

Durable chemical sensors based on field-effect transistors [☆]

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Abstract

The design of durable chemical sensors based on field-effect transistors (FETs) is described. After modification of an ion-sensitive FET (ISFET) with a polysiloxane membrane matrix, it is possible to attach all electroactive components covalently. Preliminary results of measurements with a sodium-selective CHEMFET have shown that the durability is improved by the covalent attachment of the electroactive components (>90 days).

Keywords: Chemical sensors; Field-effect transistors; Polysiloxanes

1. Introduction

A chemical sensor connects the chemical domain and the physical domain. Our work is aimed at the design and synthesis of molecular receptors that can selectively recognize a guest species. When such a guest carries a charge, as in cations, the chemical recognition process converts the neutral receptor into a charged species. This allows the use of field-effect transistors for the transduction of the (chemical) complexation into an electronic signal [1].

Supramolecular chemistry involves chemistry above the molecular level and allows molecules to be designed that selectively recognize certain species by using the principle of mutual complementarity of the receptor and the guest. Factors that determine the complementarity are the size of the species, the number of possible interactions between the receptor and the guest and the nature of the binding sites of both.

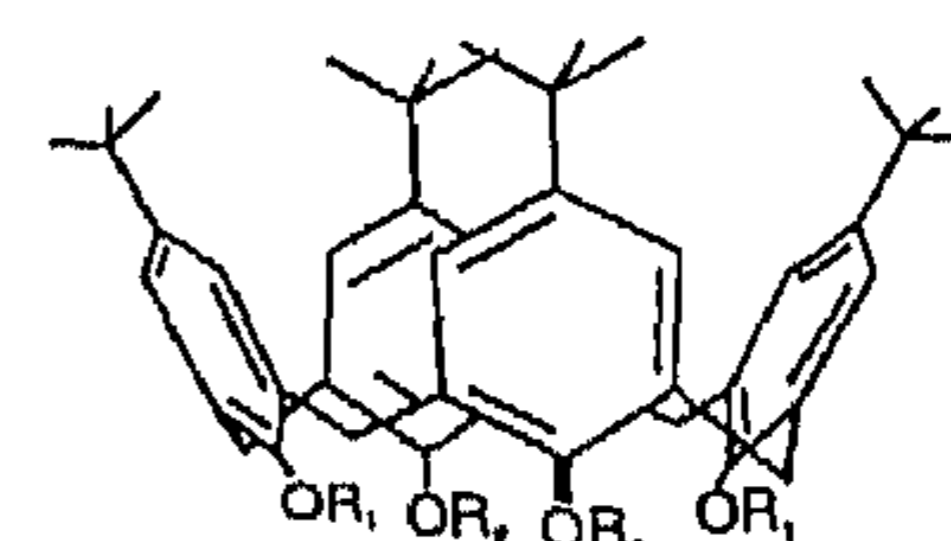
2. Cation-selective receptors based on calix[4]arenes

Most of our work in the past decade has been focused on receptors for cationic guest species and we have been able to obtain receptors that can discriminate with a high degree of selectivity between the different alkali-metal cations (e.g., Na⁺ and K⁺) [2,3]. The molecular platform that we use for the synthesis of

such receptors is a calix[4]arene, a molecule with a high hydrophobicity and four positions for chemical modification. The latter introduces the desired selectivity. Based on calix[4]arenes, we have developed both Na⁺-selective and K⁺-selective receptor molecules (1 and 2), respectively (Fig. 1). More recently this work has been extended [4] to molecules that selectively recognize heavy-metal ions, 3 for Ag⁺, 4 for Cu²⁺, 5 for Cd²⁺ and 6 for Pb²⁺ (Fig. 1).

3. CHEMFET architecture

When these molecules are incorporated in a membrane that covers the gate oxide of an ISFET, the reversible complexation of the (primary) cation by these receptors induces a constant free Mⁿ⁺ concentration in this membrane, even when the Mⁿ⁺ concentration in the aqueous phase is varied over several decades. In order to eliminate undesired interferences of other



- 1 R₁ = R₂ = CH₂C(O)OCH₂CH₃
 2 R₁, R₂ = CH₂CH₂(OCH₂CH₃), R₃ = CH₃
 3 R₁ = CH₂CH₂SCH₃, R₂ = CH₂CH₂CH₃
 4 R₁ = R₂ = OCH₂CH₂SC(S)N(CH₃)₂
 5 R₁ = R₂ = OCH₂CH₂OCH₂C(S)N(CH₃)₂
 6 R₁ = R₂ = CH₂C(S)N(CH₃)₂

Fig. 1. Structures of ionophores 1-6.

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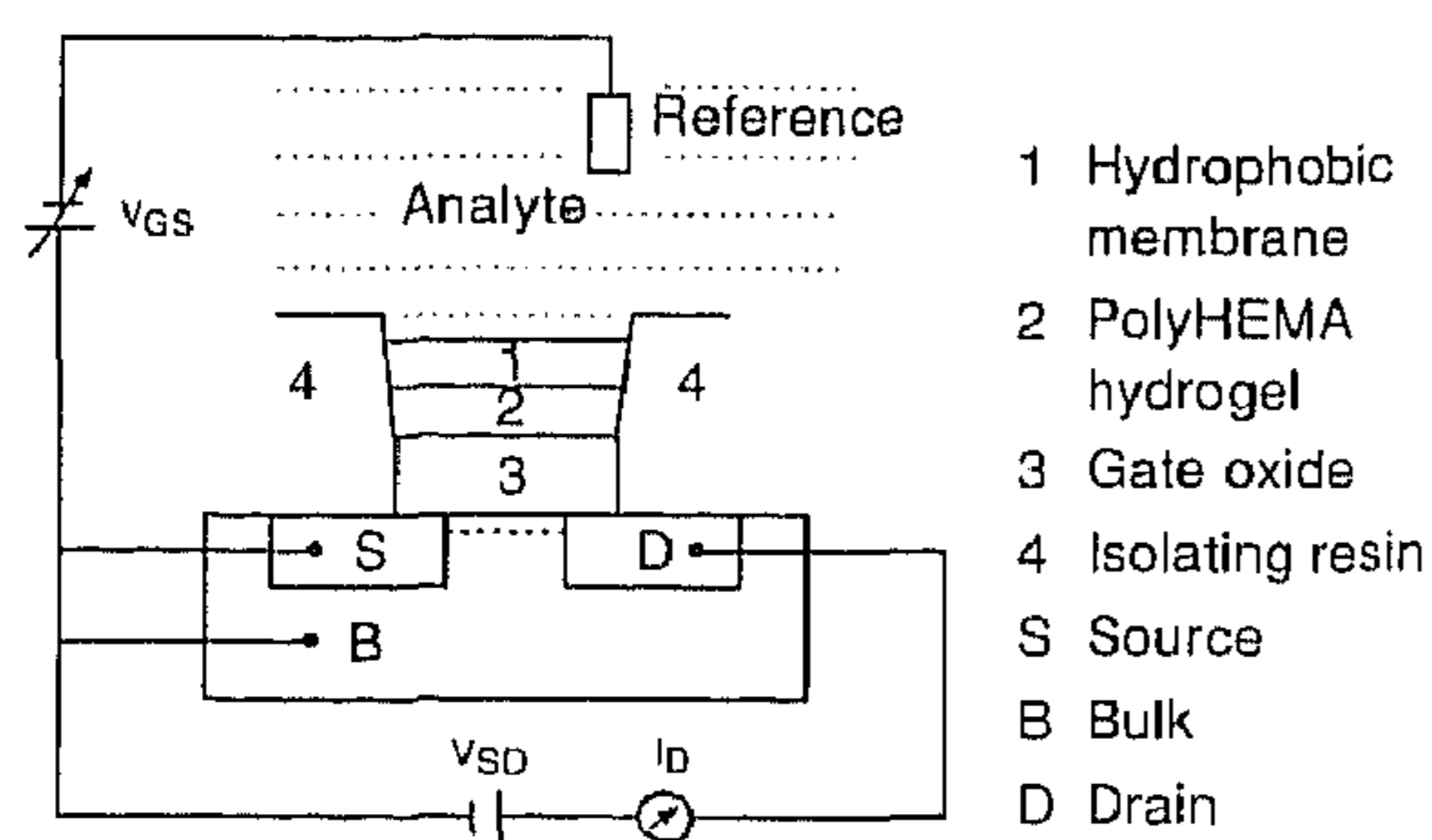


Fig. 2. Schematic representation of a CHEMFET.

cations, the selectivity of the recognition process should be high and binding should be fast and reversible.

In order to eliminate the undesired response to pH variations (and CO_2 interference), we have introduced a hydrophilic polyhydroxyethyl methacrylate (polyHEMA) layer between the sensing membrane and the gate oxide of the ISFET (Fig. 2). Such a layer is conditioned in a pH buffered solution of the primary ion, which maintains the pH at the gate oxide at a constant value. Moreover, the presence of the primary salt in the hydrogel fixes the inner membrane potential of the hydrophobic sensing membrane [5,6]. This hydrophobic sensing membrane contains the selective molecular receptor (e.g. 1–6) and a hydrophobic anion (tetraphenyl borate anion), which is commonly applied in ion-selective electrodes to eliminate the interference of sample anions. With these CHEMFETs we have measured fast and selective responses (≤ 250 ms) on changing ion concentrations with selectivities (Na^+/K^+ , K^+/Na^+) of more than 10^3 under laboratory conditions. CHEMFETs based on the calix[4]arene (3) with two diametrically substituted thioether functionalities responded selectively ($60 \text{ mV decade}^{-1}$) to a change in silver activity in the aqueous solution in the presence of potassium, calcium, cadmium and copper ions ($\log K_{i,j} < -4$). The selectivity towards mercury ($\log K_{i,j} = -2.7$) is comparable to the best neutral-carrier-based ISE so far. The calix[4]arene (4), with four dithiocarbomoyl groups, incorporated in a CHEMFET had a Nernstian response ($30 \text{ mV decade}^{-1}$) to a change in copper activity. The calix[4]arene (5), which has four dimethylthiocarbomoylmethoxyethoxy substituents, is selective in a CHEMFET ($30 \text{ mV decade}^{-1}$) towards cadmium in the presence of calcium and potassium ions. Tetrasubstitution of the calix[4]arene with thioamide groups (6) is a prerequisite for the selective detection of lead and leads to a highly selective CHEMFET ($\log K_{i,j}$ between -3.4 and -5.2) [4].

4. Novel membrane material

For practical applications of this CHEMFET technology, the lifetime of such a sensor should be at least

six and preferably nine months. The hydrophobic membranes should be very thin in order to reduce the electrical resistance. However, in continuous contact with aqueous sample solutions, the sensor response tends to deteriorate in time because of the leaching of the essential electroactive components from the membrane. Our attention has been focused on rubber-like materials that do not require the presence of additional plasticizer and are compatible with IC manufacturing techniques. Polyacrylates and polysiloxanes appeared to be the most promising [7]. Simple polysiloxanes such as polydimethylsiloxane are very apolar materials. A low polarity of the membrane favours the association of ion pairs, which affects the electronic properties and the ion-sensitivity of the membrane [8]. The polarity of polysiloxane membranes can be enhanced by the incorporation of polar cyanopropyl groups. We have recently developed a reproducible synthesis for well-defined siloxane copolymers based on anionic copolymerization of cyclic tetrasiloxanes. The cyclic tetrasiloxanes can be monofunctionalized with a methyl, a cyanopropyl or a methacrylate substituent [9]. This novel membrane material does not require additional plasticizer, is IC compatible and, in addition, can be covalently attached to the gate oxide of the ISFET or the polyHEMA hydrogel.

5. Durable CHEMFETs

The use of siloxane copolymers with methacrylate side groups enables the membrane to be attached covalently to the polyHEMA surface. When the electroactive components also possess photopolymerizable groups, e.g., methacrylate groups, they can be linked covalently to the membrane matrix during the photopolymerization process. Therefore, calix[4]arene receptors and tetraphenylborate anions have been synthesized [10]. These molecules can be covalently attached to the membrane matrix, which renders these CHEMFETs very promising as durable sensors.

This new CHEMFET architecture for the detection of Na^+ is depicted in Fig. 3. These CHEMFETs showed Nernstian responses and a good Na^+ -selectivity with respect to the interfering ions (Table 1). The lifetime experiments, which are still running at the present time, strongly indicate that chemical binding of the electroactive components results in an improved durability. After exposure to 0.1 M NaCl for 90 days, CHEMFETs with both electroactive components chemically attached to the polysiloxane matrix showed no decrease in sensitivity and Na^+/K^+ -selectivity (Table 1). This membrane architecture in which both electroactive components are covalently bound to the membrane matrix is very promising for the further development of stable, durable sensors.

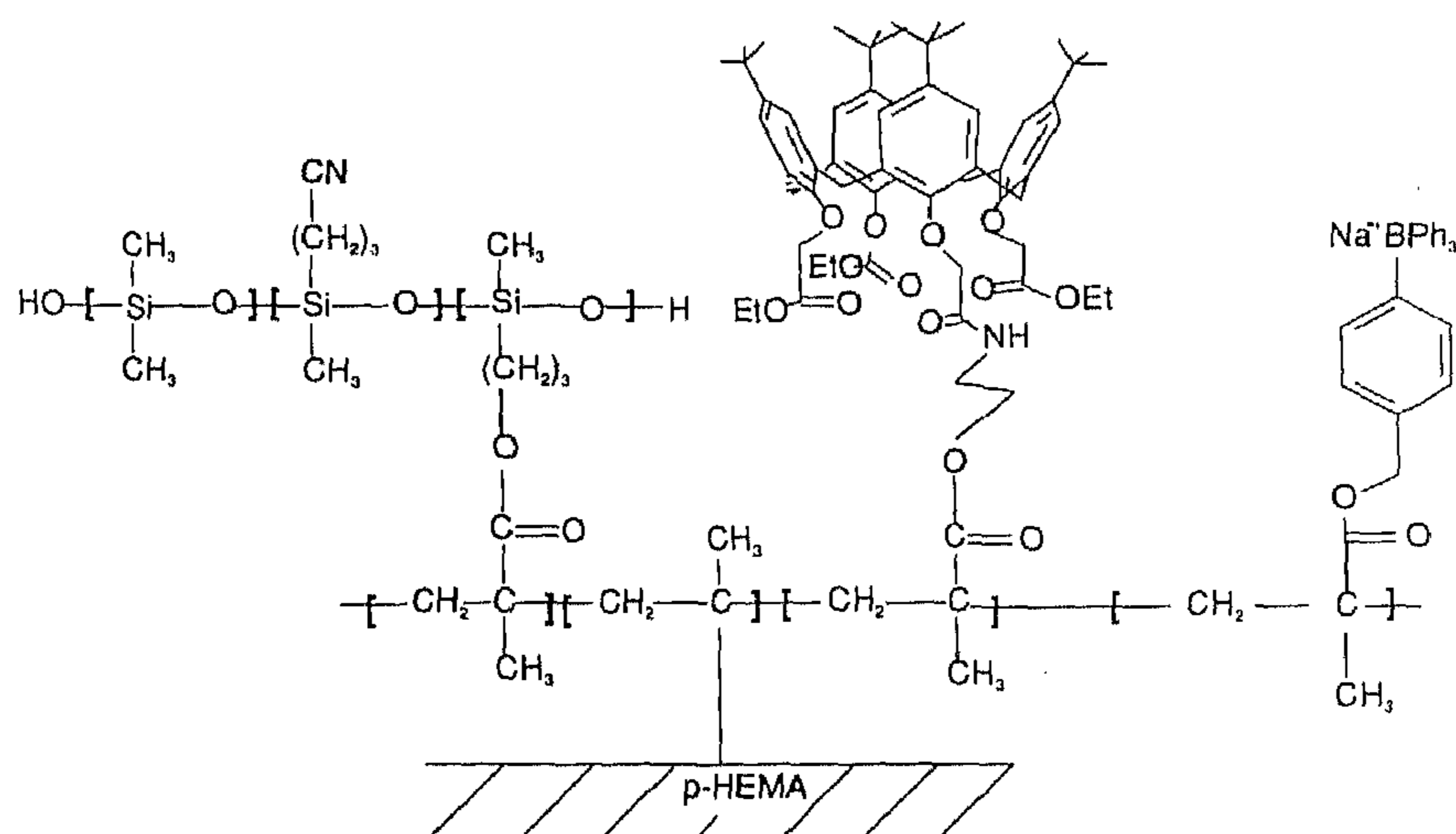


Fig. 3. Schematic representation of the Na^+ -sensing membrane after photocrosslinking.

Table 1
Response characteristics for CHEMFETs modified with polysiloxane membranes containing 10 mol% of cyanopropyl copolymer

Interfering ion, j	$\log K_{\text{Na}^+,j}^{\text{pot}}$ [slope mV decade^{-1}]					
	Cs^+	Rb^+	K^+	Li^+	Ca^{2+}	Mg^{2+}
After conditioning	-2.6 [58]	-2.9 [58]	-2.3 [57]	-2.9 [56]	-3.1 [56]	-3.3 [56]
After 90 days in 0.1 M NaCl	-2.4 [55]	-2.7 [56]	-2.4 [57]	-2.8 [55]	-3.0 [55]	-3.6 [55]

6. Experimental

6.1. Reagents

All silane and siloxane reagents were purchased from Petrarch systems. The polysiloxane copolymers were synthesized according to the method of Gankema et al. [9]. The sodium-selective ionophore and the potassium triphenyl 1-(4-methacryloxymethylphenyl) borate were prepared according to literature procedures [10,11]. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl before use. The pH 4 buffer was purchased from Yokogawa. The chloride salts of the alkali and alkaline-earth metals used were of analytical grade (Merck-Schuchardt), except for sodium which was of even higher purity (Suprapur, Merck-Schuchardt). All solutions were made with deionized, doubly distilled water.

6.2. ISFETs

The ISFETs used in this study have dimensions of $1.2 \text{ mm} \times 3 \text{ mm}$. Details of the fabrication and the modification of ISFETs by covalent anchoring of poly(hydroxyethyl methacrylate) hydrogel are as de-

scribed previously [6,7]. Subsequently, the CHEMFETs were mounted on a support, a printed circuit board, wire bonded and encapsulated with epoxy resin (Hysol H-W796/C8 W795). The ISFETs were encapsulated with silicone rubber (Dow Corning 3140 RTV). The modification of ISFETs with ion-sensitive membranes is as described previously [10].

6.3. ISFET measurements

The output signal of the CHEMFETs was measured in a constant-drain-current mode ($I_d = 100 \mu\text{A}$), with a constant drain-source potential ($V_{ds} = 0.5 \text{ V}$). This was achieved using a CHEMFET amplifier of the source-drain follower type (Electro Medical Instrumentation, Enschede, The Netherlands). The developed membrane potential was compensated by an equal and opposite potential (ΔV_{gs}) via the reference electrode. A saturated calomel electrode (SCE) was used as a reference, connected to the sample solution via a salt bridge filled with 1.0 M LiOAc. The potentiometric selectivity coefficients, $K_{i,j}^{\text{pot}}$, were determined by the fixed interference method (FIM). The constant background concentration of the interfering ion was 0.5 M, unless stated otherwise.

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