Supporting Information

Analysis of phenolic polymers as model melanins

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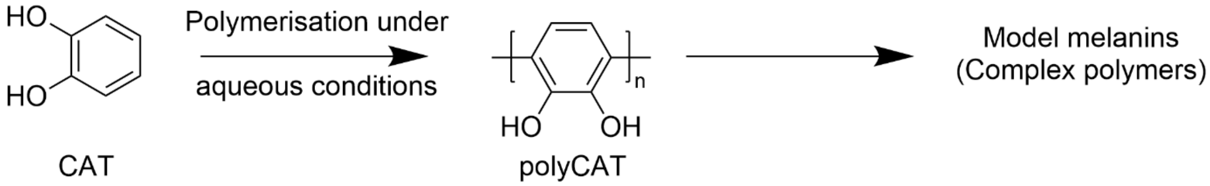
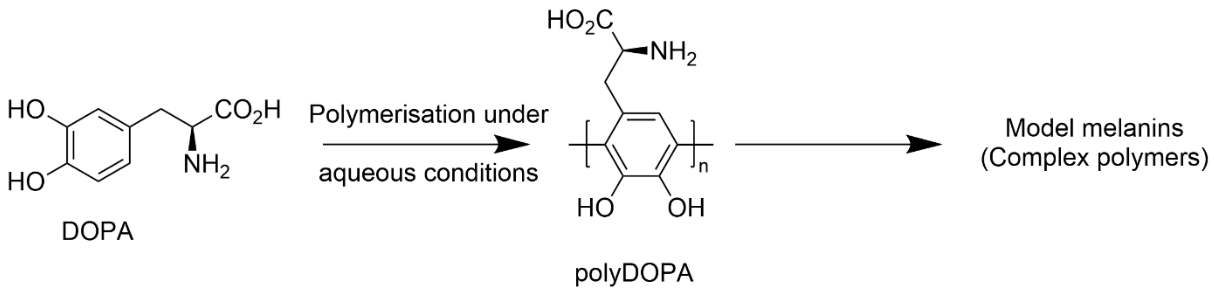
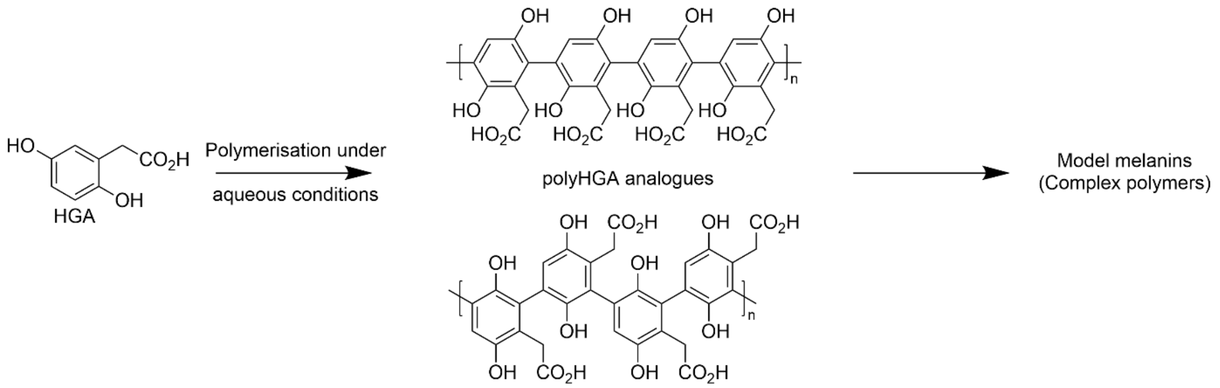


Scheme S1. A schematic of the polymerization of catechol (CAT) to form polyCAT, a simplified model melanin.



Scheme S2. A schematic of the polymerization of levodopa (DOPA) to form polyDOPA, a simplified model melanin. It is important to note that in vivo DOPA is converted to dopaquinone, then 5,6-dihydroxyindole-2-carboxylic acid (DHICA) followed by spontaneous decarboxylation resulting in 5,6-dihydroxyindole (DHI) in the final eumelanin. Moreover, the melanins formed in vivo may contain other monomers depending on the precise conditions under which they are formed in vivo.



Scheme S3. A schematic of the polymerization of homogentisic acid (HGA) to form polyHGA, a simplified model of pyomelanin. It is important to note that pyomelanin may contain other monomers depending on the conditions under which they are formed in vivo.

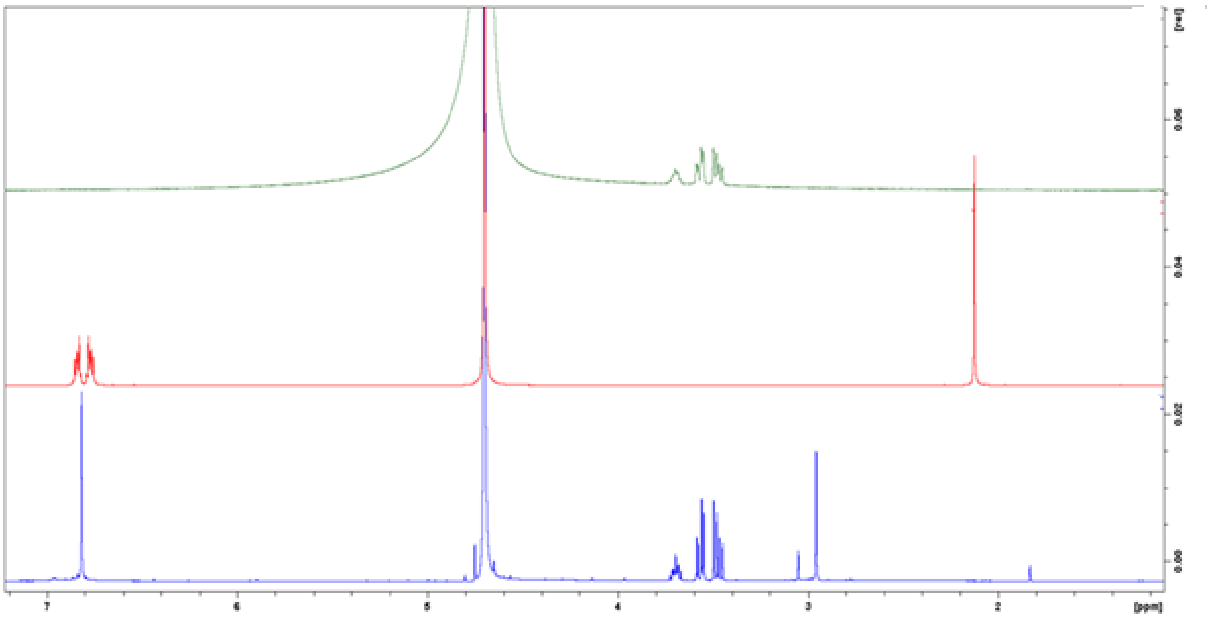


Figure S1. ^{1}H NMR of CAT (red, includes trace of acetone), polyCAT-HS (blue) and polyCAT-LS (green) in D_2O.

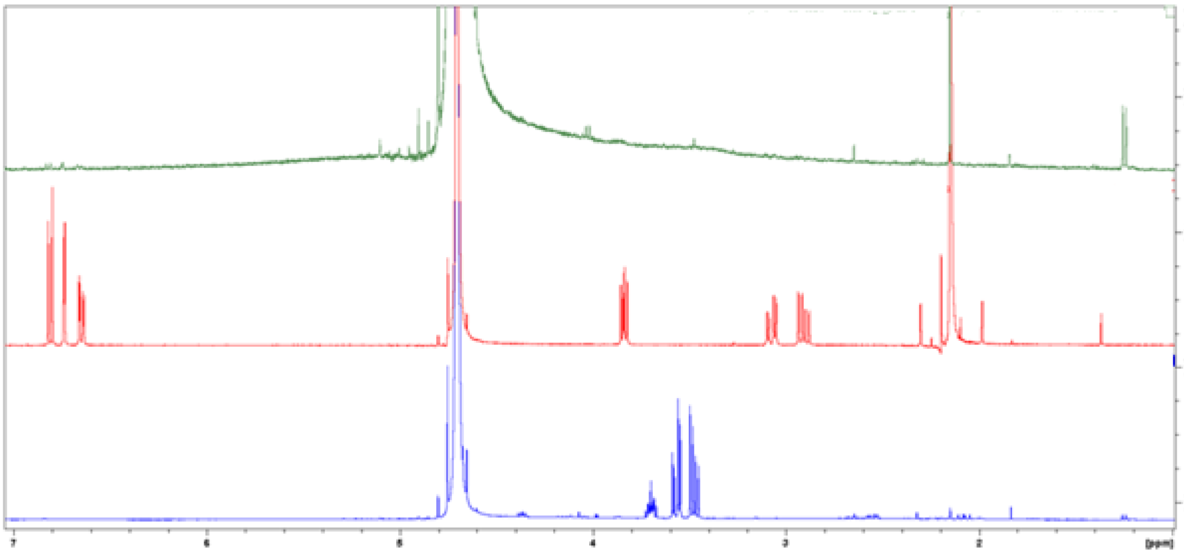


Figure S2. ^{1}H NMR of L-DOPA (red), polyLDOPA-HS (blue) and polyLDOPA-LS (green) in D_2O.

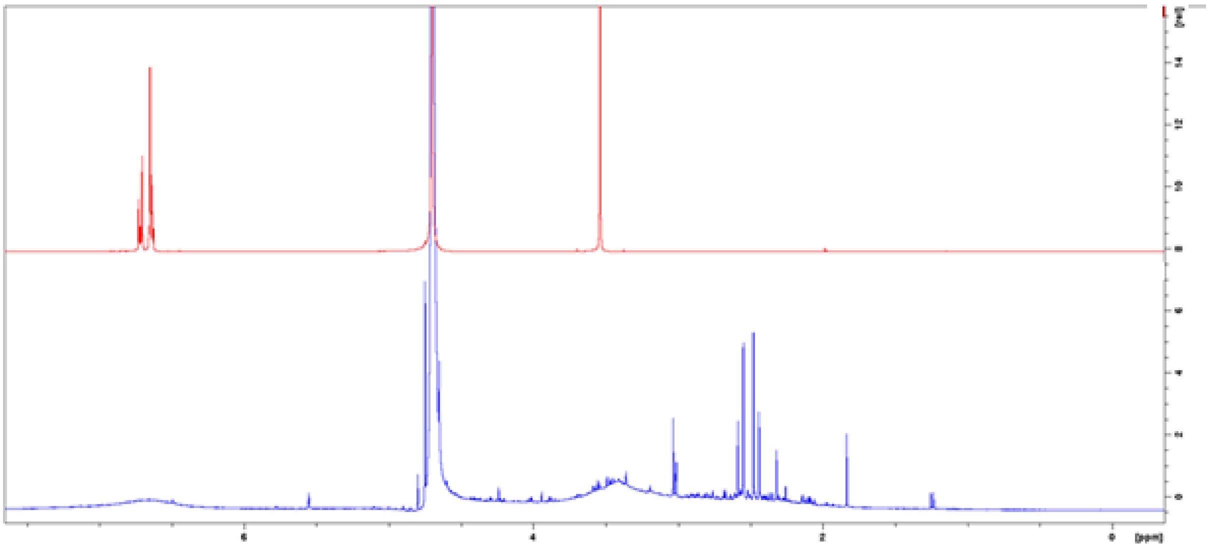


Figure S3. ^{1}H NMR of HGA (red) and polyHGA-HS (blue) in D_2O.

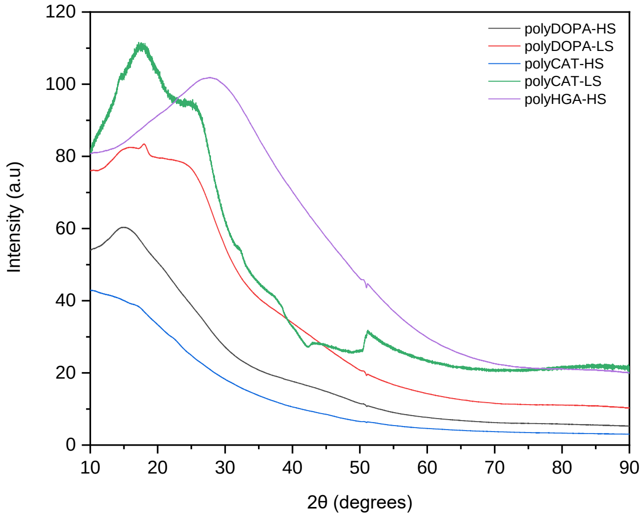


Figure S4. X-ray diffractograms of samples studied herein.

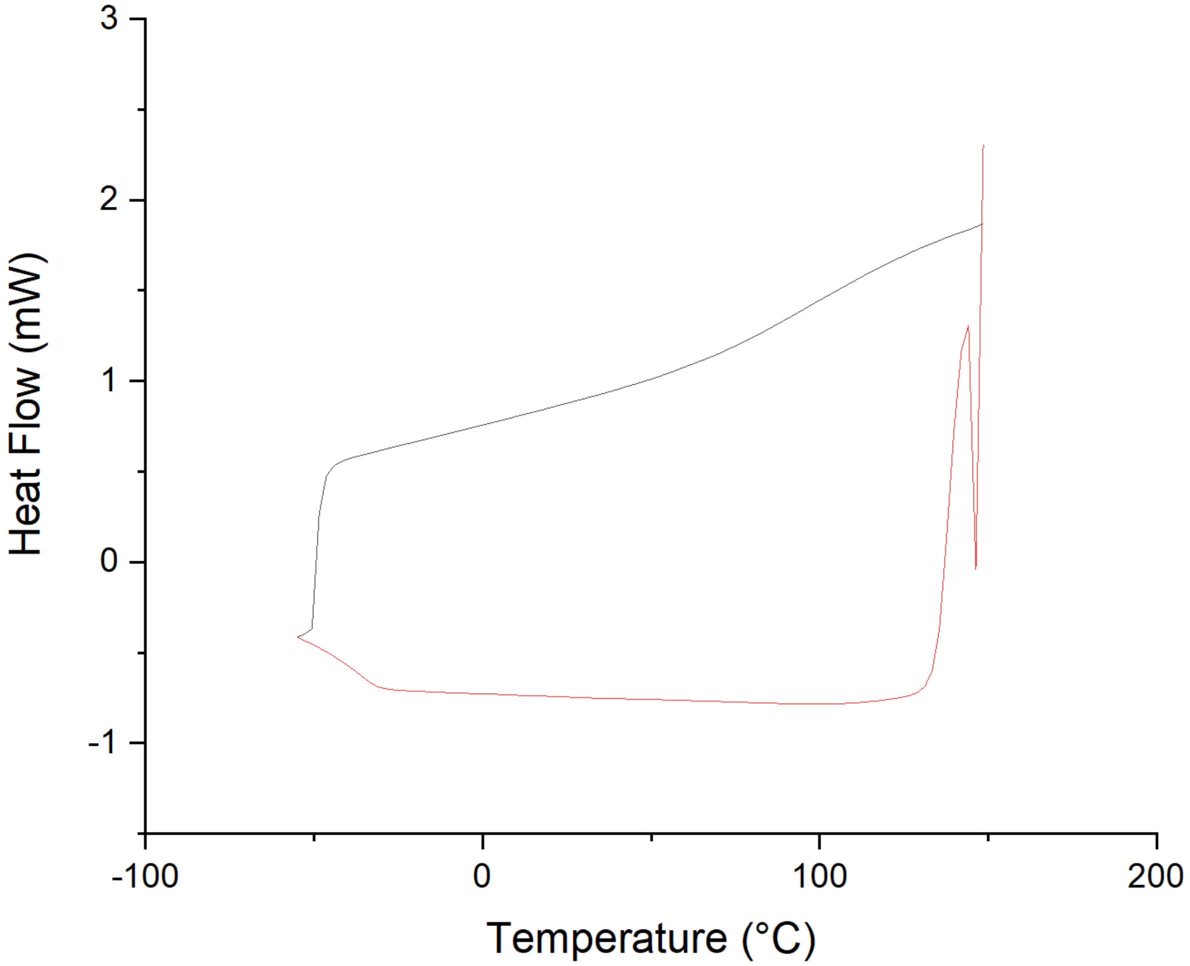


Figure S5. DSC thermograph of the second heating/cooling cycle of polyCAT-HS.

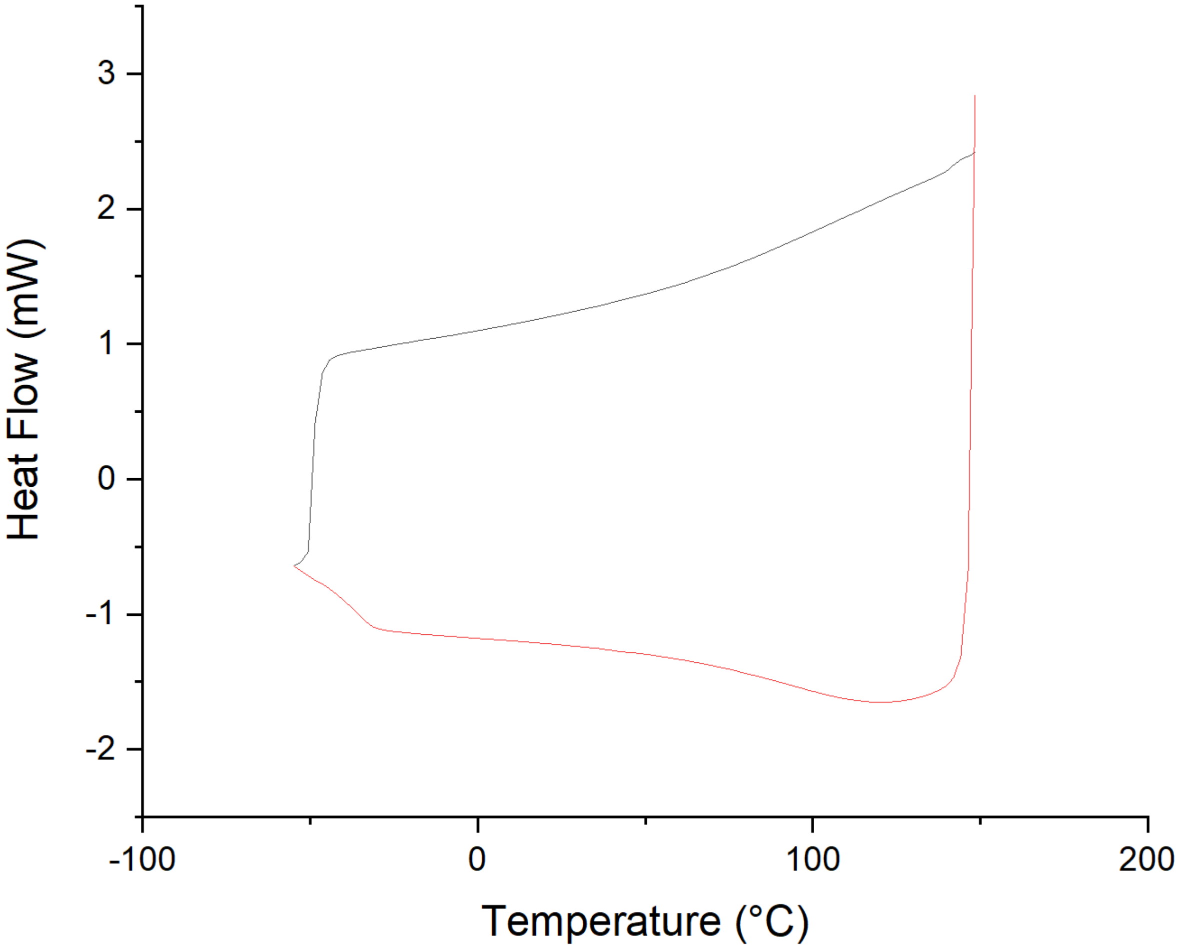


Figure S6. DSC thermograph of the second heating/cooling cycle of polyCAT-LS.

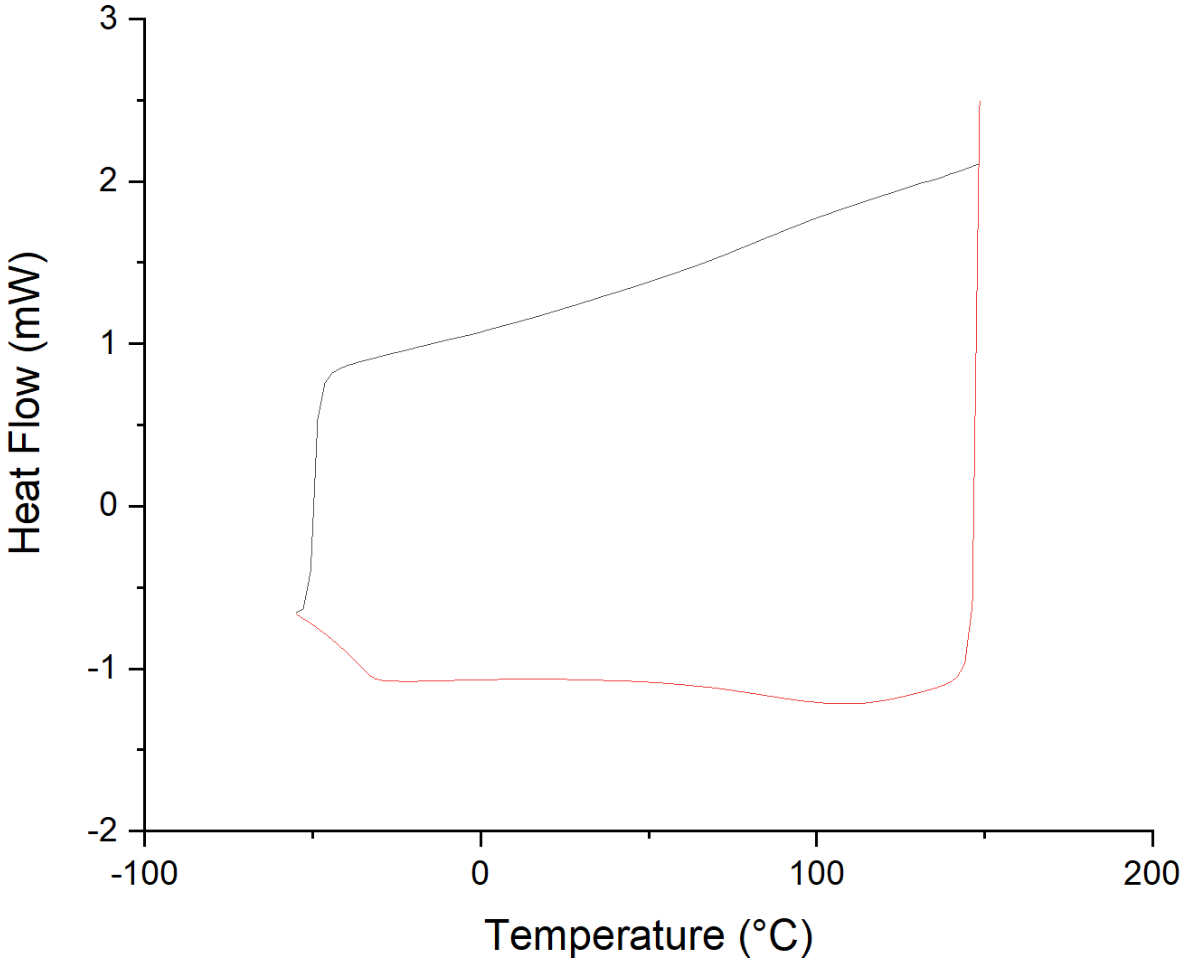


Figure S7. DSC thermograph of the second heating/cooling cycle of polyDOPA-HS.

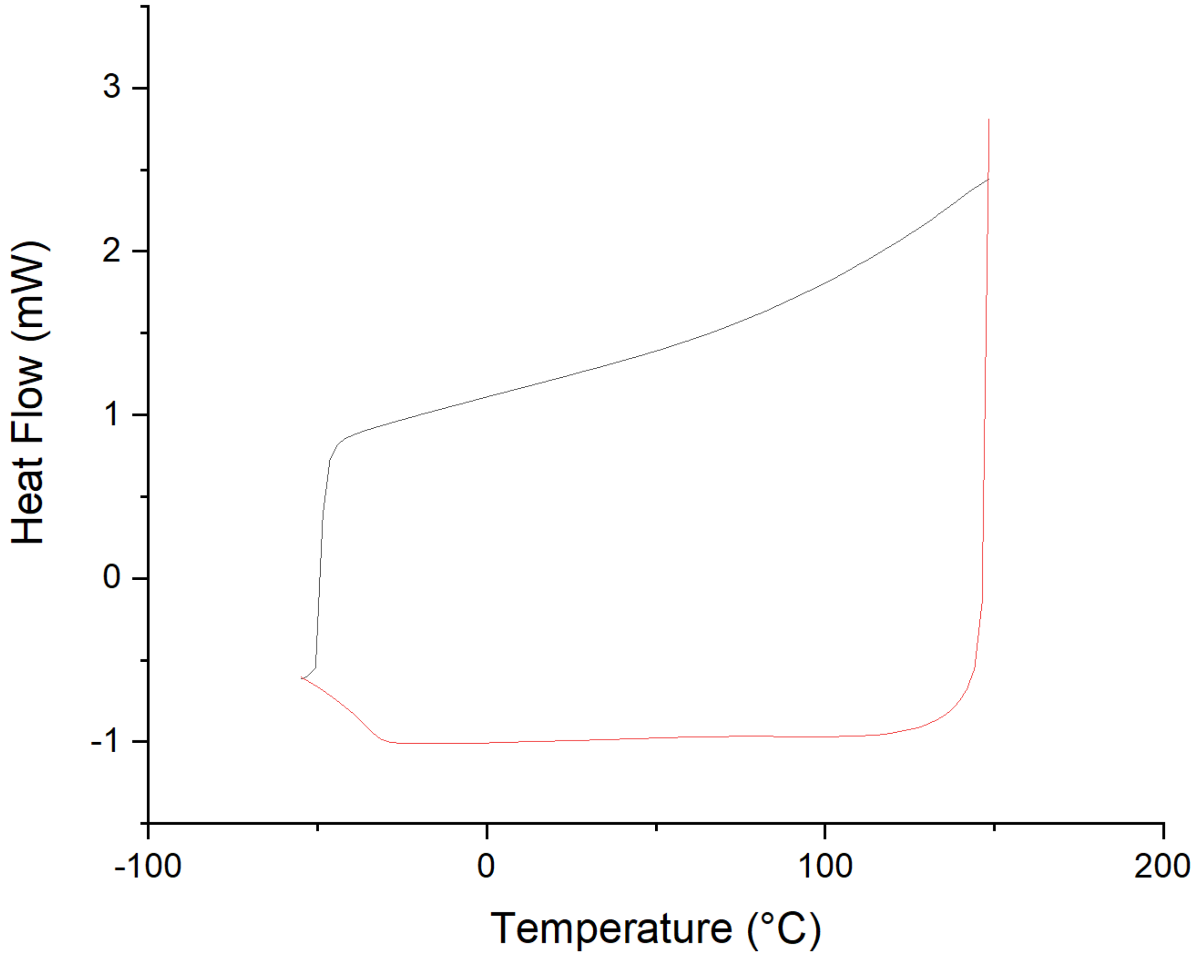


Figure S8. DSC thermograph of the second heating/cooling cycle of polyDOPA-LS.

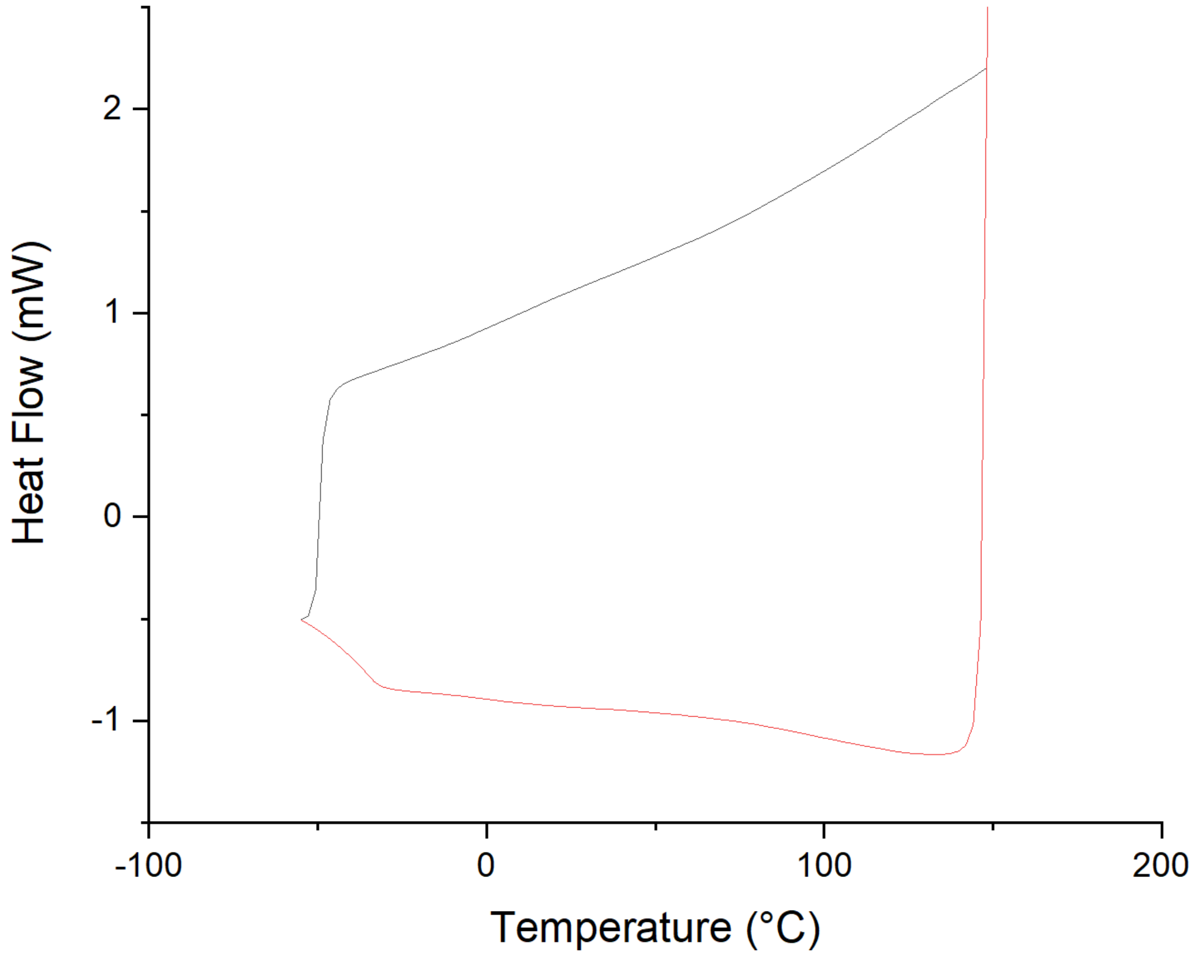


Figure S9. DSC thermograph of the second heating/cooling cycle of polyHGA-HS.

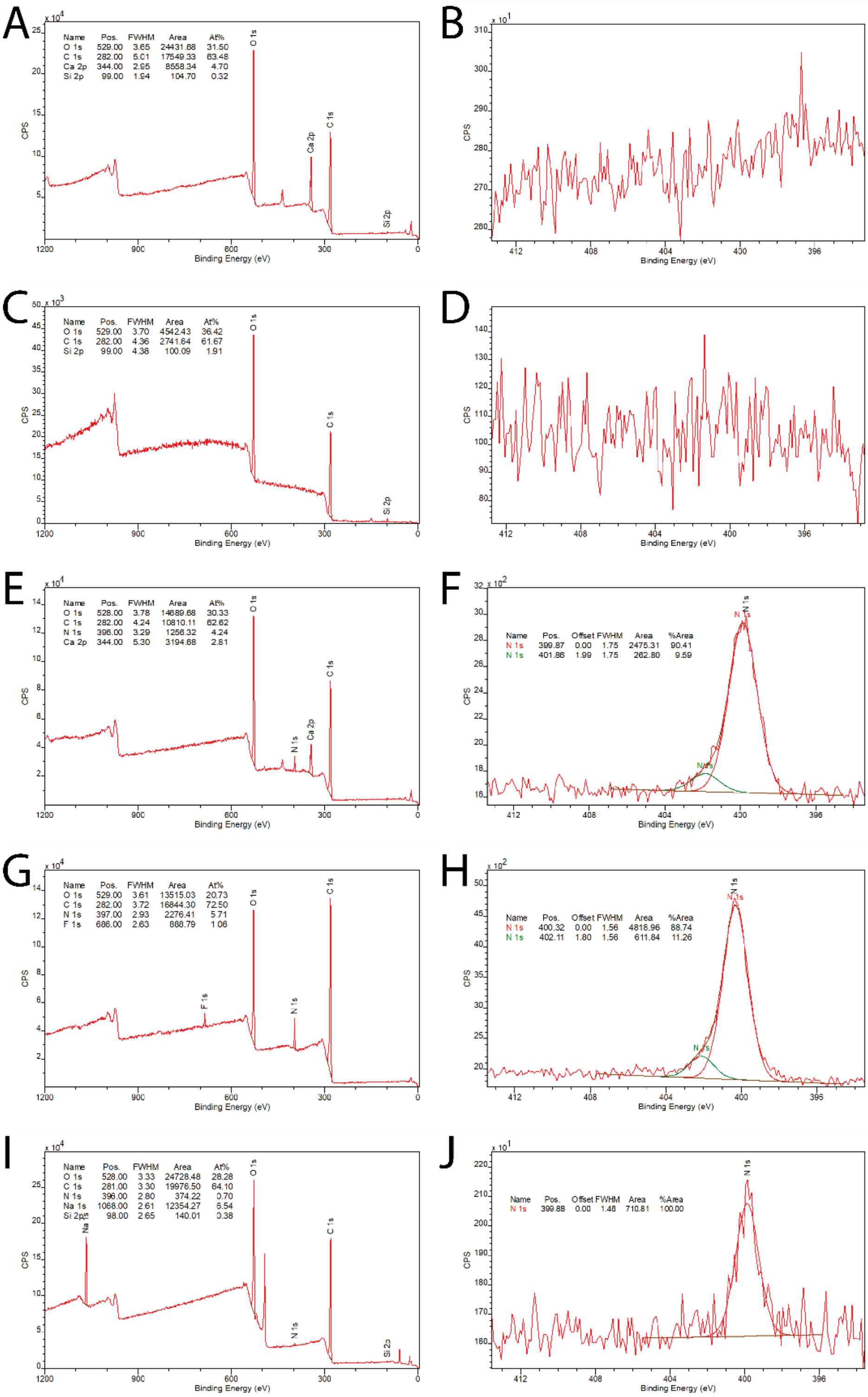


Figure S10. XPS spectra. XPS spectra. A) polyCAT-HS wide scan. **B)** polyCAT-HS N 1s core line spectra. **C)** polyCAT-LS wide scan. **D)** polyCAT-LS N 1s core line spectra. **E)** polyDOPA-HS wide scan. **F)** polyDOPA-HS N 1s core line spectra. **G)** polyDOPA-LS wide scan. **H)** polyDOPA-LS N 1s core line spectra. **I)** polyHGA-HS wide scan. **J)** polyHGA-HS N 1s core line spectra.

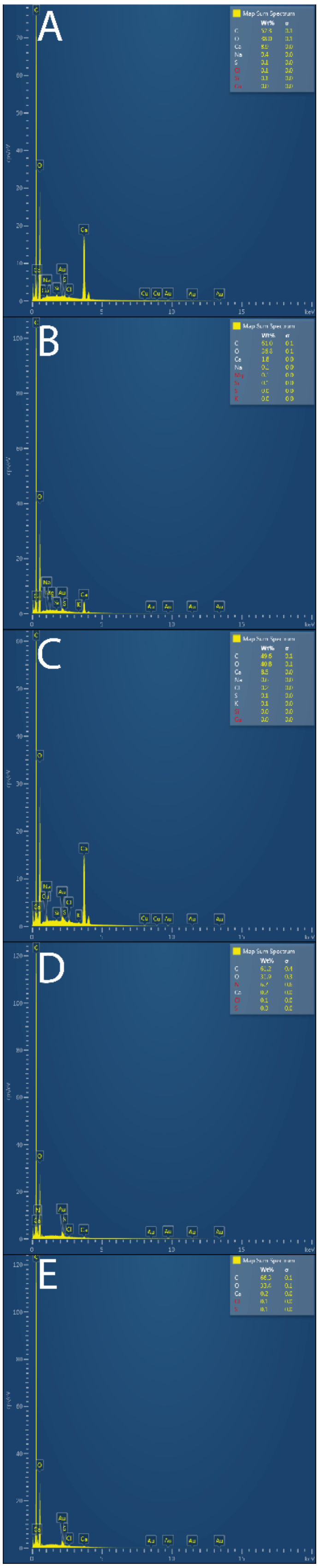


Figure S11. EDX spectra of samples studied herein. **A)** polyCAT-HS. **B)** polyCAT-LS. **C)** polyDOPA-HS. **D)** polyDOPA-LS. **E)** polyHGA-HS.

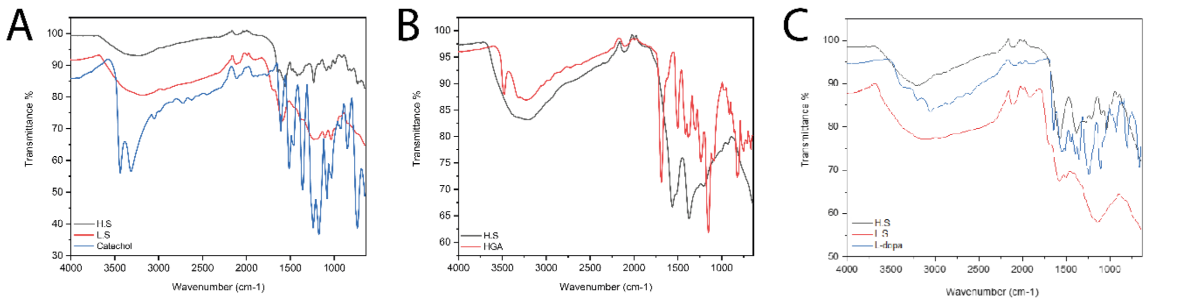


Figure S12. FTIR spectra of monomers and polymers. A) CAT, polyCAT-HS and polyCAT-LS. B) DOPA, polyDOPA-HS and polyDOPA-LS. C) HGA and polyHGA-HS.

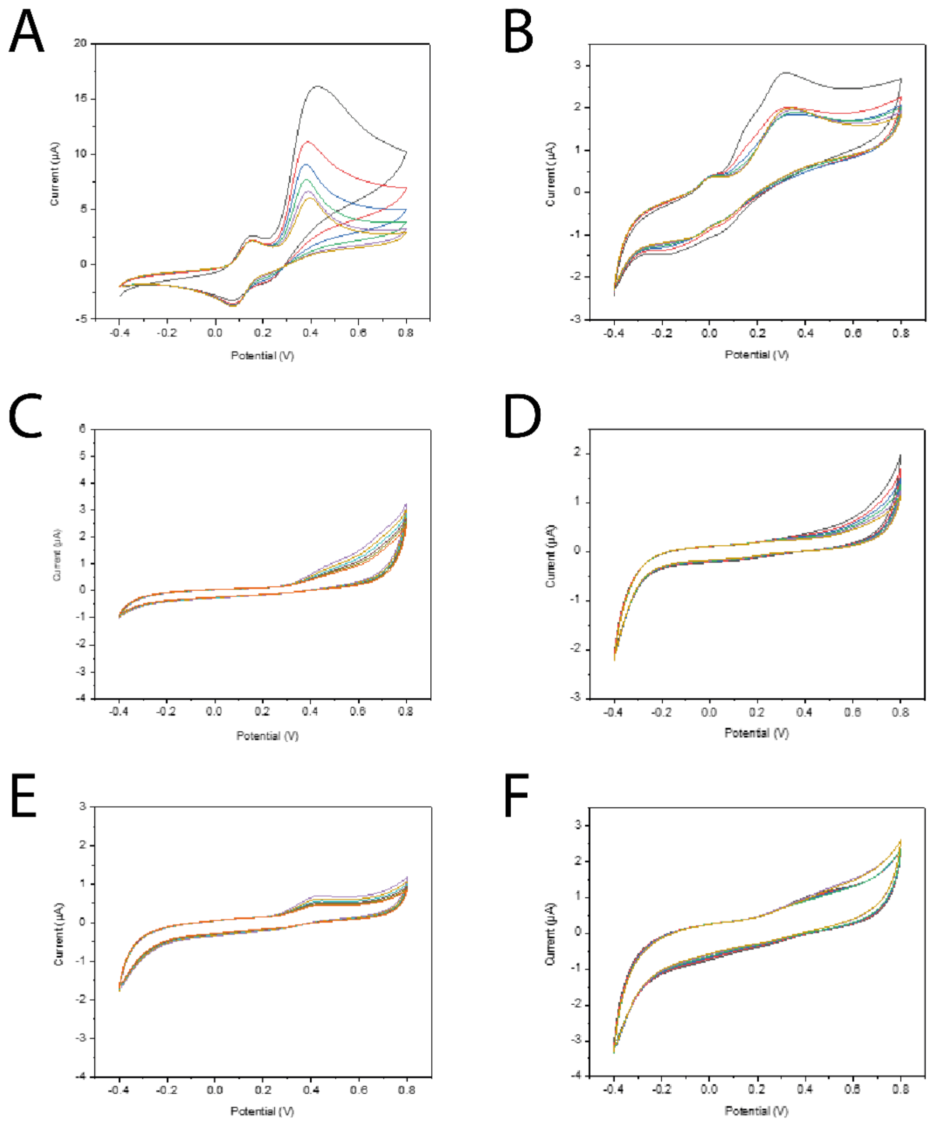


Figure S13. Cyclic voltammograms of monomers and polymers studied herein. Cathodic and anodic peaks reported vs. Ag/AgCl (reference electrode). **A)** CAT pH5 (anodic peaks at ca. 0.15V and 0.4V, and cathodic peaks at ca. 0.1V and 0.2V). **B)** CAT pH 7.4 (anodic peaks at ca. 0V and 0.3V, and cathodic peaks at ca. -0.1V and 0.1V). **C)** polyCAT-HS pH 5 (anodic peak at ca. 0.4V, and cathodic peaks at ca. 0V). **D)** polyCAT-HS pH 7.4 (anodic peak at ca. 0.4V, and cathodic peaks at ca. 0V). **E)** polyCAT-LS pH 5 (anodic peak at ca. 0.4V, and cathodic peaks at ca. 0V). **F)** polyCAT-LS pH 7.4 (anodic peak at ca. 0.4V, and cathodic peaks at ca. 0V).

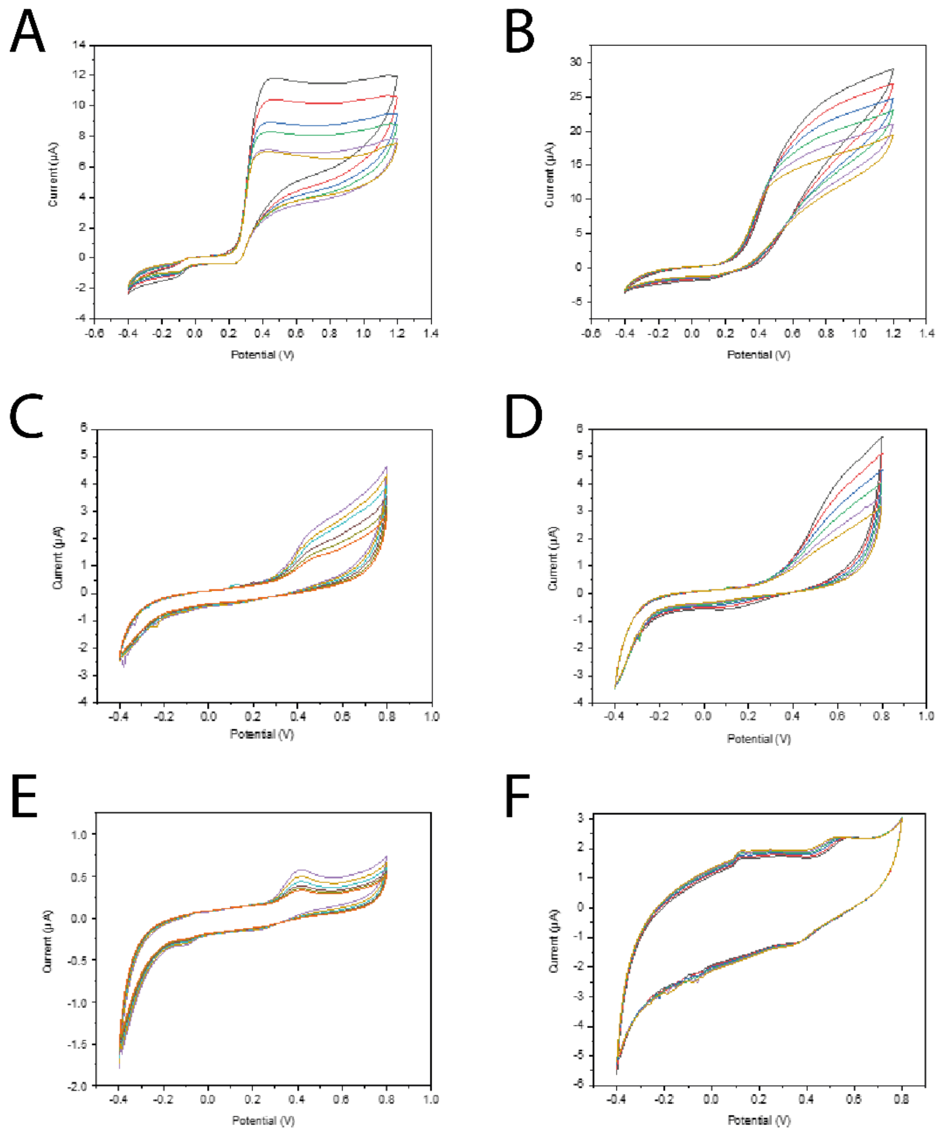


Figure S14. Cyclic voltammograms of monomers and polymers studied herein. Cathodic and anodic peaks reported vs. Ag/AgCl (reference electrode). **A)** DOPA pH5 (anodic peak at ca. 0.4V, cathodic peak at ca. -0.15V). **B)** DOPA pH 7.4 (anodic peak at ca. 0.4V, cathodic peak at ca. -0.15V). **C)** polyDOPA-HS pH 5 (anodic peak at ca. 0.4V, cathodic peak at ca. -0.15V). **D)** polyDOPA-HS pH 7.4 (anodic peak at ca. 0.4V, cathodic peak at ca. -0.15V). **E)** polyDOPA-LS pH 5 (anodic peak at ca. 0.4V, cathodic peak at ca. -0.15V). **F)** polyDOPA-LS pH 7.4 (anodic peak at ca. 0.4V, cathodic peak at ca. -0.15V).

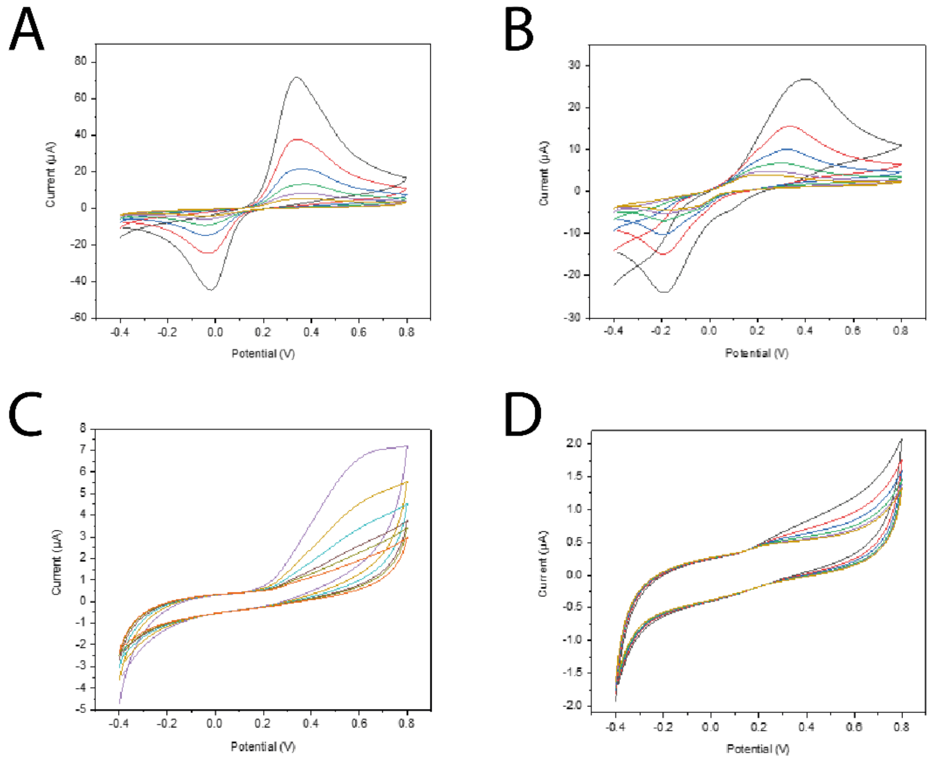


Figure S15. Cyclic voltammograms of monomers and polymers studied herein. Cathodic and anodic peaks reported vs. Ag/AgCl (reference electrode). **A)** HGA pH 5 (anodic peak at ca. 0.4V, cathodic peak at ca. 0V). **B)** HGA pH 7.4 (anodic peak at ca. 0.4V, cathodic peak at ca. -0.2V). **C)** polyHGA-HS pH 5 (anodic peak at ca. 0.56V, cathodic peak at ca. 0V). **D)** polyHGA-HS pH 7.4 (anodic peak at ca. 0.56V, cathodic peak at ca. 0V).

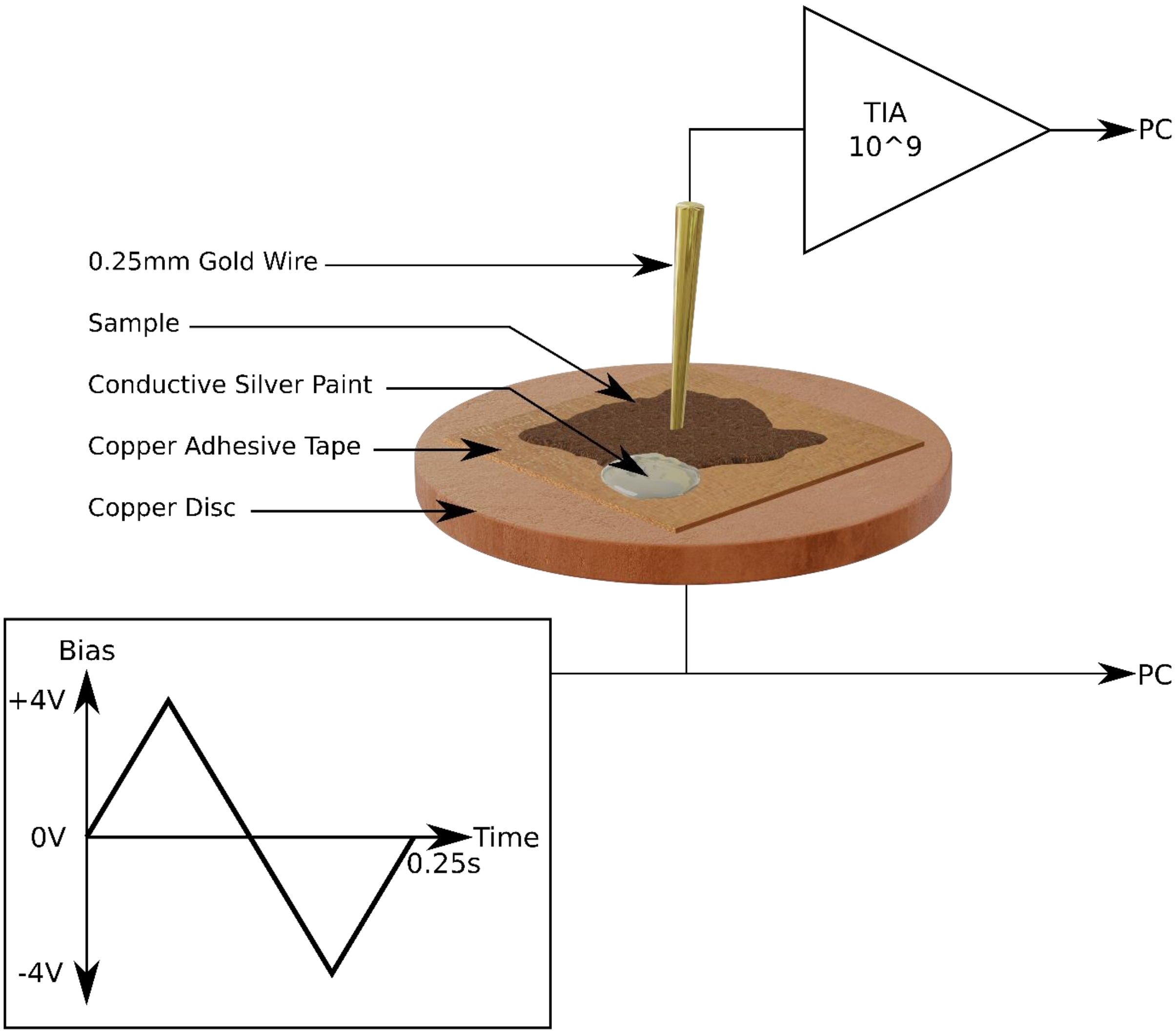


Figure S16. An illustration of the apparatus used in the conductance measurements.