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**Interfacial Self-Assembly**

# Interfacial Self-Assembly of Water-Soluble Cationic Porphyrins for the Reduction of Oxygen to Water**

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Studying the structure and the dynamical behavior of self-assembled porphyrins is an attractive subject in many fields of research.[1] In particular, the quest for new organometallic catalysts to reduce oxygen to water is a major challenge and has a large range of applications, especially in energy research where porphyrins and corroles have been widely studied.[2] The selectivity towards the four-electron reduction of oxygen of synthetic binuclear complexes, such as $[Co_2(FTF_4)]$ and Pacman porphyrins adsorbed onto edge plane pyrolytic graphite electrodes, is about 100% and 80%, respectively.[2d,e,3] "Hangman" porphyrins offer a selectivity of about 50%,[2b] and cobalt(II) tetraphenylporphyrins trapped in a thin-layer conducting polymer and deposited on an indium tin oxide (ITO) electrode have shown a selectivity of 86%.[4]

The oxygen reduction reaction (ORR) can be performed homogeneously in solutions, heterogeneously on solid electrodes, but also at soft interfaces such as the interface between two immiscible electrolyte solutions (ITIES). Operating at a soft liquid–liquid interface compared to within a bulk solution offers an extra degree of freedom, as the interface electrical polarization can be controlled to drive the reaction. The ORR can be performed at ITIES by aqueous protons and sacrificial lipophilic electron donors, such as ferrocene (Fc)[5] and decamethylferrocene (DMFc),[5c,6] and using porphyrins as catalysts.[5b,7] In most cases, $H_2O_2$ is the main reaction product. Recently, we have shown that the lipophilic electron donor tetrathiafulvalene (TTF)[7c,8] performs the direct four-electron ORR selectively, albeit slowly,[7c] and this reaction can be efficiently catalyzed at ITIES by the formation of self-assembled "molecular rafts" between two oppositely charged water-soluble porphyrins.[8d]

The present work focuses on the interfacial self-assembly of the water-soluble cobalt *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin ($[CoTMPyP]^{4+}$) at a water | 1,2-dichloroethane interface, assisted by its electrostatic interaction with the lipophilic anion tetrakis(pentafluorophenyl)borate ($TB^-$) dissolved in the organic phase, and its catalytic activity in the four-electron ORR.

Catalytic tests were performed under aerobic conditions using the cells illustrated in Scheme 1. In cell I, $[CoTMPyP]^{4+}$ was contacted first with lithium tetrakis(pentafluorophenyl)borate diethyl etherate (LiTB) and hydrochloric acid in the aqueous phase, and then with TTF dissolved in 1,2-dichloroethane (DCE). In cell II, $[CoTMPyP]^{4+}$ was contacted first with DCE containing bis(triphenylphosphoranylidine)ammonium tetrakis(pentafluorophenyl)borate (BATB) and TTF, followed by the addition of LiTB and HCl to the aqueous phase. In both cases, $TB^-$ is distributed between both phases polarizing the interface positively (water versus DCE 0.67 V[9]).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 50 μM $CoTMPyP^{4+}$<br>pH 2 (HCl)<br>10 mM LiTB | ‖ | 1 mM TTF | I | 50 μM $CoTMPyP^{4+}$<br>pH 2 (HCl)<br>10 mM LiTB | ‖ | 1 mM TTF<br>5 mM BATB | II |
| *Water* | | *DCE* | | *Water* | | *DCE* | |

***Scheme 1.*** Initial composition of the cells for the biphasic reactions. See text for details.

The catalytic activity and selectivity of $[CoTMPyP]^{4+}$ on the four-electron ORR was calculated with respect to the production of $TTF^{\bullet +}$ and $H_2O_2$[7c,8d] (Supporting Information, Figure S1). Interestingly, the catalytic activity and selectivity to water, obtained by using cell I (36% and 55%, respectively), were significantly lower than those obtained by using the cell II (84% and 82%, respectively), indicating that adding $TB^-$ to the initial composition of the organic phase enhances significantly the performance of $[CoTMPyP]^{4+}$ in the four-electron ORR. It is remarkable that such selectivity is higher than that reported for the cofacial porphyrins $Co_2DPX$ and $Co_2DPOx$ when tested in the same conditions.[8d]

Considering that in these systems the catalyst and the sacrificial electron donor are located in opposite phases, the ORR is only expected to occur at the interface where $[CoTMPyP]^{4+}$ is adsorbed between an excess of lipophilic

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electron donors and aqueous protons. Thus, surface second harmonic generation (SSHG) a technique inherently selective for interfacial species was used to characterize the adsorbed [CoTMPyP]$^{4+}$. SSHG is a nonlinear optical process whereby two photons at a fundamental frequency are converted into one photon at the harmonic frequency.[10]

Figure 1a displays the SSHG spectra of 100 μM [CoTMPyP]$^{4+}$ recorded at the [water|DCE], [water(TB$^-$)|DCE], and [water|DCE(TB$^-$)] interfaces. The fundamental beam was linearly polarized ($p$); that is, parallel to the plane of incidence, and no analyzer was placed on the harmonic beam path in whose case the SSHG intensity can be written as:[10a]

$$I_{\mathrm{SSHG}}(2\omega) = K[a\cos^2\gamma + b\sin^2\gamma + c\sin^2\gamma]^2 \tag{1}$$

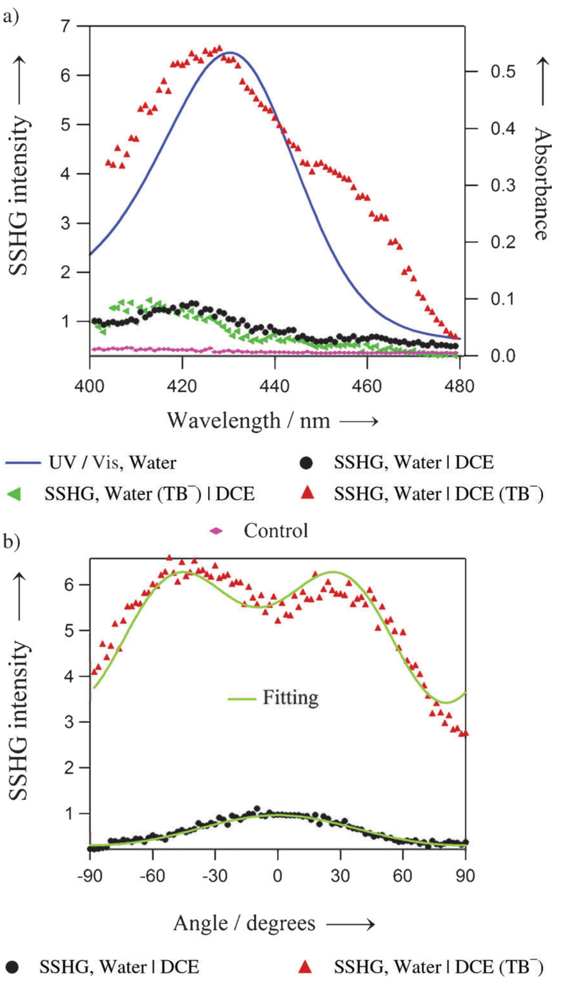

***Figure 1.*** a) UV/Vis absorption spectrum of 100 μM [CoTMPyP]$^{4+}$ in water (optical path: 1 mm) and SSHG spectra of 100 μM [CoTMPyP]$^{4+}$ recorded at the [water|DCE], [water(TB$^-$)|DCE], and [water|DCE(TB$^-$)] interfaces. The control spectrum was recorded at the neat (in the absence of porphyrin) water|DCE interface; the same spectrum was obtained for the neat [water(TB$^-$)|DCE] and [water|DCE(TB$^-$)] interfaces. b) Polarization angle dependence of the fundamental beam on the SSHG intensity for 100 μM [CoTMPyP]$^{4+}$ at the [water|DCE] and [water|DCE(TB$^-$)] interfaces.

where $K$ is a general constant and $a$, $b$, and $c$ are three complex coefficients that depend on the surface density of the porphyrins, their first hyperpolarizability at the interface, and their orientation with respect to the interface.[10a] The SSHG spectra of [CoTMPyP]$^{4+}$ at the [water|DCE] interface in Figure 1a resembles previous results.[8d] A similar spectrum was recorded at the [water(TB$^-$)|DCE] interface, where the main resonance is shifted to the blue for about 10 nm (432 nm), suggesting association between TB$^-$ and [CoTMPyP]$^{4+}$. Interestingly, the spectrum recorded at the [water|DCE(TB$^-$)] interface also shows two resonances at 426 nm and 456 nm, but 78% more intense than those recorded at the [water|DCE] and [water(TB$^-$)|DCE] interfaces, suggesting that the presence of TB$^-$ in the organic phase leads to an increase of the number density of porphyrins and its first hyperpolarizability at the interface; that is, the organic TB$^-$ significantly enhances the interfacial self-assembly of [CoTMPyP]$^{4+}$.

To investigate the interfacial self-assembly of [CoTMPyP]$^{4+}$, the dependence of the SSHG intensity on the fundamental input angle of polarization was determined at the fundamental wavelengths of 844 nm and 852 nm for the [water|DCE] and [water|DCE(TB$^-$)] interfaces, respectively (Figure 1b). The experimental data were fitted by using Equation (1) to estimate the coefficients $a$, $b$, and $c$ describing the microscopic parameters. The coefficients obtained at the [water|DCE] interface (Table 1) correlate rather well with previous results.[8d] Interestingly, for the [water|DCE(TB$^-$)] interface, a negative $c$ value was determined, whereas a vanishing value was measured for the [water|DCE] interface, indicating that the electrostatic interaction between aqueous [CoTMPyP]$^{4+}$ and organic TB$^-$ leads to species with a remarkably different electronic structure from the porphyrins adsorbed at a pristine organic phase. Furthermore, the behavior of [CoTMPyP]$^{4+}$ at the [water|DCE(TB$^-$)] interface resembles the self-assembled system [CoTMPyP]$^{4+}$/[CoTPPS]$^{4-}$.[8d] On the other hand, when comparing the SSHG spectrum of 100 μM [CoTMPyP]$^{4+}$ with that of 50 μM [CoTMPyP]$^{4+}$, both recorded at the [water|DCE(TB$^-$)] interface (Figure 2), a blue-shift was observed for both maxima when increasing the concentration, with a difference of about 59% in the SSHG intensity, which suggests H-aggregation.

***Table 1:*** Parameters obtained by fitting Eq. (1) to the polarization plots of [CoTMPyP]$^{4+}$ at the [water|DCE] and [water|DCE(TB$^-$)] interfaces.[a]

| System | $a$ | $b$ | $c$ |
|---|---|---|---|
| [water\|DCE] | 1 | 0.52 | 0 |
| [water\|DCE (TB$^-$)] | 1 | 0.79 | −0.56 |

[a] Values are normalized with respect to the coefficient $a$.

To explain the interfacial behavior of aqueous [CoTMPyP]$^{4+}$ when contacted with the organic TB$^-$, we have to consider the electrical positive polarization of the interface induced by the adsorption of the positively charged porphyrins. This adsorption is accompanied by the adsorption of TB$^-$ on the organic side of the interface to compensate the positive

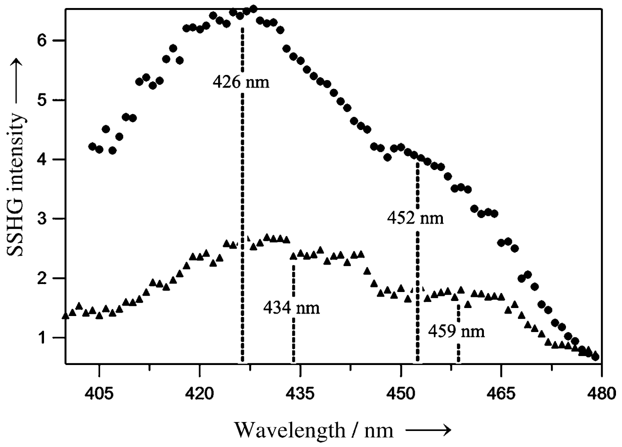

**Figure 2.** SSHG spectra of 50 μм (▲) and 100 μм (●)$[CoTMPyP]^{4+}$ (P) recorded at the [water | DCE(TB⁻)] interface.

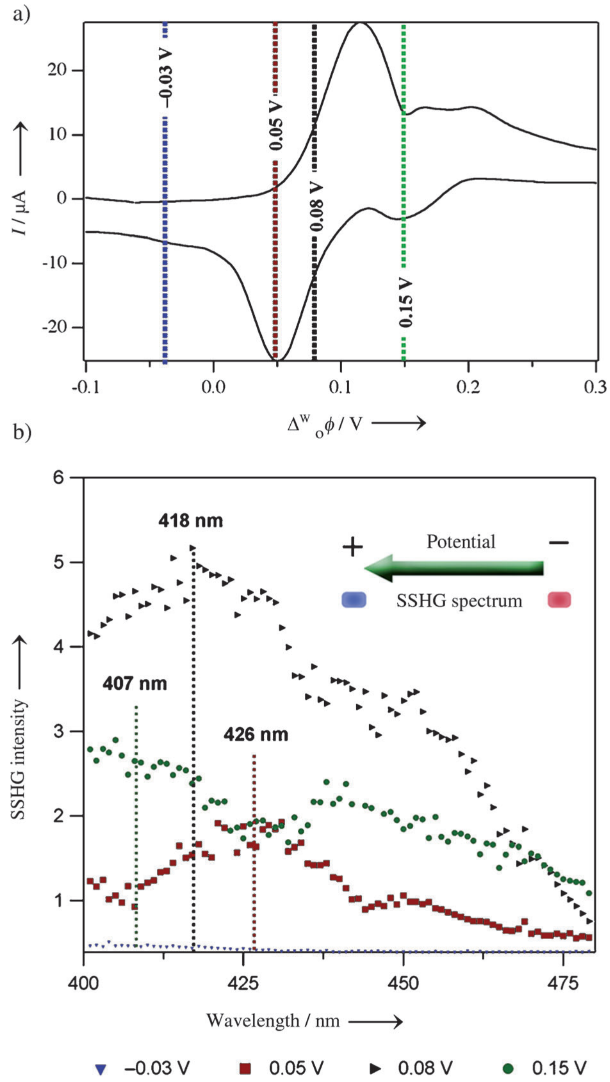

**Figure 3.** a) Ion-transfer voltammogram of 50 μм $[CoTMPyP]^{4+}$ at neutral pH (sweep rate 50 mV s$^{-1}$). b) SSHG spectra of 50 μм $[CoTMPyP]^{4+}$ recorded under polarization of the interface by using a four-electrode system.

charges by forming interfacial ion-pairs, which brings in turn more $[CoTMPyP]^{4+}$ driving its self-assembly. Despite the electrostatic repulsive force expected in such supramolecular structures, other cationic porphyrins have been reported to self-aggregate in pure water[11] promoted by the strong cohesive interaction of water and van der Waals interactions.[11b]

The role of the electrical polarization of the interface on the interfacial self-assembly of $[CoTMPyP]^{4+}$ was studied by recording the SSHG spectrum of $[CoTMPyP]^{4+}$ at different applied potentials (Supporting Information, Sections S2 and S3).[10c] Figure 3 a shows the ion-transfer voltammogram of 50 μм $[CoTMPyP]^{4+}$. The transfer of the porphyrin from the aqueous to the organic phase is observed at 0.08 V, while the post peaks around 0.15 V and 0.20 V correspond to adsorption of $[CoTMPyP]^{4+}$ at the aqueous side of the liquid–liquid junction.[8d] As reported by Nagatani et al.,[10c] the intensity of the main SSHG resonance increases as the porphyrin approaches the interface owing to an increase in the number density of porphyrins at the interface, and decreases when the porphyrins cross the interface (Figure 3 b). Furthermore, we found that positive polarization induces H-aggregation of $[CoTMPyP]^{4+}$ (the main resonance shifts to the blue), confirming the behavior observed when increasing the concentration of porphyrins. This indicates that $[CoTMPyP]^{4+}$ stack face-to-face, forming a sandwich-type arrangement similar to that reported for the self-assembled $[CoTMPyP]^{4+}/[CoTPPS]^{4-}$;[8d] in that case, DFT calculations suggested that the metal–metal distance was appropriated to drive the four-electron ORR by the formation of an *endo* oxygen adduct.[8d] In the case of the self-assembled $[CoTMPyP]^{4+}$, theoretical attempts to determine the geometry of the interfacial complexes were not conclusive. However, considering the catalytic activity results, the similarity between the self-assembled $[CoTMPyP]^{4+}$ and the self-assembled $[CoTMPyP]^{4+}/[CoTPPS]^{4-}$,[8d] and the evidence of the face-to-face aggregation, it sould be expected that in this case two cobalt atoms also participate in the reduction of one molecule of oxygen, and that the distance between them is appropriated to drive the ORR to water.

Secondary-electron SEM images of $[CoTMPyP]^{4+}$ at the [water | DCE] and [water | DCE(TB⁻)] interfaces, crystallized on a silicon substrate from a biphasic emulsion obtained by vigorous stirring, are shown in Figure 4. The image at the [water | DCE] interface (Figure 4 a) shows microstructures grown on silicon with a leaf-like asymmetric morphology. The most interesting SEM images were obtained at the [water | DCE(TB⁻)] interface (Figure 4 b), in which the microstructures surround bright circles that correspond to holes left behind after the evaporation of a drop of DCE containing BATB. The tree-like morphology of those assemblies is more complex than those obtained from the porphyrin in the bulk phase. This corroborates with the proposal that TB⁻ in the organic phase is assisting the self-assembly of $[CoTMPyP]^{4+}$.

In summary, the interfacial self-assembly of $[CoTMPyP]^{4+}$ is assisted and enhanced by its electrostatic interaction with the coordinating TB⁻ located in the organic phase. The catalytic structure formed by the self-assembling at the

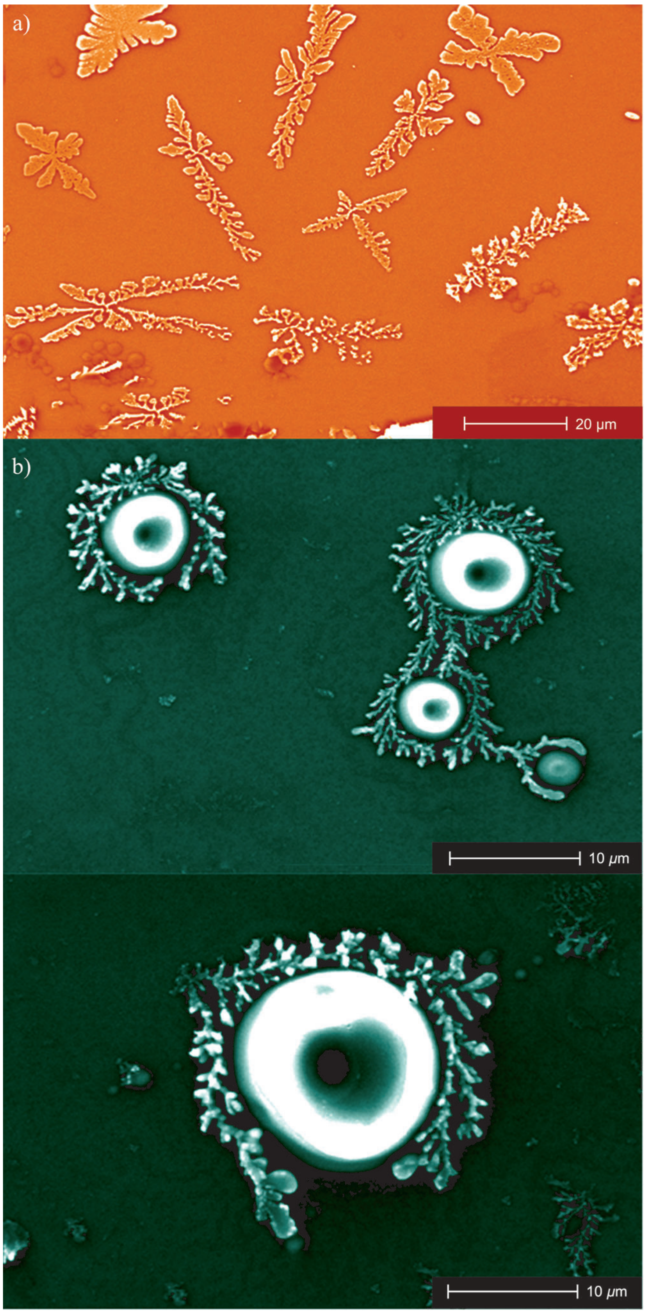

***Figure 4.*** Secondary-electron SEM images (10 kV) of $[\text{CoTMPyP}]^{4+}$ at the a) [water|DCE] and b) [water|DCE ($\text{TB}^-$)] interfaces.

interface proved an excellent selectivity to the four-electron ORR, being better than some synthetic cofacial porphyrins. This is important from a technological point of view, as it is an easy and relatively cheap way to form supramolecular catalysts. Furthermore, this work shows the potential of liquid|liquid interfaces as support media for the formation of supramolecular structures to carry out complex catalytic reactions.

## Experimental Section

Specifications of the reactants and description of the equipment and methods used are provided in the Supporting Information. The synthesis of BATB and $[\text{CoTMPyP}]^{4+}$, and a description of the setup used for the SSHG experiments, are reported in Ref. [8d].

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**Keywords:** interfaces · liquid–liquid interfaces · oxygen reduction reaction · porphyrins · self-assembly

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