Electronic Supplementary Material (ESI) for Analytical Methods

Pyrene based Selective - Ratiometric Fluorescent Sensing of Zinc and Pyrophosphate ions.

Gandhi Sivaraman, Thangaraj Anand and Duraisamy Chellappa*

Electronic Supporting Information

Materials and methods:

All reagents and solvents were used as such without further purification. Pyrene-1-carboxaldehyde, Cystamine hydrochloride were purchased from Aldrich, whereas Tri ethyl amine and Metal chloride salts was obtained from Merck chemicals. Absorption measurements were carried out in JASCO V-550 UV-vis spectrophotometer. Fluorescence spectra were recorded in F-4500 Hitachi fluorescence spectrophotometer. The slit width was kept as 5 nm for both excitation and emission. NMR spectra were recorded in Bruker (Avance) 300 MHz instrument using TMS as internal standard. ESI-MS spectral analysis was performed in positive ion as well as negative ion mode on a liquid chromatography-ion trap mass spectrometer (LCQ Fleet, Thermo Fisher Instruments Limited, US).

Preparation of metal ion solutions for photophysical studies:

Metal Chloride salts (Ag^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, $Pb^{2+}$and Zn^{2+}) were used as the source for metal ions. 10mM of metal ion stock solutions were prepared in distilled water. 1mM of PDP-1 was prepared in ACN/H_2O (7:3) was buffered with PBS buffer (pH=7.4).

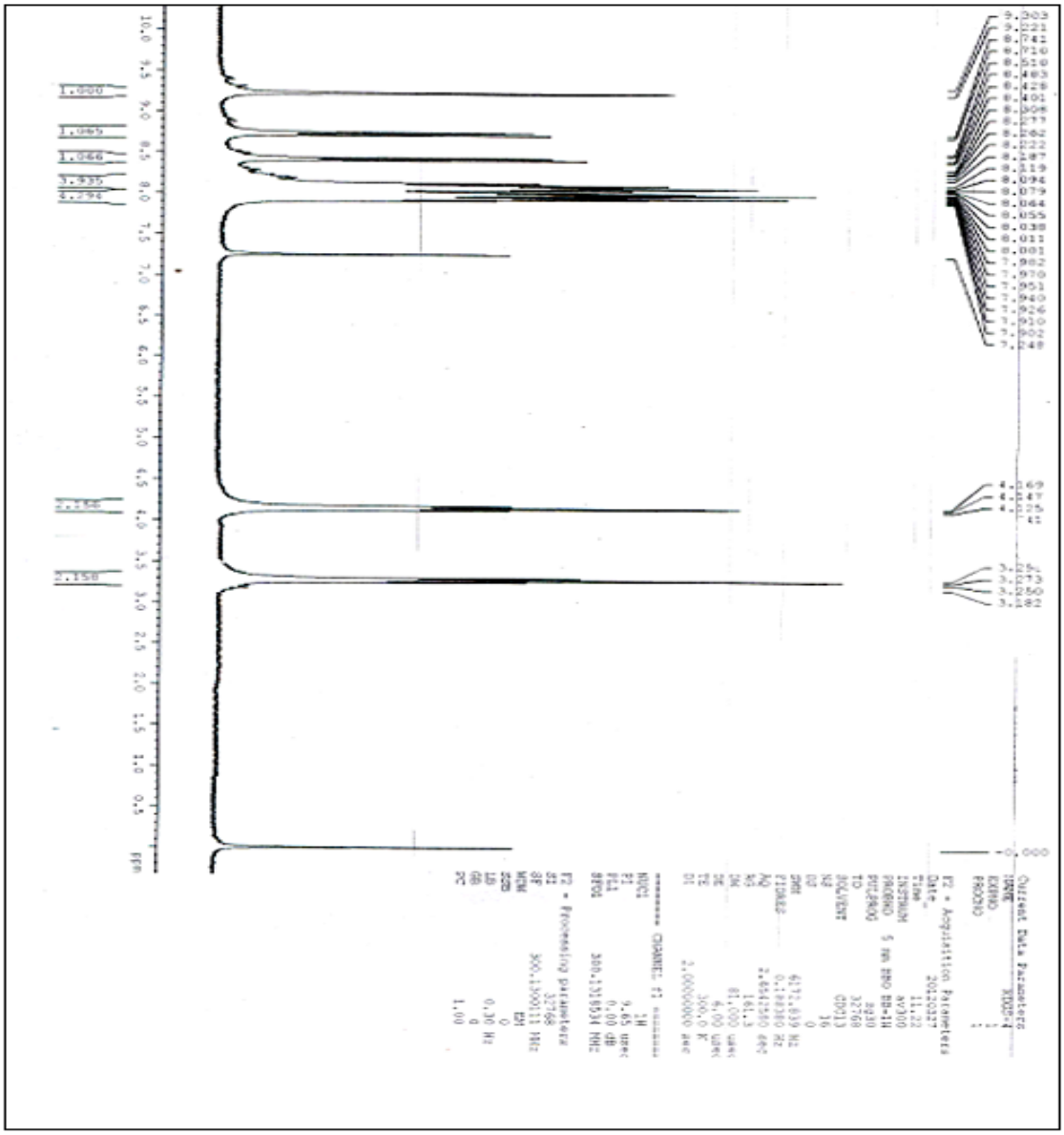

Fig-S1: ^{1}H-NMR spectrum of PDP-1

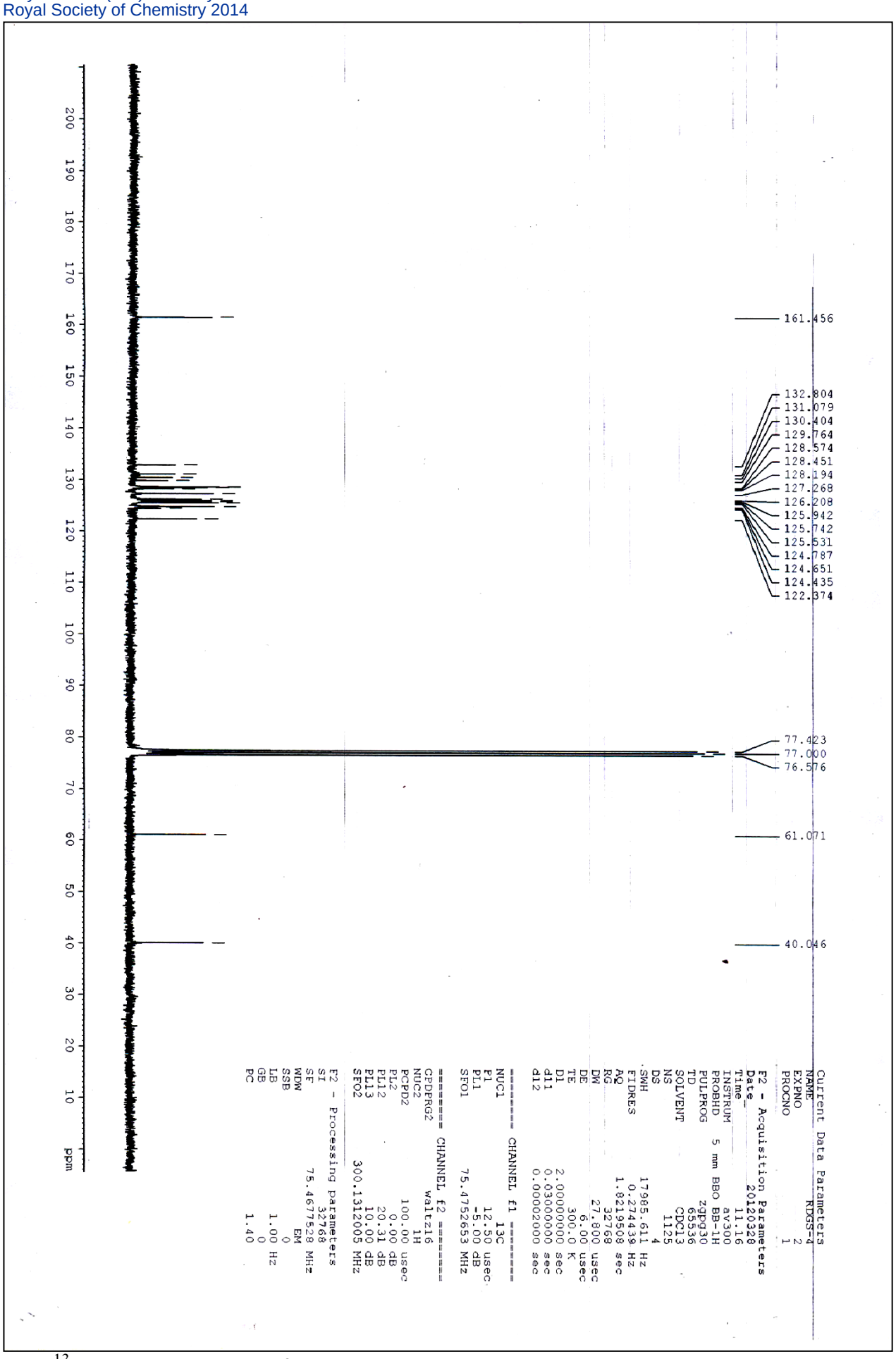

Fig-S2: ^{13}C-NMR spectrum of PDP-1

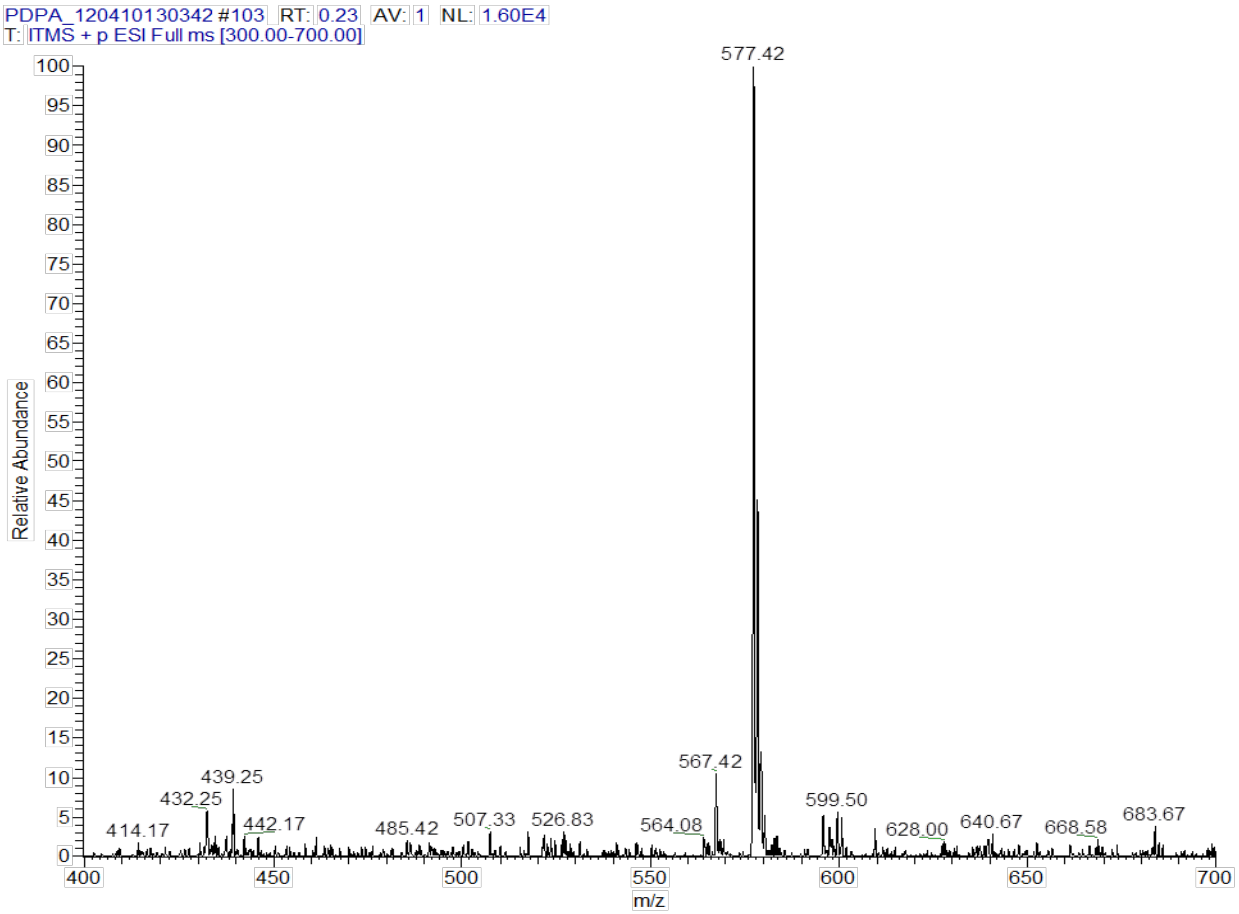

Fig-S3: ESI-MS spectrum of PDP-1

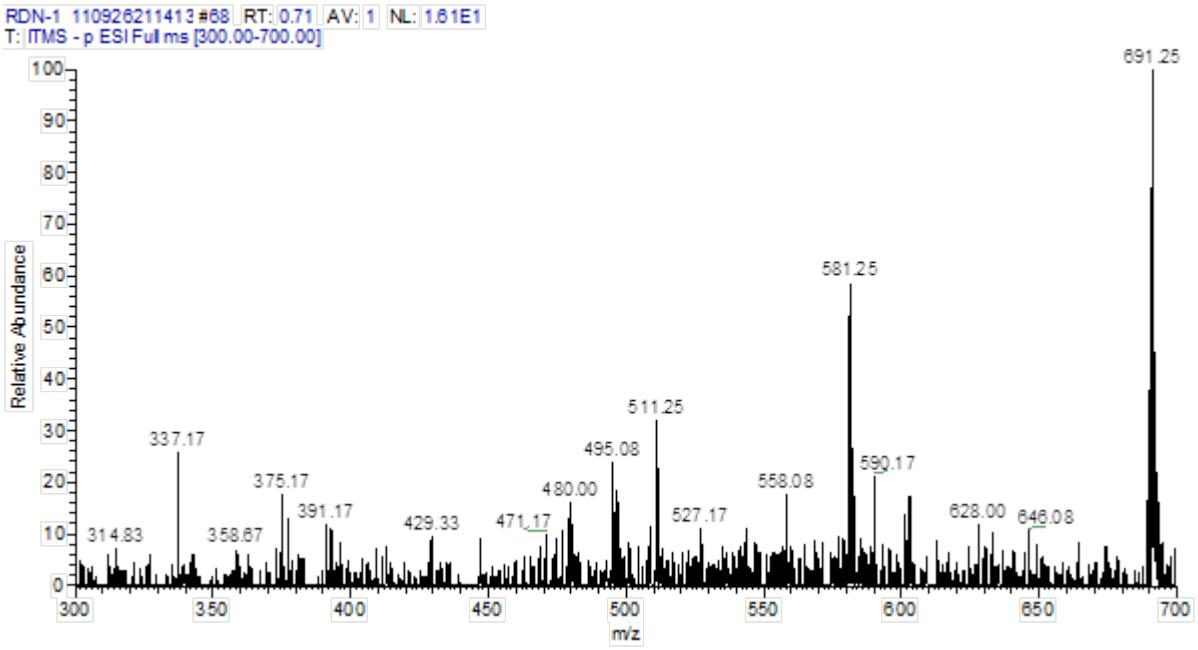

Fig-S4:ESI-MS spectrum of PDP-1 + Zn^{2+}.

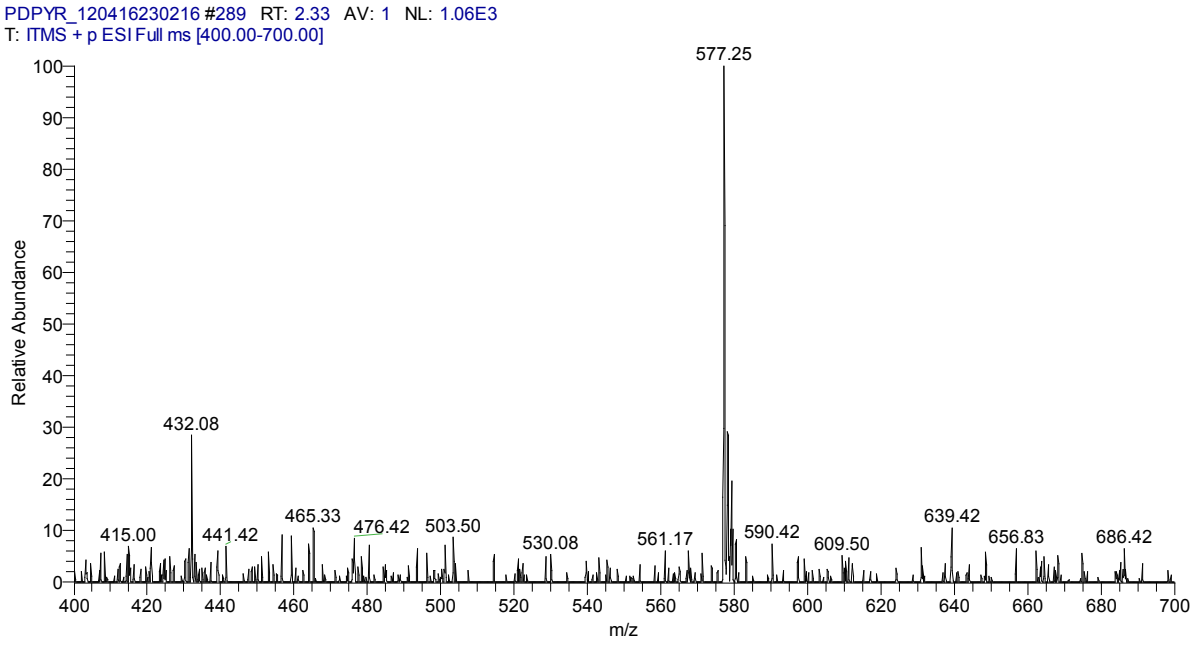

Fig-S5:ESI-MS spectrum of PDP-1 + Zn^{2+} + ppi (After addition of 100 Equivalents).

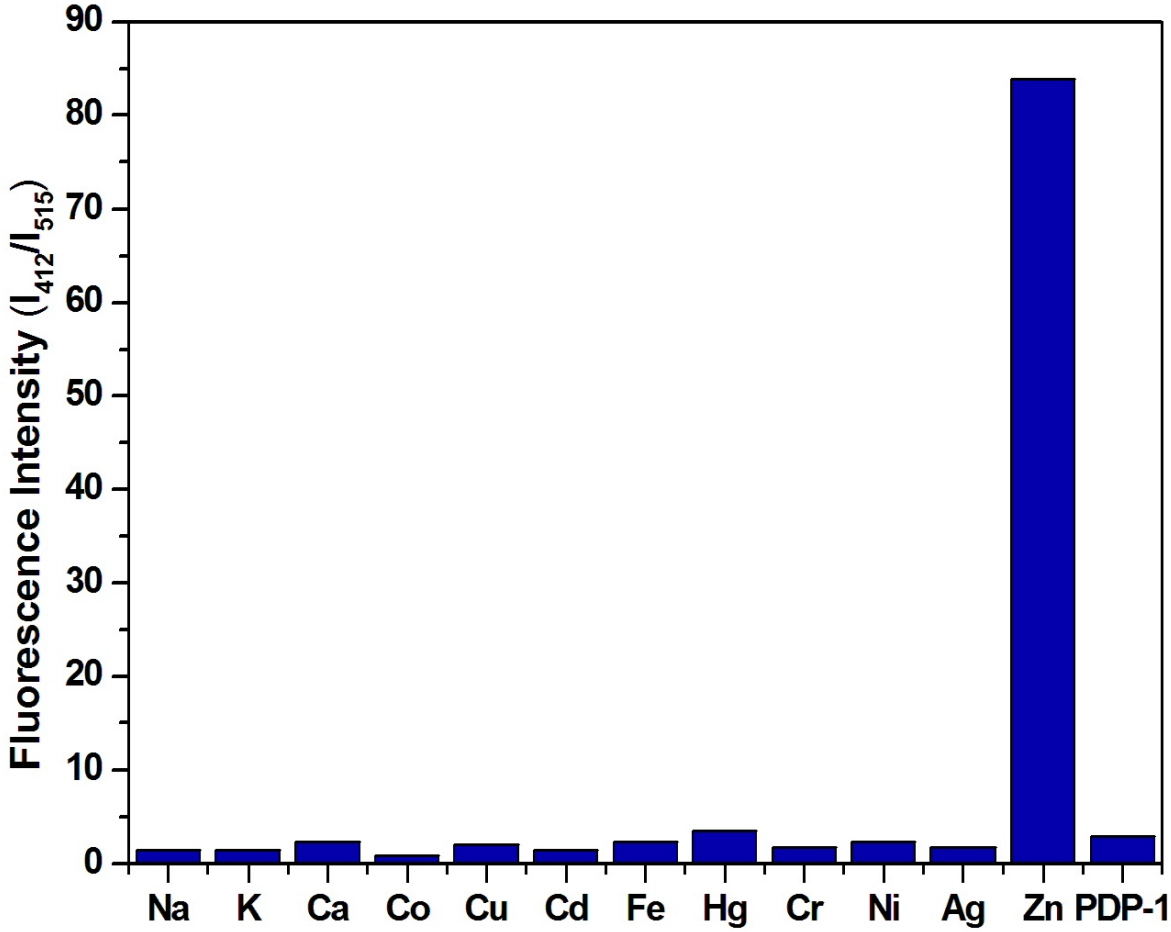

Figure-S6: Fluorescence response (I/I_0) of PDP-1 (10 µM) in CH_3CN/H_2O (30:70 v/v) to 10 µM of various tested metal ions (Blue bar)

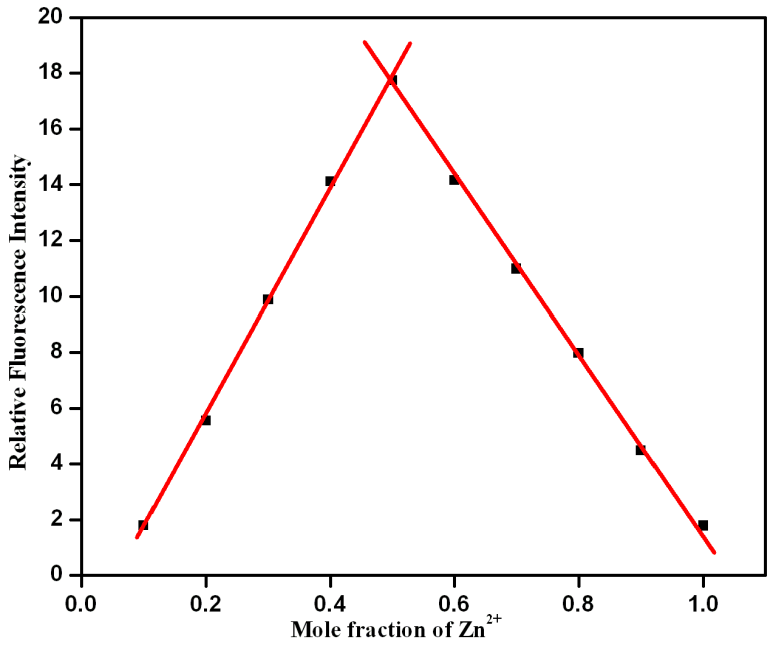

Figure-S7: Job's plot between PDP-1and Zn^{2+}.

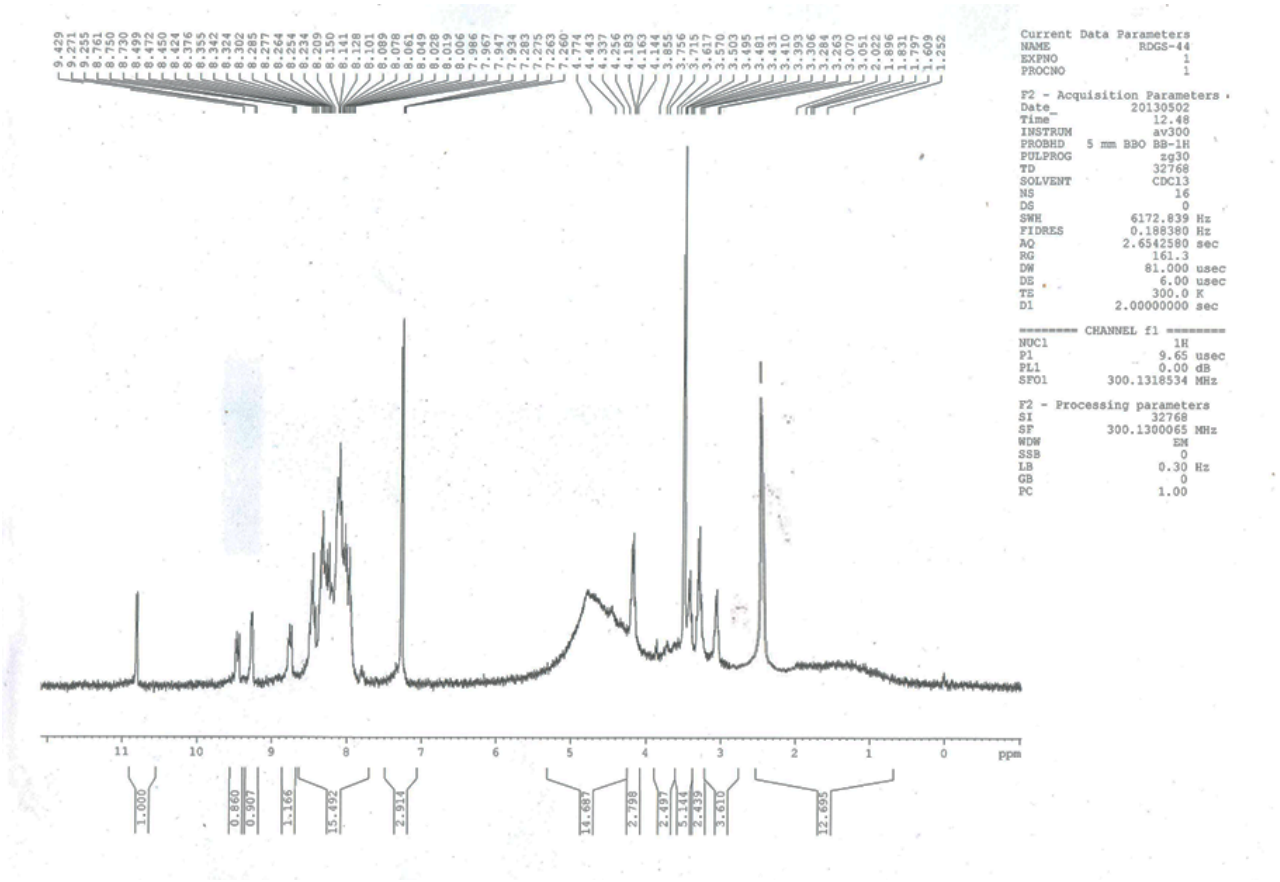

Fig-S8 : ^{1}H-nmr spectrum of PDP-1 + Zn^{2+} in DMSO-d^{6}.

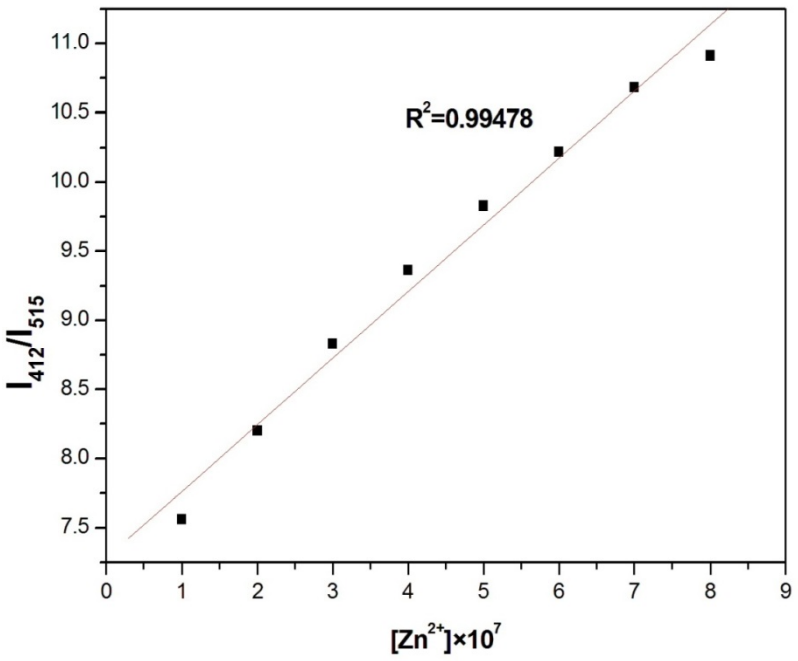

Fig-S9: Plot of fluorescence emission intensity ratio (I_{412}/I_{515}) *vs* concentration of zinc ions

Calculation of Binding constant:

The binding constant K was determined from the plot of the linear regression of log [(F - F0) / (Fm - F)] vs. log [M] in equation to obtain the intercept as log K and the slope as n.

$$\log \frac{F - F_0}{F_m - F} = \log K + n \log [M]$$

Calculation of Detection limit:

The limit of detection was found using this equation.[S1]

$DL = C_L \times C_T$

C_L = Conc. of Ligand; C_T = Conc. of Titrant at which change observed.

Thus; $DL = 1 \times 10^{-6} \times 0.085 \times 10^{-6} = 0.085 \times 10^{-6} = 8.5 \times 10^{-8}$

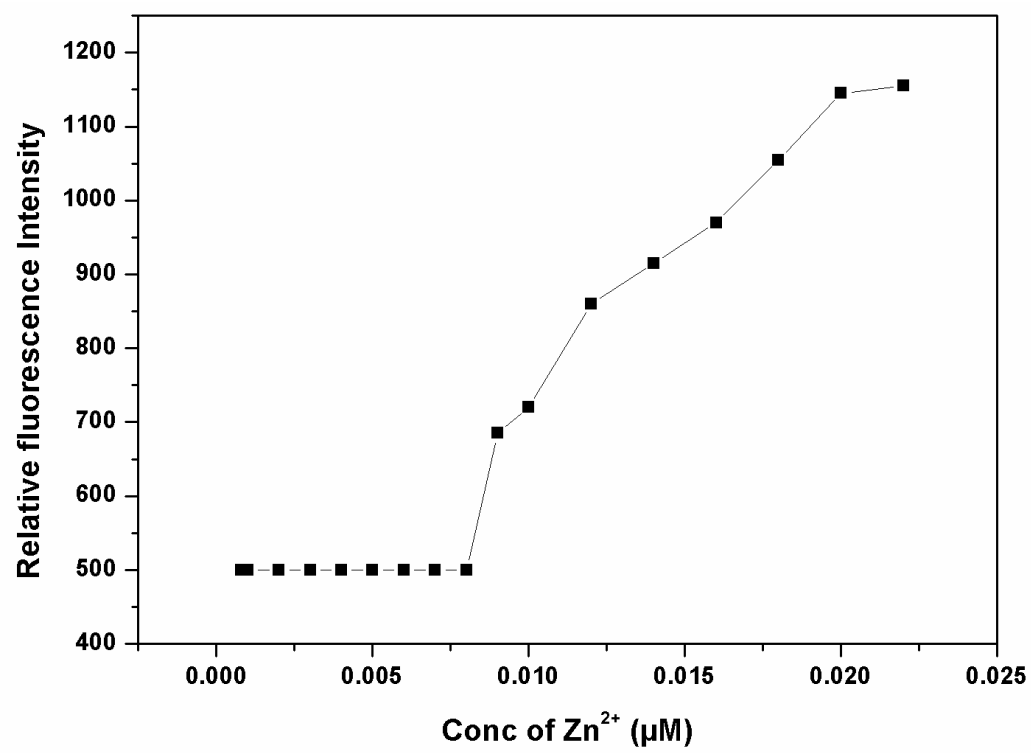

Fig-S10: Plot of fluorescence emission intensity ratio (I_{412}/I_{515}) *vs* low level concentration of zinc ions

Figure-S11 : DFT optimized geometries and distance between two pyrene rings in PDP-1, PDP-1+ $Zn^{2+}$and PDP-1 + Cu^{2+}

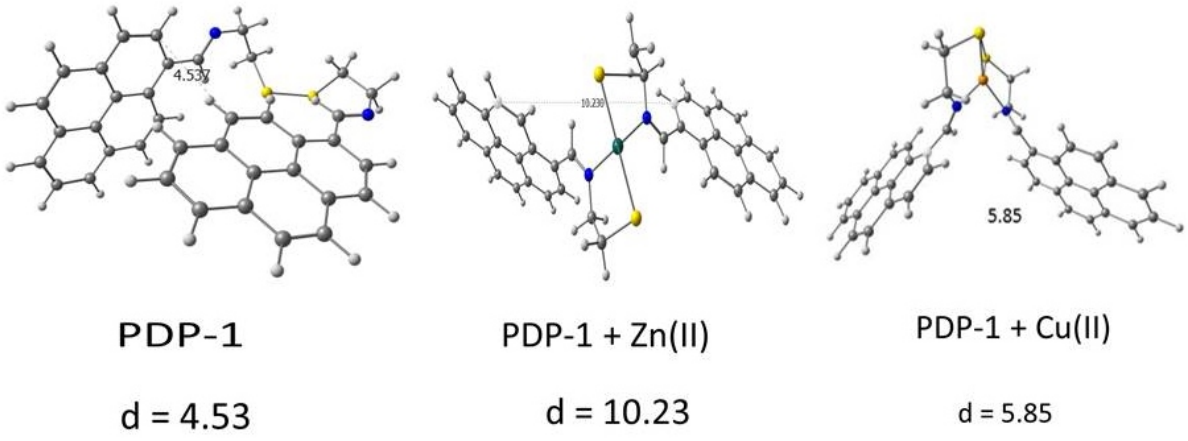

Table S1: **Determination of Zn^{2+} in drinking water, tap water and river water samples with PDP-1.**

Sample	Zn^{2+} added (μgL^{-1})	Zn^{2+} found (μgL^{-1})	Recovery (%)
Drinking water			
A	0	-	-
B	50	$50.06^{a} \pm 0.01^{b}$	98.9
C	100	$100.09^{a} \pm 0.03^{b}$	99.0
Tap water			
A	0	-	-
B	50	$50.02^{a} \pm 0.05^{b}$	99.7
C	100	$100.00^{a} \pm 0.07^{b}$	99.56
River water			
A	0	-	-
B	50	$50.09^{a} \pm 0.015^{b}$	97.8
C	100	$100.04^{a} \pm 0.06^{b}$	97.91
Human urine			
A	0	-	-
B	50	$49.99^{a} \pm 0.02^{b}$	100
C	100	$50.10^{a} \pm 0.01^{b}$	100.2

[a] Average of 3 measurements. [b] Standard deviation.

Table S2: **Determination of PPi ions in drinking water, tap water and river water samples with PDP-1+ Zn(II) .**

Sample	PPi added (μgL^{-1})	PPi found (μgL^{-1})	Recovery (%)
Drinking water			
A	0	-	-
B	50	$49.98^{a} \pm 0.01^{b}$	99.8
C	100	$99.97^{a} \pm 0.05^{b}$	99.97
Tap water			
A	0	-	-
B	50	$50.11^{a} \pm 0.04^{b}$	100.2
C	100	$101.00^{a} \pm 0.03^{b}$	101.0
River water			
A	0	-	-
B	50	$49.99^{a} \pm 0.02^{b}$	99.98
C	100	$100.00^{a} \pm 0.02^{b}$	100
Human urine			
A	0	-	-
B	50	$50.03^{a} \pm 0.021^{b}$	100.10
C	100	$50.06^{a} \pm 0.01^{b}$	100.14

[a] Average of 3 measurements. [b] Standard deviation.

References:

1. V. Bhalla, A. Gupta, M. Kumar., Chem. Commun.,2012,48, 11862.