

Supporting Information

Ion-Selective Electrodes Based on Hydrophilic Ionophore-Modified Nanopores

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Author Contributions

G.J. Methodology: Supporting.

Supporting information

Chemicals and reagents

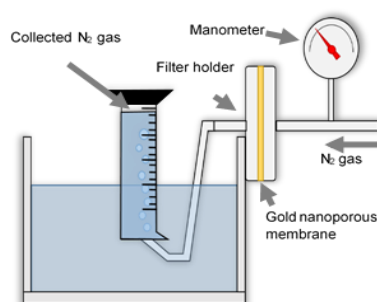
The Cys-Gly-Gly-Gly-His peptide was custom-synthesized by Bio Basic Inc. (Markham ON, Canada). 1-propanethiol (PT), 1-octanethiol (OT), 1-dodecanethiol (DT), 1-hexadecanethiol (HDT), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (PFT) was purchased from Sigma-Aldrich. Absolute ethanol (AR grade) was purchased from Molar Chemicals Ltd. (Halásztelek, Hungary). Mercaptodecanesulfonic acid sodium salt (MDSA) was synthesized according to the recipe reported by Turyan and Mandler^[1]. The electroless gold plating solution (Oromerse SO Part B) was purchased from Technics Inc. (Cranston, RI, USA). Conventional ion-selective membrane components: Copper(II) ionophore I (*o*-xylylene bis(*N,N*-diisobutyldithiocarbamate)), 2-Nitrophenyl octyl ether, potassium tetrakis(4-chlorophenyl)borate, and high molecular weight poly(vinyl chloride), were Selectrophore® grade and purchased from Sigma-Aldrich. Titriplex® III solution for metal titration (c(Na₂EDTA·2 H₂O)= 0.1 mol L⁻¹ Titripur® Reag. Ph Eur grade) was purchased from Merck Millipore (Billerica, MA). All salts were of highest analytical grade, and were purchased from Sigma-Aldrich or Merck. Solutions were made using deionized water of 18.2 MΩ cm resistivity at 25°C, produced by a Millipore Direct-Q 3 UV water purification system (Merck Millipore, Billerica, MA).

Electroless gold plating

6 μm thick and 25 mm diameter track-etched polycarbonate membranes with pore density of 6 × 10⁸ pore/cm², and nominal pore diameter of 30 nm were purchased from Whatman (Maidstone, UK). Gold nanoporous membranes were formed by electroless gold plating within the pores of track-etched polycarbonate membranes. The electroless plating procedure followed a slightly modified version of the original protocol published by the group of Martin^[2], i.e., an additional drying step in N₂ atmosphere was performed before immersing the sensitized membranes into the gold plating solution. The gold plating was done at pH 10 and 1°C for 6 hours. After the gold plating the membranes were rinsed thoroughly with deionized water and dried in an exicator.

Determination of the effective pore radius of the gold-plated nanoporous membranes

The effective pore radius (average inside radius) after the gold plating was determined by N₂ permeation. The membranes were first mounted in a commercial filter holder (Whatman, Maidstone, UK), and one side of the membrane was pressurised with N₂. The gas was collected on the other side of the membrane, so the gas flux could be determined from the volume of the collected gas and the elapsed time (Scheme S1).



Scheme S1. Schematic of the N₂ permeation setup used for the determination of the effective pore diameter of the gold-plated membranes.

The effective pore radius, r (m) was calculated according to Knudsen equation:

$$r = \left\{ \frac{3}{4} Q \left(\frac{MRT}{2\pi} \right)^{1/2} \frac{l}{n\Delta p} \right\}^{1/3}$$

where Q is the flux of the gas (mol s^{-1}), M is the molecular weight of the gas (kg mol^{-1}), R is the universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K), l is the membrane thickness (m), n is the number of pores, Δp is the pressure drop through the membrane (Pa). A close to linear dependence was found between the decrease of the pore diameter and the gold plating in the size range shown in Figure S1.

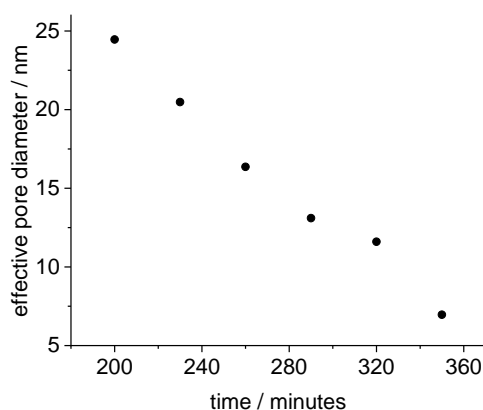


Figure S1. Effective pore diameter determined by gas permeation experiments as a function of the gold plating time.

Functionalization of the gold nanoporous membranes

The gold nanoporous membranes were immersed into an ethanolic solution of the thiol functionalized compounds for 20 hours at 25°C. The total concentration of these solutions was kept constant in all experiments at 0.1 mM varying only the molar ratio of the components to find the optimal composition. After removal from the modifier solutions, the membranes were first rinsed with ethanol and then with deionized water. Finally, the membranes were dried in vacuum (ca. 50-60 mbar).

Contact angle measurements

To confirm macroscopic mixing of thiols with widely different polarity in the self-assembled monolayers a planar gold surface was modified with mixture of a hydrophilic and a hydrophobic thiol (MDSA/PFT; CGGGH-peptide/PFT) in various molar ratios at a total concentration of 0.1 mM as described above. After the modification advancing water contact angle measurements were performed on the gold surface with sessile water droplets of 1-2 μl at room temperature and atmospheric pressure (Figure S2). The fractional surface coverage of the hydrophilic thiols in these binary mixtures were estimated by the Cassie equation^[3] (Figure S2; insets). This show a noticeable dominance of the linear PFT on the surface over a wider range of molar ratios than the hydrophilic thiols (MDSA or peptide). The surface coverage of hydrophilic thiols starts to increase at molar fractions of the hydrophilic thiols exceeding 0.5 in the modifying solution. A similar result was found when the PFT was changed to HDT as the hydrophobic component (Figure S3).

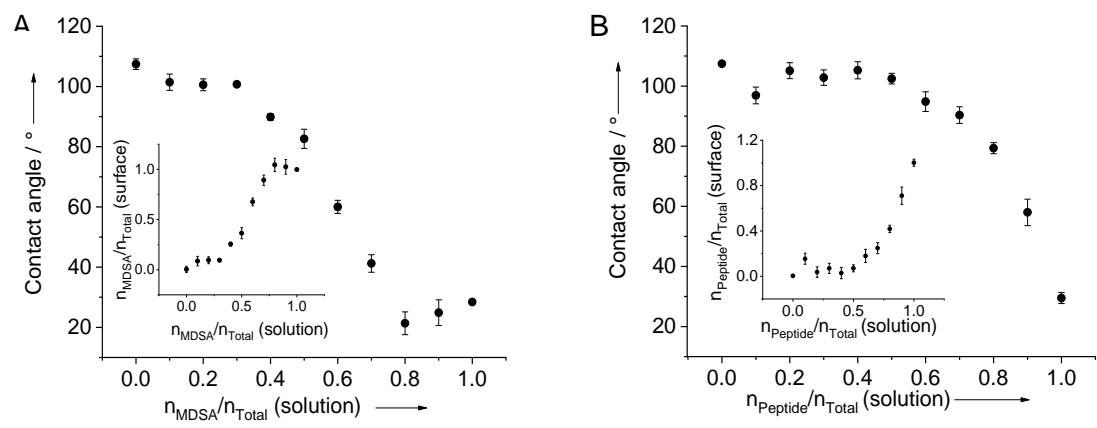


Figure S2. Water contact angle measurements on planar gold surfaces modified with solutions containing MDSA/PFT (A) and CGGGH peptide/PFT (B) in different molar ratio as a function of the modifying solution composition. Insets: The respective molar fraction of the hydrophilic component on the gold surface estimated by Cassie's law.

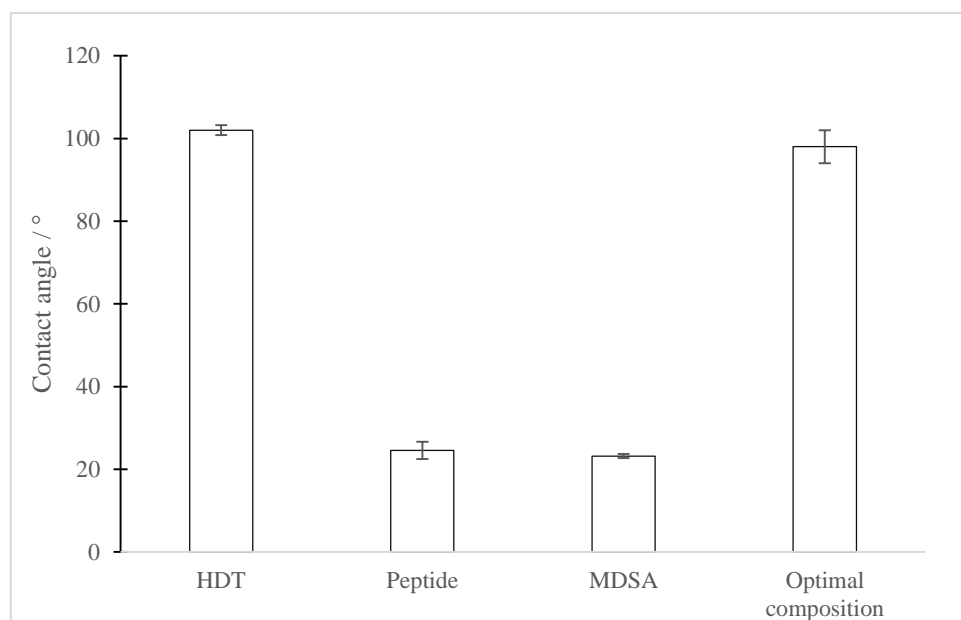


Figure S3. Water contact angles of different thiol-functionalized gold surfaces. The optimal composition stands for a modifier solution with a molar ration of 6:3:1 of the CGGGH peptide, HDT, and MDSA.

Determination of the resistance of chemically modified nanoporous gold membranes

Electrochemical impedance spectroscopy (EIS) was performed by mounting the membranes into an electrochemical cell to separate two electrolyte compartments filled with 10 mM KCl. Each compartment was electrically contacted via Ag/AgCl wire to a Reference 600 Potentiostat/Galvanostat (Gamry Instruments, Warminster, PA, USA). The impedance spectra were obtained within the frequency range of 100 kHz and 100 mHz, using a 50 mV AC amplitude. The spectra were evaluated with Gamry Echem Analyst (version 6.03) software. The resistances of chemically modified gold nanoporous membranes were determined by fitting the impedance data using an equivalent circuit (Figure S4 inset), consisting of the membrane resistance (R_p) in parallel with a constant phase element standing for the double layer capacitance (Y_0) that are in series with the electrolyte solution resistance (R_u). Figure S4 shows that for the same molar ratio of the peptide, linear alkanethiol, cation-exchanger (MDSA) the resistance of the nanopore increases with the length of the alkanethiol from C8 to C16 (Figure 1).

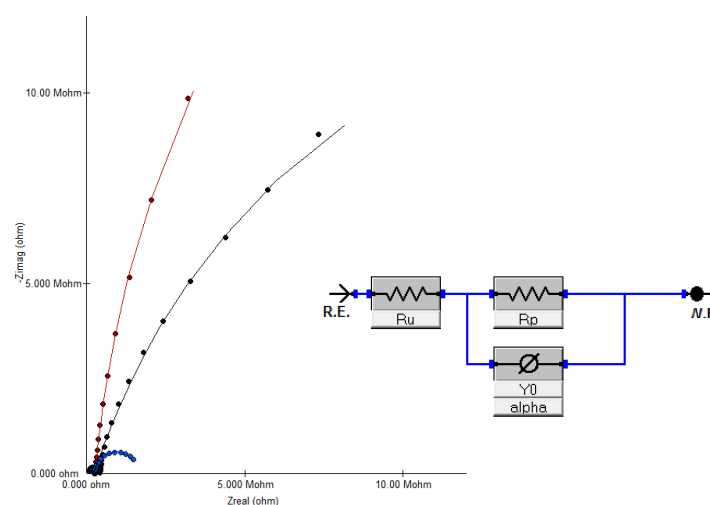


Figure S4. Typical Nyquist plots of the gold nanoporous membranes modified with a mixture of Cys-Gly-Gly-Gly-His peptide, an alkanethiol and MDSA in molar ratio 6:3:1. The length of the alkanethiols was varied in these experiments (red curve: HDT (C16); black: C12; blue: C8). The data was fitted with the equivalent circuit shown in the inset.

Preparation of the conventional plasticised PVC-based Cu^{2+} -selective membranes

The conventional poly(vinyl chloride) membrane based Cu^{2+} -selective membrane were prepared according to Kamata et al^[4], using 6.90 wt% Copper(II) ionophore I, 34.30 wt% 2-nitrophenyl octyl ether, 1.60 wt% potassium tetrakis(4-chlorophenyl)borate, 57.20 wt% poly(vinyl chloride) high molecular weight. The membrane components were dissolved in tetrahydrofuran and cast in a 24 mm diameter glass ring fixed on a glass plate. After the tetrahydrofuran was left to slowly evaporate overnight the resulting membrane disk was peeled off from the glass plate.

Preparation of ion-selective electrodes

Disks with 7 mm diameter were cut off either from the conventional polymeric ion-selective membranes or from the chemically modified nanoporous membranes and mounted into commercial Philips IS 561 liquid membrane electrode bodies (Möller Glasbläserei, Zürich, Switzerland). To have proper sealing, the chemically modified gold nanoporous membranes were sandwiched between a 1 mm thick outer and an inner silicone rubber rings and this assembly was then secured in the electrode body. Both rings had an inner diameter of 4 mm while the outer diameters were 7 mm and 6 mm, for the outer (facing the sample) and inner silicon rubber ring, respectively. The

inner reference compartment was filled with 1 mM KCl for potentiometric experiments. The electrodes were conditioned in 1 mM KCl before use.

EMF measurements

Potentiometric measurements were performed by connecting the assembled Philips electrode bodies to a 16-channel high-resolution high input impedance ($10^{15} \Omega$) pH-meter (Lawson Labs, Malvern, PA, USA), along with a double junction reference electrode (Ag/AgCl; 3 M KCl inner electrolyte, 0.1 M KCl outer electrolyte; No. 6.0729.100, Metrohm AG, Herisau, Switzerland). The calibrations were typically performed using 500 mL solutions of CuCl_2 in the range of $10^{-9} \text{ M} - 10^{-1} \text{ M}$.

Selectivity coefficients were determined by separate solution method (SSM)⁵, using a three-point calibration for the Cu^{2+} and the interfering ions (J) in their chloride salt solutions in the range of $10^{-5} \text{ M} - 10^{-3} \text{ M}$. The selectivity coefficients were calculated using the individual potentials extrapolated to 1 M activity.

Potentiometric titration

In order to demonstrate the utility of the assembled copper(II)-selective electrodes they were used as indicator electrodes during complexometric back-titration of Fe^{3+} . 10 mL of 0.1 M Na_2EDTA (excess amount in respect of Fe^{3+}) was added to 100 mL of 5 mM Fe^{3+} solution (pH was set to 4.4 with 0.15 M acetic acid/sodium-acetate buffer), then the excess amount of EDTA (0.5 mmol) was titrated back with 0.1 M Cu^{2+} . The assembled copper(II)-selective electrodes served as indicator electrodes, and a double junction electrode of the same kind as described above was used as a reference electrode. The titrants were added automatically using a Dosino 700 (Metrohm, Herisau, Switzerland) with a 10 mL dispensing unit controlled by a Liquino 711 (Metrohm, Herisau, Switzerland). The inflection point is perfectly observable in accordance with the stoichiometry of the reaction (Figure S5) at an added titrant volume of 5 mL as theoretically predicted.

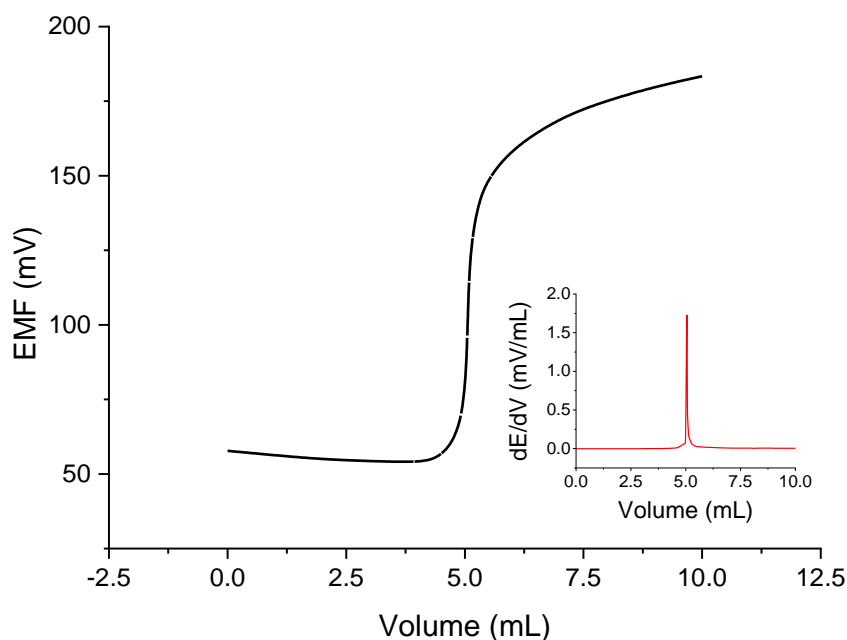


Figure S5. Potentiometric titration curve recorded using the peptide-modified gold nanoporous membrane based Cu^{2+} selective electrode during the back titration of Fe^{3+} , i.e., the excess of EDTA (10 mL, 100 mM) added to the Fe^{3+} solution (100 mL, 5 mM) is titrated with 0.1 M Cu^{2+} solution as indicator electrode. The inset shows the derivative of the titration curves that confirms the agreement of the determined equivalence volume with the calculated volume of titrant (5.0 mL).

Stability of the potentiometric response of the peptide-modified gold nanoporous membranes-based Cu²⁺ ISEs

We could use peptide-modified gold nanoporous Cu²⁺-selective electrodes for up to three months with little change in potentiometric sensitivity (Figure S6). While not in use these ISEs were stored in 1 mM KCl.

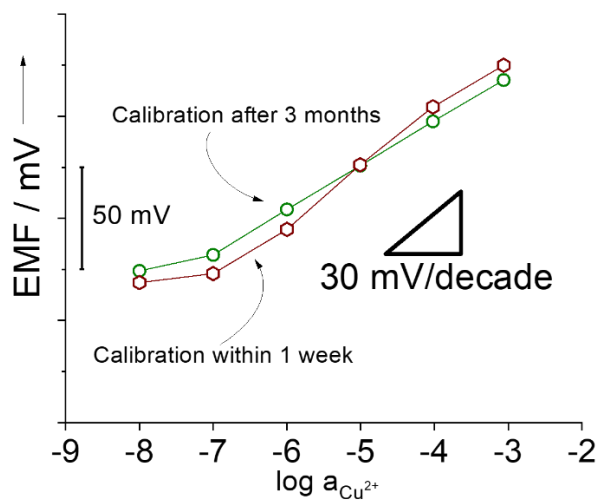


Figure S6. Calibration curves of peptide-modified gold nanoporous membrane-based Cu²⁺-selective electrodes within 1 week from assembly (red) and 3 months after the assembly (green). The assembled electrodes were stored in 1 mM KCl between the measurements.

References

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