

Supporting Information

Dye Sensitized Nanostructured Crystalline Mesoporous Tin-doped Indium Oxide Films with Tunable Thickness for Photoelectrochemical Applications

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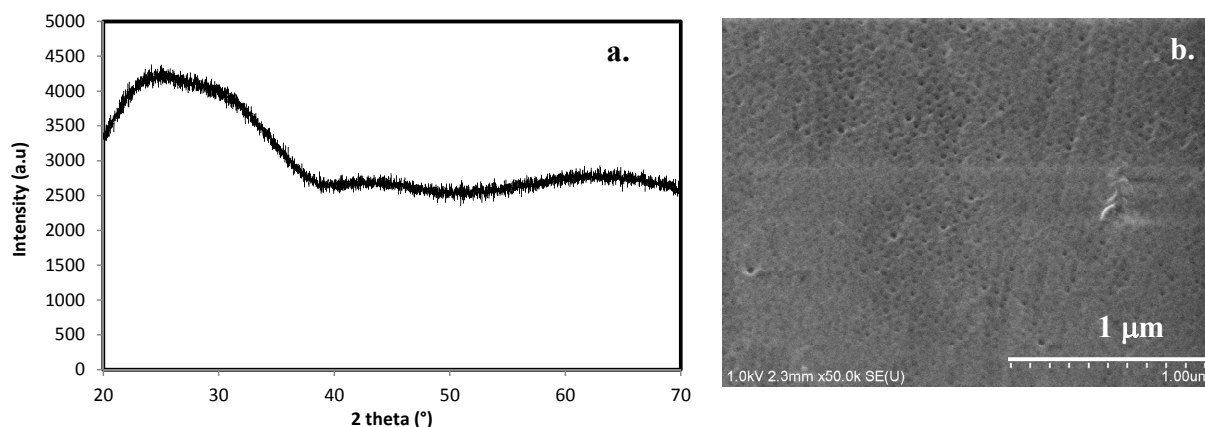


Figure S1. X-Ray diffraction patterns (a) and FE-SEM images (b) of *templated nano-ITO* films before thermal treatment.

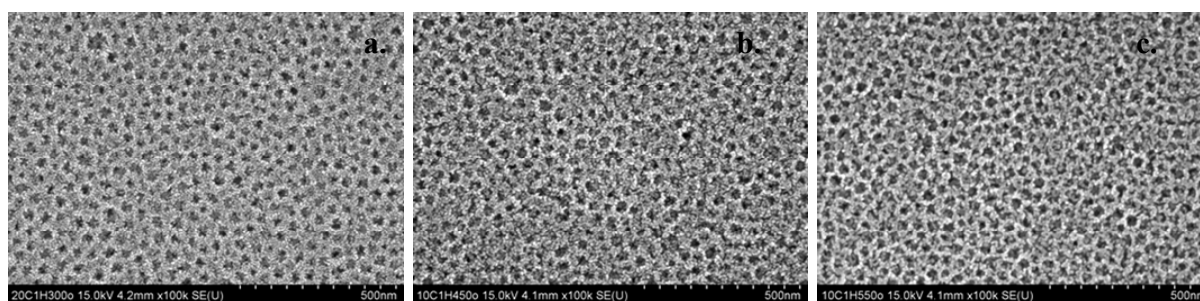


Figure S2. FE-SEM images of *templated nano-ITO* films treated at various temperatures a) 300°C, b) 450°C, c) 550°C in air

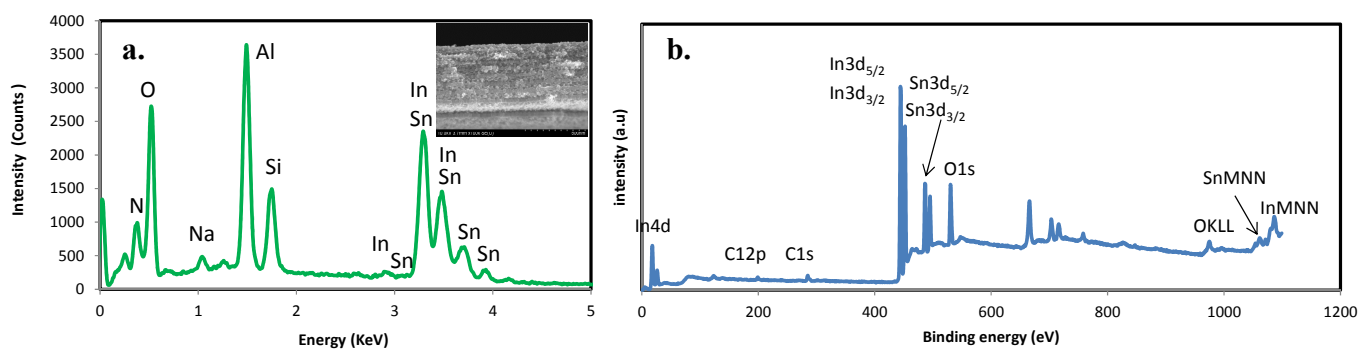


Figure S3. EDX (a) and XPS (b) analyses for *templated nano-ITO* films heat-treated at 450°C in air

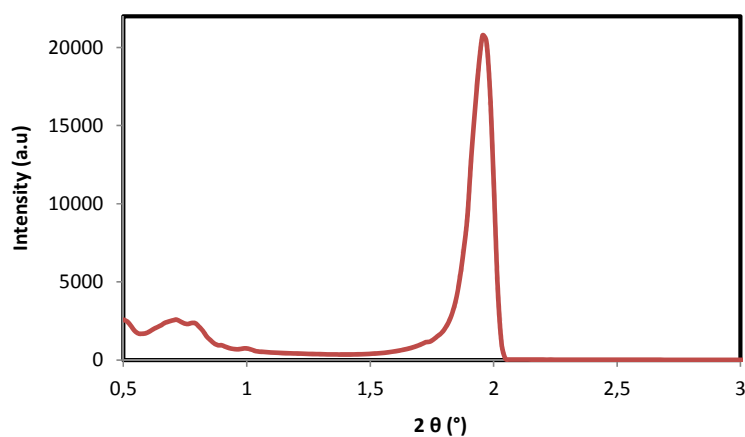
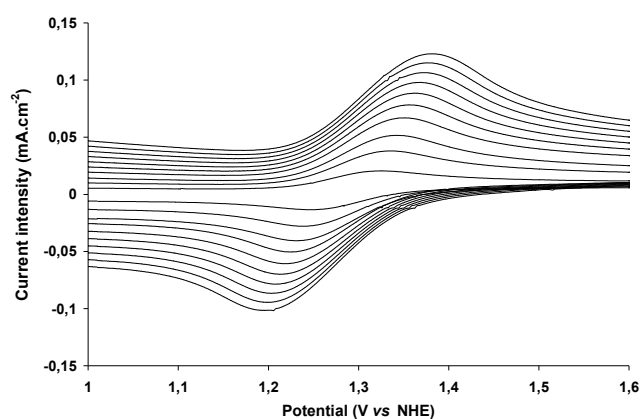


Figure S4. Small-angle X-ray diffraction of *templated nano*-ITO films calcined at 450°C. The most intense peak can be attributed to the (220) of mesopores organized into a cubic structure. The peaks before are due to interference.

Table 1. Crystallites size as function of the heat-treatment. Evolution of the crystallites size as function of the heat-treatment, determined from Debye and Scherrer formula (noted D(222)sherrer in the table), Dmean corresponds to mean diameter obtained by this method, and from Williamson et al. approach (noted D Williamson et hall in Table 1).

| Temperature | D (222)-Scherrer | D mean | D williamson et Hall |
|-------------|------------------|---------|----------------------|
| 300 °C | 15 nm | 15,6 nm | 16,6 nm |
| 450 °C | 21 nm | 20,4 nm | 25 nm |
| 550 °C | 23 nm | 21,5 nm | 30 nm |



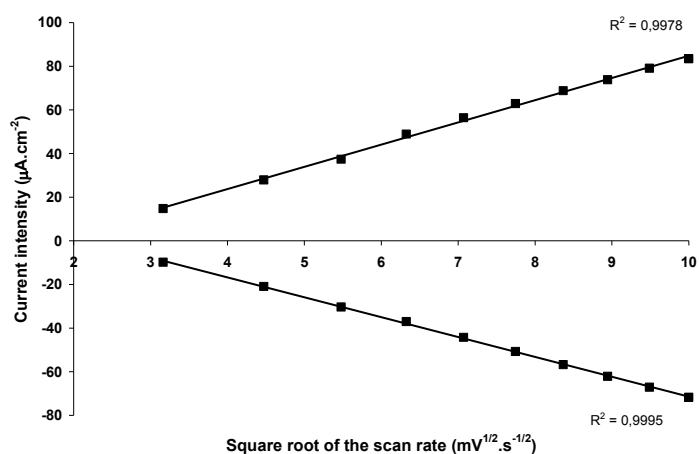


Figure S5. *Top* Cyclic voltammograms of [Ru(bpy)₃]Cl₂, 1 mM in 0.1M aqueous HOTf at scan rates varying from 10 to 100 mV.s⁻¹, recorded at a non-functionalized nanostructured ITO electrode (10 layers, treated at 450°C for 1 hour in air; electrode surface: 1 cm²). *Bottom* Linear evolution with the square root of the scan rate of the cathodic and anodic peak currents (capacitive current subtracted) related to the Ru^{III}/Ru^{II} couple.

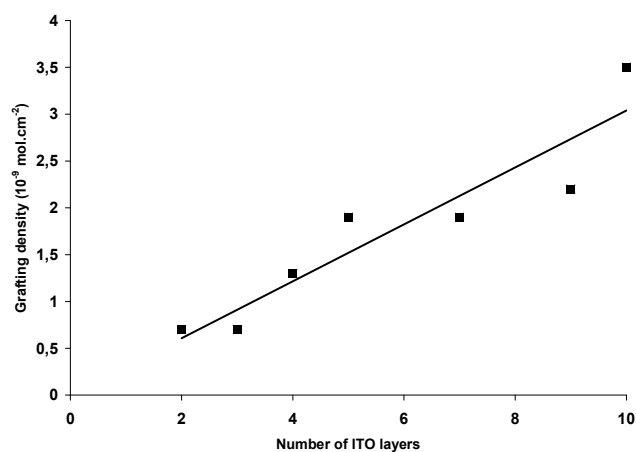
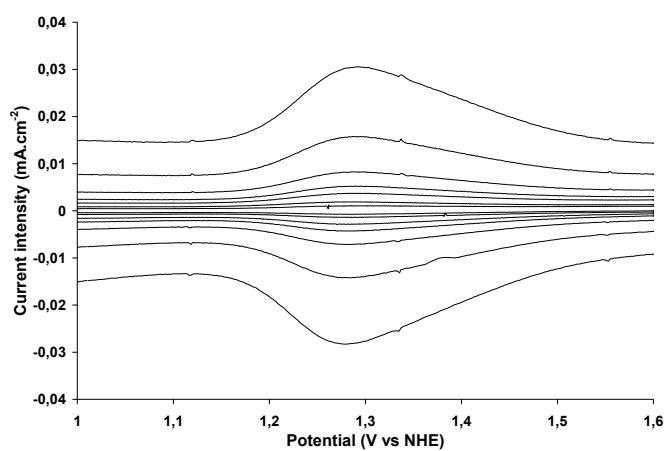


Figure S6. Dependence of the grafting density on the number of layers for multi-layered nanostructured ITO films.



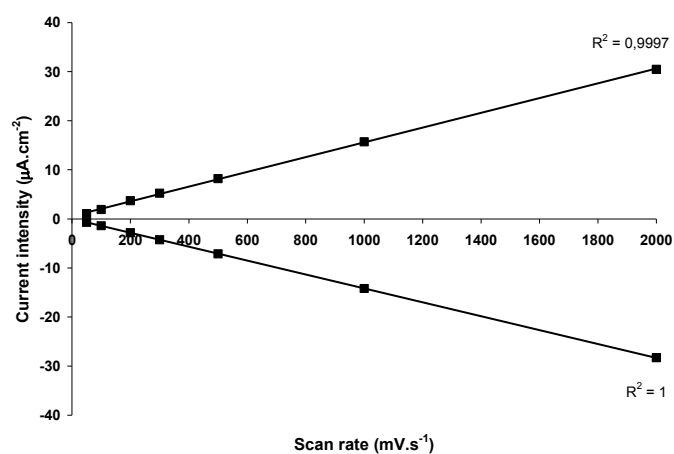


Figure S7. *Top* Cyclic voltammograms of complex **1** adsorbed on planar ITO (electrode surface: 1 cm^2), recorded in 0.1M aqueous HOTf at scan rates varying from 50 to $2000\text{ mV}\cdot\text{s}^{-1}$. *Bottom* Linear evolution with the scan rate of the cathodic and anodic peak currents related to the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ couple.

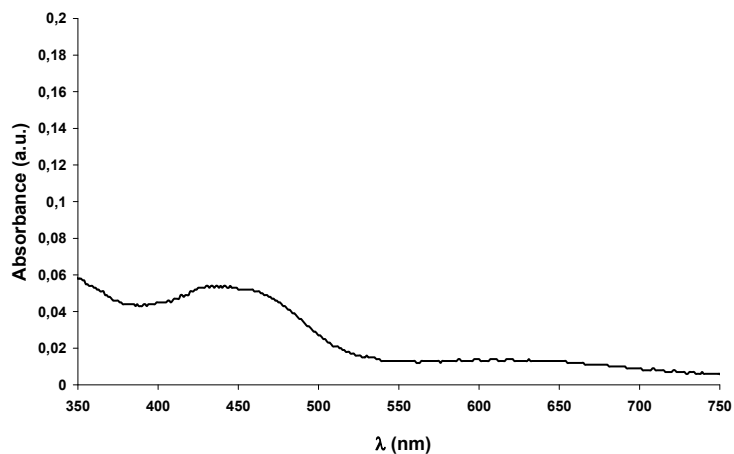


Figure S8. Absorption spectrum of complex **1** adsorbed on *templated nano-ITO* (10 layers, treated at 450°C for 1 hour in air), after subtraction of the absorption of the non-functionalized *templated nano-ITO* film.

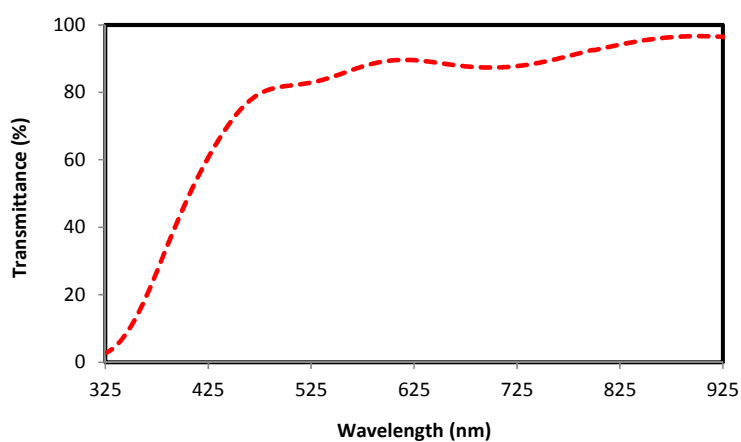


Figure S9. Transmittance for the 10-layers *dense nano-ITO* film heat-treated at 450°C for 1 h in air

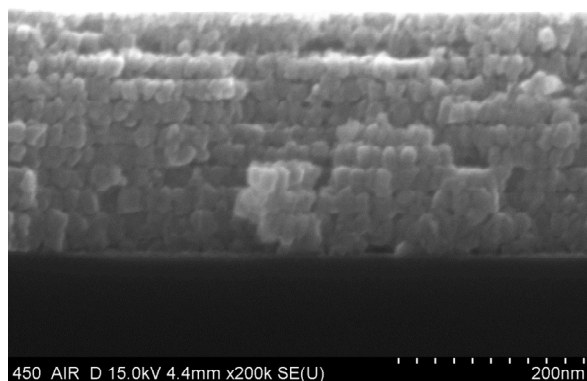


Figure S10. FE-SEM image (cross section view) of a 10 layers *dense nano-ITO* film treated at 450°C, in air.

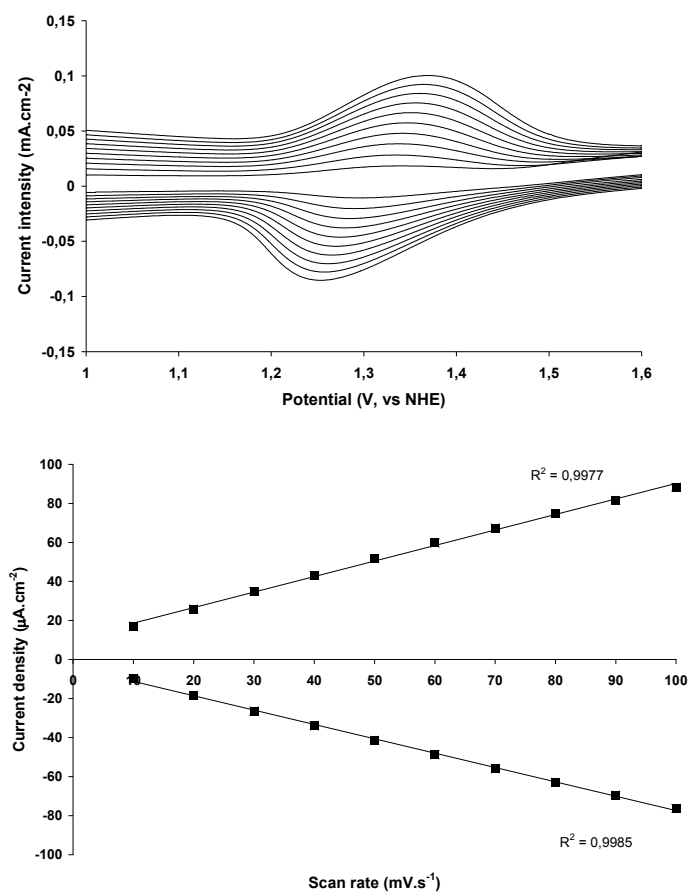


Figure S11. *Top* Cyclic voltammograms of complex **1** adsorbed on *dense nano-ITO* (10 layers prepared in the absence of template, treated at 450°C for 1 hour in air; electrode surface: 1 cm²), recorded in 0.1M aqueous HOTf at scan rates varying from 10 to 100 mV.s⁻¹. *Bottom* Linear evolution with the scan rate of the cathodic and anodic peak currents related to the Ru^{III}/Ru^{II} couple.

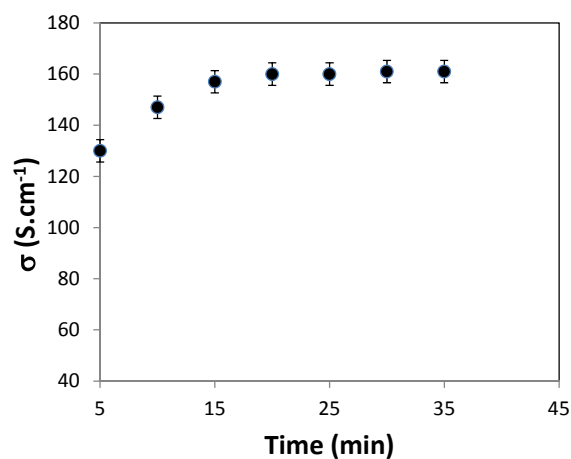


Figure S12. *In situ* electrical conductivity of films (thickness = 470 nm) heat-treated in air at 450°C: Evolution of the conductivity as a function of time for 10-layer templated nano-ITO films heated in 5% of H_2 in Ar at 200°C.

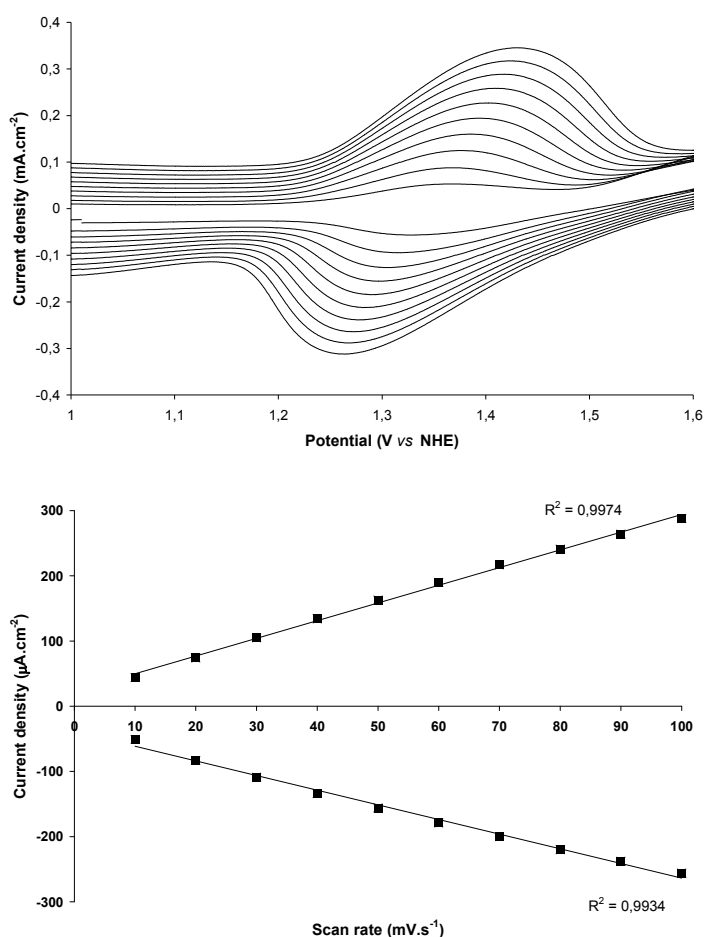


Figure S13. *Top* Cyclic voltammograms of complex 1 adsorbed on H_2 -treated templated nano-ITO (10 layers, treated at 450°C for 1 hour in air then under 5% H_2 in Ar at 200°C for 30 min; electrode surface: 1 cm^2), recorded in 0.1M aqueous HOTf at scan rates varying from 10 to 100 $\text{mV}\cdot\text{s}^{-1}$. *Bottom* Linear evolution with the scan rate of the cathodic and anodic peak currents related to the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ couple.

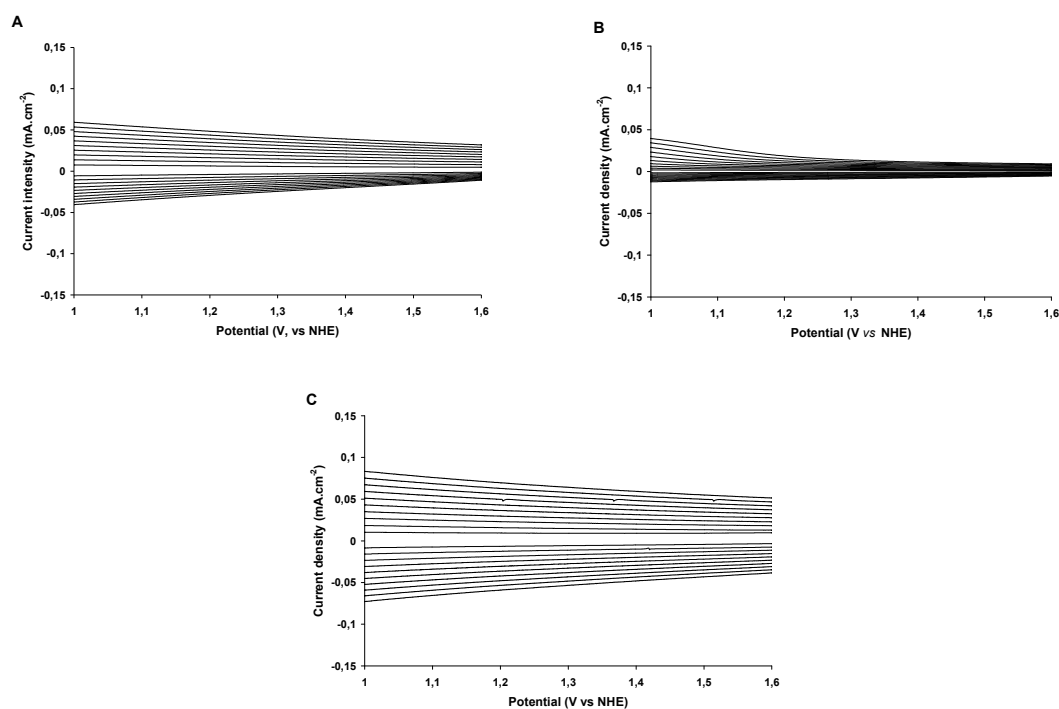


Figure S14. Sections of the cyclic voltammograms of non-functionalized **A)** 10-layer *templated nano-ITO*, **B)** 10-layer *dense nano-ITO*; **C)** 10 layers H_2 -treated *templated nano-ITO*; recorded in 0.1M aqueous HOTf at scan rates varying from 10 to 100 $mV.s^{-1}$ (electrode surface: 1 cm^2).

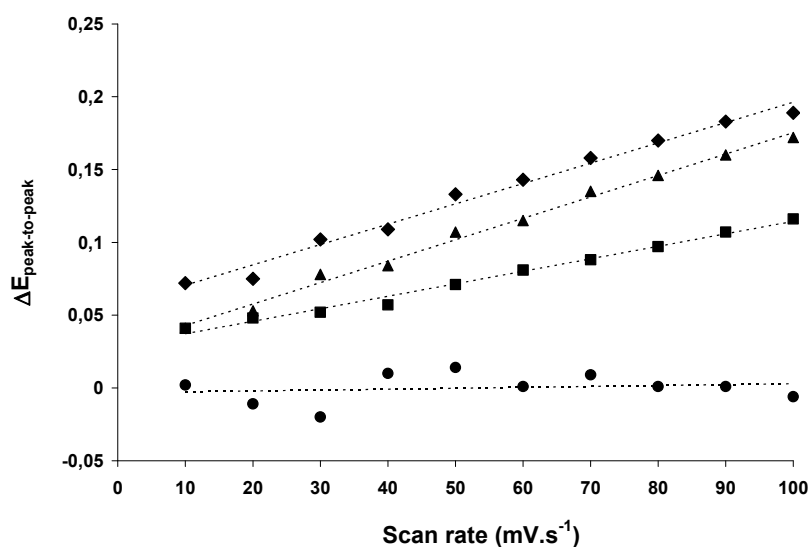


Figure S15. Peak-to-peak splitting between the oxidation and the reduction peak of complex **1** grafted on a 10-layer *templated nano-ITO* electrode (\blacklozenge), a 10-layer H_2 -treated *templated nano-ITO* electrode (\blacktriangle), a 10-layer *dense nano-ITO* electrode (\blacksquare) or a planar ITO electrode (\bullet) (recorded in 0.1M aqueous HOTf at scan rates varying from 10 to 100 $mV.s^{-1}$).