Electronic Supplementary Information

Solid-State Electropolymerization and Doping of Triphenylamine as a Route for Electroactive Thin Films

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1. Experimental details:

Electrochemical Quartz Crystal Microbalance (EQCM)

According to Sauerbrey equation, the shift in the vibration frequency (Δf) suffered by a quartz plate can be used to calculate the change of the electrode mass (Δm) that results from the deposition (or dissolution) of a rigid, homogeneous, thin film:

$$\Delta f = [-2 f_0^2 / A \, (p_q \mu_q)^{1/2}] \, \Delta m = -C_f \, \Delta m \qquad \text{(S1)}$$

where f_0 is the resonant frequency of the quartz plate, A the piezoelectrically active area, and $p_q \mu_q$ the product of the density and the shear modulus of quartz, respectively. C_f is called the sensitivity factor of the crystal and has a value of 56.6 Hz μg^{-1} cm^2 at room temperature for the quartz crystals used in this study.

In addition to the aforementioned mass effect, the QCM is also sensitive to changes in the viscosity of the film and/or the QCM surrounding liquid medium. As the Sauerbrey equation is valid exclusively if the loaded film is rigid, it is important to establish whether this requirement is satisfied in our case. Equivalent electrical circuit parameters have been employed to characterize the QCM behavior with simultaneous mass and liquid loading effects. When the QCM response is completely governed by variations of solution density and viscosity at the electrode surface, it has been established that[1-4]

$$\frac{\Delta f}{\Delta R} = -\frac{1}{4\pi L_q} \frac{\sqrt{\bar{c}_{66} f_{sg}}}{\sqrt{f \mu_q}} \qquad \text{(S2)}$$

where Δf and ΔR are the shifts of the quartz crystal resonant frequency and motional resistance, respectively. L_q is the motional inductance of the quartz crystal in air (30 mH, according to the QCM200 operation manual), $\bar{c}_{66}$ is the lossy piezoelectrically stiffened quartz elastic constant ($2.957 \cdot 10^{10}$ N·m^{-2}), μ_q is the shear modulus for AT-cut

quartz ($2.947 \cdot 10^{10}$ N·m^{-2}), f_{sg} is the series resonant frequency in air (5 MHz in our case). According to these values, equation S2 can be approximated to

$$\frac{\Delta f}{\Delta R} \approx -\frac{1}{4\pi L_q} = -2.65 \, Hz \cdot \Omega^{-1}$$

This value can be used as a criterion to ascertain the film rigidity. The experimental value should be much larger than this one in order to ascribe the resonant frequency changes exclusively to mass effects.
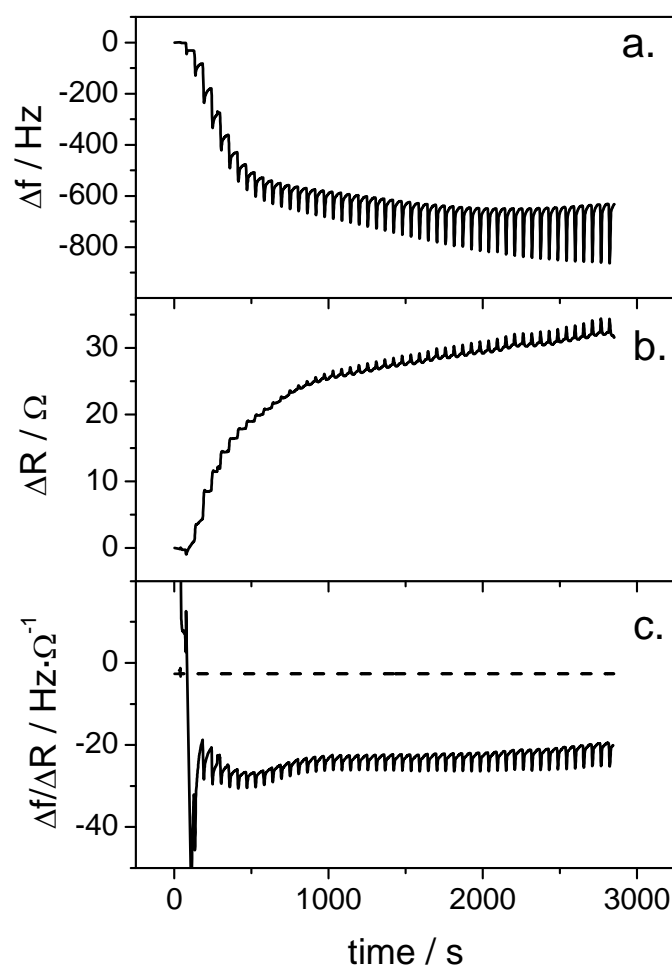
Figure S1. Time-resolved resonance frequency (Δf) (a.), resistance (ΔR) (b.) shifts and ($\Delta f / \Delta R$) (c.) for a 5 MHz quartz crystal plate coated with thin solid films of TPA during its cyclic voltammetry evolution at 50 mVs^{-1} in a N$_2$-purged NaClO$_4$ 0.5 M solution. The dashed line in figure c. represents the threshold value ($-2.65 \, Hz \cdot \Omega^{-1}$).

Figure S1 shows the time-resolved shifts of frequency (Δf) and resistance (ΔR) and the ratio $\Delta f / \Delta R$ for a quartz crystal electrode covered by a TPA corresponding to fig. 7. As observed, $\Delta f / \Delta R$ is about ten times larger than the value expected for a net viscous effect, suggesting that the TPA film behaves as a rigid layer.

During doping, the ratio $\Delta f / \Delta R$ is $-105\ Hz\cdot\Omega^{-1}$, indicating that the film is highly rigid and the Sauerbrey equation can be used accurately to estimate the changes in mass, i.e. the number of perchlorate anions from the electrolyte that ingress in the film to compensate the positive doping charge.

Atomic Force Microscopy

In order to perform the thickness measurements, a line was marked on the thin films supported on silicon wafers with a razor blade and one of the resulting parts wiped off with acetone, creating a sharply delineated step that was imaged by AFM.

Contact Angle Measurements

Under the assumptions that the drops formed are symmetric about a central vertical axis and that viscosity or inertia are not playing a significant role in determining their shape (i.e. the drop is not in motion), the shape is just defined by gravity and interfacial tension. Provided the necessary optical amplification by means of a lens and a high resolution camera, the contact angle is obtained as the slope of the tangent to the drop profile at the liquid-solid-vapor interface.

Static contact angle measurements were performed for TPA and TTA thin films (before and after the electrochemical treatment) by using an Optical Contact Angle and Surface Tension Meter CAM 101 from KSV Instruments. This is a fully computer

controlled instrument based on the capture and automatic analysis of video images. The

drop profile is extracted from the stored image (captured by a high resolution CCD

camera) with subpixel accuracy. Contrary to other tradicional approaches as circular,

polynomial or Bashforth-Adams fitting, which only use parts of the drop profile and

may often produce erroneous results (especially for large drops), the curve is fitted to

the Young-Laplace equation. Thus, contact angle data is easily obtained from the fitted

curve.

2. Schemes.

**Triphenylamine**   **Tri-p-tolylamine**
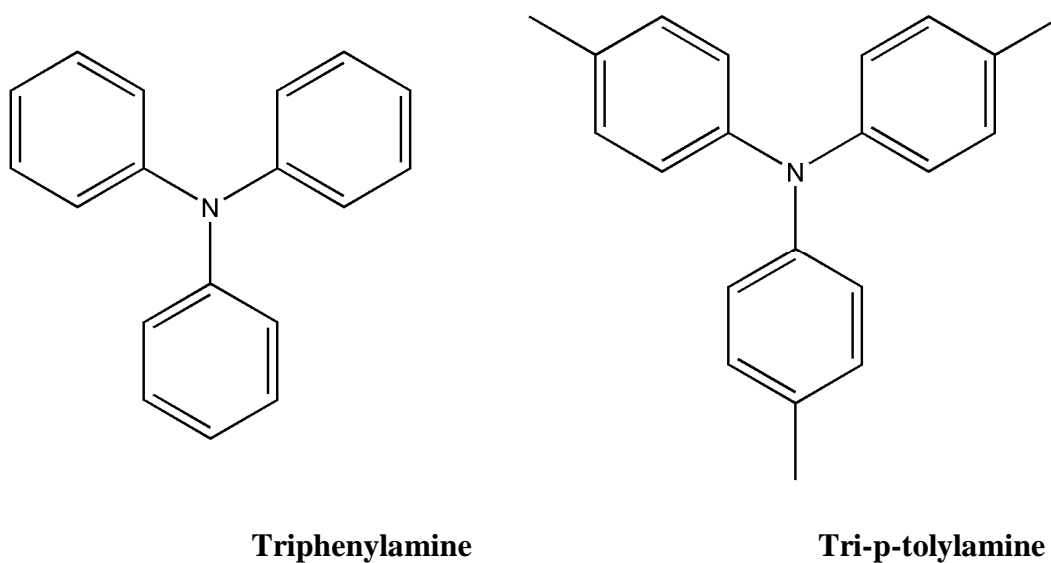
Scheme S1. Structure of triphenylamine and its corresponding para-methyl substituted derivative, tri-p-tolylamine.
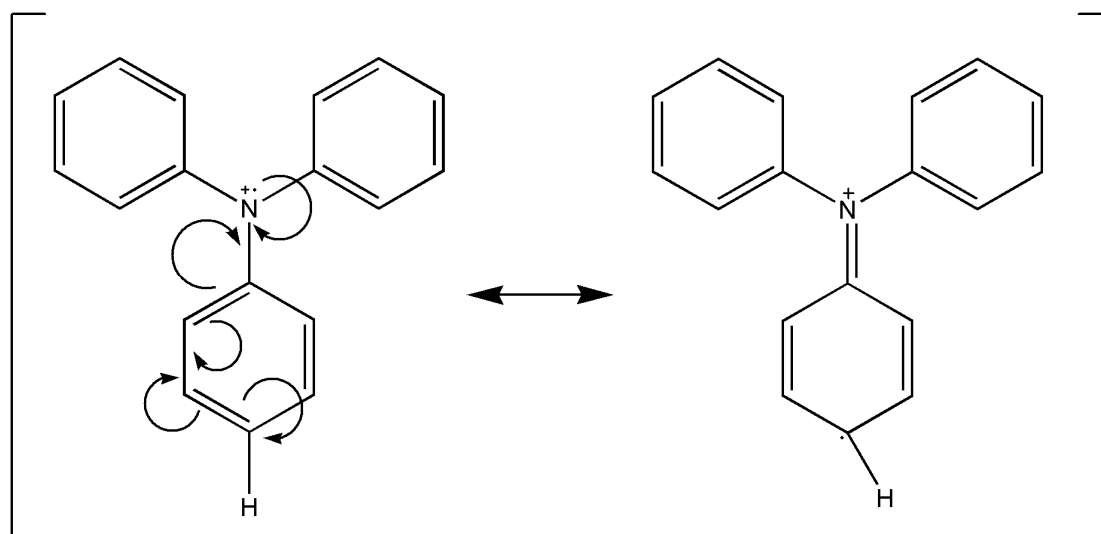
Scheme S2. Art model illustrating π-cloud electron density delocalization in the monocation radical formed after the one-electron oxidation of TPA. The model shows that the unpaired electron can be effectively delocalized to the *para* positions through this conjugated system, explaining their high reactivity.

### 3. Evolution of the voltammogram for TPA electrodes in NaCl solutions
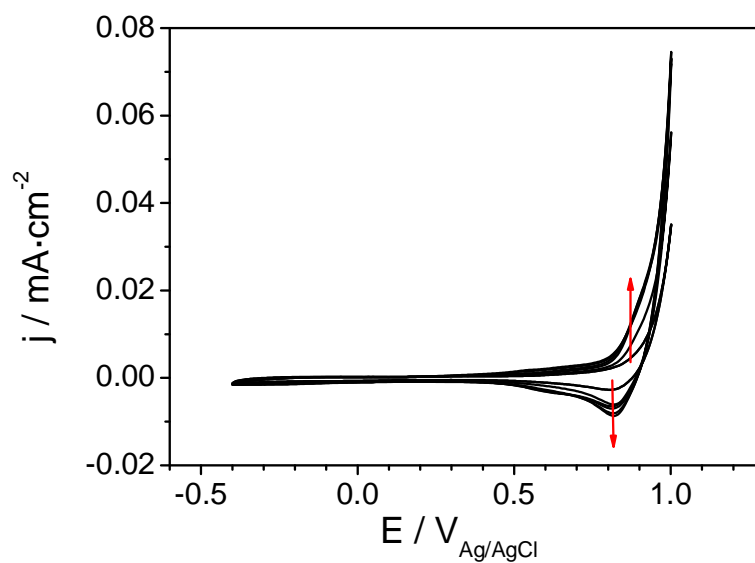
Figure S2. Evolution of cyclic voltammograms of a TPA thin solid film in 0.5 M NaCl aqueous solution. Scan range: -0.4 to 1.0 V at 50 mV·s^{-1}; 30 cycles. The arrows indicate the direction of growth of the current density with an increasing number of cycles (The figure corresponds to the cycles 2, 6, 10, 16, 20, 26 and 30).

## 4. Effect of scan rate on the evolution of the TTA and TPA thin film electrodes
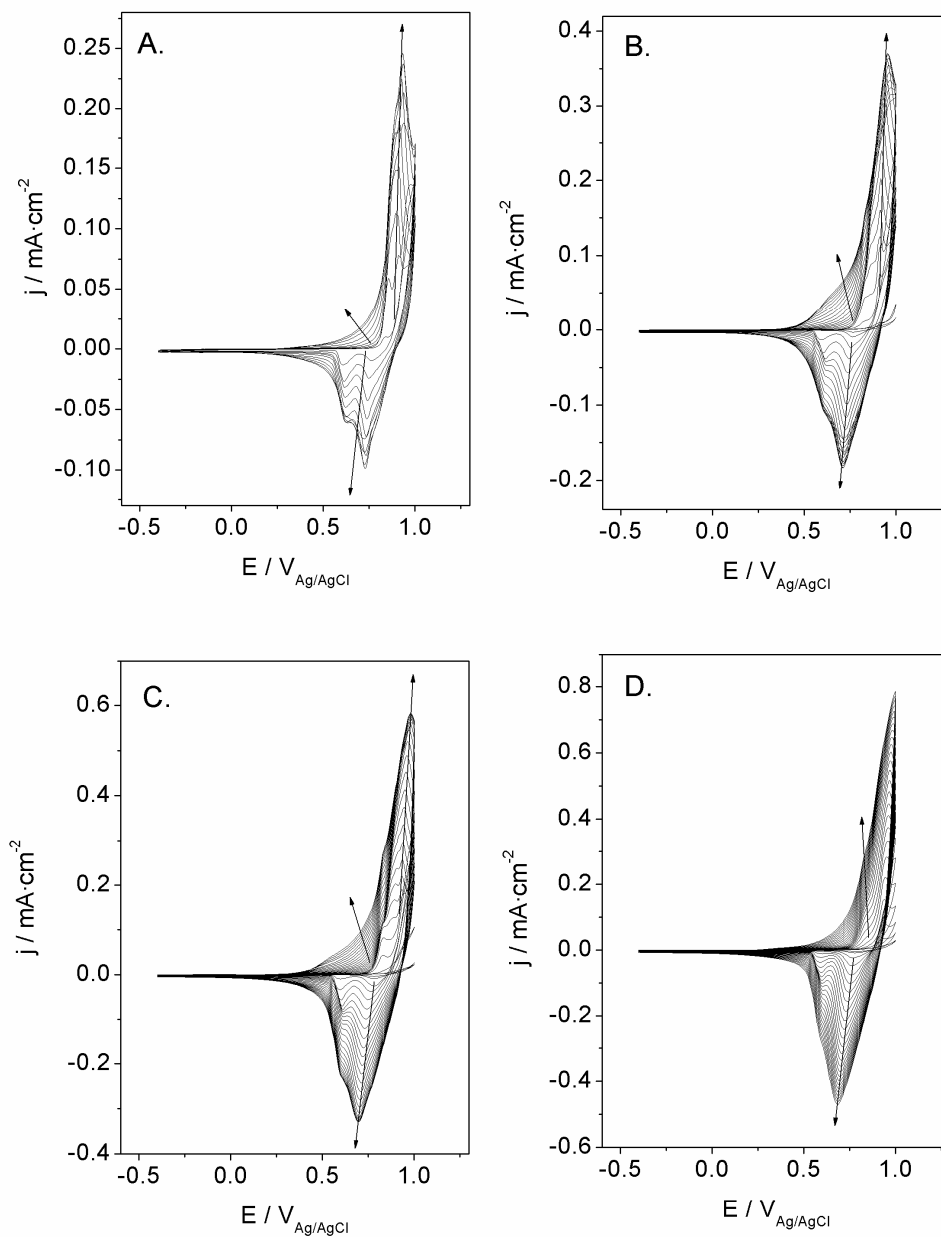
Figure S3. CVs obtained in $NaClO_4$ 0.5 M aqueous solution by cycling TPA thin solid films on FTO between -0.4 and 1.0 V (50 cycles) at 5 (A), 10 (B), 20 (C) and 50 (D) mVs^{-1}.
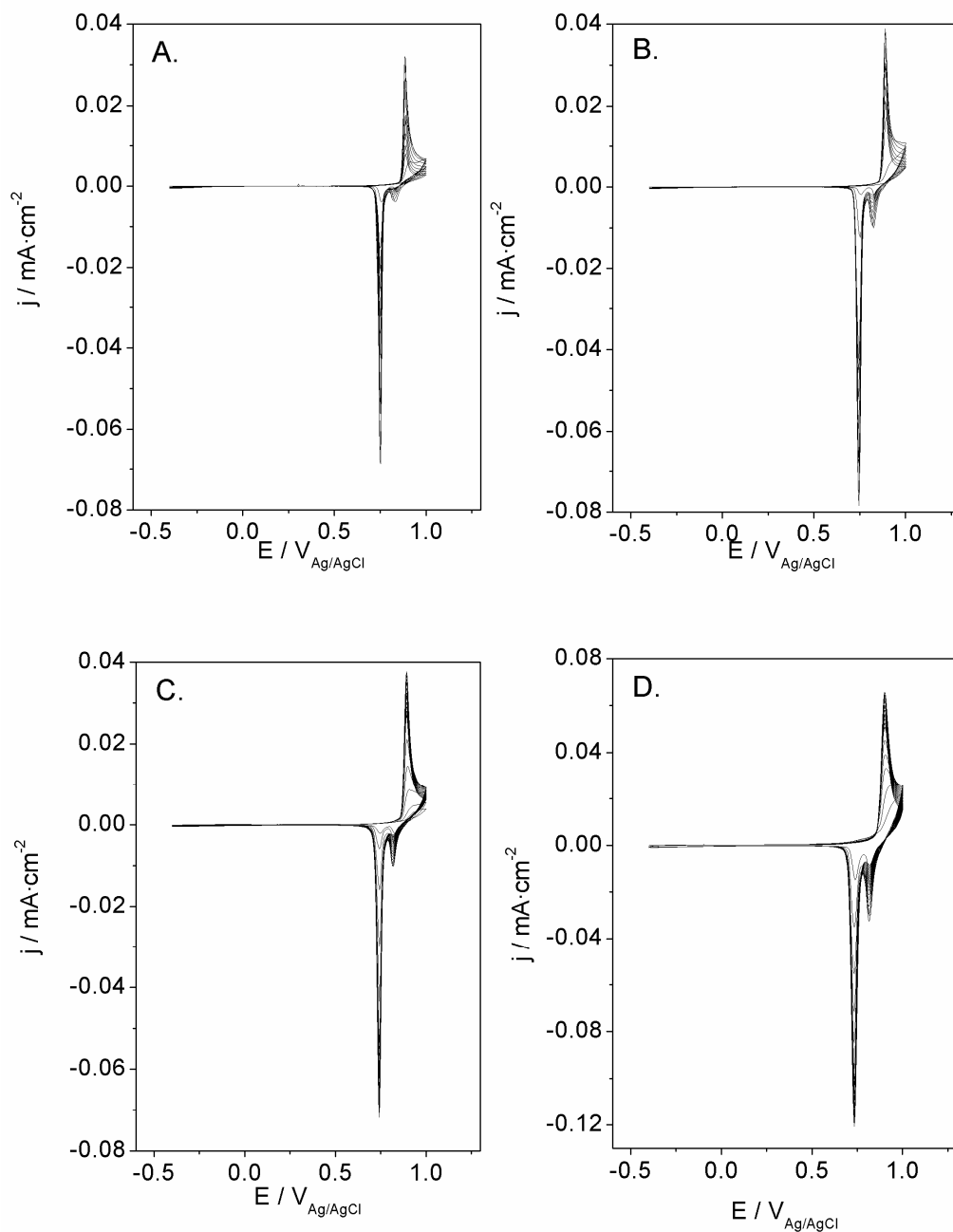
Figure S4. CVs obtained in 0.5 M NaClO$_4$ aqueous solution by cycling TTA thin solid films on FTO between -0.4 and 1.0 V (50 cycles) at 5 (A), 10 (B), 20 (C) and 50 (D) mVs^{-1}.

## 5. Spectral and mass changes associated to voltammetry
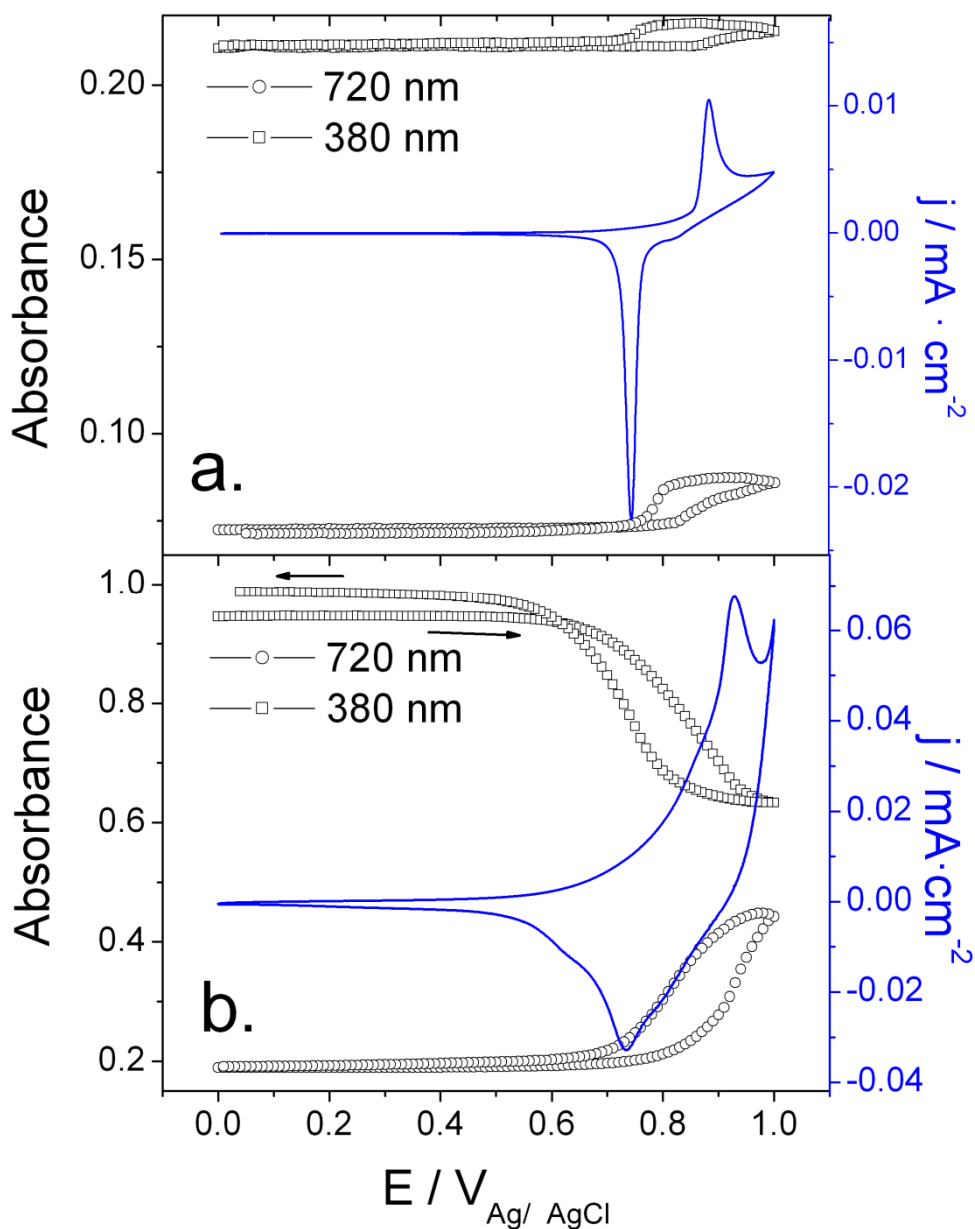
Figure S5. Changes induced in the absorbance at 380 (squares) and 720 nm (circles) by cycling the potential between -0.4 and 1.0 V at 5 mVs[-1] (blue lines) for TTA (a) and TPA (b) FTO electrodes previously submitted to 40 cycles between -0.4 and 1 V at 50 mVs[-1], in N_2 purged 0.5 M $NaClO_4$ aqueous solution.
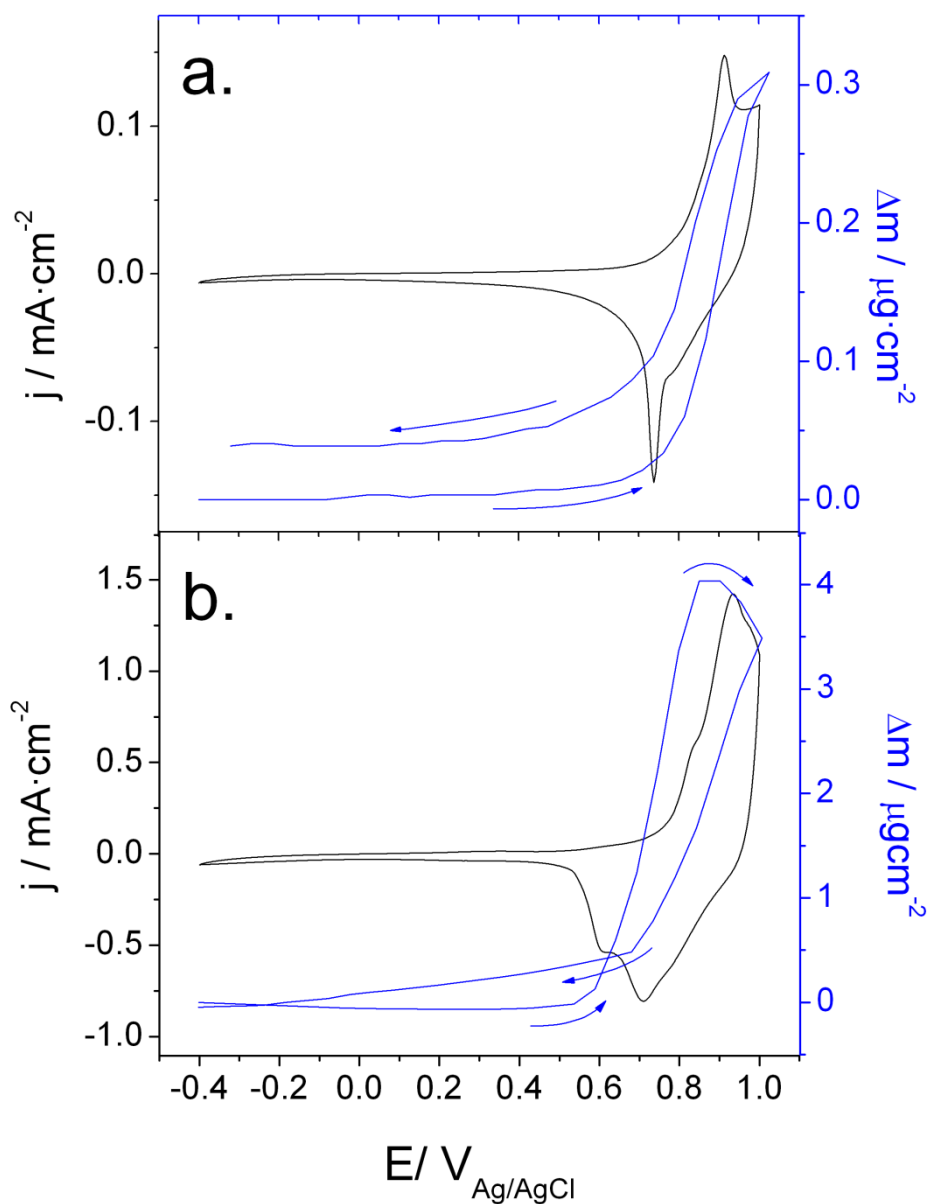
Figure S6. Mass changes induced by cycling the potential between -0.4 and 1.0 V at 5 mVs^{-1} (blue lines) for TTA (a) and TPA (b) FTO electrodes previously submitted to 40 cycles between -0.4 and 1 V at 50 mVs^{-1} in N$_2$ purged 0.5 M NaClO$_4$ aqueous solution.

6. Water contact angle measurements
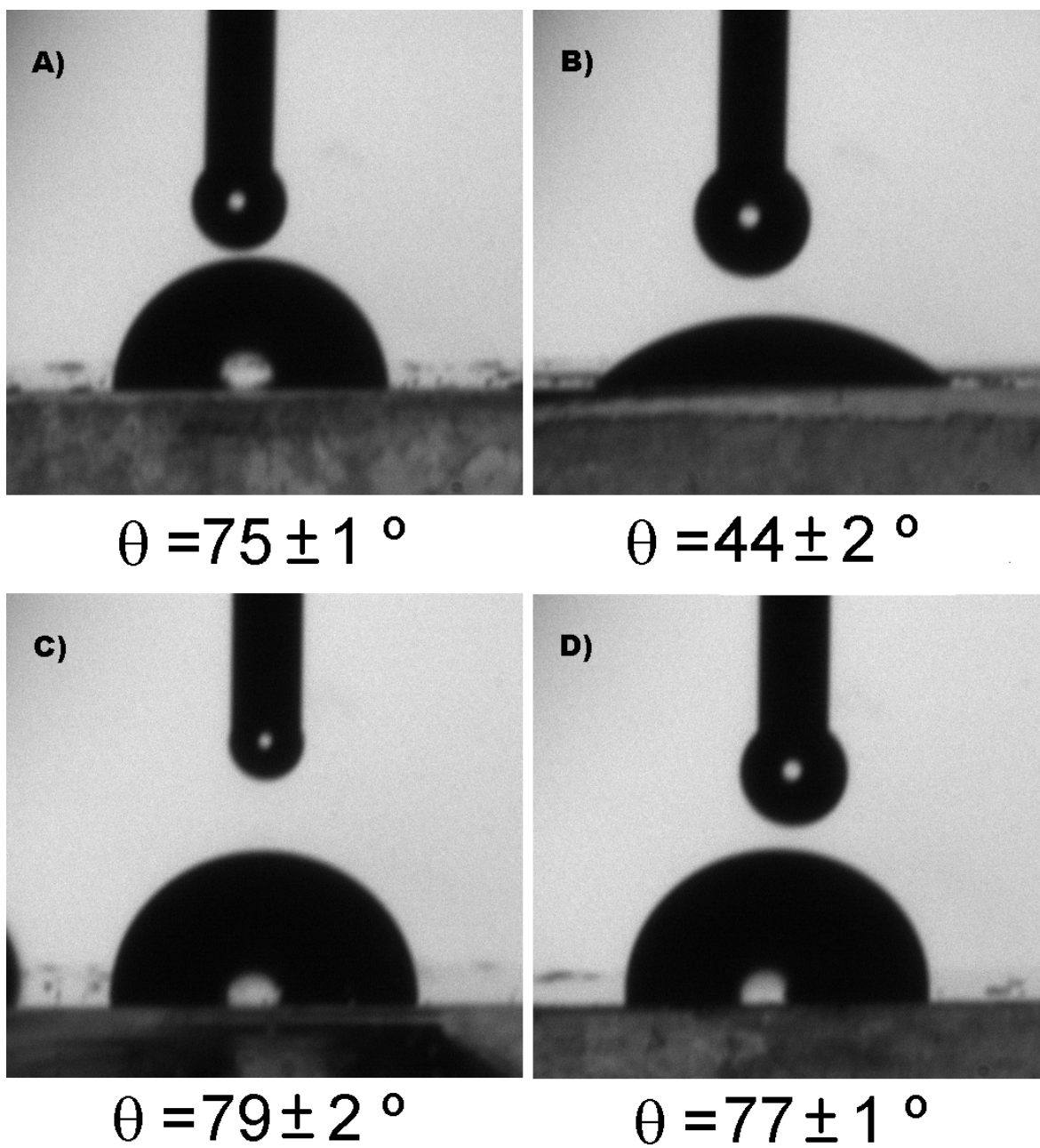
Figure S7. Changes in the contact angle measured for surfaces modified with TTA (A, B) and TPA (C, D) films before (A, C) and after (B, D) the electrochemical treatment (50 cycles between -0.4 and 1.0 V at 50 mV·s^{-1} in 0.5 M NaClO$_4$) and doping at 1 V.

7. Cross sections of the films
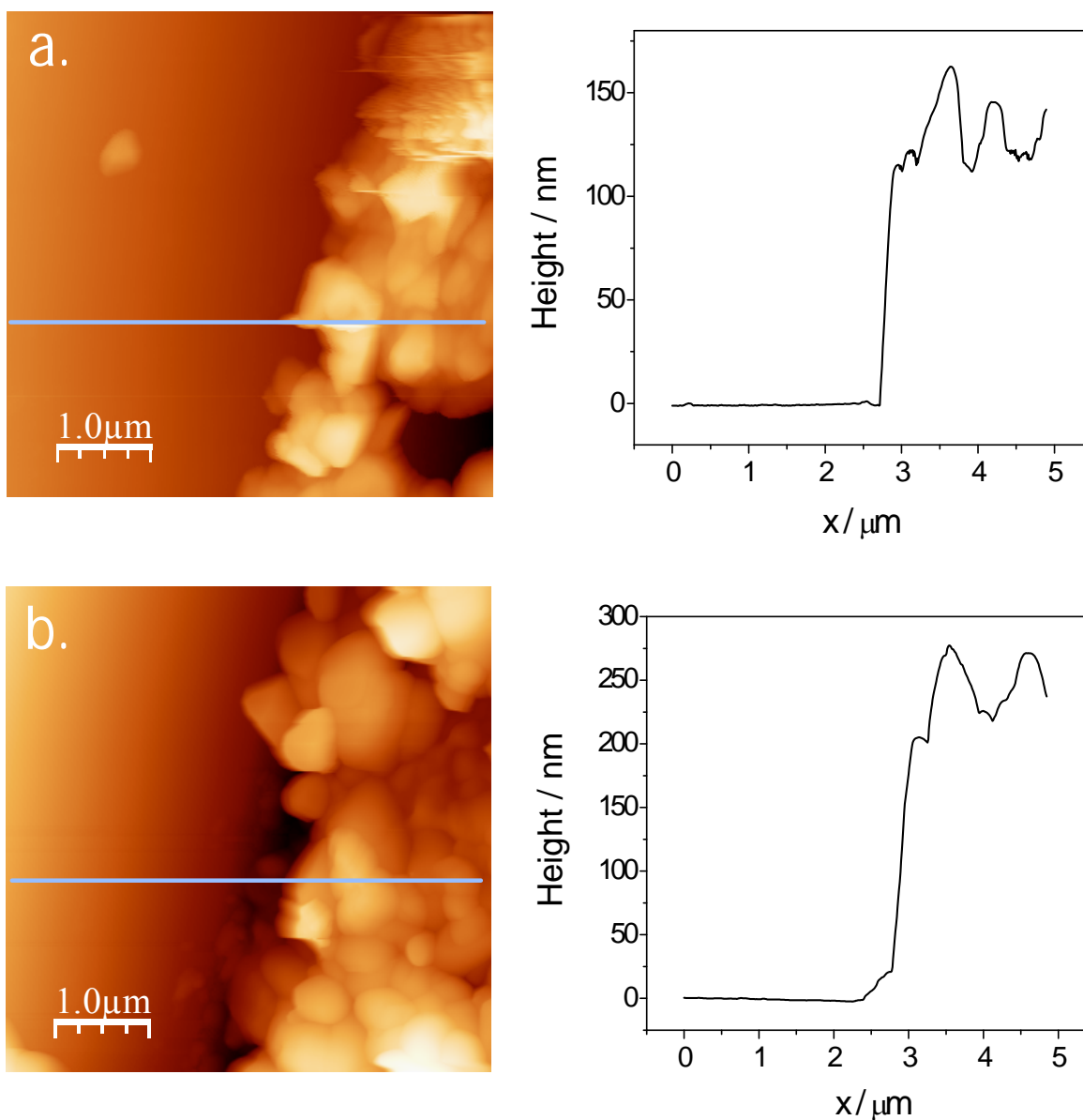
Figure S8. Cross section analysis of the AFM images obtained for a TPA (a.) and a

TTA (b.) thin films deposited on silicon wafers.

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[3] X. Tu, Q. Xie, C. Xiang, Y. Zhang and S. Yao, *J. Phys. Chem. B*, 2005, **109**, 4053.

[4] Q. Xie, Z. Li, C. Deng, M. Liu, Y. Zhang, M. Ma, S. Xia, X. Xiao, D. Yin and S. Yao, *J. Chem. Educ.*, 2007, **4**,681.