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An aggregation-induced emission based "turn-on" fluorescent chemodosimeter for the selective detection of Pb^{2+} ions†

Dipratn G. Khandare,‡[a] Hrishikesh Joshi,‡[a] Mainak Banerjee,*[a] Mahesh S. Majik[b] and Amrita Chatterjee*[a]

An aggregation-induced emission (AIE) based "turn-on" fluorescent chemodosimeter for selective detection of Pb^{2+}ions has been developed by making use of the strong affinity of lead ions for phosphate residues. The probe is a phosphate functionalized tetraphenylethylene derivative and the resulting lead–TPE complex has very low solubility in working solvent and triggers aggregation induced emission. The probe is highly efficient, cost-effective and shows a low detection limit of 10 ppb.

1. Introduction

Heavy metal ions that are used in industry pose a huge threat to public health and the environment. Lead is an element with pronounced industrial application and is extensively used in storage batteries, alloys, lead wires, paints, high quality glasses, for soldering of electronic devices, and in foundries.[1] Lead is recognized as one of the most hazardous metals to humans. It accumulates in liver, kidney and in the central nervous system, and interferes[2] with a variety of physiological processes such as biosynthesis of haemoglobin.[2b] Long exposures to high concentration of lead can cause many health diseases such as hemotoxic effects, reproductive dysfunction, gastrointestinal tract alterations and nephropathies.[2c] In particular, Pb^{2+} is dangerous for children, causing mental retardation.[2,3] While US Environmental Protection Agency (EPA) set safe threshold level for lead as 15 ppb in drinking water, International Agency for Research on Cancer (IARC) has much lower threshold (10 ppb).[4] It is therefore very important to develop lead sensors with high selectivity and sensitivity that are addressable at these concentrations.

So far, a variety of techniques have been developed for selective detection of Pb^{2+}, which include potentiometry,[5] X-ray fluorescence Raman spectroscopy,[6] isotope dilution mass spectrometry,[7] electrochemical detection,[8] nanoparticle based sensors,[9] and many others.[10] However, fluorimetric sensing by harnessing appropriate organic probes has drawn much more attention because it is simple, sensitive, and cost-effective,[11] and this technique is useful for detection of lead ions as well.[12] However, traditional fluorescent probes often suffer from the aggregation-caused quenching (ACQ) effect, when dispersed in appropriate solvent or incorporated into solid matrices, resulting in huge drop in the performance and sensitivity.[13] The ACQ effect poses huge concern in real life applications, particularly, in the *in vivo* detection of analytes.[13] Recently, a group of molecules, non-emissive in solution, have been found to luminescence intensively upon molecular aggregation, showing an aggregation-induced emission (AIE) characteristic.[14] Restriction of intramolecular rotation is proposed as the main reason behind this phenomenon. As their emission is turn-on in nature, instead of quenching, AIE-active materials have found enormous application in various fields[15–18] such as efficient sensitive chemo/biosensors,[16,18a,b,d,g] electroluminescent materials,[17f,18e] cell imaging,[17a,d,e,18i] optical devices[18h,j] *etc.* Among the reported AIE active molecules, tetraphenylethylene (TPE), due to its easy synthesis and also for simple functionalization strategies, is one of the most studied luminophore for detection of various analytes[16] and other applications.[17] However, to the best of our knowledge, AIE property of these molecules has not been exploited for the detection of Pb(II) ions. In the current endeavor, as a part of our continued effort for the development of fluorescent sensors for biologically/environmentally important analytes,[16l,19] we planned to design a TPE-based fluorescent chemodosimeter for selective and sensitive detection of Pb^{2+} ions. The literature survey reveals that alkyl phosphates have a very high affinity to Pb^{2+} ions and resulting lead phosphates

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[a] Department of Chemistry, BITS Pilani, K. K. Birla Goa Campus, NH 17 B Bypass Road, Zuarinagar, Goa 403726, India. E-mail: amrita@goa.bits-pilani.ac.in; mainak@goa.bits-pilani.ac.in; Fax: +91-832-2557-033; Tel: +91-832-2580-320; +91-832-2580-347

[b] Bio-organic Chemistry Laboratory, CSIR-National Institute of Oceanography, Dona-Paula, Goa 403 004, India

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‡ These authors contributed equally to this work.

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have very low solubility product (in the range of 10^{-10} to 10^{-50}).[9a] Hence we envisioned, probe **1**, a TPE monoester of phosphoric acid (Fig. 1), can be used for the detection of Pb^{2+} ions in aqueous media as low solubility of corresponding TPE–Pb complex will trigger aggregation of molecules in solution and serve as AIE based sensor for lead ions.

Probe **1** was successfully synthesized following a three-step procedure in high yield (Scheme 1) (see ESI†). First, TPE-OH (**2**) was prepared adopting a reported synthetic route.[20] The spectra were in good agreement with the reported values. The compound **2** was smoothly converted to diethyl-TPE-phosphate (**3**) by reaction with diethylchlorophosphate followed by deprotection of ethyl groups of **3** by trimethylsilyl iodide (TMSI) to produce desired probe **1**. Both the compounds were characterized by ^{1}H NMR, ^{13}C NMR and ESI-MS. Attachment of phosphate ester group in TPE-OH (**2**) to form **3** was indicated by the presence of a methyl triplet at δ 1.32 and a methylene quartet at δ 4.19 in ^{1}H NMR. Similarly, the signals at 16.08 and 64.56 ppm were assigned as the carbons of the ethyl groups of phosphate ester **3** in ^{13}C NMR. More importantly, the expected coupling of ^{31}P and ^{13}C nuclei was apparent in proton decoupled ^{13}C NMR. It was observed that both the carbons of ethyl groups and the aromatic carbon attached to phosphorous appeared as doublets with coupling constant, $J = 6.8$ Hz. The NMR spectra clearly suggested the presence of a phosphate moiety in compound **3**. A base peak at *m*/*z* 485.0 (corresponds to $[M + H]^+$) in ESI-MS further supported the formation of the desired product. The peaks of ethyl groups disappeared completely in the NMR spectra of **1** indicating successful deprotection. Otherwise, the NMR spectra of both of the compounds have close resemblance. The presence of $[M + H]^+$ peak at 428.9 as the base peak in ESI-MS was also in support of the formation of probe **1**. The sensing behaviour of the probe (**1**) towards lead ions was investigated by conducting various studies as described below.

The solvent effect on the aggregation behaviour of probe **1** was examined using variable proportions of THF in water. As expected, probe **1** was completely soluble and non-fluorescent in THF solution. Since the solubility of the compound is very poor in water the fluorescence intensity can be tuned by the increment of water in the solvent mixture as the compound starts aggregating at higher percentage of water. As shown in Fig. 2, the fluorescence intensity of probe **1** upon photo excitation at 370 nm was negligible in THF. On continuous addition of water into it, keeping the concentration of probe **1** fixed at 50 μM, sharp increase in fluorescence intensity was observed over 95% water–THF. This indicates that probe **1** is AIE active and therefore, useful for sensing studies.

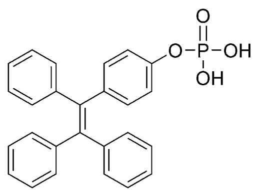

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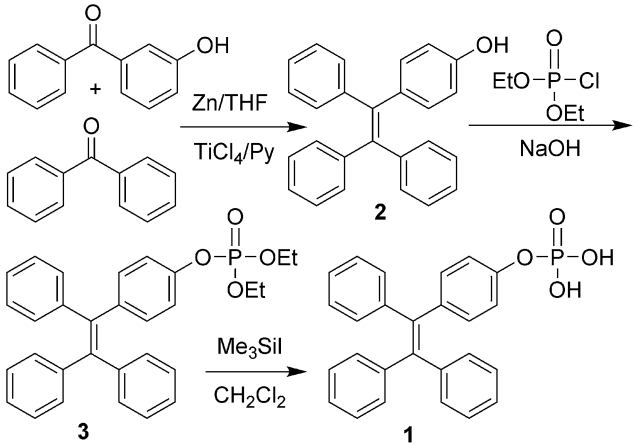
Fig. 1 Structure of the TPE derivative (**1**) used for the sensing purpose of lead ions.



Scheme 1 The synthetic route to probe **1**.

To understand the sensing characteristic of probe **1** an equivalence study was conducted. The fluorescence intensities of probe **1** (50 μM each) in 95% water–THF mixture upon addition of Pb^{2+} ions (0 to 2 equiv.) was plotted (Fig. 3). It was observed that the fluorescence response from the system slowly intensified upon gradual addition of lead ions. Presumably, the sensing mechanism is based on two simple facts: (a) TPE monoester of phosphoric acid, **1** has a strong affinity towards Pb^{2+} ions and (b) the resulting lead phosphate is insoluble in water or the working solvent system. Therefore, probe **1** readily undergoes complexation with the available Pb^{2+} ions in the solution. As soon as Pb(II)-complex is formed it goes out of the working solvent system and forms a dispersed phase in which further aggregation between the molecules of TPE–Pb complex occurs. The aggregated form of TPE–Pb complex regains planarity due to restricted rotational freedom triggering aggregation induced emission. The AIE-based sensing mechanism of probe **1** with Pb(II) ions is schematically represented in Fig. 4.

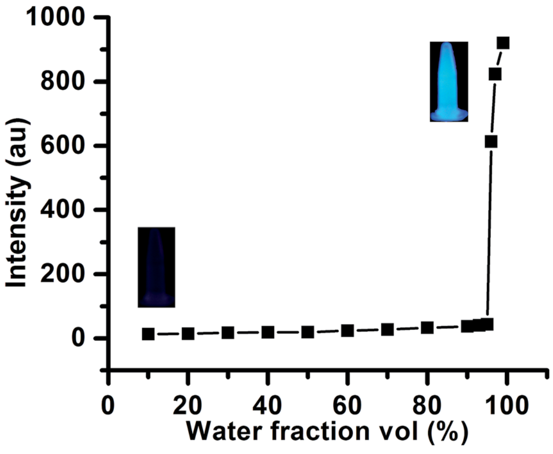


Fig. 2 Fluorescence response of probe **1** (50 μM) in different solvent compositions of water–THF at 474 nm (λ_{ex} 370 nm).

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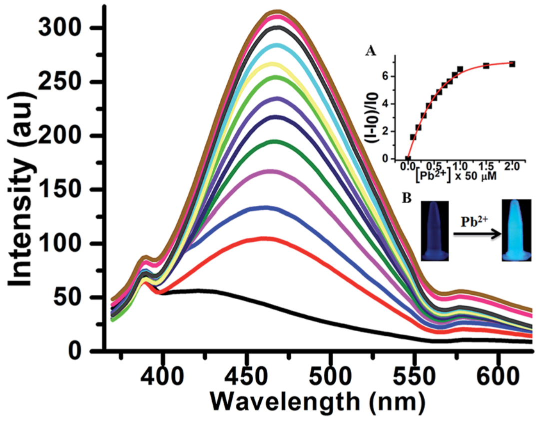

Fig. 3 Fluorimetric response of probe **1** (50 μM) upon addition of Pb^{2+} (0–100 μM) in 95% water–THF [λ_{ex} 370 nm; λ_{em} 474 nm]. Inset: (A) a plot of the increment in fluorescence intensity against the concentration of lead ions; (B) a picture of fluorescence change of **1** (50 mM) upon addition of 1.0 equiv. of Pb^{2+} ion in 95% water–THF after 5 min.

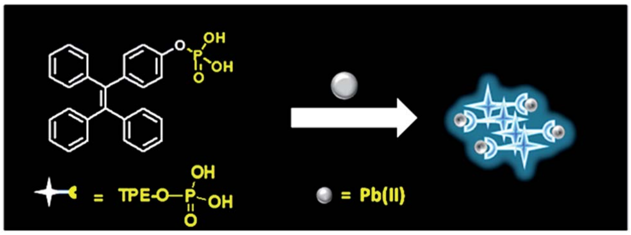

Fig. 4 Sensing process of probe **1** based on AIE mechanism.

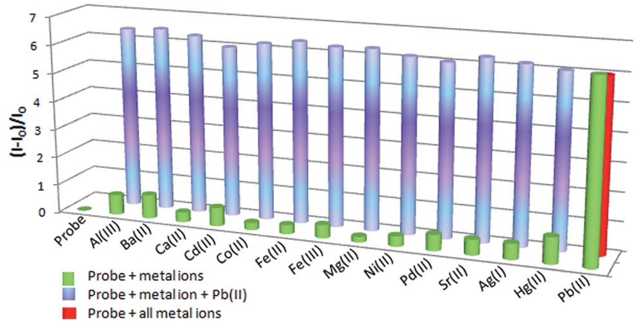

Fig. 6 Maximum fluorescence response of a probe 1 (50 μM) in 95% H_2O–THF upon addition of different metal ions (50 μM each) (Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Sr^{2+}, Ag^{+}, Hg^{2+}, Pb^{2+}) and fluorescence response of probe **1** + Pb^{2+} + all metal ions.

The extent of aggregation of probe **1** is directly dependent on the concentration of lead ions and corresponding output holds a linear relationship till the addition of 1 equiv. of Pb^{2+} (*i.e.* 50 μM) (Fig. 3, inset). At higher concentration of Pb^{2+} ions no significant change in fluorescence intensity was observed indicating full utilization of available probe molecules for complex formation.

A DLS study was followed next to verify Pb^{2+} derived aggregation of probe **1**. DLS of probe **1** in 95% water–THF was measured before and after the addition of equimolar Pb^{2+} ions (Fig. 5). From the particle size analysis the formation of nanoscale aggregates was confirmed. Before addition of Pb^{2+}, the average particle size of around 60 nm was detected in the solution of probe **1** (50 μM), which increases 16-fold after the addition of Pb^{2+} (50 μM, 1 equiv.) [mean diameter is 947 nm]. The above experimental facts strongly support spontaneous formation of a TPE-based lead phosphate, which aggregates further and shows fluorescence by the AIE mechanism.

After successfully establishing the detection ability of the probe towards Pb^{2+}, the selectivity of the probe was assessed by challenging it with several other environmentally relevant metal ions. The experiment was conducted by adding 50 μM of various metal ions like Ca^{2+}, Fe^{2+}, Mg^{2+}, Ag^{+}, Mn^{2+}, Fe^{3+} *etc.*, one at a time, into a solution of probe **1** (50 μM) in 95% water–THF and measuring the fluorescence output of the system. As shown in Fig. 6, the fluorescence intensities of all the solutions other than Pb^{2+} are very nominal. This study reveals that probe **1** is highly selective to Pb^{2+} ions. Even the probe could detect Pb^{2+} ions with similar efficiency in the presence of all metal ions (50 μM each). Hence, none of the metal ions interferes in the spontaneous complexation of Pb^{2+} ions with probe **1**.

Limit of detection for any probe is an important characteristics that needs to be defined. Under the optimal condition mentioned above, the capability of our analytical tool for quantitative detection of Pb(II) ions has been evaluated by plotting relative fluorescence intensity against concentration of

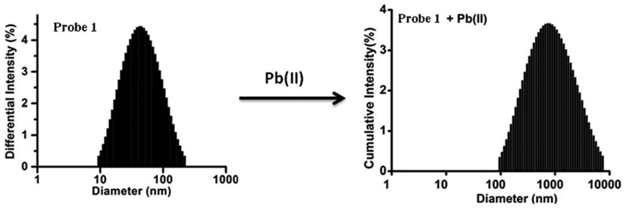

Fig. 5 Particle size analysis of a probe **1** and reaction mixture after addition of 1.0 equiv. of Pb^{2+} in 95% H_2O–THF.

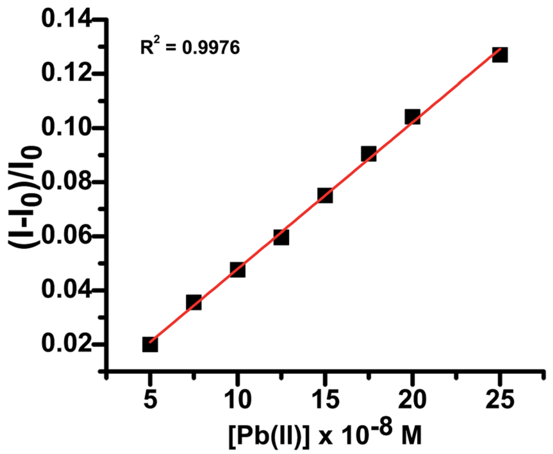

Fig. 7 The relative fluorescence response of probe **1** at lower concentration range of Pb(II) [concentration range: 50–250 nM].

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Pb(II) ions at lower concentration range (Fig. 7). A good linear correlation ($R^2 = 0.9967$) was observed even at the nanomolar concentration range (50–250 nM), from which the limit of detection has been calculated as 10 ppb.

To demonstrate potential application of the probe as an analytical tool for the detection of Pb^{2+} in various water bodies, lead nitrate was spiked with water samples (for details, see ESI†). Pre-spiked lead ion concentrations could be easily detected by probe **1** in the contaminated water samples with as high as 99–102% recovery.

2. Conclusion

In conclusion, an AIE-based fluorescence chemodosimeter has been successfully developed for the detection of Pb^{2+} ions. The probe is a tetraphenylethylene phosphate monoester and was designed keeping in mind the strong affinity of lead ions towards phosphate residue. The probe spontaneously forms water insoluble salt of lead ions and thereby, detects Pb^{2+} ions in 95% water–THF by turn-on type fluorescence response. The probe is extremely sensitive and highly selective to Pb^{2+} ions. The limit of detection of this probe is found to be 10 ppb. The present method offers simple, cost-effective and efficient way for detection of Pb^{2+} in aqueous media.

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