Electronic Supplementary Material (ESI) for Analyst.

# Electronic Supplementary Information for: Detection of *Pseudomonas aeruginosa* quorum sensing molecules at an electrified liquid|liquid micro-interface through facilitated proton transfer.

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## 1. Determination of microchannel radius

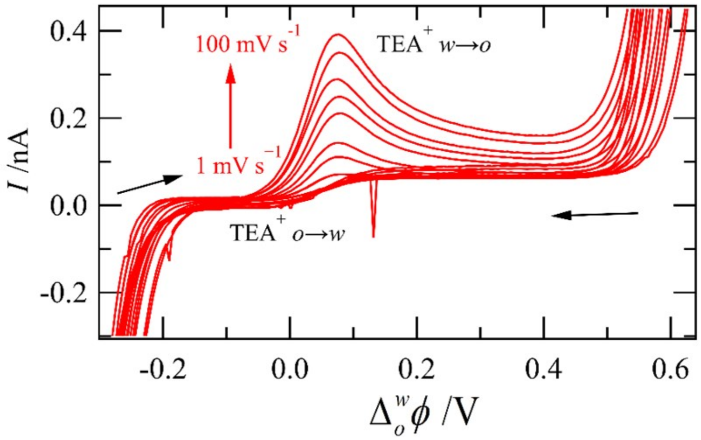

**Figure S1:** Cyclic voltammograms obtained using Cell S1 and varying the scan rate from 1-100 mV s$^{-1}$.

$$\mathrm{Ag}\Bigg|\mathrm{AgCl}\Bigg|\begin{array}{c}0.3\text{ mM TEACl}\\ 10\text{ mM LiCl}\\ (aq)\end{array}\Bigg\|\begin{array}{c}5\text{ mM BATB}\\ (DCE)\end{array}\Bigg|\begin{array}{c}\text{Sat. BACl}\\ 10\text{ mM LiCl}\\ (aq\sim ref.)\end{array}\Bigg|\mathrm{AgCl}\Bigg|\mathrm{Ag}\qquad[\text{Cell S1}]$$

$$\mathrm{Ag}\Bigg|\mathrm{AgCl}\Bigg|\begin{array}{c}0.3\text{ mM NaOBSA}\\ 10\text{ mM LiCl}\\ (aq)\end{array}\Bigg\|\begin{array}{c}5\text{ mM BATB}\\ (DCE)\end{array}\Bigg|\begin{array}{c}\text{Sat. BACl}\\ 10\text{ mM LiCl}\\ (aq\sim ref.)\end{array}\Bigg|\mathrm{AgCl}\Bigg|\mathrm{Ag}\qquad[\text{Cell S2}]$$

Figure S1 shows the CVs generated using Cell S1 and by scanning the potential between roughly –0.35 and 0.55 V. During the forward scan (from low to high potentials) a peak-shaped wave was observed with a half-wave potential at 0.049 V.[1] Meanwhile, a steady state or s-shaped wave was observe when scanning from 0.55 V to –0.35 V. Owing to the asymmetric geometry of the capillary, this leads to linear diffusion of ions leaving the pipette (crossing the interface from w→o, egress) and hemispherical diffusion of ions entering the pipette (crossing the interface from o→w, ingress). Therefore, the peak-shaped wave is the transfer of TEA$^+$ from w→o, while the sigmoidal wave is the ingress of TEA$^+$ from o→w.

The radius of the microchannel formed at the tip of the pulled borosilicate glass capillary was confirmed using cyclic voltammetric (CV) measurements of the peak-shaped ion transfer wave of tetraethylammonium (TEA$^+$) from w→o by varying the scan rate $(v)$ as shown in Figure S1 and comparing the change in peak current intensity $(i_p)$ in amperes to the Randles-Sevcik equation[2] below,

$$i_p = 0.4463\left(\frac{F^3}{RT}\right)^{\frac{1}{2}} n^{3/2} A D_{i,\alpha}^{1/2} c_{i,\alpha}^{*} v^{1/2} \qquad [\text{S1}]$$

where $A$, $F$, $R$, $T$, and $n$ are the interfacial surface area, Faraday's constant (96485.33 C mol$^{-1}$), Universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), absolute temperature (298.15 K), and the charge on the ion transferred (+1), respectively. $D_{i,\alpha}$ and $c^{*}_{i,\alpha}$ are the diffusion coefficient and initial/bulk concentration of species $i$ in phase $\alpha$. The diffusion coefficient of TEA$^{+}$ in water was taken to be $9.8\times10^{-6}$ cm$^{2}$ s$^{-1}$.[3] $i_p$ was plotted against $v^{1/2}$ in Figure S2. Using the slope obtained from linear regression analysis in Figure S2 (dashed line), the radius of the microchannel was calculated to be ~11.9 µm which is within experimental error of the commercially obtained 12.5 µm radius Pt wire used to form the microchannel.

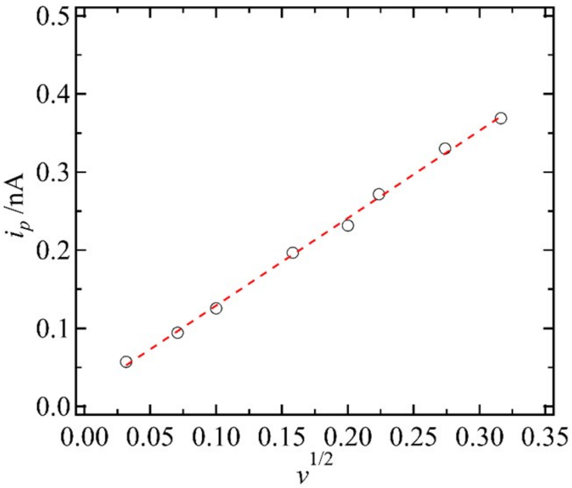

**Figure S2:** Plot of $i_p$ versus $v^{1/2}$ from Figure S1. Dashed, red curve is the product of linear regression analysis with an R$^2$ value of 0.998.

## 2. Asymmetric Diffusion Regime

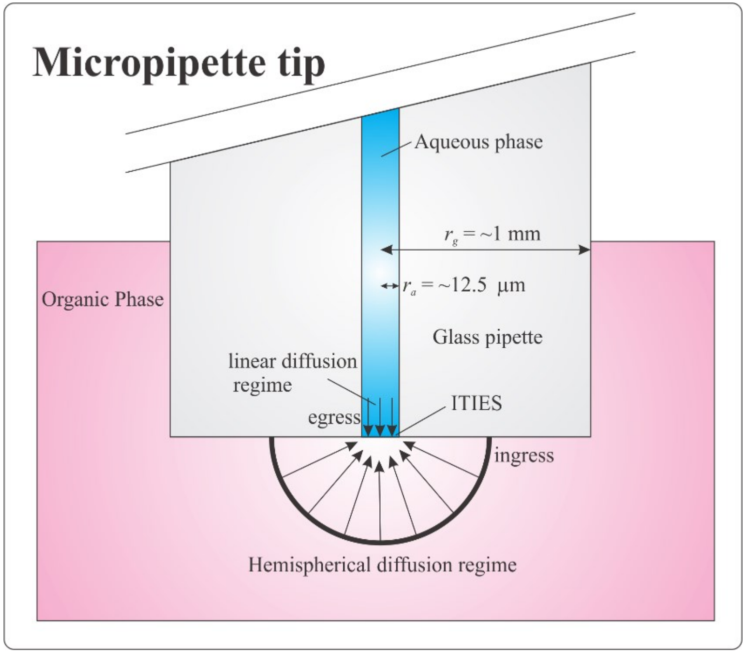

**Figure S3:** Schematic of the asymmetric diffusion regimes for egress and ingress of material across the ITIES held at the tip of a micropipette with external glass radius ($r_g$) and an internal microchannel radius ($r_a$) as indicated.

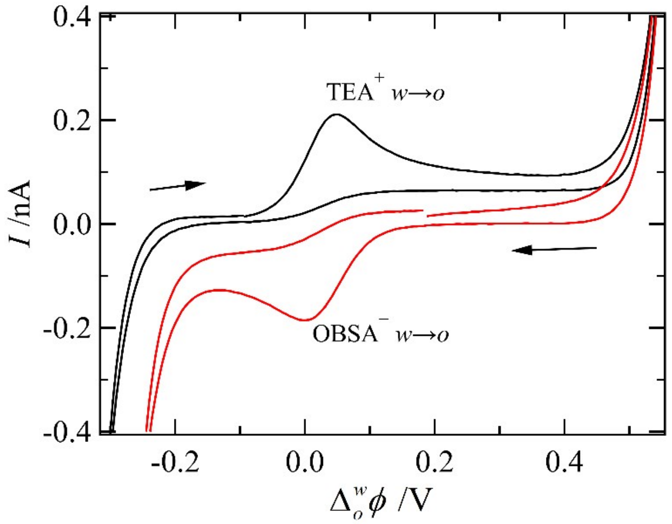

**Figure S4:** CVs recorded using Cell S1 and S2 with a scan rate of 25 and 50 mV s$^{-1}$ for the black and red trace demonstrating the TEA$^{+}$ (tetraethylammonium) and OBSA$^{-}$ (4-octylbenzenesulfonate) asymmetric ion transfer peak current responses, respectively, based on charge and the pipette geometry as shown in Figure S3.

## 3. Investigation of proton sources on ligand complexation

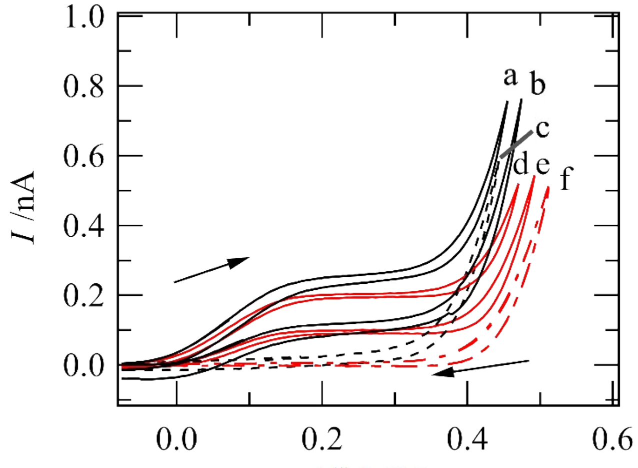

**Figure S5:** CVs using Cells 1 (curves d, e, f) and 2 (curves a, b, c) with the pH adjusted to 3.5 using HCl and citric acid, respectively, and $L$ = HHQ at 25 (b and e) and 50 µM (a and d). Curves c and f were recorded without HHQ in the DCE phase (blank curves). All other experimental parameters are the same as in Figure 1 of the main text.

## 4. Cyclic voltammetric response moving from [H$^+$] ≫ [ligand] to the [H$^+$] ≈ [ligand] regime

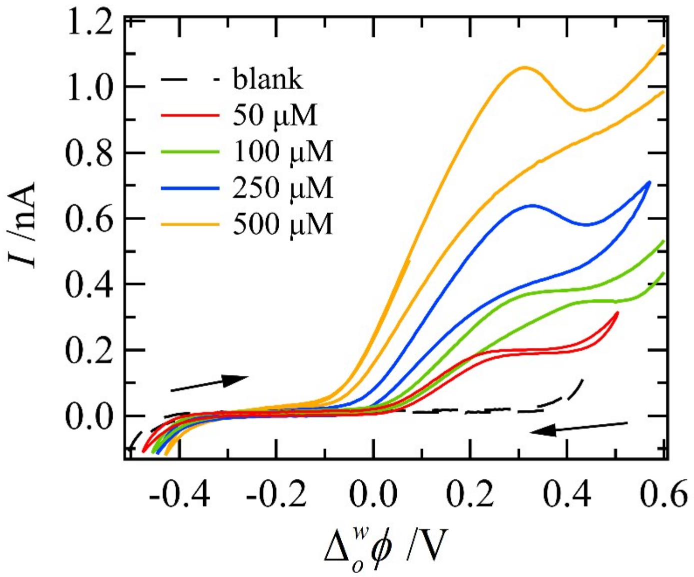

**Figure S6:** CVs recorded using Cell 1 with $L$ = HHQ and [HHQ] varied from 0-500 µM as indicated inset with a scan rate of 25 mV s$^{-1}$.

## 5. Linear regression error analysis

The upper and lower associated error with the *line-of-best-fit* (LOBF) was determined using a method described in Skoog *et al.*[4] where the standard deviation $(s_c)$ about the LOBF is defined as,

$$s_c = s_r\sqrt{\frac{1}{N}+\frac{N(x-\bar{x})^2}{N\sum x^2-\left(\sum x\right)^2}}$$

where $s_r$ is the standard error from linear regression statistics and the upper and lower error bounds are,

Upper LOBF+ = $y = mx + b + ts_c$
Lower LOBF– = $y = mx + b - ts_c$

In this case, $t$ is students $t$ value taken from standard tables using a 99.8% confidence interval and *degrees-of-freedom* as defined as N–2, where N is the population or number of data points used to construct the curve.

## References

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2. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley, New York, 2nd edn., 2001.
3. J. Strutwolf, M. D. Scanlon and D. W. M. Arrigan, *Analyst*, 2009, **134**, 148-158.
4. D. A. Skoog, *Principles of instrumental analysis*, Fourth edition. Fort Worth : Saunders College Pub., [1992] ©1992, 1992.