Tetrahedron 74 (2018) 1668–1680

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

The turn-off fluorescent sensors based on thioether-linked bisbenzamide for Fe^{3+} and Hg^{2+}

Hehong Lv [b], Ziqi Ren [b], Heng Liu [a, b], Ganbing Zhang [a, b, **], Hanping He [a, b, *], Xiuhua Zhang [a, b], Shengfu Wang [a, b]

[a] Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei University, Youyi Road 368, Wuchang, Wuhan, Hubei 430062, PR China

[b] Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, College of Chemistry and Chemical Engineering, Hubei University, Youyi Road 368, Wuchang, Wuhan, Hubei 430062, PR China

ARTICLE INFO

Article history:
Received 1 December 2017
Received in revised form
4 February 2018
Accepted 14 February 2018
Available online 16 February 2018

Keywords:
Fluorescent sensor
Metal ion
Fe^{3+}
Hg^{2+}
Bisbenzamide

ABSTRACT

Some dibenzamide derivatives with a thioether linker were designed, synthesized and characterized. The specific responses to Hg^{2+} and Fe^{3+} were investigated by fluorescence. According to fluorescence titration, the Job plot, ^{1}H NMR, and ESI-mass analysis, the derivative with mono-hydroxyl substituent (**1b**) on the aromatic ring has high selectivity for Fe^{3+} ion with the formation of 1:1 **1b**-Fe^{3+} complexes. The specificity of **1c** for Hg^{2+} could be switched by swapping the substituent from hydroxyl to amino, and a 1:2 (**1c**-Hg^{2+}) complex was formed. Along with the obtained results, density functional theory (DFT) and natural bond orbital (NBO) analyses, Time-dependent (TD) DFT and natural transition orbital (NTO) analyses were employed to explore the geometric structures, properties and possible mechanisms.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Fluorescent sensors for metal ions have been widely applied not only in environmental monitoring but also in biological studies.[1-3] Especially in recent years, selective and sensitive detection of heavy and transition metal ions has been received considerable attention because these metals caused adverse health and environmental problems.[4-9] Particularly, Hg (II) was regarded as one of the most toxic metal ions. Due to its accumulative and highly toxic character, mercury can cause serious health problems like prenatal brain damage, cognitive and motion disorder, minamata diseases, etc.[10-12] Fe (III) is an essential trace element in fundamental physiological processes, being indispensable for all living systems. It performs the oxygen-carrying capacity of heme as well as acts as a cofactor in many enzymatic reactions.[13,14] However, its deficiency or overload has a toxic effect on living organisms and causes diseases such as anemia and hemochromatosis.[15,16] Because of these environmental and health problems of Hg^{2+} and Fe^{3+}, designing highly selective and sensitive chemosensors for these two metals has been still a challenge.

Up to now, significant progress was achieved in the selective detection of Hg^{2+} and Fe^{3+}.[17-27] Most of them were based on different organic molecular systems/materials that included azo-derivatives[17,25,20], crown-ethers[24,26], naphthalimide[19], anthraquinone[21], rhodamine[23,18], benzothiazole[27], BODIPY[25,26] and so on. Among these ion recognition units, crown ethers-based chemosensors were widely used due to their advantageous characteristics: the ability to coordinate the cations of alkaline metals, high selectivity and accessibility. So far, Crown ether derivatives incorporating a fluorescent moiety have been attractive tools for optical sensing of all kinds of ions, such as Hg^{2+}, Fe^{3+}, Ag^{+}, Pb^{2+}.[28] In 2008, Zhu et al. designed a novel dye containing dithia-dioxa-monoaza crown ether moiety that can perform highly sensitive detection of Hg^{2+} ion in the NIR region.[29] In 2014, Sui et al. presented a new Fe^{3+}-recognizing cryptand with high selectivity, sensitivity, and reversibility toward Fe^{3+} detection.[30] However, for most fluorescent sensors of Hg^{2+} and Fe^{3+}, a common limitation is that they are

---

* Corresponding author. Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei University, Youyi Road 368, Wuchang, Wuhan, Hubei 430062, PR China.

** Corresponding author. Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei University, Youyi Road 368, Wuchang, Wuhan, Hubei 430062, PR China.

E-mail addresses: gbzhang@hubu.edu.cn (G. Zhang), hehanping@hubu.edu.cn (H. He).

https://doi.org/10.1016/j.tet.2018.02.031

0040-4020/© 2018 Elsevier Ltd. All rights reserved.

rather complicated, delayed response to the ion, and that their analytical results are easily influenced by coexisting ions.[9] Additionally, most of sensors only worked well in the organic medium due to their poor aqueous solubility. Therefore, development of fluorescent sensors with more sensitivity, reliability, and aqueous medium solubility is in high demand for the detection of Fe^{3+} and Hg^{2+}.

In addition, podands linked different fluorescein are also used to identify various kinds of metal. Chang group previously reported a series of copper-responsive indicators containing both BODIPY and the double ethanedithiol units.[31,32] Nolan and co-workers synthesized a fluorescent sensor based on polioxo ethylene chain, which was used with alkaline earth cations was examined.[33] Inspired by these concepts, we have focused our interest on designing simple molecules which could serve as receptors to recognize Fe^{3+} based on a fluorescence 'on-off' mechanism. Herein we synthesized some ethanedithiol derivatives **1a-g** (Scheme 1) with two substituted benzamide units for detecting Fe^{3+} and Hg^{2+} ions in aqueous solution. The chelating groups like carbonyl and carboxamide had high binding affinity to transition metal ions in comparison with alkali and alkaline earth metal ions. Furthermore, the ethanedithiol linker is flexible, which is helpful to chelate Hg^{2+} and Fe^{3+} ions.[34] In this work, the changes of substituent groups on the benzene ring ortho of **1** significantly altered the fluorescence response toward the metal ions. To our surprise, compared to other six sensors, **1b** with hydroxyl substituent showed remarkable selective response toward Fe^{3+}. **1c** with amine enhanced the selectivity for Hg^{2+} ions over Fe^{3+} ions, when the hydroxyl is replaced with amino.

2. Results and discussion

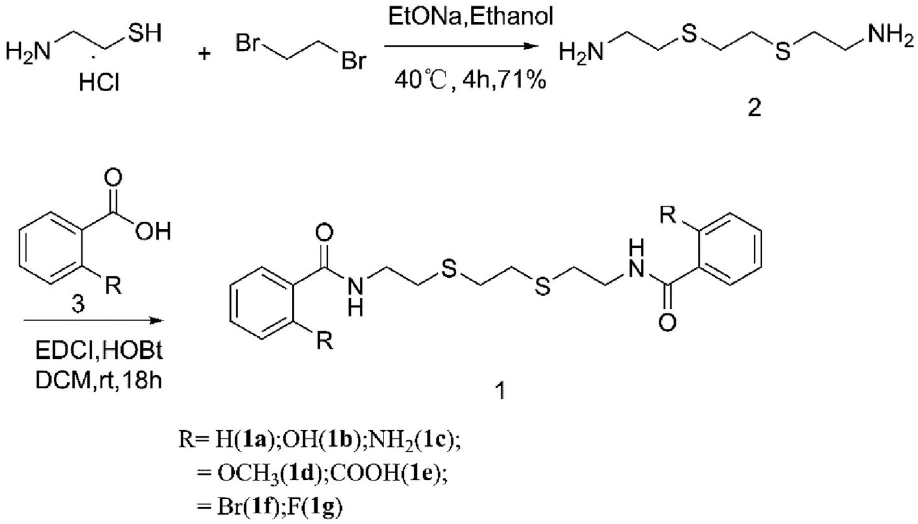
2.1. Synthesis

The compounds **1a**-**1g** featured with the thioether linker and dibenzamide units. Their synthetic pathways were similar (as shown in Scheme 1). Compound **2** was readily obtained by the reaction of cysteamine hydrochloride and1,2-dibromoethane in ethanol with a satisfied yield of 71%. Compound **2** was then reacted with different substituents of benzoic acid derivatives to give **1a,1b,1c,1d,1e,1f,1g**, respectively. The chemical structures of compounds **2** and **1a**-**1g** were characterized by ^{1}H NMR, ^{13}C NMR and ESI-MS (Figs. S1–S24, Supplementary data).

*2.2. Spectral studies and specificity of **1a-1g** to metal ions*

At first, the binding of probes **1a-1g** with metal ions was investigated by fluorescence spectroscopic measurements in DMSO/H_2O (5:95; v/v) mixed solution. As shown in Fig. 1 and Fig. S25, the probes (10 μM) exhibited better fluorescence. Particularly, the 10 μM free ligands **1b, 1c** and **1d** with electron-donating groups exhibited higher fluorescence emission intensities on excitation at 297, 317 and 290 nm, respectively. On the contrary, **1a, 1e, 1f** and **1g** with electron-accepting groups showed lower fluorescence emission intensities. The interaction of all the probes and various ions were investigated by fluorescence spectra. In the presence of excess metal ions (100 μM), it was found that the addition of Fe^{3+} into the receptors solution resulted in a varying decrement of fluorescence for free receptors **1a-1g**. Especially for probe **1b**, the fluorescence was almost quenched completely. The result indicated the probe **1b** exhibited an excellent selectivity for Fe^{3+}. Similarly, probe **1c** had good selectivity for Hg^{2+} as shown in Fig. 1. Pleasantly, for other ions including Na^{+}, K^{+}, Cu^{2+}, Fe^{2+}, Ba^{2+}, Mg^{2+}, Mn^{2+}, Ca^{2+}, Cr^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2}+, Co^{2+} and Cd^{2+}, the receptors (**1a-1g**) showed no apparent fluorescence intensity alternation. In addition, other +3 cations (such as Tm^{3+}、Gd^{3+}、Y^{3+}、Sc^{3+} and La^{3+}) didn't interfere the fluorescent emission (Fig. S26).

The detail fluorescence changes of the probes in the presence of Fe^{3+} and Hg^{2+} were analyzed as shown in Fig. 2. Here, the value of F/F_0 was used to represent fluorescence quenching degree, where F and F_0 represent the fluorescence intensity in the presence and absence of metal ions respectively. Although the fluorescence of these probes was quenched some certain after addition of Fe^{3+}, quenching of probe **1b** was most ($F/F_0 = 0.04791$) compared to other six probes. When the interactions of these probes and Hg^{2+} were analyzed, probe **1c** with amine substituent exhibited most binding to Hg^{2+} interestingly. The quenching was also studied using some different excitation wavelengths (260, 280, 330, 350 nm) again in a broad range. It was found that the fluorescence was similarly quenched by the addition of Fe^{3+} or Hg^{2+} (as shown in Fig. S27). The photos obviously showed the quenching (as shown in Fig. 2B and C). We didn't find obvious color changes in 1b or 1c solution when metal ions were added. The data of UV–vis spectrometry (Fig. S28) also showed that no significant changes were observed even in the presence of Fe^{3+} or Hg^{2+}. A small hyperchromicity was observed for 1b, the intensity of absorption peak



Scheme 1. Synthesis route to compounds **1a-1g.**

Download English Version:

https://daneshyari.com/en/article/7827423

Download Persian Version:

https://daneshyari.com/article/7827423

Daneshyari.com