Supporting information for:

Molecular porphyrinic freestanding buckypaper electrodes from carbon nanotubes for glucose fuel cells

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1. Materials and Instrumentation:

Chemicals used in this work were purchased from Sigma-Aldrich and used as received unless mentioned otherwise.

The morphology was observed using scanning electron microscopy SEM (JEOL, JSM-6700F, 5 kV) and TEM (JEOL, JEM-2010, 200 kV). Nuclear magnetic resonance (NMR) spectroscopy was carried out with Bruker Avance 400 NMR spectrometer operating at 400.0 MHz. ESI mass spectra were recorded with a Bruker APEX-Qe ESI FT-ICR mass spectrometer. Brunauer–Emmett–Teller (BET) specific surface area of samples was measured at 77 K with a Micromeritics ASAP 2020 HD88 system. The electric resistance was measured by a DC voltage/current four-point probe method using a Jandel (RM3). UV-vis spectra were measured using a UV-1500 PC photodiode array spectrophotometer equipped with a quartz cell (light path = 1 cm). All Electrochemical measurements were performed at room temperature with an Autolab electrochemical analyzer (Eco Chemie, Utrecht, and The Netherlands

2. Synthesis:

the synthesis and characterization of Co(TCPP)pyr_4 have been previously described.[15] The synthesis of Rh(TCPP)pyr_4 was performed by slightly modifications of established literature reported method[15] using the following procedure: 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 nitrogen. After concentrating the solution in a stream of dry nitrogen then under high vacuum, 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 nitrogen overnight. The solution was concentrated and respectively washed with 10% citric acid, 1N NaOH, and dichloromethane (50 mL). The crude product was dissolved again in 50 ml of dry DMF and $Rh_2Cl_2(CO)_4$ (15.0 mg) was added, stirred and refluxed for 7 h. After evaporation of the solvent, column chromatography was eluted with dichloromethane then dichloromethane/ethanol (15:1) to afford the desired Rh(TCPP)pyr_4 complex (29 mg).

^{1}H NMR (400 MHz, DMSO-d6, δ): 9.78 (s, 4H), 8.91 (s, 8H), 8.59-7.86 (m, 44H), 7.66 (d, 4H), 7.58 (d, 4H), 5.44 (d, 8H).

MS (ESI) (DMSO) m/z: $[Rh(TCPP)pyr_4]^+$ calcd for C116H80N8O4Rh, 1752.5; found, 1752.9.

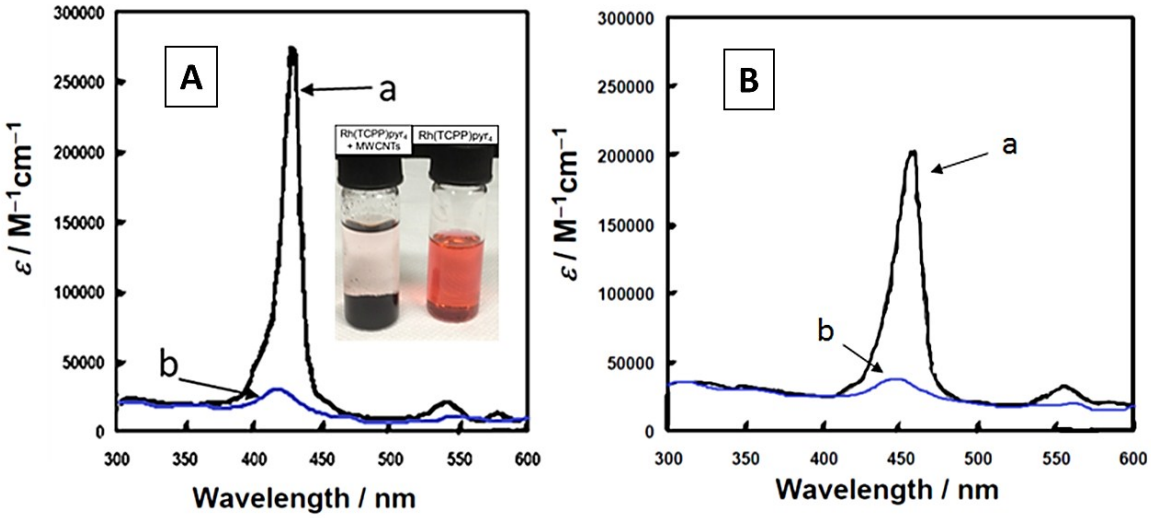

Figure S1. UV spectra of A: Rh(TCPP)pyr_4 a) solution before filtration b) outflow collection solution (Inset before and after adding MWCNT to an initial solution of Rh(TCPP)pyr_4) . B) Co(TCPP)pyr_4 a) solution before filtration b) outflow collection solution. The measurements were performed in DMF.