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Synthesis and complexation of amphiphilic calix[4]arene phosphonates with organic molecules in solutions and Langmuir-Blodgett films

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ABSTRACT

A family of amphiphilic alkoxycalix[4]arenes bearing phosphonyl groups directly attached to *para* positions of the aromatic rings is synthesized by the Arbuzov reaction of *para*-bromoalkoxycalix[4]arenes with alkyl esters of phosphorus (III) acid in the presence of $NiBr_2$. Amphiphilicity of the calixarene phosphonates is controlled by varying the quantities of the hydrophilic phosphoryl groups at the upper rim and the hydrophobic alkyl groups at the lower rim. Complexation of the calixarenes with benzene derivatives and *iso*-butanol in solutions is studied by RP HPLC and IR spectroscopy methods. Langmuir-Blodgett films of the calixarene phosphonates are prepared. Physical characteristics and complexation of the films with volatile organic molecules are characterized.

1. Introduction

Calixarenes are macrocyclic compounds of great interest in supramolecular chemistry as bowl-shape platform for construction of new molecules with remarkable host properties [1–5]. The ability to form host-guest type complexes from a gas mixture [6], solutions [7,8], crystalline state [9] and in the two-dimensional thin films [10–13] have been reported. The calixarene thin films have been used to create devices capable of recognizing cations, anions or neutral molecules in solutions (*artificial tongue*) or in a gas mixture (*artificial nose*) [14,15]. A common method of the thin film formation is based on the Langmuir-Blodgett technique (LB), using amphiphilic calixarenes simultaneously possessing hydrophilic and hydrophobic groups at the opposite rims of the macrocycle.

In this paper we describe the synthesis of a family of amphiphilic calix[4]arenes possessing hydrophilic phosphoryl groups at the upper rim and hydrophobic alkyl chains at the lower rim of the calixarene core. The binding properties of the calixarene phosphonates with benzene derivatives and *iso*-butanol in solutions have been studied. The self-assembly of calixarene phosphonates at the water–air interface, and LB film formation were investigated. Receptor properties of the calixarene LB films towards chloroform or acetone vapor in air have been investigated by the sensory system based on quartz crystal microbalance technique.

2. Experimental

2.1. General

All reactions were carried out under nitrogen. Solvents were dried and distilled by standard methods. ^{1}H NMR spectra were recorded on a Varian VXR instrument at 300 MHz. The ^{1}H NMR data are referenced to tetramethylsilane and ^{31}P NMR data are referenced relative to H_3PO_4 (85%) as the external standard. MS spectra were recorded on a single-stage quadruple mass spectrometer using DCI technique. IR spectra were recorded on M-80 spectrometer. CCl_4 for spectroscopy measurements was distilled over P_2O_5 and stored over molecular sieves 3 Å to condition in which water absorption bands ν_a and ν_{as} in this solvent (thickness of absorption layer 10 cm) were absent. The melting points determined on a Boetius apparatus were uncorrected. Analytical thin layer chromatography was performed on precoated silica gel plates (Silufol). Silica gel (L 40/100) was used for column chromatography.

Molecular modeling experiments of the phosphorylated calixarenes were carried out using HyperChem 8.0 (PM3). (The evaluations copy is free for download at http://www.hyper.com/Download/tabid/357/Default.aspx). RMS gradient was equal to 0.01 kcal/A mol.

Bromocalixarenes **1-4** [16,17] and calixarene phosphonates **5a**, **6b**, **9a**, **9b** [18,19] were synthesized according the published procedures.

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2.2. Materials

2.2.1. General procedure for the preparation of calix[4]arene phosphonates 5-9

To melted bromotetraheptyloxy(octyloxy)calix[4]arenes **1b,c** and **4 b,c** (0.01 mmol) or to solutions of bromotetrapropoxycalix[4]arenes **2** and **3** (0.01 mmol) in benzonitrile (10 mL) in the presence of $NiBr_2$ (0.002 mmol for each bromine atom of the calix[4]arene), the phosphites (0.12, 0.24, 0.48 mmol accordingly) were added dropwise at 170 °C. The resulting solutions were kept at the temperature for 1 h. The reaction mixture was evaporated in vacuum (0.05 mm, 100 °C) resulting in an oil. The oil was then dissolved in methylene chloride, and that the solution was washed with NH_4OH, water and subsequently dried over Na_2SO_4. The solution was evaporated to dryness and a residue was purified by column chromatography. Yields were calculated to be 40–70%.

2.2.2. 5-Dibutyloxyphosphonyl-25,26,27,28-tetrapropoxycalix[4]arene (5b)

Purification by column chromatography (CH_2Cl_2/acetone 10:1), R_f 0.5. Oil: yield 50%; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 6 H, J 7.2 Hz, C***H***$_3$CH$_2$CH$_2$CH$_2$O), 0.97, 1.07 (two t, 6 H + 6 H, J 7.5 Hz, C***H***$_3$CH$_2$CH$_3$O), 1.36 (m, 4 H, CH$_3$C***H***$_2$CH$_2$CH$_2$O), 1.60 (m, 4 H, CH$_3$CH$_2$C***H***$_2$CH$_2$O), 1.92 (m, 8 H, CH$_3$C***H***$_2$CH$_2$O), 3.15, 3.19 (two d, 2 H + 2 H, J 13.2 Hz, ArCH$_{2eq}$), 3.89 (m, 12 H, CH$_2$O), 4.44, 4.46 (two d, 2 H + 2 H, J 13.2 Hz, ArCH$_{2ax}$), 6.50 (m, 6 H, ArH-m + ArH-p), 6.62 (t, 1 H, J 7.0 Hz, ArH-p), 6.70 (d, 2 H, J 7.0 Hz, ArH-m), 7.18 (d, 2 H, J_{PH} 13 Hz, ArH-m); ^{31}P NMR δ 20.6; MS (CI) *m/z* 786 (M^+, 100%). M calculated 783.975. Anal. Calcd. for $C_{48}H_{65}O_7P$: C, 73.44; H, 8.35; P, 3.95 Found: C, 73.21; H, 8.33; P, 3.85.

2.2.3. 5-Diethoxyphosphonyl-25,26,27,28-tetraheptyloxycalix[4]arene (5c)

Purification by column chromatography (CH_2Cl_2/CH_3OH 20:1), R_f 0.5. Oil: yield 65%; ^{1}H NMR ($CDCl_3$) 0.93 (m, 12 H, C***H***$_3$(CH$_2$)$_6$O), 1.27 (t, 6 H, J 7.2 Hz, C***H***$_3$CH$_2$O), 1.34, 1.40 (two m, 32 H, CH$_2$), 1.95 (m, 8 H, C***H***$_2$CH$_2$O), 3.17, 3.21 (two d, 2 H + 2 H, J 13.2 Hz, ArCH$_{2eq}$), 3.91 (m, 12 H, CH$_2$O), 4.45, 4.48 (two d, 2 H + 2 H, J 13.2 Hz, ArCH$_{2ax}$), 6.59 (m, 9 H, ArH), 7.17 (d, 2 H, J_{PH} 13 Hz, ArH-m); ^{31}P NMR δ 20.1; MS (CI) *m/z* 954 (M^+, 100%). M calculated 953.35. Anal. Calcd. for $C_{60}H_{89}O_7P$: P, 3.25 Found: P, 3.12.

2.2.4. 5-Diethoxyphosphonyl-25,26,27,28-tetraoctyloxycalix[4]arene (5d)

Purification by column chromatography (CH_2Cl_2/acetone 20:1), R_f 0.6. Oil: yield 60%; ^{1}H NMR ($CDCl_3$) 0.93 (m, 12 H, C***H***$_3$(CH$_2$)$_7$O), 1.28 (t, 6 H, J 7.2 Hz, C***H***$_3$CH$_2$O), 1.34, 1.40 (two m, 40 H, CH$_2$), 1.94 (m, 8 H, C***H***$_2$CH$_2$O), 3.18, 3.22 (two d, 2 H + 2 H, J 13.2 Hz, ArCH$_{2eq}$), 3.92 (m, 12 H, CH$_2$O), 4.46, 4.49 (two d, 2 H + 2 H, J 13.2 Hz, ArCH$_{2ax}$), 6.60 (m, 9 H, ArH), 7.19 (d, 2 H, J_{PH} 13 Hz, ArH-m); ^{31}P NMR δ 20.75; MS (CI) *m/z* 1010 (M^+, 100%). M calculated 1009.45. Anal. Calcd. for $C_{64}H_{97}O_7P$: P, 3.07 Found: P, 2.96.

2.2.5. 5-Phenylisopropoxyphosphonyl-25,26,27, 28-tetrapropoxycalix[4]arene (5e)

Purification by column chromatography (CH_2Cl_2/acetone 5:1), R_f 0.4. White solid: yield 50%; m.p. 55–58 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (m, 12 H, CH$_3$), 1.27, 1.29 (two d, 3 H + 3 H, J 7.5 Hz, diastereotopic C***H***$_3$CH), 1.93 (m, 8 H, C***H***$_2$CH$_2$O), 3.17, 3.21 (two d, 2 H + 2 H, J 13.5 Hz, ArCH$_{2eq}$), 3.85 (m, 8 H, CH$_2$O), 4.45 (d, 4 H, J 13.5 Hz, ArCH$_{2ax}$), 4.55 (m, 1 H, CH$_3$C***H***), 6.51 (m, 7 H, ArH-m + ArH-p), 6.72 (d, 2 H, J 7.0 Hz, ArH-m), 7.17, 7.35 (two d, 1 H + 1 H, J_{PH} 13 Hz, diastereotopic ArH-m), 7.43 (m, 2 H, *meta* protons of C_6H_5 group), 7.51 (m, 1 H, *para* proton of C_6H_5 group), 7.69, 7.71 (two d, 1 H + 1 H, J $_{PH}$ 13 Hz, diastereotopic *ortho* protons of C_6H_5 group); ^{31}P NMR δ 31.6; Anal. Calcd. for $C_{49}H_{59}O_6P$: C, 75.94; H, 7.67; P, 3.99 Found: C, 75.88; H, 7.75; P, 3.97.

2.2.6. 5,17-Bis(diethoxyphosphonyl)-25,27-dipropoxycalix[4]arene (6a)

Purification by column chromatography (CH_2Cl_2/acetone 5:1), R_f 0.6. White solid: yield 70%; m.p. 160–163 °C; ^{1}H NMR ($CDCl_3$) 0.95 (t, 6 H, J 7.0 Hz, C***H***$_3$CH$_2$CH$_2$O), 1.36 (t, 12 H, J 7.0 Hz, C***H***$_3$CH$_2$O), 1.86 (m, 4 H, CH$_3$C***H***$_2$CH$_2$O), 3.25 (d, 4 H, J 13.0 Hz, ArCH$_{2eq}$), 3.70 (t, 8 H, J 7.0 Hz, CH$_2$O), 4.15 (m, 8 H, CH$_2$OP), 4.47 (d, 4 H, J 13.0 Hz, ArCH$_{2ax}$), 6.85 (t, 2 H, J 7.0 Hz, ArH-p), 7.05 (d, 4 H, J 7.0 Hz, ArH-m), 7.57 (d, 4 H, J_{PH} 13.2 Hz, ArH), 9.00 (s, 2 H, OH); ^{31}P δ 19.6; MS (CI) *m/z* 782 (M^+, 100%). M calculated 780.84. Anal. Calcd. for $C_{42}H_{54}O_{10}P_2$: P, 7.93 Found: P, 7.68.

2.2.7. 5,17-Bis(diethoxyphosphonyl)-25,26,27, 28-tetrapropoxycalix[4]arene (7a)

Purification by column chromatography (CH_2Cl_2/acetone 5:1), R_f 0.6. White solid: yield 70%; m.p. 159–162 °C; ^{1}H NMR ($CDCl_3$) 0.90 (t, 6 H, J 7.0 Hz, C***H***$_3$CH$_2$CH$_2$O), 1.10 (t, 6 H, J 7.0 Hz, C***H***$_3$CH$_2$CH$_2$O), 1.37 (t, 12 H, J 7.0 Hz, C***H***$_3$CH$_2$O), 1.90 (m, 8 H, CH$_3$C***H***$_2$CH$_2$O), 3.22 (d, 4 H, J 13.0 Hz, ArCH$_{2eq}$), 3.69 (t, 4 H, J 7.0 Hz, CH$_2$O), 4.18 (m, 12 H, CH$_2$O + CH$_2$OP), 4.46 (d, 4 H, J 13.0 Hz, ArCH$_{2ax}$), 6.10 (d, 4 H, J 7.2 Hz, ArH-m), 6.23 (t, 2 H, J 7.2 Hz, ArH-p), 7.56 (d, 4 H, J_{PH} 13.2 Hz, ArH-m); ^{31}P NMR δ 20.1; MS (CI) *m/z* 866 (M^+, 100%). M calculated 865.01. Anal. Calcd. for $C_{48}H_{66}O_{10}P_2$: P, 7.16 Found: P, 7.08.

2.2.8. 5,17-Bis(diphenylphosphonyl)-25,26,27, 28-tetrapropoxycalix[4]arene (7b)

Purification by column chromatography (CH_2Cl_2/CH_3OH/acetone 30:1:1), R_f 0.3. White solid: yield 50%; m.p. 107–109 °C; ^{1}H NMR ($CDCl_3$) 0.91 (t, 6 H, J 7.0 Hz, C***H***$_3$CH$_2$CH$_2$O), 1.08 (t, 6 H, J 7.0 Hz, C***H***$_3$CH$_2$CH$_2$O), 1.83 (m, 4 H, CH$_2$), 1.98 (m, 4 H, CH$_2$), 3.14 (d, 4 H, J 13.0 Hz, ArCH$_{2eq}$), 3.62 (t, 4 H, J 7.0 Hz, CH$_2$O), 4.11 (t, 4 H, J 7.0 Hz, CH$_2$O), 4.44 (d, 4 H, J 13.0 Hz, ArCH$_{2ax}$), 6.04 (d, 4 H, J 7.2 Hz, ArH-m), 6.26 (t, 2 H, J 7.2 Hz, ArH-p), 7.42 (d, 4 H, J_{PH} 13.2 Hz, ArH-m), 7.55 (m, 12 H, *meta* + *para* protons of C_6H_5 groups), 7.73, 7.76 (two d, 4 H + 4 H, J_{PH} 13 Hz, diastereotopic *ortho* protons of C_6H_5 group); ^{31}P NMR δ 30.5. Anal. Calcd. for $C_{64}H_{66}O_6P_2$: P, 6.2. Found: P, 6.16.

2.2.9. 5-Bromo-11,17,23-tris(diethoxyphosphonyl)-25,26,27, 28-tetraheptyl-oxycalix[4]arene (8a)

Purification by column chromatography (CH_2Cl_2/CH_3OH 3:1), R_f 0.4. Oil: yield 25%; ^{1}H NMR ($CDCl_3$) 0.92 (m, 12 H, C***H***$_3$(CH$_2$)$_5$CH$_2$O), 1.10 (t, 6 H, J 7.0, C***H***$_3$CH$_2$O), 1.33 (m, 12 H + 24 H, C***H***$_3$CH$_2$O + CH$_3$ (C***H***$_2$)$_4$CH$_2$CH$_2$O), 1.96 (m, 8 H, CH$_3$(CH$_2$)$_4$C***H***$_2$CH$_2$O), 3.30, 3.33 (two d, 2 H + 2 H, J 13.0 Hz, CH$_{2eq}$), 3.71 (m, 8 H, CH$_3$(CH$_2$)$_4$CH$_2$C***H***$_2$O), 4.13 (t, 12 H, J 7.0 Hz, CH$_3$C***H***$_2$O), 4.46, 4.49 (two d, 2 H + 2 H, J 13.0 Hz, ArCH$_{2ax}$), 6.53 (s, 2 H, ArH-m), 6.91 (d, 2 H, J_{PH} 13.2 Hz , ArH-m), 7.55, 7.57 (two d, 4 H, J_{PH} 13.2 Hz, C_6H_2); ^{31}P NMR δ 19.5. Anal. Calcd. for $C_{68}H_{106}BrO_{13}P_3$: C, 62.61 H, 8.19 P, 7.12 Found: C, 62.58 H, 8.23 P, 7.06.

2.2.10. 5-Bromo-11,17,23-tris(diethoxyphosphonyl)-25,26,27, 28-tetraoctyl-oxycalix[4]arene (8b)

Purification by column chromatography (CH_2Cl_2/CH_3OH 25:1), R_f. 0.5. Oil: yield 30%; ^{1}H NMR ($CDCl_3$) 0.93 (m, 12 H, C***H***$_3$(CH$_2$)$_6$CH$_2$O), 1.12 (t, 6 H, J 7.0 Hz, C***H***$_3$CH$_2$O), 1.34 (m, 12 H + 30 H, C***H***$_3$CH$_2$O + CH$_3$ (C***H***$_2$)$_5$CH$_2$CH$_2$O), 1.98 (m, 8 H, CH$_3$(CH$_2$)$_5$C***H***$_2$CH$_2$O), 3.35, 3.38 (two d, 2 H + 2 H, ArCH$_{2eq}$), 3.80 (m, 8 H, CH$_3$(CH$_2$)$_5$CH$_2$C***H***$_2$O), 4.20 (t, 12 H, J 7.0 Hz, CH$_3$C***H***$_2$O), 4.47, 4.49 (two d, 2 H + 2 H, ArCH$_{2ax}$), 6.61 (s, 2 H, ArH-m), 7.00 (d, 2 H, J_{PH} 13.2 Hz, ArH), 7.58, 7.61 (two d, 2 H + 2 H, J_{PH} 13.2 Hz, ArH); ^{31}P NMR δ 19.7. Anal. Calcd. for $C_{72}H_{114}BrO_{13}P_3$: C, 64.25 H, 9.17 P, 6.28 Found: C, 62.31 H, 9.12 P, 7.14.

2.2.11. 5,11,17,23-Tetrakis(diethoxyphosphonyl)-25,26,27, 28-tetraheptyloxy-calix[4]arene (9c)

Purification by column chromatography (CH_2Cl_2/CH_3OH 3:1), R_f 0.2. White solid: yield 60%; m.p. 110–112 °C; ^{1}H NMR ($CDCl_3$) 0.91

(t, 12 H, J 7.5 Hz, C***H***$_3$(CH$_2$)$_6$O), 1.21 (t, 24 H, J 7.5 Hz, C***H***$_3$CH$_2$O), 1.32, 1.38 (two m, 32 H, CH$_3$(C***H***$_2$)$_5$CH$_2$O), 1.95 (m, 8 H, CH$_3$(CH$_2$)$_5$C***H***$_2$O), 3.32 (d, 4 H, J 13.0 Hz, ArCH$_{2eq}$), 3.96 (m, 24 H, CH$_2$OP), 4.48 (d, 4 H, J 13.0 Hz, ArCH$_{2ax}$), 7.27 (d, 8 H, J$_{PH}$ 13 Hz , ArH-m); ^{31}P NMR δ 19.9. Anal. Calcd. for $C_{72}H_{116}O_{16}P_4$: P, 9.10 Found: P, 8.76.

2.2.12. 5,11,17,23-Tetrakis(diethoxyphosphonyl)-25,26,27,28-tetraoctyloxy- calix[4]arene (9d)

Purification by column chromatography (CH_2Cl_2/CH_3OH 25:1), R_f 0.2. White solid: yield 55%; m.p. 95–97 °C; ^{1}H NMR ($CDCl_3$) 0.92 (m, 12 H, C***H***$_3$(CH$_2$)$_6$CH$_2$O), 1.23 (t, 24 H, J 7.5 Hz, C***H***$_3$CH$_2$O), 1.33, 1.40 (two m, 40 H, CH$_3$(C***H***$_2$)$_6$CH$_2$O), 1.98 (m, 8 H, CH$_3$(CH$_2$)$_6$C***H***$_2$O), 3.33 (d, 4 H, J 13.0 Hz, ArCH$_{2eq}$), 3.98 (m, 24 H, CH$_2$OP), 4.49 (d, 4 H, J 13.0 Hz, ArCH$_{2ax}$), 7.28 (d, 8 H, J$_{PH}$ 13 Hz, ArH-m); ^{31}P NMR δ 19.3; MS (CI) *m/z* 1418 (M^+, 100%). M calculated 1417.73. Anal. Calcd. for $C_{76}H_{124}O_{16}P_4$: P, 8.74 Found: P, 8.56.

2.3. Methods

2.3.1. RP HPLC

The association constants of the complexes of calixarene tetraphosphonate **9a** with a series of benzene derivatives (Table 1) were determined by the RP HPLC method using analysis of the linear dependence of a capacity factor of the aromatic guest versus the calixarene concentration in a mobile phase. The association constants K_A were calculated according the published procedure [20,21] using Eq. (1)

$$K_A = \frac{k_0'\left(1/k' - 1/k_0'\right)}{[CA]} \quad (1)$$

where k'_o and k' are capacity factors in the absence and the presence of the calixarene additive in the mobile phase respectively; [CA] is the calixarene concentration in the mobile phase.

The liquid chromatographic system consisted of a high-pressure pump HPP 4001 (Laboratorni Pristroje, Praha) connected to a Rheodyne sample 7120 injector with a 20 μL loop (Rheodyne, Berkeley) and an ultraviolet–visible (UV–VIS) detector LCD 2563 (Laboratorni Pristroje, Praha). The column (150×3.3 mm i.d.) was packed with Separon SGX C18 (5 μm) (Lachema). Acetonitrile–water (86:14, v/v) mixture was used as a blank mobile phase. The calixarene contained mobile phases were prepared by dissolving **9a** in an acetonitrile–water (86:14, v/v) mixture to give the calixarene concentrations $0.76,\times10^{-3}$M, 1.45×10^{-3}M, 2.15×10^{-3}M and 3.05×10^{-3}M. The analytes for injections were dissolved in the same acetonitrile–water (86:14, v/v) mixture ($C=0.3\times10^{-4}$). The amount of the sample injected was 20 μL. Each of the samples was analyzed five times. All chromatograms were obtained at 22 °C. The flow rate was 0.5 mL/min, and the UV detector was operated at 254 nm. The dead time (t_0) was measured with $NaNO_2$. The mobile phase which contained the calixarene as additive was equilibrated for 10 h before analysis. Under these conditions the column was saturated with the calixarene additive.

Table 1
The association constants of the host-guest complexes of calixarene **9a** in acetonitrile–water (86:14, v/v) solution.

No	Guest	K_A, M^{-1} (RSD, %)	No	Guest	K_A, M^{-1} (RSD, %)
1	Trichloromethylbenzene	13 (17)	20	*o*-Fluorophenol	105 (13)
2	*p*-Chloroaniline	14 (16)	21	Dimethyl-*p*-toluidine	107 (5)
3	*o*-Dibromobenzene	15 (6)	22	Chlorobenzene	114 (7)
4	Hexafluorobenzene	23 (15)	23	Guaiacol	130 (17)
5	*p*-Bromophenol	29 (25)	24	Trifluoromethylbenzene	142 (18)
6	*p*-Chlorophenol	31 (18)	25	*p*-Fluorophenol	146 (9)
7	Benzene	32 (8)	26	Toluene	152 (4)
8	Phenol	32 (12)	27	*o*-Phenylenediamine	178 (8)
9	*m*-Nitrophenol	39 (2)	28	*m*-Dinitrobenzene	197 (4)
10	*p*-Xylene	44 (16)	29	*m*-Toluidine	201 (7)
11	*iso*-Propylbenzene	49 (12)	30	*p*-Bromotoluene	217 (5)
12	Benzyl alcohol	61 (10)	31	Anisaldehyde	224 (4)
13	Benzaldehyde	65 (13)	32	Veratrole	263 (3)
14	Iodobenzene	70 (7)	33	*o*-Bromotoluene	268 (6)
15	*p*-Toluidine	71 (9)	34	*m*-Xylene	294 (5)
16	*p*-Methoxytoluene	84 (16)	35	*p*-Cyanophenol	311 (3)
17	Veratraldehyde	86 (8)	36	Aniline	328 (3)
18	N,N-Dimethylaniline	93 (3)	37	*p*-Aminophenol	329 (8)
19	Salicyl aldehyde	94 (17)			

2.3.2. Langmuir-Blodgett films formation and investigation

The behavior of the calixarene molecules on a water surface has been investigated by π–A Langmuir isotherm experiments with R&K (Wiesbaden, Germany) equipment for LB film preparation [11]. Surface tension was registered by the Wilhelmy method. Chloroform solutions of the calixarenes (C = 0.5 mg/ml) were used for the monolayer formation on the bi-distilled water sub-phase. The hydrophobized silicon wafer (for ellipsometry measurements) and quartz crystal resonators with hydrophilic surface (for investigation of receptor properties) were used as substrates. The silicon wafer was hydrophobized by treatment with boiling HCl:H_2O_2:H_2O mixture and then exposed with the hexamethyldisilazan vapor during 30 min. Newly Ag (or Ni) deposited quartz surface possesses hydrophilic features and does not require any treatment.

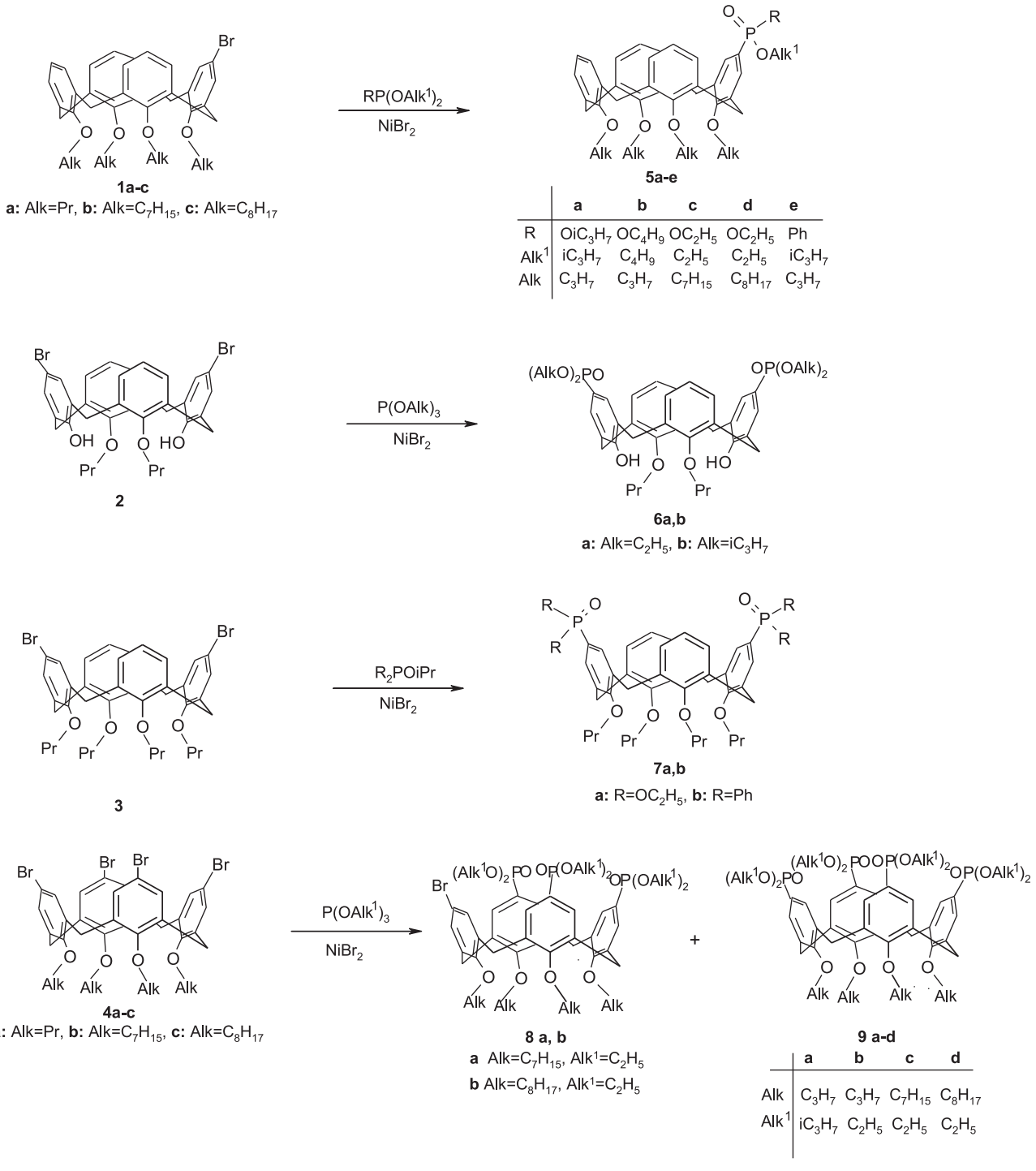
Receptor properties of the phosphonylcalixarene molecules towards organic volatiles were studied by Quartz Crystal Microbalance (QCM) technique. QCM technique uses the proportionality between a mass loaded onto quartz surface and an oscillations frequency shift as a basis [22]. By measuring the frequency shift, one can easily investigate an adsorption-desorption processes occurring onto the sensor's surface. Sensitivity of this method is a quite high — about 1 ng/Hz, which allows for the detection of very low concentration of organic vapors. The 8-channel QCM array with all necessary equipment (gas cell, gas-supplying system and electronic circuits, etc.) has been designed in the Institute of Semiconductor Physics NAS of Ukraine. Experiment control and data acquisition were implemented with PC by means of domestic software. The gas-supplying regime chosen for the experiment was non-flow type — after rapidly injecting the analyte the gas cell cuts off from the pipeline and no gas flow occurs during measuring period. Detailed description of device and gas supplying regime can be found in [23].

3. Results and discussion

3.1. Synthesis and stereochemistry

Several methods of the calixarene upper rim phosphorylation have been described [24]. The most convenient of these employs the nickel catalyzed Arbuzov reaction of the easily accessible *para*-bromoalkoxycalixarenes [18,19,25–29]. Dialkoxy- and tetraalkoxycalix[4]arenes **5-9** containing one, two, three or four hydrophilic phosphoryl groups have been synthesized by the reaction of bromocalixarenes **1-4** with alkyl esters of phosphorus (III) acid in the presence of a catalytic amount of $NiBr_2$ at 170 °C in benzonitrile solution (Scheme 1). (Phosphorylation of the low melting tetraheptyloxy(octyloxy)bromocalix[4]arenes **1b,c** and **4 b,c** was performed without solvent). The yields of phosphorylated calix[4]arenes **5-7** and **9** were in the range of 40–70%. In case of tetrabromocalix[4]arenes **4b,c** the triphosphorylated calixarenes **8a,b** were also isolated with 25 or 30% yields respectively.

In accordance with the NMR data, the macrocyclic skeleton of calixarenes **5-9** exists in the *cone* shaped conformation. This is confirmed by the presence of two doublets of the AB spin system for axial and equatorial protons of the methylene bridges in the ^{1}H NMR



	a	b	c	d	e
R	OiC_3H_7	OC_4H_9	OC_2H_5	OC_2H_5	Ph
Alk^1	iC_3H_7	C_4H_9	C_2H_5	C_2H_5	iC_3H_7
Alk	C_3H_7	C_3H_7	C_7H_{15}	C_8H_{17}	C_3H_7

	a	b	c	d
Alk	C_3H_7	C_3H_7	C_7H_{15}	C_8H_{17}
Alk^1	iC_3H_7	C_2H_5	C_2H_5	C_2H_5

Scheme 1.

spectra, and the presence of only one signal in the ^{31}P NMR spectra. Coupling constants of the axial and equatorial protons are 13 Hz, the difference of their chemical shifts $\Delta\delta$ is in the range 0.8–1.2 ppm. The parameter $\Delta\delta \approx 0.8$ ppm for dialkoxycalixarenes **6** confirms the stereochemically rigid *flattened cone* (C_{2v} symmetry) conformation (Fig. 1a) [30]. In this conformation phosphorylated benzene rings are forced to the coplanar orientation due to formation of the intramolecular hydrogen bonds OH···OPr at the macrocyclic lower rim. For tetraalkoxycalixarenes **5, 7-9** the parameter $\Delta\delta \approx 1.2$ ppm indicates the *regular cone* (C_{4v} symmetry) conformation (Fig. 1b) [31].

3.2. Investigation of the complexation by IR spectroscopy

In contrast to the well-documented complexation of phosphorylated calixarenes with metal cations, their complexation with organic molecules is less investigated [25]. The presence of the rather basic P=O moieties reveals the calixarenes as receptors of organic molecules possessing CH, NH, OH protonodonor groups. Binding of *iso*-butanol or phenol H-donor molecules with mono-, di-, and tetraphosphorylated calix[4]arenes **5a, 6b, 9a** was investigated by the IR spectroscopy in CCl_4 solutions. Calixarenes **5a, 6b, 9a** possess

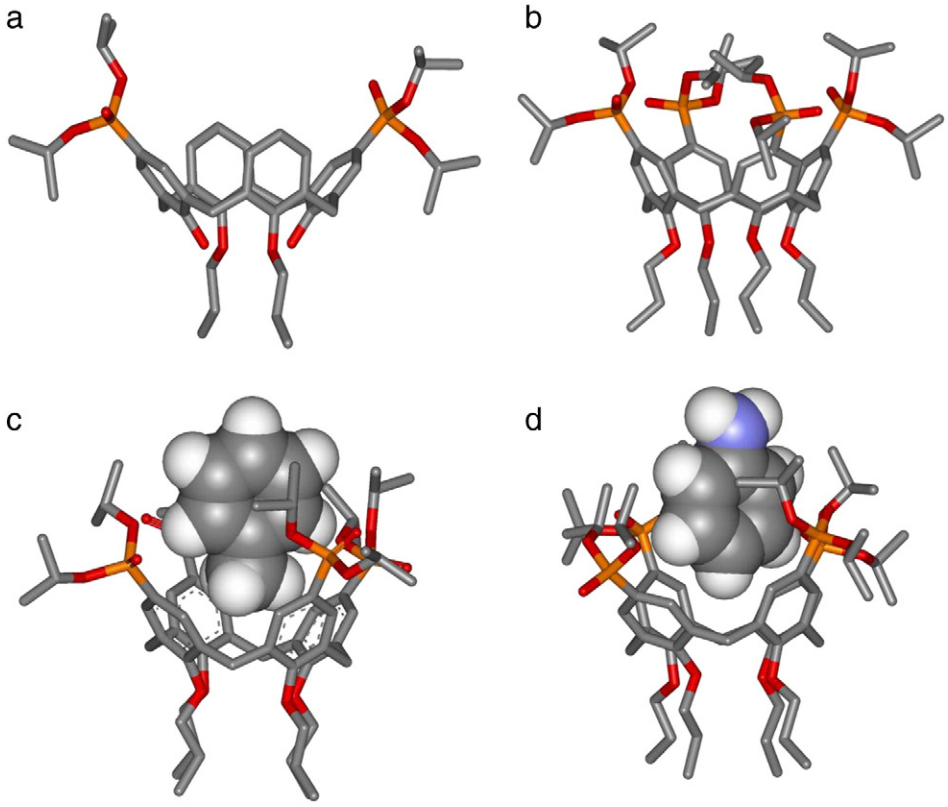
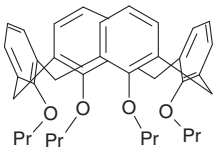


Fig. 1. Energy minimized structures of dipropoxycalixarene diphosphonate 6b (a), tetrapropoxycalixarene tetraphosphonate 9a (b) and the host-guest inclusion complexes of 9a with toluene (c) and aniline (d) molecules (HyperChem 8.0, PM3).

two types of proton acceptor centers: oxygen atoms at the lower rim of the macrocycle and oxygen atoms of P=O groups at the upper rim. As shown by the model experiment with the upper rim unsubstituted tetrapropoxycalixarene **10,** the proton acceptor ability of the ether oxygens at the lower rim is not significant.



10

In the IR spectra of the mixtures **10** ($1 \cdot 10^{-2}$ M) with *iso*-butanol ($5 \cdot 10^{-5}$ M) or with phenol ($5 \cdot 10^{-5}$ M) in CCl_4 solutions no shift of the absorption band of the hydroxyl groups induced by hydrogen bonding was observed. However, IR spectra of mixtures of phosphorylated calixarenes **5a, 6b, 9a** ($1 \cdot 10^{-2}$–$1 \cdot 10^{-3}$ M) with *iso*-butanol or phenol ($1 \cdot 10^{-2}$–$5 \cdot 10^{-3}$ M) reveal the presence of the strong hydrogen bonds. The $\Delta\nu$ (OH) values for butanol and phenol consist of 220 cm^{-1} and 390 cm^{-1} respectively. The optical density of the hydroxyl absorption bands increases along with the number of phosphoryl groups in calixarenes **5a**<**6b**<**9a**.

The absorption band shifts of P=O groups in calixarenes **5a, 6b** induced by the hydrogen bonding with *iso*-butanol or phenol molecules are 29 cm^{-1} and 37 cm^{-1} respectively.

The association constant K_a for complexation of monophosphonylcalixarene **5a** with iso-butanol and phenol molecules were calculated according to Eq. (2)

$$K_a = \frac{\left[C_{complex}\right]}{\left[C_{calix}\right] \cdot \left[C_{guest}\right]} \tag{2}$$

where $[C_{calix}]$, $[C_{guest}]$, $[C_{complex}]$ are the equilibrium concentrations of the calixarene host, the iso-butanol or phenol guest molecules and their host–guest complex respectively determined by the IR spectroscopy method from adsorption intensity of the guest's free and the guest's associated OH groups.

Enthalpy ΔH of the complexation was calculated using Eq. (3)

$$-\Delta H = R\, tg\, a \tag{3}$$

where the *tg* α parameter was determined from a linear dependence of $\ln K_a$ *vs* 1/T.

So, the association constant K_a and enthalpy ΔH for complexation of monophosphonylcalixarene **5a** with iso-butanol are 15.8 L mol^{-1} and 2.4 kcal mol^{-1}, respectively. Phenol forms a more stable complex with calixarene **5a** (K_a = 2200 L mol^{-1} and ΔH = 6.5 kcal mol^{-1}).

3.3. Investigation of the complexation by RP HPLC and molecular modeling methods

The stability constants of calixarene complexes with neutral organic molecules in solutions are usually determined by NMR spectroscopy [31] or microcalorimetry [19] methods. Nevertheless, it has been documented [20,21,32,33] that under reversed-phase liquid chromatography conditions the addition of a calixarene to a mobile phase leads to decreasing sorption of organic solutes on a sorbent surface due to formation of the host-guest inclusion complexes of the calixarene host with the organic guest. Stability constants of the 1:1 complexes can be determined from a linear dependence between the guest capacity factors and the calixarene concentration in the mobile phase (see Experimental).

The association constants K_A of the complexes of calixarene **9a** with a series of benzene derivatives determined by the RP HPLC method in acetonitrile–water (86:14, v/v) solution as the mobile

phase are presented in (Table 1). The constants are in the range of 13–329 M^{-1}. Their values depend upon electronic nature, size, quantity and geometrical position (*ortho, meta, para*) of substituents at benzene ring of the guest molecules.

The lowest K_A value (13 M^{-1}) was estimated for the calixarene **9a** complex with trichloromethylbenzene. The trifluoromethylbenzene–**9a** complex was determined to be almost 10-fold more stable (K_A 142 M^{-1}). The toluene–**9a** complex has K_A 152 M^{-1} which is larger than for benzene complex (K_A 32 M^{-1}). Two methyl groups in *meta*-position of the benzene ring increase K_A of *meta*-xylene to 294 M^{-1}. Substitution of benzene ring in *para*-position with methyl or methoxyl groups leads to the decreasing K_A to 44 M^{-1} (*para*-xylene) and 84 M^{-1} (*para*-methoxytoluene). The replacement of the bromine atom in *ortho*-dibromobenzene ($K_A = 15$ M^{-1}) by the methyl group increases K_A to 268 M^{-1} (*ortho*-bromotoluene). The largest values of the association constants are reported for the calixarene complexes with *para*-cyanophenol (311 M^{-1}) and *para*-aminophenol (329 M^{-1}). The observed relationship between the nature of the guest molecule and K_A values reflects the complicated character of the complexation process.

The mode of the host-guest complexation is illustrated by the molecular modeling calculations (Fig. 1c,d). As it is shown, the toluene molecule is included into the calixarene **9a** cavity by methylene group forming CH–π bonds with aromatic rings of the macrocyclic skeleton. In the inclusion complex with the aniline molecule its NH_2 group is oriented outside the calixarene cavity.

3.4. The calixarene Langmuir-Blodgett films and their receptor properties

The π–A (π — the pressure inside the film, A — the area per one molecule) Langmuir isotherm experiments with amphiphilic calixarenes **5a,e** and **9a** on a water surface confirm the Langmuir monolayer formation (Fig. 2). The area per molecule (A) for closely packed layers are 1.75 ± 0.05 nm^2 (**5a**), 1.30 ± 0.05 nm^2 (**5e**) and 2.07 ± 0.05 nm^2 (**9a**) that corresponds with our previous experiments on the similar calix[4] arenes [11].

The Langmuir-Blodgett films of calixarenes **5a,e** and **9a** have been prepared and investigated as well. The calixarene LB films were formed on the polished silicon plates coated with a native oxide by immersing the plates using vertical transfer procedure. The LB films are formed at π 18–20 mN/m and dipping speed 2 mm/min. The LB film thicknesses of **5a,e** and **9a** on the silicon substrates as measured by the optical ellipsometry method are 1.0 ± 0.1 nm.

In order to investigate the calixarenes **5a,e** and **9a** receptor features their multilayered films (25–30 monolayers) were formed on the quartz resonator surfaces of the QCM-based sensory systems [23].

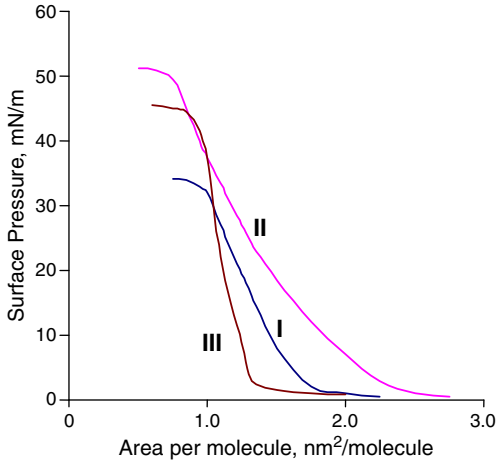


Fig. 2. π–A Langmuir isotherms of monolayers of compounds **5a** (I), **9a** (II), and **5e** (III).

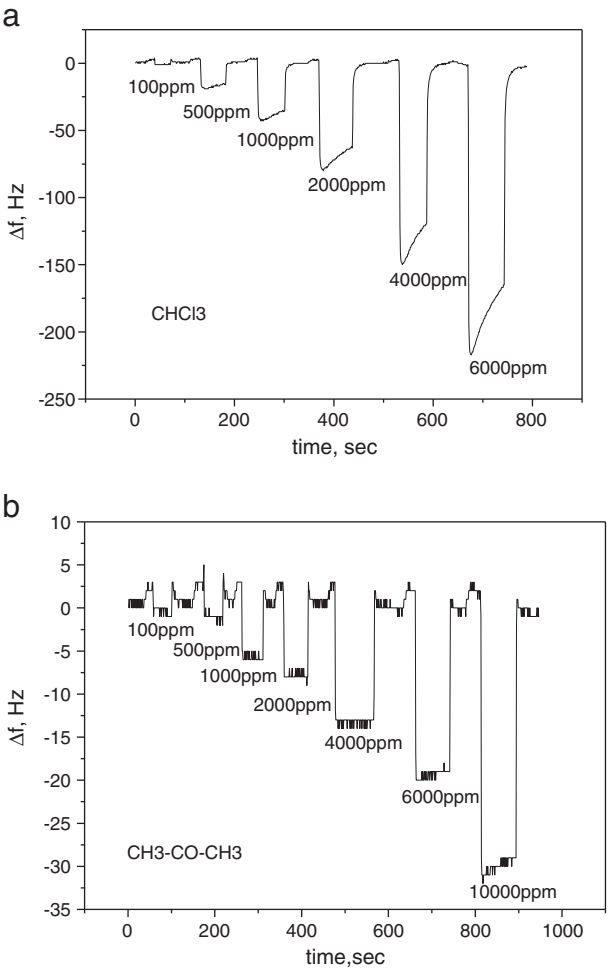


Fig. 3. Kinetic responses of the QCM sensors covered with calixarene **5a** (30 monolayers) to sorption of chloroform (a) and acetone (b) at different concentrations in air.

The kinetic responses of **5a** coated sensors to different concentrations (100–10,000 ppm) of acetone and chloroform in air are presented in Fig. 3. The sensor has a quick kinetic response (less than a second), high reversibility and reproducibility.

The stoichiometry of the analyte–calixarene (S) in the LB films has been estimated using the QCM sensor responses to chloroform and acetone at concentrations close to their saturated vapor pressure [34]. Taking into account linearity of Sauerbrey equation [22] the stoichiometry S can be calculated from expression (4)

$$S = \frac{M_{calix} / M_{anal}}{\Delta f_{calix} / \Delta f_{anal}} \quad (4)$$

Table 2
Responses of the QCM sensors on the calixarene LB films deposition (Δf_{calix}), the analytes sorption (Δf_{anal}) and stoichiometry of analyte–calixarene (S).

Sensor parameters	Chloroform			Acetone		
	5a	5e	9a	5a	5e	9a
Δf_{calix}, Hz	2056	4646	7000[a]	2056	4646	4600[a]
Δf_{anal}, Hz	850	1750	850	180	250	120
$\Delta f_{calix}/\Delta f_{anal}$	2.4	2.6	8.2	11.4	17.2	38.3
M_{calix}/M_{anal}	6.4	6.6	10.6	13	13.3	21.5
S	2.7	2.5	1.3	1.1	0.8	0.6

[a] The quartz sensors with different number of the calixarene **9a** LB monolayers onto their surfaces were used for the chloroform and acetone experiments.

where Δf_{calix} and Δf_{anal} are frequency shift caused by the calixarene LB films deposition and the analyte molecules sorption onto the sensor surface. M_{calix} and M_{anal} are molecular weights of the calixarene and analyte respectively.

The S data obtained from Eq. (4) are presented in Table 2. The stoichiometry of chloroform–calixarene equals to 1.3 for **9a**, 2.5 for **5e** and 2.7 for **5a**. The stoichiometry of acetone–calixarene is 0.6, 0.8 and 1.1 for **9a, 5e** and **5a** respectively.

4. Conclusion

The amphiphilic calix[4]arene phosphonates easily synthesized by the Arbuzov reaction of the *para*-bromoalkoxycalixarenes form the host-guest inclusion complexes with different organic molecules in solution. The calixarene Langmuir-Blodgett films layered onto QCM chemosensor surface can reversibly adsorb vapors of volatile organic compounds in air.

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