

Supporting Information

for

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

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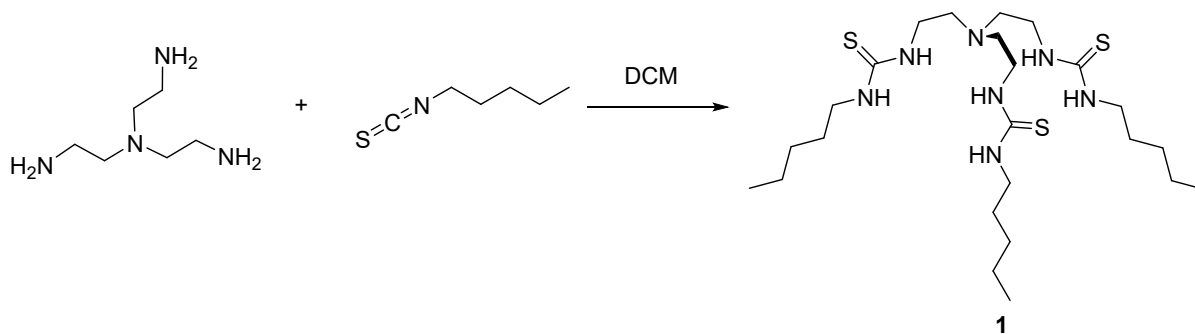
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1. Preparation of receptor **1**.

Receptor **1** was prepared by a method previously reported¹, 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 (SiO₂, 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 ¹H NMR data coincided with those previously reported. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 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).



2. Facilitated Cl^- transfer limited by concentration of receptor **1**.

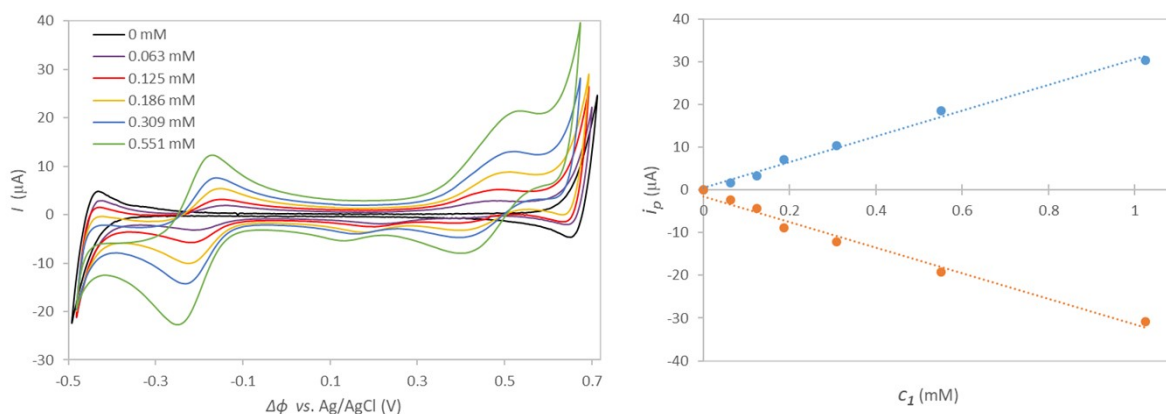


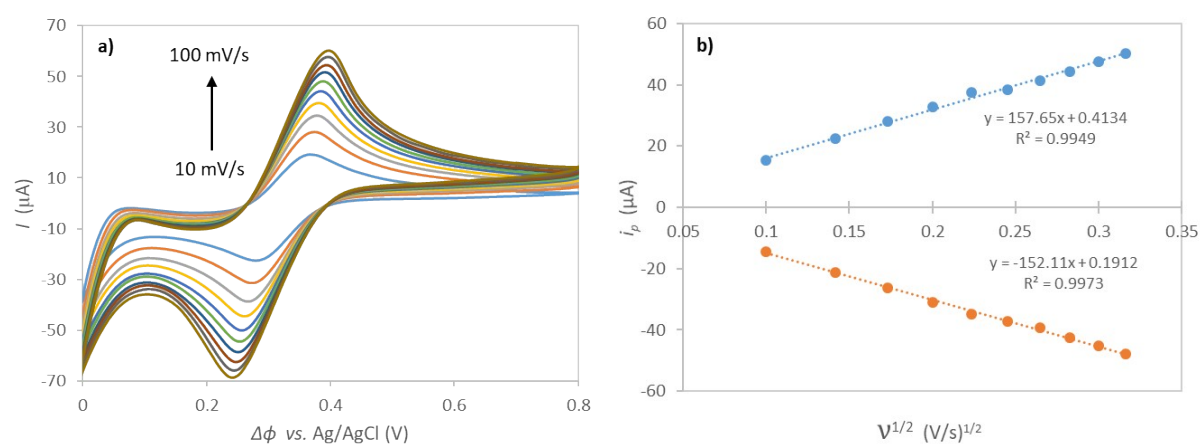
Figure S1. **Left**) CVs of Cell 1 in the presence of the electrolytes 20mM $\text{NaCl}_{(\text{aq})}$ | 10mM $\text{BTTPATFPB}_{(\text{DCB})}$ and various concentrations of receptor **1**_(DCB). CVs were calibrated in accordance with the formal transfer potential of TMA^+ at the water | DCB interface. **Right**) Plot of the peak current of Cl^- —**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,

$$i_p = 0.4463 \left(\frac{z^3 F^3}{RT} \right)^{1/2} A.C (D.v)^{1/2} \quad \text{Equation S1}$$

Where i_p is the peak current of the facilitated anion transfer, v 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 BTTPATFPB_(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 ($v^{1/2}$) for the forward and reverse peaks. Scan rates were from 10-100 mV/s (increments of 10 mV/s).

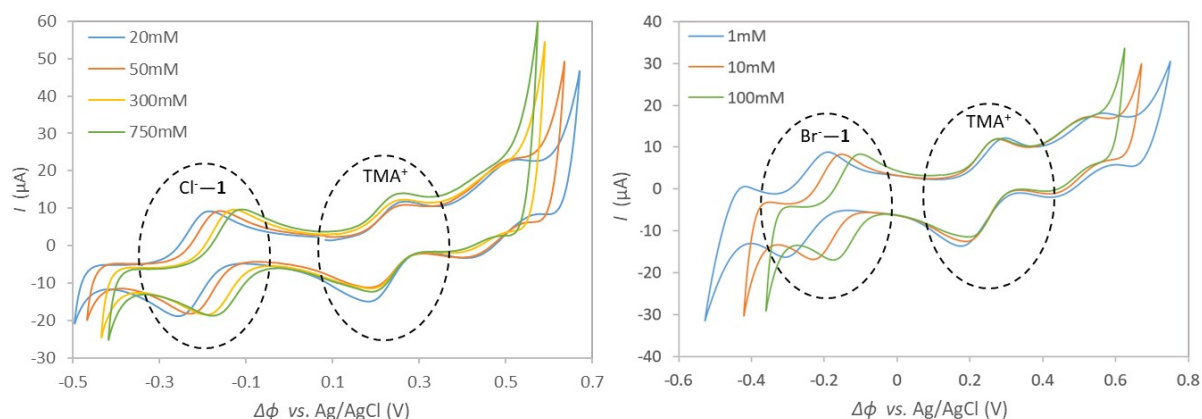
4. Stoichiometry and association constant (K_a).

For the stoichiometry and association constant determination, Equation 1 in the main text was used.

These calculations require $\Delta_o^w \phi_{A^-}^{\circ}$ of the anion at the studied aqueous|organic interface (see section 4 below), and $\Delta_o^w \phi^{1/2}$ 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⁺, $\Delta_o^w \phi_{TMA^+}^{\circ} = 0.226 V$)² 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 CH₃COO⁻ is shown in Figure S4.

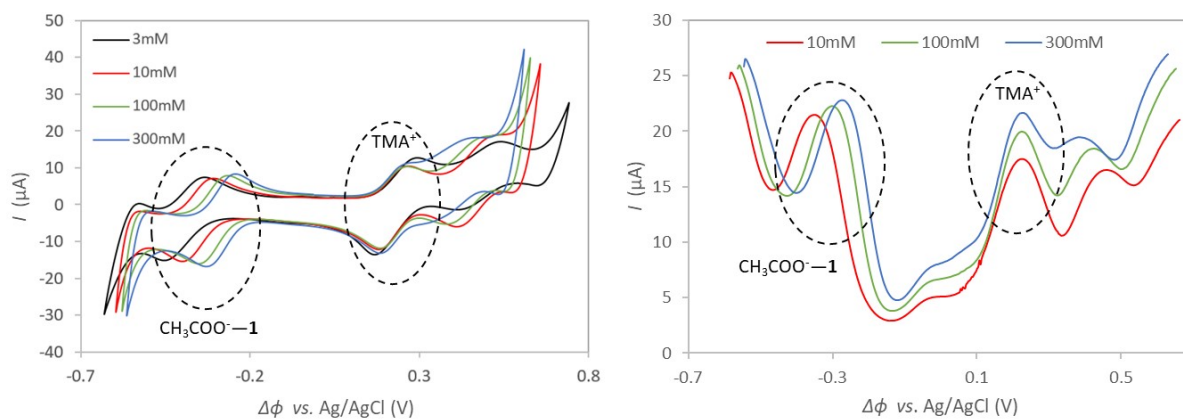


Figure S4. (Left) CVs of Cell 1 for $\text{CH}_3\text{COOLi}_{(\text{aq})}$ at various concentrations in the presence of 0.5mM receptor $\mathbf{1}_{(\text{DCB})}$ and the calibrator cation 0.2mM $\text{TMA}^+_{(\text{aq})}$. Scan rate = 10 mV/s. **(Right)** DPV curve of the cell at various concentrations. Scan rate = 50 mV/s.

5. Correlations of the standard Gibbs energy of ion transfer ($\Delta G_{tr}^{\ominus, w \rightarrow o}$).

Due to the lack of the data of the standard anion transfer potential ($\Delta_o^w \phi_{A^-}^{\ominus}$) from water to DCB for Br⁻, CH₃COO⁻ and SO₄²⁻, $\Delta_o^w \phi_{A^-}^{\ominus}$ data from other solvents were used to estimate the required data in DCB. That is, plots of the standard Gibbs energy of ion transfer ($\Delta G_{tr}^{\ominus, w \rightarrow o}$) from water to different solvents were found to provide linear correlations, allowing to estimate $\Delta G_{tr}^{\ominus, w \rightarrow o}$ of unknown data in one solvent relative to a known one of another solvent^{3,4}. $\Delta G_{tr}^{\ominus, w \rightarrow o}$ data are more widely reported for 1,2-dichloroethane (DCE) and nitrobenzene (NB) solvents, unlike DCB. Thus, $\Delta G_{tr}^{\ominus, w \rightarrow NB}$ and $\Delta G_{tr}^{\ominus, w \rightarrow DCE}$ data were plotted in relation to $\Delta G_{tr}^{\ominus, w \rightarrow DCB}$ of some reported data (Fig. S5). The average $\Delta G_{tr}^{\ominus, w \rightarrow DCB}$ values for transfer from water to DCB for Cl⁻, Br⁻, CH₃COO⁻ and SO₄²⁻ were estimated to equal 63.05, 51.01, 53.47 and 139.41 kJ/mol, respectively. Subsequently, $\Delta_o^w \phi_{A^-}^{\ominus}$ values were calculated from,

$$\Delta_o^w \phi_{A^-}^{\ominus} = \frac{\Delta G_{tr}^{\ominus, w \rightarrow o}}{zF} \quad \text{Equation S2}$$

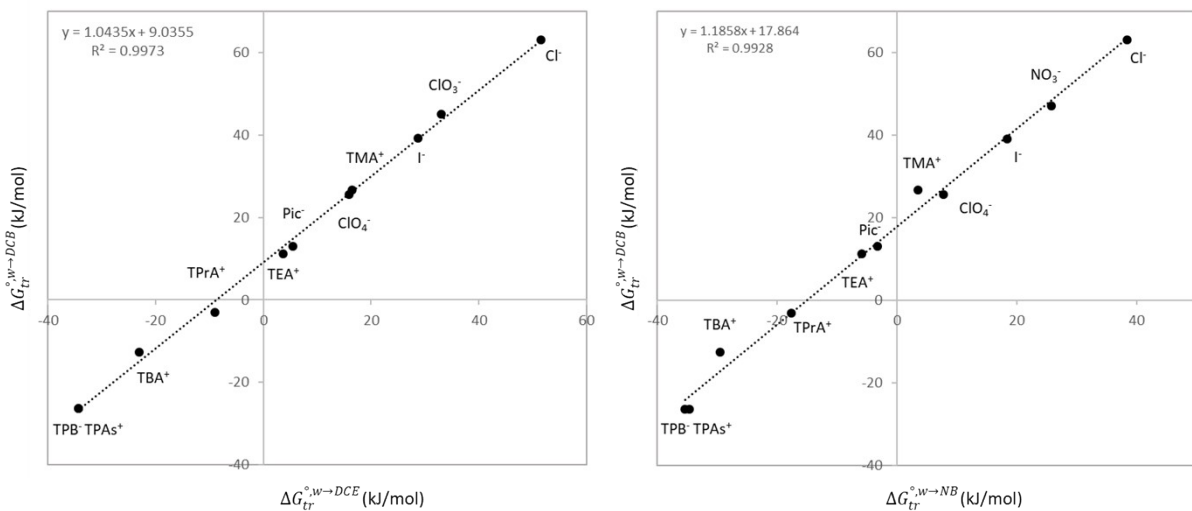


Figure S5. Plots of the standard Gibbs energy of ion transfer ($\Delta G_{tr}^{\ominus, w \rightarrow o}$) of various ions showing the linear correlations. Data were collected from several references^{2,5,14,6-13} and the average value was plotted.

6. Facilitated phosphate ion transfer by *N,N'*-di(*n*-butyl)thiourea.

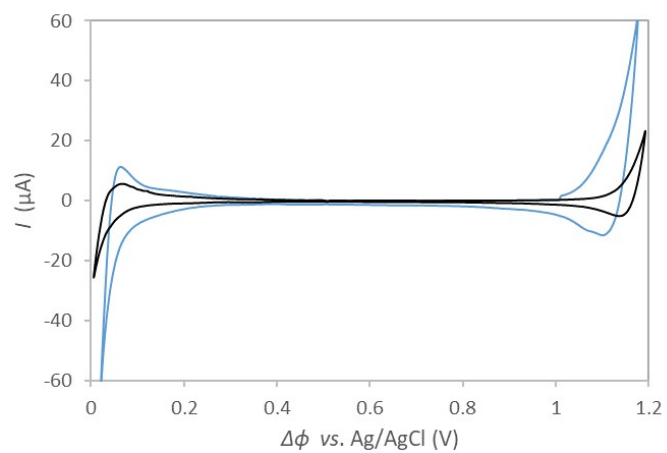


Figure S6. CVs of Cell 1 in the presence of only the supporting electrolytes 1M (pH 7) phosphate buffer_(aq) | 10mM BTPTATFPB_(DCB) (**black**) and after the addition of 1mM dibutylthiourea_(DCB) (**blue**). Scan rate = 50 mV/s. It can be seen that after the addition of the receptor, no interfacial reactions took place within the potential window, and only the current limits increased.

7. References

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