Dalton Transactions

RSC Publishing

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c2dt32531d

Received 23rd October 2012,
Accepted 14th November 2012

DOI: 10.1039/c2dt32531d

www.rsc.org/dalton

A highly sensitive and selective fluorescent chemosensor for Pb^{2+} ions in an aqueous solution†

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A new fluorescent sensor based on the BODIPY fluorophore and the polyamide receptor for Pb^{2+} was designed and synthesized. The sensor is highly selective for Pb^{2+} over relevant competing metal ions, and sensitive to ppb levels of Pb^{2+}. It features the most sensitive probe to date for Pb^{2+} ions in water.

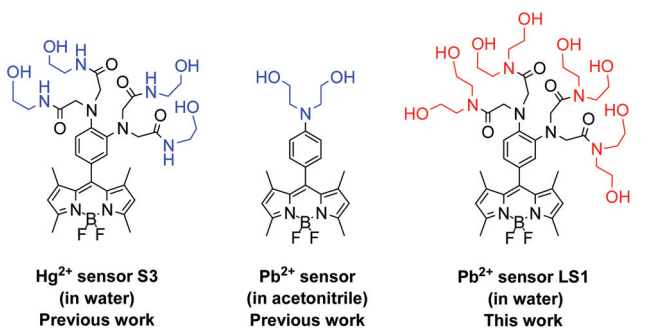
Introduction

Lead, which is widely distributed in the environment such as the air, soil, and water due to its use in batteries, gasoline, and pigments,[1] is one of the most ubiquitous and poisonous heavy metals.[2] Lead poisoning may induce anemia, neurological damage, physical growth impairments, nerve disorders, memory loss, kidney disorders, and reduced IQ.[3] Despite efforts to reduce global emissions, lead poisoning remains one of the top environmental health problems.[4] Due to the toxicity of Pb^{2+}, the determination of lead in biological and environmental samples is crucial both to the monitoring of environmental pollution and to the diagnosis of clinical disorders. However, standard techniques, such as atomic absorption spectrometry,[5] inductively coupled plasma mass spectrometry,[6] and anodic stripping voltammetry,[7] often require expensive and sophisticated instrumentation, and/or sample preparation, and are therefore not suitable for real-time and *in situ* analysis.

Optical sensors involving fluoroionophores are becoming popular because of their ease of application in solution as well as their high sensitivity to and selectivity for trace analytes with spatial and temporal resolution.[8] In the past several years, considerable efforts have been made to develop fluorescent chemosensors for Pb^{2+} ions based on peptide,[9] protein,[10] DNAzyme,[11] polymer,[12] and small-molecule scaffolds.[13] However, most of them are limited by interfering background fluorescence, nonspecific quenching from competing metal ions, and/or incompatibility with water. We now present the synthesis and properties of a new Pb^{2+}-ion specific fluorescent chemosensor Leadsensor-1 (**LS1**) that has visible wavelength excitation and emission profiles, excellent selectivity for Pb^{2+} ions over relevant competing metal ions, a 19-fold turn-on response, and high sensitivity to ppb levels of Pb^{2+} in water.

In 2006, Qian *et al.*[14] disclosed that polyamide receptor (**MR**) based fluorescent molecule sensors featured high water solubility, unique Hg^{2+} ion selectivity, and significant signal response upon Hg^{2+} ion complexation. We noticed that one of the fluorescent sensors **S3** also has slight fluorescence enhancements by Pb^{2+} ions (I/I_0 = 1.4) in neat water solution.[14c] Inspired by this, we designed a new fluorescent sensor for Pb^{2+} (**LS1**) by introducing a diethanolamine group to the polyamide receptor (Scheme 1). We reasoned that the introduction of the diethanolamine group would potentially enhance the selectivity of the sensor to Pb^{2+} ions while retaining its water solubility because the diethanolamine group has been used as a receptor for Pb^{2+} in acetonitrile which shows selectivity but is limited by the relatively low sensitivity and quenching in aqueous media.[13j]

Herein, the preparation and fluorescence responses of the new Pb^{2+}-ion-responsive chemosensor **LS1** are reported below.



Scheme 1 **LS1** design inspired by previous work.

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†Electronic supplementary information (ESI) available: Fluorescence properties of **LS2**, and copies of NMR and MS spectra. See DOI: 10.1039/c2dt32531d

Results and discussion

LS1 has been synthesized as shown in Scheme 2. Alkylation of **1** with ethyl bromoacetate affords tetraester **2** in 67% yield. Vilsmeier formylation of **2** using $POCl_3$–DMF followed by basic workup generates aldehyde **3** in 40% yield. BODIPY **4** is obtained in a one-pot, three-step procedure *via* condensation of **3** with 2,4-dimethylpyrrole, followed by DDQ oxidation and boron insertion with $BF_3{\cdot}OEt_2$ (20% overall yield for three steps). Ester ammonolysis of **4** gives **LS1** (**5**) in 23% yield.

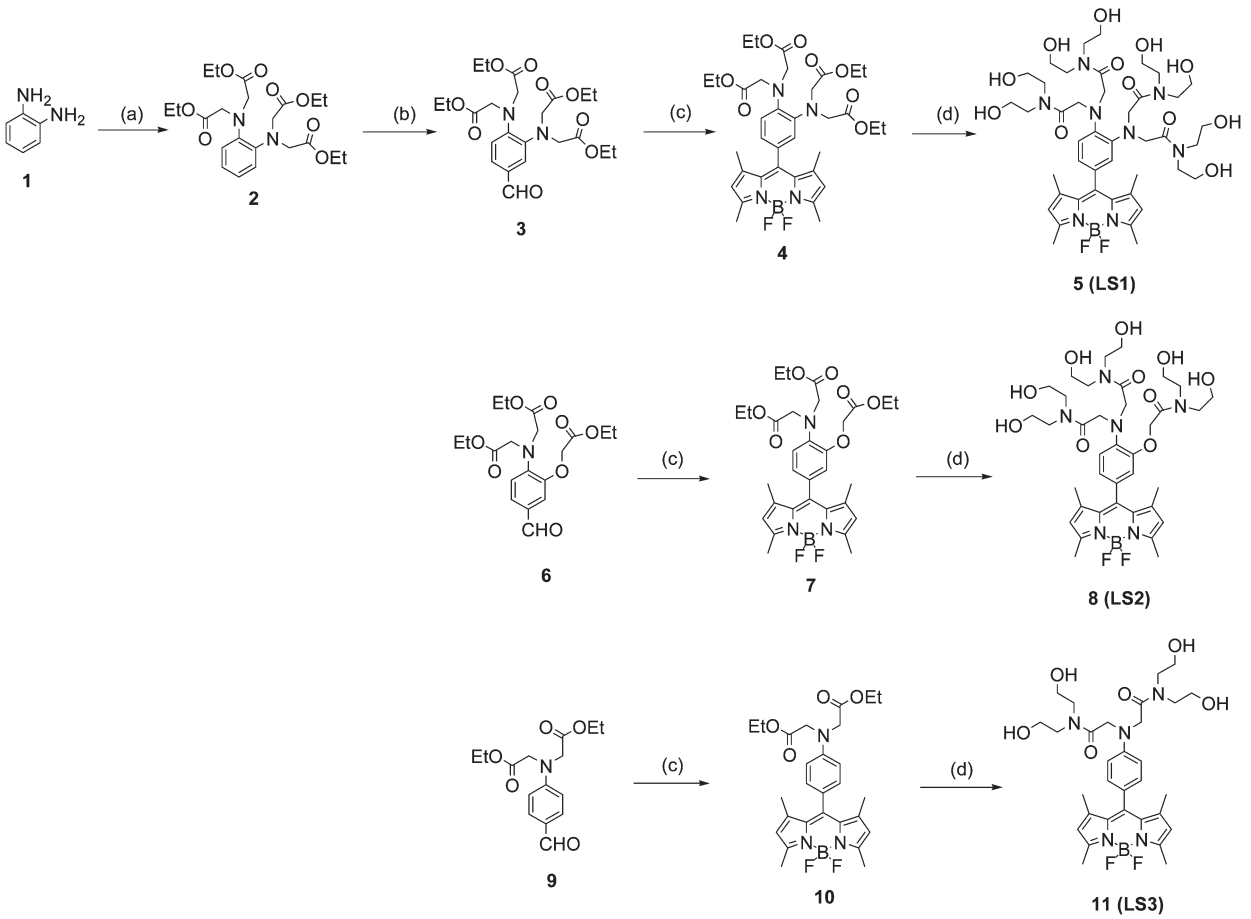
Spectroscopic measurements for **LS1** were performed in neutral aqueous media (0.1 M PBS buffer, pH 7.2) for **LS1** is inert to pH in the range of 6.5–8.0 (Fig. 1). **LS1** alone shows a visible absorption band centered at 497 nm ($\varepsilon = 4.0 \times 10^4$ M^{-1} cm^{-1}) and is almost nonfluorescent (λ_{em} = 510 nm, Φ = 0.006), indicative of efficient photoinduced electron transfer (PET) quenching of the excited BODIPY fluorophore by the electron-donating polyamide receptor.[14c]

However, addition of 2 equiv. of Pb^{2+} triggers a *ca.* 19-fold (Φ = 0.112, Fig. 2a and Table S1, ESI†) increase in integrated emission for **LS1** with the same absorption (λ_{abs} = 496 nm) and emission maxima (λ_{em} = 510 nm), indicating that the PET quenching pathway is efficiently blocked by Pb^{2+} ion complexation. The enhancement of fluorescence intensity of **LS1** is linear to the corresponding lg[Pb^{2+}] (0.05–1.25 μM) (R^2 = 0.99294) (Fig. 2b). The association constants K_{11} and K_{21} were determined by a nonlinear least-squares analysis of fluorescence intensity *versus* Pb^{2+} ion concentration to be 5.3×10^8 and 8.0×10^6, respectively (ESI†).[15]

Moreover, the selectivity of **LS1** toward different metal ions was examined. Much to our delight, the turn-on response of **LS1** is highly specific for Pb^{2+} and no obvious change of fluorescent emission was observed when it is treated with Hg^{2+}, Ag^{+}, Zn^{2+}, Sn^{4+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Ca^{2+}, Fe^{3+}, Na^{+}, Ni^{2+}, Cd^{2+}, Cr^{3+}, Bi^{3+}, Fe^{2+}, and Mg^{2+} (Fig. 3a). It should be mentioned that **LS1** still responds to Pb^{2+} sensitively even in the presence of other relevant competing ions (Fig. 3b).

Furthermore, binding analysis using the method of continuous variations (Job's plot) establishes that a 1 : 2 **LS1** : Pb^{2+} complex is responsible for the observed fluorescence enhancement (Fig. 4).

To clarify the actual polyamide–Pb^{2+} interactions, **LS2** and **LS3** bearing three and two amide arms into the polyamide receptors were synthesized (Scheme 2). The results showed that **LS3** is unable to form a complex with Pb^{2+} ions while **LS2** forms a 1 : 1 complex with Pb^{2+} ions ($K_{11} = 2.8 \times 10^3$)



Scheme 2 Synthesis of **LS1**, **LS2**, and **LS3**: (a) ethyl bromoacetate–KI–DIPEA, CH_3CN, reflux, 8 h; (b) $POCl_3$–DMF, 2 h; (c) (1) 2,4-dimethylpyrrole–TFA, CH_2Cl_2, rt, 10 h; (2) DDQ, rt, 4 h; (3) NEt_3–$BF_3{\cdot}OEt_2$, rt, 2 h; (d) diethanolamine, CH_3CN, reflux, 24 h.

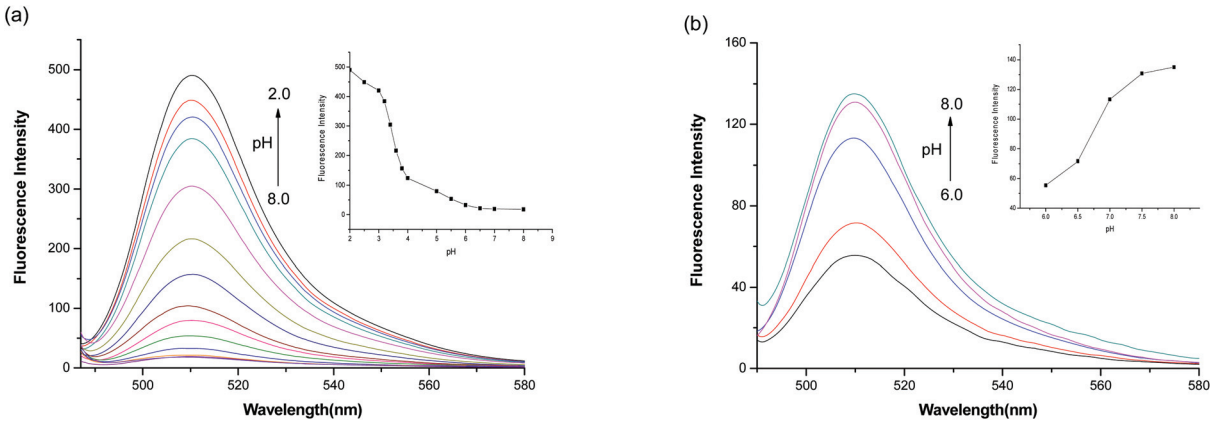


Fig. 1 (a) Effect of the pH on the fluorescence emission of **LS1** (0.05 μM) in a buffer solution. (b) Effect of the pH on the fluorescence emission of **LS1**–Pb^{2+} complex (2.0 equiv. of Pb^{2+}) in a buffer solution.

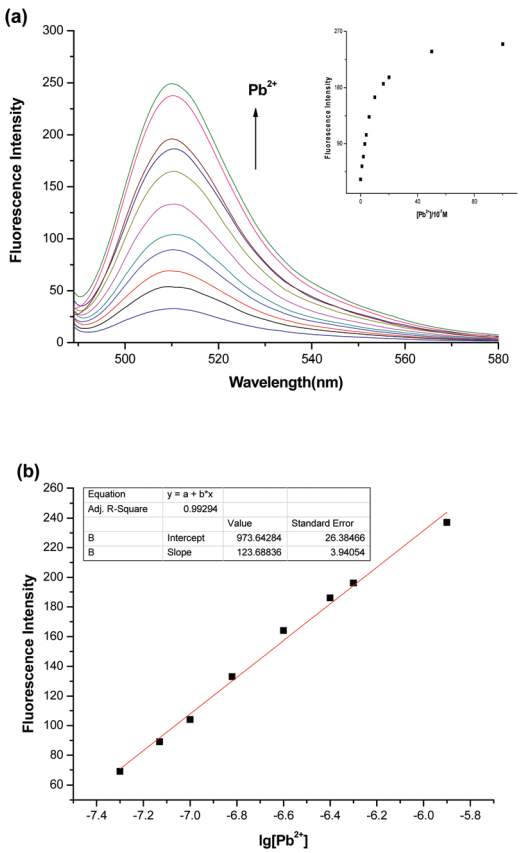


Fig. 2 (a) Fluorescence emission spectra (λ_{ex} = 470 nm) of **LS1** (0.05 μM) in neutral aqueous media (0.1 M PBS buffer, pH 7.2) upon the addition of Pb^{2+} (0–2.5 μM). Inset: binding isotherm between **LS1** and Pb^{2+} with emission intensity at 510 nm. (b) Fluorescence intensity of **LS1** at 510 nm as a function of lg[Pb^{2+}] (0.05–1.25 μM) under the same condition as the Pb^{2+} titration.

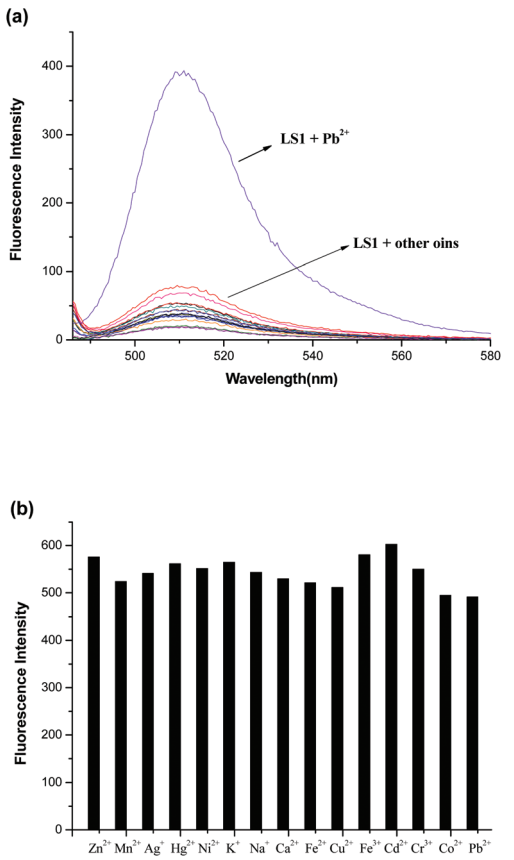


Fig. 3 (a) Fluorescence responses of **LS1** (0.25 μM) with 2.0 equiv. of metal ions in 0.1 M PBS (pH 7.2). Metal ions include Pb^{2+}, Hg^{2+}, Ag^{+}, Zn^{2+}, Sn^{4+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Ca^{2+}, Fe^{3+}, Na^{+}, Ni^{2+}, Cd^{2+}, Cr^{3+}, Bi^{3+}, Fe^{2+}, and Mg^{2+}. λ_{ex} = 470 nm. (b) The fluorescence intensity of **LS1** (0.25 μM) at 510 nm with 40 equiv. of the competing metal ions, followed by 2.0 equiv. of Pb^{2+}.

(Fig. S1–S3, ESI†), indicating that the amide arms play a key role in the stability and binding mode of coordination complexes. We recorded the ^{1}H NMR spectra of **LS1** and its complex with Pb^{2+} in D_2O (Fig. 5). Three aromatic protons attributed to the polyamide receptor were distinctly downfield shifted from δ 6.50–6.94 ppm to 7.52–7.88 ppm due to the localization of the aniline nitrogen lone-pair electrons by the Pb^{2+} ions. The two single peaks assigned for the eight H_d protons showed a slight upfield shift and split into two peaks, indicating the electron shielding effect by the amide groups in the complexation form. Accordingly, the structure of the **LS1**–Pb^{2+} complex has been proposed (Fig. 6).

Owing to its excellent optical properties, **LS1** is sensitive enough to detect environmentally relevant concentrations of Pb^{2+} ions in an aqueous solution. As shown in Fig. 2b, addition of 15 ppb of Pb^{2+} ions, the maximum US EPA limit for allowable levels of lead in drinking water, to a 0.05 μM solution of **LS1** affords a 276% emission increase.[16] Furthermore, the detection limit was calculated to be 1.34×10^{-8} M according to a reported method,[17] which indicates that **LS1** features the most sensitive probe to date for Pb^{2+} ions in water.

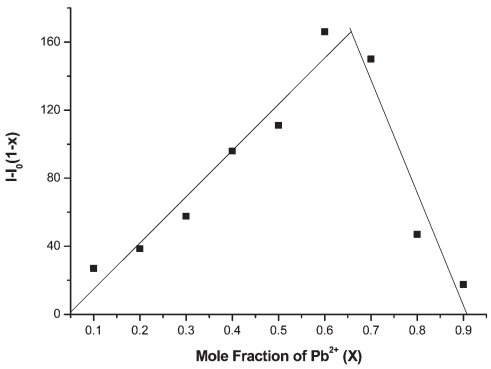


Fig. 4 Job's plot showing the 1 : 2 binding of **LS1** with Pb^{2+}. The total concentration of the sensor and Pb^{2+} is 0.5 μM in neutral aqueous media (0.1 M PBS buffer, pH 7.2).

Conclusion

In conclusion, we have designed and synthesized a new fluorescent sensor (**LS1**) for Pb^{2+} ions in water. **LS1** is a unique Pb^{2+}-responsive small-molecule indicator that features visible wavelength excitation and emission profiles, a selective turn-on response to Pb^{2+} compared to relevant competing metal ions, a 19-fold turn-on response, and sensitivity to ppb levels of Pb^{2+} ions in water. Titration experiments show that **LS1** can be used to detect changes of Pb^{2+} levels in drinking water, illustrating its feasibility as a versatile tool to monitor Pb^{2+} widely in the environment. In addition, comparison of the

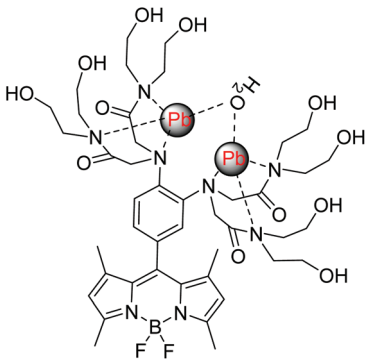


Fig. 6 A proposed structure of **LS1**–Pb^{2+} complex.

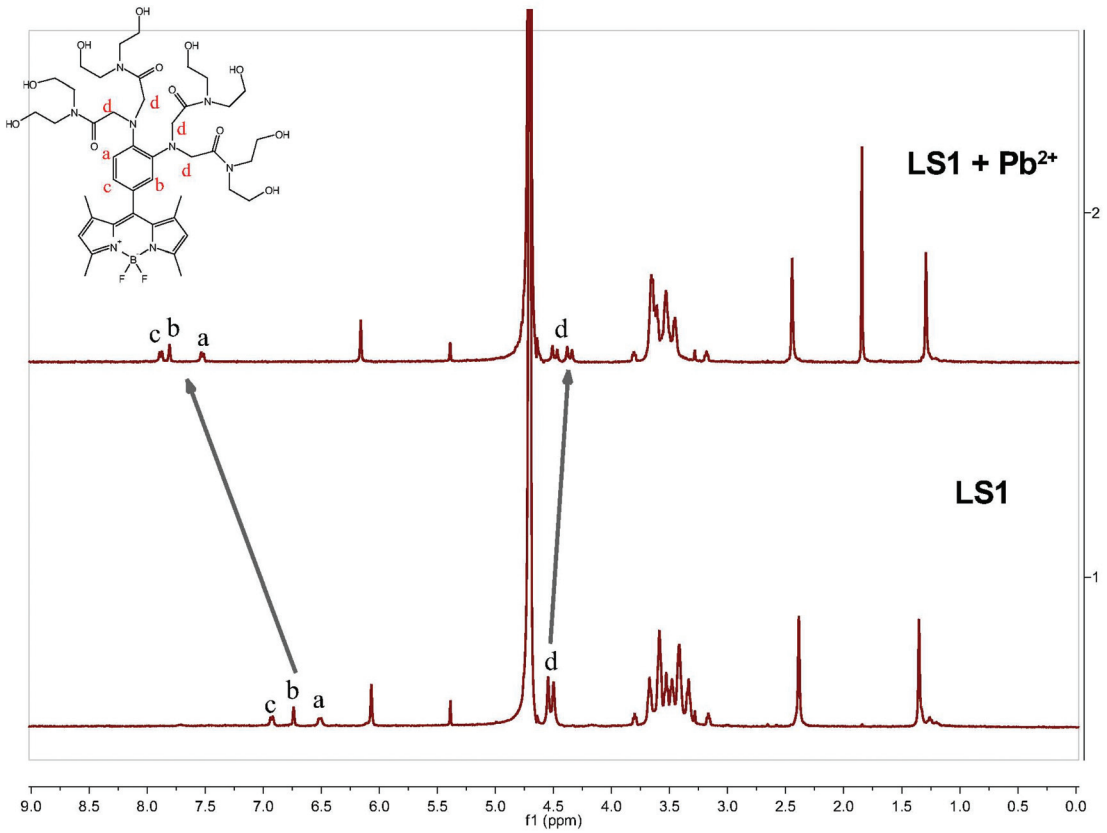


Fig. 5 ^{1}H NMR spectra of **LS1** and **LS1** + Pb^{2+} complex.

structure of **LS1** to that of **S3**, which is a chemosensor for Hg^{2+} ions, reveals that the slight difference in appended amide arms of a polyamide receptor can thoroughly change the recognition preference of sensors. We anticipate that the experimental results of this study should find utility in the future design of metal-ion sensors in water for a variety of chemical and biological applications.

Experimental section

Materials and measurements

All the solvents were of analytical grade. NMR experiments were carried out on a Bruker AV-400 NMR spectrometer with chemical shifts reported in ppm (in D_2O, $CDCl_3$, and CD_3OD). Mass spectra were measured on an Agilent 1290 LC-MS spectrometer. All pH measurements were made with a Sartorius basic pH-Meter PB-10. Fluorescence spectra were determined on a PerkinElmer LS55 Fluorescence spectrophotometer. Absorption spectra were collected on a Shimadzu UV 2501(PC) S UV-Visible spectrophotometer. The excitation and emission widths for **LS1–LS3** were all 5 nm.

Synthesis

Compound 3. Compound **3** was synthesized according to the literature.[14c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.60 (d, J = 1.2 Hz, 1H), 7.49 (dd, J = 8.4, 1.2 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 4.42 (s, 4H), 4.28 (s, 4H), 4.12 (m, 8H), 1.21 (t, J = 7.2 Hz, 12H).

Compound 4. 2.6 g of **3** (5.4 mmol) and 1.4 mL (15.9 mmol) of 2,4-dimethylpyrrole were dissolved in 30 mL of absolute dichloromethane under a nitrogen atmosphere, three drops of trifluoroacetic acid were added and the solution was stirred at ambient temperature for 10 h. A solution of dichlorodicyanobenzoquinone (DDQ, 1.2 g, 5.3 mmol) in 10 mL dichloromethane was added and stirring was continued for 4 h, followed by the addition of triethylamine (10.0 mL, 71.9 mmol) and BF_3-OEt_2 (10.0 mL, 79.6 mmol). After stirring for another 2 h, the reaction mixture was washed with 200 mL water, extracted with dichloromethane (3 × 100 mL). The extract was dried over sodium sulfate and then concentrated under vacuum. The product was purified by flash chromatography using petroleum ether–ethyl acetate (4 : 1, v/v) as the eluant to give 0.8 g (20%) of **4** as a red solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.0 Hz, 1H), 6.93 (s, 1H), 6.83 (d, J = 8.0 Hz, 1H), 5.95 (s, 2H), 4.34 (s, 4H), 4.28 (s, 4H), 4.16–4.01 (m, 8H), 2.54 (s, 6H), 1.40 (s, 6H), 1.19 (m, 12H).

Compound 5 (LS1). 68.0 mg of **4** (0.1 mmol) was dissolved in 5 mL acetonitrile, and 10 mL diethanolamine was added. The solution was refluxed under nitrogen for 24 h, cooled and concentrated under vacuum to get rid of the acetonitrile, then poured into 50 mL saturated brine. The mixture was neutralized with sodium dihydrogen phosphate, and extracted with dichloromethane (10 × 50 mL). The extract was dried over sodium sulfate and then concentrated under vacuum. The product was purified by flash chromatography using dichloromethane–methanol–triethylamine (10 : 3 : 1, v/v/v) as the eluant to give 21.0 mg (23%) of **LS1** as a red solid; ^{1}H NMR (400 MHz, D_2O) δ 6.82 (brs, 1H), 6.69 (s, 1H), 6.34 (brs, 1H), 5.98 (s, 1H), 5.97 (s, 1H), 4.49 (s, 4H), 4.45 (s, 4H), 3.56 (m, 16H), 3.37 (m, 16H), 2.30 (s, 6H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, D_2O) δ 172.74, 172.58, 155.46, 144.61, 142.69, 141.82, 141.75, 131.35, 127.34, 121.39, 121.20, 121.01, 119.69, 59.19, 59.13, 59.06, 53.95, 51.42, 50.14, 49.85, 48.48, 48.33, 13.78; HRMS (ESI) Calcd for $([M + H])^+$, 935.4861; Found, 935.4880.

The procedures of the synthesis of **LS2** and **LS3** were the same as **LS1**.

Compound 6. Compound **6** was synthesized according to the literature.[14c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.19 (s, 1H), 6.73 (d, J = 8.0 Hz, 1H), 4.58 (s, 2H), 4.26–4.07 (m, 10H), 1.19 (t, J = 6.8 Hz, 9H).

Compound 7. Red solid (13%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, J = 8.0 Hz, 1H), 6.81 (dd, J = 8.0, 1.6 Hz, 1H), 6.65 (d, J = 1.6 Hz, 1H), 5.97 (s, 2H), 4.62 (s, 2H), 4.30–4.12 (m, 10H), 2.54 (s, 6H), 1.44 (s, 6H), 1.26 (d, J = 7.2 Hz, 9H).

Compound 8 (LS2). Red solid (33%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.32 (d, J = 8.4 Hz, 1H), 6.97 (s, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.05 (s, 2H), 4.27 (s, 4H), 3.70 (m, 13H), 3.53 (m, 13H), 2.47 (s, 6H), 1.49 (s, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ 173.32, 170.98, 156.55, 152.46, 144.88, 142.04, 132.85, 122.53, 122.11, 114.02, 60.81, 60.54, 60.14, 56.07, 51.53, 50.96, 50.21, 49.76, 14.88; HRMS (ESI) Calcd for $([M + H])^+$, 791.3963; Found, 791.3968.

Compound 9. Compound **9** was synthesized according to the literature.[14c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.75 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 4.34–4.15 (m, 8H), 1.29 (t, J = 7.2 Hz, 6H).

Compound 10. Red solid (28%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.2 Hz, 2H), 6.71 (d, J = 8.2 Hz, 2H), 5.96 (s, 2H), 4.30–4.14 (m, 8H), 2.54 (s, 6H), 1.45 (s, 6H), 1.28 (t, J = 7.2 Hz, 6H).

Compound 11 (LS3). Red solid (48%); ^{1}H NMR (400 MHz, CD_3OD) δ 6.93 (d, J = 8.4 Hz, 2H), 6.73 (d, J = 8.4 Hz, 2H), 5.92 (s, 2H), 4.40 (s, 4H), 3.66 (m, 8H), 3.58–3.44 (m, 8H), 2.36 (s, 6H), 1.39 (s, 6H); HRMS (ESI) Calcd for $([M + H])^+$, 630.3274; Found, 630.3280.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant no. 20902082) and the Zhejiang Provincial Natural Science Foundation of China (Grant no. Y3100416).

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16 $\lg[Pb^{2+}] = -7.14$, the fluorescence intensity $I = 90.49$ ($I/I_0 \approx 2.76$, where $I_0 = 32.79$, is the emission intensity in the absence of Pb^{2+}).
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