

A Low Band Gap Conjugated Polymer for Supercapacitor Devices[†]

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We present the electrochemical polymerization and characterization of a stable and dopable polyindophenine derivative starting from monomer **5**. The fabrication of supercapacitor devices was carried out by direct electrochemical polymerization on an ITO-coated slide. Furthermore, the galvanostatic and potentiostatic experiments conducted on these supercapacitors have shown that the polyindophenine-derivative material has very good cyclability, over a potential range of 1.4 V, and a maximum capacitance of 140 F g⁻¹.

Introduction

In the energy storage research field, supercapacitors, also known as electrochemical capacitors, are among the most studied electrochemical devices. The possibility to use these systems to power hybrid electric vehicles (HEVs), camera flash bulbs, pulsed lasers, or any other device that requires a large amount of charge delivered in a very short time could be realized with supercapacitors.¹

Electronically conducting polymers (CPs) are, among a wide list of candidates, some of the most promising materials for the production of high-performance supercapacitors.^{2–5} They generally offer three important properties: (i) high specific capacitance, due to involvement of the whole polymer mass in the charging process; (ii) high conductivity in the doped state; and (iii) fast charge/discharge electron-transfer kinetics. Depending on the characteristics of the starting monomer, different synthetic methodologies can be utilized to obtain the polymeric material.

Electrochemical polymerization⁶ provides a convenient way to synthesize a conducting polymer (CP) directly on the electrode, offering at the same time a fine control over the amount of deposited material and over the degree of doping.

In this work, we present the electrochemical polymerization and characterization of an n/p-type supercapacitor device based on a new electrosynthesized indophenine-based polymer.⁷ Figure 1.

Experimental Details

All chemicals used in the synthesis were purchased from Aldrich. Tetrahydrofuran (THF) was distilled over sodium benzophenone before use, whereas all other solvents were purified using an engineering solvent purification system. All new compounds were characterized by ¹H, ¹³C NMR, EI-MS, and elemental analysis. NMR spectra were taken on a Bruker ARX 400 spectrometer. All chemical shifts were reported relative to tetramethylsilane (TMS). Melting points were measured using a capillary melting point apparatus (MelTemp from Laboratory Devices) and were uncorrected. Elemental analysis results were obtained from Desert Analytics Co. Chemicals used in the electrochemical experiments: poly(methyl methacrylate) (PMMA) 25 000 from Polysciences, Inc., lithium

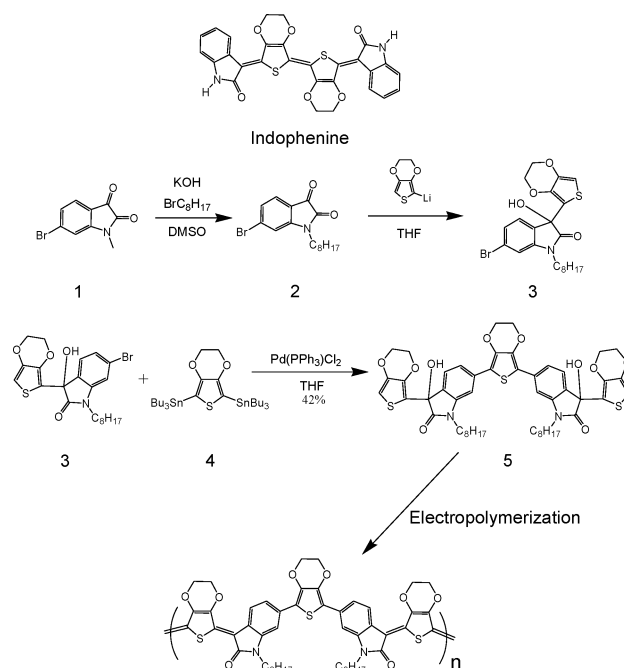


Figure 1. Synthesis and structure of monomer **5**, indophenine and electrosynthesized polymer.

perchlorate (LiClO₄) 99.99% from Aldrich, tetrabutylammonium hexafluorophosphate (TBAPF₆) electrochemistry grade from Fluka, and anhydrous propylene carbonate (PC) 99.7% from Aldrich were used as received. Potentiostatic experiments were carried out on a BAS100B/B potentiostat, whereas an EG&G Princeton Applied Research model 263A was used for galvanostatic experiments. A three-electrode configuration cell with Pt wire as counter electrode and Ag wire as pseudoreference electrode was used during the electropolymerization as well as monomer-free solution characterization of the polymer. Pt gauze (100 mesh, 99.9%) from Aldrich and ITO-coated slides (7 mm × 50 mm × 0.7 mm, 5–15 Ω per square) from Delta Technologies were used as working electrodes. Polymer-coated ITO slides were then used, after careful cleaning in DCM, as supercapacitor electrodes. Polymer-coated electrodes were dried at room temperature overnight in the laboratory environment. Considering that the solvent used during the electropolymerization was DCM, it should definitely have evaporated during

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this amount of time without heating the sample. The amount of material deposited on the electrode was determined by two different approaches: (i) using charge vs weight curves obtained preparing different Pt grid electrodes (previously weighed) coated with different amounts of polymer; (ii) scraping the electropolymerized material from the ITO slide and weighing it directly using a very sensitive microbalance. Several experiments using different amounts of material deposited onto the electrode gave results in good agreement with the previous approach, and no large discrepancy was observed. Since a considerable number of experiments to determine the amount of polymer present on the electrode and the reproducibility of the charge vs weight curves were performed, we believe our results are a reasonable estimate with error no bigger than 10% on the capacitance measurements. A microporous polypropylene membrane (Cellgard 2500, thickness 25 μm , porosity 55%), treated with a plasticized gel AN/PC/PMMA/LiClO₄ with weight ratio 70:20:7:3, was used as a separator in the supercapacitor device.

Hitachi S4700 field emission scanning electron microscopy (SEM) was used for morphological imaging.

Synthesis of *N*-Octyl-6-bromoisatin 2. A sample of 6-bromoisatin⁸ **1** (5.5 g, 24.3 mol) dissolved in 80 mL DMSO was treated with a solution of 1.36 g KOH (24.3 mol) and 25 mL ethanol at room temperature. After 10 min, a solution of 5.63 g 1-bromooctane (29.2 mmol) and 20 mL DMSO was added. The mixture was stirred at room temperature for 3 days, then 200 mL diethyl ether and 150 mL water were added. The organic layer was washed with brine and dried with anhydrous sodium sulfate. After the solvent was evaporated, the residue was purified by column chromatography with CH₂Cl₂. The product was recrystallized in hexane to afford 5.8 g orange crystals of *N*-octyl-6-bromoisatin **2** (75%), mp 74–76 °C. ¹H NMR (CDCl₃): δ 7.46 ppm (d, J = 7.9 Hz, 1H), 7.27 ppm (dd, J = 1.5 Hz, J = 7.1 Hz, 1H), 7.06 ppm (d, J = 1.5 Hz, 1H), 3.69 ppm (t, J = 7.1 Hz, J = 7.6 Hz, 2H), 1.69 ppm (m, 3H), 1.25–1.40 ppm (m, 13H), 0.88 ppm (t, J = 6.4 Hz, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃): δ 182.4, 115.9, 147.7, 133.5, 126.8, 126.4, 116.3, 113.8, 40.5, 31.7, 29.1, 27.2, 26.8, 22.6, 20.0, 14.1. EI-MS m/z : 337 (M^+ for C₁₆H₂₆⁷⁹BrNO₄S). Anal. Calcd for C₁₆H₂₆BrNO₄S: C, 56.82; H, 5.96; Br, 23.62; N, 4.14. Found: C, 56.81; H, 5.81; Br, 23.86; N, 4.11.

Synthesis of *N*-Octyl-6-bromo-3-hydroxy-3-thienyl-2-indolinone 3. *n*-BuLi (6.2 mL, 2.5 M in hexane) was dropped into a stirring solution of 1.09 g 3,4-ethylenedioxythiophene (13.0 mmol) and 30 mL dry THF at –78° under argon atmosphere. The temperature of the mixture was raised to 20 °C and kept for 1 h. The mixture was added slowly into a solution of 4.0 g *N*-octyl-6-bromoisatin (11.8 mmol) and 100 mL dry THF with a syringe at –78 °C under argon protection. After 4 h, the mixture was extracted with 150 mL diethyl ether, and the organic layer was washed with water. After evaporating the solvent, the product was purified by column chromatography with hexane/ethyl acetate (7:2) to give 3.36 g white needle crystals of compound **3** (59%), mp 109–111 °C. ¹H NMR (CDCl₃): δ 7.29 ppm (d, J = 8.1 Hz, 1H), 7.21 ppm (dd, J = 1.5 Hz, J = 7.9 Hz, 1H), 7.00 ppm (d, J = 1.7 Hz, 1H), 6.25 ppm (s, 1H), 4.17 ppm (m, 4H), 3.93 ppm (s, 1H), 3.75 ppm (m, 1H), 3.56 ppm (m, 1H), 1.67 ppm (m, 2H), 1.23–1.45 ppm (m, 10H), 0.87 ppm (t, J = 6.6 Hz, J = 7.2 Hz, 3H). ¹³C NMR (CDCl₃): δ 175.5, 147.7, 145.7, 144.5, 138.3, 130.6, 128.4, 126.8, 125.8, 124.0, 112.2, 98.8, 74.9, 64.8, 64.4, 40.4, 31.8, 29.2, 27.1, 26.8, 22.6, 14.1. EI-MS m/z : 479 (M^+ for C₂₂H₂₆⁷⁹BrNO₄S). Anal. Calcd for C₂₂H₂₆BrNO₄S: C, 55.00; H, 5.45;

Br, 16.63; N, 2.92; S, 6.67. Found: C, 55.44; H, 5.30; Br, 10.94; N, 3.01; S, 6.28.

Synthesis of Monomer 5. Compound **3** (2.0 g, 4.17 mmol), 1.44 g 2,5-bis(tributylstannyl)-3,4-ethylenedioxythiophene **4**^{9,10} (2.0 mmol) and 146 mg dichlorobis(triphenylphosphine)-palladium (II) were dissolved in 150 mL THF. The mixture was refluxed overnight; upon cooling, 100 mL diethyl ether and 150 mL water were added. The organic layer was separated, washed with water, and dried with anhydrous sodium sulfate. After evaporating the solvent, the crude product was purified by column chromatography with hexane/ethyl acetate (3:1). 0.82 g of yellow crystals was obtained as compound **5** (44%), mp 124–126 °C. ¹H NMR (CDCl₃): δ 7.46 ppm (d, J = 6.6 Hz, 2H), 7.43 ppm (d, J = 7.9 Hz, 2H), 7.29 ppm (s, 1H), 6.34 ppm (s, 2H), 6.24 ppm (s, 2H), 4.41 ppm (s, 4H), 4.18 ppm (m, 8H), 4.01 ppm (s, 2H), 3.82 ppm (m, 1H), 3.66 ppm (m, 1H), 1.74 ppm (m, 4H), 1.20–1.41 ppm (m, 20H), 0.86 ppm (t, J = 6.6 Hz, J = 7.2 Hz, 6H). ¹³C NMR (CDCl₃): δ 175.7, 143.6, 141.6, 141.7, 139.2, 134.8, 132.7, 127.7, 125.67, 125.6, 120.7, 120.6, 115.9, 115.7, 106.5, 98.6, 75.2, 64.7, 64.6, 64.5, 64.4, 40.2, 31.8, 29.3, 29.2, 27.8, 27.2, 26.9, 26.8, 22.6, 17.5, 14.1, 13.6. EI-MS m/z : 940 (M^+). Anal. Calcd for C₅₀H₅₆N₂O₁₀S₃: C, 63.81; H, 6.00; N, 2.98; S, 10.22. Found: C, 63.98; H, 6.24; N, 3.01; S, 10.04.

Results and Discussion

Indophenine polymers have been reported over the years^{11–14} but have not been fully characterized, very likely due to their insolubility. Besides their pressed pellet conductivity, other potentially important properties such as electrochemistry and spectroscopy have not been reported. In the recent past, we have begun a project to prepare low band gap conjugated polymers based on highly colored (hence low band gap) monomers.¹⁵ Indophenine (Figure 1) is a deep blue-colored, insoluble material. Its insolubility can be ascribed to a combination of hydrogen bonding and π – π stacking. One of the strategies developed in our group for the incorporation of indophenine in a conjugated polymer is shown in Figure 1.

The monomer **5** was synthesized by Stille coupling between compound **3** and 2,5-bis(tributylstannyl)-3,4-ethylenedioxythiophene (**4**) catalyzed by dichlorobis(triphenylphosphine)palladium (II) in a purified yield of 42%. The organotin compound **4**^{9,10} was readily obtained in high yield by direct lithiation of 3,4-ethylenedioxythiophene, followed by reaction with stannyl chloride. 6-Bromoisatin **1** was synthesized through a two-step procedure, known as Sandmeyer reaction, using 3-bromoaniline as starting material.⁸ *N*-Octyl-6-bromoisatin **2** was obtained by the reaction of 6-bromoisatin with potassium hydroxide and 1-bromooctane in DMSO. The tertiary alcohol **3** was synthesized in analogy to Cava's report¹⁶ in two steps starting from compound **2** as described in the experimental details.

The electropolymerization of monomer **5** was carried out potentiodynamically on ITO-coated slides and Pt grids in a potential window between –0.3–1.2 V vs SCE at 100 mV/s. Figure 2 shows the first 10 cycles of polymer growth on a Pt grid electrode starting from a 2×10^{-3} M dichloromethane (DCM) solution of monomer, containing 0.2 M TBAPF₆. After the first irreversible process at 1.15 V vs SCE, due to the EDOT units contained in the monomer, a constant growth of multi-electronic processes starting at –0.2 V, due to the oxidations of the conjugated EDOT units now forming the polymer backbone, appeared as a result of continuous oxidation of the polymeric material formed on the ITO electrode. The entire electrode set used in the construction of supercapacitor devices

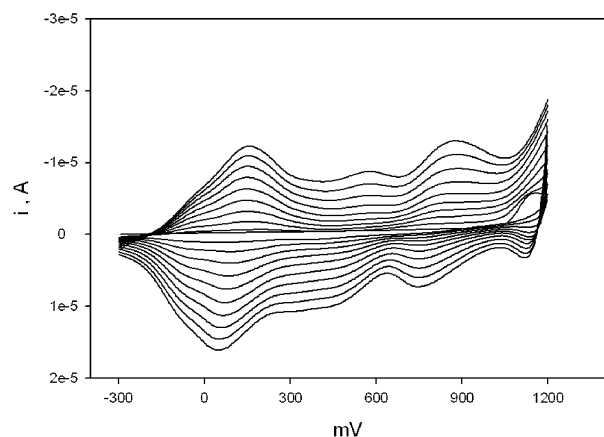


Figure 2. First ten electropolymerization cycles of a 2×10^{-3} M solution of **5**; Pt grid, 100 mV s^{-1} DCM/TBAPF₆.

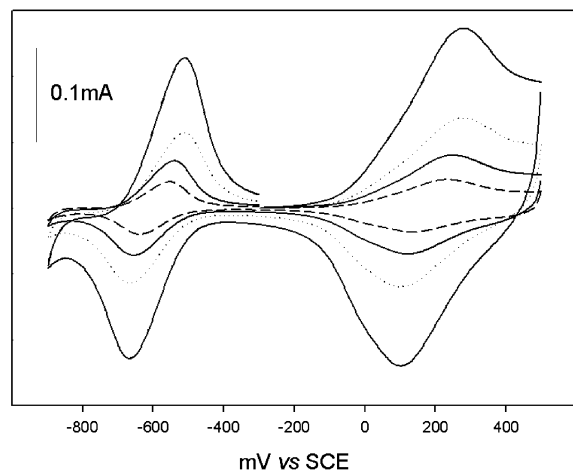


Figure 3. Cyclic voltammograms of the polymer, directly electrosynthesized on Pt grid, in a monomer-free DCM/TBAPF₆ solution at different scan rates: 50, 100, 200, and 400 mV s^{-1} .

was prepared by potentiodynamic electropolymerization as described above. The amount of polymer synthesized onto the electrode was monitored by the charge passed through the solutions during the electropolymerization process. The deposit material was weighed using a microbalance after washing the byproducts from the electrochemical process.

In Figure 3 are shown the cyclic voltammograms of the synthesized polymer, on Pt grid and in a monomer-free DCM solution, at 50, 100, 200, and 400 mV s^{-1} . In the investigated potential window between 0.6 and -1.0 V vs SCE , the polymers have shown one reversible oxidation processes, at 0.18 V vs SCE , and one reversible reduction process at -0.60 V vs SCE . Integration of the charge under the cathodic peak in both oxidation and reduction processes is, within the experimental error, identical to the charge under the anodic peaks, confirming the good reversibility of these electrochemical processes at the electrode–polymer interface. The value of peak current as a function of scan rate ($20\text{--}400 \text{ mV s}^{-1}$) shows a linear relationship indicating that the electron-transfer processes are fast on the examined time scale for both oxidation and reduction processes.

The absorption properties of the monomer **5** in DCM, together with the absorption properties of the polymer on ITO, are reported in Figure 4. Whereas the monomer spectrum (inset) shows a lower wavelength absorption band with maximum at 370 nm , the spectrum of the polymer looks completely different. A new absorption band having maximum at 890 nm and a tail

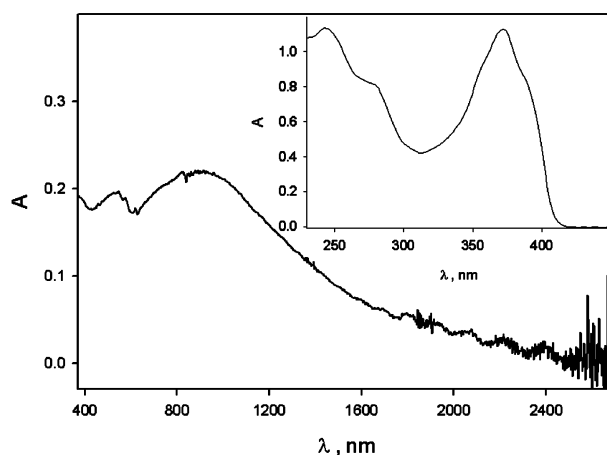


Figure 4. Absorption spectra of the polymer directly synthesized on ITO slide and of the monomer (inset) in DCM solution.

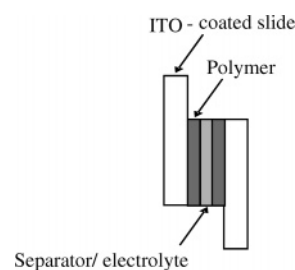


Figure 5. Schematic representation of the electrochemical supercapacitor.

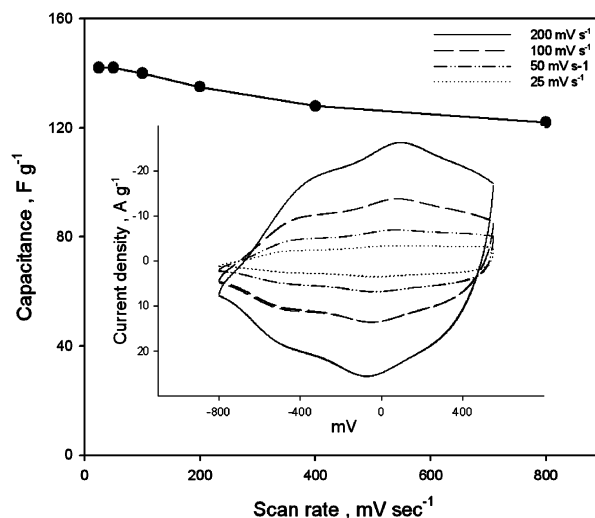


Figure 6. Scan rate dependence of the specific capacitance (F g^{-1}) in the supercapacitor device. Cyclovoltammetry of the capacitor device at different scan rates: 25, 50, 100, and 200 mV s^{-1} ; inset.

which extends up to 2400 nm appears as a result of the extended conjugation of the polymer backbone. Using the onset of the absorption tail, an optical band gap of 0.5 eV was calculated, which is in good agreement with the value obtained by the electrochemical measurements.

A schematic representation of the electrochemical supercapacitor¹⁷ is shown in Figure 5. Two sets of ITO electrodes coated with the same amount of polymer were electrically insulated by a microporous polypropylene membrane pretreated in a plasticized electrolyte solution; see experimental details. In Figure 6, the inset shows the cyclovoltammetry of the supercapacitor device at different scan rates (25, 50, 100, 200 mV s^{-1}). Even if the voltammogram's shape is not perfectly

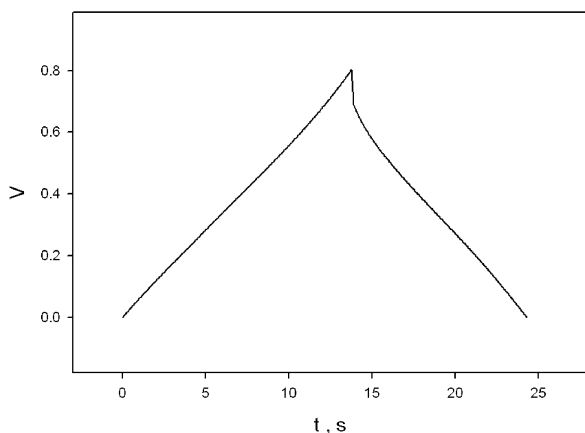


Figure 7. Galvanostatic charge and discharge cycle of the supercapacitor device at 0.1 mA cm^{-2} .

rectangular, as predicted from theory in the case of a pure capacitive process, the rapid increase of the current upon application of the potential followed by a plateau are distinctive signs of the capacitive nature of these electrochemical processes. Normalizing the CV curves in Figure 6 (inset) resulted in only a minor change in shape, indicating a reliable stability of the capacitor versus scan rate in all the investigated potential range ($-0.6/+0.6 \text{ V}$). Also reported in Figure 6 are the changes in maximum capacitance versus scan rate calculated for the CV experiments. The maximum capacitance is observed at low scan rate. At 25 mV s^{-1} , the device shows a maximum capacitance of 140 F g^{-1} ; increasing the scan rate by an order of magnitude gives a decrease in capacitance of only 8%, showing that most of the capacitance is still available even under fast charge/discharge conditions.

Galvanostatic charge/discharge cycles, at various current densities, were conducted on the device in order to better characterize the behavior of this material for capacitor applications. Figure 7 shows the galvanostatic cycle performed at 0.1 mA cm^{-2} . The galvanostatic measurements agreed with the potentiostatic experiments. The symmetry of the charge/discharge cycle (Figure 7), and the respective discharge capacitance 130 F g^{-1} at 0.1 mA cm^{-2} , show that the material releases 90% of the stored charge. A slight decrease of 15% of the total amount of stored charge was observed in the range of current density from 0.02 to 2 mA cm^{-2} , confirming the high power performance of the capacitor. A maximum capacitance of 140 F g^{-1} was obtained, in agreement with the CV analysis, from the charge/discharge experiments. Additionally, a capacitance decrease of 10% was observed during the first 1000 cycles. The observed gradual decrease of capacitance with time is most likely due to side reactions with moisture or oxygen during the continuous charge/discharge experiments.

The morphology of the electrosynthesized material, shown in Figure 8, was investigated by scanning electron microscopy (SEM) on both the ITO- and Pt-coated electrodes, and the results reported in Figure 8. Despite the two different substrates, the material always exhibits a highly porous open structure having a nonuniform polymer grain size in the micrometer and submicrometer range that provides a large and effective electrolyte-accessible surface area helping the fast charge/discharge dynamics. The polymer synthesized on Pt grid shows the presence of a few fibril-like structures, also observed in other organic polymers.^{2,18,19} However, the materials exhibits mostly a grapelike structure.

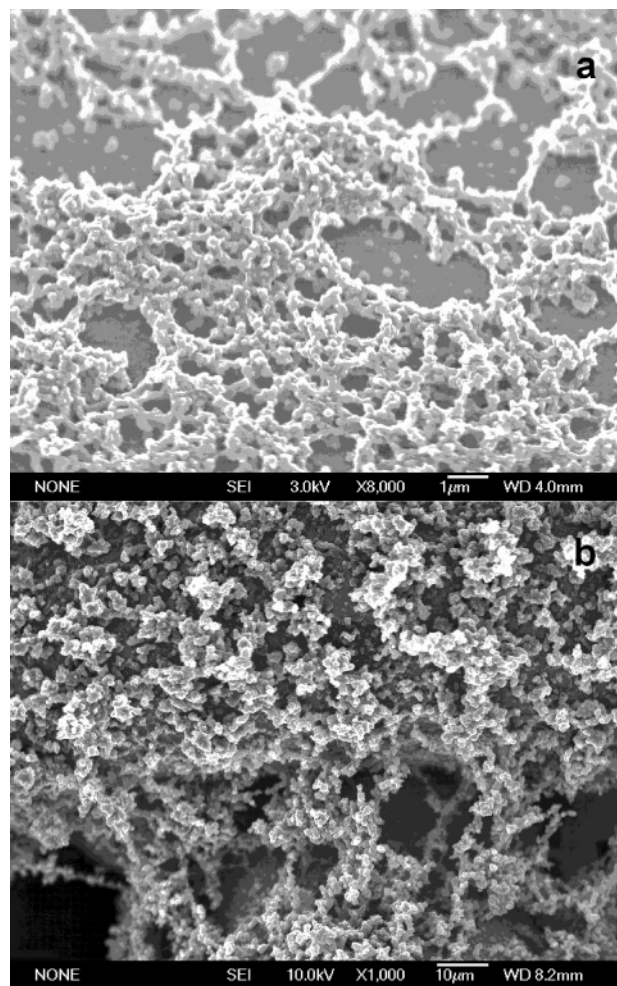


Figure 8. SEM pictures of the electrosynthesized polymer on (a) ITO coated slide, (b) Pt grid.

Conclusion

A new conjugated polymer containing indophenine repeat units was electrochemically potentiodynamically synthesized on ITO or Pt electrodes starting from a tertiary alcohol **5**. The symmetric polymer/polymer supercapacitor device exhibits squarelike cyclic voltammograms and a good stability over a potential window of 1.4 V . A maximum specific capacitance of 140 F gr^{-1} obtained by both potentiostatic and galvanostatic techniques together with good stability under different current densities demonstrates that the electrosynthesized material shows promising properties for supercapacitor applications.

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