

Supporting Information

From gold porphyrin to gold nanoparticles: application to glucose oxidation

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Experimental

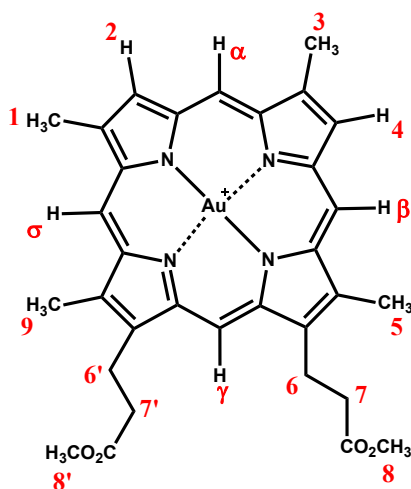
1. Materials

Commercially available reagents, α -D-Glucose, anhydrous NaOAc, H₂AuCl₄, Nafion®, 1-methyl-2-pyrrolidinone (NMP), and potassium hydroxide (KOH) were of analytical grade and purchased from Sigma-Aldrich. 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 was purchased from ABCR. All other reagents, solvents, acids, and bases were of special grade and were used as received.

2. Preparation of Gold(III) Porphyrin Complexes

The synthesis of the gold(III) porphyrins was conducted under an inert atmosphere. The **(DPDE)Au(III)** complexes were prepared according to the following protocol:

H₂AuCl₄ (91 mg, 0.27 mmol) and anhydrous NaOAc (73 mg, 0.88 mmol) were dissolved in acetic acid (5 mL). The mixture was protected from light and stirred for 10 min at room temperature. Deuteroporphin IX dimethyl ester (50 mg, 0.11 mmol) was added and the mixture was heated to 120°C over 4 h under argon. Complete metallation of the porphyrins was checked by disappearance of two Q bands of H₂(DPDE) using UV-Vis spectroscopy. Upon removal of the solvent under vacuum, the residue was dissolved in CH₂Cl₂ (50 mL). The organic phase was washed with saturated aqueous Na₂CO₃ and water. The organic phase was dried over MgSO₄ and evaporated. The crude mixture was purified by column chromatography with CH₂Cl₂ as eluant to remove unreacted compounds. Finally, (DPDE)Au(III) was then collected using a CH₂Cl₂/MeOH (99:1, v/v) mixture, affording the desired porphyrin as a reddish-purple solid (55 mg, 0.075 mmol, 68 %).



NMR δ_{H} (400 MHz; CDCl_3): 10.2-10.6 (3s, 4H, $\underline{\alpha-\beta-\gamma-\sigma}$), 9.1 (s, 2H, $\underline{2-4}$), 4.52 (t, 4H, $\underline{6-6'}$), 3.77 (s, 6H, $\underline{8-8'}$), 3.69 (s, 6H, $\underline{5-9}$), 3.52 (s, 6H, $\underline{1-3}$), 3.34 (t, 4H, $\underline{7-7'}$).

UV-vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \text{ mM}^{-1} \text{ cm}^{-1}$): 388 (120), 507 (15), 543 (22).

ESI-MS m/z (acetonitrile): 733.3 [(DPDE)Au(III)]⁺.

2. General Methods

Ultrapure water was obtained from a Milli-Q Purelab UHQ (Elga) with a resistivity of 18.2 $\text{M}\Omega \text{ cm}^{-1}$. Electrochemical measurements were performed at 20 °C with an Autolab electrochemical analyzer (Eco Chemie, Utrecht, The Netherlands) controlled by GPES software (Eco Chemie). X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Surface Science Instruments (SSI) spectrometer employing monochromatic Al $K\alpha$ radiation as the X-ray source. Electrodes for XPS measurements were fabricated using the following procedure: MWCNTs (5 mg) were added to 1 mL of NMP solvent containing 1 mg of the product (without Nafion[®]). The suspension was homogenized by an ultrasonic generator for 30 min. A portion (50 μL) of this suspension was dropped onto carbon felts. The solvent was removed under reduced pressure.

NMR spectra were recorded on a Bruker AVANCE 400 operating at 400.0 MHz for ^1H . ESI mass spectra were recorded with a Bruker APEX-Qe ESI FT-ICR mass spectrometer. UV-visible spectra were recorded with a Carry 1 spectrophotometer with a quartz cuvette (1 cm thickness).

The morphology of the MWCNT electrodes was investigated by scanning electron microscopy (SEM) using a Zeiss ULTRA 55 FESEM equipped with the GEMINI column with a beam booster (Nanotechnology Systems Division, Carl Zeiss NTS GmbH, Germany). For transmission electron microscopy (TEM) observation, drops of dilute MWCNT/(DPDE)Au(III) suspension in THF was deposited onto glow-discharged carbon-coated electron microscopy grids and allowed to dry. The samples were observed using a Philips CM200 microscope (FEI Company, Hillsboro, OR, USA) operating at 80 kV. Micrographs were recorded on Kodak SO163 films. The samples used for electrochemical investigations or modification were prepared for TEM by scraping off the deposited MWCNTs films from the GC electrodes and dispersed by sonication in THF for 2 min. Then, a drop of this suspension was put onto a Cu grid and allowed to dry in air.

3. Electrochemical Measurements

Cyclic voltammetry (CV) was performed in a conventional three-electrode cell equipped with a glassy carbon (GC) electrode (geometric area = 0.071 cm²), a platinum wire counter-electrode and a saturated calomel electrode (SCE) as reference electrode for aqueous media. The electrochemical experiments, performed in organic media, were carried out in a three-electrode electrochemical cell under a dry argon atmosphere and in a glove box ([O₂] < 20 ppm). A Pt wire placed in a separated compartment was used as counter electrode, and the Ag/AgNO₃ 10 mmol L⁻¹ in DMF + TBAP (0.1 M) served as reference electrode. Potentials given are referred to this (Ag/AgNO₃) electrode.

The GC electrodes were polished with 2 μm diamond paste, purchased from Presi (France), followed by rinsing thoroughly with Milli-Q water using ultrasound. After further rinsing with acetone and ethanol, the GCs were dried at room temperature.

Electrocatalytic experiments were performed in aqueous KOH solutions at pH = 13. All E_{1/2} values reported in this work were determined from cyclic voltammogram as an average of the oxidative and reductive peak potentials (E_{p,a}+E_{p,c})/2. The aqueous solutions were deoxygenated by purging with argon prior to each experiment and an argon flow was kept over the solution during the whole experiment.

4. Fabrication of MWCNT/(DPDE)Au(III) electrodes

MWCNT/(DPDE)Au(III) electrodes were fabricated using the following procedure: MWCNTs (5 mg) were added to 1 mL of NMP solvent containing 1 mg of the (DPDE)Au(III) complex and 5 μ L Nafion® (the Nafion® solution contains 5% Nafion, 25% 2-propanol, 25% n-propanol, 45% water). The suspension was homogenized by an ultrasonic generator for 30 min. The resulting supernatant was used as catalyst ink. For electrochemical investigations, a portion (20 μ L) of this suspension was dropped onto a freshly polished GC disk electrode (3 mm in diameter). The solvent was removed under reduced pressure.