Voltammetric, Spectroscopic and Microscopic Investigations of Electrocrystallized forms of Semiconducting, AgTCNQ (TCNQ=7,7,8,8-tetracyanoquinodimethane) Exhibiting Different Morphologies and Colors

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## **Supporting Information**

Figures S1-S4: Raman and IR spectra and powder XRD of chemically synthesised AgTCNQ (Figure S1). Cyclic voltammetry at a gold electrode in acetonitrile (Figure S2) and at a chemically modified electrode in water (Figure S3). Optical microscopy of electrochemically synthesized AgTCNQ (Figure S4).

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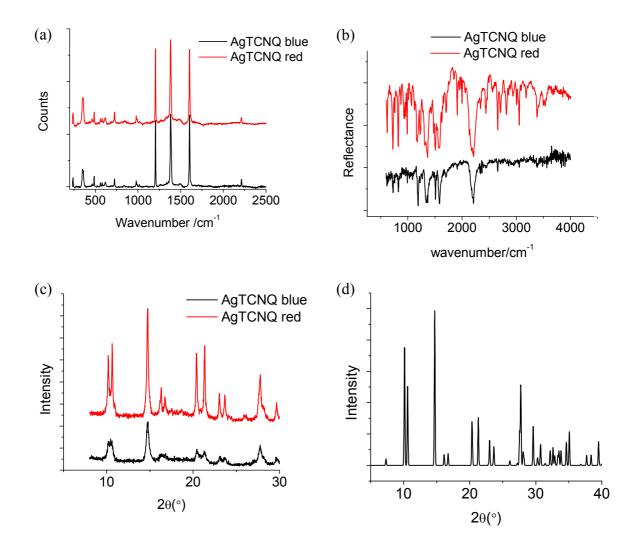


Figure S1: (a) Raman spectroscopy, (b) infrared spectroscopy and (c) powder XRD from chemically synthesized AgTCNQ blue and red forms according to reference 20 and (d) powder XRD calculated from single crystal data from reference 17.

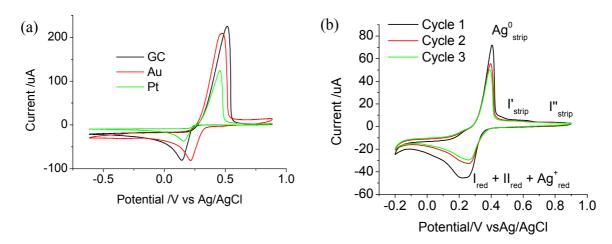


Figure S2: Cyclic voltammetry in acetonitrile (0.1 M Bu<sub>4</sub>NBF<sub>4</sub>) (a) second cycles of potential at a scan rate of 100 mV s<sup>-1</sup> for 10 mM  $Ag^{+}_{(MeCN)}$  at 1.5 mm diameter GC, 1.5 mm diameter gold and 1 mm diameter platinum electrodes and (b) potential cycles 1, 2 and 3 for equi-molar 9.1 mM  $TCNQ_{(MeCN)}$  and  $Ag^{+}_{(MeCN)}$  at a 1.5 mm diameter gold electrode using a scan rate of 20 mV s<sup>-1</sup>.

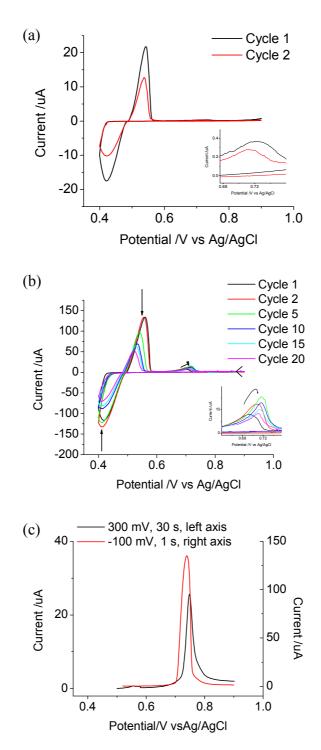


Figure S3: Cyclic voltammograms obtained in water (0.1 AgNO<sub>3(aq)</sub>) at a 3 mm diameter GC electrode at a scan rate of 20 mV s<sup>-1</sup> from (a) a drop cast  $TCNQ_{(s)}$ -modified electrode (b) a mechanically attached  $TCNQ_{(s)}$ -modified electrode (c) a modified electrode consisting of electrocrystallized AgTCNQ obtained from equi-molar 9.1 mM  $TCNQ_{(MeCN)}$  and  $Ag^{+}_{(MeCN)}$  in acetonitrile (0.1 M Bu<sub>4</sub>NBF<sub>4</sub>) when the potential is held for 30 s at 300 mV or 1 s at -100 mV.

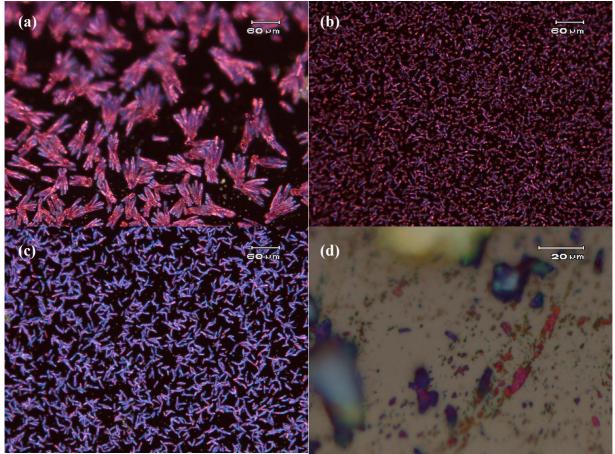


Figure S4: Optical microscopy of AgTCNQ generated as follows on a 3 mm diameter GC electrode (a)  $Ag_{(metal)}$  deposited from 10 mM  $Ag_{(MeCN)}^+$  in acetonitrile (0.1 M  $Bu_4NBF_4$ ) at -100 mV for 10 s, rinsed in acetonitrile and placed in 10 mM  $TCNQ_{(MeCN)}$  for a further 60 s. (b-c) Electrocrystallized from equi-molar 9.1 mM  $TCNQ_{(MeCN)}$  and  $Ag_{(MeCN)}^+$  in acetonitrile (0.1 M  $Bu_4NBF_4$ ) by (b) linear sweep voltammetry over the potential range of 1.1 V to 0 V and (c) cyclic voltammetry from 1.1 V to -300 mV at a scan rate of 100 mV s<sup>-1</sup>. (d) in 0.1 M  $AgNO_{3(aq)}$  via linear sweep voltammetry from 900 to 400 mV at a scan rate of 20 mV s<sup>-1</sup> of mechanically adhered  $TCNQ_{(s)}$ .