

Controlling Supramolecular Structures in Iron Tetrasulfonated Phthalocyanine Films through pH Variation: Implications for Thin-Film Device Performance

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Raman band assignments

Table S1. Raman band assignments for FeTsPc powder and PAH/FeTsPc LbL films.

Powder (cm ⁻¹)	PAH/FeTsPc film			Assignments
	pH 2.5	pH 6.0	pH 9.0	
507	507	504	504	Isoindole deformation ^{1,2}
600	604	602	603	Macrocycle vibration ^{1,2} , macrocycle breathing ³
683	689	689	690	Macrocycle vibration ^{1,2} , Pc breathing ⁴
749	751	752	752	Macrocycle vibration ¹⁻³ , C-H out-of-plane bending ^{4,5}
1327	1337	1339	1338	Pyrrole stretching ¹⁻⁴
1522	1533	1533	1533	C=C, C=N pyrrole stretching ¹⁻⁴

Molecular Organization: of PAH/FeTsPc LbL film at pH 2.5.

The molecular Organization of PAH/FeTsPc LbL film (at pH 2.5) was also evaluated by FTIR measurements (Figure S1), considering the surface selection rules^{6,7}. The surface selection rules for FTIR measurements are based on the scalar product of dipole moment (μ) and the electric field of the beam (E), following $I = \mu \cdot E \cos \theta$. Thus, the maximum band intensity is observed for μ parallel to the E . Here, differences in the relative intensity of key bands from Pc indicate anisotropy of the casting film and preferential molecular orientation in the LbL films. For instance, the phthalocyanine bands assigned to in-plane C-H bending (1109 cm⁻¹), Pc ring breathing (759 cm⁻¹) (also in the plane of the FeTsPc macrocycle), and out-of-plane C-H wagging (700 cm⁻¹) are evident in the FTIR spectra at transmission mode. However, the C-H out-of-plane band almost vanishes in reflection

mode, and the Pc ring breathing at 759 cm^{-1} predominates. Thus, the FTIR measurements suggest the FeTsPc molecules must be with the macrocycle, preferably oriented at an angle of $45\text{-}90^\circ$ at the substrate surface. In our case, the FTIR results agree with Raman analysis, revealing a tendency of the Pc macrocycle to tilt toward the substrate surface. The FTIR spectra also showed a shift in the band ascribed to SO_3^- stretching (1192 to 1181 cm^{-1}) when comparing FeTsPc casting and PAH/FeTsPc LbL film (Figure 6), which gives evidence of the formation of “saline bridges” – interaction between NH_3^+ of PAH and SO_3^- of FeTsPc ⁸.

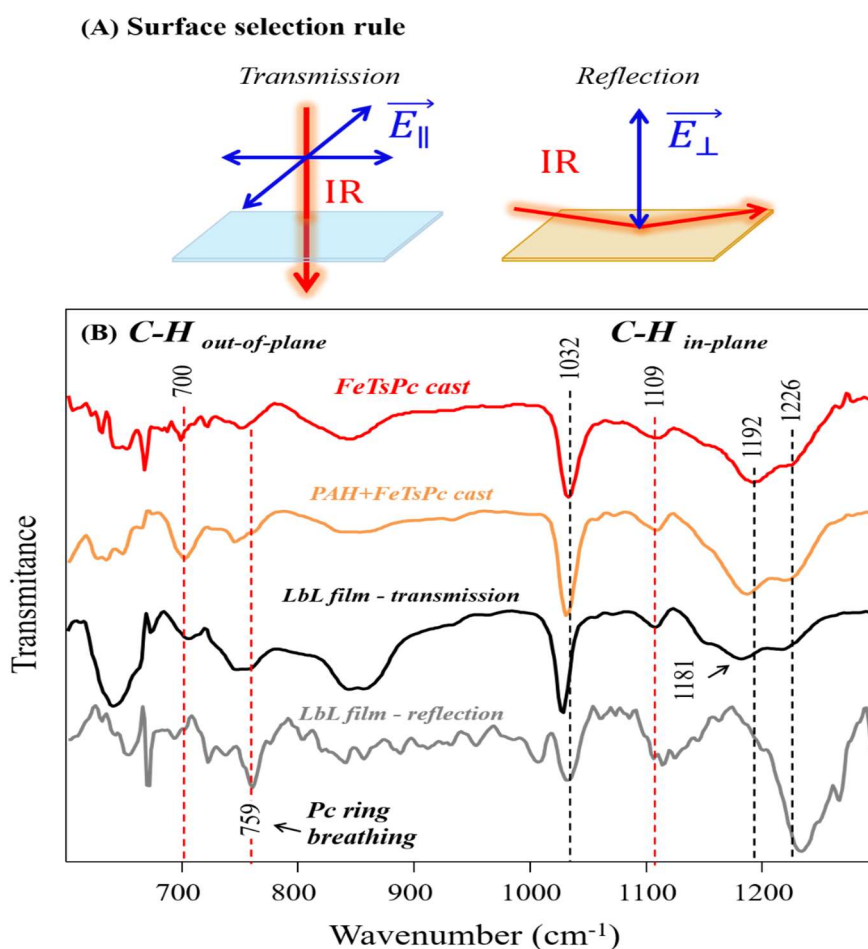


Figure S1. (A) Schematic representation of surface selection rule for transmission and reflection infrared spectroscopy, following $I = \mu \cdot E \cos \theta$. (B) FTIR spectra for FeTsPc casting (red), PAH+FeTsPc casting (orange), and PAH/FeTsPc LbL film (at pH 2.5) (black and gray). The transmission mode was performed to the film onto the Ge substrate and the reflection mode onto the Au substrate. PAH/FeTsPc LbL film has 30 bilayers for transmission mode and 60 for reflection mode measurements. All the spectra are plotted with normalized intensity.

Surface coverage (Laviron equation)⁹

$$\Gamma = Q/nFA$$

The charge Q (C) was calculated by the integration of the anodic peak obtained from the cyclic voltammogram in HCl using a scan rate of 50 mV/s; n is the number of electrons transferred (assumed to be 1); F the Faraday constant (96485 C/mol), and A the geometry area of the working electrode (1 cm²).

Thickness (from Faraday equation)

$$h = wQ/nFA\rho = w\Gamma/\rho$$

The Γ (surface coverage) was obtained using the relation of $\Gamma = Q/nFA$ as described above, w is the sum of molecular weight of monomers (FeTsPc (942.60 g/mol) and PAH (56 x 10³ g/mol)), and ρ the film density normalized to be 1 (g/cm³).

AFM images

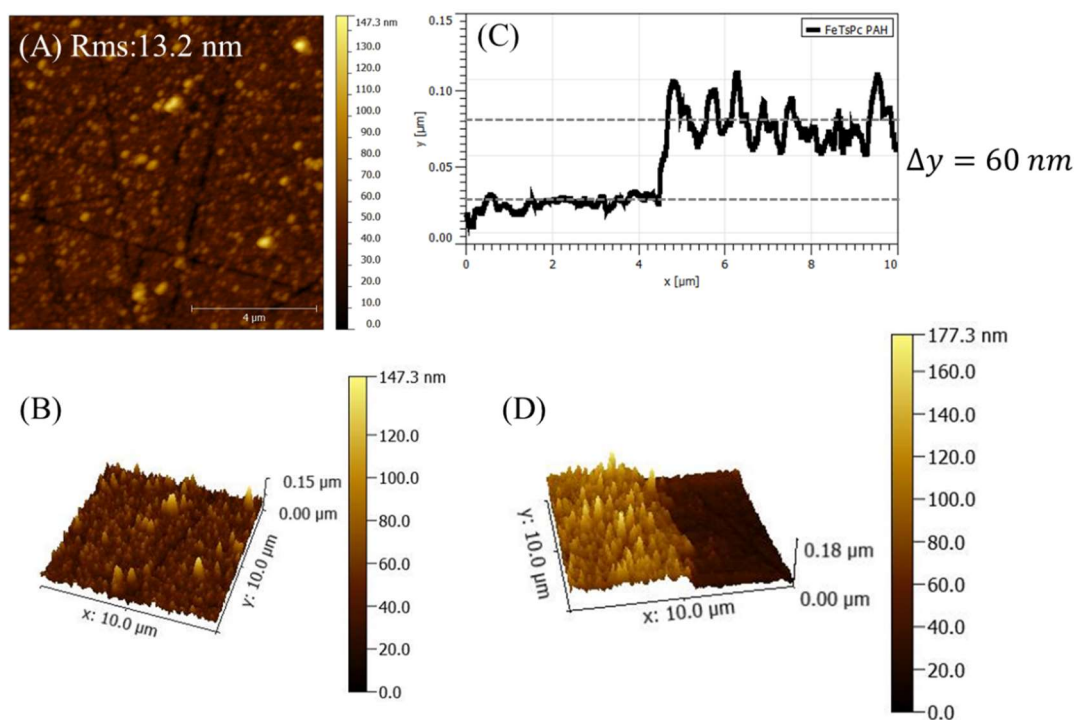


Figure S2. AFM images of topography (A, B) and thickness (C, D) of PAH/FeTsPc(2.5) film. The AFM images were collected using a Nanosurf microscope model Easyscan2 in tapping mode with a resolution of 512 dots/line and an area of 10x10 μm. The images were processed using the Gwyddion 2.9 software.

ITO bare electrode in the presence of catechol

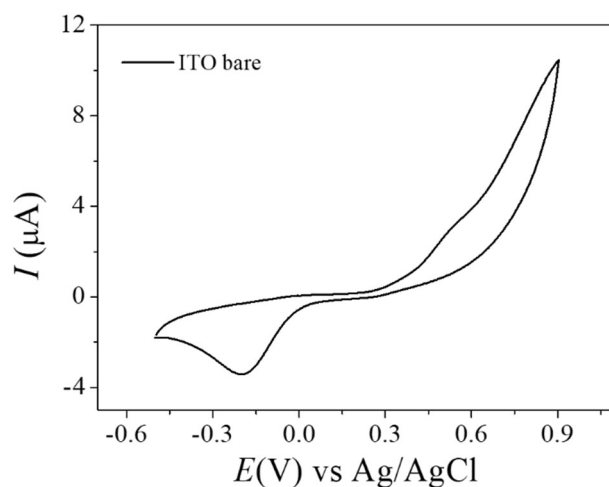


Figure S3. Cyclic voltammograms ITO bare electrode recorded in the presence of 1.0×10^{-4} mol/L of catechol at 50 mV/s using the 1 mmol/L HCl as supporting electrolyte.

Scan rate effect – modified electrodes

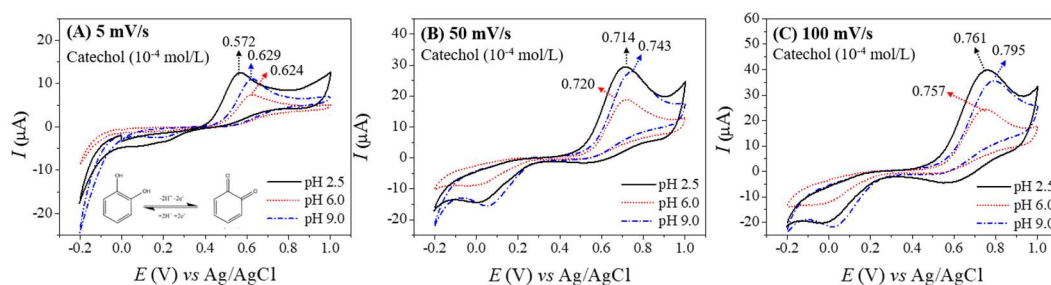


Figure S4. Cyclic voltammograms PAH/FeTsPc(2.5), PAH/FeTsPc(6.0), and PAH/FeTsPc(9.0) onto ITO recorded in the presence of 1.0×10^{-4} mol/L of catechol at 50 mV/s using 1 mmol/L HCl as supporting electrolyte.

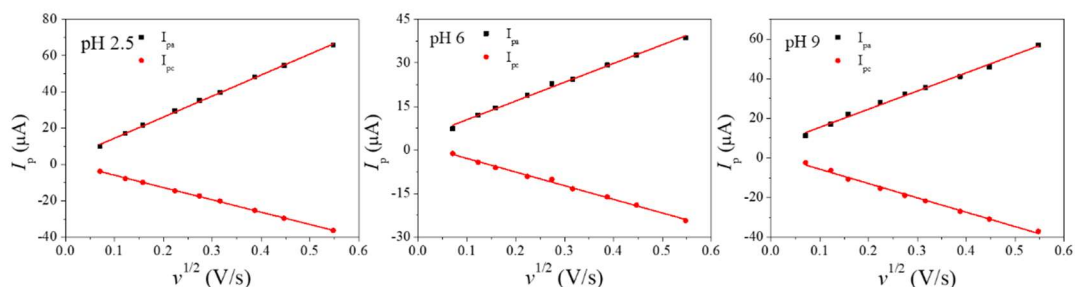


Figure S5. Peak current in the function of the square root of scan rate.

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