Supplementary Data

"Self-Assembled Naphthalenediimide Derivative Films for Light-Assisted Electrochemical Reduction of Oxygen."

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Synthesis of N,N'-(ethyl-N",N",N''-dimethyloctadecaneammonium)-1,4,5,8-naphthalene diimide bromide

→ 1,4,5,8-naphthalic dianhydride [Aldrich] $(3.7 \times 10^{-2} \text{ mol}, 10 \text{ g})$ reacted with N,N-dimethylethylenediamine (Aldrich) (excess of four equivalents) in 300 mL of water under vigorous stirring and heating (75 °C) for 2 h. An orange solid was obtained, filtered and washed with 500 mL of distilled water. It was dried at 70 °C. Yield = 87%.



Fig. 1 Synthesis of precursor 1.

¹**H-NMR** - (CDCl₃) δ (ppm): 2.3 (s, 12H, N-CH₃), 2.6 (t, 4H, CH₂), 4.3 (t, 4H, N(imide)-CH₂), 8.7 (s, 4H, Ar).

Mass Spectrum - $\frac{m}{z}$: 408 M⁺, 377, 249, 153, 58.

- **Infrared** (KBr) ν (cm⁻¹): 3078, 2821, 2771, 1700, 1663, 1450, 1349, 1243, 1070.
- Elementar Analysis calc. (%): C 64.69, H 5.92, N 13.72; found: C 64.62, H 5.89, N 13.77.

 \rightarrow Compound 1 was treated with 1-bromooctadecane (excess of four equivalents) in acetonitrile under reflux for 12 h. The yellow product was filtered, washed with cold acetonitrile and dried at 70 °C. Yield = 87%.



Fig. 2 DC18, N,N-ethyl-N',N'-dimethyloctadecylammonium-1,4,5,8-naphthalene diimide bromide.

¹**H-NMR** - (DMSO-d6) δ (ppm): 0.8 (t, 6H, CH₃); 1.2 - 1.3 (m, 60H, CH₂); 1.7 (m, 4H, CH₂) 3.5 (s, 12H, N-CH₃); 3.3 (t, 4H, CH₂); 3.5 (t, 4H, CH₂); 4.4 (t, 4H, CH₂); 8.7 (s, 4H, ar).

Mass Spectrum - $\frac{m}{2z}$: 457 M²⁺.

- **Infrared** (KBr) ν (cm⁻¹): 2970, 2821, 1705, 1667, 1448, 1350, 1243, 1070.
- Elementar Analysis calc. (%): C 76.15, H 10.80, N 6.12, O 6.80; found: C 76.10, H 10.79, N 6.12, O 6.99.

Experimental details

Electrochemical experiments were carried out on a μ Autolab III/FRA2 in a conventional three electrodes arrangement. A Ag|AgCl (KCl 3.0 mol dm⁻³; E_{ref}^{\ominus} = 0.22 vs SHE) reference electrode was used with a Pt wire counter-electrode in KCl 0.1 mol dm⁻³ aqueous electrolyte. Spectroelectrochemical (in situ UV-Vis spectra) experiments were realized with an Ocean Optics USB 4000 spectrophotometer equipped with a wand optical-fiber probe. The same arrangement was used to illuminate the electrode's surface (Fig. 4). AFM images were obtained on a Shimadzu SPM 9600 microscope (dynamic sweep mode). ¹H-NMR data were obtained with a Bruker AC-200 spectrophotometer in DMSO-d₆. Mass spectra were measured in a Shimadzu CG/EM 14B/QP5050A equiped with an ion trap analyser LC-MS(n)-Bruker Daltonics Esquire 3000 plus spectrometer. SEM images were obtained in a Shimadzu SS-550 microscope. Infrared spectra were measured in a Bomem MB 100 using KBr pellets.



Fig. 3 Cyclic voltammograms of a DC18-modified glassy carbon electrode at different sweep rates (from 10 to 50 mV s⁻¹). Inset: current intensity at -0.69 V vs sweep rate.

Fig. 3 shows the electrochemical response of a DC18 film on a GCE electrode (d = 2 mm, $\Gamma = 4 \times 10^{-9} mol cm^{-2}$), in pure electrolyte at different sweep rates. The current intensities are linearly dependent of the sweep rate, which demonstrates that the electroactive species are in fact immobilzed over the electrode's surface. AFM images (Fig. 5) reveal a homogeneous surface after electrochemical conditionement and shows that this material is composed by successive layers as well. This feature is not observed before electrochemical conditionement(Fig. 6).



Fig. 4 Illustration of the spectroelectrochemical cell used.



Fig. 5 AFM image of a $4 \times 10^{-9} mol cm^{-2}$ DC18 film on a GCE electrode, showing its regular layered structure.



Fig. 6 AFM image of the same film before electrochemical conditionement.