Supporting Information

Proton Coupled Oxygen Reduction

at Liquid-Liquid Interfaces Catalyzed by Cobalt Porphine

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1. Synthesis and Characterization of Cobalt Porphine

1.1. Instrumentation. $^1$H NMR spectra were recorded on a Bruker DRX-500 AVANCE transform spectrometer at the “Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne (PACSMUB)”; chemical shifts are expressed in ppm relative to chloroform (7.258 ppm). UV-visible spectra were recorded on a Varian Cary 1 spectrophotometer. Mass spectra were obtained on a Bruker Daltonics Ultraflex II spectrometer at the PACSMUB in the MALDI/TOF reflectron mode using dithranol as a matrix. Accurate mass measurements (HR-MS) were carried out in the same conditions as previously using PEG ion series as internal calibrant.

1.2. Chemicals and Reagents. Silica gel (Merck; 70-120 mm) was used for column chromatography. Analytical thin layer chromatography was performed using Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by mass spectrometry, thin-layer chromatography and UV-visible spectroscopy.

1.3. Synthesis

Scheme S-1.

The cobalt porphine was prepared by transmetallation of the magnesium complex. The magnesium porphine was prepared as recently described in the literature.$^{[s1]}$ Magnesium porphine (80 mg, 0.241 mmole) was dissolved under argon in 10 ml of benzonitrile in the
presence of 5 equivalents of cobalt acetate tetrahydrate and 2.5 equivalents of sodium acetate. The resulting solution was then heated at 140°C for 2 h 30, the transmetallation being monitored by MALDI/TOF mass spectrometry. At the end of the reaction, the solvent was removed under vacuum and the crude product was dissolved in dichloromethane (50 ml) and washed three times with water (3 x 200 ml) then dried over MgSO\(_4\). The solvent was removed in vacuo and the residue was purified on a silica plug (CH\(_2\)Cl\(_2\) as eluent). The cobalt porphine was isolated in 36% yield (32 mg, 0.087 mmol).

The spectroscopic data of the cobalt porphine are in agreement with the literature values. \(^{[a2-s4]}\)MS (MALDI-TOF): \(m/z = 367.67\) [M]\(^+\); 367.27 calcd. for C\(_{20}\)H\(_{12}\)N\(_4\)Co. HR-MS (MALDI-TOF): \(m/z = 367.0370\) [M]\(^+\); 367.0394 calcd. for C\(_{20}\)H\(_{12}\)N\(_4\)Co. UV-visible (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}\) nm \((\varepsilon, \%) = 386\) (100), 507 (4.4), 537 (4.4).

2. **Calculation of the Galvani Potential Difference across the Liquid-Liquid Interface**

As shown in the paper, two-phase reactions were performed, where the Galvani potential difference across the liquid-liquid interface was controlled by the distribution of all of ions between two phases. In order to calculate this potential, we first considered the Nernst equation for the different ionic species \(i\) present in the system:

\[
\Delta_w^w \phi = \Delta_w^w \phi_{\text{dil}}^{w \rightarrow o} - \frac{RT}{z_i F} \ln \frac{c_i^o}{c_i^w}
\] (SI 1)

At the same time, the mass balance for the different species was considered:

\[
\frac{V_o}{V_w} c_{i, \text{ initial}}^o + c_{i, \text{ initial}}^w = \frac{V_o}{V_w} c_i^o + c_i^w
\] (SI 2)
where $c_{i,\text{initial}}^o$ and $c_{i,\text{initial}}^w$ stand for the concentrations of $i$ initially added in the organic and aqueous phases, respectively. The concentrations at the equilibrium are denoted as $c_i^o$ and $c_i^w$. In our particular case, the volume ratio between the organic and the aqueous phase ($V_o/V_w$) was always unitary, ergo it will be no further considered. On the other hand, the calculations are always performed assuming equilibrium conditions; therefore the mass balance equilibrium concentrations correspond to those involved in the Nernst equation for the ion transfer process. Additionally, the electroneutrality condition must be fulfilled and reads:

$$\sum_i z_i c_i^w = 0 \quad (\text{SI 3})$$

which after being combined with eqs. (SI 1) and (SI 2) finally yields

$$\sum_i z_i \frac{c_i^{\text{total}}}{1 + \exp\left[\frac{F}{RT} \left(\Delta_i^w \phi - \Delta_i^w \phi_{\text{tr},i}^{o\rightarrow w}\right)\right]} = 0 \quad (\text{SI 4})$$

Thus, after solving eq. (SI 4), the potential drop across the interface can be obtained. Nonetheless, prior knowledge of the standard ion transfer potential is required for all the ionic species. Taking this into account, the formal standard ion transfer potentials of BA$^+$ was assumed to be 60 mV more negative that of Cl$. Analogously, this value for TB$^-$ was taken as 60 mV more positive than that of Li$^+$. This assumption is quite reasonable since it is found experimentally in routinary cyclic voltammograms that the potential window is limited by the transfer of Li$^+$ and Cl$^-$ in its positive and negative edges, respectively. Finally, from the potential value obtained, the concentrations for all the ions in both phases were calculated after applying eqs. (SI 1) and (SI 2), as shown in Tables 1, 2 and 3.
3. Compared Two-Phase Reactions: TMA$^+$ versus TB$^-$ as common ions

![Graph showing UV-visible spectra](image)

**Figure S-1.** (a) Two-phase reaction controlled by TMA$^+$ (flask 1) and TB$^-$ (flask 2) partition after instant mixing. The top aqueous phase contained 5 mM TMACl/LiTBB + 10 mM HCl + 1 M H$_2$O$_2$ and the bottom DCE phase contained 5 mM TMATB/BATB + 5 mM Fc, as illustrated by the cartoon under the figure; (b) UV-visible spectra of the DCE phases separated from flask 1 (black) and flask 2 (red).
4. Heterogeneous reaction between Fc in DCE and H$_2$O$_2$ in Water

In order to know whether Fc located in DCE reacts heterogeneously with H$_2$O$_2$ in the acidic water, cyclic voltammetry measurements were performed with the electrochemical cell illustrated in Scheme S-2. The results in Figure S-2 show no difference in the absence and presence of H$_2$O$_2$ in water, proving that in the available potential window no heterogeneous reaction between Fc and H$_2$O$_2$.

Scheme S-2.

![Scheme S-2](image)

Figure S-2. Cyclic voltammetry at a water-DCE interface with the electrochemical cell illustrated in Scheme S-1 in the absence (black) and presence (red) of H$_2$O$_2$. Scan rate 50 mV s$^{-1}$. 
5. Standard redox potentials of oxygen reduction reactions in the organic phase

The calculation of the standard redox potential in the organic phase can be regarded in general as follows:

$$\text{O}_\alpha (\alpha) + e^- \rightarrow \text{R}_\alpha (\alpha) \quad \left[ E^{\alpha}_\text{SHE} \right]$$ (SI 5)

where the specie O is reduced to R, both present in the phase \(\alpha\). Thus, the formal standard redox potential for this system can be expressed as:

$$E^{\alpha}_\text{O \rightarrow R} \text{SHE} = \frac{1}{nF} \left[ (\mu^{\alpha}_\text{O} + 2\mu^{\alpha}_\text{H}^+ - \mu^{\alpha}_\text{H}_2\text{O}) - 2\left( \mu^{\alpha}_\text{H}^+ - \frac{1}{2} \mu^{\alpha}_\text{H}_2\text{O} \right) \right]$$ (SI 6)

In the particular case of two-electron oxygen reduction, we have:

$$\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \quad \left[ E^{\alpha}_\text{O}_2/\text{H}_2\text{O}_2 \text{SHE} \right] = 0.695 \text{ V}$$ (SI 7)

Furthermore, the standard redox potential in the organic phase can be interpreted as:

$$E^{\alpha}_\text{O}_2/\text{H}_2\text{O}_2 \text{SHE} = \frac{1}{2F} \left[ (\mu^{\alpha}_\text{O}_2 + 2\mu^{\alpha}_\text{H}^+ - \mu^{\alpha}_\text{H}_2\text{O}_2) - 2\left( \mu^{\alpha}_\text{H}^+ - \frac{1}{2} \mu^{\alpha}_\text{H}_2\text{O}_2 \right) \right]$$ (SI 8)

and that in water as:

$$E^{\alpha}_\text{O}_2/\text{H}_2\text{O}_2 \text{SHE} = \frac{1}{2F} \left[ (\mu^{\alpha}_\text{O}_2 + 2\mu^{\alpha}_\text{H}^+ - \mu^{\alpha}_\text{H}_2\text{O}_2) - 2\left( \mu^{\alpha}_\text{H}^+ - \frac{1}{2} \mu^{\alpha}_\text{H}_2\text{O}_2 \right) \right]$$ (SI 9)

which after being combined yield eq. (SI 10), further simplified to equation (SI 11).

$$E^{\alpha}_\text{O}_2/\text{H}_2\text{O}_2 \text{SHE} = \left[ E^{\alpha}_\text{O}_2/\text{H}_2\text{O}_2 \text{SHE} \right] + \frac{1}{2F} \left[ \left( \mu^{\alpha}_\text{O}_2 + 2\mu^{\alpha}_\text{H}^+ - \mu^{\alpha}_\text{H}_2\text{O}_2 \right) - \left( \mu^{\alpha}_\text{H}_2\text{O}_2 - \mu^{\alpha}_\text{H}_2\text{O}_2 \right) \right]$$ (SI 10)

$$E^{\alpha}_\text{O}_2/\text{H}_2\text{O}_2 \text{SHE} = \left[ E^{\alpha}_\text{O}_2/\text{H}_2\text{O}_2 \text{SHE} \right] + \frac{1}{2F} \left[ \left( \mu^{\alpha}_\text{O}_2 + 2\mu^{\alpha}_\text{H}^+ - \mu^{\alpha}_\text{H}_2\text{O}_2 \right) - \left( \mu^{\alpha}_\text{H}_2\text{O}_2 - \mu^{\alpha}_\text{H}_2\text{O}_2 \right) \right]$$ (SI 11)

Taking into account that $\Delta G_{\text{tr,H}^+} = \mu^{\alpha}_\text{H}^+ - \mu^{\alpha}_\text{H}_2\text{O}_2$ and $\Delta G_{\text{tr, H}_2\text{O}_2} = \mu^{\alpha}_\text{H}_2\text{O}_2 - \mu^{\alpha}_\text{H}_2\text{O}_2$, eq. (SI 12) can also be written as:
\[
\left[ E^{\circ}_{\text{O}_2/H_2O_2} \right]_{\text{SHE}}^0 = \left[ E^{\circ}_{\text{O}_2/H_2O_2} \right]_{\text{SHE}}^w + \frac{1}{2F} \left[ 2\Delta G^{\circ , \text{H}_2O} - \Delta G^{\circ , \text{H}_2O} \right]
\] (SI 12)

In such a way and knowing that \( \Delta G^{\circ , \text{H}_2O} = 53 \text{ kJ} \cdot \text{mol}^{-1} \) and \( \Delta G^{\circ , \text{H}_2O} \approx 15 \text{ kJ} \cdot \text{mol}^{-1} \), finally we obtain,

\[
\left[ E^{\circ}_{\text{O}_2/H_2O_2} \right]_{\text{SHE}}^0 = 1.165 \text{ V}
\] (SI 13)

Proceeding in a similar way for the four-electron reduction of oxygen,\[s5\]

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{H}_2\text{O}
\]

\[
\left[ E^{\circ}_{\text{O}_2/H_2O} \right]_{\text{SHE}}^w = 1.229 \text{ V}
\] (SI 14)

It is finally obtained

\[
\left[ E^{\circ}_{\text{O}_2/H_2O} \right]_{\text{SHE}}^0 = \left[ E^{\circ}_{\text{O}_2/H_2O} \right]_{\text{SHE}}^w + \frac{1}{4F} \left[ 4\Delta G^{\circ , \text{H}_2O} - \Delta G^{\circ , \text{H}_2O} \right]
\] (SI 15)

where the value for the Gibbs free energy of transfer of water (\( \Delta G^{\circ , \text{H}_2O} \)) herein employed was derived from its solubility in DCE\[s7\] and replaced into the eq. (SI 15). Finally, we obtain:

\[
\left[ E^{\circ}_{\text{O}_2/H_2O} \right]_{\text{SHE}}^0 = 1.749 \text{ V}
\] (SI 16)

References