



Journal Name

SUPPORTING INFORMATIONS

Experimental

Materials

Acetonitrile (MeCN) (HPLC grade) used for electrochemistry was obtained from VWR chemicals and used without further purification. Tetrabutylammonium perchlorate (Fluka) [Bu₄N]ClO₄ (TBAP) was used as supporting electrolyte in organic media. All reagents, chemicals products and enzyme, purchased from Aldrich, were of reagent grade quality 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.

Electrochemistry Measurements

The electrochemical experiments in organic media were performed in MeCN in a three-electrode electrochemical cell under a dry argon atmosphere and in a glovebox ([O₂] < 20 ppm) using in both cases an Autolab pgstat100 potentiostat. 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/AgNO₃ 10 mM in MeCN + TBAP (0.1 M) served as a reference electrode in organic media.

For electrochemical experiments performed in aqueous media, a Biologic VMP3Multi Potentiostat was used. Experiments were performed in 0.1 M phosphate buffer (pH 7). A platinum grid was used as the counter electrode and an SCE served as the reference electrode.

Potentials in organic and aqueous media are referred to the (Ag/AgNO₃) electrode and the (Ag/AgCl) electrode, respectively.

Data fitting was performed with OriginPro9.

The morphology of the modified MWCNTs electrodes was investigated by SEM using an ULTRA 55 FESEM based on the GEMINI FESEM column with beam booster (Nanotechnology Systems Division, Carl Zeiss NTS GmbH, Germany) and tungsten gun.

Synthesis

1-(11-bromoundecyl)-1H-pyrrole was synthesized according to previously described procedures¹.

Synthesis of 1-(11-(1H-pyrrol-1-yl)undecyl)-1H-imidazole (imidazole-pyrrole): 340 mg of imidazole (5 mmol) and 280 mg of K₂CO₃ (2 mmol) were dissolved in 30 mL of MeCN. Then, 150 mg of 1-(11-bromoundecyl)-1H-pyrrole (0.5 mmol) were added to the mixture. The reaction mixture was then refluxed under argon atmosphere for 24h. The suspension was then filtered

and the solvent removed under vacuum. The crude product was then extracted with 60 mL of CH₂Cl₂ and washed with H₂O saturated with K₂CO₃ (3x50 mL). The organic phase was then dried over MgSO₄ and under vacuum to yield to 130 mg of a pale yellow oil as the pure product (90% yield).

¹H NMR: δH/ppm (400 MHz, CDCl₃): 1.20-1.30 (m, 14H), 1.75 (q, j = 6.4Hz, 2H), 1.82 (q, J = 7.2Hz, 2H), 3.85 (t, J = 7.2 Hz, 2H), 4.11 (t, J = 7.6 Hz, 2H), 6.12 (t, J = 2Hz, 2H), 6.64 (t, J = 2Hz, 2H), 7.02 (s, 1H), 7.25 (s, 1H), 8.46 (s, 1H).

¹³C NMR: δC/ppm (400 MHz, CDCl₃): 26.33, 26.73, 28.92, 29.13, 29.27, 29.32, 29.33, 29.36, 30.6, 31.52, 48.59, 49.6, 107.74 and 120.43.

MS (ESI+): 288⁺ (M+H⁺)

Preparation of MWCNT electrodes

Commercial grade thin multi-walled carbon nanotubes (9.5 nm diameter, purity >95%) were obtained from Nanocyl and used as received without any purification step. MWCNT films were prepared by drop coating 20 μL of a 5 mg mL⁻¹ dispersion of MWCNTs in N-methyl pyrrolidinone (NMP) onto the glassy carbon (GC) electrode surface. The deposit was then allowed to dry under vacuum.

Functionalization of Electrodes with polypyrrole-imidazole (p-Im) and p-[(Im)(PP)Fe^{III}]

The p-Im-modified MWCNTs electrode (p-Im-MWCNTs) was obtained by electrodeposition of the imidazole-pyrrole monomer from a 2 mM solution in MeCN 0.1 M TBAP. In order to saturate the surface with the p-Im polymer, 80 scans between 0 and 0.9 V Vs Ag/AgNO₃ were performed.

The pi-stacking of (PP)Fe^{III} onto the MWCNT-modified electrode was performed by incubating the non-functionalized electrode in a solution of (PP)Fe^{III} in DMF (0.05 ; 0,1 ; 0,5 ; 1 ; 2,5 ; 5 and 10 mM) for several minutes. In order to generate the formation of the p-[(Im)(PP)Fe^{III}], the same procedure was repeated with p-Im-MWCNT-modified electrode with an incubating time of 3 hours.

References

- 1 J. S. Lee, Y. S. Chi, J. Kim, W. S. Yun and I. S. Choi, *Phys. Chem. Chem. Phys.*, 2008, **10**, 3138–3149.