

Bis[di-*n*-alkyl(fluoro)stannyl]methanes, (R₂FSn)₂CH₂ (R = *n*-octyl, *n*-dodecyl): Stable Fluoride-Selective Carriers

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The synthesis of bis[di-*n*-alkyl(fluoro)stannyl]methanes, [(R₂FSn)₂CH₂, (**3**, R = *n*-octyl; **4**, R = *n*-dodecyl), is reported and their unprecedented dimeric structure in solution with pentacoordinate tin atoms is rationalized on the basis of ¹⁹F and ¹¹⁹Sn NMR spectroscopy, osmometric molecular mass determination and electrospray mass spectrometry (ESMS). ¹⁹F and ¹¹⁹Sn MAS NMR and Mössbauer spectroscopy also indicate pentacoordinate tin atoms for the solid state. The

ability of compounds **3** and **4** to bind fluoride ion selectively and reversibly is evaluated through potentiometric measurements. Compared with the previously reported organotin(IV)-based fluoride ionophore [Cl(Ph)₂Sn]₂CH₂, **3** and **4** exhibit a drastically improved lifetime, while retaining their high preference for fluoride over all other lipophilic anions evaluated. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Various recent publications deal with the anion recognition properties of organotin compounds. As shown, mainly by variable-temperature NMR spectroscopy and single-crystal X-ray diffraction analysis, open-chain as well as cyclic bis(haloorganostannyl)alkanes function as bicentric Lewis acids towards Lewis bases such as fluoride and chloride ions^[1–7]. The methylene-, dimethylene- and *o*-phenylene-bridged ditin derivatives [Ph₂(X)Sn]₂CH₂,^[3] Ph₂XSnCH₂CH₂SnXPh₂,^[4] and *o*-C₆H₄(SnXMe₂)₂^[1] (X = F, Cl), respectively, preferably chelate fluoride over chloride ions. Moreover, bis[chloro(diphenyl)stannyl]methane, [Cl(Ph)₂Sn]₂CH₂, and bis[dichloro(phenyl)stannyl]methane, [Cl₂(Ph)Sn]₂CH₂, when incorporated into polymeric-membrane ion-selective electrodes, are highly selective carriers for fluoride^[8] and phosphate ions,^[9] respectively. When these carriers are used to develop chemical sensors, the observed signal is unstable over prolonged periods, while re-

peated use influences both the sensitivity (the slope of the calibration curve expressed in mV per –log[anion] units) and detection limit of the sensor. This signal drift could be due to carrier decomposition, ligand exchange, or poisoning due to the very strong binding to the primary ion^[10]. Such signal drift is the only obstacle to the application and commercialization of these ionophores in chemical sensors. The origin of the carrier instability in the sensor membrane is not completely understood, but is postulated to be hydrolysis for [Cl₂(Ph)Sn]₂CH₂. Furthermore, with both [Cl₂(Ph)Sn]₂CH₂ and [Cl(Ph)₂Sn]₂CH₂, chloride exchange with other anions present in the solution to be analyzed could occur. Additionally, the stability problem might originate from anion-induced organic group migration^[11] and also from too low a lipophilicity of the carriers. Low carrier lipophilicity facilitates leaching from the organic phase, drastically influencing membrane characteristics.^[12] We present here the synthesis and structure of bis[di-*n*-alkyl(fluoro)stannyl]methanes [F(R₂)Sn]₂CH₂ (**3**, R = *n*-octyl; **4**, R = *n*-dodecyl) designed to overcome the above-mentioned problems. Their higher lipophilicity, in combination with an improved membrane composition, gives an optimal fluoride-selective electrode.

Results and Discussion

Synthesis of the Title Compound and Its Structure in Solution and in the Solid State

Bis[dibromo(phenyl)stannyl]methane, [Br₂(Ph)Sn]₂CH₂,^[13] and four equivalents of *n*-octylMgBr react to give bis[di-*n*-

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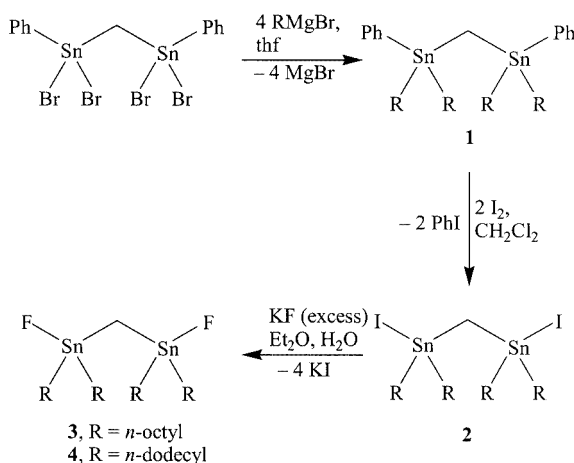
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octyl(phenyl)stannyl]methane, $[n\text{-octyl}_2(\text{Ph})\text{Sn}]_2\text{CH}_2$ (**1**) which was subsequently treated with iodine to provide bis[iodo(di-*n*-octyl)stannyl]methane, $[\text{I}(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2$ (**2**). Reaction of the latter with excess of potassium fluoride then gave bis[fluoro(di-*n*-octyl)stannyl]methane, $[\text{F}(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2$ (**3**) (Scheme 1). Bis[di-*n*-dodecyl(fluoro)stannyl]methane, $[(n\text{-dodecyl})_2\text{FSn}]_2\text{CH}_2$, (**4**), was prepared analogously.



Scheme 1. Synthesis of bis[fluoro(di-*n*-octyl)stannyl]methane (**3**) and bis[di-*n*-dodecyl(fluoro)stannyl]methane (**4**)

Compounds **3** and **4** were obtained as colorless amorphous materials that are sparingly soluble in common organic solvents such as CH_2Cl_2 and CHCl_3 . The ^{119}Sn NMR spectrum at ambient temperature ($\text{CH}_2\text{Cl}_2/\text{D}_2\text{O}_{\text{capillary}}$) of compound **3** reveals a doublet of doublet of doublets at $\delta = 38.8$ ppm [$^1J(^{119}\text{Sn}-^{19}\text{F})$ 690, 1468, $^3J(^{119}\text{Sn}-^{19}\text{F})$ 107 Hz]. The essentially concentration-independent ^{19}F NMR spectrum (CDCl_3) shows two triplet resonances of equal integral ratio at -112.9 ppm [$^1J(^{19}\text{F}-^{119/117}\text{Sn}) = 683$, $^2J(^{19}\text{F}-^{19}\text{F}) = 71$ Hz] and -157.2 ppm [$^1J(^{19}\text{F}-^{119/117}\text{Sn}) = 1474$, $^2J(^{19}\text{F}-^{19}\text{F}) = 69$ Hz]. The satellite-to-signal-to-satellite integral ratio (15:70:15) for both resonances indicates that each fluorine atom couples with two ^{117}Sn and two ^{119}Sn nuclei. Based on these spectroscopic data and osmometric molecular weight determinations in chloroform (1336 g/mol) and *n*-hexane (1493 g/mol) compound **3** probably adopts the dimeric structure (A) (Figure 1) in solution. This is supported by the electrospray mass spectrometric studies reported below.

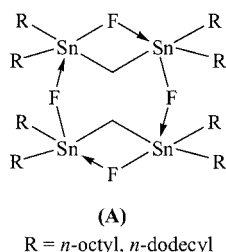


Figure 1. Dimeric structure of **3** in solution

The ^{19}F and ^{119}Sn NMR spectra of compound **4** are similar (see Exp. Sect.).

The ^{119}Sn MAS NMR spectrum of **3** is dominated by anisotropy of chemical shift interaction. The isotropic peak shows a triplet at $\delta = 2.4$ ppm [$\nu_{1/2}$ 325, $J(^{119}\text{Sn}-^{19}\text{F}) = 1270$ Hz]. From the intensities of the corresponding triplet-shaped spinning side bands the main components of the shielding tensor were estimated to be $\delta = 261.9$, -113.0 and -141.7 ppm, respectively. The solid-state ^{19}F NMR spectrum recorded at a spinning rate of 30 kHz exhibits a singlet at $\delta = -142.1$ ppm ($\nu_{1/2}$ 150 Hz) with unresolved $J(^{19}\text{F}-^{117/119}\text{Sn})$ satellites of 1272 Hz (satellite-to-signal-to-satellite ratio 12.6:74:13.4). These spectroscopic data are reasonably consistent with the polymeric structure (B) shown in Figure 2, with, at least on the ^{19}F and ^{119}Sn time scales, symmetric Sn–F–Sn bridges. This view is further supported by the Mössbauer spectrum (I.S. 1.34 mm/s, Q.S. 3.69 mm/s), which unambiguously indicates pentacoordinate tin atoms. Similar spectroscopic data have been reported for dimethylphenyltin fluoride^[14]

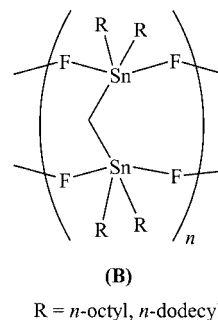
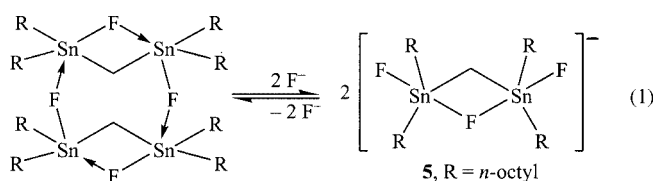


Figure 2. Polymeric structure of **3** in the solid state

The ^{119}Sn NMR spectrum of **3** at room temperature in CD_2Cl_2 solution to which had been added one molar equivalent of $\text{Bu}_4\text{NF}\cdot 2\text{H}_2\text{O}$ shows a complex resonance (four lines with different half widths) centered at $\delta = -38$ ppm, which upon cooling to -80°C turns into a doublet of doublets at $\delta = -32$ ppm [$^1J(^{119}\text{Sn}-^{19}\text{F})$ 648, 1946, $^3J(^{119}\text{Sn}-^{19}\text{F})$ 121 Hz]. These findings are consistent with the formation of the organostannate complex **5** [Equation (1)].



The ^{119}Sn NMR spectrum was unchanged upon addition of a second molar equivalent of $\text{Bu}_4\text{NF}\cdot 2\text{H}_2\text{O}$. Compound **4** behaves analogously upon addition of one molar equivalent of $\text{Bu}_4\text{NF}\cdot 2\text{H}_2\text{O}$ [$\delta(^{119}\text{Sn}) = -40$ ppm at room temperature in CD_2Cl_2 solution, complex pattern with four lines].

Chloride ions can break the fluoride bridges in the A-type dimer. Thus, the ^{119}Sn NMR spectrum of **3** at room temperature in CD_2Cl_2 solution to which had been added one molar equivalent Ph_4PCl shows a broad resonance at $\delta = -19$ ppm that upon cooling to -20°C turns into a complex pattern centered at $\delta = -20$, which was not analyzed further.

The ESMS spectrum (negative mode) of a solution of **3** and Ph_4PCl in acetonitrile shows the following mass clusters with the expected isotopic patterns: $\{[\text{F}(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2\cdot\text{F}\}^-$ (761.6), $\{[\text{F}(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2\cdot\text{Cl}\}^-$ (777.5), $\{[\text{Cl}(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2\cdot\text{F}\}^-$ (793.6), $\{[\text{F}(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2\cdot\text{F}\}^-$ (1502.7), and $\{[\text{F}(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2\cdot\text{Cl}\}^-$ (1520.3). The latter two support the dimeric structure (A) (Figure 1) of compound **3** in solution (see above).

Potentiometric Studies

Bis[fluoro(di-*n*-octyl)stannyl]methane, $[\text{F}(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2$, (**3**), and bis[di-*n*-dodecyl(fluoro)stannyl]methane, $[(n\text{-dodecyl})_2\text{FSn}]_2\text{CH}_2$, (**4**), were used to develop a solvent polymeric membrane electrode that was examined for its selectivity and sensitivity (slope) to fluoride. The results are compared with previously obtained potentiometric data based on bis[chloro(diphenyl)stannyl]methane, $[\text{Cl}(\text{Ph})_2\text{Sn}]_2\text{CH}_2$.^[8] Compounds **3** and **4** are more lipophilic than $[\text{Cl}(\text{Ph})_2\text{Sn}]_2\text{CH}_2$ and do not favor halide exchange. Therefore, they are expected not only to preserve the excellent fluoride selectivity obtained with the $[\text{Cl}(\text{Ph})_2\text{Sn}]_2\text{CH}_2$ -based system, but also to exhibit a considerably longer lifetime within the organic membrane layer.

Potentiometric Response

The potentiometric response of a liquid polymeric membrane doped with an ion carrier provides direct evidence of the interaction of the carrier with the ions in solution. Based on these data, one can determine the selectivity, the binding constant in the organic phase, the reversibility and the stability of the ionophore–anion complex. Thus, the overall potentiometric response (ΔE), the calibration curve, and the base line return and stability of the electrodes based on carriers **3** and **4**, were monitored and analyzed. Figure 3 shows the potential changes observed and the resulting calibration curve of the ion-selective electrodes (ISEs).

Figure 3 shows that the two sensors have different analytical characteristics. The slope of the calibration curves for the ISEs based on carriers **3** and **4** are -87.8 and -68.2 $\text{mV}/-\log[\text{F}^-]$, respectively. Carrier **3** with the octyl substituents shows a higher sensitivity to fluoride anion, indicating that the organic substituents R have little influence on the coordination of the carrier to fluoride. The slope to fluoride of both carriers is higher than can be explained by the Nernst theory, according to which the sensitivity for monovalent anions such as fluoride is -59.16 $\text{mV}/-\log[\text{anion}]$. The high sensitivity of organometallic carriers to anions observed previously^[15–17] is suggested to be connected with a less than one-to-one complex formed between the carrier and the primary ion in the polymeric membrane

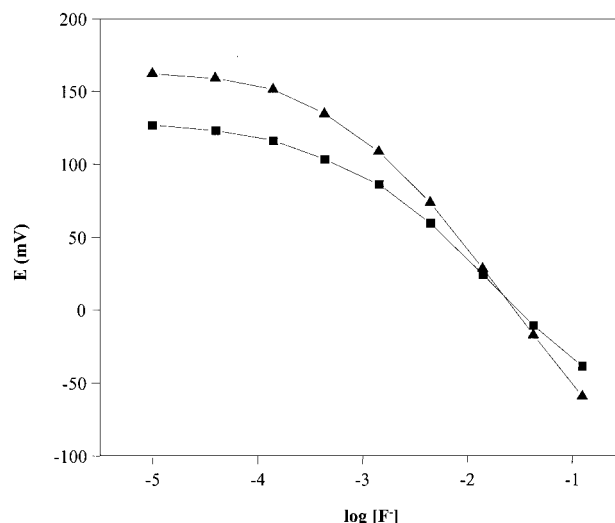


Figure 3. Calibration curves of the ISEs based on compounds **3** (solid triangle) and **4** (solid square) in aqueous solutions buffered with MES to pH 5.5

phase of the sensor.^[18,19] This stoichiometry was not observed in the NMR titrations performed in CD_2Cl_2 .

Ionophore Stability Studies: A very important characteristic of an ionophore is its stability (chemical and structural) over time under operational conditions, which can be very well studied using potentiometry. The interfacial potential generated due to the ability of the carrier to complex the ion under investigation is directly related to the state of the ionophore. Any signal drift, loss in sensitivity or selectivity is thus a measure of the ionophore's instability. Therefore, the sensitivity of ISEs based on carriers **3** and **4** was monitored for a period of 40 days. Figure 4 shows that the sensitivity of the membrane to fluoride remained practically unchanged for over 20 days of continuous use, the slope remaining above 50 $\text{mV}/-\log[\text{F}^-]$.

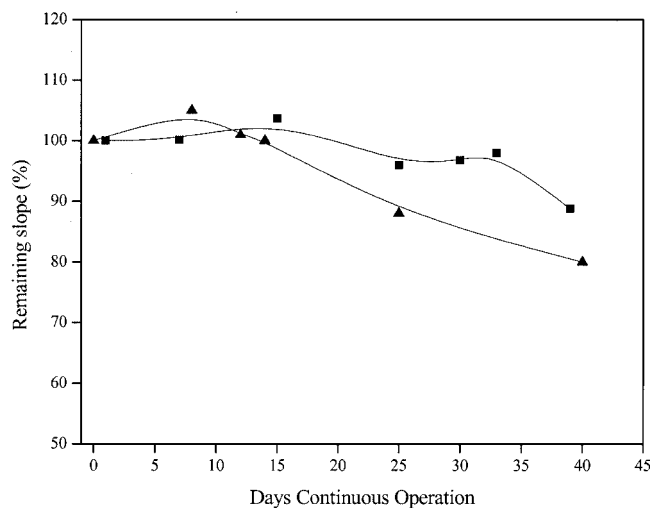


Figure 4. Stability of the ISE1 and ISE2 sensors, based on carriers **3** (solid triangle) and **4** (solid square), respectively, according to the sensitivity of the sensor over time under continuous monitoring in MES (buffered to pH 5.5)

The effect is even more obvious when the more lipophilic dodecyl-substituted carrier (carrier **4**) is used. This is a large improvement when compared with the previously reported carrier $[(\text{ClPh}_2\text{Sn})_2\text{CH}_2]$ which showed a lifetime of not longer than 4 days.

Ionophore Selectivity: The selectivity of the ionophore was studied using the overall potentiometric response of the membrane between a solution of plain buffer, and that containing 0.01 M of the salt under study. Figure 5 shows the overall potentiometric response (in ΔE) of sensors based on carriers **3** and **4**. Based on these data, the logarithms of the potentiometric selectivity coefficients $\log K_{F,J}^{\text{pot}}$ were determined according to the Nikolskii–Eisenman equation (Equation 2) (Table 1 and 2).

$$E_M = E^0 + \frac{RT}{zF} \ln(a_i + K_{ij}^{\text{pot}} a_j^{\frac{z_i}{z_j}}) \quad (2)$$

E_M is the membrane potential in mV, a_i the activity (concentration) of the primary ion, a_j the activity of the interfering ion and z_i and z_j the charge of the primary and interfering ions, respectively. Negative potentiometric selectivity coefficients $K_{F,J}^{\text{pot}}$ indicate that the ISE is more selective to the

Table 1. Potentiometric selectivity coefficients $K_{F,J}^{\text{pot}}$ of the ISE based on carrier **3**.

Anion	$\log K^{\text{pot}}$
NO_3^-	-1.9
Cl^-	-1.0
F^-	0.0
ClO_4^-	-1
I^-	-0.1
SCN^-	0.8

Table 2. Potentiometric selectivity coefficients $K_{F,J}^{\text{pot}}$ of the ISE based on carrier **4**.

Anion	$\log K^{\text{pot}}$
NO_3^-	-1.6
Cl^-	-1.3
F^-	0.0
ClO_4^-	-1.2
I^-	-0.9
SCN^-	-0.4

primary ion (fluoride in this study), whereas positive values indicate that the ISE is more selective to the interfering ion. The selectivity order based on the overall potentiometric response in a MES-buffered solution at pH 5.5 for both ISEs is similar, $\text{F}^- \approx \text{SCN}^- > \text{I}^- > \text{ClO}_4^- > \text{Cl}^- > \text{NO}_3^-$. For comparison, the classical Hofmeister selectivity order for a quaternary ammonium ion-based sensor is $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Cl}^- > \text{F}^-$.

Evidently, from the overall potentiometric response and the calculated selectivity coefficients, the fluoride ion is preferred over several other more lipophilic ions, such as perchlorate, nitrate, and iodide. The anti-Hofmeister selectivity sequence obtained for **3** and **4** is closely related to that obtained for the less stable ionophore $[\text{Cl}(\text{Ph}_2\text{Sn})_2\text{CH}_2]$.^[8]

These results clearly show that, even though the sensor based on ionophore **3** has a good sensitivity and selectivity for fluoride, an improved sensor in terms of selectivity and stability over time is produced when the membrane is doped with ionophore **4**.

Conclusion

The stability of previously evaluated highly selective fluoride carriers can be drastically improved by the use of lipophilic organic substituents. The closely related carriers $(\text{FR}_2\text{Sn})_2\text{CH}_2$ (**3**, R = *n*-octyl; **4**, R = *n*-dodecyl) and the previously reported $[\text{Cl}(\text{Ph}_2\text{Sn})_2\text{CH}_2]$ are compared for their fluoride selectivity and their ability to develop stable fluoride-selective electrodes. Based on spectroscopic studies, in organic phases these carriers form a reversible one-to-one complex with fluoride anions. Furthermore, the stability of the sensors depends on the lipophilicity of the carrier, which in turn can be controlled by the organic substituents attached to the tin atoms. However, the selectivity is not influ-

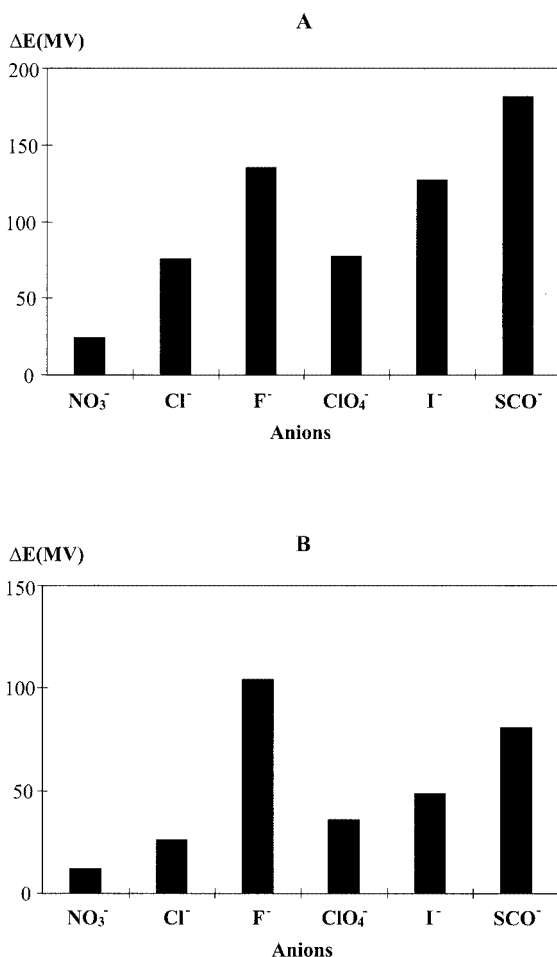


Figure 5. Overall potentiometric response of the ISEs based on carriers **3** (A) and **4** (B) towards several anions at pH 5.5 (MES, 0.001 M).

enced drastically, allowing the development of a robust and highly selective liquid polymeric fluoride-selective electrode. This result will be useful in improving the stability and lifetime of other ionophores that are highly selective for anions such as phosphate and chloride.

Experimental Section

General Remarks: All manipulations were performed under nitrogen using standard Schlenk and vacuum line techniques. Solvents were distilled from the appropriate desiccants prior to use. Literature procedures were used to prepare bis[dibromo(phenyl)stannyl]methane, $[\text{Br}_2\text{Ph}]\text{Sn}_2\text{CH}_2$.^[13] NMR spectra were recorded in CDCl_3 using a spectrometer at 500.13 (^1H), 100.63 (^{13}C) 182.36 (^{19}F), 111.92 and 149.21 (^{119}Sn) MHz. Chemical shifts (δ ppm) were referenced to Me_4Sn (^{119}Sn), CFCl_3 (^{19}F) and Me_4Si (^{13}C , ^1H). ^{119}Sn MAS NMR spectra were recorded with a Varian Unity-plus 500 spectrometer at 186.40 MHz using a Doty supersonic CP/MAS probe (rotor diameter 5 mm) with a 10 kHz spinning rate. The corresponding ^{19}F MAS NMR spectra were recorded with a Bruker Avance 400 spectrometer at 376.52 MHz using rotors of 2.5 mm diameter with spinning rates of up to 32 kHz. Elemental analyses were performed with an instrument from Carlo Erba Instrumentation (model 1106). Molecular weight determinations were carried out with a Knauer Dampdruck-Osmometer K-7000. The calibration standard was Polystyrene 2000 (Fluka) with *n*-hexane and chloroform as solvents.

Electrochemical Studies: Instrumentation: Potentiometric measurements were performed with a XENON CI-317 8-channel electrometer (Halandri, Athens, Greece) versus an Orion Research (Beverly, MA, USA) 900200 double junction reference electrode. Data were collected with a personal computer program written in BASIC for storage and further analysis.

Reagents: High purity potassium salts (p.a. Fluka, p.a. Merck) were used for the preparation of electrolyte solutions. 2-Morpholinoethanesulfonic acid (MES) (Merck) was used as the pH buffer. The membranes were constructed from poly(vinyl chloride) (PVC) (high molecular weight, Selectophore, Fluka), as membrane matrix, bis(2-ethylhexyl) sebacate (DOS) (Selectophore, Fluka) as plasticizer, and tetrahydrofuran (THF) (p.a. Merck), doubly distilled before use, as membrane solvent.

Membrane preparation: All the membranes examined had the following composition: 2% carrier, 33% PVC and 65% DOS. The mixture of components (100 mg) was dissolved in THF (ca. 1.5 mL), and the resultant solution was poured into a glass ring (i.d. 17 mm), the latter being placed on a glass plate. Membranes were formed after solvent evaporation. Circular pieces (diameter 7 mm) of the membranes were cut off and mounted for testing on type IS 561 Phillips electrode bodies (from Willi Möller AG, Glasbläserei, Zürich, Switzerland). The internal solution of the electrode was 0.01 M KCl.

Selectivity measurements and calibration curves: All electrodes were tested without prior pretreatment, except when specifically mentioned. All electrolyte solutions were 10^{-2} , and buffered with MES 10^{-3} M (pH = 5.5). The potential was monitored and the potential difference recorded when the readings were stable in either the calibrating or test solutions. The selectivity coefficients were determined by the separate solution method (SSM)^[20], as-

suming that the electrode shows a theoretical slope of -59.16 mV for monovalent anions.

Synthesis of Bis[di-*n*-octyl(phenyl)stannyl]methane, $[(n\text{-octyl})_2(\text{Ph})\text{Sn}]_2\text{CH}_2$ (1): A solution of *n*-octylmagnesium bromide prepared from *n*-octyl bromide (5.01 g, 25.9 mmol) and magnesium (0.63 g, 25.9 mmol) in THF (50 mL) was added to a solution of bis[dibromo(phenyl)stannyl]methane^[13] (4.70 g, 6.48 mmol) in THF (150 mL). After stirring at room temperature (4 h) the resulting mixture was hydrolyzed with water (50 mL). The organic layer was then separated, dried with Na_2SO_4 and filtered. Evaporation of the solvent gave 3.9 g (70% yield) of bis[di-*n*-octyl(phenyl)stannyl]methane (1) as a colorless oil. ^1H NMR (500.13 MHz, CDCl_3 , 300 K): δ = 0.12 [s, $^2J(^1\text{H}\text{-}^{119}\text{Sn})$ = 57.4 Hz, 2 H, $\text{Sn-CH}_2\text{-Sn}$], 0.92 [t, $^2J(^1\text{H}\text{-}^1\text{H})$ = 7 Hz, 12 H, $-\text{CH}_3$], 0.99–1.63 [m, J = 56 Hz, $-\text{CH}_2-$], 7.26–7.55 [m, 10 H, Sn-Ph] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CDCl_3 , 300 K): δ = -19.5 [$^1J(^{13}\text{C}\text{-}^{117}\text{Sn})$ = 226.9, $^1J(^{13}\text{C}\text{-}^{119}\text{Sn})$ = 236.7 Hz, $\text{Sn-CH}_2\text{-Sn}$], 11.67 [$^1J(^{13}\text{C}\text{-}^{117}\text{Sn})$ = 337.2, $^1J(^{13}\text{C}\text{-}^{119}\text{Sn})$ = 253.3 Hz, C-1], 14.12 (C-8), 22.71 (C-7), 26.82 [$^2J(^{13}\text{C}\text{-}^{117/119}\text{Sn})$ = 20.1 Hz, C-2], 29.18–29.73 (C-4, C-5), 31.96 (C-6), 34.44 [$^3J(^{13}\text{C}\text{-}^{117/119}\text{Sn})$ = 59.4 Hz, C-3], 127.93 [$^3J(^{13}\text{C}\text{-}^{117/119}\text{Sn})$ = 41.8 Hz, C_m], 128.10 [C_p], 136.24 [$^2J(^{13}\text{C}\text{-}^{117/119}\text{Sn})$ = 32.7 Hz, C_o], 142.92 [C_j] ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CDCl_3): δ = -16.5 [$^2J(^{117}\text{Sn}\text{-}^{119}\text{Sn})$ = 239 Hz] ppm. $\text{C}_{45}\text{H}_{80}\text{Sn}_2$ (858.5): calcd. C 63.0, H 9.4; found C 63.7, H 9.9.

Synthesis of Bis[iodo(di-*n*-octyl)stannyl]methane, $[(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2$ (2): Iodine (3.61 g, 10.22 mmol) was added in small portions under ice-cooling to a stirred solution of 1 (6.10 g, 7.11 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was then stirred overnight, after which the solvent and the iodobenzene were removed in vacuo. Addition of CH_2Cl_2 (20 mL), filtration and evaporation of the solvent then afforded 6.4 g (94% yield) bis[iodo(di-*n*-octyl)stannyl]methane (2) as a light yellow oil. ^1H NMR (500.13 MHz, CDCl_3 , 300 K): δ = 0.87 [t, $^2J(^1\text{H}\text{-}^1\text{H})$ = 7 Hz, 12 H, $-\text{CH}_3$], 1.19–1.65 (m, 56 H, $-\text{CH}_2-$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CDCl_3 , 300 K): δ = -3.01 [$\text{Sn-CH}_2\text{-Sn}$], 14.09 (C-8), 19.45 [$^1J(^{13}\text{C}\text{-}^{117}\text{Sn})$ = 334.0, $^1J(^{13}\text{C}\text{-}^{119}\text{Sn})$ = 349.3 Hz, C-1], 22.63 (C-7), 26.83 [$^2J(^{13}\text{C}\text{-}^{117/119}\text{Sn})$ = 25.9 Hz, C-2], 28.90–29.18 [C-4–C-5], 31.84 (C-6), 33.44 [$^3J(^{13}\text{C}\text{-}^{117/119}\text{Sn})$ = 70.1 Hz, C-3] ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.92 MHz, CDCl_3): δ = 87.3 ppm. $\text{C}_{33}\text{H}_{70}\text{I}_2\text{Sn}_2$ (958.14): calcd. C 41.4, H 7.4; found C 42.0, H 7.5.

Synthesis of Bis[fluoro(di-*n*-octyl)stannyl]methane, $[(n\text{-octyl})_2\text{Sn}]_2\text{CH}_2$ (3): A solution of bis[iodo(di-*n*-octyl)stannyl]methane (5 g, 5.23 mmol) in diethyl ether (50 mL) was poured into a solution of potassium fluoride (2.98 g, 52.2 mmol) in water (50 mL). The resultant mixture was stirred for 24 h, and then the organic layer was separated, washed with water (2×50 mL), filtered and dried with sodium sulfate. After removing the solvent, the remaining residue was washed with dichloromethane (20 mL), filtered and dried in vacuo to give 2.3 g (60%) of compound 3. ^1H NMR (400.13 MHz, CDCl_3): δ = 0.87 [t, $^2J(^1\text{H}\text{-}^1\text{H})$ = 7 Hz, 24 H, $-\text{CH}_3$], 1.05–1.65 [m, 14 H, $-\text{CH}_2-$] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CDCl_3): δ = 14.12 (C-8), 20.23 (t, C-1), 22.72 (C-7), 25.53 [$^2J(^{13}\text{C}\text{-}^{117/119}\text{Sn})$ = 26.2 Hz, C-2], 29.32–29.44 (C-4, C-5), 31.99 (C-6), 34.14 [$^3J(^{13}\text{C}\text{-}^{117/119}\text{Sn})$ = 80.7 Hz, C-3] ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (282.36 MHz, CDCl_3): δ = -115.1 [t, $^2J(^{19}\text{F}\text{-}^{119}\text{F})$ = 71.2, $^1J(^{19}\text{F}\text{-}^{119}\text{Sn})$ = 686.6 Hz], -159.3 [$^2J(^{19}\text{F}\text{-}^{119}\text{F})$ = 68.9, $^1J(^{19}\text{F}\text{-}^{119}\text{Sn})$ = 1472.0 Hz] ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CH_2Cl_2 , $\text{D}_2\text{O}_{\text{capillary}}$): δ = 38.1 [ddd, $^1J(^{19}\text{F}\text{-}^{119}\text{Sn})$ = 1468, $^1J(^{19}\text{F}\text{-}^{119}\text{Sn})$ =

690, $^3J(^{19}\text{F}-^{119}\text{Sn}) = 107 \text{ Hz}$] ppm. $\text{C}_{33}\text{H}_{70}\text{F}_2\text{Sn}_2$ (742.33): calcd. C 53.4, H 9.5; found C 53.2, H 9.6.

Synthesis of Bis[di-*n*-dodecyl(fluoro)stannyl]methane, [(*n*-dodecyl) $_2\text{FSn}$] $_2\text{CH}_2$ (4): Compound 4 was prepared by a procedure analogous to that for 3. Thus, bis[dibromo(phenyl)stannyl]methane (9.4 g, 13.0 mmol) was reacted with the Grignard reagent made from 1-dodecyl bromide (1.34 g, 56.0 mmol) and magnesium turnings to give bis[di-*n*-dodecyl(phenyl)stannyl]methane (7.4 g, 53%) as a viscous oil ($^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.92 MHz, CDCl_3): $\delta = -15.1$), which was used for the subsequent reaction without further purification. Treatment of bis[di-*n*-dodecyl(phenyl)stannyl]methane (6.40 g, 5.9 mmol) with iodine (3.00 g, 11.8 mmol) gave bis[iodo(di-*n*-dodecyl)stannyl]methane (6.9 g, 93%) as a slightly yellow oil ($^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.92 MHz, CDCl_3): $\delta = 85.8$ ppm) that was used without further purification for the subsequent reaction.

A solution of bis[iodo(di-*n*-dodecyl)stannyl]methane (1.67, 1.4 mmol) in diethyl ether (30 mL) was added to a solution of potassium fluoride (0.82, 14.1 mmol) in water (20 mL). The mixture was then stirred for 24 h followed by the workup procedure described for compound 3 to give bis[di-*n*-dodecyl(fluoro)stannyl]methane (1.07 g, 79%) as a colorless amorphous solid. ^1H NMR (400.13 MHz, CDCl_3): $\delta = 0.86$ [t, $^2J(^1\text{H}-^1\text{H}) = 6 \text{ Hz}$, 12 H, $-\text{CH}_3$], 1.05–1.65 [m, 84 H, $-\text{CH}_2-$] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CDCl_3): $\delta = 14.12$ (C-12), 20.26 (t, C-1), 22.72 (C-11), 25.54 [$^2J(^{13}\text{C}-^{117/119}\text{Sn}) = 26.2 \text{ Hz}$, C-2], 29.36–29.45 (C-4–C-9), 31.97 (C-10), 34.15 [$^3J(^{13}\text{C}-^{117/119}\text{Sn}) = 80.2 \text{ Hz}$, C-3] ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (282.36 MHz, CDCl_3): $\delta = -115.0$ [t, $^2J(^{19}\text{F}-^{19}\text{F}) = 68.8$, $^1J(^{19}\text{F}-^{119}\text{Sn}) = 686.6 \text{ Hz}$], -159.3 [t, $^2J(^{19}\text{F}-^{19}\text{F}) = 66.6$, $^1J(^{19}\text{F}-^{119}\text{Sn}) = 1479.1 \text{ Hz}$] ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CH_2Cl_2 , $\text{D}_2\text{O}_{\text{capillary}}$) $\delta = 38.2$ [ddd, $^1J(^{19}\text{F}-^{119}\text{Sn}) = 1466$, $^1J(^{19}\text{F}-^{119}\text{Sn}) = 688$, $^3J(^{19}\text{F}-^{119}\text{Sn}) = 105 \text{ Hz}$]. $\text{C}_{49}\text{H}_{102}\text{F}_2\text{Sn}_2$ (965.9): calcd. C 59.9, H 10.5; found C 59.5, H 10.6.

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