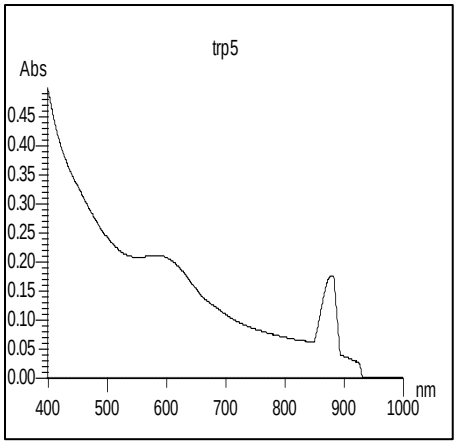
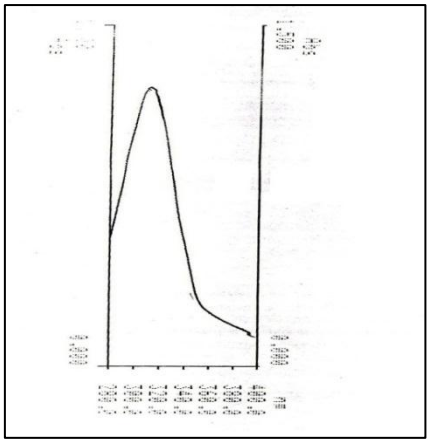
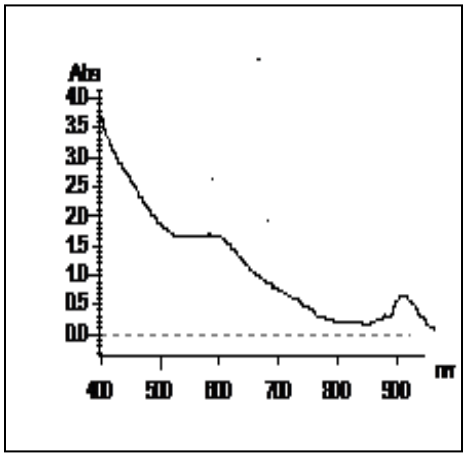


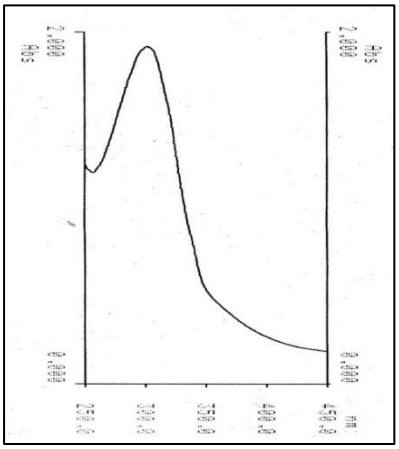
(a)



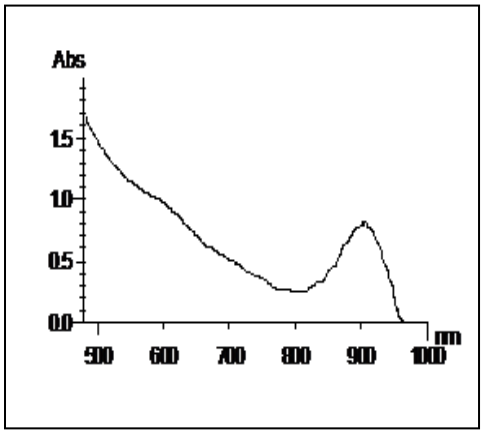
(b)



(c)

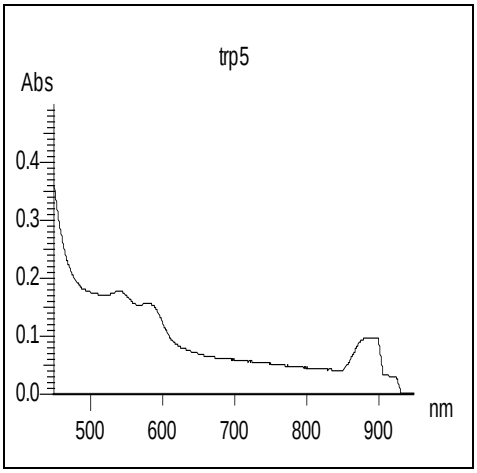


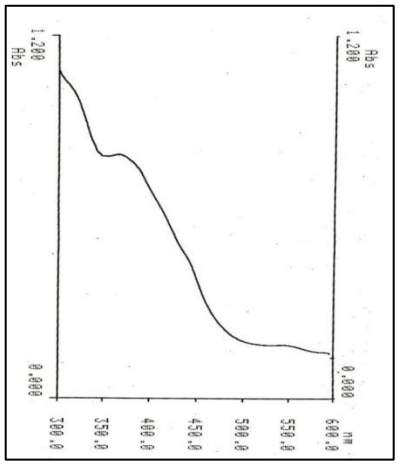
(d)



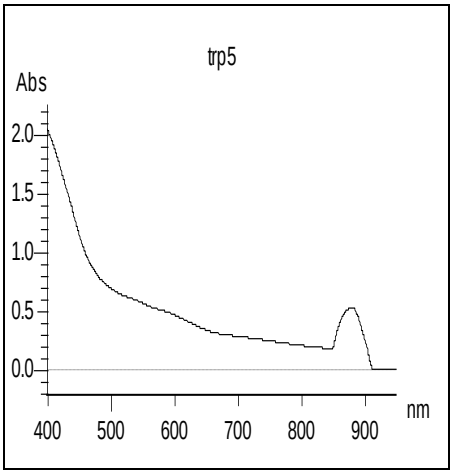
(e)

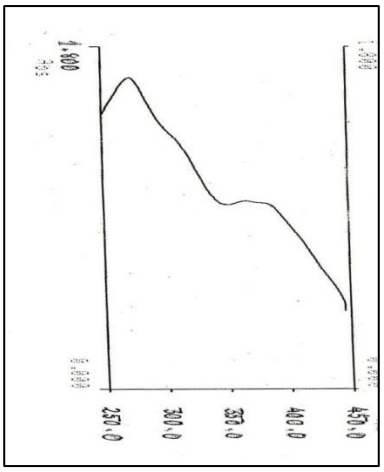
Fig. S1. Electronic spectra of Fe(acac)$(tbh)_2$ in benzene (a & b), acetonitrile (c & d), DMSO (e)



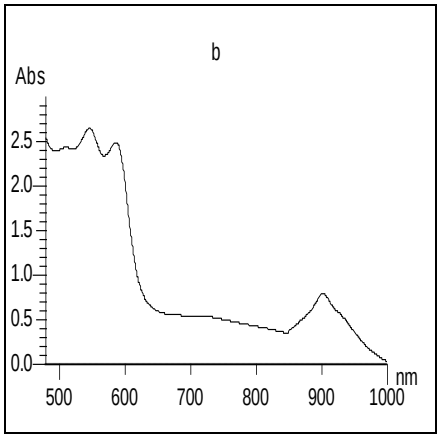


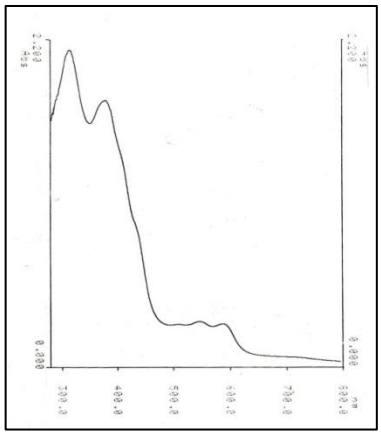
(a) (b)





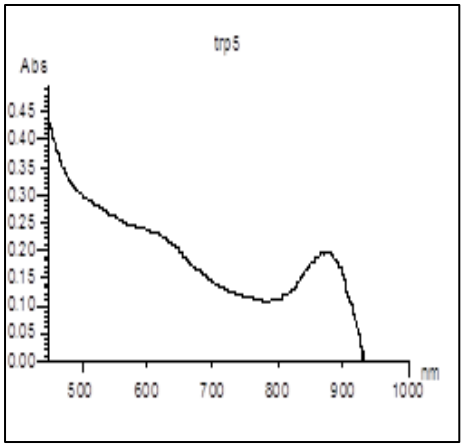
(c) **(d)**



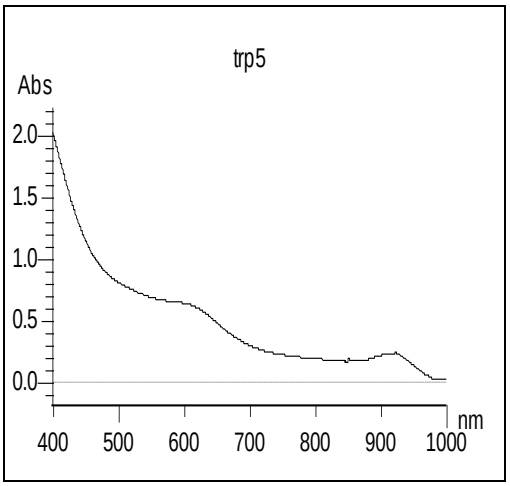


(e) **(f)**

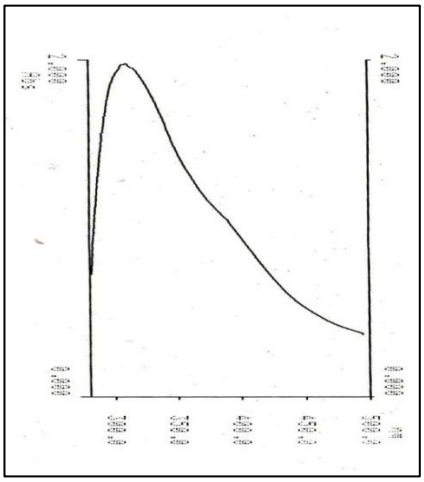
Fig. S2. Electronic spectra of Fe(acac)(htbh)$_2$ in benzene (a & b), in acetonitrile (c & d), in DMSO (e & f)



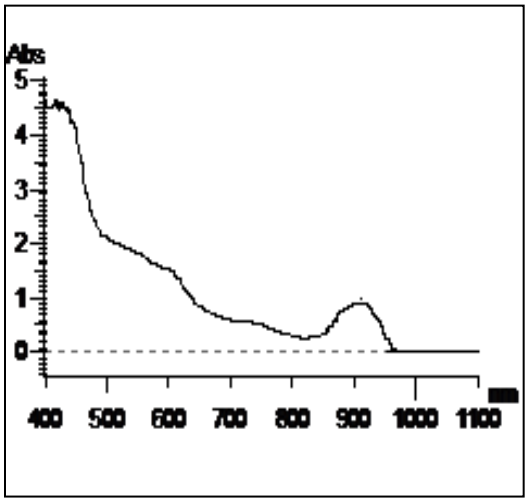
(a)



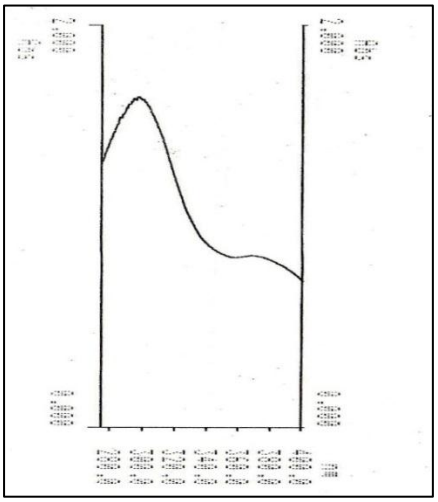
(b)



(c)

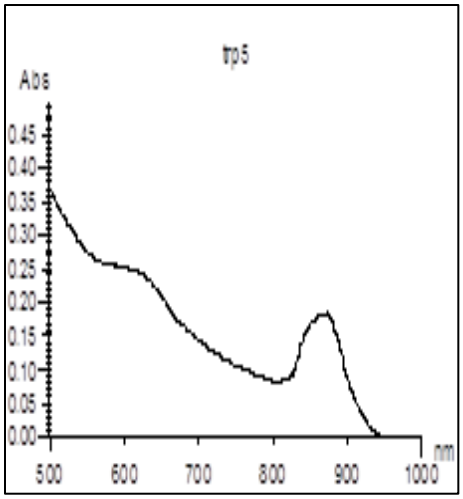


(d)

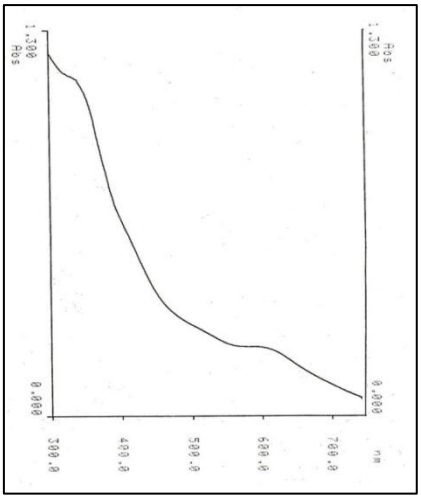


(e)

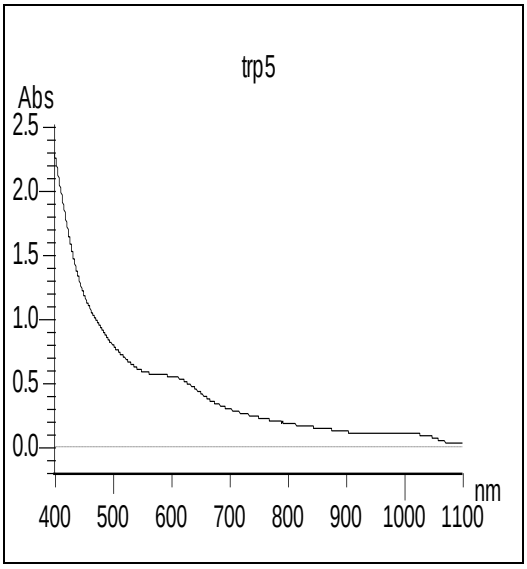
Fig. S3. Electronic Spectra of Fe (acac)$(fth)_2$ in benzene (a), in acetonitrile (b & c), DMSO (d & e)



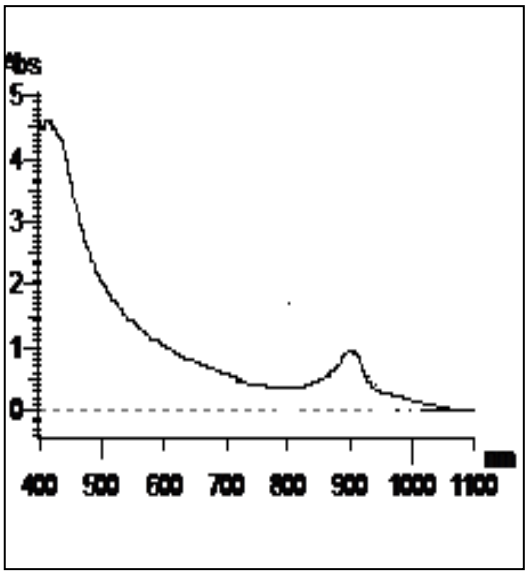
(a)



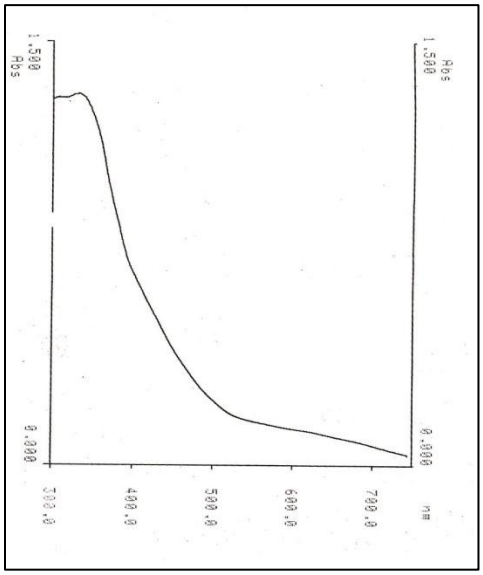
(b)



(c)

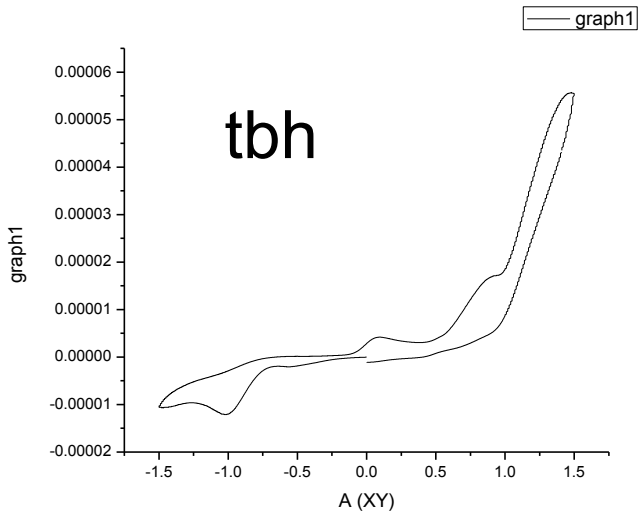


(d)



(e)

Fig. S4. Electronic spectra of Fe(acac)(tth)$_2$ in benzene (a & b), acetonitrile (c), DMSO (d & e)



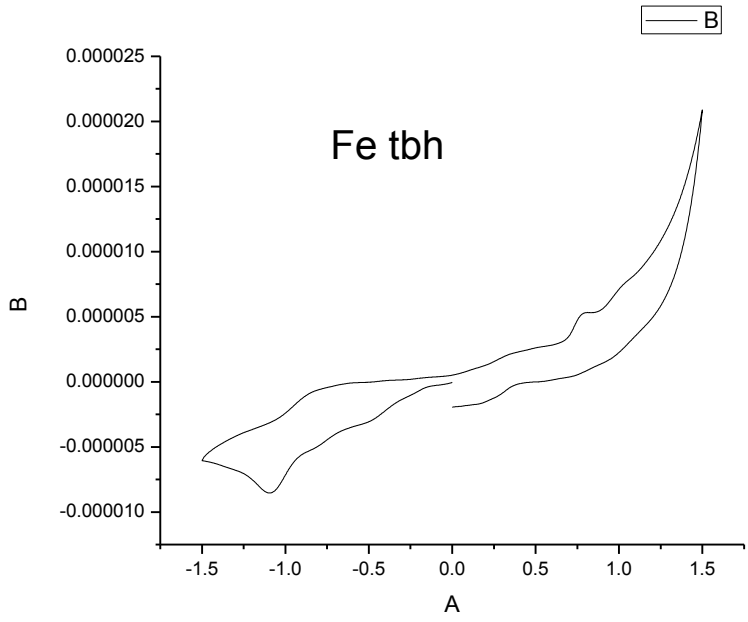


Fig. S5. Cyclic Voltammograms of thiobenzhydrazide and (acetylacetonato)bisthiobenzhydrazido iron(III) complex (scan rate 100 mv sec^{-1})

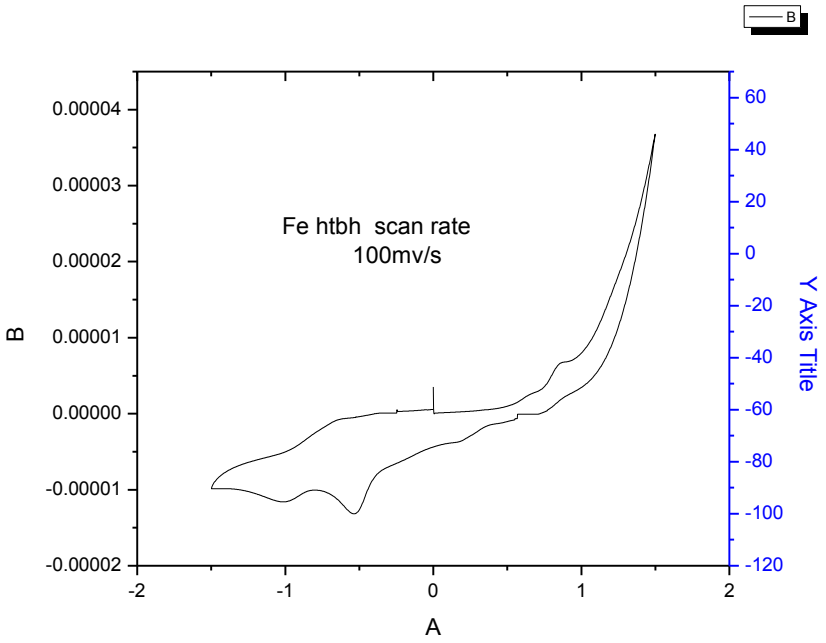


Fig. S6. Cyclic Voltammogram of (acetylacetonato)bis-2-hydroxythiobenzhydrazido iron(III) complex (scan rate 100 mv sec^{-1})

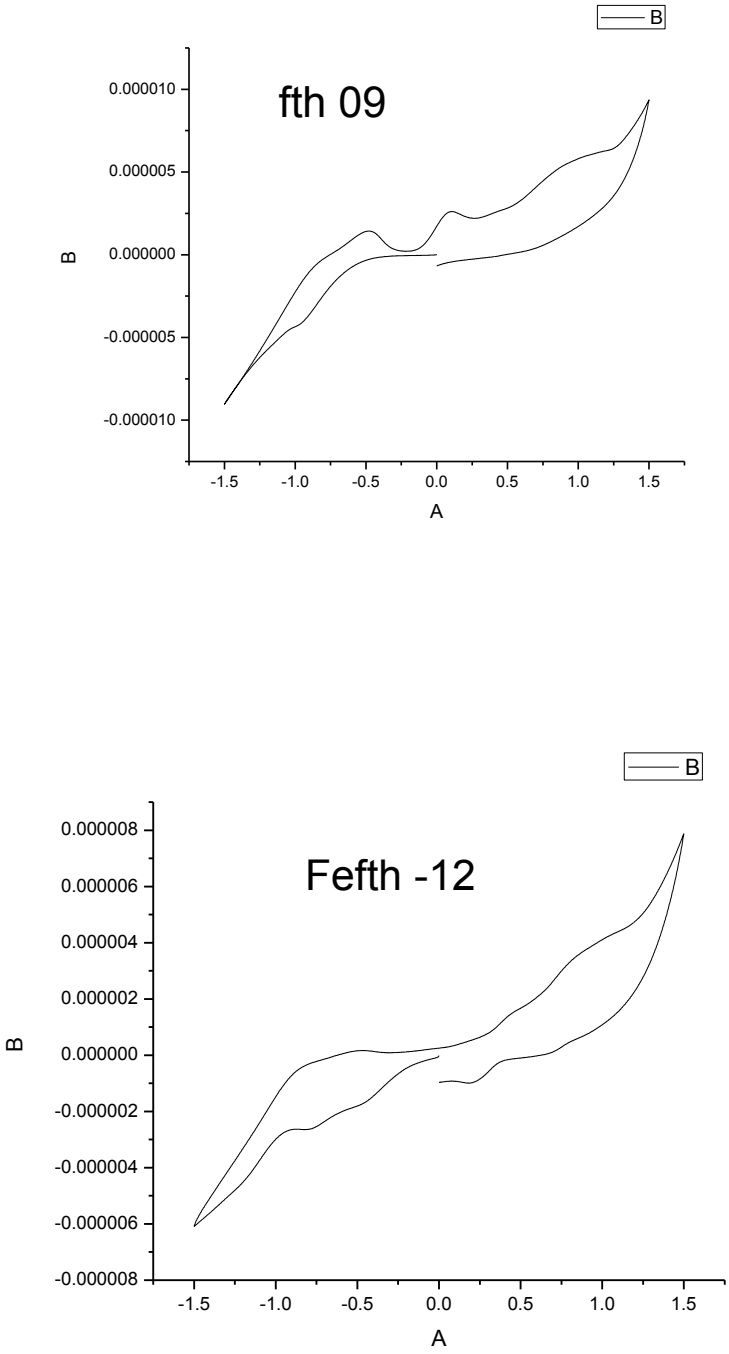
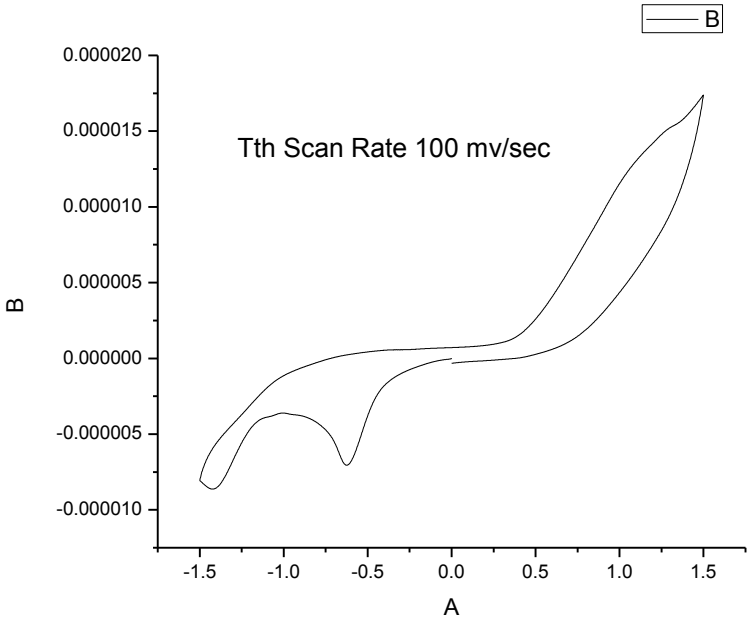


Fig. S7. Cyclic Voltammograms of furan-2-thiohydrazide and (acetylacetonato)bisfuran-2-thiohydrazido iron(III) complex (scan rate 100 mv sec^{-1})



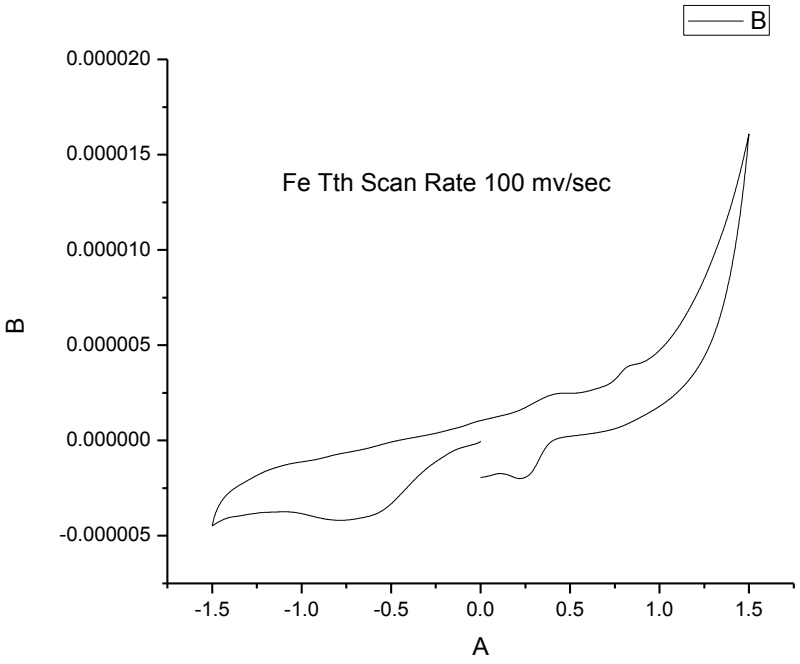


Fig. S8. Cyclic Voltammograms of thiophen-2-thiohydrazide and (acetylacetonato)bisthiophen-2-thiohydrazido iron(III) complex (scan rate 100 mv sec^{-1})

Table S1 The Cartesian coordinates of the optimized structure for acetylacetonatobis-2-hydroxythiobenzhydrazidoiron(III) [Fe(acac)(htbh)$_2$] calculated from DFT studies

Atom	x	y	z
Fe	-0.07433682	-0.21682177	-0.01651677
O	-1.87759685	-0.88248246	0.42594413
O	-0.67445953	0.71090692	-1.61095448
C	-1.89535363	0.80306798	-2.01750438
C	-2.08247878	1.64135026	-3.27678029
H	-3.12538042	1.63989301	-3.62729990
H	-1.77492244	2.68196723	-3.07495920
H	-1.43046937	1.25857806	-4.07982105
C	-3.01742667	0.19346472	-1.39765554
H	-3.99146899	0.33410791	-1.86853126
C	-2.95898355	-0.61871534	-0.25018962
C	-4.22016904	-1.28946067	0.28221512
H	-5.12721087	-0.93760355	-0.23161763
H	-4.14142019	-2.38308022	0.15086625
H	-4.32279537	-1.10222565	1.36478380
S	0.53341550	-2.08017714	-1.21075482
N	0.38149042	-1.38316333	1.57934404
H	0.86361136	-0.93181804	2.37035699
H	-0.55358803	-1.66563768	1.92260468
C	1.15283413	-3.03614986	0.15191690
C	1.77848790	-4.36021574	-0.16175722
C	2.72030202	-4.46113624	-1.21107665
C	1.44507630	-5.54442431	0.55473514
C	3.33702531	-5.67827283	-1.53903910
H	2.96722941	-3.55332137	-1.76608897
C	2.05974213	-6.76928625	0.21920711
C	3.00290120	-6.83715254	-0.81745571
H	4.06944336	-5.72024612	-2.34938342
H	1.78940902	-7.67328636	0.77811734
H	3.47035910	-7.79649678	-1.05863916
O	0.49533608	-5.47352318	1.55245185
H	0.35643001	-6.38389740	1.89171792
S	1.96450676	0.66423785	-0.10560940
N	-0.57818277	2.80207965	0.54469379
N	1.13176385	-2.66239391	1.40423914
C	1.80374441	2.37167472	-0.05338260
H	2.73669062	2.92012116	-0.21693004
C	0.60430264	3.16603268	0.06121880
N	-0.57149662	1.47045843	1.13998220
H	0.05282080	1.49991406	1.96563753
H	-1.52740891	1.33747041	1.49385796
C	0.67852649	4.58596852	-0.43082210
C	1.14476976	4.84759199	-1.73842264
C	0.30988744	5.69315686	0.38227311

C	1.23147936	6.15344703	-2.24858059
H	1.42844159	3.99611478	-2.36334737
C	0.39774195	7.00564202	-0.12749918
C	0.85247860	7.23523566	-1.43548939
H	1.58717094	6.32260156	-3.26822536
H	0.11292724	7.84940029	0.51236491
H	0.91176727	8.26049764	-1.81242648
O	-0.09794215	5.45297974	1.67881710
H	-0.27264498	6.32152172	2.10092921

Table S2 Atomic Spin Population (Major contribution shown in bold)

Atom	Atomic Number	Atomic Spin Population
Fe	**26.0**	**-0.67705**
O	8.0	0.00300
O	8.0	-0.00539
C	6.0	0.01122
C	6.0	0.00018
H	1.0	0.00031
H	1.0	0.00033
H	1.0	0.00049
C	6.0	-0.01378
H	1.0	0.00033
C	6.0	0.00033
C	6.0	-0.00049
H	1.0	0.00010
H	1.0	0.00060
H	1.0	0.00040
S	16.0	0.01126
N	7.0	0.01181
H	1.0	-0.00040
H	1.0	0.00054
C	6.0	0.00332
C	6.0	0.00034
C	6.0	0.00059
C	6.0	0.00028
C	6.0	-0.00016
H	1.0	-0.00004
C	6.0	0.00001
C	6.0	0.00038
H	1.0	0.00001
H	1.0	0.00001
H	1.0	-0.00002
O	8.0	0.00010
H	1.0	-0.00001
S	**16.0**	**0.13714**
N	**7.0**	**0.22218**
N	7.0	-0.00070
C	**6.0**	**0.31681**
H	1.0	-0.01260
C	6.0	-0.03273
N	7.0	0.00142
H	1.0	0.00945
H	1.0	-0.00085
C	6.0	0.00391
C	6.0	-0.00102
C	6.0	-0.00247
C	6.0	0.00213
H	1.0	0.00084
C	6.0	0.00190

C	6.0	-0.00275
H	1.0	-0.00017
H	1.0	0.00005
H	1.0	0.00016
O	8.0	-0.00030
H	1.0	0.00028

Table S3 DFT Final Molecular Orbital Analysis for Alpha spin:

Vector 130 Occ=1.000000D+00 E=-1.255216D-01

MO Center= 3.0D-01, -2.2D-01, -1.1D-01, r^2= 4.2D+00

Bfn.	Coefficient	Atom+Function	Bfn.	Coefficient	Atom+Function
28	0.278013	1 Fe d 2	160	-0.263605	16 S px
33	0.252804	1 Fe d 2	24	-0.226740	1 Fe d -2
38	0.214356	1 Fe d 2	29	-0.205838	1 Fe d -2
320	-0.203045	33 S pz	34	-0.176704	1 Fe d -2
362	0.154625	36 C pz			

Vector 131 Occ=0.000000D+00 E=-1.049618D-01

MO Center= 2.9D-01, 2.9D-01, -7.0D-02, r^2= 3.6D+00

Bfn.	Coefficient	Atom+Function	Bfn.	Coefficient	Atom+Function
27	0.342616	1 Fe d 1	32	0.312785	1 Fe d 1
320	0.300270	33 S pz	37	0.264875	1 Fe d 1
324	0.197539	33 S pz	362	-0.151274	36 C pz

Table S4 DFT Final Molecular Orbital Analysis for Beta spin:

Vector 130 Occ=1.000000D+00 E=-1.380487D-01

MO Center= 1.3D-01, -8.5D-01, -2.4D-01, r^2= 3.2D+00

Bfn.	Coefficient	Atom+Function	Bfn.	Coefficient	Atom+Function
160	0.316982	16 S px	24	0.261983	1 Fe d -2
28	-0.261636	1 Fe d 2	29	0.237967	1 Fe d -2
33	-0.238488	1 Fe d 2	34	0.196638	1 Fe d -2
38	-0.197367	1 Fe d 2	164	0.188286	16 S px
161	0.169096	16 S py	346	-0.153328	35 N px

Vector 131 Occ=0.000000D+00 E=-1.071531D-01

MO Center= 9.1D-01, 1.7D+00, 7.6D-02, r^2= 4.6D+00

Bfn.	Coefficient	Atom+Function	Bfn.	Coefficient	Atom+Function
320	0.392515	33 S pz	362	-0.324178	36 C pz
366	-0.305638	36 C pz	334	0.285828	34 N pz
324	0.278240	33 S pz	338	0.241887	34 N pz