

# Unique norbornene based triazole molecule for selective Fe(II) sensing

Sourav Bhattacharya and Raja Shunmugam\*

## Supporting Information

1. Experimental Section.....	S1
2. Schematic representation of homopolymer of NFTZ.....	S2
3. <sup>1</sup> H NMR spectra of NFTZ monomer.....	S3
4. <sup>13</sup> C NMR spectra of protected NFTZ monomer.....	S4
5. GPC analysis of NFTZH.....	S5
6. Quenching constat plot of NFTZ monomer.....	S6
7. FTIR spectra of NFTZ monomer and NFTZ-Fe (II) complex .....	S7
8. UV-Visible spectra of NFTZ in THF.....	S8
9. ESI-Mass spectra of NFTZ-Fe (II) complex.....	S9
10. Unique bluish-white fluorescence of NFTZ monomer and its corresponding flurescence quenching by Fe (II).....	S10
11. Determiation of detection limit from fluorescence intensity of NFTZ	

### Experimental Section:

**Materials:** Exo-oxabicyclo- [2.2.1] hept-5-ene-2, 3 - dicarboxylic anhydride<sup>1</sup>, P-amino benzoic acid, acetic anhydride, sodium acetate, 3-amino-1,2,4-triazole-5-thiol, second generation Grubbs' catalyst, were purchased from Sigma Aldrich. dicyclohexyl carbodiimide (DCC), dimethylsulfoxide (DMSO), dichloromethane (DCM), methanol, CDCl<sub>3</sub> were purchased as reagent grade from Aldrich, Acros, Merck and used as received. Dichloromethane (DCM) was distilled over calcium hydride and used for reaction.

### **Characterization:**

**Gel Permeation Chromatography (GPC).** Molecular weights and PDIs were measured by Waters gel permeation chromatography in THF relative to PMMA standards on systems equipped with Waters Model 515 HPLC pump and Waters Model 2414 Refractive Index Detector at 350C with a flow rate of 1 mL/min.

**ESI-MS** - MS analyses were performed with Q-TOF YA263 high resolution (Waters Corporation) instruments by +ve mode electrospray ionization.

**Fluorometry.** Fluorescence emission spectra were recorded on a Fluorescence spectrometer (Horiba Jobin Yvon, Fluoromax-3, Xe-150 W, 250-900 nm).

**Nuclear Magnetic Resonance (NMR).** The <sup>1</sup>H NMR spectroscopy was carried out on a Bruker 500 MHz spectrometer using CDCl<sub>3</sub> as a solvent. <sup>1</sup>H NMR spectra of solutions in CDCl<sub>3</sub> were calibrated to tetramethylsilane as internal standard ( $\delta$ H 0.00).

**Fourier Transform Infra Red (FT-IR).** FT-IR spectra were obtained on FT-IR Perkin-Elmer spectrometer at a nominal resolution of 2 cm<sup>-1</sup>.

**Ultra Violet (UV) Spectroscopy.** UV-visible absorption measurements were carried out on U-4100 spectrophotometer HITACHI UV-vis spectrometer, with a scan rate of 500 nm/min.

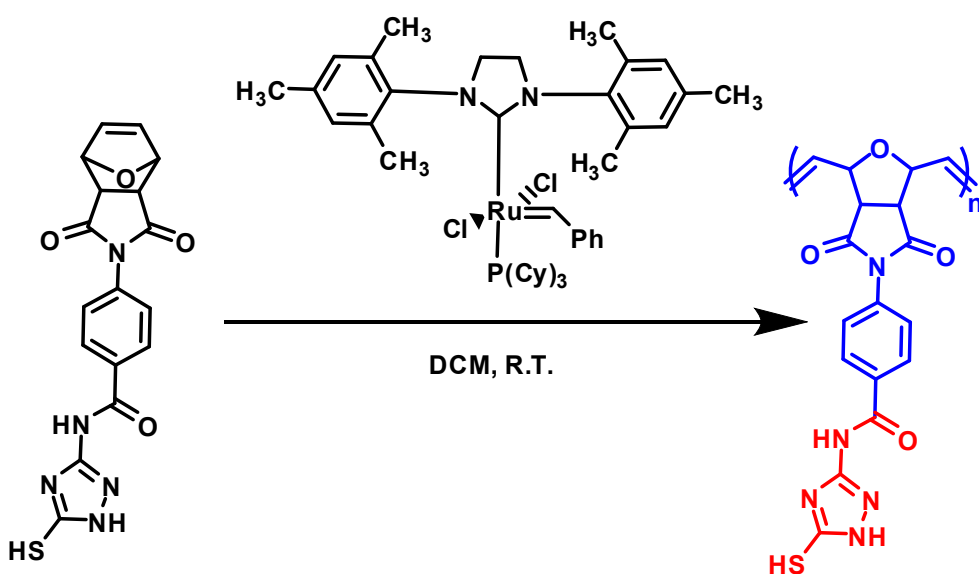
**Synthesis of compound 2** (Scheme 1): Exo - oxabicyclo- [2.2.1] hept-5-ene-2, 3 - dicarboxylic anhydride, 1.914 g (11.5 mmol) was taken in 4 neck reaction flask. 35 ml of acetone was added to it and heated until it became clear solution. After that para amino benzoic acid 1.605 g (11.5 mmol) was added to the reaction mixture with stirring. After fifteen minutes heating was stopped and reaction mixture was allowed to stir for about 30 minutes. The solid was filtered and dried under oven at 55 °C under vacuum. The dried intermediate was then dissolved in 30 ml of dimethyl formamide and heated to 50 °C. Acetic anhydride 15 ml (158.97 mmol) and sodium acetate 0.635 g (7.743 mmol) were charged under stirring. The reaction mixture was allowed to stir for three hours at 55 °C. After 3 h the reaction mixture was poured into 500 ml of water acidified by addition of 5 ml concentrated HCl. White colour solid was precipitated immediately and filtered the solid and washed with water and dried at 90 °C, under vacuum (80 % yield). <sup>1</sup>H

NMR (DMSO-D<sub>6</sub>, 400 MHz):  $\delta$  13.1 (bs, 1H), 8.0 - 8.2 (m, 2H), 7.4 - 7.5 (m, 2H), 6.6 (s, 2H), 3.1 (s, 2H). <sup>13</sup>C NMR (DMSO-D<sub>6</sub>, 400 MHz):  $\delta$  175.43, 166.59, 136.65, 135.78, 130.0, 126.79, 80.86, 47.58. IR (KBr, cm<sup>-1</sup>): 3236, 2635, 2073, 1954, 1826, 1780, 1729, 1698, 1607, 1515, 1418, 1218, 1144, 1125, 1020, 975, 950, 912, 883, 878, 804, 726, 672, 633, 598, 541, 521. MS (ESI) calculated for C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>Na [M + H]<sup>+</sup> : 285.05 ; observed 284.95.

**Synthesis of compound NFTZ:** 1 g (3.5 mmol) of compound **1** was taken into 6 ml of dimethyl formamide. 0.86 g (4.17 mmol) of Dicyclohexylcarbodiimide (DCC) in to the reaction mixture. Reaction mixture allowed to stir for 15 min to form the white precipitate at room temperature. Reaction mixture was cooled to 0-5 °C. 3-amino-1,2,4-triazole-5-thiol 0.45 g (3.85 mmol) dissolved in dimethyl formamide and this solution was added to the reaction mixture and continued the Reaction mixture overnight. EtOAc followed by water was added to the reaction mixture. Organic layer was washed with 2 x 10 ml of water followed by sodium bicarbonate wash. Finally organic layer was washed with brine solution. Organic layer concentrated under vacuum to yield a off-white colour solid which is purified which is purified through column chromatography using 25% DCM, MeOH mixture as mobile phase and silica as stationary phase. (700 mg, 70% yield). <sup>1</sup>H NMR (DMSO-D<sub>6</sub>, 500 MHz):  $\delta$  7.82 (s, 1H), 7.52 (s, 2H), 7.23 (s, 2H), 6.5 (s, 2H), 5.22 (s, 2H), 3.11 (s, 2H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  175.48, 167.39, 139.42, 138.64, 132.23, 128.32, 126.67, 80.85, 45.27, IR (KBr, cm<sup>-1</sup>): 3268, 2922, 2849, 2098, 1712, 1620, 1509, 1370, 1216, 770, MS (ESI) calculated for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>O<sub>4</sub>SNa<sup>+</sup> [M + Na]<sup>+</sup> : 406.38 ; observed 406.34.

**Homopolymerization of norbornene derived triazole monomer (NFTZH):** 10 mg (0.0347 mmol) of Monomer **1** was weighed into a separate Schlenk flask, placed under an atmosphere of nitrogen, and dissolved in 1 ml of dry DCM. Into another Schlenk flask, a desired amount of second generation Grubbs' catalyst 1.4 mg (G2, 20 mol %) was added, flushed with nitrogen, dissolved in minimum (0.5 ml) anhydrous dichloromethane. All two flasks were degassed three times by freeze-pump-thaw cycles. The Monomer **1** was transferred to the flask containing the catalyst via a cannula. The reaction was allowed to stir at room temperature until the polymerization was complete (50 minutes) before it was quenched with vinyl ethyl ether (0.5 ml). An aliquot was taken for GPC analysis, and the remaining product was precipitated with diethyl ether, dissolved it again THF, passed it through neutral alumina to remove the catalyst

and precipitated again with diethyl ether to get pure polymer (8 mg, 80% yield). Gel permeation chromatography (GPC) was done in tetrahydrofuran (flow rate = 1ml/1min). The molecular weight of homopolymer 1, was measured using polystyrene standards.  $M_n = 18,000$  and PDI = 1.2 suggested the homopolymerization of **NFTZ**.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  3.2 (s, 2H), 4.9 (s, 2H), 5.4 (s, 2H), 7.5-7.2 (m, 4H), 7.9 (s, 1H).



**Scheme 2: Schematic representation of homopolymerization of NFTZ**

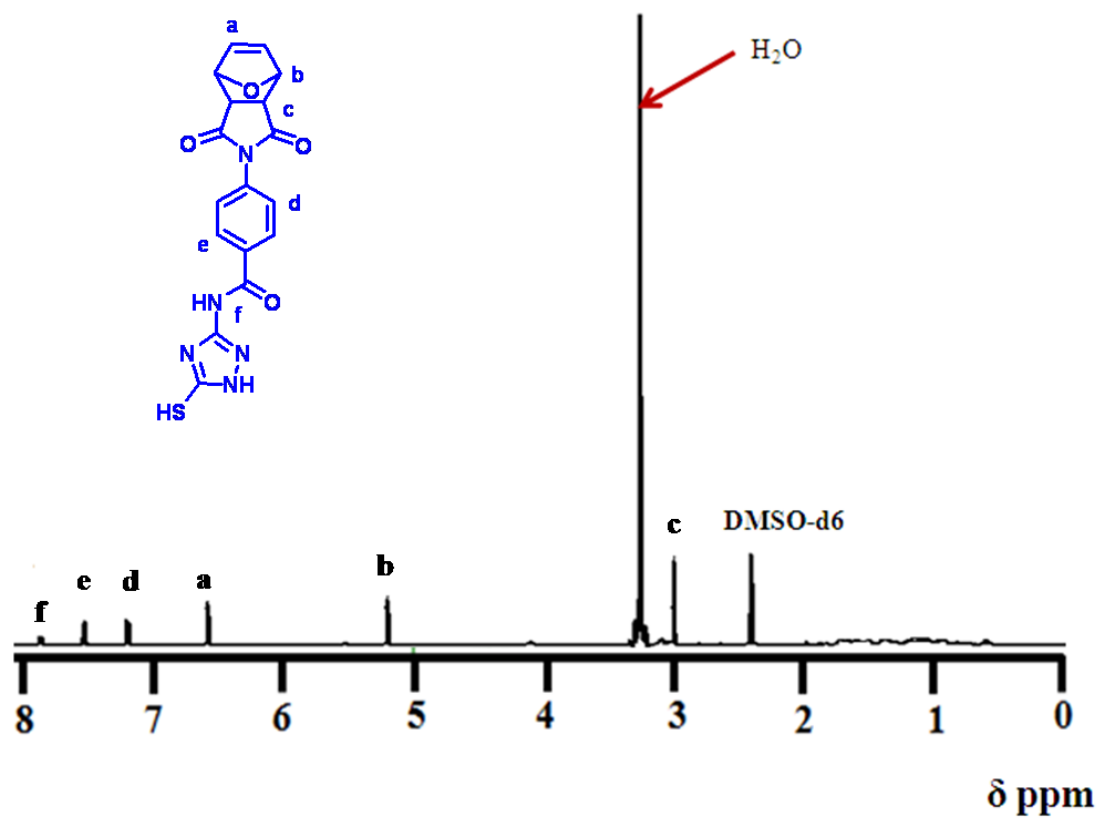


Figure S1:  $^1\text{H}$  NMR of NFTZ in  $\text{DMSO-d}_6$

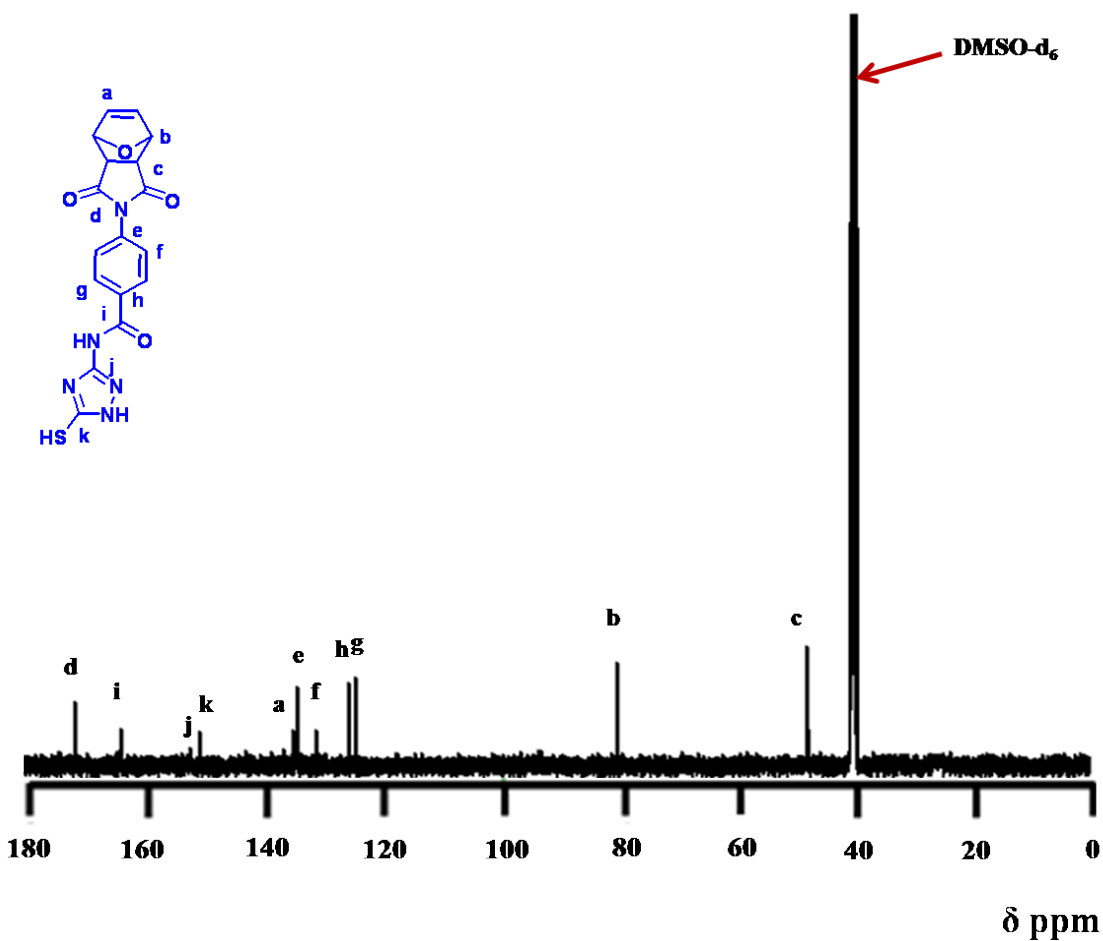
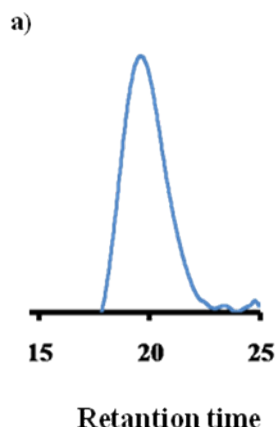


Figure S2:  $^{13}\text{C}$  NMR of NFTZ in  $\text{DMSO-d}_6$



b)

Polymer	$M_n$ (Target)	$M_n$ (Observed)	PDI
NDTZH1	20000	19,000	1.2
NDTZH2	15000	16,000	1.1
NDTZH3	10000	9,000	1.2

Figure S3: a) GPC chromatogram of triazole based norbornene polymer (TZP)  $M_n = 19000$  PDI= 1.2. b) Table comprising molecular weight and PDI of NFTZH.

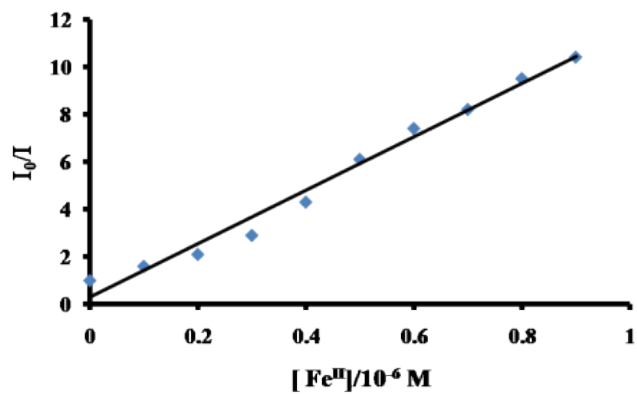


Figure S4: Plot of Fe<sup>II</sup> vs. I<sub>0</sub>/I that gives the value of quenching constant.

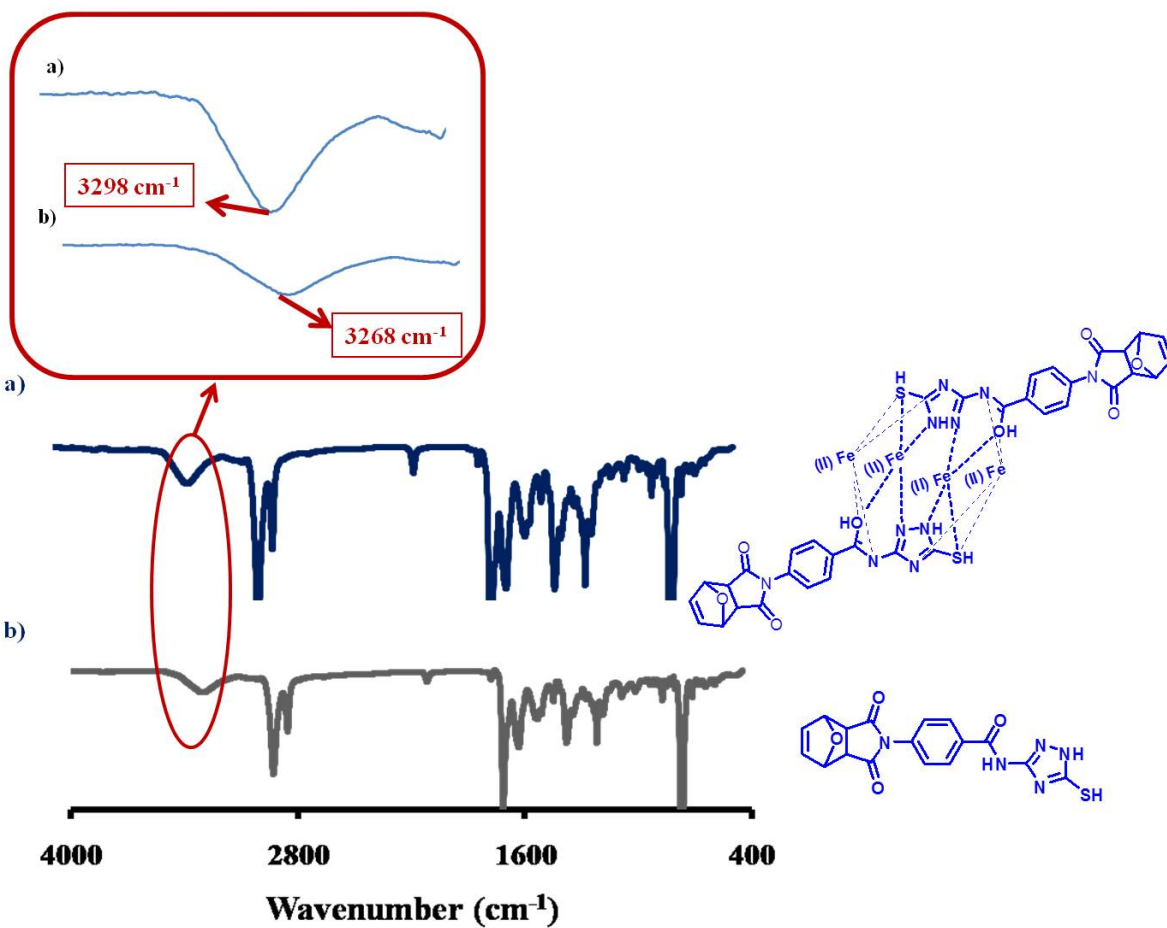


Figure S5: UV-Visible spectroscopy of NFTZ in THF

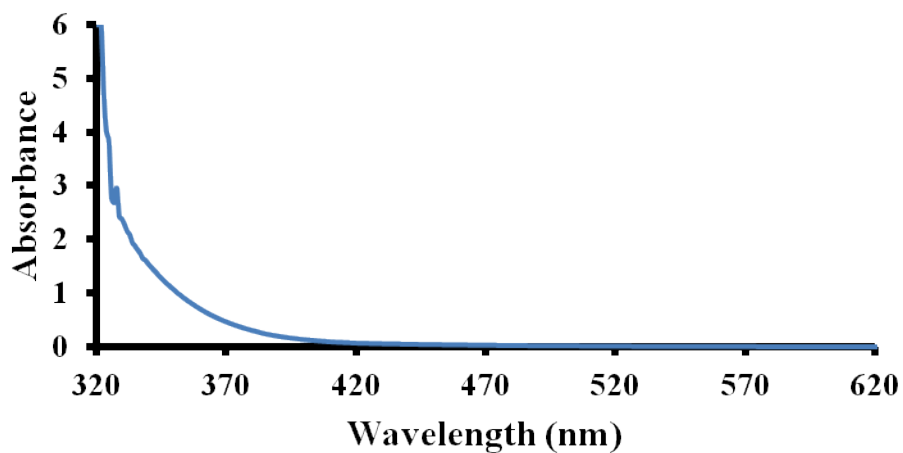


Figure S6: UV-Visible spectra of NFTZ in THF

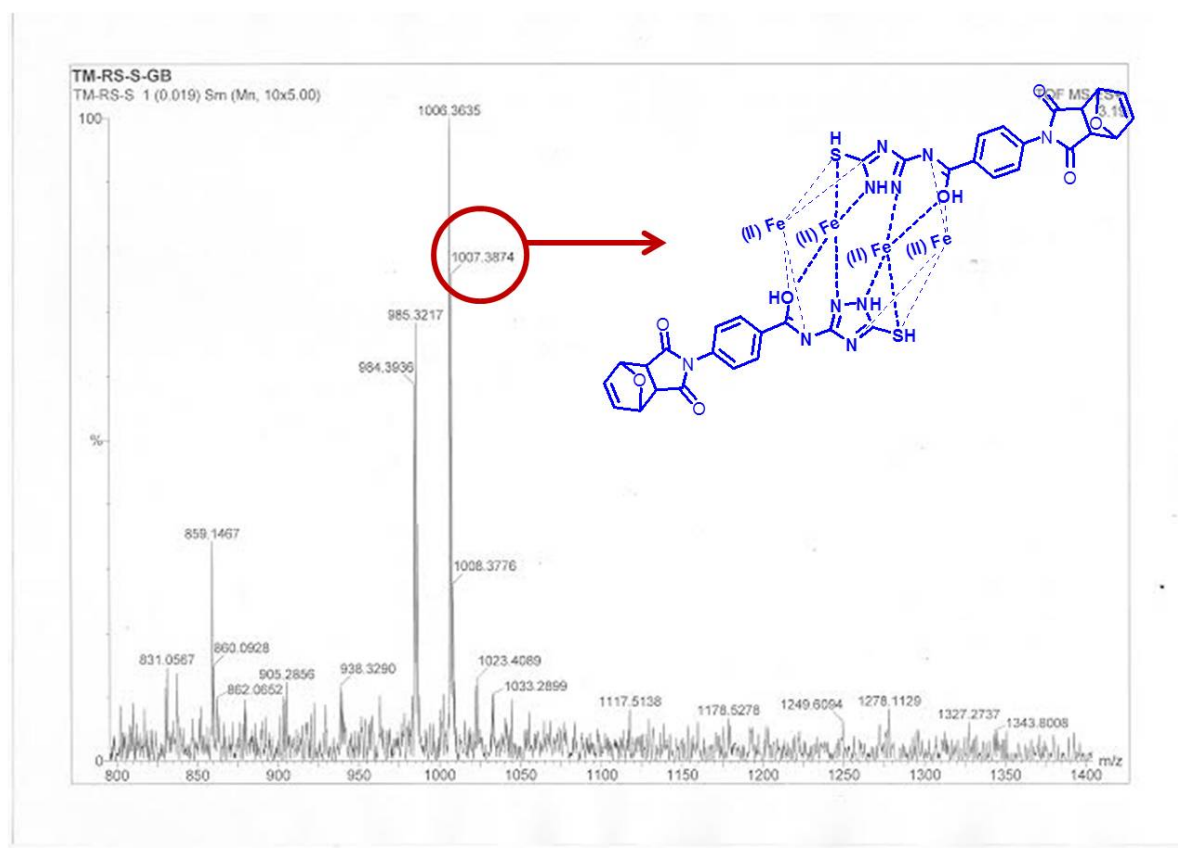


Figure S7: ESI-Mass spectra of NFTZ-Fe (II) complex



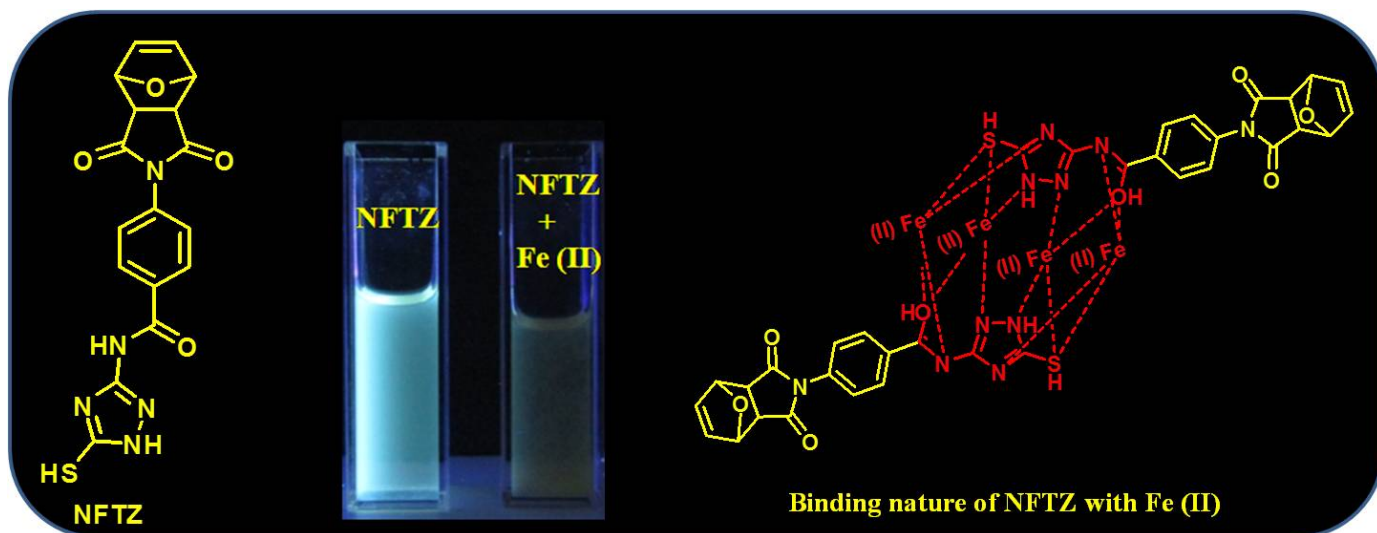


Figure S8: Unique bluish-white fluorescence of NFTZ monomer and its corresponding fluorescence quenching by Fe (II).

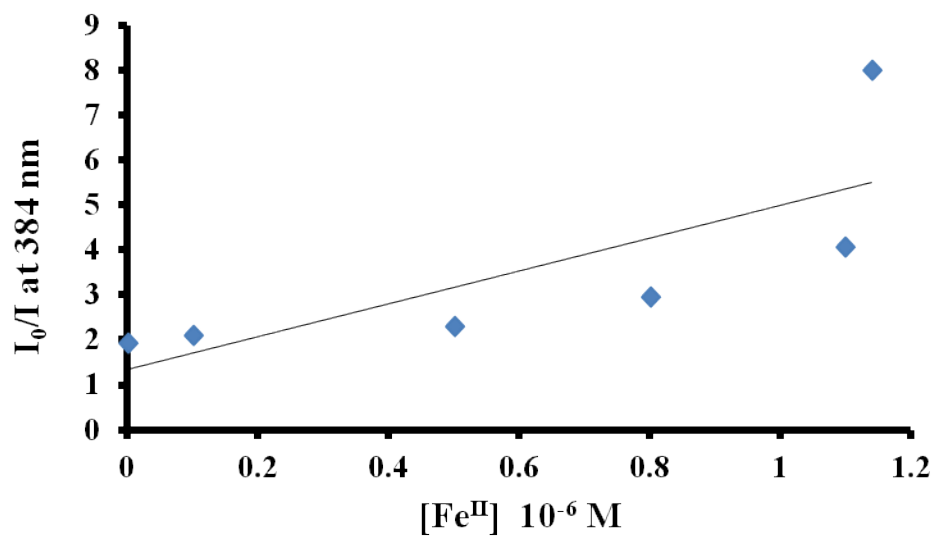


Figure S9: Determination of detection limit from fluorescence intensity of NFTZ in THF/H<sub>2</sub>O (1:1).