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Formation of perfluorinated polyphenylenes by multiple pentafluorophenylation using $C_6F_5Si(CH_3)_3$

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ABSTRACT

Pentafluorophenylation of perfluoroarenes with $C_6F_5Si(CH_3)_3$ was investigated by using NMR and MALDI–TOF–MS techniques. Successive multiple pentafluorophenylation easily occurred not only on the *para*-position but also on the *ortho*-positions to provide perfluorinated *p*-phenylene and *m*-phenylene compounds. The perfluoroarenes having electron-withdrawing substituents provided oligo- to poly-(phenylene)s depending on the added amounts of $C_6F_5Si(CH_3)_3$, while the perfluoroarenes having electron-donor substituents gave $H(C_6F_4)_nF$ polymers produced from C_6F_5H, which was the decomposed product of $C_6F_5Si(CH_3)_3$.

1. Introduction

Polyphenylene compounds are known to be conductive polymers, as are other π-conjugated oligomers, such as polyacetylene, polypyrrole, polythiophene, and polyaniline. Such conductive polymers are expected to find application in organic electronics for controlling electronic functions by molecular and supermolecular complexity [1]. For example, hybrid nanocomposites with a π-conjugated unit have been investigated for opto-electronic devices [2]. Research on liquid-crystalline conjugated polymers has been reported, focusing on ferroelectric and photoresponsive materials [3]. In recent years, various conductive polymers have been investigated for use in organic electroluminescence devices [4]. Because of the strong electronegativity of a fluorine atom, introduction of fluorine atoms into materials is expected to improve their electronic properties. The effect of fluorine atoms on electronic and opto-electronic materials has been reviewed for poly(phenylenevinylene)s, poly(phenyleneethylene)s, polythiophenes, and polyphenylenes [5]. Perfluorinated polyphenylene compounds in particular have higher electronegativity and durability. Therefore, perfluorinated oligo-(*p*-phenylene)s [6] and phenylene dendrimers [7] could be used not only as the electron-transport layer but also as an *n*-type organic semiconductor. Moreover, in a recent study of materials having perfluoroaryl units aimed at electronic materials, the synthesis of poly(phenylene ethylene)s with aryl-perfluoroaryl units [8] and polyphenylene dendrimers with pentafluorophenyl units [9] was reported.

Recent years have seen dramatic developments in synthesis of polyfluoro aromatics as well as in properties [10]. The polyfluoro aromatics have been also investigated in the view of the C–F bond activation [11]. For synthetic studies on the perfluorinated polyphenylenes mentioned above, the organocopper cross-coupling method has often been used [6,7]; however, this method is a step-wise reaction and needs bromide and organocopper precursors that are difficult to prepare. As a reagent for introducing the C_6F_5 group into perfluoroarenes, substituted perfluoro-(biphenyl) and -(terphenyl) compounds were obtained in a reaction of C_6F_5Li at −78 °C [12]. A GC-MS study revealed that the reaction of perfluoroarenes with C_6F_5Li at 25 °C after slowly warming from −78 °C gave mixtures of oligo(phenylene)s up to quinquephenyl [13]. Perfluoro-(*p*-terphenyl) and -(*p*-quaterphenyl) were also prepared by the reaction of nonafluorobiphenyl with C_6F_5MgBr [14]. It was reported that decomposition of C_6F_5MgBr in refluxing THF yielded high molecular weight (up to 15,000) polymer [15]. The reactions of these organometallics, C_6F_5Li and C_6F_5MgBr, required inert conditions and/or controlling the reaction temperature. A silicon-based reagent for pentafluorophenylation, $(C_6F_5)Si(CH_3)_3$, was prepared by the reaction of C_6F_5Br, $ClSi(CH_3)_3$, and $P[N(CH_3)_2]_3$ [16]. The pentafluorophenylation using $(C_6F_5)Si(CH_3)_3$ could be easily performed without any special equipment. We have previously demonstrated a useful pentafluorophenylating reagent for perfluorinated carbonyl compounds [17] and perfluorinated 3,6-dihydro-2*H*-1,4-oxazine [18]. In the

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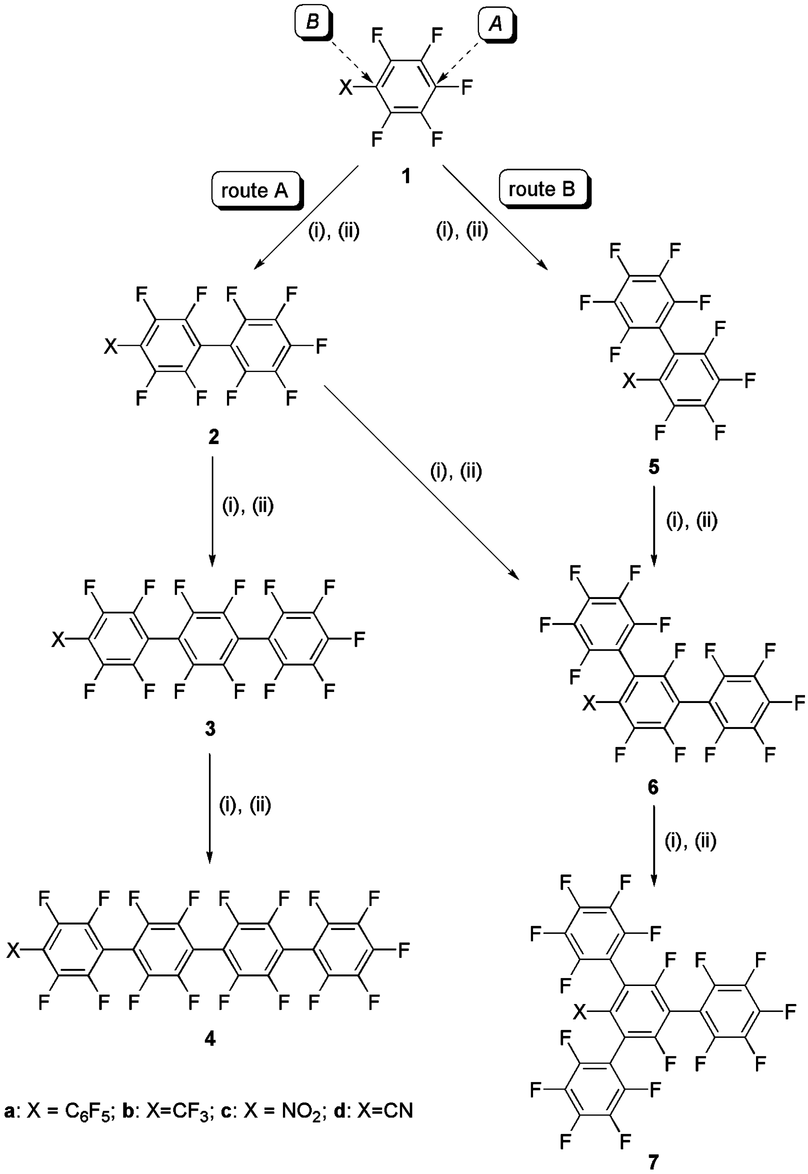


Scheme 1. (i) $C_6F_5Si(CH_3)_3$/cat. KHF_2/DMF; (ii) $-F^-$.

reaction of the latter compound with $(C_6F_5)Si(CH_3)_3$, multiple pentafluorophenylation at the *para*-positions occurred to provide nonafluorobiphenylyl derivatives, the structures of which were determined by NMR and DFT analyses. In the present study, we target several perfluoroarenes as possible precursors of perfluoro(polyphenylene)s and furthermore investigate a substituent effect in the aromatic ring for the multiple pentafluorophenylation of $(C_6F_5)Si(CH_3)_3$, mainly using NMR and the MALDI–TOF–MS techniques.

2. Results and discussion

In our pentafluorophenylation method using $C_6F_5Si(CH_3)_3$ described herein, a straightforward reaction procedure was used which differed from the previously reported unstable organometallics, C_6F_5Li and C_6F_5MgBr. The pentafluorophenylation with $C_6F_5Si(CH_3)_3$ was performed in a Teflon® vessel at ambient temperature without an inert atmosphere. The reactions usually proceeded as a two layer mixture, thus pentafluorophenylated products were easily separated from the lower layer in most cases. As the first examination, several perfluoroarenes having an electron-withdrawing substituent were reacted with equimolar to several equivalents of $C_6F_5Si(CH_3)_3$ (Scheme 1). The results of reactions of these perfluoroarenes with $C_6F_5Si(CH_3)_3$ are summarized in Table 1. The use of 1.1 equiv. against decafluorobiphenyl (**1a**) provided pentafluorophenyl derivative **2a** as the main product, accompanied by nonafluorobiphenyl derivative **3a** *via* successive pentafluorophenylation against the *para*-position of **2a** (Table 1, Entry 1). Furthermore, multiple attack of $C_6F_5Si(CH_3)_3$ against the terminal positions occurred for **3a** to provide tridecafluoroterphenyl derivative **4a** (Table 1, Entries 2 and 3). Although these perfluorinated oligo(phenylene)s **2a**–**4a** have been reported previously [6,14], detailed assignments of ^{19}F NMR peaks have not been established. We assigned the ^{19}F NMR peaks of linear perfluoroaryl compound **2a**–**4a** using a ^{19}F–^{19}F homodecoupling method and employed the assignments of our previous study [18]. In similar fashion to **1a**, octafluorotoluene (**1b**) provided linear perfluoroaryl derivatives **2b**, **3b**, and **4b** by the terminal position attack of $C_6F_5Si(CH_3)_3$ (Table 1, Entries 4 and 5). In the ^{19}F NMR spectra, although CF_3 groups of the linear perfluoroaryl compound **2a**–**4a** appeared as triplet peaks coupled with the *ortho*-fluorines, a weak doublet CF_3 peak appeared in the

Table 1
Pentafluorophenylation by the reaction of perfluoroaromatics **1** with trimethyl(pentafluorophenyl)silane.

Entry	Aromatics (mmol)	$C_6F_5Si(CH_3)_3$ (mmol)	KF (mmol)	Yield (%)[a]
1	**1a** (1.00)	1.09	0.19	**2a** (47), **3a** (19)
2	**1a** (0.72)	1.44	0.14	**2a** (14), **3a** (44), **4a** (15)
3	**1a** (0.65)	1.95	0.13	**3a** (19), **4a** (73)
4	**1b** (1.02)	1.10	0.19	**2b** (55), **3b** (19)
5	**1b** (1.05)	2.16	0.19	**2b** (32), **3b** (32), **4b** (9)[b]
6	**1c** (1.03)	1.14	0.19	**2c** (67), **6c** (5)
7	**1c** (0.73)	1.49	0.15	**2c** (63), **6c** (20), **7c** (9)
8	**1d** (1.03)	1.11	0.19	**2d** (67), **5d** (6), **6d** (12), **7d**(2)
9	**1d** (0.78)	1.57	0.15	**2d** (49), **6d** (21), **7d** (14)

[a] Determined by ^{19}F NMR.

[b] The CF_3 peaks indicated possible formation of trace amounts of **5b** and **6b**.

^{19}F NMR spectrum of the reaction mixture. Considering the coupling pattern of the *ortho*-substituted CF_3 group of the aromatic ring [19], trace amounts of **5b** and **6b** possibly formed in the reaction with 2.0 equiv. against **1b** by the *ortho*-position attack of $C_6F_5Si(CH_3)_3$ (Table 1, Entry 5), but the ^{19}F NMR peaks about **5b** and **6b** could not be completely assigned because several peaks overlapped with those of **2b**–**4b**.

In the reaction of pentafluoronitrobenzene (**1c**), although $C_6F_5Si(CH_3)_3$ also attacked on the *para*-position at first (Table 1, Entry 6), successive $C_6F_5Si(CH_3)_3$ attack occurred at the *ortho*-fluorine (the 3,5-positions) predominantly over the substitution at the terminal position (the 4′-position) to provide a bent biphenyl derivative **6c** and a branched terphenyl derivative **7c** (Table 1, Entry 7). In the case of pentafluorobenzonitrile (**1d**), the *ortho*-fluorine attack of $C_6F_5Si(CH_3)_3$ occurred more easily than for the other perfluoroarenes to provide perfluoro-(2-cyano-[1,1′]biphe-]biphenyl) (**5d**) as a side-product (Table 1, Entry 8) and to produce a bent biphenyl derivative **6d** and a branched terphenyl derivative **7d** similarly to **1c** (Table 1, Entry 9). The bent biphenyls **6c** and **6d** had characteristic ^{19}F NMR peaks at *ca.* −110 ppm assigned as the 2′-F and from −123 ppm to −125 ppm as the 6′-F. On the other hand, the ^{19}F NMR peaks of the branched terphenyls **7c** and **7d** were symmetrical and characteristic at *ca.* −100 ppm assigned as the 2′,6′-F. The tendency of the *ortho*-fluorine attack could be explained by the steric hindrance of the electron-withdrawing substituent, which more significantly influences the *ortho*-positions than the *meta*- and *para*-positions. Thus, because of larger steric hindrance of the nitro group than the cyano group, the nitro group suppressed the *ortho*-fluorine attack to a greater extent, resulting in reduced formation of *ortho*-substituted products. Furthermore, the perfluoroarens **1a** and **1b**, which have much larger substituents, C_6F_5 and CF_3, produced trace amounts of the *ortho*-substituted products, if any. The tendency of orientation as dominant at the para-position was also reported in several perfluoro aromatics [11].

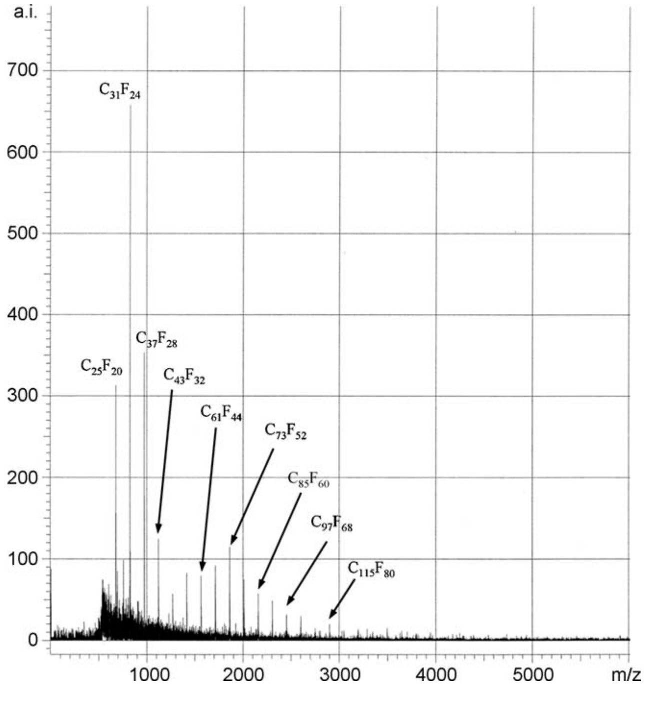
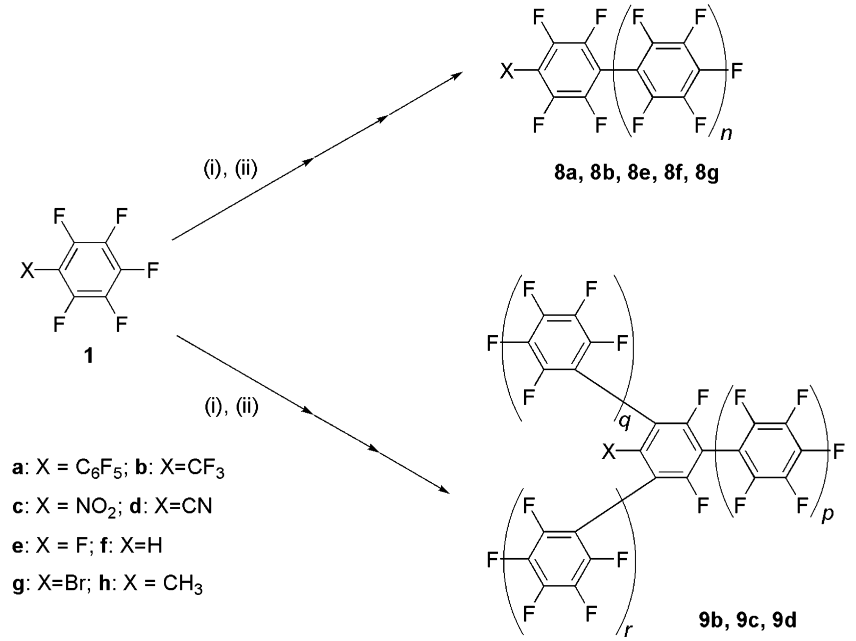


Fig. 1. MALDI–TOF mass spectra of the reaction products by the reaction of **1b** with 10 equiv. of $C_6F_5Si(CH_3)_3$.

As shown above, the successive pentafluorophenylation proceeded depending on the amount of $C_6F_5Si(CH_3)_3$ to provide the linear perfluoro(oligophenylene) by the attack on the terminal fluorine and/or the branched perfluoro(oligophenylene) by the attack on both *ortho*- and *para*-fluorines. In order to study the details and limitation of this successive pentafluorophenylation, we examined reactions of perfluoroarenes with an excess amount (10 equiv.) of $C_6F_5Si(CH_3)_3$ (Scheme 2). Yields and the mean numbers of the introduced C_6F_5 groups were determined by MALDI–TOF–MS analysis and are presented in Table 2. In the case of using 10 equiv. of $C_6F_5Si(CH_3)_3$ to **1a** (Table 2, Entry 1), the attack of $C_6F_5Si(CH_3)_3$ on the terminal fluorine proceeded to give linear perfluoro(polyphenylene) **8a**, the structure of which was determined by ^{19}F NMR and MALDI–TOF–MS analyses as follows. The ^{19}F NMR peaks were classified into three aromatic fluorine groups: the terminal fluorine at *ca.* −150 ppm; the fluorines next to the terminal fluorine at *ca.* −160 ppm; and the remaining interior fluorines from −136 ppm to −138 ppm. The TOF–MS peaks showed two series such as $C_{6m}F_{4m+2}$ (the parent peak) and $C_{6m}F_{4m+1}$ (the cleavage peak of fluorine) and the mean m value was about 5.3; that is, the number of introduced C_6F_5 groups (n) was about 3.3. On the other hand, in the reactions of **1c** and **1d** with 10 equiv. of $C_6F_5Si(CH_3)_3$ (Table 2, Entries 3 and 4), results of ^{19}F NMR and MALDI–TOF–MS analyses indicated the formation of branched perfluoro(polyphenylene)s **9c** and **9d**, which also had characteristic 4′,6′-F peaks in the range from −98 ppm to −110 ppm in the ^{19}F NMR spectra, similar to **7c** and **7d**. The mean numbers of the introduced C_6F_5 groups into **1c** and **1d** estimated by the TOF–MS were from about twice to three times (**9c**: $p + q + r = 9.5$; **9d**: $p + q + r = 8.3$) that of **1a**. If a highly branched polymer, such as a dendrimer, formed in the pentafluorophenylation, the peak intensity of the region from −98 ppm to −110 ppm would increase to a level similar to that from −136 ppm to −138 ppm [7]. In the cases under study, such increment of the peak intensity was not observed, thus, the possibility of forming the highly branched polymer appears to be low. In the reactions of **1b** with 10 equiv. of $C_6F_5Si(CH_3)_3$ (Table 2, Entry 2), TOF–MS peaks of the reaction products were distributed in a diphasic pattern as shown in Fig. 1. In the ^{19}F NMR spectra of the reaction products, there appeared a triplet and a doublet CF_3 peak. Together with the TOF–MS data analysis, it was considered



Scheme 2. (i) $C_6F_5Si(CH_3)_3$/cat. KHF_2/DMF; (ii) $-F^-$.

Table 2
Formation of perfluoroaryl oligomers by the reaction of perfluoroaromatics **1** with trimethyl(pentafluorophenyl)silane.

Entry	Aromatics (mg)	$C_6F_5Si(CH_3)_3$ [mg (mol equiv.)]	Yield (mg)	Formed polyphenylenes (the mean number of C_6F_5 groups introduced)[a]
1	**1a** (78)	574 (10)	421	**8a** ($n = 3.3$)
2	**1b** (56)	567 (10)	160	**8b** ($n = 4.3$), **9b** ($p + q + r = 11.6$)
3	**1c** (45)	512 (10)	423	**9c** ($p + q + r = 9.5$)
4	**1d** (49)	610 (10)	498	**9d** ($p + q + r = 8.7$)
5	**1e** (46)	598 (10)	551	**8e** ($n = 4.4$), **8f** ($n = 4.6$)
6	**1f** (172)	275 (1.1)	176	**8f** ($n = 4.7$)
7	**1g** (247)	266 (1.1)	154	**8f** ($n = 4.7$), **8g** ($n = 4.9$)
8	**1h** (180)	262 (1.1)	212	**8f** ($n = 4.4$)

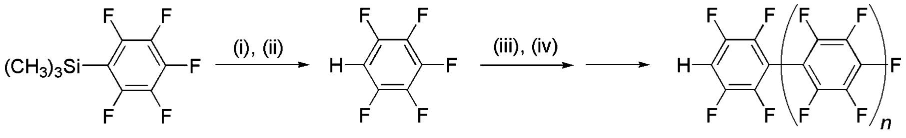
[a] Determined by MALDI–TOF–MS analysis.

that the former corresponded to **8b** ($n = 4.3$) and the latter corresponded to **9b** ($p + q + r = 11.6$), but their product distributions probably overlapped and an accurate analysis method that is applicable for such polyphenylenes will be explored in future work.

Collectively, these perfluoroarenes **1a**–**1d** having electron-withdrawing substituents provided linear and/or branched perfluoro(polyphenylene)s by the reaction of excess amounts of $C_6F_5Si(CH_3)_3$. These results showed that the introduction of a C_6F_5 group into the mono-ring (C_6F_5X type) could occur both at the *para*-position and at the *ortho*-positions, whereas the introduction of a C_6F_5 group into the connected ring ($C_6F_5C_6F_4X$ type) could occur at the terminal position, most obviously in the case of decafluorobiphenyl (**1a**). This is because the introduction of the C_6F_5 groups at 2,6- and 2′,6′-positions (the *ortho*-like positions) of the $C_6F_5C_6F_5$ ring is disadvantageous in regard to the steric effect, and the introduction of the C_6F_5 groups at 3,5- and 3′,5′-positions (the *meta*-like positions) of the $C_6F_5C_6F_5$ ring is disadvantageous in regard to the inductive effect. Consequently, the perfluorinated poly(*m*-phenylene)s were obtained without formation of any dendrimers.

In order to further investigate the inductive effect of the substituent upon the successive pentafluorophenylation, reactions of other perfluoroarenes, especially those having less electronegative substituents, were examined. In the case of pentafluorobenzene (**1f**) (Table 2, Entry 6), even using 1.1 equiv. of $C_6F_5Si(CH_3)_3$, the successive introduction of C_6F_5 groups at the terminal positions gave **8f** ($n = 4.7$). Although hexafluorobenzene (**1e**) is the same kind of compound as **1a**, an unexpected product **8f** was obtained in addition to **8e** by the reaction of **1e** with 10 equiv. of $C_6F_5Si(CH_3)_3$ (Table 2, Entry 5). It is considered that hydrogenation of $C_6F_5Si(CH_3)_3$ resulting in formation of **1f** caused this additional perfluoro(polyphenylene) **8f** shown in Scheme 3. The hydrogenation of $C_6F_5Si(CH_3)_3$ also occurred in the reaction of bromopentafluorobenzene (**1g**) (Table 2, Entry 7) to provide a mixture of **8f** (from the decomposition product **1f**) and **8g** (from the starting material **1g**); the TOF–MS data of the reaction mixture are shown in Fig. 2. In reaction of 2,3,4,5,6-pentafluorotoluene (**1h**) with $C_6F_5Si(CH_3)_3$ (Table 2, Entry 8), the hydrogenation of $C_6F_5Si(CH_3)_3$ predominated over the pentafluorophenylation; **8f** was only a polymerized product without formation of **8h**.

To summarize the substituent effect on multiple pentafluorophenylation, when the electronegativity of the substituent in the perfluoroarene was weaker, the hydrogenation of $C_6F_5Si(CH_3)_3$ predominated to provide large amounts of **8f**. The formation of **8f** from $C_6F_5Si(CH_3)_3$ was also reported in the attempted synthesis of $[(CH_3)_3Si(C_6F_5)_2]^-$ anion [20]. In this previous report, even using a fluoride ion source having no hydrogen atoms, such as CsF, formation of **8f** could not be prevented. Thus, in both the previously reported results and in the cases presented here, it is considered that adventitious water molecules attacked the $C_6F_5Si(CH_3)_3$ in the presence of a catalytic amount of fluoride anion before the reaction of perfluoroarenes with $C_6F_5Si(CH_3)_3$; then, the hydrogenation product C_6F_5H reacted with another



1f **8f**

Scheme 3. (i) cat. KHF_2/DMF; (ii) $-FSi(CH_3)_3$; (iii) $C_6F_5Si(CH_3)_3$/cat. KHF_2/DMF; (iv) $-F^-$.

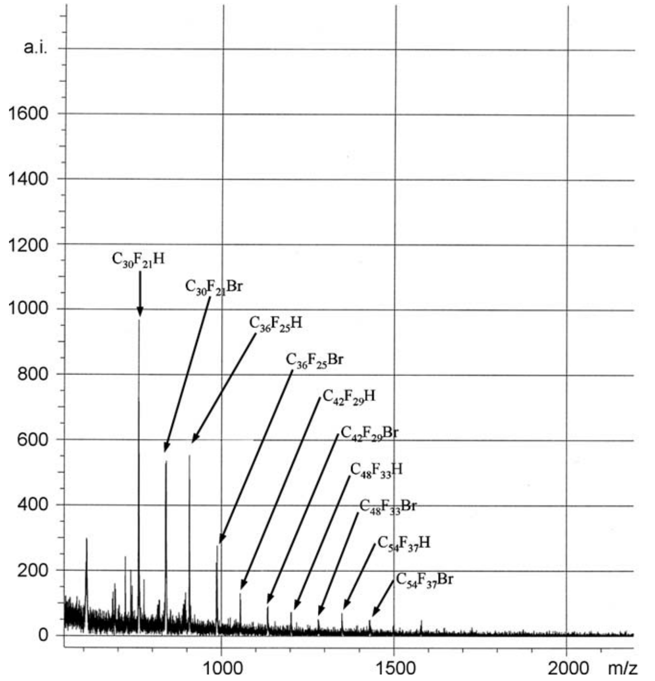


Fig. 2. MALDI–TOF mass spectra of the reaction products by the reaction of **1g** with 1.1 equiv. of $C_6F_5Si(CH_3)_3$.

molecule of $C_6F_5Si(CH_3)_3$ resulting in the formation of p-$H(C_6F_4)_nF$ (**8f**). The electronegative substituent stabilizes the addition–elimination intermediate proposed in our previous report [18]; therefore, the intermediate easily formed before the hydrogenation of $C_6F_5Si(CH_3)_3$ to prevent the formation of C_6F_5H and p-$H(C_6F_4)_nF$.

3. Conclusions

In the reaction of perfluoroarenes having an electronegative substituent with $C_6F_5Si(CH_3)_3$, multiple pentafluorophenylation at the *para*-position and the *ortho*-positions of the C_6F_5 ring are introduced. By reactions with up to 3 equiv. of $C_6F_5Si(CH_3)_3$, only linear perfluorinated oligophenylenes were obtained from $C_6F_5C_6F_5$, while perfluorinated bent and branched oligophenylenes were mainly obtained from $C_6F_5NO_2$ and C_6F_5CN. Further multiple pentafluorophenylation occurred by the addition of 10 equiv. of $C_6F_5Si(CH_3)_3$; similar to the tendency observed at lesser amounts, perfluoronated poly(p-phenylene)s were obtained from $C_6F_5C_6F_5$, whereas perfluoronated poly(m-phenylene)s were obtained from $C_6F_5NO_2$ and C_6F_5CN. The regioselectivity of $C_6F_5CF_3$ was somewhat lower; both perfluoronated poly(p-phenylene)s and poly(m-phenylene)s were obtained using 10 equiv. of $C_6F_5Si(CH_3)_3$. In cases of perfluoroarenes having a less electronegative substituent, hydrogenation of $C_6F_5Si(CH_3)_3$ competitively occurred to provide C_6F_5H, which could be perfluorinated by $C_6F_5Si(CH_3)_3$. Consequently, C_6F_6 and C_6F_5Br provided p-$H(C_6F_4)_nF$, accompanied by the corresponding poly(p-phenylene)s; furthermore, $C_6F_5CH_3$ only gave p-$H(C_6F_4)_nF$ without the formation of any polymerized products starting from $C_6F_5CH_3$.

4. Experimental

4.1. General remarks

The ^{13}C NMR spectra were measured on a Varian INOVA-300 spectrometer operated at 75.42 MHz with $CDCl_3$ as the solvent. The ^{19}F NMR spectra were measured on a Varian INOVA-300 spectrometer at 282.24 MHz with $CDCl_3$ as the solvent; positive δ values were downfield from the internal reference, $CFCl_3$. The GC-MS data were obtained with a Shimadzu QP-5000 quadrupole mass spectrometer by electron-impact ionization at 70 eV (column: 60 m × 0.25 i.d., 1.5 μ NEUTA BOND-1, GL Science). The DI-MS data were obtained with a Shimadzu QP-1100EX quadrupole mass spectrometer by electron-impact ionization at 70 eV. The TOF–MS data were obtained with a Bruker Daltonics AutoFLEX time-of-flight mass spectrometer using the matrix-assisted laser desorption ionization (MALDI) method (matrix: *trans*-3-indole-acrylic acid). Trimethyl(pentafluorophenyl)silane was prepared by a reaction of bromopentafluorobenzene with chlorotrimethylsilane and phosphorus tris(diethylamide) using tetraglyme as a solvent instead of benzonitrile because of facility of isolation [16]. All solvents were purchased as anhydrous solvents commercially and were used without further purification.

4.2. Reaction of decafluoro-(1,1-biphenyl) (1a) with 2 equiv. of $C_6F_5Si(CH_3)_3$

A solution of **1a** (241 mg, 0.72 mmol) and $C_6F_5Si(CH_3)_3$ (347 mg, 1.44 mmol) with 3 ml of an anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (11 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 3 h, the reaction mixture turned to a white suspension. A 447 mg of white solid was collected by filtration. The white solid consisted of a mixture of 14% of **2a**, 44% of **3a**, and 15% of **4a** determined by ^{19}F NMR spectroscopy and MS analysis. While **2a** was isolated by Kur-gel Rohr distillation, **3a** and **4a** were analyzed as a mixed form.

4.2.1. Perfluro-(1,1′:4′,1″:4″,1‴-quaterphenyl) (3a)

^{19}F NMR (282 MHz, $CDCl_3$): δ −136.79 (4F, m, 3′,5′-F and 2″,6″-F), −136.93 (4F, m, 2,6-F and 2‴,6‴-F), −137.31 (4F, m, 2′,6′-F and 3″,5″-F), −149.69 (2F, t, J = 21.5, 4-F and 4‴-F),−160.62 (m, 4 F, 3,5-F and 3‴,5‴-F); ^{13}C NMR (75.42 MHz, $CDCl_3$): δ 101.85, 108.84, 108.85, 138.04, 142.84, 144.25, 144.38, 144.58; QP-MS (m/z, %): 630 [M^+, 100], 315 [$C_6F_5C_6F_4^+$, 48].

4.2.2. Perfluoro-(1,1′:4′,1″:4″,1‴:4‴,1⁗-quinquephenyl) (4a)

^{19}F NMR (282 MHz, $CDCl_3$,): δ −136.51 (4F, m, 2″,6″-F and 3″,5″-F), −136.71 (4F, m, 3′,5′-F and 2⁗,6⁗-F), −136.86 (4F, m, 2,6-F and 2⁗,6⁗-F), −149.61 (2F, t, J = 19.5, 4-F and 4⁗-F), −160.45 (4F, m, 3,5-F and 3⁗,5⁗-F); ^{13}C NMR (75.42 MHz, $CDCl_3$): δ 101.82, 108.84, 108.90, 109.12, 138.05, 142.84, 144.26, 144.30, 144.38, 144.59; TOF–MS (m/z, %): 778 [M^+, 100].

4.3. *Reaction of octafluorotoluene (**1b**) with 2 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1b** (249 mg, 1.05 mmol) and $C_6F_5Si(CH_3)_3$ (506 mg, 2.11 mmol) with a 1 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (15 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 3 h, the reaction mixture turned to a light-yellow suspension. A white solid was collected by filtration. The white solid consisted of a mixture of 32% of **2b**, 32% of **3b**, 9% of **4b** determined by ^{19}F NMR spectroscopy and MS analysis. While **3b** was isolated by Kur-gel Rohr distillation, **2b** and **4b** were collected as a mixture with **3b**, so they were analyzed as a mixed form. The CF_3 peaks of the ^{19}F NMR also indicated possible formation of small amounts of isomers **5b** and **6b**, but their ^{19}F NMR spectra could not be assigned because of overlapping aromatic ring fluorine peaks.

4.3.1. *Perfluoro-(4-methly-[1,1′:4′,1″]terphenyl) (**3b**)*

^{19}F NMR (282 MHz, $CDCl_3$): δ −56.96 (3F, t, *J* = 22.4 Hz, 4-CF_3), −135.52 (2F, m, 2 F, 2,6-F), −136.65 (2F, m, 2′,6′-F), −136.77 (2F, m, 3′,5′-F), −137.34 (2F, m, 2″,6″-F), −139.07 (2F, m, 3,5-F), −149.57 (1F, t m, *J* = 19.8 Hz, 1 F, 4″-F), −160.55 (2F, 2 F, 3″,5″-F); ^{13}C NMR (75.42 MHz, $CDCl_3$): δ 101.74, 108.15, 109.30, 110.93, 112.10, 114.60, 120.56, 138.09, 142.93, 144.15, 144.44, 144.44, 144.52; QP-MS (*m*/*z*, %): 630 [M^+, 100], 315 [$C_6F_5C_6F_4^+$, 48]. 532 [M^+, 100], 512 [M^+-F, 13], 481 [M^+-CF_2, 16], 266 (13), 241 (19), 69 (18).

4.3.2. *Perfluoro-(4-methyl-[1,1′:4′,1″:4″,1‴]quaterphenyl) (**4b**)*

^{19}F NMR (282 MHz, $CDCl_3$): δ −56.94 (3F, t, *J* = 21.7 Hz, 1-CF_3), −135.42 (2F, m, 2,6-F), −136.20 (2F, m, 2′,6′-F), −136.50 (2F, m, 2″,6″-F), −136.75 (2F, m, 3′,5′-F), −136.78 (2F, m, 3″,5″-F), −137.31 (2F, m, 2‴,6‴-F), −139.00 (2F, m, 3,5-F), −149.49 (1F, t, *J* = 21.5 Hz, 4‴-F), −160.40 (2F, m, 3‴,5‴-F); ^{13}C NMR (75.42 MHz, $CDCl_3$): δ 101.61, 108.38, 108.66, 109.01, 109.54, 110.87, 112.11, 117.35, 120.52, 138.06, 142.87, 114.18, 144.24, 144.33, 144.42, 144.50, 144.59; QP-MS (*m*/*z*, %): 680 [M^+, 100], 340 (43), 330 (17), 315 (30), 298 (12), 69 (18).

4.4. *Reaction of pentafluoronitrobenze (**1c**) with 2 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1c** (156 mg, 0.73 mmol) and $C_6F_5Si(CH_3)_3$ (359 mg, 1.49 mmol) with a 2 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (12 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 3 h, the reaction mixture turned to an orange suspension. The Kur-gel Rohr distillation provided a mixture of 63% of **2c**, 20% of **6c**, and 9% of **7c** determined by ^{19}F NMR spectroscopy and MS analysis.

4.4.1. *Perfluoro-(4′-nitro-[1,1′;3′,1″]terphenyl) (**6c**)*

^{19}F NMR (282 MHz, $CDCl_3$,): δ −108.96 (1F, m, 2′-F), −123.04 (1F, m, 6′-F), −137.06 (2F, m, 2″,6″-F), −138.31 (2F, m, 2,6-F), −144.93 (1F, m, 5′-F), −148.33 (1F, t m, *J* = 21.5 Hz, 4″-F), −148.88 (1F, t m, *J* = 21.5 Hz, 4-F), −159.82 (2F, m, 3″,5″-F), −159.89 (2F, m, 3,5-F); QP-MS (*m*/*z*, %): 509 [M^+, 100], 434 (59), 413 (52), 403 (67), 296 (50), 265 (20), 140 (37), 93 (44), 69 (52).

4.4.2. *Perfluoro-(2′-nitro-5′-phenyl-[1,1′;3′,1″]terphenyl) (**7c**)*

^{19}F NMR (282 MHz, $CDCl_3$): δ −99.23 (2F, m, 2′,6′-F), −136.83 (2F, m, 2‴,6‴-F), −138.17 (4F, m, 2,6-F and 2″,6″-F), −148.44 (1F, t m, *J* = 21.5 Hz, 4‴-F), −148.93 (2F, t m, *J* = 21.5 Hz, 4-F and 4″-F), −159.86 (4F, m, 3,5-F and 3″,5″-F), −159.94 (2F, m, 3‴,5‴-F); QP-MS (*m*/*z*, %): 657 [M^+, 71], 582 (69), 532 (48), 492 (45), 246 (36), 140 (82), 93 (58), 69 (62).

4.5. *Reaction of pentafluorobenzonitrile (**1d**) with 2 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1d** (151 mg, 0.78 mmol) and $C_6F_5Si(CH_3)_3$ (378 mg, 1.57 mmol) with a 3 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (12 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 3 h, the reaction mixture turned to an orange suspension. The Kur-gel Rohr distillation provided a mixture of 63% of **2d**, 20% of **6d**, and 9.1% of **7d** determined by ^{19}F NMR spectroscopy and MS analysis.

4.5.1. *Perfluoro-[1,1′;3′,1″]terphenyl-4′-carbonitrile (**6d**)*

^{19}F NMR (282 MHz, $CDCl_3$): δ −109.08 (1F, m, 2′-F), −124.85 (1F, m, 6′-F), −130.15 (1F, m, 5′-F), −137.01 (2F, m, 2,6-F), −137.82 (2F, m, 2″,5″-F), −148.29 (1F, t m, *J* = 19.4 Hz, 4″-F), −148.35 (1F, t m, *J* = 21.5 Hz, 4-F), −159.61 (2F, m, 3″,5″-F), −159.86 (2F, m, 3,5-F); QP-MS (*m*/*z*, %): 489 [M^+, 100], 420 [M^+-CF_3, 11], 244 (15).

4.5.2. *Perfluoro-(5′-phenyl-[1,1′;3′,1″]terphenyl-2′-carbonitrile) (**7d**)*

^{19}F NMR (282 MHz, $CDCl_3$): δ −100.54 (2F, m, 4′,6′-F), −136.85 (2F, m, 2‴,6‴-F), −137.61 (4F, m, 2,6-F and 2″,6″-F), −148.38 (1F, t m, *J* = 19.5 Hz, 4‴-F), −148.50 (2F, t m, *J* = 21.5 Hz, 4-F and 4″-F), −159.68 (4F, m, 3,5-F and 3″,5″-F), −159.81 (2F, m, 3‴,5‴-F); QP-MS (*m*/*z*, %): 637 [M^+,100], 568 [M^+-CF_3, 11], 318 (39), 284 (16).

4.6. *Reaction of decafluoro-(1,1-biphenyl) (**1a**) with 10 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1a** (78 mg, 0.23 mmol) and $C_6F_5Si(CH_3)_3$ (574 mg, 2.39 mmol) with 3 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (5 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 10 min, the DMF solution turned to an orange solution, and then to a white suspension for 5 h. After constant stirring for 24 h, the white solid formed (421 mg) was collected by filtration, washed with DMF, and dried. The ^{19}F NMR and TOF–MS analyses indicated that the white solid consisted of **8a**.

Data of **8a**: ^{19}F NMR ($CDCl_3$, 282 MHz): δ −136.60, −136.78, −137.01, −137.32 (22F, m), −149.63 (2F, t m, *J* = 19.5 Hz), −160.51 (4F, m); TOF–MS (M^-): 611 [26, $C_{24}F_{17}$], 630 [37, $C_{24}F_{18}$($n = 2$)], 759 [100, $C_{30}F_{21}$], 778 [70, $C_{30}F_{22}$ ($n = 3$)], 907 [67, $C_{36}F_{25}$], 926 [26, $C_{36}F_{26}$ ($n = 4$)], 1055 [12, $C_{42}F_{29}$], 1074 [4.4, $C_{42}F_{30}$ ($n = 5$)], 1203 [4.3, $C_{48}F_{33}$], 1222 [2.0, $C_{48}F_{34}$ ($n = 6$)], 1352 [3.5, $C_{54}F_{37}$], 1371 [2.3, $C_{54}F_{38}$ ($n = 7$)].

4.7. *Reaction of octafluorotoluene (**1b**) with $C_6F_5Si(CH_3)_3$ with 10 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1b** (56 mg, 0.24 mmol) and $C_6F_5Si(CH_3)_3$ (567 mg, 2.36 mmol) with a 3 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (5 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 1 h, the DMF solution turned to a white suspension, and a white solid precipitated for 3 h. After constant stirring for 24 h, the white solid (160 mg) was collected by filtration, washed with DMF, and dried under vacuum. The ^{19}F NMR and TOF–MS analyses indicated that the white solid consisted of a mixture of **8b** and **9b**.

Data of the polymerized products (the mixture of **8b** and **9b**): ^{19}F NMR ($CDCl_3$, 282 MHz): δ −56.94 (3F, t, *J* = 21.5 Hz), −58.20 (3F, br d, *J* = 19.5 Hz), −109.40 (1F, br s), −111.39 (1F, m), −136.0 to −138.0 (64F, m), −149.55 (6F, m), −160.42 (12F, m); TOF–MS (M^-): 680 [45, $C_{25}F_{20}$, ($n = 3$)], 828 [100, $C_{31}F_{24}$ ($n = 4$)], 976 [53, $C_{37}F_{28}$ ($n = 5$)], 1124 [17, $C_{43}F_{32}$ ($n = 6$)], 1272 [6.7, $C_{49}F_{36}$

($n = p + q + r = 7$)], 1421 [11, $C_{55}F_{40}$ ($n = p + q + r = 8$)], 1569 [11, $C_{61}F_{44}$ ($n = p + q + r = 9$)], 1717 [13, $C_{67}F_{48}$ ($p + q + r = 10$)], 1865 [18, $C_{73}F_{52}$ ($p + q + r = 11$)], 2013 [11, $C_{79}F_{56}$ ($p + q + r = 12$)], 2161 [8.2, $C_{85}F_{60}$ ($p + q + r = 13$)], 2309 [7.1, $C_{91}F_{64}$ ($p + q + r = 14$)], 2457 [4.4, $C_{97}F_{68}$ ($p + q + r = 15$)], 2605 [4.3, $C_{103}F_{72}$ ($p + q + r = 16$)], 2753 [1.5, $C_{109}F_{76}$ ($p + q + r =17$)], 2901 [2.6, $C_{115}F_{80}$ ($p + q + r = 18$)].

*4.8. Reaction of pentafluoronitrobenze (**1c**) with10 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1c** (45 mg, 0.21 mmol) and $C_6F_5Si(CH_3)_3$ (512 mg, 2.13 mmol) with 3 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (5 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 3 h, the DMF solution turned to a light-yellow solution. After stirring for 24 h, the reaction mixture became a blue-violet solution. To remove the solvent from the reaction mixture, 423 mg of light-yellow solid was collected by filtration, washed with ether twice, and dried. The ^{19}F NMR and TOF–MS analyses indicated that the white solid consisted of a mixture of **9c**.

Data of **9c**: ^{19}F NMR ($CDCl_3$, 282 MHz): δ −98.0 to −104.0 (2F, m), −134.0 to −140.0 (23F, m), −146.3 to −149.8 (3F, m), −158.2 to −160.5 (6F, m); TOF–MS (M^-): 934 [16, $C_{36}F_{24}NO_2$], 1082 [35, $C_{42}F_{28}NO_2$], 1230 [70, $C_{48}F_{32}NO_2$], 1249 [14, $C_{48}F_{33}NO_2$ ($p + q + r = 7$)], 1351 [16, $C_{53}F_{36}NO$], 1379 [100, $C_{54}F_{36}NO_2$], 1398 [21, $C_{54}F_{37}NO_2$ ($p + q + r = 8$)], 1499 [15, $C_{59}F_{40}NO$], 1526 [90, $C_{60}F_{40}NO_2$], 1546 [18, $C_{60}F_{41}NO_2$ ($p + q + r = 9$)], 1647 [17, $C_{65}F_{44}NO$], 1675 [78, $C_{66}F_{44}NO_2$], 1694 [17, $C_{66}F_{45}NO_2$ ($p + q + r = 10$)], 1795 [15, $C_{71}F_{48}NO$], 1823 [76, $C_{72}F_{48}NO_2$], 1842 [17, $C_{72}F_{49}NO_2$ ($p + q + r = 11$)], 1943 [9.8, $C_{77}F_{52}NO$], 1971 [66, $C_{78}F_{52}NO_2$], 1990 [13, $C_{78}F_{53}NO_2$ ($p + q + r = 12$)], 2119 [27, $C_{84}F_{56}NO_2$], 2267 [14, $C_{90}F_{60}NO_2$], 2415 [5.1, $C_{96}F_{64}NO_2$].

*4.9. Reaction of petafluorobenzonitrile (**1d**) with 10 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1d** (49 mg, 0.25 mmol) and $C_6F_5Si(CH_3)_3$ (610 mg, 2.54 mmol) with 3 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (5 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 3 h, the DMF solution turned to a light-yellow solution. After stirring for 24 h, the reaction mixture became an orange solution. To remove the solvent from the reaction mixture, 498 mg of light-yellow solid was collected by filtration, washed with ether twice, and dried. The ^{19}F NMR and TOF–MS analyses indicated that the white solid consisted of a mixture of **9d**.

Data of **9d**: ^{19}F NMR ($CDCl_3$, 282 MHz): δ −99.0 to −110.0 (2F, m), −134.0 to −139.0 (24F, m), −146.4 to −149.8 (3F, m), −158.2 to −161.0 (6F, m); TOF–MS (M^-): 766 [15, $C_{31}F_{20}N$], 785 [26, $C_{31}F_{21}N$ ($p + q + r = 4$)], 914 [19, $C_{37}F_{24}N$], 933 [65, $C_{37}F_{25}N$ ($p + q + r = 5$)], 1062 [21, $C_{43}F_{28}N$], 1081 [94, $C_{43}F_{29}N$ ($p + q + r = 6$)], 1210 [19, $C_{49}F_{32}N$], 1229 [100, $C_{49}F_{33}N$ ($p + q + r = 7$)], 1359 [16, $C_{55}F_{36}N$], 1378 [89, $C_{55}F_{37}N$ ($p + q + r = 8$)], 1507 [12, $C_{61}F_{40}N$], 1526 [88, $C_{61}F_{41}N$ ($p + q + r = 9$)], 1655 [9.6, $C_{67}F_{44}N$], 1674 [57, $C_{67}F_{45}N$ ($p + q + r = 10$)], 1803 [7.2, $C_{73}F_{48}N$], 1822 [50, $C_{73}F_{49}N$ ($p + q + r = 11$)], 1970 [48, $C_{79}F_{53}N$ ($p + q + r = 12$)], 2118 [40, $C_{85}F_{57}N$ ($p + q + r = 13$)], 2266 [31, $C_{91}F_{61}N$ ($p + q + r = 14$)], 2414 [25, $C_{97}F_{65}N$ ($p + q + r = 15$)], 2562 [21, $C_{103}F_{69}N$ ($p + q + r = 16$)], 2710 [9.7, $C_{109}F_{73}N$ ($p + q + r = 17$)], 2858 [5.8, $C_{115}F_{77}N$ ($p + q + r = 18$)].

*4.10. Reaction of hexafluorobenzene (**1e**) with 10 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1e** (46 mg, 0.24 mmol) and $C_6F_5Si(CH_3)_3$ (598 mg, 2.49 mmol) with a 5 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (5 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 2 h, the DMF solution turned to a white suspension. After stirring for 24 h, the white solid formed (551 mg) was collected by filtration, washed with DMF, and dried. The ^{19}F NMR and TOF–MS analyses indicated that the white solid consisted of a mixture of **8a** and **8f** by the TOF–MS analysis.

*4.11. Reaction of pentabenzene (**1f**) with 1.1 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1f** (172 mg, 1.02 mmol) and $C_6F_5Si(CH_3)_3$ (275 mg, 1.14 mmol) with 3 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (15 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 3 h, the reaction mixture turned to a light-yellow suspension. A white solid (176 mg) was collected by filtration. The ^{19}F NMR and TOF–MS analyses indicated that the white solid consisted of **8f**.

Data of **8f**: ^{19}F NMR ($CDCl_3$, 282 MHz): δ −136.64, −137.03, −137.32, −137.68, −137.94, −138.34 (m), −148.69 (t m, J = 20.6 Hz), −150.81 (t m, J = 21.5 Hz), −160.57 (m), −161.15 (m); TOF–MS (M^-): 760 [100, $C_{30}F_{21}H$ ($n = 4$)], 908 [70, $C_{36}F_{25}H$ ($n = 5$)], 1056 [7.8, $C_{42}F_{29}H$ ($n = 6$)], 1204 [7.2, $C_{48}F_{33}H$ ($n = 7$)], 1353 [4.4, $C_{54}F_{37}H$ ($n = 8$)].

*4.12. Reactions of bromopetafluorobenzene (**1g**) and 2,3,4,5,6-pentafluorotoluene (**1h**) with 1.1 equiv. of $C_6F_5Si(CH_3)_3$*

A solution of **1g** (247 mg, 1.00 mmol) and $C_6F_5Si(CH_3)_3$ (266 mg, 1.11 mmol) with a 2 ml of anhydrous DMF was placed in a 10 ml Teflon vessel, and then a catalytic amount (15 mg) of KHF_2 was added vigorously stirring with a magnetic stirrer. After stirring at room temperature for 3 h, the reaction mixture turned to a white suspension and the white solid (154 mg) was collected by filtration. It was considered that the white solid consisted of a mixture of **8e** and **8g** by the following TOF–MS (M^-) data: 760 [100, $C_{30}F_{21}H$ ($n = 4$)], 839 [54, $C_{30}F_{21}Br$ ($n = 4$)], 908 [56, $C_{36}F_{25}H$ ($n = 5$)], 987 [27, $C_{36}F_{25}Br$ ($n = 5$)], 1056 [12, $C_{42}F_{29}H$ ($n = 6$)], 1135 [7.1, $C_{42}F_{29}Br$ ($n = 6$)], 1204 [5.6, $C_{48}F_{33}H$ ($n = 7$)] 1283 [3.6, $C_{48}F_{33}Br$ ($n = 7$)], 1353 [6.2, $C_{54}F_{37}H$ ($n = 8$)], 1431 [3.7, $C_{54}F_{37}Br$ ($n = 8$)], 1501 [1.7, $C_{60}F_{41}H$ ($n = 9$)], 1579 [3.6, $C_{60}F_{41}Br$ ($n = 9$)].

Because of low reactivity of perfluoroaromatic compounds having an electron-donor substituent, the reaction of 2,3,4,5,6-pentafluorotoluene (**1h**) with 1.1 equiv. of $C_6F_5Si(CH_3)_3$ could not provide the corresponding oligomers but formed **8e** by the reaction of **1e**, which is a decomposed product of $C_6F_5Si(CH_3)_3$, based on the results of TOF–MS analysis.

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