donor groups in the center of their helical column (Fig. 21). This arrangement provides a dramatic increase of the charge carrier mobility of the donor or acceptor groups from the center of the helical columns when compared with the mobility of the same compound in its native state. Co-assembly of donor and acceptor dendrons self-organize a donor-acceptor complex in the center of the helical column. This complex has also a dramatically increased charge carrier mobility when compared with that of the parent non-dendronized complex. Polymers containing electron-acceptor and electron-donor side groups were also synthesized and characterized for their charge carrier mobility to display as expected low mobilities. However, the complementary donor-polymer co-assemble with the acceptor-dendrons and the acceptor-polymer co-assemble with the donor-dendrons

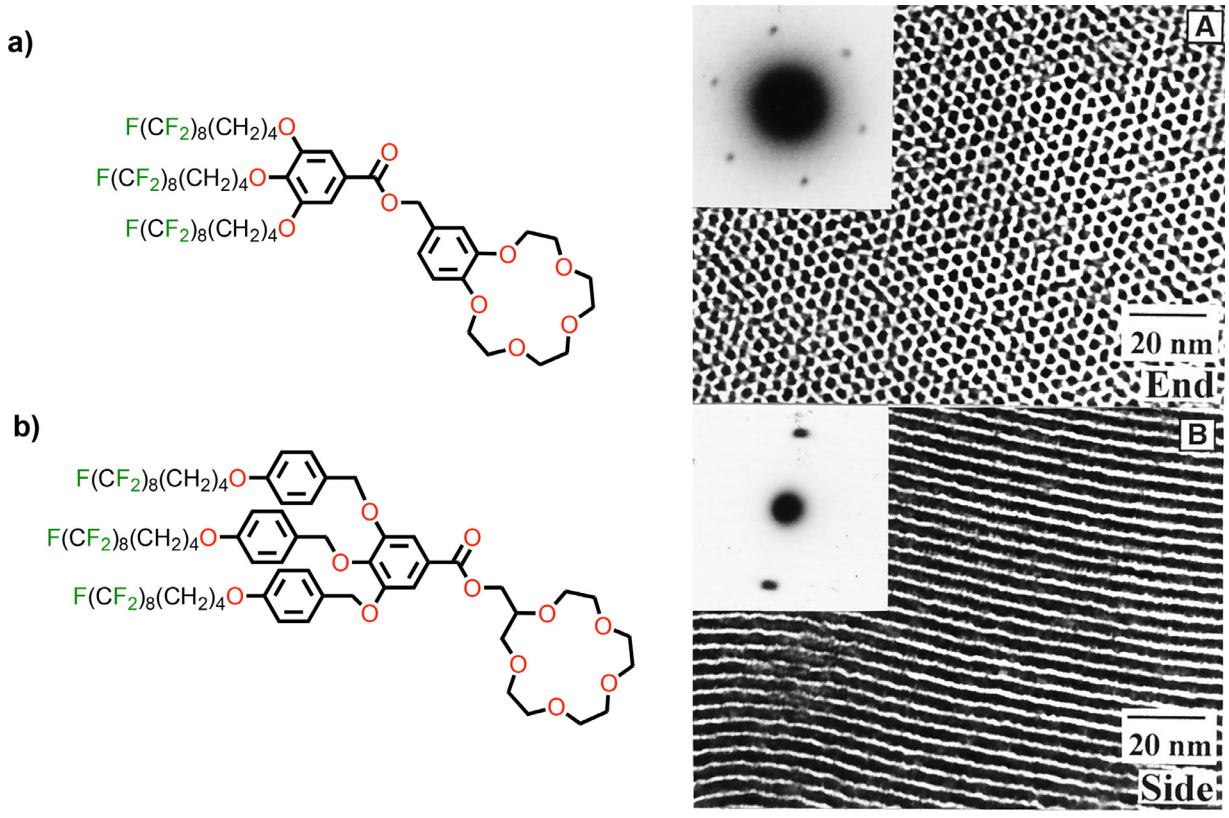


Fig. 20

Phase-contrast micrograph of (a) homeotropically and (b) planar-aligned LC assemblies generated by supramolecular cylinders self-assembled. This figure was adapted and modified from reference 450. Copyright © 1997, he American Association for the Advancement of Science.

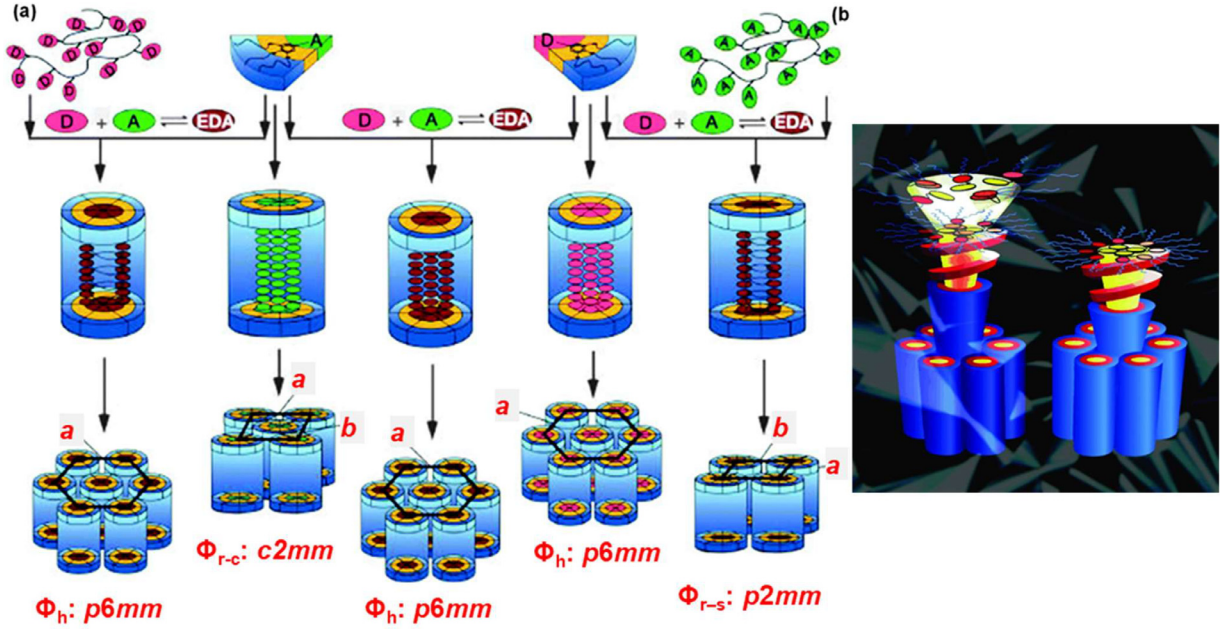


Fig. 21

Schematic illustration of complex electronic supramolecular materials mediated by dendrons containing donor (D) and acceptor (A) groups, and their co-assembly with complementary amorphous polymers containing D and A side groups (a). The different systems forms hexagonal columnar (Φ_h), centred rectangular columnar ($\Phi_{r\text{-}c}$) and simple rectangular columnar ($\Phi_{r\text{-}s}$) arrays; a and b are lattice dimensions. The self-repairing process of back-folded (brown) electronically active supramolecular helical pyramidal columns self-assembled by semifluorinated minidendron attached to the acceptor groups (b). This figure was adapted and modified from references 491 and 492. Copyright © 2002, Macmillan Magazines Ltd. Copyright © 2006 John Wiley & Sons, Inc.

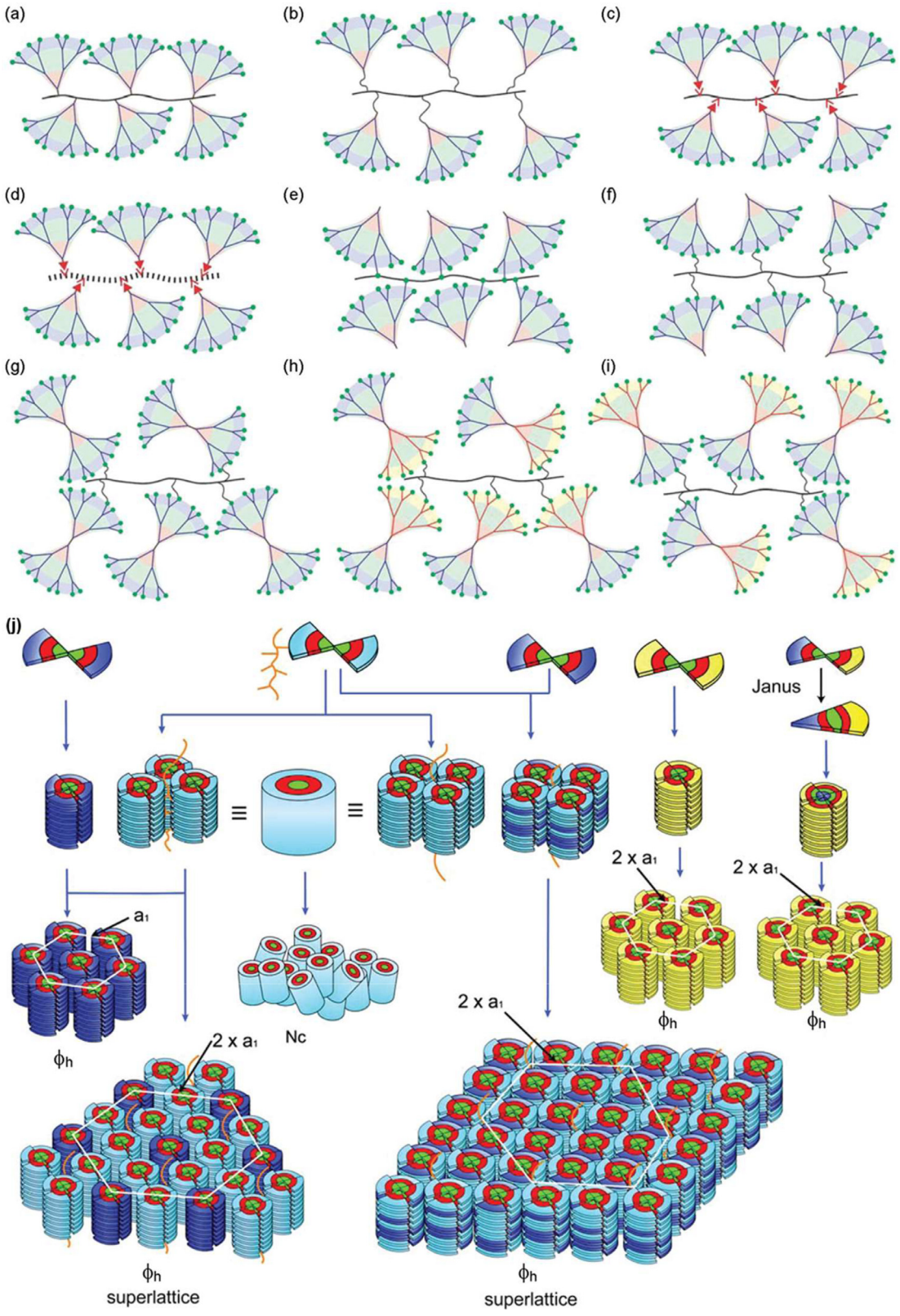


Fig. 22

(*a–i*) The diversity of possibilities for the attachment of a self-assembling dendron or dendrimer to a covalent or supramolecular backbone. Topologies generated from linear covalent and supramolecular polymers dendronized with self-assembling dendrons, twin dendritic molecules, and Janus dendrimers. (j) Self-assembly of hydrogenated twin dendritic molecules, of polymers dendronized with hydrogenated twin dendritic molecules, and their coassembly (all in blue). Self-assembly of fluorinated twin dendritic molecules (in yellow) and of semifluorinated Janus dendrimers (half in blue and half in yellow). This figure was reproduced with permission from reference 495. *Copyright © 2012, American Chemical Society*.

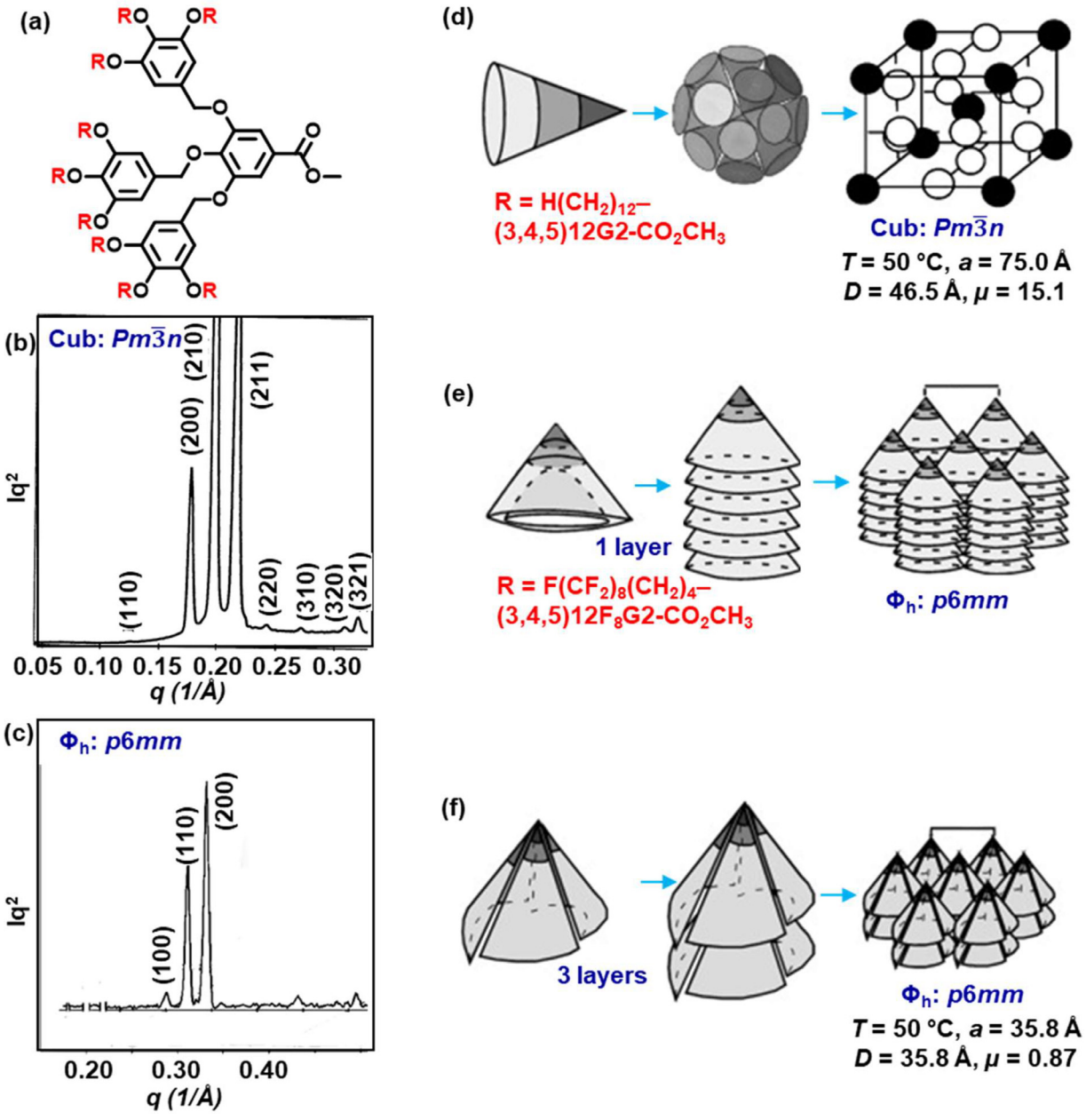


Fig. 23

Chemical composition affecting the structure of self-organized supramolecular dendrimers. Structures, self-assembly, and self-organization of the second generation dendrons: (a) structure of $(3,4,5)^2$12G2-CO_2Me; (b) radial plot from XRD of the Cub: *Pm*$\bar{3}$*n* phase; (c) Radial plot from XRD of the hexagonal: *P6mm* phase; (d) all-trans cone conformation of $(3,4,5)^2$12G2-CO_2Me; (e) all gauche-crown conformation of $(3,4,5)^2$12F8G2-CO_2Me; (f) all trans-taper conformation of $(3,4,5)^2$12F8G2-CO_2Me. Parts of this figure were adapted from reference 442 and modified.

incorporating the polymer backbone and its donor-acceptor complex in the center of the helical supramolecular columns. An increased conductivity was observed also in these cases. These structural organizations were elucidated by a complementary combination of oriented fiber X-ray diffraction and solid-state ^{1}H-NMR experiments. This structural analysis methodology demonstrated for the case of supramolecular columns containing acceptors a backfolded structural defect of the acceptor on the donor part of the dendron. However, a heating-cooling and reheating process was demonstrated to self-repair these structural defects. Fig X illustrated schematically this concept. Libraries of donor-dendrons and acceptor-dendrons were synthesized and their self-assembly analyzed to demonstrate the generality of this concept [492,493].

4.7 Twin-fluorinated and Janus fluorinated-hydrogenated minidendritic benzamides

Both twin-hydrogenated and twin-fluorinated minidendritic benzamides self-assemble into helical columns self-organizing columnar hexagonal periodic arrays (Fig. 22) [446,494]. Janus fluorinated-hydrogenated minidendritic benzamides self-assemble into bilayered vesicular pyramidal columns with double

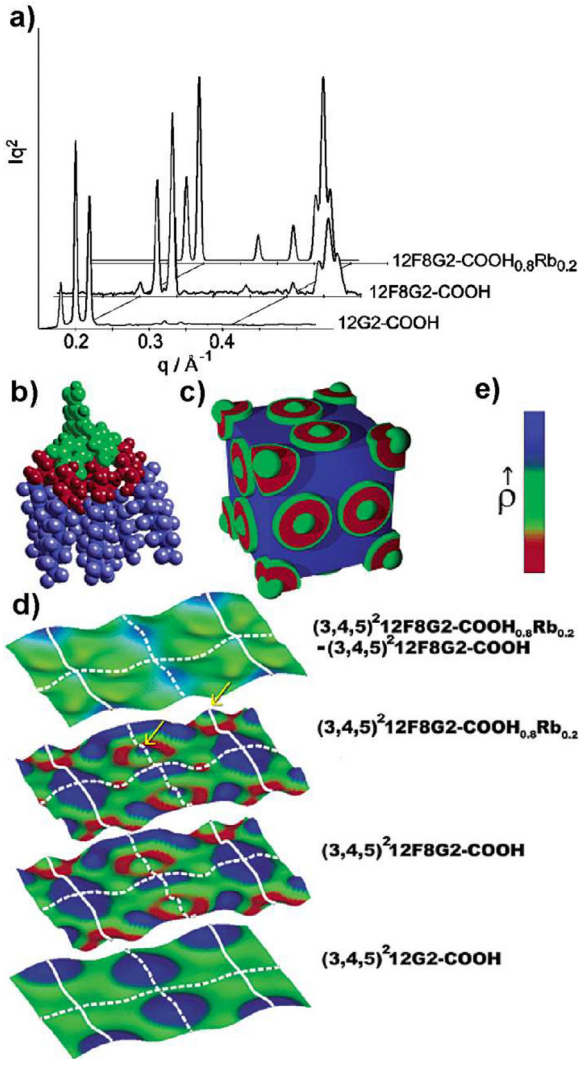


Fig. 24

(a) Small-angle X-ray powder diffractograms of the $Pm\bar{3}n$ phase. Expected and observed electron density (ρ) distributions. (b) Molecular model of **(3,4,5)²12F8G2-CO₂H** (c) Expected $\rho(x,y,z)$ distribution in a $Pm\bar{3}n$ unit cell of **(3,4,5)²12F8G2-CO₂H**according to the spheres model. (d) 2-Dimensional $\rho(x,y)$ maps of the $z = 0$ level. (e) Color coding. Adapted with permission from reference 511. Copyright 2003, American Chemical Society.

column diameter from their twin-fluorinated or hydrogenated homologues (Fig. 22) [494].

This is a very simple concept employed in the design and prediction of the columnar supramolecular assemblies with numerous applications in even more complex architectural design to be discussed in the following subchapters.

4.8 Self-organizable vesicular columns assembled from polymers dendronized with fluorinated-hydrogenated Janus dendrimers provide access to the first examples of reverse thermal actuators or reverse molecular machines

Top of Fig. 22 outlines all topologies generated from linear covalent and supramolecular polymers dendronized with self-assembling dendrons, twin dendrimers and Janus dendrimers [495]. Covalent polymers dendronized with twin dendrons self-organize polymers jacketed with bundles of supramolecular columns which can program by co-assembly new supramolecular columnar hexagonal superlattices (Fig. 22) [452,496,497]. Polymers dendronized with Janus fluorinated-hydrogenated dendrimers self-organize self-repairing vesicular assemblies (Fig. 22). Fibers of these supramolecular columns act as reverse thermal actuators or reverse molecular machines [495]. They contrast polymers dendronized with self-assembling dendrons that generate conventional molecular machines that expand on heating [126–128,443,498,499]. Janus fluorinated-hydrogenated dendrimers were also developed as promising ^{19}F-MRI traceable probes [500]. Fluorinated dendrimers and dendrons can be considered to act as a fluorous phase since their immiscibility to the hydrogenated part may mediate their unusual assembly and co-assembly [501]. Closely related examples of semifluorinated Janus dendrimers were also reported from other laboratories [502].

4.9 Transformation of a spherical supramolecular dendrimer into a pyramidal column by fluorination

Higher generation self-assembling dendrons and dendrimers or even minidendrons with strong interacting groups at their apex [444] self-assemble into spherical supramolecular dendrimers that self-organize a diversity of cubic periodic arrays or even liquid quasicrystals [15,213,215,450,503].

Self-organizable dendronized polymers also can form supramolecular spheres self-organizing similar periodic and quasiperiodic arrays [206–211,214,465,470,504,505]. We will not discuss them here [211,453,464,465,467–470,473,504–521].

Although their mechanism was elucidated by investigating rational libraries they are outside of the scope of this Perspective. A supramolecular orientational memory effect at the transition from spherical to columnar assemblies was also discovered to generate unprecedented columnar hexagonal arrangements of helical columns [522–525] and it will not be discussed here. However, we would just like to mention the spherical supramolecular dendrimers received substantial theoretical interest from many laboratories [526–528] and their periodic and quasiperiodic arrays were in the meantime discovered in block copolymers [529–532], surfactants [533–535], giant molecules [536,537], and became an active topic of research in self-organized soft matter. Fluorination of a second generation dendron that self-organizes spherical supramolecular dendrimers transforms it from sphere into a pyramidal column when the functional group at its apex is –$COOCH_3$ and therefore non-interacting (Fig. 23) [442]. However, when the –$COOCH_3$ group was transformed into a –COOH interacting group the self-organization of the fluorinated dendron into a supramolecular sphere was reestablished (Fig. 24) [511]. In order to clarify and elucidate this very interesting result, additional work on the reversibility of spherical to pyramidal assembly via fluorination is required.

4.10 Application of fluorination as an isomorphic replacement tool in the analysis of the cubic $Pm\bar{3}n$ or A15 Frank-Kasper phase generated from spherical supramolecular dendrimers

Two models were original propose when the $Pm\bar{3}n$ phase was discovered in potentially spherical supramolecular dendrimers

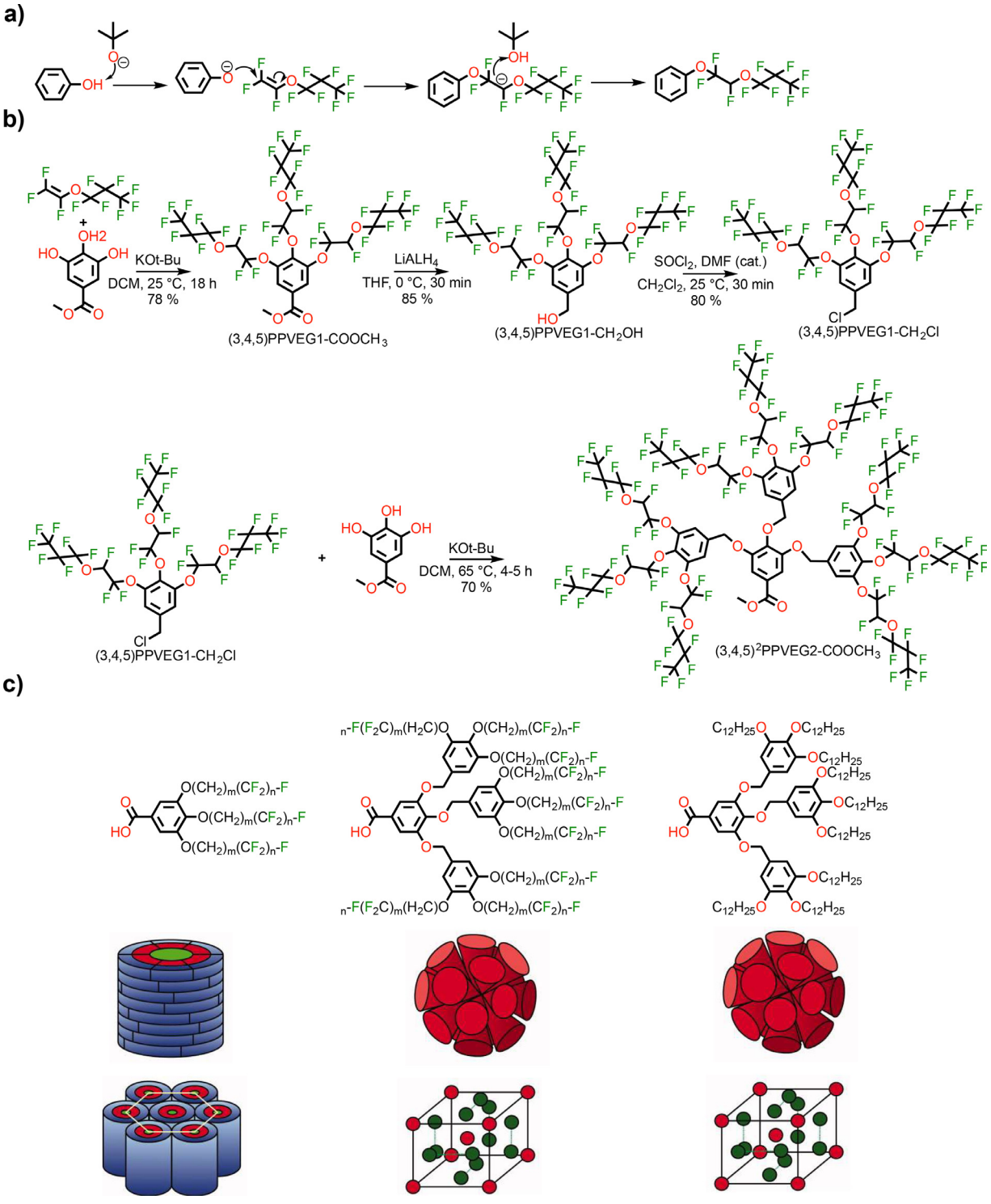


Fig. 25

(a) The mechanism of addition of phenol to perfluoropropyl vinyl ether. (b) Synthesis of the first generation dendritic benzyl chlorides (3,4,5)PPVEG1-CH_2Cl and second generation AB_3 (3,4,5)2PPVEG2-$COOCH_3$; c) comparison of the self-assembly of (3,4,5)RfG1-CO_2H, (3,4,5)2RfG2-CO_2H, and (3,4,5)212G2-CO_2H. Adapted with permission from reference 538. Copyright 2010, John Wiley & Sons, Inc.

[15]. One model was based on spherical supramolecular dendrimers and the second model was based on distorted supramolecular columns. No method to discriminate between these two models was available at the submission for publication time. One of the co-authors of the paper (VP) made the decision to favor the spherical assembly. The justification for this decision in front of all other co-authors was very simple. The paper will be rejected by the dendrimer community if we claim that high generation supramolecular dendrimers are not spherical. This idea was protected by a previous publication demonstrating that

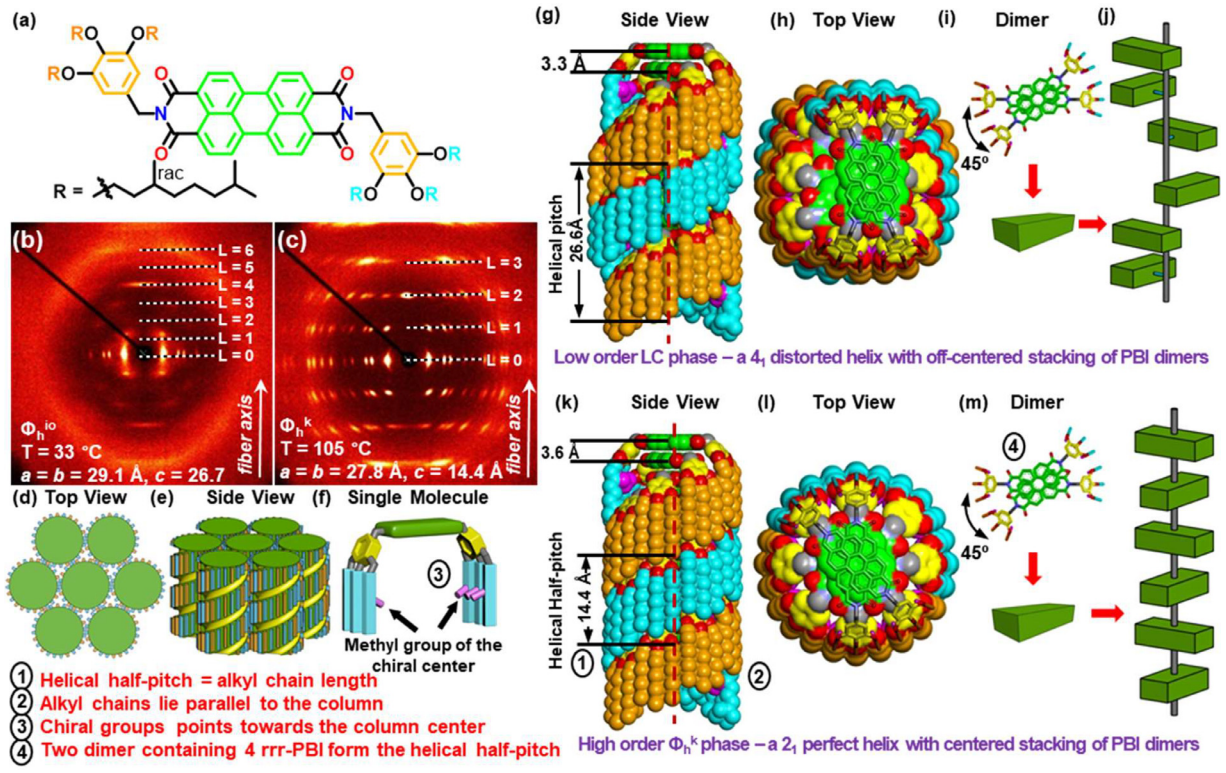


Fig. 26

Molecular structure of dendronized PBI (a); (b) wide-angle X-ray diffraction (WAXS) pattern in the Φ_h^{io} phase (b) and wide-angle X-ray diffraction (WAXS) pattern in Φ_h^{k} phase (c). The cogwheel model of helical self-organization accompanied by deracemization that disregards chirality (d to m). This figure was adapted and modified from reference 539.

"willow-like" dendrimers [354] fold into conventional nematic and smectic phases, but I (VP) considered that this was too early to convince the dendrimer community about the inability of high generation dendrimers to form non-spherical assemblies. The first definitive support for the spherical supramolecular dendrimers came from transmission electron microscopy [450]. The second evidence for the spherical supramolecular dendrimer came from the transformation of the apex group of the fluorinated dendrimer reported to transform the spherical shape into a pyramidal shape from $-COOCH_3$ to –COOH (Fig. 25). This transformation regenerated the X-ray diffraction of the $Pm\bar{3}n$ phase. The –COOH group at the apex was transformed into –COORb and therefore heavy atoms were available both at the periphery of the supramolecular dendron and at its apex. This allowed the combination of X-ray diffraction and electrondensity maps via isomorphic replacement to complement the transmission electron microscopy work and definitively demonstrate that the $Pm\bar{3}n$ phase is in fact an A15 Frank-Kasper phase generated from spherical supramolecular dendrimers (Fig. 25) [511]. The supramolecular spherical dendrimers are generated by maximizing their entropy by minimizing their area or surface (spherical supramolecular dendrimers received substantial theoretical interest from many laboratories [526,527]. Since due to their helicity perfluoroalkyl groups are more rigid than the hydrogenated alkyl groups they are not as suitable as the alkyl groups in maximizing entropy and therefore, they favour columnar assemblies. Additional work on this hypothesis is also required in order to support this reassembly concept by fluorination.

4.11 From amplified self-assembly of dendrons and dendrimers to their disassembly via an environmentally friendly perfluoropropyl alkyl group

Perfluoroalkyl groups larger than perfluorooctyl are biopersistent and bioaccummulative and therefore, are considered environmentally unfriendly although they are lipophilic and of biological interest for this physical property. Our laboratory elaborated a method to functionalize dendrons and dendrimers as well as Janus dendrimers by addition of their phenolates to perfluoropropyl vinyl ether (Fig. 26) [538]. Regardless of their generation number the resulting dendrons are liquid although they are a fluorous material. Therefore, this semifluorination provides a disassembly effect since it does not mediate the self-assembly in a supramolecular architecture. However, as it will be shown in additional subchapters, they mediate self-assembly in water. A disassembly followed by reassembly was previously designed in our laboratory for the deracemization process in the crystal state mediated by a columnar hexagonal crystal phase assembled from hat-shaped dendrimers [466]. This process transforms a syndiotactic or atactic supramolecular polymer into an isotactic or in other words a homochiral supramolecular polymer with numerous practical applications including in recycling. It is expected that this process can be perfected by engineering and design by fluorination.

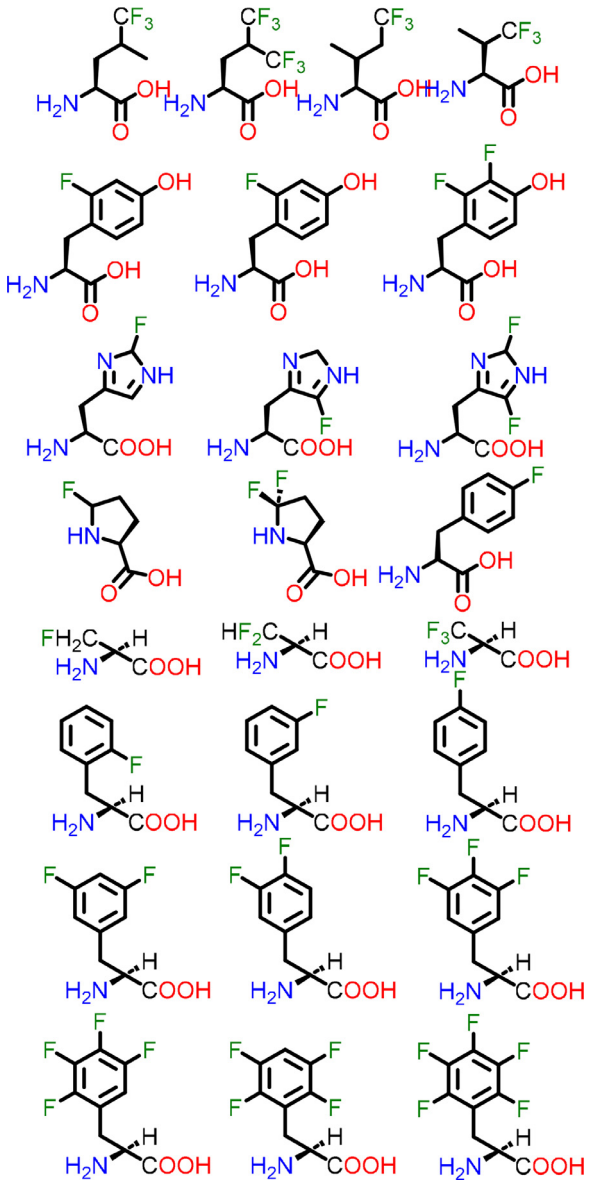


Fig. 27

Selected examples of fluorinated amino acids.

4.12 The cogwheel mechanism of self-assembly and the perfluorinated alkyl coat

Extensive screening through libraries of dendronized arylene bisimides including perylene bisimides (PBI) and naphthalene bisimides (NBI) via structural and retrostructural analysis [447,540–544] led to the discovery of the cogwheel mechanism [466] of helical self-organization that is accompanied by helical deracemization and therefore, disregards chirality. The cogwheel mechanism of helical self-organization is the second mechanism discovered in our laboratory that is accompanied by deracemization in the crystal state. The first one is based on a hat-shape conformation of the self-assembling dendrimer [466]. The cogwheel mechanism assemble helical columns with the alkyl groups of the dendron jacketing the column in a parallel way to the long axis of the column. The structural requirement for the cogwheel mechanism of self-assembly requires that the alkyl coat must have a length equal to half the helical pitch of the helical column [539] (Fig. 26). Any deviation from this strict rule decreases the rate of helical self-organization. A perfect agreement between the length of the alkyl coat and the half pitch of the helix was accomplished by sequence-defined self-assembling dendrons. This perfectly designed coat provides an extraordinary acceleration of the cogwheel helical self-organization [545,546]. While elucidating the molecular structure of the cogwheel coat we also screened through libraries of semifluorinated arylene bisimides in order to functionalize the coat while maintaining a thermodynamic control for its self-organization [547]. Rewardingly, it was discovered that the perfluoropropyl vinyl ether derived fluorinated alkyl group containing 6 atoms including one oxygen mediates the helical self-organization of dendronized PBI and of tetrachlorinated PBI (Cl_4PBI) via a cogwheel mechanism even if the helical coat does not contain the minimum of 8 carbons of its alkyl chain demanded in the original discovery [539]. This most probably may mean that the higher stiffness of the perfluoro alkyl helps to fill the space better than the nonfluorinated longer alkyl. This remarkable discovery illuminated the capabilities available for the design of functionalized helical cogwheel coats of interest for numerous potential applications.

5 Fluorine and fluorinated components in biological sciences

5.1 Fluorinated amino acids in proteins, peptides and peptoids

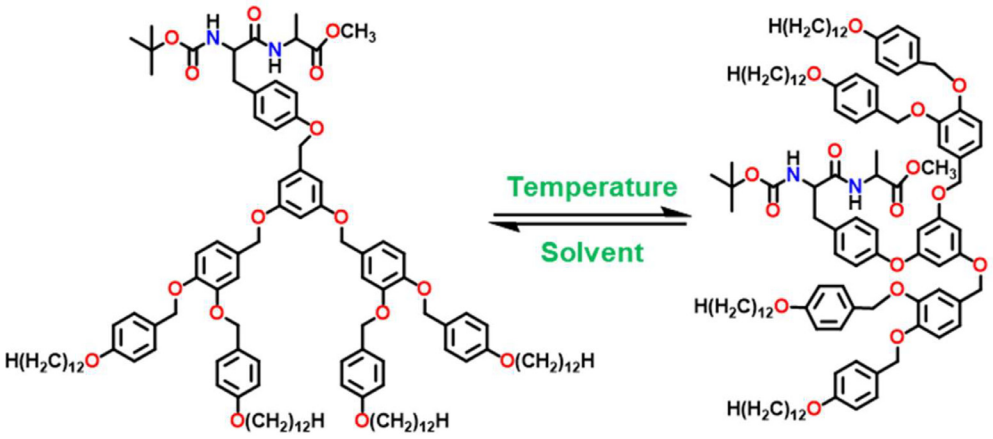
The development of fluorinated amino acids and their incorporation in peptides, proteins and peptoids is part of the general effort to incorporate non-canonical or unnatural amino acids into proteins in order to search for the limits of the synthetic capabilities of the living organism and expand it with the help of more than the 20 natural amino acids. The general endeavor of this synthetic effort is to provide an expansion of the genetic code beyond the 20 natural amino acids. According to our knowledge this effort started almost simultaneously and independently in in the late 1980th in the laboratories of Peter G. Schultz and David A. Tirrell (Fig. 27) [548–565].

This field expanded immediately in many laboratories around the world [566–576]. Soon after this field expanded from proteins and peptides to peptoids [577–587].

One general conclusion was obtained both for fluorinated peptides, proteins and peptoids. Fluorination enhances the hydrophobic effect and through it increases the rate of folding and the stability of the folded proteins. A brief report the current status of on the expansion of the genetic code was recently published [588]. This is a very important combination of effects expected to provide a diversity of new functions not only in proteins but also in peptides, peptoids and in their conjugates.

5.2 Self-assembly of amphiphilic dendritic dipeptides into aquaporin mimics

The amphiphilic dendritic dipeptide (4-3,4-3,5)12G2-CH_2-Boc-L-Tyr-L-Ala-OMe was designed to self-assemble in bulk and in the hydrophobic bilayer of a phospholipid vesicle into a helical porous cylinder [589] that mimics the structure



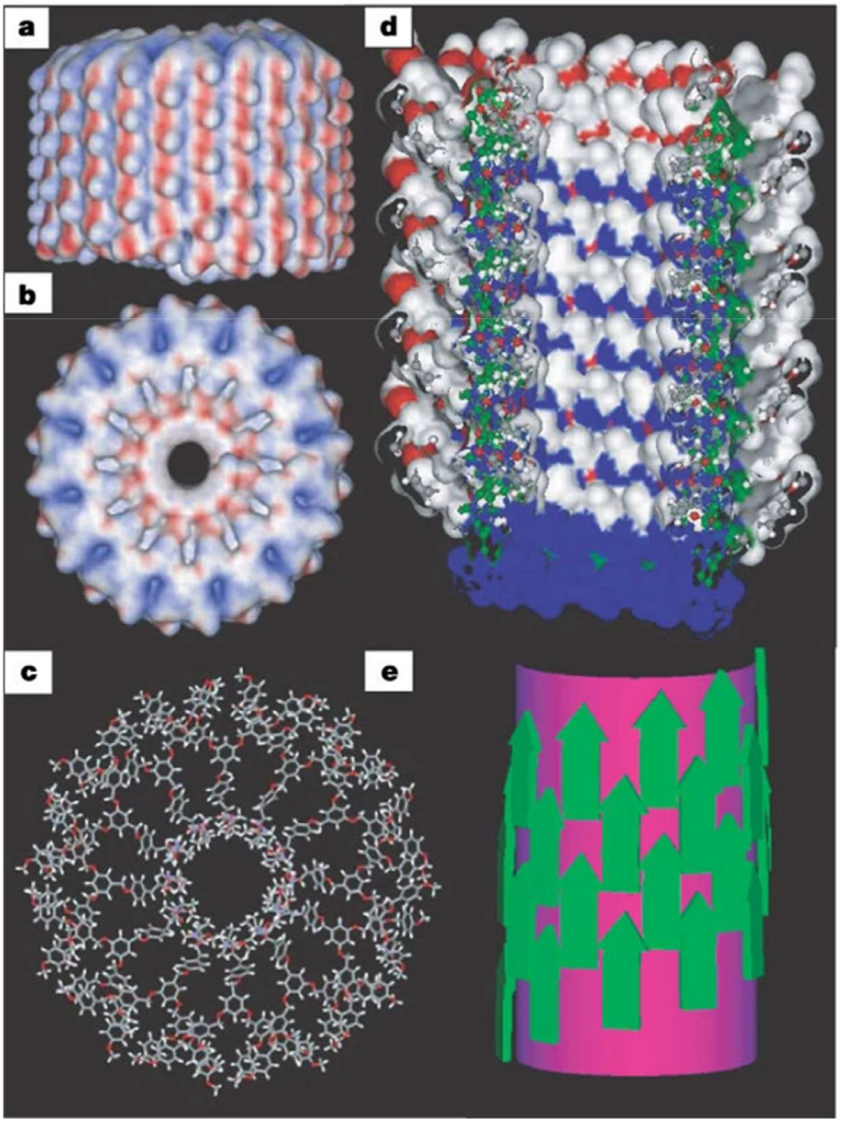


Fig. 28

Trans-tapered low-temperature (top-left), and *cis*-globular high-temperature (top-right), conformers of the l-l stereoisomer of (4-3,4-3,5)12G2-CH_2-Boc-l-Tyr-l-Ala-OMe and (4-3,4-3,5)12G2-CH_2-Boc-l-Tyr-d-Ala-OMe. **a**, Side view of the right-handed supramolecular column. **b**, Top view of **a. c**, Top view of a single porous column layer. **d**, Cross-section through the hydrophobic pore (without dendrons) showing its β-barrel structure (CH_3 of Ala is white, CH_3 of Boc are blue, O is red, C-N of dipeptide are green, aromatic groups are grey) assembled from the β-helical dipeptides. **e**, Schematic model for the self-assembly of the dipeptidic β-barrel pore. The green arrows indicate the dipeptides. The Figure was adapted and modified from reference 603.

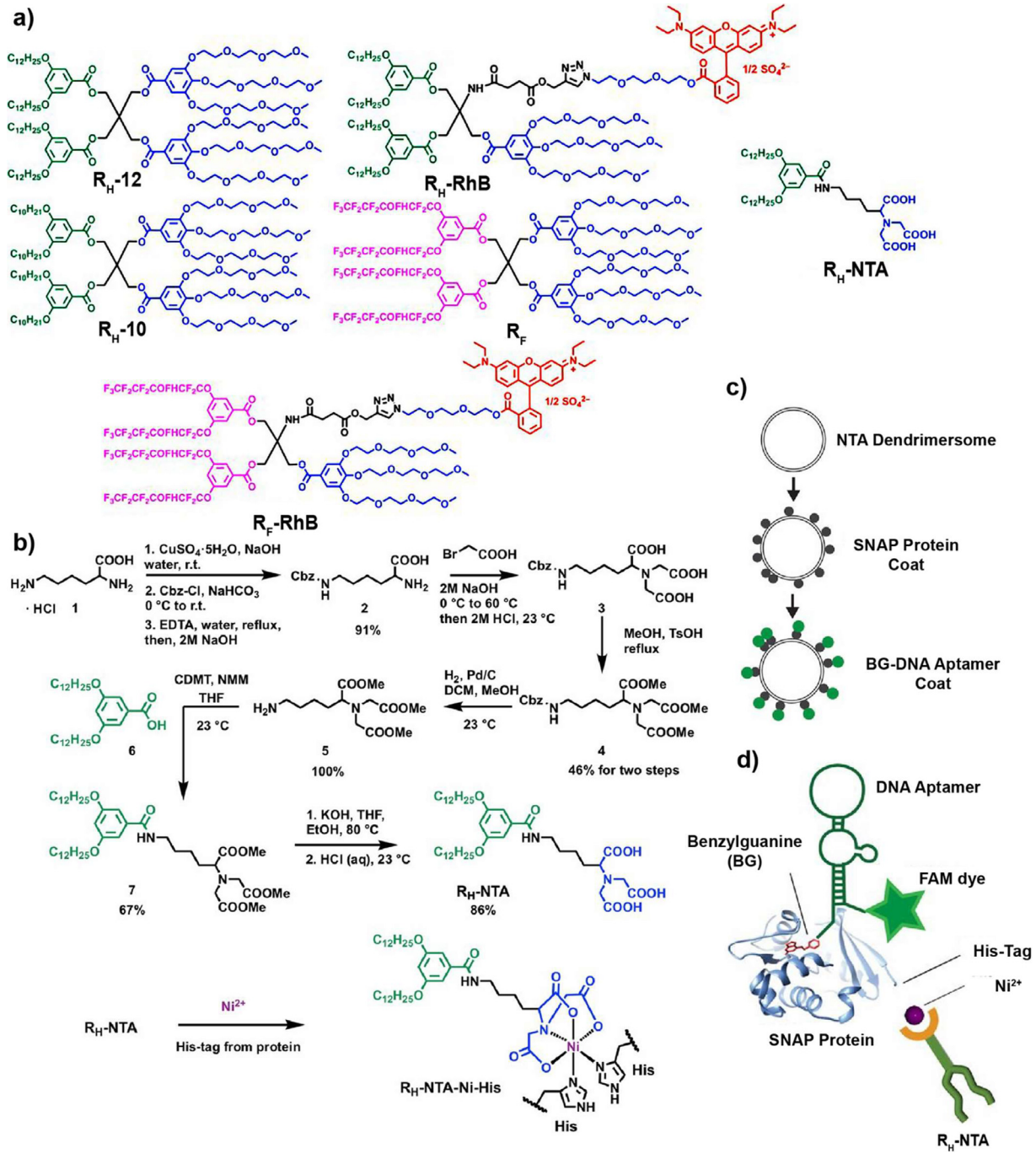


Fig. 29

Chemical structures of amphiphilic Janus dendrimers used for vesicle assembly, fluorescent labeling, and chelating. b) Synthesis of a Janus dendrimer conjugated to a nitrilotriacetic acid (NTA) ligand (RH-NTA) and scheme of RH-NTA binding to histidine (His) residues from proteins. c) Schematic showing layering of a protein and DNA coat to dendrimersome vesicle. d) His-SNAP proteins binds to RH-NTA to form the initial protein layer. Adapted with permission from reference 622. Copyright 2017, National Academy of Sciences of the United States of America (NAS).

of the transmembrane protein Aquaporin [589,590]. Selective transport for water but not for alkali metal ions and halides was demonstrated for this simple Aquaporin mimic [591]. The principles of self-assembly of this dendritic dipeptide were investigated [81,430,472,592–598] and will not be repeated here. The single handed helical confomation and its hydrophobic channel seems to be responsible for its water transport selectivity and activity (Fig. 28). This work inspired laboratories from around the world to develop related supramolecular assemblies for selective water transport [599–602] and most recent results demonstrated higher rate of water transport than even Aquaporin and the same selectivity. The question we have is the following. If fluorination stabilized the folded structure of proteins and enhances their hydrophobic effect, would replacing the $-CH_3$

group from alanine from the dendritic dipeptide (4-3,4-3,5)12G2-CH_2-Boc-L-Tyr-L-Ala-OMe with $-CF_3$ group via trifluoroalanine provide the most selective, active and the simplest to synthesize ionic channel for water purification? The answer to this question depends on the ability of the trifluoro methyl part of alanine from the fluorinated dipeptide to replace the nonfluorinated methyl group in exactly the same part of the supramolecular dendritic dipeptide channel (Fig. 28) [603,591]. This question deserves to be answered by performiong this experiment.

5.3 Semifluorinated amphiphilic Janus dendrimers as models of biological membranes including for cell fusion and fission

Amphiphilic Janus dendrimers (IDs) were discovered in 2010 in our laboratory [391,604–613]. They provide very simple amphiphilic molecules that generate access to programmed vesicles, named dendrimersomes, with monodisperse molar mass distribution and predicted dimensions by simple injection of their ethanol solution in water or in buffer. Janus glycodendrimers (JGDs) including sequence-defined JGDs assembling glycodendrimersomes were subsequently elaborated [614–626] and expanded in one of the most successful mimics of the glycan of biological membranes. Janus dendrimers and Janus glycodendrimers co-assemble with both bacterial and human cells generating mixed cell with numerous potential applications [606,607,627,628]. Dendrimersomes assembled from Janus dendrimers engulf living bacteria by endocythosis [629] providing access to biomedical applications while co-assembly of liposomes, dendrimersomes and polymersomes with JDs conjugated to mono- and tris-nitrilotriacetic acid (NTA and trisNTA) enhances protein recruitment [630]. They are also of great interest in other areas of chemical biology [631]. Aside from entirely hydrogenated JDs and JGDs, semifluorinated and hybrid semifluorinated JDs and JGDs were also elaborated (Fig. 29). The most suitable fluorinated fragment for this construction is based on the perfluoropropyl vinyl ether discussed in subchapter 4.9. Due to the fluorophobic effect of the fluorinated JD self-sorting and co-assembly of fluorinated, hydrogenated and hybrid JDs into dendrimersomes were observed [632]. JDs co-assembled from fluorinated, hydrogenated and hybris JDs were elaborated as models for cell fusion and fission [633]. Semifluorinated JDs were also shown to encapsulate hydrophobic components in dendrimersomes and also decorate their surface with proteins and nucleic acids (Fig. 29) [622]. Semifluorinated JDs exhibit a lamellar to sponge phase transition [634].

These experiments demonstrate the remarkable potential of semifluorinated JDs and JGDs in numerous biomedical applications and we expect that they might also impact the field of mRNA delivery with one component sequence defined ionizable amine amphiphilic Janus dendrimers (IAJDs) that were recently elaborated in our laboratory [635–640].

6 Conclusions

This Perspective is a very personalized view of the research involving completely different, but many times complementary areas of fluorine chemistry performed mostly in our laboratory. This is not a review article but a Perspective and therefore, contains only very few mentions of related research performed in other laboratories. We apologize for being very restricted in our discussions and for missing excellent work perfomed in numerous other laboratories. Representative research that impacted this field mostly during this century and was performed in other laboratories was briefly discussed in the Introduction chapter. Some additional laboratories influential in this area are mentioned here [641–661]. Nevertheless, we hope that this Perspective, wich attempts to cover even unpublished events that fovored success and failures, provides a very broad view on the unlimited capabilities of fluorine chemistry via a multitude of methodologies covering aspects from organic, molecular, macromolecular, supramolecular and biological sciences and providing a mechanism to bridge in between all these disciplines, with a single element, Fluorine, in order to generate functions. This Perspective is based on Invited Lectures invited by Pierangelo Metrangolo and Giuseppe Resnati and presented at the International Symposium of Fluorine Chemistry in Como, Italy, August 23-28, 2015 and by Veronique Gouverneur and presented during the International Symposium on Fluorine Chemistry in Oxford, UK, July 22-27, 2018. The contents of these lectures were never published in the Proceedings of these International Symposia but provided the outline of this Perspective. I (VP) thank again the organizers of these International Symposia for their invitations. Many generations of very dedicated, hard working and gifted high school, undergraduate and graduate students, postdocs and research scholars from all over the world were involved in this work and I would like to use this opportunity to thank to all of them for their excellent contributions to the work presented here and also for creating the most multinational-international and challenging scientific environment in my (VP) laboratories at Case Western Reserve University and at the University of Pennsylvania.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.giant.2023.100193.

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