Accepted Manuscript

Selective detection of Hg(II) with benzothiazole-based fluorescent organic cation and the resultant complex as a ratiometric sensor for bromide in water

Amanpreet Singh, Ajnesh Singh, Narinder Singh, Doo Ok Jang

PII: S0040-4020(16)30371-4

DOI: 10.1016/j.tet.2016.04.082

Reference: TET 27725

To appear in: *Tetrahedron*

Received Date: 23 March 2016

Revised Date: 29 April 2016

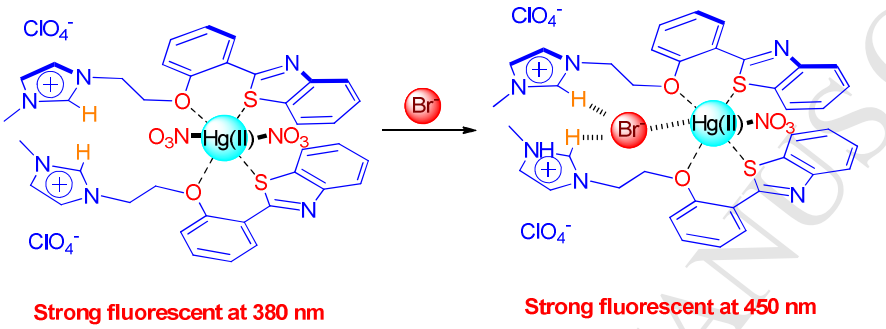
Accepted Date: 30 April 2016

Please cite this article as: Singh A, Singh A, Singh N, Jang DO, Selective detection of Hg(II) with benzothiazole-based fluorescent organic cation and the resultant complex as a ratiometric sensor for bromide in water, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.04.082.

Graphical Abstract

Selective detection of Hg(II) with benzothiazole-based fluorescent organic cation and the resultant complex as a ratiometric sensor for bromide in water

Amanpreet Singh, Ajnesh Singh, Narinder Singh* and Doo Ok Jang*



Selective detection of Hg(II) with benzothiazole-based fluorescent organic cation and the resultant complex as a ratiometric sensor for bromide in water

Amanpreet Singh,[a] Ajnesh Singh,[b] Narinder Singh,[a,*] and Doo Ok Jang[c,*]

Email: ***nsingh@iitrpr.ac.in; dojang@yonsei.ac.kr***

[a]Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar, Punjab 140001, India

[b]Department of Applied Science & Humanities, Jawaharlal Nehru Govt. Eng. College, Sundernagar, India

[c]Department of Chemistry, Yonsei University, Wonju 220−710, Republic of Korea

Abstract: A benzothiazole−based receptor conjugated with an imidazolium cation, receptor **N1**, was synthesized. Receptor **N1** is capable of selectively binding Hg(II) in the presence of other metal ions in water, with a large enhancement in fluorescence intensity at 380 nm via a PET mechanism. The resulting Hg(II) complex of receptor **N1** showed a selective ratiometric response upon addition of Br^- ions. The Hg(II) complex of receptor **N1** was used to determine the concentration of Br^- ions in the presence of other anions, with a detection limit of 22 nM. ^{1}H NMR studies showed that the imidazolium hydrogen in the Hg(II) complex of receptor **N1** participates in the recognition of Br^- ions. In the absence of Hg(II), receptor **N1** did not recognize Br^- ions.

Keywords: *fluorescence, ratiometric, receptor, recognition, bromide, water*

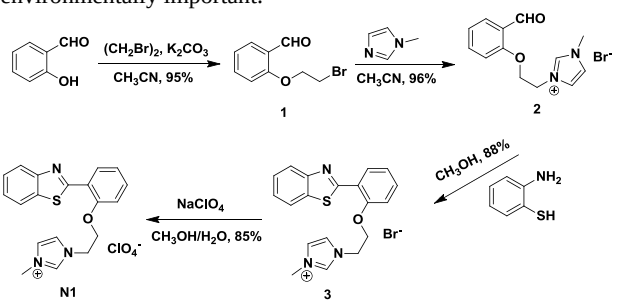
Introduction

The design and synthesis of heteroditopic receptors with binding sites for simultaneously complexation with cationic and anionic species have attracted a great deal of attention in supramolecular chemistry.[1–4] These receptors can interact with a single heteroditopic guest such as amino acids and nucleotides or can bind with non−identical guest molecules.[5,6] Such systems are interesting due to their direct applications as molecular sensors and membrane transport agents for extracting ion pairs and enhancing the solubility of insoluble ions.[7–9] Despite a number of practical applications, sensors for ion-pairs are rare, particularly in water.[10–13]

Due to the diverse range of anion shapes and sizes, their recognition using an organic receptor is a difficult task.[14–16] The recognition of anions is problematic in aqueous medium, particularly when using a receptor relying purely on hydrogen bonding, because of competition between anions and polar solvent molecules for binding sites on the receptor. Ion−pair recognition may improve the binding affinity of an anion by providing extra electrostatic interactions from the cation, as electrostatic interactions are generally less influenced by solvent than hydrogen bonding.[17–19] Another advantage of extra electrostatic interactions is the cooperative effect. The ion-pair receptor has sites for a cation and an anion. Upon binding of one guest molecule (cation), the affinity of the receptor for the second guest (anion) is increased.[20–22]

Ion-pair recognitions have been attained by conjugating a cation receptor with some hydrogen bond donor substitute groups.[23–26] Thordarson *et al.* examined the binding of Cl^- with a tetratopic ion-pair host in the presence of Ca(II).[27] The tetratopic receptor underwent conformational changes that allowed the receptor to bind Cl^-. Smith *et al.* found that association of an alkali metal ion with a receptor enhances the binding affinity of an anion.[28] In addition, a number of receptors have been reported for recognition of anions.[29–32] However, only a few of these receptors were developed for detection of Br^- due to the lack of suitable binding sites, low charge density, and a weak tendency to form hydrogen bonds.[33–35] Due to these challenging properties, the design of sensors for Br^- has been difficult. Moreover, receptors for Br^- suffer from competition with water molecules in an aqueous medium.

Inspired by previous reports on imidazolium−conjugated fluorescent sensors and in continuation of our research activities with benzimidazole/benzothiazole−based receptors,[36–40] we developed a simple organic receptor **N1** that has proficient binding sites for cation recognition, as shown in Scheme 1. The distal part of the receptor is tailored with an imidazolium group that is well-known to provide anion recognition. Another advantage of this approach lies in the fact that the imidazolium moiety may impart solubility of the receptor in an aqueous medium. Sensor activity in aqueous media is mandatory if the targeted analyte is biologically or environmentally important.[41,42]



Scheme 1. Synthesis route of receptor **N1**.

Experimental

General

All chemicals were purchased from Aldrich Chemical Co. and were used as−received without further purification. ^{1}H NMR spectra were recorded with a JEOL spectrometer operated at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. CHN analysis was performed using a Perkin Elmer 2400 CHN Elemental Analyzer, while pH measurements were carried out with a ME/962P instrument. A PerkinElmer L55 fluorescence spectrophotometer equipped with quartz cuvettes (path length = 1 cm) was employed for fluorescence measurements, with a xenon lamp as the excitation source. X−ray diffraction data for **N1** were collected on a Bruker X8 APEX II KAPPA CCD diffractometer at 293 K using graphite monochromatized Mo−Kα radiation (λ = 0.71073 Å). IR spectra were recorded using a Bruker Tensor 27 spectrometer. Binding constant was calculated using nonlinear regression analysis using Hyperspec program. Atomic absorption spectroscopy experiments were performed using Perkin Elmer AAS. Concentration of bromide was measured using Inductively Coupled Plasma.

Synthesis of compound 1:[43] A solution of salicylaldehyde (10.6 mL, 100 mmole) and anhydrous K_2CO_3 (13.8 g, 100 mmole) in CH_3CN (20 mL) was heated to reflux for 1 h, and then 1,2−dibromoethane (86.17 mL, 1000 mmole) was added. The reaction mixture was refluxed for 10 h under argon. The reaction mixture was cooled to room temperature and filtered, and the volatiles were evaporated under vacuum. The resulting crude product was purified using column chromatography on silica gel to produce compound **1** (21.8 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (t, *J* = 8.0 Hz, 2H, CH_2), 4.41 (t, *J* = 8.0 Hz, 2H, CH_2), 6.94 (d, *J* = 16 Hz, 1H, Ar−H), 7.52 (t, *J* = 16 Hz, 1H, Ar−H), 7.84 (d, *J* = 16 Hz, 1H, Ar−H), 10.53 (s, 1H, CHO); ^{13}C NMR (100 MHz, DMSO−d_6) δ 28.8, 68.3, 112.7, 121.6, 125.3, 128.6, 136.0, 160.7, 189.7.

Synthesis of compound 2: A solution of compound **1** (4.52 g, 20 mmol) and *N*−methyl imidazole (1.68 g, 20 mmol) in CH_3CN (40 mL) was heated to reflux for 10 h under argon. After completion of the reaction, the solvent was evaporated using a rotatory evaporator. The product was recrystallized from EtOH to yield compound **2** (6.01 g, 96%). Mp: 106−108 ^{o}C; FT−IR ν 3147 (=CH), 2994 (−CH), 2969 (−CH_3), 1723 (C=O), 1591, 1508, 1378 (C−O), 1153 (C−N), 1119, 952, 841 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (s, 3H, CH_3), 4.54 (t, *J* = 8.0 Hz, 2H, CH_2), 5.05 (t, *J* = 8.0 Hz, 2H, CH_2), 7.01 (d, *J* = 8.0 Hz, 1H, ArH), 7.14-7.20 (m, 2H, ArH), 7.20 (s, 1H, ArH), 7.58 (t, *J* = 8.0 Hz, 1H, ArH), 7.72 (d, *J* = 8.0 Hz, 1H, imdazolium−H), 8.12 (s, 1H, imdazolium−H), 10.12 (s, 1H, imdazolium−H), 10.52 (s, 1H, CHO); ^{13}C NMR (100 MHz, DMSO−d_6) δ 36.8, 49.3, 67.0, 112.8, 121.8, 123.0, 124.3, 124.7, 132.7, 136.4, 138.0, 158.7, 190.4. Anal. Calcd for $C_{13}H_{15}BrN_2O_2$: C, 50.18; H, 4.86; N, 9.00. Found: C 50.11; H, 4.80; N, 8.91.

Synthesis of compound 3: In a two−neck round-bottom flask equipped with a reflux condenser, 2−aminothiophenol (1.25 g, 10 mmol) was dissolved in dry MeOH (20 mL). A solution of aldehyde **2** (3.13 g, 10 mmol) in dry MeOH (10 mL) was added to the above reaction mixture. A balloon filled with argon was affixed to the condenser, and the reaction mixture was heated to reflux for 6 h. Reaction progress was monitored using TLC. After completion of the reaction, the solvent was evaporated to yield semi−solid compound **3** (3.68 g, 88%). Mp: 87−88 ^{o}C; FT−IR ν 3125 (=CH), 3049 (=CH), 1675 (C=N), 1607, 1561, 1317 (C−O), 1164 (C−N), 1004, 805, 729; ^{1}H NMR (400 MHz, DMSO−d_6) δ 3.79 (s, 3H, CH_3), 4.72−4.78 (m, 4H, CH_2), 7.17 (t, 1H, *J* = 8.0 Hz, Ar−H), 7.30 (d, 1H, *J* = 16 Hz, Ar−H), 7.43 (t, 1H, *J* = 16 Hz, Ar−H), 7.49−7.55 (m, 2H, Ar−H), 7.70 (t, 1H, *J* = 8.0 Hz, Ar−H), 7.94 (t, 1H, *J* = 8.0 Hz, Ar−H), 8.01 (d, 1H, *J* = 16 Hz, Ar−H), 8.07 (d, 1H, *J* = 16 Hz, Ar−H), 8.35 (d, 1H, *J* = 16 Hz, Ar−H), 9.34 (s, 1H, imdazolium−H); ^{13}C NMR (100 MHz, DMSO−d_6) δ 36.2, 49.0, 67.3, 114.0, 121.9, 122.2, 123.0, 123.2, 124.3, 124.5, 126.8, 129.6, 132.8, 135.6, 137.7, 152.1, 155.8, 162.5. Anal. Calcd for $C_{19}H_{18}BrN_3OS$: C, 54.81; H, 4.36; N, 10.09. Found: C, 54.67; H, 4.25; N, 9.99.

Synthesis of receptor N1:[44] Sodium perchlorate (0.85 g, 7.0 mmol) was added to a solution of compound **3** (2.10 g, 5.0 mmol) in 25 mL of H_2O:MeOH (1:1, v/v). The reaction mixture was stirred at room temperature for 2 h. Volatiles were removed under reduced pressure, and CH_3CN (20 mL) and $MgSO_4$ (1.0 g) were added to the remaining suspension. After standing for 1 h, the suspension was filtered. Volatiles were evaporated under reduced pressure, and the resulting light yellow powder was recrystallized from MeOH to produce yellow crystals of **N1** (1.86 g, 85%). Mp: 104−106 °C; FT−IR ν 3079 (=CH), 2873 (−CH), 1680 (C=N), 1591, 1340 (C−O), 1179 (C−N), 1103, 920, 775, 706 cm^{-1}; ^{1}H NMR (400 MHz, DMSO−d_6) δ 3.79 (s, 3H, CH_3), 4.72−4.76 (m, 4H, CH_2), 7.13 (t, 1H, *J* = 16 Hz, Ar−H), 7.26 (d, 1H, *J* = 16 Hz, Ar−H), 7.42 (t, 1H, *J* = 16 Hz, Ar−H), 7.48−7.51 (m, 2H, Ar−H), 7.68 (t, 1H, *J* = 8.0 Hz, Ar−H), 7.93 (t, 1H, *J* = 8.0 Hz, Ar−H), 7.98 (d, 1H, *J* = 16 Hz, Ar−H), 8.04 (d, 1H, *J* = 16 Hz, Ar−H), 8.35 (d, 1H, *J* = 16 Hz, Ar−H), 9.36 (s, 1H, imdazolium−H); ^{13}C NMR (100 MHz, DMSO−d_6) δ 36.3, 49.0, 67.3, 114.2, 121.9, 122.3, 122.4, 123.1, 123.2, 124.3, 125.7, 127.0, 129.59, 133.0, 135.7, 137.8, 132.1, 155.9, 162.5. Anal. Calcd for $C_{19}H_{18}ClN_3O_5S$: C, 52.35; H, 4.16; N, 9.64. Found: C, 52.26; H, 4.10; N, 9.48.

Binding studies: Binding studies with receptor **N1** were performed using fluorescence spectroscopy in an aqueous medium. Binding studies were performed at 25±1 ^{o}C, and the solutions were shaken for a sufficient time before recording the spectra. UV−vis absorption spectra of receptor **N1** exhibited a maximum absorption peak at 260 nm. In fluorescence spectroscopy, receptor **N1** exhibited a weak emission at 380 nm when excited at 260 nm. For cation binding studies, a 20 μM solution of receptor **N1** was prepared in water. Fluorescence spectra were recorded upon addition of 0.6 equivalents (12 μM) of metal ions. HEPES buffer solution was used to maintain a pH value of 7.4 in all experiments.

Results and Discussion

Syntheses

Receptor **N1** was synthesized as shown in Scheme 1. Salicylaldehyde was converted to compound **1** using our previously developed method.[43] An imidazolium ring was conjugated to compound **1** through a substitution reaction of compound **1** with *N*−methylimidazole. A benzothiazole moiety was introduced through reaction of compound **2** with 2−aminothiophenol. The Br^- ion in compound **3** was

exchanged with ClO_4^- using a reported method to produce receptor **N1**.[44]

Structure characterization

Receptor **N1** was crystallized in an orthorhombic crystal system with the Pbca space group (Table S1). The asymmetric unit contained one cationic moiety of receptor **N1** and one ClO_4^- as counter ion. The ORTEP diagram along with the atom numbering scheme is shown in Figure 1 (disordered ClO_4^- ion is not shown for clarity). The benzothiazole and phenyl moieties are coplanar, while the plane containing the *N*−methylimidazole has a dihedral angle of 75.46° with the plane containing the benzothiazole and phenyl moieties. Selected bond lengths and bond angles are given in Table S2. The packing of receptor **N1** was not determined due to the disordered nature of ClO_4^-. Packing diagram is shown in Figure 2.

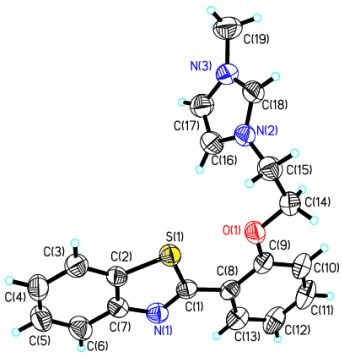


Figure 1. ORTEP view of receptor **N1** (CCDC 1408239) with 40% probability of thermal ellipsoids and atom numbering scheme (disordered ClO_4^- ion is not shown for clarity).

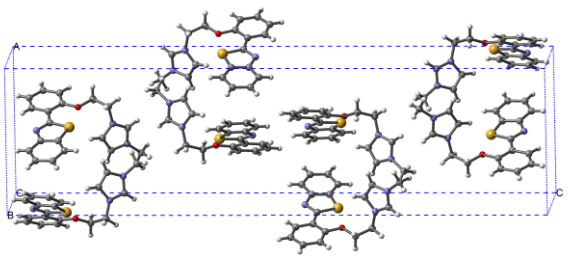


Figure 2. Packing diagram of receptor **N1**.

Binding properties of receptor N1

Cation recognition studies were performed using fluorescence spectroscopy. Fluorescence spectra were recorded upon addition of 0.6 equivalents of different cations including Ni(II), Ag(I), Ca(II), Cu(II), Na(I), K(I), Sr(II), Th(II), Fe(III), Cd(II), Cr(II), Mn(II), Co(II), and Hg(II). Upon addition of various cations to a 20 μM solution of receptor **N1**, no changes in the emission profile were observed with the exception of Hg(II). When Hg(II) was added, an approximately three−fold enhancement in the emission profile of receptor **N1** was observed, as shown in Figure 3. The large enhancement in fluorescence intensity is attributed to cancelation of photo−induced electron transfer (PET) by the benzothiazole sulfur atom. The selectivity of receptor **N1** for Hg(II) can be explained on the basis of cavity size and Pearson's hard-soft acid-base theory.[45] While sulfur is a soft center that interacts with soft acids, the receptor did not show any significant changes in fluorescence with other soft metal ions such as Ag(I), Cu(II), Th(II), and Cd(II). This result might be due to the size of the receptor cavity.

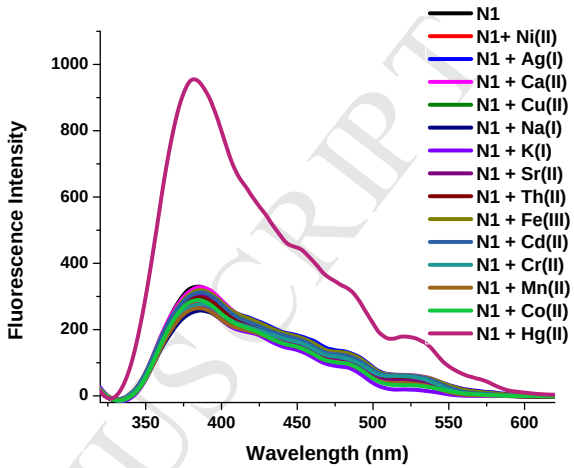


Figure 3. Changes in emission spectra upon addition of 0.6 equivalents of different metal ions to a 20 μM solution of receptor **N1** in water (HEPES 10 mM, pH = 7.4) excited at λ_{ex} = 260 nm.

To determine the binding stoichiometry, a Job's plot[46] was constructed using fluorescence enhancement data, as shown in Figure S1, confirming that Hg(II) ions bind to receptor **N1** in a ratio of 1:2, *i.e.*, two molecules of receptor **N1** bind to one Hg(II) ion. This result was confirmed by mass spectrometry. To take mass spectra, Hg(II) complex of ligand **N1** was prepared by dissolving 324 mg of $Hg(NO_3)_2$ and 872 mg of **N1** in methanol, resulting mixture was stirred for 60 minutes. Dark yellow precipitate was collected after filtration of mixture. Mass analysis of the complex of Hg(II) with receptor **N1** showed m/z = 499, which corresponds to [2**N1**·Hg(II)$(NO_3)_2$−2ClO_4^-] (Figure S2). The stoichiometry of the complex was also confirmed using elemental analysis, the results of which were in good agreement with the chemical formula of the complex: 2**N1**·Hg(II)$(NO_3)_2$ ($C_{39}H_{42}Cl_2HgN_8O_{16}S_2$) (Table S3). The data revealed that a mercury ion was attached to two **N1** receptors and two NO_3^- ions with two ClO_4^- counter ions to compensate for the charges on the imidazolium rings.

Upon successive addition of Hg(II) 0 to 12 μM (0−0.6 equiv) to a 20 μM solution of receptor **N1**, a gradual increase in emission intensity was observed (Figure 4). Different species formed on different concentration of Hg(II) was find out using Hyperspec software.[47] A plot of the concentration of Hg(II) and the fluorescence intensity at 380 nm showed a linear incremental increase in fluorescence intensity in the range of 0−12 μM. As shown in Figure 5, the Y-axis on the left represents the fluorescence intensity, whereas the Y-axis on the right represents the percentage of different species present at different concentrations of Hg(II). Binding constants for the **N1**+Hg(II) complex and 2**N1**+Hg(II) were determined using

nonlinear least-squares regression analysis, which was found to be 9.53 x 10^3 and 3.54 x 10^4, respectively. The detection limit was calculated to be 48 nM using the 3σ method (black dotted curve in Fig. 5).[48]

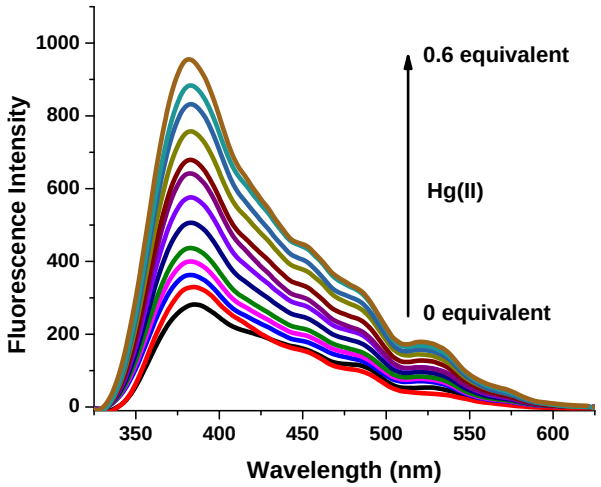


Figure 4. Effect of gradual addition of Hg(II) (0−0.6 equiv) on the emission profile of receptor **N1** (20 μM) in water (HEPES 10 mM, pH = 7.4).

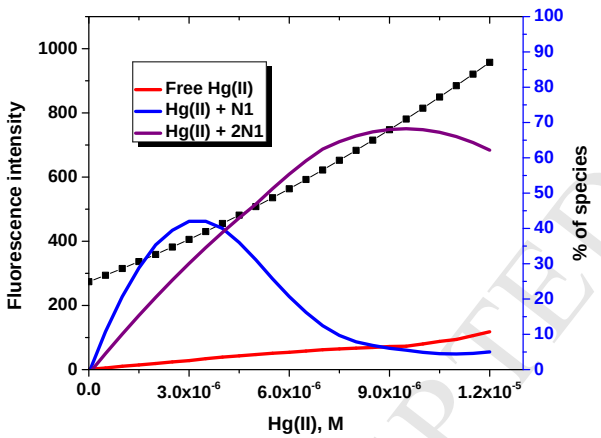


Figure 5. Linear relationship between Hg(II) concentration and fluorescence intensity at 380 nm with excitation at λ_{ex} = 260 nm (left Y-axis) and the percentage of species formed at different concentrations of Hg(II) (right Y-axis).

To examine possible interference from different metal ions with Hg(II) recognition of receptor **N1**, competitive binding studies were performed by adding Hg(II) ions to the solution of receptor **N1** in the presence of other metal ions. The results are presented in Figure 6. There were no significant changes in fluorescence intensity at 380 nm, indicating that the coexistence of other metal ions had no significant interference on Hg(II) recognition.

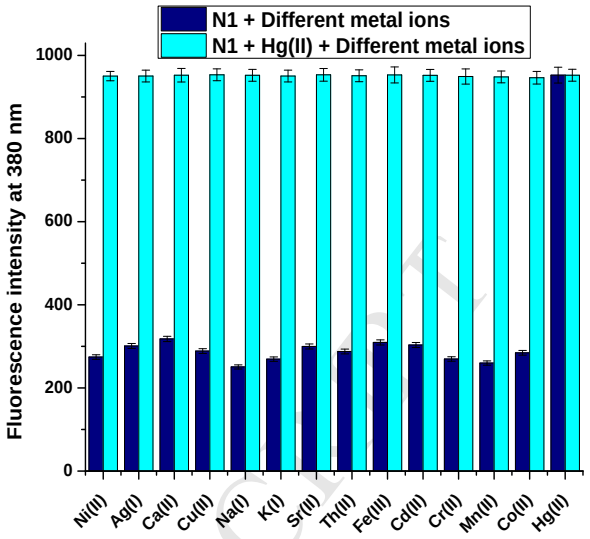


Figure 6. Comparison of the fluorescence intensity of receptor **N1** (20 μM) at 380 nm in the presence of Hg(II) (0.6 equiv) and other analytes (0.6 equiv) in water (HEPES 10 mM, pH = 7.4) with excitation at λ_{ex} = 260 nm.

Binding properties of the Hg(II) complex of receptor N1

The Hg(II) complex of receptor **N1** was further subjected to anion recognition using fluorescence spectroscopy. A solution of the complex was screened with tetrabutyl ammonium salts of several anions ($CH_3CO_2^-$, ClO_4^-, HSO_4^-, NO_3^-, Cl^-, Br^-, I^-, and F^-). None of the anions caused any changes in the intensity or wavelength of the parent band of the complex. However, upon addition of Br^- ions, the parent band at 380 nm was shifted to 450 nm, as shown in Figure 7. The bathochromic shift was attributed to Br^- ion stabilization of the mercury complex of receptor **N1**, which leads to a decrease in the band gap, resulting in a shift of the fluorescence band to higher wavelength.

To study the interaction of Br^- ions with the Hg(II) complex of receptor **N1**, titration was performed by adding small aliquots of Br^- ions to a solution of receptor **N1** (20 μM) and Hg(II) 12 μM (0.6 equiv). The intensity of the band at 380 nm decreased on addition of Br^- ions, and a new band at 450 nm emerged, as shown in Figure 9. An isosbestic point at 412 nm implied that there was an interaction of Br^- ions with the Hg(II) complex of receptor **N1**. To obtain a calibration curve, the ratio of F_{450}/F_{380} was plotted against the concentration of Br^- (Figure 10), which showed that the Hg(II) complex of receptor **N1** could be used for selective determination of Br^- ions in aqueous media, with a detection limit of 22 nM.

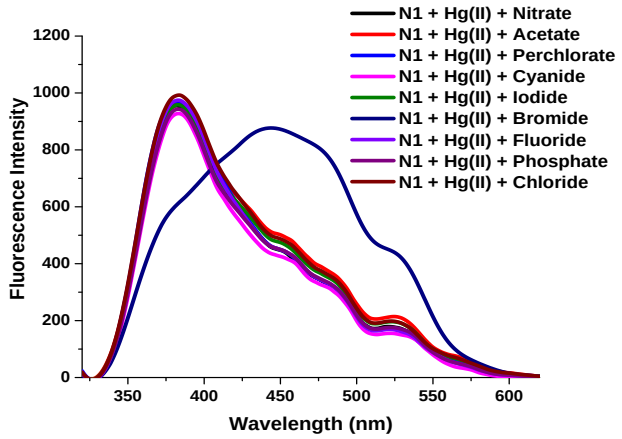


Figure 7. Changes in fluorescence spectra of a solution of receptor **N1** (20 μM) and Hg(II) (0.6 equiv) upon addition of different anions (0.75equiv, 15 μM).

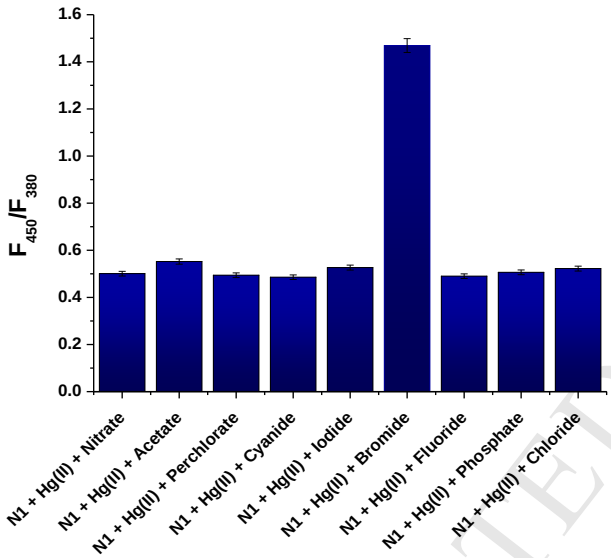


Figure 8. Comparison of the fluorescence intensity (F_{450}/F_{380}) in the presence of receptor **N1** (20 μM), Hg(II) 12 μM (0.6 equiv) and 0.75 equiv of different anions in water (HEPES 10 mM, pH = 7.4) with excitation at λ_{ex} = 260 nm.

A Job's plot analysis revealed that the binding stoichiometry of the Hg(II) complex of receptor **N1** to Br^- ions was 1:1 (Figure S3a). This stoichiometry was confirmed using elemental analysis, which indicated the formation of a new complex with chemical formula 2**N1**·$Hg(NO_3)(Br^-)$ ($C_{38}H_{36}BrCl_2HgN_7O_{13}S_2$) (Table S3). The association constant calculated with a Benesi−Hildebrand plot was K_a = 4.42 x 10^4 M^{-1} (Figure S3b).[48]

To examine interference from different anions with Br^- ion recognition of the Hg(II) complex of receptor **N1**, competitive binding studies were performed by recording fluorescence spectra in presence of receptor **N1** (20 μM), Hg(II) (12 μM, 0.6 equiv), different anions (15 μM, 0.75 equiv) and Br^- ions (0.75 equiv). There were no significant changes in fluorescence intensity ratio (F_{450}/F_{380}) of receptor **N1**, indicating that there is no significant interference on Br^- recognition (Figure 11).

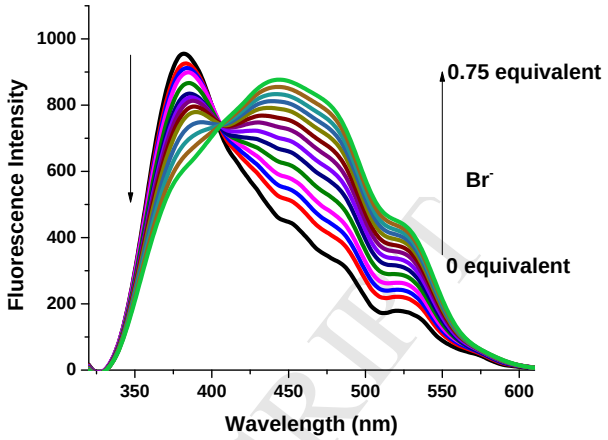


Figure 9. Changes in fluorescence spectra of a solution of receptor **N1** (20 μM) and Hg(II) (0.6 equiv, 12 μM) upon successive addition of Br^- ions (0.75equiv, 15 μM).

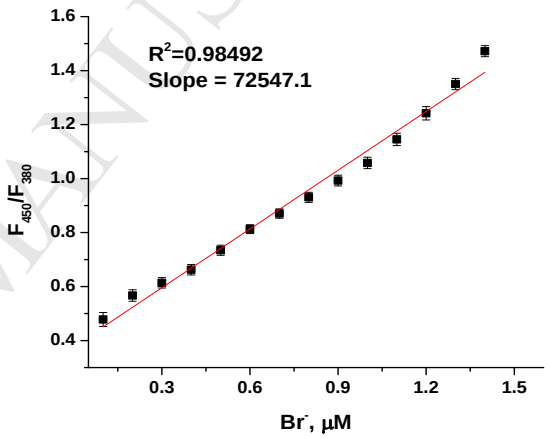


Figure 10. A linear plot of F_{450}/F_{380} of a solution of **N1** (20 μM) and Hg(II) (0.6 equiv, 12 μM) upon successive addition of Br^- ions.

The ^{1}H NMR spectra of receptor **N1** were recorded in DMSO−d_6:D_2O (95:5, v/v) in the presence and absence of Hg(II) and TBA-Br (Figure 12). Upon addition of 2 equiv of Br^- ions to a solution of receptor **N1**, no significant changes were observed. When 2 equiv of Hg(II) was added to a solution of receptor **N1**, small shifts of the aliphatic protons were observed. A shift of the imidazolium hydrogen from 9.26 to 9.72 ppm indicated an interaction of receptor **N1** with Hg(II). The ^{1}H NMR spectrum of receptor **N1** was recorded in the presence of both Hg(II) and TBA-Br, which showed changes in the aliphatic and aromatic regions. Two triplets at 4.73 and 4.77 ppm shifted to 4.64 and 5.01 ppm, respectively. The imidazolium proton shifted from 9.26 ppm to 10.11 ppm, confirming that Br^- ions interact with receptor **N1** only in the presence of Hg(II).

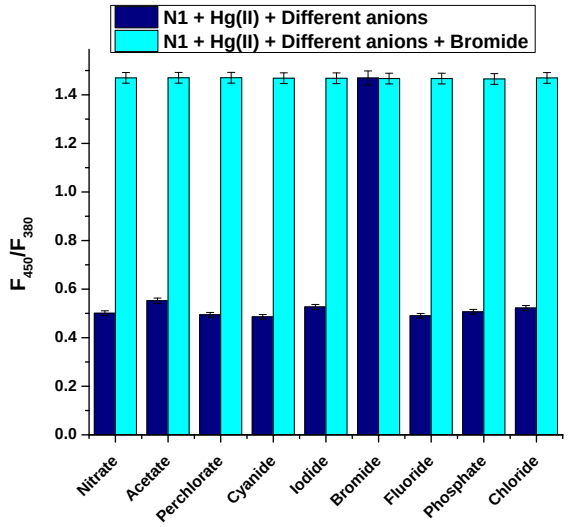


Figure 11. Fluorescence intensity ratio (F_{450}/F_{380}) of receptor **N1** (20 μM) in the presence of Hg(II) (0.6 equiv) and Br^- ions (15 μM, 0.75 equiv) along with other anions (0.75 equiv) in water (HEPES 10 mM, pH = 7.4) with excitation at λ_{ex} = 260 nm.

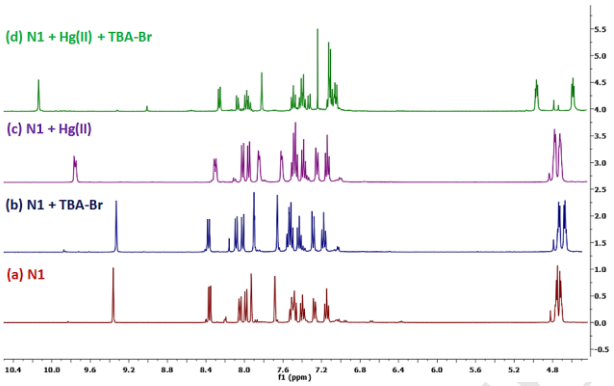
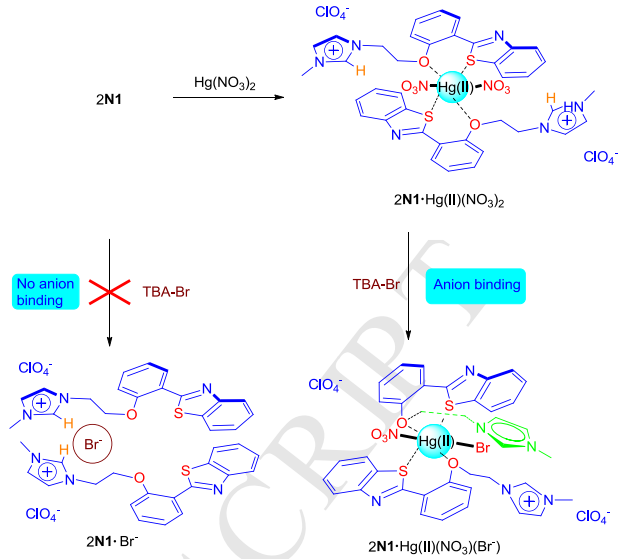


Figure 12. ^{1}H NMR spectra in DMSO−d_6:D_2O (95:5, v/v): (a) **N1** only, (b) **N1**+TBA-Br (2.0 equiv), (c) **N1**+Hg(II) (2.0 equiv), and (d) **N1**+Hg(II) (2.0 equiv)+TBA-Br (2.0 equiv).

Absorption and fluorescence spectra were also recorded with/without Hg(II) and/or Br^- ions. The results indicate that Hg(II) ion is essential for recognizing Br^- ions with receptor **N1** in water (Figures S4 and S5). The binding modes of receptor **N1** involving Hg(II) and Br^- ions are shown in Scheme 2. Receptor **N1** selectively binds to Hg(II) to form 2**N1**·Hg(II)$(NO_3)_2$, which was confirmed using elemental analysis. The Hg(II) complex of receptor **N1** selectively recognizes Br^- ions to produce 2**N1**·Hg$(NO_3)(Br^-)$. In the absence of Hg(II), receptor **N1** does not recognize Br^- ions.



Scheme 2. Plausible binding modes of receptor **N1** to Hg(II) and Br^- ions.

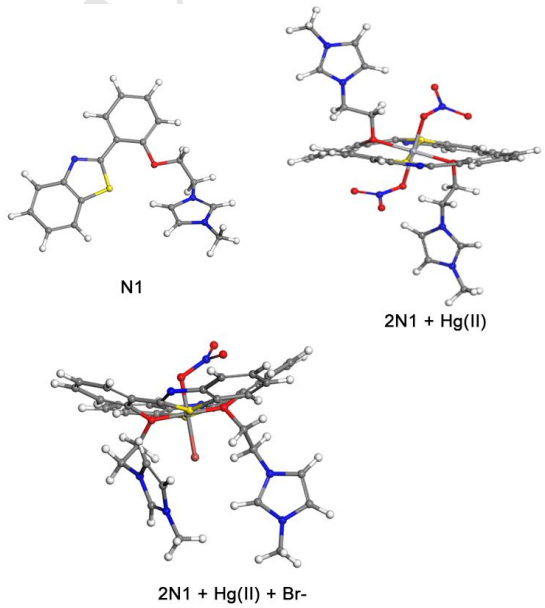


Figure 13. DFT computed optimized structure of **N1**, 2**N1**+ $Hg(NO_3)_2$, and 2**N1**+ $Hg(NO_3)_2$ + Br^-.

In order to explain the electronic spectra of the complexes, theoretical calculations were carried out by using the DMol 3 package with density functional theory (DFT). All calculations were done via generalized gradient approximations (GGA) with double numeric plus polarization (DNP).[49] The geometry of the structures was minimized to calculate the HOMO-LUMO gap. From the optimized structures, it was observed that two ligand molecules coordinated with Hg(II), along with two nitrate ions (Figure 13). The benzothiazole ligand coordinates to Hg(II) in such a way that cationic moieties are opposite to each other. However, on substitution of the nitrate with bromide ions, both imidazolium cations rearrange to form a cavity for the bromide ion. Here, the bromide ion interacts with Hg(II) through ionic

interaction, whereas the positive charge of the imidazolium ring provides the cavity for the anion. The HOMO-LUMO diagram of **N1** shows that the HOMO is spread over the benzothiazole moiety, whereas the LUMO is on the imidazolium cation (Figure 14). On complexation with Hg(II) and bromide, the HOMO shifts toward the metal and bromide ion, whereas the LUMO spreads over the aromatic ring (benzothiazole). The change in the HOMO-LUMO orbitals causes the change in the emission profile of the receptor.

To evaluate the present sensor in real time analysis, water samples were collected from different resources and used for preparation of the **N1** solution (20 μM). Different concentrations of Hg(II) were spiked to this solution, and the fluorescence intensity was recorded at 380 nm. By comparing fluorescence intensity with the calibration curve in Figure 10, the amount of Hg(II) was determined. The high percentage of recovery for Hg(II) indicates the authentication of receptor **N1** for real time analysis. Similarly, for real time evaluation of bromide ions in the river water sample, an **N1** solution (20 μM) also containing 12 μM of Hg(II) was prepared. Different concentrations of bromide ions were spiked into the samples **1b**, **2b**, **3b**, **1b'**, **2b'** and **3b'**, and the fluorescence spectra were recorded. By comparing the fluorescence intensity at 450 nm with the calibration curve in Figure 10, the amount of bromide was determined.

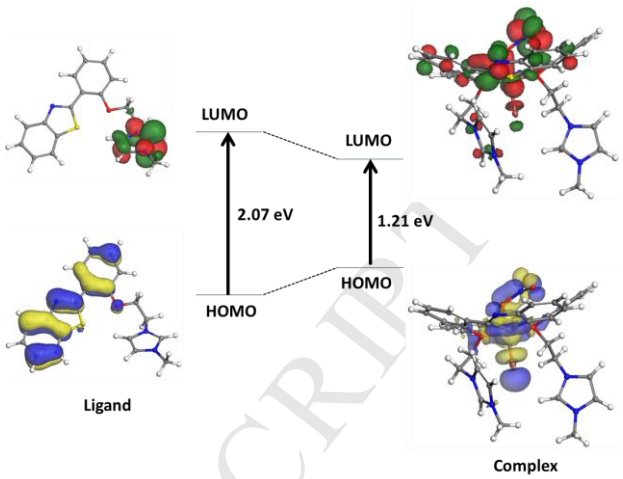


Figure 14. Energy correlation of HOMO-LUMO gap between ligand **N1** and **N1** complex of Hg(II)-Br.

To authenticate the experiments, the found concentrations of Hg(II) and bromide were also determined using AAS (atomic absorption spectroscopy) and ICP (inductively coupled plasma), respectively, which was in agreement with the presented methods (Table 1).

Table 1. Result of Hg(II) and bromide sensing in real samples.

Sample	Hg(II) added (μM)	Hg(II) found (μM)		Recovery (%)	Sample	Bromide added (μM)	Bromide found (μM)		Recovery (%)
		Present method	AAS				Present Method	ICP	
Tap water									
1a	0	-	-		**1b**	0	0.9	0.91	
2a	5	4.97	4.92	99.4	**2b**	10	10.3	10.2	94.5
3a	10	9.95	9.93	99.5	**3b**	15	15.7	15.7	98.7
River water									
1a'	0	-	-		**1b'**	0	0.5	0.5	
2a'	5	4.97	4.95	99.4	**2b'**	10	10.1	10.2	96.2
3a'	10	9.96	9.96	99.6	**3b'**	15	15.4	15.3	96.4

Conclusion

We synthesized a novel benzothiazole-based receptor **N1** that incorporated an imidazolium cation. Receptor **N1** was investigated for sensing cations and anions in water. Receptor **N1** selectively recognized Hg(II), with a large enhancement in emission intensity at 380 nm. The Hg(II) complex of receptor **N1** selectively recognized Br^- ions in water in a ratiometric manner. The ratiometric plot of F_{450}/F_{380} and interference studies showed that the Hg(II) complex of receptor **N1** could be used for selective analysis of Br^- ions in water, even in the presence of other anions, with a detection limit of 22 nM. ^1H NMR studies showed that the imidazolium hydrogen in the Hg(II) complex of receptor **N1** participates in the recognition of Br^- ions. In the absence of Hg(II), receptor **N1** did not recognize Br^- ions.

Acknowledgements

A.S. is thankful to CSIR−New Delhi, India, for his fellowship. Authors are thankful to S. Kaur of Panjab University Chandigarh for help in evaluation of binding constant.

References

1. Gale, P. A.; Caltagirone, C. *Chem. Soc. Rev.* **2015**, *44*, 4212.
2. Molina, P.; Tárraga, A.; Alfonso, M. *Dalton Trans.* **2014**, *43*, 18.
3. Hargrove, A. E.; Nieto, S.; Zhang, T.; Sessler, J. L.; Anslyn, E. V. *Chem. Rev.* **2011**, *111*, 6603.
4. Elmes, R. B. P.; Jolliffe, K. A. *Chem. Commun.* **2015**, *51*, 4951.
5. Romański, J.; Trzaskowski, B.; Piątek, P. *Dalton Trans.* **2013**, *42*, 15271.

6. Evans, A. J.; Beer, P. D. *Dalton Trans.* **2003**, 4451.
7. Kim, S. K.; Sessler, J. L. *Chem. Soc. Rev*. **2010**, *39*, 3784.
8. Thomas, J. A. *Dalton Trans.* **2011**, *40*, 12005.
9. Rommel, S. A.; Sorsche, D.; Rau, S. *Dalton Trans.* **2016**, *45*, 74.
10. Wang, H. H.; Gan, Q.; Wang, X. J.; Xue, L.; Liu, S. H.; Jiang, H. *Org. Lett.* **2007**, *9*, 4995.
11. Singh, A.; Singh, A.; Singh, N.; Jang, D. O. *RSC Adv.* **2015**, *5*, 72084.
12. Singh, J.; Singh, A.; Singh, N. *RSC Adv.* **2014**, *4*, 61841.
13. Singh, J.; Yadav, M.; Singh, A.; Singh, N. *Dalton Trans.* **2015**, *44*, 12589.
14. Lim, J. Y. C.; Cunningham, M. J.; Davis, J. J.; Beer, P. D. *Chem. Commun.* **2015**, *51*, 14640.
15. Yoon, J.; Kim, S. K.; Singh, N. J.; Lee, J. W.; Yang, Y. J.; Chellappan, K.; Kim, K. S. *Science* **2004**, *80*, 581.
16. Anzenbacher, P.; Palacios, M. A.; Jursíková, K.; Marquez, M. *Org. Lett.* **2005**, *7*, 5027.
17. Shang, X. F.; Li, J.; Lin, H.; Jiang, P.; Cai, Z. S.; Lin, H. K. *Dalton Trans.* **2009**, 2096.
18. Zhang, Z. H.; Liu, J.; Wan, L. Q.; Jiang, F. R.; Lam, C. K.; Ye, B. H.; Qiao, Z.; Chao, H. Y. *Dalton Trans.* **2015**, *44*, 7785.
19. Shi, H. Y.; Huang, Y. L.; Sun, J. K.; Jiang, J. J.; Luo, Z. X.; Ling, H. Y.; Lam, C. K.; Chao, H. Y. *Dalton Trans.* **2015**, *44*, 7785.
20. Romański, J.; Piątek, P. *J. Org. Chem.* **2013**, *78*, 4341.
21. Sadhu, B.; Sundararajan, M.; Velmurugan, G.; Venuvanalingam, P. *Dalton Trans.* **2015**, *44*, 15450.
22. Piątek, P.; Karbarz, M.; Romański, J. *Dalton Trans*. **2014**, *43*, 8515.
23. Fu, Y.; Mu, L.; Zeng, X.; Zhao, J. L.; Redshaw, C.; Ni, X. L.; Yamato, T. *Dalton Trans.* **2013**, *42*, 3552.
24. Wan, Q.; Zhuo, J. B.; Wang, X. X.; Lin, C. X.; Yuan, Y. F. *Dalton Trans.* **2015**, *44*, 5790.
25. Alfonso, M.; Ferao, A. E.; Tárraga, A.; Molina, P. *Inorg. Chem*. **2015**, *54*, 7461.
26. Jia, C.; Hay, B. P.; Custelcean, R. *Inorg. Chem.* **2014**, *53*, 3893.
27. Howe, E. N. W.; Bhadbhade, M.; Thordarson, P. *J. Am. Chem. Soc*. **2014**, *136*, 7505.
28. Mahoney, J. M.; Beatty, A. M.; Smith, B. D. *J. Am. Chem. Soc*. **2001**, *123*, 5847.
29. Zhang, D.; Jiang, X.; Yang, H.; Su, Z.; Gao, E.; Martinez, A.; Gao, G. *Chem. Commun*. **2013**, *49*, 6149.
30. Wang, H.; Xue, L.; Jiang, H. *Org. Lett*. **2011**, *13*, 3844.
31. Zhang, M.; Yu, M.; Li, F.; Zhu, M.; Li, M.; Gao, Y.; Li, L.; Liu, Z.; Zhang, J.; Zhang, D. Yi, T.; Huang, C. *J. Am. Chem. Soc.* **2007**, *129*, 10322.
32. Lou, X.; Ou, D.; Li, Q.; Li, Z. *Chem. Commun.* **2012**, *48*, 8462.
33. Singh, N.; Jang, D. O. *Org. Lett.* **2007**, *9*, 1991.
34. Mahapatra , A. K.; Roy, J.; Sahoo, P.; Mukhopadhyay, S. K.; Chattopadhyay, A. *Org. Biomol. Chem.* **2012**, *10*, 2231.
35. Barman, S.; Sadhukhan, M. *Mater. Chem.* **2012**, *22*, 21832.
36. Lu, Q. S.; Dong, L.; Zhang, J.; Li, J.; Jiang, L.; Huang, Y.; Qin, S.; Hu, C. W.; Yu, X. Q. *Org. Lett.* **2009**, *11*, 669.
37. Kim, S. K.; Singh, N. J.; Kwon, J.; Hwang, I. C.; Park, S. J.; Kim, K. S.; Yoon, J. *Tetrahedron* **2006**, *62*, 6065.
38. Singh, A.; Singh, A.; Singh, N. *Dalton Trans.* **2014**, *43*, 16283.
39. Wang, S.; Chang, Y. T. *J. Am. Chem. Soc.* **2006**, *128*, 10380.
40. Busschaert, N.; Caltagirone, C.; Rossom, W. V., Gale, P. A. *Chem. Rev.* **2015**, *115*, 8038.
41. Sharma, H.; Kaur, N.; Singh, N. *Anal. Methods*. **2015**, *7*, 7000.
42. Hamilton, G. R. C.; Sahoo, S. K.; Kamila, S.; Singh, N.; Kaur, N.; Hyland, B. W.; Callan, J. F. *Chem. Soc. Rev.* **2015**, *44*, 4415.
43. Singh, N.; Kumar, M.; Hundal, G. *Tetrahedron* **2004**, *60*, 5393.
44. Dupont, J.; Consorti, C. S.; Suarez, P. A. Z.; Souza, R. F. D. *Org. Synth.* **2002**, *79*, 236.
45. Pearson, G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
46. Renny, J. S.; Tomasevich, L. L.; Tallmadge, E. H.; Collum, D. B. *Angew. Chemie. Int. Ed.* **2013**, *52*, 11998.
47. Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739.
48. Singh, A.; Raj, T.; Aree, T.; Singh, N. *Inorg. Chem.* **2013**, *52*, 13830.
49. Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett*. **2003**, *91*, 146401.