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Supplementary information

Non-covalent double functionalization of carbon nanotubes with a NADH oxidation Ru(II)-based molecular catalyst and a NAD-dependent glucose dehydrogenase

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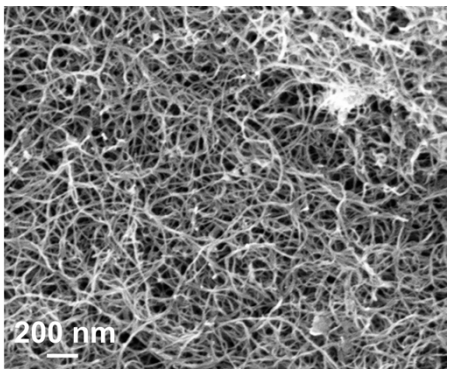

Figure S1. SEM image of functionalized MWCNT electrode

Experimental

Materials and methods

Acetonitrile (HPLC grade) used for electrochemistry measurements was obtained from Rathburn and used without further modification. Tetrabutylammonium perchlorate (Fluka) [Bu4N]ClO4 (TBAP) was used as supporting electrolyte in organic media. All chemical products and GDH from *Pseudomonas sp.* (235 U mg^{-1}) were purchased from Aldrich and used as received unless it is mentioned. 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-visble spectra were recorded with a Perkin Elmer Lambda 650 spectrophotometer with a quartz cuvette (1 cm depth).

Electrochemistry measurements

The electrochemical experiments performed in MeCN were carried out in a three-electrode electrochemical cell under dry argon atmosphere and in a glove box ([O_2] <20 ppm). The surface of GC electrodes were polished with a 2 µm diamond paste purchased from Presi (France), and rinsed successively with water, acetone and ethanol.
A Pt wire placed in a separated compartment was used as counter electrode and the $Ag/AgNO_3$ 10 mM in MeCN + TBAP (0.1 M) served as reference electrode in organic media. Potentials given in organic and aqueous media are referred to the (Ag/AgNO3) electrode and the saturated calomel electrode (SCE) respectively.

For electrochemical experiments performed in aqueous media a platinum grid was used as the counter electrode and a saturated calomel electrode served as reference electrode.
All electrochemical experiments were recorded on a Autolab PGSTAT100 potentiostat.

Synthesis

[$Ru(Phendion)_2Cl_2$] and 4,4'-bis(4-pyrenyl-1-ylbutyloxy)-2,2'-bipyridine) were synthesized according to previously described procedures[1,2].
Synthesis of [(1,10-phenathroline-5,6-dione)$_2$((4,4'-bis(4-pyrenyl-1-ylbutyloxy)-2,2'-bipyridine)Ru(II)]$(PF_6)_2$ (RuQ-pyrene): A solution of 4,4'-bis(4-pyrenyl-1-ylbutyloxy)-2,2'-bipyridine) (48mg) and [$Ru(Phendion)_2Cl_2$] (40mg) in ethylene glycol (3 mL) was refluxed for 1.5h under argon. After cooling down to room temperature, a 10mL aqueous solution of saturated NH_4PF_6 was added, allowing the as-formed product to precipitate. The orange brown precipitate was then filtrated, washed with water and Et_2O, yielding 70mg of product (68% yield). ^{1}H NMR: δ_H/ppm (400 MHz, CD_3CN): 1.98-2.01 (m, 8H), 3.43 (d, J = 8Hz, 4H), 4.22-4.26 (m, 4H), (dd, J = ,2H), 7.53 (d, J = 6.4Hz 2H), 7.57-7.64 (m, 4H), 7.91-7.96 (m, 4H), 7.97-8.02 (m, 4H), 8.04-8.06 (m, 6H), 8.09-8.14 (m, 4H), 8.15-8.21 (m, 6H), 8.33 (d, J = 10Hz, 2H), 8.50 (d, J = 7.6Hz, 2H) ; MS (ESI+): 611.2 (M-2PF_6^{2+}), 1367.3 (M-PF_6^+) ; UV/Vis (DMF) : λmax / nm (ε / M^{-1} cm^{-1}) = 312 (42700), 328 (61800), 345 (80900), 442 (14700)

Fabrication of the electrodes

Commercial grade thin Multi-Walled Carbon Nanotubes (9.5nm diameter, purity > 95 %,) were obtained from Nanocyl. The MWCNT electrodes were obtained by dropcasting 20 µL of a MWCNT dispersion in 1-methyl-2-pyrrolidinone (5mg mL^{-1}), affording a 5-µm–thick homogeneous MWCNT film on GC electrode.

The RuQ-pyrene/MWCNTs electrodes were prepared by successive incubation in a RuQ-pyrene solution in DMF starting from 0 to 8mM for 1h. After each incubations, the electrodes were rinsed several times with deionized water.

The RuQ-pyrene/GDH MWCNTs electrodes were prepared by incubation in different ratios of RuQ-pyrene/Pyrene-NHS in DMF. The bi-functionalized electrodes were then incubated for 6h in 40µL of a 2mg mL^{-1} solution of GDH in phosphate buffer pH7 at 4°C.

After each incubations, the electrodes were rinced several times with deionized water.

References

1. C. A. Goss and H. D. Abruna, *Inorg. Chem.*, 1985, **24**, 4263–4267.
2. A. Le Goff, K. Gorgy, M. Holzinger, R. Haddad, M. Zimmerman, and S. Cosnier, *Chem. Eur. J.*, 2011, 10216–10221.