Supporting Information

Anion Transfer at a Micro-Water/1,2-Dichloroethane Interface Facilitated by β-Octafluoro-*meso*-octamethylcalix[4]pyrrole

Renfa Cui,[†] Qing Li,[†] Dustin E. Gross,[‡] Xin Meng,[†] Bo Li,[†] Manuel Marquez,[§] Ronghua Yang,[*†] Jonathan L. Sessler,[*‡] and Yuanhua Shao[*†]

[†]*College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China,* [‡]*Department of Chemistry and Biochemistry, Institute for Cellular and Molecular Biology, The University of Texas at Austin, Austin 78712,USA,* [§]*Harrington Department of Bioengineering, Arizona State University, Tempe, Arizona 85287, USA*

yhshao@ pku.edu.cn, yangrh@pku.edu.cn, sessler@mail.utexas.edu

Phone: +86-10-62759394
Fax: +86-10-62751708

Table of contents

I. Fabrication of micropipets

A Model P-2000 laser puller (Sutter Instruments) was used to fabricate micropipets with an orifice radius in the range of 2–25 μm from borosilicate glass capillaries (o.d./i.d., 1.0/0.58 mm); this was done by controlling the pulling parameters. The aqueous solution was filled from the back of the micropipet using a 10 μL syringe. The micropipette was inspected with an optical microscope (BX-51, Olympus) prior to each measurement; this inspection was also used to measure the orifice radius and to ensure there were no bubbles trapped inside.

II. Electrochemical cell and electrochemical measurements

The receptors employed in our study were *meso*-octamethylcalix[4]pyrrole **1** and its β-perfluorinated analogue **2** (see Figure 1A in the text). They were prepared and purified as described previously (Gale, P. A.; Sessler, J. L.; Král, V.; Lynch, V. *J. Am. Chem. Soc.* **1996**, *118*, 5140-5141 for **1**. Anzenbacher, P., Jr.; Try, A. C.; Miyaji, H.; Jurisíková, K.; Lynch, V. M.; Marquez, M.; Sessler, J. L. *J. Am. Chem. Soc*. **2000**, *122*, 10268-10272 for **2**).

Bis(triphenylphosphoranylidene)ammonium chloride (BTPPACl, 98%), potassium tetrakis(4-chlorophenyl)borate (KTPBCl, 98%) and tetramethyllammonium chloride (TMACl, 98%) were purchased from Fluka. Bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl) borate (BTPPATPBCl) was synthesized according to a published procedure (Li, F.; Chen,Y.; Zhang, M.; Jing, P.; Gao, Z.; Shao, Y. *J. Electroanal. Chem.* **2005**, *579*, 89-102) and used as the supporting electrolyte in the DCE phase. Tetramethylammonium tetrakis(4-chlorophenyl)borate (TMATPBCl) was synthesized via the metathesis of tetramethylammonium chloride and potassium tetrakis(4-chlorophenyl)borate, and was used as the inner reference salt in the DCE phase. Sodium chloride (NaCl, AR), sodium bromide (NaBr, AR), sodium nitrite ($NaNO_2$，AR), and sodium acetate (CH_3CO_2Na, AR) were purchased from Beijing Chemicals Co. Normal precautions were taken when

dealing with DCE and other hazardous chemicals.

Voltammetric experiments involving the micropipettes were carried out in a two-electrode system inside a Faraday cage. An Ag wire (0.125 mm in diameter) coated with AgCl was inserted into the aqueous phase inside the micropipet and used as the aqueous reference electrode. Another Ag wire coated with AgTPBCl was immersed in the outside organic phase and used as the organic reference electrode. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a computer-controlled BAS 100 B (Bioanalytical Systems) electrochemical workstation. All experiments were carried out at room temperature (22 ± 2 °C).

III. Evaluation of the association constants $\log \beta^{o}_{AR^-}$ corresponding to the interaction between various test anions and receptors 1 and 2

We have tested the receptor 1 for FAT. It is clear that no FATs can be observed within the potential window when using receptor 1 (see Figure S1). This may be because the association constants between receptor 1 and anions are not big enough to facilitate anion transfers to an observable potential within the potential window. As noted earlier (Levitskaia, T. G.; Marquez, M.; Sessler, J. L.; Shriver, J. A.; Vercouter, T.; Moyer, B. A. *Chem. Commun*. **2003**, 2248-2249), a 1:1 complex between **2** and various anions can be formed under interfacial conditions. For a facilitated anion transfer process involving a similar stoichiometric receptor-ion ratio (i.e., 1:1), the relationship between the concentration of an anion C_{A^-} and the half wave potential of the facilitated anion transfer $E^{1/2}_{AR^-}$ is expected to obey the following equation, S1, provided that $C_{A^-} >> C_2$ (Matsuda, H.; Yamada, Y.; Kanamori, K.; Kudo, Y.; Takeda, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1497-1508):

$$E^{1/2}_{AR^-} = \Delta^{w}_{o}\phi^{0'}_{A^-} - \frac{RT}{2F}\ln\frac{D_R}{D_{AR^-}} + \frac{RT}{F}\ln\beta^{o}_{AR^-}C_{A^-} \qquad \text{S1}$$

where $\Delta^{w}_{o}\phi^{0'}_{A^-}$ refers to the formal potential of transfer of the anion. D_R and D_{AR^-} are the diffusion coefficients of **2** and the complex AR^- formed by the interaction between **2** and the targeted anion in the DCE phase, respectively. In the present instance, D_R is expected to be almost equal to D_{AR^-} due to the fact that receptor **2** is relatively large compared to the size of the anions in question.

In order to evaluate the half-wave potential of the facilitated anion transfer ($E^{1/2}_{AR^-}$) on the TATB (tetraphenylarsonium tetraphenylborate) scale, TMA^+ was used as an internal reference ion in the DCE phase in Cell 1 and differential pulse voltammetry (DPV) was employed (Figure **S2**). The following equation was used to determine the formal potential of the facilitated anion transfer $E^{1/2}_{AR^-}$

$$E^{1/2}_{AR^-} - E^{1/2}_{TMA^+} = \Delta^{w}_{o}\phi^{o'}_{AR^-} - \Delta^{w}_{o}\phi^{o'}_{TMA^+} \qquad \text{S2}$$

where $E^{1/2}_{TMA^+}$ is the experimental half-wave potential of TMA^+. The value of $E^{1/2}_{AR^-} - E^{1/2}_{TMA^+}$ is equal to the difference between the respective potential peak value of AR^- and TMA^+ in the DPV curve (see Figure S2). $\Delta^{w}_{o}\varphi^{o'}_{TMA^+}$ is equal to 160 mV at the W/DCE interface (cf. Samec, Z. *Pure Appl. Chem.* **2004**, *76*, 2147-2180).

Based on equation S1, the association constant and the stoichiometric ratio between anions and **2** can be calculated. By varying the concentrations of anions (y = 40, 100, 200, 500, 1000, respectively), while fixing x = 2, a series of $E^{1/2}_{AR^-}$ values was obtained. Plotting $E^{1/2}_{AR^-}$ versus log C_{A^-} gave rise to four linear relationships for the respective four anions (see Figure S3). From the slopes (54.6, 52.2, 68.8, 66.0 for Cl^-, Br^-, NO_2^-, $CH_3CO_2^-$, respectively, which are close to the theoretical value of 59 mV/dec for monovalent ions), it was concluded that the stoichiometric ratio between the anion and **2** is 1:1. From the intercepts, the

association constants ($\log \beta^{o}_{AR^-}$) corresponding to the interaction between the anion in question

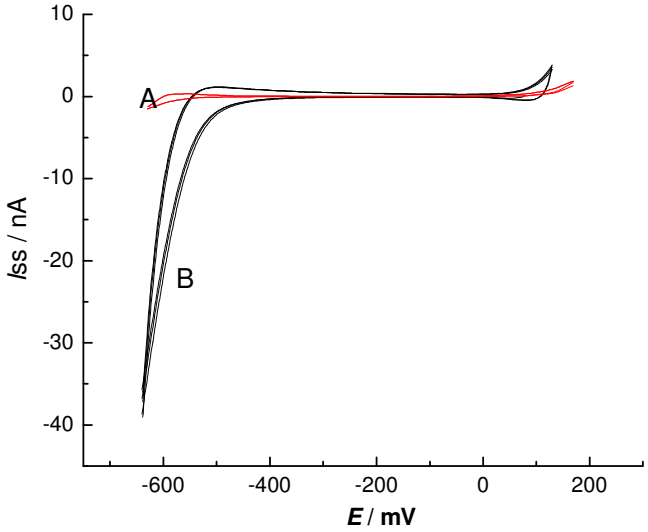

Figure S1 The potential windows in the presence of **1** (B) and without **1** or **2** (A) with Cell 1 (shown in the main text), in which A = Cl^-, x = 2, y = 100, r =20 μm. The scan rate is 50 mV/s.

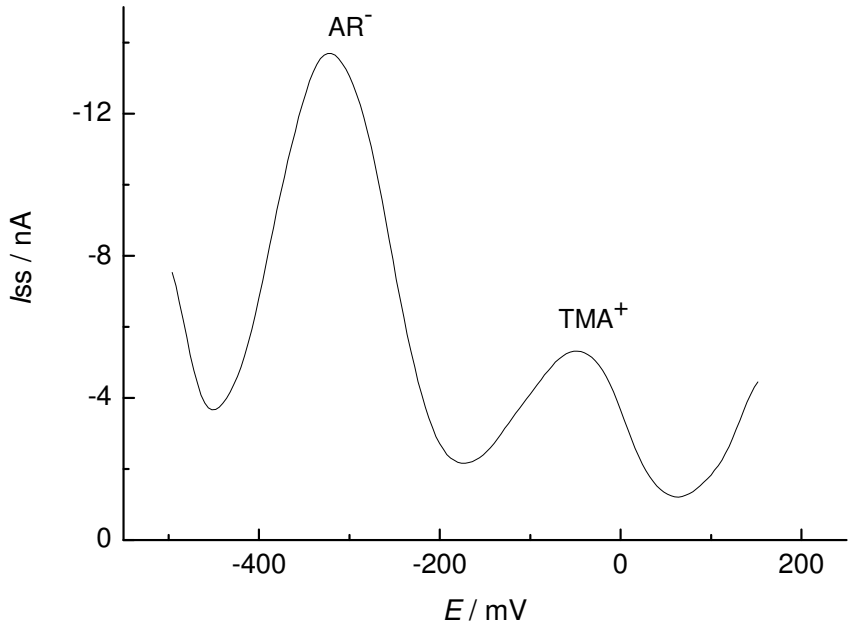

Figure S2 DPV curve of Cl^- transfer across the μ-W/DCE interface facilitated by **2** using Cell 1 with TMATPBCl added in the DCE phase up to a concentration of 0.2 mM, and where x = 2, y = 100. The scan rate is 50 mV/s and r is 20 μm.

and **2** were calculated as 8.26, 6.52, 3.28, 5.77 for Cl^-, Br^-, NO_2^-, $CH_3CO_2^-$, respectively.

These results are summarized in Table 1 in the text.

Due to the specific geometry of the micropipet, the diffusion field for an ion transfer from outside to the inside of the pipette is hemispherical, whereas that from the inside to the outside is linear. This is expected to result in an asymmetric cyclic voltammogram. However, it is clear that the voltammograms in Figure 1B in the text for the facilitated transfer of the four anions in question are all steady-state voltammograms. Thus, the mechanism of their FATs can be verified to be a Transfer by Interfacial Complexation (TIC) and Transfer by Interfacial Dissociation (TID) using published methods (Shao, Y. H.; Osborne, M. D.; Girault, H. H. *J. Electroanal. Chem.* **1991**, *318*, 101-109).

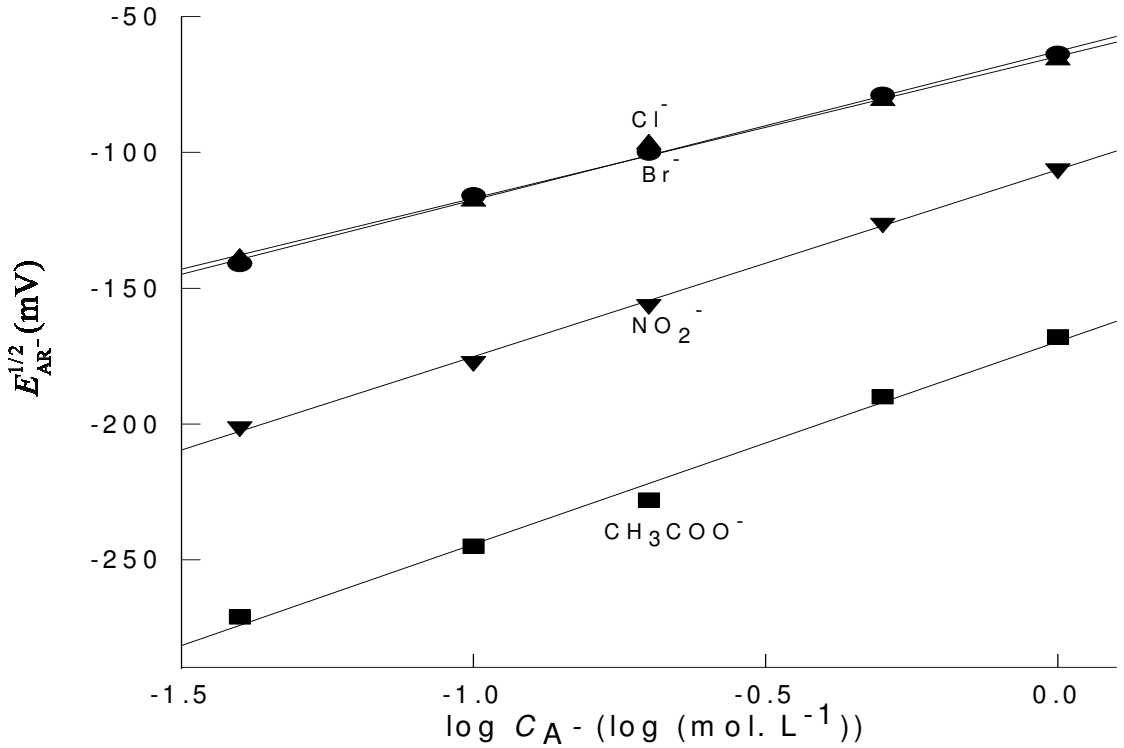

Figure S3 Dependence of the experimental half-wave potentials of the proposed facilitated anions transfer ($E^{1/2}_{AR^-}$) on the logarithm of concentration of anion (log C_A^-) using Cell 1, where x = 2, y = 40, 100, 200, 500, 1000, respectively. The scan rate is 50 mV/s and r = 10-25 μm.

IV. Evaluation of the diffusion coefficient D_R of receptor 2 in the DCE phase

If the outer wall of the micropipet is not silanized, the relationship between the limiting current *Iss* and the concentration of **2**, when $C_A^- >> C_2$, can be expressed in terms of the following equation, S3 (Beattie，P. D.; Delay A.; Girault, H. H. *J.Electroanal.Chem.* **1995**, *380*, 167-175):

$$Iss = 3.35\pi nFDcr \qquad \text{S3}$$

where *n* is the charge number, *F* is the Faraday constant, *c* is the bulk concentration of **2** in the DCE phase, and *r* is the radius of the micropipet.

Figure S4 shows the cyclic voltammograms for facilitated Cl^- transfer effected using Cell 1 and **2** as the receptor. The half-wave potentials ($E^{1/2}_{AR^-}$) were found to be insensitive to differences in the concentration of **2**. Such a finding provides further support for the conclusion that the stoichiometric ratio between Cl^- and **2** is 1:1. The inset to Figure S3 shows the dependence of the steady-state current on the concentration of **2** in the DCE phase. From the slope of this line, the diffusion coefficient of **2** in the DCE phase could be obtained. Analogous analyses were carried out for the other anions, giving rise to values for the diffusion coefficient, *D*, for **2** in the DCE phase of 4.2×10^{-6}, 3.6×10^{-6}, 3.2×10^{-6}, 3.0×10^{-6} cm^2/s for Cl^-, Br^-, NO_2^-, $CH_3CO_2^-$, respectively. The mean value is $(3.5 \pm 0.5) \times 10^{-6}$ cm^2/s. These findings are summarized in Table 1 in the text.

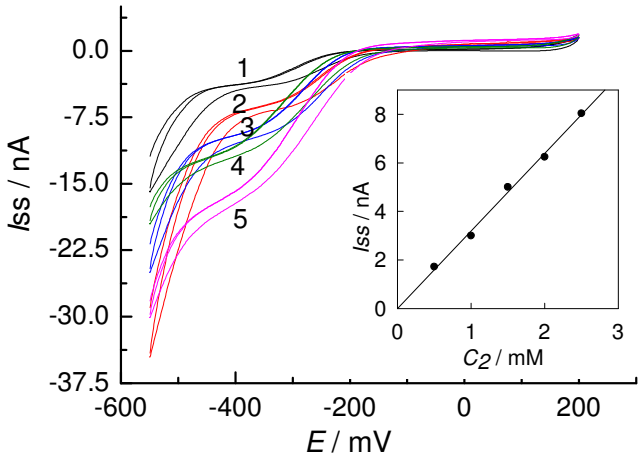

Figure S4 Cyclic voltammograms corresponding to the facilitated transfer of Cl^- anion effected using different concentrations of **2** in Cell 1, where x = 0.5, 1.0, 1.5, 2.0, 2.5, respectively, and y = 1000. The inset shows the linear line obtained from a plot of *Iss* vs. C_R. The scan rate is 50 mV/s and r = 20 μm.

V. Measurements of kinetic parameters

From Figure 1B in the text, we can see that the steady-state voltammograms are rather close to the negative side of the potential window. Therefore, it is hard to analyze them and evaluate kinetic data. Based on equation S1, the half-wave potential will be shifted to more positive potential as the concentration of the anion increases. Using Cell 1 as described in the text (where x = 2, y = 5000 and the scan rate is 50 mV/s), the kinetic parameters for the FAT of Cl^- and Ac^- at the μ-W/DCE interface by **2** have been evaluated and listed in Table T1. They are 1-2 orders smaller than those obtained for cations using crown ether as the receptor. For the rest of the anions, it is hard to get useful kinetic information by this way because no reasonable steady-state voltammograms could be obtained.

Table T1. Kinetic Parameters for the FAT of Cl^- and Ac^- at the μ-W/DCE Interface by **2**.

	r /μm	$\lvert\Delta E_{1/4}\rvert$ /mV	$\lvert\Delta E_{3/4}\rvert$ /mV	a	K^0 ($\times10^{-2}$/ cm s^{-1})
Cl^-	4	30.8	32.3	0.55	3.40
	7	31.2	32.4	0.61	1.21
	9	30.7	31.5	0.71	1.04
	5	32.1	34.4	0.52	1.76
	4	31.2	33.6	0.51	2.95
	2	33.0	36.0	0.52	2.64
	0.6[a]	44.0	46.0	0.59	1.75
mean				0.57±0.07	2.11±0.90
CH_3COO^-	8	32.9	34.5	0.62	0.52
	4	33.3	35.8	0.56	1.41
	5	31.4	32.8	0.65	1.39
	10	34.6	36.0	0.67	0.28
	13	33.0	35.5	0.57	0.47
	0.9[a]	44.0	45.0	0.61	0.70
	2	39.0	40.0	0.67	0.49
mean				0.62±0.04	0.75±0.50

[a] when the r is less than 1 μm, we used the following conditions to obtain steady-state voltammograms: x = 10, y = 5000 for Cell 1 as described in the main text.

It is also interesting to comparing the cyclic voltammograms of FCT of potassium by DB18C6 (diphenyl 18-crown-6) with that of FAT of chloride by receptor **2** (see Figure S5,

curves A and B) (they are included here together for comparison, but do not necessarily have the correct potentials) using the following cells S1 and S2:

Ag|AgTPBCl | x mM R + 2 mM BTPPATPBCl (DCE) || y mM NaA (W) | AgCl|Ag Cell S1

Ag|AgTPBCl | x mM DB18C6 + 2 mM BTPPATPBCl (DCE) || y mM KCl (W) | AgCl|Ag Cell S2

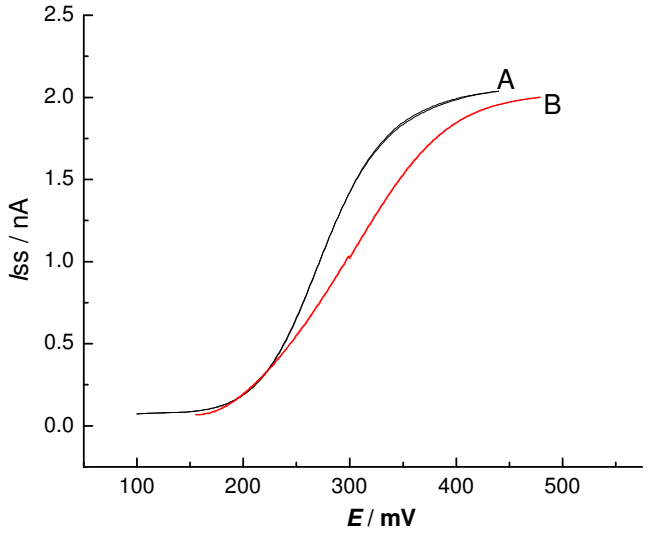

Figure S5 A comparison of the steady state voltammograms obtained for K^+ facilitated by DBC18C6 and Cl^- by receptor **2**; A: CV curve of K^+ facilitated by DB18C6 using Cell 2 with x = 2, y = 100, r =2 μm ; B: CV curve of Cl^- facilitated by receptor **2** using Cell 1 with x = 4, y = 5000, r = 2 μm. In both cases, the scan rate is 50 mV/s.

From curve A of this figure, we can obtain the values of $|\Delta E_{1/4}=E_{1/2}-E_{1/4}|$ and $|\Delta E_{3/4}=E_{3/4}-E_{1/2}|$ are 30.2 and 29.6 mV, which are less than 30.5 and 31 mV. This means that the CV A shows a reversible process, and we cannot calculate the k^0 value from data obtained using a micro-sized pipet. In order to evaluate the k^0 value, we have to use smaller size of pipet, for example, a nanopipet. This is what we usually do for the case of facilitated cation transfer. In the case of CV B in the Figure, we are dealing with the facilitated transfer of chloride by receptor 2. Obviously, a quick comparison with CV A confirms that we are not looking at a truly reversible process; therefore we can evaluate the kinetic rate constant (k^0) associated with this process by using a micropipet (i.e., cell S1). The values of $|\Delta E_{1/4}=E_{1/2}-E_{1/4}|$ and $|\Delta E_{3/4}=E_{3/4}-E_{1/2}|$ are 32.5 and 34 mV, which are bigger than 30.5 and 31 mV. Usually, it is

much easily to handle a micropipet than a nanopipet. Thus, we are gratified that we could evaluate the k^0 value in our studies using micropipets. This comparison further confirms that our conclusion in the text is correct, that is, the FATs of anions are slower than that of FCT of alkali metal ion.

In order to simplify the comparison, we used the concentration in Cell S1 is 4 mM. which is different from that shown in Table T1. This is because of the different of diffusion coefficient of DB18C6 (5.2 x 10^{-6} cm^2/s) (see Shao, Y.; Mirkin, M.V. *J.Am.Chem.Soc*., **1997**, *119*, 8103-8104) with receptor **2**.