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Highly Effective Fluorescent Sensor for Hg^{2+} in Aqueous Solution

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A new anthracene fluorophore senses Hg^{2+} selectively in aqueous solution. Among the metal ions examined, fluorescent chemosensor 1 shows selective large CHEQ effects with Hg^{2+} and Ag^{+} at pH 7.

Keywords: Fluorescent chemosensor; Fluorescent receptor; Anthracene; Ligand immobilization; Hg(II) detection

INTRODUCTION

Detection of metal ions with high specificity under physiologically relevant conditions is an important aspect in the design of fluorescent chemosensors for biological and environmental applications [1–5]. In particular, mercury contamination occurs through oceanic and volcanic emission [6], gold mining [7], solid waste incineration, etc. Because of the high toxicity of mercury, considerable attention has been focused on the development of new fluorescent chemosensors [8–20] and colorimetric sensors [21–24] for the detection of mercury and mercuric salts with sufficient selectivity.

Czarnik [18], Yoon [25] and colleagues have reported that the introduction of polyamine ligands and azacrown ligands to the 1,8-positions of the anthracene moiety Au: the anthracene moiety of what? changed the binding properties of these ligands towards metal ions. Shinkai *et al.* [26,27] reported azoarene-capped analogues of 1.10-diaza-4,7,14,17-tetrathiacyclooctadecane, which was also used in the present work. The conformation of the capped ligand according to its X-ray structure was reported to be substantially different from that of the free ligand [27]. 1.10-Diaza-4,7,14,17-tetrathiacyclooctadecane derivatives have also been reported by other groups [28–32].

We report here the binding properties of a new anthracene derivative that bears an azathiacrown ligand on the 1,8-positions of the anthracene framework. Compared to Shinkai's azopyridine-capped analogue [27], the thiaazacrown ligand in host **1** should be in a more rigid form; in addition, the anthracene moiety in host **1** acts not only as a fluorescent source but also as a template for introducing binding selectivity. Our fluorescent chemosensor **1** displays extreme selectivity for Hg^{2+} ions in aqueous solution at physiological pH.

RESULTS AND DISCUSSION

We prepared ligand **1** by reaction of 1.10-diaza-4,7,14,17-tetrathiacyclooctadecane with 1,8-bis-(bromomethyl)anthracene **2** as shown in Scheme 1. Our synthesis began with 1,8-bis(hydroxymethyl)anthracene, which was then transformed to **2** using the procedures of Nakagawa and co-workers [33–35]. Compound **1** was synthesized in 60% yield by the addition of **2** to a mixture of 1.10-diaza-4,7,14,17-tetrathiacyclooctadecane (1 equiv.), K_2CO_3 and $CHCl_3$ at room temperature.

From the pH-fluorescence profile, the pK_a of compound **1** was calculated as 7.2. An observed fluorescence dependence on pH is in keeping with the intramolecular amine quenching mechanism that has been described previously. Protonation of an amine group in fluorophore-amine conjugates results in the elimination of photoinduced electron

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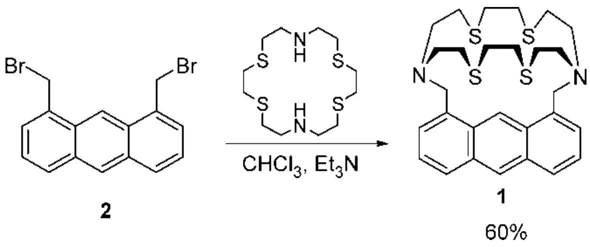

SCHEME 1 Synthesis of compound **1**.

transfer [28–32]. Therefore, fluorescence is expected to be a function of pH, and pH measurement using anthrylamines has been described by de Silva *et al.* [36]. To evaluate metal ion binding in aqueous solution, we measured the fluorescence change of compound **1** at pH 7 as both CHEF (chelation-enhanced fluorescence) and CHEQ (chelation-enhanced quenching) effects can be observed at this pH. If a quenching metal ion (e.g. Hg^{2+} via enhanced spin-orbital coupling [37], Cu^{2+} via energy or electron transfer [38]) binds tightly to the immobilized ligand **1**, intracomplex quenching takes place.

Ag^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+} and Zn^{2+} ions were used to evaluate the metal ion binding properties of **1**. All titration studies were conducted in 0.1 M HEPES (pH 7):DMSO (8:2, v/v) and using a 6 μM concentration of compound **1**. Using these metal ions (1 equiv.), compound **1** displayed large CHEQ effects with Hg^{2+} and Ag^{+}, even though there was a relatively small CHEQ effect with Cu^{2+} (Fig. 1). Fluorescent emission changes of compound **1** upon the addition of Hg^{2+} ions are shown in Fig. 2. From the fluorescent titrations, the association constants for Hg^{2+} and Cu^{2+} ions were calculated as 195 000 and 2100 M^{-1} (errors $<10\%$), respectively (Fig. 3) [39,40]. The selectivity for Hg^{2+} ions is almost 100 times that for Cu^{2+}. Overall emission change was almost 10-fold in the case of Hg^{2+}. Unfortunately, we were not able to obtain a consistent and reliable association constant for Ag^{+} from fluorescent titration experiments as the emission intensity did not consistently decrease upon the increase of Ag^{+} ion concentration.

Emission intensities of **1** with 6 μM Hg^{2+} in the presence of 600 μM of Ca^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+} and Zn^{2+} ions were the same as that using 6 μM Hg^{2+} alone (±5%).

In conclusion, an azathiacrown ligand **1** senses Hg^{2+} selectively in aqueous solution. Among the metal ions examined, fluorescent chemosensor **1** shows selective large CHEQ effects with Hg^{2+} ($K_a = 195\ 000\ M^{-1}$) and Ag^{+} at pH 7. In our case, the anthracene moiety in host **1** acts not only as a fluorescent source but also as a template for introducing the binding selectivity. These results suggest that the rigid capping of the azacrown ligand onto a fluorophore framework may be used successfully in the creation of selective chemosensors. Such selectivity is not yet predictable, but may be readily established by screening techniques.

EXPERIMENTAL

General Methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was

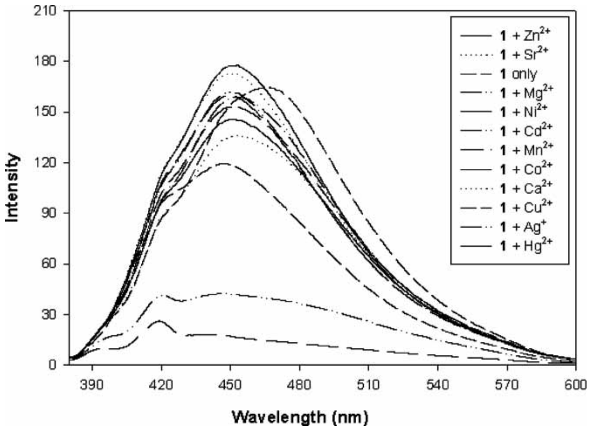

FIGURE 1 Fluorescent emission changes of **1** (6 μM) upon addition of Ag^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+} and Zn^{2+} (1 equiv.) in 0.1 M HEPES (pH 7):DMSO (8:2, v/v) (excitation at 365 nm).

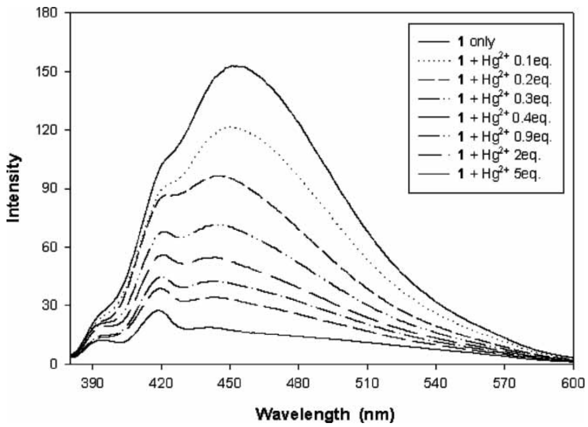

FIGURE 2 Fluorescent titrations of **1** (6 μM) upon addition of Hg^{2+} in 0.1 M HEPES (pH 7):DMSO (8:2, v/v) (excitation at 365 nm).

carried out on silica gel 60 (230–400 mesh ASTM; Merck). Thin layer chromatography (TLC) was carried out using Merck 60 F_{254} plates with a thickness of 0.25 mm. Preparative TLC was performed using Merck 60 F_{254} plates with a thickness of 1 mm.

Melting points were measured using a Büchi 530 melting point apparatus, and are uncorrected. ^1H and ^{13}C NMR spectra were recorded using a Bruker 500 spectrometer. Chemical shifts were expressed in ppm, using TMS as internal standard. Mass spectra were obtained using a JMS-HX 110A/110A Tandem Mass Spectrometer (JEOL).

Most of the chemicals including metal salts and HEPES were obtained from Sigma-Aldrich Chemical Company, Milwaukee, WI, USA. 1,8-Bis(hydroxymethyl)anthracene was purchased from TCI (Tokyo Kasei Organic Chemicals). $CHCl_3$, CH_2Cl_2 and MeOH were distilled from CaH_2. Compound **2** was prepared as described in the literature.

CAUTION. Although we have not experienced any problems with the perchlorate salts described herein, the usual precautions should be taken when handling these compounds [41].

1,8-(1.10-Diaza-4,7,14,17-tetrathiacyclooctadecane) bismethylanthracene (1)

To a solution of 1.10-diaza-4,7,14,17-tetrathiacyclooctadecane (0.44 g, 1.4 mmol) in triethylamine (0.38 ml, 2.8 mmol) and anhydrous $CHCl_3$ (200 ml) was added 1,8-bis(bromomethyl)anthracene (0.5 g, 1.4 mmol). The reaction mixture was stirred at room temperature for 4 h. The solution was concentrated in vacuo to yield a tan solid, which was loaded onto a silica gel column and eluted with 10% MeOH/$CHCl_3$. The appropriate fractions were combined, and concentrated in vacuo to yield **1** as an oily solid (0.44 g, 60%): ^1H NMR ($CDCl_3$, 500 MHz) δ 9.54 (s, 1H), 8.46 (s, 1H), 7.98 (d, $J = 7.8$ Hz, 2H), 7.40 (m, 4H), 4.26 (s, 4H), 2.94 (t, $J = 7.8$ Hz, 8H), 2.76 (m, 8H), 2.60 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.3, 134.5, 132.2, 130.9, 129.6, 129.4, 128.9, 128.4, 128.0, 127.8, 125.2, 120.9, 59.5, 55.9, 32.2, 30.3; FAB mass

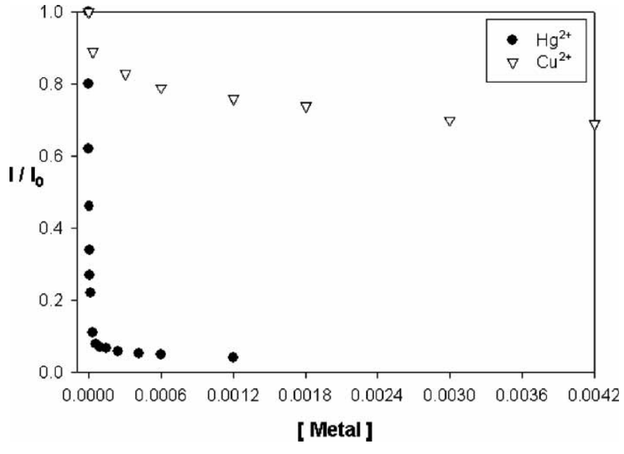

FIGURE 3 Fluorescent titrations of **1** (6 μM) in 0.1 M HEPES (pH 7):DMSO (8:2, v/v) as a function of metal concentration.

spectrum m/e 529.1844 $[M+H]^+$, calcd for $C_{28}H_{37}N_2S_4$ 529.1840.

Preparation of Fluorometric Metal Ion Titration Solutions

Stock solutions (1 mM) of the perchlorate salts of Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+} and Zn^{2+} ions in pH 7.0 HEPES (0.1 M) were prepared. Stock solution of **1** (0.1 mM) was also prepared in DMSO. Test solutions were prepared by placing 4–40 μL of the probe stock solution into a test-tube, adding an appropriate aliquot of each anion stock, and diluting the solution to 4 mL with pH 7.0 HEPES (0.1 M) and DMSO (8:2, v/v). For all measurements, excitation was at 365 nm; emission was measured at 451 nm. Both excitation and emission slit-widths were 5 nm.

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