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Electronic Supplementary Information

Highly-organized stacked multilayers via layer-by-layer assembly of lipid-like surfactants and polyelectrolytes. Stratified supramolecular structures for electrochemical nanoarchitectonics

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Supplementary figures

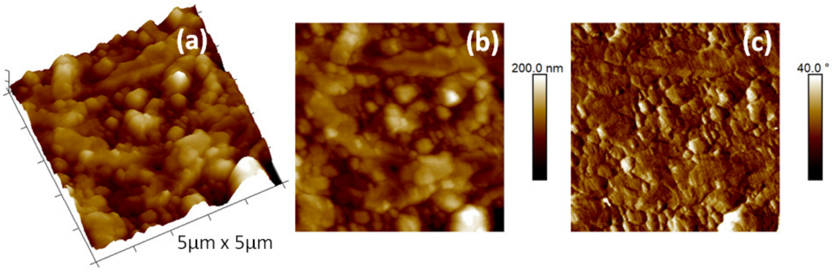

Figure S1. AFM images of the (DP/PAH)$_9$ multilayered film: surface plot of the topography (a), height (b) and phase (c) channels. Scan size 5 × 5 µm^2, z-scale indicated on each image.

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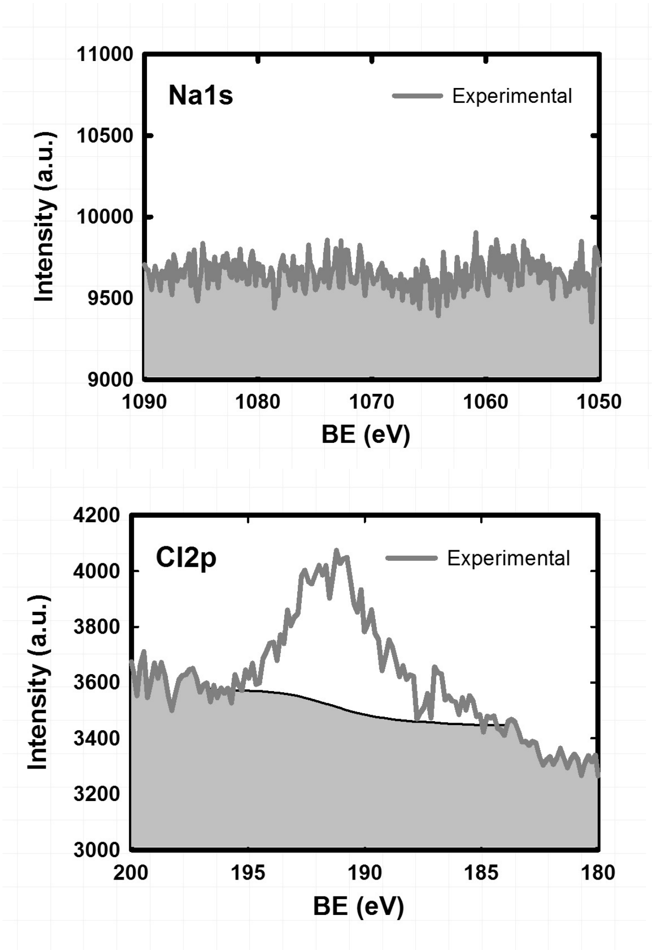

Figure S2. XPS results in the Na1s (top) and Cl2p (bottom) core binding energy regions of Si/PEI/(DP/PAH)$_5$. The presence of chloride (and the absence of Na), as revealed by the XPS, confirms the idea that the PAH layer contains some proportion of anions from solution that compensate the excess of positive charge

Table S1. ATR-FTIR. The band positions of the methylene stretching and the intensity ratio reveals that the packing of the aliphatic chains of DP in the assemblies is similar to that in the solid.

Sample	ν(CH_3)	ν(CH_2 asym)	ν(CH_2 sym)	Int(CH_2 asym)/ Int(CH_2 sym)
Solid DP	2950.5 cm^{-1}	2916.0 cm^{-1}	2848.5 cm^{-1}	1.42
(DP/PAH)$_5$	2954.5 cm^{-1}	2917.5 cm^{-1}	2849.5 cm^{-1}	1.48
(DP-Fc/PAH)$_5$	2953.5 cm^{-1}	2921.5 cm^{-1}	2853.0 cm^{-1}	1.60

Comparison between (OsPA/DP/OsPA/GOx)$_5$ and (OsPA/GOx)$_5$ - Electrochemical response

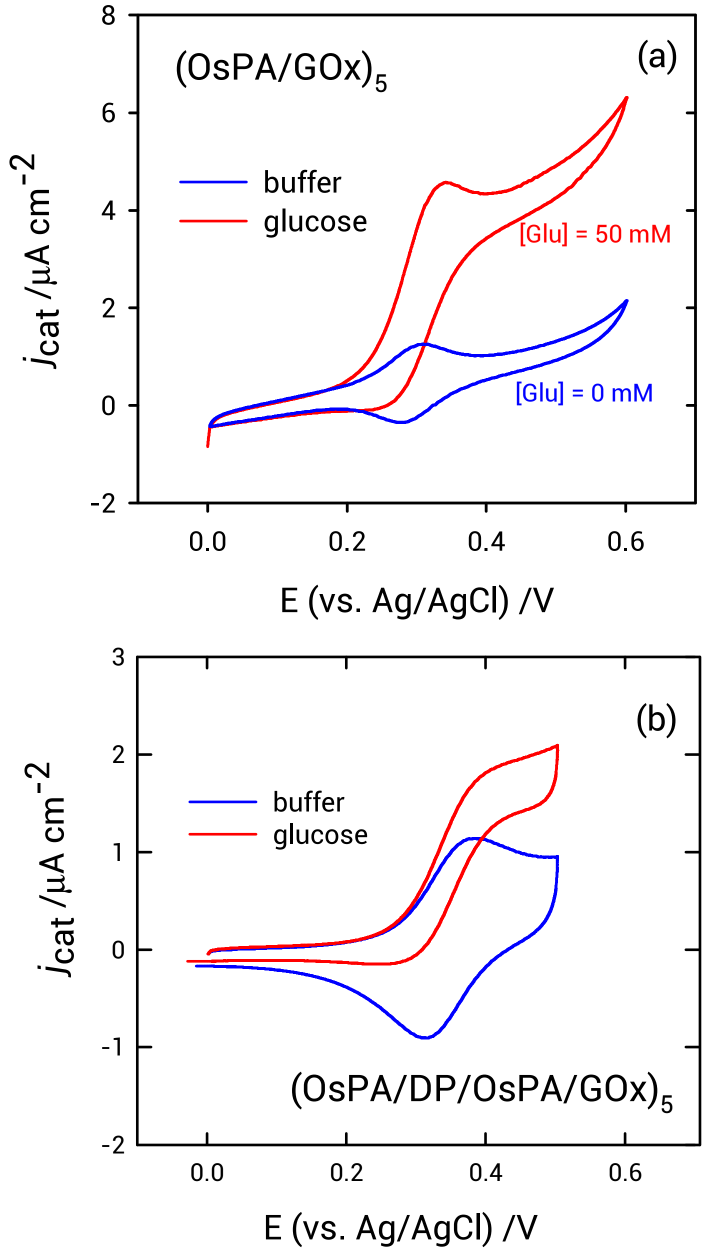

Figure S3. Cyclic voltammograms corresponding to: (a) $(OsPAGOx)_5$ and (b) $(OsPA/DP/OsPA/GOx)_5$. The blue trace refers to voltammetric measurements performed in the absence of glucose whereas the red trace refers voltammetric measurements performed in the presence of 50 mM glucose.

GISAXS characterization of $(DP/PAH)_5$ multilayer

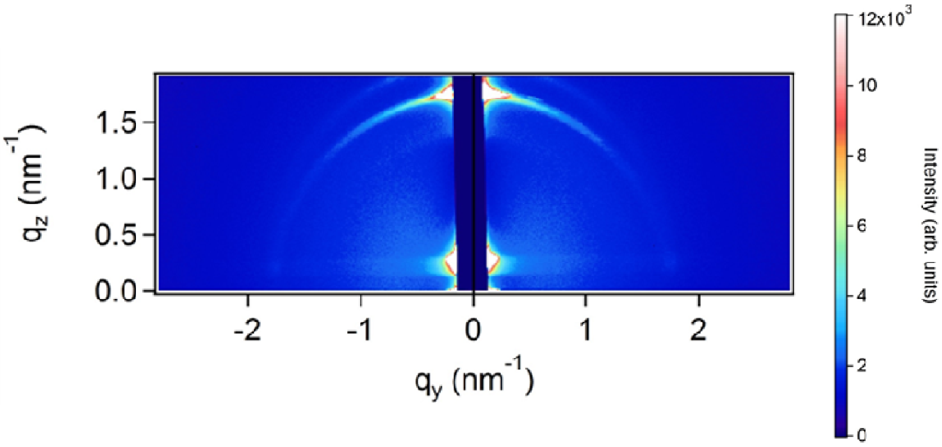

Figure S4. GISAXS pattern corresponding to a $(DP/PAH)_5$ multilayer.

Experimental Procedures

Materials

Poly(allylamine) hydrochloride (PAH, average Mw ~58 kDa), sodium dodecylphosphate (DP), polyethylenimine (PEI, Mw 10 kDa), ferrocene (Fc), 3-mercapto-1-propanesulfonic acid sodium salt (MPS) and glucose were purchased from Aldrich, glucose oxidase (GOx) from Aspergillus niger was purchased from Biozyme. The redox polymer [Os(bpy)2ClpyNH]–poly(allylamine) (OsPA) was synthesized as previously reported.[1] The pH of stock solutions of PAH (1 mg mL^{-1}) and DP (26 mM) were adjusted to 8 by adding 10% KOH. All chemicals were of analytical grade.

Layer-by-layer assembly of films

The Au substrates (for FTIR and electrochemical measurements) and the Si substrates (for AFM images, ellipsometry, XRR, GISAXS, XPS and contact angle measurements) were first coated with PEI. After the initial modification all the substrates were rinsed with Milli-Q water. Multilayer films were assembled by a sequential dip-coating process, alternating between DP solution (26mM, pH 8, 70°C, 10 min) and PAH solution (1 mg mL^{-1}, pH 8, 70°C, 10 min). The substrates were rinsed with Milli-Q water (70°C) after each absorption step.

In the electrochemical experiment with $(DP\text{-}Fc/PAH)_5$, DP-Fc deposition solutions were 1 mM Fc in DP 26mM, pH8, 70°C.

In the bioelectrocatalytic experiment with $(OsPA/DP/OsPA/GOx)_5$, the Au substrates were first coated with 20 mM MPS in 10 mM H_2SO_4. After the initial modification the substrates were rinsed with Milli-Q water. Multilayer films were assembled by a sequential process, alternating between DP solution, OsPA solution and GOx solution with concentrations 10mM, 0.4% w/v, and 1mg/ml, respectively. The substrates were rinsed with Milli-Q water after each absorption step.

Ellipsometry

Ellipsometry was performed with a spectroscopic ellipsometer (alpha-SE) from J. A. Woollam Co with an incidence angle of 70°. Samples were prepared on Si substrates by dip-coating at 70°C. Results were analysed employing the CompleteEASE software (J.A.Woollam Co., Inc.). Data from 500 to 900 nm were fitted employing a Cauchy model for the optical constants of the assembled layer. Three different points per substrates were averages.

Atomic Force Microscopy (AFM)

AFM images were acquired with a Multimode 8 AFM (Nanoscope V Controller, Bruker, Santa Barbara, CA). Tapping mode imaging was conducted under dry nitrogen by using silicon probes (RTESP, 40N/m spring constant, 12 nm tip radius, Bruker). AFM measurements in buffer solution (HEPES 50 mM, pH 7.4) were performed in the peak force tapping mode (PeakForce- Quantitative NanoMechanics, PF-QNM) using V-shaped AFM probes (SNML, 0.07 N/m spring constant, 2 nm tip radius, Bruker). Each sample was imaged several times at different locations on the substrate to ensure reproducibility.

Contact Angle measurements

The contact angle measurements were performed with an automated goniometer Ramè Hart model 290 with Drop Image Advanced v2.7 software. Samples were prepared on Si substrates by dip-coating at 70°C.

X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was performed using a SPECS SAGE HR 100 system spectrometer. A Mg Kα (1253.6 eV) X-ray source was employed operating at 12.5kV and 10mA. Survey spectra were obtained with pass energy of 30 eV whereas 15 eV was employed for detailed spectra of some core regions. The take-off angle was 90° and operating pressure was 8 10^{-8} mbar. Quantitative analysis of spectra was carried out with the Casa XPS 2.3. 16 PR 1.6 software. Shirley baselines and Gaussian\Lorentzian (30%) product functions were employed. To compensate surface-charging effects, the binding energy (BE) of the aliphatic core level C1s was set at 285 eV.[2] For N/P, more precise calculations were performed by recording the XPS spectrum $(NH_4)_2HPO_4$ (Sigma Aldrich) powder in the same conditions as internal reference. Samples were prepared on Si substrates by dip-coating at 70°C.

FTIR Spectroscopy

Fourier transform infrared spectroscopy in the Attenuated Total Reflectance mode (ATR-FTIR) was performed using a Varian 600 FTIR spectrometer equipped with a ZnSe ATR crystal with a resolution of 4cm^{-1}. Background-subtracted spectra were corrected for ATR acquisition by assuming a refractive index of 1.45 for all of the samples. Samples were prepared on Au substrates by dip-coating at 70°C.

Grazing-Incidence Small-Angle X-ray Scattering (GISAXS)

GISAXS measurements were performed at the D10A-XRD2 beamline of Laboratório Nacional de Luz Síncrotron (LNLS, Campinas, Brazil). A monochromatic beam of 7689 eV (λ = 1.6124 Å) was used to perform the experiments. Large size (2 x 2 cm^2) silicon wafers were used as GISAXS simple substrates. GISAXS scattering intensities were recorded using a Pilatus 100 K detector (DECTRIS Ltd – Baden, Switzerland) at a distance of 631 mm from the sample (calibration: 64 pixel per degree). Exposure times under these conditions ranged from 60s to 80s depending on the contrast and sample quality. The beam size was 150 µm x 4 mm. Lamellar spacings were determined according to the procedure described by Di *et al.*[3]

Cyclic Voltammetry (CV)

Cyclic voltammetry experiments were performed with a TEQ-04 potentiostat using a conventional three electrode cell equipped with a Ag/AgCl reference electrode and a platinum counter electrode. Cyclic voltammograms were registered at 25 °C, at a scan rate of 0.050 and 0.100 Vs^{-1}, in 0.1M KCl.

References

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