Supporting Information

for

Potentiometric Sensors Based on Fluorous Membranes Doped with Highly Selective Ionophores for CO_3^{2-}

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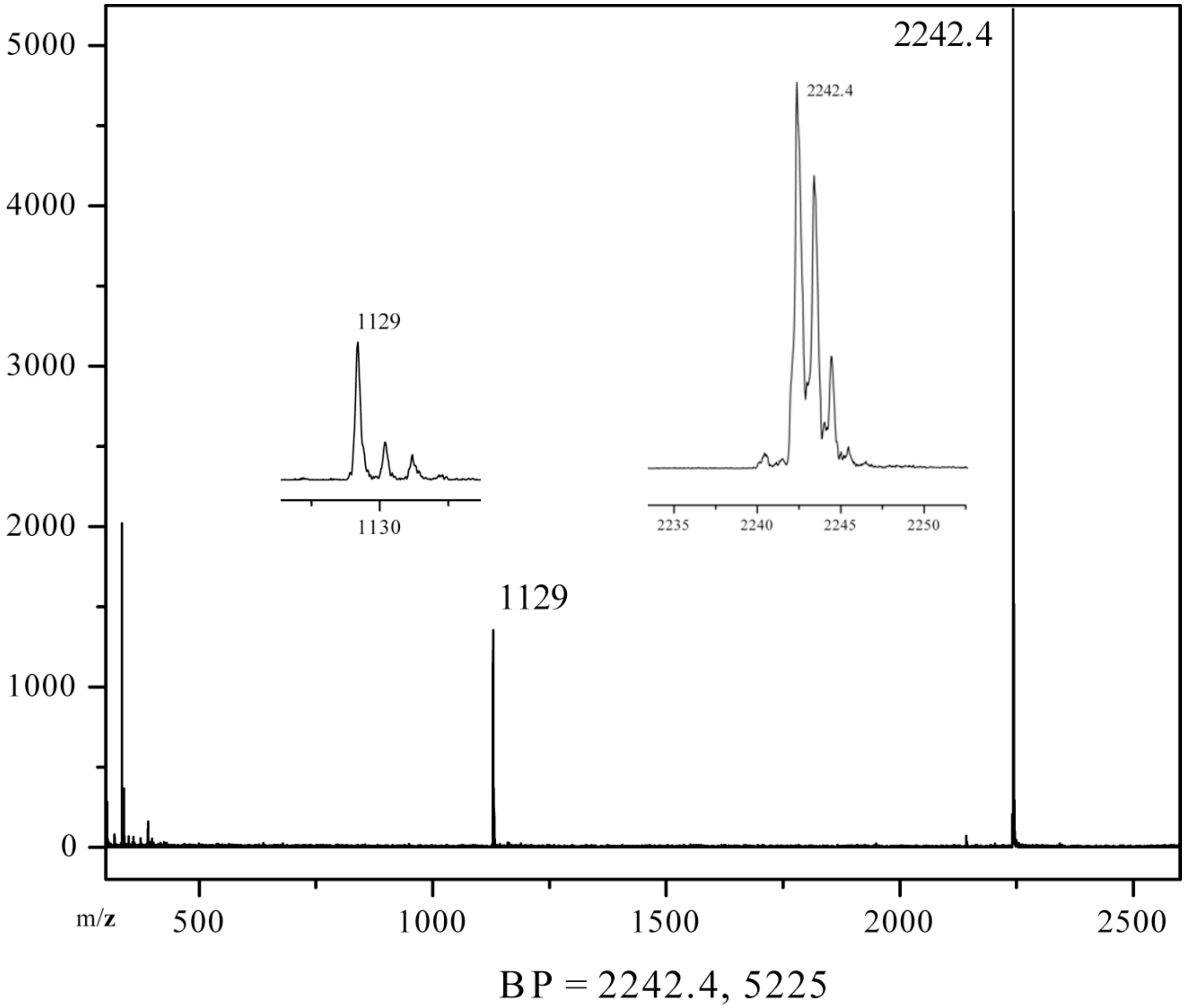

Figure S1. MALDI-TOF mass spectrum of fluorophilic salt **1**.

Table S1. CO_3^{2-} Selectivities ($\log K^{pot}_{co_3^{2-},J}$) of Conventional Ionophore-Doped ISEs and Fluorous Ionophore-doped ISEs with Perfluoroperhydrophenanthrene as Membrane Matrix

ion J	CO_3^{2-} Selectivities ($\log K^{pot}_{co_3^{2-},J}$)		
	Conventional ISE[a]	Fluorous ISE No. 1 (**Mn-1**) [b]	Fluorous ISE No. 2 (**Mn-2**)[c]
Cl^-	-4.80	-6.87 ± 0.26	-5.46 ± 0.21
Br^-	-3.50	-4.97 ± 0.26	-6.90 ± 0.22
NO_3^-	-1.60	-5.13 ± 0.17	-6.58 ± 0.20
SCN^-	0.70	-1.59 ± 0.16	-2.78 ± 0.20
Sal^-	3.80	-2.19 ± 0.27	-2.36 ± 0.28

[a] Ionophore: heptyl 4-trifluoroacetylbenzoate[1]; [b] fluorophilic ionophore **Mn-1** (1.5 mM) and cationic sites, **1** (1.0 mM); [c] fluorophilic ionophore **Mn-2** (4.0 mM) and anionic sites, **2** (1.0 mM)

Table S2. BPh_4^+ Selectivities ($\log K^{pot}_{BPh_3^-,J}$) of Fluorous Ionophore-Free Ion-Exchanger Membranes and Fluorous Ionophore-Doped Membranes with Perfluoroperhydrophenanthrene as Membrane Matrix.

Membrane Composition		BPh_4^+ Selectivities ($\log K^{pot}_{BPh_3^-,J}$)		
ionophore	Ionic sites	CO_3^{2-}	SCN^-	OH^-
none	**1** (2 mM)	-9.90 ± 0.10	-5.80 ± 0.10	-10.93 ± 0.16
Mn-1 (1.5 mM)	**1** (1 mM)	-4.27 ± 0.11	-5.07 ± 0.05	-3.74 ± 0.08
Mn-1 (1.5 mM)	**1** (2 mM)	-8.65 ± 0.16	-5.85 ± 0.13	-7.05 ± 0.15
Mn-1 (4.0 mM)	**2** (1 mM)	-1.86 ± 0.06	-0.22 ± 0.08	0.71 ± 0.09
Mn-2 (1.5 mM)	**1** (1 mM)	-6.02 ± 0.09	-5.79 ± 0.05	-4.07 ± 0.05
Mn-2 (1.5 mM)	**1** (2 mM)	-7.08 ± 0.15	-5.81 ± 0.13	-5.55 ± 0.25
Mn-2 (4.0 mM)	**2** (1 mM)	-0.11 ± 0.08	-1.50 ± 0.05	3.50 ± 0.09
Mn-3 (4.0 mM)	**2** (1 mM)	2.39 ± 0.05	-1.88 ± 0.10	0.75 ± 0.10

Binding Constant Derivation

When determined with respect to a noncomplexing ion such as tetraphenylborate, the selectivity of an ionophore-based ISE membrane for an ion that forms a complex with the ionophore can be used to determine the binding constant of the ion–ionophore complex. The relevant theory has been reported in the literature.[2-6] Here, binding constants are derived considering a rather complicated case in which the ionophores can function as both positively and negatively charged ionophores.

According to the phase boundary potential model, the selectivity coefficient for an ionophore-free ion-exchanger membrane $K_{JI}^{pot}(IE)$ is given by[7]

$$K_{JI}^{pot}(IE) = \frac{[J^{-}(J)]^{z}}{K_{JI}[I^{z-}(I)]} \tag{S1}$$

where I^{z-} is the anion of charge z that the ionophore can bind (in our case, CO_3^{2-}), and J^{-} is the reference ion that we assume not to interact with the ionophore (BPh_4^-). $[I^{z-}(I)]$ and $[J^{-}(J)]$ refer to free ion concentrations in the membrane phase when there is only one kind of the two anions, I^{z-} or J^{-}, present in the membrane, and K_{IJ} is the equilibrium constant for the exchange of I^{z-} and J^{-} between the membrane and the sample phase. Since there is no ionophore in the membrane, $[J^{-}(J)]$ equals R_T, the total concentration of ionic site in the ion exchanger membrane, while $[I^{z+}(I)]$ equals R_T / z.

$$K_{JI}^{pot}(IE) = \frac{zR_T{}^{z}}{K_{JI}R_T} \tag{S2}$$

In the same way, we can get the selectivity coefficient of the equivalent membrane doped with positively charged ionophore, which is given by

$$K_{JI}^{pot}(L) = \frac{(L_{tot}^{+} + z_R[R_T^{z_R}])^{z}}{K_{JI}[I^{z-}(I)]} \tag{S3}$$

where L_{tot}^{+} is the total concentration of ionophore and $[R_T^{z_R}]$ is the total concentration of ionic sites with a charge sign of z_R in the membrane. Assuming that J^{-} does not bind to the ionophore, $[J^{-}(J)]$ is equal to $L_{tot}^{+} + z_R[R_T^{z_R}]$. Combining equations S2 and S3 gives

$$[I^{z-}(I)] = \frac{(L_{tot}^{+} + z_R[R_T^{z_R}])^{z}}{zR_T}\frac{K_{JI}^{pot}(IE)}{K_{JI}^{pot}(L)} \tag{S4}$$

Since more specific situations are of particular interest here , I^{2-} (representing CO_3^{2-}) will be used for following discussion. Panel A in Figure 4 of the associated full paper shows that in the membrane with an anionic site-to-ionophore ratio of 1:4, the dominant complex is $L_2^{+}I^{2-}$. Thus, the cumulative binding constant, β_{IL_2}, is given by

$$\beta_{IL_2} = K_{L^{+}-I^{z-}}K_{L^{+}I^{z-}-L^{+}} = \frac{[L_2^{+}I^{z-}]}{[L^{+}]^{2}[I^{z-}]} \tag{S4}$$

where $[L^{+}]$ is the concentration of free ionophore in the membrane.

Since there is a large excess of L^{+} in an ideally selective membrane, the concentration of 1:1 stoichiometry complex of ionophore and the anion, $L^{+}I^{2-}$, resulting from dissociation of $L_2^{+}I^{2-}$, is very low. Thus, we can assume that $[L^{+}I^{2-}]$ is ≈0 M. From the mass and charge balance in the membrane, $[L_2^{+}I^{2-}]$ and $[L^{+}]$ can be expressed by

$$[L_2^{+}I^{z-}] = [L_{tot}^{+}] - [R_T^{-}] - 2\,[I^{2-}] \tag{S5}$$

and

$$[L^{+}] = 2\,[I^{2-}] + [R_T^{-}] \tag{S6}$$

Combining equations S4, S7, and S8 gives

$$\beta_{IL_2} = \frac{[L_{tot}^{+}] - [R_T^{-}] - 2[I^{2-}]}{(2[I^{2-}] + [R_T^{-}])^{2}[I^{z-}]} \tag{S7}$$

Substituting $[I^{z+}]$ as calculated from Equation S4 into Equation S7, the binding constant β_{IL_2} is obtained.

In the ionophore-based membranes with a cationic site-to-ionophore ratio of 2:3, complexes of the type $L_2^+I^{2-}$ and L^+I^{2-} coexist. Using β_{IL_2} and the mass and charge balance in the membrane to solve for $[L^+]$ gives

$$[L^+] = \frac{-2 + \sqrt{4 - 4\beta_{IL_2}[I^{2-}]([R_T^+] - [L_{tot}^+] - 2[I^{2-}])}}{2\beta_{IL_2}[I^{2-}]} \tag{S8}$$

Expressions for $[L_2^+I^{2-}]$ and $[L^+I^{2-}]$ can now be obtained by insert of $[I^{2+}]$ from equation S4 and $[L^+]$ from equation S8 into the following two equatons:

$$[L_2^+I^{2-}] = [L_{tot}^+] - [R_T^+] + 2[I^{2-}] - 2[L^+] \tag{S9}$$

$$[L^+I^{2-}] = [L^+] - [R_T^+] - 2[I^{2-}] \tag{S10}$$

Note that the resulting expressions for $[L_2^+I^{2-}]$ and $[L^+I^{2-}]$ are very lengthy, and are therefore not reproduced here. The same applies for several other expressions shown in the following.

With expressions for $[L^+]$, $[I^{2+}]$, $[L^+I^{2-}]$ and $[L_2^+I^{2-}]$ known, $K_{L^+-I^{2-}}$ and $K_{L^+I^{2-}-L^+}$ can be calculated from

$$K_{L^+-I^{2-}} = \frac{[L^+I^{2-}]}{[L^+]\,[I^{2-}]} \tag{S11}$$

and

$$K_{L^+I^{2-}-L^+} = \frac{[L_2^+I^{2-}]}{[L^+][L^+I^{2-}]} \tag{S12}$$

Complexes of the type $L^+I_2^{2-}$ (i.e., one ionophore bound to two CO_3^{2-}) are formed in the membranes with 4:3 cationic site-to-ionophore ratio. The binding constant, $K_{L^+I^{2-}-I^{2-}}$, is given by

$$K_{L^+I^{2-}-I^{2-}} = \frac{[L^+I_2^{2-}]}{[I^{2-}][L^+I^{2-}]} \tag{S13}$$

In membranes with this ionic site-to-ionophore ratio (see panel A, Figure 4, of the associated full paper), $[L^+I_2^{2-}]$ and $[L^+I^{2-}]$ are the dominant species and one may assume that $[L^+]$ is equal to ≈0 M. Therefore, the mass balance and charge balance in the membrane can be used to give $[L^+ I_2^{2-}]$ as

$$[L^+ I_2^{2-}] = \frac{[R_T^+] - [L_{tot}^+] - 2[I^{2-}]}{2} \tag{S14}$$

and $[L^+ I^{2-}]$ is given by

$$[L^+ I^{2-}] = \frac{3[L_{tot}^+] - [R_T^+] + 2[I^{2-}]}{2} \tag{S15}$$

Substituting equations S4, S14 and S15 into equation S13 gives the binding constant $K_{L^+I^{2-}-I^{2-}}$.

The mechanism of the super-Nernstian responses exhibited by the membranes with a 1:4 ratio of anionic sites and ionophore was further confirmed by the fact that at low pH, these electrodes exhibited nearly Nernstian responses of about 50 mV/decade for SCN$^-$ at high concentrations from 10^{-1} to 10^{-3} (where a majority of the ionophore forms [LSCN]$^-$ complexes) and slopes of -87 mV/decade and -71 mV/decade for **Mn-1** and **Mn-2** for SCN$^-$ concentrations in the range from $10^{-3.5}$ to $10^{-4.5}$ M (where the ionophore forms 1:2 and 1:1 or $[L_n(OH)_{n-1}]^+$ complexes and no free ionophore is left in the membranes.

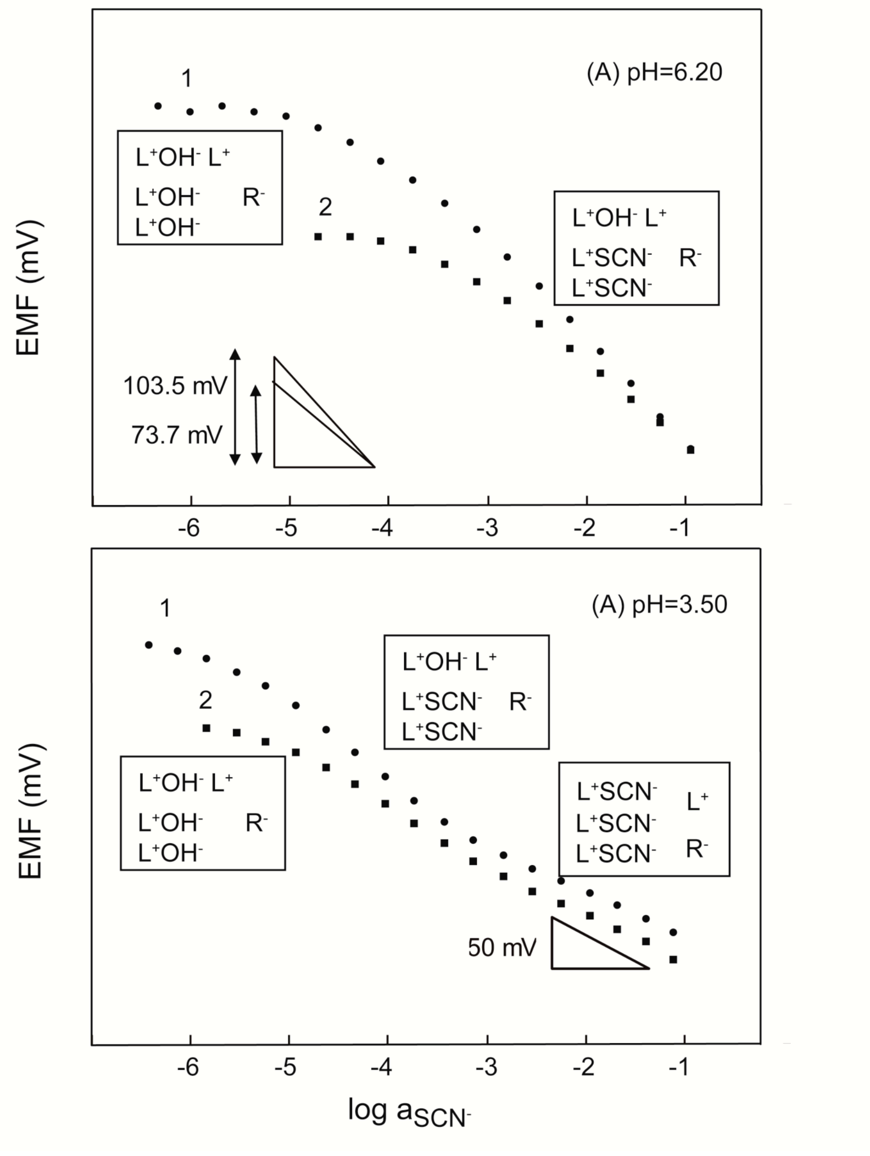

Figure S2. Potentiometric SCN$^-$ response of an ISE based on a liquid membrane with perfluoroperhydrophenanthrene doped with: (1) 4.0 mM ionophore **Mn-1** and 1.0 mM anionic sites, **2**;(2) 4.0 mM ionophore **Mn-2** and 1.0 mM anionic sites, **2** at (A) pH=6.20 and (B) pH=3.50.

References

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