

# ORR Activity of Metalated Phenanthroline-Strapped Porphyrin Adsorbed on Carbon Nanotubes

Manel Hanana,<sup>a</sup> Christophe Kahlfuss,<sup>b</sup> Jean Weiss,<sup>b</sup> Renaud Cornut,<sup>a</sup> Bruno Jusselme,<sup>a</sup> Jennifer A. Wytko<sup>b,\*</sup> and Stéphane Campidelli<sup>a,\*</sup>

<sup>a</sup>Université Paris-Saclay, CEA, CNRS, NIMBE, LICSEN, 91191, Gif-sur-Yvette, France. Telephone: +33 (0)1-69-08-51-34

<sup>b</sup>Institut de Chimie de Strasbourg, UMR 7177 CNRS-Université de Strasbourg, 4 rue Blaise Pascal, 67008 Strasbourg, France. Telephone: +33-(0)3-68-85-14-24

Email: [stephane.campidelli@cea.fr](mailto:stephane.campidelli@cea.fr); [jwytko@unistra.fr](mailto:jwytko@unistra.fr)

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## Synthesis.

**Synthesis of Fe-P.** A suspension of strapped porphyrin **H<sub>2</sub>P** (51 mg, 49  $\mu$ mol) was in DMF was degassed by bubbling Ar through it for 30 min. The mixture was heated at 160 °C, then FeCl<sub>2</sub> (62 mg, 0.49 mmol) was added through a solid addition tube. The mixture was stirred at the same temperature for 18 h under Ar, then cooled to rt and exposed to air for 1 h. The solvent was evaporated under reduced pressure and the crude product was taken in CH<sub>2</sub>Cl<sub>2</sub> and washed with 2M HCl<sub>(aq)</sub>. The organic phase was filtered over an alumina plug (CH<sub>2</sub>Cl<sub>2</sub>) and evaporated under reduced pressure. The product was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and HCl was bubbled through the solution for 15 min at rt. The solvent was evaporated under reduced pressure to yield **Fe-P** (44 mg, 38  $\mu$ mol, 80%) as a brownish solid. MS (ESI+) m/z calc. for [M+H]<sup>+</sup>: 1136.42, found: 1136.42; MS (MALDI-TOF): m/z calc. for [M-Cl]<sup>+</sup>: 1110.444, found: 1100.473.

**Synthesis of Cu/Fe-P.** Tetrakis(acetonitrile)copper(I) hexafluorophosphate (15 mg, 40  $\mu$ mol) was added through a solid addition tube to a degassed solution of **Fe-P** (45 mg, 40  $\mu$ mol) in dry dichloromethane. The resulting mixture was stirred at rt for 18 h under argon and then evaporated to dryness to yield **Cu/Fe-P** (50 mg, 40  $\mu$ mol, 100%) as a brown solid. MS (MALDI-TOF) m/z calc. for [M-Cl]<sup>+</sup>: 1198.342, found: 1198.430.

## Sample preparation.

**MWNT.** MWNTs (Nanocyl NC3100™) (60 mg) were sonicated in nitric acid (35 vol %) (150 mL) with an ultrasound bath (Fisherbrand, 37 kHz, power 100% for 10 min and then 40% for 30 min) and then heated at 100 °C for 5 h. The suspension was then cooled and filtered under vacuum through a 0.2  $\mu$ m PTFE membrane and washed with water. The nanotubes were redispersed in 2 M NaOH (100 mL) using the ultrasound bath (100% for 10 min) and then filtered through a PTFE membrane and washed with deionized water, and then 1 M HCl followed by deionized water until the filtrate was neutral.

**MWNT-Fe-P and MWNT-Cu/Fe-P.** A mixture of purified **MWNT** (9 mg) and porphyrin **Fe-P** or **Cu/Fe-P** (3 mg) in dry THF (10 mL) was homogenized using an ultrasound bath (Fisherbrand, 37 kHz, power 100%) for 15 min. The THF was gently evaporated with a stream of N<sub>2</sub> and the mixtures were dried under vacuum.

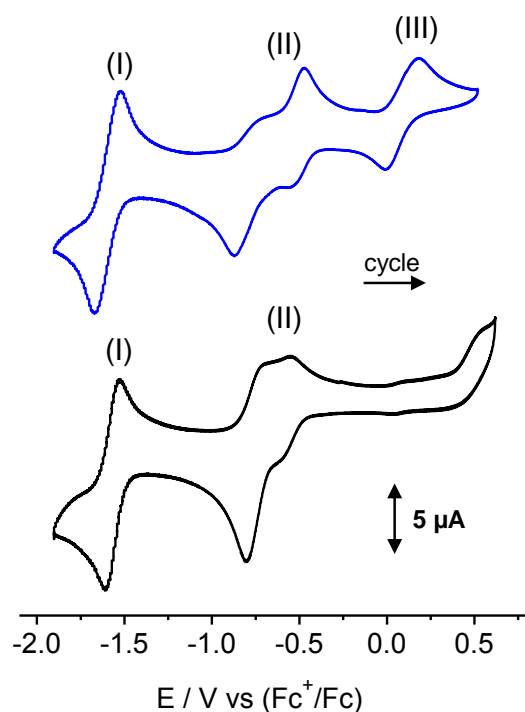
Three milligrams of each mixture (**MWNT-Fe-P** and **MWNT-Cu/Fe-P**) were dispersed in 750 µL of ethanol and 75 µL of Nafion solution (5% in alcohol). The mixtures were homogenized using an ultrasound bath until they formed homogenous inks. For the **MWNT** ink, the same procedure was followed but without adding porphyrins. For the reference **Fe-P** and **Cu/Fe-P** inks, 3 mg of porphyrin were directly dispersed in 750 µL of ethanol and 75 µL of Nafion solution (5% in alcohol)

#### **Electrochemical experiments.**

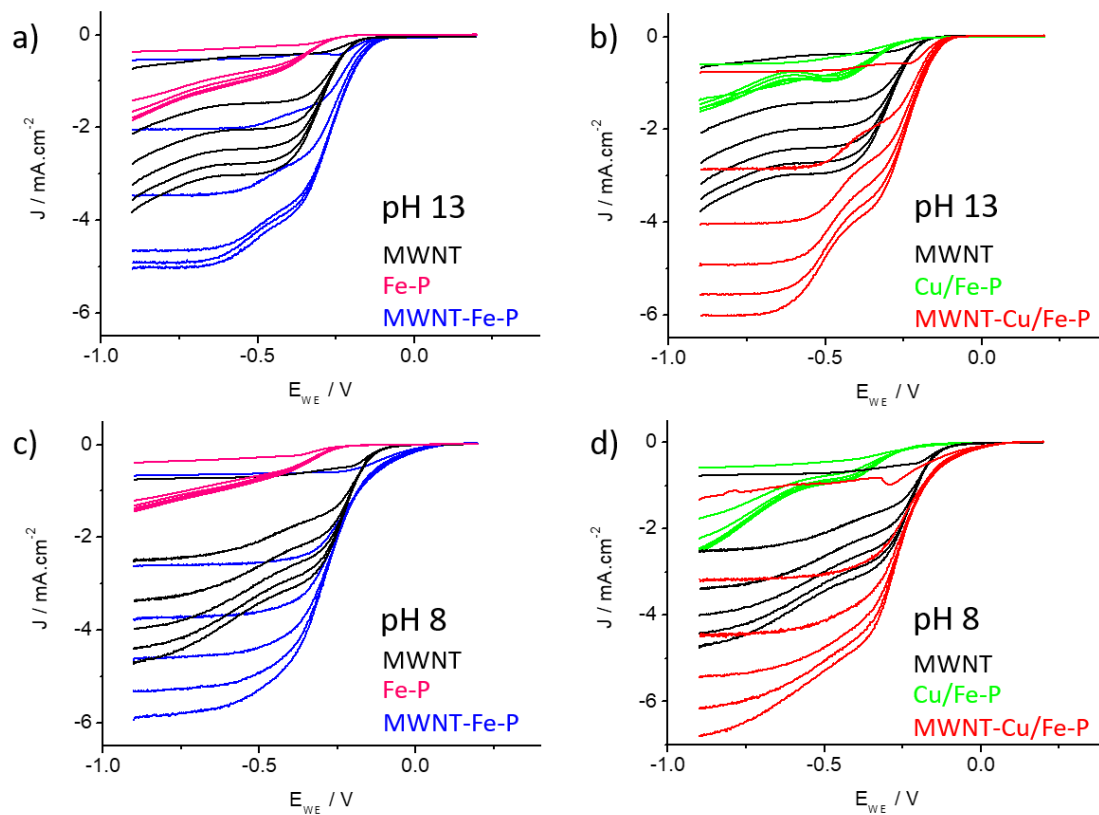
**Electrode preparation.** Before each measurement, the glassy carbon (GC) disk (5 mm, 0.196 cm<sup>2</sup>) used as rotating electrode was polished with aqueous dispersions of synthetic diamonds (1 µm), then rinsed and sonicated with water. Aliquots (5 µL) of the catalyst inks were deposited by drop-casting onto the GC disk, then air-dried. For experiments at pH 6, a new ink was deposited onto the GC disk for each rotation step.

**Electrochemical measurements.** The instrument used was a VSP bipotentiostat (Bio-Logic SAS). The CVs of **Fe-P** and **Cu/Fe-P** were performed in a 0.1 M tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) THF solution in an electrochemical cell equipped with a glassy carbon working electrode, a platinum counter electrode and an Ag/AgNO<sub>3</sub> (10 mM) reference electrode. The potentials are reported vs ferrocene used as internal reference. The solutions were degassed by bubbling argon and the cyclic voltammetry was performed at a scan rate of 20 mV/s. For ORR, the electrochemical tests were carried out on solutions at pH 13 (0.1 M NaOH), 10 and 8 (phosphate buffers) in a three electrode glass cell, thermostated at 25 °C. A “CE to Ground” connection with a saturated KCl - Ag/AgCl electrode as reference and a graphite plate as counter electrode was used. As working electrode, a Pine rotating ring disk electrode (RRDE) with catalyst-loaded GC disk (0.196 cm<sup>2</sup>) and Pt

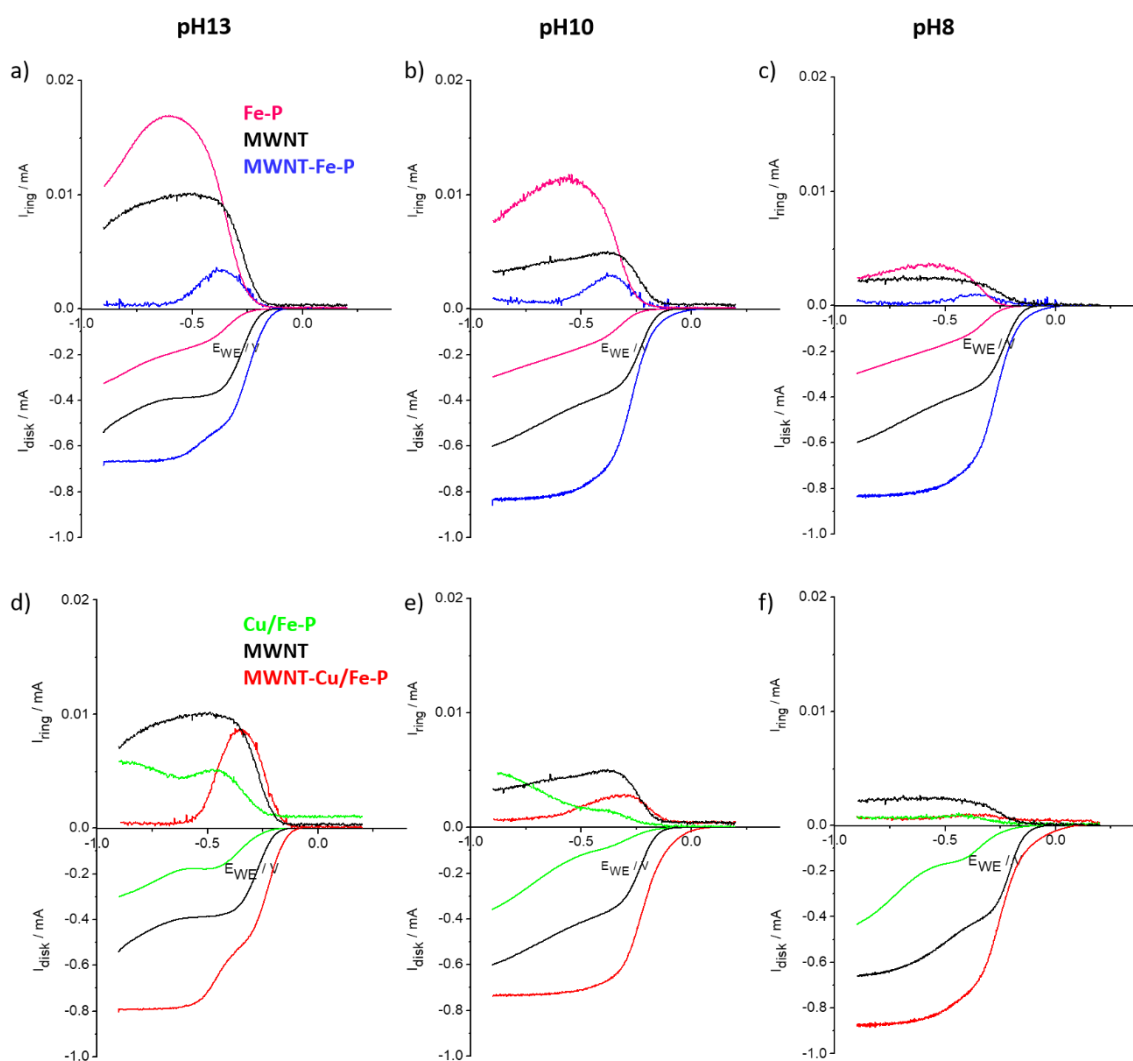
ring (0.110 cm<sup>2</sup>) was controlled by a speed control unit from Princeton Applied Research Model 636 Electrode Rotator. The voltammograms were recorded at 5 mV.s<sup>-1</sup> in stationary conditions (with various rotating rates: 0, 400, 800, 1200, 1600, and 2000 rpm) in O<sub>2</sub>-saturated solutions. An average current was calculated from the forward and backward scans. All potentials reported in this paper refer to that of the Ag/AgCl electrode. H<sub>2</sub>O<sub>2</sub> production was monitored in the RRDE configuration at 400 rpm with a CV at the GC disk (5 mV.s<sup>-1</sup>). The collection coefficient of the RRDE (0.20) was measured using the one-electron [Fe(CN)<sub>6</sub>]<sup>3-</sup>/[Fe(CN)<sub>6</sub>]<sup>4-</sup> redox couple, according to the manufacturer's instructions.



**Fig. S1** Cyclic voltammetry (second cycle) of 1 mM **Fe-P** (black curve) and **Cu/Fe-P** (blue curve) in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> THF solution at 20 mV/s under argon.



**Fig. S2** Polarization curves at different rotation rates (0, 400, 800, 1200, 1600 and 2000 rpm) for **Fe-P** (pink curves), **MWNT** (black curves) and **MWNT-Fe-P** (blue curves) and for **Cu/Fe-P** (green curves), **MWNT** (black curves) and **MWNT-Cu/Fe-P** (red curves) recorded for ORR in  $O_2$ -saturated phosphate buffer solutions at different pH (scan rate = 5 mV/s, room temperature).



**Fig. S3** (a-c) RRDE curves with disk and ring currents for **MWNT-Fe-P** (blue), **MWNT** (black) and **Fe-P** (pink) at pH 13, 10 and 8, respectively with a rotation rate of 800 rpm; (d-f) RRDE curves with disk and ring currents for **MWNT-Cu/Fe-P** (red), **MWNT** (black) and **Cu/Fe-P** (green) at pH 13, 10 and 8, respectively with a rotation rate of 800 rpm.