Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPORTING INFORMATION

Design, Synthesis, and Characterization of Fe(II)-Polymer of Redox Non-Innocent, Heteroatomic, Polydentate Schiff's base Ligand: Negative Differential Resistance and memory behaviour

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SUPPORTING INFORMATION

List of Contents:

1. Determination of molecular weight by SLS:

Molecular weight of the polymer sample was investigated using Berry Plot. For this, a stock solution was prepared by dissolving 15mg of the polymer sample in 30 ml DMSO. This stock solution was filtered through 0.2 micron Nylon filter. Then six concentration series was prepared from this stock solution using filtered DMSO solvent, and analysed at different angles through SLS. The polymer solution depicts the molecular weight of (6.81± 0.40) x 10^4 g/mol and the berry plot is shown in ESI Fig. S1.

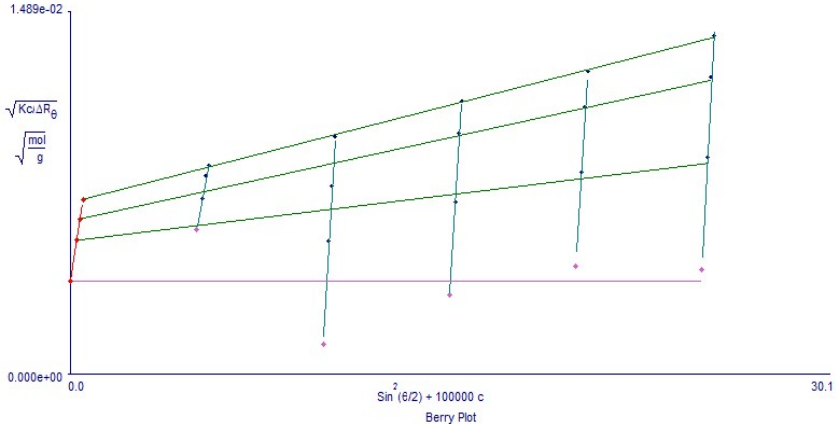


Fig. S1: Berry plot of Fe(II)-poly solution in DMSO.

2. FTIR analysis of ligand & Fe(II)-poly:

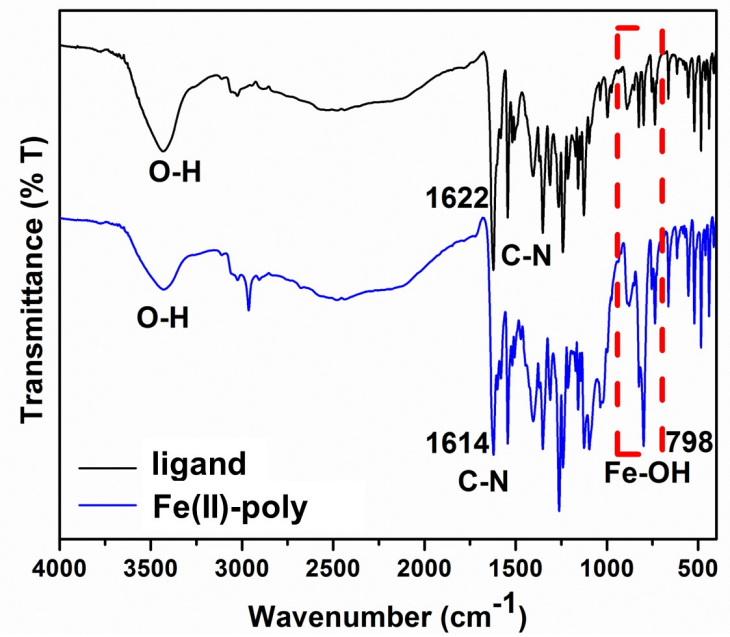


Fig. S2: FTIR spectra of ligand (L1) and Fe(II)-poly

3. ^{13}C NMR & H-H COSY NMR of ligand (L1):

The ^{13}C NMR of the ligand (L1) is shown below. The total peaks that appear in the spectra are 17, which confirm the formation of the ligand.

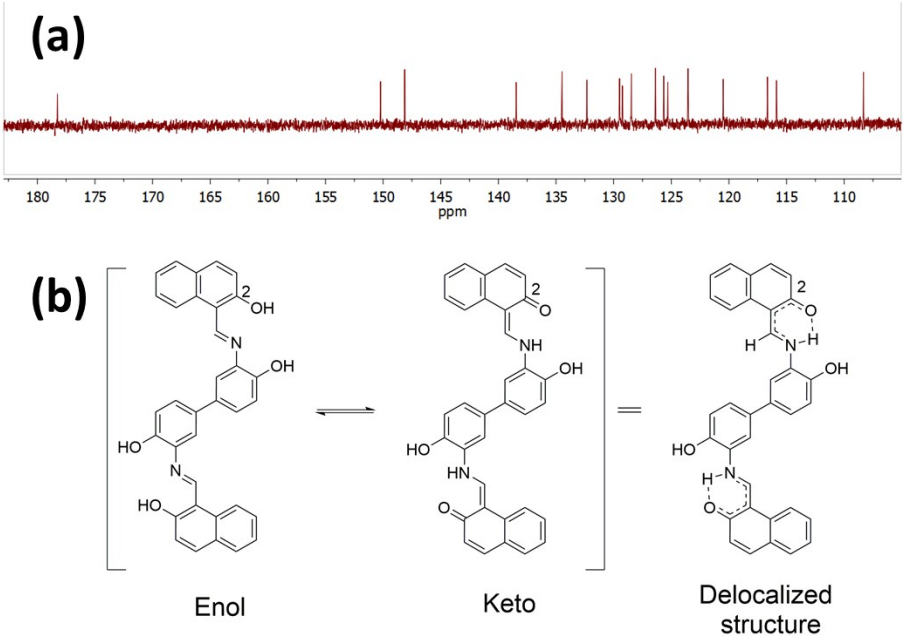


Fig. S3: (a) ^{13}C NMR of ligand (L1), (b) keto-enol tautomerism present in ligand (L1) structure.

COSY of ligand depicts a total of 11 diagonal peaks and all the cross peaks show the symmetry with their corresponding peaks in the correlation spectra, thereby confirming the synthesis of the ligand.

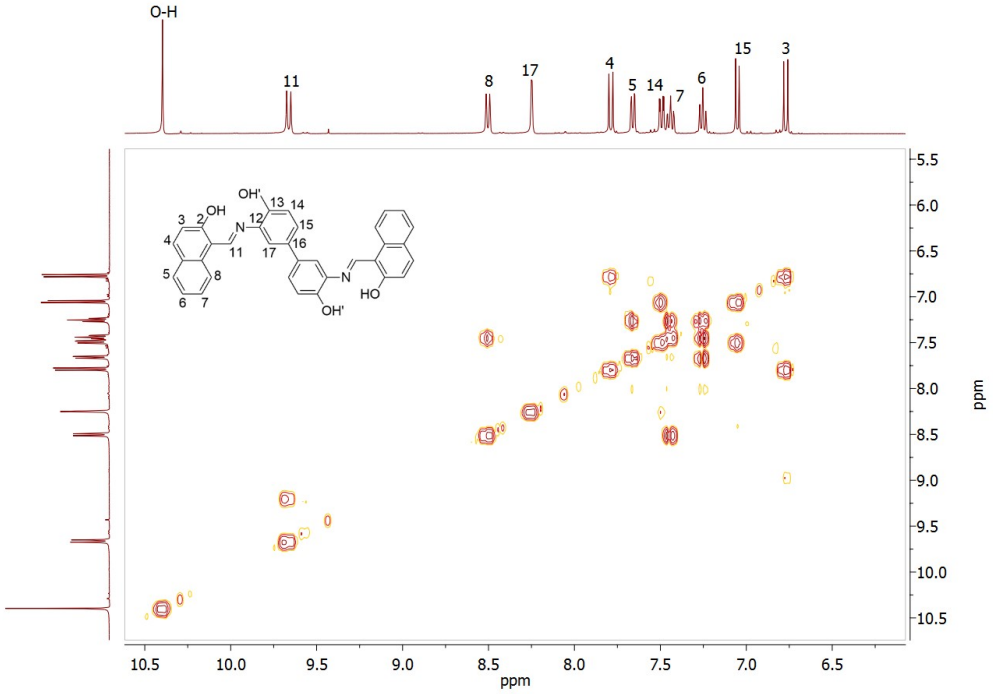
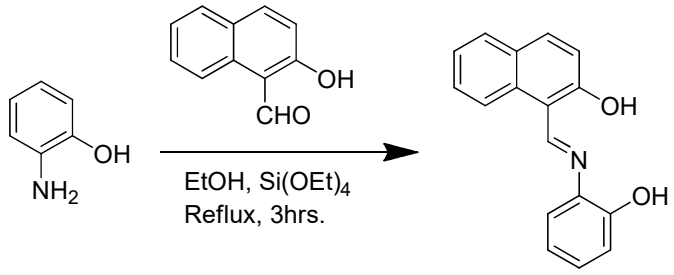


Fig. S4: H-H COSY spectra of the ligand (L1).

4. Synthesis of model ligand (L2):

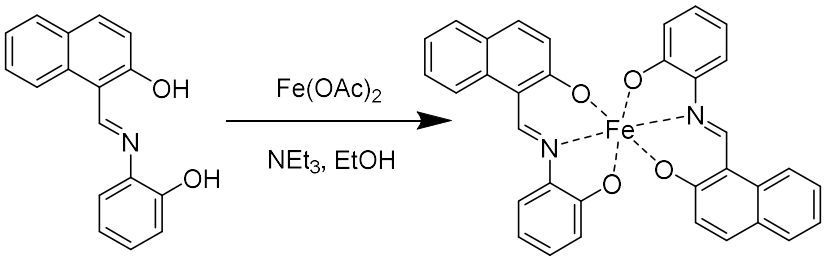
To the ethanolic solution of 2-aminophenol (10 mmol, 1.09 gm) in a three neck flask equipped with condenser, a solution of 1.72 gm (10 mmol) of 2-hydroxy naphthaldehyde in ethanol was added, followed by the addition of 3 ml of tetraethyl orthosilicate and the reaction mixture was stirred for four hours under nitrogen atmosphere. After the completion of reaction (monitored by TLC), reaction mixture was cooled to room temperature and then the solvent was removed by rotary evaporator and later dried in oven. The crude product so obtained was recrystalized by using ethanol to give 2.5 gm of the product. Yield 90%. (ethyl acetate: DCM, 3:7) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.67 (d, 1 H), 10.27 (s, 1 H), 9.45 (d, 1 H), 8.34 (d, 1 H), 7.90 (d, 1 H), 7.75 (s, 1 H), 7.64 (d, 1 H), 7.44 (t, 1 H), 7.22 (t, 1 H), 7.06 (t, 1 H), 6.96 (d, 1 H), 6.91 (t, 1 H) and 6.75 (d, 1 H).



Scheme S1: Synthesis of model ligand (L2)

5. Synthesis of monomeric paramagnetic iron complex of model ligand & NMR:

To the ethanolic solution of model ligand (100 mg, 0.38 mmol), 3 ml of triethyl amine was added followed by addition of 0.067 g of $Fe(OAc)_2$ and mixture was refluxed in nitrogen atmosphere for 12 hrs. Then the dark coloured solution was removed and solvent was rotary evaporated. The obtained compound was then washed with hot ethanol and dried in oven. Yield 90% (0.12 g). ^{1}H NMR (400 MHz, DMSO) δ: -10(s), -6 (s), 12 (s), 31.4 (s).



Scheme S2: Synthesis of monomeric paramagnetic iron complex of model ligand (L2)

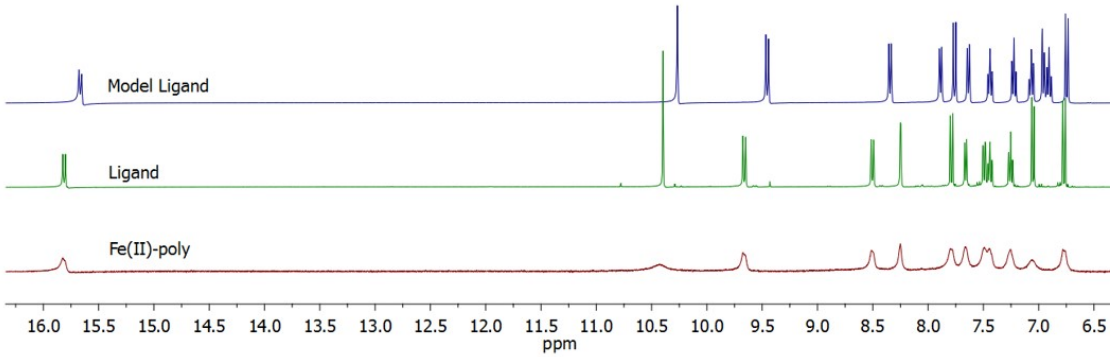


Fig. S5: Overlay ^{1}H NMR spectra of ligand, model ligand and Fe(II)-poly.

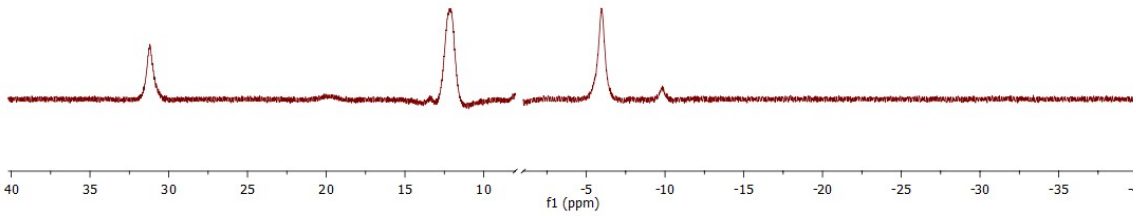


Fig. S6: ^{1}H NMR spectra of monomeric paramagnetic iron complex of model ligand.

6. VSM analysis of monomeric paramagnetic iron complex of model ligand:

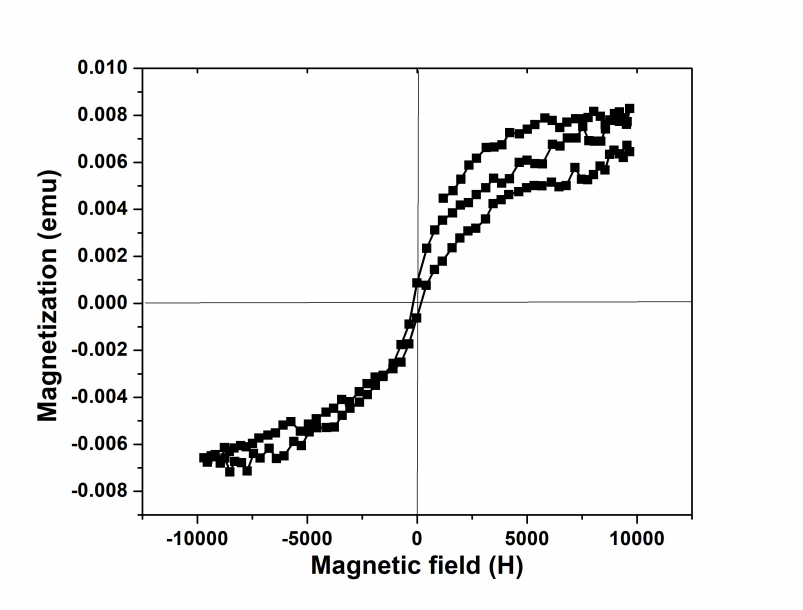


Fig. S7: VSM plot of monomeric paramagnetic iron complex of model Ligand.

7. UV-Vis-NIR of Fe(II)-poly:

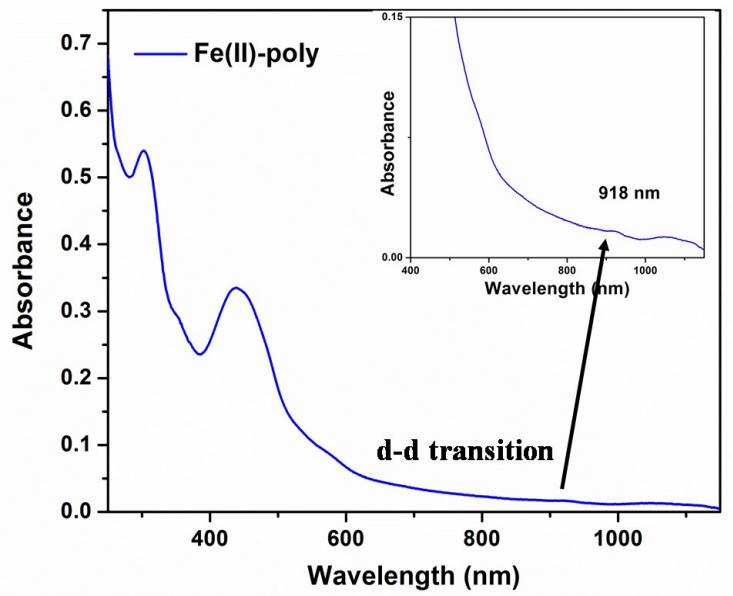


Fig. S8: UV-Vis-NIR absorbance spectrum of Fe(II)-poly

8. FESEM analysis of Fe(II)-poly:

ESI Fig. S9 shows the FESEM image of the polymeric powder sample. The picture reveals the formation of aggregates in the sample. However, a clear pattern connected in a regular fashion, as expected in polymer, can be seen from the image.

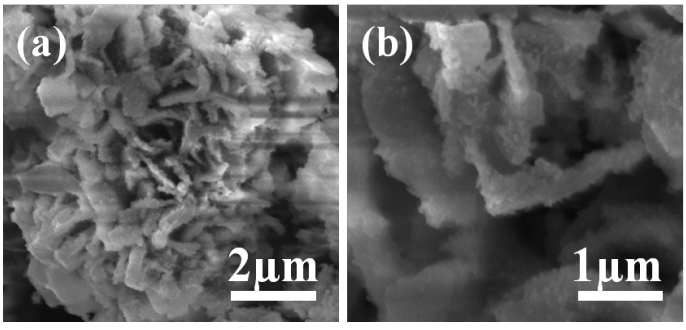


Fig. S9: FESEM image of powdered sample of Fe(II)-poly

9. EDX report of Fe(II)-poly:

To obtain the elemental composition of the polymer, thin film of the Fe(II)-poly solution (10^{-5} M) has been obtained on glass plate. The EDX report has been summarized below in ESI Table S1. Since we have used the glass surface, therefore EDX data also shows the elemental composition of glass.

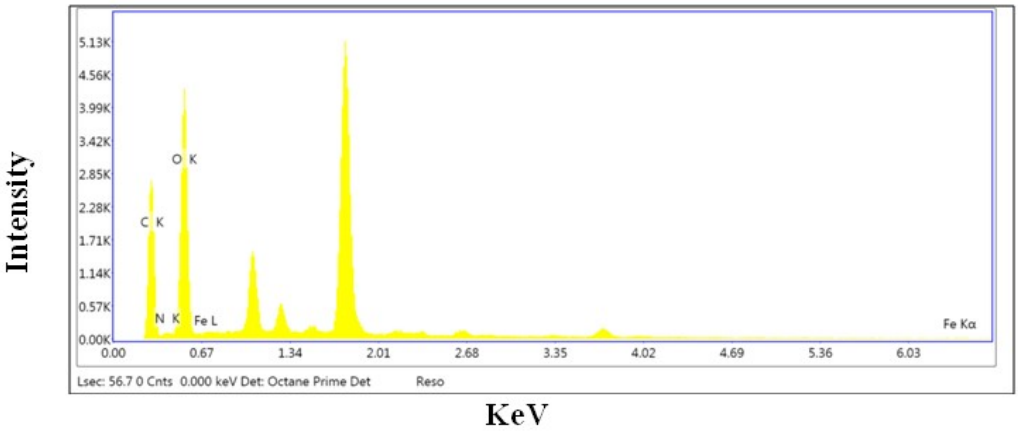
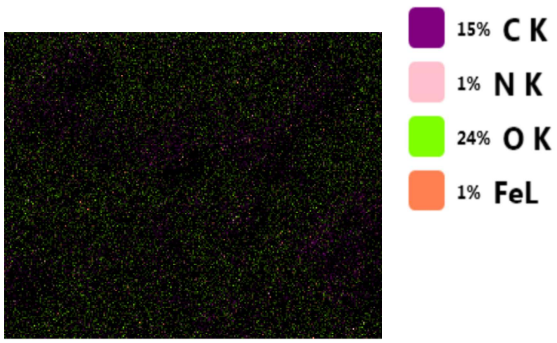


Fig. S10: EDX report of Fe(II)-poly.

Table S1: Elemental Composition of Fe(II)-poly obtained by EDX report:

Element	Weight %	Atomic %
C K	32.38	38.89
N K	8.14	8.39
O K	58.05	52.35
Fe L	1.43	0.37
Total	100	

Element Overlay:



10. AFM measurement of Fe(II)-poly:

The polymeric structure was confirmed by AFM analysis. The dimension obtained from the section profile of AFM, was compared with those obtained from calculated model structure. The AFM section profile showed that the thickness of the polymer is 1.4 nm.

Two units of the polymer chain were taken for minimizing their energy. When the minimized structure was optimized by MOPAC calculation, then thickness of the polymer unit was found to be 1.39 nm. This calculated thickness matches with that observed by section profile of AFM analysis. Therefore, it clearly supports presence of single polymeric strand observed on HOPG surface.

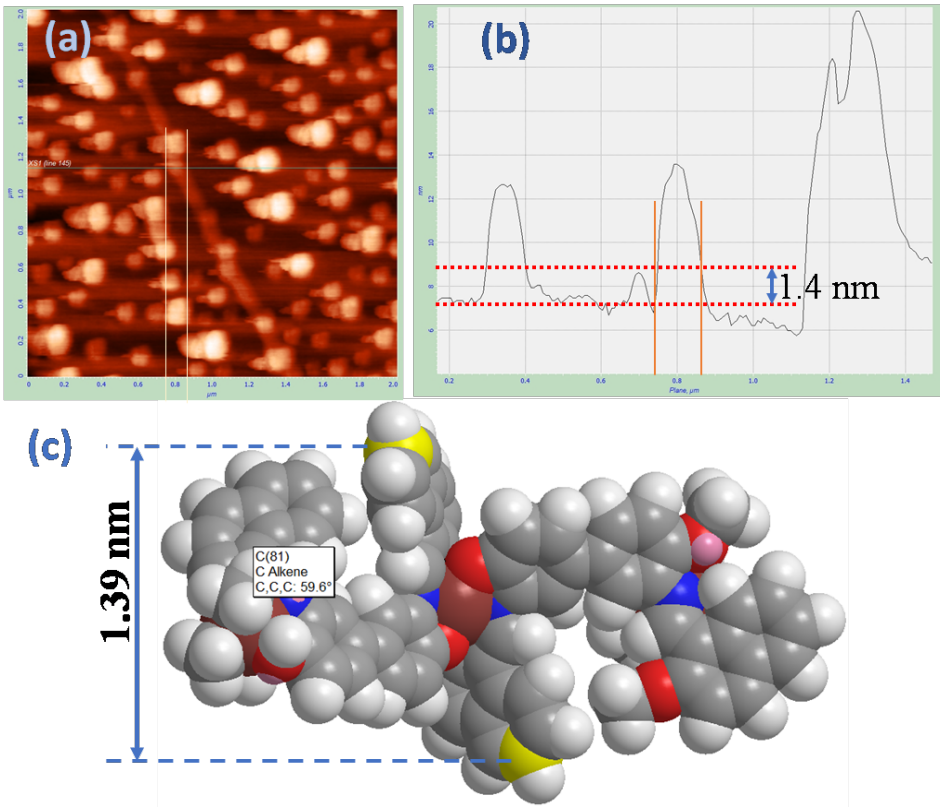


Fig. S11: Section profile of Fe(II)-poly AFM (a) and (b), and optimized structure of the two units of polymer units.

11. Cyclic voltammetry of ligand, model ligand & iron complex of model ligand :

The Cyclic voltammogram of the ligand in both oxidation and reduction sweep is given below. Ligand does not show any oxidation sweep. However, two reduction peaks at -0.768 V and another at -1.75 V, due to reduction of two imine groups.

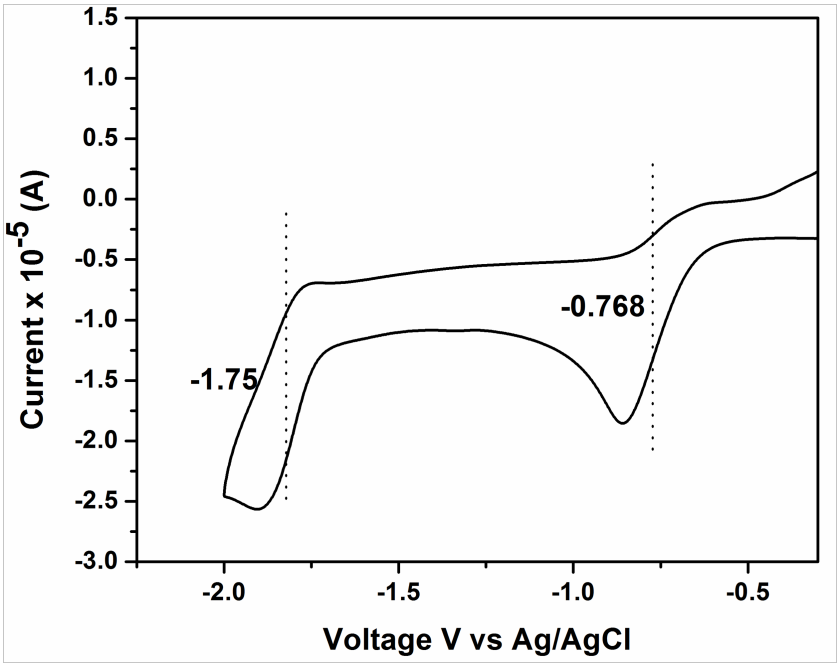


Fig. S12: CV of ligand in reduction sweep in acetonitrile containing 0.1 M TBAP at 100 mV/s with Glassy carbon as working electrode and Ag/AgCl as reference electrode.

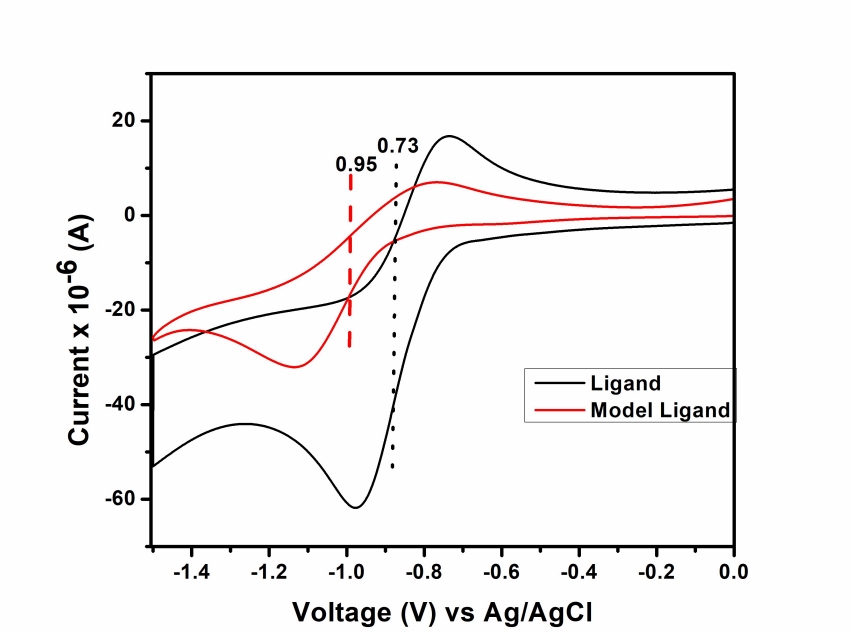


Fig. S13: CV of ligand and model ligand in reduction sweep in acetonitrile containing 0.1 M TBAP at 50 mV/s with Glassy carbon as working electrode and Ag/AgCl as reference electrode.

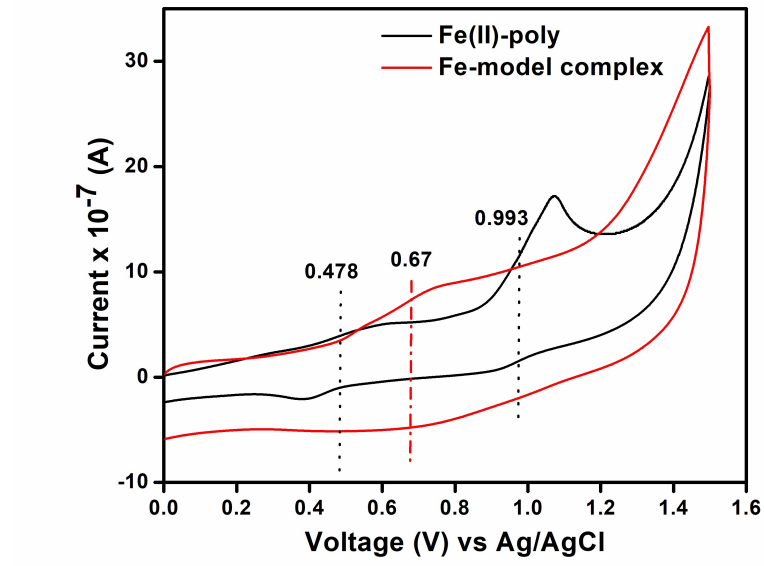


Fig. S14: CV of Fe(II)-poly and Fe-model complex in reduction sweep in acetonitrile containing 0.1 M TBAP at 50 mV/s with Glassy carbon as working electrode and Ag/AgCl as reference electrode.