



Fluorescent sensors for Ca²⁺ and Pb²⁺ based on binaphthyl derivatives

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ABSTRACT

Two novel binaphthyl compounds have been synthesized for the selective fluorescent recognition of Ca²⁺ or Pb²⁺. By introducing different terminal groups to the receptor unit, the fluorescence signals of the receptors are significantly changed: **1** is fluorescence enhancement for Ca²⁺, **2** is fluorescence quenching for Pb²⁺. The binding properties for metal ions were examined by the absorption and fluorescence spectra. The fluorescence intensity enhancement was ascribed to the complex formation between Ca²⁺ and **1** which blocked the photo-induced electron transfer process.

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1. Introduction

Calcium ion play an important role as a messenger in biological systems. Many physiological processes are triggered, regulated, or influenced by calcium ion [1,2]. Lead ion is the most toxic heavy metal ion causing adverse environmental and health problems. A wide variety of symptoms (which include memory loss, irritability, anemia, muscle paralysis, and mental retardation) have been attributed to lead poisoning, suggesting that Pb²⁺ affects multiple targets *in vivo* [3]. Therefore, it is important to explore new methods for analyzing Ca²⁺ and Pb²⁺ *in vitro* and *in vivo*. Because of the importance of ionic calcium and lead in biological processes, chemists have been interested in the design of chemosensors for the specific detection of them.

Design of chemosensors for the selective detection of a specific analyte is a topic of considerable interest, due to their wide ranging application in the broad areas of chemistry, biology and optics [4–11]. In optical sensors, the use of fluorescence as detecting method offers distinct advantages in terms of sensitivity, selectivity and response time. Fluorescent molecular sensors have attracted considerable interest because of their intrinsic sensitivity and selectivity [4,6,7]. They are also called fluoroionophores because they consist in a recognition moiety (ionophore) linked to a transducing moiety (fluorophore). The choice of the fluorophore is of major importance because it governs the recognition event

into an optical signal owing to the change of its photophysical characteristics due to the perturbation by the bound cation of various photoinduced processes (electron transfer, energy transfer, charge transfer). The recognition moiety is responsible for the efficiency and selectivity of binding. Among ionophores for metal ions, binaphthyl-based ligands offer numerous advantages because of the rigidity of the complexing unit and tuneable strategies to obtain molecules with appropriate substituents. Although the beginning of the development can be traced back to the enantioselective quenching of binaphthyl-based fluorescence first reported about 30 years ago [12]. Only recently binaphthyl-based fluorescent sensors have been used for the monitoring of many chemical species [13–24].

In the early reports some fluorescent molecular sensors have been designed for Ca²⁺ or Pb²⁺, which include derivatives of crown ether [25–28], calixarene [29–32], anthracene [33–35], squaraine [36–39] and so on. Despite having many sensors, chemists continue endeavoring to design new ones and to improve their sensitivity, selectivity and reliability in order to satisfy various needs. In connection with our developments of fluorescent sensors for metal ions [40,41], and studies about binaphthyl-based ligands for luminescent lanthanide complexes [42–44], we designed and synthesized two binaphthyl-based compounds in a novel but simple approach as fluorescent sensors for Ca²⁺ and Pb²⁺, which show distinctly different optical properties. To best of our knowledge, much less attention has been paid to binaphthyl-based compounds as fluorescent sensors for metal ions. And to our surprise, only having different terminal groups, sensor **1** show selectivity and response toward Ca²⁺ with fluorescence enhancement, but sensor **2** is fluorescence quenching for Pb²⁺.

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2. Experimental

2.1. Materials

All commercially available chemicals were of A.R. grade and all solvents used were purified by standard methods.

2.2. Methods

IR-spectra were measured on Nicolet Nexus 670 FT-IR using KBr pellets in the range of 400–4000 cm^{-1} . The ^1H NMR spectra were recorded on a Varian Mercury plus 300BB spectrometer in CDCl_3 or d_6 -DMSO solution with TMS as internal standard. Fluorescence measurements were performed on a Hitachi F-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The excitation and emission slit widths were 5.0 nm. Absorption spectra were made on a Shimadzu UV-240 spectrophotometer. HRMS were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer.

2.3. Synthesis: compounds **1** and **2**

Compounds **1** and **2** were readily prepared according to Scheme 1. We introduced two different terminal groups into the 1, 1'-binaphthyl framework to construct the fluorescent receptors. All of the compounds were characterized by ^1H NMR, ^{13}C NMR, IR and HRMS. They were all obtained in high yield and were soluble in common organic solvents such as CHCl_3 , MeOH and DMSO.

2.4. Syntheses: compounds **1–4**

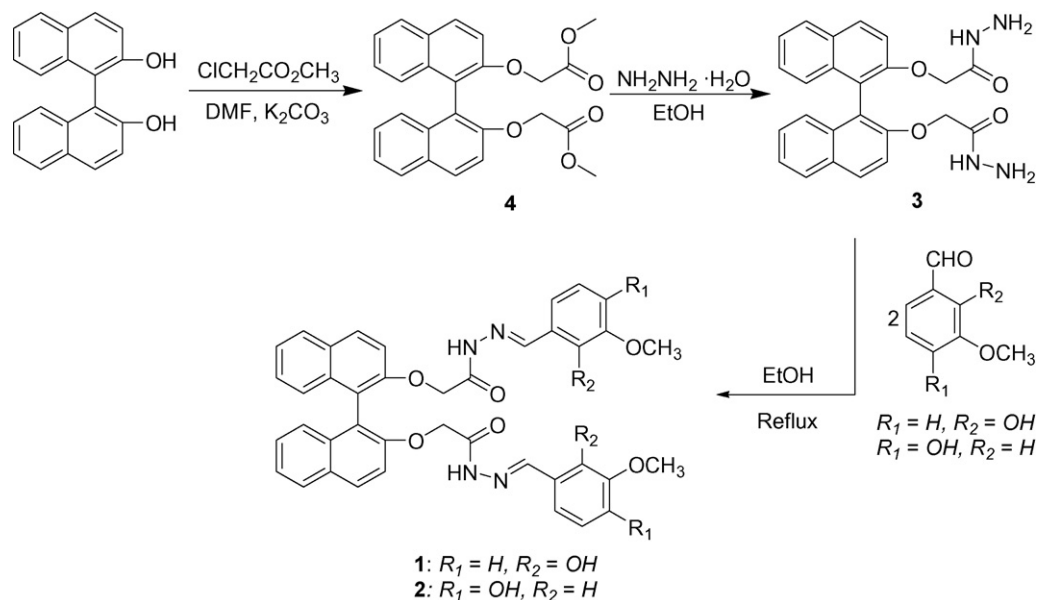
Anhydrous K_2CO_3 (9.5 g, 70.98 mmol) was added into the 10 mL DMF solution of 1, 1'-bi-2-naphthol (5 g, 17.48 mmol) at 80 °C. After two hours, a solution of methyl chloroacetate (4 g, 36.89 mmol) in 10 mL DMF was added dropwise to the mixture and maintained at 100 °C for 4 h. When cooled, 60 ml distilled water was poured and the turbid solution was extracted by 40 mL chloroform three times. Organic phase combined was washed with water and dried with anhydrous Na_2SO_4 . Solvent removed, the crude residue was purified by flash column chromatography on silica gel (Petroleum ether/AcOEt = 5:1 to 3:1) to afford the compound **4**; Yield: 65%. ^1H

NMR (300 MHz, CDCl_3): δ 7.96 (d, J = 9.0 Hz, 2H), 7.88 (d, J = 7.8 Hz, 2H), 7.39–7.34 (m, 4H), 7.25 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 4.57 (s, 2H), 4.56 (s, 2H), 3.64 (s, 3H), 3.64 (s, 3H) ppm. IR (KBr film): ν_{max} 2953, 1755, 1621, 1592, 1508, 1434, 1377, 1333, 1288, 1213, 1149, 1107, 1091, 1001, 819, 749 cm^{-1} . The hydrazine hydrate (1.5 g, 1.4 mL) was added to **4** (5 g, 11.63 mmol) in dry ethanol (10 mL) at 80 °C. Then the mixture was allowed to reflux for 4 h to afford **3** as a white solid; Yield: 91%. ^1H NMR (300 MHz, d_6 -DMSO): δ 8.73 (s, 2H, -NH-), 8.05 (d, J = 9.0 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.22 (t, J = 8.4 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 4.58 (d, J = 14.7 Hz, 2H), 4.44 (d, J = 14.7 Hz, 2H), 4.24 (brs, 4H, -NH₂) ppm. IR (KBr film): ν_{max} 3428, 3274, 3051, 2921, 1661, 1622, 1594, 1532, 1509, 1264, 1219, 1147, 1086, 985, 802, 737 cm^{-1} .

Compounds **1** and **2** were prepared according to the literature [45].

Compound **1**: yield: 92%. ^1H NMR (300 MHz, d_6 -DMSO): δ 11.57 (s, 1H, -N=CH-), 11.48 (s, 1H, -N=CH-), 11.29 (s, 1H, -N=C-OH), 10.89 (s, 1H, -N=C-OH), 10.69 (s, 1H, -NH-), 10.59 (s, 1H, -NH-), 9.36 (s, 2H, -OH), 8.33–8.27 (m, 2H), 8.15–8.01 (m, 2H), 7.99–7.93 (m, 2H), 7.60 (d, J = 8.1 Hz, 1H), 7.54–7.46 (m, 1H), 7.40–7.20 (m, 4H), 7.14–6.95 (m, 4H), 6.85–6.74 (m, 2H), 5.27–5.08 (m, 2H), 4.82–4.62 (m, 2H), 3.80 (s, 6H) ppm. ^{13}C NMR (75 MHz, d_6 -DMSO): δ 169.4, 164.5, 164.3, 153.9, 153.6, 148.2, 148.0, 147.1 (2C), 146.0, 141.4, 133.5, 133.4, 129.6, 129.4, 128.9, 128.1, 126.6, 125.2, 124.9, 124.7, 124.1, 123.6, 120.7, 120.5, 120.1, 119.2, 119.1, 118.8, 118.7, 118.0, 117.8, 116.4, 115.7, 113.9, 112.9, 68.4, 67.6, 56.2, 55.8 ppm. IR (KBr film): ν_{max} 3319, 3217, 3056, 2932, 2836, 1691, 1612, 1584, 1530, 1508, 1465, 1362, 1327, 1255, 1219, 1149, 1079, 946, 809, 778, 733 cm^{-1} . HRMS (ESI) m/z obsd 699.2443([M+H]⁺), calcd 699.2449 for $\text{C}_{40}\text{H}_{35}\text{N}_4\text{O}_8$.

Compound **2**: yield: 90%. ^1H NMR (300 MHz, d_6 -DMSO): δ 11.41 (s, 1H, -N=CH-), 11.29 (s, 1H, -N=CH-), 10.78 (s, 1H, -NH-), 10.18 (s, 1H, -NH-), 9.54–9.44 (m, 2H, -OH), 8.07–8.06 (m, 1H), 8.01–7.89 (m, 2H), 7.84–7.81 (m, 1H), 7.57–7.49 (m, 2H), 7.44–7.08 (m, 6H), 7.06–6.95 (m, 4H), 6.80–6.73 (m, 2H), 5.27–5.00 (m, 2H), 4.76–4.55 (m, 2H), 3.78 (s, 3H), 3.75 (s, 3H) ppm. ^{13}C NMR (75 MHz, d_6 -DMSO): δ 170.0, 169.7, 164.7, 164.5, 154.8, 154.5, 149.8, 149.5, 149.4, 149.0, 145.1 (2C), 134.0 (2C), 130.3, 130.0, 129.9, 129.6, 129.4, 128.7, 127.3, 126.1, 125.8, 125.4, 125.2, 124.6, 124.2, 123.0, 122.2, 120.4, 119.8, 118.5, 116.5, 116.1, 110.0, 109.5, 68.8, 68.2, 56.2, 56.1 ppm. IR



Scheme 1. The synthesis of receptors **1** and **2**.

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