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A new class of fluorogenic thiazolo[2,3-*b*] quinazolinone receptor: selective detection towards mercury and hydrogen bisulfate ions in aqueous medium†

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A series of fluorophoric and structurally diverse thiazoloquinazoline derivatives were synthesized in a one-pot multicomponent cascade reaction using a microwave irradiation technique. The unique structural arrangement of the synthesized compounds encouraged us to design a new type of bioactive molecular receptor. This receptor interacts with HSO_4^- in 1 : 1 and Hg^{2+} in 1 : 2 binding stoichiometric ratios resulting in a change in fluorescence as well as absorption spectra in aqueous medium. The ion bonded receptor complex possibly enhances the fluorescence signal of the receptor *via* H-bonded complex formation with HSO_4^- ions and co-ordinate complex formation with Hg^{2+} ions.

Introduction

Gradual developments in the design and synthesis of novel organic fluorophores are essential for their flawless progress in chemistry, biology, and functional-materials research.[1] Extensive use of metal ions and their subsequent pollution trigger severe environmental and health problems[2] in day to day life. As a consequence, construction of highly selective and sensitive fluorescence sensors based on organic frameworks that are proficient in detecting metal ions has been the subject of keen interest. In particular, thiazolo[2,3-*b*]quinazolinone represents a prominent framework due to its prevalence in bioactive substances.[3–5] In spite of diverse applications in the field of biology and pharmacy, there are limited reports on the photophysical properties of such fused heterocycles. Since a single receptor for multiple analytes[6] has drawn extensive attention amongst analytical chemists, it is quite demanding and challenging for developing such molecular sensors. Nevertheless, the approach for the construction of novel fluorophoric and structurally diverse thiazoloquinazolines towards the development of chemosensors for multiple analytes still remains a mystery.

Hydrogen sulfate is one of the deleterious pollutants[7] in agricultural fertilizers, industrial raw materials and nuclear fuel waste. It eventually gets into the environment and causes several problems such as skin irritation, eye damage and respiratory paralysis.[8] Thus, it is necessary to detect hydrogen sulfate in real time from environmental and biological samples in the presence of other competitive ions though it is an exigent task due to its large standard Gibbs energy of hydration (-1080 kJ mol^{-1}).[9]

Conversely, mercury is a highly toxic heavy transition metal and a kind of persistent toxic substances (PTS) owing to its characteristics such as environmental persistence, long-range transportation, bioaccumulation, and high toxicity.[10–13] Its exposure can have numerous adverse effects on health, such as brain damage, kidney failure, various cognitive and motion disorders.[14] The consequences of its toxicity has been revealed by Minamata disease and mercury poisoning in Iraq.[15–17] Moreover, Hg^{2+} can be converted into the more toxic methylmercury (MeHg) *via* chemical or biological pathways, causing further harm to organisms with high trophic level after bioaccumulation and biomagnification.[18–21] Therefore, developing effective and sensitive analytical methods for HSO_4^- and Hg^{2+} ions determination in water is of great significance.

In continuation of our interest in exploring the synthesis and study of fluorogenic properties of unique thiazolo[2,3-*b*]quinazolinones *via* one-pot cascade reaction under microwave irradiation technique,[22] in this context, we expanded the range of accessible angular –OH functionalized thiazolo[2,3-*b*]quinazolinone analogues using 2-amino thiazole precursor. Accumulating evidences towards the formation of thiazolo[2,3-*b*] quinazolinones having unique structural arrangement and interesting fluorescence properties, we have investigated the selectivity and sensitivity of HSO_4^- and Hg^{2+} ions in aqueous (H_2O : MeOH, 20 : 80 v/v) medium using this novel receptor.

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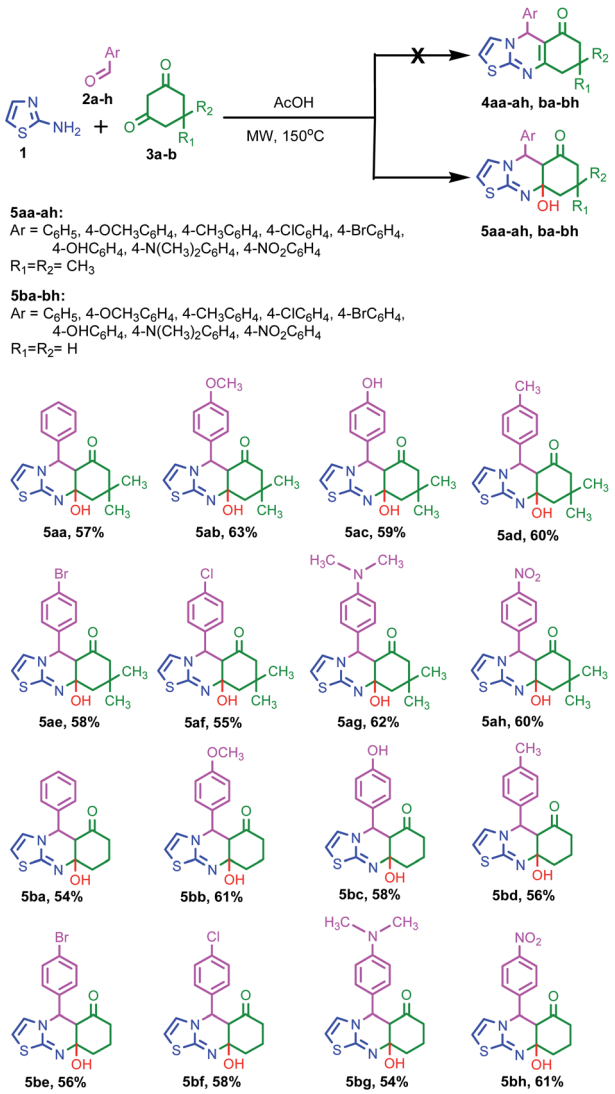
Results and discussion

Taking our previously reported results into consideration,[22] we attempted analogous one pot three component cascade reaction of equimolar mixture of 2-amino thiazole **1**, aryl aldehydes **2a-h** and cyclic-1,3-dicarbonyls **3a-b** under acid mediated microwave heating at 150 °C in a microwave synthesizer. Here also, unexpected formation of a series of compound **5** was achieved in spite of compound **4** (Scheme 1). The isolated target molecules are elucidated unambiguously using NMR and mass spectroscopy. Two different series of thiazoloquinazolinone derivatives **5aa-5ah** and **5ba-5bh** were synthesized in good yields on heating the mixture of **1**, **2a-h** separately with dimedone **3a** and 1,3-cyclohexanedione **3b** respectively (Scheme 1).

Interestingly, an additional experiment was done to know the presence of –OH group leading a crucial role for the distinct photophysical property of the thiazoloquinazolinone (I) (Fig. 1).



Scheme 1 Synthesis of 9a-hydroxy-5-phenyl-5,5a,7,8,9,9a-hexahydrothiazolo[2,3-*b*]quinazolin-6-ones **5aa-5ah**, **ba-5bh** from 2-amino thiazole **1**, cyclic 1,3-diketones **2a-h** and aromatic aldehydes **3a-b**.

Benzothiazoloquinazolinone (II) (Fig. 1) was also synthesized by previously reported procedure.[22] Fluorescence spectra of benzothiazoloquinazolinone (II) were then measured upon addition of 5 equivalents various metal ions. From the fluorescence spectra, it was observed that no such significant change in emission intensities at 395 nm was occurred after addition of the metal ions (see Fig. S49 in the ESI†).

Perceiving the significance of –OH bond formation, we have investigated the sensing mechanism of the synthesized compounds possessing different substituents in compounds **5aa**, **5ac**, **5ag**, **5ah** and **5ba**. All the derivatives of the thiazolo[2,3-*b*]quinazolinones besides, compounds **5ag**, **5ah**, **5bg** and **5bh** displayed cyan colour fluorescence under UV lamp. The initial solvatochromism studies of compound **5aa** (R) was performed in acetonitrile, chloroform, DMSO, 1,4-dioxan, ethanol, hexane and methanol–water. In the UV-visible spectra, two strong absorption band appeared at 286 and 404 nm in H_2O : MeOH (20 : 80 v/v) solvent medium may be attributed to $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transition. The fluorescence emission spectrum of receptor R was measured in the same solvent medium with an excitation wavelength 404 nm and maximum fluorescence emission intensity was observed at 460 nm. Further, the receptor R possessing sulfur, nitrogen atoms and one free –OH group appended to one side of the molecule may act as suitable binding site for cation in accordance with soft acid soft base (SASB) concept and for anions by non-covalent interaction such as hydrogen bonding.

Consequently, we have investigated the binding affinity of receptors **5aa**, **5ac**, **5ag**, **5ah** and **5ba** towards various anions and cations. The anion and cation binding affinity of different receptors was primarily examined by fluorescence and UV-vis spectroscopic techniques. Fluorescence and UV-visible spectra were measured upon addition of 5 equivalents various anions such F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- in the form of their tetrabutylammonium (TBA) salts and CN^- ion as potassium salt to a 10 μM receptor solutions in H_2O/MeOH (20 : 80 v/v) solvent medium. Similarly, the spectroscopic responses were also monitored by adding 5 equivalents of different metal ions such as Na^+, K^+, Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Pd^{2+}, Zn^{2+} in the form of their perchlorate/chloride//nitrate salts (10^{-3} to 10^{-4} M) dissolved in Milli-Q water. From the fluorescence spectra, it was observed that the emission intensities at 460 nm were increased by about 10 fold in presence of 5 equivalents of HSO_4^- or Hg^{2+} ions (Fig. 2) when added separately to the receptor solutions, however other ions could not produce any significant changes in the fluorescence spectra of the receptor solution under an

Fig. 1 Structures of thiazoloquinazolinone (I) and benzothiazoloquinazolinone (II).

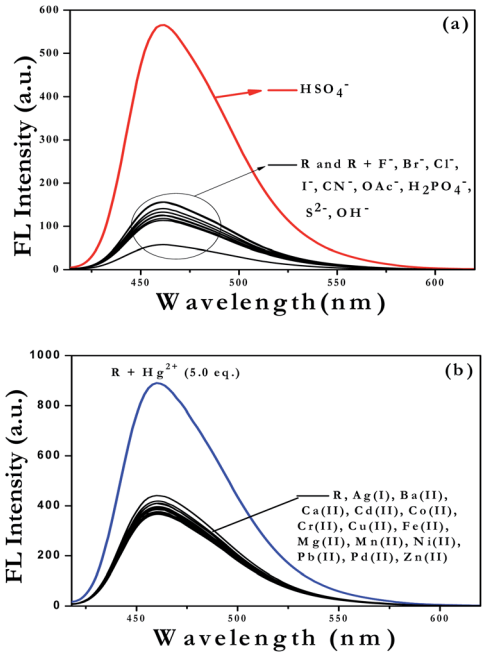


Fig. 2 Fluorescence spectra of receptor R (10 μM) in presence of 5.0 equivalents of various anions (a) and cations (b) in MeOH/H_2O (20 : 80) as solvent medium (λ_{ex} = 404 nm).

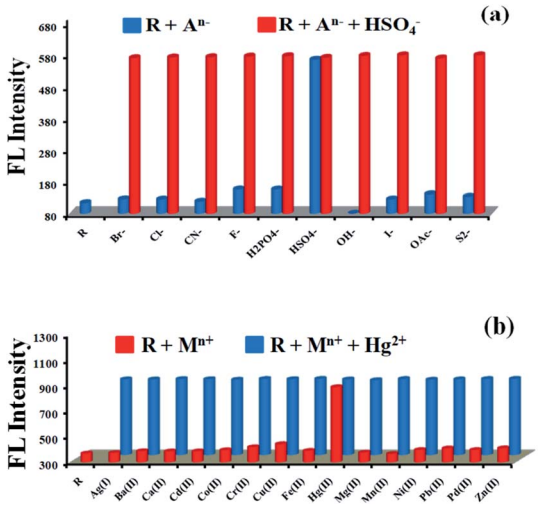


Fig. 3 (a) Histogram for receptor R (10 μM) in presence of 5.0 equivalents various anions (blue bars) and 5.0 equivalents various anions plus 5.0 equivalents HSO_4^- ions (red bars) and (b) histogram for receptor R (10 μM) in presence of 5.0 equivalents various cations (red bars) and 5.0 equivalents various cations plus 5.0 equivalents Hg^{2+} ions (blue bars) in MeOH/H_2O (20 : 80 v/v) (λ_{ex} = 404 nm).

identical condition. On the other hand in the UV-vis studies, it was observed that the absorption band at 404 nm was decreased to a smaller extent while the absorption band at 286 nm shows a significant decrease with a hypsochromic shift of 21 nm from 286 nm to 265 nm only in presence of HSO_4^- ion (see Fig. S50a in the ESI†). Moreover, in case of 5 equivalents of Hg^{2+} ions a hypsochromically shifted (59 nm) new and hence a distinct absorption band was appeared at 345 nm (see Fig. S50b in the ESI†) with simultaneous disappearance of the absorption band at 404 nm. These findings clearly indicated that the receptor has a very high selectivity and significant affinity towards HSO_4^- and Hg^{2+} ions.

Furthermore, in order to check the interference of other ions, competitive binding studies were carried out by monitoring the fluorescence spectra of receptor in presence of 5 equivalents various anions having 5 equivalents of HSO_4^- ions and 5 equivalents various cations including 5 equivalents Hg^{2+} ions separately in MeOH/H_2O (20 : 80 v/v) solvent medium upon excitation at 404 nm. From the histograms (Fig. 3), it was observed that the fluorescence intensity at 460 nm was enhanced only by 5 equivalents of HSO_4^- or Hg^{2+} ions (Fig. 3a and b) indicating a high selectivity of the receptors towards these ions. Besides, the receptor R (compound **5aa**), the sensing properties of thiazoloquinazolinone derivatives possessing electron rich (compound **5ac** and **5ag**) and electron deficient (compound **5ah**) phenyl substituents have been investigated for sensing. From the results, it was concluded that the compound **5ac** showed similar type of optical responses as the compound **5aa**. No satisfactory results were obtained in case of **5ag** and **5ah** as the compounds are poorly emissive/non-emissive in nature. In addition, the anion and cation selectivities of the compound **5ba** also checked whether this compound offers steric hindrance towards binding (ESI, Fig. S60†). The findings suggest that the compounds **5aa** and **5ba** show similar fluorescence responses. Thus, the steric hindrance does not interfere the binding. As a result, only the compound **5aa** was taken for further investigation towards sensing.

The fluorescence intensity at 460 nm is nearly the same as receptor R in presence of 5 equivalents HSO_4^- or Hg^{2+} ion even in the presence of 5 equivalents other interfering ions (Fig. 3a and b). These findings further supported that, presence of other ions in the analytical sample could not produce any interference in the detection of HSO_4^- or Hg^{2+} ion and hence the receptor is found to be highly selective towards HSO_4^- and Hg^{2+} ion when analyzed separately.

Additionally, the interference of cations for HSO_4^- and anions for Hg^{2+} ion were also checked by measuring fluorescence spectra in presence of 5 equivalents various cations with receptor solution having 5 equivalents of HSO_4^- ions and 5 equivalents various anions with receptor solution having 5 equivalents of Hg^{2+} ions separately in MeOH/H_2O (20 : 80 v/v) solvent medium upon excitation at 404 nm. From the histograms (see Fig. S51 in the ESI†), the fluorescence intensity at 460 nm is nearly the same as receptor R in presence of 5 equivalents HSO_4^- ions and 5 equivalents of other cations having 5 equivalents of Hg^{2+} ions.

Similarly, the fluorescence intensity at 460 nm is nearly the same as receptor R in presence of 5 equivalents Hg^{2+} and 5 equivalents of other anions having 5 equivalents of HSO_4^- ion. These findings further supported that presence of other anions in the analytical sample could not produce any interference in the detection of Hg^{2+} ion except HSO_4^- ion and presence of other cations could not produce any interference in the detection of HSO_4^- ion except Hg^{2+} ion. Thus, we can envisage that

the receptor can be utilized for selective and sensitive detection of HSO_4^- or Hg^{2+} with only exception when both are present.

In order to understand the binding characteristics of the receptors and HSO_4^- or Hg^{2+} ions, fluorescence titration experiments were conducted upon gradual addition of a standard solution of HSO_4^- or Hg^{2+} ions to the receptor solution separately. On gradual addition of a standard solution of HSO_4^- ion to a 10 μM receptor R solution indicated a progressive increase in intensity of the receptor emission band at 460 nm (see Fig. S52 in the ESI†). A fluorescence change from weakly emissive to bright cyan was observed with increasing concentration of HSO_4^- ion upon UV-illumination. From the fluorescence titration spectra, the binding constant of receptor-HSO_4^- was estimated to be 2.79×10^6 with a nonlinear regression fit of $R^2 = 0.998$ (see Fig. S52 in the ESI†). Conversely, an initial increase in intensity of the receptor emission band at 460 nm was observed for gradual addition of two equivalents of Hg^{2+} ions to a 10 μM receptor R solution (Fig. 4a). On further addition of Hg^{2+} ions beyond two equivalents to the 1 : 2 receptor–Hg^{2+} complex exhibited a subsequent decrease in intensity at 460 nm (Fig. 4a). Here, we can suggest that after binding of two equivalents of mercury ions, additional Hg^{2+} ions remain in the vicinity of the solution of the complex that quenches the intensity possibly due to heavy metal ion effect acting as a self-quencher. In order to understand the quenching behavior, an additional experiment was carried out taking copper as quencher. Upon gradual addition of Cu^{2+} ions to a 1 : 2 receptor–Hg^{2+} complex solution, it was observed that the fluorescence intensity at 460 nm get quenched as was observed in case of Hg^{2+} ion addition beyond 2 equivalents (Fig. 4b). These findings suggest that the fluorescence quenching is due to the presence of heavy metal ions in the vicinity of the 1 : 2 receptor–Hg^{2+} complex in the solution. From the Benesi–Hildebrand plot, the binding constant was estimated to be 2.29×10^4 M^{-1} with linear regression fit of $R^2 = 0.985$ for Hg^{2+} ion as measure of fluorescence intensity at 460 nm (see Fig. S53 in the ESI†). Such a very high binding constant indicated a very strong affinity of the receptor R towards HSO_4^- or Hg^{2+} ion.

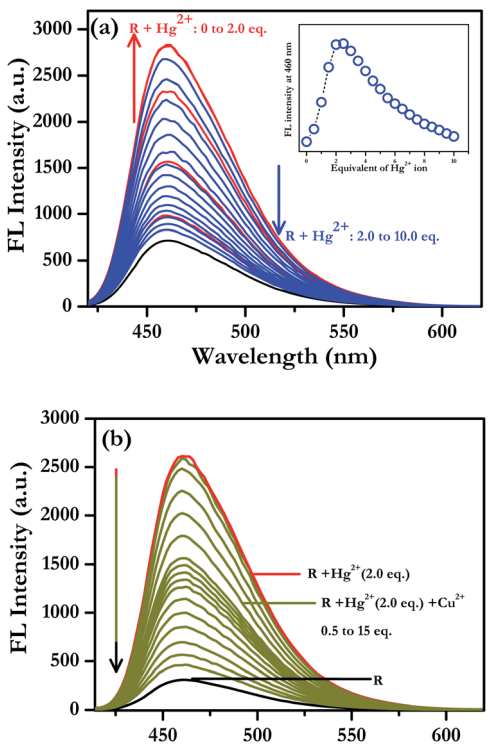


Fig. 4 Fluorescence titration spectra of (a) receptor R (10 μM) upon addition of 0.2 to 10.0 eq. of Hg^{2+} ions in MeOH/H_2O (20 : 80) solvent medium. Inset shows the corresponding increase in fluorescence intensity at 460 nm (λ_{ex} = 404 nm). (b) receptor R (10 μM) + 2.0 equivalents of Hg^{2+} upon addition of 0.5 to 15.0 eq. of Cu^{2+} ions in MeOH/H_2O (20 : 80) solvent medium (λ_{ex} = 404 nm).

In the UV-visible titration of receptor R, it was observed that the receptor absorption band at 404 nm gradually decreases along with the simultaneous increase of a hypsochromically shifted new absorption band at 345 nm with incremental concentration of Hg^{2+} ion by the gradual addition of Hg^{2+} ions (see Fig. S54 in the ESI†). The UV-visible titration profile is in accordance with the fluorescence titration profile that further supported a certain interaction of the receptor R with Hg^{2+} ions. Thus, we can propose that the sulfur (S), nitrogen (N) and hydroxyl oxygen (O) binding sites of the receptor R bind with the Hg^{2+} ions through co-ordinate interaction due to soft acid soft base concept.

The binding stoichiometry of receptor R with HSO_4^- or Hg^{2+} ions was quantitatively analyzed by Job's continuous variation plot. It revealed that maximum fluorescence intensity at 460 nm for 0.5 mole fractions of HSO_4^- or Hg^{2+} ions indicating the binding ratios between R with HSO_4^- ion and R with Hg^{2+} ion in 1 : 1 and 1 : 2 respectively (see Fig. S55 in the ESI†). Further, the sensitivity of the receptor R has been evaluated by determining the detection limit. From the fluorescence measurement the detection limit for HSO_4^- and Hg^{2+} ion by the receptor R were found to be 3.6 μM and 17.1 μM respectively (see Fig. S56 in the ESI†). This limit of detection HSO_4^- is far below the permissible concentration of HSO_4^- ion (1000–1200 mg L^{-1} = 0.01 M) in drinking water as recommended by WHO.[23]

To further elucidate the binding mode of the receptor R with HSO_4^-, ^1H NMR-titration experiment has been performed which illustrated that the chemical shift of the –OH group shifted towards downfield region. Moreover, after the continuous addition of HSO_4^- anion of 0.5, 1.0 and 2.0 equiv. to the receptor solution, the resonance at δ11.18 ppm shifted towards downfield to δ11.21, 11.23 and 11.26 ppm respectively.

In order to gain insight into the structural basis of photophysical properties of receptor R, theoretical calculations of R, R + Hg^{2+} and R + HSO_4^- were performed using Gaussian 09 program. The structures of R, R + Hg^{2+} and R + HSO_4^- were optimized using B3LYP and B3LYP/LANL2DZ basis sets respectively. The frontier molecular orbital analysis reveals that in receptor R, HOMO is spread over thiazole and pyridine scaffolds where as the LUMO is located only over pyridine ring (Fig. 5d). Moreover, in R + Hg^{2+} (1 : 2) HOMO appears over thiazole and pyridine moieties, where as LUMO is located over mercury (Fig. 5f). Moreover, the calculated HOMO–LUMO energy gap difference for R + Hg^{2+} (1 : 2) (3.15 eV) is lesser than

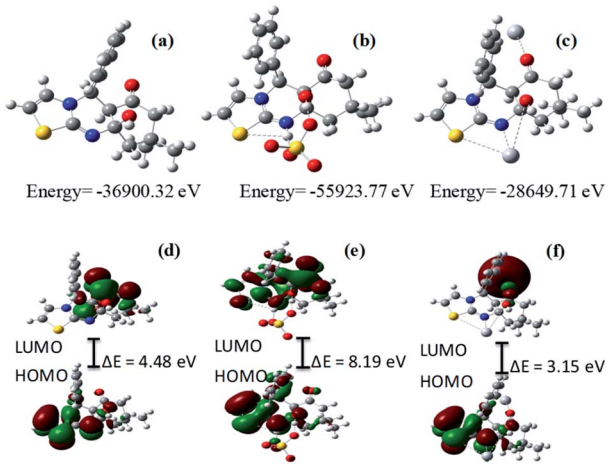


Fig. 5 Optimized structure of (a) R, (b) R + HSO_4^- and (c) R + Hg^{2+}. Frontier molecular orbital of (d) receptor R (e) R + $HSO_4^-$and (f) R + Hg^{2+}.

that of the receptor R (4.48 eV) which indicates favorable coordination between the receptor R and Hg^{2+} in 1 : 2 ratio. However, in R + HSO_4^- HOMO is found over the thiazole and pyridine moieties and LUMO spreads all over the molecules (Fig. 5e). The calculated energy difference between HOMO and LUMO for R + HSO_4^- (8.19 eV) is higher than that of the receptor R (4.48 eV). The larger HOMO–LUMO gap refers to higher kinetic stability and lower chemical reactivity. The molecule binding with HSO_4^- is definitely stable.

Conclusions

In summary, we were able to extend our methodology for the synthesis of –OH functionalized thiazoloquinazolinone derivatives under one-pot multicomponent cascade reaction using 2-amino thiazole precursor. The unique structural arrangement of the synthesized compounds stimulated us to design a new type of bioactive novel molecular receptor. All the experimental findings clearly suggested that this receptor interact with HSO_4^- in 1 : 1 and with Hg^{2+} in 1 : 2 binding stoichiometric ratio resulting in a change in fluorescence as well as absorption spectra in aqueous medium. The ion bonded receptor complex possibly enhances the fluorescence signal of the receptor at 460 nm *via* H-bonded complex formation with HSO_4^- ions and co-ordinate complex formation with Hg^{2+} ions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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