Multifunctional metallo-supramolecular interlocked hexagonal microstructures for the detection of lead and thiols in water

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EXPERIMENTAL SECTION

Measurements and Methods

Chemicals and solvents (reagent grade) were obtained from common suppliers such as Sigma-Aldrich, S D Fine-Chem Limited (SDFCL), Spectrochem and were used without further purification, unless otherwise stated. All reactions were performed under N_2. N-Methyl-2-pyrrolidone (NMP) was dried over 4Å molecular sieves. THF, DMSO and CH_3CN solvents were of HPLC grade. Deionized water was obtained from ULTRA UV/UF Rions Lab Water System Ultra 370 series device.

Chromatography

Chromatographic purification was performed with silica gel 60-120 mesh. TLC was performed on aluminium sheets coated with silica gel 60 F254 (Merck, Darmstadt).

NMR Spectroscopy

^1H and ^{13}C NMR spectra were recorded on a BRUKER Biospin AVANCE-III FT-NMR HD-500 spectrophotometer using $CDCl_3$ or DMSO(d_6) as solvent. The peak values were obtained as ppm (δ), and referenced to tetramethylsilane (TMS) for ^1H NMR spectroscopy and the residual solvent signal for ^{13}C NMR spectroscopy. Data are reported as follows: chemical shifts in ppm, coupling constant J in Hz; multiplicity (s = singlet, bs = broad singlet, t = triplet, q = quartet, m = multiplet). Concentration based ^1H NMR spectroscopic titration of **PDI-HQ** and ^1H NMR spectroscopic titration of **PDI-HQ** against Pb^{2+} were performed in DMSO(d_6)-H_2O (9:1 v/v) on Bruker-AVANCE-II FT-NMR AL400 spectrometer. All data were then processed in delta

software to draw the stacking spectra of **PDI-HQ** and **PDI-HQ** + Pb^{2+} complex at different concentrations.

UV-Vis and Fluorescence Spectroscopy measurements

The absorption spectra were recorded on SHIMADZU-2450 spectrophotometer equipped with a Peltier system to control the temperature. Quartz cells of 1 cm in length were used for sample measurements. The spectral bandwidth and the scan rate were fixed at 2 nm and 140 nm min^{-1}, respectively. Fluorescence titrations were performed on a CHRONOS-BH and PerkinElmer LS-55 fluorescence spectrophotometers (slit width: excitation = 10 nm, emission = 2.5 nm) with excitation at 490 nm, unless otherwise stated. Quartz cells of 1 cm in length were used for sample measurements. The concentration of HEPES buffer (pH 7.2) was 0.01 M. Stock solutions for various measurements of **PDI-HQ** were prepared in CH_3CN and DMSO. For experiments with **PDI-HQ**, we have taken 3 mL of the solution that contains 30 µL **PDI-HQ** in acetonitrile and 2.97 mL of HEPES-buffer (0.01 M, pH = 7.2) in cuvette. Typically aliquots of freshly prepared standard solutions (10^{-1} M to 10^{-3} M) of Ag^{+}, Mg^{2+}, Cs^{+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+}, K^{+}, Mn^{2+}, Hg^{2+}, Sr^{2+}, Cd^{2+}, Zn^{2+}, Li^{+}, Cu^{2+} and Ba^{2+} as perchlorate or nitrate salts, unless otherwise stated, were prepared in deionized Millipore water and were diluted as required. The stock solution of **PDI-HQ**–Pb^{2+} was prepared by mixing of **PDI-HQ** and Pb^{2+} (1:30) in 99.9% HEPES-buffer (0.1% CH_3CN) (0.01 M, pH = 7.2). Typically aliquots of freshly prepared standard solutions (10^{-1} M to 10^{-3} M) of Cl^{-}, $H_2PO_4^{-}$, HPO_4^{2-}, I^{-}, NO_2^{-}, NO_3^{2-}, F^{-}, Br^{-}, CO_3^{2-}, ClO_4^{-}, CN^{-}, OH^{-}, AcO^{-}; thiols viz. propanethiol, Cys, bovine serum albumin (BSA), $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-} and $S_2O_5^{2-}$ in deionized Millipore water were used to record UV-Vis and fluorescence spectra.

IR Spectroscopy and Mass Spectrometry

Fourier transform infrared (FT-IR) spectra were recorded on PerkinElmer 92035 spectrometer. High resolution mass spectra (HRMS) results were recorded on a BRUKER DALTONIK micrOTOF-Q11 spectrometer.

Dynamic Light Scattering Measurements

DLS measurements were performed at (25.0±0.1) ^{o}C by using a light-scattering apparatus (Zetasizer Nano ZS Malvern Instrument). The stock solutions of **PDI-HQ** (1 mM, CH_3CN) and

water were filtered through Millipore membrane filter (Acrodisc syringe filter, 0.45 μm Supor membrane) before measurements to remove interfering impurities. Solutions of **PDI-HQ** in acetonitrile and its mixtures with water or solutions of **PDI-HQ** in $CH_3CN:H_2O$ (0.1:99.9, v/v) + Pb^{2+} were prepared. 2 mL of each of these solutions was taken in glass cuvette to record the DLS spectrum. The samples were thermally equilibrated for 10 min before each measurement, and an average of 10 measurement runs were considered to be data. The temperature was controlled to an accuracy of ±0.1 °C using an inbuilt Peltier device. Data was analyzed using the standard algorithms.

Microscopic Measurements

Field-emission scanning electron microscopic (FE-SEM) measurements were performed on a JEOL JSM-6610LV (ZEISS SUPRA^{TM}55) operating at an acceleration voltage of 10 kV with a tungsten filament as the electron source. High-resolution transmission electron microscopic (HR-TEM) images were obtained with a JEOL JEM-2100 electron microscope operating at an acceleration voltage of 200 kV. The solutions prepared for DLS experiments were used for SEM and TEM. 5 μL of each of the solution was added on the pre-cleaned surface of the separate glass slide using drop cast method and was allowed to dry in the incubator at 25 ^{o}C. SEM images were taken after sputtering with Au. For preparation of samples for recording TEM images, 1 μL of the solution was added on carbon coated Cu-grid which was allowed to dry in the incubator at 25 ^{o}C.

Detection limit

The detection limit was calculated based on the absorbance or fluorescence titration. To determine the S/N ratio, the absorbance or emission intensity of **PDI-HQ** (10 μM) or **PDI-HQ**+Pb^{2+} was measured by 3 times and the standard deviation of blank solution (without addition of Pb^{2+} for **PDI-HQ** or without addition of cysteine for **PDI-HQ**+Pb^{2+}) measurements was determined. The detection limit was then calculated with the equation

Detection limit = $3\sigma bi/m$

Where, σbi is the standard deviation of blank solution (without addition of Pb^{2+} for **PDI-HQ** or without addition of cysteine for **PDI-HQ**+Pb^{2+}) measurements; m is the slope between intensity versus sample concentration.

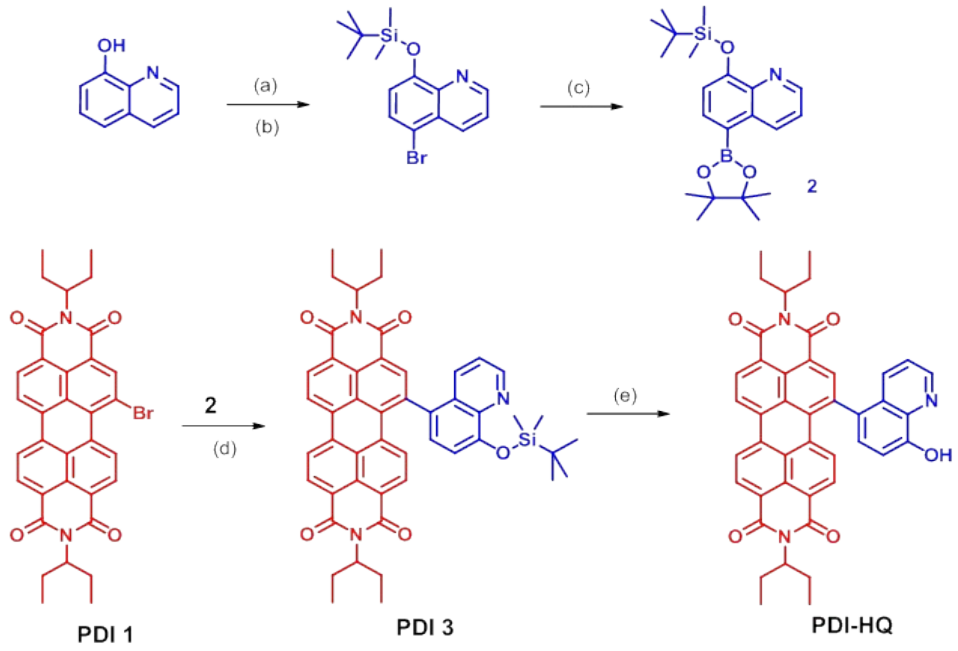
Urine sample

A real urine sample of a medically fit person was used for the experiments. For experiments with urine sample we have taken 3 mL of the solution that contains 30 µL **PDI-HQ** in acetonitrile, 1.5 mL of urine and 1.47 mL of HEPES-buffer (0.01 M, pH = 7.2) in cuvette and fluorescence value obtained was compared with the calibration curve to quantify the Pb^{2+} ions.

Data Analysis

All absorption and fluorescence scans were saved as ACSII files and further processed in Excel™ to produce all graphs shown in the chapter. The spectral data were analysed through curve fitting procedures by using non-linear regression analysis SPECFIT 3.0.36 to determine the stability constants and the distribution of various species.

MATERIAL SYNTHESIS

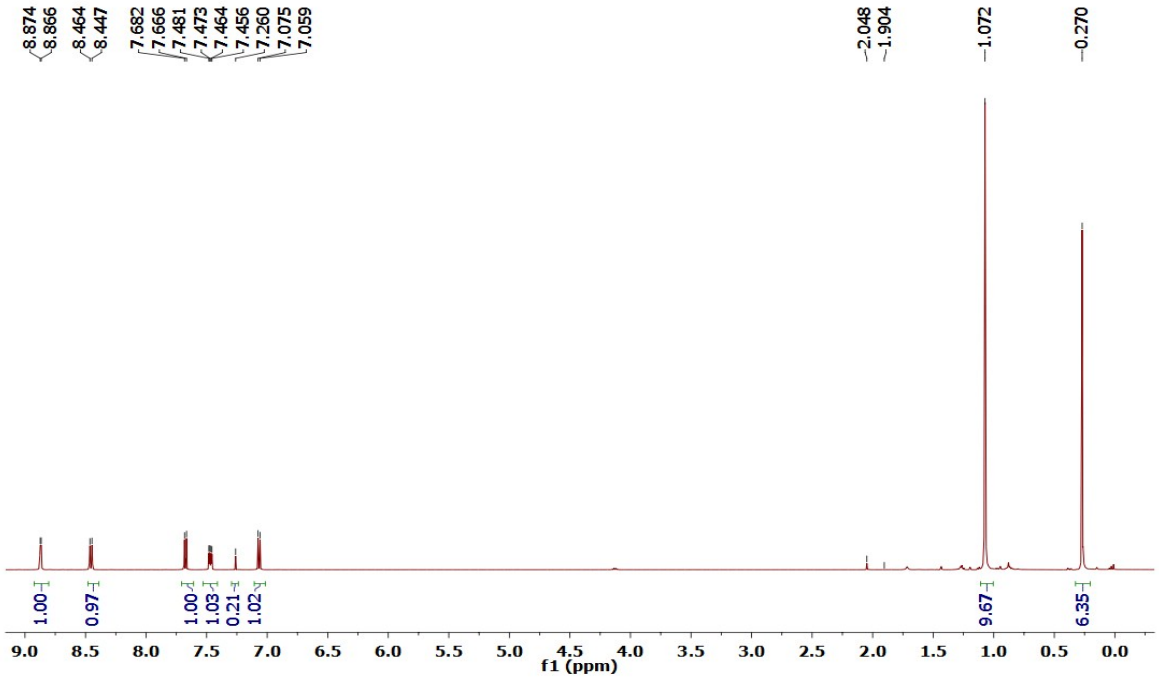


Scheme 1: Synthesis and chemical structure of **PDI-HQ**.

8-hydroxyquinoline (5 g, 0.034 mmol) was taken in dicholormethane (150 mL, dry) and tert-butyl dimethylsilyl chloride (5.7 g, 0.038 mol), imidazole (2.46 g, 0.036 mol) were added all at once. The reaction mixture was stirred for 48 hour at RT. After this time interval, the reaction mixture was quenched with 0.1 N HCl solutions, washed with brine solution and crude product silylated 8-hydroxyquinoline was

concentrated under high vacuum. Compound silylated 8-hydroxyquinoline was Isolated as colorless liquid, yield is 80.1% (7.2 g, 0.025 mol); R_f = 0.3 (Et_2O:hexane 2:98 v/v).

Crude product (5.0 g, 0.019 mol) was dissolved in dichloromethane (120 mL, dry) under nitrogen atmosphere. Bromine (0.49 mL, 0.019 mol) in dichloromethane (20 mL, dry) was added drop-wise at RT under nitrogen atmosphere. The reaction mixture was stirred for 10 h at RT. After this interval, quenched the reaction mixture with saturated solution of sodium thiosulfate, washed with brine and crude product was concentrated under high vacuum. The crude product was purified by column chromatography (ethyl acetate:hexane, 1:99 v/v) to obtained compound **2** as pale yellow liquid; Yield is 92% (6.0 g, 0.017 mol); R_f = 0.6 (Ethyl acetate:hexane 1:99); HRMS (TOF, ESI) *m/z* found 339.04; calcd. 340.06 for $C_{12}H_{20}BrNOSi$; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.27 (s, 6H), 1.07 (s, 9H), 7.07 (d, J = 8.0 Hz, HQ-H7, 1H), 7.47 (dd, J_1 = 8.5 Hz, J_2 = 4.0 Hz, HQH-3, 1H), 7.67 (d, J = 8 Hz, HQH-6, 1H), 8.45(d, J = 8.5 Hz, HQH-4, 1H), 8.87(d, J = 4 Hz, HQH-2, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = -3.8, 19.0, 26.0, 112.4, 118.4, 122.4, 128.6, 130.6, 135.4, 143.0, 149.1, 153.0 ppm.



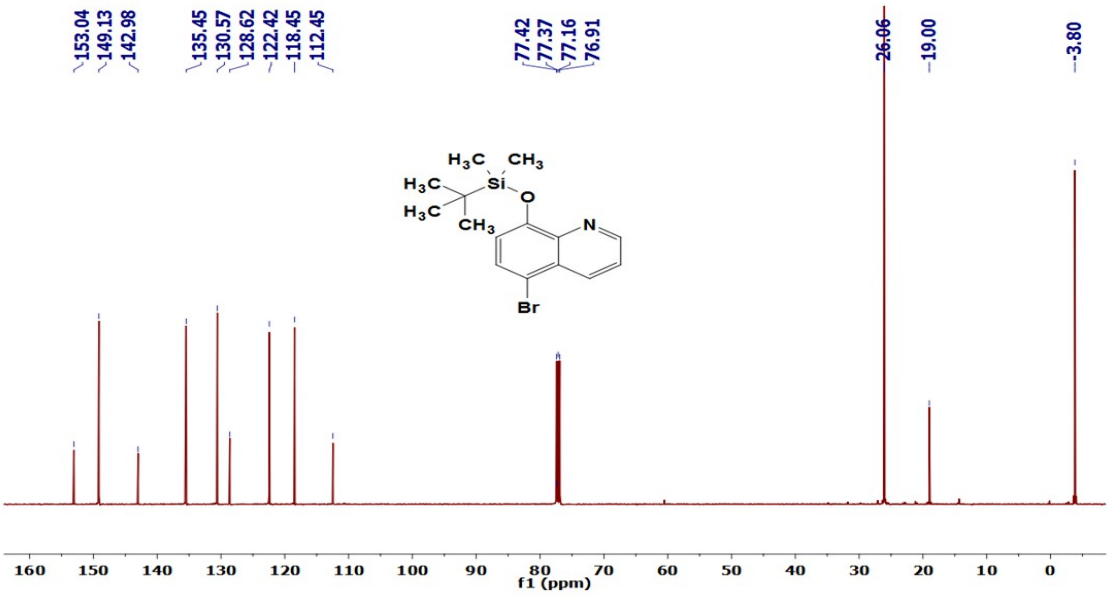
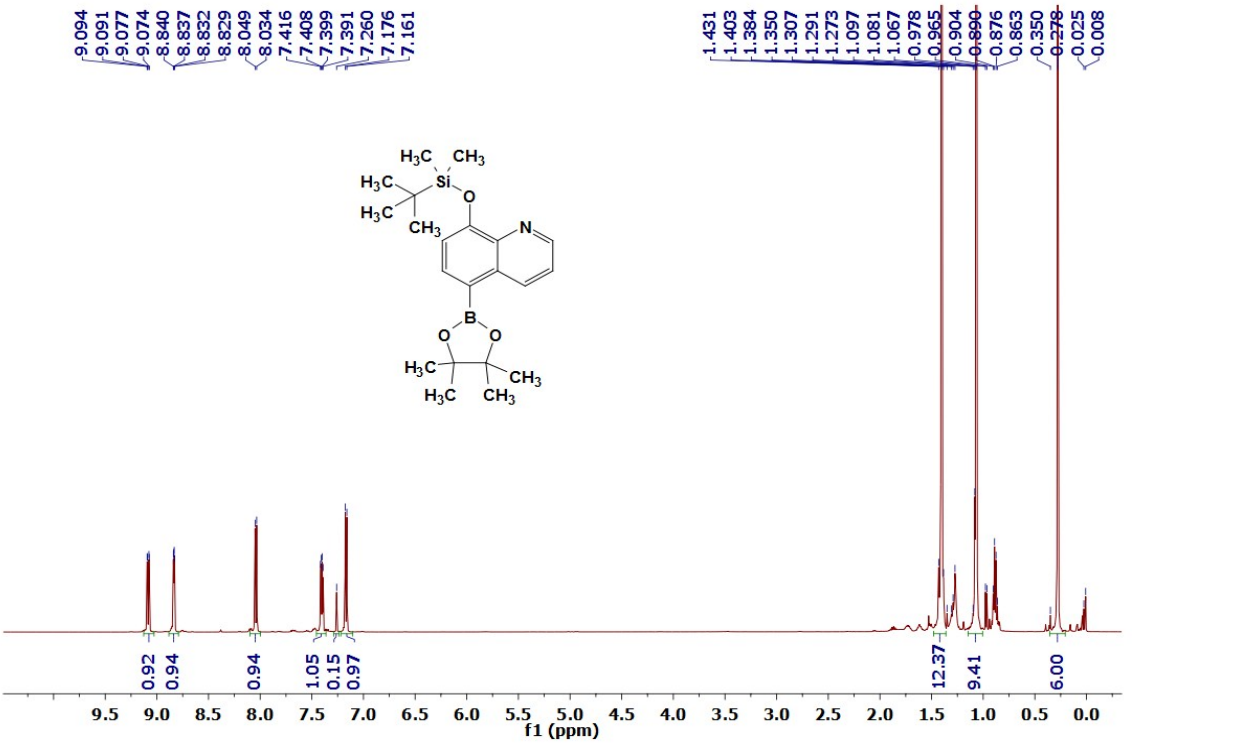


Figure S1: ^{1}H and ^{13}C NMR spectra of compound **4**.

5-Bromo-8-(*tert*-butyldimethylsilyloxy) quinoline (**4**) (5.0 g, 14.8 mmoles) and catalyst $PdCl_2(PPh_3)_2$ (0.5 g, 0.71 mmoles) were dissolved in anhydrous 1,4-dioxane (50 mL) under N_2 at RT. Subsequently, triethylamine (7.75 mL, 55.56 mmoles) and bis(pinacolatoboron) (5.39 g, 21.2 mmoles) were added to the reaction mixture and stirred overnight at 90^0 C. The reaction mixture was cooled and poured into water (100 mL), extracted with chloroform and concentrated under high vacuum. The residue was column chromatographed (ethyl acetate/hexane 4:96) to isolate **3** as a pale yellow solid, yield 3.5 g (9.08 mmoles, 61.2%); R_f = 0.5 (ethyl acetate/hexane 4:96); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.27 (s, 6H), 1.06 (s, 9H), 1.39 (s, 12H), 7.20 (d, J = 7.5 Hz, 1H), 7.39 (dd, J_1 = 8.5 Hz, J_2 = 4.0 Hz, HQH-3, 1H), 8.03 (d, J = 7.5 Hz, HQH-6, 1H), 8.83 (dd, J_1= 4.0 Hz, J_2 = 1.5 Hz, HQH-4, 1H), 9.08 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, HQH-2, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = -3.70, 19.10, 22.79, 25.11, 26.12, 31.73, 34.82, 83.73, 117.34, 121.61, 133.93, 136.63, 137.44, 142.15, 148.10, 156.18 ppm; HR-MS: *m/z* found 386.2332 (M^++1); calcd. 385.2245 for [$C_{21}H_{32}BNO_3Si$].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9.091
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9.074
8.840
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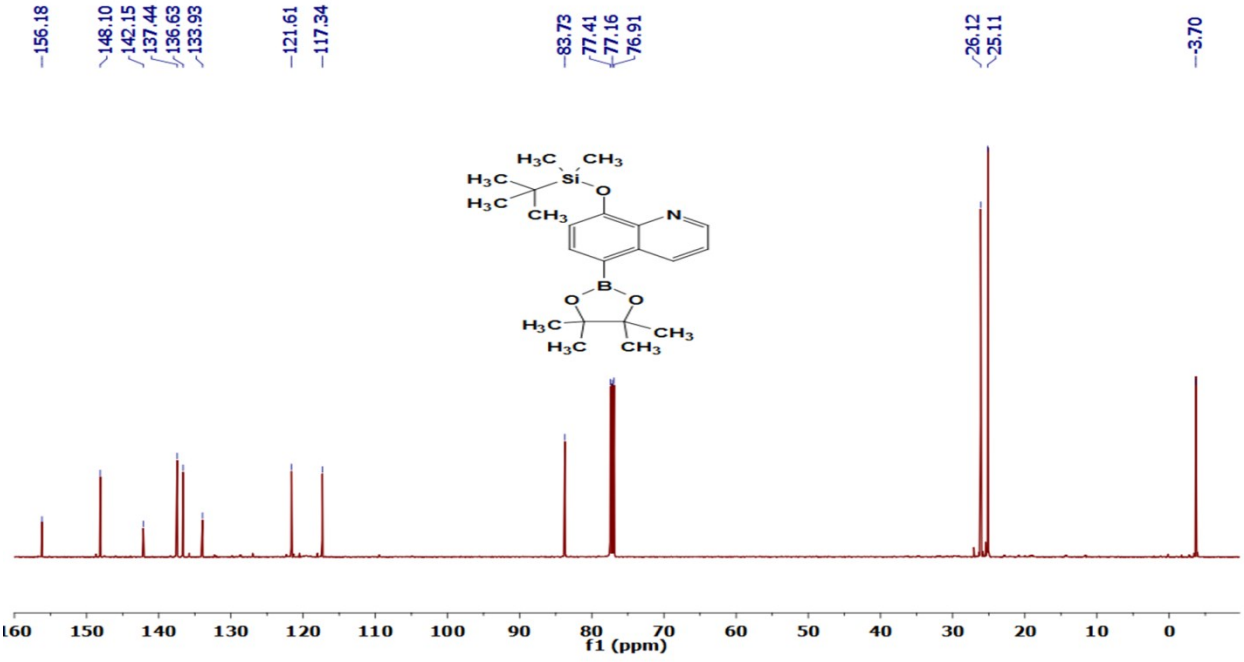
7.391
7.260
7.176
7.161
1.431
1.403
1.384
1.350
1.307
1.291
1.273
1.097
1.081
1.067
0.978
0.965
0.904
0.890
0.876
0.863
0.350
0.278
0.025
0.008
0.92
0.94
0.94
1.05
0.15
0.97
12.37
9.41
6.00
f1 (ppm)


156.18
148.10
142.15
137.44
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77.41
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25.11
3.70
f1 (ppm)

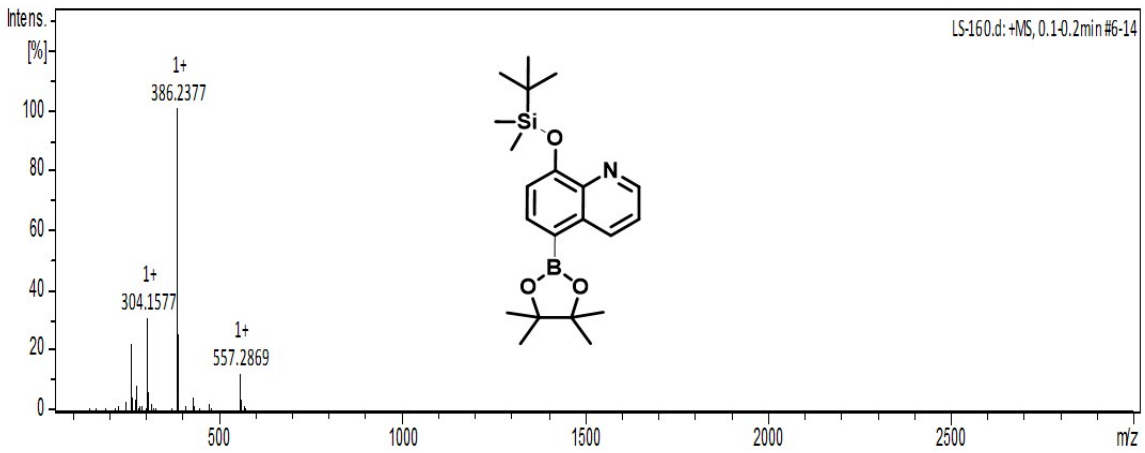
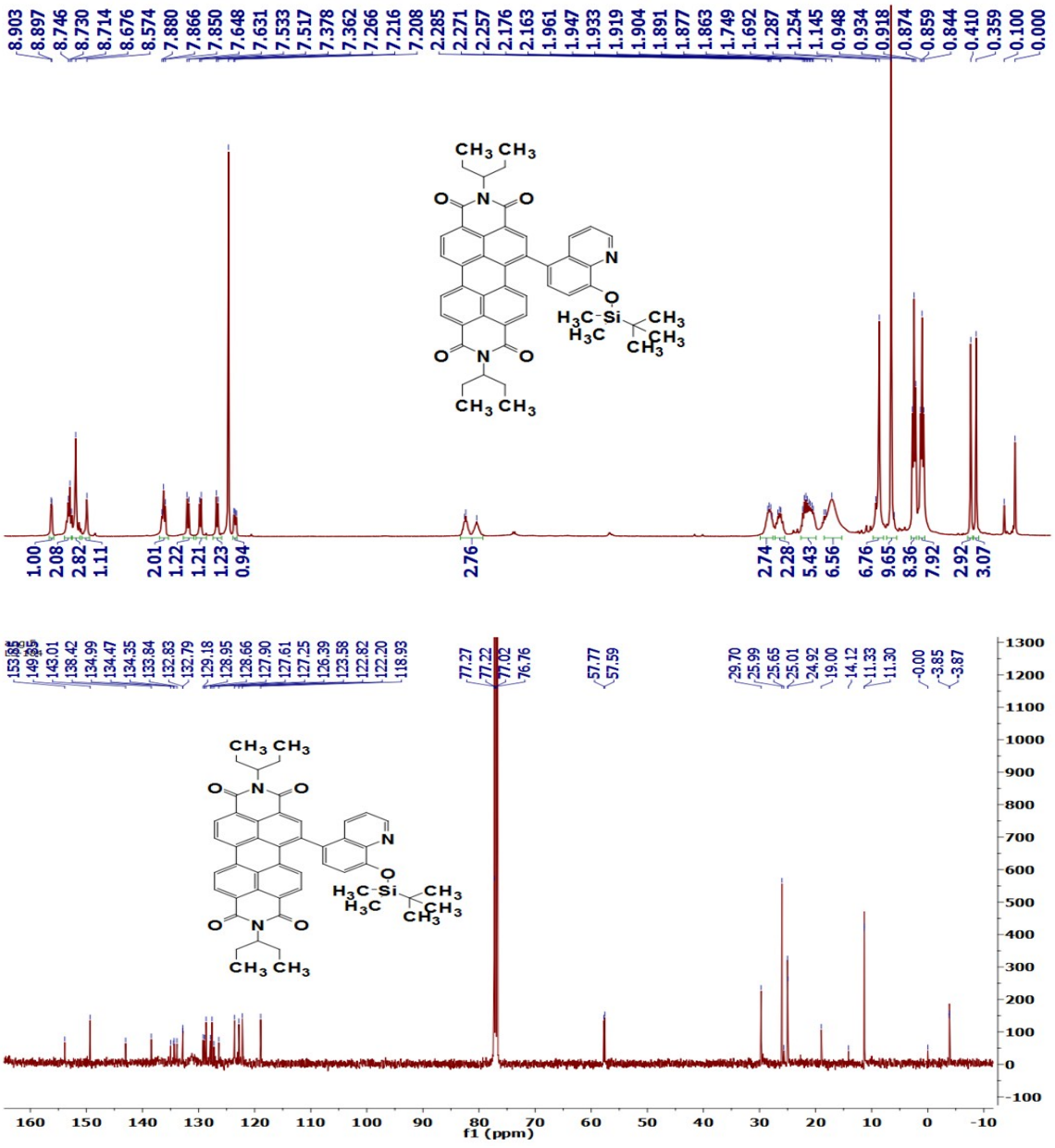


Figure S2: ^{1}H, ^{13}C NMR and Mass spectra of compound **3**.

Synthesis of PDI 1

PDI 2 (1.0 gm, 1.64 mmoles) and Na_2CO_3 (1.77 g, 16.70 mmoles) were dissolved in toluene (50 mL), ethanol (15 mL) and water (25 mL) mixture and solution was purged with N_2 for 10 min. Subsequently, compound **3** (0.94 g, 2.44 mmoles) and catalyst $Pd(PPh_3)_4$ (0.37 g, 0.32 mmoles) were added to the reaction mixture and stirred at 70 ^{0}C for 10 h. After this time interval the reaction mixture was evaporated under vacuum. The remaining residue was poured into water, extracted with chloroform, dried and concentrated under vacuum. The residue was further purified by column chromatography (SiO_2, $CHCl_3$/hexane 10:90) to isolate PDI-SiHQ as a red solid, yield 600 mg (0.762 mmol, 46.3%); R_f = 0.45 ($CHCl_3$/hexane 10:90); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.36 (s, 3 H), 0.41 (s, 3H), 0.86 (t, J = 7.5 Hz, 6H), 0.93 (t, J = 7.5 Hz, 6H), 1.14 (s, 9H), 1.85-1.97 (m, 4H), 2.15-2.30 (m, 4H), 4.97-5.09 (m, 2H), 7.20 (dd, J_1 = 8.5 Hz, J_2 = 4.0 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.85-7.88 (m, 2H), 8.57 (s, 1H), 8.64-8.76 (m, 4H), 8.90 (d, J = 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 153.99, 149.49, 143.15, 138.57, 135.13, 134.61, 134.50, 133.98, 132.97, 132.93, 129.32, 129.10, 128.80, 128.05, 127.75, 127.40, 126.53, 123.72, 122.96, 122.34, 119.07, 77.37, 57.91, 57.73, 29.84, 26.13, 25.16, 25.06, 15.47, 11.44, -3.70, -3.73 ppm.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1.00 2.08 2.82 1.11 2.01 1.22 1.21 1.23 0.94 2.76 2.74 2.28 5.43 6.56 6.76 9.65 8.36 7.92 2.92 3.07
153.85 149.85 143.01 138.42 134.99 134.47 134.35 133.84 132.83 132.79 129.18 128.95 128.66 127.90 127.61 127.25 126.39 123.58 122.82 122.20 118.93
77.27 77.22 77.02 76.76 57.77 57.59 29.70 25.99 25.65 25.01 24.92 19.00 14.12 11.33 11.30 -0.00 -3.85 -3.87
f1 (ppm)

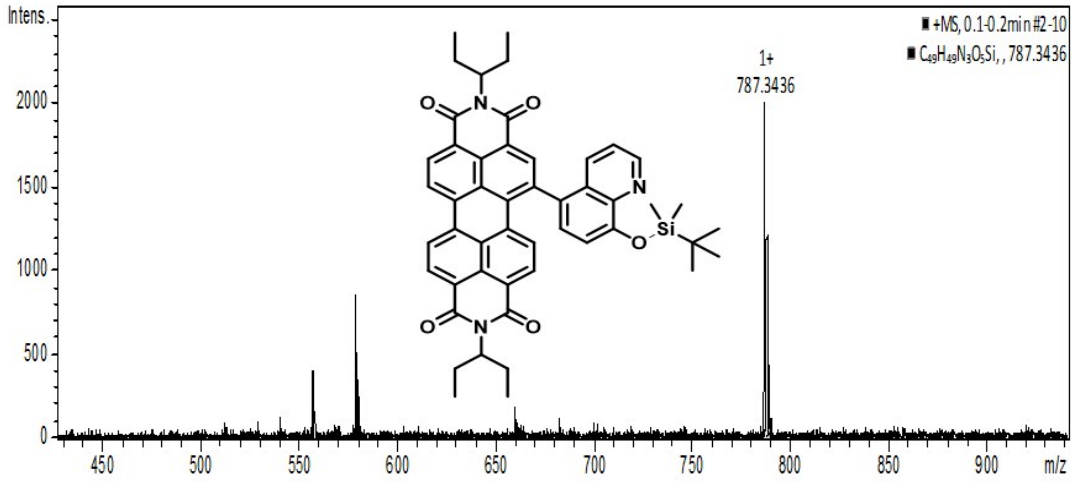


Figure S3: ^{1}H, ^{13}C NMR and Mass spectra of compound PDI **1**.

Synthesis of PDI-HQ

In a 50 mL round bottom flask, **PDI 1** (100 mg, 0.127 mmol) was dissolved in THF (10 mL). Then 1.0 M solution of *tert*-butyl ammonium fluoride in THF (15 mL) was added and mixture was stirred for 24 h at RT. After this interval, the solvent was removed and residue was dissolved in chloroform and washed with water. The organic solvent dried over Na_2SO_4 and solvent was removed by rotary evaporation. The crude product was purified by column chromatography (SiO_2, chloroform/ hexane) to isolate **PDI-HQ**, as a red solid (60 mg, 0.089 mmol, 70.2%), R_f = 0.4 (methanol/chloroform 0.5:9.5).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.86 (t, J = 7.5 Hz, 6H 2xCH_3 ethylpropyl), 0.93 (t, J = 7.5 Hz, 6H, 2xCH_3 ethylpropyl), 1.86-1.96 (m, 4H, 2xCH_2 ethylpropyl), 2.25-2.28 (m , 4H, 2xCH_2 ethylpropyl), 4.97-5.10 (m, 2H, 2xCH ethylpropyl), 7.27 (m, 1H, HQ), 7.38 (d, J = 8.0 Hz, 1H, HQ), 7.62 (d, J = 8.0 Hz, 1H, Perylene ArH), 7.69 (d, J = 8.0 Hz, 1H, HQ), 7.89 (dd, J_1 = 8.5 Hz, J_2 = 1.0 Hz, 1H, HQ), 7.92 (d, J = 8.0 Hz, 1H, Perylene ArH), 8.58 (s, 1H, Perylene ArH), 8.67-8.74 (m, 4H, Perylene ArH), 8.82 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, HQ, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 11.42, 11.46, 25.07, 25.16, 29.08, 57.74, 57.92, 111.27, 122.95, 123.75, 125.40, 127.38, 128.06, 128.72, 128.83, 129.07, 129.31, 130.79, 131.31, 133.52, 134.00, 134.48, 134.61, 135.09, 138.16, 139.19, 148.78, 153.28 ppm

Mass Spectrum: *m/z* found 674.2658 [M^++1]; calcd. 673.2577 for [$C_{43}H_{35}N_3O_5$]

UV-Vis (99.9% H_2O:CH_3CN): λ_{max} = 492 nm

Fluorescence (99.9% H_2O:CH_3CN): λ_{max} = 660 nm (weak band).

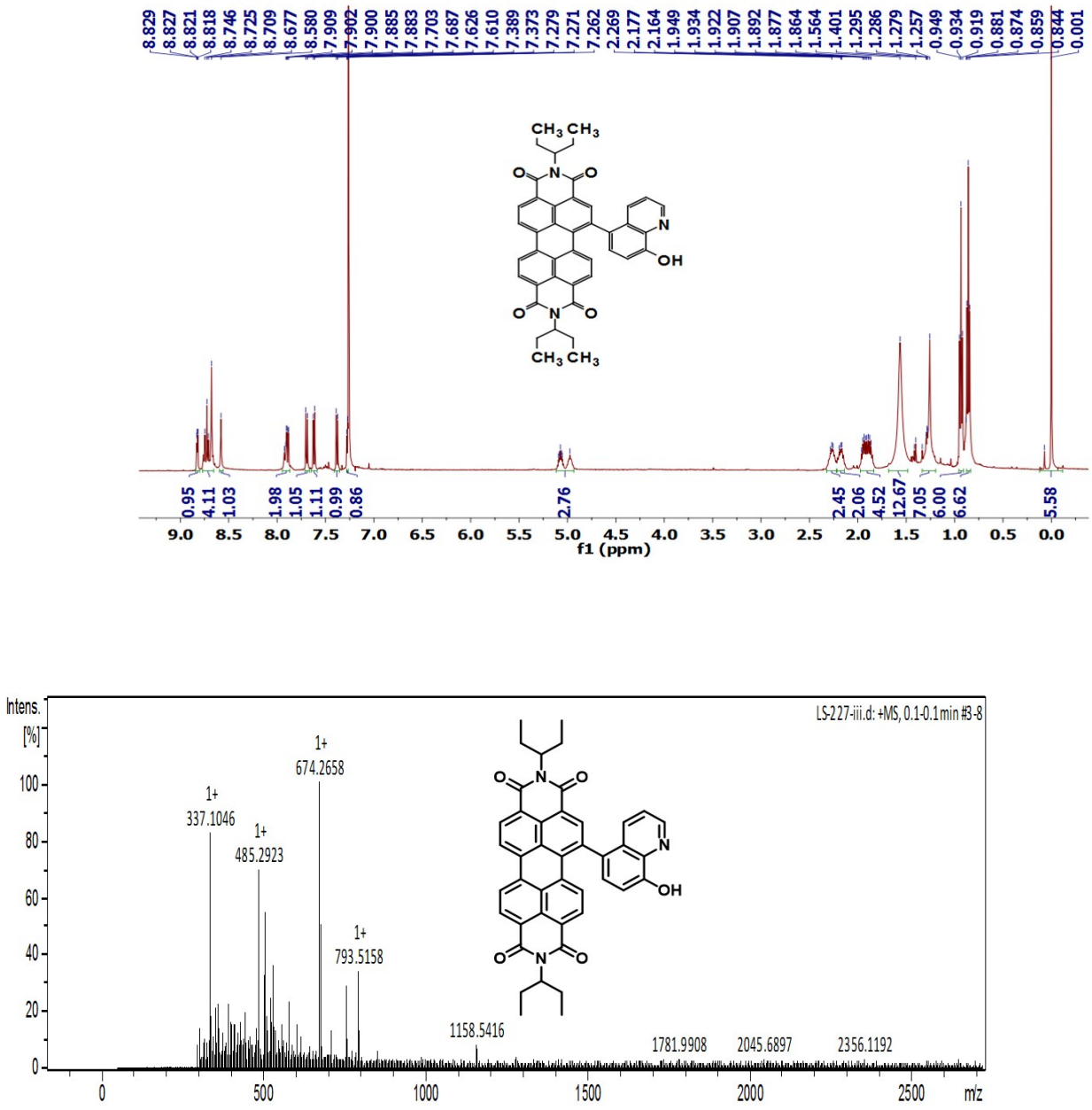


Figure S4: ^{1}H, ^{13}C NMR and Mass spectra of compound **PDI-HQ**.

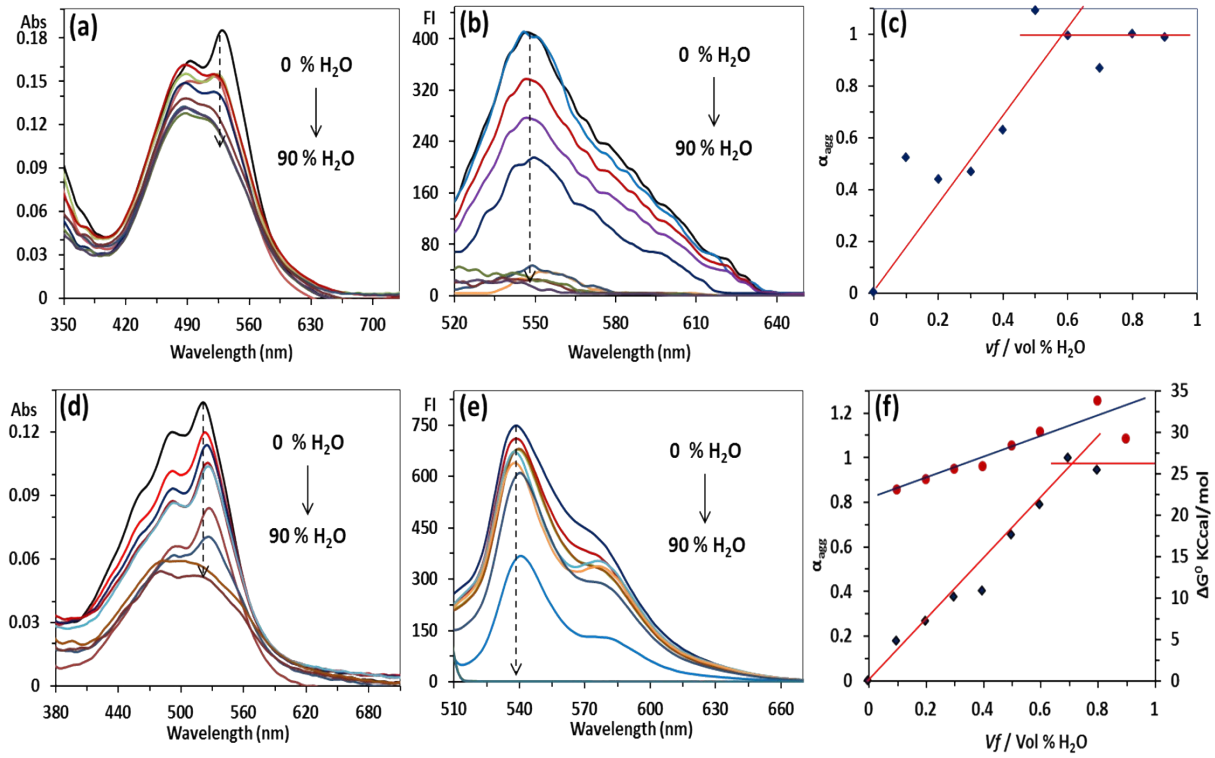


Figure S5. Absorption and emission changes in **PDI-HQ** (10 μM) after incremental addition of H_2O to (a,b) DMSO and (d,e) CH_3CN; Plot of degree of aggregation (α_{agg}) *vs.* water fraction in (c) DMSO and (f) CH_3CN. (Slit width Ex/Em = 15/9)

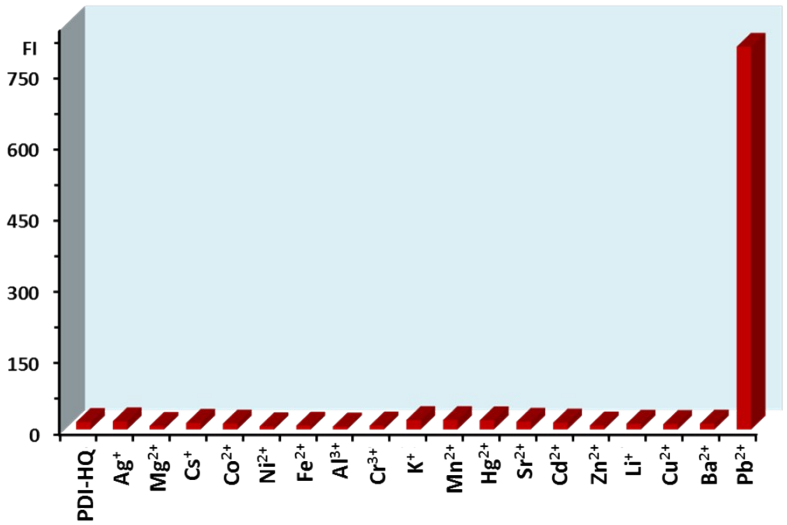


Figure S6. Fluorescence intensity changes as observed in **PDI-HQ** (10 μM) in the presence of various metal ions recorded in HEPES buffer (0.1% CH_3CN, pH 7.2).

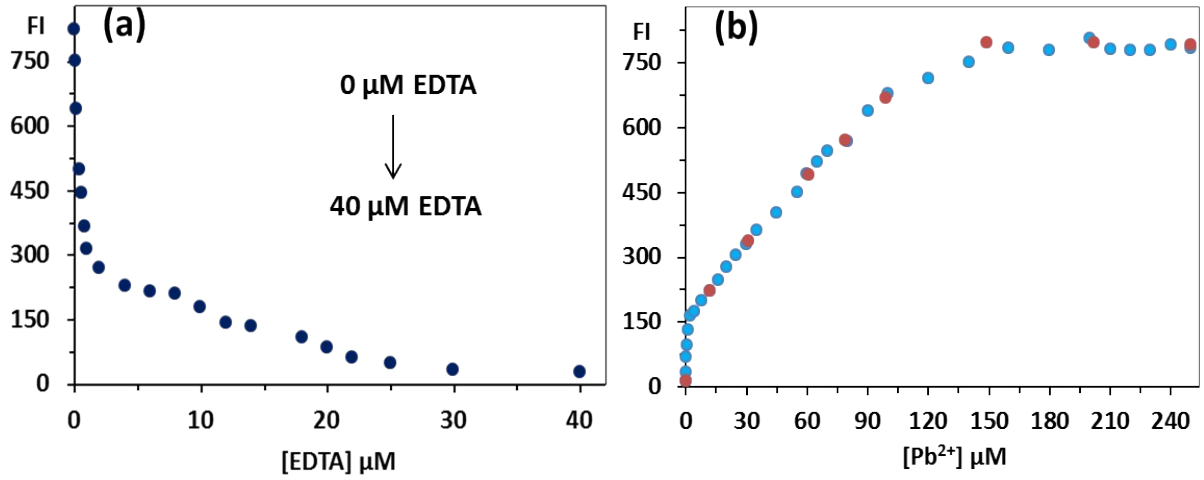


Figure S7. (a) Plot of fluorescence intensity of **PDI-HQ**–Pb^{2+} aggregates (1:30), HEPES buffer (0.1% CH_3CN, pH 7.2) on addition of EDTA; (b) Graph showing percentage recovery of Pb^{2+} ions in urine samples using calibration curve.

Table S1: Application of **PDI-HQ** in determination of Pb^{2+} ions in spiked urine samples along with percentage recovery values of Pb^{2+} ions in urine samples.

Sr. No.	Concentration of Pb^{2+} ions added (µM)	Concentration of Pb^{2+} ions obtained (µM)	Recovery of Pb^{2+} (%)
1	12	11.8	98.33
2	30	31	103.33
3	60	61	101.66
4	80	79	98.75
5	100	99	99.00
6	160	149	93.12
7	200	202	101.00
8	250	251	100.40

Table S2: Change in chemical shift (δ) of perylene P1-P6 protons and 8-hydroxyquinoline protons as observed in ^{1}H NMR titration of **PDI-HQ** with Pb^{2+} ions recorded in DMSO(d_6)/H_2O (9:1, v/v).

Equivalents of Pb^{2+}	P1[a] (Δδ)[b]	P2[a] (Δδ)[b]	P3[a] (Δδ)[b]	P4[a] (Δδ)[b]	P5[a] (Δδ)[b]	P6[a] (Δδ)[b]
1 equiv. (10µM)	7.558 (0.063)	7.758 (0.072)	8.539 (0.036)	8.600 (0.041)	8.902 (0.074)	8.932 (0.080)
2 equiv. (20µM)	7.543 (0.078)	7.731 (0.101)	8.530 (0.045)	8.590 (0.051)	8.875 (0.101)	8.915 (0.097)
3 equiv. (30µM))	7.504 (0.117)	7.692 (0.140)	8.505 (0.070)	8.565 (0.076)	8.854 (0.122)	8.882 (0.130)
4 equiv. (40µM)	7.461 (0.160)	7.652 (0.180)	8.477 (0.098)	8.537 (0.104)	overlap	overlap
5 equiv. (50µM)	7.364 (0.257)	7.567 (0.265)	8.407 (0.168)	8.472 (0.169)	8.698 (0.278)	8.720 (0.292)

Equivalents of Pb^{2+}	HQ-7[a] (Δδ)[b]	HQ-3[a] (Δδ)[b]	HQ-6[a] (Δδ)[b]	HQ-4[a] (Δδ)[b]	HQ-2[a] (Δδ)[b]	P7[a] (Δδ)[b]
1 equiv. (10µM)	7.287 (0.033)	7.350 (0.005)	7.637 (0.023)	7.907 (0.036)	8.862 (0.012)	8.299 (0.025)
2 equiv. (20µM)	7.271 (0.049)	7.346 (0.010)	7.628 (0.032)	7.895 (0.048)	8.857 (0.017)	8.292 (0.032)
3 equiv. (30µM))	7.243 (0.077)	7.338 (0.018)	7.606 (0.054)	7.870 (0.073)	8.839 (0.035)	8.276 (0.048)
4 equiv. (40µM)	7.224 (0.096)	7.330 (0.026)	7.580 (0.080)	7.842 (0.100)	overlap	8.259 (0.065)
5 equiv. (50µM)	7.175 (0.145)	7.310 (0.046)	7.509 (0.150)	7.782 (0.161)	8.823 (0.051)	8.218 (0.106)

[a]Chemical shift (δ) in ppm; [b]Change in chemical shift (Δδ) in ppm

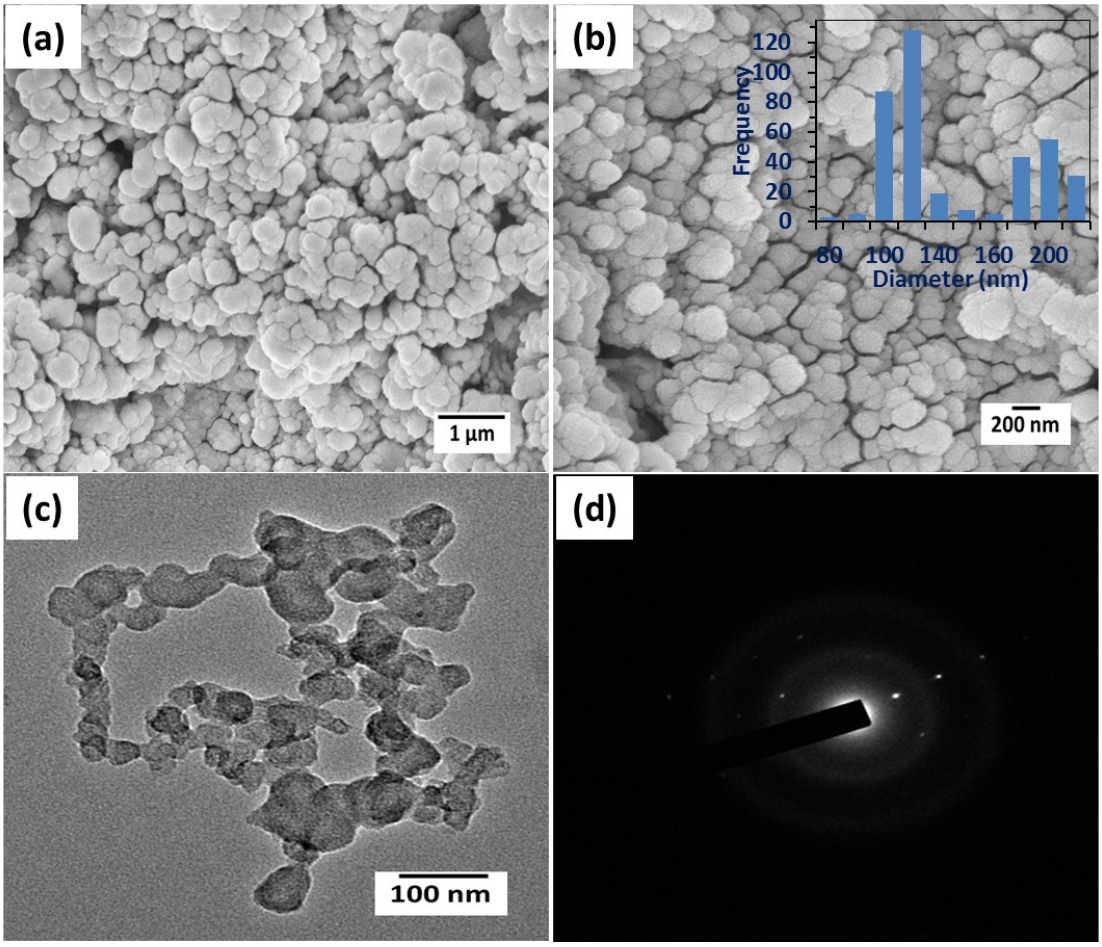


Figure S8. SEM (a-b) and TEM (c) micrographs of thin films obtained from drop cast of solution of **PDI-HQ** (10 µM) in water (0.1% CH_3CN) showing spherical morphology; (d) SAED pattern recorded in HRTEM.

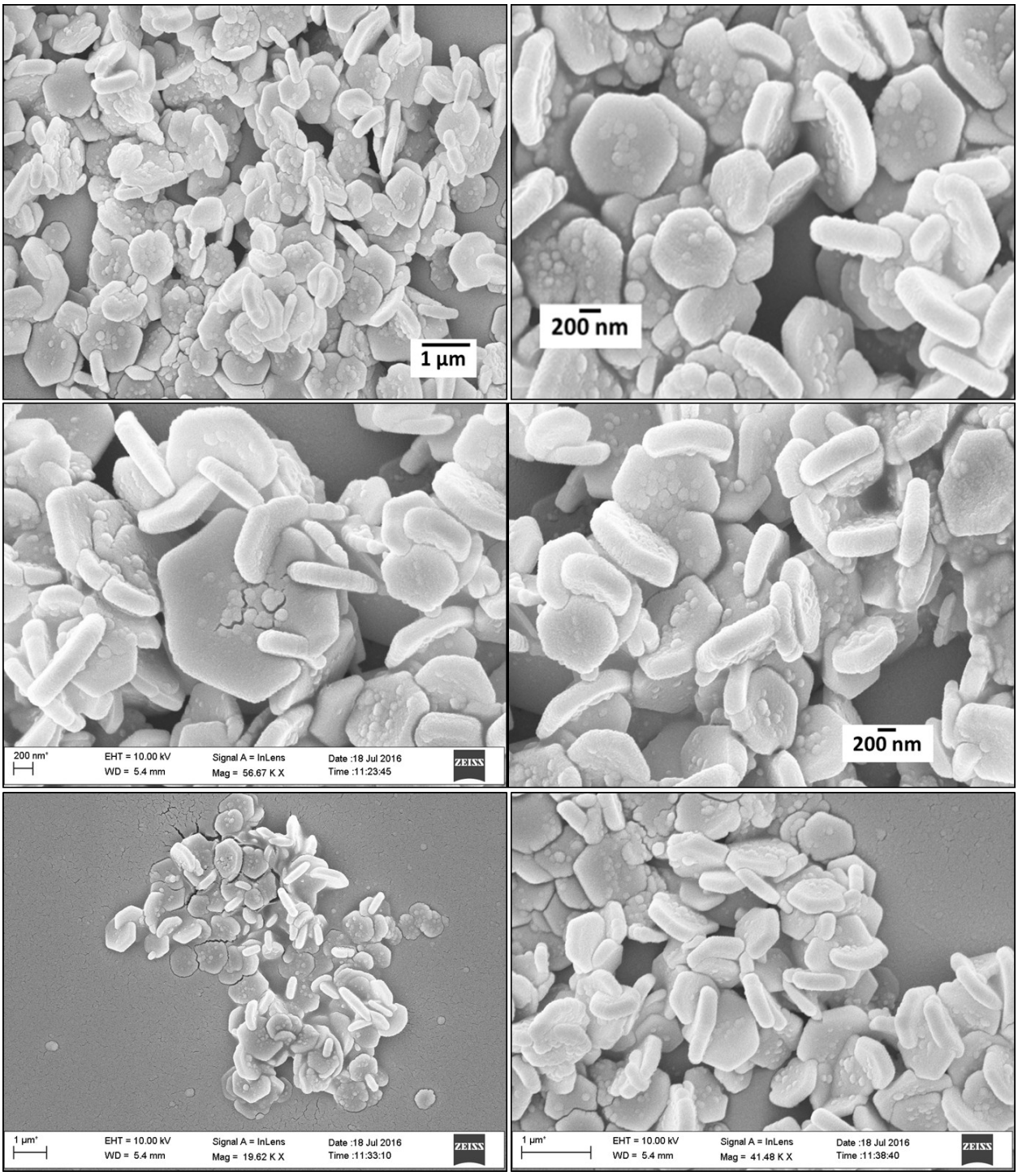
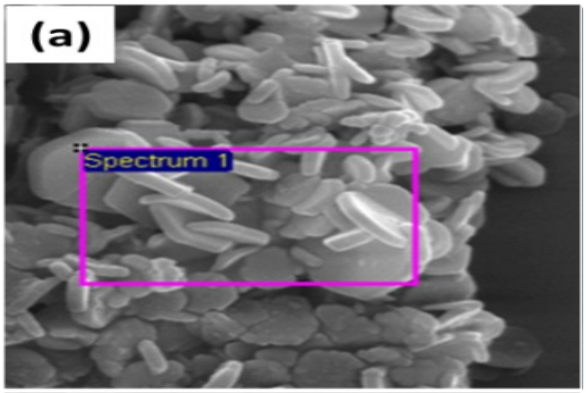
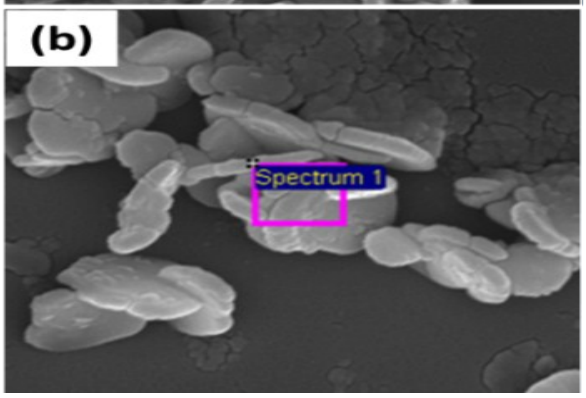


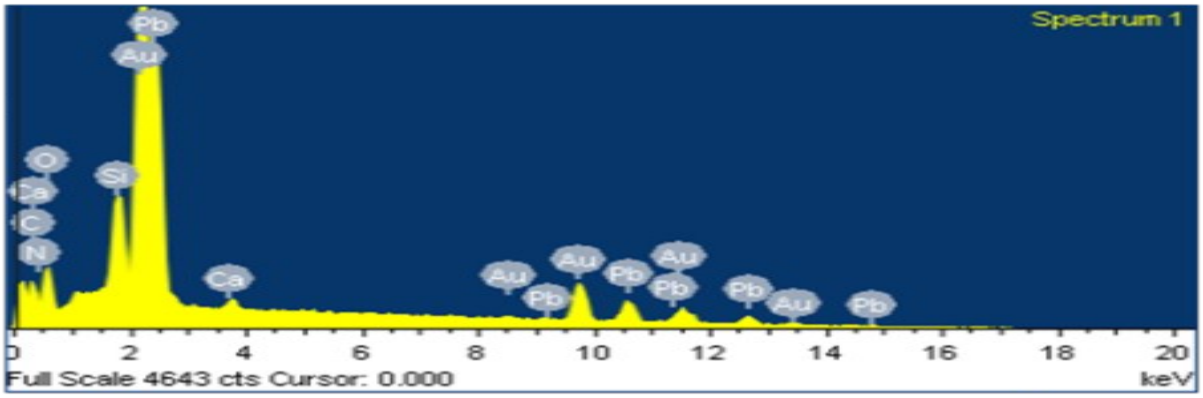
Figure S9. SEM micrographs of thin films obtained from drop cast of 6 µl solution of [**PDI-HQ** (10 µM) + $Pb(ClO_4)_2$ (300 µM)] in water (0.1% CH_3CN) showing interlocked hexagonal metallo-supramolecular self-assemblies



Element	Weight%	Atomic%
C K	11.21	41.81
N K	-0.44	-1.41
O K	13.38	37.47
Si K	3.37	5.37
Ca K	0.74	0.83
Au M	38.11	8.67
Pb M	33.63	7.27
Totals	100.00	



Element	Weight%	Atomic%
C K	13.79	34.10
N K	2.70	5.72
O K	20.60	38.25
Si K	13.83	14.63
Au M	35.89	5.41
Pb M	13.20	1.89
Totals	100.00	



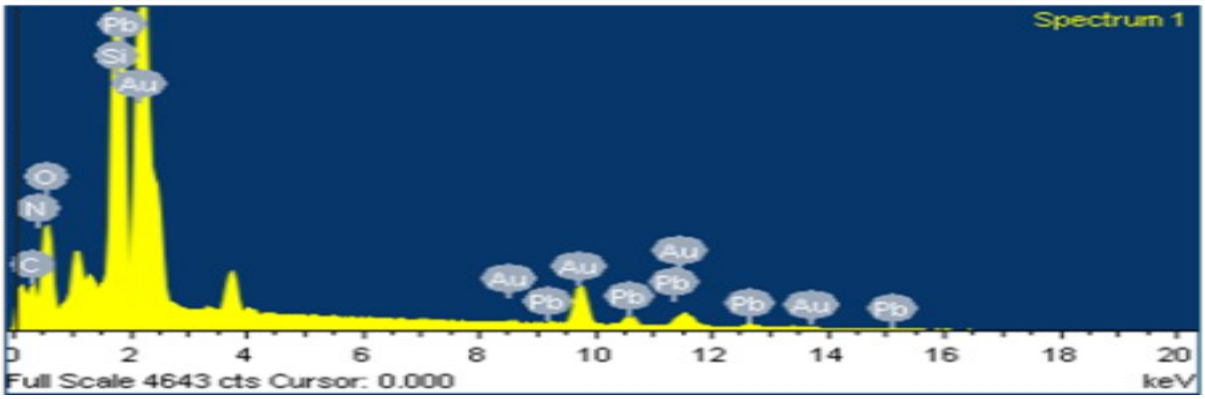


Figure S10. (a-b) EDAX spectrum of **PDI-HQ**–Pb^{2+} aggregates recorded on FESEM.

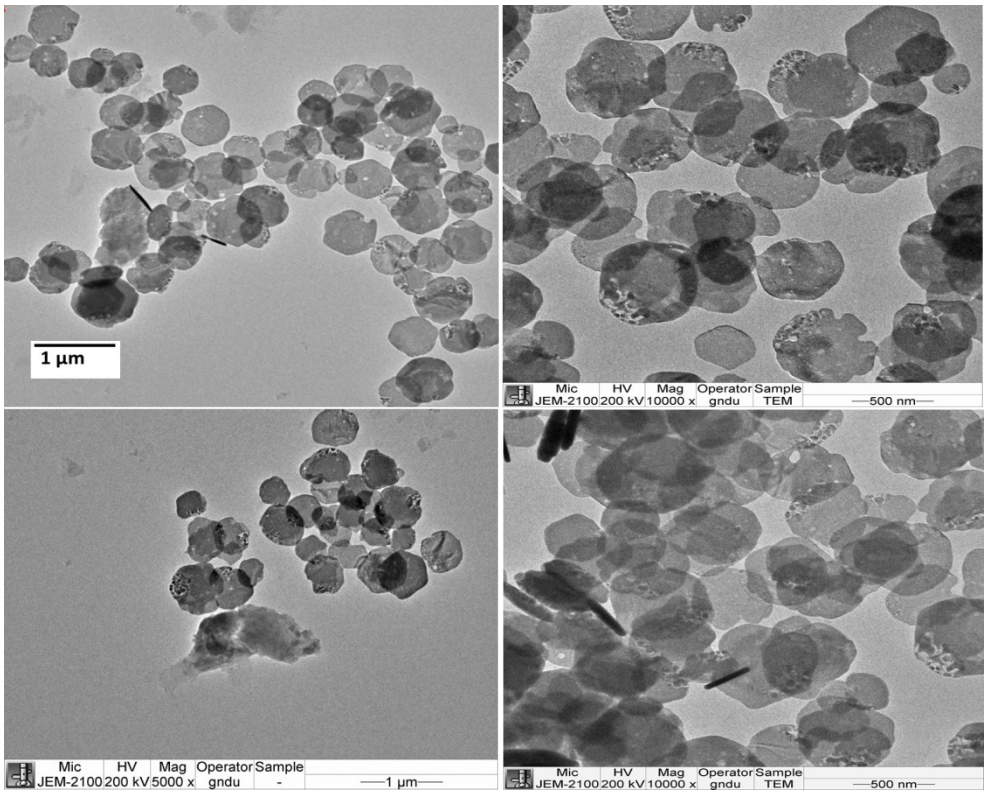


Figure S11. TEM micrographs of thin film obtained from drop cast of 6 µl solution of [**PDI-HQ** (10 µM) + $Pb(ClO_4)_2$ (300 µM)] in water (0.1% CH_3CN) showing interlocked hexagonal metallo-supramolecular self-assemblies.

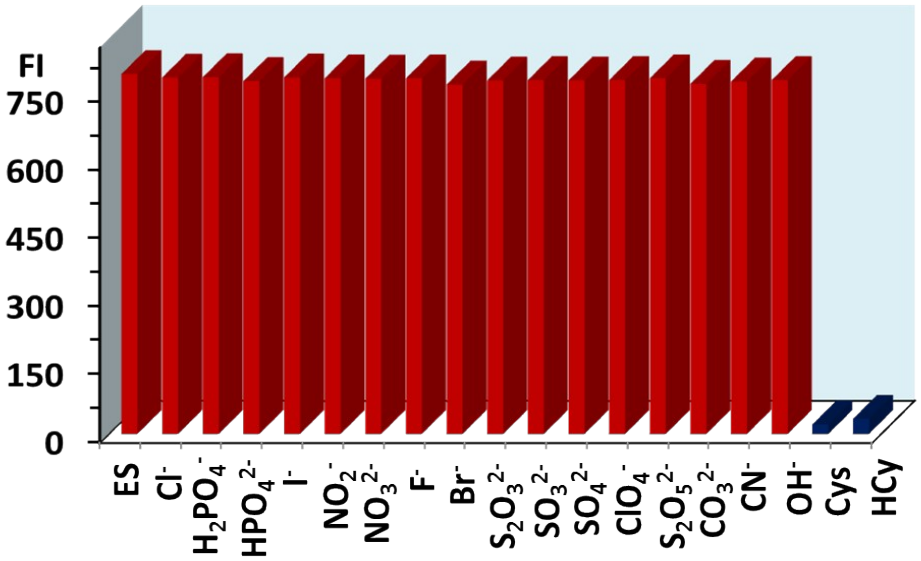


Figure S12. Fluorescence intensity changes as observed in **PDI-HQ**+Pb^{2+} ensemble **(ES)** (10 µM) in the presence of various anions/thiols recorded in HEPES buffer (0.1% CH_3CN, pH 7.2).

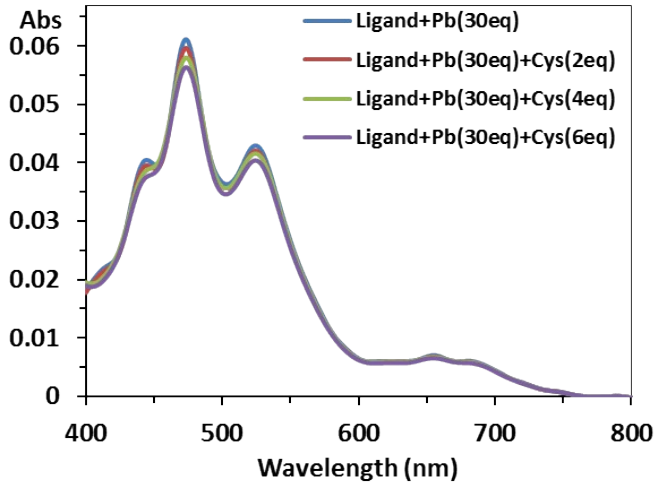


Figure S13. Absorbance spectra of **PDI-HQ**-Pb^{2+} ensemble (10 μM) after the incremental addition of cysteine recorded in HEPES buffer (0.1% CH_3CN), pH 7.2.

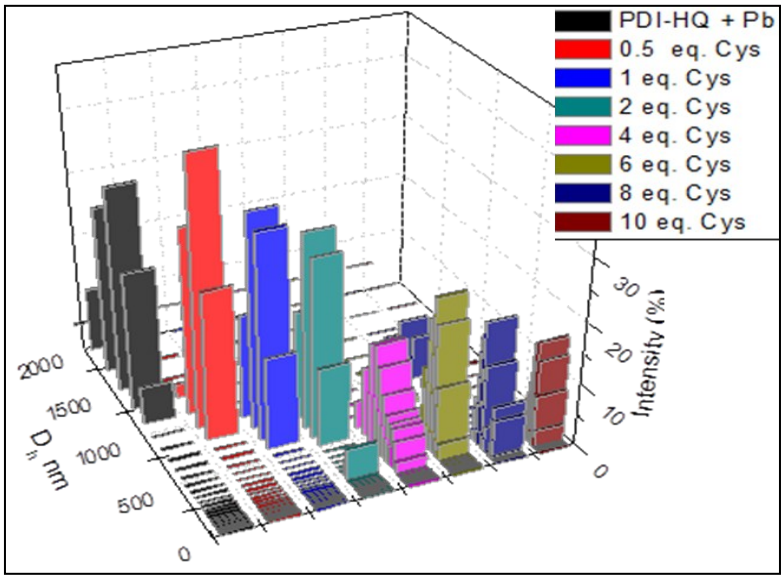


Figure S14. DLS titration showing gradual decrease in the aggregate size upon titration of **PDI-HQ**+Pb^{2+} ensemble with Cysteine.

Table S3: Table showing the Z average value for the aggregates in nm for titration of **PDI-HQ** with Pb^{2+} and titration of **PDI-HQ**+Pb^{2+} complex with Cys.

	Z Aggregates (nm)		Z Aggregates (nm)
PDI-HQ	128.26	**PDI-HQ** – Pb^{2+} (50 Equiv.)	1579.656
PDI-HQ – Pb^{2+} (1 Equiv.)	157.553	**PDI-HQ** – Pb^{2+} + Cys (0.5 Equiv.)	1150.324
PDI-HQ – Pb^{2+} (3 Equiv.)	275.157	**PDI-HQ** – Pb^{2+} + Cys (1 Equiv.)	990.565
PDI-HQ – Pb^{2+} (5 Equiv.)	318.653	**PDI-HQ** – Pb^{2+} + Cys (2 Equiv.)	865.364
PDI-HQ – Pb^{2+} (10 Equiv.)	461.965	**PDI-HQ** – Pb^{2+} + Cys (4 Equiv.)	571.234
PDI-HQ – Pb^{2+} (15 Equiv.)	619.56	**PDI-HQ** – Pb^{2+} + Cys (6 Equiv.)	498.139
PDI-HQ – Pb^{2+} (20 Equiv.)	776.979	**PDI-HQ** – Pb^{2+} + Cys (8 Equiv.)	353.774
PDI-HQ – Pb^{2+} (22.5 Equiv.)	890.199	**PDI-HQ** – Pb^{2+} + Cys (10 Equiv.)	215.376
PDI-HQ – Pb^{2+} (25 Equiv.)	1030.920		
PDI-HQ – Pb^{2+} (30 Equiv.)	1193.88		
PDI-HQ – Pb^{2+} (35 Equiv.)	1290.556		
PDI-HQ – Pb^{2+} (40 Equiv.)	1382.61		
PDI-HQ – Pb^{2+} (50 Equiv.)	1618.454		

Table S4: Comparison of literature reports for sensing of Pb2+ ions.

	Journal	**Fluorophore**	**Solvent**	**LOD**	**λ_{em} (nm)**	**Metallo-supramolecular assembly**	**SEM/ TEM studies**	**Application**
1	Present work	Perylene diimide	99.9 % Water	$2.5x10^{-8}$ M	660	Hexagons (interlocked)	Yes	Yes
2	*RSC Adv.* **2016**, *6*, 656	Rhodamine	HEPES	$1.5x10^{-8}$ M	552	No	No	Yes
3	*Dalton Trans.* **2015**, *44*, 17326	Rhodamine	99% water	$2.5x10^{-7}$ M Cu^{2+} interferes	576	No	No	Yes
4	*RSC Adv.* **2015**, *5*, 101802	Anthraquinone-CD	Water	$9.0x10^{-8}$ M	557	No	No	Yes
50-33% aqueous medium								
5	*J. Photochem. Photobio.* A **2018**, *355*, 101	Methyl red	$CH_3CN:H_2O$ (1:1)	$5.4x10^{-6}$ M Cr^{3+}, Hg^{2+}, Cu^{2+} interferes	513 (UV)	No	No	Yes
6	*Dalton Trans.* **2016**, *45*, 9187	Hydroxyl-quinoline based	$CH_3OH:H_2O$ (1:1)	$1.5x10^{-7}$ M	407	No	No	No

7	*Chem. Asian J.* **2014**, *9*, 3397	Naphthalimide	CH_3CN:H_2O (1:1)	$1.6x10^{-7}$ M Ca^{2+}, Cd^{2+} interfere	538	No	No	Yes
8	*Analytica Chimica Acta* **2012**, *751*, 135	Pyrene (quenching)	DMSO:H_2O (2:3)	$1.0x10^{-5}$ M	481	No	No	No
9	*Anal. Methods* **2016**, *8*, 2032	Azino bis-schiff base	CH_3OH:H_2O (2:1)	$8.0x10^{-9}$ M	442	No	No	No
10	*Anal. Methods* **2013**, *5*, 169		DMSO:H_2O (2:1)	$1.8x10^{-7}$ M		No	No	Yes
Pure organic solvent or < 20% water								
11	*Inorg. Chem.* **2017**, *56*, 14533	Phthalocyanin-Porphyrin	THF:CH_3OH (4:1)	$2.2x10^{-8}$ M $3.4x10^{-9}$ M	605	No	No	No
12	*Analyst* **2016**, *141*, 4388	Quinoline-2-carbohydrazide	CH_3OH:H_2O (4:1)	$3.2x10^{-6}$ M Zn^{2+}, Cd^{2+} interfere	582	No	No	No
13	*New J. Chem.* **2017**, *41*, 12198	Naphthalene	CH_3CN:H_2O (9:1)	$9.63x10^{-10}$ M Ni^{2+}, Sn^{2+}, Cu^{2+}, Fe^{3+} interfere	358	No	No	No
14	*Tetrahedron Lett.* **2017**, *58*, 252	Schiff-base	CH_3CN:H_2O (95:5)	$3.8x10^{-7}$ M	508	No	No	No
15	*RSC Adv.* **2016**, *6*, 112728	Rhodamine-quinoline	CH_3CN:H_2O (95:5)	$7.0x10^{-9}$ M	570	No	No	Yes
16	*Sens. Actuator B*, **2015**, *208*, 258	Naphthalimide	CH_3CN:H_2O (99:1)	$5.1x10^{-6}$ M Fe^{3+}, Hg^{2+} interfere		No	No	Yes He
17	*Sens. Actuator B*, **2018**, *258*, 648	Spiropyran (UV)	CH_3CN	$4x10^{-8}$ M Cr^{3+} interfere	482	No	No	No
18	*RSC Adv.* **2017**, *7*, 35528	Thiacalixarene	CH_2Cl_2-CH_3CN (1:1)	Zn^{2+}, Cd^{2+} interfere	427	No	No	No
19	*Dalton Trans.* **2015**, *44*, 5790	Diferrocenyl propane	CH_3CN	$4.4x10^{-7}$ M Cu^{2+}, Hg^{2+} interfere	420	No	No	No
20	*Talanta* **2014**, *130*, 103	Triphenyamine-bisthiophenol	CH_3CN	$1.8x10^{-5}$ M	529	No	No	No