Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Benzimidazolyl terpyridine-Fe^{2+} system and its recognition driven molecular model of a traffic light

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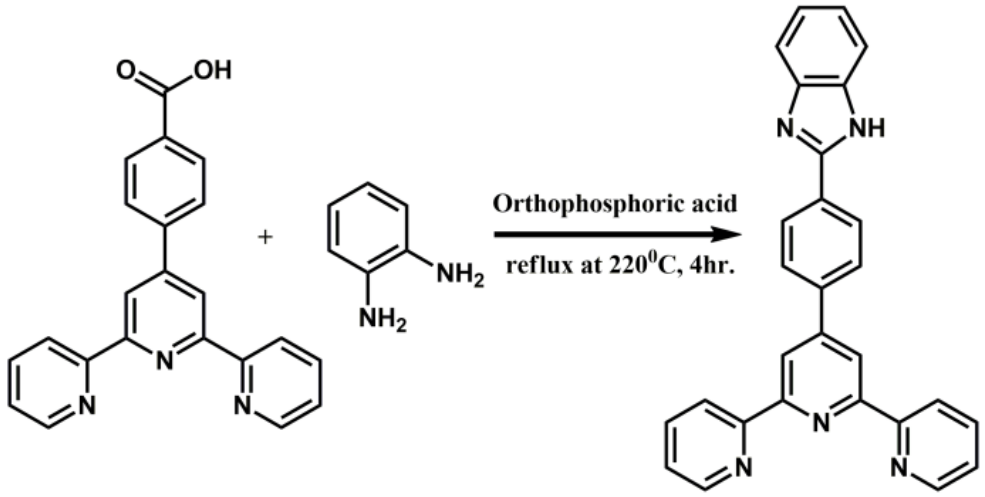

Scheme S1: Synthetic procedure for **BIT**.

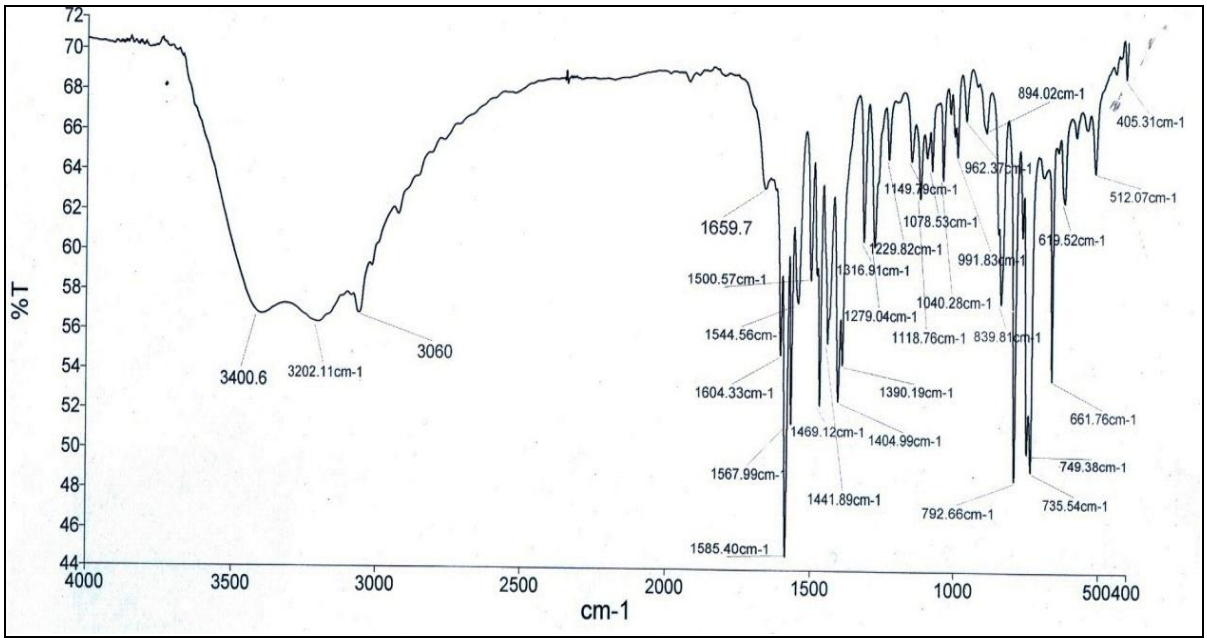

Fig. S1:IR spectrum of **BIT**.

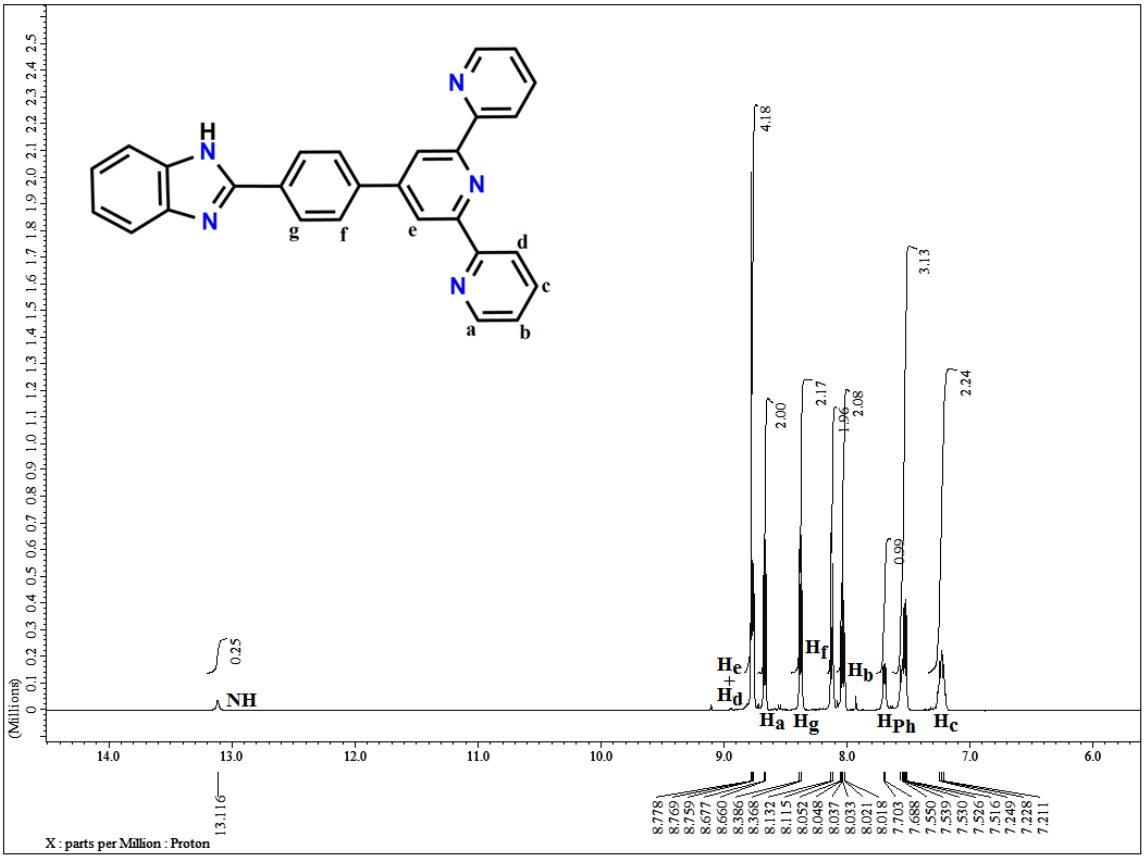

Fig. S2: ^{1}H NMR spectrum of **BIT** in DMSO-d_6 at room temperature.

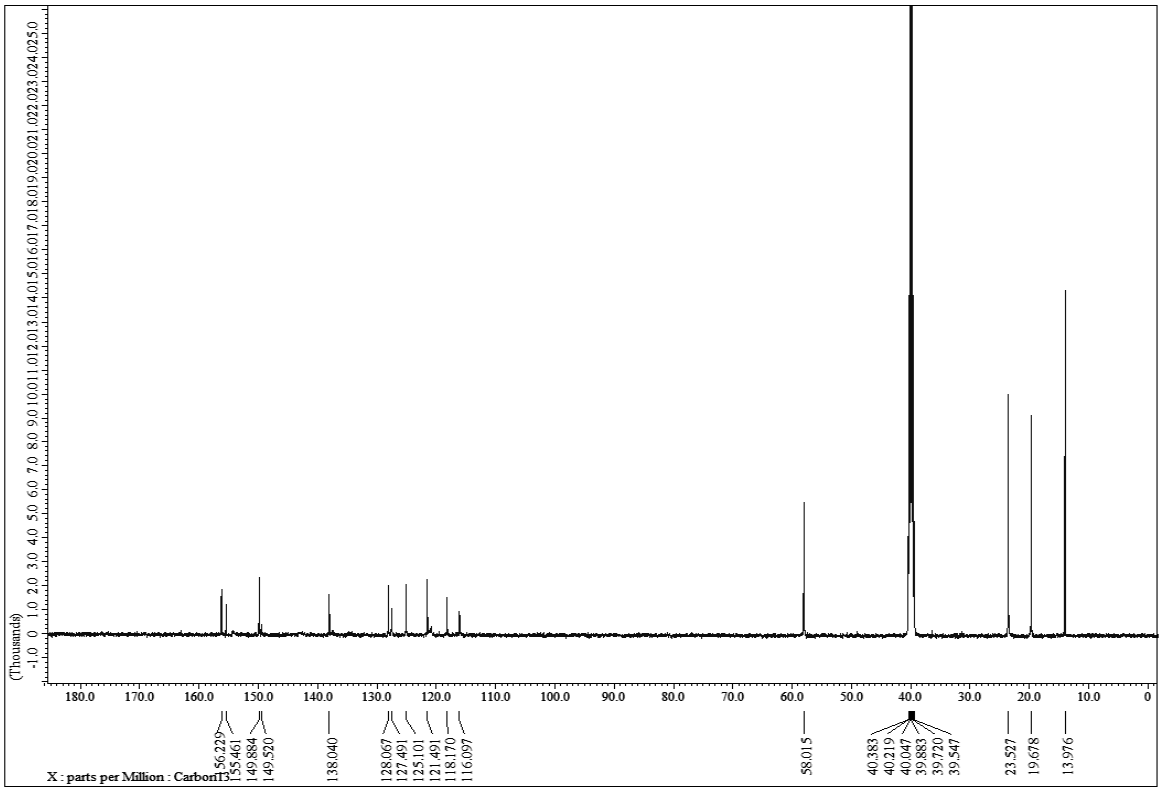

Fig. S3: ^{13}C NMR spectrum of **BIT** in DMSO-d_6 at room temperature.

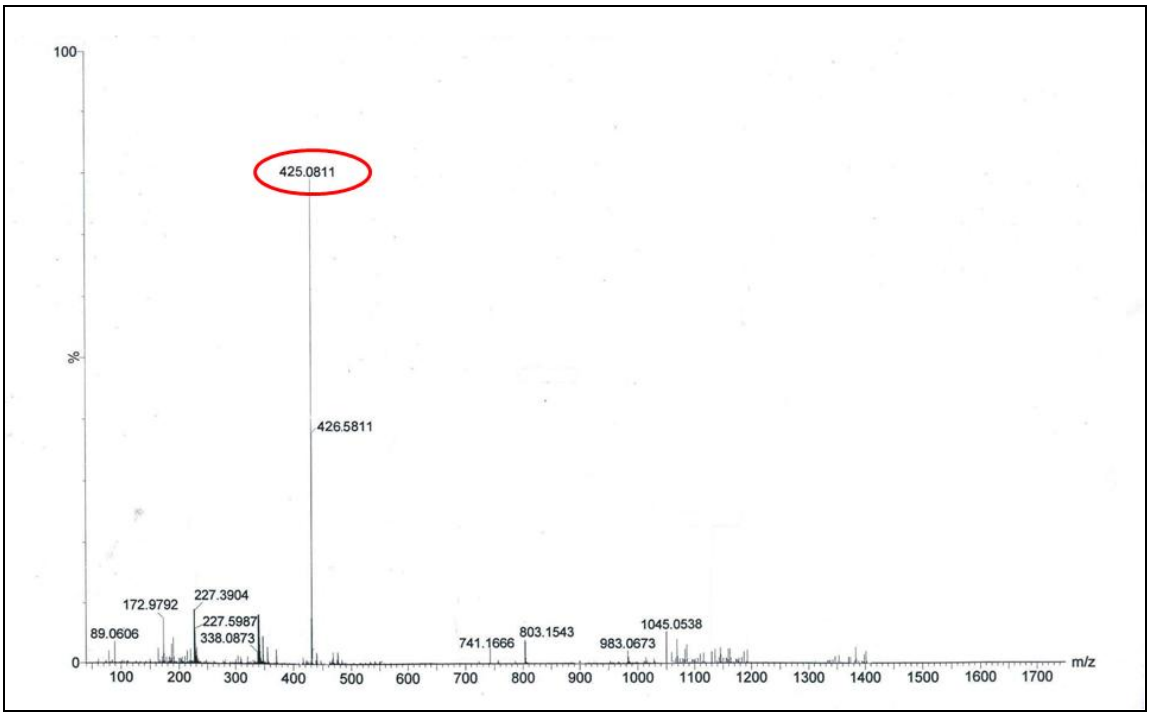

Fig. S4:HRMSspectrum of **BIT**.

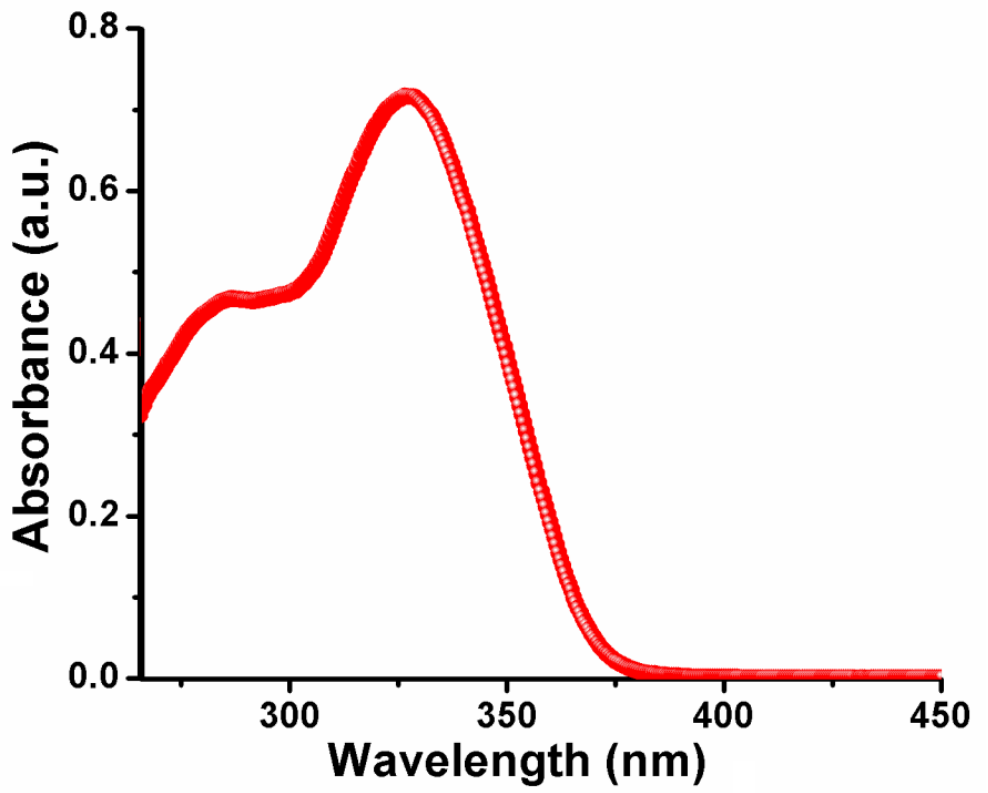

Fig. S5:UV-vis spectrum of **BIT** (2.0 x 10^{-5} M, DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2) at room temperature.

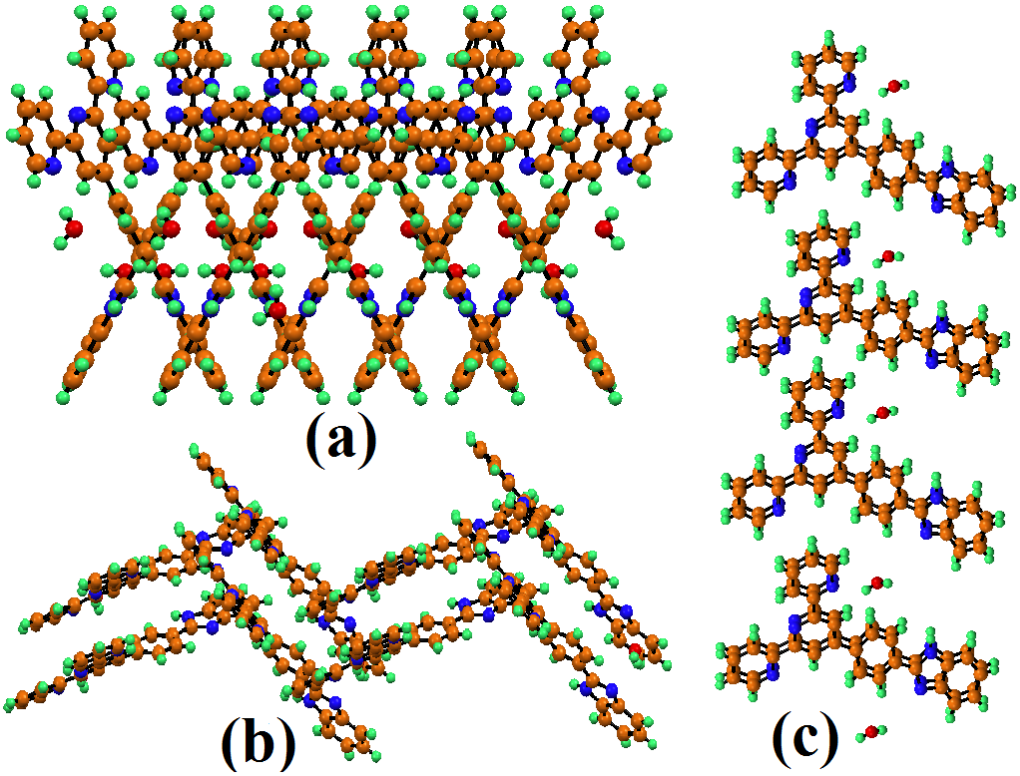

Fig. S6: Supramolecular architectures of **BIT** along a**(i),** b**(ii)** and c**(iii)** crystallographic axes, respectively.

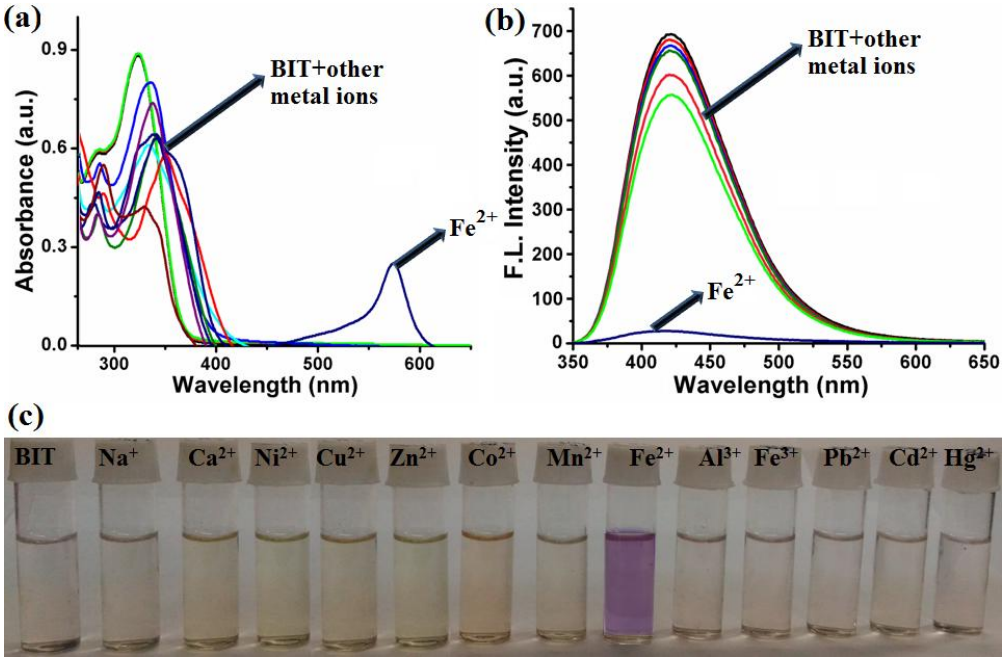

Fig. S7: Changes in (a) UV-vis, (b) Fluorescence spectra and (c) visual colour in solution of **BIT** (2.0 x 10^{-5} M, DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2)upon the addition of 2 equiv. of different metal ions as their perchlorate salt(1.0 x 10^{-2}M in H_2O).

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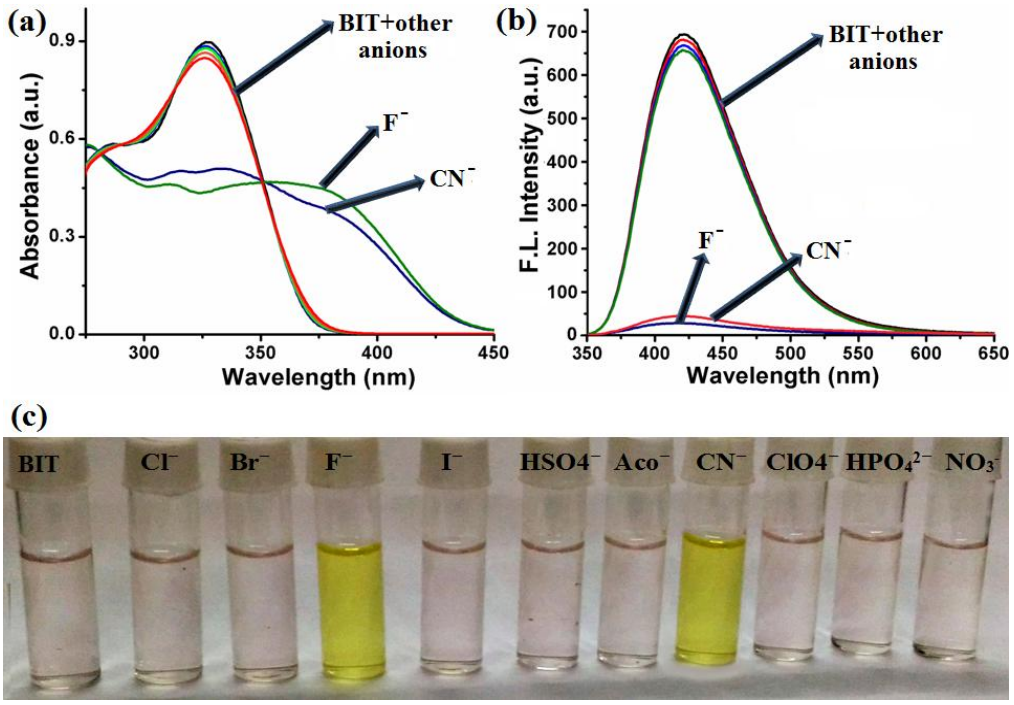

Fig. S8: Changes in (a) UV-vis, (b) Fluorescence spectra and (c) visual colour in solution of **BIT** (2.0 x 10^{-5} M, DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2)upon the addition of 10 equiv. of different anions as their TBA salt(1.0 x 10^{-2} M in acetonitrile)

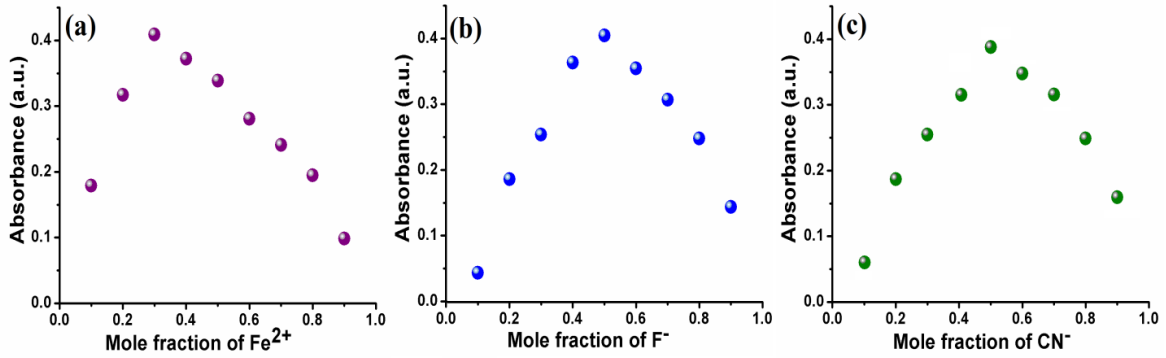

Fig. S9: Job's plot obtained for**BIT**(2.0 x 10^{-5} M,DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2)on variation of its absorbance *vs* mole-fraction of Fe^{2+}(1.0 x 10^{-3}M in H_2O)at λ_{max} = 579nm (a), F^-(1.0 x 10^{-2} M in acetonitrile)at λ_{max} = 381 nm (b), and CN^-(1.0 x 10^{-2} M in acetonitrile)at λ_{max} = 383 nm (c).

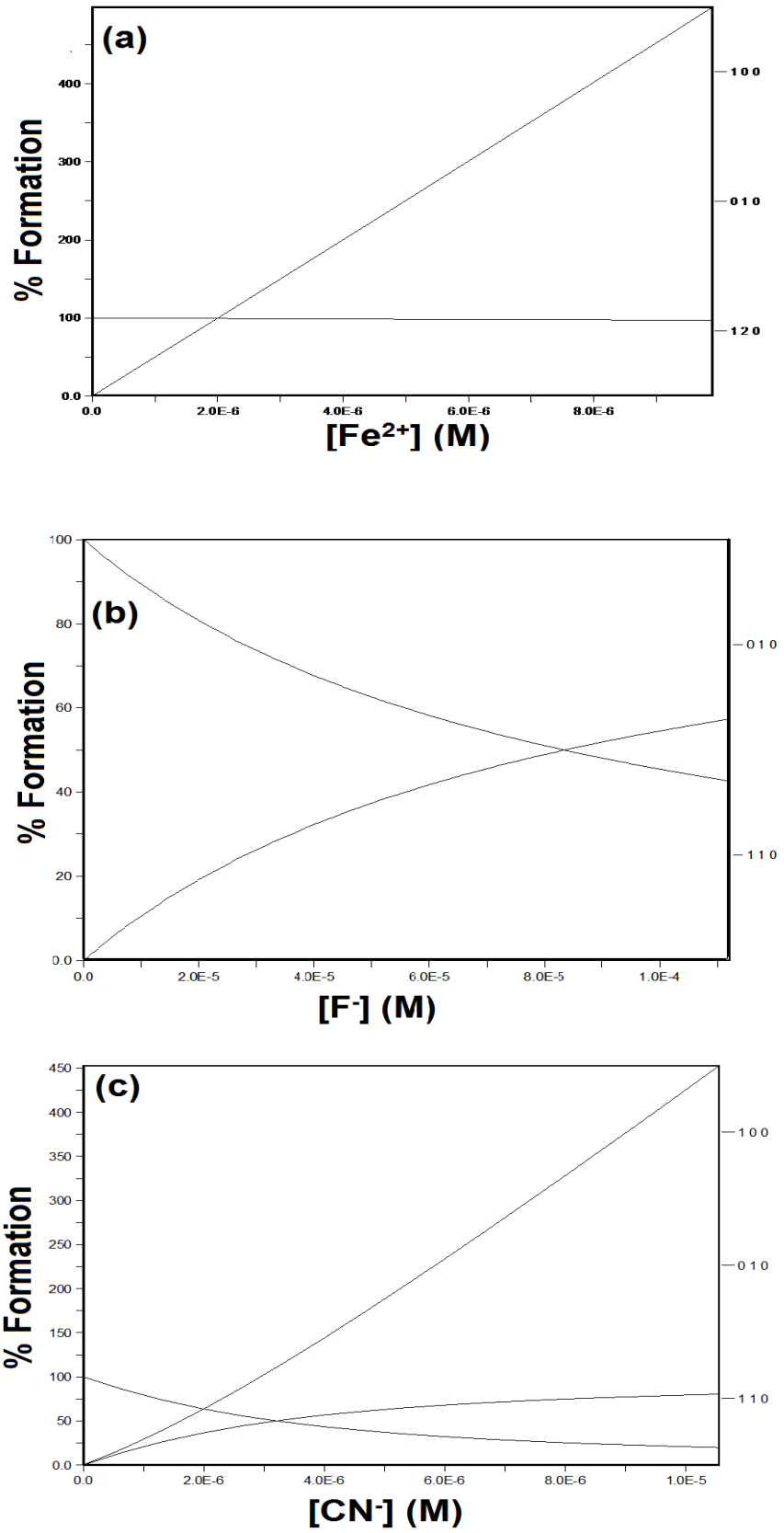

Fig. S10: Fitting diagram for the binding of **BIT** with Fe^{2+}(a), F^-(b) and CN^-(c) ions obtained using SPECFIT software.

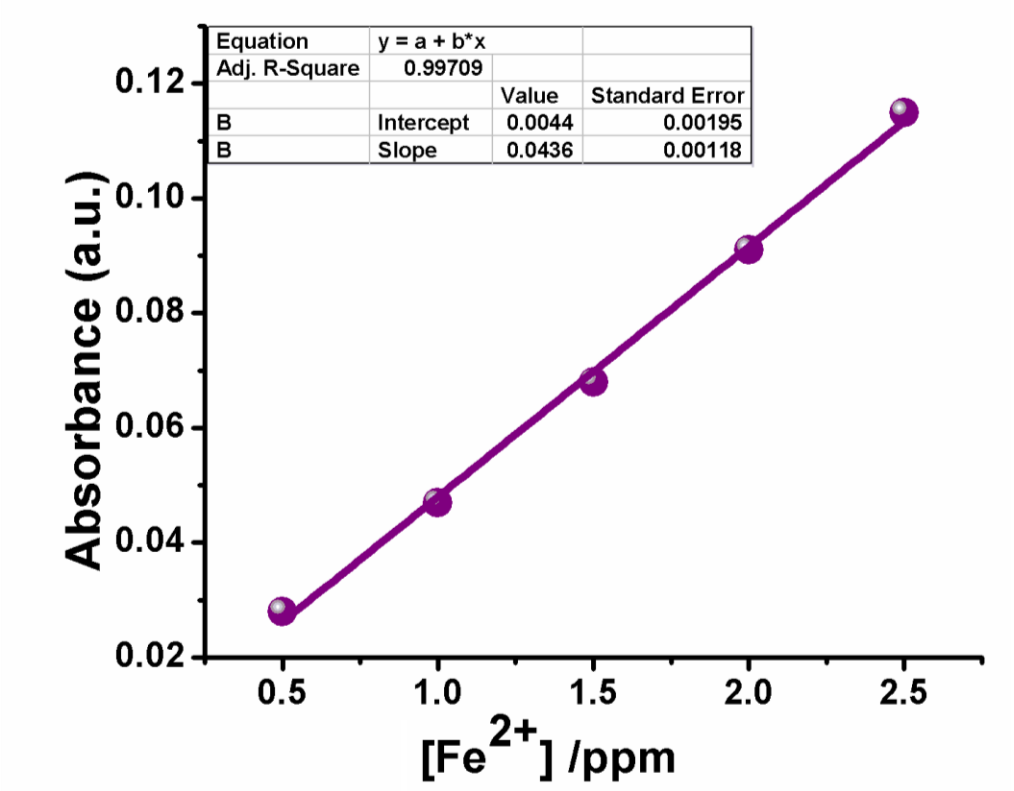

Fig.S11: Graph showing the variation of absorbance of**BIT** (2.0×10^{-5} M, DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2)*vs*[Fe^{2+}](R^2 = 0.985) at low concentration level used for the determination of detection limit λ_{max} 579nm.

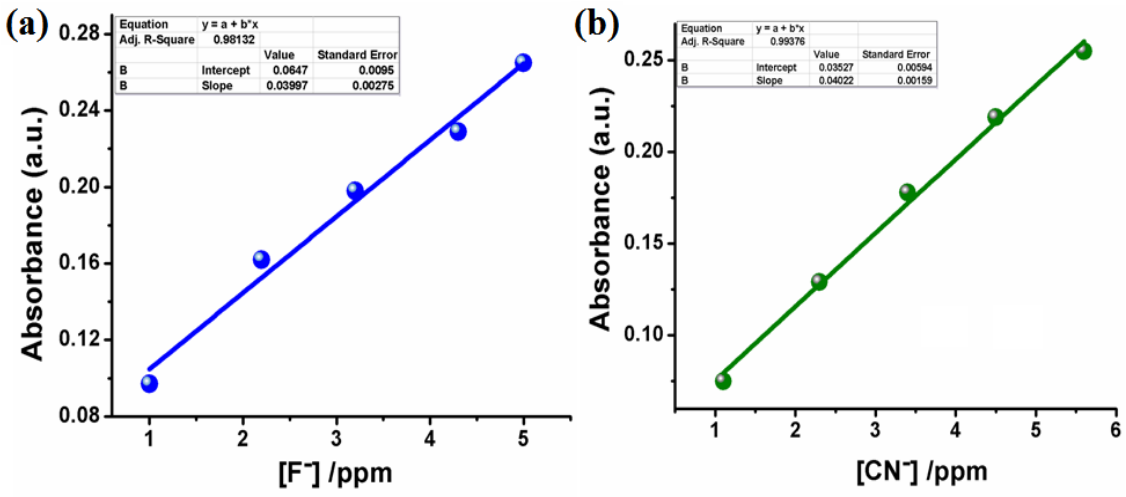

Fig. S12: Graph showing the variation of absorbance **BIT**(2.0×10^{-5} M,DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2)vs (a) [F^-](R^2= 0.986) and (b) [CN^-](R^2= 0.992) at low concentration level used for the determination of detection limit at λ_{max} 381 and 383 nm, respectively.

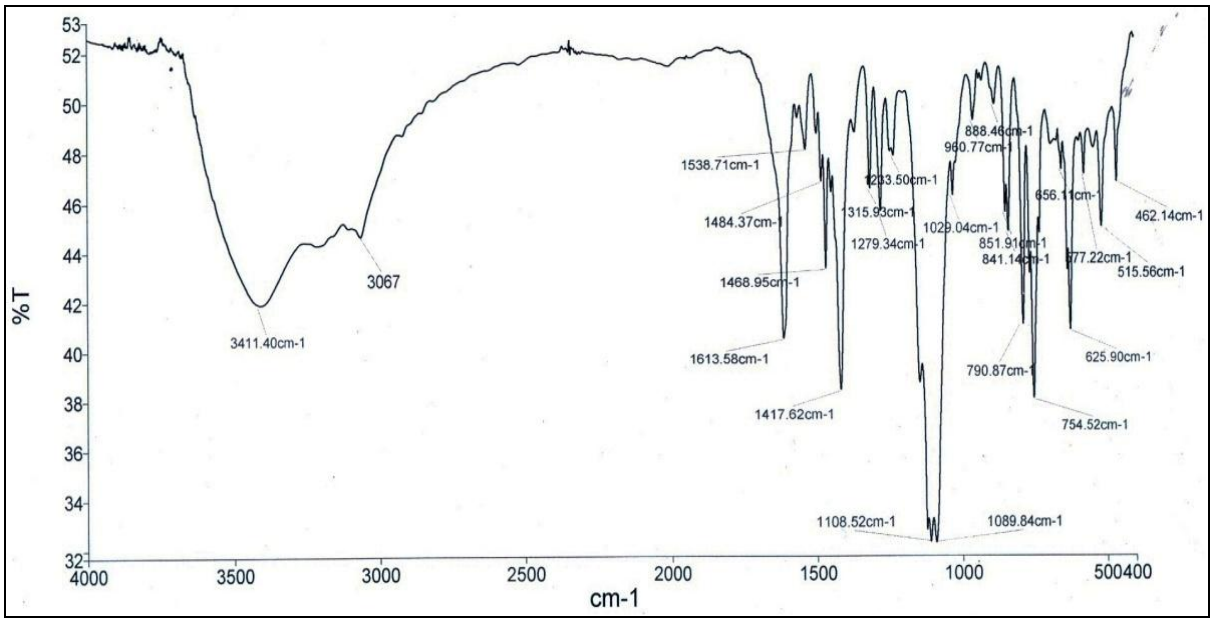

Fig. S13:IR spectrum of complex **1**.

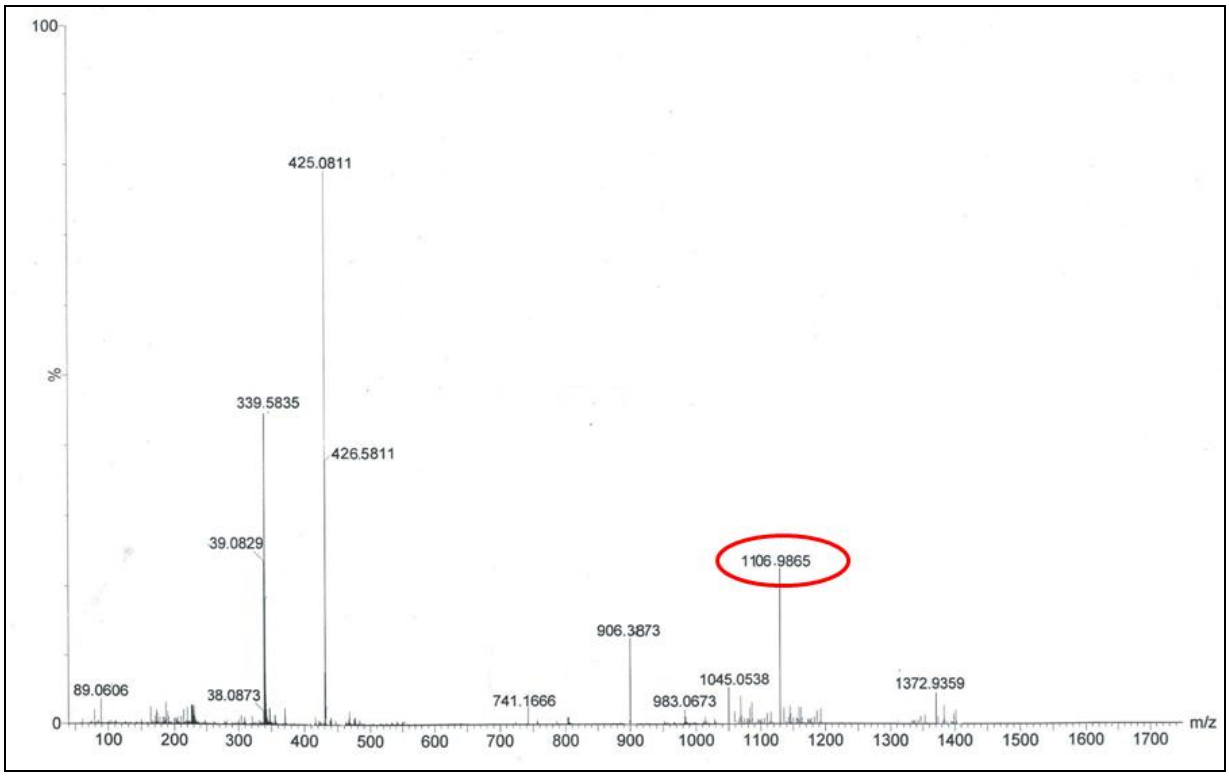

Fig. S14: HRMS spectrum ofcomplex **1**.

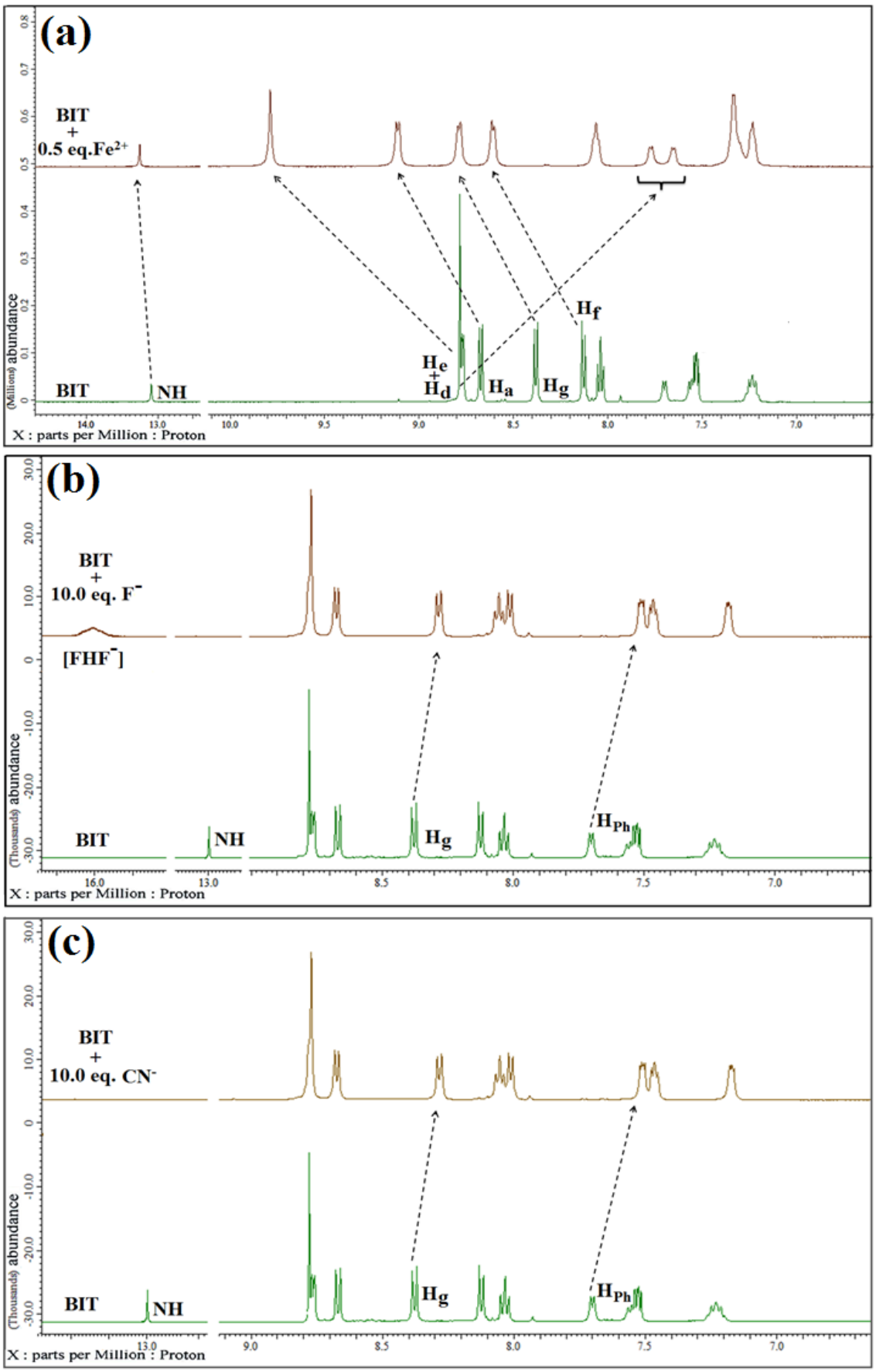

Fig. S15: Partial ^{1}H NMR spectra of **BIT** before and after the addition of Fe^{2+} (a), F^{-} (b) and CN^{-} (c) ions in DMSO-*d6*.

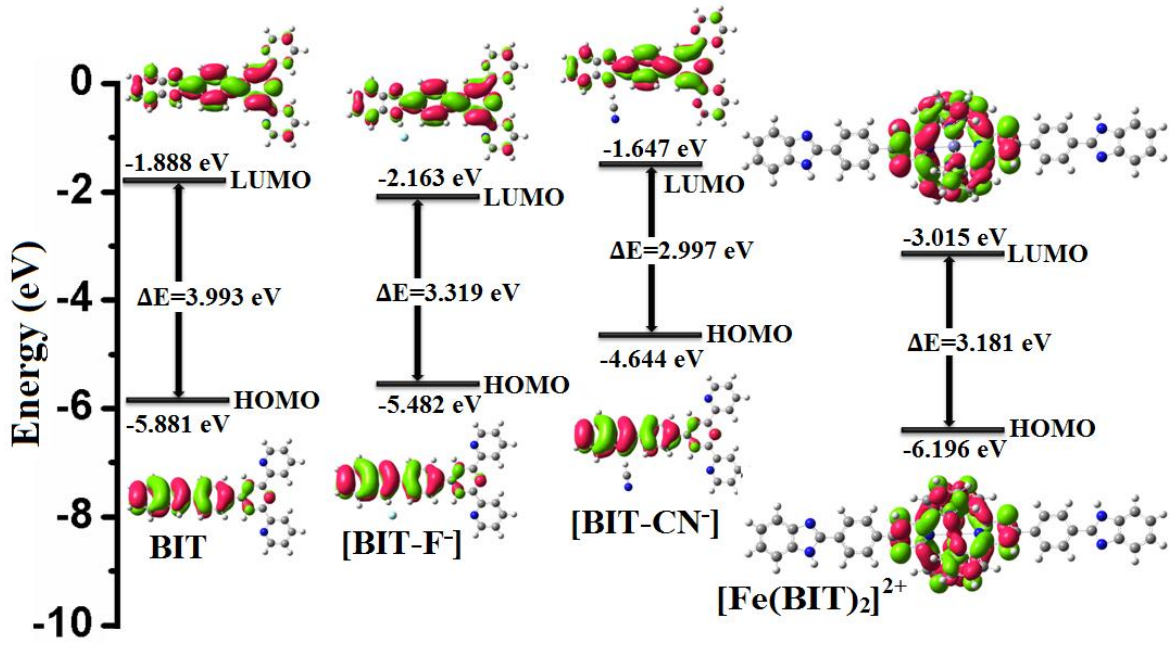

Fig. S16: Energy level diagrams of **BIT**, [**BIT-F⁻**], [**BIT-CN⁻**], and [Fe(**BIT**)$_2$]$^{2+}$ calculated at DFT level in acetonitrile (using a B3LYP/6-31G** and LANL2DZ basis set).

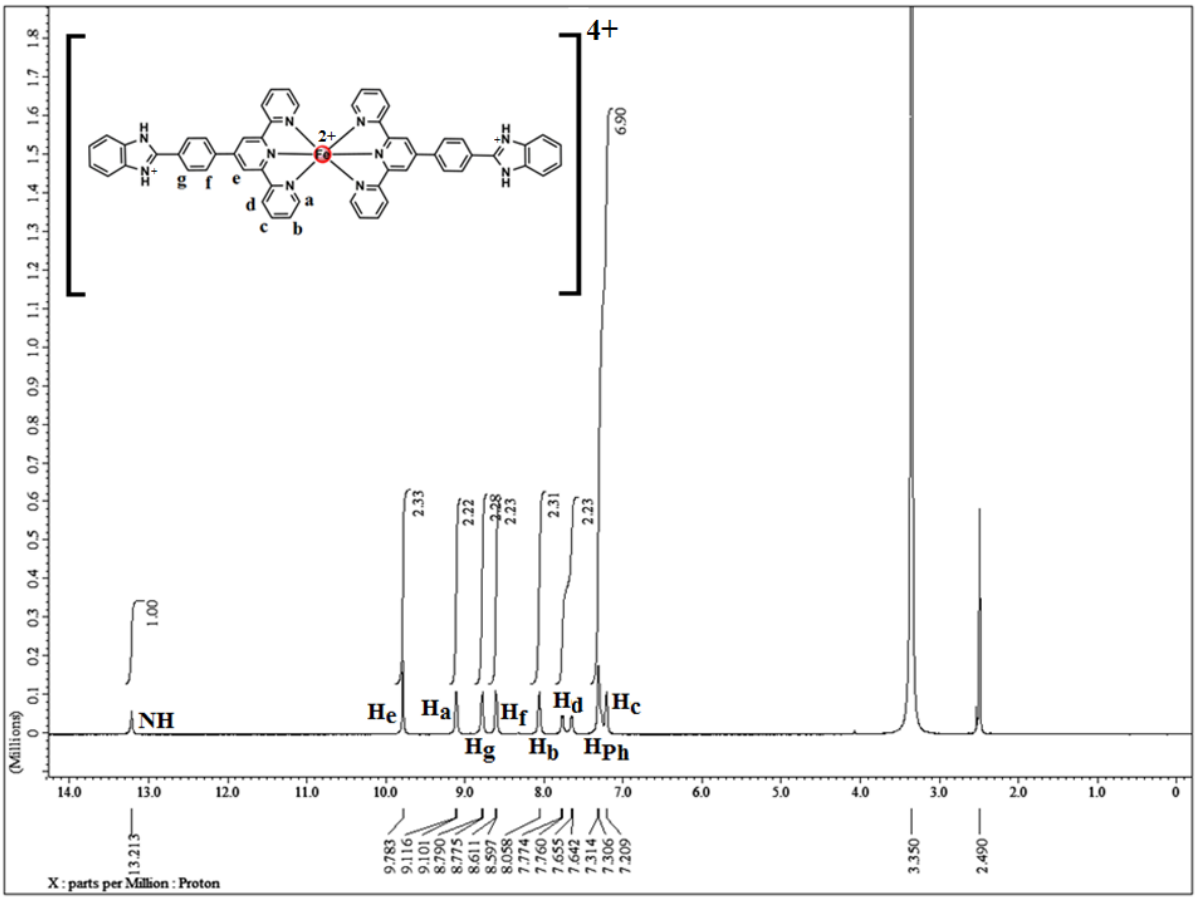

Fig. S17: ^{1}H NMR spectrum of complex**1** recorded in DMSO-d$_6$ at room temperature.

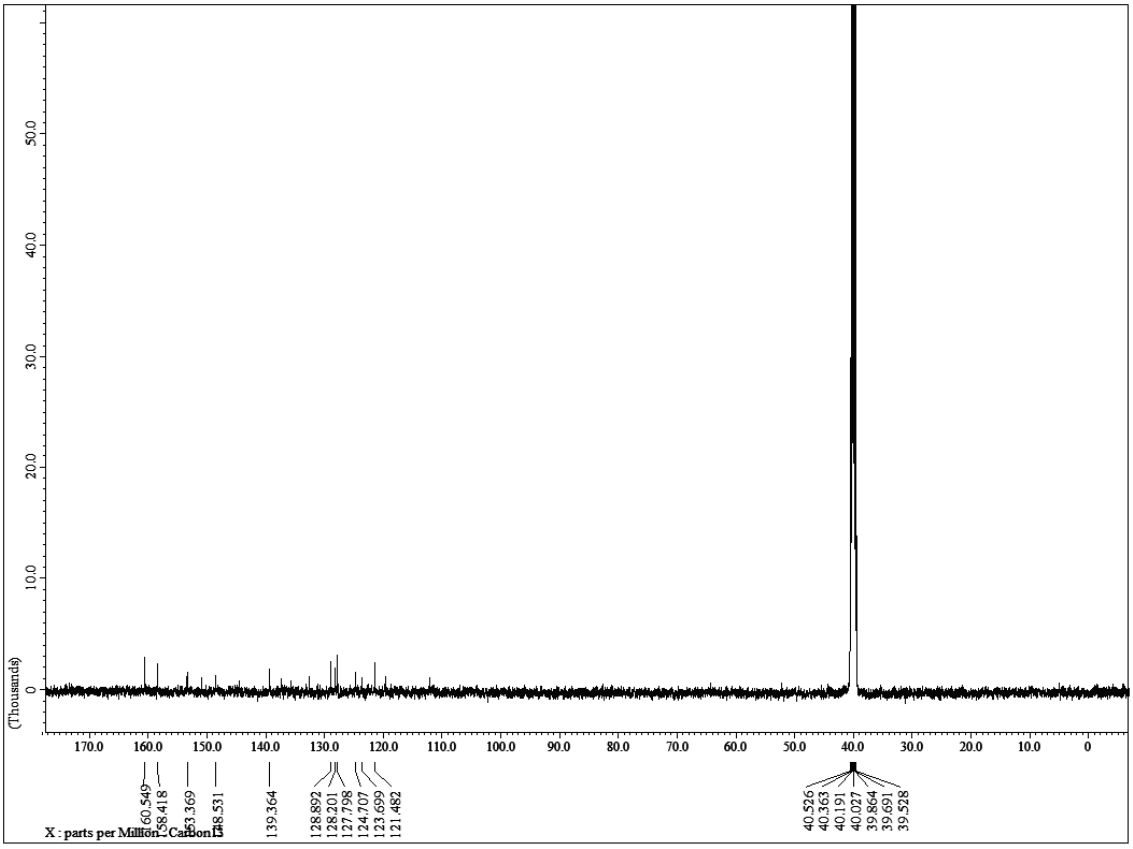

Fig S18: ^{13}C NMR spectrum of complex**1** recordedin DMSO-d_6 at room temperature.

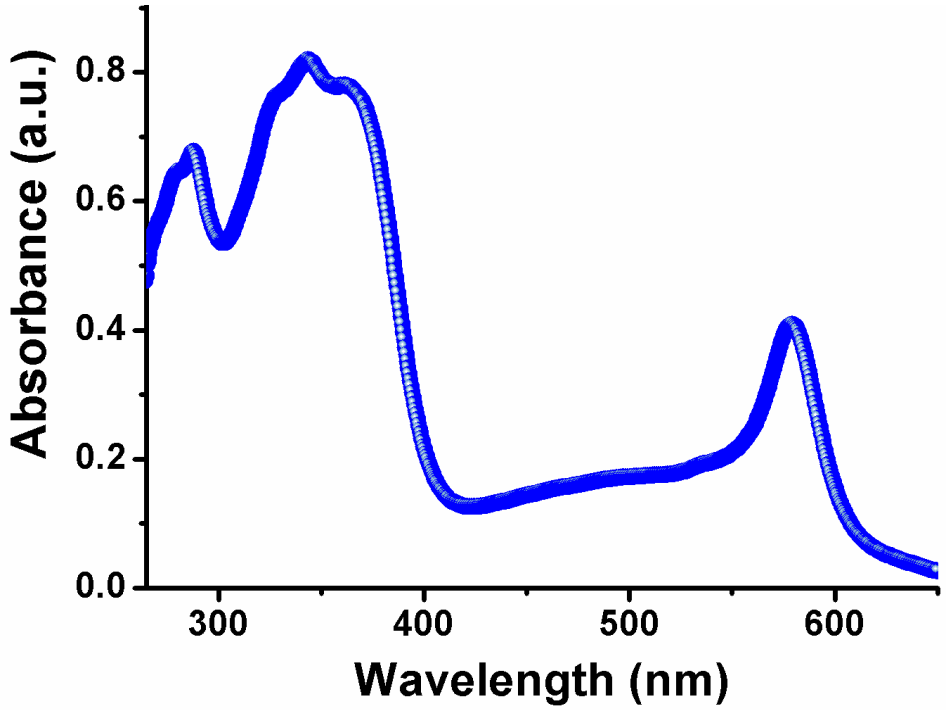

Fig. S19: UV-vis spectrum of complex**1** (2.0 x 10^{-5} M, DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2) at room temperature.

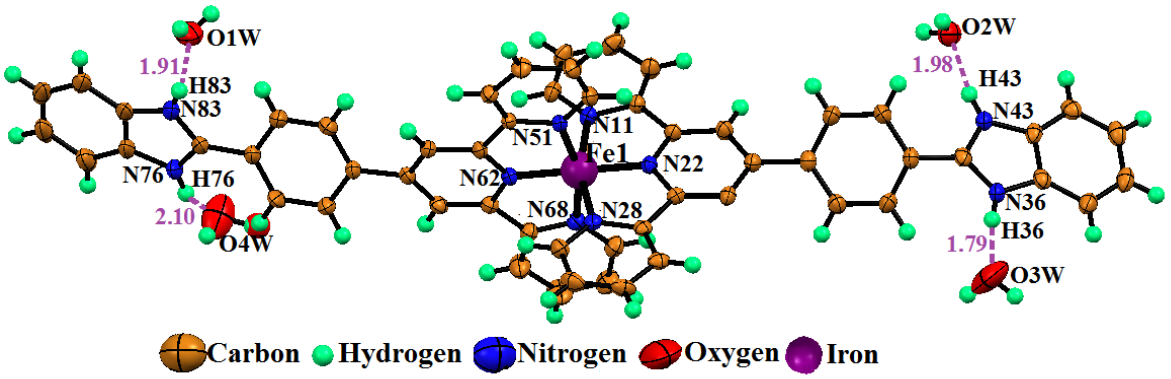

Fig. S20: Molecular structure (ORTEP Diagram) of complex **1**,[Fe(H-**BIT**)$_2$].4ClO_4 with four hydrogen bonded water molecules at 50% probability level. The perchlorate ions are omitted for clarity.

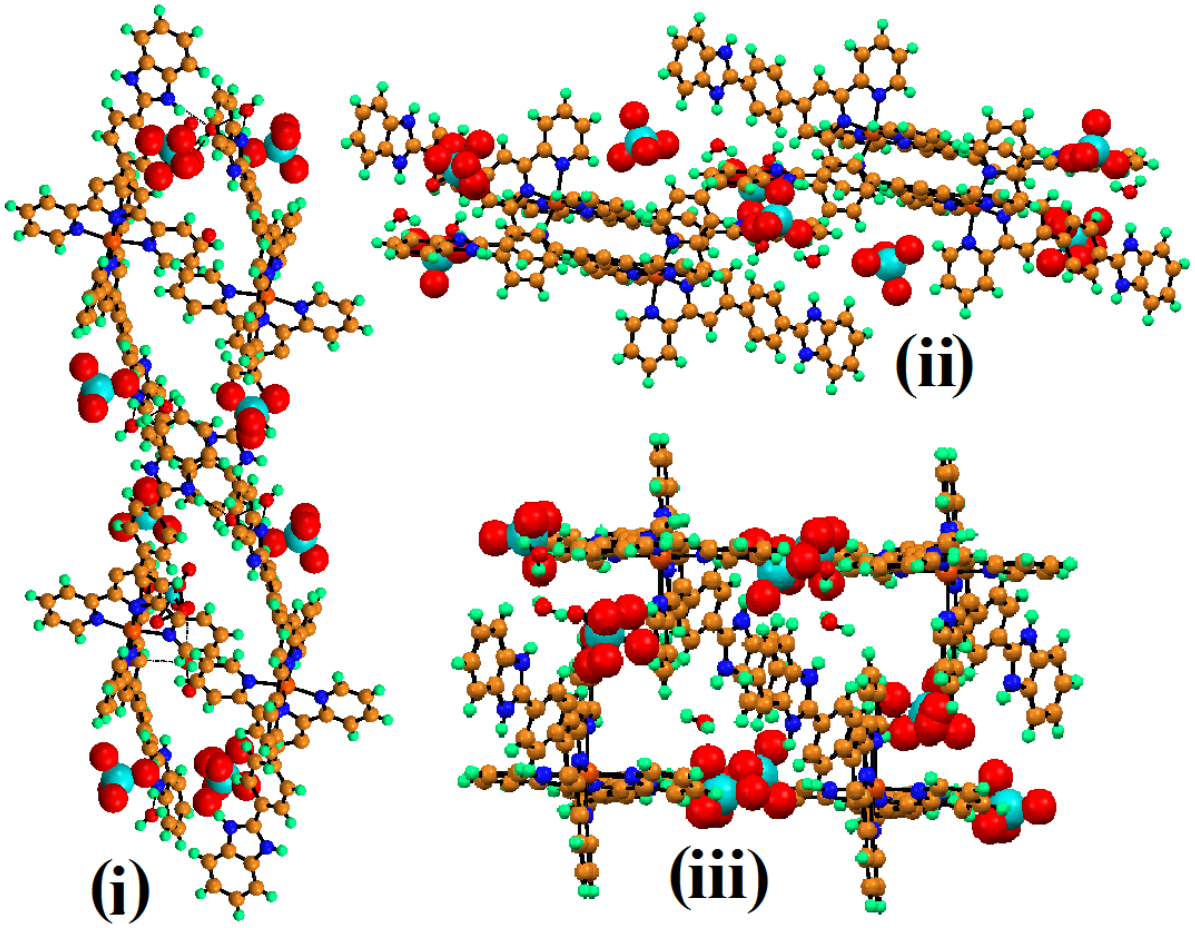

Fig. S21: Supramolecular architectures of complex**1** along a(i) b(ii) and c(iii) crystallographic axes, respectively.

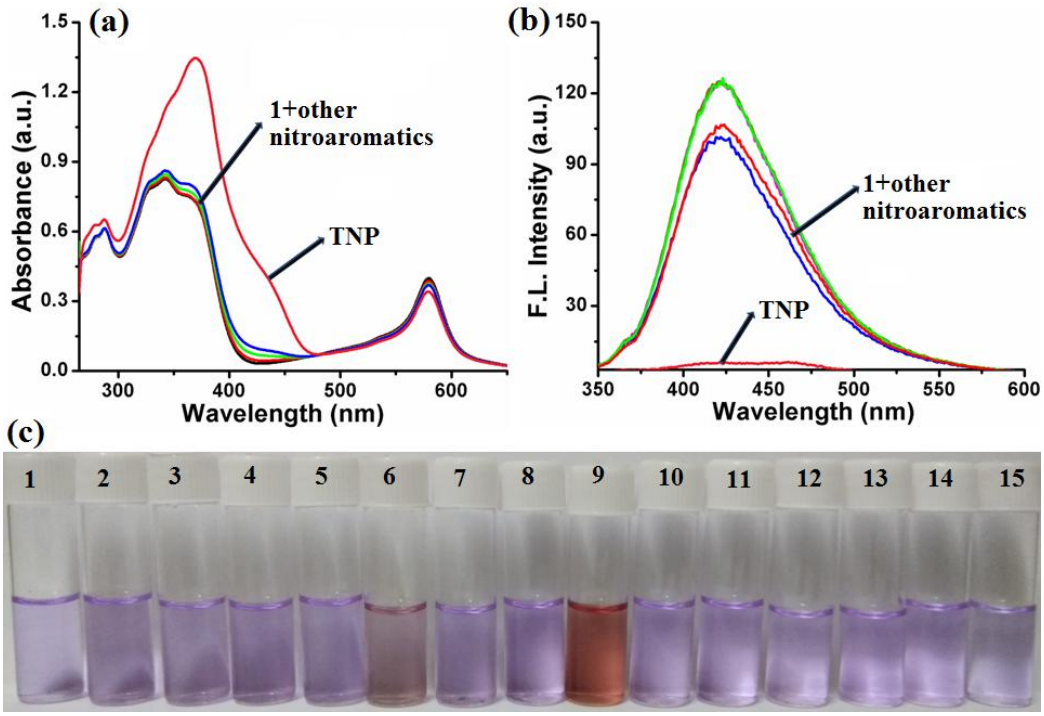

Fig. S22: Changes in (a) UV-vis, (b) Fluorescence spectra and (c) visual colour change of complex**1** (2.0 x 10^{-5} M, DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2) upon the addition of different nitroaromatics (1.0 x 10^{-2}M in MeOH) along with carboxylate(1.0 x 10^{-2}M in acetonitrile) and phosphate(1.0 x 10^{-2}M in acetonitrile). (1=none, 2=4-nitrobenzene, 3=1,3-dinitrobenzene, 4=4-nitrotoluene, 5= 2,4-dinitrotoluene, 6=DNP (2,6-dinitrophenol),7=phenol, 8=4-nitrophenol(NP)9=2,4,6-trinitrophenol (TNP),10=2,4,6-trinitrotoluene(TNT), 11=4-methoxyphenol(MP), 12=tetrabutylammonium acetate (TBAAc), 13=benzoic acid (BA), 14=tetrabutylammonium phosphate (TBAPO),15=tributylammonium pyrophosphate (TBAPy) .

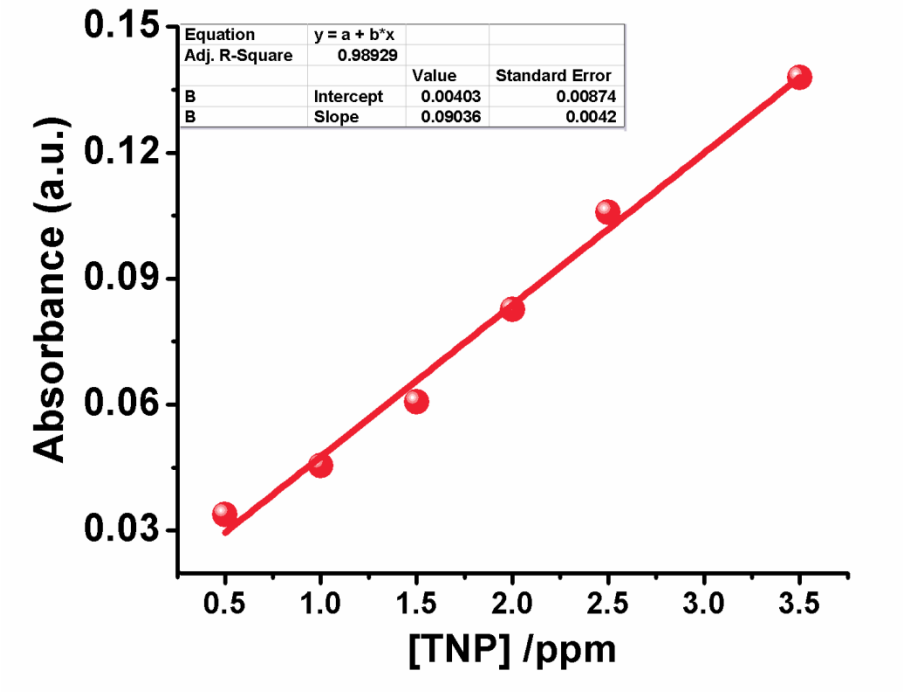

Fig. S23: Graph showing the variation of absorbance forcomplex**1**(2.0 x 10^{-5}M, DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2)vs [TNP]at low concentration level (R^2= 0.986) used for the determination of detection limit at λ_{max} 425nm.

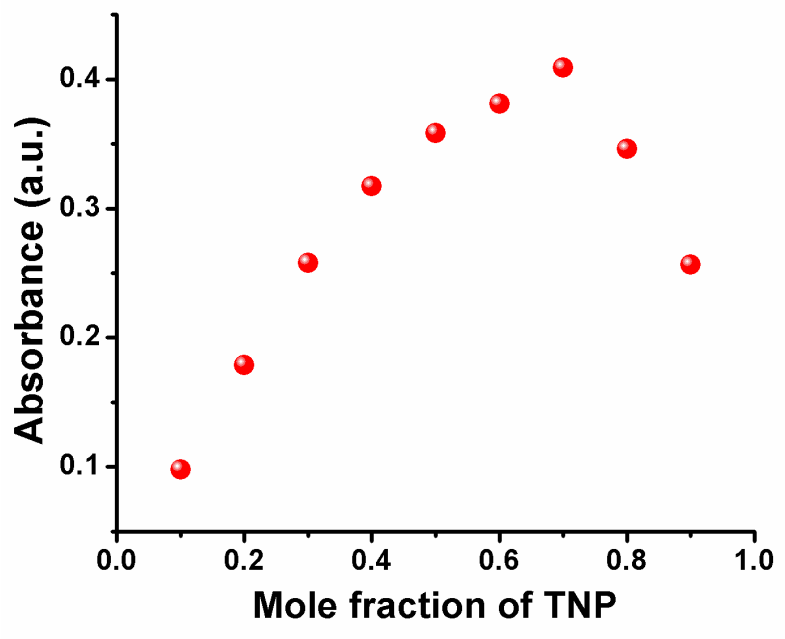

Fig. S24: Job's plot showing the variation of absorbance of complex **1** at λ_{max} = 425 nm *vs* mole fraction of TNP.

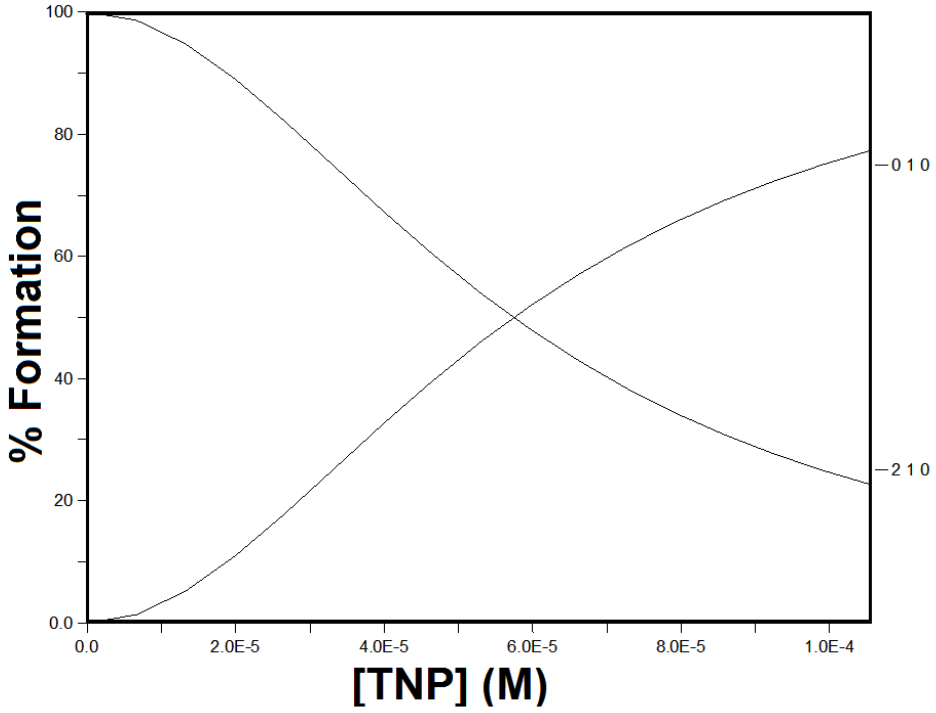

Fig. S25: Fitting diagram for the binding of complex **1** with TNP obtained using SPECFIT software.

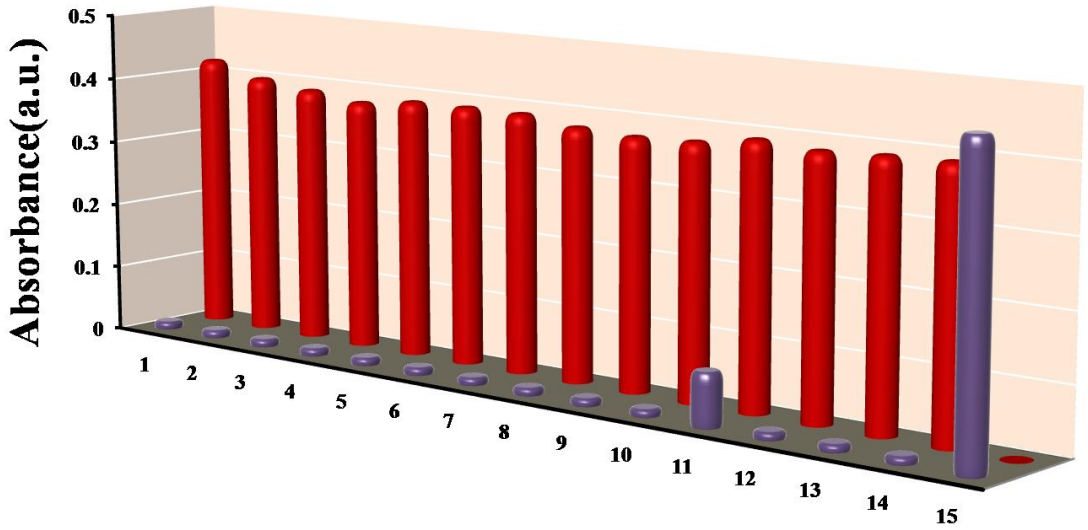

Fig. S26: Representative bar chart showing absorbance changes at λ_{max}=425 nm on the addition of various nitroaromatics (3eq. in H_2O) (purple bars) and in the presence of TNP(red bars)in the solution of complex**1** ($2.0x10^{-5}$M, DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9,v/v, HEPES buffer, pH 7.2).(1=none, 2=4-nitrobenzene, 3=1,3-dinitrobenzene, 4=4-nitrotoluene, 5= 2,4-dinitrotoluene, 6= 4-methoxyphenol(MP), 7=phenol, 8=4-nitrophenol(NP) 9= tributylammonium pyrophosphate (TBAPy), 10=2,4,6-trinitrotoluene(TNT), 11=DNP (2,6-dinitrophenol), 12=tetrabutylammonium acetate (TBAAc), 13=benzoic acid (BA), 14=tetrabutylammonium phosphate (TBAPO),15=2,4,6-trinitrophenol(TNP))

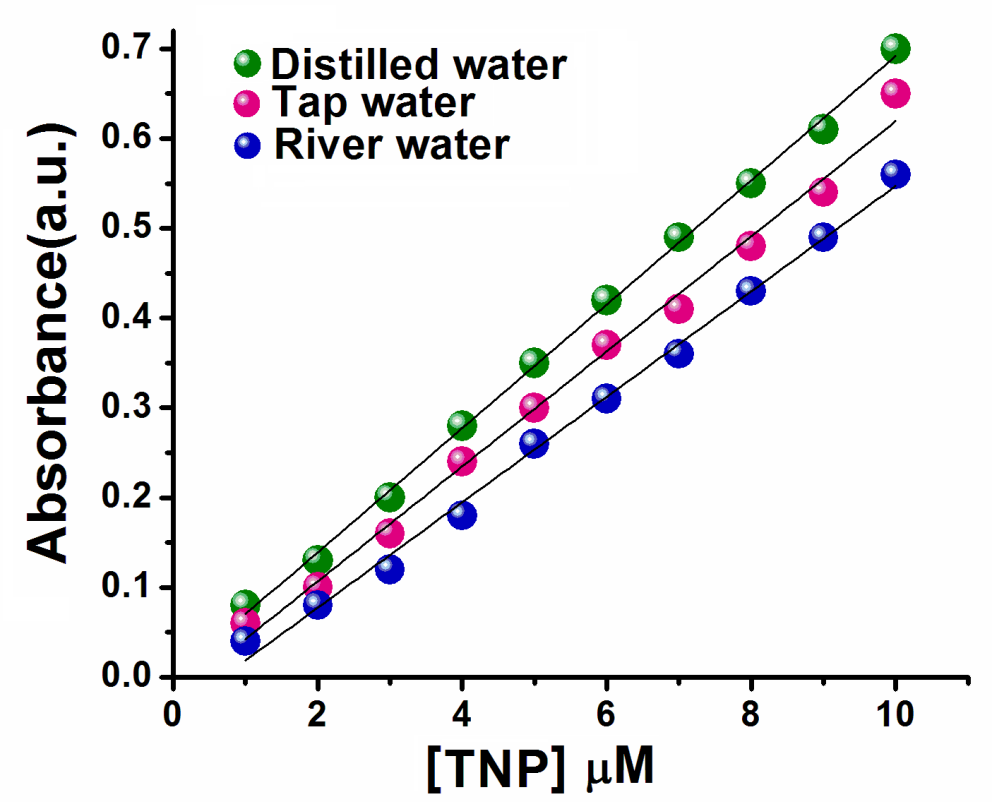

Fig. S27: Proof-of-concept experiments with complex **1**(1.0×10^{-3} M,DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2) λ_{max}425nmfor determination of [TNP](R^2=0.99) in water samples.

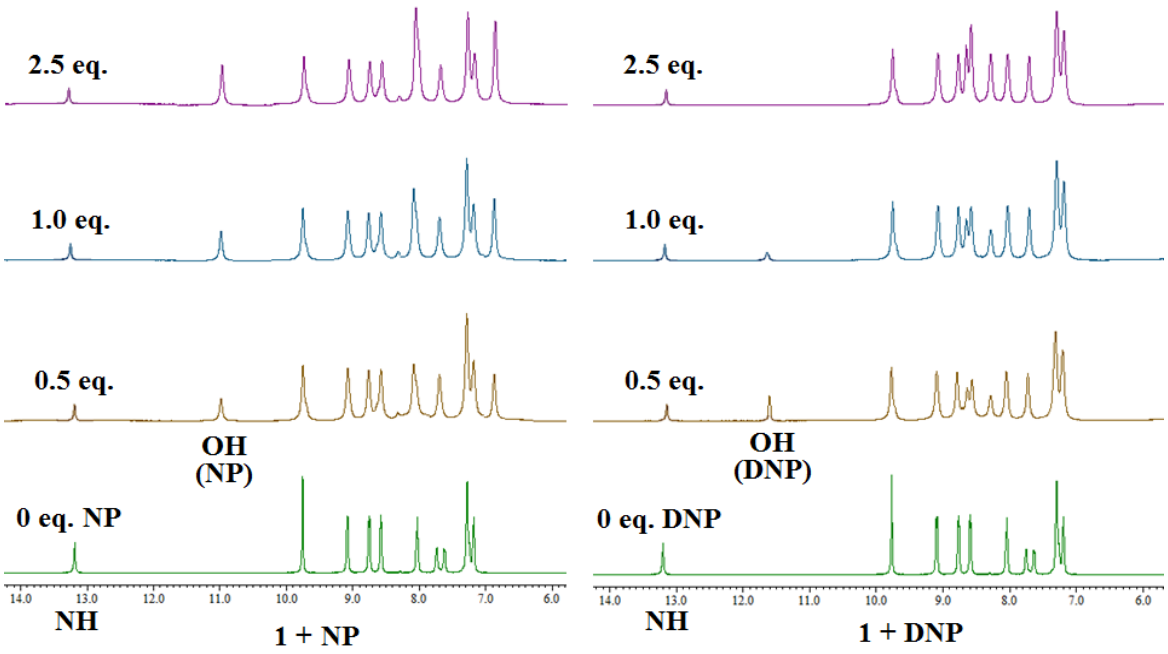

Fig. S28: Partial ^{1}H NMR titrations of **1** with 4-nitrophenol (NP) and 2,4-dinitrophenol (DNP) recorded in DMSO,$d_6$at room temperature.

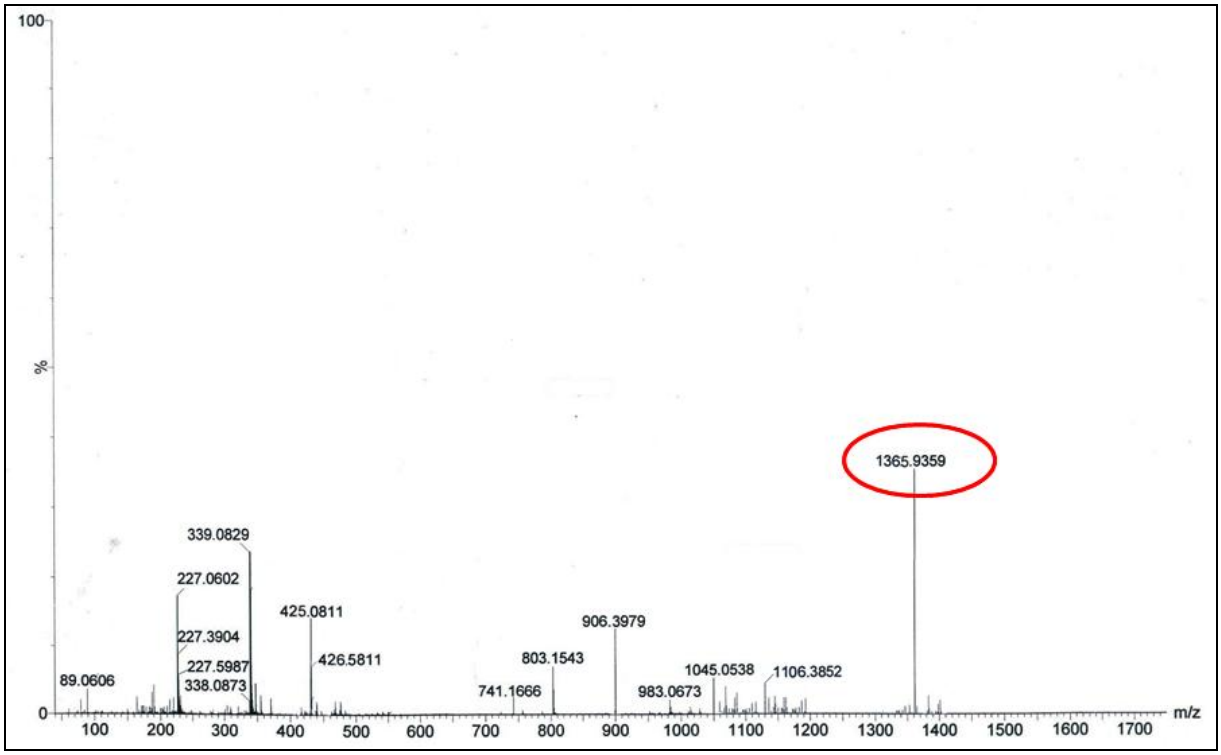

Fig. S29:HRMS ofcomplex**1**+TNP.

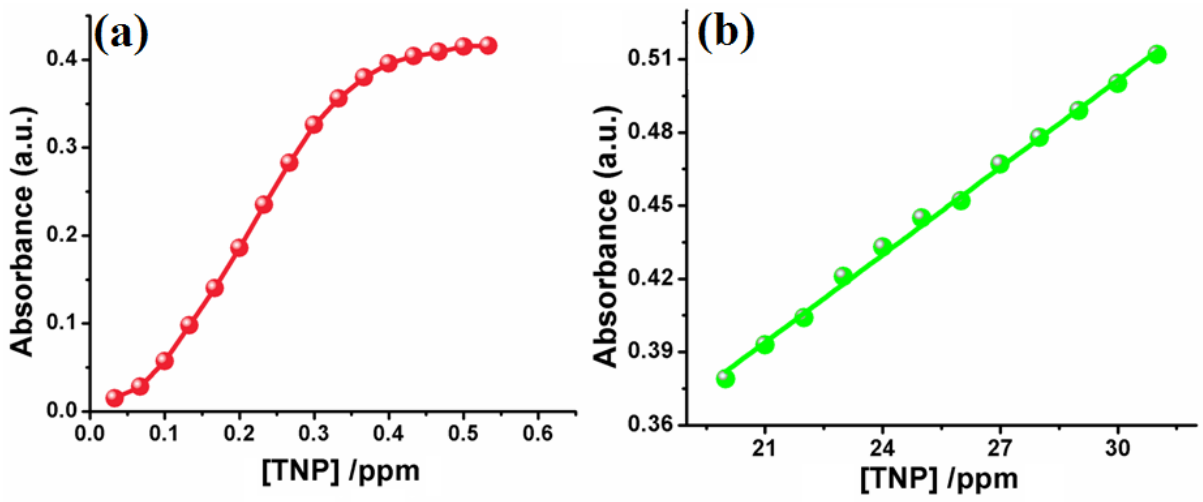

Fig. S30: The variation of absorbance of [TNP] in the presence(a)and absence(b) of complex **1**(2 x10^{-5}M,DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2) at λ_{max} 425nm.

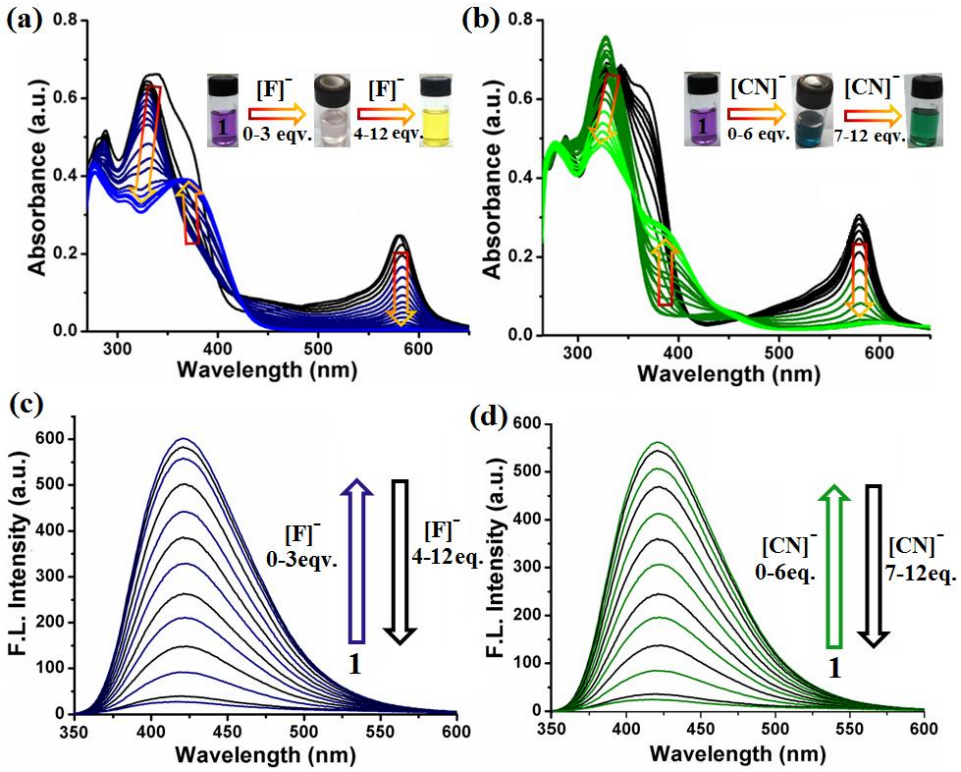

Fig.S31: Changes in absorbance and emission intensity of **1** (2.0 x 10^{-5} M, DMF-H_2O-acetonitrile, 0.5 : 0.5 : 9, v/v, HEPES buffer, pH 7.2) on additionof12.0 equiv. of F^- (a,c) and CN^-(b,d) ions (1.0 x 10^{-2} M in acetonitrile).

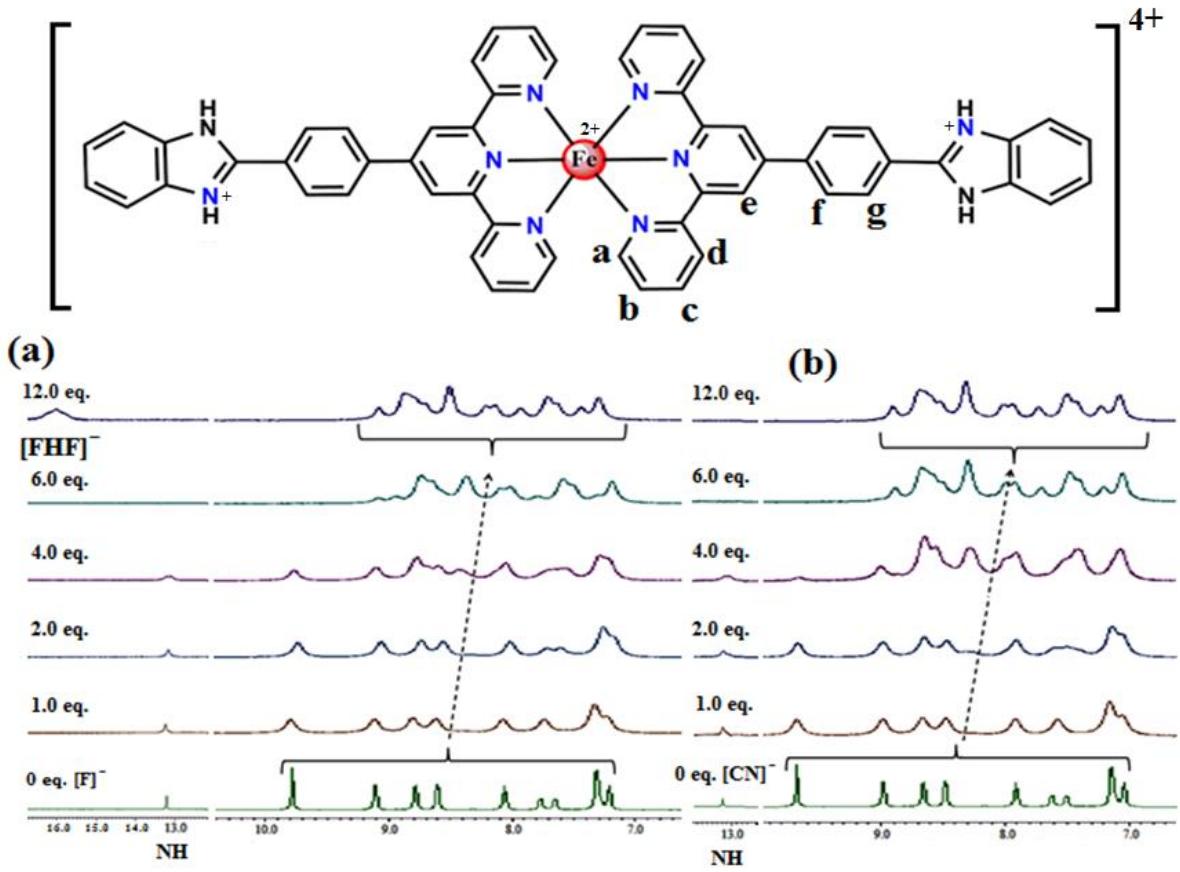

Fig. S32: Partial ^{1}H NMR titrations of **1** with F^-**(a)** and CN^-**(b)** ions recorded in DMSO,d_6 at room temperature.

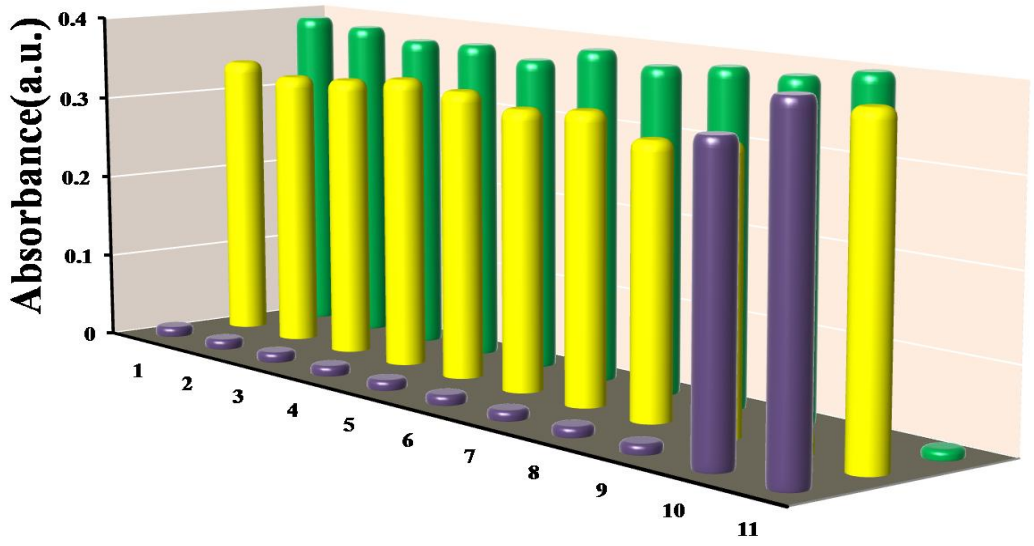

Fig. S33: Representative bar chart showing absorbance changes at λ_{max}=380 nm on the addition of various anions (12eq. in acetonitrile) (purple bars), in the presence of F^- (yellow bars) and CN^- (green bars) in the solution of complex **1** ($2.0x10^{-5}$M in acetonitrile). (1= none, 2= Cl^-, 3= Br^-, 4 = I^-, 5 = HSO_4^-, 6= Aco^-, 7= ClO_4^-, 8= HPO_4^{2-}, 9 = NO_3^-, 10= F^-, 11=CN^-).

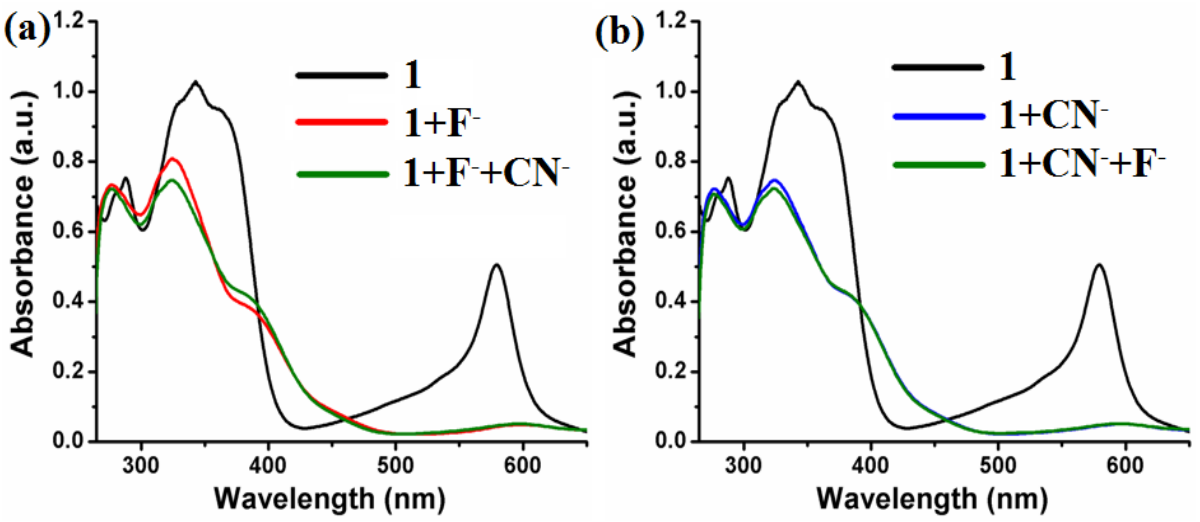

Fig. S34: Absorption spectra of **1** showing the changes in its absorbance in the presence of F^- followed by the addition of CN^- ions**(a)** and in the presence of CN^- followed by the addition of F^- ions**(b)**.

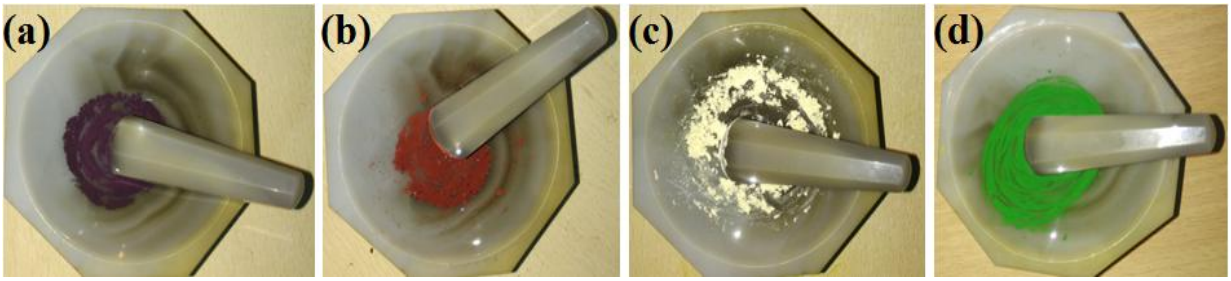

Fig. S35: Visual color changes upon mechanical grinding of complex**1** (a) separately with TNP (**b**),F^-(**c**) and CN^- (d)ionsastheir tetrabutylammoniumsalts.

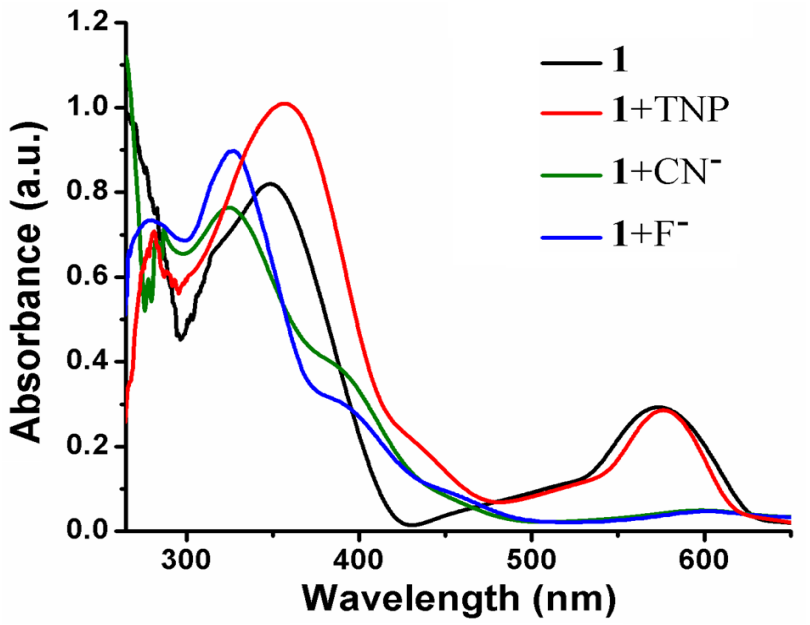

Fig. S36: Solid state UV-vis spectral changes recorded on the mechanical grinding of complex **1**separatelywith TNP, tetrabutylammoniumsalts of F^- and CN^- ions.

Table S1. Selected Crystallographic Data for **BIT,** complex **1** and complex **2**

Parameters.	**BIT**	Complex **1**	Complex **2**
Formula.	$C_{28}H_{25}N_5O_3$	$C_{56}H_{52}Cl_4FeN_{10}O_{22.5}$	$C_{72.5}H_{53.5}FeN_{18}O_{21.5}$
M.	479.53	1422.72	1576.68
Crystal system.	Orthorhombic	Triclinic	Triclinic
Temperature(°K)	296	273	293
Space group.	*Pna2₁*	*P*-1	*P*-1
a/Å	19.159(3)	10.8611(5)	13.6844(5)
b/Å	4.1134(6)	17.4221(8)	18.0033(7)
c/Å	30.426(5)	18.0546(8)	28.3883(10)
α(°)	(90)	62.612(1)	101.503(1)
β(°)	(90)	81.047(1)	93.773(1)
γ(°)	(90)	85.646(1)	95.517(1)
V/Å^3	2397.8(6)	2996.4(2)	6795.7(4)
Z	4	2	4
D_c, g cm^{-3}	1.179	1.577	1.541
Reflns.collected/Unique	11917/3883	46277/14978	107375/26653
Data/restraints/Parameters.	3883/1/325	14978/26/897	266531/145/19737
R(int)	0.0304	0.0434	0.0464
Limiting indices	-23<=h(<=23	-14<=h<=14	-18<=h<=18
	-4<=k<=2	-23<=k<=23	-23<=k<=23
	-36<=l<=29	-24<=l<=24	-37<=l<=37
ϑrange for data collection(°)	2.48-25.21	2.217-28.377	2.253-26.000
Completeness to ϑ=25.00	99.9	99.9	99.9
Refinement method	Full-matrix, least-squares on F^2	Full-matrix, least-squares on F^2	Full-matrix, least-squares on F^2
Final R indices[I>2σ(I)]	R_1= 0.0415	R_1= 0.0681	R_1= 0.0682
	wR_2=0.1091	wR_2=0.1639	wR_2=0.1755
R indices(all data)	R_1=0.0638	R_1=0.0977	R_1=0.0911
	wR_2=0.1196	wR_2=0.1809	wR_2=0.1961
GoF	1.024	1.022	1.035
Residual electron density e/A^3	0.167,-0.155	1,586, -1.798	1.317, -1.073

Table S2. Dimensions in the coordination spheres of complexes **1** and **2**

Bond lengths(Å)			
	1	**2A**	**2B**
Fe-N11	1.979(3)	1.976(3)	1.982(3)
Fe-N22	1.877(2)	1.876(3)	1.872(3)
Fe-N28	1.961(3)	1.983(3)	1.978(3)
Fe-N51	1.964(3)	1.967(3)	1.973(3)
Fe-N62	1.876(2)	1.8753)	1.878(3)
Fe-N68	1.970(3)	1.972(3)	1.969(3)
Bond Angles(^{0})			
N62-Fe-N22	177.75(11)	178.40(11)	179.48(12)
N62-Fe-N28	100.25(11)	97.68(11)	98.62(11)

N22-Fe-N28	80.96(11)	80.90(11)	80.86(11)
N62-Fe-N51	80.75(11)	80.97(10)	80.78(11)
N22-Fe-N51	101.19(11)	98.25(11)	99.19(11)
N28-Fe-N51	89.80(11)	88.8997(11)	93.72(11)
N62-Fe-N68	81.28(11)	80.49(11)	81.05(11)
N22-Fe-N68	96.82(11)	100.29(11)	98.99(11)
N28-Fe-N68	91.40(11)	93.79(10)	90.59(12)
N51-Fe-N68	161.91(11)	161.46(11)	161.76(11)
N62-Fe-N11	97.73(11)	101.03(11)	99.69(11)
N22-Fe-N11	81.07(11)	80.37(11)	80.82(11)
N28-Fe-N11	162.02(11)	161.21(11)	161.69(11)
N51-Fe-N11	93.23(11)	92.28(11)	89.23(11)
N68-Fe-N11	91.18(11)	90.90(11)	92.23(11)

Table S3 Hydrogen bond dimensions (A, deg) in **BIT**, **1** and **2**

BIT					
D-H…A (D= donor, A = acceptor)	D-H	H…O	D…A	D-H…A	symmetry element
N43-H43 O1W	0.83(2)	2.09(3)	2.917(6)	170(4)	
O1W-H1W…O3W	0.85(3)	2.63(4)	3.050(9)	112(3)	x+1/2, -y-1/2, z
O2W-H21W…N11	0.85(3)	2.02(5)	2.833(7)	161(12)	
O2W- H22W…O3W	0.84(3)	2.63(13)	2.855(11)	97(9)	x+1/2, -y+1/2, z
O3W- H32W…O2W	0.89	2.14	2.855(11)	137	x-1/2, -y+1/2, z
Complex **1**					
N36-H36…O3W	0.86	1.79	2.644(4)	173	
N43- H43…O2W	0.86	1.98	2.820(4)	164	
N83- H83…O1W	0.86	1.91	2.749(4)	165	
N76- H76…O4W	0.86	2.10	2.865(6)	149	
O1W- H11W…O2W	0.83	2.04	2.858(4)	171	1-x, 1-y, -z
O2W- H21W…O31	0.85	2.14	2.900(4)	149	1+x,y,z
O2W- H22W…O23	0.86	1.89	2.723(7)	163	1-x, 1-y, 1-z
O2W- H22W…O28	0.86	1.95	2.777(14)	159	1-x, 1-y, 1-z
O3W- H32W…O33	0.85	2.57	3.160(5)	128	1-x, -y, 1-z
O3W- H32W…O34	0.85	2.06	2.869(4)	159	1-x, -y, 1-z
O4W- H41W…O5W	0.94	1.75	2.681(9)	172	x, y, -1+z
O5W- H51W…O13	0.82	2.49	3.191(9)	144	
O6W-H61W…O41	0.82	2.02	2.787(6)	155	
O6W-H62W…O22	0.83	2.02	2.839(6)	172	
O6W-H62W…O27	0.83	2.41	3.196(11)	159	
Complex **2**					
N36A-H36A…O92D	0.88	2.03	2.901(5)	171	2-x, -y, 1-z
N76A-H76A…O2W	0.88	1.92	2.768(4)	161	
N36B-H36B…O3W	0.88	1.97	2.736(5)	147	
N76B-H76B…O1W	0.88	2.01	2.889(6)	176	
N76B-H76B…O4W	0.88	1.99	2.766(9)	146	
O2W-H2W1…O91E	0.87	1.93	2.792(4)	168	2-x, 1-y, 2-z
O2W-H2W2…O92C	0.87	2.26	2.998(5)	143	1-x, 1-y, 2-z

[a] There were close contacts between other solvent water molecules but as their hydrogen atoms could not be located, they are not listed here.

TableS3: Data of SPECFIT for calculation of binding constant of **BIT** with Fe^{2+} at λ_{max} 579nm.

When [Fe^{2+}]: [BIT] = 1:2

[PROGRAM]
Name = SPECFIT
Version = 3.0

[FILE]
Name = BIT+FE2+.FAC
Path = C:\Program Files\SPECFIT\DATA\
Date = 26-Aug-07
Time = 8:43:42 PM
Ncomp = 2
Nmeas = 16
Nwave = 761

[FACTOR ANALYSIS]
Tolerance = 1.000E-09
Max.Factors = 10
Num.Factors = 8
Significant = 4
Eigen Noise = 4.837E-04
Exp't Noise = 4.837E-04

#	Eigenvalue	Square Sum	Residual	Prediction
1	1.486E+03	9.105E+01	8.648E-02	Data Vector
2	9.079E+01	2.621E-01	4.640E-03	Data Vector
3	1.805E-01	8.163E-02	2.590E-03	Data Vector
4	7.878E-02	2.848E-03	4.837E-04	Data Vector
5	1.240E-03	1.608E-03	3.635E-04	Possibly Data
6	2.796E-04	1.328E-03	3.304E-04	Probably Noise
7	2.075E-04	1.121E-03	3.035E-04	Probably Noise
8	1.660E-04	9.548E-04	2.801E-04	Probably Noise

[MODEL]
Date = 26-Aug-07
Time = 8:44:04 PM
Model = 0
Index = 3
Function = 1
Species = 3
Params = 3

[SPECIES]	[COLORED]	[FIXED]	[SPECTRUM]
1 0 0	False	False	
0 1 0	True	False	
1 2 0	True	False	

[SPECIES]	[FIXED]	[PARAMETER]		[ERROR]
1 0 0	True	0.00000E+00	+/-	0.00000E+00
0 1 0	True	0.00000E+00	+/-	0.00000E+00
1 2 0	False	8.89448E+00	+/-	5.06828E-01

[CONVERGENCE]
Iterations = 6
Convergence Limit = 1.000E-04
Convergence Found = 2.223E-05
Marquardt Parameter = 0.0
Sum(Y-y)^2 Residuals = 3.48348E+00
Std. Deviation of Fit(Y) = 1.69150E-02

[STATISTICS]
Experimental Noise = 4.837E-04
Relative Error Of Fit = 4.7046%
Durbin-Watson Factor = 0.4200
Goodness Of Fit, Chi^2 = 1.223E+03
Durbin-Watson Factor (raw data) = None
Goodness Of Fit, Chi^2 (raw data) = None

[COVARIANCE]
4.895E+00

[CORRELATION]
1.000E+00

[END FILE]

TableS4: Data of SPECFIT for calculation of binding constantof**BIT** with F^- at λ_{max} 381nm.

[F^-]:BIT]=1:1
[PROGRAM]
Name = SPECFIT
Version = 3.0

[FILE]
Name = BIT+F-.FAC
Path = C:\Program Files\SPECFIT\DATA\
Date = 26-Aug-07
Time = 8:55:18 PM
Ncomp = 2
Nmeas = 18
Nwave = 377

[FACTOR ANALYSIS]
Tolerance = 1.000E-09
Max.Factors = 10
Num.Factors = 8
Significant = 4
Eigen Noise = 6.247E-04
Exp't Noise = 6.247E-04

#	Eigenvalue	Square Sum	Residual	Prediction
1	8.826E+02	4.075E+01	7.749E-02	Data Vector
2	4.071E+01	3.474E-02	2.263E-03	Data Vector
3	2.838E-02	6.363E-03	9.686E-04	Data Vector
4	3.717E-03	2.646E-03	6.247E-04	Data Vector
5	9.044E-04	1.742E-03	5.068E-04	Possibly Data
6	4.292E-04	1.313E-03	4.400E-04	Probably Noise
7	2.587E-04	1.054E-03	3.943E-04	Probably Noise
8	1.667E-04	8.873E-04	3.618E-04	Probably Noise

[MODEL]
Date = 26-Aug-07
Time = 8:55:43 PM
Model = 0
Index = 3
Function = 1
Species = 3
Params = 3

[SPECIES]	[COLORED]	[FIXED]	[SPECTRUM]
1 0 0	False	False	
0 1 0	True	False	
1 1 0	True	False	

[SPECIES]	[FIXED]	[PARAMETER]		[ERROR]
1 0 0	True	0.00000E+00	+/-	0.00000E+00
0 1 0	True	0.00000E+00	+/-	0.00000E+00
1 1 0	False	4.08395E+00	+/-	3.37167E-02

[CONVERGENCE]
Iterations = 6
Convergence Limit = 1.000E-04
Convergence Found = 1.106E-06
Marquardt Parameter = 0.0
Sum(Y-y)^2 Residuals = 2.17449E-01
Std. Deviation of Fit(Y) = 5.66114E-03

[STATISTICS]
Experimental Noise = 6.247E-04
Relative Error Of Fit = 1.5348%
Durbin-Watson Factor = 1.0779
Goodness Of Fit, Chi^2 = 8.214E+01
Durbin-Watson Factor (raw data) = None
Goodness Of Fit, Chi^2 (raw data) = None

[COVARIANCE]
6.517E-03

[CORRELATION]
1.000E+00

[END FILE]

Table S5: Data of SPECFIT for calculation of binding constant of **BIT** with CN^- at λ_{max} 383nm.

[CN^-]:BIT]=1:1

[PROGRAM]
Name = SPECFIT
Version = 3.0

[FILE]
Name = BIT+CN-.FAC
Path = C:\Program Files\SPECFIT\DATA\
Date = 26-Aug-07
Time = 8:52:04 PM
Ncomp = 2
Nmeas = 17
Nwave = 377

[FACTOR ANALYSIS]
Tolerance = 1.000E-09
Max.Factors = 10
Num.Factors = 5
Significant = 3
Eigen Noise = 9.985E-04
Exp't Noise = 9.985E-04

#	Eigenvalue	Square Sum	Residual	Prediction
1	8.371E+02	3.376E+01	7.258E-02	Data Vector
2	3.373E+01	2.763E-02	2.077E-03	Data Vector
3	2.124E-02	6.387E-03	9.985E-04	Data Vector
4	3.997E-03	2.391E-03	6.110E-04	Possibly Data
5	6.470E-04	1.744E-03	5.218E-04	Probably Noise

[MODEL]
Date = 26-Aug-07
Time = 8:52:19 PM
Model = 0
Index = 3
Function = 1
Species = 3
Params = 3

[SPECIES]	[COLORED]	[FIXED]	[SPECTRUM]
1 0 0	True	False	
0 1 0	True	False	
1 1 0	True	False	

[SPECIES]	[FIXED]	[PARAMETER]		[ERROR]
1 0 0	True	0.00000E+00	+/-	0.00000E+00
0 1 0	True	0.00000E+00	+/-	0.00000E+00
1 1 0	False	5.65745E+00	+/-	1.98385E-01

[CONVERGENCE]
Iterations = 11

Convergence Limit = 1.000E-04
Convergence Found = 2.235E-05
Marquardt Parameter = 0.0
Sum(Y-y)^2 Residuals = 4.01996E-01
Std. Deviation of Fit(Y) = 7.92044E-03

[STATISTICS]
Experimental Noise = 9.985E-04
Relative Error Of Fit = 2.1490%
Durbin-Watson Factor = 1.5689
Goodness Of Fit, Chi^2 = 6.292E+01
Durbin-Watson Factor (raw data) = None
Goodness Of Fit, Chi^2 (raw data) = None

[COVARIANCE]
3.353E-01

[CORRELATION]
1.000E+00

[END FILE]

TableS6 Selected UV-vis absorption energy transitions at the TD-DFT/B3LYP level for **BIT,** [**BIT**+F]$^-$, [**BIT**+CN]$^-$ and [Fe(**BIT**)$_2$]$^{2+}$.in acetonitrile.

Excited state	λ_{ex}(nm)/ (eV)	Oscillator strength(f)	λ_{exp}(nm)/ ε_{exp}($M^{-1}cm^{-1}$)	Key transitions
BIT				
S_9	325/3.8125	0.0404	326/89700	H-4→L+1(2%), H-2→L(37%), H→L+1(58%)
S_{15}	287/4.3129	0.3021	287/58500	H-5→L(4%), H-5→L+2(2%), H-2→L(44%), H-2→L+1(16%), H→L+2(29%),
[**BIT**+F]$^-$				
S_5	369/3.3550	0.9281	375/45000	H→L(56%) H-2→L+1(43%)
S_{19}	268/4.6230	0.4612	276/58200	H-13→L(2%), H-6→L+1(9%), H-3→L+1(56%), H-2→L+2(7%), H-2→L+3(6%), H→L+4(14%)
[**BIT**+CN]$^-$				
S_7	381/3.2478	0.8103	390/43000	H-1→L(87%), H→L(12%)
S_{25}	269/4.5979	0.2501	275/58000	H-2→L+1(3%), H-1→L+2(2%), H→L+2(36%), H-2→L+5(54%)
[Fe(**BIT**)$_2$]$^{2+}$				
S_9	573/2.5324	0.0079	579/40900	H-2→L(15%), H-2→L+1(2%), H→L+1(72%)
S_{64}	343/3.6091	0.3629	344/82000	H-4→L+4(2%), H-3→L+5(3%), H-1→L+4(43%), H→L+5(45%)

TableS7: Data of SPECFIT for calculation of binding constant of complex **1** with TNP at λ_{max} 425nm

[TNP] :[Complex 1]=2:1

[PROGRAM]
Name = SPECFIT
Version = 3.0

[FILE]
Name = COMPLEX1+TNP NEW.FAC
Path = C:\Program Files\SPECFIT\DATA\
Date = 26-Aug-07
Time = 8:59:30 PM
Ncomp = 2
Nmeas = 17
Nwave = 761

[FACTOR ANALYSIS]
Tolerance = 1.000E-09
Max.Factors = 10
Num.Factors = 7
Significant = 4
Eigen Noise = 4.488E-04
Exp't Noise = 4.488E-04

#	Eigenvalue	Square Sum	Residual	Prediction
1	3.076E+03	5.958E+01	6.787E-02	Data Vector
2	5.906E+01	5.185E-01	6.331E-03	Data Vector
3	3.727E-01	1.458E-01	3.357E-03	Data Vector
4	1.432E-01	2.605E-03	4.488E-04	Data Vector
5	8.228E-04	1.782E-03	3.712E-04	Probably Noise
6	2.714E-04	1.511E-03	3.418E-04	Probably Noise
7	2.114E-04	1.299E-03	3.170E-04	Probably Noise

[MODEL]
Date = 26-Aug-07
Time = 8:59:56 PM
Model = 0
Index = 3
Function = 1
Species = 3
Params = 3

[SPECIES]	[COLORED]	[FIXED]	[SPECTRUM]
1 0 0	False	False	
0 1 0	True	False	
2 1 0	True	False	

[SPECIES]	[FIXED]	[PARAMETER]		[ERROR]
1 0 0	True	0.00000E+00	+/-	0.00000E+00
0 1 0	True	0.00000E+00	+/-	0.00000E+00
2 1 0	False	8.51229E+00	+/-	2.43517E-01

[CONVERGENCE]
Iterations = 5
Convergence Limit = 1.000E-04
Convergence Found = 2.926E-05
Marquardt Parameter = 0.0
Sum(Y-y)^2 Residuals = 5.95728E+01
Std. Deviation of Fit(Y) = 6.78616E-02

[STATISTICS]
Experimental Noise = 4.488E-04
Relative Error Of Fit = 13.9156%
Durbin-Watson Factor = 1.9261
Goodness Of Fit, Chi^2 = 2.286E+04
Durbin-Watson Factor (raw data) = None
Goodness Of Fit, Chi^2 (raw data) = None

[COVARIANCE]
5.654E-01

[CORRELATION]
1.000E+00

[END FILE]

Table S8: Recovery data of TNP in real sample by complex **1**.

S.N.	Samples	TNP added (μM)	TNP found (μM)	% Recovery
1.	Distilled Water	0	0	-
		2	1.96	98%
		4	3.94	98.5%
		6	5.89	98.16%
2.	Tap water	0	0	-
		2	1.82	91%
		4	3.79	94.75%
		6	5.86	97.66%
3.	River water	0	0	-
		2	1.85	92.5%
		4	3.98	99.5%
		6	5.87	97.83%

Table S9: Binding constants and detection limits of **BIT** and complex **1** in the presence of different analytes.

Receptors	Analytes	Binding Constant (log β)	Detection limits	
			(ppm)	Concentration (M)
BIT	Fe^{2+}	8.89±0.50	0.42	$4.2x10^{-7}$
	F^-	4.08±0.03	5.9	$5.9x10^{-6}$
	CN^-	5.65±0.19	7.2	$7.2x10^{-6}$
Complex **1**	TNP	8.51±0.24	0.14	$1.4x10^{-7}$