

Electronic supplementary information

An aggregation-induced emission based “turn-on” fluorescent chemodosimeter for the selective detection of Pb²⁺ ions

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Experimental

Chemicals

4-Hydroxybenzophenone, benzophenone and diethylchlorophosphate were purchased from Sigma Aldrich (India). TiCl_4 was purchased from Spectrochem Pvt. Ltd. Mumbai (India). Zn powder and lead nitrate were purchased from SD Fine Chemicals Ltd. Mumbai (India). All other chemicals and solvents were obtained from different commercial suppliers and were used without further purification.

Instrumentation

NMR spectra were recorded on Bruker Avance 300 MHz NMR spectrometer. Mass spectra were obtained from Agilent 6400B LC-MS (ESI^+). Fluorescence spectra were taken on a JASCO FP-6300 spectrofluorometer, the slit width was 2.5 nm for both excitation and emission. Absorption spectra were recorded on a JASCO V570 UV/Vis/NIR spectrophotometer at room temperature. IR spectra were recorded on Shimadzu DR-8031 FT-IR Spectrophotometer.

General Procedure

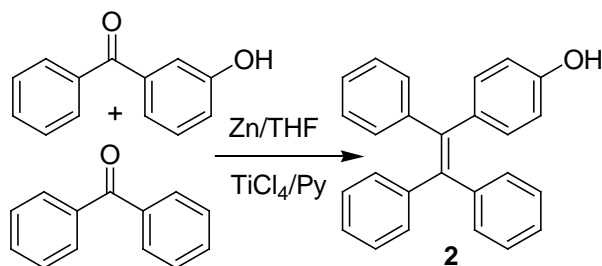
THF was dried over sodium and was freshly distilled before use. Thin layer chromatography (TLC) was used for monitoring progress of the reactions and during purification of products by column chromatography. TLC was carried out on 0.25-mm silica gel plates (60F-254) and UV light (254 or 365 nm) was used for visualization. Stock solutions of probe **1** (1 mM) was prepared in THF and that of lead nitrate (1 mM) was prepared in deionized water (MilliQ, 18 Ω). For study of the effect of different metal ions stock solutions were prepared by dissolving corresponding metal salts in deionized water (MilliQ, 18 Ω). The solutions of real samples were prepared by spiking $\text{Pb}(\text{NO}_3)_2$ in tap water and river water. All solutions were subjected to filtration through 0.22 μm syringe filter in order to avoid any interference by any particulate matter in fluorescence measurement.

Procedure for fluorescence study

The fluorescence study was carried out by addition of 150 μL of probe **1** (1 mM, in THF) in deionised water (2.7 mL) in a 3 mL cuvette. To this solution required volume of Pb^{2+} solution

(1 mM) was added and adjusted with water to make it 3 mL of 95% H₂O–THF solution. The solution was incubated for 5 min at room temperature and then, the fluorescence response was measured. For equivalent study concentration of Pb²⁺ ions was changed from 0-2 equivalent. For each reaction mixture fluorescence response was recorded. The same procedure was followed for comparative study with other metal ions.

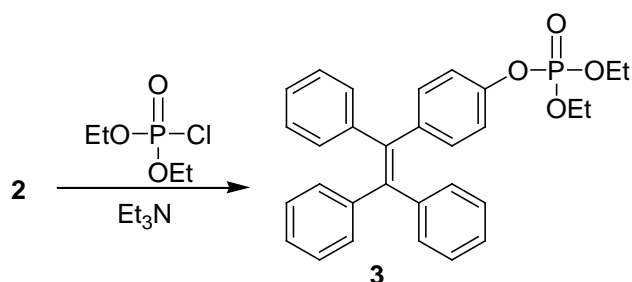
Synthesis of 4-(1,2,2-triphenylvinyl)phenol (**2**):¹



A three-necked flask equipped with a magnetic stirrer was charged with zinc powder (1.56 g, 24 mmol) and 20 mL anhydrous THF under nitrogen atmosphere. The mixture was cooled to 0 to -5 °C and TiCl₄ (1.2 mL, 12 mmol) was slowly added by a syringe. The suspension was warmed to room temperature and stirred for 30 min, then heated at reflux for 2.5 h. The mixture was again cooled to 0 to -5 °C, charged with pyridine (0.47 mL, 6 mmol) and stirred for 10 min. The solution of a mixture of benzophenone (436, 2.4 mmol) and 4-hydroxybenzophenone (475 mg, 2.4 mmol) in 20 mL of THF was added slowly. After addition, the reaction mixture was heated at reflux until both the starting materials were consumed as revealed by TLC (~8 h). The reaction was quenched by addition of excess of 10% aqueous K₂CO₃ solution and product was taken up with CH₂Cl₂ (50 mL). The organic layer was collected and concentrated. The crude product was purified by column chromatography to give the desired product, TPE-OH (**2**, 583 mg, yield: 70%).

White solid, mp 212-214 °C (decompose); ¹H NMR (300 MHz, CDCl₃): δ (ppm) 4.82 (s, 1H), 6.56 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.98-7.16 (m, 15H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 114.63, 126.42, 126.60, 127.65, 127.75, 131.36, 131.38, 131.40, 132.76, 136.37, 140.21, 140.48, 143.93, 143.94, 144.04, 154.08; Mass spectrum (ESI-MS): *m/z* 348.9 [M + H]⁺; IR (ν, KBr): 1246, 1441, 1516 and 3345 cm⁻¹.

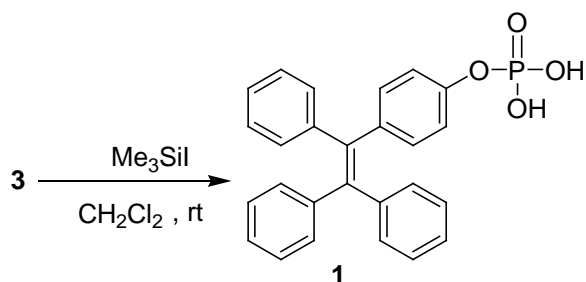
Synthesis of diethyl 4-(1,2,2-triphenylvinyl)phenyl phosphate (3):



In a single neck round bottom flask 100 mg (0.29 mmol) of compound **2** was taken in 5 mL of dry chloroform under nitrogen atmosphere. Triethyl amine (78 μ L, 0.58 mmol) and diethylchlorophosphate (50 μ L 0.344 mmol) were added slowly one after another into a stirred solution of **2** at 0 $^{\circ}$ C. The reaction mixture was brought to room temperature and stirred overnight. The reaction mixture was then concentrated under reduced pressure. The residue was re-dissolved in dichloromethane, washed with brine followed by water and the collected organic layer was dried over sodium sulphate and filtered. The organic solvent was concentrated under reduced pressure to afford the crude product, which was purified by flash chromatography to obtain the desired TPE-ester derivative **3** as sticky liquid (132 mg, 95%).

^1H NMR (300 MHz, CDCl_3): δ (ppm) 1.32 (t, $J = 7.2$ Hz, 6H), 4.19 (q, $J = 7.2$ Hz, 4H), 6.99-7.10 (m, 19H); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 16.08 ($J = 6.8$ Hz), 64.56 ($J = 6.8$ Hz), 119.19, 119.25, 126.51, 126.55, 127.66, 127.71, 127.75, 131.27, 131.30, 132.60, 139.89, 140.53, 141.27, 143.39, 143.55, 149.13 ($J = 6.8$ Hz); Mass spectrum (ESI-MS): m/z 485.0 [$\text{M} + \text{H}$] $^+$; IR (ν , KBr): 1024, 1218, 1281, 1447, 1598, 2361 and 2984 cm^{-1} .

Synthesis of 4-(1,2,2-triphenylvinyl)phenyl dihydrogen phosphate (1):



Compound **3** (100 mg, 0.21 mmol) was taken in 2 mL of dry DCM under nitrogen atmosphere. To it trimethylsilyl iodide (TMSI, 59 μ L 0.41 mmol) was added slowly at 0 $^{\circ}$ C. The reaction mixture was brought to room temperature and stirred for 2 h. The reaction

mixture was then concentrated under reduced pressure and the crude residue was directly subjected to flash chromatography to afford pure probe **1** (76 mg, 86%).

^1H NMR (300 MHz, CDCl_3): δ (ppm) 6.88-7.11 (m, 19H); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 119.55, 126.48, 126.58, 127.67, 127.72, 127.84, 131.27, 131.34, 132.57, 139.93, 140.47, 141.04, 141.18, 143.51, 143.64, 143.73, 149.24; Mass spectrum (ESI-MS): m/z 428.9 $[\text{M} + \text{H}]^+$; IR (ν , KBr): 1079, 1218, 1441, 1516, 1648, 2922 and 3503 cm^{-1} .

UV-vis Spectra

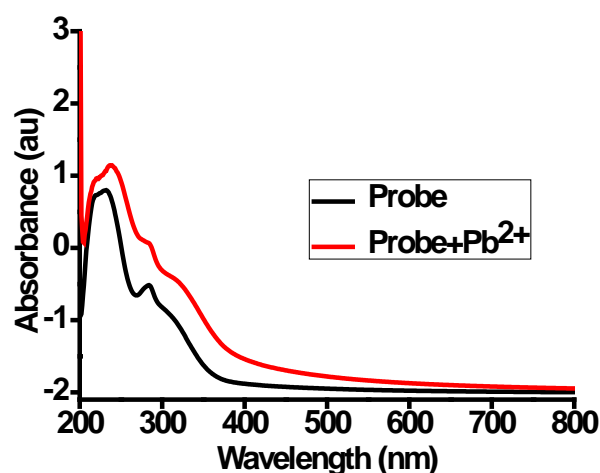


Figure S1. Overlaid UV-vis absorption spectra of **1** (black) and a mixture of both probe and Pb^{2+} (red). Both spectra were recorded in 95% H_2O -THF as solvent system.

Limit of Detection (LOD)

For determination of LOD the response of probe **1** was examined at nanomolar concentration range of $\text{Pb}(\text{II})$ ions. First, 1 mM stock solution of $\text{Pb}(\text{NO}_3)_2$ was further diluted to 0.1 mM and 0.01 mM, respectively and used for sensing studies. Under the optimal condition, $\text{Pb}(\text{II})$ ions were gradually added to a probe solution (50 μM , in 95% water-THF) and incubated for 5 min and then fluorescence response of the solution was measured. The observed fluorescence intensities were plotted against concentrations of $\text{Pb}(\text{II})$ ions. A good linear correlation ($R^2 = 0.9967$) was observed at the concentration range 50–250 nM. Below 50 nM concentration the curve gradually deviated from linearity (Fig. S2). Therefore, the limit of detection of the probe was considered as 50 nM of Pb^{2+} ions or ~ 10 ppb.

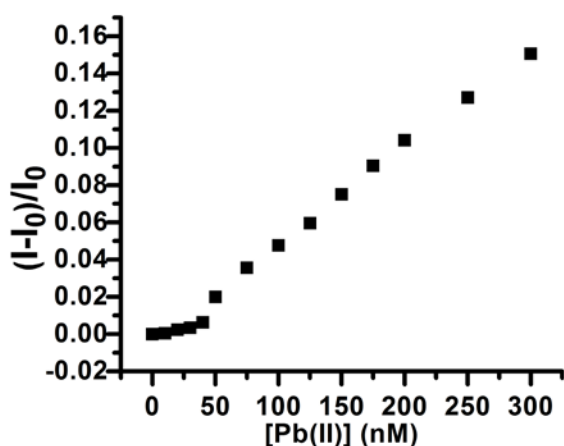


Figure S2: A plot of relative fluorescence response of probe **1** at lower concentration range of Pb(II) [concentration range: 0-300 nM]. The linearity is maintained from 50 nM concentration of Pb²⁺ ions.

Detection of Pb(II) ions in different water samples

For real sample analysis water samples were collected from Zuari river (Goa, India) and tap and were filtered through 0.22 μm syringe filter before analysis. A stock solution of Pb(NO₃)₂ (10 mL, 50 μM) in DI water was prepared. 30 μL of this solution was added to 10 mL of river water and 50 μL to tap water and it was mixed thoroughly. 2.85 mL of each of the samples was taken in cuvette and 150 μL of probe **1** (1 mM in THF) was added and the solution was incubated for 5 min before fluorescence measurement. The observed fluorescence intensity was plotted in the standard curve. The concentration of Pb(II) in two different water samples were closely matched with the amount of Pb(II) spiked showing a recovery of 99-102%.

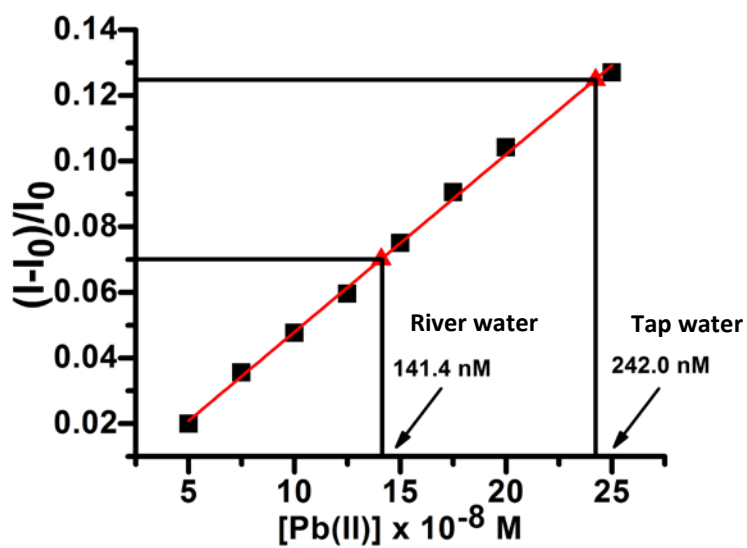


Figure S3: The relative fluorescence intensity from real samples (marked in red) was plotted in the standard curve to obtain the concentration of Pb(II) ions in the real samples.

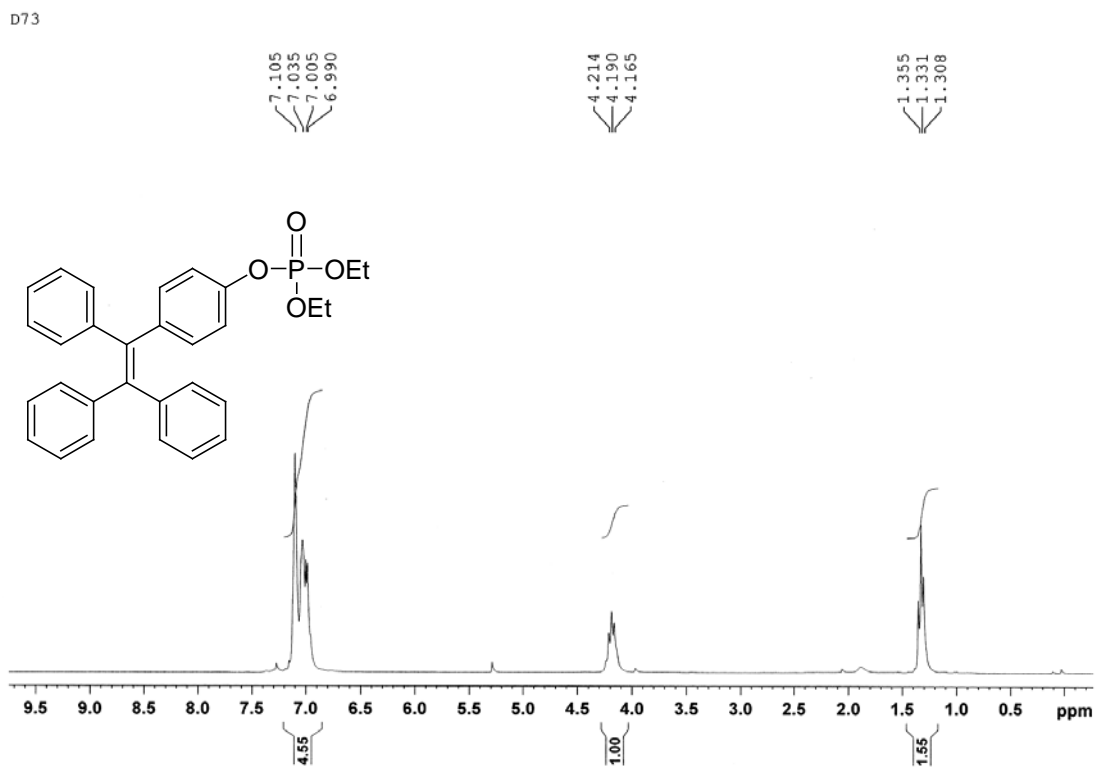
Table S1. Real sample analysis

Sl. no.	Sample	Concentration found from graph (nM)	Actual concentration (nM)	Recovery %
1.	Tap water	242.0	237.5	101.89%
2.	River water	141.4	142.5	99.22%

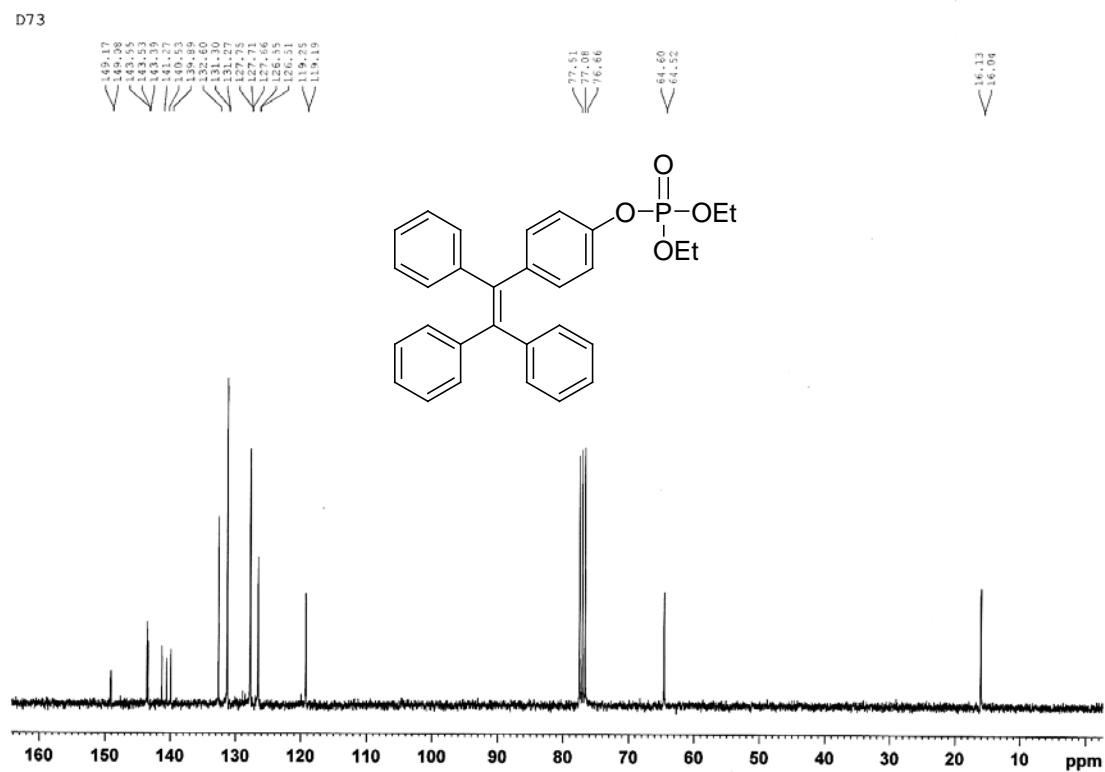
References

1. X.-F. Duan, J. Zeng, J.-W. Lu and Z.-B. Zhang, *J. Org. Chem.*, 2006, **71**, 9873.

¹H NMR of diethyl 4-(1,2,2-triphenylvinyl)phenyl phosphate (3):

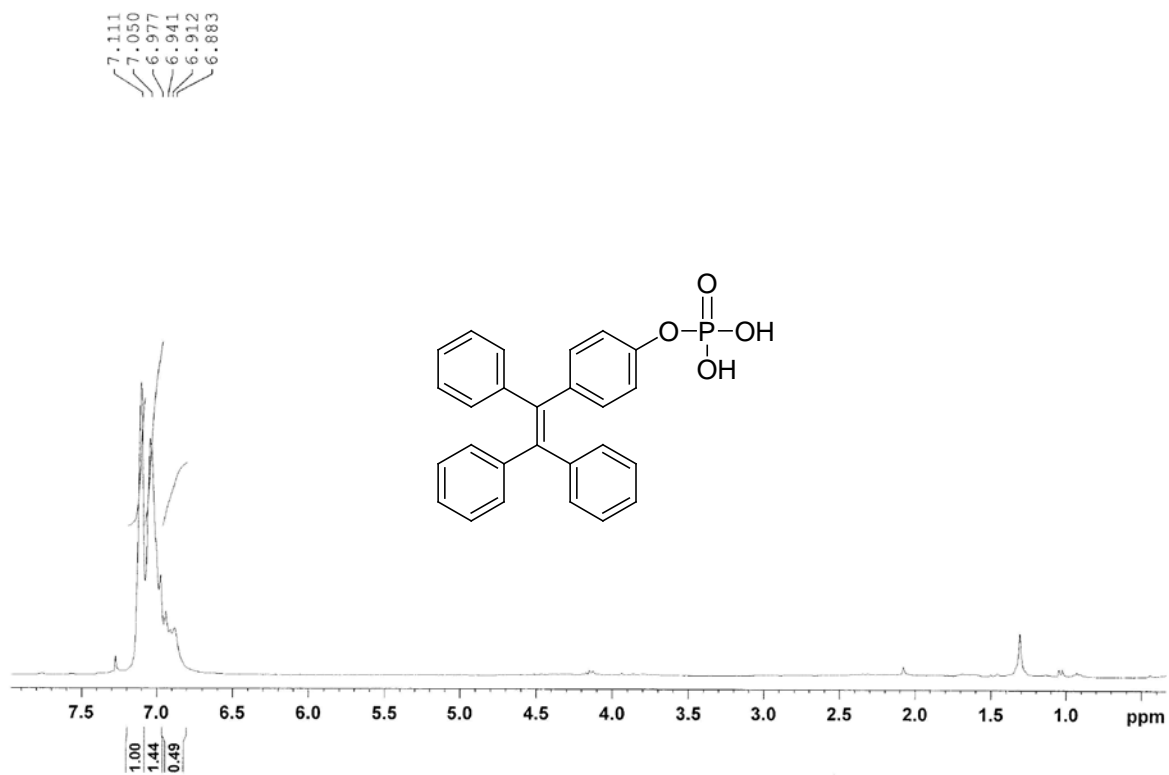


¹³C NMR of diethyl 4-(1,2,2-triphenylvinyl)phenyl phosphate (3):



¹H NMR spectrum of 4-(1,2,2-triphenylvinyl)phenyl dihydrogen phosphate (1):

D79



¹³C NMR spectrum of 4-(1,2,2-triphenylvinyl)phenyl dihydrogen phosphate (1):

D79

