

Redox-active self-assembled monolayers as novel solid contacts for ion-selective electrodes†

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A new methodology to fabricate solid-contact ion-selective electrodes (SC-ISEs) using SAMs of a lipophilic redox-active compound to facilitate the charge transfer across the interface leads to improved potential stability and prevents redox or O₂ interference of valinomycin-based SC-ISEs.

In conventional solvent polymeric ion-selective electrodes (ISEs), the membrane is in electrical contact with the internal reference electrode through an inner solution. This arrangement provides stable potentials at the membrane/solution and solution/internal electrode interfaces.¹ For an ISE whose membrane is in direct contact with the inner electrode (coated wire electrodes),² however, the potential stability is generally not satisfactory owing to poorly defined redox reactions at the metal surface and formation of a thin aqueous layer between this metal and the membrane.^{3a–c} ISFETs with an immobilized buffered hydrogel layer between the PVC membrane and the SiO₂ surface showed improved stability^{3d} but since the need for an inner solution impedes true miniaturization of ISEs, several approaches to improve the EMF stability of solid-contact electrodes have been suggested.^{3b,4,5}

Here, we introduce a novel approach to prepare SC-ISEs using redox-active self-assembled monolayers (SAMs). A lipophilic and redox-active compound (a fullerene **1** or tetrathiafulvalene, (TTF) **2** derivative, Fig. 1) is attached by self-assembly to the inner gold electrode (gold film or gold bead), and a conventional ion-selective membrane (with polyurethane matrix) is deposited on the modified solid substrate. The redox properties of the SAMs guarantee a stable potential, while their lipophilicities prevent the formation of an aqueous layer between the membrane and the metal electrode. Two new compounds were designed in view of their easy reduction (of fullerene in **1**) or oxidation (of TTF in **2**).

Compound **1** was synthesized by converting 8-chlorooctanol to the *S*-acetyl protected 8-mercaptooctanol⁶ and then into the malonate derivative, which was added in a modified Bingel reaction to C₆₀.⁷ Acidic deprotection of the monoadduct yielded **1**. The synthesis of **2** is described in the literature.^{8–10} Detailed procedures, spectroscopic and voltammetric data are included in the electronic supplementary information.†

SAMs of **1** and **2** were formed by dipping freshly evaporated Au films (2000 Å, vacuum-deposited on glass slides with a buffer layer of 60 Å Cr) or glass-sealed ultra-clean spherical Au bead (diameter of exposed area ca. 1 mm) electrodes into a 1 mM CH₂Cl₂ solution of the respective compound for 24 h, followed by rinsing with large amounts of CH₂Cl₂ and drying under Ar.¹⁰ The resulting modified surfaces were characterized by contact-angle measurements, ellipsometry and IR spectroscopy (for Au films) or voltammetry (for Au films and beads).

† Electronic supplementary information (ESI) available: synthetic and spectroscopic data for **1** and **2** is available from the RSC web site: <http://www.rsc.org/suppdata/a9/a909532b/>

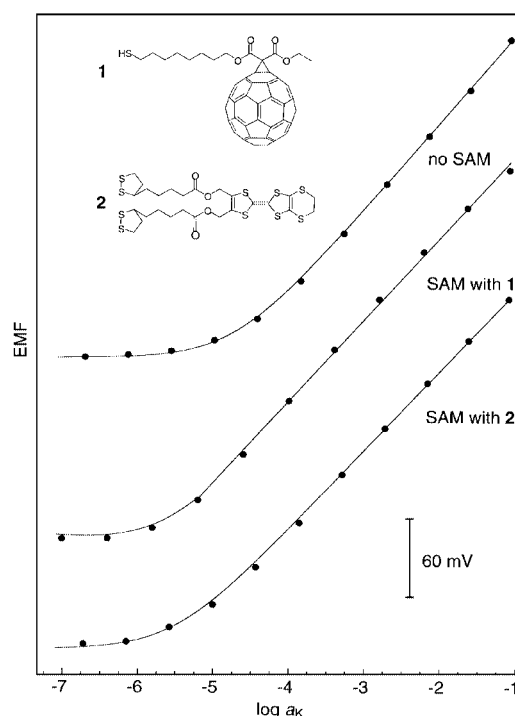


Fig. 1 K⁺-Calibration curves of a valinomycin-based SC-ISE membrane with no SAM, and with a SAM of the fullerene derivative **1** or TTF derivative **2** (curves offset for clarity).

The cyclic voltammograms (CVs) recorded in a solution of 0.1 M NBu₄PF₆ in CH₂Cl₂ show a linear increase of the peak current related to the fullerene-based first reduction (for **1**) or TTF-based first oxidation (for **2**) with the scan rate, indicative of a surface-confined behavior (Fig. 2).¹¹ This was also confirmed by the small potential difference between the anodic and cathodic peaks: 22 mV for the fullerene reduction at $E_{1/2} = -680$ mV and 35 mV for the TTF oxidation at $E_{1/2} = +575$ mV (vs. an aqueous Ag/AgCl reference electrode at a scan rate of 1 V s⁻¹; Fig. 2). The SAMs derived from compounds **1** and **2** proved to be stable, exhibiting almost the same current responses after several scan cycles. The surface coverages¹² were found to be 3.9×10^{-10} and 1.9×10^{-10} mol cm⁻² (estimated values for a monolayer: 1.9×10^{-10} and 3.6×10^{-10} mol cm⁻²)¹³ for **1** and **2**, respectively.^{8,14} The advancing contact angles of water revealed a higher lipophilicity ($71 \pm 2^\circ$ for **1** and $70 \pm 2^\circ$ for **2**)¹⁵ compared to that of the unmodified Au electrode, but a lower one than reported for highly hydrophobic surfaces ($>100^\circ$),¹⁶ which apparently reflects the aromatic character of the terminal fullerene and TTF groups.

Both SAM-modified Au films and beads were used as internal electrodes for the potentiometric measurements¹⁷ with

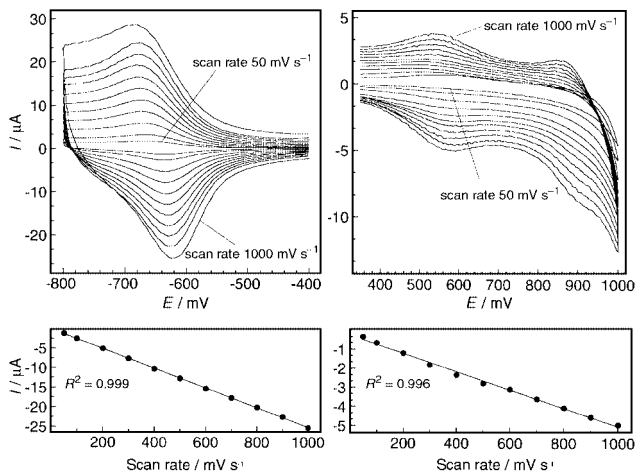


Fig. 2 Cyclic voltammograms of a SAM of **1** (left) or **2** (right) on a gold bead recorded in 0.1 M NBu₄PF₆ in CH₂Cl₂ with scan rates between 1000 (first scan) and 50 mV s⁻¹ (last scan). All measurements were started at 0 mV.

K⁺ selective polyurethane membranes.¹⁸ Fig. 1 shows calibration curves for the SC-ISEs with different interfaces after conditioning in a 10⁻³ M KCl solution for 12 h. The SC-ISEs with SAMs exhibit linear responses down to 10⁻⁵ M K⁺ with Nernstian slopes (the lower detection limit is due to H⁺ interference¹⁷). Since the membrane composition for these SC-ISEs is the same as for conventional liquid-contact ISEs, the selectivity coefficients are also the same within experimental error. The EMF values of these SC-ISEs are more stable (long term drifts over 100 h 85 μV h⁻¹ as compared to 220 μV h⁻¹ without SAM) and not influenced by changes in the ratio of Fe(III)/Fe(II) in solutions of constant ionic strength (0.1 M KCl) and constant total amount of the redox couple (10⁻² M FeCl₃/FeCl₂). In the absence of the redox-active SAM, the linear response range was reduced by about an order of magnitude (Fig. 1, the lower detection limit is no more due to H⁺ interference) and strongly drifting signals (> 5 mV min⁻¹) were observed when interfering ions were measured. Both of these effects can be explained by the presence of an aqueous layer between the polyurethane membrane and the gold surface. The composition of this layer changes upon contact of the SC-ISE with interfering sample ions and thereby affects both the phase boundary potential at the interface of the membrane and the aqueous layer as well as the interfacial potential at the metal surface, which is apparently determined by the reaction of O₂.^{3b} The strong influence of O₂ on the EMF of coated wire electrodes^{3b,5a} (Fig. 3, top curve) is effectively reduced by the SAMs of **1**, **2** or *n*-C₈H₁₇SH (Fig. 3), indicative of the absence of an aqueous layer. However, no Nernstian response could be obtained with the latter monolayer, corroborating the need for the redox active SAM.

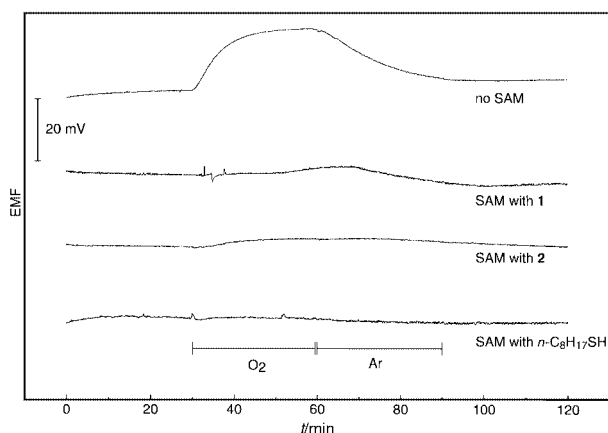


Fig. 3 EMF response of various SC-ISEs on introducing O₂ or Ar into a 10⁻³ M KCl solution (curves offset for clarity).

In summary, we have developed a new methodology to fabricate solid-contact ion-selective electrodes using SAMs of redox-active compounds. All the valinomycin-based SC-ISEs studied show Nernstian responses down to 10⁻⁵ M K⁺, with improved stability, and no redox or O₂ interference.

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