Supporting Information

Glucose fuel cell based on carbon nanotube-supported pyrene-metalloporphyrin catalysts

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1. Materials and methods

Commercially available reagents form Aldrich were used as received unless mentioned otherwise. Commercial grade thin Multi-Walled Carbon Nanotubes (MWNT) (9.5 nm diameter, purity >95%), obtained from Nanocyl were used as received without any further purification step. Deuteroporphin IX dimethyl ester, and meso-tetrakis-(4-carboxyphenyl) porphyrin were purchased from ABCR. All other reagents, solvents, acids, and bases were of special grade and were used as received. NMR spectra were recorded on a Bruker AVANCE 400 operating at 400.0 MHz for ^{1}H. ESI mass spectra were recorded with a Bruker APEX-Qe ESI FT-ICR mass spectrometer. Electrochemical measurements were performed at room temperature with an Autolab electrochemical analyzer (Eco Chemie, Utrecht, The Netherlands) controlled by GPES software (Eco Chemie).

2. Electrochemical Experiments

Aqueous solutions were prepared using Milli-Q purified water (>18 MΩ cm^{-1}). Experiments at neutral condition (pH 7) and alkaline conditions (pH 13) were performed in phosphate buffer solution and in KOH (0.1 M) diluted with Milli-Q water, respectively. Rotating disk electrode (RDE) electrochemical experiments were performed by using a glassy carbon working electrode (A =0.071 cm^2), a Pt wire counter electrode separated by a glass frit, and a saturated calomel electrode (SCE) as reference electrode.

RDE experiments were performed in a three electrode electrochemical cell setup connected to a MSR rotator (Pine Instruments). The surface of GC electrodes were polished with a 2 µm diamond paste purchased from Presi (France), washed with water using ultrasound, and rinsed with acetone and ethanol. The solutions were deoxygenated by purging with argon prior to each experiment and an argon flow was kept over the solution during the whole experiment. The solutions were oxygenated by purging with oxygen gas prior to each experiment and an oxygen flow was kept over the solution during the oxygen electroreduction experiments.

3. Preparation of metalloporphyrin electrodes

MWCNT electrodes modified catalysts with or without pyrenes were fabricated using the following procedure: First, MWCNTs (5 mg) were added to 1 ml of NMP solvent. The suspension was homogenized by an ultrasonic generator for 30 minutes to ensure maximum dispersion. To this suspension was added 1 mg of the catalyst as a

solid. Non-covalent immobilization of each catalyst was allowed to occur for 2 h and the resulting suspensions were used as electrocatalytic ink.

For cathodic or anodic electrochemical investigations, a portion (20 µL) of this ink was dropped onto a freshly polished GC disk electrode and the solvent was removed under reduced pressure. The functionalized electrodes were rinsed several times with NMP, DMF, and then with pure water.

For glucose fuel cell experiments, the electrocatalytic inks were deposited on GC electrodes as anodic and cathodic compartments using the same aforementioned drop casting technique. The catalysts were deposited at room temperature and the solvent was removed under vacuum. The fuel cell electrolyte, containing 0.5M glucose in 0.1 M KOH solution or 0.5M glucose in phosphate buffer solution, was oxygenated by an oxygen flow kept over the solution during the whole fuel cell experiments. The active area of the fuel cell is 0.071 cm^2. The fuel cells are tested in ambient conditions at 20°C.

4. Preparation of pyrene-metalloporphyrin complexes

4.1. Pyrene-functionalized rhodium deuteroporphyrin (Rh(DP)pyr_2).

Deuterioporphyrin dimethyl ester (100 mg, 0.186 mmol) was dissolved in THF (20 mL). After the addition of 5 N aq. KOH (20 mL), the reaction mixture was vigorously stirred under argon at 70 °C for 18 h. The reaction was monitored by TLC: in CH_2Cl_2/MeOH (100:1) in order to control the migration of the diacid formed compared to the ester reagent. The formed diacids were extracted with 400 ml of ethyl acetate which was washed three times with H_2O. The organic phase was dried over Na_2SO_4 and the solvent was removed yielding the violet product which was treated with diethyl ether. After filtration through a frit, the collected solid was washed several times with diethyl ether, H_2O and methanol. Drying under high vacuum gave 60 mg (63%).

^{1}H NMR (DMSO): δ 12.1 (s, 2H), 10.26, 10.23, 10.19, 9.27 (4s, 6H), 4.35 (t, 4H), 3.72, 3.7, 3.62, 3.60 (4s, 12H), 3.2 (t, 4H) and -4.24 (s, 2H).

ESI-MS m/z (H_2O/DMSO): 509.0 $[M-H]^-$.

Pyrene-methylamine was obtained from pyrene-methylamine hydrochloride by extraction with dichloromethane from a NaOH aqueous solution as follows. Pyrenemethylamine hydrochloride (268 mg, 1.0 mmol) was added to a solution of NaOH (60 mg, 1.5 mmol) in water (30 mL). The resulting suspension was extracted with CH_2Cl_2 (3×20 mL). Removal of the solvent under vacuum yielded a white power of pyrenemethylamine (205 mg, 0.9 mmol).

Dicyclohexylcarbodiimide (103 mg, 0.5 mmol) was added to deuterioporphyrin diacid (50 mg, 0.1 mmol) dissolved in 20 mL of dry DMF in an ice bath. The solution was stirred under argon for 1 h at 0 °C and then N-hydroxysuccinimide (0.34 mg, 0.3 mmol) was added. The reaction mixture was agitated for 2 h under argon at room temperature. Thereafter pyrenemethylamine (68 mg, 0.30 mmol) and triethylamine (0.1 mL) dissolved in DMF (2 mL) were added. The reaction mixture was stirred overnight at room temperature. The reaction mixture was then concentrated in a vacuum to a volume of 1 mL, diethyl ether (10 mL) was added and the crude product precipitated as a dark-brown solid. The solid residue was filtered and washed with 1 N aq. HCl, 0.1M KOH and saturated sodium hydrogen carbonate solution. The solid residue was chromatographed on silica gel eluting with dichloromethane/ethanol (100/1) to give 57 mg (60%) (DP)pyr_2 as a red-brown solid.

^{1}H NMR (DMSO): δ -3.78 (s, 2 H), 3.13 (t, 4 H), 3.54 (s, 3 H,), 3.56 (s, 3 H), 3.77 (s, 3 H), 3.82 (s, 3 H),4.38 (t, 4 H), 4.59 (t, 4 H), 5.05 (d, 2 H), 6.45-8.45 (m, 18 H), 9.36 (s, 1H), 9.44 (s, 1H), 10.26 (s, 1H), 10.28 (s, 1H), 10.46 (s, 1H), 10.49 (s, 1H).

ESI-MS m/z (DMSO): 936.0 $[DP(pyr)_2]^-$.

$RhDP(pyr)_2$ metalloporphyrin was prepared by refluxing the metal-free $DP(pyr)_2$ (15mg, 0.016 mmol) with Rh2Cl2(CO)4 (10.0 mg, 0.026 moml) in ethanol (60 mL) for 5 hours. After reflux, the solvent was removed under reduced pressure. It was taken up in dichloromethane (50 mL washed with water. The organic phase was concentrated and the residue was chromatographed eluting with dichloromethane. Finally, the metaled product $RhDP(pyr)_2$ was obtained as a reddish solid (13 mg, 76%).

^{1}H NMR ($CDCl_3$): δ 3.07 (t, 4 H), 3.54 (s, 3 H,), 3.69 (s, 3 H), 3.81 (s, 3 H), 3.82 (s, 3 H),4.38 (t, 4 H), 4.59 (t, 4 H), 5.04 (d, 2 H), 6.5-8.14 (m, 18 H), 9.15 (s, 1H), 9.20 (s, 1H), 10.21 (s, 1H), 10.29 (s, 1H), 10.34 (s, 1H), 10.45 (s, 1H).
ESI-MS m/z (DMSO): 1037.0 $[RhDP(pyr)_2]^+$, 1065.0 $[RhDP(pyr)_2)(EtOH)]^+$.

4.2. Pyrene-functionalized cobalt tetracarboxyphenyl porphyrin (Co(TCPP)pyr4).

Meso-tetrakis-(4-carboxyphenyl) porphyrin (100 mg, 0.125 mmol) was dissolved in 10 ml of anhydrous methylene chloride. 1.5 ml of a 2 M solution of oxalyl chloride in methylene chloride (3 mmol) and a catalytic amount of DMF (1 μl) was added. The mixture was stirred overnight under an atmosphere of nitrogen. After concentrating the solution in a stream of dry nitrogen and drying the green solid under high vacuum, which it was used in the next step without further purification.

The crude acid chloride was redissolved in 10 ml of dry DMF. A solution of the pyrenemethylamine (227.7 mg, 1 mmol, 8 equivalents) and 500 μl of triethylamine in 5ml of dry DMF were added. The resulting mixture was stirred under an inert atmosphere for 2 days. After completion of the reaction, the solution was concentrated and respectively washed with 10% citric acid, 1N NaOH, and dichloromethane (50 mL). The crude product was redissolved again in 10 ml of dry DMF and cobalt acetate (88 mg, 0.625 mmol) was added, stirred and refluxed for 5 h. after evaporation of the solvent, column chromatography with methylene chloride/methanol(15:1) afforded the desired $Co(TCPP)pyr_4$ compound (45 mg, 21%).

^{1}H NMR (DMSO): δ: 9.62 (s, 4H), 8.84 (s, 8H), 8.39-7.96 (m, 44H), 7.59 (d, 4H), 7.56 (d, 4H), 5.41 (d, 8H).

MALDI-TOF m/z (DMSO): 1703 $[Co\ (TCPP)pyr_4]$.