Evidence of tetraphenylporphyrin monoacids by ion-transfer voltammetry at polarized liquid|liquid interfaces†

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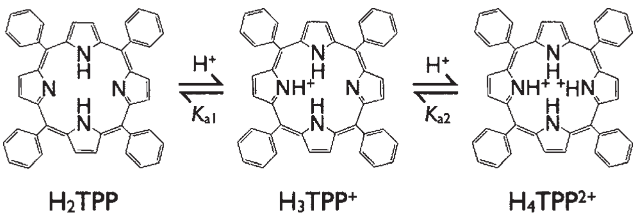
We present a simple methodology to illustrate the existence of tetraphenylporphyrin monoacid based on ion-transfer voltammetry at a polarized water|1,2-dichloroethane interface and organic p*K* values are also estimated.

The acid–base property of free-base porphyrins has been widely investigated, but the subject is still the matter of some controversy.[1] The tetrapyrrole ring of a free-base porphyrin contains two tertiary nitrogen atoms, which allows the gain of protons to form a monoacid and a diacid, as illustrated for the free-base 5,10,15,20-*meso*-tetrapehenylporphyrin (H_2TPP) in Scheme 1, and the existence of monoacids has received considerable attention. By titrating H_2TPP usually one isosbestic point due to H_2TPP and H_4TPP^{2+} is observed, whereas the intermediate H_3TPP^+ could not be clearly detected.[2]

The existence of H_3TPP^+, as well as pK_{a1} and pK_{a2} values, has been reported in a few cases,[3–6] one of which is based on the ion-transfer voltammetry at a polarized water|nitrobenzene interface.[6] Since the pioneering work of Koryta *et al.*,[7] ion transfer voltammetry at the liquid|liquid interface (also called the Interface between Two Immiscible Electrolyte Solutions (ITIES)) has become a well-established method to study the acid–base properties of molecules dissolved in an organic phase in contact with an aqueous electrolyte. As shown by Reymond *et al.* for the study of therapeutic molecules, this methodology allows the determination of p*K* values, and the drawing of ionic partition diagrams.[8] Herein, using this simple methodology, we illustrate the existence of H_3TPP^+ in 1,2-dichloroethane (DCE) and pK_{a1} and pK_{a2} values are also estimated.

An ITIES is formed when an aqueous solution containing hydrophilic ions is put in contact with an organic solution containing lipophilic ions. Electrochemical polarization supplied by an external voltage can give a polarizable potential window, the width of which is defined by the transfer reactions of the electrolyte ions across the interface. The potential dependence for ion transfer across the interface follows a Nernst equation. For example, using 10 mM LiCl and 100 mM HCl as the aqueous electrolytes and bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BTPPATPFB, 5 mM) as the lipophilic electrolyte in DCE, a potential window ranging from −0.5 to 0.4 V can be obtained, as shown by the dotted line in Fig. 1(a). This window is determined by the transfer of H^+ and Cl^- from water to DCE at positive and negative potentials, respectively. With the help of an ionophore present in DCE that can complex with H^+, the transfer of H^+ will be facilitated and a wave will appear in the middle of the potential window. Stated in another way, H^+ will transfer at less positive potentials in this case, due to the presence of a proton acceptor in the organic phase. This phenomenon is usually called facilitated ion transfer reaction (or Transfer by Interfacial Complexation, TIC)[9] and the shift of the transfer potential provides information on the complexation constant between the ionophore and H^+.

By dissolving 50 μM H_2TPP in a DCE solution containing a lipophilic salts (BTPPATPFB, 5 mM) in contact with an acidic aqueous solution (10 mM LiCl and 100 mM HCl), two waves can be observed in the cyclic voltammogram, as illustrated by the full line in Fig. 1(a). The two waves, featuring the same current magnitude, lie at 0.046 V ($\Delta_o^w\phi_1$) and 0.262 V ($\Delta_o^w\phi_2$), respectively. First of all, the peak-to-peak potential separations for the two waves are approximately 60 mV, which complies with the conditions for a reversible transfer of a singly charged ion. The maximum peak currents are in good agreement with the Randles–Sevcik equation as shown by the linear dependence on the square root of scan rate, indicating that both waves originate from diffusion-controlled reactions. The measured peak currents also linearly increase with the H_2TPP concentration in the range 50 to 200 μM. This confirms that the ion transfer reactions are limited by the diffusion of H_2TPP species in the organic phase. Indeed, the proton concentration in water is in excess compared with that



Scheme 1 Protonation of H_2TPP to form monoacid and diacid.

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† Electronic supplementary information (ESI) available: Fig. S1: Cyclic voltammetry of 50 μM H_2TPP at various scan rates. Fig. S2: Cyclic voltammetry at various concentrations of H_2TPP. Fig. S3: CVs at various aqueous pH. See DOI: 10.1039/b811886h

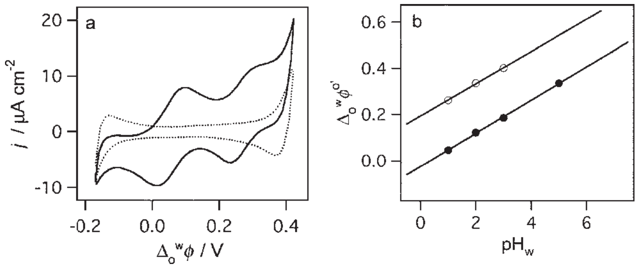
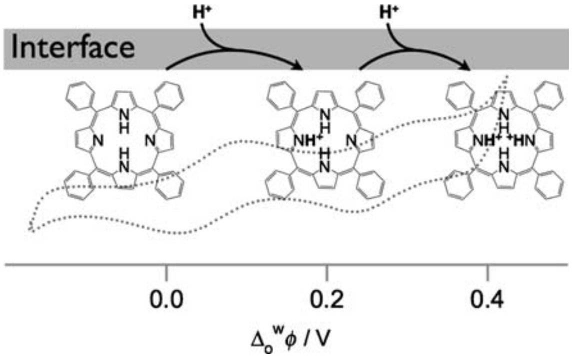


Fig. 1 (a) Cyclic voltammograms in the absence (···) and presence (—) of 50 μM H_2TPP in DCE at a scan rate of 0.025 V s^{-1}. Electrolytes: 10 mM LiCl and 100 mM HCl in water and 5 mM BTPPATPFB in DCE. (b) pH dependence of the half-wave potentials of the two waves.



Scheme 2 Illustration of interfacial formation of H_3TPP^+ and H_4TPP^{2+}.

of H_2TPP in DCE. Furthermore, the two waves shift with the acidity of aqueous phase by approximately 60 mV pH^{-1}, as illustrated in Fig. 1(b), confirming that both waves correspond to a facilitated proton transfer reaction. As illustrated in Scheme 2, the first wave represents the transfer of a proton from water to DCE facilitated by H_2TPP that in fact is the first protonation of H_2TPP to form the monoacid H_3TPP^+ in DCE, and the second one represents the facilitated transfer of a second proton by H_3TPP^+. These two processes can be expressed as:

$$H_2TPP_{(DCE)} + H^+{}_{(W)} \rightleftharpoons H_3TPP^+{}_{(DCE)} \qquad (1)$$

$$H_3TPP^+{}_{(DCE)} + H^+{}_{(W)} \rightleftharpoons H_4TPP^{2+}{}_{(DCE)} \qquad (2)$$

As illustrated in Fig. 1(a), the facilitated transfer of H^+ in the presence of H_2TPP and H_3TPP^+ is occurring at lower potentials than that of H^+ alone.

In addition, considering the two processes represent a 1 : 1 complexation reaction controlled by the diffusion of the porphyrin species in the organic phase, K_{a1} and K_{a2} can be estimated by exploring the pH dependence of the apparent transfer potential according to the following equation:[10]

$$\Delta_o^w\phi_{LH^+}^{1/2} = \Delta_o^w\phi_{H^+}^{o'} + \frac{RT}{2F}\ln\left(\frac{D_L}{D_{LH^+}}\right) - \frac{2.303RT}{F}pK_a^{DCE} + \frac{2.303RT}{F}pH^w \qquad (3)$$

where $\Delta_o^w\phi_{LH^+}^{1/2}$ is the half-wave transfer potential of the respective facilitated proton transfers. $\Delta_o^w\phi_{H^+}^{o'}$ is the formal transfer potential for the transfer of H^+. D_L and D_{LH^+} (L = H_2TPP, H_3TPP^+) represent the diffusion coefficients of the proton acceptor ligand and its protonated form, and for simplicity it can be assumed that $D_L \approx D_{LH^+}$; pH^w is the aqueous pH. The relationship between $\Delta_o^w\phi$ and the pH^w is found to be linear, and the intercept allows the determination of the pK_a in the organic phase. K_a^{DCE} is defined by:

$$K_a^{DCE} = \frac{a_L^{DCE}a_{H^+}^{DCE}}{a_{LH^+}^{DCE}} \qquad (4)$$

Doing so, as shown in Fig. 1(b), pK_{a1}^{DCE} and pK_{a2}^{DCE} here are found to be equal to 9.8 and 6.0, which show that both H_3TPP^+ and H_4TPP^{2+} are very weak acids in DCE. Meanwhile, it suggests that both H_2TPP and H_3TPP^+ are weak bases, having a small affinity for protons. It is worthwhile to mention that the proton activity in DCE is very small and the lack of hydrogen bonds in DCE prevents the stabilization of the protonated species and favours the presence of neutral or low charges species.

In conclusion, we present a simple methodology to illustrate the existence of H_3TPP^+ in DCE, based on ion-transfer voltammetry at the water|1,2-dichloroethane interface. K_{a1} and K_{a2} values can be accurately determined.

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