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A new selective fluorescent probe for lead ions

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Abstract

A new fluorescent probe (BPb_1) for Pb^{2+} has been synthesized, where diethanolamine (receptor) is linked with 4,4-difluoro-4-bora-3a, 4a-diaza-s-indacene (BODIPY) (fluorophore) via a methylene group (spacer). The absorption (496 nm) and emission (505 nm) wavelengths are in visible range. The fluorescence quantum yields of the lead-free and lead-bound states of BPb_1 in acetonitrile are 0.013 and 0.693, respectively. The large chelation enhanced fluorescence effect (CHEF) with Pb^{2+} can be explained by the blocking of the photoinduced electron transfer (PET) process.

Keywords: Probe; Pb^{2+}; Selectivity; Photo-induced electron transfer; Fluorescence

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At present, the development of fluorescence probes for sensing of metal ions is an important goal in chemistry and biology due to their relatively high sensitivity, selectivity and short response time, local observation, etc [1]. Even though fluorescent probes for various metal ions have been developed over the last decades, there have been relatively few reports on Pb^{2+} selective fluorescent probes [2–20].

BODIPY dyes have excellent photophysics and photochemistry properties [21], so a few BODIPY-based fluorescence probes have been reported recently [22–27]. Herein, we reported a new BODIPY incorporated Pb^{2+} fluorescence probe based on photoinduced electron transfer mechanism. Synthesis of probe BPb_1 is shown in Scheme 1.

1. Experimental

All reactions were carried out under a nitrogen atmosphere with dry, freshly distilled solvents under anhydrous conditions. All the materials were obtained from commercial suppliers and were used without further purification.

^1H NMR and ^{13}C NMR spectra were obtained on a Varian INVOA 400 MHz spectrometer. High resolution mass spectra were obtained using Q-TOF mass spectrometry (Micromass, England). UV absorption spectra were obtained on a Perkin Elmer Lambda 35 spectrophotometer. Fluorescence emission spectra were recorded with a PTI-700 fluorimeter. Melting point was determined by an X-6 micro-melting point apparatus and was uncorrected.

Chloroacetyl chloride (1.94 mmol) and 1,4-dimethylpyrrole (3.9 mmol) were dissolved in 150 mL of absolute CH_2Cl_2 under a nitrogen atmosphere, the absolute CH_2Cl_2 was bubbled with N_2 for 0.5 h prior to use. Then the mixture

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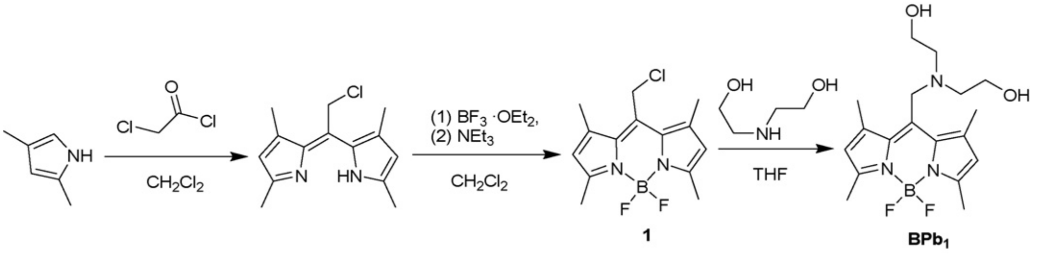

Scheme 1. Synthesis of probe BPb_1.

was stirred for 5 h at room temperature. The black solution was added 4 mL of triethylamine, followed by 8 mL of $BF_3·OEt_2$. The mixture was stirred under a N_2 atmosphere for another 4 h at room temperature. Finally, the reaction mixture was filtered, and evaporated to dryness. The crude compound was purified by flash column chromatography on silica gel (16:1 hexanes–EtOAc) to afford a red solid **1** in ca. 43% yield. A suspension of compound **1** (0.34 mmol), 2-(2-hydroxyethylamino)-ethanol (0.34 mmol), potassium iodide (0.10 mmol) and potassium carbonate (0.34 mmol) in 30 mL THF was stirred for 8 h at room temperature under N_2 atmosphere. After filtration, THF was removed by evaporation. The crude compound was purified by flash column chromatography (200:1 CH_2Cl_2–MeOH) to afford a yellow solid compound BPb_1 in ca. 53% yield. mp: 142–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.16 (s, 1H, CH), 6.15 (s, 1H, CH), 3.73 (t, 4H, $J = 4.6$ Hz, OCH_2), 2.96 (t, 4H, $J = 4.6$ Hz, CH_2N), 2.80 (s, 2H, NCH_2C), 2.63 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.44 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 149.14, 126.37, 125.99, 125.03, 122.24, 120.92, 117.99, 60.2, 45.98, 31.13, 21.41, 14.73, 13.65. HRMS: calcd. for $C_{18}H_{26}BF_2N_3O_2$ $[M + H]^+$, 366.2164; found, 366.2152.

2. Results and discussion

The absorption maximum wavelength of BPb_1 was 496 nm. The maintaining of the maximum absorption wavelength upon the binding of Pb^{2+} indicates a PET mechanism [1].

The fuorescence spectra of BPb_1 were obtained by excitation at 496 nm (Fig. 1.). BPb_1 showed a large CHEF effect with Pb^{2+}. The fluorescence quantum yield was improved from $\varphi_F = 0.013$ to $\varphi_F = 0.693$ when the Pb^{2+} was added [28]. During the complexation, the position of the fluorescence maximum emission wavelength did not change, which indicating that the large CHEF effects with Pb^{2+} can be explained by the blocking of the PET process. PET fluorescent probes are of great interest and promise because of their various applications. The electron transfer between the fluorophore (as signaling unit) and the receptor results in ‘‘switching off’’ of the fluorescence intensity. The presence of guests (metal ions or proton) capable of binding with the lone pair electrons of the receptor causes the PET

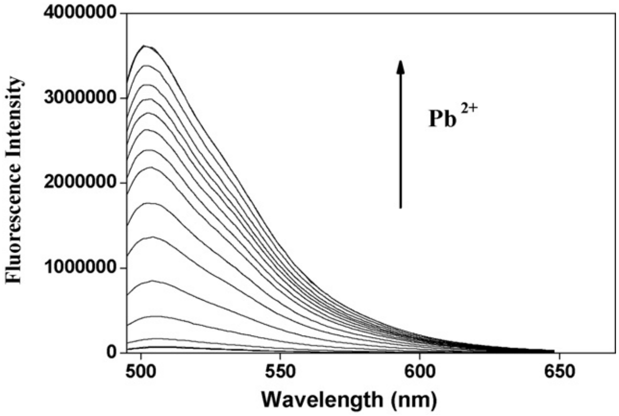

Fig. 1. Emission spectra of 1 μmol/L BPb_1 in the presence of 0–300 eq. of Pb^{2+}. These spectra were measured in acetonitrile (excitation at 496 nm). The slit width was 4 nm for both excitation and emission.