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Synthesis and spectroscopic-electrochemical properties of novel ratiometric Hg (II) chemosensor containing Bodipy and the N-phenylaza-15-crown-5 moiety

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Abstract

The aryl-amine containing azacrown ether ring and alkyl-chloro boradiazaindacene (Bodipy) were synthesized by Schiff base condensation. The absorption and emission of a novel Schiff base derivative (based on azacrown-Bodipy) were performed in presence of different cations such as Zn^{2+} , Ga^{3+} , Pb^{2+} , Hg^{2+} , NH_4^+ , Ca^{2+} , Cu^{2+} , Na^+ , Ni^{2+} , Cd^{2+} and Cr^{3+} . The complexation property of the Schiff base was studied in dimethylformamide (DMF) by interacting azacrown-ether group and transition metal nitrates-ammonium chloride. The electrochemical behavior of the Schiff base has also been investigated by cyclic voltammetry. All experimental results indicated that the new compound act as a selective ratiometric chemosensor for Hg^{2+} .

Keywords

Bodipy; Azacrown Ether; Chemosensor; Absorption; Emission; Cyclic voltammetry

1. Introduction

Chemosensor compounds have been utilized mainly for the detection of toxic metal ions in macromolecular chemistry just as they have in pharmacology, environmental chemistry and biochemistry [1–5]. Multi-systems containing some fluorophore groups are extensively investigated as both theoretical and experimental applications. Most works have concerned the binding of various fluorescent dyes to the azacrown ethers and their spectroscopic-electrochemical properties due to the complex reactions [6–9]. These compounds are commonly considered functional cages because of their ability to heavy or alkali metal sensors by using light [10–12]. Among the functional cages that reacted with the fluorescent dyes, Bodipy is certainly one of the most important. However, the studies on azacrown ether ring-containing Bodipy as a fluorescent sensor has been rarely reported [13–16]. Bodipy dyes as a special class of fluorophores are synthesized for desired photophysical changes (Stoke's shift etc.) through binding of the analyte. A large number of the donor fluorophores have been developed for selective detection of Hg^{2+} ions [17–20]. Due to their intense fluorescence, Bodipy's have been found useful in the synthesis of novel fluorescent sensor for Hg^{2+} cation and the energy transfer from Bodipy-terminal to metal ion detected. Binding of the analyte to Bodipy as fluorescent sensor can be caused in either enhancement or

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quenching of the emission [21, 22]. The Bodipy-terminal behaves as an antenna complex capable of light harvesting and other units serve as fluorophore (by the binding of analyte) [23, 24]. Analyte binding to the potential chelate group (azacrown) will cause some changes in absorption and fluorescence spectra [25]. The changes in the emission spectra occur via a process such as charge transfer, electron transfer, through-space energy-transfer or through-bond energy-transfer [26–28].

This paper concerns the synthesis and spectroscopic-electrochemical properties of a novel combination of N-phenylaza-15-crown-5 and Bodipy units. We aimed to synthesize the Bodipy derivative that carried out energy transfer and ion binding from donor part as molecular sensor. The Schiff base prepared by several techniques shows a ratiometric fluorescent behavior toward Hg (II) cation such as classical reaction of complexation. To the best of our knowledge, this is an important fixation Crown-Bodipy based reactive sensor for Hg (II) cation.

2. Experimental Section

Absorbance spectra are collected by a *Perkin Elmer Lambda 25 UV-vis spectrophotometer* using quartz cells of 1.0 cm path length. Fluorescence measurements are carried out in a *PerkinElmer LS 55 spectrofluorimeter*. The fluorescence spectra are recorded in a 1 cm quartz cuvette at room temperature. The excitation and emission slits are set at 5 nm. ^1H and ^{13}C NMR spectra were recorded on *Varian 400 MHz NMR*. All reagents are purchased from *Sigma-Aldrich (MO, USA)*, *Fisher Scientific (USA)*, *Merck (Germany)* and *Acros Organics (USA)* in analytical grade and used as received, unless otherwise stated. The percentages of carbon, hydrogen and nitrogen in all compounds were determined using a *TruSpec* elemental analyzer. Moreover, the solutions of Bodipy-metal ion were mixed by *Kudos Ultrasonic Cleaner 53 kHz*. The metal ions in DMF solution were prepared from their nitrate salts. All electrochemical experiments were performed using a CH Instruments electrochemical analyzer (*Model 600C Series*) equipped with a *BAS C3* cell stand. The working electrode was a bare glassy carbon disk (*BAS Model MF-2012*) with a geometric area of 0.027 cm². The reference electrode was Ag/AgCl/KCl_(sat.) and the counter electrode was a Pt wire. Glassy carbon electrodes were polished first using fine wet emery papers with grain size of 4000 (Buehler, Lake Bluff, IL, USA) then with 0.1 μm and 0.05 μm alumina slurry on a polishing pad (Buehler, Lake Bluff, IL, USA) to give them a mirror-like appearance. The electrodes were sonicated for 15 min in water and in 50:50 (v/v) isopropyl alcohol and acetonitrile (IPA + MeCN) solution purified over activated carbon.

2.1. The synthesis of 8-{4-(Chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (1)

To a stirred solution of 2,4-dimethyl-3-ethylpyrrole (2.5 mL) in dry dichloromethane (100 mL), 4-(chloromethyl)benzoyl chloride (1.875 g, 10 mmol) was added drop wise at room temperature and under N₂. The solution was heated and stirred to 60 °C for 2 h. After cooling of the solution, triethylamine (TEA) (5 equiv.) was added to the residual solid, the mixture was stirred at room temperature for 30 min under N₂, and boron trifluoride diethyl etherate (7 equiv.) was then added. The solution was stirred at 60 °C for 2 h and the final residue was purified by column chromatography (petroleum ether-EtOAc; in 8:1 ratio) and obtained to reddish an adhesive material. ^1H NMR [400 MHz, CDCl₃]: δ (ppm) 7.41 (d, 2H, ArH), 7.18 (d, 2H, ArH), 4.63 (s, 2H, CH₂), 2.44 (s, 6H CH₃), 2.21 (q, 4H, CH₂), 1.27 (s, 6H, CH₃), 0.89 (t, 6H, CH₃). ^{13}C NMR [100 MHz, CDCl₃]: δ (ppm); 153.81, 139.42, 138.42, 136.12, 135.81, 132.83, 130.62, 129.02, 128.78, 45.59, 17.07, 14.43, 12.43, 11.62. Anal.Calc. for (%) C₂₄H₂₈N₂F₂ClB: C, 67.23; H, 6.58; N, 6.53; Found: C, 66.82; H, 6.98; N, 6.12.

2.2. The synthesis of 8-{4-(benzyloxy)benzaldehyde}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (2)

1 (0.429 g, 1.00 mmol, 1 equiv.) was dissolved in DMF (70 mL), 4-hydroxybenzaldehyde (0.183 g, 1.5 equiv.) was added to this solution followed by 5 equivalents K_2CO_3 as solid. The mixture was refluxed 24 h. The acetone was then removed under vacuo and ethylacetate (100 mL) was added to the residue. The solution was extracted with ethylacetate (200 mL) and water (2x200 mL) and brine (1x200 mL). The organic layer was collected and dried over anhydrous magnesium sulphate. Then, the solvent of the filtration was removed, after which the residue was purified through a column eluting with 4:1; petroleum ether:ethyl acetate. The relevant fractions were collected and the solvent was removed by evaporation. A red solid was obtained.

1H NMR [400 MHz, $CDCl_3$]: δ (ppm) 9.90 (s, 1H, CHO), 7.81 (d, 2H, ArH), 7.55 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.08 (d, 2H, ArH) 5.25 (s, 2H, CH_2), 2.52 (s, 6H, CH_3) 2.27 (q, 4H, CH_2) 1.26 (s, 6H, CH_3) 0.96 (t, 6H, CH). ^{13}C NMR [100 MHz, $CDCl_3$]: δ (ppm); 189.33, 161.31, 139.24, 137.42, 135.43, 134.12, 133.51, 132.83, 131.44, 130.62, 129.02, 128.78, 117.55, 57.59, 18.57, 15.33, 13.93, 12.82. Anal.Calc. for (%) $C_{31}H_{33}N_2O_2BF_2$: C, 72.38; H, 6.47; N, 5.45; Found: C, 71.92; H, 6.98; N, 5.12.

2.3. The synthesis of N-(4-aminophenyl)aza-15-crown-5 (3)

This compound was prepared according to the literature procedure [29, 30] N-(4-nitrosophenyl)aza-15-crown-5 (1.60 g, 4.90 mmol) was dissolved in 3 mL hydrochloric acid (37%) and 1.6 mL water. $SnCl_2$ (2.60 g, 14.00 mmol) was then added in portions under stirring at 40°C. Water (20 mL) was added to dilute the solution after 20 min and the mixture was allowed to continue being stirred for another 30 min. After addition of NaOH (40%), the crude product appeared as a brown oil.

The mixture was extracted with dichloromethane several times, and the combined dichloromethane extracts were dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to dryness leaving brown oils. Subsequent recrystallization from MeCN gave the product as brown crystals.

1H NMR [400 MHz, $CDCl_3$]: 6.54–6.62 (m, 4H, ArH), 3.62–3.72 (m, 16H, CH_2CH_2O), 3.48 (t, 4H, NCH_2CH_2O), 3.22(s, 2H, NH_2). ^{13}C NMR [100 MHz, $CDCl_3$]: δ (ppm); 141.74, 136.77, 117.25, 113.65, 71.47, 70.45, 69.23, 52.95. Anal.Calc. for $C_{16}H_{26}N_2O_4$: C, 61.91, H, 8.44, N, 9.03; Found C, 61.15, H, 8.48, N, 9.39.

2.4. The Synthesis of Schiff base (based on N-(4-aminophenyl)aza-15-crown-5 and Bodipy) (4)

The Schiff base was prepared by the usual condensation reaction in methanol (50 mL) of **2** (0.257 g, 0.5 mmol) with **3** (0.155 g, 0.5 mmol). The solutions were stirred and refluxed for 6 h. The solvent was evaporated and the residue was purified by column chromatography (eluent ethylacetate) and a red solid material was obtained.

1H NMR [400 MHz, $CDCl_3$]: δ (ppm) 8.86 (s, 1H, $CH=N$), 8.23 (d, 2H, ArH), 7.99 (d, 2H, ArH), 7.74 (d, 2H, ArH), 7.65 (d, 2H, ArH), 7.48 (d, 2H, ArH), 7.14 (d, 2H, ArH), 5.68 (s, 2H, CH_2), 4.08 (m, 20H, Crown CH), 2.69 (s, 6H, CH_3) 2.42 (q, 4H, CH_2) 1.38 (s, 6H, CH_3) 1.29 (t, 6H, CH_3). ^{13}C NMR [100 MHz, $CDCl_3$]: δ (ppm); 163.39, 161.23, 148.12, 147.70, 141.54, 135.97, 132.03, 130.12, 128.87, 127.87, 127.77, 126.53, 123.49, 123.21, 119.87, 114.43, 70.88, 70.47, 66.43, 54.32, 18.72, 16.43, 14.33. Anal.Calc. for (%) $C_{47}H_{57}N_4O_5BF_2$: C, 69.97; H, 7.12; N, 6.94; Found: C, 69.54; H, 7.38; N, 6.82.

3. Results and Discussion

3.1. The spectroscopic studies

The recognition behavior of the Schiff base toward different cations was investigated. Briefly, DMF solutions of the Schiff base (1 μ M) and metal nitrate and ammonium chloride (20 equiv.) were prepared. UV-visible absorption, emission and excitation spectra were then obtained.

3.1.1. The absorption studies—The absorption properties of the Schiff base-cation mixtures are demonstrated in Fig. 1. Although the N-phenylaza-15-crown-5 compounds are well known to recognize sodium, potassium, calcium, lead and mercury ions [7, 8]; our compound only selective mercury ion. So, a shift in absorption band could not be observed in these experiments except for mercury (Fig. 1). The Schiff base and other cations mixture exhibit an absorption maximum at 525 nm, whereas the Schiff base-Hg(II) mixture appears to have an absorption maximum at 495 nm. The absorption spectrum of Schiff base-Hg(II) mixture is hypsochromically shifted to blue (the maximum band was significantly blue-shifted by 30 nm) due to an extended conjugation of the π -system of the Bodipy-benzene groups with the nitrogen-oxygen atoms of the azacrown ether. This can be ascribed to selective binding of mercury (II) ion by the azacrown unit of the Schiff base, which inhibits the intra-molecular charge transfer process. The most intense band around 525 nm and a shoulder shorter wavelength around 495 nm can be attributed to a strong S_0 – S_1 transition.

3.1.2. The emission and excitation studies—The emission measurements were performed at fixed excitation wavelength (470 nm). The emission spectra are similarly useful and the potential chemosensor shows two emission peaks. The peaks were observed around 480 nm (weak band) and 540 nm (strong band) in all fluorescence spectra of Schiff base-cation mixtures, except for mercury. In contrast to other mixtures, the emission spectrum of mercury-ligand mixture has a broad-strong peak at 480 nm and a medium-intensity peak at 535–540 nm as shown Fig.2.

In the presence of mercury ions, the most intense peak of the emission spectra shifts hypsochromically to 485 nm. Moreover, the peak intensity is significantly enhanced. The amplification of the fluorescence intensity of Schiff base by binding of Hg^{2+} can be attributed to the CHEF (chelation-induced enhanced fluorescence) mechanism. When the mercuric ions interact with nitrogen and oxygen atoms of the azacrown unit, the PET (photo-induced electron transfer) from nitrogen-oxygen atoms to Bodipy group is decreased or stopped. On the contrary mercury, the Schiff base does not adopt toward other cations; because, the conjugated bond between the Bodipy terminal and azacrown terminal is very long; the internal charge transfer (ICT) of the ligand has a minor influence upon metal ion binding.

The excitation change results are represented at fixed emission (500 nm) in Fig. 3 which shows a pronounced selectivity and sensitivity for mercury. The excitation graphs of other cations give similar curves such as ligand, while the addition of Hg^{2+} results give a large increase in excitation intensity. The increase of shorter wavelength emitting Schiff base is also remarkable, as it indicates energy transfer efficiency due to broader spectral overlaps between the donor and fluorophore when the mercuric ion is bound to the aza-crown. The excitation spectrum of only Schiff base-Hg(II) mixture compared to that of the Schiff base solution presents an effective energy transfer with in the target complex compound.

Once binding with mercury ions, if the azacrown-terminal is assumed as an ampule due to its high fluorescence; Bodipy-terminal may be considered the diode of the ampule owing to cathc-able photon.

The binding in the 8-position of Bodipy (meso) in many cases results in PET process whereas binding derivatives in other positions would cause intramolecular charge transfer [31]. Here, it is attributed that PET carried out between the functionalized aza-crown group in the 8-position and the Bodipy terminal once held to mercury ions with nitrogen-oxygen atoms. This binding state of mercury ions affects the fluorescence intensity whereas other cations do not. Coordination of Schiff base to Hg (II) having d^{10} -electronic configuration is likely to induce PET to give a remarkable fluorescence increase. The fluorescence quantum yield of Schiff base is determined to be 0.029, which is indicative of PET quenching from the azacrown to the fluorophore (Bodipy). The phenyl groups are only a linker, as the stereo-effect of CH_2 groups turn the aryl groups non-planar with Bodipy terminal.

Then, we carried out the titration of chemosensor Schiff base with mercury ions. The peak at 525 nm is clearly shifted (hypsochromically) to blue and the absorption intensity is increased with the concentration increase of the metal ion; resulting isosbestic point appeared at 502 nm (Fig. 4). All absorption spectra present a selective opportunity of ratiometric sensing of mercury ions.

The titration process between Hg^{2+} ions and Schiff base is fluorometrically performed (Fig. 5), the results clearly justify our target molecule. When the concentration of Hg(II) ions increases, the peak intensity in shorter wavelength enhance whereas the intensity of peak in longer wavelength decreases. This is attributed to more efficient energy transfer.

Moreover, the binding stoichiometry is calculated with Job plotting and as expected, detected at a 1:1 ratio. Fig. 6 was obtained with maximum peaks at 495 nm. The total concentration of the compound Schiff base and Hg (II) ion was constant (0.01 mM), with a continuous variable molar fraction of guests.

To confirm Schiff base as an ion-selective fluorescence chemosensor for mercury (II) ions the effect of competing metal ions was determined. Schiff base (1 μM) was treated with 20 equiv. Hg (II) in the presence of other cation ions (20 equiv), respectively. As shown in Fig. 7, the presence of other cation ions on the detection of Hg (II) ions had generally a minor effect and competing ions had practically no effect on the emission intensity at 480 nm.

3.1.3. Analysis of ^1H -NMR spectra of free form and Hg (II) complex—We carried out the ^1H -NMR experiments of Schiff Base in the absence of mercury ions in order to understand the binding behavior. ^1H -NMR titrations were performed with increasing quantities of Hg(II) to the macrocyclic signals changes upon addition of increasing quantities of Hg (II) (free, 0.5, 1 and 2 equiv.). The data of complex obtained are shown in Fig. 8. The CH_2 signals of N-phenylaza-15-crown-5 moiety were shifted to lowfield or highfield (as shown Fig. 8) Moreover, the little signal changes of the protons in the aromatic rings can be realized with increasing quantities of Hg(II). As shown Fig. 8 (d), no extra changes in 2 equiv (unlike Fig. 8 (c)).

3.2. The effect of pH on the fluorescence intensity

Titration of Schiff base with Hg^{2+} in DMF:water containing 7 % (v/v) pH 7.0 HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer solution revealed that, as shown in Fig. 9, the emission peak increased at 480 nm when excited at 470 nm. The fluorescence intensity of Schiff base reaches almost a constant minimal value at pH 6.9. The maximum intensity of Schiff base was observed in pH: 4. The pH-insensitivity of fluorescence in weak acidic media is of importance for the chemosensor's studies in health applications.

3.3. Stern-Volmer kinetics

Stern-Volmer analysis was utilized to chemosensor the nature of fluorescence enhancement in the complexation of metal ions. The plots obtained emission intensities (I_0/I) against mercury concentration and showed a linear graph (Fig. 10).

$$I_0/I = 1 + K_{sv}[M]$$

In Eq., I_0 ; the emission intensity of Schiff base in the absence Hg^{2+} ; I ; in the presence Hg^{2+} , K_{sv} static quenching constant. Linear behavior was shown in graphic. The static quenching constants (K_{sv}) are calculated -8.19×10^5 .

3.4. Electrochemical investigations

Electrochemical properties of the **4** (Schiff base) was investigated by the cyclic voltammetry (CV) technique in dry DMF containing 0.2 M tetrabutylammonium-tetrafluoroborate (TBATFB) electrolyte at glassy carbon electrode. This compound displayed upon reductive scanning a clear irreversible wave at around -0.83 V that is assigned to the redox processes associated with formation of the Bodipy radical anion. During the anodic scan, an irreversible oxidation peak observed at 1.23 V was attributed to the radical cation ($BODIPY^{+ \cdot}$) formation which is consistent with the reported Bodipy derivatives [32, 33]

4. Conclusion

Based on azacrown and Bodipy fluorophore combined with classic Schiff base condensation, we have synthesized a new ratiometric fluorescence chemosensor for mercury ion detection. The spectroscopic-electrochemical properties of the chemosensor were studied in several forms. When coordinated with Hg^{2+} to nitrogen-oxygen of aza-crown, target molecule exhibit the blue-shift of emission wavelengths and the fluorescence increases for ratiometric measurements. These results and observations give remarkable evidence for the argument that the direct interaction between fluorophore and Hg^{2+} in solution medium leads to the energy transfer-based fluorescence modulation. The electrochemical behaviors were also investigated. As expected, during the anodic scan, an observed irreversible oxidation peak was attributed to the radical Bodipy cation.

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References

1. Bingol H, Kocabas E, Zor E, Coskun A. *Talanta*. 2010; 82:1538. [PubMed: 20801369]
2. Wu S-P, Wang T-H, Liu S-R. *Tetrahedron*. 2010; 66:9655.
3. Atilgan S, Kutuk I, Ozdemir T. *Tetrahedron Lett*. 2010; 51:892.
4. Sakamoto T, Inoue M, Ojida A, Hamachi I. *Bioorg. Med. Chem. Lett*. 2009; 19:4175. [PubMed: 19546004]
5. Kandaz M, Guney O, Senkal FB. *Polyhedron*. 2009; 28:3110.
6. Ando Y, Homma Y, Hiruta Y, Citterio D, Suzuki K. *Dyes Pigments*. 2009; 83:198.
7. Deveci P, Taner B, Kılıç Z, Solak AO, Arslan U, Özcan E. *Polyhedron*. 2011; 30:1726.
8. Batista RMF, Oliveira E, Costa SPG, Lodeiro C, Raposo MMM. *Tetrahedron*. 2011; 67:7106.
9. Ocak U, Ocak M, Başoğlu A, Parlayan S, Başaran D, Alp H, Kantekin H. *Polyhedron*. 2010; 29:1069.
10. Blakemore JD, Chitta R, D'Souza F. *Tetrahedron Lett*. 2007; 48:1977.
11. Gámez F, Hurtado P, Haya BM, Berden G, Oomens J. *Int. J. Mass Spectrom*. 2011; 308:217.

12. Jaggernauth GE, Fairman RA. *Inorg. Chem. Comm.* 2011; 14:79.
13. Danjoua P-E, Lyskawaa J, Delattrea F, Becuwea M, Woisela P, Ruellana S, Fourmentina S, Cazier-Dennin F. *Sensor Actuat. B.* 2012; 171–172:1022.
14. Moczar I, Huszthy P, Maidics Z, Kadar M, Toth K. *Tetrahedron.* 2009; 65:8250.
15. Guler H, Hayvali Z, Dal H, Hokelek T. *Polyhedron.* 2012; 31:688.
16. Kim HJ, Kim SH, Kim JH, Lee E-H, Kim K-W, Kim JS. *Bull. Korean Chem. Soc.* 2008; 29:1831.
17. Kalai T, Hideg K. *Tetrahedron.* 2006; 62:10352.
18. Fan J, Guo K, Peng X, Du J, Wang J, Sun S, Li H. *Sensors Actuat B-Chem.* 2009; 142:191.
19. Coskun A, Akkaya EU. *J. Am. Chem. Soc.* 2006; 128:14474. [PubMed: 17090027]
20. Atilgan S, Ozdemir T, Akkaya EU. *Org. Lett.* 2010; 12:4792. [PubMed: 20936821]
21. Mbatia HW, Kennedy DP, Camire CE, Incarvito CD, Burdette SC. *Eur. J. Inorg. Chem.* 2010; 32:5069.
22. Kursunlu AN, Guler E, Ucan HI, Boyle RW. *Dyes Pigments.* 2012; 94:496.
23. Suzuki S, Kozaki M, Nozaki K, Okada K. *J. Photoch. Photobio. C.* 2011; 12:269.
24. Ye Z, Wang G, Chen J, Fu X, Zhang W, Yuan J. *Biosens. Bioelectron.* 2010; 26:1043. [PubMed: 20846845]
25. Lee JCI, Choi K-S, Cho H-K, Kang J-G. *J Lumin.* 2007; 127:332.
26. Pfennig BW, Norris MR, Zimmerman N, Gallagher JR, McCloskey AI. *Inorg. Chim. Acta.* 2009; 362:1701.
27. Cao X, Wei T, Chen Y, Yin M, Guo C, Zhang W. *J. Rare Earth.* 2011; 29:1029.
28. Purkayastha P. *J. Photoch. Photobio. A.* 2010; 212:43.
29. Vladimirova MP, Simova SD, Stanoeva ER, Mitewa MI. *Dyes Pigments.* 2001; 50:157.
30. Lu XX, Qin SY, Zhou ZY, Yam VWW. *Inorg. Chim Acta.* 2003; 346:49.
31. Xie X, Qin Y. *Sensors Actuat B-Chem.* 2011; 156:213.
32. Lai RY, Bard AJ. *Phys. Chem. B.* 2003; 107:5036.
33. Burghart A, Kim H, Welch MB, Thoresen LH, Reibenspies J, Burgess K, Bergstrom F, Johansson LB-A. *J. Org. Chem.* 1999; 64:7813.

Highlights

► The Schiff base prepared by several techniques shows a ratiometric fluorescent behavior toward Hg (II) cation such as classical reaction of complexation. ► To the best of our knowledge, this is an important fixation Crown-Bodipy based reactive sensor for Hg (II) cation.

Fig. 1.
The absorption spectra of Schiff base and Schiff base-cation ions.

Fig. 2. Emission spectra of the Schiff base in DMF (1 μM) in DMF in the absence and presence of various cations. Added cation ion concentrations were 20 μM. Excitation wavelength is 470 nm.

Fig. 3. Excitation spectra of target Schiff base in DMF (1 μ M) in DMF in the absence and presence of various cations. The emission data were collected at 500 nm.

Fig. 4. Hg(II) titration of the chemosensor Schiff base. Hg(II) concentration is varied with 0, 2, 5, 7, 10, 12, 15, 18 and 20 μM

Fig. 5. Hg(II) titration of the chemosensor Schiff base in DMF. Hg(II) concentration is varied with 0, 2, 5, 7, 10, 12, 15, 18 and 20 μM in DMF.

Fig. 6.
Job's plot for Schiff Base/mercury ion, 0.01 mM in DMF.

Fig. 7. Schiff base concentration was set at 1 μM and the concentration of Hg (II)-competing cations was 20 μM , respectively. (The fluorescence intensity was around 480 nm).

Fig. 8. (a) ¹H-NMR spectrum in the free form (b) ¹H-NMR spectrum in the presence of Hg²⁺ with 0.5 equiv. (c) ¹H-NMR spectrum in the presence of Hg²⁺ with 1 equiv. (d) ¹H-NMR spectrum in the presence of Hg²⁺ with 2 equiv. [in (CD₃)₂SO].

Fig. 9. Dependence of the fluorescence intensity of Schiff base on pH in DMF:water (1:10) solution containing 7 % HEPES (with 20 equiv. Hg ion, excitation was provided at 470 nm and emission was integrated at 480 nm).

Fig. 10.
Stern-Volmer plot for the fluorescence enhancement of Hg^{2+} by Schiff base in DMF.

Fig. 11.

Cyclic voltammograms recorded for **4** in dry DMF containing 0.2 M TBATFB background electrolyte at a glassy carbon electrode and an Ag/AgCl reference electrode. All the measurements were carried out in 1 mM solutions of the ligand at room temperature in the potential range from **a)** 0 to -1 V **b)** 0 to 2V with a scan rate of 100 mV s⁻¹.

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

Scheme 2.
The synthesis of **3**.

Scheme 3.
The synthesis of Schiff base ligand.