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## SUPPLEMENTARY MATERIAL TO Electrical, optical and structural characterization of interfaces containing poly(3-alkylthiophenes) (P3ATs) and polydiphenylamine on ITO/TiO<sub>2</sub>: Interaction between P3ATs polymeric segments and TiO<sub>2</sub>

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Fig. S-1. Impedance magnitude (A) and Bode-Phase (B) diagrams at open-circuit potential and constant temperature of 22 °C for the ITO/TiO<sub>2</sub> system.

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**Fig. S-2.** Raman spectra of the ITO/TiO2/PDPA system. Post-synthesis analysis times were a) 0 h, b) 1 h, c)5 h, d) 10 h, e) 15 h, f) 24 h, g) 30 h and h) 97 h at excitation of 532 nm. Insert 5. Deconvoluted Raman spectra for the ITO/TiO2/PDPA system after A) 0 h and B) 97 h.



**Fig. S-3.** Raman spectra of the ITO/TiO<sub>2</sub>/PDPA/P3HT system. Post-synthesis analysis times were a) 0 h, b)1 h, c) 5 h, d) 10 h, e) 15 h, f) 24 h, g) 30 h and h) 97 h, at excitation of 532 nm. Insert 6. Deconvoluted spectra for the ITO/TiO<sub>2</sub>/PDPA/P3HT after A) 0 h and B) 97 h.

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**Fig. S-4.** Impedance magnitude (A) and Bode-Phase (B) diagrams at open-circuit potential and constant temperature of 22 °C for the ITO/TiO<sub>2</sub>/PDPA/P3HT system. Post-synthesis analysis times were a) 0 h (solid square), b) 1 h (empty square), c) 5 h (solid circle), d) 10 h (empty circle), e) 15 h (solid triangle), f) 24 h (empty triangle), g) 30 h (empty lozenge) and h) 97 h (solid lozenge), after electrochemical synthesis.



**Fig. S-5.** Raman spectra of the ITO/TiO<sub>2</sub>/PDPA/P3MT system. Post-synthesis analysis times were a) 0 h, b) 1 h, c) 5 h, d) 10 h, e) 15 h, f) 24 h, g) 30 h and h) 97 h, at excitation of 532 nm.

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**Fig. S-6.** Impedance magnitude (A) and Bode-Phase (B) diagrams at open-circuit potential and constant temperature of 22 °C for the ITO/TiO<sub>2</sub>/PDPA/P3MT system. Post-synthesis analysis time were a) 0 h (solid square), b) 1 h (empty square), c) 5 h (solid circle), d) 10 h (empty circle), e) 15 h (solid triangle), f) 24 h (empty triangle) and g) 30 h (empty lozenge), after electrochemical synthesis.

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