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ORIGINAL ARTICLE

A Single Fluorescent Sensor for Hg^{2+} and Discriminately Detection of Cr^{3+} and Cr(VI)

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Abstract An iminocrown ether was synthesized and its fluorescence properties were studied in the presence of a variety of cations and anions in 99 % aqueous medium. The results revealed the interesting ability of the iminocrown ether in discriminately detection of Cr(III) and Cr(VI) ions in addition to detection of Hg^{2+} ion. Among various environmentally relevant metal ions, Cr^{3+} and Hg^{2+} enhanced and quenched the fluorescence emission, respectively and among anions only dichromate ion, Cr(VI), quenched the emission while the rest of ions insignificantly influenced the fluorescence emission. Selectivity of the iminocrown ether was also investigated and proved in the presence of excess of common competing ions. Furthermore, the fluorescence intensity of the iminocrown ether was studied as a function of concentrations of the three ions by performing a titration experiment for each one of them. The detection limits of 5.36×10^{-8}, 2.06×10^{-6}, and 7.49×10^{-8} mol L^{-1} were also calculated for Hg^{2+}, Cr^{3+}, and Cr(VI), respectively.

Keywords Fluorescent sensor · Iminocrown ether · Mercury · Chromium

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Introduction

Transition metals are significantly important mostly due to their either hazardous nature or crucial roles in environmental and biological systems [1, 2]. Mercury and chromium are two of these metal-ions which have attracted a great deal of attention. Mercury as Hg^{2+} inorganic salt is one of the most abundant toxic metals and causes environmental problems [3], in addition to a wide variety of health issues such as severe damage in central nervous system, heart, kidney, and genes even in low concentrations [4–6]. Furthermore, among the different valence states of chromium, Cr(III) and Cr(VI) are the most stable and hence the most prevalent ones in nature. Cr^{3+} as an essential trace element for biochemical processes, in addition to improving insulin sensitivity plays a vitally important role in metabolism of carbohydrates, proteins, and lipids [7]. Deficiency of chromium leads to a series of health problems such as diabetes and cardiovascular disease [8]. On the other hand, Cr(VI) easily finds its way into the environment as a pollutant because of its widespread utilization in surface industry, batteries, welding, corrosion control, catalysis, and etc. [9, 10]. Cr(VI) is more hazardous to the environment and humans compared to the other valence states of chromium and leads to severe damages in liver, kidney, and DNA [11, 12]. Hence, development of efficient methods for monitoring trace amounts of mercury and chromium ions has gained considerable attention.

A wide variety of methods such as atomic absorption [13, 14], coupled plasma-mass spectroscopy [15, 16], and voltammetry [17, 18] have been used for mercury and chromium detection in solutions. These methods are costly, time consuming and require precise pretreatments, trained operators and complicated instrumentation. Fluorescent sensors have proved to be convenient alternatives for these methods due to fast response times, low costs, easy detection, high sensitivity, and high selectivity [19, 20]. Thus, development of novel fluorescent sensors is of remarkable interest. Though, a series of fluorescent sensors have been reported for individually detection of Hg^{2+}, Cr^{3+} and Cr(VI) ions [21–26], to the best of our knowledge, no fluorescent sensor has been reported capable of detecting these three ions simultaneously. Moreover, most of the reported sensors for these ions suffer from poor solubility and applicability in aqueous media [27–30]. Also some reports have been published for detection of both Hg^{2+} and Cr^{3+} ions, [31, 32] which fail in distinguishing between the two ions. On the other hand, most of the fluorescent sensors reported for Cr^{3+} are of the quenching type because of its paramagnetic nature. Thus, it is an impressive challenge to develop sensors of enhancing type for Cr^{3+}. Considering the vitally important role of Cr^{3+} in biological processes and the toxic nature of Cr(VI), distinguishing between the two valence states is significantly important and demanded. As far as we are aware, some reports have been published for distinguishing between Cr^{3+} and Cr(VI) [33, 34], but no claim has been published reporting a fluorescent sensor capable of discriminating between Cr(III) and Cr(VI) ions, meanwhile differentiating them from rest of the ions. Designing a single sensor capable of discriminately detection of Cr(III) and Cr(VI) in addition to detection of Hg^{2+} with functionality in mostly aqueous medium can facilitate detection of the three ions and reduce the costs considerably beside saving the time and trouble of several sample preparation.

Crown ethers, first discovered by Pedersen [35], have been the subject of many studies in various fields such as chromatography [36, 37], phase transfer catalysis [38], ion extraction and transport [39, 40], membranes [41], and electrochemistry [42, 43]. Crown ethers are well-known for selectively formation of complexes with metal ions by electrostatic ion-dipole interaction between metal-ions and electron rich donor atoms of the crown ether. Complex formation of crown ethers is highly influenced by different parameters including the relative size of the crown ether cavity and the metal ion radius, number and type of electron donor atoms in the ring, basicity of the donor atoms, coplanarity of the crown ring, and the electrical charge on the metal ion [35]. These unique properties of crown ethers in complex formation make them promising compounds for selectively detection of metal ions. Nitrogen-containing crown ethers (imino/azacrown ethers) are particularly known for their high affinity toward transition metals [44] and have been the subject of a series of studies in metal recognition area [45]. To date a number of fluorescent sensors based on nitrogen-containing crown ethers have been published for detection of various metal-ions [46, 47] but, only few of them contained imino groups [48]. The interaction of these imino groups with-metal ions result in dramatic changes in the fluorescence properties of the fluorophore which is the key factor in the fluorescent sensors. Herein, we report application of an iminocrown ether as a fluorescent sensor in both cation and anion recognition in 99 % aqueous medium. The three benzo groups, in addition to the quite fixed cavity of the iminocrown ether result in a solid structure and hence a selective sensor. Besides, the two nitrogen atoms in the structure of iminocrown ether enhance its affinity toward transition metals.

Experimental

Materials and Reagents

Salicylaldehyde, O-phenylenediamine (Sigma Aldrich), potassium carbonate, 1,2-diaminobenzene, methanol, dimethylformamide (Merck), and dibromoethane (Acros Organics) were purchased and used without further purification. Stock solutions of all cations were prepared using their nitrate salts, and those of anions were prepared using their sodium or potassium salts.

Aparatus

FT-IR spectra were obtained in KBr disks on a WQF-510A FTIR spectrometer in 400–4000 cm^{-1} region. Fluorescence measurements were collected on a Cary Eclipse Fluorescent Spectrophotometer. UV-vis absorption spectra were obtained using an Analytik Jena Specord S600 spectrophotometer.

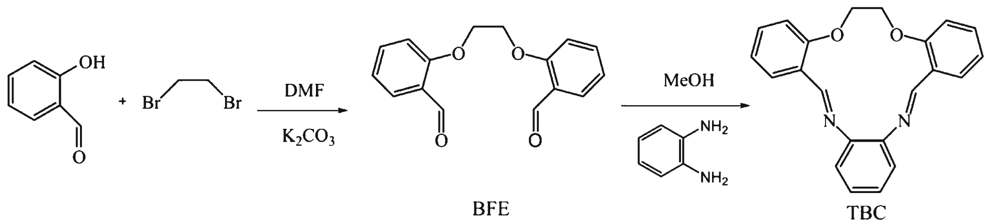
Synthesis of BFE

1,2-Bis(2-formylphenoxy)ethane (**BFE**) was synthesized based on a previous report [49] with slight modification. Salicylic aldehyde (1.560 g, 12.77 mmol) and 1,2-dibromoethane (1.0 g, 5.32 mmol) were added to dimethylformamide (8.0 mL) containing potassium carbonate (1.765 g, 12.77 mmol), and the mixture solution was stirred for 24 h at 50 °C under nitrogen protection. The resulted dark brown solution was then poured onto 200 mL water while stirring, and 1,2-bis(2-formylphenoxy)ethane was collected by filtration as a brown powder. Finally, colorless crystals were obtained after recrystallization from ethanol and subsequently from ethyl acetate. Yield: 1.09 g (75 %). M.p.: 144–146 °C (lit. [49] 146–148 °C). IR (KBr, cm^{-1}): 3083, 2949, 2870, 1688, 1598, 1483, 1455, 1407, 1250, and 1067.

Synthesis of TBC

3,4:9,10:13,14-Tribenzo-1,12-diaza-5,8-dioxacyclotetradecane-1,11-diene (**TBC**) was synthesized similar to the procedure reported before [50]. To a solution of BFE (2.7 g, 10 mmol) in 150 mL methanol, (1.08 g, 10 mmol) ortho-phenylene diamine in 30 mL methanol was added and the mixture was

Scheme 1 synthetic procedure of TBC



refluxed for 3 h. The solvent was evaporated to 30 mL and cooled to room temperature and then 60 mL of water was added while stirring. The suspension was let stand at 0 °C to yield a precipitate which was filtered off and dried at ambient temperature. Yield: 2.4 g (70 %). M.p.: 177–179 °C (lit. [51] 179–180 °C). IR (KBr, cm^{-1}): 3064, 2925, 2880, 1641, 1600, 1585, 1483, 1455, 1407, 1231, and 1052. The overall synthetic procedure of TBC is depicted in Scheme 1.

Results and Discussion

Cation Sensing

Sensing properties of TBC toward cations were studied in EtOH/H_2O (1:99, *v*/*v*) solution following excitation at 290 nm which caused an emission with a maximum at 373 nm. The fluorescence emission changes were monitored upon individually addition of 20 equivalents of different cations including Hg^{2+}, Cr^{3+}, Mn^{2+}, Mg^{2+}, Na^+, K^+, Ca^{2+}, Cd^{2+}, Pb^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} to 3 mL 1×10^{-5} M solution of TBC. The results (Fig. 1) revealed that the fluorescence intensity of TBC quenched in the presence of Hg^{2+} ions,

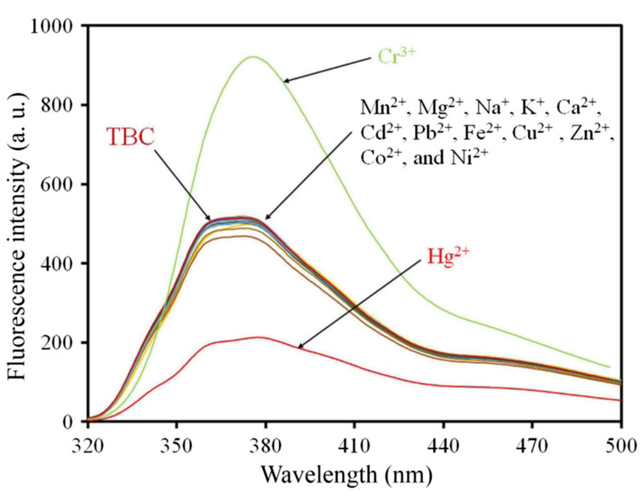


Fig. 1 Fluorescence emission of TBC in the presence of different metal ions including Hg^{2+}, Cr^{3+}, Mn^{2+}, Mg^{2+}, Na^+, K^+, Ca^{2+}, Cd^{2+}, Pb^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} in EtOH/H_2O (1:99, *v*/*v*) solution, [TBC] = 1×10^{-5} M and [M^{n+}] = 1×10^{-4} M (20 eq.) (λ_{ex} : 290 nm and λ_{em} : 373 nm)

whereas the presence of Cr^{3+} ions had an opposite effect on the spectrum and enhanced the intensity. The rest of ions negligibly influenced the fluorescence spectrum of TBC. The quenching effect of Hg^{2+} ion can be attributed to the interaction of the ion with electron-donor oxygen and nitrogen atoms of TBC and heavy atom effect [52]. On the other hand, the enhancement of the fluorescence intensity in the presence of Cr^{3+} is probably due to the chelation of TBC with Cr^{3+} ion and inhibition of lone-pair electrons of the imine nitrogen atoms from taking part in photoinduced electron transfer (PET) process [53]. The strong affinity of Cr^{3+} to bind with receptors containing sp^2 nitrogen atoms is already well-known [54].

The quenching mechanism of the sensor with Hg^{2+} was further investigated using the following Stern-Volmer equation (1):

$$F_0/F = 1 + K_{sv}[Q] \quad (1)$$

where F_0 and F are the fluorescence intensities in the absence and presence of the quencher, respectively. [Q] is the concentration of the quencher, i.e. Hg^{2+} and K_{sv} is the quenching constant. Plotting the F_0/F versus concentration of Hg^{2+} ion gave a linear plot (Fig. 2). The linearity of the plot indicates that the quenching mechanism is either purely static or purely dynamic. To determine the right mechanism, absorption spectra of TBC was recorded in absence and presence of Hg^{2+} ion. The absorption spectrum of TBC in presence of Hg^{2+} is distorted from that of TBC in absence of Hg^{2+} ion (Fig. 3) which results from a complex formation between TBC and Hg^{2+} ion before the excitation and suggests that a static quench has taken place. The quenching constant for Hg^{2+} was calculated to be 5.03×10^4 mol^{-1} by Stern-Volmer equation.

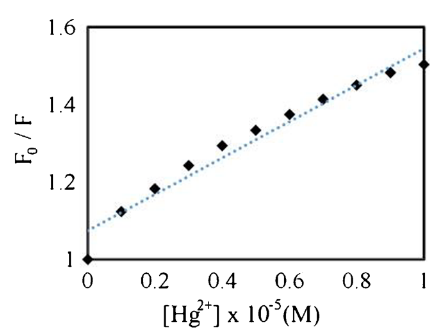


Fig. 2 Stern-Volmer plot for titration of TBC with different concentrations of Hg^{2+} ion

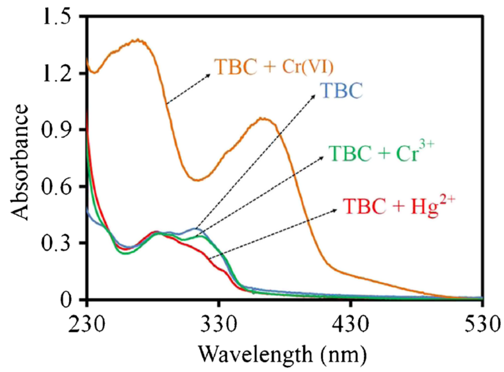


Fig. 3 The absorption spectra of TBC in absence and presence of Hg^{2+}, Cr^{3+}, and Cr(VI)

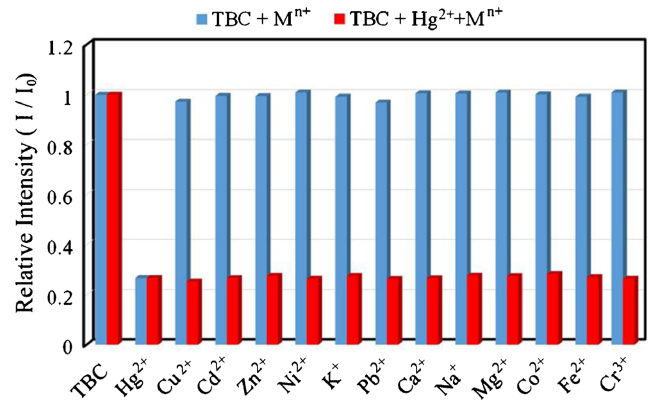


Fig. 5 Selectivity of TBC for Hg^{2+} (1 eq.) in the presence of other metal ions (5 eq. except for Cr^{3+} (1 eq.)) in EtOH/H_2O (1:99, *v*/*v*) solution (λ_{ex} : 290 nm and λ_{em} : 373 nm)

To determine the stoichiometry between TBC and the two metal-ions, the Job's plot method was applied (Fig. 4). For both Cr^{3+} and Hg^{2+} a 1:1 complexation was obtained.

Binding Constant

The binding constants of TBC to both Hg^{2+} and Cr^{3+} were calculated by Benesi-Holdebrand equation (2):

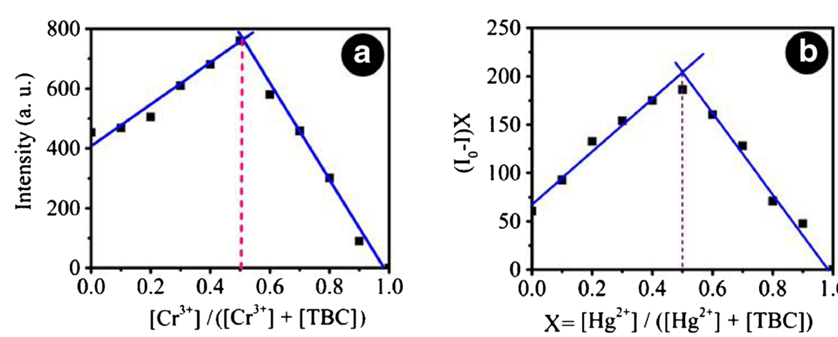
$$1/\Delta F = (1/\Delta F_{max}) + (1/K[C]^n)\,(1/\Delta F_{max})$$
$$\Delta F = (F_x - F_0),\ \text{and}\ \Delta F_{max} = (F_\infty - F_0). \qquad (2)$$

where F_0, F_x, and F_∞ are the emission intensities in absence, at an intermediate, and at a metal-ion concentration of a complete interaction, respectively. K is the binding constant, [C] is the concentration of the metals, and n is the number of binding metal-ions to TBC (here $n = 1$). The values of K obtained from the slopes were 1.16×10^5 and 1.32×10^4 mol^{-1} for Hg^{2+} and Cr^{3+}, respectively.

Selectivity of the sensor toward Hg^{2+} and Cr^{3+} was also investigated in the presence of 5 equivalents of competing metal-ions (except for Hg^{2+} and Cr^{3+} competition which was performed in presence of 1 equivalent of each ion) in EtOH/H_2O (1:99, *v*/*v*) solution. The results (Fig. 5) demonstrated that even much higher concentrations of the competing ions barely affected the fluorescence intensity of Hg^{2+} + TBC systems and proved the high selectivity of the sensor toward Hg^{2+} ion. Furthermore, equivalent amounts of Cr^{3+} did not interfere in Hg^{2+} detection which means TBC has more affinity toward Hg^{2+} than Cr^{3+}. The results of selectivity experiment for Cr^{3+} (Fig. 6) also revealed the selectivity of the sensor toward Cr^{3+} ion except in presence of Hg^{2+} ion.

To evaluate the influence of Hg^{2+} and Cr^{3+} concentrations on the fluorescence intensity of the TBC, titration experiment was performed in EtOH/H_2O (1:99, *v*/*v*) solution for each ion. The sensor demonstrated higher sensitivity toward Hg^{2+} compared to Cr^{3+} and it was observed that relatively lower starting concentrations of Hg^{2+} ions were utilized for the experiment. With increasing the ions concentration, the emission intensity of TBC decreased gradually (Fig. 7) and a good linearity was obtained between Hg^{2+} concentrations and reduction in the fluorescence intensity of the sensor (Fig. 7, inset). As for Cr^{3+} ions, with the increase of the ion concentration, the fluorescence emission intensity increased (Fig. 8) and resulted in a linear plot of the Cr^{3+} concentrations versus the fluorescence intensity (Fig. 8, inset). Furthermore, detection limits (DL) were calculated for both Hg^{2+} and Cr^{3+} in EtOH/H_2O (1:99, *v*/*v*) solution on the basis of DL = 3σ/m, where σ is the standard deviation of blank solutions and m is the slope of fluorescence intensity against concentration of the target ion. The detection limit values obtained as 5.36×10^{-8} and 2.06×10^{-6} mol L^{-1} were for Hg^{2+} and Cr^{3+}, respectively which show the sensitivity of the sensor toward both ions particularly Hg^{2+}.

Fig. 4 Job's plots for the complexation of TBC with Cr^{3+} (**a**) and Hg^{2+} (**b**), where I and I_0 are the fluorescence intensities in the presence and absence of the metal-ions



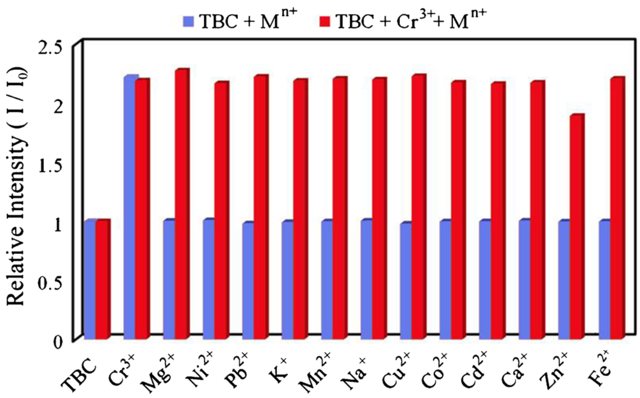


Fig. 6 Selectivity of TBC for Cr^{3+} (1 eq.) in the presence of other metal ions (5 eq.) in EtOH/H_2O (1:99, *v/v*) solution (λ_{ex} : 290 nm and λ_{em} : 373 nm)

Anion Sensing

The sensing properties of TBC were also investigated toward anions under the same conditions as for cations. Fluorescence emission of TBC was studied in the presence of a variety of anions including $Cr_2O_7^{2-}$, CN^-, HCO_3^-, CO_3^{2-}, HPO_4^{2-}, $CH_3CO_2^-$, NO_3^-, $H_2PO_4^-$, $S_2O_3^{2-}$, F^-, Cl^-, Br^-, I^-, SO_4^{2-}, SCN^-, and NO_2^- (Fig. 9). It was observed that the fluorescence emission interestingly quenched in the presence of dichromate ions, Cr(VI), which is a stable form of chromium other than Cr(III). The rest of anions either slightly increased or negligibly decreased the intensity, meaning no interference in Cr(VI) detection. The quenching mechanism of TBC with Cr(VI) was further investigated by the same procedure previously applied for Hg^{2+} ion using the Stern-Volmer equation (1). Results (Fig. 10) show a linear plot of F_0/F against the concentration of Cr(VI) ion which indicates an either purely static or purely dynamic quench as the quenching mechanism

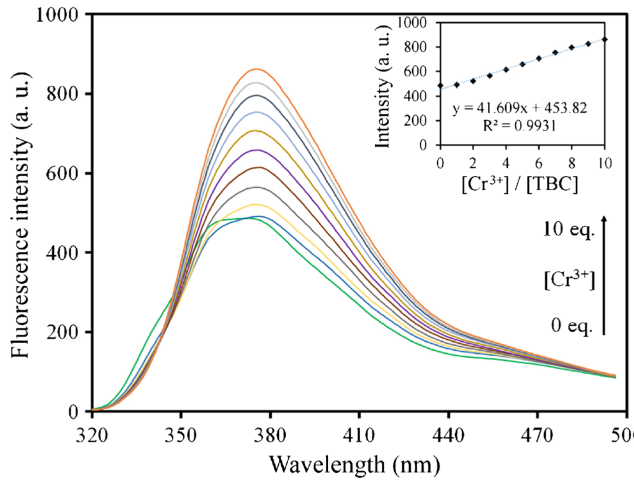


Fig. 8 Fluorescence emission of TBC upon addition of Cr^{3+} ions in EtOH/H_2O (1:99, *v/v*) solution, [TBC] = 1×10^{-5} M, [Cr^{3+}] = (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and10 eq.). Inset: fluorescence emission as a function of Cr^{3+} concentration (0–10 eq.) (λ_{ex} : 290 nm and λ_{em} : 373 nm)

of TBC emission by Cr(VI) ion. Since the absorption spectrum of TBC in the presence of Cr(VI) ion distorts from that of TBC in absence of the ion, a static quench occurs. The value of quenching constant was also calculated as 2.37×10^5 mol^{-1}. The complexation between TBC and Cr(VI) was also determined by Job's plot method and results showed a 1:1 stoichiometry (Fig. 11).

Binding Constant

The binding constant of TBC to Cr(VI) was also estimated by the same procedure illustrated before for Hg^{2+} and Cr^{3+} ions, using the Benesi-Hidebrand equation (2). The value of the binding constant was obtained as 9.97×10^4 mol^{-1}.

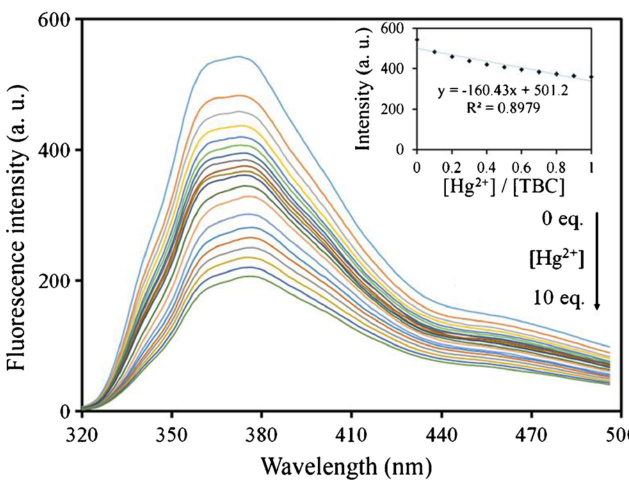


Fig. 7 Fluorescence emission of TBC upon addition of Hg^{2+} ions in EtOH/H_2O (1:99, *v/v*) solution, [TBC] = 1×10^{-5} M, [Hg^{2+}] = (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, 6, 7, 8, 9 and10 eq.). Inset: fluorescence emission as a function of Hg^{2+} concentration (0–1 eq.) (λ_{ex} : 290 nm and λ_{em} : 373 nm)

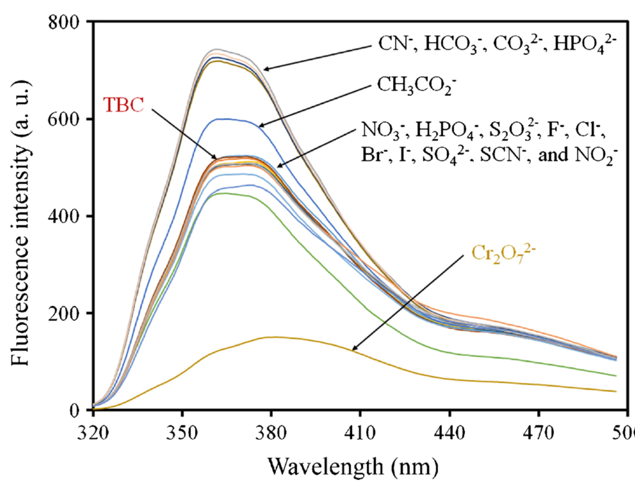


Fig. 9 Fluorescence emission of TBC in the presence of different anions including $Cr_2O_7^{2-}$, CN^-, HCO_3^-, CO_3^{2-}, HPO_4^{2-}, $CH_3CO_2^-$, NO_3^-, $H_2PO_4^-$, $S_2O_3^{2-}$, F^-, Cl^-, Br^-, I^-, SO_4^{2-}, SCN^-, and NO_2^- in EtOH/H_2O (1:99, *v/v*) solution, [TBC] = 1×10^{-5} M and [A^{n-}] = 1×10^{-4} M (20 eq.) (λ_{ex} : 290 nm and λ_{em} : 373 nm)

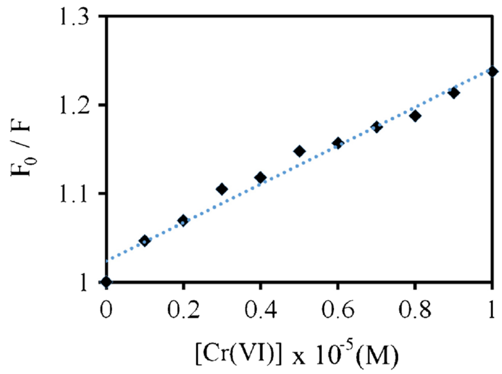


Fig. 10 Stern-Volmer plot for titration of TBC with different concentrations of Cr(VI) ion

To ensure the lack of interference by common accompanying anions in detection of dichromate, selectivity test was also performed in which the fluorescence emission changes of Cr(VI) + TBC system were examined in the presence of various competing ions. The obtained results (Fig. 12) revealed that competing anions even in much higher concentrations (5 eq.) insignificantly affected the emission of the system and this fact proved high selectivity of the sensor toward Cr(VI) ion.

A titration experiment was also performed to evaluate the effect of Cr(VI) concentration on the fluorescence intensity. As presented (Fig. 13), upon addition of Cr(VI) concentrations to TBC solution, the fluorescence emission intensity decreased gradually. Also, plotting the concentrations of dichromate ions against the emission intensity (Fig. 13, inset), showed a linear relationship between the two factors. The detection limit was then calculated for Cr(VI) ion by a similar method applied for Hg^{2+} and Cr^{3+} before and 7.49×10^{-8} mol L^{-1} was obtained which shows high sensitivity of the sensor toward Cr(VI) ion.

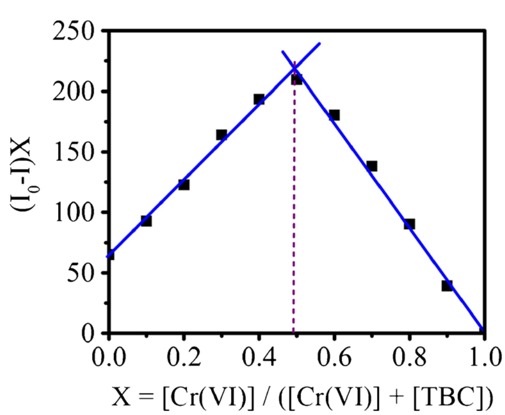


Fig. 11 Job's plots for the complexation of TBC with Cr(VI), where I and I_0 are the fluorescence intensities in the presence and absence of the metal-ions

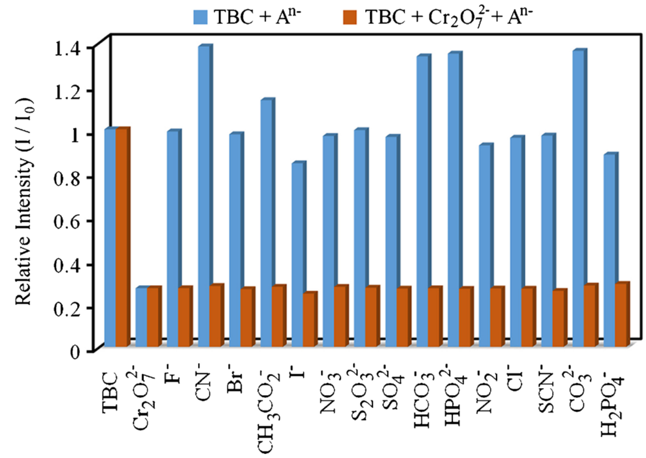


Fig. 12 Selectivity of TBC for Cr(VI) (1 eq.) in the presence of other anions (5 eq.) in EtOH/H_2O (1:99, *v*/*v*) solution (λ_{ex} : 290 nm and λ_{em} : 373 nm)

Conclusion

TBC was synthesized with a two-step procedure. The fluorescence properties of the synthesized iminocrown ether were investigated in the presence of a variety of cations and anions and results revealed its capability in selectively detection of Hg^{2+}, Cr^{3+}, and Cr(VI) in 99 % aqueous media. Quenching mechanisms were also determined to be of static type for Hg^{2+} and Cr(VI) ions with $K_{sv} = 5.03 \times 10^4$ and 2.37×10^5 mol^{-1}, respectively. The binding constants were also estimated as 1.16×10^5, 1.32×10^4, and 9.97×10^4 mol^{-1} for Hg^{2+}, Cr^{3+}, and Cr(VI), respectively. Furthermore, in the selectivity experiment, even 5 equivalents of the common competing ions did not interfere in recognition of the target ions which proves the high selectivity of the sensor toward the ions. Titration experiments demonstrated a linear relationship

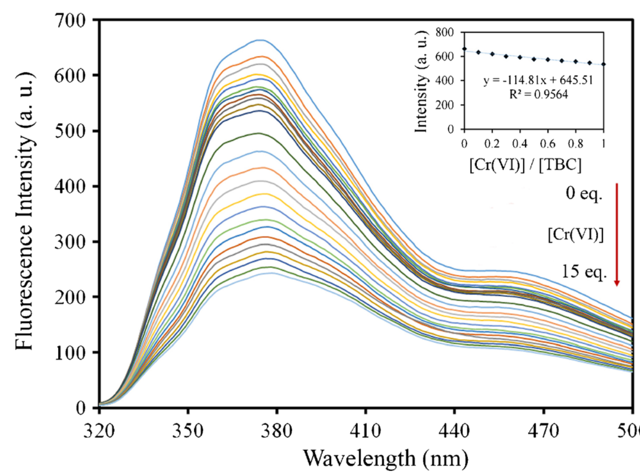


Fig. 13 Fluorescence emission of TBC upon addition of Cr(VI) ions in EtOH/H_2O (1:99, *v*/*v*) solution, [TBC] = 1×10^{-5} M, [Cr(VI)] = (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 eq.). Inset: fluorescence emission as a function of Cr(VI) concentration (0–1 eq.) (λ_{ex} : 290 nm and λ_{em} : 373 nm)

between the concentration of the ions and the fluorescence intensity variation. Finally, the limits of detection were calculated as 5.36×10^{-8}, 2.06×10^{-6} and 7.49×10^{-8} mol L^{-1} for Hg^{2+}, Cr^{3+}, and Cr(VI), respectively. Quite low detection limits acquired, showed the high sensitivity of the sensor toward the three ions, particularly Hg^{2+} and Cr(VI).

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