Online Supporting Information for:

## Enhanced performance of triarylamine redox electrodes through directed electrochemical polymerization

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The following figures show the complete cyclic voltammetry set for the data presented in manuscript figure 2. Figure S1 below shows the multiple CV scans recorded for each scan rate (100 mV/s, 30 mV/s, and 10 mV/s) for 4Me-TTPA (left) and TTPA (right). Note that the first scan at 100 mV/s gives a slightly higher current do to the presence of monomer remaining in the film after electrochemical deposition. Figure S2 shows extended cycling of each film over 200 cycles at 100 mV/s. Cycling measurements were performed in ambient conditions and no attempt was made to eliminate oxygen from the system.



**Figure S1**. Multiple current-voltage measurements recorded at multiple scan rates (100, 30, 10 mV/s) for 4Me-TTPA (left) and TTPA (right) films on a 1.6mm diameter Pt electrodes. The potentials are referenced to a pseudoreference electrode (Ag/Ag<sup>+</sup> in  $10^{-2}$  M silver nitrate, ferrocene E<sub>1/2</sub> = 0.100V).



**Figure S2**. Current-Voltage properties during extended voltage cycling (200 cycles) at 100 mV/s for 4Me-TTPA (left) and TTPA (right) films on a 1.6mm diameter Pt electrodes. The potentials are referenced to a pseudoreference electrode (Ag/Ag<sup>+</sup> in 10<sup>-2</sup> M silver nitrate, ferrocene  $E_{1/2}$  = 0.100V).

Figure S3 shows the shift in the peak oxidation potential with scan rate from v=10 mV/s to v=100 mV/s.



Figure S3. Redox potential (for peak current) vs scan rate (v) for each film.

The following figures show the possible molecular structures of the polymers formed during electrochemical polymerization of each monomer on a polished Pt electrode in a solution containing 0.1 M TBAF in solutions of acetonitrile and methylene chloride. Polymerization is carried out at a constant potential of 0.9 V vs. Ag/Ag+.



**Figure S4**. Molecular structures of polymers produced during the electrochemical synthesis of the monomer TTPA.



**Figure S5**. Molecular structures of polymers produced during the electrochemical synthesis of the monomer 4Me-TTPA.



**Figure S6**. Molecular structures of polymers produced during the electrochemical synthesis of the monomer 5Me-TTPA.