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## Electronic Supplementary Information

# Electrochemical Nanoarchitectonics through Polyaminobenzylamine-Dodecyl Phosphate Complexes: Redox Activity and Mesoscopic Organization in Self-Assembled Nanofilms

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## 1. XPS

The components and relative proportions employed for fitting the N1s core spectra of PABA and PABA:DP films are presented in **Table S1**. The spectra were deconvoluted as reported previously.[1,2] The lower BE component at 398.6 eV has been attributed to the neutral N backbone (=N- bound to C).[3–6] The following component at 399.8 eV has been assigned to the neutral amine, which is expected to appear at about 1eV higher BE than the imine.[4,6] Charged nitrogen species are expected to appear at higher BE than neutral ones, so the components at 400.3 and 402.5 eV have been referred as positive nitrogen species.[4–7] The peak at about 400.3 eV has been assigned to oxidized secondary amines (delocalized polaron-type structure) whereas the other peak at about 402 eV would be due to protonated imine (localized bipolaron-type structure).[4,6] Finally, the contributions of the pendant amino groups are expected to appear at about 399 eV for the unprotoned form (indistinguishable from the backbone neutral amines) and 401.5 eV for the protonated form.[8,9]

**Table SI 1.** Components employed for fitting the XPS N1s core level of the PABA and PABA:DP assembled films.

| BE / eV | 398.6 | 399.8 | 400.3 | 401.5 | 402.5 | % Positive N species |
|---|---|---|---|---|---|---|
| *Sample* | Atomic composition (%) | | | | | |
| PABA-DP 1-10 | 9 | 24 | 13 | 26 | 28 | 67 |
| PABA-DP 1-5 | 9 | 26 | 23 | 29 | 13 | 65 |
| PABA-DP 1-2 | 11 | 4 | 18 | 36 | 31 | 85 |
| PABA | 14 | 22 | 28 | 29 | 7 | 64 |

## 2. Ellipsometry

Ellipsometry was performed with a spectroscopic ellipsometer (alpha-SE) from J. A. Woollam Co. A beta-spline model was employed for the description of the assembled layer to take into account the absorption of the PABA component (**Fig. S2**).[2] The ellipsometric response was measured at three different incident angles of incidence (65, 70 and 75°) and the whole data were employed for fitting the thickness (**Fig. S3**). At least 5 different spots were measured for each modified Au substrate and the average results are reported in **Table S2**.

**Table S2.** Average thickness of the assembled films deposited on Au substrates as determined from spectroscopic ellipsometry

| Sample | Ellipsometric Thickness |
|---|---|
| PABA-DP 1:2 | 10.5±1 nm |
| PABA-DP 1:5 | 22±2 nm |
| PABA-DP 1:10 | 34±3 nm |

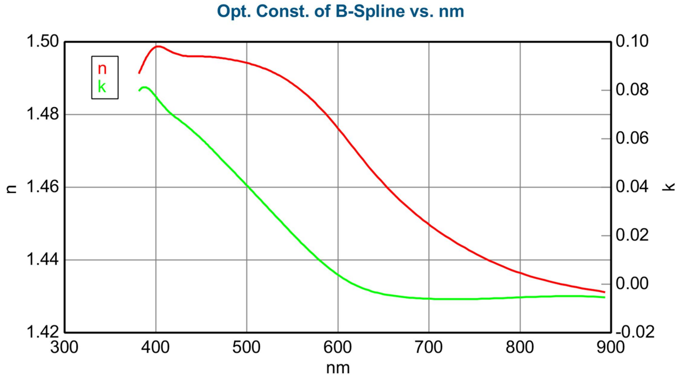

**Fig. S2.** Optical constants employed for fitting the ellipsometric data of PABA/DP assembled films.

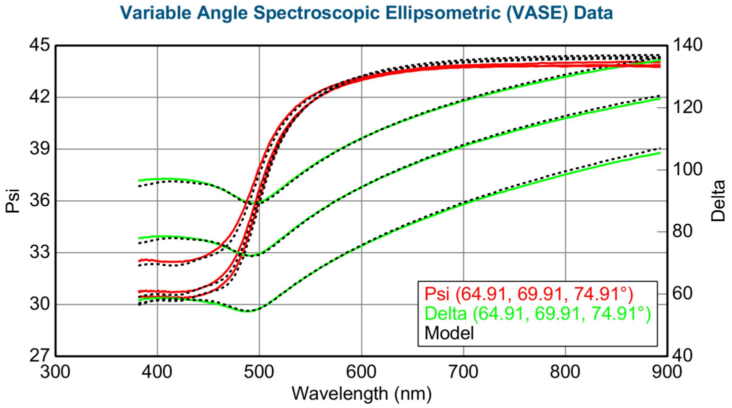

**Fig. S3.** Fitting of the ellipsometric data of the Au/PABA-DP 1:2 film.

## 3. XRR

The X-Ray reflectivity diagrams for the PABA-DP assembled films are reported **in Fig. S4**.

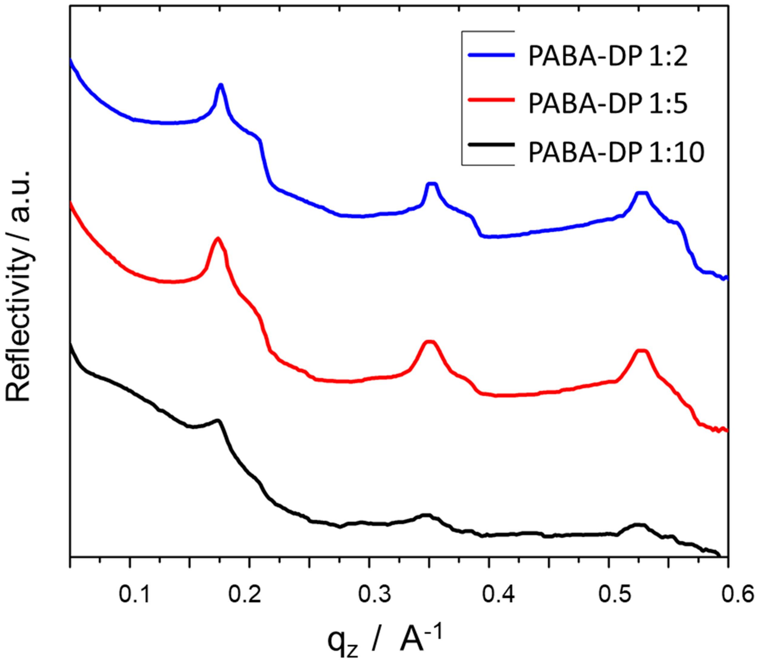

**Fig. S4.** XRR spectra of the PABA-DP assembled films formed from different proportion of polyelectrolyte:surfactant.

## 4. GISAXS

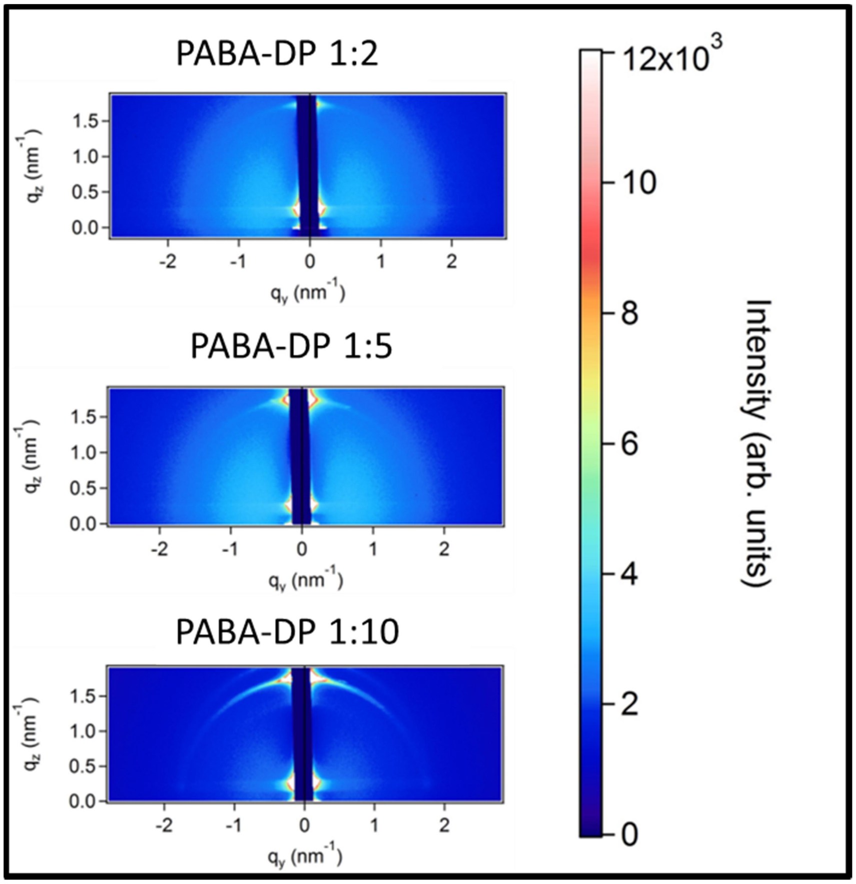

**Fig. S5.** GISAXS spectra of the PABA-DP assembled films formed from different proportion of polyelectrolyte:surfactant.

## 5. WAXS

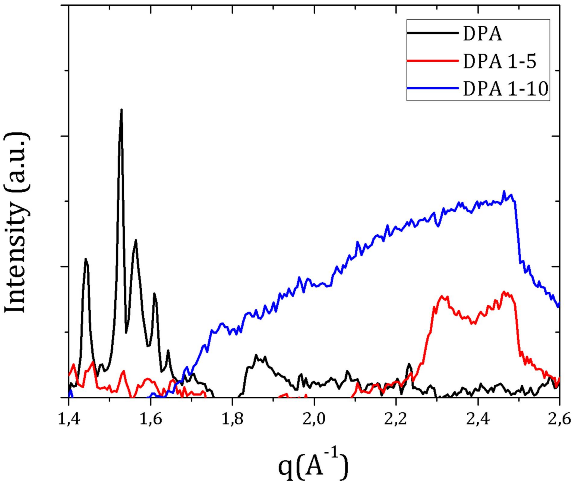

**Fig. S6.** WAXS spectra of solid DP and the PABA-DP assembled films formed from different proportion of polyelectrolyte:surfactant on Mylar.

## 6. Electrochemical stability of the assembled films

We have performed several successive voltammetric experiments without perceiving any loss of electrochemical signal upon cycling. As an example, we show below the comparison of initial and final responses at 20 mV $s^{-1}$ for a particular PABA-DP 1:10 film in 0.1M KCl solution (**Fig. S7**). There, the initial voltammogram refers to that obtained from the first cycling routine in this medium, whereas the final voltammogram refers to that recorded after more than 200 cycles (at different scan rates) in the same potential window. As can be seen, the voltammetric response displays no significant changes, thus evidencing the absence of film degradation or dissolution during the electrochemical cycling.

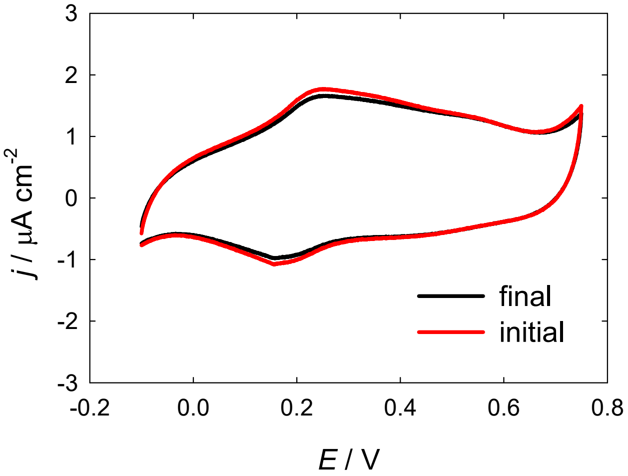

**Fig. S7.** Voltammetric response at 20 mV $s^{-1}$ for a particular PABA-DP 1:10 film before (initial) and after (final) performing more than 200 voltammetric cycles.

## 7. Copper UPD

Under Potential Deposition (UPD) of Cu (II) was employed as a tool to study the effective coverage of the assembled films.[10] The electrodes were exposed to a 0.06 mM $CuSO_4$ solution in 0.5 M $H_2SO_4$ and a linear sweep voltammetry was performed from 0.8 to 0 V vs Ag/AgCl (**Fig. S8**). During this negative scan, Cu(II) ions are reduced and deposited just on the regions of the gold substrate that are directly exposed to the solution. The lower potential limit is higher than the required for the massive deposition of copper in these conditions, so just an atomic layer of Cu is formed. Then, the scan was reversed and the deposited Cu was re-dissolved. The area of this re-dissolution peak (integrated voltammetric charge) at about 0.3 V was employed as a measure of the exposed gold surface. The relative area of this peak for the film-covered electrodes ($A_{film}$) compared with that obtained on a clean gold electrode ($A_{Au}$) allows estimating the coverage as

$$\text{Coverage} = (1 - A_{film}/A_{Au})\ 100\%$$

Values obtained in this way for the assembled films are reported in **Table S3**.

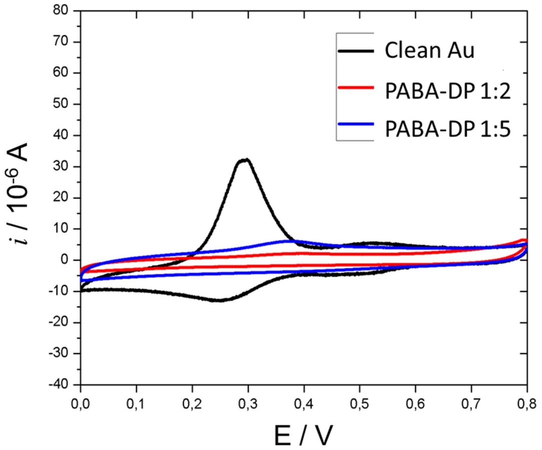

**Fig. S8.** Cu UPD voltammograms at 0.2 Vs$^{-1}$.

**Table S3.** Coverage of the assembled films as determined from the Cu UPD results

| Sample | Coverage |
|---|---|
| PABA-DP 1:2 | 98.1 % |
| PABA-DP 1:5 | 97.5 % |
| PABA-DP 1:10 | 98.5 % |

## References

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