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Synthesis of phosphate-type fluorocarbon–hydrocarbon hybrid surfactants and their adsorption onto calcium hydroxyapatite

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Abstract

Five novel phosphate-type hybrid surfactants, $C_mF_{2m+1}C_6H_4CH[OPO_2(OC_6H_5)Na]C_nH_{2n+1}$ (F*m*PH*n*PPhNa: $m = 4, 6, 8$; $n = 3, 5$), have been synthesized. When compared with sulfate-type hybrid surfactants, $C_mF_{2m+1}C_6H_4CH(OSO_3Na)C_nH_{2n+1}$ (C_6H_4 = *p*-phenylene), the new hybrid surfactants were found to have comparable abilities to lower the surface tension of water. The critical micelle concentrations of F*m*PH*n*PPhNa followed Klevens' rule and their occupied areas per molecule increased with increasing *m* and *n*. Calcium hydroxyapatite (CaHAp) pellets modified with F*m*PH3PPhNa gave high hydro and lipophobic surfaces. The hybrid surfactants are expected to be useful as new dental reagents for oral hygiene.

Keywords: Hybrid surfactant; Phosphate-type; Fluorocarbon; Calcium hydroxyapatite; Human teeth; Hydro and lipophobic surface; Plaque-controlling surface

1. Introduction

Hybrid surfactants with a fluorocarbon chain and a hydrocarbon chain in one molecule have unique properties such as simultaneous emulsification of hydrocarbon oil/fluorocarbon oil/water [1], formation of small micelles with unusually long lifetime [2], and very high viscosity of the surfactant solution at body temperature [3–7]. These properties cannot be shown by the mixture of fluorocarbon surfactants and hydrocarbon surfactants.

Yoshino et al. have so far synthesized fluorinated silane coupling agents and modified bovine teeth using the silanes [8–10]. The silanes gave hydrophobicity and lipophobicity to the tooth surface and restrained dental plaque formation. This result suggests that the fixation of fluorocarbons onto teeth is effective in keeping oral cavities clean. Hybrid surfactants have also been reported to solubilize hydrocarbon molecules in their micelles, suggesting that they can serve as a drug carrier [11,12]. On the other hand, 2-methacryloyloxyethyl hydrogen phenyl phosphate ($CH_2{=}C(CH_3)COOC_2H_4[OPO_2(OC_6H_5)H$]: phenyl-P) is widely used as a dental adhesive because its phenyl phosphate group strongly adsorbs to human teeth [13–16]. Then, hybrid surfactants having a phenyl phosphate group, if synthesized, would be useful in the field of dentistry. It is expected that such surfactants adsorb on teeth to give hydrophobicity and lipophobicity to the surface and their micelles solubilizing dental drugs can penetrate into periodontal pockets to cure periodontal disease.

The present paper reports the synthesis of five novel phenyl phosphate-type hybrid surfactants, $C_mF_{2m+1}C_6H_4CH[OPO_2(OC_6H_5)Na]C_nH_{2n+1}$ (F*m*PH*n*PPhNa: $m = 4, 6, 8$; $n = 3, 5$), the physicochemical properties of their solutions, and their adsorption to calcium hydroxyapatite (CaHAp) pellets as a model of human teeth.

2. Results and discussion

2.1. Synthesis of hybrid surfactants

Scheme 1 shows the synthetic route of the hybrid surfactants. Hybrid alcohols, F*m*PH*n*A, were prepared according to the previous paper [17]. The introduction of a phosphate group to the hybrid alcohol was performed using diphenyl

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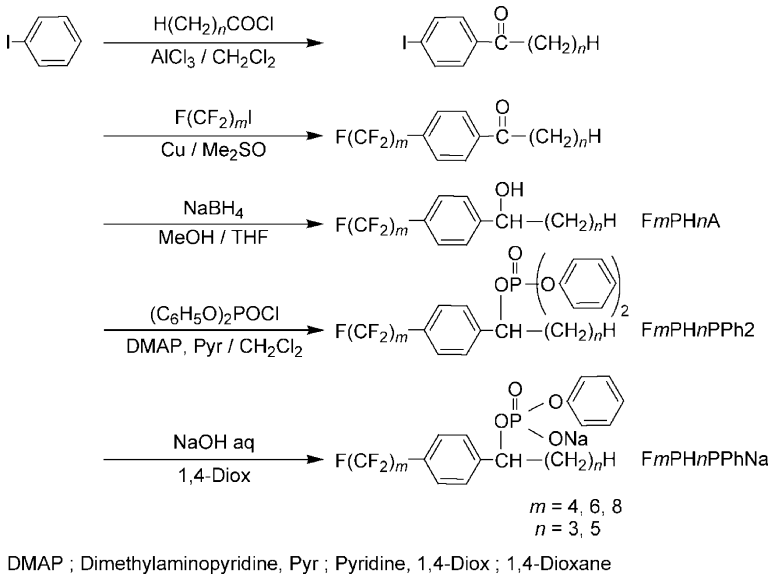


Scheme 1. Synthesis of F*m*PH*n*PPhNa.

phosphorochloridate with dimethylaminopyridine (DMAP) as catalyst at 35 °C. The obtained triesters, $C_mF_{2m+1}C_6H_4$-CH[OPO(OC_6H_5)$_2$]C_nH_{2n+1} (F*m*PH*n*PPh2), were easily alkalized with NaOH to give the desired phosphate-type hybrid surfactants, F*m*PH*n*PPhNa, in a high yield (ca. >70%).

2.2. Krafft point, cmc and surface tension of FmPHnPPhNa

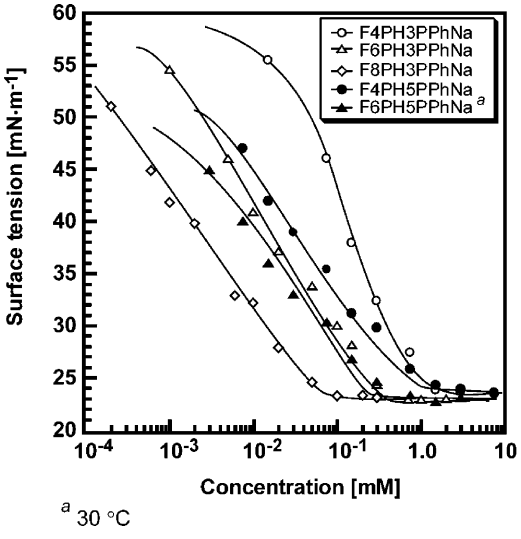
Table 1 lists the Krafft points (K_p), cmcs, and surface tension values at cmc (γ_{cmc}) of F*m*PH*n*PPhNa together with the corresponding data of $C_mF_{2m+1}C_6H_4CH(OSO_3Na)$-$C_nH_{2n+1}$ (F*m*PH*n*OS: $m = 4, 6, 8$; $n = 3, 5$; $C_6H_4 = p$-phenylene) [17]. The value of K_p increased with increasing *m* and *n*, and F*m*PH*n*PPhNa having long hydrophobic chains ($m + n > 10$) showed K_p values higher than room temperature. The K_p values of F*m*PH*n*PPhNa are higher than those of the corresponding F*m*PH*n*OS. This is because phenyl phosphate group is less hydrophilic compared with sulfate group. The cmcs of F*m*PH*n*PPhNa were lower than those of F*m*PH*n*OS due to the higher hydrophobicity. Moreover, the γ_{cmc} values for F*m*PH*n*PPhNa were about 20 mN m^{-1}, which are almost the same as those for the conventional single-chain fluorinated surfactants [18].

Fig. 1 shows the relationship between surface tension and concentration for F*m*PH*n*PPhNa aqueous solutions at 25 °C. The occupied areas (A_{Air}) per molecule of F*m*PH*n*PPhNa were calculated from the surface excess concentration at air/water interface (Γ_{Air}). The value of Γ_{Air} was calculated

Table 1
Krafft point (k_p), cmc, and γ_{cmc} of F*m*PH*n*PPhNa at 25° C

Surfactant		K_p[a] (°C)	Cmc (mM)	γ_{cmc} (mN/m)
F4PH3PPhNa	<0	(14 mM)	1.4	24
F6PH3PPhNa	13	(3.5 mM)	0.35	23
F8PH3PPhNa	22	(0.74 mM)	0.074	22
F4PH5PPhNa	<0	(9.7 mM)	0.97	24
F6PH5PPhNa	27	(2.1 mM)	0.21[b]	23[b]
F8PH5PPhNa[c]	37	(0.45 mM)	–	–
F4PH3OS[d]	<0	(35 mM)	7.0	19
F6PH3OS[d]	<0	(4.5 mM)	0.90	18
F8PH3OS[d]	16	(0.4 mM)	0.08	20
F4PH5OS[d]	<0	(10 mM)	3.0	19
F6PH5OS[d]	14	(1.5 mM)	0.34	20
F8PH5OS[d]	32	(0.2 mM)	–	–

[a] K_p was measured in the concentration shown in parenthesis.
[b] 30 °C.
[c] The data were not obtained because of high K_p.
[d] From Ref. [17].



[a] 30 °C

Fig. 1. Surface tension plot of F*m*PH*n*PPhNa aq. against surfactant concentration at 25 °C.

Table 2
Adsorbed amount (Γ_{Air}) and occupied area (A_{Air}) per molecule at air/water interface at 25 °C

Surfactant	Γ_{Air} (μmol/m^2)	A_{Air} (nm^2)
F4PH3PPhNa	1.61	1.03
F6PH3PPhNa	1.23	1.34
F8PH3PPhNa	0.96	1.73
F4PH5PPhNa	0.90	1.85
F6PH5PPhNa[a]	0.86	1.93
F4PH3OS[b]	2.5	0.66
F6PH3OS[b]	2.1	0.80
F8PH3OS[b]	1.8	0.94
F4PH5OS[b]	1.7	0.99
F6PH5OS[b]	1.6	1.04

[a] 30°C.
[b] From Ref. [17].

using the Gibbs adsorption isotherm (1) [18],

$$\Gamma_{Air} = -\frac{1}{4.606RT}\left(\frac{\partial\gamma}{\partial \log C}\right) \quad (1)$$

Here, γ is the surface tension of water, C is the concentration of FmPHnPPhNa aqueous solution, R is the gas constant, and T is the absolute temperature. The value of A_{Air} relates to the adsorption amount Γ_{Air} via the following Eq. (2) [18],

$$A_{Air} = \frac{1}{\Gamma_{Air} N_A} \quad (2)$$

where N_A is Avogadro's number. Table 2 shows the values of Γ_{Air} and A_{Air}. The A_{Air} increased with increasing m and n. FmPHnPPhNa had a large A_{Air} value compared with the corresponding FmPHnOS. Phenyl phosphate group is structurally larger than sulfate group. This would be the reason for the larger A_{Air} values for FmPHnPPhNa.

Fig. 2 shows the logarithmic plots of the cmc determined by surface tension measurements against m and n. Klevens found that log(cmc) was empirically related to the hydrophobic chain length N in Eq. (3),

$$\log(\text{cmc}) = a - bN \quad (3)$$

where a and b are constants [18]. In the case of FmPH3PPhNa, log(cmc) decreased linearly with increasing m, obeying Klevens' rule (4)

$$\log(\text{cmc}) = -1.56 - 0.319\,m \ (\text{correlation coefficient}, 0.999) \quad (4)$$

Eq. (4) suggests that the cmc decreases by 52% when the number of CF_2 group in the hydrophobic chain increases by one. Moreover, the following three Eqs. (5)–(7) are obtained assuming that Klevens' rule holds for FmPH5PPhNa ($n = 5$), F4PHnPPhNa ($m = 4$), and F6PHnPPhNa ($m = 6$).

$$\text{F}m\text{PH5PPhNa} : \log(\text{cmc}) = -1.68 - 0.333\,m \quad (5)$$

$$\text{F4PH}n\text{PPhNa} : \log(\text{cmc}) = -2.62 - 0.080\,n \quad (6)$$

$$\text{F6PH}n\text{PPhNa} : \log(\text{cmc}) = -3.12 - 0.111\,n \quad (7)$$

These equations give the rates of cmc decrease of 54%/CF_2 group, 17%/CH_2 group, and 23%/CH_2 group for FmPH5PPhNa, F4PHnPPhNa and F6PHnPPhNa, respectively. For FmPHnOS, the cmc decreases by 66–67%/CF_2 group and 34–38%/CH_2 group. The contribution to cmc of both CF_2 and CH_2 groups in FmPHnPPhNa is smaller than that in FmPHnOS. This result would be brought about by the introduction of a spatially large phenyl group into phosphate group, thereby causing the hydrophobic interaction between hydrophobic chains to become weaker than that in FmPHnOS.

2.3. Modification of CaHAp pellets with FmPHnPPhNa

Table 3 gives the contact angles of water and oleic acid on the modified pellet after being dipped in water for 12 h. The contact angle of water increased with increasing m and n, while the contact angle of oleic acid increased with increasing m and decreased with increasing n. The pellet surface modified with FmPH3PPhNa was highly hydrophobic and oil-repellent. In contrast, whereas the pellets modified with FmPH5PPhNa were highly hydrophobic, they were lipophilic compared to those pellets modified with FmPH3PPhNa.

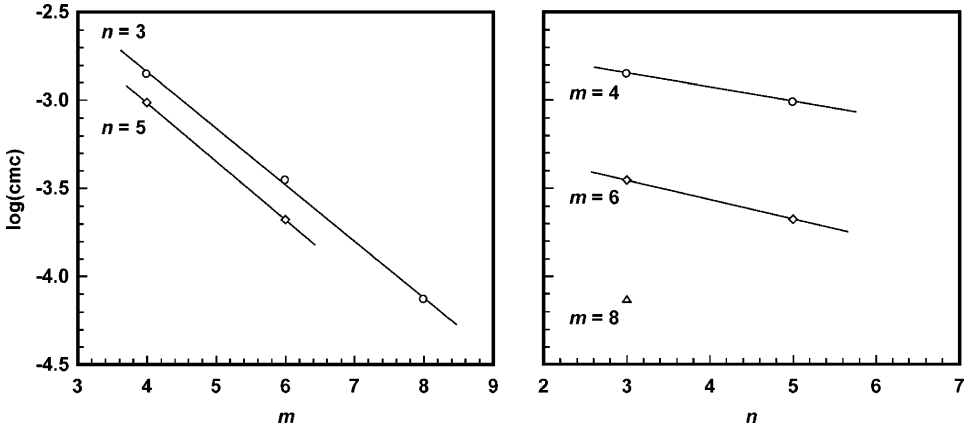


Fig. 2. Log(cmc) plots of FmPHnPPhNa aq. against hydrophobic chain length m or n.

Table 3
Contact angles of CaHAp pellets modified by F*m*PH*n*PPhNa at 25 °C

Compound	Water (°)	Oleic acid (°)
F4PH3PPhNa	70 ± 5	48 ± 3
F6PH3PPhNa	77 ± 4	74 ± 4
F8PH3PPhNa	91 ± 5	82 ± 2
F4PH5PPhNa	80 ± 2	44 ± 3
F6PH5PPhNa	92 ± 2	48 ± 3
Unmodified	55 ± 4	24 ± 4

We previously reported that the hydrophobic and lipophobic tooth surface markedly inhibits plaque formation on it. In particular, CaHAp pellets modified with F*m*PH3PPhNa remained highly hydro and lipophobic even after being dipped in water for 12 h. F*m*PH3PPhNa are thus expected to be a useful dental reagent from a viewpoint of oral hygiene.

3. Experimental section

3.1. Materials

$IC_6H_4COC_nH_{2n+1}$ ($n = 3, 5$), $C_mF_{2m+1}C_6H_4COC_nH_{2n+1}$ ($m = 4, 6, 8$; $n = 3, 5$), and $C_mF_{2m+1}C_6H_4CH(OH)C_nH_{2n+1}$ (F*m*PH*n*A: $m = 4, 6, 8$; $n = 3, 5$) were synthesized as reported previously [17]. DMAP (TCI) and diphenyl phosphorochloridate (Kanto Chemical) were used without further purification. Dichloromethane (bp 40 °C), 1,4-dioxane (bp 101 °C), and pyridine (bp 83 °C) were purified before use by distillation after being dehydrated with calcium hydride.

3.2. Measurements and instruments

3.2.1. Characterization of FmPHnPPhNa

A Nicolet Avatar 360-FT-IR spectrometer was used to measure FT-IR spectrum with the ATR method. A Bruker DPX-400 spectrometer was used to measure 400 MHz ^{1}H-NMR spectrum at 30 °C in $CDCl_3$ and CD_3OD (with tetramethylsilane (TMS) as internal standard). The same spectrometer was also used to measure 376 MHz ^{19}F-NMR spectrum at 30 °C in $CDCl_3$ and CD_3OD (with trifluoroacetic acid as external standard). GC–mass spectrum (GC–MS) was measured with a Hewlett Packard HP6890 series GC System (Hewlett Packard 5973 Mass Selective Detector). MS measurement (FABMS) using the fast atom bombardment (FAB) method was performed with a JEOL JMS SX102A.

3.2.2. Measurement of cmc, surface tension, and K_p

Surface tension was measured at 25 °C by the Wilhelmy method using a Krüss Model K12 surface tensiometer. Electroconductivity measurement was conducted on surfactant solution as a function of temperature with a DKK-TOA conductivity meter CM-60S and the temperature at which the conductivity abruptly changes was defined as the K_p value of the surfactant.

3.2.3. Contact angle of water on CaHAp pellet modified with FmPHnPPhNa

A CaHAp pellet (Cellyard pellet, Pentax) with a diameter of 13 mm and a height of 2 mm was introduced in 10 cm^3 of F*m*PH*n*PPhNa aqueous solution whose concentration was twice as high as the cmc. After being dipped in the solution for 6 h at 25 °C, the modified pellet was taken out and dried for 30 min at room temperature in vacuo. Only with F6PH5PPhNa, the pellet was dipped in surfactant solution at 30 °C because the K_p of the surfactant was 27 °C. The modified pellet was soaked in 10 cm^3 of pure water for 12 h at 25 or 30 °C (for F6PH5PPhNa). The contact angles of water and oleic acid were measured using 0.9 mm^3 droplets of the liquids after the washed pellet was dried for 30 min in vacuo.

3.3. Synthesis of FmPHnPPh2

3.3.1. Synthesis of diphenyl 1-[(4-perfluorobutyl)phenyl]-1-butylphosphate (F4PH3PPh2)

F4PH3A (4.7 g, 12.7 mmol), dichloromethane (50 cm^3), pyridine (1.51 cm^3, 19.1 mmol), and DMAP (2.3 g, 19.1 mmol) were placed in a 100 ml eggplant-shaped flask equipped with an isobaric dropping funnel under nitrogen atmosphere. Diphenyl phosphorochloridate (5.1 g, 19.1 mmol) was then slowly added through the funnel. The reaction mixture was stirred for 10 h at 35 °C, and flash column chromatography (eluent is mixture (v/v) of chloroform:acetone = 90:1) performed on silica gel (Wakogel C-300, Wako pure chemical industries) gave F4PH3PPh2 as a white solid. Yield 6.2 g (81%); IR (cm^{-1}): 1089 (ν_{P-O}), 1132 ($\nu_{P=O}$), 1264 (ν_{C-F}), 1488 (ν_{Ph-O}); ^{1}H-NMR ($CDCl_3$): δ 0.78 (3H, t, $J = 7.4$ Hz, a), 1.18 (2H, m, b), 1.77 (2H, dd, c), 5.44 (1H, m, d), 6.85 (4H, m, *o*-proton from –OPO(O–)$_2$), 6.97 (2H, t, $J = 7.3$ Hz, *p*-proton from –OPO(O–)$_2$), 7.18 (4H, m, *m*-proton from –OPO_3–), 7.30 (2H, d, $J = 8.2$ Hz, *m*-proton from C_4F_9–), 7.40 (2H, d, $J = 8.2$ Hz, *o*-proton from C_4F_9–) for $CH_3{}^aCH_2{}^bCH_2{}^cCH^d[OPO_3(C_6H_5)_2]C_6H_4C_4F_9$; ^{19}F-NMR ($CDCl_3$): δ −85.8 (3F, s, a), −129.9 (2F, s, b), −126.9 (2F, s, c), −114.7 (2F, s, d) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dC_6H_4$-$CH[OPO(OC_6H_5)_2]C_3H_7$; GC–MS 70 eV, *m/z* (rel. int.): 600 $[M]^+$ (12), 557 $[M-C_3H_7]^+$ (5), 350 $[M-OPO(OC_6H_5)_2]^+$ (25), 309 $[C_4F_9C_6H_4CH_2]^+$ (30), 251 $[OPO(OC_6H_5)_2]^+$ (100).

3.3.2. Synthesis of diphenyl 1-[(4-perfluorohexyl)phenyl]-1-butylphosphate (F6PH3PPh2) etc.

The methods of synthesis and purification were the same as those in Section 3.3.1.

F6PH3PPh2: white solid, yield 77%; IR (cm^{-1}): 1089 (ν_{P-O}), 1143 ($\nu_{P=O}$),1241 (ν_{C-F}), 1488 (ν_{Ph-O}), 2960(ν_{C-H});

^{1}H-NMR ($CDCl_3$): δ 0.81 (3H, t, $J = 7.4$ Hz, a), 1.28 (2H, m, b), 1.81 (2H, dd, c), 5.49 (1H, m, d), 6.89 (4H, m, *o*-proton from –OPO(O–)$_2$), 7.01 (2H, t, $J = 7.3$ Hz, *p*-proton from –OPO(O–)$_2$), 7.22 (4H, m, *m*-proton from –OPO_3–), 7.33 (2H, d, $J = 8.2$ Hz, *m*-proton from C_4F_9–), 7.43 (2H, d, $J = 8.2$ Hz, *o*-proton from C_4F_9–) for $CH_3{}^aCH_2{}^bCH_2{}^c$-$CH^d[OPO(OC_6H_5)_2]C_6H_4C_6F_{13}$; ^{19}F-NMR ($CDCl_3$): δ −85.6 (3F, s, a), −130.4 (2F, s, b), −127.0 (2F, s, c), −126.0 (2F, s, d), −125.6 (2F, s, e), −114.5 (2F, s, f) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fC_6H_4CH[OPO(OC_6H_5)_2]C_3H_7$; GC–MS 70 eV, *m/z* (rel. int.): 700 $[M]^+$ (20), 657 $[M-C_3H_7]^+$ (5), 450 $[M-OPO(OC_6H_5)_2]^+$ (25), 409 $[C_6F_{13}C_6H_4CH_2]^+$ (30), 251 $[OPO(OC_6H_5)_2]^+$ (100).

F8PH3PPh2: white solid, yield 78%; IR (cm^{-1}): 1092 (ν_{P-O}), 1147 ($\nu_{P=O}$), 1247 (ν_{C-F}), 1484 (ν_{Ph-O}), 2959 (ν_{C-H}); ^{1}H-NMR ($CDCl_3$): δ 0.81 (3H, t, $J = 7.4$ Hz, a), 1.26 (2H, m, b), 1.80 (2H, dd, c), 5.48 (1H, m, d), 6.87 (4H, m, *o*-proton from –OPO(O–)$_2$), 7.09 (2H, t, $J = 7.3$ Hz, *p*-proton from –OPO(O–)$_2$), 7.22 (4H, m, *m*-proton from –OPO_3–), 7.33 (2H, d, $J = 8.2$ Hz, *m*-proton from C_4F_9–), 7.43 (2H, d, $J = 8.2$ Hz, *o*-proton from C_4F_9–) for $CH_3{}^aCH_2{}^bCH_2{}^c$-$CH^d[OPO(OC_6H_5)_2]C_6H_4C_8F_{17}$; ^{19}F-NMR ($CDCl_3$) δ −85.5 (3F, s, a), −130.4 (2F, s, b), −126.8 (2F, s, c), −126.0 (6F, s, d, e and f), −125.3 (2F, s, g), −114.5 (2F, s, h) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fCF_2{}^gCF_2{}^hC_6H_4CH[O$-$PO(OC_6H_5)_2]C_3H_7$; GC–MS 70 eV, *m/z* (rel. int.): 800 $[M]^+$ (20), 757 $[M-C_3H_7]^+$ (5), 550 $[M-OPO(OC_6H_5)_2]^+$ (30), 509 $[C_8F_{17}C_6H_4CH_2]^+$ (30), 251 $[OPO(OC_6H_5)_2]^+$ (100).

F4PH5PPh2: white solid, yield 76%; IR (cm^{-1}): 1090 (ν_{P-O}), 1147 ($\nu_{P=O}$), 1240 (ν_{C-F}), 1483 (ν_{Ph-O}), 2967 (ν_{C-H}); ^{1}H-NMR ($CDCl_3$): δ 0.74 (3H, t, $J = 7.4$ Hz, a), 1.13 (6H, m, b, c, and d), 1.79 (2H, dd, e), 6.14 (1H, m, f), 6.87 (4H, m, *o*-proton from –OPO(O–)$_2$), 6.99 (2H, t, $J = 7.3$ Hz, *p*-proton from –OPO(O–)$_2$), 7.21 (4H, m, *m*-proton from –OPO_3–), 7.31 (2H, d, $J = 8.2$ Hz, *m*-proton from C_4F_9–), 7.41 (2H, d, $J = 8.2$ Hz, *o*-proton from C_4F_9–) for $CH_3{}^aCH_2{}^bCH_2{}^cCH_2{}^dCH_2{}^eCH^f[OPO(OC_6H_5)_2]C_6H_4C_4F_9$; ^{19}F-NMR ($CDCl_3$): δ −85.9 (2F, s, a), −130.0 (2F, s, b), −126.9 (2F, s, c), −114.7 (3F, s, d) for $CF_3{}^aCF_2{}^b$-$CF_2{}^cCF_2{}^dC_6H_4CH[OPO(OC_6H_5)_2]C_5H_{11}$; GC–MS 70 eV, *m/z* (rel. int.): 628 $[M]^+$ (15), 557 $[M-C_5H_{11}]^+$ (5), 378 $[M-OPO(OC_6H_5)_2]^+$ (25), 309 $[M-OPO(OC_6H_5)_2]^+$ (30), 251 $[OPO(OC_6H_5)_2]^+$ (100).

F6PH5PPh2: white solid, yield 78%; IR (cm^{-1}): 1093 (ν_{P-O}), 1147 ($\nu_{P=O}$), 1237 (ν_{C-F}), 1492 (ν_{Ph-O}), 2959 (ν_{C-H}); ^{1}H-NMR ($CDCl_3$): δ 0.75 (3H, t, $J = 7.4$ Hz, a), 1.16 (6H, m, b, c, and d), 1.82 (2H, dd, e), 5.46 (1H, m, f), 6.87 (4H, m, *o*-proton from –OPO(O–)$_2$), 7.02 (2H, t, $J = 7.3$ Hz, *p*-proton from –OPO(O–)$_2$), 7.18 (4H, m, *m*-proton from –OPO_3–), 7.33 (2H, d, $J = 8.2$ Hz, *m*-proton from C_4F_9–), 7.43 (2H, d, $J = 8.2$ Hz, *o*-proton from C_4F_9–) for $CH_3{}^aCH_2{}^bCH_2{}^cCH_2{}^dCH_2{}^eCH^f[OPO(OC_6H_5)_2]C_6H_4C_6F_{13}$; ^{19}F-NMR ($CDCl_3$): δ −85.4 (3F, s, a), −130.4 (2F, s, b), −127.0 (2F, s, c), −126.0 (2F, s, d), −125.6 (2F, s, e), −114.5 (2F, s, f) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fC_6H_4$-$CH[OPO(OC_6H_5)_2]C_5H_{11}$; GC–MS 70 eV, *m/z* (rel. int.): 728 $[M]^+$ (20), 657 $[M-C_5H_{11}]^+$ (5), 478 $[M-OPO$-$(OC_6H_5)_2]^+$ (25), 409 $[M-OPO(OC_6H_5)_2]^+$ (30), 251 $[OPO(OC_6H_5)_2]^+$ (100).

F8PH5PPh2: white solid, yield 74%; IR (cm^{-1}): 1089 (ν_{P-O}), 1147 ($\nu_{P=O}$), 1241 (ν_{C-F}), 1483 (ν_{Ph-O}), 2963 (ν_{C-H}); ^{1}H-NMR ($CDCl_3$): δ 0.82 (3H, t, $J = 7.4$ Hz, a), 1.22 (6H, m, b, c, and d), 1.90 (2H, dd, e), 5.53 (1H, m, f), 6.94 (4H, m, *o*-proton from –OPO(O–)$_2$), 7.11 (2H, t, $J = 7.3$ Hz, *p*-proton from –OPO(O–)$_2$), 7.31 (4H, m, *m*-proton from –OPO_3–), 7.40 (2H, d, $J = 8.2$ Hz, *m*-proton from C_4F_9–), 7.50(2H, d, $J = 8.2$ Hz, *o*-proton from C_4F_9–) for $CH_3{}^aCH_2{}^bCH_2{}^cCH_2{}^dCH_2{}^eCH^f[OPO(OC_6H_5)_2]C_6H_4C_8F_{17}$; ^{19}F-NMR ($CDCl_3$): δ −85.5 (3F, s, a), −130.4 (2F, s, b), −126.8 (2F, s, c), −126.0 (6F, s, d, e and f), −125.3 (2F, s, g), −114.5 (2F, s, h) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fCF_2{}^g$-$CF_2{}^hC_6H_4CH[OPO(OC_6H_5)_2]C_5H_{11}$; GC–MS 70 eV, *m/z* (rel. int.): 828 $[M]^+$ (20), 757 $[M-C_5H_{11}]^+$ (5), 578 $[M-OPO(OC_6H_5)_2]^+$ (25), 509 $[M-OPO(OC_6H_5)_2]^+$ (30), 251 $[OPO(OC_6H_5)_2]^+$ (100).

3.4. Synthesis of FmPHnPPhNa

3.4.1. Synthesis of sodium phenyl 1-[(4-perfluorobutyl)phenyl]-1-butylphosphate (F4PH3PPhNa)

F4PH3PPh2 (7.6 g, 12.6 mmol), 1,4-dioxane (50 cm^3), 4N-sodium hydroxide aqueous solution (25 cm^3) were mixed and the mixture was heated for 2 h at 50 °C. After 1N-hydrochloric acid was added to the mixture until the value of pH attained 4, the precipitate formed was filtrated. Sodium hydrogencarbonate solution (1.0 g in 10 cm^3 water) was introduced to an aqueous suspension of the precipitate (5.2 g) to make an aqueous solution. After a stirring for 20 min at 25 °C, the solution was evaporated to dryness at 120 °C and obtained a white solid. The methanol soluble components of this white solid were extracted with methanol. The pure white solid, F4PH3PPhNa, was obtained as reprecipitation product by adding 500 cm^3 of hexane to 5 cm^3 of the methanol solution. Yield 5.40 g (78%); IR (cm^{-1}): 1089 (ν_{P-O}), 1132 ($\nu_{P=O}$), 1264 (ν_{C-F}), 1488 (ν_{Ph-O}); ^{1}H-NMR (CD_3OD): δ 0.87 (3H, t, $J = 7.4$ Hz, a), 1.32 (2H, m, b), 1.80 (2H, dd, c), 5.30 (1H, m, d), 7.11 (2H, t, $J = 8.2$ Hz, *m*-proton from –OPO_2(O–)), 6.92 (2H, d, $J = 8.2$ Hz, *o*-proton from –OPO_2(O–)), 6.98 (1H, $J =$ 7.3 Hz, t, *p*-proton from –OPO_2(O–)), 7.50 (4H, m, e) for $CH_3{}^aCH_2{}^bCH_2{}^cCH^d[OPO_2(OC_6H_5)Na]C_6H_4{}^eC_4F_9$; ^{19}F-NMR ($CD_3OD$): δ −85.8 (2F, s, a), −129.9 (2F, s, b), −126.9 (2F, s, c), −114.7 (2F, s, d) for $CF_3{}^aCF_2{}^bCF_2{}^c$-$CF_2{}^dC_6H_4CH[OPO_2(OC_6H_5)Na]C_3H_7$; FABMS *m/z* (rel. int.): 1069 $[2M-Na]^-$ (18), 523 $[M-Na]^-$ (100), 79 $[PO_3]^-$ (26).

3.4.2. Synthesis of sodium phenyl 1-[(4-perfluorohexyl)-phenyl]-1-butylphosphate (F6PH3PPhNa) etc.

The methods of synthesis and purification were the same as those in Section 3.4.1.

F6PH3PPhNa: white solid, yield 72%; IR (cm^{-1}): 1089 (ν_{P-O}), 1143 ($\nu_{P=O}$),1241 (ν_{C-F}), 1488 (ν_{Ph-O}), 2960(ν_{C-H}); ^{1}H-NMR (CD_3OD): δ 0.85 (3H, t, $J = 7.4$ Hz, a), 1.33 (2H, m, b), 1.80 (2H, dd, c), 5.34 (1H, m, d), 7.13 (2H, t, $J = 8.2$ Hz, *m*-proton from –OPO_2(O–)), 6.92 (2H, d, $J = 8.2$ Hz, *o*-proton from –OPO_2(O–)), 6.97 (1H, $J = 7.3$ Hz, t, *p*-proton from –OPO_2(O–)), 7.50 (4H, m, e) for $CH_3{}^aCH_2{}^bCH_2{}^cCH^d[OPO_2(OC_6H_5)Na]C_6H_4{}^eC_6F_{13}$; ^{19}F-NMR ($CD_3OD$): δ −85.6 (3F, s, a), −130.4 (2F, s, b), −127.0 (2F, s, c), −126.0 (2F, s, d), −125.6 (2F, s, e), −114.5 (2F, s, f) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fC_6H_4$-$CH[OPO_2(OC_6H_5)Na]C_3H_7$; FABMS *m/z* (rel. int.): 1269 $[2M-Na]^-$ (7.5), 563 $[M-Na]^-$ (100), 79 $[PO_3]^-$ (44).

F8PH3PPhNa: white solid, yield 75%; IR (cm^{-1}): 1092 (ν_{P-O}), 1147 ($\nu_{P=O}$), 1247 (ν_{C-F}), 1484 (ν_{Ph-O}), 2959 (ν_{C-H}); ^{1}H-NMR (CD_3OD): δ 0.87 (3H, t, $J = 7.4$ Hz, a), 1.31 (2H, m, b), 1.82 (2H, dd, c), 5.32 (1H, m, d), 7.12 (2H, t, $J = 8.2$ Hz, *m*-proton from –OPO_2(O–)), 6.93 (2H, d, $J = 8.2$ Hz, *o*-proton from –OPO_2(O–)), 6.96 (1H, $J = 7.3$ Hz, t, *p*-proton from –OPO_2(O–)), 7.50 (4H, m, e) for $CH_3{}^aCH_2{}^bCH_2{}^cCH^d[OPO_2(OC_6H_5)Na]C_6H_4{}^eC_8F_{17}$; ^{19}F-NMR ($CD_3OD$) δ −85.5 (3F, s, a), −130.4 (2F, s, b), −126.8 (2F, s, c), −126.0 (6F, s, d, e and f), −125.3 (2F, s, g), −114.5 (2F, s, h) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^f$-$CF_2{}^gCF_2{}^hC_6H_4CH[OPO_2(OC_6H_5)Na]C_3H_7$; FABMS *m/z* (rel. int.): 1469 $[2M-Na]^-$ (18), 763 $[M-Na]^-$ (100), 79 $[PO_3]^-$ (30).

F4PH5PPhNa: white solid, yield 72%; IR (cm^{-1}): 1090 (ν_{P-O}), 1147 ($\nu_{P=O}$), 1240 (ν_{C-F}), 1483 (ν_{Ph-O}), 2967 (ν_{C-H}); ^{1}H-NMR (CD_3OD): δ 0.81 (3H, t, $J = 7.3$ Hz, a), 1.28 (6H, m, b, c and d), 1.86 (2H, dd, e), 5.31 (1H, m, f), 7.11 (2H, t, $J = 8.2$ Hz, *m*-proton from –OPO_2(O–)), 6.94 (2H, d, $J = 8.2$ Hz, *o*-proton from –OPO_2(O–)), 6.99 (1H, $J = 7.3$ Hz, t, *p*-proton from –OPO_2(O–)), 7.50 (4H, m, g) for $CH_3{}^aCH_2{}^b$-$CH_2{}^cCH^dCH_2{}^eCH^f[OPO_2(OC_6H_5)Na]C_6H_4{}^gC_4F_9$; ^{19}F-NMR ($CD_3OD$): δ −85.9 (2F, s, a), −130.0 (2F, s, b), −126.9 (2F, s, c), −114.7 (2F, s, d) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dC_6H_4CH[O$-$PO_2(OC_6H_5)Na]C_5H_{11}$; FABMS *m/z* (rel. int.): 1125 $[2M-Na]^-$ (5), 551 $[M-Na]^-$ (100), 79 $[PO_3]^-$ (78).

F6PH5PPhNa: white solid, yield 73%; IR (cm^{-1}): 1093 (ν_{P-O}), 1147 ($\nu_{P=O}$), 1237 (ν_{C-F}), 1492 (ν_{Ph-O}), 2959 (ν_{C-H}); ^{1}H-NMR (CD_3OD): δ 0.82 (3H, t, $J = 7.3$ Hz, a), 1.28 (6H, m, b, c and d), 1.87 (2H, dd, e), 5.31 (1H, m, f), 7.12 (2H, t, $J = 8.2$ Hz, *m*-proton from –OPO_2(O–)), 6.92 (2H, d, $J = 8.2$ Hz, *o*-proton from –OPO_2(O–)), 6.98 (1H, $J = 7.3$ Hz, t, *p*-proton from –OPO_2(O–)), 7.50 (4H, m, g) for $CH_3{}^aCH_2{}^bCH_2{}^cCH^dCH_2{}^eCH^f[OPO_2(OC_6H_5)Na]C_6H_4{}^g$-$C_6F_{13}$; ^{19}F-NMR ($CD_3OD$) δ −85.4 (3F, s, a), −130.4 (2F, s, b), −127.0 (2F, s, c), −126.0 (2F, s, d), −125.6 (2F, s, e), −114.5 (2F, s, f) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fC_6H_4$-$CH[OPO_2(OC_6H_5)Na]C_5H_{11}$; FABMS *m/z* (rel. int.): 1325 $[2M-Na]^-$ (16), 651 $[M-Na]^-$ (100), 79 $[PO_3]^-$ (25).

F8PH5PPhNa: white solid, yield 80%; IR (cm^{-1}): 1089 (ν_{P-O}), 1147 ($\nu_{P=O}$), 1241 (ν_{C-F}), 1483 (ν_{Ph-O}), 2963 (ν_{C-H}); ^{1}H-NMR (CD_3OD): δ 0.83 (3H, t, $J = 7.3$ Hz, a), 1.28 (6H, m, b, c and d), 1.87 (2H, dd, e), 5.34 (1H, m, f), 7.12 (2H, t, $J = 8.2$ Hz, *m*-proton from –OPO_2(O–)), 6.93 (2H, d, $J = 8.2$ Hz, *o*-proton from –OPO_2(O–)), 6.99 (1H, $J = 7.3$ Hz, t, *p*-proton from –OPO_2(O–)), 7.52 (4H, m, g) for $CH_3{}^aCH_2{}^bCH_2{}^cCH^dCH_2{}^eCH^f[OPO_2(OC_6H_5)Na]C_6H_4{}^g$-$C_8F_{17}$; ^{19}F-NMR ($CD_3OD$) δ −85.5 (3F, s, a), −130.4 (2F, s, b), −126.8 (2F, s, c), −126.0 (6F, s, d, e and f), −125.3 (2F, s, g), −114.5 (2F, s, h) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fCF_2{}^g$-$CF_2{}^hC_6H_4CH[OPO_2(OC_6H_5)Na]C_5H_{11}$; FABMS *m/z* (rel. int.): 1525 $[2M-Na]^-$ (12), 751 $[M-Na]^-$ (100), 79 $[PO_3]^-$ (32).

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