

Supporting Information

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

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# Supporting Information

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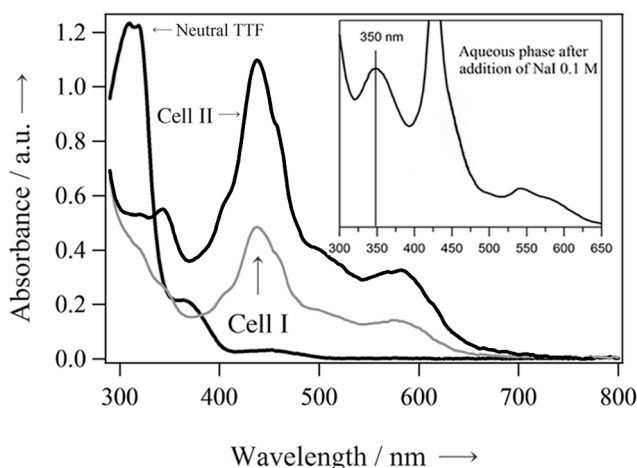
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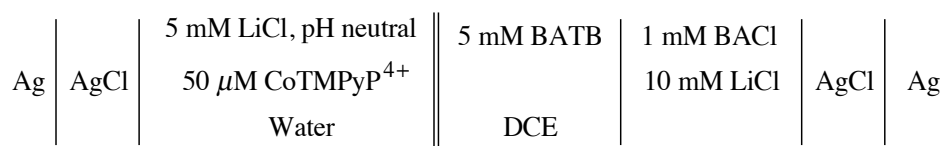
## SI1. Catalytic activity results



**Figure SI1.** UV-visible absorption spectra of the organic phase after 1 h of biphasic reaction by using the cells illustrated in Scheme 1 on the manuscript. The inserted figure corresponds to the aqueous phase (cell I) after 1 h of reaction and titration with sodium iodide (NaI).

## SI2. Ion-transfer voltammetry at ITIES.

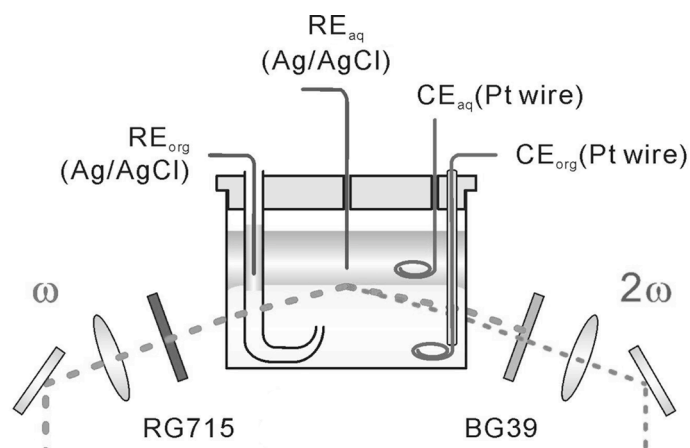
The transfer of  $\text{CoTMPyP}^{4+}$  at the water | DCE interface was studied by using the four-electrode cell described previously by Hatay et. al.<sup>[1]</sup> where two reference electrodes polarize the interface and two platinum counter electrodes provide the current. The external potential is applied by means of two silver/silver chloride (Ag/AgCl) reference electrodes, which are connected to both phases by means of a Luggin capillary. A commercial potentiostat (PGSTAT 30, Metrohm, CH) was used. The Galvani potential difference was estimated by taking the formal ion transfer potential of TMA<sup>+</sup> as 0.18 V. The schematic representation of the initial composition of the four-electrode cell is illustrated in Figure SI2.



**Figure SI2.** Initial composition of the electrochemical cell used to study the transfer of CoTMPyP<sup>4+</sup>.

**SI3. Dependence of the SSHG spectrum of CoTMPyP<sup>4+</sup> on the polarization of the interface.**

The cell used for studying the dependence of the SSHG spectrum of CoTMPyP<sup>4+</sup> on the polarization of the interface was previously described by Nagatani et. al [2]. and follows the same configuration described in Section SI2, see Figure SI2 for the composition of the cell and Figure SI3 for a schematic representation of the cell. SSHG spectra of 50 CoTMPyP<sup>4+</sup> were recorded at different potentials. In order to ensure the accuracy of the results, each SSHG spectrum (at a determined potential) was recorded using fresh solutions after cleaning carefully the cell. The equilibration time before recording each spectrum under at a specified potential was 15 seconds and the potential was applied by using chronoamperometry. The SSHG signal was averaged over 300 laser shots.



**Figure SI3.** Electrochemical SSHG cell used to study the dependence of the SSHG spectrum of  $\text{CoTMPyP}^{4+}$  on the polarization of the interface. RE: Reference electrode, CE: counter electrode.

#### SI4. Reactants.

All solvents and chemicals were used as received without further purification. Bis(triphenylphosphoranylidene)ammonium chloride (BACl 98%), tetrakis(pentafluorophenyl)-borate ethyl etherate (LiTB purum) and lithium chloride (LiCl >99%) were purchased from Fluka. Chlorhydric acid (37-38%) and 1,2-dichloroethane (DCE, grade HPLC) were purchased from Merck and Applichem respectively. Tetrathiafulvalene (TTF 99+%) was purchased from Acros and sodium iodide (NaI 98%) was purchased from Aldrich.

#### SI5. Biphasic Reactions.

The composition of the cells is illustrated in Scheme 1 on the main manuscript and all the experiments were performed with air-saturated solutions at room temperature ( $21 \pm 2$  °C). The biphasic reactions were performed in glass flasks with a volume of 4 mL (2mL each phase) under stirring at 900 rpm. In order to perform the analysis of the

products of the reaction, the aqueous and organic solutions were isolated from each other after 1 hour of reaction. The organic phase was directly subjected to the UV-visible spectroscopy in order to confirm formation of the radical cation TTF<sup>•+</sup> (1 mm optical path), while the aqueous phase was treated with NaI in excess (equivalent to 0.1 M) prior to the UV-visible spectroscopic measurement in order to detect the formation of from the oxidation of I<sup>-</sup> by H<sub>2</sub>O<sub>2</sub> (10 mm optical path). The UV-visible absorption spectra were recorded with a standard spectrophotometer (Ocean Optical, model Chem2000) using quartz cells.

#### **SI6. Scanning Electron Microscopy (SEM) of the self-assembled CoTMPyP<sup>4+</sup>.**

For the SEM analyses the samples were prepared by shaking the interface formed between 50 μM of the porphyrin and pure DCE or BATB in DCE. Afterwards, drops of the resultant emulsion were placed on a silicon film and allowed dry slowly at room temperature. The images were acquired using a Philips FEI XLF-30 microscope at 10 kV.

#### **References**

- [1] I. Hatay, B. Su, F. Li, M. A. Mendez, T. Khoury, C. P. Gros, J. M. Barbe, M. Ersoz, Z. Samec, H. H. Girault, *J. Am. Chem. Soc.* **2009**, *131*, 13453.
- [2] H. Nagatani, A. Piron, P. F. Brevet, D. J. Fermin, H. H. Girault, *Langmuir* **2002**, *18*, 6647.