Supporting Information

Trivial Positional Isomerism in Ligands Triggering Different Properties in Fe(II)-Metallopolymers; Design, Synthesis, and Characterization

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1. ^{13}C-NMR spectrum of Ligand L_1 and HRMS of Ligand L_1

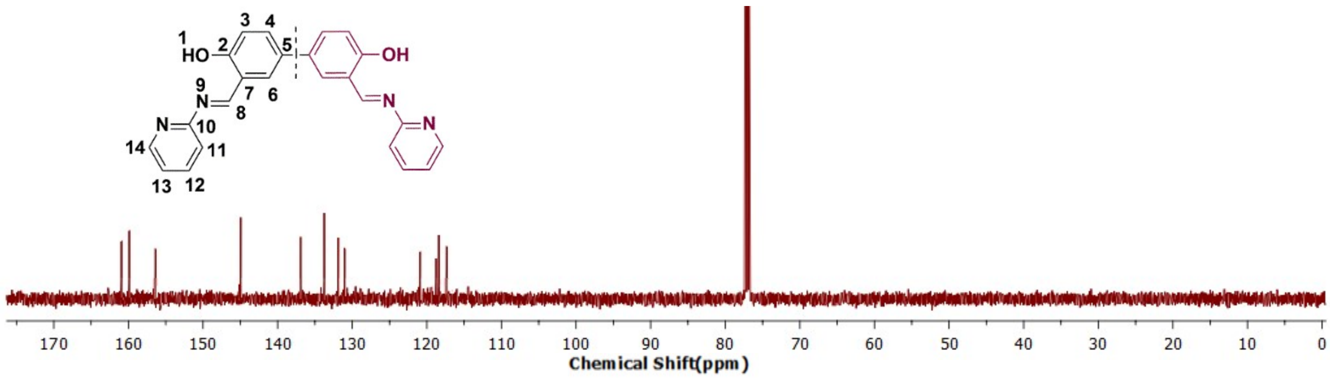

Figure .S-1. ^{13}C-NMR spectrum (125 MHz, $CDCl_3$) of Ligand L_1

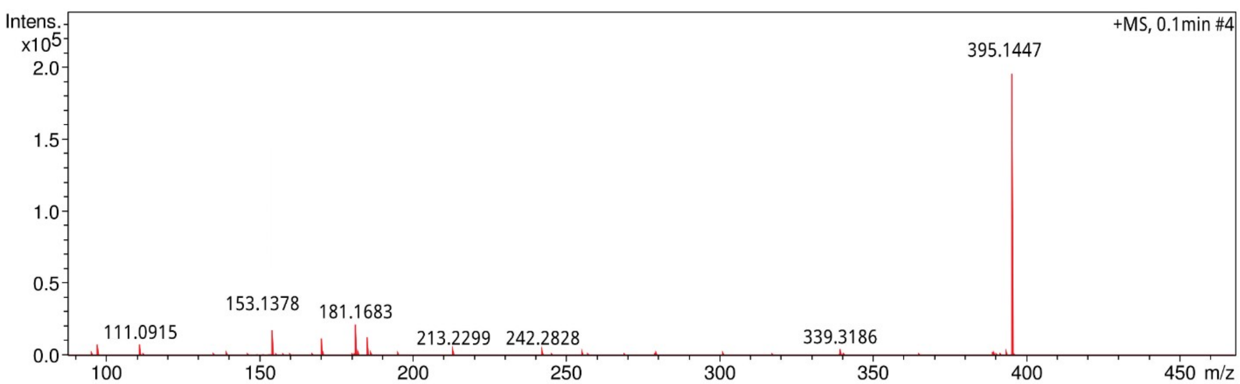

Figure .S-2. HRMS of Ligand L_1

2. ^{13}C-NMR spectrum of Ligand L_2 and HRMS of Ligand L_2

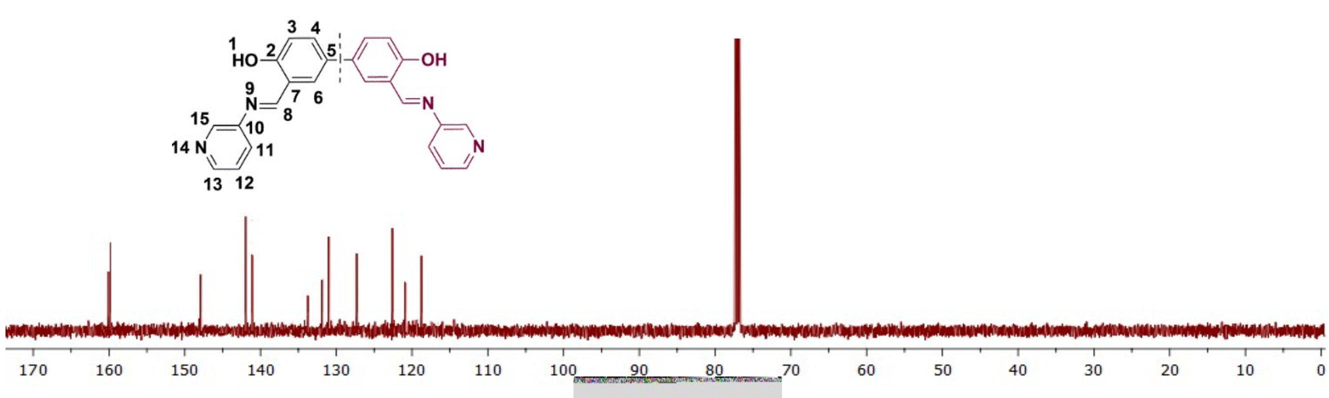

Figure .S-3. ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of Ligand L_2

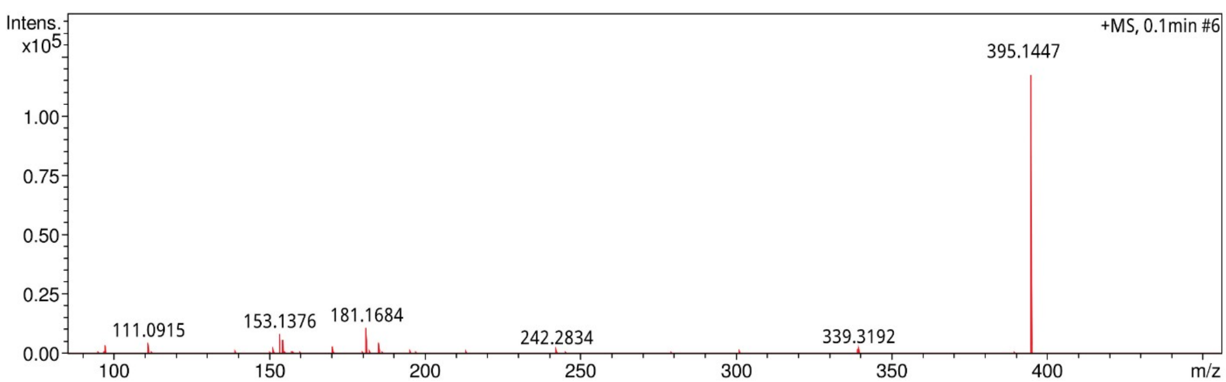

Figure .S-4. HRMS of Ligand L_2

3. ^{1}H-NMR spectrum of Ligands, Fe(II)-poly and schematic their coordination

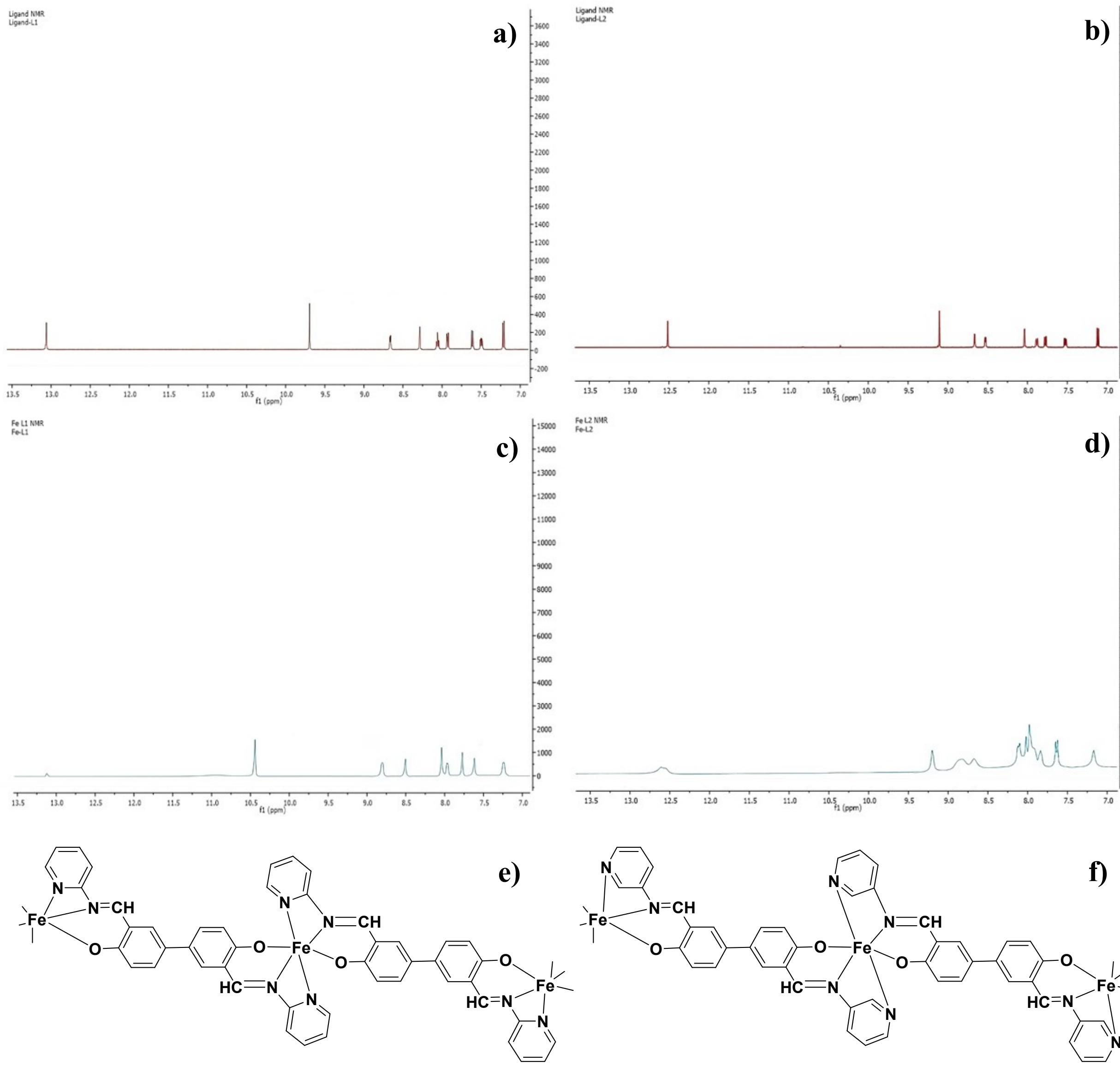

Figure .S-5. ^{1}H NMR spectra of a) Ligand L_1 b) Fe(II)-L_1 poly c) Ligand L_2 and d) Fe(II)-L_2 poly and schematic coordination of e) Fe(II)-L_1 poly f) Fe(II)-L_2 poly

4. Molecular Weight of Fe(II)-L_1 poly and Thermal analysis

Molecular Weight determination:

The Static light scattering (SLS) technique was used to determine the Weight Average molecular weight of the Fe(II)-L_1 poly and Fe(II)-L_2 poly. For both polymers, two different stock solutions were prepared by dissolving 15 mg of polymer in 30 ml of THF that were then filtered through a 0.2-micron Nylon filter to remove solid particles to obtain a homogeneous solution. Then six different concentration solutions were prepared from this stock solution with filtered THF solvent used as dilution. Both the polymers were analyzed at different angles by SLS technique gives the (3.7± 0.8) x 10^4 g/ mol for Fe(II)- L_1 poly (Fig-S-6) and (4.04± 0.8) x 10^4 g/ mol for Fe(II)- L_2 Poly (Fig-S-8) shown in Berry plot.

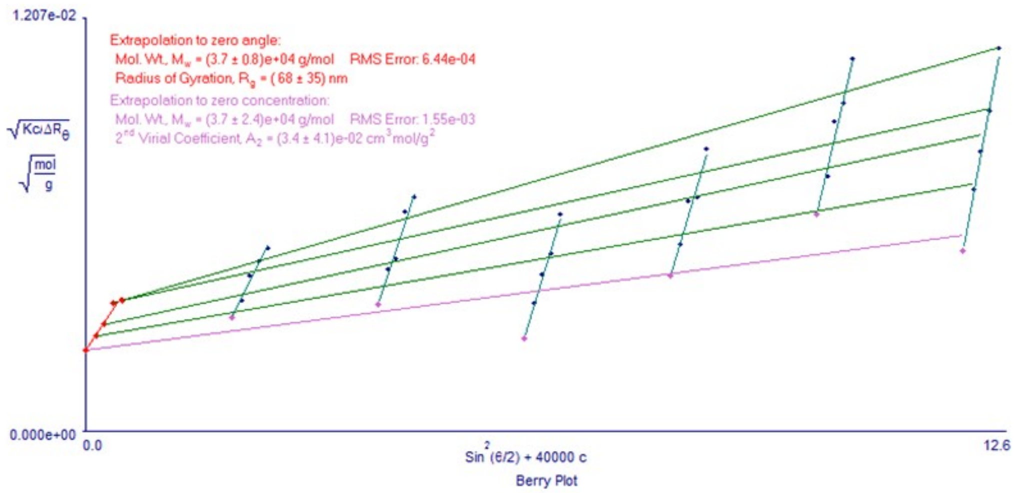

Figure .S-6. Berry Plot of Fe (II)-L_1 poly in batch mode (THF solution)

Thermal analysis

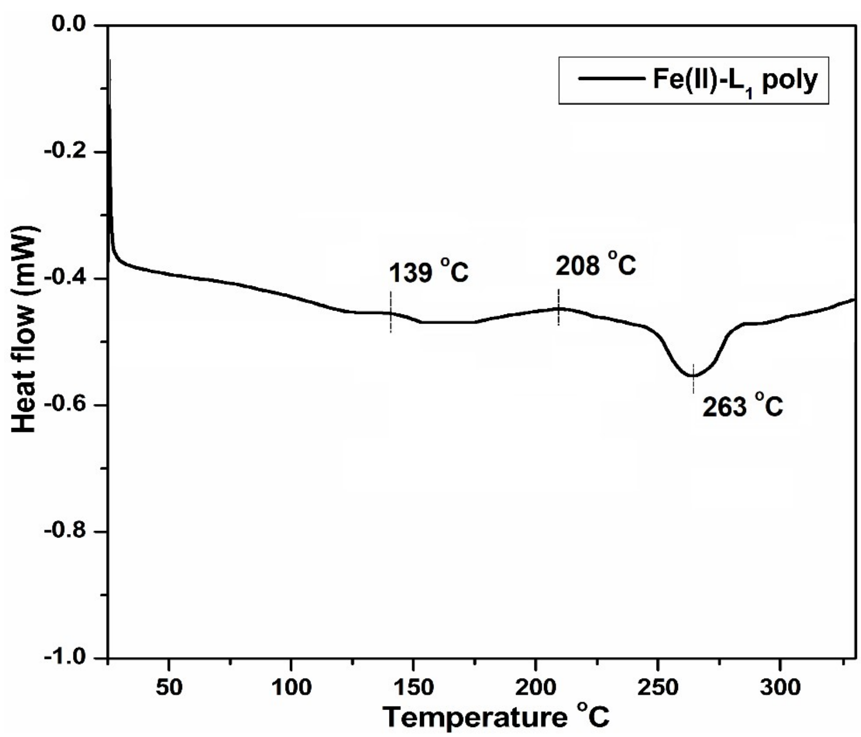

Figure .S-7. DSC Thermogram of Fe(II)-L_1 poly

5. Molecular Weight of Fe(II)–L_2 poly and Thermal analysis

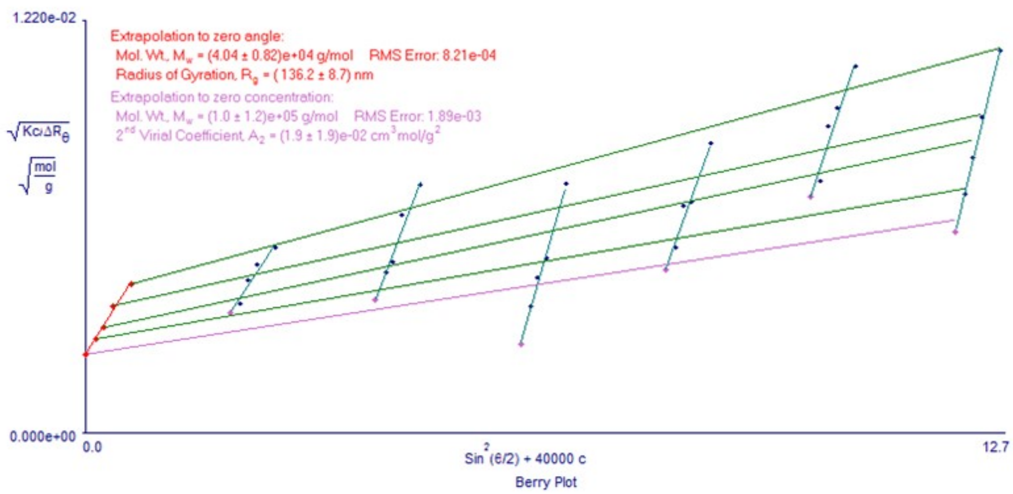

Figure .S-8. Berry Plot of Fe (II)-L_2 poly in batch mode with a solution prepared in THF

Thermal Analysis:

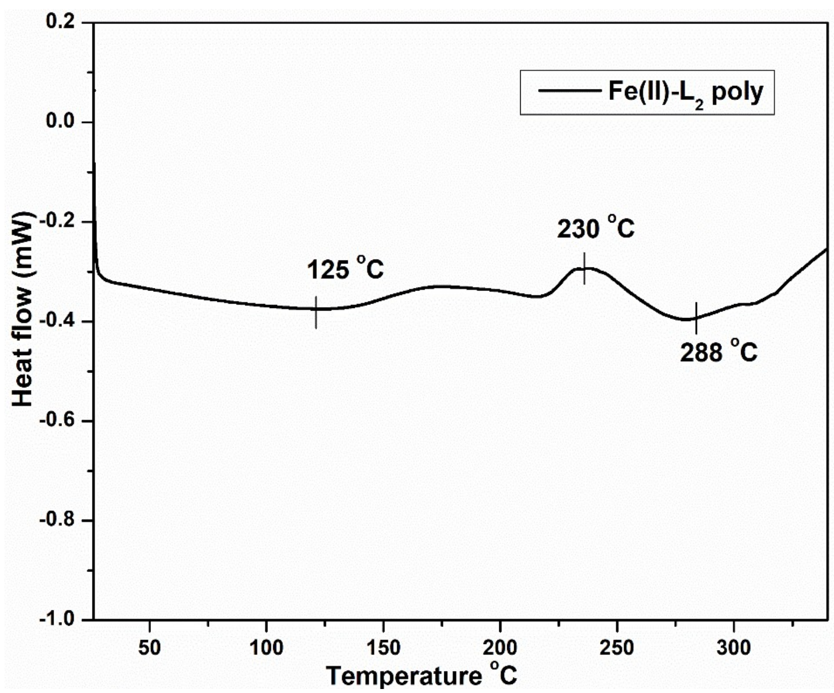

Figure .S-9. DSC Thermogram of Fe(II)-L_2 poly

6. Cyclic voltammetry of Ligand L_1 and Ligand L_2

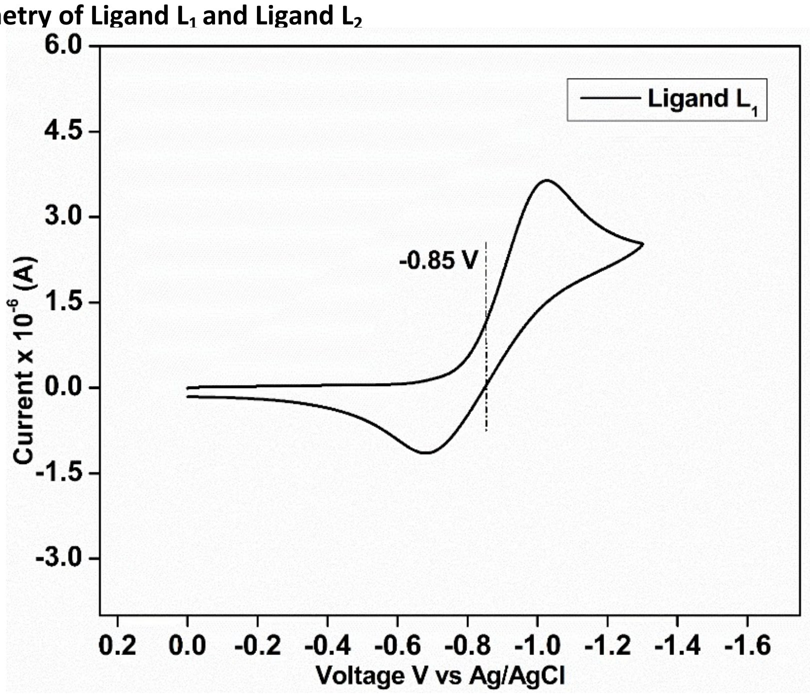

Figure .S-10. Cyclic Voltammogram of Ligand L_1 in dichloromethane containing 0.1 M TBAP at 100mV/s with Glassy Carbon working electrode and Ag/AgCl reference electrode

The Cyclic voltammogram of the ligand L_1 is shown in Figure .S-10. Ligands do not generally show any oxidation response. A reduction peak at -0.85 V was observed, corresponding to the reduction of the imine bond.

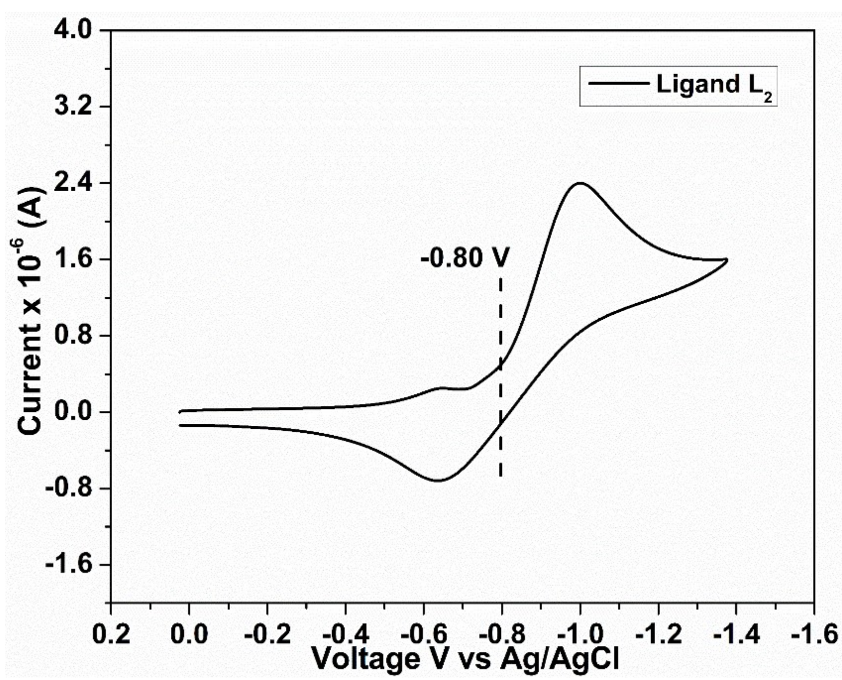

Figure .S-11. Cyclic Voltammogram of ligand L_2 in dichloromethane containing 0.1 M TBAP at 100mV/s with Glassy Carbon working electrode and Ag/AgCl reference electrode

Similarly, the cyclic voltammogram of the Ligand L_2 is shown in Figure .S-11. A reduction response at -0.80 V was observed, corresponding to the reduction of imine bonds.

7. Repeatable Cyclic voltammetry of Fe(II)-L_1 and Fe(II)-L_2 Poly

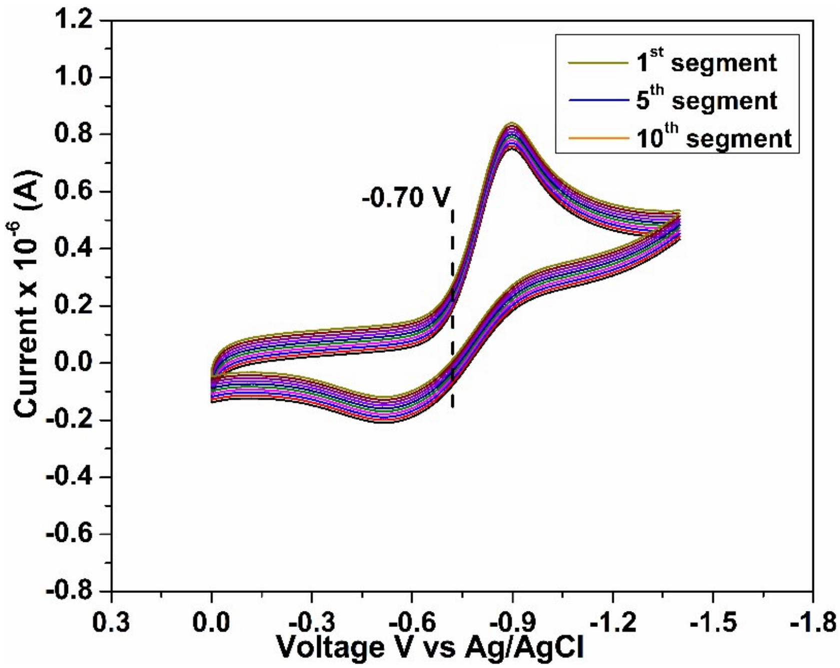

Figure .S-12. 10 segment reduction Cyclic Voltammogram of Fe(II)-L_1 poly

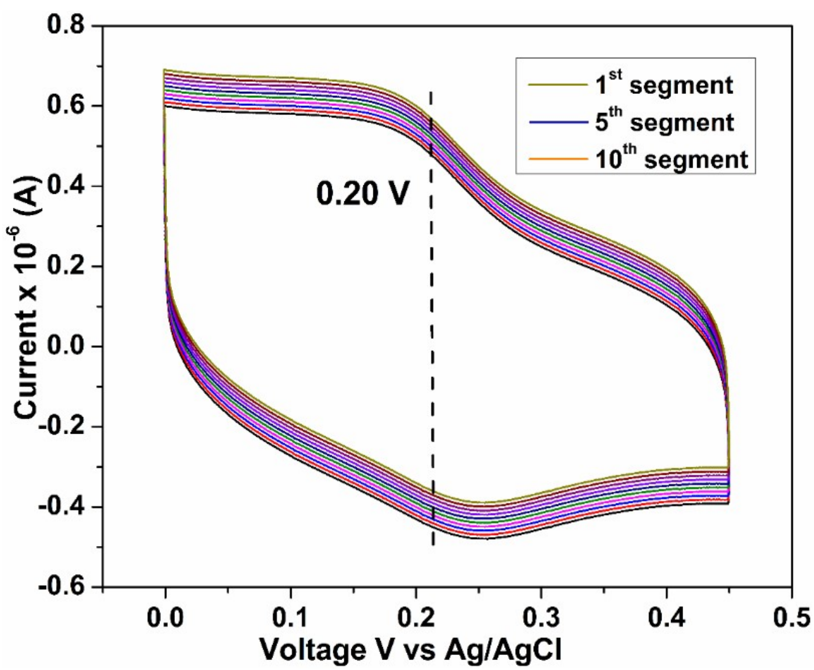

Figure .S-13. 10 segment oxidation Cyclic Voltammogram of Fe(II)-L_1 poly

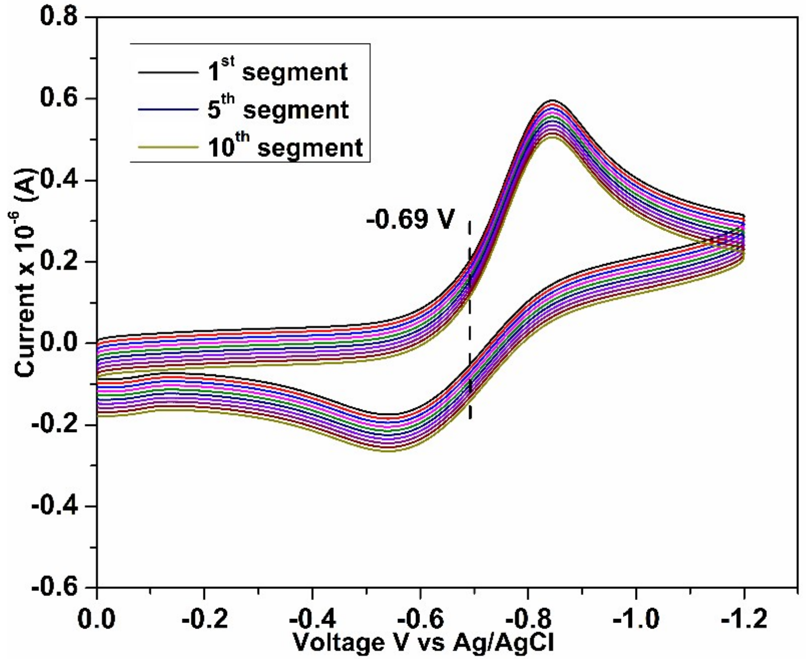

Figure .S-14. 10 segment reduction Cyclic Voltammogram of Fe(II)-L_2 poly

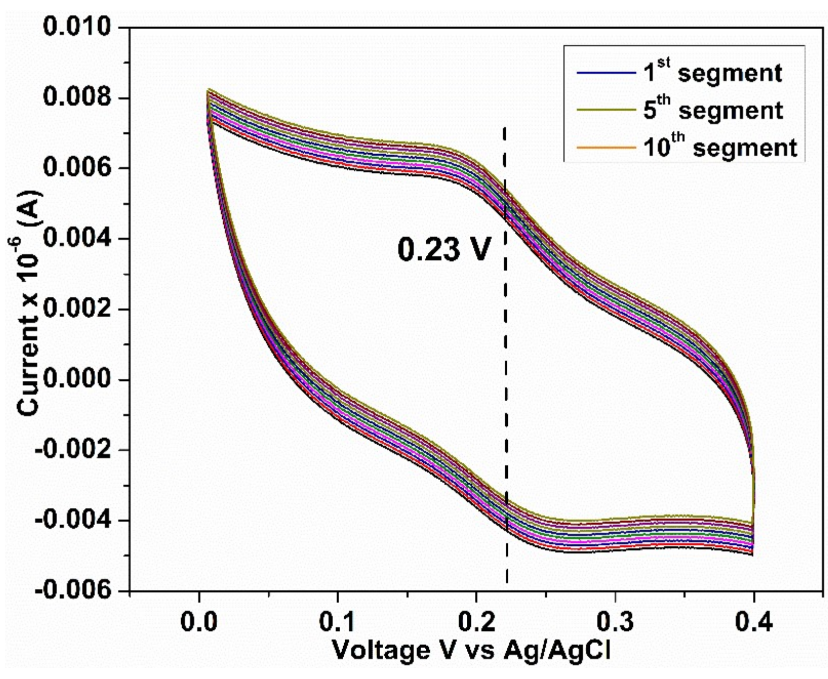

Figure .S-15. 10 segment oxidation Cyclic Voltammogram of Fe(II)-L_2 poly

8. Conductivity Experiment and Counter ion detection of Fe(II)-L_1 poly and Fe(II)-L_2 poly solutions

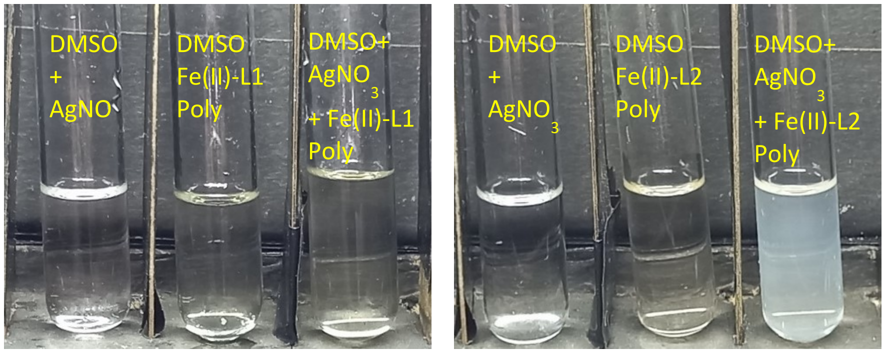

Figure .S-16. Counter ion detection of Fe(II)-L_1 poly and Fe(II)-L_2 poly solutions

Two experiments were conducted to verify the presence of Cl^- counter anion; precipitation test by $AgNO_3$ followed by conductivity measurement experiment. A ubiquitous test used to detect Cl^- ions in solution is the $AgNO_3$ test. On adding AgNO3 solution to Fe(II)-L_1 Poly solution, no turbidity was observed, which indicates the absence of Cl- as counter anion indicating Fe(II)-L_1 poly as a neutral polymer; however, in the case of Fe(II)-L_2 poly, slight turbidity was observed (as shown in pic) on the addition of $AgNO_3$ which indicates the presence of Cl^- as a counter anion. This test was also supported by conductivity measurement of different concentrations for both polymeric solutions (Table S-1 below). In the case of Fe(II)-L_1 poly, a minimal change in conductivity measurements was observed that indicates the polymer being neutral. In the case of Fe(II)-L_2 poly, conductivity change with change in concentration was high, which could only be possible because of counter Cl^- anions. Secondly, for the same concentration of polymeric solutions conductivity difference was quite large, indicating the presence of Cl- counter anion for Fe(II)-L_2 poly.

Table .S-1. Conductivity measurements of Fe(II)-L_1 and Fe(II)-L_2 Poly

Sr. No.	Concentration	Conductivity (μS) Fe(II)-L_1 Poly	Conductivity (μS) Fe(II)-L_2 Poly
1	1 x 10^{-4} M	6.34	14.13
2	2 x 10^{-4} M	7.35	17.07
3	3 x 10^{-4} M	7.15	34.40
4	4 x 10^{-4} M	7.77	43.42

9. DRS of Fe(II)-L_1 and Fe(II)-L_2 poly

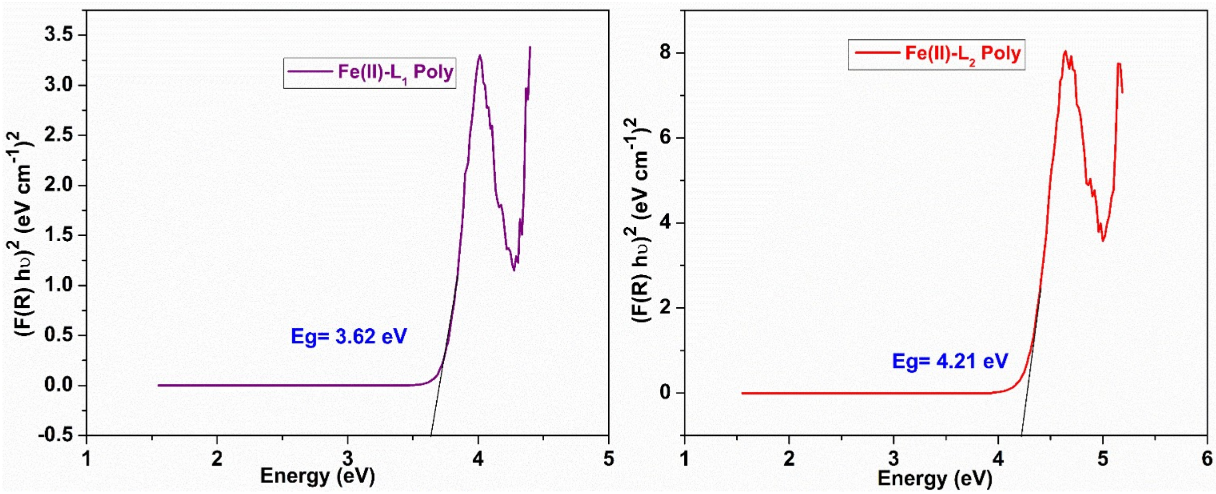

Figure .S-17. DRS of Fe(II)-L_1 poly and Fe(II)-L_2 poly

10. XPS of Fe(II)-L_1 and Fe(II)-L_2 poly

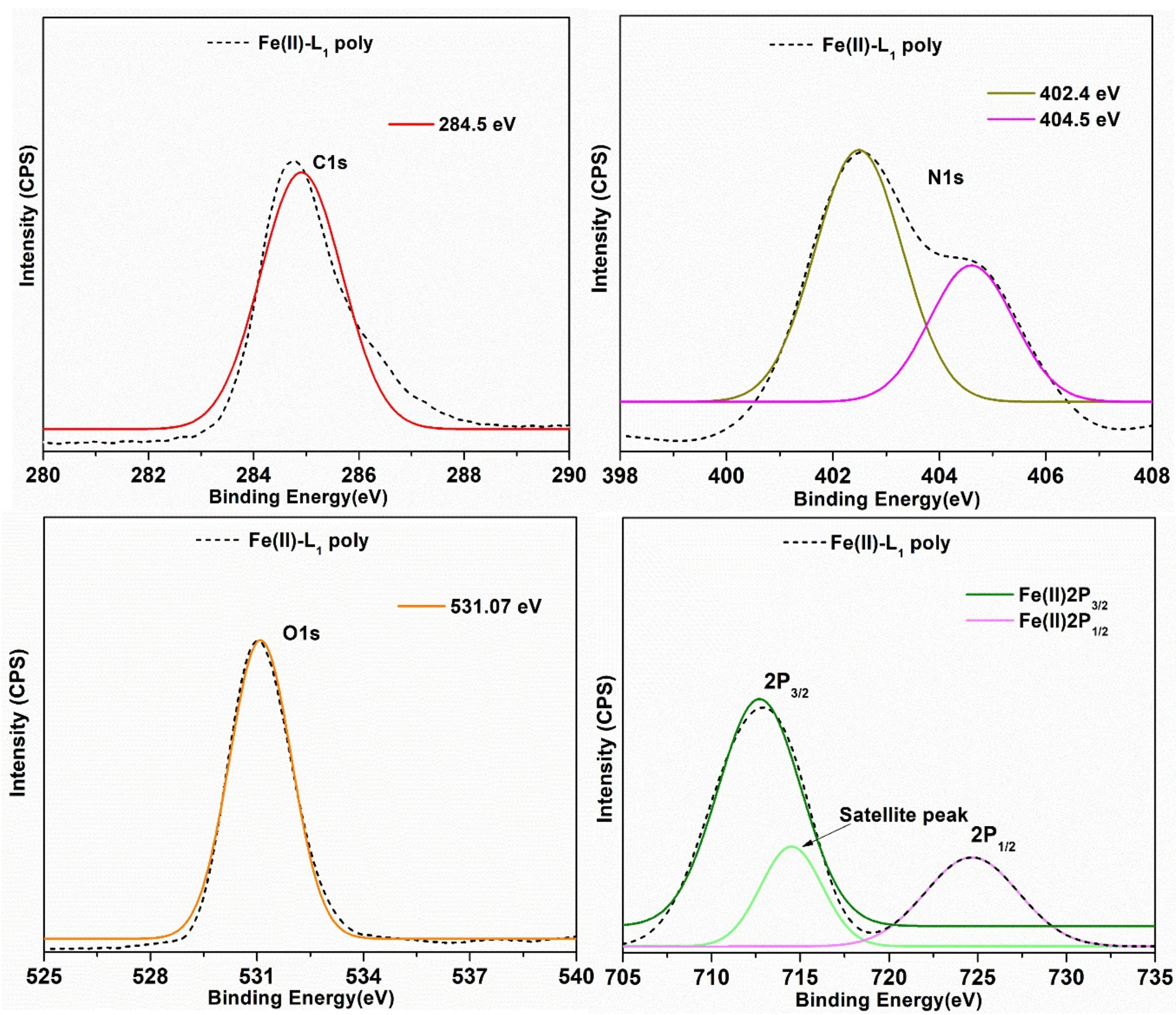

Figure .S-18. XPS of Fe(II)-L_1 poly of a) Carbon b) Nitrogen c) Oxygen and d) Iron element

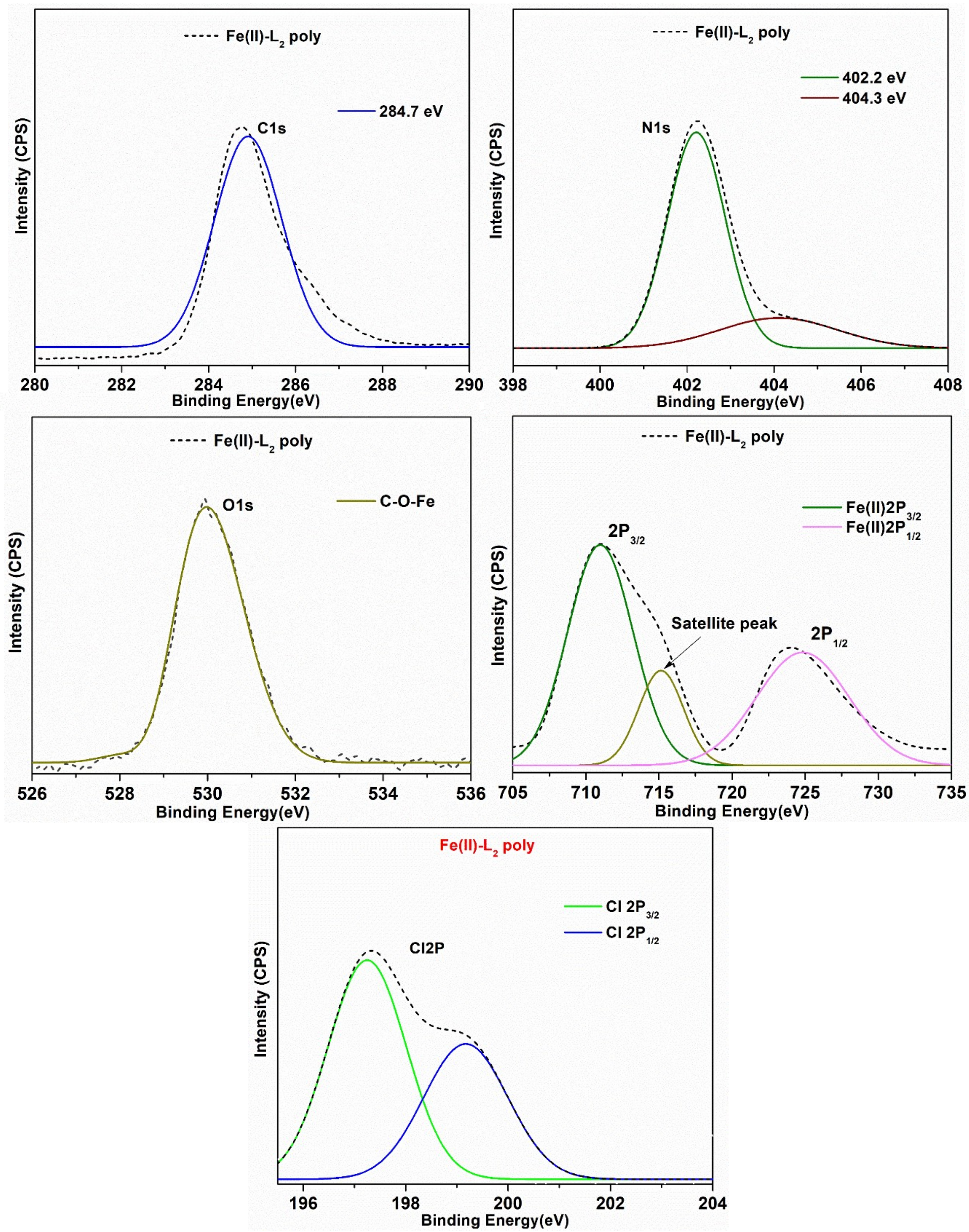

Figure .S-19. XPS of Fe(II)-L_2 poly of a) Carbon b) Nitrogen c) Oxygen d) Iron and e) Chlorine element

11. Spectroelectrochemical studies upon sequential voltage increase of Fe(II)-L_1 poly and Fe(II)-L_2 poly

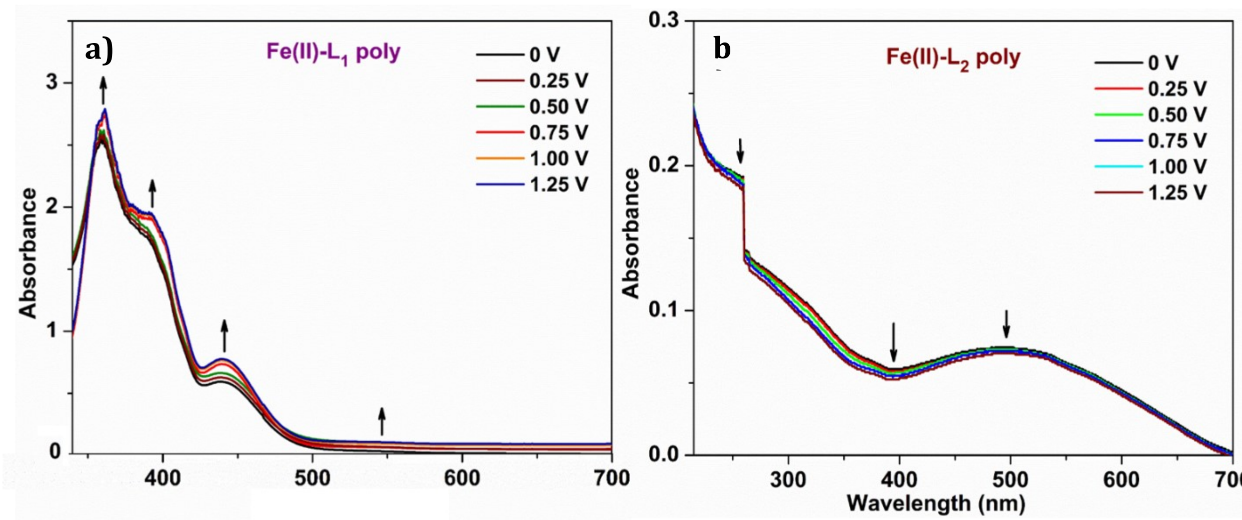

Figure .S-20. Spectroelectrochemical experiment studies upon sequential voltage increase (a) Fe(II)-L_1 poly showing incremental changes in spectra in between 0 V to 0.9 V and (b) Fe(II)-L_2 poly showing a decrease in spectra in between 0 V to 0.9 V

12. Effect of mass loading and scan rate on capacitance value of Fe(II)-L_1 poly and Fe(II)-L_2 poly

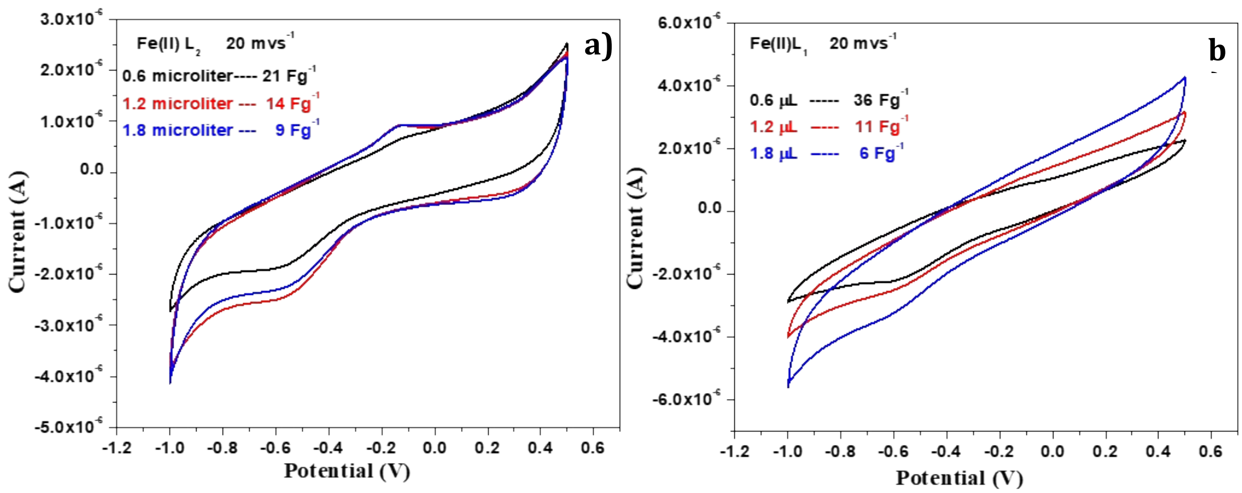

Figure .S-21. Effect of mass loading and scan rate on capacitance value of Fe(II)-L_1 poly and Fe(II)-L_2 poly