Experimental

All materials were purchased from Aldrich or Acros and used as received unless otherwise noted.

Tris(4-(thiophen-2-yl)phenyl)amine (TTPA) solutions were prepared by dissolving 50 mg TTPA with 330 mg tetrabutylammonium tetrafluoroborate (TBABF$_4$) in 5 mL dry acetonitrile (MeCN) with 5 mL anhydrous methylene chloride (CH$_2$Cl$_2$), yielding solutions with 10 mM TTPA and 100 mM TBABF$_4$. Initial cyclic voltametry characterization was performed using a 2 mm diameter Pt working electrode (Pt mesh counter electrode and Ag/Ag$^+$ (0.3 M AgNO$_3$) reference electrode).

Two types of substrates were prepared for film deposition. On a homemade sputter system (details), 5 nm Ti and 500 nm Au were deposited on planar polyimide (Au/PI) substrates (Dupont Kapton® HN) and anodic alumina membranes (Au/Ano) (Whatman Anodisc 60 μm thick with 0.2 μm pores). The substrates were fastened in a Teflon well with a 0.5 cm$^2$ opening (toward the solution) with a Teflon O-ring. Au/PI were placed in the substrate holder with the gold film facing the solution and the Au/Ano substrates were placed in the holder with the gold film away from the solution (the solution gains access to the electrode through the pores). The TTPA solution was then added to the Teflon well, followed by the counter and reference electrodes. Films were deposited with chronoamperometry (0.7 V bias) and cyclic voltammetry (0 to 1 V, 100 mV/s). Following film deposition, the Teflon well (including the mounted substrate) was rinsed with dry acetonitrile numerous times and dried under a stream of nitrogen. In the 200 nm AAO membranes, the deposition was terminated when the polymer completely filled the pores, which was indicated by a sharp increase in current as the electrodes gained access to the bulk solution (approx. 600 sec).

The electrolyte solution for electrochemical characterization was prepared by dissolving 0.66 g TBABF$_4$ in 20 mL dry MeCN yielding 100 mM TBABF$_4$ solutions. The electrolyte was added to the Teflon well with the TTPA coated substrate. Cyclic voltammetry (CV), electrical impedance spectroscopy (EIS) and charge-discharge measurements were performed on a Princeton Applied Research VersaSTAT3 potentiostat. Similar to previously, a platinum mesh was used as the counter electrode with an Ag/Ag$^+$ (0.3 M AgNO$_3$) reference electrode. Cyclic voltametry scans were recorded between 0 and 1 V with scan rates of 5, 10, 30, 50, 100 mV/s (not all experiments used every scan rate). EIS was performed between 10 kHz and 0.1 Hz and charge discharge measurements were recorded between 0 and 0.9 V with current densities of 1, 2, and 4 mA/cm$^2$. 
Scanning electron microscopy (SEM) was performed on a Zeiss Supra 55VP Field Emitter Gun (FEG) SEM. Images of polymer films on Au/PI were recorded on the planar substrates. Cross-section images of the polymer in the alumina membranes were recorded after cleaving the membrane.

**Additional electrical characteristics**

**CV plots during film growth**

![CV plots](image)

Figure SI-1. (left) Initial 10 CV scans on 2mm dia. Pt working electrode. (right) CV during film deposition (100 mV/s, 50 cyc) on 0.5 cm$^2$ Au/PI. The red trace is the final scan.

The redox peak around 0.6 V shifts to a higher potential as the thickness of the film increases, due to the mass-transport limitations of the ion. An additional redox peak forms upon deposition due to the polymerization of the terminal thiophene groups. This process also experience transport limitations toward the conclusion of the deposition, as shown in the CV deposition curves consisting of 50 cycles (right).

**Electrical Impedance Spectroscopy**

![Impedance plots](image)

Figure SI-2. (left) The Nyquist plot of 3 films, nanotubes in 200 nm AAO (red) and porous films deposited via chronoamperometry (black) and cyclic voltammetry (blue), is presented. (right) The phase vs. frequency of the same devices (on left) is shown.