A Soft On/Off Switch Based on the Electrochemically Reversible H-J Interconversion of a Floating Porphyrin Membrane

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Soft molecular assemblies that respond reversibly to external stimuli are attractive materials as on/off switches, in optoelectronic, memory and sensor technologies. In this article, we present the reversible structural rearrangement of a soft porphyrin membrane under an electrical potential stimulus in the absence of solid-state architectures. The free-floating porphyrin membrane lies at the interface between immiscible aqueous and organic electrolyte solutions and is formed through interfacial self-assembly of zinc(II) meso-tetrakis(4-carboxyphenyl)porphyrins (ZnPor). A potential difference between the two immiscible electrolyte solutions induces the intercalation of bis(triphenylphosphoranylidene)ammonium cations from the organic electrolyte that exchange with protons in the porphyrin membrane. In situ UV/vis absorbance spectroscopy shows that this ionic intercalation and exchange induces a structural interconversion of the individual porphyrin molecules in the membrane from an H- to a J-type molecular configuration. These structural rearrangements are reversible over 30 potential cycles. In situ polarisation-modulation fluorescence spectroscopy further provides clear evidence of structural interconversion of the porphyrin membrane, as intercalation of the organic electrolyte cations significantly affects the latter’s emissive properties. By adjusting the pH of the aqueous phase, additional control of the electrochemically reversible structural interconversion can be achieved, with total suppression at pH 3.

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A Soft On/Off Switch Based on the Electrochemically Reversible H-J Interconversion of a Floating Porphyrin Membrane

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Abstract

Soft molecular assemblies that respond reversibly to external stimuli are attractive materials as on/off switches, in optoelectronic, memory and sensor technologies. In this article, we present the reversible structural rearrangement of a soft porphyrin membrane under an electrical potential stimulus in the absence of solid-state architectures. The free-floating porphyrin membrane lies at the interface between immiscible aqueous and organic electrolyte solutions and is formed through interfacial self-assembly of zinc(II) meso-tetrakis(4-carboxyphenyl)porphyrins (ZnPor). A potential difference between the two immiscible electrolyte solutions induces the intercalation of bis(triphenylphosphoranylidene)ammonium cations from the organic electrolyte that exchange with protons in the porphyrin membrane. In situ UV/vis absorbance spectroscopy shows that this ionic intercalation and exchange induces a structural interconversion of the individual porphyrin molecules in the membrane from an H- to a J-type molecular configuration. These structural rearrangements are reversible over 30 potential cycles. In situ polarisation-modulation fluorescence spectroscopy further provides clear evidence of structural interconversion of the porphyrin membrane, as intercalation of the organic electrolyte cations significantly affects the latter’s emissive properties. By adjusting the pH of the aqueous phase, additional control of the electrochemically reversible structural interconversion can be achieved, with total suppression at pH 3.
Introduction

Controlling the molecular arrangements of chromophores in supramolecular assemblies remains a grand challenge with functional dyes such as porphyrins. In these assemblies, non-covalent intermolecular interactions precisely control the position and orientation of single molecules, thereby governing the physicochemical and photophysical properties of the ensemble. For example, in the solid-state, changes in molecular packing may turn non-emissive organic molecules such as terpyridine into good emitters, or impact significantly the emission of anthracene assemblies. Methodologies that reversibly modulate such arrangements using external stimuli are long sought after given their potential importance in the development of on/off switching behaviour in optoelectronic, memory and sensor technologies. Among these stimuli, light, pH, and electric fields can provide flexible external control with a certain degree of reversibility.

Compared to the interface between solid electrodes and electrolytes, the interface between two immiscible electrolyte solutions (ITIES) is dynamic and lacks inherent defects such as step edges, domain boundaries, terraces and kinks. Thus, the uniform templating of adsorbed molecules at such “soft” interfaces can provide a pathway to molecular assemblies with unique structural arrangements and functionalities. Given the weak interaction with the interface, intermolecular interactions in molecular assemblies adsorbed at the ITIES can be externally manipulated by applying an electrical potential stimulus across the liquid|liquid boundary. Recently, we developed an experimental approach to induce the self-assembly of Zn(II) meso-tetrakis(4-carboxyphenyl)porphyrin (ZnPor) through a hydrogen bond-mediated mechanism at the ITIES. By optimising the pH of the aqueous phase to closely match the pKₐ of the carboxyl groups (pKₐ = 5.8), films of ZnPor nanostructures self-assembled at the liquid|liquid interface creating a porphyrin membrane intermediate between the two electrolyte solutions. Upon polarisation, carboxyl groups in the ZnPor membrane act as cationic exchange sites and give rise to purely ionic electrochemical signals resembling those of redox-type reactions in solid substrates.

In this article, we use in situ spectroelectrochemical techniques to demonstrate that ion intercalation and exchange reactions in these soft ZnPor membranes are accompanied by a change in the stacking arrangement of the individual porphyrin molecules within the nanostructures. In situ UV/vis absorbance and polarisation-modulation fluorescence spectroscopies in total internal reflection mode (TIR-UV/vis and PM-TIRF, respectively) show that exchange of protons in the porphyrin membrane by bulky...
bis(triphenylphosphoranylidene)-ammonium cations (R₂N⁺) from the organic electrolyte induces a stacking interconversion of the porphyrins from a compact H-type nanostructure to an open J-type. This interconversion can be manipulated by an interfacial Galvani potential difference between the two electrolyte solutions (Δϕ) and is reversible over 30 potential cycles.

Results and Discussion

Monitoring reversible H- to J-type interconversion of the interfacial porphyrin membrane by in situ UV/vis spectrophotometry. The potential induced interconversion between H- and J-type nanostructures in the ZnPor membrane was analysed in a 4-electrode configuration by cyclic voltammetry (CV), and in situ TIR-UV/vis and PM-TIRF; the configuration of the electrochemical cell used is presented schematically in Fig. 1 and in detail in Fig. S1 of the Supporting Information (SI). Schematics and experimental optimisation procedures for the in situ TIR-UV/vis absorbance and PM-TIRF spectroelectrochemical setups, respectively, are detailed in Figs. S2-S6. Soft ZnPor membranes were obtained from the self-assembly of ZnPor at the water|α,α,α-trifluorotoluene (TFT) interface as described in detail in the SI and our previous work. For CV and TIR-UV/vis absorbance experiments, ZnPor molecules not adsorbed at the liquid|liquid interface were flushed out, leaving only the membrane between the two electrolyte solutions of approximately 200 nm in thickness (Fig. S7). For PM-TIRF experiments, after the ZnPor membrane was self-assembled, non-adsorbed ZnPor molecules remained in the aqueous phase during the course of the experiment.
**Fig. 1.** Schematic configurations for spectroelectrochemical studies with the ZnPor membrane system. The techniques used were cyclic voltammetry (CV), in situ UV/vis absorbance and polarisation-modulation fluorescence spectroscopies in total internal reflection mode (TIR-UV/vis and PM-TIRF, respectively). The organic phase was α,α,α-trifluorotoluene (TFT) containing 5 mM bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (R$_2$NTB). The aqueous phase was 10 mM lithium citrate (Li$_2$HCit) at pH 5.8, or 10 mM citric acid (H$_3$Cit) at pH 3.0. The ZnPor membrane was prepared from 10 μM solutions of ZnPor in contact with the TFT as described in the SI.

Fig. 2a shows CVs in the presence and absence of the ZnPor membrane, respectively. At potentials where the aqueous phase is polarised negatively with respect to the organic phase ($\Delta_{o}^{w}\phi < 0$), an increase in the interfacial concentration of R$_2$N$^+$ near the organic electrolyte-membrane interface leads to a reversible intercalation/exchange reaction associated with peaks A and B in the voltammogram.$^{19}$ Scanning negatively, R$_2$N$^+$ ions penetrate the membrane binding to anionic carboxyl sites and displacing protons through ion exchange at neutral carboxyl sites producing peak A. The latter process reverses as the potential direction is switched and scanned to more positive potentials, yielding peak B.$^{19}$
Fig. 2. (a) Cyclic voltammetry (CV) in the absence and presence of the ZnPor membrane in the configuration presented schematically in Fig. 1a. The scan rate was 25 mV·s⁻¹. The 4-electrode electrochemical cell setup used for these measurements is presented in Fig. S1. (b) Differential TIR-UV/vis absorbance spectra of the ZnPor membrane at different $\Delta_o\phi$. The spectrum of the membrane at +0.50 V was taken as a blank.

In situ TIR-UV/vis absorbance measurements were carried out at different $\Delta_o\phi$, as presented in Fig. 2b. Differential spectra were obtained by subtracting the spectrum of the ZnPor membrane obtained at +0.5 V from spectra obtained at each $\Delta_o\phi$. A stepwise interconversion between three dominant supramolecular nanostructures is observed. Using the $\lambda_{\text{max}}$ of ZnPor in solution at pH 5.8 ($\lambda_{\text{max}} = 422$ nm) as a reference (Fig. S8), these supramolecular nanostructures were assigned as either H-type ($\lambda_{\text{max}} = 414$ nm) or J-type ($J_1$, $\lambda_{\text{max}} = 435$ nm and $J_2$, $\lambda_{\text{max}} = 448$ nm). Control differential spectra in the absence of the ZnPor film were featureless (Fig. S4).
The differential TIR-UV/vis absorbance spectra in Fig. 2b indicate that the structure of the ZnPor membrane is dynamic across the whole potential range studied. The potential of zero charge (PZC) at pH 5.8 in the presence of the ZnPor membrane was determined previously as +0.25 V. At potentials approaching or more positive than the PZC, i.e., +0.2 and +0.5 V, ZnPor molecules primarily adopt a compact H-type configuration as observed for other porphyrin assemblies at the ITIES. Note that at these positive potentials, no electrochemical signals were observed in the presence of the ZnPor membrane, and thereby a more compact structure could be expected. At potentials more negative than the PZC, i.e., 0 and –0.30 V, R2N+ accumulates at the organic electrolyte|membrane interface. We propose that electrostatic interactions with R2N+ cause a partial opening of the nanostructures in the membrane and the appearance of an initial J-type structure (J1). The subsequent intercalation of bulky R2N+ species and their exchange with substantially smaller protons in the membrane cause further structural rearrangements into a more open J-type configuration (J2). Of particular note is that differential TIR-UV/vis absorbance measurements clearly indicate that H-J interconversion begins to take place even at potentials considerably positive of peaks A and B. The latter is due to the continuous change in the double layer and the gradual build-up of R2N+ species at the organic electrolyte|membrane interface as Δwφ is scanned negatively.

The reversibility of the structural H-J interconversion was demonstrated by comparing the magnitude of the absorbance of the H and J2 nanostructures as a function of the number of potential cycles, as presented in Fig. 3a (one cycle = potential steps from +0.50 V to –0.25 V to +0.50 V). A near constant absorbance value for 30 cycles indicates an excellent, robust reversibility of the optical properties of the membrane. This observation is in line with the negligible charge differential (ΔQ ≈ 0 μC·cm⁻²) determined electrochemically for peaks A and B in the voltammogram, presented in Fig. S9. The electrochemically reversible H-J interconversion of the ZnPor membrane at the water|TFT interface is shown schematically in Fig. 3b.
Fig. 3. (a) Reversible H-J interconversion of the ZnPor membrane as a function of the potential cycle. One cycle = potential steps from +0.50 V to −0.25 V to +0.50 V. The absorbance of H and J₂ was measured at 414 and 448 nm, respectively, from the differential TIR-UV/vis absorbance spectra presented in Fig. S10 and animated in a Movie, see SI. (b) Schematic of the electrochemically reversible H-J interconversion of the ZnPor membrane at the water|TFT interface.

**Suppression and reactivation of the interfacial porphyrin membrane H-J interconversion by pH.** The pH of the aqueous phase significantly effects the structural interconversion and electrochemistry of the ZnPor membrane. As presented in Fig. 4, by decreasing the pH from 5.8 to 3.0, the electrochemical ion intercalation/exchange was supressed with all electrochemical signals related to the presence of the ZnPor membrane disappearing. Furthermore, the H-J interconversion was suppressed at pH 3.0, with no changes in the differential absorbance spectra observed at different $\Delta \phi$. Thus, the spectroelectrochemical analysis clearly demonstrates that the potential induced intercalation/exchange reaction is responsible for the H-J interconversion observed. Consequently, when the former is supressed, the porphyrin membrane retains a compact H-type configuration. Control TIR-UV/Vis absorbance experiments show that even though the ZnPor membrane initially self-assembles only at a pH value near the pKₐ of the carboxyl groups (pKₐ = 5.8), once assembled, the membrane is stable even at very acidic conditions (Fig. S11). This excludes any effects of redissolution of the membrane on the analysis presented.
Fig. 4. Suppression and reactivation of the ZnPor membrane H-J interconversion monitored by CV and differential TIR-UV/vis absorbance. The scan rate for the CV was 5 mV·s\(^{-1}\). Inset: differential absorbance of the membrane at pH 3.0 with \(\Delta_{o}^{w}\phi\) equal to –0.30 V and +0.50 V, respectively. The TIR-UV/vis absorbance spectrum at +0.50 V was taken as the blank, and spectra at other \(\Delta_{o}^{w}\phi\) across the full potential range studied are shown in Fig. S12.

Both the applied \(\Delta_{o}^{w}\phi\) and pH of the aqueous phase shift the chemical equilibrium involving carboxyl groups in the ZnPor membrane, aqueous protons, and bulky organic R\(_2\)N\(^+\) cations. The overall equilibrium of the ion exchange in the membrane, \(m\), can be represented as follows

\[
-\text{COOH}_m + R_2N_m^+ \rightleftharpoons -\text{COOR}_2N_m^+ + H_m^+ \quad (1)
\]

This equilibrium is similar to that present in membranes used in ion selective electrodes (ISE).\(^{21}\) In effect, within a certain potential range, the porphyrin membrane acts as an intermediate phase separating the aqueous and organic electrolyte solutions.\(^{19}\) The ion exchange reaction can be considered as the combination of acid dissociation

\[
-\text{COOH}_m \rightleftharpoons -\text{COO}^-_m + H_m^+ \quad (2)
\]

and binding of the organic cation

\[
-\text{COO}^-_m + R_2N_m^+ \rightleftharpoons -\text{COOR}_2N_m^+ \quad (3)
\]

In turn, the equilibrium constant of the acid dissociation reaction is dictated by ionic equilibrium at the membrane|aqueous electrolyte interface

\[
-\text{COOH}_m \rightleftharpoons -\text{COO}^-_m + H_{aq}^+ \quad (4)
\]
where \textit{aq.} is the aqueous phase. Furthermore, the equilibrium constant of the binding reaction is dictated by ionic equilibrium at the organic electrolyte|membrane interface (\textit{i.e.} intercalation)

\begin{equation}
-COO^-_m + R_2N^+_{org} \rightleftharpoons -COOR_2N^+_m
\end{equation}

where \textit{org.} is the organic phase. The interfacial Galvani potential difference necessary for the ion exchange reaction (\(\Delta^w_o \phi^{IE}\)) is therefore a function of the concentration of the carboxyl groups in the ZnPor membrane, organic \(R_2N^+\) cations, and aqueous protons. As the pH of the aqueous phase decreases, more energy is required to shift the chemical equilibria described in Equations (1) to (5) to favour acid dissociation and \(R_2N^+\) binding in the membrane. Thus, \(\Delta^w_o \phi^{IE}\) shifts to more negative potentials and eventually falls outside the polarisable potential window, as observed when the pH of the aqueous electrolyte is 3.0 in Fig. 4.

\textit{In situ} polarisation-modulation fluorescence spectroscopy of the interfacial porphyrin membrane H-J interconversion. Further spectroelectrochemical evidence of the reversible structural interconversion of the ZnPor membrane was obtained using PM-TIRF to probe the effect of interfacial polarisation on the emitted fluorescence. PM-TIRF signals (\(\Delta F^{p-s}\)) as a function of emission wavelength (PM-TIRF spectra) were recorded at different \(\Delta^w_o \phi\) (Fig. 5a.). As demonstrated in previous works, PM-TIRF spectra are interface-specific, with signals arising from randomly oriented molecules in the bulk phases effectively cancelled out.\(^{22,23}\) At \(\Delta^w_o \phi = +0.59, +0.29, -0.06\) and \(-0.15\) \text{V}, two emission peaks were observed (\(\lambda_{em.} = 613\) and 663 nm), similar to the emission peaks for the monomeric porphyrin (see Fig. S13). The negative values of \(\Delta F^{p-s}\) at each \(\Delta^w_o \phi\) confirm the relatively horizontal orientation of individual ZnPor molecules within the membrane with respect to the plane of the interface.\(^{23}\) PM-TIRF spectra measured at \(-0.06\) and \(-0.15\) \text{V} show a major decrease in \(-\Delta F^{p-s}\) compared to the spectrum at \(+0.29\) \text{V}, with no spectral shift. The decrease in \(-\Delta F^{p-s}\) may be associated with a change in molecular orientation of the ZnPor molecules within the membrane at the more negative potentials. The lack of a spectral shift indicates association of the ZnPor molecules in the membrane mainly through hydrogen bonds between their carboxyl groups.\(^{16}\) This finding is in line with the pH dependency of the ZnPor membrane formation, as detailed in our recent work,\(^{17}\) and the cooperative hydrogen bonding model proposed by Girault and co-workers in their photoelectrochemical studies of ZnPor at a polarised water|1,2-dichloroethane interface.\(^{24}\) At \(\Delta^w_o \phi < -0.30\) \text{V}, the PM-TIRF spectra red-shifted and a third emission peak (\(\lambda_{em.} = 694\) nm) appeared, confirming close \(\pi-\pi\) stacking of the porphyrin ring at the interface and the formation of J-type nanostructures.
Fig. 5. (a) PM-TIRF spectra of the ZnPor membrane at different $\Delta \omega \phi$. (b) PM-TIRF spectra of the ZnPor membrane after a potential cycle from +0.29 V to –0.30 V and back to +0.59 V. $\lambda_{\text{exc.}} = 404$ nm.

As presented in Fig. 5b, by switching the potential across the interface between the positive and negative potentials, the emission peak at 694 nm can be effectively controlled, further demonstrating the reversibility of the structural interconversion and the control over the emission properties of the porphyrin membrane. The rate of the dissociation of the J-aggregate was rather slow at +0.29 V, and therefore a higher positive potential of +0.59 V was applied on switching back from negative to positive potentials.

Conclusions

In this article, we demonstrate the reversible structural interconversion of a soft porphyrin membrane from an H- to a J-type molecular configuration in the absence of any
solid-state architectures. The interconversion was controlled by applying an interfacial Galvani potential difference between two immiscible electrolyte solutions. The potential difference induced an ion intercalation/exchange reaction that affected reversibly the supramolecular structure of the membrane. The latter was demonstrated electrochemically by cyclic voltammetry and spectroscopically by in situ UV/vis absorbance and polarisation-modulated fluorescence spectroscopies in total internal reflection mode. The H- to J-interconversion was robust and repeatable over at least 30 potential cycles. The interconversion was suppressed within the polarisable potential window at pH 3.0, but recoverable by returning the pH of the aqueous phase to pH 5.8.

The work herein opens new opportunities to investigate the use of structurally dynamic soft supramolecular porphyrin assemblies at the ITIES as switchable on/off responsive nanomaterials, with applications in optoelectronic, memory and sensor devices. An ITIES can be easily supported on a solid electrode, such as a flexible indium tin oxide (ITO) electrode, for device integration using organogel thin films. Future work will involve self-assembly of the porphyrin membrane at an aqueous|organogel interface on flexible ITO electrodes leading to flexible on/off switches based on electrochemically driven ion intercalation/exchange reactions of the soft porphyrin membrane.

**Conflicts of interest**

There are no conflicts to declare.

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Table of Contents Graphic

![Diagram showing H-type and J-type nanostructures with change in voltage](image)

- Water
  - ZnPor membrane
  - $\Delta \phi$
  - Oil
  - $+0.50 \text{ V}$
  - $-0.30 \text{ V}$
  - H-type nanostructures
  - J-type nanostructures

![Graph showing absorbance over cycles with voltages](image)
Supporting Information (SI)

A Soft On/Off Switch Based on the Electrochemically Reversible H-J Interconversion of a Floating Porphyrin Membrane

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S1. Experimental methods

S1.1 Chemicals. All reagents were used as received without further purification. Zinc \( \text{meso-tetrakis(4-carboxyphenyl)porphyrin (ZnPor, } \geq 98\%) \) was obtained from Porphychem. Lithium hydroxide (LiOH, \( \geq 98\% \)), citric acid (H\(_3\)Cit, \( \geq 99.5\% \)) and bis(triphenylphosphoranylidene) ammonium chloride (R\(_2\)NCl, 97%), were purchased from Sigma-Aldrich. Lithium tetrakis(pentafluorophenyl)borate diethyletherate (LiTB) was purchased from Boulder scientific, and \( \alpha,\alpha,\alpha \)-trifluorotoluene (TFT, \( \geq 99\% \)) from Acros Organics. All aqueous solutions were prepared using Milli-Q® deionized water (18.2 MΩ). Aqueous solutions of ZnPor were prepared by directly dissolving the solid in the lithium citrate buffer pre-adjusted to the desired pH, followed by sonication of the solution for three minutes.

The organic electrolyte was obtained by a metathesis reaction between R\(_2\)NCl and LiTB. In a typical procedure, equimolar quantities of LiTB and R\(_2\)NCl were dissolved separately in a mixture of CH\(_3\)OH:H\(_2\)O 2:1 (v/v). The solutions obtained were mixed together and stirred for 30 minutes at room temperature. After this time, a white powder in suspension was obtained. This suspension was then filtered and the solid obtained collected in a beaker. Acetone was added drop-wise to this solid until most of it was dissolved. The solution obtained was filtered again and water was added drop-wise to precipitate the solid. The acetone in the mixture was then evaporated by gently heating (50°C) and stirring. The solid obtained was pure R\(_2\)NTB, and vacuum dried for two hours to obtain a fine white powder.

S1.2 Self-assembly of the zinc porphyrin membrane (ZnPor membrane). The porphyrin membrane self-assembled from aqueous solutions of 10 \( \mu \text{M} \) of ZnPor. The self-assembly was carried out at the water|TFT interface for 30 minutes. Critically, the pH of the aqueous solution was adjusted using a 10 mM Li\(_2\)HCit (lithium citrate buffer) to match the pKa of the 4-carboxyphenyl substituents (pKa\(_{\text{COOH}} = 5.8\)).\(^1\) Subsequently, this solution was contacted with TFT (an organic solvent that is immiscible with water) for 30 minutes, leading to the formation of a well-defined aqueous|organic interface. Upon contact, the clear formation of interfacial nanostructures was immediately seen visually. The water|TFT interface took on a yellow/green complexion, easily distinguishable from the purple colour of bulk ZnPor aqueous solution. The intensity of the interfacial colouration increased with time, ultimately leading to the formation of a ZnPor membrane. For cyclic voltammetry and in situ TIR-UV/vis absorbance experiments,
porphyrin not adsorbed at the interface was carefully removed and replaced with Li$_2$HCit buffer. This procedure was repeated until no porphyrin was detectable by UV/vis spectroscopy in the aqueous phase.

**S1.3 Electrochemical measurements.** Electrochemical measurements at the interface between two immiscible electrolyte solutions (ITIES) were carried out with a PGSTAT204 Autolab Metrohm potentiostat using a four-electrode electrochemical cell (see Fig. S1). The reference electrodes used were Ag/AgCl for the organic side and Ag/AgCitrate(Ag$_3$Cit) for the aqueous side. The counter electrodes were Pt. The electrolyte in the aqueous phase was a 10 mM buffer of Li$_2$HCit at different pH values. In the organic phase, the solvent used was TFT, and the organic electrolyte was 5 mM R$_2$NTB. The electrochemical cell configuration investigated in this communication is presented in Fig. S1a, where each vertical line represents a phase boundary and the double vertical line represents the polarisable interface between the membrane and the aqueous and organic electrolyte solutions.

![Diagram showing the electrochemical cell configuration](image)

**Fig. S1.** (a) Four-electrode electrochemical cell configuration used for electrochemical measurements. (b) Schematic, (c) and (d) pictures of the cell. CE = counter electrode, RE = reference electrode. R$_2$N = bis(triphenylphosphoranylidene)ammonium cation. TB = tetrakis(pentafluorophenyl)borate anion. Organic solvent = $\alpha,\alpha,\alpha$-trifluorotoluene.
S1.4 *In situ* UV/vis spectroscopy in total internal reflection (TIR-UV/vis) at the bare ITIES and the membrane|organic electrolyte interface. In order to analyse the effect of the applied interfacial Galvani potential difference (Δ°wφ) on the structure of the ZnPor membrane, *in situ* TIR-UV/Vis absorbance at the polarised water|TFT and membrane|TFT interfaces was used. In this configuration, the light source was directed towards the interface with the aid of focusing lenses, diaphragm and mirrors (see Fig. S2) at an angle of incidence (AOI) calculated using Snell’s law and the refractive indexes of water (ηH2O) and TFT (ηTFT) as follows:

\[ η_TFT \sin θ_1 = η_{H_2O} \sin θ_2 \]

If θ2 is assumed to be 90°

\[ θ_2 = 90° \]
\[ \sin θ_2 = 1 \]

Applying Snell’s law, with ηH2O and ηTFT equal to 1.330 and 1.414, respectively, the critical angle was determined as follows:

\[ \sin θ_1 = \frac{η_{H_2O}}{η_{TFT}} = \frac{1.330}{1.414} = 0.940 \]
\[ θ_1 = \sin^{-1}(0.940) = 70.05° \]

The light source (Xe lamp HPX-2000, Ocean Optics) was guided by an optical fiber with a 200 µm core (Newport) and focused on the water|TFT and membrane|TFT interfaces through plano-convex (Thorlabs) and achromatic lenses (Newport), see Fig. S2. All lenses were placed at their confocal lengths. The longer wavelengths (λ > 700 nm) were cut by a Hot Mirror (Thorlabs) to avoid heating of the interfacial region. The reflected light was focused onto an optical fiber with a 1500 µm core (Thorlabs). The AOI to the interface was set as 75°. A neutral density (ND) filter (Thorlabs) was used to reduce the intensity of the light beam; the ND filter was placed directly after the source to avoid photobleaching of the porphyrin. The absorption spectra were recorded by a Maya 2000Pro (Ocean Optics).
Fig. S2. Optical setup for in situ UV/vis absorbance measurements in total internal reflection (TIR-UV/vis absorbance). (1) Xe light source (Ocean optics HPX-2000), (2) UVFS coated plano convex lenses, (3) neutral density (ND) filter, (4) iris diaphragm, (5) “Hot” mirror (cut-off wavelength 800 nm), (6) Achromatic doublets, and (7) Ocean Optics Maya2000 Pro spectrometer. The angle of incidence (AOI) was set to 75°.

S1.5 Minimising baseline drift and artifacts for TIR-UV/vis absorbance measurements. The baseline for the TIR-UV/vis absorbance measurements was affected by heating of the interface with infrared radiation and changes in the surface tension at different $\Delta \omega$. To minimise the former, a hot mirror was placed between the light source and the interface. As presented in Fig. S3a, the hot mirror effectively cut off wavelengths in the infrared region above 700 nm. Using this configuration, the drifting of the spectral baseline was significantly reduced over time and no artifact was observed in the region of interest (see Fig. S3b).

Fig. S3. Xe lamp emission after being reflected at the water|TFT interface. (a) Emission using a “hot” mirror that cuts off wavelengths above 700 nm. (b) Variation of the emission spectra over a 10 minutes period. Spectra were taken every 60 seconds.
The effect of the polarisation potential on the baseline drift and possible spectral artifacts was analysed at the ITIES in the absence of the ZnPor membrane at the interface. The CV recorded under these conditions shows no electrochemical signals in a potential range between –0.2 and 0.6 V (see Fig. S4a). Additionally, taking as a reference the spectrum at +0.40 V, in situ TIR-UV/vis spectra at different potentials presented in Fig. S4b show only small variations in the spectral baseline at +0.4 and +0.2 V. At –0.25 and –0.30 V, some baseline drift at the bare liquid|liquid interface was observed. However, as conclusively shown vide infra in Fig. S12, the presence of the ZnPor membrane stabilises the interface with no baseline shift observed in the presence of the latter at negative applied potentials. Furthermore, no significant variations over time were observed for the spectral baseline at each of the potentials used in the analysis as presented in Figs. S4c and S5. Any variations are in the order of 0.005 A.U. and represent only 5 to 10% of the spectral shifts observed in the presence of the ZnPor membrane.

**Fig. S4.** Stability of the spectral baseline for in situ TIR-UV/vis experiments at different \( \Delta \omega \phi \) in the absence of the ZnPor membrane. (a) CV obtained in the absence of the ZnPor membrane using the configuration of the 4-electrode electrochemical cell employed outlined in Fig. S1a. The scan rate used was 20 mV·s\(^{-1}\) and the pH of the aqueous phase was 5.8. (b) Raw baseline obtained during in situ TIR-UV/vis absorbance experiments at different \( \Delta \omega \phi \), taking as a reference the spectrum obtained at +0.40 V. (c) Influence of time on the spectral baseline drift during in situ TIR-UV/vis experiments at different \( \Delta \omega \phi \). Spectra were taken at 6 second intervals for one minute and the first spectra (at \( t = 0 \)) was used as the reference.
Fig. S5. The variation of Xe light source emission spectra after being reflected at the water|TFT interface polarized at different $\Delta \phi$. For each potential, the spectra were taken at 6 second intervals for one minute. Insets show a magnification region demonstrating the minimal variation of the spectra over time.
S1.6 Polarisation-modulation total internal reflection fluorescence (PM-TIRF) measurements at the ITIES. Periodic modulation between the p- and s-polarised incident beams was performed by a liquid crystal retarder (LCR) (Thorlabs, LCC1111T-A, LCC25/TC200) at 13 Hz. The excitation light source was a cw laser diode at 404 nm (Coherent, CUBE 405-50C). The output power was attenuated to < 25 mW to avoid photobleaching of ZnPor. The AOI was approximately 75°. The fluorescence signal from the interfacial region was measured perpendicularly to the interface by an optical fiber and a monochromator equipped with a photomultiplier tube (Shimadzu, SPG-120S), see Fig. S6. The polarisation-modulated fluorescence signal from the interfacial region was analysed by a digital lock-in amplifier (NF, LI5640) as a function of modulation frequency of the incident beam. The polarization-modulation efficiency ($P_m$) of LCR was obtained as 0.95 at 404 nm, indicating that 5% of the s-polarized component remain in the p-polarized mode of LCR or vice versa.³

![Diagram](image)

**Fig. S6.** (a) Schematic representation and (b) experimental setup of the spectroelectrochemical cell for PM-TIRF experiments.
S2. Supporting Figures

**Fig. S7.** Scanning electron microscopy (SEM) image of a ZnPor membrane transferred from the water|TFT interface to a copper grid with a holey carbon substrate. Images were obtained on a FEI Quanta 650 FEG high resolution SEM.

**Fig. S8.** UV/vis absorption spectrum of 10 µM ZnPor in an aqueous solution at pH 5.8.
Fig. S9. Charge measured for each of the peaks observed in the presence of the ZnPor membrane. The configuration of the 4-electrode electrochemical cell employed is outlined in Fig. S1a. The scan rate used was 5 mV·s⁻¹ and the start potential was +0.30 V.

Fig. S10. Differential in situ TIR-UV/vis absorbance spectra of the ZnPor membrane as a function of the potential cycle number. The potential difference between the two electrolyte solutions was stepped between +0.50 and −0.30 V and back to +0.50 V during a single cycle. An animation of the change in the differential in situ TIR-UV/vis absorbance spectra with potential cycling is provided as an additional supporting information movie file.
Fig. S11. *In situ* TIR-UV/vis absorbance spectra of a ZnPor membrane self-assembled from 50 μM ZnPor in solution at pH 5.8 for 30 minutes at open circuit potential (OCP). After self-assembly, the pH of the aqueous phase was adjusted to progressively more acidic pH values.

Fig. S12. **pH suppression of the ion intercalation/exchange.** (a) CV at 25 mV·s⁻¹ obtained in the presence and absence of the ZnPor membrane at pH 3.0 using the configuration of the 4-electrode electrochemical cell employed outlined in Fig. S1. (b) Differential *in situ* TIR-UV/vis absorbance spectra of the ZnPor membrane at pH 3.0 and at different applied Δφ. The spectrum of the ZnPor membrane at +0.50 V was taken as the baseline.
Fig. S13. Fluorescence emission spectrum of ZnPor in an aqueous solution, with [ZnPor] = 50 µM and a pH of the aqueous phase of 5.8. The excitation wavelength was 418 nm.

S3. Supporting References

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### Other files

| AVI animation of Figure S10.avi (1.51 MiB) | view on ChemRxiv | download file |
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