Supporting Information

for

**Electrochemical Assessment of a Tripodal Thiourea-Based Anion Receptor at the Liquid | Liquid Interface**

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1. Preparation of receptor 1.

Receptor 1 was prepared by a method previously reported\(^1\), with a modified purification process. A solution of tris(2-aminoethyl)amine (200 mg, 1.37 mmol) and \(n\)-pentylisothiocyanate (613 mg, 4.51 mmol) in dichloromethane (DCM) (10 mL) was stirred for 72 h. The solvent was evaporated, resulting in a light yellow oil. The residue was purified by column chromatography (SiO\(_2\), DCM-AcOEt 1:1), precipitated from DCM-hexane, and dried under vacuum to afford the product as a white solid. Yield: 607 mg (83%). The \(^1^H\) NMR data coincided with those previously reported. \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.48\) (s, 3H), 7.18 (s, 3H), 3.45 (s, 6H), 2.62 (t, \(J = 6.6\) Hz, 6H), 1.56 – 1.38 (m, 6H), 1.36 – 1.14 (m, 12H), 0.87 (t, \(J = 6.9\) Hz, 9H).

![Chemical structure of receptor 1](image-url)
2. Facilitated Cl\textsuperscript{-} transfer limited by concentration of receptor 1.

Figure S1. **Left**) CVs of Cell 1 in the presence of the electrolytes 20mM NaCl\textsubscript{(aq)} | 10mM BPATFPB\textsubscript{(DCB)} and various concentrations of receptor 1\textsubscript{(DCB)}. CVs were calibrated in accordance with the formal transfer potential of TMA\textsuperscript{+} at the water| DCB interface. **Right**) Plot of the peak current of Cl\textsuperscript{-}—1 complex (\(i_p\)) as a function of the concentration of receptor 1 (\(c_1\)). Scan rate = 10 mV/s.
3. Diffusion coefficient ($D$) calculation.

The diffusion coefficient of receptor 1 can be estimated from the Randles-Ševčík equation,

$$i_p = 0.4463 \left( \frac{Z^3 F^3}{RT} \right)^{1/2} A C (D \nu)^{1/2}$$

*Equation S1*

Where $i_p$ is the peak current of the facilitated anion transfer, $\nu$ is the scan rate of the voltammetric measurements, $A$ is area of the aqueous | organic interface, $C$ concentration of the ionophore, $D$ is the diffusion coefficient of the ionophore in the organic interface, $F$ is the Faraday constant, $Z$ is the charge of the ion, $T$ is the temperature in Kelvin and $R$ is the universal gas constant.

*Figure S2. a) CVs of Cell 1 in the presence of the electrolytes 20mM NaCl$_{aq}$ | 10mM BTPATFPB$_{DCB}$ and 1mM receptor 1$_{DCB}$ showing the facilitated Cl$^-$ transfer peak. b) Plot of Randles-Ševčík equation of the peak current ($i_p$) as a function of the square root of the scan rate ($\nu^{1/2}$) for the forward and reverse peaks. Scan rates were from 10-100 mV/s (increments of 10 mV/s).*
4. Stoichiometry and association constant ($K_a$).

For the stoichiometry and association constant determination, Equation 1 in the main text was used. These calculations require $\Delta^{w}_{\phi} \phi^o_{A^-}$ of the anion at the studied aqueous | organic interface (see section 4 below), and $\Delta^{w}_{\phi} \phi^{1/2}$ of the anion of the calibrated CV.

Calibration of the CVs is a mandatory practice for the analysis calculations, since the absolute scale of the Galvani potential difference is not accessible by direct measurements. In this context, a calibrator ion of known and defined standard transfer potential can be used to scale the CV data. Herein, the CVs were calibrated by adding tetramethylammonium cation (0.2mM TMA$^+$, $\Delta^{w}_{\phi} \phi^o_{TMA^+} = 0.226 \text{ V}$) during the voltammetric measurements. Calibrated CVs for the facilitated Cl$^-$ and Br$^-$ transfer in presence of TMA$^+$ are shown in Figure S3.

**Figure S3.** CVs of Cell 1 for NaCl$_{aq}$ (Left) and NaBr$_{aq}$ (Right) at various concentrations in the presence of 0.5mM receptor 1$_{[DCB]}$ and the calibrator cation 0.2mM TMA$^+_{[aq]}$. Scan rate = 10 mV/s.

Differential pulse voltammetry (DPV) was also employed to extract accurate half-wave potential data, especially in case of overlapping of the transfer wave of TMA$^+$ with other peaks. An example which involves the facilitated transfer of CH$_3$COO$^-$ is shown in Figure S4.
Figure S4. (Left) CVs of Cell 1 for CH$_3$COOLi$_{(aq)}$ at various concentrations in the presence of 0.5mM receptor 1$_{(DCB)}$ and the calibrator cation 0.2mM TMA$^+_{(aq)}$. Scan rate = 10 mV/s. (Right) DPV curve of the cell at various concentrations. Scan rate = 50 mV/s.
5. Correlations of the standard Gibbs energy of ion transfer ($\Delta G^{\omega\rightarrow\omega}_{tr}$).

Due to the lack of the data of the standard anion transfer potential ($\Delta \phi^0_{A^-}$) from water to DCB for Br$^-$, CH$_3$COO$^-$ and SO$_4^{2-}$, data from other solvents were used to estimate the required data in DCB.

That is, plots of the standard Gibbs energy of ion transfer ($\Delta G^{\omega\rightarrow\omega}_{tr}$) from water to different solvents were found to provide linear correlations, allowing to estimate $\Delta G^{\omega\rightarrow\omega}_{tr}$ of unknown data in one solvent relative to a known one of another solvent$^{3,4}$. $\Delta G^{\omega\rightarrow\omega}_{tr}$ data are more widely reported for 1,2-dichloroethane (DCE) and nitrobenzene (NB) solvents, unlike DCB. Thus, $\Delta G^{\omega\rightarrow\omega}_{tr}$ for DCE and $\Delta G^{\omega\rightarrow\omega}_{tr}$ for NB data were plotted in relation to $\Delta G^{\omega\rightarrow\omega}_{tr}$ of some reported data (Fig. S5). The average $\Delta G^{\omega\rightarrow\omega}_{tr}$ values for transfer from water to DCB for Cl$^-$, Br$^-$, CH$_3$COO$^-$ and SO$_4^{2-}$ were estimated to equal 63.05, 51.01, 53.47 and 139.41 kJ/mol, respectively. Subsequently, $\Delta \phi^0_{A^-}$ values were calculated from,

$$\Delta \phi^0_{A^-} = \frac{\Delta G^{\omega\rightarrow\omega}_{tr}}{zF}$$

Equation S2

**Figure S5.** Plots of the standard Gibbs energy of ion transfer ($\Delta G^{\omega\rightarrow\omega}_{tr}$) of various ions showing the linear correlations. Data were collected from several references$^{2,5,14,6–13}$ and the average value was plotted.
6. Facilitated phosphate ion transfer by \(N,N'-\text{di}(n\text{-butyl})\text{thiourea}\).
7. References


