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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: $m = 4, 6, 8$; $n = 3, 5$; C_6H_4 = *p*-phenylene, C_6H_5 = phenyl), 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 are found to have comparable abilities to lower surface tension of water. The critical micelle concentrations of F*m*PH*n*PPhNa follow Klevens rule and their occupied areas per molecule increase with increasing *m* and *n*. Calcium hydroxyapatite (CaHAp) pellets modified with F*m*PH3PPhNa gives high hydrophobic and lipophobic surfaces. The hybrid surfactants are expected 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], the 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 showed by the mixture of fluorocarbon surfactants and hydrocarbon surfactants.

The authors 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 surfaces and restrained dental plaque formation. This result suggests that the fixation of fluorocarbons onto teeth is effective to keep oral cavities clean. We have also reported that hybrid surfactants can solubilize hydrocarbon molecules in their micelles and thus the hybrid surfactant micelles serve as drug carriers [11,12]. On the other hand, phenyl-P is widely used as a dental adhesive because its phenyl phosphate group strongly adsorbs to human teeth [13–16]. Hybrid surfactants having a phenyl phosphate group would be useful in the field of dentistry. It is expected that not only the surfactants adsorb on teeth to give hydrophobicity and lipophobicity, but also the surfactant 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: $m = 4, 6, 8$; $n = 3, 5$; C_6H_4 = *p*-phenylene, C_6H_5 = phenyl), the physicochemical properties of their solutions and the adsorption to calcium hydroxyapatite (CaHAp) pellet as a model of human teeth.

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2. Results and discussion

2.1. Synthesis of hybrid surfactants

Scheme 1 shows the synthetic route of the hybrid surfactants. The alcohol, F*m*PH*n*A, was prepared according to the previous paper [17]. The introduction of a phosphate group to hybrid alcohol F*m*PH*n*A was performed using diphenyl phosphorochloridate under the catalyst of dimethylaminopyridine (DMAP) at 35 °C. The obtained triester, $C_mF_{2m+1}C_6H_4CH[OPO(OC_6H_5)_2]C_nH_{2n+1}$ (F*m*PH*n*PPh2), was easily alkalized with NaOH to give the phosphate-type hybrid surfactant F*m*PH*n*PPhNa in a high yield (ca. >70%).

2.2. Krafft point, cmc and surface tension of FmPHnPPhNa

Table 1 shows Krafft point (K_p), cmc, and surface tension at cmc (γ_{cmc}) of F*m*PH*n*PPhNa aqueous solutions 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 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 of F*m*PH*n*PPhNa is higher than that of the corresponding F*m*PH*n*OS. This is because phenyl phosphate group was less hydrophilic compared with sulfate group. By the hydrophobicity of F*m*PH*n*PPhNa, the cmc was lower than that of F*m*PH*n*OS. Moreover the γ_{cmc} for F*m*PH*n*PPhNa was about 20 mN m^{-1}, almost same as that 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.

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^{-1})
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 (3.5 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 concentration shown in parenthesis.
[b] 30 °C.
[c] The data were not obtained because of high K_p.
[d] From Ref. [17].

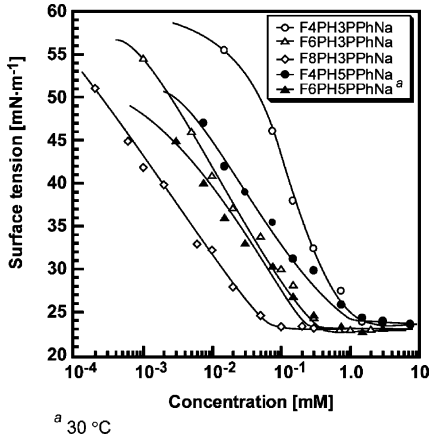
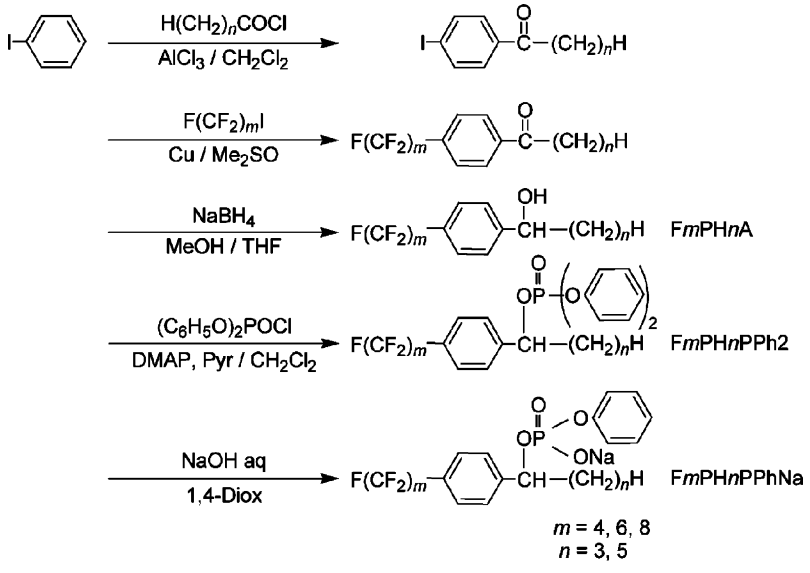


Fig. 1. Surface tension plots of F*m*PH*n*PPhNa aq. against surfactant concentration at 25 °C.



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

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].

The occupied area (A_{Air}) per molecule of F*m*PH*n*PPhNa was calculated from the surface excess concentration at air/water interface (Γ_{Air}). The value Γ_{Air} was calculated 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 the concentration of F*m*PH*n*PPhNa aqueous solutions, R the gas constant and T the absolute temperature. The value 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 value of Γ_{Air} and A_{Air}. The A_{Air} increased with increasing m and n. F*m*PH*n*PPhNa has a large A_{Air} value compared with the corresponding F*m*PH*n*OS. Phenyl phosphate group is structurally larger than sulfate group. This will be the reason for the larger A_{Air} values of F*m*PH*n*PPhNa.

Fig. 2 shows the logarithmic plots of the cmc determined by surface tension measurement against m and n. Klevens has found that log(cmc) was empirically related to a 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 F*m*PH3PPhNa, log(cmc) decreased linearly with increasing m, obeying Klevens rule (4),

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

Eq. (4) suggests that when the number of CF_2 group in the hydrophobic chain increases by one, the cmc decreases by 52%. Moreover, assuming that Klevens rule hold for F*m*PH5PPhNa ($n = 5$), F4PH*n*PPhNa ($m = 4$), and F6PH*n*PPhNa ($m = 6$), the following three Eqs. (5)–(7) are obtained.

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

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

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

These equations give the rates of cmc decrease of 54%/CF_2 group, 17%/CH_2 group, and 23%/CH_2 group for F*m*PH5PPhNa, F4PH*n*PPhNa and F6PH*n*PPhNa, respectively. For F*m*PH*n*OS, the cmc decreases by 66–67%/CF_2 group and 34–38%/CH_2 group. The contribution to cmc of both CF_2 group and CH_2 group in F*m*PH*n*PPhNa is smaller than that in F*m*PH*n*OS. This result would be brought about by the introduction of a spatially large phenyl group into phosphate group, thereby causing weakened hydrophobic interaction between hydrophobic chains as compared with that for F*m*PH*n*OS.

2.3. Modification of CaHAp pellets with FmPHnPPhNa

Table 3 shows the contact angles of water and oleic acid on the modified pellet after being dipped in water for 12 h. The contact angles of water increased with increasing value

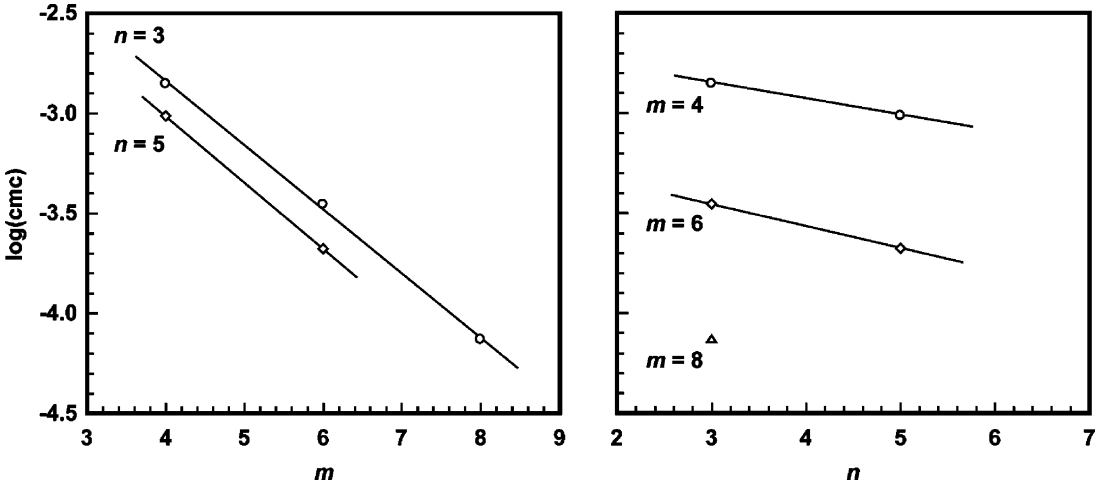


Fig. 2. Log(cmc) plots of F*m*PH*n*PPhNa aq. against hydrophobic chain length m or n.

Table 3
Contact angles on modified surface 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

of *m* and *n*, and the contact angles of oleic acid increased by increasing *m*, while decreased as value *n* increased. The modified pellet surface with F*m*PH3PPhNa was highly hydrophobic and oil-repellent. In contrast, although the pellets modified by F*m*PH5PPhNa are highly hydrophobic, those showed lipophilicy compared to pellets modified by F*m*PH3PPhNa. We previously reported that the hydro- and lipophobic tooth surface markedly inhibits plaque formation on it. In particular, the CaHAp pellets modified by F*m*PH3PPhNa remained highly hydro- and lipophobic even after being dipped in water for 12 h. F*m*PH3PPhNa is expected to be a useful dental reagent from the 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 $C_mF_{2m+1}C_6H_4CH(OH)C_nH_{2n+1}$ ($m = 4, 6, 8$, $n = 3, 5$: F*m*PH*n*A) were synthesized as reported previously [15]. 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 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 the 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 angles of water and oleic acid on the CaHAp pellet modified by FmPHnPPhNa

The 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 for 6 h at 25 °C, the pellets were dried for 30 min at room temperature in vacuo. Only for F6PH5PPhNa, the pellet was dipped in the 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 (the case of F6PH5PPhNa). The contact angles of water and oleic acid were measured using 0.9 mm^3 of droplets after the pellets were 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 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_3–), 6.97 (2H, t, $J = 7.3$ Hz, *p*-proton from –OPO_3–), 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 $CF_3^aCF_2^bCF_2^cCF_2^dC_6H_4CH[OPO_3(C_6H_5)_2]C_3H_7$; GC–MS 70 eV, *m*/*z* (rel. int.): 600 $[M]^+$ (12), 557 $[M–C_3H_7]^+$ (5), 350 $[M–OPO_3(C_6H_5)_2]^+$ (25), 309 $[C_4F_9C_6H_4CH_2]^+$ (30), 251 $[OPO_3(C_6H_5)_2]^+$ (100).

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

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_3–), 7.01 (2H, t, J = 7.3 Hz, *p*-proton from –OPO_3–), 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 $CH_3{}^aCH_2{}^bCH_2{}^cCH^d[OPO_3(C_6H_5)_2]C_6H_4C_6F_{13}$; ^{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 $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fC_6H_4CH[OPO_3(C_6H_5)_2]C_3H_7$; GC–MS 70 eV, *m/z* (rel. int.): 700 $[M]^+$ (20), 657 $[M–C_3H_7]^+$ (5), 450 $[M–OPO_3(C_6H_5)_2]^+$ (25), 409 $[C_6F_{13}C_6H_4CH_2]^+$ (30), 251 $[OPO_3(C_6H_5)_2]^+$ (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_3–), 7.09 (2H, t, J = 7.3 Hz, *p*-proton from –OPO_3–), 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 $CH_3{}^aCH_2{}^bCH_2{}^cCH^d[OPO_3(C_6H_5)_2]C_6H_4C_8F_{17}$; ^{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 $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fCF_2{}^gCF_2{}^hC_6H_4CH[OPO_3(C_6H_5)_2]C_3H_7$; GC–MS 70 eV, *m/z* (rel. int.): 800 $[M]^+$ (20), 757 $[M–C_3H_7]^+$ (5), 550 $[M–OPO_3(C_6H_5)_2]^+$ (30), 509 $[C_8F_{17}C_6H_4CH_2]^+$ (30), 251 $[OPO_3(C_6H_5)_2]^+$ (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_3–), 6.99 (2H, t, J = 7.3 Hz, *p*-proton from –OPO_3–), 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 $CH_3{}^aCH_2{}^bCH_2{}^cCH_2{}^dCH_2{}^eCH^f[OPO_3(C_6H_5)_2]C_6H_4C_4F_9$; ^{19}F-NMR ($CDCl_3$): δ −85.9 (3F, s, a), −130.0 (2F, s, b), −126.9 (2F, s, c), −114.7 (2F, s, d) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dC_6H_4CH[OPO_3(C_6H_5)_2]C_5H_{11}$; GC–MS 70 eV, *m/z* (rel. int.): 628 $[M]^+$ (15), 557 $[M–C_5H_{11}]^+$ (5), 378 $[M–OPO_3(C_6H_5)_2]^+$ (25), 309 $[M–OPO_3(C_6H_5)_2]^+$ (30), 251 $[OPO_3(C_6H_5)_2]^+$ (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_3–), 7.02 (2H, t, J = 7.3 Hz, *p*-proton from –OPO_3–), 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 $CH_3{}^aCH_2{}^bCH_2{}^cCH_2{}^dCH_2{}^eCH^f[OPO_3(C_6H_5)_2]C_6H_4C_6F_{13}$; ^{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 $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fC_6H_4CH[OPO_3(C_6H_5)_2]C_5H_{11}$;GC–MS 70 eV, *m/z* (rel. int.): 728 $[M]^+$ (20), 657 $[M–C_5H_{11}]^+$ (5), 478 $[M–OPO_3(C_6H_5)_2]^+$ (25), 409 $[M–OPO_3(C_6H_5)_2]^+$ (30), 251 $[OPO_3(C_6H_5)_2]^+$ (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_3–), 7.11 (2H, t, J = 7.3 Hz, *p*-proton from –OPO_3–), 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 $CH_3{}^aCH_2{}^bCH_2{}^cCH_2{}^dCH_2{}^eCH^f[OPO_3(C_6H_5)_2]C_6H_4C_8F_{17}$; ^{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 $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fCF_2{}^gCF_2{}^hC_6H_4CH[OPO_3(C_6H_5)_2]C_5H_{11}$; GC–MS 70 eV, *m/z* (rel. int.): 828 $[M]^+$ (20), 757 $[M–C_5H_{11}]^+$ (5), 578 $[M–OPO_3(C_6H_5)_2]^+$ (25), 509 $[M–OPO_3(C_6H_5)_2]^+$ (30), 251 $[OPO_3(C_6H_5)_2]^+$ (100).

3.4. Synthesis of FmPHnPPhNa

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

F4PH3PPh2 (3.0 g, 5.0 mmol), 1,4-dioxane (50 cm^3), 4N-sodium hydroxide aqueous solution (25 cm^3) was heated for 2 h at 50 °C. After 1N-hydrochloric acid was added to the mixture by pH = 4, the precipitation was filtrated. The sodium hydrogencarbonate (1.0 g) in water (10 cm^3) was introduced to aqueous solution dispersed the precipitation (5.2 g). The precipitation of methanol-soluble part from hexane was preformed to give F4PH3PPhNa as white solid. 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_3–), 6.92 (2H, d, J = 8.2 Hz, *o*-proton from –OPO_3–), 6.98 (1H, J = 7.3 Hz, t, *p*-proton from –OPO_3–), 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 (3F, s, a), −129.9 (2F, s, b), −126.9 (2F, s, c), −114.7 (2F, s, d) for $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dC_6H_4CH[OPO_2(OC_6H_5)Na]C_3H_7$; 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) and others

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_3–), 6.92 (2H, d, J = 8.2 Hz, *o*-proton from –OPO_3–), 6.97 (1H, J = 7.3 Hz, t, *p*-proton from –OPO_3–), 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 ($\nu_{P–O}$), 1147 ($\nu_{P=O}$), 1247 ($\nu_{C–F}$), 1484 ($\nu_{Ph–O}$), 2959 ($\nu_{C–H}$); ^{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 $–OPO_3–$), 6.93 (2H, d, J = 8.2 Hz, *o*-proton from $–OPO_3–$), 6.96 (1H, J = 7.3 Hz, t, *p*-proton from $–OPO_3–$), 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 $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dC$-$F_2{}^eCF_2{}^fCF_2{}^gCF_2{}^hC_6H_4CH[OPO_2(OC_6H_5)Na]C_3H_7$; 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 ($\nu_{P–O}$), 1147 ($\nu_{P=O}$), 1240 ($\nu_{C–F}$), 1483 ($\nu_{Ph–O}$), 2967 ($\nu_{C–H}$); ^{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 $–OPO_3–$), 6.94 (2H, d, J = 8.2 Hz, *o*-proton from $–OPO_3–$), 6.99 (1H, J = 7.3 Hz, t, *p*-proton from $–OPO_3–$), 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 (3F, 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 ($\nu_{P–O}$), 1147 ($\nu_{P=O}$), 1237 ($\nu_{C–F}$), 1492 ($\nu_{Ph–O}$), 2959 ($\nu_{C–H}$); ^{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 $–OPO_3–$), 6.92 (2H, d, J = 8.2 Hz, *o*-proton from $–OPO_3–$), 6.98 (1H, J = 7.3 Hz, t, *p*-proton from $–OPO_3–$), 7.50 (4H, m, g) for $CH_3{}^aCH_2{}^bCH_2{}^cCH^d$-$CH_2{}^eCH^f[OPO_2(OC_6H_5)Na]C_6H_4{}^gC_6F_{13}$; ^{19}F-NMR ($CD_3$ OD) 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 $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fC_6H_4CH[OPO_2(OC_6H_5)$-$Na]C_5H_{11}$; 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 ($\nu_{P–O}$), 1147 ($\nu_{P=O}$), 1241 ($\nu_{C–F}$), 1483 ($\nu_{Ph–O}$), 2963 ($\nu_{C–H}$); ^{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 $–OPO_3–$), 6.93 (2H, d, J = 8.2 Hz, *o*-proton from $–OPO_3–$), 6.99 (1H, J = 7.3 Hz, t, *p*-proton from $–OPO_3–$), 7.52 (4H, m, g) for $CH_3{}^aCH_2{}^bCH_2{}^cCH^d$-$CH_2{}^eCH^f[OPO_2(OC_6H_5)Na]C_6H_4{}^gC_8F_{17}$; ^{19}F-NMR ($CD_3$ OD) 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 $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fCF_2{}^gCF_2{}^hC_6H_4CH[O$-$PO_2(OC_6H_5)Na]C_5H_{11}$; FABMS *m/z* (rel. int.): 1525 $[2M–Na]^-$ (12), 751 $[M–Na]^-$ (100), 79 $[PO_3]^-$ (32).

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