Electronic Supplementary Information (ESI)

An INHIBIT logic gate from thiophene derivative using iron and zinc ions as input: Tuning the efficiency on moving from naphthalene to anthracene to pyrene for green luminescent detection of intracellular iron

Arnab Banerjee[a], Animesh Sahana[a], Sudipta Das[a], Sisir Lohar[a], Bidisha Sarkar[b], Subhra Kanti Mukhopadhyay[b], Jesús Sanmartín Matalobos[c]* and Debasis Das[a*]

[a]*Department of Chemistry, The University of Burdwan, Burdwan, West Bengal, India*

[b]*Department of Microbiology, The University of Burdwan, Burdwan – 713104, West Bengal, India,*

[c]*Departamento de Química Inorgánica, Facultade de Química, Avda. Das Ciencias s/n, 15782, Santiago de Compostela, Spain.*

Debasis Das <e-mail: ddas100in@yahoo.com>; Tel: +91-342-2533913; Fax: +91-342-2530452

1. Calculation of Quantum Yield

Fluorescence quantum yields (Φ) were estimated by integrating the area under the fluorescence curves using the equation[1],

$$\phi_{sample} = \phi_{ref} \times \frac{OD_{ref} \times A_{sample} \times \eta^2_{sample}}{OD_{sample} \times A_{ref} \times \eta^2_{ref}}$$

whereA was the area under the fluorescence spectra and OD was optical density of the compound at the excitation wavelength. Anthracene has been used as quantum yield standard(quantum yield is 0.27 in ethanol)[2]for measuring the quantum yields of **PTA** and its

Zn^{2+}adduct. For [**PTA**- Fe^{3+}]adduct, tris(2,2'-bipyridyl)ruthenium(II) (Φ = 0.042 in water) has been used.[3]

2. Calculation of detection limit

To determine the detection limit, fluorescence titration of **PTA** with $Fe^{3+}$is carried out by adding aliquots of micro-molar concentration of Fe^{3+}. From the concentration at which there was a sharp change in the fluorescence intensity multiplied with the concentration of **PTA**gave the detection limit.[4]

3. Equations used for calculating detection limit (DL)

$DL = C_L \times C_T$

C_L = Conc. of **PTA**; C_T = Conc. of iron at which fluorescence enhanced.

Thus;

$DL = 1\ \mu M \times 0.01\ \mu M = 0.01\ \mu M = 1 \times 10^{-8}$ M

4. X-ray crystal structural parameters

Crystal parameters	**PTA**	**ANTA**
Molecular formula	$C_{22}H_{15}NS$	$C_{20}H_{15}NS$
Formula weight	325.41	301.39
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	12.6935 (18)	4.3718 (4)
b/Å	9.3300 (12)	13.1396 (12)
c/Å	13.2778 (17)	25.912 (2)

α/°	90.0	90.0
β/°	95.55 (1)	93.433 (5)
γ/°	90.0	90.0
Z	4	4
V/ Å^3	1565.1 (4)	1485.8 (2)
T/K	100	100
λ/Å	0.7107	0.7107
ρ/mg m^{-3}	1.381	1.347
μ/mm^{-1}	0.21	0.21
Crystal size/mm	0.68 × 0.37 × 0.02	0.52 × 0.11 × 0.08
h/k/l	−15→15/0→11/0→16	−5→5/0→16/0→32
F(000)	680	632
θ range/°	2.7–24.5°	2.2–26°
T_{min} and T_{max}	0.607 and 1.0	0.953 and 1.0
Reflection collected	33038	22444
Independent reflection	3092	3068
R factor (all data)	0.058	0.037
R factor (final)	0.150	0.096

Geometry

All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimatedusing the full covariance matrix. The cell s.u.'s are taken into account individually in theestimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cellparameters are only used

when they are defined by crystal symmetry. An approximate (isotropic)treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement

Refinement of F2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F2, conventional R-factors R are based on F, with F set to zero for negative F2. The threshold expression of F2 >2σ(F2) is used only for calculating R factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Figures

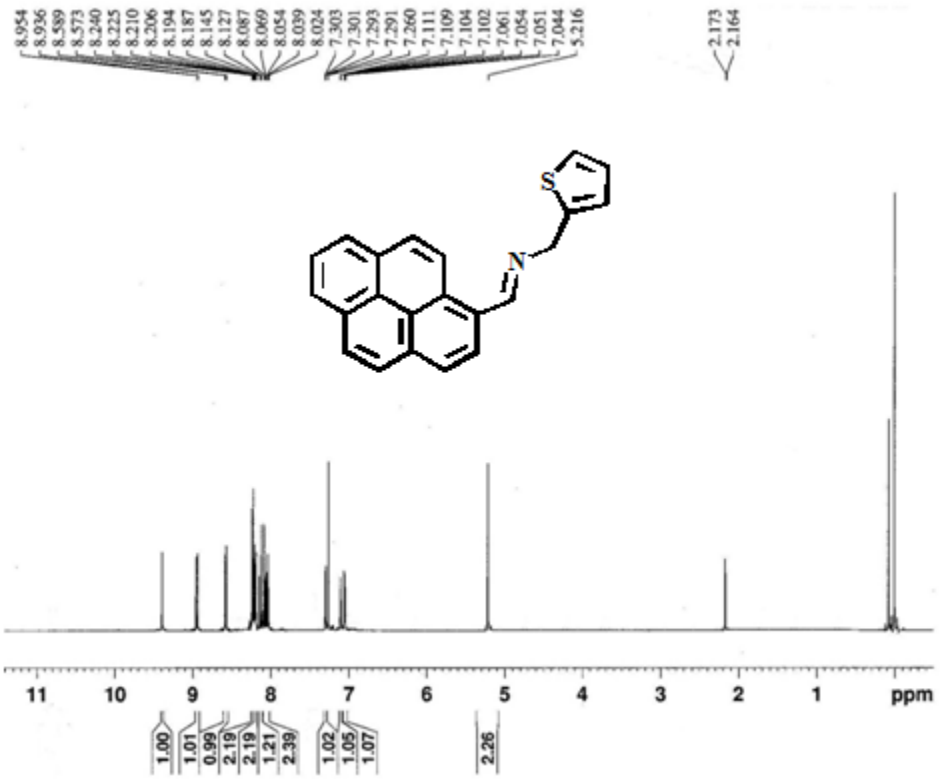

Figure S1. ^{1}H NMR spectrum of **PTA** in $CDCl_3$

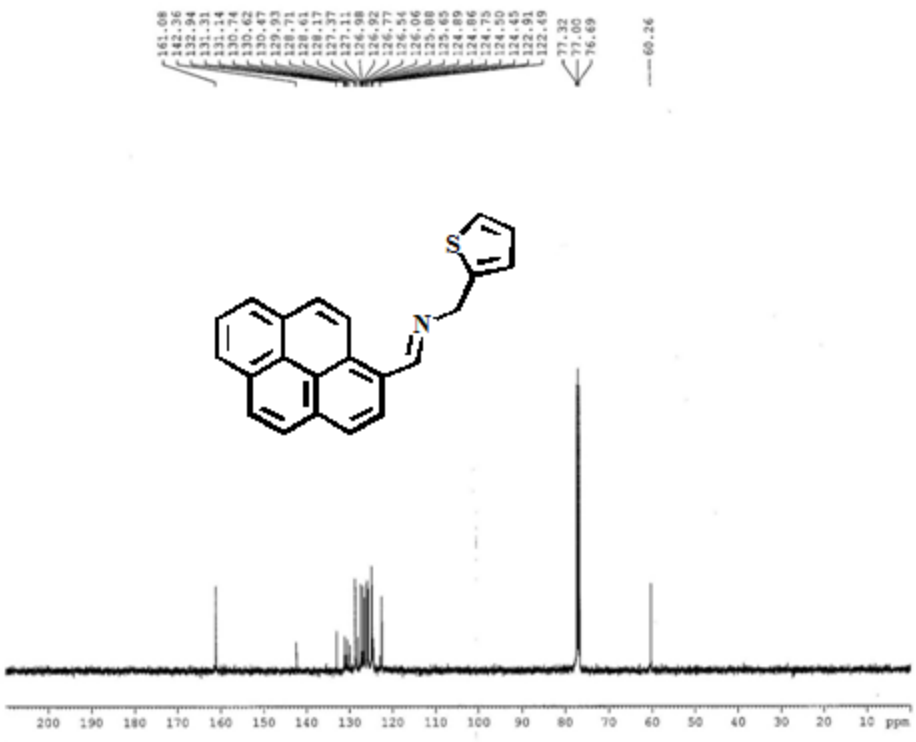

Figure S2. ^{13}C NMR spectrum of **PTA** in $CDCl_3$

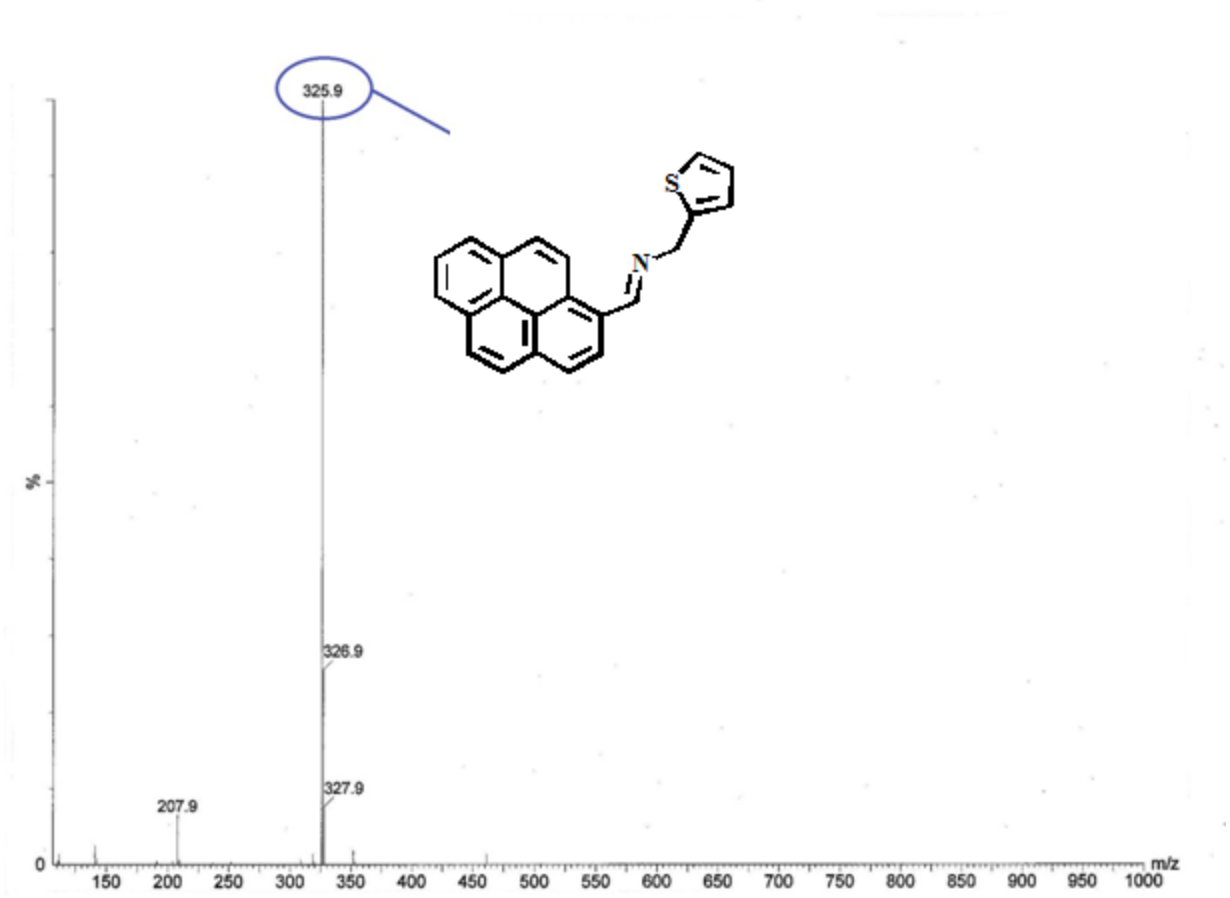

Figure S3. QTOF –MS ES^+ spectrum of **PTA**

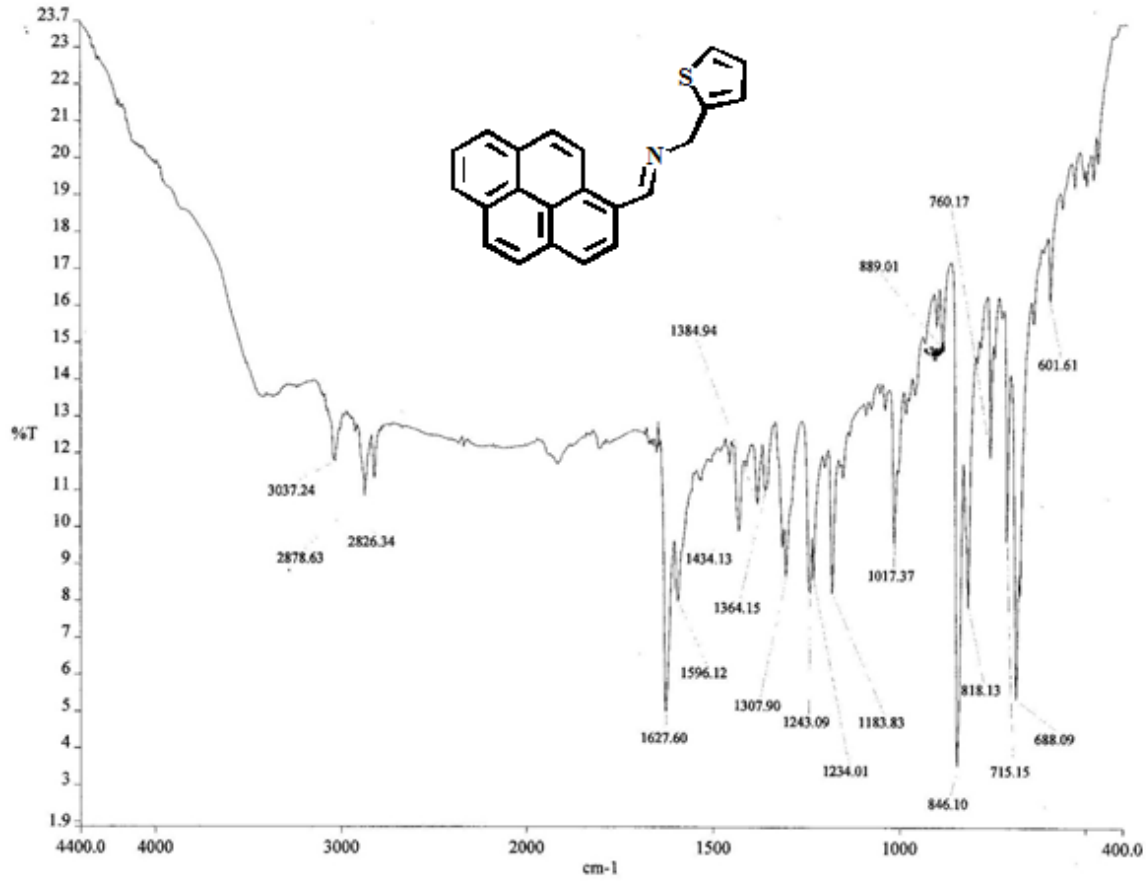

Figure S4. FTIR spectrum of **PTA**

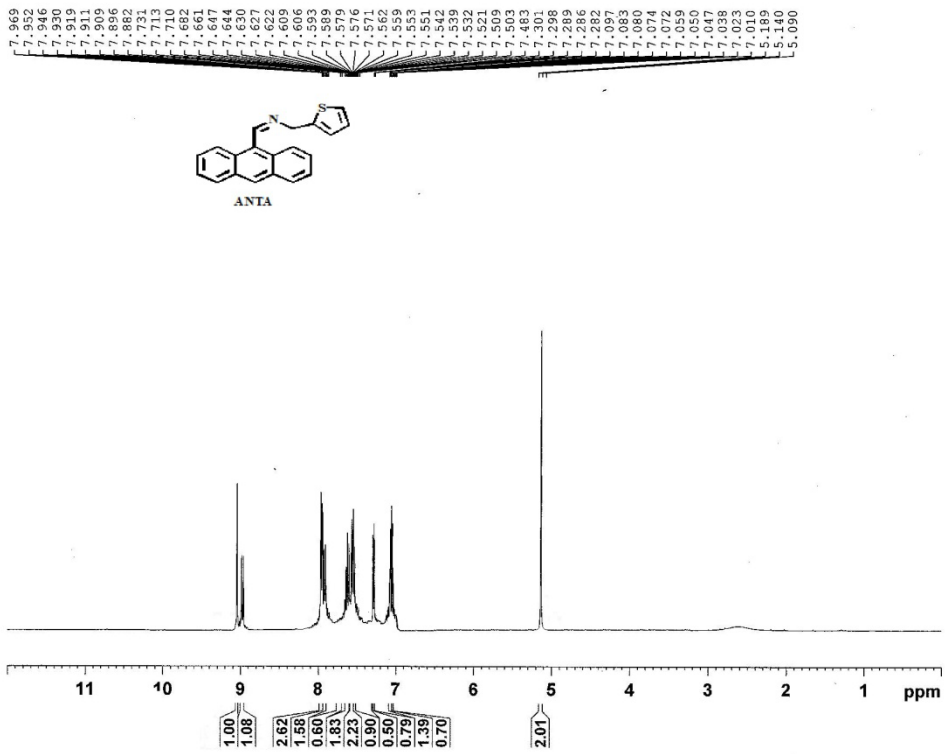

Figure S5. ^{1}HNMR spectrum of **ANTA** in $CDCl_3$

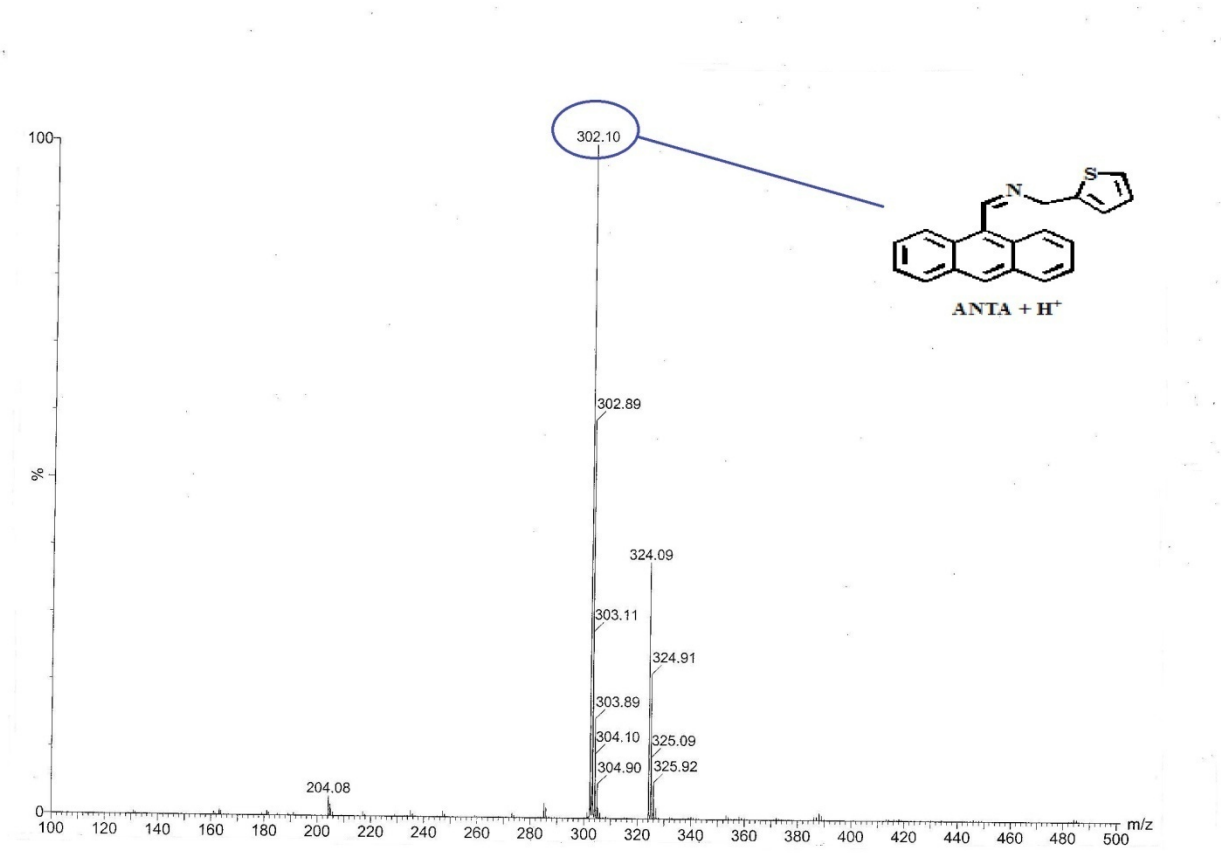

Figure S6. QTOF –MS ES^+ spectrum of **ANTA**

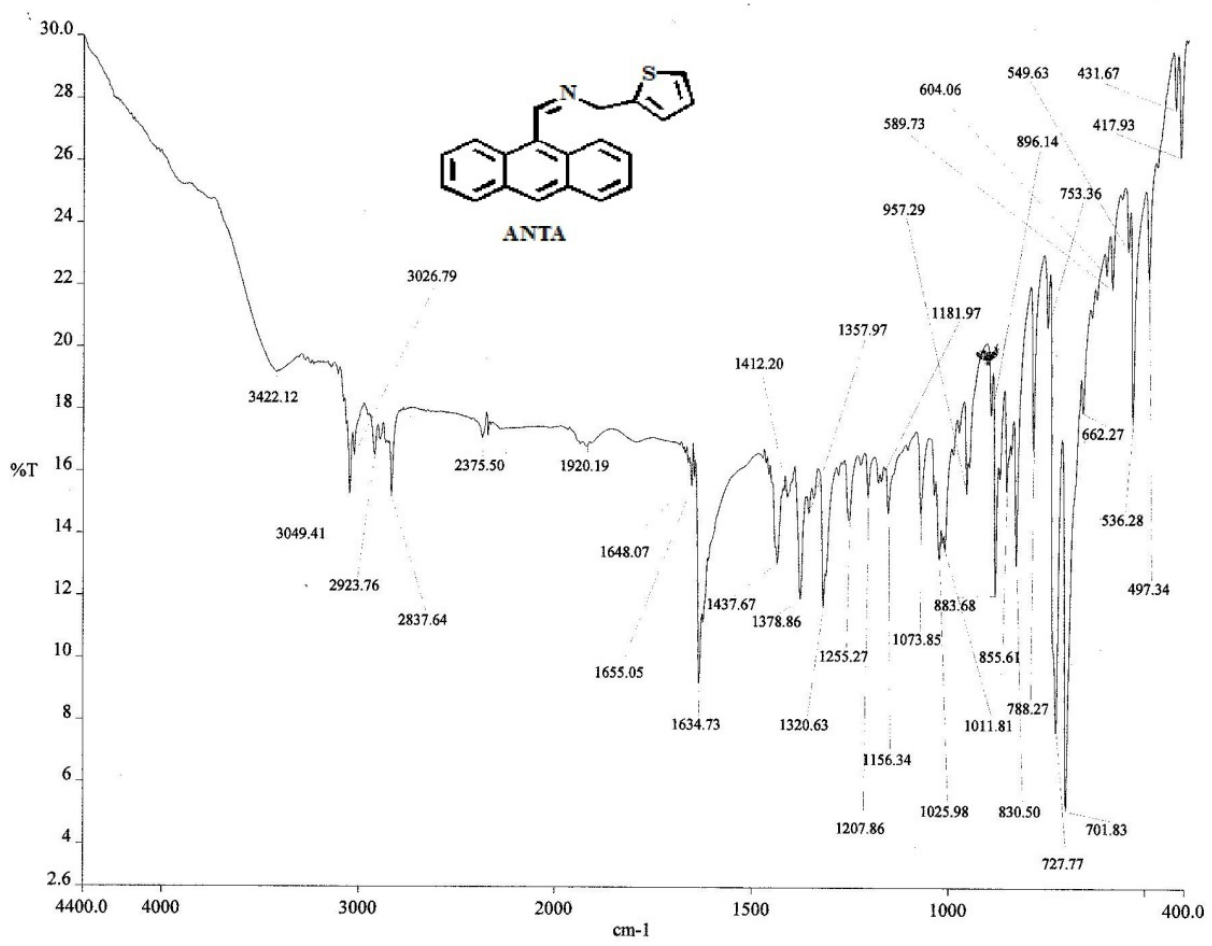

Figure S7. FTIR spectrum of **ANTA**

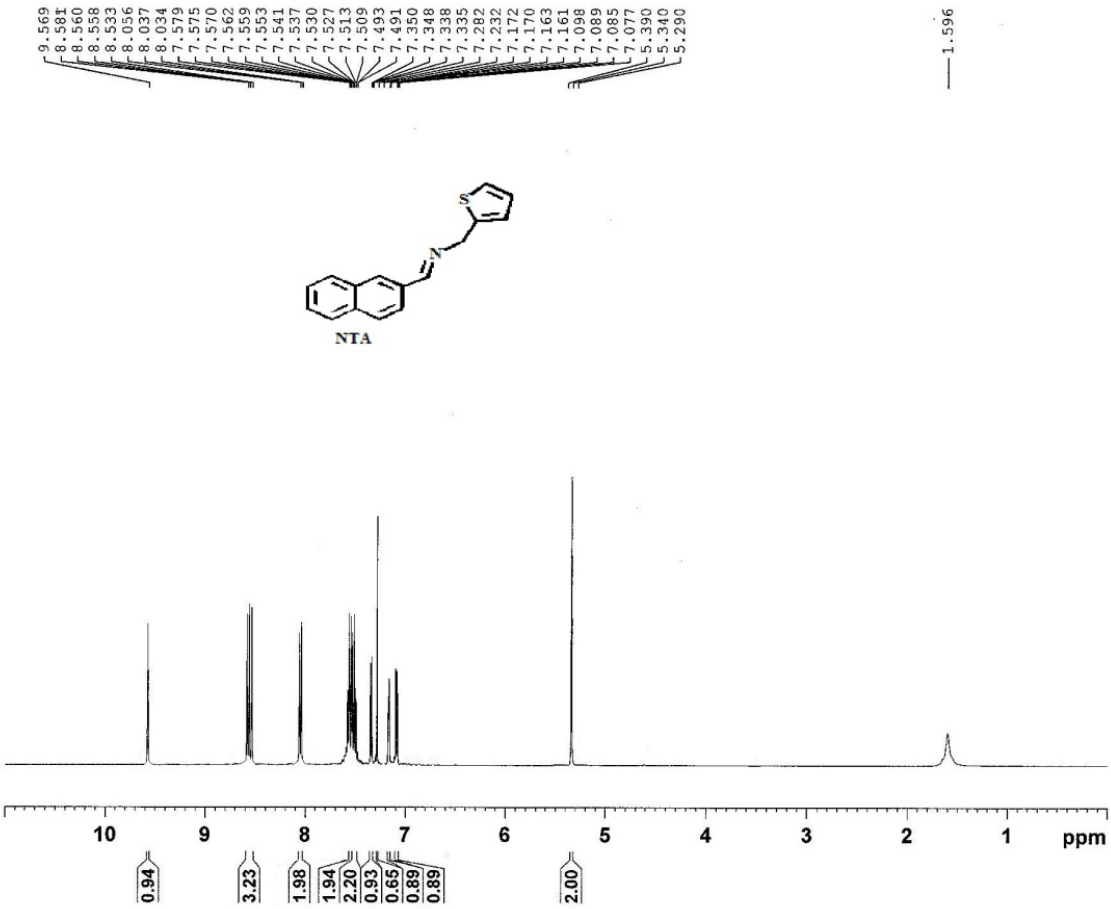

Figure S8. ^{1}H NMR spectrum of **NTA** in $CDCl_3$

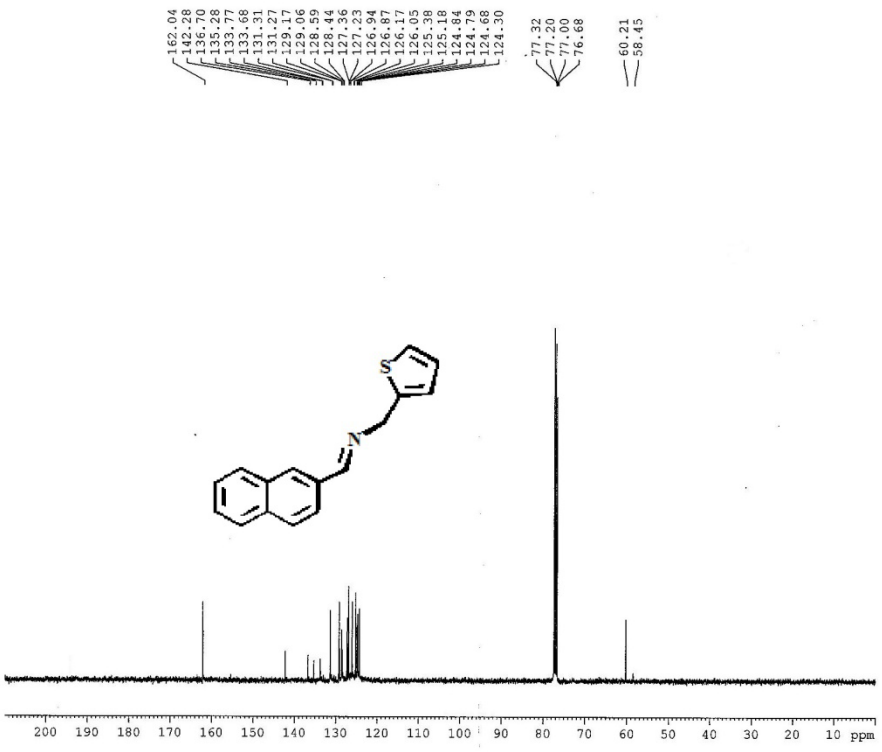

Figure S9. ^{13}C NMR spectrum of **NTA** in $CDCl_3$

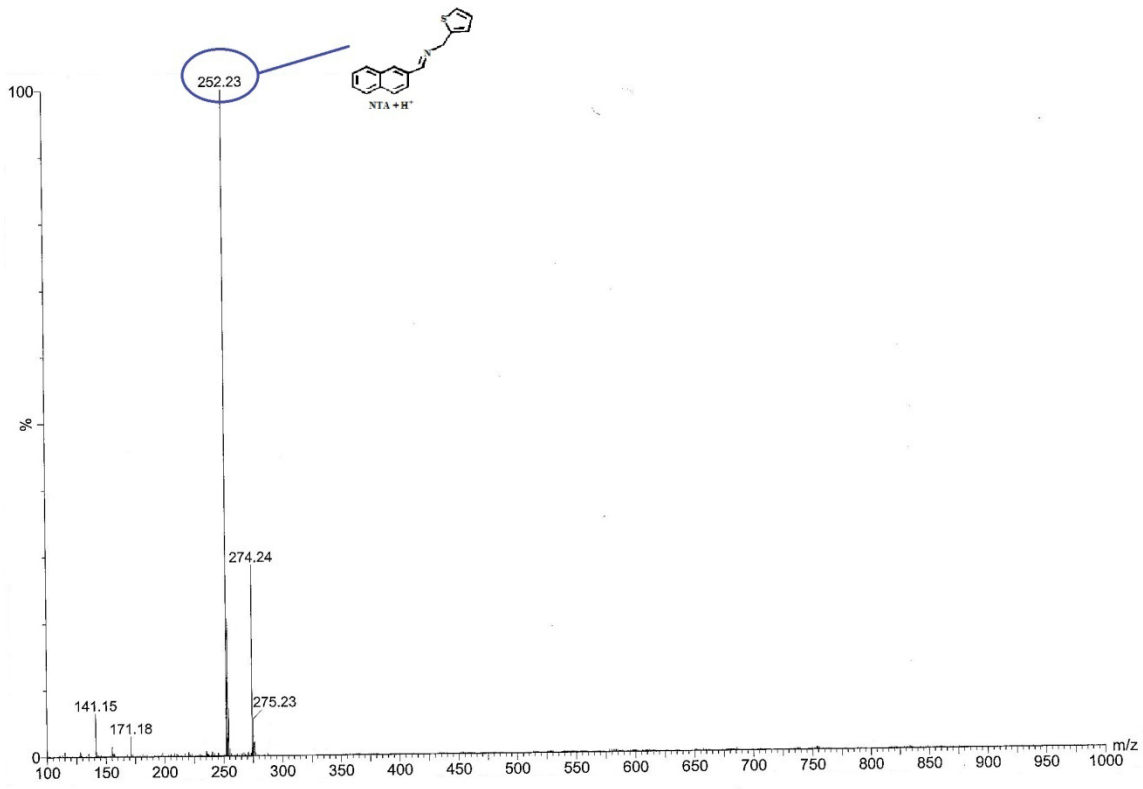

Figure S10. QTOF –MS ES$^+$ spectrum of **NTA**

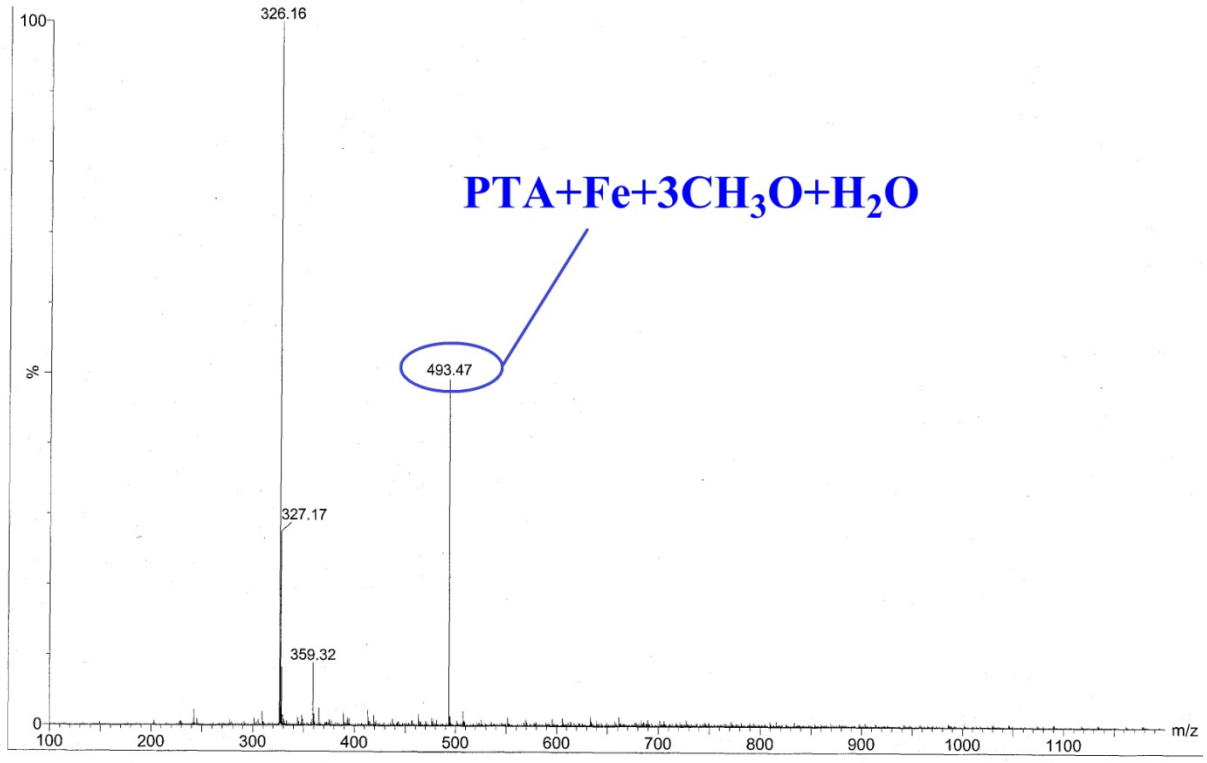

Figure S11. QTOF –MS ES^+ spectrum of **[PTA-Fe^{3+}]** adduct

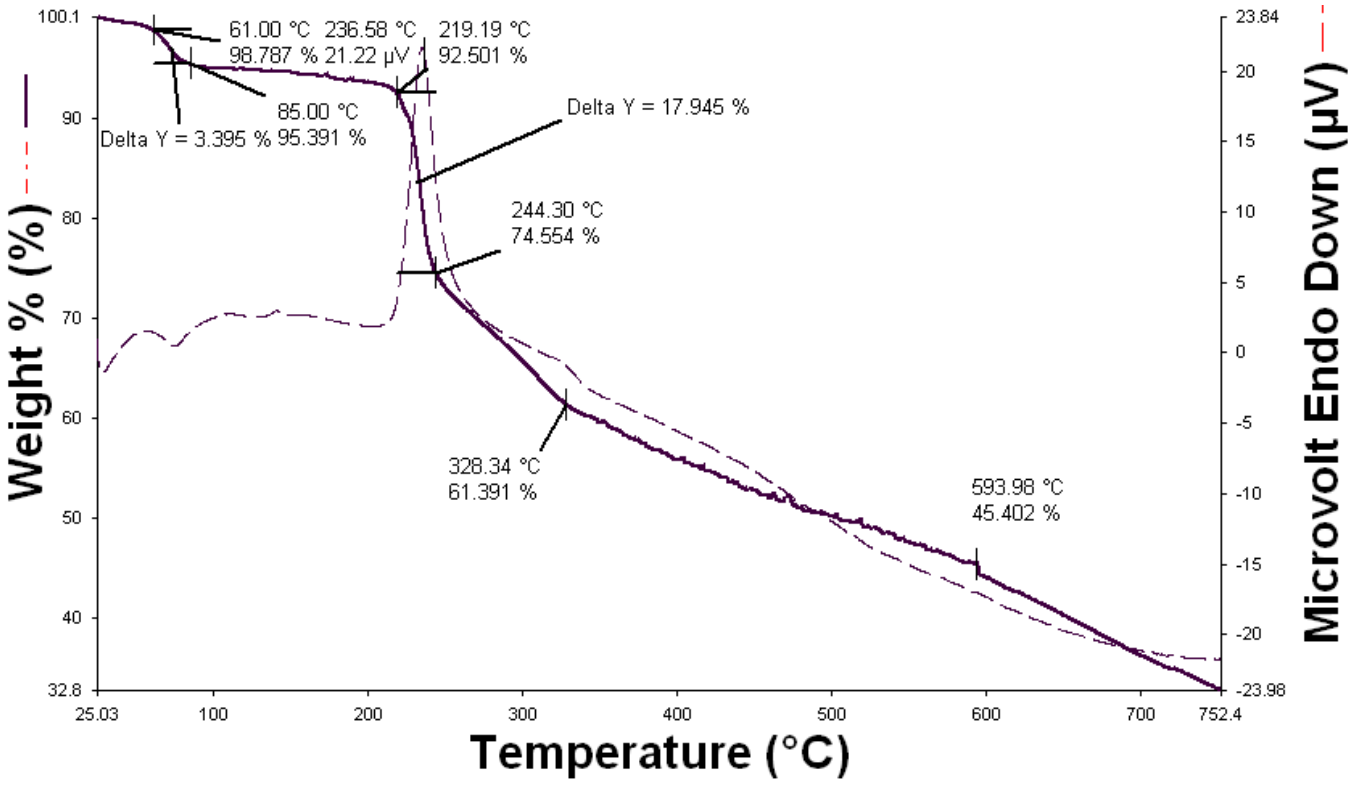

Figure S12. Thermogram of the **[PTA-Fe^{3+}]** adduct

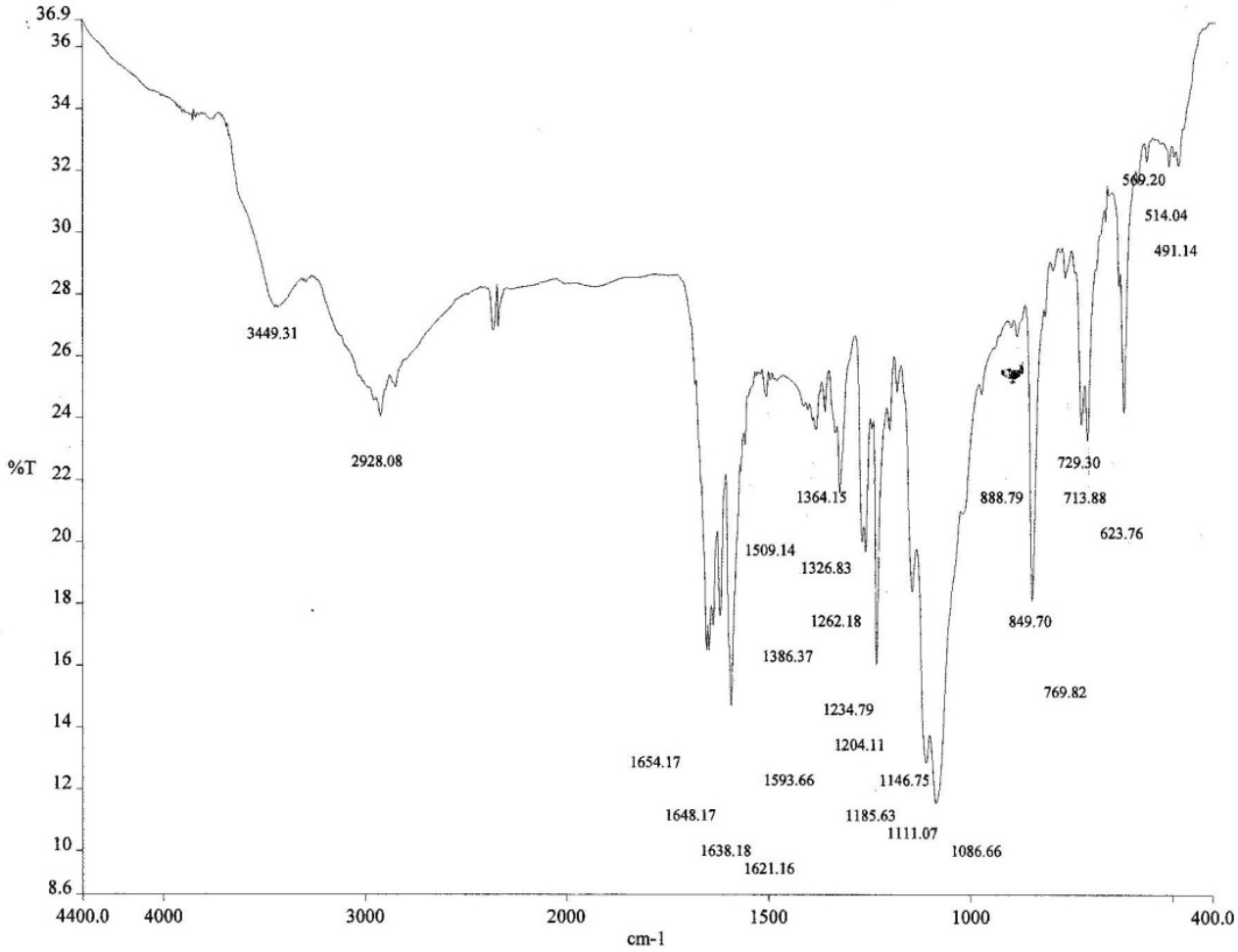

Figure S13. FTIR spectrum of the **[PTA-Fe^{3+}]** adduct

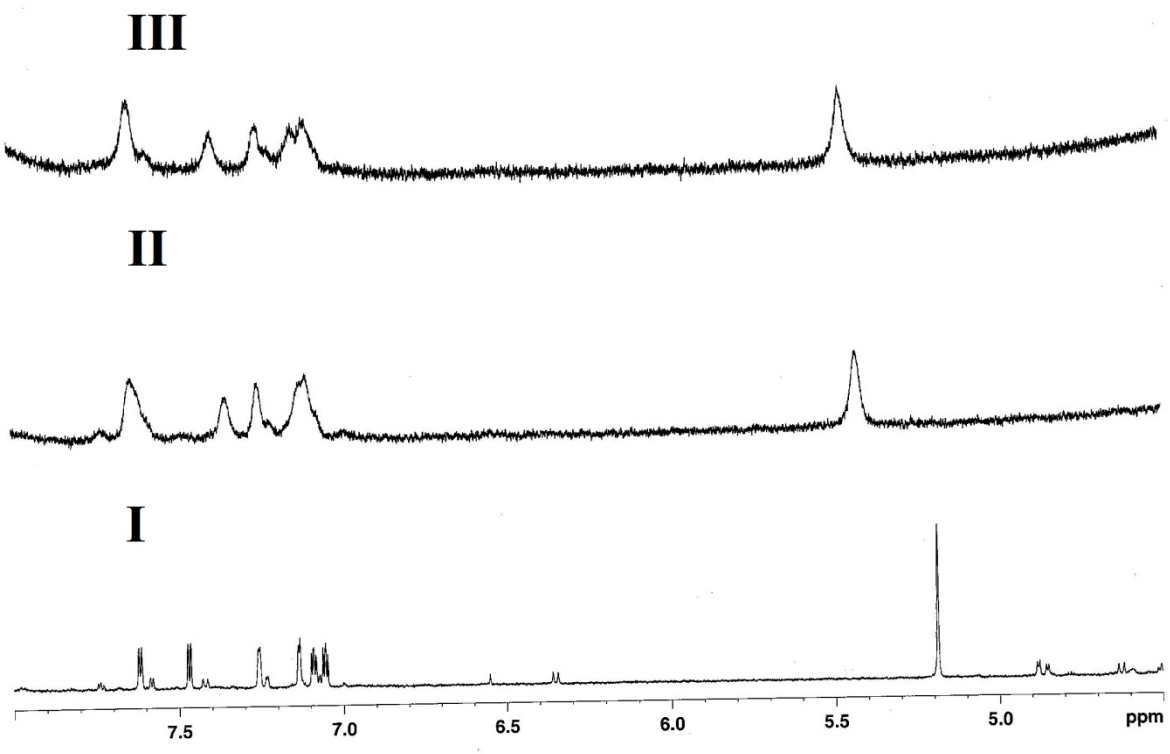

Figure S14. ^{1}H NMR spectra of **PTA**with Fe^{3+} in DMSO-d_6: (I) only **PTA**; (II) **PTA** with 1 equiv. of Fe^{3+}; (III) **PTA** with 2.0 equiv. of Fe^{3+}.

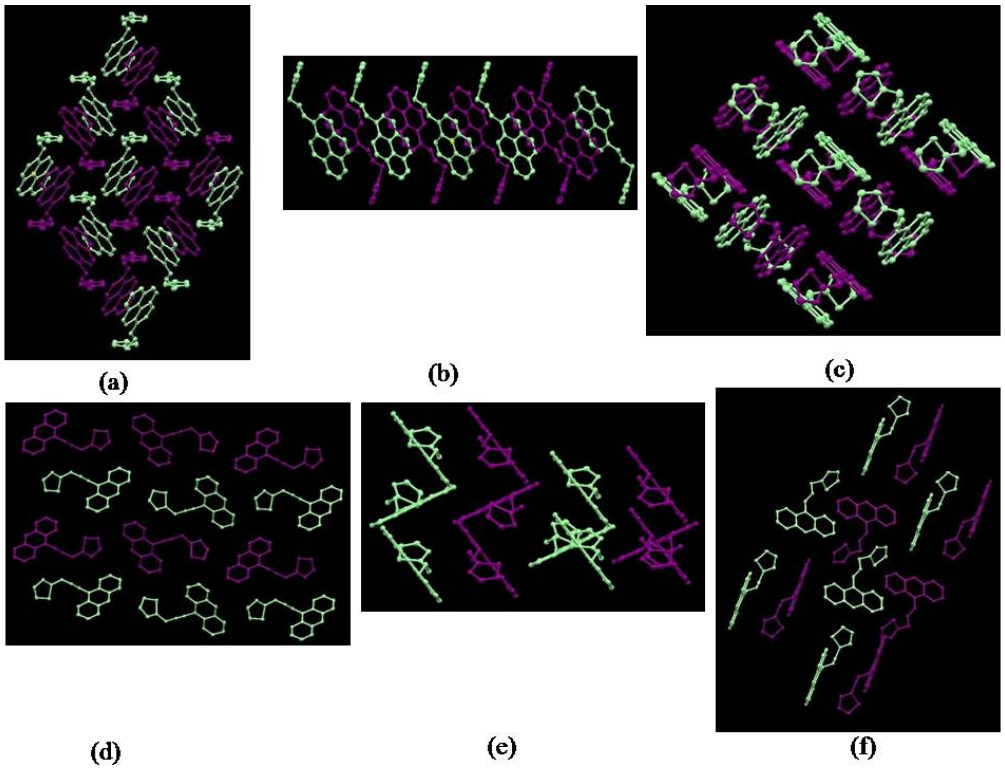

Figure S15. Crystal packing diagram of **PTA** (a), (b) and (c) and **ANTA** (d), (e) and (f) along three different axis a, b and c respectively.

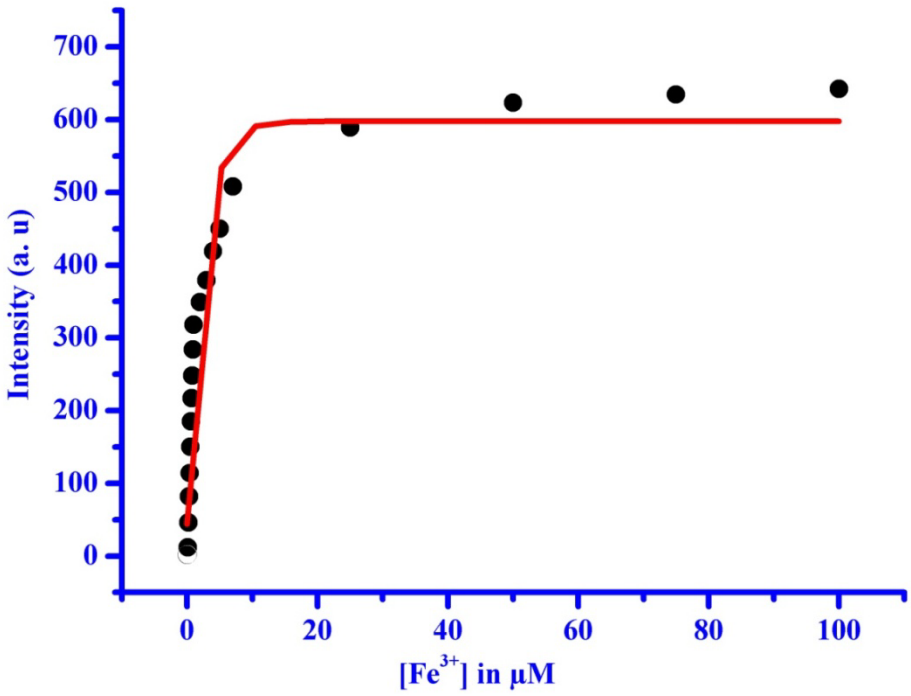

Figure S16. Plot of fluorescence intensity *vs.*externally added [Fe^{3+}](1-100 µM)

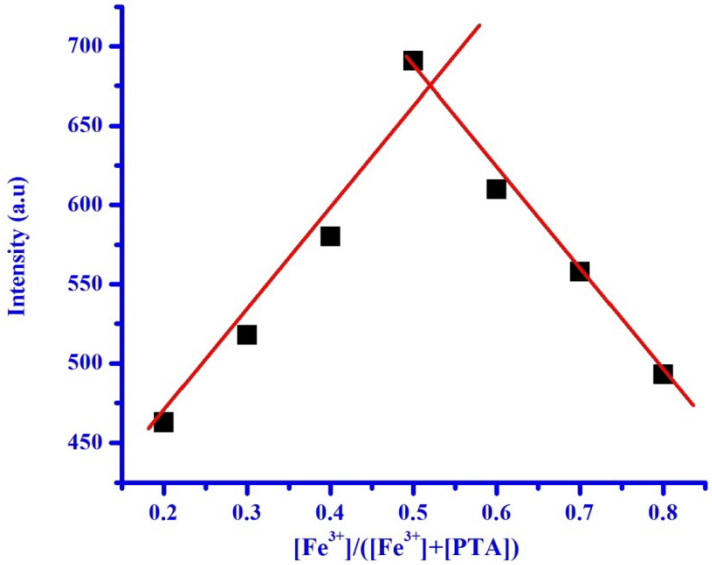

Figure S17. Job's plot for determination of stoichiometry of the [**PTA**-Fe^{3+}] system.

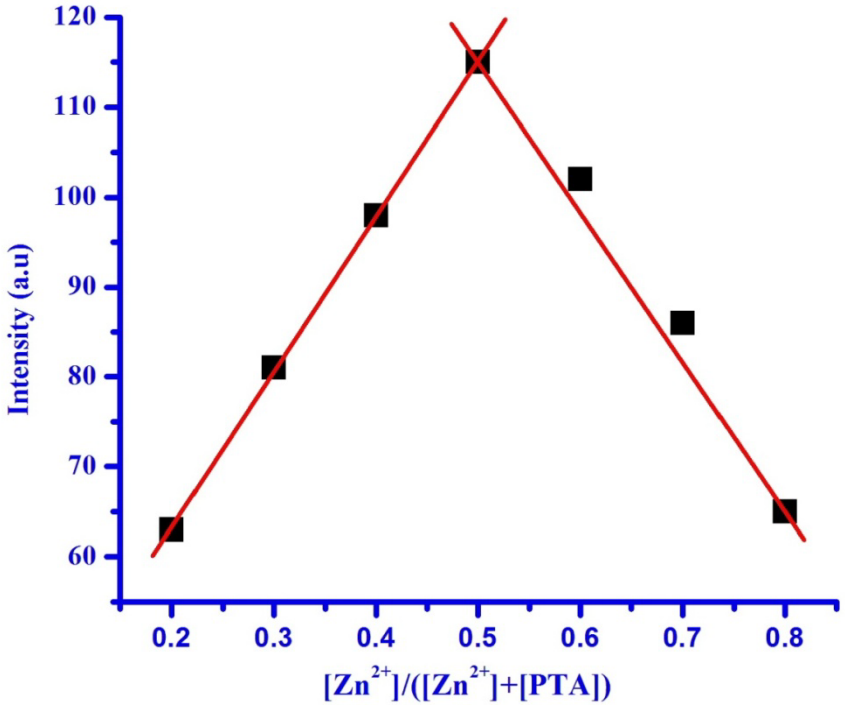

Figure S18. Job's plot for determination of stoichiometry of the [**PTA**-Zn^{2+}] system

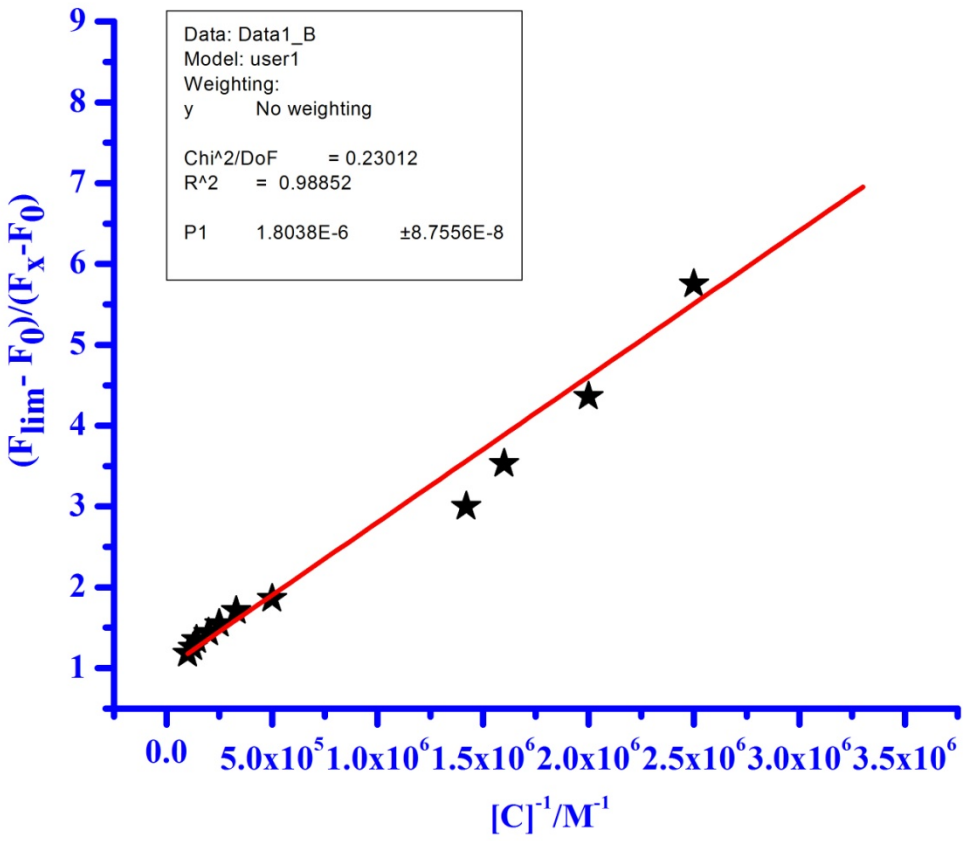

Figure S19. Determination of the binding constant of **PTA** with Fe^{3+} using $(F_{max} - F_0)/ (F_x - F_0) = 1 + (1/K) \times (1/[M]^n)$, where F_{max}, F_0 and F_x are fluorescence intensities of **PTA** in presence of Fe^{3+} at saturation, free **PTA** and at any intermediate Fe^{3+}concentration, respectively.

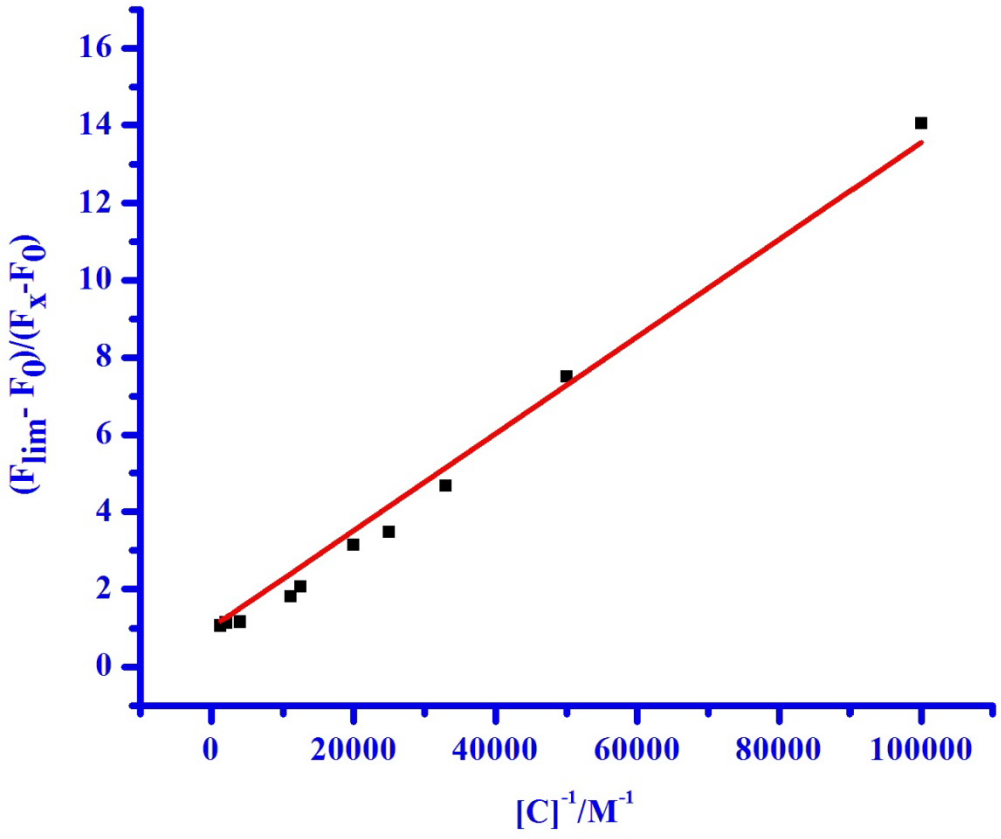

Figure S20. Determination of the binding constant of **PTA** with Zn^{2+} using $(F_{max} - F_0)/ (F_x - F_0) = 1+ (1/K) \times(1/[M]^n)$, where F_{max}, F_0 and F_x are fluorescence intensities of **PTA** in presence of Zn^{2+}at saturation, free **PTA** and at any intermediate Zn^{2+}concentration, respectively.

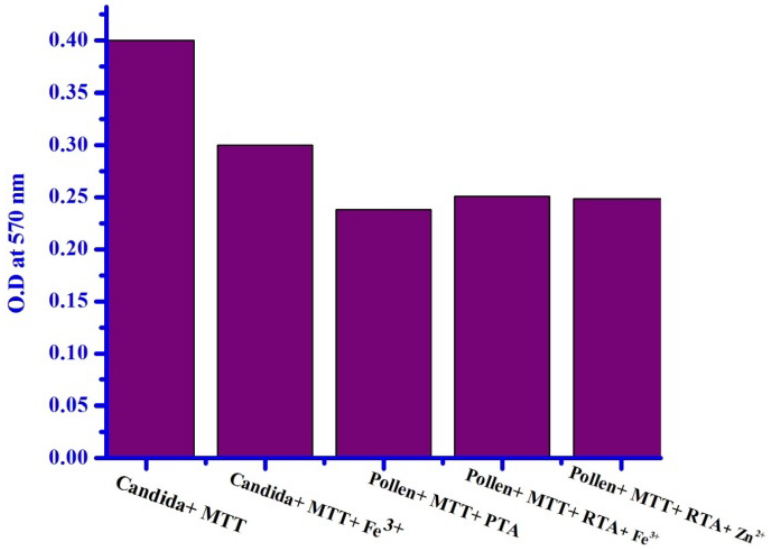

Figure S21. MTT assay studies of **PTA.**

References

1. E. Austin, M. Gouterman, *Bioinorg. Chem.*,1978, **9**, 281.

2. W. H. Melhuish, *J. Phys. Chem.*, 1961, **65,** 229.

3. J. V. Houten, R. J. Watts, *J. Am. Chem. Soc.*, 1976, **98**, 4853.

4. G. L. Long, J. D. Winefordner, *Anal. Chem*., 1983, **55**, 712A.