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# Synthetic studies on the molybdenum cofactor: Total synthesis of pterindithiolenes by direct dithiolene formation from suitable pterin alkynes

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**ABSTRACT**

A novel, efficient total synthesis of a series of pterindithiolenes (**15, 16, 17** and **18**) [(5,6-dihydro-[1,4]dithiin or 6,7-dihydro-5H-[1,4]dithiepin systems respectively for six and seven membered dithiolenes] has been reported. The six membered quinoxaline thioketal **9** and seven membered quinoxaline dithiolene **11** have also been synthesized from quinoxaline acetylenic alcohol **5** and the corresponding acetylenic ketone **10** respectively. The synthesis of five membered pterin thioketals **12** and **13** along with the conversion of **13** to the dithiolene **14** by the reaction with NBS is also reported.

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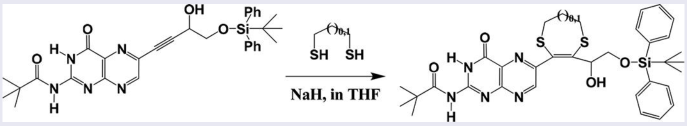
**KEYWORDS**
Moco; six and seven membered pterindithiolenes; six membered quinoxaline dithiolenes

**GRAPHICAL ABSTRACT**



## Introduction

All molybdenum-containing enzymes[1] except nitrogenase, complex the metal through the enedithiol moiety attached to a unique pterin nucleus termed molybdopterin (MPT).[2] The molybdopterin derivatives Form A, Form B, urothione and camMPT have been isolated[3,4] and the suggested ligation of molybdenum to sulphur ligands of molybdopterin is in accordance with the results of EXAFS (Extended X-ray Absorption Fine Structure) studies.[5a] The isolated C(6)-substituted pterins possess unsaturated carbon atoms α and β to the pterin ring. Sulfur functionalities are associated with these unsaturated carbons in camMPT, Form B and urothione and the formation of these compounds is consistent with the decomposition of proposed 1,2-ene-dithiolate structure of Moco.[5b]

Extensive review articles have been devoted to the discussions of biochemistry, spectroscopy, mechanism and recent advances of the Moco containing enzymes and the structure of the Moco.[6–22] Several oxidative degradation products of molybdopterin have been isolated. The basic structure of the molybdenum cofactor (Moco) is shown in

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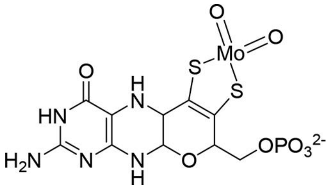


Figure 1. Basic structure of the Moco.

Figure 1. Two of these derivatives, Form A and Form B are the oxidative degradation products of the cofactor. Urothione, the third derivative, is a metabolic product of the molybdopterin excreted in urine. The fourth one, camMPT was obtained by the carboxamidomethyl derivatisation of the cofactor. The structures of the Form A, Form B, urothione and the dephospho Form A (in its homochiral form) have been confirmed by the chemical synthesis by Taylor et al.[23–26] The decomposition of Moco-containing molybdoenzymes was carried out in absence of iodine and a degradation product dephospho Form B was obtained which contains only one of the two sulfur atoms present in molybdopterin itself, for which the structure is shown in Figure 2.

One of these oxidation products of Moco has been suggested to be a thieno[3,2-g]pterin, termed Form B. The only sulfur-containing pterin natural product previously known is the thieno[3,2-g]pterin derivative urothione, which was first isolated from human urine in 1940[27] and synthesized 27 years later in 0.3% yield from a pteridine intermediate.[28–32]

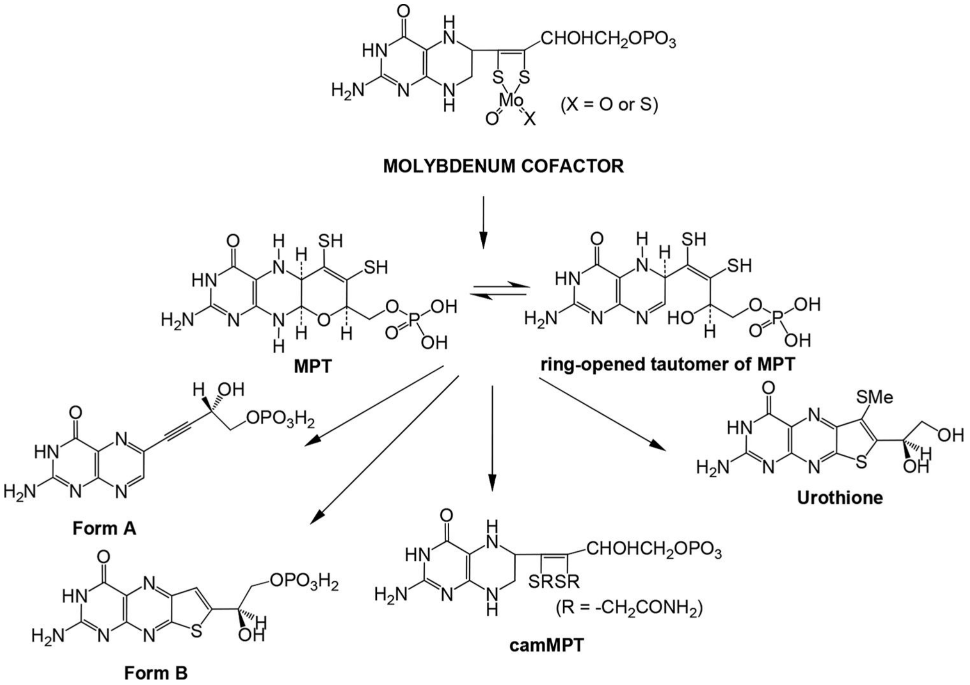


Figure 2. A tentative structure for the active cofactor.

Urothione was ultimately assigned the structure (Figure 1) which received strong support through comparison with deoxyurothione, which Taylor *et al.* synthesized several years ago by an unambigous route,[33] and has been rigorously confirmed by direct comparison with (±)-urothione prepared by a new and unequivocal total synthesis by his group.[34a] The discovery that children suffering from biochemical abnormalities due to combined deficiencies of sulfite oxidase and xanthine dehydrogenase lacked the active molybdenum cofactor, and that their urine samples were devoid of urothione, confirmed that this latter compound was the urinary metabolite of molybdenum cofactor.[34b] On the basis of the structural aspects of the degradation products; Form A, Form B and Urothione a tentative structure for the active molybdenum cofactor, shown in the Figure 2 was proposed by Johnson and Rajagopalan.[34c,35] It is interesting to note that the protein crystallographic studies have subsequently revealed the remarkable accuracy of these proposals.

Recently we published a convenient and concise total synthesis of thienopterins and (±) Form B (dephospho) from the suitable acetylene moiety attached with pterin ring system.[36] In this paper, we have shown the advantages of conjugated acetylene moiety at the 6-position of the pterin system for thiophene annulation. We describe in this paper a novel, concise and convenient total synthesis of pterindithiolenes (**11, 14, 15, 16, 17** and **18**) by a new direct dithiolene annulation from suitable alkyne substituted pterins.

## Results and discussion

In our retrosynthetic strategy for dithiolene annulation, we conceptualized that direct nucleophilic Michael attack by one sulphide ion of the dithiolate to the substituted acetylene moiety at the 6-position of conjugated pterin ring could follow further attack by the other sulphide ion under suitable reaction condition and variation of substituents (steric hindrance and electronic factors around the triple bond) at the adjacent carbon of acetylene moiety resulting direct dithiolene formation rather than preferring attack at the same carbon (for formation of thioketal). Thus when pterin at its 6-position is conjugated with suitably substituted acetylene moiety [e.g., more bulky TBDPS group (for protection) at α or β hydroxy groups instead of TBDMS (smaller) or α methyl groups], direct dithiolene annulation was observed as a reality. In case of other pterin alkyne substrates having no such bulky TBDPS groups, thioketals are formed as usual which however can be converted to the desired dithiolenes by known NBS reaction. Similarly we anticipated direct dithiolene annulation onto pterin from suitable pterin alkynes in one step by simply sulphide ion (a very strong nucleophile). Thus we wanted to utilize the advantages of the unique pterin system [electron withdrawing as well as easy conversion of the possible corresponding pterin anion (negative charge at N5) formed by nucleophilic attack by sulphide to the triple bond or subsequently produced dihydropterin (by acceptance of protons from excess thiol used or during aqueous work-up) to aromatized pterin by oxidation (unique redox property of pterin)] as well as conjugated acetylene moiety at the 6-position.

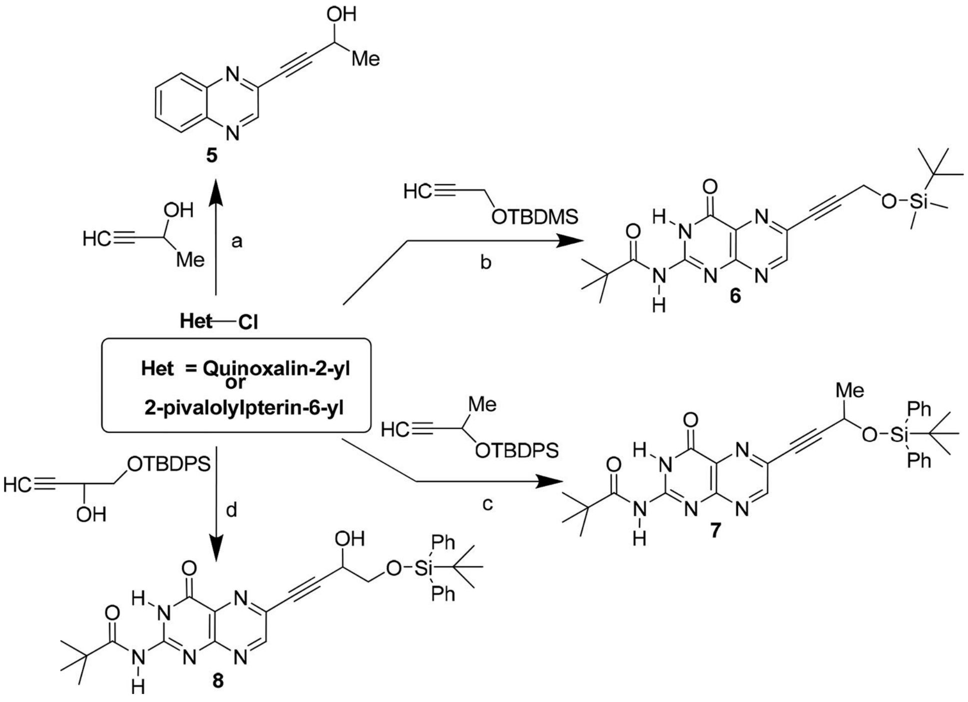
Following the above synthetic strategy, we wanted to synthesize the suitable alkyne substituted pterins for our goal to reach the stable pterin dithiolenes and thienopterin. While a broad range of *N*-pivaloylated-C(6)-alkyne substituted pterin ($PPt\text{-}C \equiv C\text{-}CHRR_1$ where - Ppt is 2-N-pivaloylpterin)[37–39] and C(2)-alkyne substituted quinoxalines ($Quin\text{-}C \equiv C\text{-}CH(OH)Me$) can be prepared, our discussion here is limited to the derivatives with R=H, $R_1 = OSiMe_2{}^tBu$; R=Me, $R_1 = OSiPh_2{}^tBu$ and R=OH, $R_1 = CH_2OSiPh_2{}^tBu$ respectively for which we published the synthetic procedure in our previous paper.[36] These R groups were selected since they possess four-carbon side chain and should allow ultimate conversion to the proposed molybdopterin side chain.

## Reagents and condition

(a) $Pd(OAc)_2$, CuI, $PPh_3$, $Et_3N$, MeCN, 80 °C, 4 h. 85%; (b) $Pd(OAc)_2$, CuI, $PPh_3$, $Et_3N$, MeCN, 60 °C, 4 h., 76%; (c) $Pd(PPh_3)_4$, CuI, $Et_3N$, MeCN, 60 °C, 3 h., 72%; (d) $Pd(OAc)_2$, $(o\text{-tolyl})_3P$, CuI, MeCN, 100 °C, 3.5 h., 62%.

Taylor and co-workers were the first to describe the synthesis of 2-alkynylquinoxalines and 6-alkynylpteridines related to molybdopterin. The alkyne functionality in compounds **5**-**8** were prepared by a palladium catalyzed coupling reaction of the corresponding terminal alkynes with C(6)-chloro-*N*-pivaloylpterin or C(2)-chloro-quinoxaline and the compounds **5**-**8** were isolated in fair yield, as shown in Scheme 1. Compounds **5** and **8** were prepared according to the procedure reported by Taylor and our group.[25b]

Turning into a different approach, we have here synthesized the stable pterin dithiolenes in 60 to 70% yield from the corresponding alkyne substituted pterin. The molybdenum dithiolene ring as well as the underlying enedithiol moiety in Moco are unique among the biomolecules hithertofore known. These functional groups pose a challenging unsolved problem in natural product synthesis. A large number of complexes of Mo in various oxidation states is known[40,41] including complexes with thiols[42,43] and thio amino acids



Scheme 1. Synthesis of alkyne substituted quinoxaline **5** and pterins **6**, **7** and **8**.

e.g., cysteine.[44] Reports have been made on molybdenum dithiolate[45–47] and Mo-pterin complexes.[48] The structures of many Mo- and W-enzymes have been investigated by protein crystallography.[49] The synthetic studies on pterin dithiolene system (pterin substituted metal coordinated dithiolenes related to the molybdenum cofactor) have been carried out by different research groups. Joule *et al.* have reported some model studies on quinoxaline dithiolene and dithiolane compounds at the 2-position of quinoxaline.[50]

## Reagents and condition

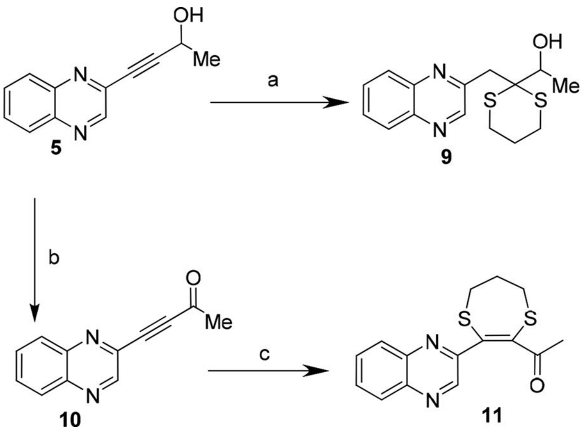
(a) 1,3-Propanedithiol, NaH, rt., 3 h., 73%; (b) $CrO_3$ / 25% $H_2SO_4$, acetone, 0 °C, 6 h., 75%; (c) 1,3-Propanedithiol, NaH, 0 °C, 2 h.

At first, we have attempted our synthetic study on quinoxaline system (Scheme 2). Thioketal compound **9** was easily prepared from 1,3-propanedithiol and compound **5** in the presence of sodium hydride instead of 1,2-ene-dithiol moiety. The work of Oconnor and Jones[51] also suggested that a necessary condition for the success of the formation of 1,2-ene-dithiol moiety is the presence of at least one electron-withdrawing substituent on the alkyne.[52] To activate the alkyne, the hydroxy group of compound **5** was oxidized to the keto compound **10** by $CrO_3$ in 25% $H_2SO_4$ (Jones' reagent).[53] Compound **11** containing dithiolene moiety was isolated from the reaction of compound **10** with 1,3-propanedithiol in presence of NaH. However, our attempt to apply this reaction to the pterin-substituted acetylene **6** (Scheme 3) resulted in obtaining the compounds **12** and **13** [hydroxy group protected by *tert*-butyldimethylsilyl (TBDMS)].

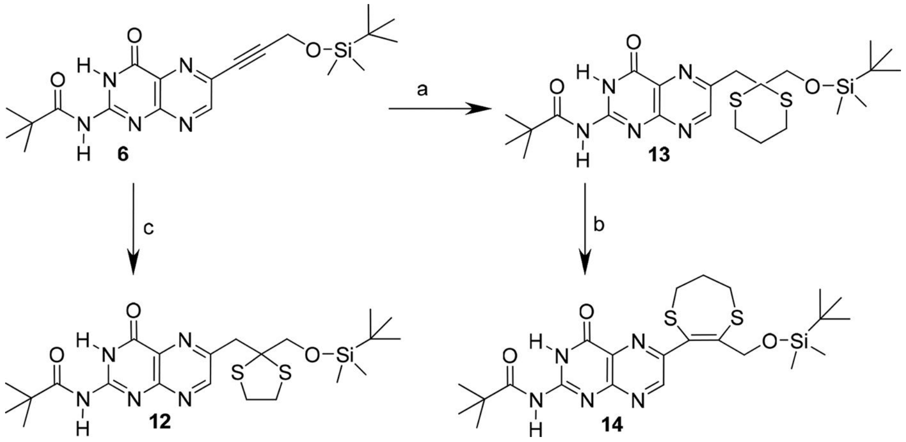
## Reagents and condition

(a) 1,3-Propanedithiol, NaH, rt., 3 h., 82%; (b) NBS, $CCl_4$, rt., 8 h., 45%; (c) 1,2-ethanedithiol, NaH, rt., 3 h., 78%.

When the compound **13** is subjected to the reaction with NBS,[54] the desired dithiolene compound **14** containing 1,2-ene-dithiol moiety was obtained in a good yield. A mechanism for the formation of *N*-pivaloylpterin dithiolene is suggested in Figure 3.



Scheme 2. Synthesis of quinoxaline thioketal **9** and dithiolene **11**.



**Scheme 3.** Synthesis of pterin thioketals **12, 13** and dithiolene **14**.

## *Reagents and condition*

(a) 1,2-ethanedithiol, NaH, dry THF, rt., 2 h., 76%; (b) 1,3-Propanedithiol NaH, dry THF, rt., 2 h., 74%.

In continuation of our work, we have got the following interesting observation when the hydroxy group adjacent to the alkyne moiety attached with pterin is protected with a bulky silyl group i.e *tert*-butyldiphenylsilyl (TBDPS) instead of TBDMS group. The first direct one step convenient and efficient synthesis of pterin dithiolenes **15** and **16** was achieved from alkynylpterin **7** and 1,2-ethanedithiol or 1,3-propanedithiol respectively as shown in Scheme 4. Also compounds **17** and **18** were isolated from alkynylpterin **8** and 1,2-ethanedithiol or 1,3-propanedithiol respectively as shown in Scheme 5. Probable mechanism

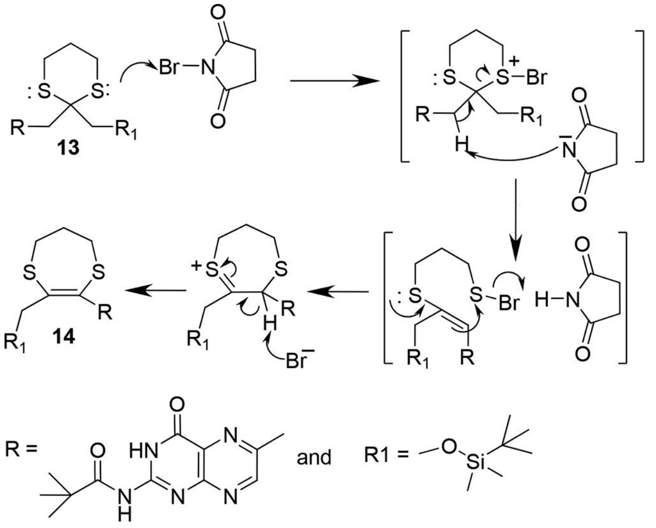
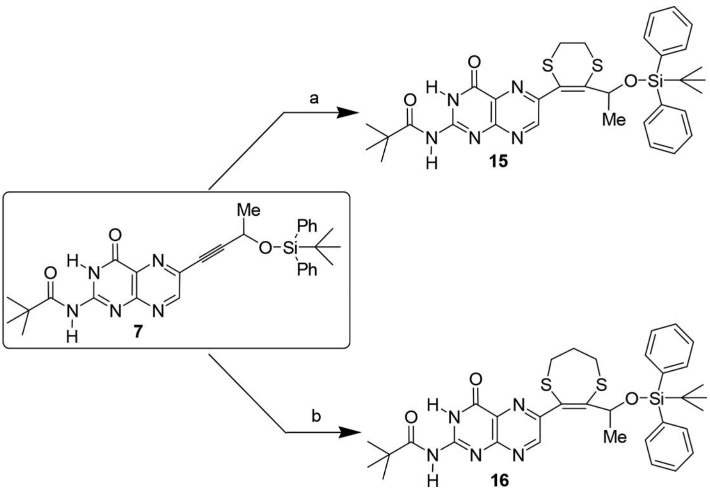


**Figure 3.** Plausible mechanism for the formation of pterin dithiolene **14** by *N*-bromo succnimide (NBS).



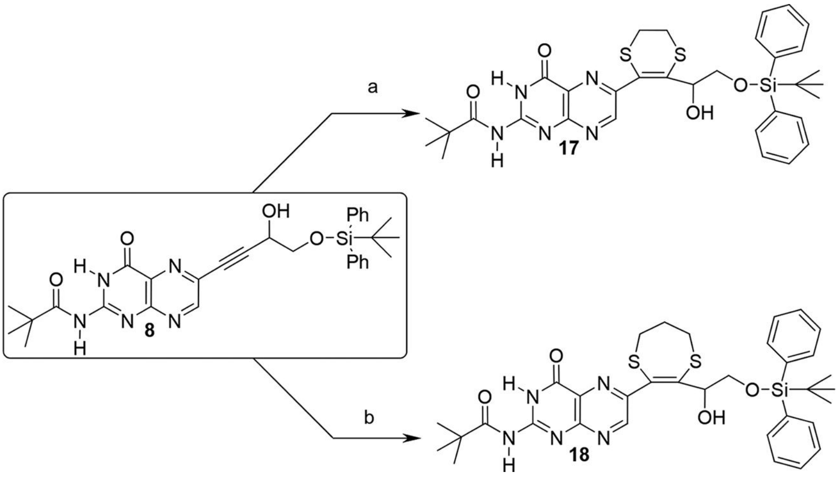
Scheme 4. New one step synthesis of pterin dithiolenes **15** and **16**.

for the formation of **12** from **6** has been proposed[51(d)] as in Figure 4 but different mode of reaction in case of formation of **15** from **7** is probably due to steric factor surrounding the reaction site.

## *Reagents and condition*

(a) 1,2-ethanedithiol, NaH, dry THF, rt., 3 h., 74%; (b) 1,3-Propanedithiol, NaH, dry THF, rt., 3 h., 72%.

Further possible ways of cleaving or exchanging the carbon atoms in the dithiine or dithiepine system by a molybdenum-containing moiety or direct annulation of dioxomolydenum dithiolene to alkynepterin **8** leading to the total synthesis of the Moco are being investigated.



Scheme 5. New one step synthesis of pterin dithiolenes **17** and **18**.

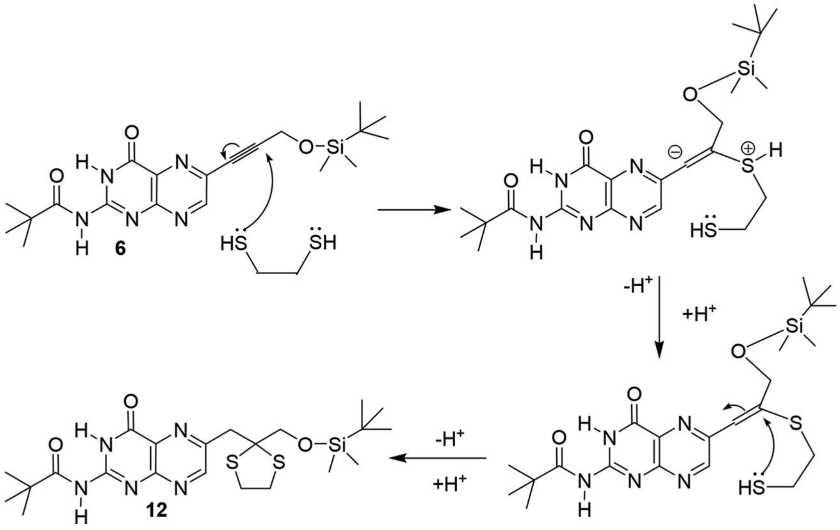


**Figure 4.** Plausible mechanism for formation of **12**.

This unique addition and cyclisation is successful only with pterin system (Figure 5) as this cyclisation is found to be unsuccessful with quinoxaline system. Thus such electron withdrawing character of pterin and oxidative more facile aromatization of partially

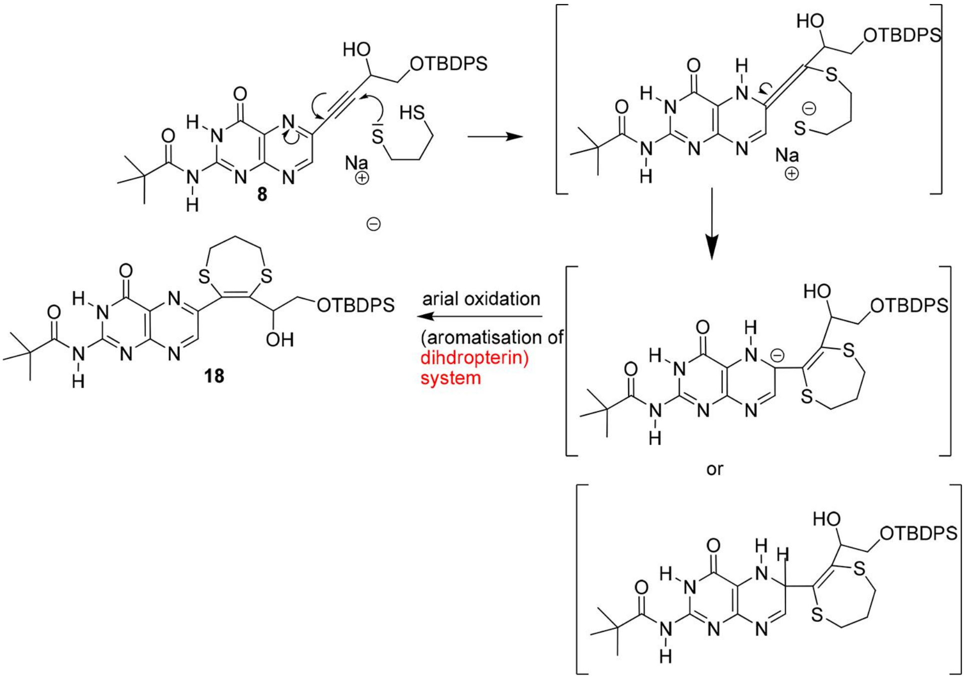


**Figure 5.** Plausible mechanism for the formation of dithiolene-mediated pterin **18** from alkyne substituted pterin **8**.

reduced pterin to pterin may be the possible driving force behind the favorable dithiolene formation from adjacent acetylene moiety of pterin system only.

## Conclusion

In summary, we report here the synthesis of a new series of six and seven membered pterindithiolenes for the development of molybdenum dithiolate and Mo-pterin complexes. The dithiolene synthesis has evolved from a simple novel method of efficient direct formation of C-S bond at the suitable acetylene moiety attached with pterin ring system. Further possible ways of direct annulation of dioxomolybdenum dithiolene to alkynepterin **8** leading to the total synthesis of the Moco are being investigated.

## Experimental section

### General experimental procedure for thioketals and dithiolenes

To a solution of 1,2 ethanedithiol/1,3-propanedithiol in dry tetrahydrofuran, sodium hydride was added and stirred under nitrogen atmosphere for one hour. The alkyne substituted pterin or quinoxaline in dry tetrahydrofuran was added dropwise to the reaction mixture under nitrogen atmosphere and stirred for 6 hours at room temperature. Tetrahydrofuran was removed under vacuum distillation and dichloromethane was added to the solid and finally washed with water. The organic layer was separated and dried over anhydrous sodium sulphate. Then the solvent was removed and the residue was purified by column chromatography.

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# Dual-mode chemosensor for the fluorescence detection of zinc and hypochlorite on a fluorescein backbone and its cell-imaging applications†

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and Nandan Bhattacharyya[d]

Fluorescein coupled with 3-(aminomethyl)-4,6-dimethylpyridin-2(1*H*)-one (**FAD**) was synthesized for the selective recognition of $Zn^{2+}$ over other interfering metal ions in acetonitrile/aqueous buffer (1 : 1). Interestingly, there was a significant fluorescence enhancement of **FAD** in association with $Zn^{2+}$ at 426 nm by strong chelation-induced fluorescence enhancement (CHEF) without interrupting the cyclic spirolactam ring. A binding stoichiometric ratio of 1 : 2 for the ligand **FAD** with metal $Zn^{2+}$ was proven by a Jobs plot. However, the cyclic spirolactam ring was opened by hypochlorite ($OCl^-$) as well as oxidative cleavage of the imine bond, which resulted in the emission enhancement of the wavelength at 520 nm. The binding constant and detection limit of **FAD** towards $Zn^{2+}$ were determined to be $1 \times 10^4$ $M^{-1}$ and 1.79 μM, respectively, and the detection limit for $OCl^-$ was determined as 2.24 μM. We introduced here a dual-mode chemosensor **FAD** having both the reactive functionalities for the simultaneous detection of $Zn^{2+}$ and $OCl^-$ by employing a metal coordination ($Zn^{2+}$) and analytes ($OCl^-$) induced chemodosimetric approach, respectively. Furthermore, for the practical application, we studied the fluorescence imaging inside HeLa cells by using **FAD**, which demonstrated it can be very useful as a selective and sensitive fluorescent probe for zinc.

## Introduction

Fluorescent probes can be potentially useful for the detection of biologically important analytes by significant changes of the absorption as well as the emission signal intensities. To enrich the understanding of different biological phenomena, the design and synthesis of the new fluorescent backbones and the corresponding approaches for the selective detection of various analytes through optical sensing are key areas of interest in biology. In this respect, the most common approach is to integrate a fluorescence molecule with an appropriate channel for signal transduction with an additional functionality having high selectivity and sensitivity towards the desired analyte. Therefore, fluorometric detection is attracting growing interest for trace chemical selective detection due to its simplicity as well as high sensitivity. In particular, "*turn-on and turn-off*"-type sensors have been attracting growing interest recently for their particular advantages over other reported chemosensors due to their unambiguous assignment in detection processes.[1] In this respect fluorescein dyes are very important as bio-labelling reagents. Moreover, they have excellent photophysical properties, such as long wavelength absorption and emission maxima with a high fluorescence quantum yield and light stability. In addition, among the common fluorescent probes, fluorescein derivatives are non-toxic and can be readily prepared.[2–4] Most of the fluorescein-based chemosensors are non-fluorescent due to the closed spirolactam structure, but analytes can induce the opening of the spirolactam ring, resulting in the appearance of strong green fluorescence, which is referred to as a 'turn-on' fluorescent chemosensor.[5] However, the beauty of our present chemosensor, fluorescein coupled with 3-(aminomethyl)-4,6-dimethylpyridin-2(1*H*)-one (**FAD**), revealed a quite different mode of sensing with the simultaneous detection of the metal-ion zinc and anionic reactive oxygen species (ROS), like hypochlorite (HOCl). Among the most reactive oxygen (ROS) and reactive nitrogen species (RNS),[6] hypochlorite anion ($OCl^-$) and its protonated form hypochlorous acid (HOCl) are the biologically most important reactive oxygen species (ROS).[7] As an oxidant $OCl^-$ is very much reactive and sensitive to chemosensors having various oxidizable auxochromic groups, like *p*-methoxyphenol, thiol, dibenzoylhydrazine, hydroxamic acid, oxime derivatives, and imine bonds.[8]

Among the metal cations, $Zn^{2+}$, the second-most abundant transition-metal ion in the human body, is a particularly

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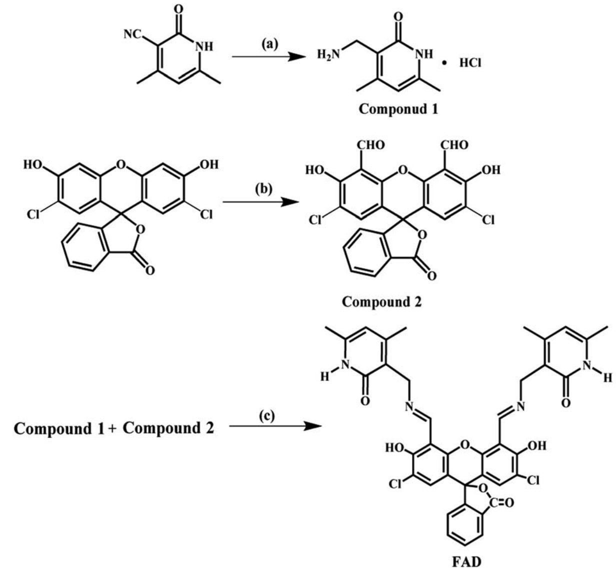


Scheme 1 . Synthesis of **FAD**. Reagents and conditions: (a) aqueous $NH_3$, $H_2$, RANEY® Ni, in MeOH, rt., 5 h, (b) TFA/AcOH, urotropine, 90 °C, 24 h and (c) reflux in ethanol, 24 h.

significant metal ion since it plays a role in a range of physiological and pathological processes, such as epilepsy, ischaemic stroke, Alzheimer's disease, and infantile diarrhoea, and is also a potent killer of neurons *via* oxidative stress.[9] On the other hand, zinc is an essential element for normal human growth as well as for the development of the body. Although, the structural chemistry of $Zn^{2+}$ is well understood, many questions related to zinc homeostasis and action remain unanswered. Thus, it is appealing to make zinc "visible" in tissues, even in living cells.[10] Therefore the development of various fluorescent chemosensors for the selective detection of $Zn^{2+}$ by *in vitro* and *in vivo* study has received great attention in recent years.[11,12] Though a number of excellent zinc sensors have been reported so far, the design of new sensors with better selectivity as well as sensitivity is still an active area of work.[13–19]

Herein, we developed a chemosensor **FAD** based on the fluoroquinolonic properties of the well-known fluorescein framework for the sensing of $Zn^{2+}$ and $OCl^-$ by a dual-mode pathway. Significantly the sensing of zinc by **FAD** is reported here in mixed aqueous solution through the fluorescence response with an unusual sensing manner in fluorescein. We devised a general methodology for preparing fluorescent sensors that is based on the fluorescein framework. **FAD** was synthesized by the reaction between fluorescein dialdehyde (compound **2**) and the amine (compound **1**) as shown in Scheme 1. The chemical structures of **FAD** and all the intermediates were established through spectroscopic studies, including $^1H$ NMR and mass (ESI) spectroscopy.

## Results and discussions

### UV-vis and fluorescence study

The sensing abilities of **FAD** ($c = 1 \times 10^{-5}$ M) in acetonitrile/aqueous HEPES buffered (1 : 1, pH 7.2) solution towards various metal ions ($c = 2 \times 10^{-4}$ M) were studied by means of the UV-vis as well as fluorescence spectra. Fig. 1 shows the absorbance changes of **FAD** upon the gradual addition of $Zn^{2+}$. The UV-vis spectrum of **FAD** showed the characteristic absorption band for the wavelength maximum at 400 nm, which upon the gradual addition of $Zn^{2+}$ was suppressed, whereas a new absorption peak at 500 nm was intensified, but no visible colour change was observed. Two well-defined isosbestic points appeared at 372 and 450 nm, respectively, in the presence of zinc ions, signifying the definite complexation between $Zn^{2+}$ and **FAD**, which indicated also the formation of a new charge–transfer complex with specific coordination numbers between the receptor **FAD** and the metal-ion $Zn^{2+}$ and this was also responsible for the generation of a significant fluorescence enhancement in the emission spectra.

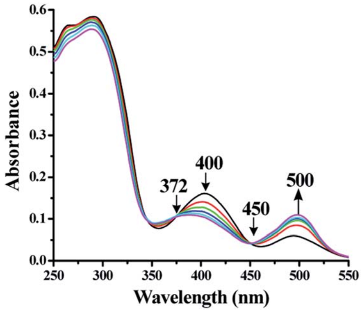


Fig. 1 UV-vis spectra of **FAD** ($c = 1 \times 10^{-5}$ M) in acetonitrile/aqueous HEPES buffered (1 : 1, pH 7.2) solution upon titration with $Zn^{2+}$ ($c = 2 \times 10^{-4}$ M).

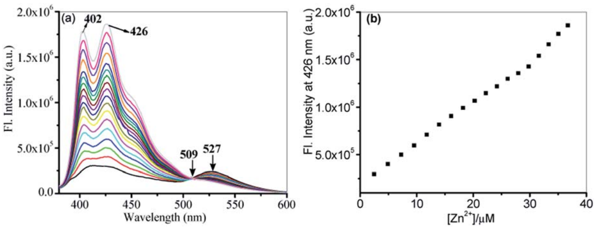


Fig. 2 (a) Fluorescence spectra of **FAD** ($c = 1 \times 10^{-5}$ M) in acetonitrile/aqueous HEPES buffered solution (1 : 1, pH 7.2) solution upon titration with $Zn^{2+}$ ($c = 2 \times 10^{-4}$ M). (b) Plot of the concentration of $Zn^{2+}$ *vs.* the fluorescence intensity changes of **FAD** at a wavelength of 426 nm.

For visualizing ions at the molecular level, fluorescent sensors are very important and useful tools. Such sensors create a perceptible luminescent signal upon selective binding with the desired analyte. Very careful modification on the molecular probes can also provide a way to study the biological relevance of any intracellular metal ions.[20] Therefore, the utility of **FAD** as a $Zn^{2+}$ sensor using its fluorescence characteristics was also studied in acetonitrile/aqueous HEPES buffered solution (1 : 1, pH 7.2) ($c = 1 \times 10^{-5}$ M) with various competing metal ions ($c = 2 \times 10^{-4}$ M).

As shown in Fig. 2a, upon excitation at 370 nm, the almost non-fluorescent **FAD** itself showed very weak emission signals around at 420 nm and 527 nm, which upon the gradual addition

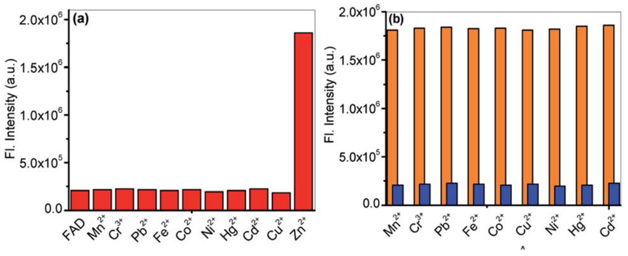


Fig. 3 (a) Bar diagram of the fluorescence response of the receptor **FAD** ($c = 1.0 \times 10^{-5}$ M) at 426 nm wavelength in acetonitrile/aqueous HEPES buffered solution (1 : 1, pH 7.2) solution upon titration with 5.0 equiv. of each of the different guest cations ($c = 2.0 \times 10^{-4}$ M). (b) Metal-ion selectivity profile of the sensor **FAD** (10 μM) with bar-scale representation: (blue bars) change of emission intensity of the sensor + 5.0 equiv. of different interfering metal ions ($M^{n+}$); (yellow bars) change of emission intensity of the sensor **FAD** + 5.0 equiv. of various interfering $M^{+n}$, followed by 5.0 equiv. $Zn^{2+}$ at 426 nm.

of $Zn^{2+}$ were suppressed along with increase in the emission intensities by 7-fold over the dual emission bands at wavelengths of 402 and 426 nm, respectively. The significant changes of the fluorescence intensity of **FAD** at 426 nm wavelength with the gradual addition of $Zn^{2+}$ is shown in Fig. 2b.

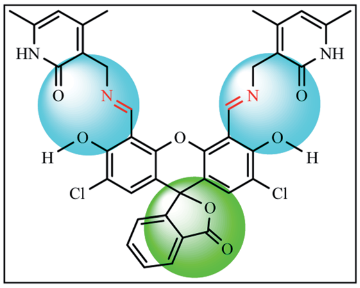
### Selectivity test and competition experiments

For the selectivity test of **FAD** with various interfering metal ions, fluorescence experiments were performed with the co-existence of different interfering metal ions. But no significant fluorescence response was observed in the presence of other interfering metal ions, including $Hg^{2+}$, $Ni^{2+}$, $Cr^{3+}$, $Cu^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Cd^{2+}$, and $Fe^{2+}$. Fig. 3a displays the change in the emission spectra of the receptor **FAD** in the presence of all the mentioned metal ions, but only strong fluorescence enhancement occurred in the presence of $Zn^{2+}$. The changes in fluorescence intensity of the receptor **FAD** at 426 nm for the various metal ions is shown by the various red bars. The longest length of the red bar indicated the strong fluorescence enhancement of **FAD** upon binding with $Zn^{2+}$ as compared to the other interfering metal ions, which showed smaller red bars length.

To further explore the selectivity of **FAD** for $Zn^{2+}$, the competition experiments were also carried out in the presence of $Zn^{2+}$ mixed with other interfering metal ions, including $Hg^{2+}$, $Ni^{2+}$, $Cr^{3+}$, $Cu^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Cd^{2+}$, and $Fe^{2+}$. As shown in Fig. 3b, the fluorescence enhancement of **FAD** upon binding with $Zn^{2+}$ was unperturbed (yellow bars) and the other interfering metal ions did not interfere with the sensing of $Zn^{2+}$ (blue bars). This indicated that the receptor **FAD** was highly sensitive for the selective detection of $Zn^{2+}$ in the presence of the other interfering metal ions.

### Dual-mode binding mode of FAD

Since the sensor **FAD** contains two modes of binding functionalities, we employed two different binding sites for sensing two different analytes utilizing two pathways as mentioned below:



Scheme 2 Schematic representation of the dual-mode binding of **FAD** with $Zn^{2+}$ (aqua colour region) by chelation and $OCl^{-}$ (green and aqua colour regions) by a chemodosimetric approach.

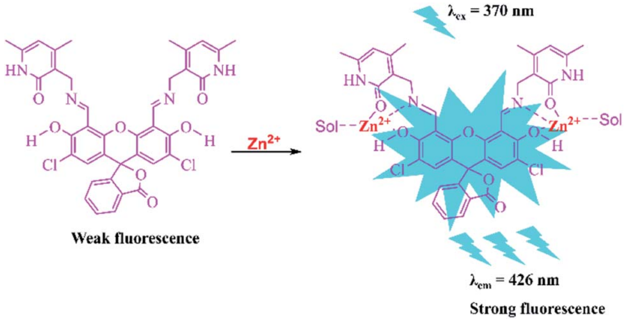
(i) The metal coordination inside the cavities (Scheme 2, aqua circle) constructed by fluorescein hydroxy, imine nitrogen, and the participation of the carbonyl group of the pyridine moieties.

(ii) An analyte-induced chemodosimetric approach by the opening of the cyclic spirolactam ring (green circle) as well as by oxidative cleavage of the "C=N" group of **FAD** (red coloured in Scheme 2).

Herein, we utilized this bimodal chemosensor for the sensing of metal ions or cations through pathway (i) and, on the contrary, the opening of the spirolactam ring as well as oxidative cleavage of "C=N" group of **FAD** by sensing various anions or reactive species by pathway (ii), as explained in detail below.

### Probable binding mode of FAD with $Zn^{2+}$ in the solution phase

To find out the plausible mechanism of the binding stoichiometry between $Zn^{2+}$ and **FAD**, Job plot analysis was carried out. The results obtained from the Job plots indicated the 1 : 2 stoichiometry for the complexation between **FAD** and $Zn^{2+}$, respectively (Fig. S1, ESI†). From the knowledge of the binding stoichiometry and spectral studies, the probable binding mode is proposed, as shown in Scheme 2. Moreover, there was no enhancement in the emission intensity at the near wavelength range at about 500–550 nm upon binding with $Zn^{2+}$, which indicated the existence of the cyclic spirolactam ring, while the cavities formed by fluorescein dialdehyde coupled with 3-(aminomethyl)-4,6-dimethylpyridin-2(1*H*)-one were responsible



Scheme 3 Probable binding mode of **FAD** with $Zn^{2+}$.

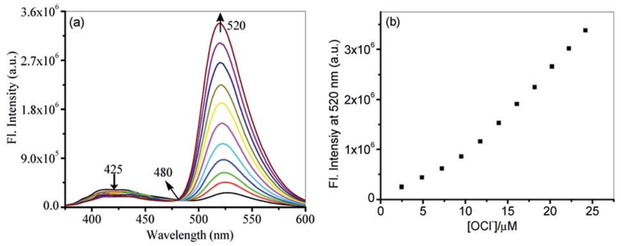


Fig. 4 (a) Fluorescence spectra of **FAD** ($c = 1 \times 10^{-5}$ M) in acetonitrile/aqueous HEPES buffered solution (1 : 1, pH 7.2) solution upon titration with $OCl^-$ ($c = 2 \times 10^{-4}$ M). (b) Concentration *vs.* Fl. intensity changes plot of **FAD** with $OCl^-$ at 426 nm wavelength.

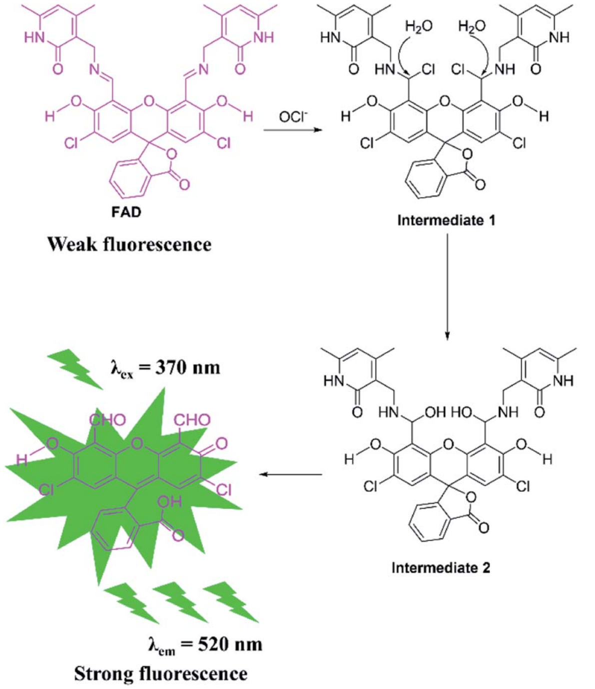
for binding with $Zn^{2+}$ (Scheme 3). The strong chelation by the coordination of $Zn^{2+}$ inside the cavities (aqua colour in Scheme 2) of **FAD** constructed by fluorescein hydroxy, imine nitrogen, and the participation of the carbonyl group of the pyridine moieties resulted in forming a semi-rigid cavity with four coordination sites (three from the ligand and one from the solvent), which was also well suited to fitting the target zinc metal ion and forming a **FAD**-$Zn^{2+}$ complex in mixed aqueous media.

Thus, $Zn^{2+}$ coordination leads to the chelation-induced fluorescence enhancement (CHEF) and strong ICT (intramolecular/intermolecular charge transfer) within the molecule, which causes the generation of high fluorescence upon metal binding (**FAD**-$Zn^{2+}$, Scheme 3). The complex formation of **FAD** with $Zn^{2+}$ was verified by the association constant value, which was as determined $1 \times 10^4$ $M^{-1}$ (Fig. S2, ESI†).[21] Moreover, the Job's plot, which exhibited a maximum at 0.3 M fraction of host, further indicated that only a 1 : 2 complex was formed between **FAD** and $Zn^{2+}$ respectively (Fig. S1, ESI†). From the fluorescence titration experiments, the detection limit of the receptor **FAD** for $Zn^{2+}$ was determined to be 1.79 μM, using the equation $DL = K \times Sb_1/S$, where $K = 3$, $Sb_1$ is the standard deviation of the blank solution, and $S$ is the slope of the calibration curve (Fig. S3, ESI†).[22]

### Probable binding mode of FAD with $OCl^-$ in the solution phase

To justify the binding mode of $Zn^{2+}$ with **FAD**, we performed a fluorescence study of **FAD** with $OCl^-$. Interestingly the hypochlorite anion ($OCl^-$), one of the reactive oxygen species (ROS) showed a very strong emission signal at 520 nm (Fig. 4a), and the emission intensity gradually increased by 13-fold upon the incremental concentration of $OCl^-$ into the **FAD** ($c = 1 \times 10^{-5}$ M) in acetonitrile/aqueous HEPES buffered solution (1 : 1, pH 7.2) (Fig. 4b). The appearance of the strong emission signal in the wavelength range near 500–550 nm indicated the rupture of the spirolactam ring of fluorescein by the gradual addition of $OCl^-$ throughout the process.

The probable mechanism for this can be explained by the chemodosimetric approach through the $OCl^-$-induced oxidative cleavage of the "C═N" group of **FAD**, which resulted in hydrolysis of the imine bond through intermediate **1** and intermediate **2** to produce fluorescein dialdehyde (**FAD**) (Scheme 4). Simultaneously, due to the basic character/oxidative properties of hypochlorite, the opening of the spirolactam ring was verified the appearance of an emission signal at 520 nm, which corresponded to the opened-structure fluorescein.[23] Opening of the spirolactam ring and the hydrolysis of the imine bonds resulted in the appearance of the strong fluorescence. From the fluorescence titration experiments, the detection limit of the receptor **FAD** for $OCl^-$ was determined to be 2.24 μM (Fig. S4, ESI†).



Scheme 4 Probable sensing mechanism of $OCl^-$ by the chemosensor FAD.

## Practical application

### Cell imaging

Owing to the favourable binding properties of **FAD** with $Zn^{2+}$ and intense emission in the visible region, it was thought that it could be exploited for practical bio-imaging, particularly for the sensitive detection of intracellular $Zn^{2+}$. In order to determine the membrane permeability of the **FAD** and its ability to specifically bind the $Zn^{2+}$ ions in living cells, human cervical cancer cells (HeLa) were taken for testing the fluorescence of **FAD** with $ZnCl_2$. HeLa cells were grown in a medium containing heat-inactivated FCS (10%; v/v), DMEM, streptomycin (100 U $mL^{-1}$), and penicillin (0.1 mg $mL^{-1}$) at 37 °C.

Confluent cells were trypsinized and seeded in 6-well plates at a density of $1 \times 10^5$ cells per $cm^3$. After 24 h cell seeding, the cells were treated with **FAD** ($c = 1 \times 10^{-5}$ M) and different concentrations of $ZnCl_2$ ($2 \times 10^{-4}$ M, $3 \times 10^{-4}$ M, $4 \times 10^{-4}$ M) and **FAD** alone ($c = 1 \times 10^{-5}$ M). After 2 h, the cells were washed with phosphate buffer saline and fresh medium was added to

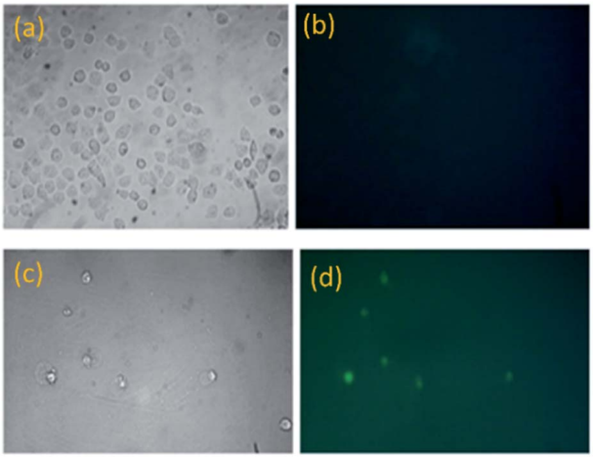


Fig. 5 HeLa cells showed no fluorescence in the (a) bright field image, (b) dark field image. HeLa cells showed intense green colour in the presence of both **FAD** ($c = 1 \times 10^{-5}$ M) and $ZnCl_2$ ($c = 2 \times 10^{-4}$ M) in the (c) bright field image, (d) dark field image. The photographs were taken using a DeWinter Victory-FL fluorescence inverted microscope using DeWinter Biowizard software v 4.4 using 40X.

each well and pictures were taken with a fluorescent microscope, as shown in Fig. 5. In the absence of $Zn^{2+}$, the cells exhibited no fluorescence in the presence of the ligand **FAD** only (Fig. 5a and b), but the addition of $Zn^{2+}$ to the ligand-incubated cells resulted in the appearance of significant green fluorescence inside the cells, corresponding to the same fluorescence colour that appeared in the *in vitro* study by fluorescence spectroscopy (Fig. 5c and d).

## Experimental

### General

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. Melting points were determined on a hot-plate melting point apparatus with open-mouth capillary and were uncorrected. $^1$H-NMR spectra were recorded on a Brucker 500 MHz instrument. For the NMR spectra, DMSO was used as a solvent with TMS as an internal standard. Chemical shifts are expressed in δ units and $^1$H–$^1$H coupling constants in Hz. UV-vis titration experiments were performed on a JASCO UV-V530 spectrophotometer and fluorescence experiments were done using a PerkinElmer LS 55 fluorescence spectrophotometer with a fluorescence cell of 10 mm path.

### General methods for the Uv-vis and fluorescence titrations

For the Uv-vis and fluorescence titrations, stock solution of the sensor (**FAD**) were made in acetonitrile/aqueous HEPES buffered solution (1 : 1, pH 7.2) solution ($c = 1 \times 10^{-5}$ M). Solutions of the guest cations were prepared ($2 \times 10^{-4}$ mL$^{-1}$) in water. The original volume of the sensor solution was 2 mL. Solutions of the sensor of various concentrations and increasing concentrations of cations were prepared separately. The spectra of these solutions were recorded by means of UV-vis methods.

### Method for the preparation of the target ligand FAD

**Synthesis of 3-(aminomethyl)-4,6-dimethylpyridin-2(1*H*)-one (compound 1).**[24] 3-Cyano-2,4-dimethyl-2-hydroxypyridine (0.3 g, 2.0 mmol) was dissolved in MeOH (5 mL), to which a catalytic amount of RANEY® Ni and aqueous $NH_3$ (0.3 mL) were added and the reaction mixture was stirred under hydrogen pressure (bladder pressure) for 5 h. After completion of the reaction, the catalyst was filtered off and the filtrate was concentrated under reduced pressure. The residue was thoroughly dried to provide the desired product (0.3 g, quantitative yield).

Compound **1**: $^1$H NMR (500 MHz, $d_6$-DMSO): δ 2.18 (s, 3H), 2.20 (s, 3H), 3.81 (s, 2H), 6.10 (s, 1H), 8.00 (br s, 2H), 11.81 (br s, 1H).

**Synthesis of 2′,7′-dichlorofluorescein (DCF) dialdehyde (compound 2):.**[25] DCF (3.15 g, 7.87 mmol) and urotropine (5.35 g, 37.55 mmol) were dissolved in trifluoroacetic acid (13 mL). The mixture was stirred and heated to 90 °C for 24 h and the mixture became sticky. Acetic acid solution (10 M in water, 100 mL) was added, and then the mixture was stirred overnight at 25 °C. The solid precipitate was filtered on a Büchner funnel and then washed three times with water. After drying under an infrared lamp under vacuum, crude DCF dialdehyde was obtained as a red solid (4 g).

Compound **2**: $^1$H NMR (500 MHz, $d_6$-DMSO): δ 12.45 (brs, 2H), 10.68 (s, 2H), 8.18 (d, $J = 8.00$ Hz, 1H), 7.82 (m, 3H), 7.41 (s, 1H), 7.22 (s, 1H).

**Synthesis of the target ligand FAD.** DCF dialdehyde (0.500 g, 1.09 mmol) and compound **1** (332.87 g, 2.18 mmol) were dissolved in EtOH (50 mL). The reaction mixture was stirred under reflux conditions for 24 h in a nitrogen atmosphere. The reaction mixture was cooled to 25 °C and the precipitate was filtered with a Büchner funnel. The crude product was washed with EtOH (20 mL × 3). After drying under vacuum, **FAD** was obtained as a solid (0.50 g, 0.68 mmol, 63% yield).

**FAD**: $^1$H NMR (500 MHz, $d_6$-DMSO): 13.90 (br s, 2H), 11.83 (br s, 2H), 9.52 (s, 2H), 7.97 (d, $J = 7.5$ Hz, 1H), 7.81–7.70 (m, 3H), 7.31 (d, $J = 8.0$ Hz, 1H), 6.61 (s, 1H), 6.03 (s, 1H), 5.98 (s, 1H), 3.78 (s, 4H), 2.30 (s, 3H), 2.20 (s, 9H). MS (ESI): *m/z* (%): 724 ($M^+$).

## Conclusion

We developed a fluorescein-based probe **FAD** for the selective detection of $Zn^{2+}$ as compared to other interfering metal ions in an acetonitrile/aqueous HEPES buffered solution (1 : 1, pH 7.2). The significant large fluorescence enhancement was due to the CHEF effect by the metal coordination to the hydroxy group of fluorescein and the functionalities connected to the pyridine moiety of the Schiff base functionalities of the ligand **FAD** without opening of the cyclic spirolactam ring. The complex formation of **FAD** with $Zn^{2+}$ having the stoichiometric ratio 1 : 2 was observed by Job plot. On the other hand, hypochlorite-induced oxidative cleavage resulted in the formation of fluorescein dialdehyde as well as spirolactam ring rupture, which led to the emission enhancement at 520 nm wavelength. Complex formation with a 1 : 2 stoichiometry of **FAD** with $Zn^{2+}$

was observed with an association constant of $1 \times 10^4$ M$^{-1}$. The sensitivity of **FAD** towards Zn$^{2+}$ and OCl$^-$ was determined by the lower detection limits of 1.79 μM and 2.24 μM, respectively. Thus, we presented here a dual-mode chemosensor **FAD** for the simultaneous detection of Zn$^{2+}$ and OCl$^-$ by employing metal coordination and analyte-induced chemodosimetric approach, respectively. Furthermore, for practical application, we studied fluorescence imaging inside HeLa cell by using **FAD** with Zn$^{2+}$, which demonstrated it can be very useful as a selective and sensitive fluorescent probe for zinc.

## Conflicts of interest

There are no conflicts to declare.

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# Computational Investigation on Lithium Fluoride for Efficient Hydrogen Storage System

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## Abstract

Lithium fluoride (LiF) serving as a template for an efficient hydrogen storage system has been expressed in this article. The structure optimization, stability, and reactivity of the derived LiF systems have been studied with density functional theory (DFT) based reactivity descriptors. The binding energy/$H_2$ gives support to the quasi-molecular type adsorption process. According to natural bond orbital (NBO) data analysis, the charge on the Li atom decreases gradually with each successive $H_2$ adsorption, and a charge transfer interaction occurs from $H_2$ molecules to the Li of the LiF. From atoms-in-molecule (AIM) analysis, molecular hydrogen interacts with building blocks through electrovalent-type interaction. The astonishing gravimetric wt% result (43.48 upon ten hydrogen adsorption in a single LiF) justifies this template to be a potential hydrogen storage material. The Gibbs free energy changes suggest a spontaneous hydrogen adsorption process at or below 54 K.

*Keywords:* Lithium fluoride; Density functional theory; Binding energy; Quasi-molecular adsorption; Gravimetric wt%.
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## 1. Introduction

Energy and climate change are the most imperative issues in the present time throughout the world. Energy consumption is increasing day by day. Within a few decades, the demand for carbon-based fossil fuels will likely outpace its rate of production. It is seen that three times of mass of gasoline is required to supply the same energy as compared to hydrogen. In addition, the emission of $CO_2$ during the combustion of fossil fuels also can't be overlooked. In a combustion reaction of hydrocarbons, the energy contribution of hydrogen per gram is more comparable to carbon. To reduce the dependency on carbon-based fossil fuels, the limelight comes to hydrogen, which might be a promising clean alternative energy carrier because of its higher energy density proficiency and sustainable environment-friendly combustible nature.[1-5] However, one of the major challenges in this context is the storage of hydrogen. On a large volumetric scale, hydrogen being gas at standard temperature and pressure is necessary to meet the same energy as provided by gasoline being liquid under the same condition.[6] To deal with this low volumetric density problem, the designing of solid-state hydrogen storage materials has drawn the keen interest of researchers.[7,8] The density of hydrogen storage becomes a key issue for its portable applications. The density of hydrogen at atmospheric pressure and temperature is very low (1/14 of the air density) and thus the hydrogen storage density of the system is a key factor for hydrogen energy applications.[9,10] Presently, for the mobile applications of hydrogen, two storage paths are established, *i.e.*, high-pressure gas storage and low-temperature liquid storage. The gas storage density, high-pressure tank, hydrogenation station, and safety, are the main challenges for a high-pressure hydrogen gas storage path.[11,12] Physisorption and chemisorption are the two storage routes for solid hydrogen storage materials and a series of materials have been theoretically predicted.[5] But high hydrogen storage capacity cannot be achieved by physisorption, although in this process, the desorption of hydrogen can occur under ambient conditions. Chemisorption is a simple way to store a large

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quantity of hydrogen. But since it's not a reversible process, chemisorption cannot satisfy the storage criteria.[13-17] It appears that for materials to possess promising storage capacity, the hydrogen adsorption process should be reversible and the concerned energy should lie in between that of physisorption and chemisorption (quasi-sorption).[18,19] Keeping in view all these things, we recently started to find out some suitable hydrogen storage materials, which can meet the target set up by the U.S. Department of Energy (DOE)[20] (6.0% in 2010, and 9.0% in 2015) with a high gravimetric wt%.[18,19] Due to the small size of lithium fluoride and greater charge density of Li, we choose this template LiF for storing hydrogen with satisfactory results. We communicate the results in this article.

## 2. Theory and Computational Details

The Gaussian 16w computer program has been used to optimize ground state geometries of all the studied systems by using numerous functionals, including B3LYP, CAM-B3LYP, *ω*B97X-D, and two distinct basis sets, LanL2DZ and 6-311+G(d,p) to get the ground state energy minima of the structures.[19,21-23] Here we have taken two basis sets to know whether there has been any significant change in reactivity parameter values. Frequency optimization is also performed in the same functional and basis set to ensure their location at the minimum of the potential energy surface. All the geometries have been optimized without any symmetry constraints and the default optimization criteria embedded in Gaussian16 software have been used.

The employment of CAM-B3LYP and *ω*B97X-D is largely to rectify the long-range interaction. All the optimized geometry along with their ground state energy and point groups are depicted in Fig. 1, Figs. S1, S2, S3, and S5. The cartesian coordinates of optimized geometries were listed in the data set. D1 of supporting information file. Hardness ($\eta$), electrophilicity ($\omega$), the average adsorption energy per hydrogen molecule ($E_{ads}/H_2$), the donor-acceptor (bonding–antibonding) charge-transfer interaction, the gravimetric wt%,

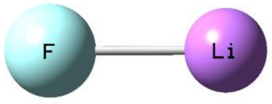
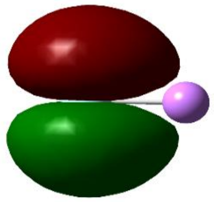
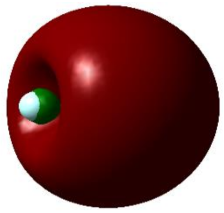
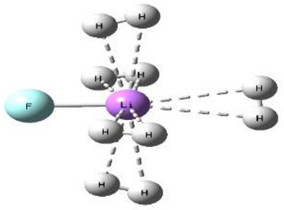
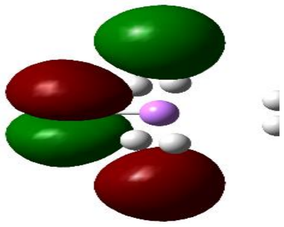
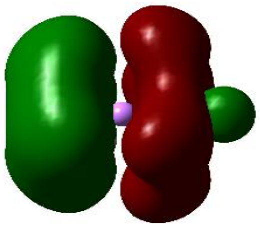
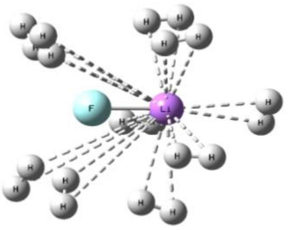
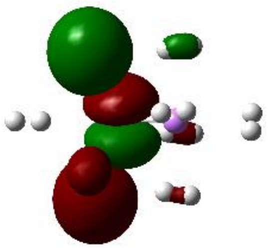
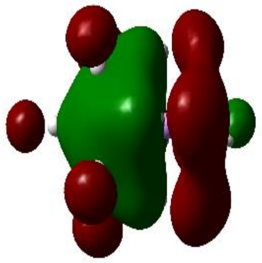
| Optimized structures | Highest occupied molecular orbital (HOMO) | lowest unoccupied molecular orbital (LUMO) | $\Delta E_{HOMO-LUMO}$ (eV) |
|---|---|---|---|
|  <br>**LiF**<br>**Point group: $C_1$**<br>**E = -2955.58 eV** | <br>**HOMO = -9.84 eV** | <br>**LUMO = - 0.21 eV** | - 9.63 eV |
| <br>**LiF@5H₂**<br>**Point group: $C_1$**<br>**E = -3084.17 eV** | <br>**HOMO = -9.81 eV** | <br>**LUMO = 0.26 eV** | - 10.07 eV |
| <br>**LiF@10H₂**<br>**Point group: $C_1$**<br>**E = -3244.57 eV** | <br>**HOMO = - 10.42 eV** | <br>**LUMO = 0.22 eV** | - 10.64 eV |

**Fig. 1** Optimized geometries, energy, point group, HOMO, LUMO, and $\Delta E_{HOMO-LUMO}$ (eV) of LiF, LiF@5$H_2$, and LiF@10$H_2$ systems at the ωB97X-D/6-311+ G (d, p) level of theory.

and the Gibbs free energy change of the LiF@n$H_2$ systems, as well as the adsorption ability (Er) of LiF, have been calculated by using standard techniques.[18,19,24-35] To understand the binding nature of this trapping mechanism, the Multiwfn package[36] was used to perform the atoms-in-molecules (AIM) analysis.[37] The Multiwfn software is an extremely powerful program for realizing electronic wavefunction analysis, which is a key ingredient of quantum chemistry. The details have been given in supporting information.

## 3. Results and discussion

### 3.1 LiF@n$H_2$: Stability, reactivity, and average adsorption energy per $H_2$ ($E_{ads}/H_2$)

The dipolar LiF molecule can adsorb up to 10 $H_2$ molecules (up to five around the Li center and after that around the whole LiF molecule). The optimized structures, energy, point group, frontier molecular orbitals such as HOMO/LUMO of the systems, and corresponding bandgap ($\Delta E_{HOMO-LUMO}$) have been given in Fig. 1 and Figs. S1, S2, and S3 (supporting information file). From Tables S1 and S2, it is evident that the hardness ($\eta$, eV) has gradually increased and electrophilicity ($\omega$, eV) has relatively decreased when molecular $H_2$ is adsorbed one after another on the LiF surface. This trend is found similar for all types of basis sets (B3LYP, CAM-B3LYP, and $\omega$B97X-D) used during the calculation. This has been perfectly manifested in Fig. S4. This is the indication of increasing stability and decreasing reactivity trends and respectively upon gradual $H_2$ adsorption. Again, the higher the bandgap ($\Delta E_{HOMO-LUMO}$) higher is the stability and the lower the reactivity,[38] which is clearly observed in Fig. 1 and detail given in Figs. S1, S2, and S3.

The average adsorption energy per molecule of hydrogen (Eads/$H_2$) of LiF@n$H_2$ systems (Fig. 2 and Table S3) is decreased with the increase of the number of adsorbed $H_2$ molecules around the Li center and whole LiF. The reason behind that with the increase of the number of adsorbed $H_2$ molecules around the Li center and whole LiF, the natural bond orbital (NBO) charges on the Li are decreased (Table 1 and Fig. S5). As a result, the dipole-induced dipole interaction decreases, which directly influences the lowering of average adsorption energy per hydrogen molecule (Eads/$H_2$). But moving from eight $H_2$ to nine and ten, the NBO charges on the Li center remain unchanged, this may be attributed to the lowering of dipole-induced dipole interaction due to the movement of adsorbed molecular hydrogen towards the fluorine (F) center. Now, another important parameter, namely adsorption ability ($E_r$), is the indication of how many adsorbed $H_2$ molecules will be considered to be calculated (Table 1). The result reflects that up to ten adsorbed $H_2$, its values are decreased; after that, its value is negligible. Thus, we have considered LiF can adsorb a maximum of ten molecular hydrogens. Next, the gravimetric wt% of all $H_2$ adsorbed systems has been recorded (Table 1). This is an excellent result when we compare it with the reference value of the U.S. D.O.E. standard value[20] as well as other reported systems[18,19] reported in Table S7.

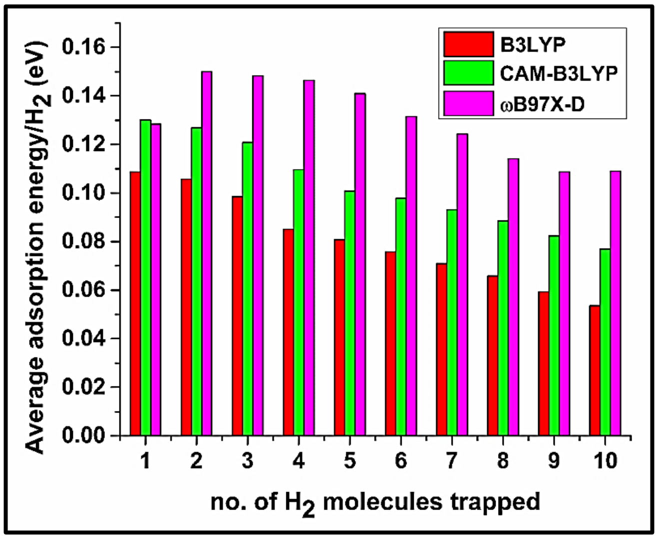


**Fig. 2** Plot of average adsorption energy/$H_2$ [eV] *vs* no. of $H_2$ molecules trapped of LiF@n$H_2$ systems at the B3LYP, CAM-B3LYP, and $\omega$B97X-D/6-311+ G(d,p) level of theory.

**Table 1.** NBO charges of LiF@n$H_2$ systems at CAM-B3LYP/6-311+G(d,p) level of theory, adsorption ability ($E_r$) of LiF@n$H_2$ systems at the B3LYP and CAM-B3LYP/6-311+G(d,p) level of theory and Gravimetric wt% of LiF@n$H_2$ systems.

| System | NBO charges | Adsorption ability ($E_r$) | | Gravimetric wt% |
|---|---|---|---|---|
| | | B3LYP | CAM-B3LYP | |
| LiF@$H_2$ | 0.96 | 0.109 | 0.130 | 7.14 |
| LiF@2$H_2$ | 0.95 | 0.103 | 0.124 | 13.33 |
| LiF@3$H_2$ | 0.93 | 0.084 | 0.109 | 18.75 |
| LiF@4$H_2$ | 0.91 | 0.045 | 0.076 | 23.53 |
| LiF@5$H_2$ | 0.89 | 0.064 | 0.065 | 27.78 |
| LiF@6$H_2$ | 0.88 | 0.051 | 0.083 | 31.58 |
| LiF@7$H_2$ | 0.88 | 0.042 | 0.065 | 35.00 |
| LiF@8$H_2$ | 0.88 | 0.029 | 0.056 | 38.10 |
| LiF@9$H_2$ | 0.89 | 0.008 | 0.033 | 40.91 |
| LiF@10$H_2$ | 0.89 | 0.001 | 0.028 | 43.48 |

### 3.1.1 Bonding nature

The delocalization correction energy ($\Delta E_{CT}$) and it's average ($\Delta E_{CT}^{av}$) values have been expressed through Fig. S6 (the detailed results in Table S4) indicating that a charge transfer interaction happened from the bonding orbital (BD) of the trapped $H_2$ molecules to the anti-bonding lone pair orbital (LP*) of $Li^+$ ions. One interesting observation here is that up to five adsorbed $H_2$, the ($\Delta E_{CT}^{av}$) values increase; after that, upon adsorption of $6H_2$ onwards, the trend decreases. This may be due to the load of the adsorbed hydrogen shift towards the F center of the LiF molecule. We used topological analysis at the bond critical point (BCP) to find the bonding nature controlling parameters like electron density [$\rho(r_c)$], Laplacian of electron density [$\nabla^2\rho(r_c)$], local electron energy density [$H(r_c)$], kinetic energy density [$G(r_c)$], and potential energy density [$v(r_c)$] of the LiF@$H_2$. Using the multi-win package,[36] we developed three figures (Fig. 3 and Figs. S7 and S8) to show the bonding behavior of LiF@$H_2$. The top and lower sections of Fig. 3 demonstrate the variations in the electron density. We can see that there is no electron density between the Li center and the adsorbed $H_2$ molecule. This supports the ionic bonding between the Li center and the adsorbed molecular hydrogen. In Fig. S7 the areas of charge depletion (green solid lines) and charge concentration (blue dotted lines) are depicted. The solid brown lines represent the bond paths, while the solid bold blue lines represent the zero-flux molecular plane surfaces.[39] The light blue spheres indicate the bond critical points (BCPs), where the bond path and zero-flux surfaces intersect. No electron density between Li and the molecular hydrogen suggests ionic bonding. Fig. S8 shows the electron localization function (ELF) of the systems. There are no localized electrons between Li and the adsorbed molecular hydrogen in this image. To determine the bonding type, $\nabla^2\rho(r_c)$, $H(r_c)$, and [$-G(r_c)/V(r_c)$] values have been calculated at the BCP [Table S5]. As the values of both $\nabla^2\rho(r_c)$ and $H(r_c)$ are positive (0.04 and 0.002) and the ratio of $-G(r_c)$ to $V(r_c)$ is larger than 1, we may assume that FLi···$H_2$ interactions are non-covalent.[40-42]

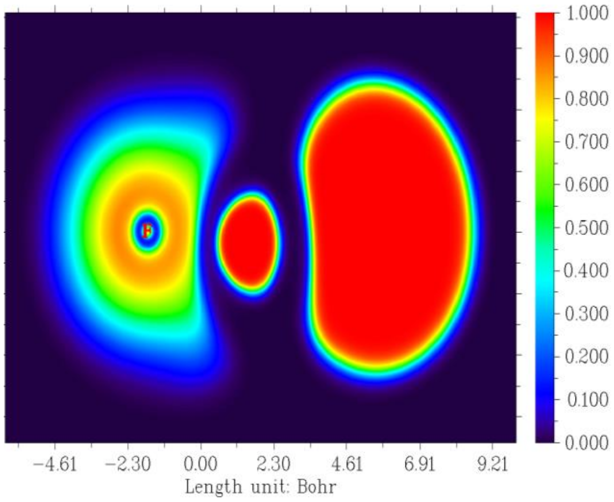


**Fig. 3** The plot of the ELF of the LiF@$H_2$ systems generated at the ωB97X-D/6-311+G(d,p) level of theory.

### 3.1.2 Effect of temperature on hydrogen adsorption

The Gibbs free energy change analysis has been carried out (Fig. 4 and Table S6) to make an idea about the spontaneous $H_2$ adsorption temperature of LiF. Results reveal that at 54 K or below this temperature, this adsorption process will be spontaneous.

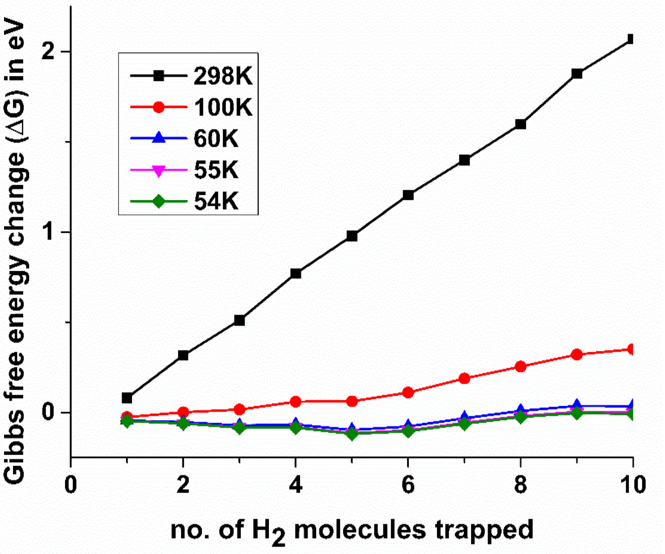


**Fig. 4** Plot of Gibb's free energy change [eV] *vs* no. of $H_2$ molecules trapped of LiF@n$H_2$ systems at the ωB97X-D/6-311+G(d,p) level of theory.

## 4. Conclusion

The LiF molecule has been identified as a promising hydrogen storage material since the average adsorption energy per $H_2$ molecule supports a quasi-molecular adsorption process. According to the NBO analysis, the charge on the Li atom progressively drops with the gradual increase of $H_2$ adsorptions, indicating that a charge transfer interaction occurs between the bonding orbitals of $H_2$ molecules and the antibonding orbitals of Li. A single LiF molecule can adsorb up to 10 $H_2$ (LiF@10$H_2$) with a high gravimetric wt% value (43.48) which is found to be a much better system than our previously reported systems (Table S7). The amazing results demonstrate the LiF molecule as a promising hydrogen storage material w.r.t U.S.D.O.E. standards.[20] According to the atoms in molecule (AIM) analysis, molecular hydrogen interacts with the building units in electrovalent interactions. At or below 54 K, the changes in Gibbs free energy indicate that the hydrogen adsorption process is spontaneous. The findings are very encouraging and exciting for synthetic chemists and technologists in terms of the possibility of synthesizing this material as a potential hydrogen storage option in the pursuit of green fuel storage. Based on the findings reported in this article we are trying to develop a study on LiF clusters, a molecule-to-material approach that may help to design a new type of gas storage device by using the material which will help the real laboratory to land application.

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## Conflict of interest

There are no conflicts to declare.

## Supporting information

Applicable.

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# Hydrogen Storage on Lithium Chloride / Lithium Bromide Surface at Cryogenic Temperature

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## Abstract

This article has expressed that Lithium chloride (LiCl) and Lithium bromide (LiBr) are good templates for low-temperature hydrogen storage. The structure and chemical reactivity of the derived templates were studied based on density functional theory (DFT). The adsorption process can be found in nature as quasisorption. The molecular hydrogen interacts with building blocks (with the $Li^+$ center) through electrovalent interaction, and a single LiCl/LiBr molecule can absorb 10 $H_2$ molecules with a high gravimetric weight percentage (32.00 for LiCl and 18.71 for LiBr), which is turn out to be promising systems according to the standard. The Gibbs free energy changes suggest a spontaneous hydrogen adsorption process at cryogenic temperature.

*Keywords:* Lithium chloride; Lithium bromide; Hydrogen storage; DFT; Binding Energy; Quasisorption, Gravimetric wt%.
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Article type: Research article

## 1. Introduction

As the transition to renewable and intermittent energy sources such as solar and wind power continues, it is becoming clear that these sources are seasonal and insufficient to meet future energy needs adequately.[1] Due to the shrinking reserves of conventional fossil fuels and their high $CO_2$ emissions, several industries feel compelled to reduce their dependence on fossil fuels.[2-4] Hydrogen is a promising candidate in this regard.

Hydrogen has the potential to play a critical role in our society, from transportation to manufacturing to power generation for household appliances. It is a completely pollution-free source of energy, with water as the end result in most circumstances. However, experts have been concerned about hydrogen storage for a long time. At room temperature and atmospheric pressure, the density of hydrogen gas is as low as 0.08988 g/L,[5] making its storage difficult and expensive. As a result, the only task at hand is to increase the storage density. Several strategies for storing hydrogen at higher densities have been proposed, but none has yet shown to be effective.[6] A given process always has a significant impact on the capital and operating costs of the storage facility.[7,8] Due to the different boundary conditions, there is room for more than one technological option for large-scale hydrogen storage.[9]

So far, there have essentially been three major hydrogen storage methods reported. The first is hydrogen gas storage at high pressure and room temperature (RT), the second is hydrogen storage in the liquid phase at low temperatures, and the third is hydrogen storage in the solid phase via adsorption at low or room temperature. As a result, each of these strategies has advantages and downsides.[10,11] There is always a massive infrastructure load involved with hydrogen storage at high pressure at room temperature; on the other hand, storing and transporting hydrogen in the liquid phase is extremely challenging. As a result, keeping it as an adsorbing material would be preferable. At room temperature, the adsorption percentage of solid hydrogen is very low (2-3%).

In our group, we are attempting to identify some suitable systems for a higher percentage of solid-phase hydrogen adsorption. The two possible hydrogen storage pathways in solid materials are physisorption and chemisorption, and a number of materials have been theoretically predicted to date.[12] High hydrogen storage cannot be achieved by physisorption, although desorption of the gas can occur under ambient conditions with this process. Conversely,

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chemisorption seems to be an effective and easy way to store a large amount of hydrogen. However, since it is not a reversible process, chemisorption cannot meet the storage criteria.[13-18] Therefore, we need to explore a new process with promising storage capacity, in which the hydrogen adsorption-desorption mechanism should be reversible, and the energy involved should be between that of physisorption and chemisorption (quasisorption).[19-22] Keeping all of these in mind, we recently revealed some promising hydrogen storage materials that can meet the target set by the United States Department of Energy (D.O.E.), 2015.[23] In a recent report, we described (using a computational approach) the surprising hydrogen storage efficacy of lithium fluoride (LiF),[24] which prompted us to compare it to Lithium chloride (LiCl) and Lithium bromide (LiBr) to determine which was the best. We believe that, the two new small systems would be promising hydrogen storage material that will make its future impact in the development of green fuel mission.

## 2. Theory and computational details

Gaussian 16w software[25] was used to optimize the ground state geometries of all studied systems using multiple functionals, including CAM-B3LYP, ωB97X-D, as well as two separate basis sets, LanL2DZ and 6-311+G (d, p) to obtain minimal energy structures in the ground state.[26] Here we have used two basis sets to justify whether there has been any notable change in the values of the reactivity parameters. The frequency calculation is also performed in the same function and basis set to ensure its position on the surface of minimum potential energy. The optimized geometry, ground-state energy, and point groups are shown in Fig. 1, Figs. S1, S2, S3, and S5 [S=supporting information].

The cartesian coordinates of some optimized geometries have been put in the data set D1 of supporting information (SI) file. Hardness ($\eta$), electronegativity ($\chi$), electrophilicity ($\omega$),[27-53] the average adsorption energy per hydrogen molecule ($E_{ads}/H_2$),[24] adsorption ability ($E_r$),[24] natural bond orbital (NBO) charge,[54] the donor-acceptor (bonding–antibonding) charge- transfer interaction,[55] the gravimetric wt%,[19-22] and the Gibbs free energy change of the LiX@nH$_2$ [X = Cl, Br and n = 1-10] systems[24] have been calculated by using the standard mathematical techniques within the conceptual DFT framework. The common equations we have used are stated below as per the reported literatures.

$$\text{Hardness } (\eta) = I - A \quad [31\text{-}34] \qquad (1)$$

$$\text{Electronegativity } (\chi) = \frac{I+A}{2} \quad [31\text{-}34] \qquad (2)$$

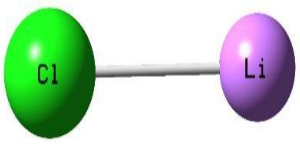
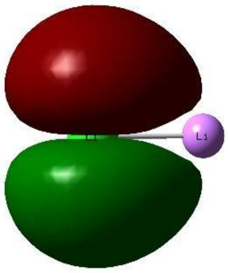
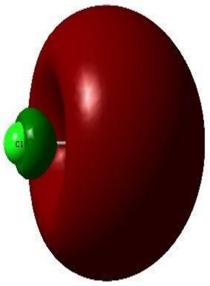
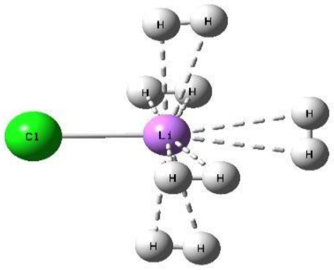
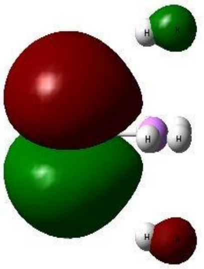
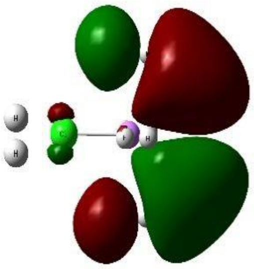
$$\text{and Electrophilicity } (\omega) = \frac{\chi^2}{2\eta} \quad [31\text{-}34] \qquad (3)$$

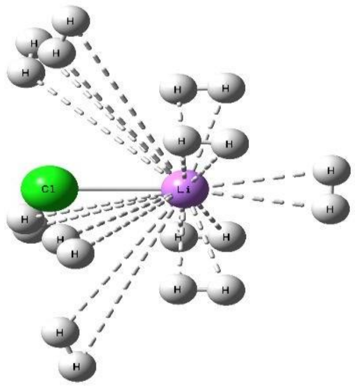
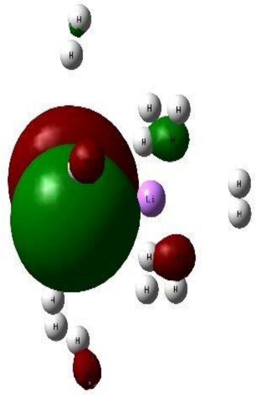
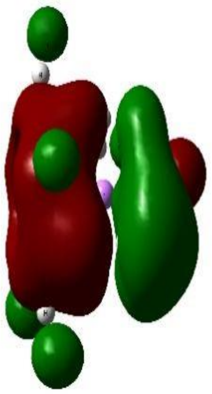
where I = ionization energy and A = electron affinity of the system. Average adsorption energy per hydrogen molecule was calculated following the equation:

$$[E_{ads}/H_2] = [(E_{LiX} + nE_{H2}) - E_{LiX@nH2}]/n \quad [24] \qquad (4)$$

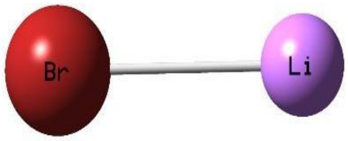
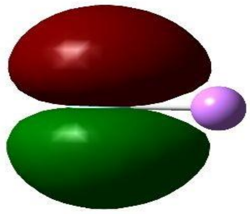
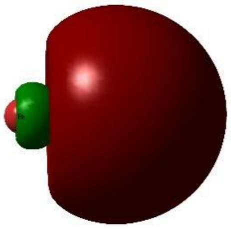
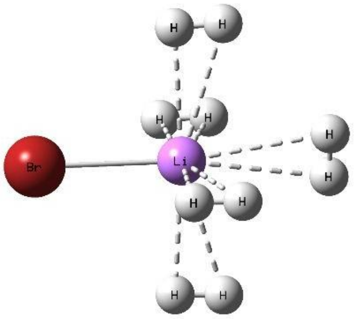
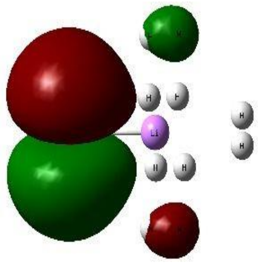
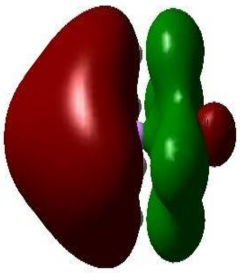
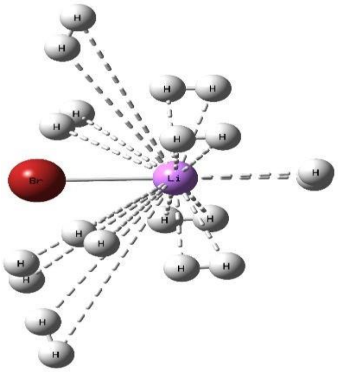
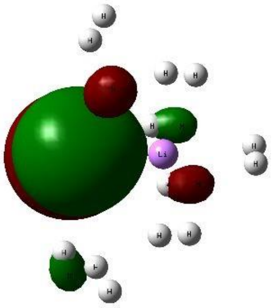
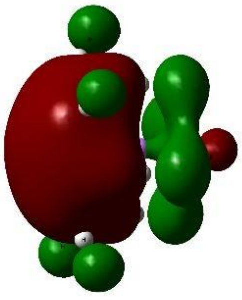
where $E_{LiX}$, $E_{H2}$, and $E_{LiX@nH2}$ are energies of the LiX [X = Cl, Br], H$_2$ molecule, and H$_2$ adsorbed LiX complexes, respectively, and n = no of adsorbed H$_2$ molecules (n = 1-10). Adsorption ability ($E_r$), Delocalization correction energy ($\Delta E_{CT}$), and Average delocalization correction energy ($\Delta E_{CT}^{av}$) were calculated using equation stated below.

$$\text{Adsorption ability } (E_r) = [E_{LiX@(n-1)H2} + E_{H2} - E_{LiX@nH2}] \quad [24] \qquad (5)$$

| Optimized structures | HOMO | LUMO | ΔEHOMO-LUMO (eV) |
|---|---|---|---|
| <br>LiCl Point group: C$_1$<br>E$_0$ = - 12729.83 eV | <br>E$_0$ = - 9.041 eV | <br>E$_0$ = - 0.377 eV | - 8.664 eV |
| <br>LiCl@5H$_2$ Point group: C$_1$ E$_0$ = - 12890.57 eV | <br>E$_0$ = -8.856 eV | <br>E$_0$ = 0.209 eV | - 9.065 eV |

| | | | |
|---|---|---|---|
| <br>$LiCl@10H_2$ Point group: $C_1$ $E_0$ = - 13050.85 eV | <br>$E_0$ = -9.133 eV | <br>$E_0$ = 0.204 eV | - 9.337 eV |

(a)

| Optimized structures | HOMO | LUMO | $\Delta E_{HOMO-LUMO}$ (eV) |
|---|---|---|---|
| <br>LiBr Point group: $C_1$<br>$E_0$ = -70253.81 eV | <br>$E_0$ = - 8.606 eV | <br>$E_0$ = - 0.437 eV | - 8.169 eV |
| <br>$LiBr@5H_2$ Point group: $C_1$ $E_0$ = - 70414.56 eV | <br>$E_0$ = - 8.409 eV | <br>$E_0$ = 0.191 eV | - 8.600 eV |
| <br>$LiBr@10H_2$ Point group: $C_1$ $E_0$ = - 70574.81 eV | <br>$E_0$ = - 8.635 eV | <br>$E_0$ = 0.198 eV | - 8.837 eV |

(b)

**Fig. 1** Optimized geometries, energy, point group, HOMO, LUMO, and $\Delta E_{HOMO-LUMO}$ (eV) of (a) LiCl, $LiCl@5H_2$, and $LiCl@10H_2$; (b) LiBr, $LiBr@5H_2$, and $LiBr@10H_2$ systems at the ωB97X-D /6-311+G(d,p) level of theory.

Delocalization correction energy,

$$(\Delta E_{CT}) = \Delta E_{ij} = q_i \frac{F\,(i,j)^2}{\varepsilon_j - \varepsilon_i} \text{ [55]} \tag{6}$$

Average delocalization correction energy,

$$(\Delta E_{CT}^{av}) = \frac{1}{n}\,\Delta E_{CT} \text{ [55]} \tag{7}$$

In equation (6), $q_i$ is the donor orbital occupancy, *F(i,j)* is the off-diagonal NBO Fock matrix element and $\varepsilon_i$ and $\varepsilon_j$ are diagonal elements (orbital energies) and 'n' is the number of adsorbed molecular hydrogen (n = 1-10). The density of adsorbed hydrogen was calculated by calculating the gravimetric wt% and Gibbs free energy was calculated as per general thermochemistry equation, which is stated below.[19-22]

$$\text{Gravimetric wt\%} = \frac{\text{Molecular weight of trapped } H_2}{\text{Molecular weight } LiX@nH_2 \text{ complex}} \times 100 \tag{8}$$

Gibbs free energy change,

$$(\Delta G_{LiX\,@nH2}) = G_{LiX\,@nH2} - G_{LiX} - nG_{H2} \text{ [19-22]} \tag{9}$$

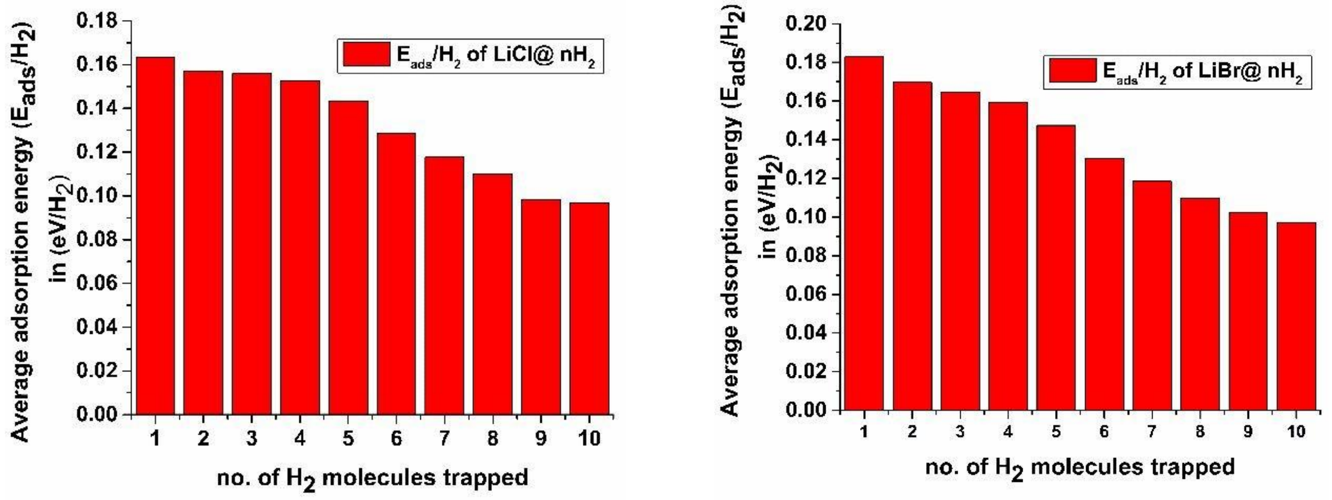
here $G_{LiX@nH2}$, $G_{LiX}$, and $nG_{H2}$ indicate Gibbs free energy of the $H_2$ adsorbed complexes, LiX [X = Cl, Br], and molecular hydrogen respectively.

The Multiwfn package[56] has been used to predict the bonding nature in between Li center and adsorbed $H_2$.[57] The Multiwfn software is a powerful tool for performing electronic wavefunction analysis, a vital component of quantum chemistry. The details have been given in supporting information.

## 3. Results and discussion

### 3.1 LiX@nH$_2$ (X = Cl, Br): Stability, reactivity, and average adsorption energy per H$_2$ (E$_{ads/H2}$)

We have successfully obtained LiX@ $nH_2$ (X = Cl, Br and n= 1-10) optimized systems, and for all systems number of imaginary frequencies turns out to be zero. However, once the structures are optimized, we can see that up to $5H_2$, $H_2$ molecules have been trapped around the Li centre. Following that, the sixth inserted $H_2$ molecule moves away from the Li centre and toward the X (X = Cl, Br) centre, and so on until the tenth $H_2$. So, after the fifth $H_2$ molecule, $H_2$ molecules were adsorbed not only around the Li centre but also across the entire polar LiX surface (X = Cl, Br). The optimized structures, point group, energy, frontier molecular orbitals such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the optimized systems, and corresponding bandgap ($\Delta E_{HOMO-LUMO}$) have been given in Fig. 1 and Figs. S1-S3. Values (in eV) of hardness (η), electronegativity (χ) and electrophilicity (ω) of LiX@ $nH_2$ (X = Cl, Br and n= 1-10) systems have been tabulated in Tables S1-S4 at both ωB97X-D/LanL2DZ and ωB97X-D/6-311+G(d,p) level of theory. In these tables, we have also supplied values (in eV) of ionization energy (I) and electron affinity (A) as the mathematical equation of hardness (η) and electronegativity (χ) depend on these two. With that, we have also plotted hardness (η), electronegativity (χ), and electrophilicity (ω) vs. no. of trapped $H_2$ molecules (Fig. S4) of LiX@ $nH_2$ (X = Cl, Br, and n = 1-10) systems at both ωB97X-D/LanL2DZ and ωB97X-D/6-311+G(d,p) level of theory. We can see from the tables and figures that the hardness gradually increases. Electronegativity and electrophilicity decrease progressively. Because hardness is related to stability and electrophilicity to reactivity, adsorption of $H_2$ increases stability while decreasing reactivity. Again, increasing stability and decreasing reactivity were supported by the gradual increase in band gap ($\Delta E_{HOMO-LUMO}$) [Fig. 1 and Figs. S1-S3]. Now, Fig. 2 and Table S5 show that as the number of adsorbed $H_2$ molecules increases near the Li center and over the LiX (X = Cl, Br), the average adsorption energy per hydrogen molecule ($E_{ads/H2}$) decreases (Fig. 2). As the number of adsorbed $H_2$ molecules surrounding the Li core and LiX increased, the charges on the natural bonding orbital (NBO) on Li decreased (Table 1 and Fig. S5). Consequently, the dipole-induced dipole interaction decreases, lowering the average adsorption energy per hydrogen molecule ($E_{ads/H2}$).



(a) (b)

**Fig. 2** Plot of average adsorption energy/$H_2$ [eV] *vs* no. of $H_2$ molecules trapped of (a) LiCl@$nH_2$ [n= 1-10] systems and (b) LiBr@$nH_2$ [n= 1-10] systems at the ωB97X-D /6- 311+G(d,p) level of theory.

**Table 1.** NBO charges and adsorption ability ($E_r$) of LiX@n$H_2$ [X= Cl, Br and n= 1-10] systems at CAM-B3LYP /6-311+G(d,p) level of theory and Gravimetric wt% of LiX@n$H_2$ [X= Cl, Br and n= 1-10] systems.

| Systems | NBO charges | Adsorption ability ($E_r$) [eV] | Gravimetric wt % |
|---|---|---|---|
| | | CAM-B3LYP | |
| LiCl@$H_2$ | 0.895 | 0.137 | 4.49 |
| LiCl@2$H_2$ | 0.870 | 0.131 | 8.60 |
| LiCl@3$H_2$ | 0.840 | 0.113 | 12.37 |
| LiCl@4$H_2$ | 0.834 | 0.059 | 15.84 |
| LiCl@5$H_2$ | 0.826 | 0.029 | 19.05 |
| LiCl@6$H_2$ | 0.825 | 0.029 | 22.02 |
| LiCl@7$H_2$ | 0.825 | 0.032 | 24.78 |
| LiCl@8$H_2$ | 0.839 | 0.040 | 27.35 |
| LiCl@9$H_2$ | 0.845 | 0.025 | 29.75 |
| LiCl@10$H_2$ | 0.827 | 0.024 | 32.00 |
| LiBr@$H_2$ | 0.873 | 0.138 | 2.25 |
| LiBr@2$H_2$ | 0.848 | 0.131 | 4.40 |
| LiBr@3$H_2$ | 0.840 | 0.111 | 6.46 |
| LiBr@4$H_2$ | 0.816 | 0.054 | 8.43 |
| LiBr@5$H_2$ | 0.809 | 0.022 | 10.32 |
| LiBr@6$H_2$ | 0.810 | 0.015 | 12.13 |
| LiBr@7$H_2$ | 0.814 | 0.030 | 13.88 |
| LiBr@8$H_2$ | 0.815 | 0.022 | 15.55 |
| LiBr@9$H_2$ | 0.814 | 0.022 | 17.16 |
| LiBr@10$H_2$ | 0.810 | 0.021 | 18.71 |

However, abnormal trends were observed in the lower parts of these tables. The NBO charges on the Li center increased rather than decreased. This is because the steric overload between the $H_2$ molecules increases with increasing $H_2$ concentration from 7 to 8, 9, and 10 $H_2$, as does the distance between the $H_2$ molecules increases with increasing $H_2$ concentration from 7 to 8, 9, and 10 $H_2$, as does the distance of the adsorbed $H_2$ molecules from the Li center. Thus, the dipole-induced dipole interaction decreases, increasing the NBO charges. The adsorption ability ($E_r$) indicates how many adsorbed $H_2$ molecules are taken up. The results (Table 1) show that concentrations of hydrogen decrease up to 10 adsorbed $H_2$ molecules, and beyond that they become insignificant. So we assumed that LiX (X = Cl, Br) could adsorb 10 $H_2$ molecules. In the next step, we measured the gravimetric wt% of all $H_2$-adsorbed systems (Table 1). This is an excellent performance compared to the standard value of the U.S. Department of Energy (D.O.E.).

### 3.1.1. Bonding nature

We plotted the average delocalization correction energy ($\Delta E_{CT}^{av}$) versus the number of trapped $H_2$ molecules (Fig. S6). We also tabulated the delocalization correction energy ($\Delta E_{CT}$) and its average values ($\Delta E_{CT}^{av}$) (Table S6). From both Figures and Tables, it can be seen that a charge transfer interaction took place from the bonding orbital (BO) of the trapped $H_2$ molecules to the antibonding orbital of the lone pair of electrons (LP*) of the Li center. However, looking at the table, it can be observed that up to five adsorbed $H_2$ the ($\Delta E_{CT}^{av}$) value increases; thereafter, its value continues to decrease as the number of $H_2$ captured increases. This is because as the trapped $H_2$ molecules increase, the position of the $H_2$ molecules moves toward the X center (X = Cl, Br). As a result, the distance between the Li center and the adsorbed $H_2$ molecules increased, which decreased the charge transfer intensity as well as the charge transfer amount. We performed the topological analysis at the critical bonding point (BCP) to learn about the bonding nature of predictive parameters such as electron density [$\rho(r_c)$], Laplacian of electron density [$\nabla^2\rho(r_c)$], local electron energy density [$H(r_c)$], kinetic energy density [$G(r_c)$], and potential energy density [$v(r_c)$] of the system LiX@$H_2$ (X= Cl, Br) using the program package multiwfn.[56] We made three maps (Fig. 3, Fig. S7, and S8) to find the electron density between Li and adsorbed $H_2$. There are two sections in Fig. S7. Both the upper and lower sections represent the electron density of LiX (X = Cl, Br), and $H_2$. We can see the electron-dense hump of LiX (X = Cl, Br), and $H_2$, but there is no electron density between the Li center and the trapped $H_2$ molecule. This suggests ionic bonding between the Li center and the adsorbed $H_2$. In Fig. S8, there are many different colored lines and detailed description[58] was given in the footnote of Fig. S8. There is no electron density between the Li center and the adsorbed $H_2$ molecule, which in turn supports the ionic bond between Li and $H_2$. Fig. 3 shows the electron localization function (ELF) of the systems. There are no localized electrons between Li and the trapped $H_2$. The

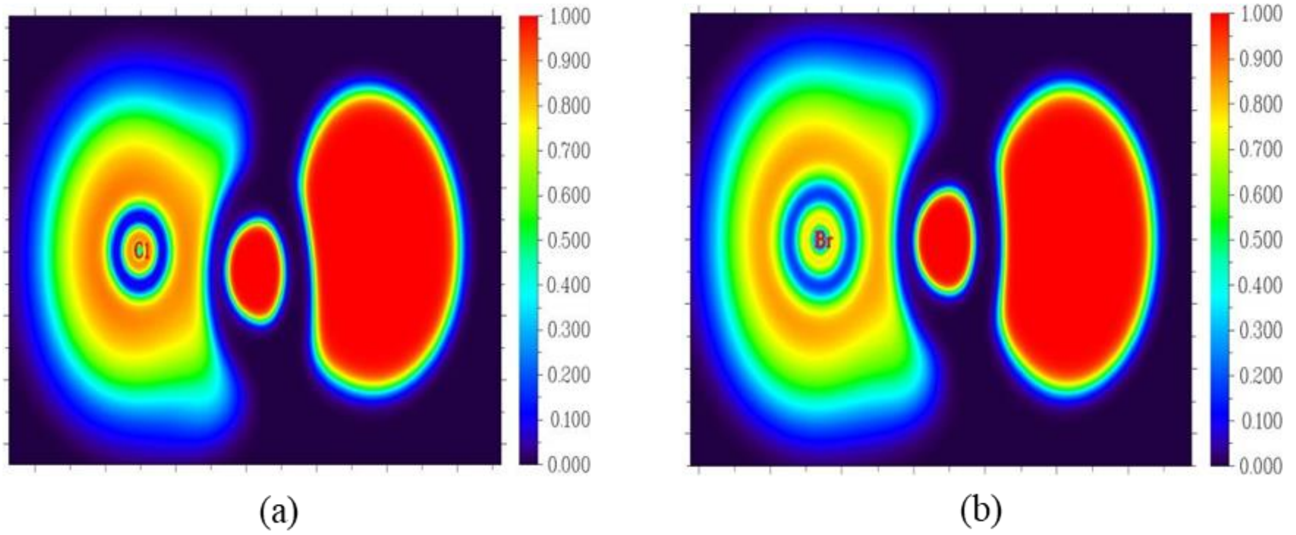


**Fig. 3** The plot of the ELF of the (a) LiCl@$H_2$ system and (b) LiBr@$H_2$ system generated at the ωB97X-D/6-311+G(d,p) level of theory.

bond between the Li center and the adsorbed $H_2$ is thus ionic in nature. Now we can get a complete idea about the bonding nature from the value of [-G(r)/V(r)] in the following way–

(i) The interaction is said to be non-covalent if [-G(r)/V(r)] > 1.

(ii) The interaction is said to be partially covalent if 0.5 < -G(r)/V(r) < 1and the strength of interaction depends on the sign of $\nabla^2\rho$ and H(r). Which is stated below-

  a) The interactions are quite strong when both $\nabla^2\rho$ and H(r) are negative.
  b) The interactions are medium when the value of H(r) is negative and the value of $\nabla^2\rho$ positive.
  c) The interactions are weak when both $\nabla^2\rho$ and H(r) are positive.

Here as the sign of both $\nabla^2\rho(r_c)$ and $H(r_c)$ is positive (Table S7) and the value of $[-G(r_c)/V(r_c)]$ (Table S7) is larger than 1, we may assume that XLi···$H_2$ [X= Cl, Br] interactions are ionic.[59-61]

### 3.1.2. Effect of temperature on hydrogen adsorption

From thermochemistry, we know that the spontaneity of a process depends on the sign of the Gibbs free energy (ΔG) change. If it is negative, then the process is spontaneous. Here we used the same concept. We have plotted the change in Gibbs free energy (ΔG) versus the number of trapped $H_2$ molecules (Fig. 4) of LiX@ n$H_2$ systems (X = Cl, Br and n = 1-10). We also tabulated the change in Gibbs free energy (ΔG) (Table S8). The figures and the tables show that at 51 K or below this temperature the adsorption process of LiCl system is spontaneous; at 49 K or below this temperature, the adsorption process of LiBr system is spontaneous.

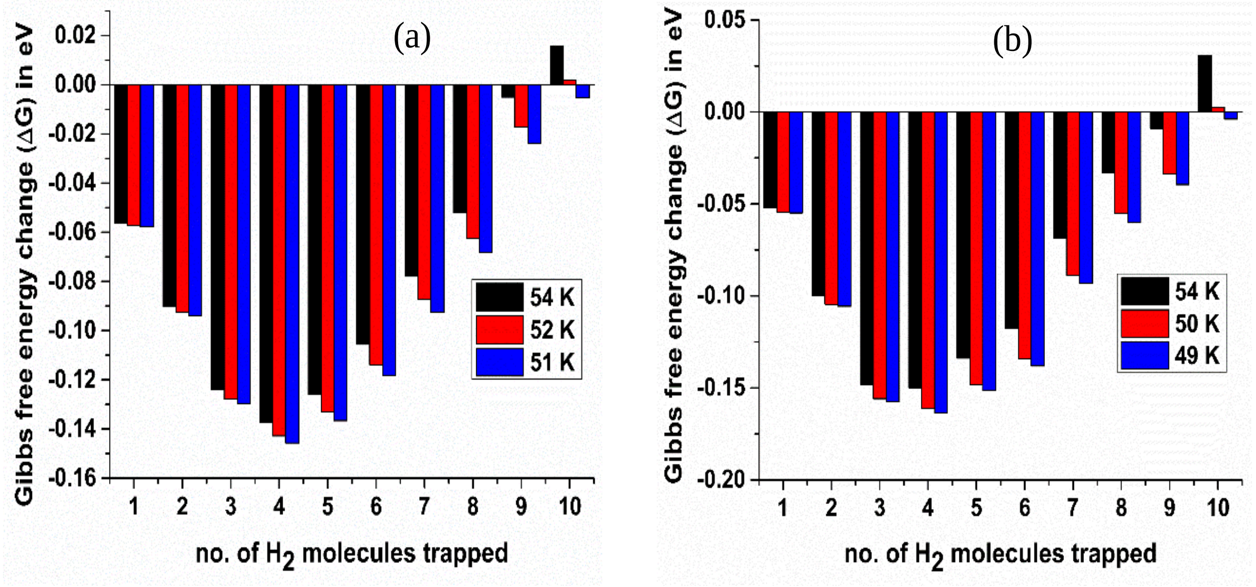


**Fig. 4** Plot of Gibbs free energy change [eV] *vs* no. of $H_2$ molecules trapped of (a) LiCl@n$H_2$ [n= 1-10] systems and (b) LiBr@n$H_2$ [n= 1-10] systems at the ωB97X-D /6-311+G(d,p) level of theory.

## 4. Conclusion

Because their adsorption energy (average adsorption energy per $H_2$ molecule) aids the quasisorption process, the LiCl and LiBr molecules are recognized as encouraging hydrogen storage templates. The positive charge on the Li atom in the overall system diminishes with the adsorption of $H_2$ molecules, according to NBO analysis (slight deviation seen in the case of @$8H_2$ and @$9H_2$). It implies that a charge transfer interaction takes place between the bonding orbitals of $H_2$ molecules and the antibonding orbitals of Li. A single LiCl or LiBr molecule can absorb $10H_2$ with a high gravimetric wt percent value (32.00 for LiCl and 18.71 for LiBr), which is found to be a sound system in comparison to the U.S. D.O.E. (2015) standard,[23] but lower than the LiF. With LiCl, it's over two-thirds, and with LiBr, it's even less than half. Electrovalent interactions between the building unit (LiCl and LiBr) and the molecular hydrogen are predicted by the Atoms in Molecules (AIM) model. The variations in Gibbs free energy indicate that the hydrogen adsorption process is spontaneous at or below 51 K for LiCl and 49 K for LiBr, demonstrating once again that LiF (54 K)[24] is the superior template of the three. In current time, whole world is focusing on $H_2$ as green fuel. So, searching for proper storage material is a well-timed topic for research. And very recent, Lyu *et. al.* and Nishihara *et al.* have testified some hydrogen storage material where theoretical findings support the experimental results.[62,63] In our current report, for all systems, the adsorption process is thermodynamically physible at cryogenic temperature, and study with synthetic approach is much easier for LiCl and LiBr as both are available common compounds. So, researchers involved in synthesizing new molecules/materials in pursuit of promising and sustainable hydrogen storage devices can learn a great deal from the results. The outcomes will allow us to investigate the hydrogen storage capacity on the surface of molecular clusters (method based on bulk materials) and finally investigate the laboratory's potential industrial uses.

## Acknowledgment

All authors are also thankful to Haldia Institute of Technology for providing research infrastructure. The article is dedicated: Author G. Roymahapatra would like to dedicate this article to the 75th Birthday of his father, Sri Sukdev Roymahapatra (popularly known as Sukdev Sir; DOB 04th November, 1948), a retired English teacher from Dakshinchak High School in Purba Medinipur, West Bengal, India. Sukdev Sir, who is currently suffering from Alzheimer's and Parkinson's disease, not only promoted GRM as a parent, but is also always by his side as a friend to motivate and encourage him through all of life's difficulties. All of the co-authors pray to the Almighty for GRM's father's speedy recovery.

## Conflict of Interest

There is no conflict of interest.

## Supporting Information

Applicable.

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# Colorimetric and theoretical investigation of coumarin based chemosensor for selective detection of fluoride

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ABSTRACT

Coumarin based **Sensor 1** has been designed and synthesized to recognize fluoride ion visually with high selectivity and sensitivity over other anionic analytes through color change from very faint yellow to pink in acetonitrile. The probable binding phenomenon in solution phase has been explained by $^1$H NMR study of **sensor 1** with different concentration of fluoride ions. The binding constant of the **sensor 1** with fluoride has been determined as $3.9 \times 10^4$ $M^{-1}$ and the lower detection limit 6.5 μM of the **sensor 1** towards fluoride, which has made the **sensor 1** as a promising backbone for selective detection of fluoride. For the practical application, test strips based on **sensor 1** were fabricated, which could act as a convenient and efficient naked eye $F^-$test kits. The experimentally observed absorption maxima along with its binding nature with fluoride ions also have been supported through theoretical calculations using density functional theory (DFT) calculations.

## 1. Introduction

Foremost importance of anion in biological, clinical, environmental, catalysis and chemical processes inspire us towards the selective and efficient recognition of anion, which is an area of growing interest in supramolecular chemistry [1–4]. Among the anions fluoride has a benign effect; especially this is used for the prevention of dental cavities [5] and treatment for osteoporosis [6]. But excessive ingestion seems to cause health hazards. For example, over-accumulation of fluoride can influence cell signaling neurological and metabolic dysfunctions [7]. It has also important applications in steel making and aluminum refining, ion batteries, photocurrent enhancing in supramolecular solar cells industries as well as in different organic synthesis [8,9]. Surrounding this industrial area fluoride contamination is often detected. Concerns for the consequences have generated wide interest in the development of rapid, selective and sensitive systems capable of selective recognition and visually noticeable sensing of fluoride in a competitive environment [10]. Being the smallest halide, the fluoride anion has a highest charge density and strong nucleophilic character. Besides this, it has highest affinity to protons among anions. All this makes fluoride fond of hydrogen bonding partners. Hydrogen bondings are really the intermolecular forces selected by Nature to bind anions to proteins [11].

Many works have been reported [12–20] but still search for structurally simple colorimetric sensor which can be synthesized easily and efficiently enables 'naked-eye' detection of fluoride ions without any special spectroscopic instrumentation has been a keen area of interest. Thus, herein we report design and synthesis of a highly selective and sensitive colorimetric **sensor 1** for recognition of fluoride ions in presence of other competing anions, along with theoretical modeling and optimization using density functional theory (DFT).

## 2. Results and discussion

### 2.1. Scheme of synthesis of sensor 1

**Sensor 1** has been synthesized by the facile Schiff base condensation reaction of 2–hydroxy-5-methylbenzene-1,3-dicarbaldehyde (2) [21] with 7-amino-4-(trifluoromethyl)–2*H*-chromen-2-one (3) in methanol under refluxing condition in presence of two drops of acetic acid as light yellowish precipitation with 56% yield

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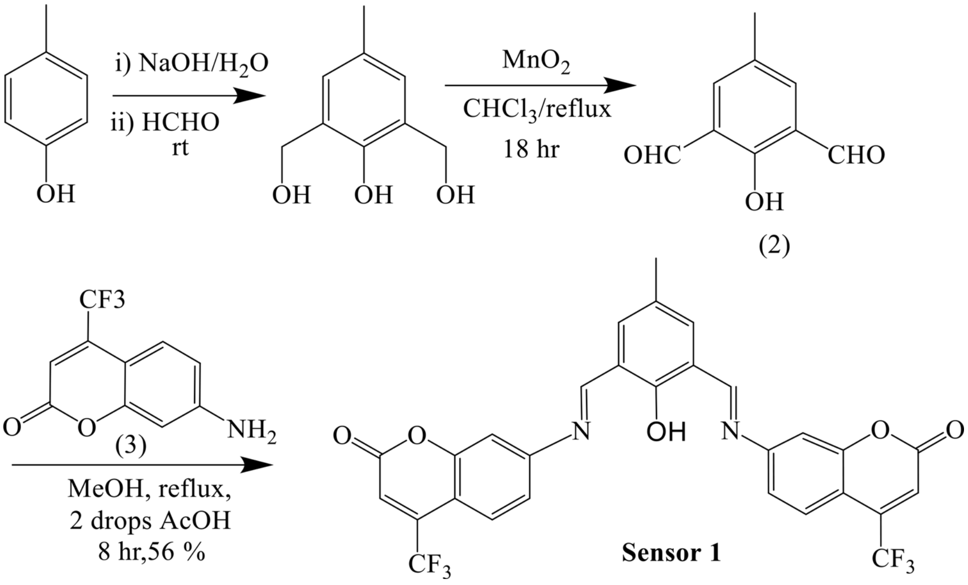


**Scheme 1.** Synthetic scheme for **sensor 1**.

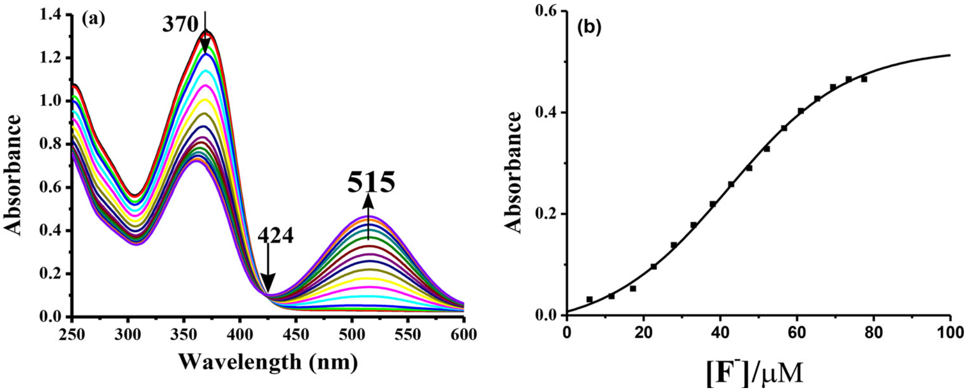


**Fig. 1.** (a) UV–vis absorption spectra of **sensor 1** ($c = 2 \times 10^{-5}$ M) upon titration with TBAF ($c = 4 \times 10^{-4}$ M) in $CH_3CN$. (b) Binding isotherm recorded at 515 nm with the change of the concentration of TBAF.

(Scheme 1). Its molecular structure and purity were established from different spectroscopic studies like $^1H$ NMR and MS (ESI).

### 2.2. Analytes binding studies

#### 2.2.1. Spectrophotometric titrations with various anions

The binding and recognition abilities of **sensor 1** towards various anions were studied by UV-vis spectroscopy. The titration was carried out in $CH_3CN$ at $2 \times 10^{-5}$(M) concentration of **sensor 1** upon the successive addition of tetrabutylammonium fluoride (TBAF) ($c = 4 \times 10^{-4}$ M) and other competing anions like $Br^-$, $Cl^-$, $I^-$, $CH_3COO^-$ as their tetrabutyl ammonium salts and $PO_4^{3-}$, $NO_3^-$, $NO_2^-$, $S^{2-}$, $OCl^-$, $CN^-$ as their sodium salts. The UV-vis spectrum of the **sensor 1** is characterized by absorption band centered at 370 nm (Fig. 1). On gradual addition of the tetrabutylammonium fluoride the band at 370 nm gradually diminished accompanied with a new band with increasing absorbance appears at 515 nm ensuing ‘naked eye’ detectable exciting color change from faint yellow to pink (Scheme 2). The absorption spectra show a distinct isosbestic point at 424 nm, which clearly indicates the formation of a new complex between the **sensor 1** and the fluoride ions. In addition, weakening of the characteristic absorption band at 370 nm suggests significant electronic perturbation occurred in the ground state of **sensor 1**[22].

The fluoride ions induced bathochromic shift of 145 nm observed in the absorption and consequent color change from very faint yellow to pink can be ascribed towards the probable hydrogen bonding interaction between the –OH proton of **sensor 1** and fluoride ion facilitated increase in electron density on phenolic ‘O’ atom of –OH group followed by improved delocalization and hence decrease in energy responsible for electronic transition. Fluoride induced deprotonation of the hydroxyl group due to strong hydrogen-bonding interaction between **sensor 1** and $F^-$resulted enhancement of $\pi$ delocalization, which was expected to reduce the energy gap of the $\pi$-$\pi^*$ transition appearing a new absorption band near 515 nm resulting in the formation of a ‘naked-eye’ color change from faint yellow to pink [23]. Thus, the new absorption band at higher wavelength appeared at 515 nm, intensity of which was enhanced about fifteen-fold with increasing addition of fluoride ions and after addition of 5 equivalent of TBAF it was saturated.

#### 2.2.2. Host-guest stoichiometric ratio, binding constant and detection limit

The binding stoichiometry between **sensor 1** and fluoride ion in acetonitrile was determined from Job’s plots [24] (Fig. 2b) and the binding affinity was calculated from a Benesi-Hildebrand plot [25] (Fig. 2a). The results suggest a 1:1 stoichiometry and the association constants (Ka) were calculated considering 1:1

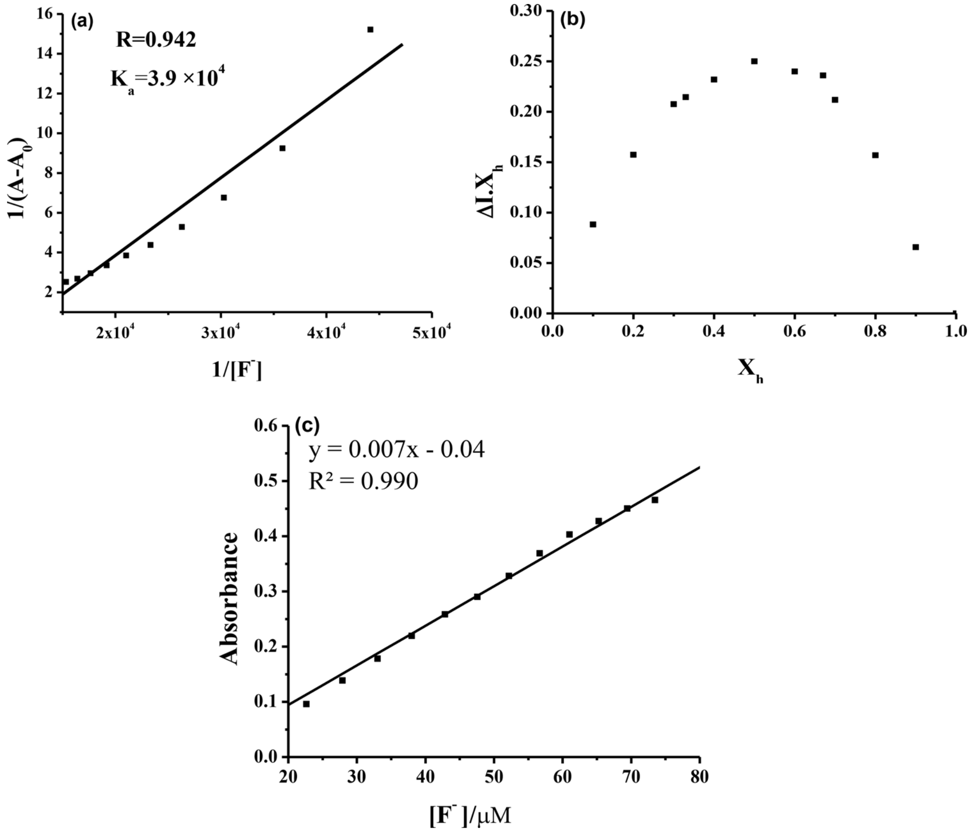


**Fig. 2.** (a) Benesi–Hildebrand plot from UV-vis titration data of **sensor 1** ($c = 2 \times 10^{-5}$ M) with $F^-$($c = 4 \times 10^{-4}$ M). (b) Jobs plot diagram of **sensor 1** with TBAF. (c) Changes of absorbance of **sensor 1** ($c = 2 \times 10^{-5}$ M) as a function of [F$^-$] ($c = 4 \times 10^{-4}$ M) at 515 nm.

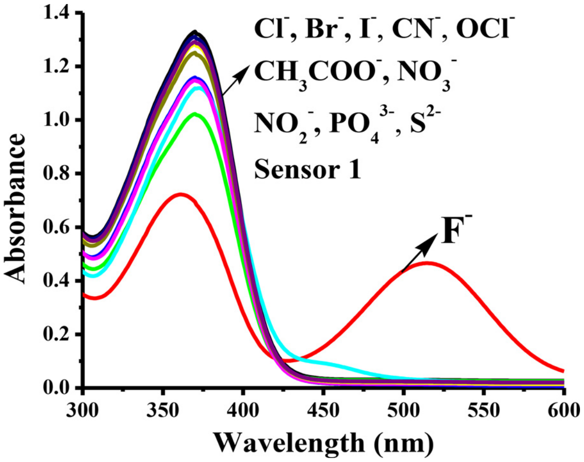


**Fig. 3.** UV-vis absorption spectra of **sensor 1** ($c = 2 \times 10^{-5}$ M) upon addition of different anions (5 equiv.) in $CH_3CN$.

complexation to be $3.9 \times 10^4$ M$^{-1}$. The detection limit [26] of **sensor 1** as a colorimetric sensor for the fluoride ion was determined to be 6.5 µM by using 20 µM of **sensor 1** solution in UV–Vis titration (Fig. 2c).

### 2.2.3. Selectivity test

The effects of interference of the previously-mentioned anionic analytes were investigated (Fig. 3) but no such characteristic response was found to sense those anions. These results confirmed that **sensor 1** possesses highly selective colorimetric response towards $F^-$. This is probably due to higher basicity of the fluoride ion among the all-other competing anions, due to which fluoride ions are capable of stronger hydrogen bonding interaction with the phenolic –OH causing such type of red shift in the absorption spectra. Whereas other competing anions having rather weak basicity could not interact enough through hydrogen bonding to facilitate improved electronic delocalization.

### 2.2.4. Competition experiment

To further explore the selectivity of **sensor 1** for $F^-$, the competition experiment was also performed in the presence of $F^-$ mixed with other interfering analytes like Br$^-$, Cl$^-$, I$^-$, $CH_3COO^-$, $PO_4^{3-}$, $NO_3^-$, $NO_2^-$, $S^{2-}$, OCl$^-$, CN$^-$. As shown in Fig. 4, absorption enhancement of **sensor 1** on binding with $F^-$remains unperturbed and other interfering anions were innocent toward the sensing with $F^-$in $CH_3CN$. This indicates that the **sensor 1** is highly selective and sensitive for $F^-$in $CH_3CN$ and the binding of **sensor 1** with $F^-$ is also independent in presence of other anions as well.

### 2.2.5. Practical application

We have also developed a colorimetric test kit for practical applications. Herein we have used TLC plate as the test kits and initially it exhibits white color in naked eye in absence of **sensor 1** (Fig. 5I).

The ligand-coated TLC paper strips were prepared by immersing them into sensor **1** solution ($c = 2 \times 10^{-5}$ M). The ligand-coated test kit shows faint yellow color due to the initial faint yellow color of the ligand solution (Fig. 5II). But when solutions of different anions were sprayed onto these strips, a notable faint yellow strip changed its color to pink exclusively when $F^-$ solution was sprayed (Fig. 5III). The development of such dipsticks or test srips is useful as instant qualitative information is obtained without resorting to the instrumental analysis.

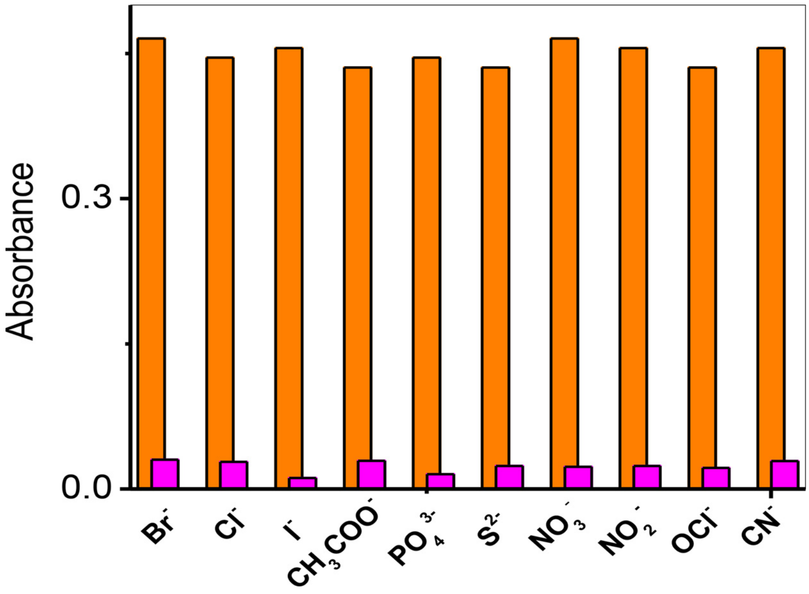


**Fig. 4.** Anion selectivity profile of the **sensor 1** ($c = 2 \times 10^{-5}$ M): (Violet bars) change of absorbance of sensor 1 + 5.0 equiv of interfering anions; (Orange bars) change of absorbance of the sensor + 5.0 equiv anions, followed by 5.0 equiv $F^{-}$ at 515 nm.

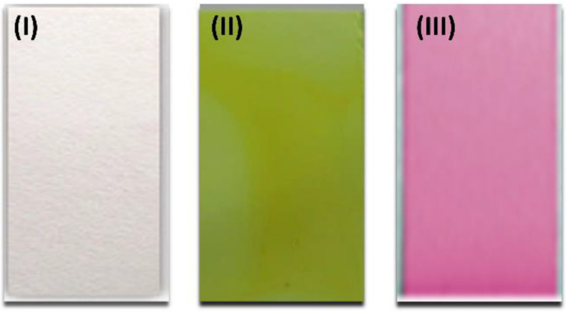


**Fig. 5.** Colorimetric test kit: Photographs of TLC plate test kit coated with sensor 1 ($c = 2 \times 10^{-5}$ M) used for the detection of $F^{-}$in $CH_3CN$ ($c = 4 \times 10^{-4}$ M): I, (control, only TLC plate); II, sprayed with sensor 1 solution ($c = 2 \times 10^{-5}$ M); III, sprayed with $F^{-}$solution to the sensor coated plate.

### 2.2.6. Binding studies by $^1H$ NMR spectra

To gain more insight into the nature of interaction of fluoride ion with **sensor 1**, we had performed $^1H$ NMR titration in $CDCl_3$ and the spectra are shown in Fig. 6. The spectrum shows that on addition of one equivalent of TBAF into the solution of **sensor 1** the signals of –OH proton ($H_a$) at 12.97 ppm disappeared but no new signal was found around 16.0 ppm [27].

From this observation it can be imagined that in presence of fluoride the deprotonation of the –OH proton does not take place rather due to strong hydogen bonding between –OH proton and fluoride ion (Scheme 2), the signal of –OH proton becomes so broadened that it is not appeared in the $^1H$ NMR spectra.

### 2.2.7. Probable host-guest binding mode

To build up the base behind the achieved experimental results, we have tried to find out the energy minimized structure of **sensor 1** and its complex focusing on the nature of bonding interaction with fluoride ions. The ground state optimization was carried out in acetonitrile for all compounds using Gaussian 09 software with B3LYP hybrid functional and 6–31 G (d,p) basis set by applying Density Functional Theory method [28].

The optimized structure of **sensor 1** shows (Fig. 7) that the two coumarin moieties keep themselves far away from each other as such a way to facilitate the incoming approach of the anions to interact with **sensor 1** through its –OH proton, as expected and also observed through theoretical modeling.

**Table 1**
Few useful optimized parameters of **sensor 1** and its complex.

| Muliken charge | O13 | O45 | |
|---|---|---|---|
| **Sensor 1** | −0.561932 | −0.514841 | |
| **Sensor 1**-F | −0.65697 | −0.522228 | |
| **Bond length (Å)** | **O13-H14** | **N15-H14** | **C6-O13** |
| **Sensor 1** | 1.0059 | 1.66538 | 1.33207 |
| **Sensor 1**-F | 1.56148 | 2.40135 | 1.2667 |

### 2.2.8. Theoretical investigation

On close inspection of the modulation of electronic charge density from Mulliken charge distribution (Table 1) it is found that negative charge on -O13 increases on binding of **sensor 1** with fluoride ions, which indicates probable hydrogen bonding between –OH proton by which this proton is being more closure to fluoride ions, which is more electronegative than oxygen atom (Scheme 2). This hydrogen bonding type interaction can be confirmed also from the optimized structure where the O13-H14 bond and N15-H14 bond distances in **sensor 1**, are 1.005 and 1.665 Å respectively (Fig. 7a) (Table S3; supplementary data), both of which are elongated whereas the C6-O13 bond is shortened from 1.33 to 1.26 Å on complexation with fluoride ions.

This hydrogen bonding drives extended electronic delocalization, which is supported by the enhanced electron density on –O45 -as found from Mulliken charge distribution – hence causes substantial red shift in absorption spectra from 370 nm to 515 nm. Computed absorption wavelengths (Table S3) which are very close to our experimentally observed findings also support the proposed mode of complexation (Fig. 7b) through hydrogen bonding type interaction between **sensor 1** and fluoride ions.

## 3. Experimental section

### 3.1. General

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purifi-

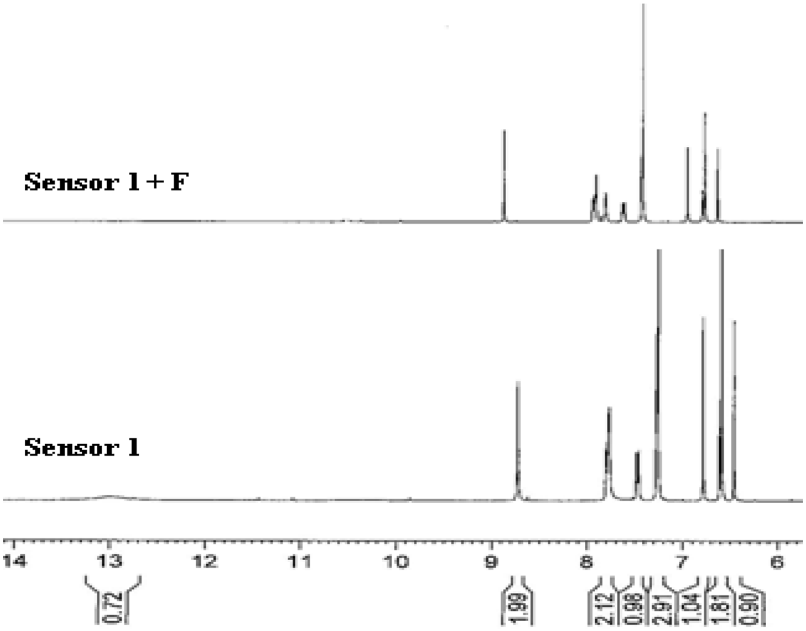
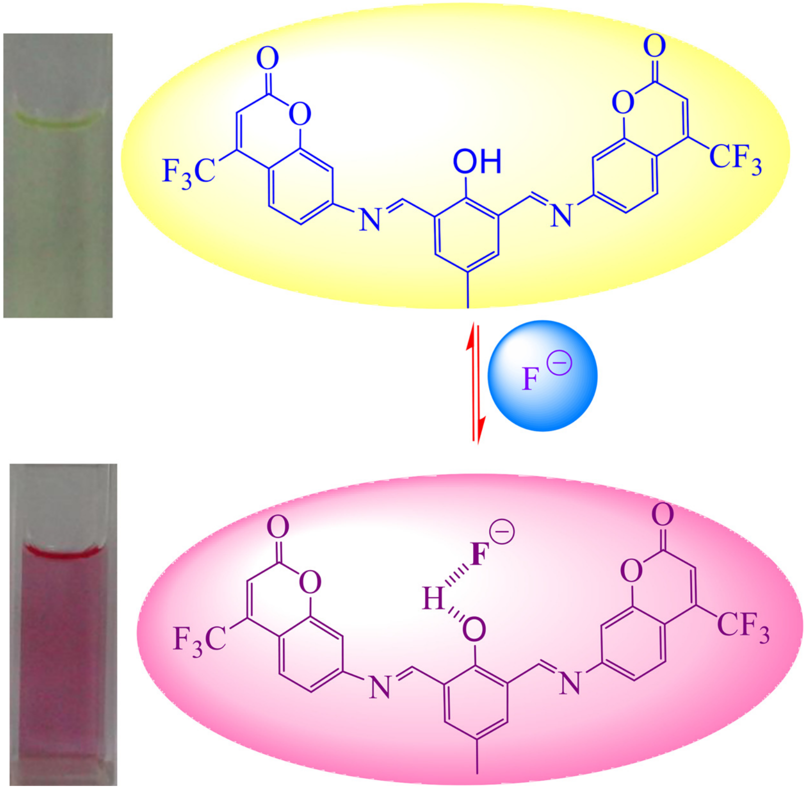


**Fig. 6.** Partial $^1$H NMR spectrum of **sensor 1** in $CDCl_3$ and with addition of TBAF (one equivalent).



**Scheme 2. Left:** Color change of the **sensor 1** on addition of *F*⁻. **Right:** Probable mode of binding of **sensor 1** with *F*⁻ in acetonitrile solution.

cation. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and were uncorrected. $^1$H NMR spectra were recorded on Brucker 400 MHz instruments. NMR titration was carried out in $CDCl_3$ solvent on 400 MHz instrument. For NMR spectra, $CDCl_3$ was used as solvent with TMS as an internal standard. Chemical shifts are expressed in $\delta$ units and $^1$H–$^1$H and $^1$H–C coupling constants in Hz. UV–vis titration experiments were performed on a JASCO UV-V530 spectrophotometer.

### 3.2. General method of UV-vis titrations

For UV-vis titration, stock solution of the sensor was prepared ($c = 2 \times 10^{-5}$ $ML^{-1}$) in $CH_3CN$. The solution of the guest anion of tetrabutyl ammonium fluoride was prepared ($4 \times 10^{-4}$ $ML^{-1}$) in $CH_3CN$. The original volume of the sensor solution was 2 ml to measure the absorbance. Solutions of the sensor of various concentrations and increasing concentrations of various anions were pre-

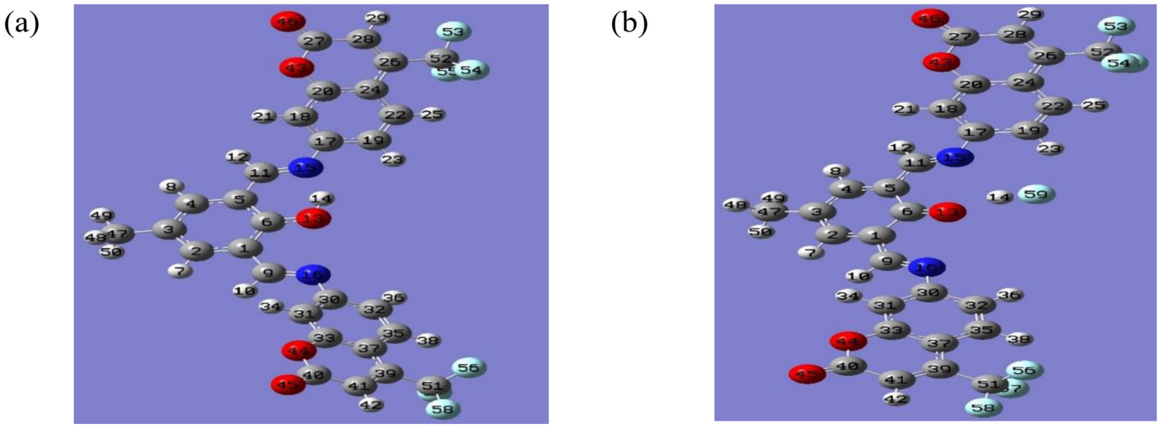


**Fig. 7.** (a) B3LYP optimized geometry of **sensor 1.** (b) B3LYP optimized geometry of **sensor 1**-fluoride complex**.**

pared separately. The titration was performed by adding different anions solutions to the solution of **sensor 1** individually. The spectra of these solutions were recorded by means of UV-vis methods.

### *3.3. Synthetic methods*

***Synthesis of 2–hydroxy-5-methyl-benzene-1,3-dicarbaldehyde (2):*** p-Cresol (10 g) was added to a solution of NaOH (3 g) in water (20 mL). Following full development of a gold color, 37% formaldehyde (20 g) was added. The mixture was stirred for 20 min and allowed to stand overnight at the ambient temperature. The yellow granular 2,6-dimethylol-5-methylphenol product was collected by vacuum filtration and washed with water-saturated sodium chloride followed by dilute HCl. In a 100 ml r.b. flask fitted with a reflux condenser, a magnetic stirrer and a dropping funnel was placed 2,6-dimethylol-5-methylphenol (1 gm). Following addition of excess $MnO_2$, it was then refluxed in $CHCl_3$ for 18 h. Finally, the product **2** was purified by 60–120 silica gel by 5% ethyl acetate in pet ether. Yield of the product was 500 mg (50%).

***Synthesis of the sensor 1***

**Sensor 1** has been synthesized by the facile Schiff base condensation reaction of 2–hydroxy-5-methylbenzene-1,3-dicarbaldehyde (2)[20] with 7-amino-4-(trifluoromethyl)–2*H*-chromen-2-one (3) in methanol under refluxing condition in presence of two drops of acetic acid as light yellowish precipitation with 56% yield.

**$^1$H NMR ($CDCl_3$, 400 MHz):** $\delta$ (ppm):12.93 (br s, 1H), 8.72 (s, 2H), 7.77 (d, 2H, $J = 4.0$ Hz), 7.48(d, 1H, $J = 10.4$ Hz), 7.27(d, 3H, $J = 7.20$ Hz), 6.78 (s, 1H,), 6.59 (d, 2H, $J = 10.4$ Hz), 6.46 (s, 1H), 2.38 (s, 3 H).

**MS (ESI$^+$): *m/z* =** 585.27 (M - $H^+$), **Anal calcd for $C_{29}H_{16}F_6N_2O_5$:** 59.39% C, 2.75% H, 19.44% F, 4.78% N,13.64% O; **found:**59.18% C, 2.65% H, 19.22% F, 4.70% N, 13.34% O.

## 4. Conclusions

In conclusion, we have synthesized a new **sensor 1** which can recognize fluoride ion by naked-eye detectable color change from very faint yellow to pink in acetonitrile. Through investigation of its binding properties we have screened a wide range of competing anions by the absorption method. The experimentally observed results have been correlated with theoretical modeling obtained from Density Functional Theory (DFT) calculation and consequent optimization findings using density functional theory and this correlation manifests that **sensor 1**-fluoride complexation occurs via 1:1 hydrogen bonding interactions facilitating the charge transfer from phenolic oxygen and hence substantial red shift in absorption maxima. In view of the high selectivity and sensitivity and quick synthetic accessibility **sensor 1** may be useful as a novel colorimetric fluoride sensor. For practical applications, we have developed a colorimetric test kit of **sensor 1** for the selective detection of $F^-$ by naked eye color change from faint yellow to pink.

## Justifications

- ➢ Coumarin based **Sensor 1** has been recognized as the selective sensor for fluoride ion by the notable visual color change from very faint yellow to pink in acetonitrile by strong hydrogen bonding interaction.
- ➢ **Sensor 1** shows unique selectivity and sensitivity towards fluoride over other anionic analytes like $Br^-$, $Cl^-$, $I^-$, $CH_3COO^-$, $PO_4{}^{3-}$, $NO_3{}^-$, $NO_2{}^-$, $S^{2-}$.
- ➢ The probable binding phenomenon in the solution phase has been explained successfully by $^1$H NMR experiments and theoretical approach.
- ➢ The high selectivity and sensitivity of the **sensor 1** with fluoride has been explained by lower detection limit as 6.5 µM and significant binding constant $3.9 \times 10^4$ $M^{-1}$.
- ➢ For the practical application, test strips based on **sensor 1** were fabricated, which could act as a convenient and efficient naked eye $F^-$test kits.
- ➢ Fluoride induced strong hydrogen bonding interaction, lower detection limit and notable binding constant has made the **sensor 1** as a promising backbone for the selective and sensitive detection of fluoride.

## Declaration of Competing Interest

The authors declare no conflict of interest.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2022.133228.

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# Hydrogen Storage Efficiency of Ag (I)/Au (I) Decorated Five-Member Aromatic Heterocyclic (AH) Compounds: A Theoretical Investigation

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## Abstract

The hydrogen ($H_2$) economy has long faced significant challenges in the areas of production, storage, and application. Extensive research efforts have been directed towards finding effective solutions. Among the various storage options, solid-state hydrogen storage has emerged as a promising alternative. In this study, we conduct a theoretical investigation on the efficiency of $H_2$ trapping in Ag(I)/Au(I)-decorated five-member aromatic heterocyclic (AH) rings. We analyze the aromaticity of the metal-decorated ring and the $H_2$-trapped metal-decorated ring using the nuclear independent chemical shift (NICS) value, to study the stability of the aromatic system. Our findings also demonstrate that these systems are capable of trapping up to five molecules of $H_2$ in a quasi-sorption manner. Furthermore, we investigate the spontaneity of $H_2$ adsorption in Ag(I)/Au(I)-decorated systems by examining the Gibbs free energy change. To understand the bonding nature, we perform an analysis using the electron localization function (ELF) and non-covalent interaction (NCI) analysis, which reveal the bonding nature of our modeled systems. It has shown the gravimetric wt% values ranging from 3.66 to 5.45. Additionally, the partial density of states (PDOS) technique is employed to identify the contributions of $H_2$, decorated metal, and the five-member AH system towards the frontier molecular orbitals of the complexes. Also, ADMP calculation indicates their stability near room temperature.

*Keywords:* AH (Aromatic heterocyclic compound); five-membered AH; Ag(I)/Au(I)-AH complex; Hydrogen adsorption.
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## 1. Introduction

Hydrogen is increasingly recognized as the preferred energy carrier for the 21st century due to its clean, abundant, and non-toxic nature. When used as a fuel cell or burner, hydrogen produces only heat and water vapor, making it environment friendly. Therefore, the successful development of the hydrogen economy offers numerous advantages for the environment. However, a key challenge in advancing the hydrogen economy lies in the development of a safe, compact, lightweight, and cost-efficient hydrogen storage system. The widespread utilization of hydrogen as a fuel requires storage systems that offer high gravimetric weight percent (wt%) and volumetric density, rapid kinetics for ambient adsorption and desorption, favorable enthalpy for hydrogen adsorption and desorption, recyclability, safety, and cost-efficiency.[1,2] Therefore, designing structures based on reported systems and developing new systems to enhance $H_2$ trapping efficiency are popular research avenues. Due to the advantages of clean, renewable, abundant, and outstanding performance in terms of environment friendly, hydrogen has received much attention.[3-5] Safety and cost-effectiveness in hydrogen storage techniques are a big problem for hydrogen use in transportation applications.[6] Conventional storage methods

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such as pressurized hydrogen gas and liquid storage systems involve high safety and cost concerns for onboard applications.[7,8]

Therefore, alternative storage methods are highly obligatory to meet the necessities of the hydrogen economy. Solid-state storage systems based on metal hydrides, organometallic compounds, and metal clusters have shown great potential for storing hydrogen securely, compactly, and reversibly, making them an interesting area of research for hydrogen storage. However, none of these schemes fully satisfy all the essential criteria for a viable and sustainable hydrogen technology. Among all reported methods, solid-state hydrogen storage materials have attracted much attention,[9-12] such as hydride complexes,[13-16] polymeric material,[17-19] carbon nanomaterial,[20-23] and metal-organic frameworks (MOF).[24,25] Solid-state hydrogen storage materials have garnered significant interest due to their impending advantages. To be granted as efficient hydrogen storage materials, these systems should exhibit fast adsorption/desorption kinetics and high gravimetric density (5.5 wt%).[26] Hydrogen storage technology mainly divided into two types: physisorption process (the host materials adsorb $H_2$ molecules via weak interaction at very low temperatures and high hydrogen gas pressure) and chemisorption process (the $H_2$ molecule dissociates into atomic stage and then is bonded to the host materials). In both processes; during application; it is difficult to release $H_2$ molecule from the host due to strong interaction and hence it is difficult to use in transportation/automobile industries. Therefore, materials with reversible adsorption energy (0.2eV/$H_2$ to 0.6 eV/$H_2$) (4.612 kcal/mol to 13.836 kcal/mol)[27, 28] tend to meet high gravimetric density and release $H_2$ easily near room temperature. Metalized siligraphene nano-sheet ($SiC_7$) is a good example of such kind. It can operate as an efficient $H_2$ storage material at ambient conditions.[29] Light metal decorated $C_4N$ nano-sheet can bind up to five $H_2$ molecules efficiently. Titanium and Boron decorated twin-graphene provides new inspiration for the discovery of carbon-based hydrogen storage materials.[30] Decoration of transition metal increases the hydrogen storage capacity at room temperature on different graphene sheets.[31] It is also found that alkali metal and transition metal decorated germanene are energetically favorable which serves as good hydrogen storage systems.[32] Transition metal doping also increases the hydrogen storage capacity of two-dimensional carbon-nitride nano-sheets.[33] Transition metal (TM= Sc, Ti, V, Cr, Mn) decorated covalent triazine-based framework shows potential hydrogen storage efficacy without cluster formation.[34] To be suitable for hydrogen storage, system must fulfill specific criteria: (a) $H_2$ adsorption occurs in the molecular state rather than atomic form, (b) cluster formation is avoided, (c) metals have a low weight, (d) they meet the targets set by the Department of Energy (DOE), and (e) adsorption occurs preferably through a quasi-adsorption process. In our group, we have recently reported many important findings regarding of Li-decorated aromatic heterocyclic systems,[35-41] which meets the target set by DOE (2025). It has also been found that clustering of Ti on a C60 surface show the high efficiency of hydrogen storage.[42] Very few works are reported on transition metal decorated heterocyclic systems because cluster formation (some of the results show that) will occur in metal complexes which lower the $H_2$ storage capacity. It is also reported that metal-metal clusters are very good materials for $H_2$ storage and in such cases material can avoid the metal aggregation problem. On the other hand; in most of the cases, the adsorption process is either physical adsorption or chemical adsorption. Through a comprehensive review of different hydrogen storage systems, it becomes apparent that metals exhibit excellent hydrogen adsorption and storage abilities. Very recently, one interesting report published in the J. Am. Chem. Soc. (2023), where scientists have synthesized and established air-stable Cu(I) metal-organic framework and it found to be excellent hydrogen storage[43] material, and it encouraged us to design and theoretically investigate the storage efficiency of various five-member aromatic heterocyclic rings decorated with coin metals, such as Ag and Au. In this paper objective is to explore their efficacy as hydrogen storage materials by analyzing their different properties and also to explore which system is more suitable for this purpose.

## 2. Theory and computational details

In this study, the designed systems were optimized to their local minimum on the potential energy surface with zero imaginary frequency using the Gaussian 16w quantum chemistry program package.[44] Density functional theory (DFT)[45] within different functional such as CAM-B3LYP, M05, and various basis sets including 6-311+g (d, p), 6-31+G*, and LanL2DZ were employed. Bare rings were optimized at CAM-B3LYP/6-311+g(d, p). On the other hand we have optimized with and without $H_2$ trapped metal decorated model systems taken two basis set 6-31+G* (for ring atoms) and LanL2DZ (for metal atom) with M05 function for DFT calculation.

The stability and chemical reactivity of the Ag(I)/Au(I)-AH systems and their $H_2$-trapped complexes were analyzed using conceptual DFT (CDFT)-based descriptors such as hardness (η) and electrophilicity (ω), calculated with standard techniques[46-48] Basically hardness and electrophilicity are the global property of model systems. Increasing value of hardness indicate the increasing stability of the systems. On the other hand decreasing value of electrophilicity indicates decreasing reactivity of the systems.

The average binding energy ($E_b$) value of each Ag(I)/Au(I)-AH systems are determined using Eq-(1)

$$E_b = [E_{(host)+@nH2} - (E_{(host)+} + nE_{H2})]/n \quad (1)$$

Where $E_{(host)+@nH2}$, $E_{(host)+}$ and $E_{H2}$ represent the energy of the gradual $H_2$ trapped Ag(I)/Au(I)decorated heterocyclic system, only Ag(I)/Au(I)decorated heterocyclic system and energy of $H_2$ molecule. ‘n’ symbolizes the number of $H_2$ molecule trapped.

The average adsorption energy (Eads) of $H_2$ molecules is calculated using the Eq-(2)

$$E_{ads} = [(E_{(host)+} + nE_{H2}) - E_{[(host)+@nH2]}]/n \quad (2)$$

Where $E_{(host)+@nH2}$, $E_{(host)+}$ and $E_{H2}$ represent the energy of the gradual $H_2$ trapped Ag(I)/Au(I)decorated heterocyclic system, only the Ag(I)/Au(I)-decorated heterocyclic system and energy of $H_2$ molecule. 'n' symbolizes the number of $H_2$ molecule trapped.

We have also calculated nucleus independent chemical shift which is also called NICS. It is a very essential computational tools for the assessment of aromaticity. This method was invented by the late Paul V.R. Schleyer in the year 1996. Currently it is the most widely used method for determining and justifying aromaticity and antiaromaticity. At the time of calculation of NICS, a ghost atom, Bq is placed at the center of ring plane (denoted as NICS(0)) which is generally account for σ aomaticity and take another ghost atom Bq1 to 1Å above the center of the molecular plane(denoted as NICS(1)) which is denoted as π aromaticity. If the NICS(0) and NICS(1) value of a ring become negative then the systems are both σ and π aromatic in nature but if the value is positive then the systems becomes antiaromatic. We have calculated the NICS (0) and NICS(1) (nucleus independent chemical shift) values to check the pattern of aromaticity and stability of the metal decorated AH-systems as well as for Ag(I)/Au(I)-AH-systems.[49-51]

Gravimetric wt% was calculated to determine the hydrogen storage potential of the materials by the Eq-(3)

$$\text{Gravimetric wt\%}=\frac{Molecular\ weight\ of\ trapped\ H_2}{Molecular\ weight\ of\ (host)+@nH2}\times 100 \quad (3)$$

To investigate the spontaneity of the hydrogen adsorption process, Gibbs free energy change with temperature was calculated using the following Eq- (4):

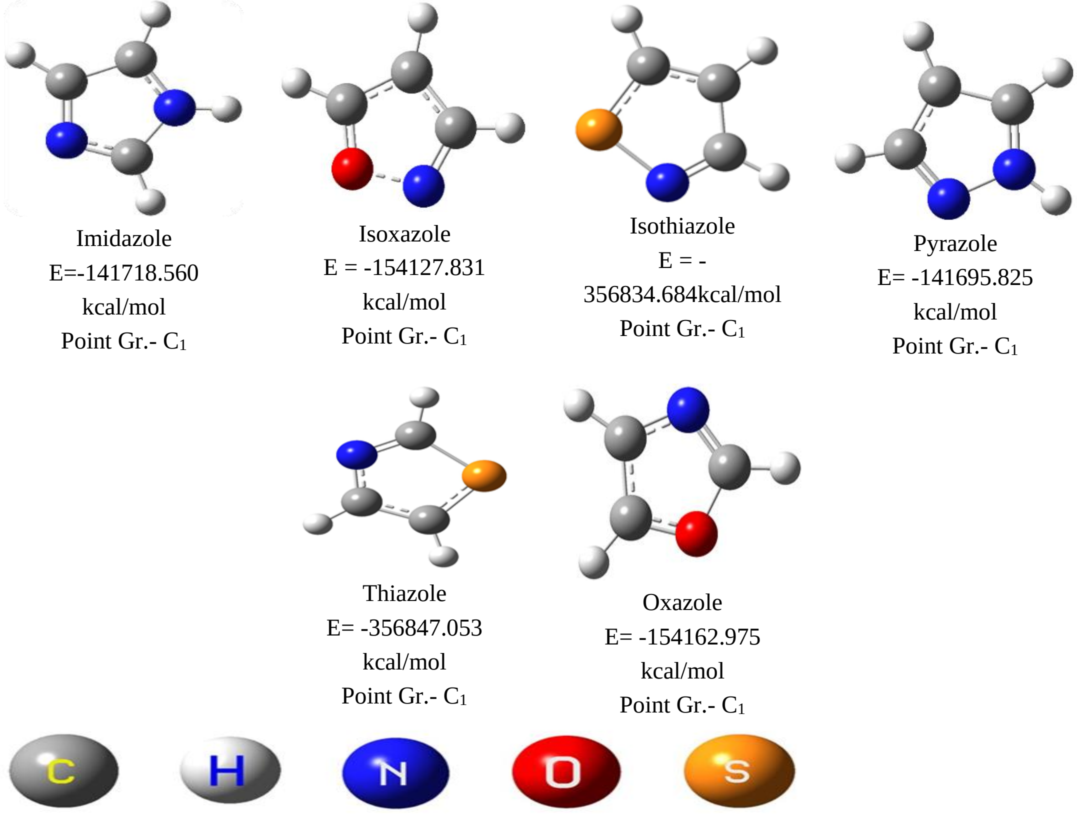
$$\Delta G_{(host@nH2)+}=[G_{(host@nH2)+}-G_{(host)+}-nG_{H2}] \quad (4)$$

To analyze the bonding nature in the different systems, topological analysis was performed using the Multiwfn package.[52] The shaded surface map and electron localization function (ELF) were calculated to provide information about the localized electron.[53] Non-covalent interaction (NCI) analysis was conducted to identify non-covalent interactions in the Ag(I)/Au(I)-AH@n$H_2$ systems. The NCI results were generated using the Multiwfn software package.[54] Atom centered density matrix propagation (ADMP)[55-57] study has been carried out to know about the kinetic stability of model systems. Partial Density of States (PDOS) can be generated for different parts of the $H_2$-trapped metal-decorated complexes to identify the contribution of trapped $H_2$, decorated metal, and aromatic heterocyclic ring to the frontier molecular orbitals of the complexes.[58]

## 3. Result and discussion

### 3.1 Stability, and reactivity of different five-member heterocyclic systems

The study investigated the ground state geometry of various five-member AH systems, including imidazole, pyrazole, isoxazole, isothiazole, thiazole, and oxazole (Fig. 1). From the


Imidazole
E=-141718.560
kcal/mol
Point Gr.- $C_1$

Isoxazole
E = -154127.831
kcal/mol
Point Gr.- $C_1$

Isothiazole
E = -
356834.684kcal/mol
Point Gr.- $C_1$

Pyrazole
E= -141695.825
kcal/mol
Point Gr.- $C_1$

Thiazole
E= -356847.053
kcal/mol
Point Gr.- $C_1$

Oxazole
E= -154162.975
kcal/mol
Point Gr.- $C_1$

**Fig. 1** Optimized geometries and energy of five-member AH-systems at the CAM-B3LYP/6-311+g (d,p) level of theory.

**Table 1.** Hardness (η);(kcal/mol), Electrophilicity (ω);(kcal/mol) and NICS(0) and NICS (1) of different five-member AH-systems. Hardness/atom & Electrophilicity/atom are in brackets.

| Heterocyclic System | η (kcal/mol) | ω (kcal/mol) | NICS(0) (ppm) | NICS(1) (ppm) |
|---|---|---|---|---|
| Imidazole | 225.593(25.065) | 130.763(14.529) | -12.679 | -10.475 |
| Isoxazole | 228.063(28.507) | 167.646(20.955) | -11.924 | -10.503 |
| Isothiazole | 221.837(27.729) | 151.734(18.966) | -12.883 | -11.093 |
| Pyrazole | 238.209(26.467) | 132.364(14.707) | -13.279 | -11.249 |
| Thiazole | 199.469(24.933) | 167.185(20.898) | -12.417 | -10.983 |
| Oxazole | 236.365(29.545) | 151.273(18.909) | -11.063 | -9.617 |

DFT calculation It was found that pyrazole exhibited the highest hardness value. As the hardness indicate the stability of the system so pyrazole is the most stable system, while isoxazole had a high electrophilicity value, suggesting it as the most reactive among the investigated systems (Table 1). All of the AH systems displayed negative NICS (0) and NICS (1) values, confirming their aromatic nature.

### 3.2 Stability, reactivity, aromaticity, and NBO of Ag(I)/Au(I) decorated differently studied five-membered aromatic heterocyclic systems

Metal-decorated systems [Ag(I)/Au(I)-AH] were created for $H_2$ adsorption by placing metal ions (Ag(I)/Au(I)) on the side and top of the five-member heterocyclic ring. After optimization, it was observed that the metal ions were predominantly bonded with the ring through the nitrogen (N) center. In case of oxazole, Ag(I)/Au(I) attached to both nitrogen (N) and oxygen (O) centers (Fig. 2), but the N-Ag(I)/Au(I) bonding was found to be the more stable isomer. Similarly, for isoxazole, isothiazole, and thiazole, Ag(I)/Au(I) primarily attached to the ring through the N atom rather than other ring electronegative atoms (O, S). The optimized structures of the metal decorated AH systems are provided in Fig. 2.

To assess the stability of the metal-decorated AH systems, various CDFT parameters such as hardness (η), electrophilicity (ω), NICS (0), NICS (1), and NBO (natural bond orbital) values were calculated (Table 2). The metal-decorated isoxazole system exhibited the highest hardness value, indicating greater stability, while Ag(I)-isoxazole system indicate higher hardness value than Au(I)-isoxazole system. The Ag(I)/Au(I)-decorated oxazole-O systems has shown higher electrophilicity, suggesting higher reactivity of the systems. On the basis of hardness value of all the Ag(I)/Au(I) decorated system, Ag(I)-decorated systems give higher stability (hardness range:73.317kcal/mol to 114.902 kcal/mol) than Au(I) decorated systems (hardness range: 54.298 kcal/mol to 103.883 kcal/mol). The negative NICS(0) and NICS(1) values confirmed aromatic nature of the investigated systems. Additionally, positive NBO charges on Ag or Au indicated the presence of an electric field, suggesting preferential $H_2$ adsorption on a metal site, enabling greater adsorption of up to five $H_2$ molecules. From Table 2, it is also

**Table 2.** Hardness (η);(kcal/mol), Electrophilicity (ω);(kcal/mol), NICS (0) and NICS (1) (ppm) and NBO charges on metal center of $Ag^+/Au^+$-decorated systems. Hardness/atom and Electrophilicity/atom values are in brackets.

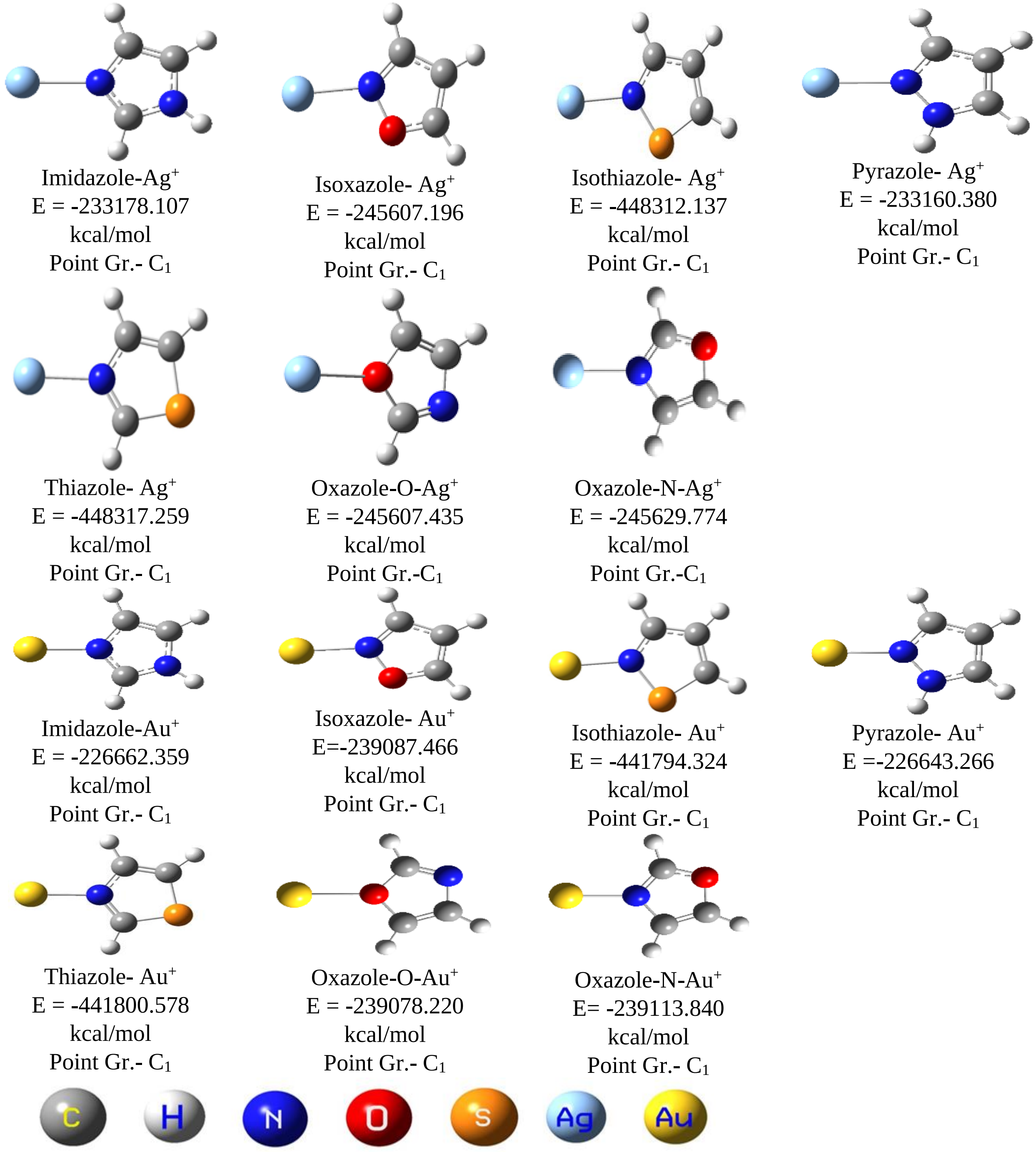
| System decorated with Ag+/Au+ | η (kcal/mol) | ω (kcal/mol) | NICS(0) (ppm) | NICS(1) (ppm) | NBO |
|---|---|---|---|---|---|
| Imidazole-$Ag^+$ | 106.688 (10.669) | 207.877 (20.788) | -13.063 | -11.149 | 0.909 |
| Isoxazole-$Ag^+$ | 114.902 (12.767) | 225.203 (25.023) | -11.753 | -10.984 | 0.931 |
| Isothiazole-$Ag^+$ | 105.609 (11.734) | 232.722 (25.858) | -12.230 | -11.798 | 0.924 |
| Pyrazole-$Ag^+$ | 101.932 (10.193) | 237.027 (23.703) | -13.161 | -11.868 | 0.911 |
| Thiazole-$Ag^+$ | 101.561 (11.285) | 235.635 (26.182) | -12.228 | -11.826 | 0.909 |
| Oxazole-O-$Ag^+$ | 73.317(8.146) | 362.944 (40.327) | -11.197 | -9.748 | 0.963 |
| Oxazole-N-$Ag^+$ | 103.425 (11.492) | 239.604 (26.603) | -11.918 | -10.458 | 0.925 |
| Imidazole-$Au^+$ | 89.840(8.984) | 285.206 (28.521) | -12.937 | -11.296 | 0.787 |
| Isoxazole-$Au^+$ | 103.883 (11.543) | 285.672 (31.741) | -11.728 | -10.899 | 0.831 |
| Isothiazole-$Au^+$ | 97.025(10.781) | 289.140 (32.127) | -12.051 | -11.580 | 0.813 |
| Pyrazole-$Au^+$ | 93.454(9.345) | 296.042 (29.604) | -13.077 | -11.696 | 0.793 |
| Thiazole-$Au^+$ | 94.778(10.531) | 289.366 (32.152) | -12.224 | -11.725 | 0.788 |

| | | | | | |
|---|---|---|---|---|---|
| Oxazole-O-$Au^+$ | 54.298(6.033) | 577.005 (64.112) | -11.296 | -9.616 | 0.897 |
| Oxazole-N-$Au^+$ | 95.487(10.610) | 299.025 (33.225) | -11.850 | -10.359 | 0.815 |

observed that, the grater NBO charges on Ag(I) rather than Au(I), indicates grater adsorption of $H_2$-molecule on Ag(I)decorated systems.

### 3.3 Stability, reactivity, aromaticity, and NBO charges of highest no. of $H_2$ trapped Ag(I)/Au(I)- decorated different five-membered aromatic heterocyclic systems

The study examined the $H_2$ trapping capacity of the metal-decorated AH systems, revealing that all systems could trap a maximum of five $H_2$ molecules. All the optimized structures of the maximum $H_2$ trapped system [Ag(I)/Au(I)-AH@5$H_2$] have been given in Fig. 3 and consequently other lower no. $H_2$ trapped systems (1-4) have been shown in Fig. S1.


Imidazole-$Ag^+$
E = -233178.107 kcal/mol
Point Gr.- $C_1$

Isoxazole- $Ag^+$
E = -245607.196 kcal/mol
Point Gr.- $C_1$

Isothiazole- $Ag^+$
E = -448312.137 kcal/mol
Point Gr.- $C_1$

Pyrazole- $Ag^+$
E = -233160.380 kcal/mol
Point Gr.- $C_1$

Thiazole- $Ag^+$
E = -448317.259 kcal/mol
Point Gr.- $C_1$

Oxazole-O-$Ag^+$
E = -245607.435 kcal/mol
Point Gr.-$C_1$

Oxazole-N-$Ag^+$
E = -245629.774 kcal/mol
Point Gr.-$C_1$

Imidazole-$Au^+$
E = -226662.359 kcal/mol
Point Gr.- $C_1$

Isoxazole- $Au^+$
E=-239087.466 kcal/mol
Point Gr.- $C_1$

Isothiazole- $Au^+$
E = -441794.324 kcal/mol
Point Gr.- $C_1$

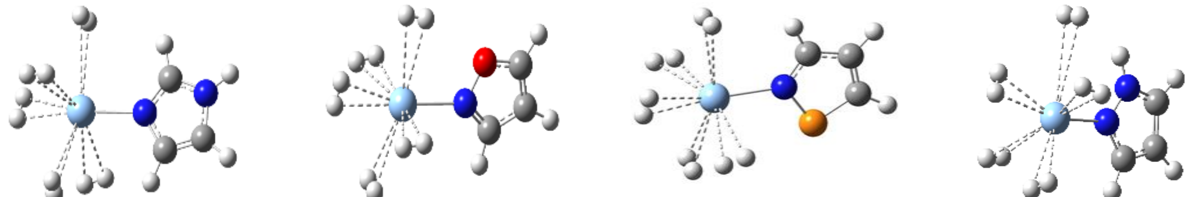
Pyrazole- $Au^+$
E =-226643.266 kcal/mol
Point Gr.- $C_1$

Thiazole- $Au^+$
E = -441800.578 kcal/mol
Point Gr.- $C_1$

Oxazole-O-$Au^+$
E = -239078.220 kcal/mol
Point Gr.- $C_1$

Oxazole-N-$Au^+$
E= -239113.840 kcal/mol
Point Gr.- $C_1$

Fig. 2 Optimized geometries and energy of $Ag^+$ and $Au^+$ decorated different five-membered AH systems at the M05/ LanL2DZ (for $Ag^+$ and $Au^+$) and 6-31+G* (for ring atom) level of theory.

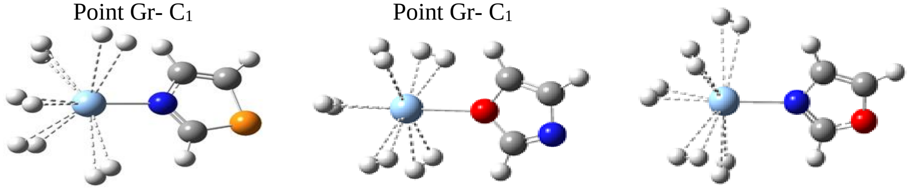


Imidazole-$Ag^+$@ $5H_2$
E = -236842.977
kcal/mol
Point Gr- $C_1$

Isoxazole-$Ag^+$@ $5H_2$
E = -249273.293
kcal/mol
Point Gr- $C_1$

Isothiazole-$Ag^+$@ $5H_2$
E = -451977.767
kcal/mol
Point Gr- $C_1$

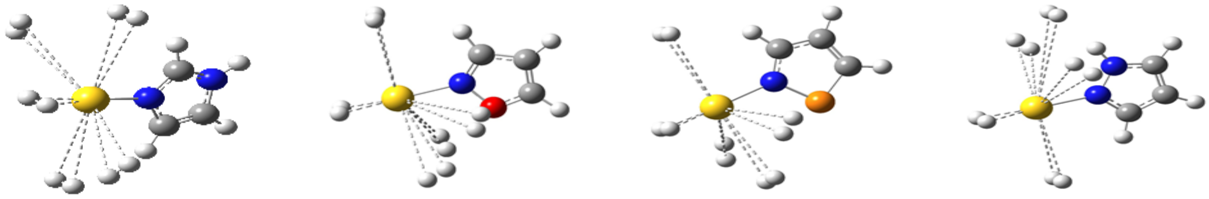
Pyrazole-$Ag^+$@ $5H_2$
E = -236826.082
kcal/mol
Point Gr- $C_1$



Thiazole-$Ag^+$@ $5H_2$
E = -451982.693
kcal/mol
Point Gr- $C_1$

Oxazole-O-$Ag^+$@ $5H_2$
E = -249276.956
kcal/mol
Point Gr.-$C_1$

Oxazole-N-$Ag^+$@ $5H_2$
E = -249297.404
kcal/mol
Point Gr-$C_1$

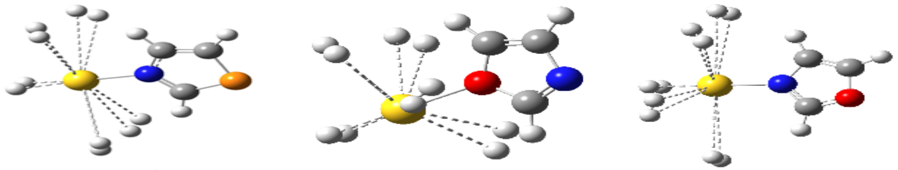


Imidazole-$Au^+$@ $5H_2$
E = -230334.146
kcal/mol
Point Gr- $C_1$

Isoxazole-$Au^+$@ $5H_2$
E = -242760.075
kcal/mol
Point Gr- $C_1$

Isothiazole-$Au^+$@ $5H_2$
E = -445466.233
kcal/mol
Point Gr- $C_1$

Pyrazole-$Au^+$@ $5H_2$
E = -230316.299
kcal/mol
Point Gr- $C_1$



Thiazole-$Au^+$@ $5H_2$
E = -445472.405
kcal/mol
Point Gr- $C_1$

Oxazole-O-$Au^+$@ $5H_2$
E = -242751.230
kcal/mol
Point Gr.-$C_1$

Oxazole-N-$Au^+$@ $5H_2$
E = -242786.330
kcal/mol
Point Gr-$C_1$

**Fig. 3** Optimized geometries and energy of highest no. of $H_2$ trapped $Ag^+$and $Au^+$-AH systems at the M05/ LanL2DZ (for $Ag^+$ and $Au^+$) and 6-31+G* (for ring atom) level of theory.

From Table 3, It is interestingly observed that Isoxazole-Ag+@$5H_2$ has the higher hardness value among other Ag(I) decorated system. Also it has observed that Isoxazole-$Au^+$@$5H_2$ system has the higher hardness value among other Au(I) decorated system. So, among Ag(I)-decorated system, Isoxazole-$Ag^+$@$5H_2$ system is the most sable systems. In other side, among Au(I)decorated system, Isoxazole-$Au^+$@$5H_2$ is most stable one. Between $H_2$ trapped Ag(I) and Au(I)decorated system, Au(I)-decorated systems exhibit higher stability (hardness range: 105.784 kcal/mol to 162.536 kcal/mol) than Ag(I)-decorated system (hardness range: 113.076 kcal/mol to 152.433 kcal/mol). If we have observed

**Table 3.** Hardness (η);(kcal/mol), Electrophilicity (ω);(kcal/mol), NICS(0) and NICS (1) and NBO charges on metal center of highest no. of $H_2$ trapped $Ag^+$/$Au^+$-AH systems. Hardness/atom & Electrophilicity/atom are in brackets.

| System decorated with $M^+$ | η(kcal/mol) | ω(kcal/mol) | NICS(0) (ppm) | NICS(1) (ppm) | NBO |
|---|---|---|---|---|---|
| Imidazole-$Ag^+$ @$5H_2$ | 133.514(6.676) | 130.262(6.513) | -12.964 | -11.690 | 0.764 |
| Isoxazole-$Ag^+$@$5H_2$ | 152.433(8.023) | 133.942(7.050) | -11.623 | -11.008 | 0.753 |
| Isothiazole-$Ag^+$@$5H_2$ | 141.860(7.466) | 137.670(7.246) | -12.115 | -12.056 | 0.807 |
| Pyrazole-$Ag^+$@$5H_2$ | 138.176(6.909) | 138.301(6.915) | -13.036 | -12.701 | 0.760 |
| Thiazole-$Ag^+$@$5H_2$ | 138.076(7.267) | 137.080(7.215) | -12.127 | -12.011 | 0.762 |
| Oxazole-O-$Ag^+$@$5H_2$ | 113.076(5.951) | 181.032(9.528) | -11.248 | -9.918 | 0.773 |
| Oxazole-N-$Ag^+$@$5H_2$ | 140.448(7.392) | 139.368(7.335) | -11.835 | -10.540 | 0.768 |
| Imidazole-$Au^+$ @$5H_2$ | 147.758(7.388) | 125.382(6.269) | -12.889 | -12.070 | 0.629 |
| Isoxazole-$Au^+$@$5H_2$ | 162.536(8.555) | 136.466(7.182) | -15.859 | -13.515 | 0.656 |
| Isothiazole-$Au^+$@$5H_2$ | 147.670(7.772) | 145.124(7.638) | -11.933 | -11.618 | 0.638 |
| Pyrazole-$Au^+$@$5H_2$ | 151.824(7.591) | 133.308(6.665) | -13.016 | -11.800 | 0.634 |
| Thiazole-$Au^+$@$5H_2$ | 148.806(7.832) | 137.061(7.214) | -12.089 | -11.577 | 0.634 |
| Oxazole-O-$Au^+$@$5H_2$ | 105.784(5.568) | 228.668(12.035) | -11.525 | -14.717 | 0.724 |
| Oxazole-N-$Au^+$@$5H_2$ | 153.550(8.082) | 136.726(7.196) | -11.808 | -10.525 | 0.643 |

the electrophilicity value of the different $H_2$ trapped metal decorated systems, then we have noticed that $H_2$ trapped Au(I) decorated imidazole system has become less reactive among other Au(I) decorated systems. On the other hand $H_2$ trapped Ag(I) decorated Imidazole system has shown less reactivity among other Ag(I) decorated systems. Between Ag(I) and Au(I) decorated systems, Ag(I) decorated model systems show the better results (electrophilicity range:130.262kcal/mol to181.032 kcal/mol) than Au(I) decorated model systems (electrophilicity range:125.382 kcal/mol to 228.668 kcal/mol).The hardness and electrophilicity values generally increased and decreased, respectively, as the number of trapped $H_2$ molecules increased, indicating chemical stability.[59,60] Fig. S2 shows the graphical representation of hardness and electrophilicity values with gradual trapping of $H_2$ molecules of Ag(I)/Au(I)-AH systems. The hardness & electrophilicity value of different studied systems with gradual trapping of $H_2$ has been shown in Table S1. From Table 3, it is also observed that, at $H_2$-trapping condition, all the metal decorated AH- systems show negative NICS value, indicating their good aromatic nature. The adsorption capacity was evaluated through the average adsorption energy ($E_{ads}$), which decreased with the gradual addition of $H_2$ molecules due to steric hindrance (Fig. 4). The value of average adsorption energy for all the $H_2$ trapped complexes are in between 0.11 eV/$H_2$ to 0.69 eV/$H_2$ (2.536 kcal/mol to 15.911 kcal/mol), which is intermediate of physisorption and chemisorption state. Thermodynamically, the adsorption process is spontaneous. The studied systems exhibited negative NICS(0) and NICS(1) values, indicating their good σ and π aromatic nature.

It is also observed that the energy of systems decreases at different stages like bare ring, metal (Ag (I)/Au (I)) decorated ring and $H_2$-trapped metal (Ag (I)/Au(I)) decorated ring. From Table 4 and 5, it has shown that the energy become decreases from bare ring to metal decorated systems and lastly it comes to the lower value in case of $H_2$ trapped metal decorated system. This study has indicated the stability of our modeled systems.

We have also studied the NBO charge calculation on metal center with gradual trapping of $H_2$ molecules. This study has graphically represented in Fig. 5. When we go through without

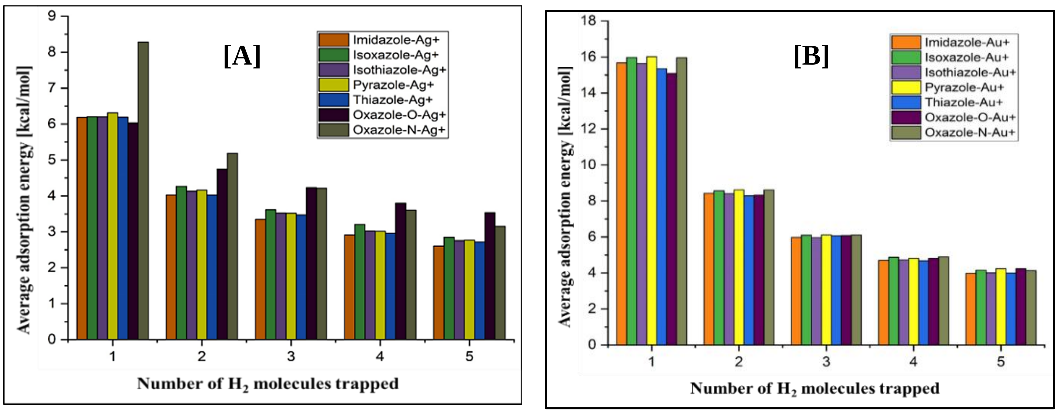


**Fig. 4** A plot of Average adsorption energy [kcal/mol] Vs. no. of $H_2$ molecules trapped with $Ag^+$[A]and $Au^+$[B]-decorated different five-membered aromatic heterocyclic systems.

**Table 4.** Energy of the different systems at different stages like bare ring, metal [Ag(I)] decorated ring and $H_2$- trapped metal [Ag(I)] decorated ring at optimized condition.

| Systems | Energy (kcal/mol) | | |
|---|---|---|---|
| | Bare ring(kcal/mol) | Metal (Ag) decorated ring(kcal/mol) | $H_2$ trapped metal (Ag) decorated ring (kcal/mol) |
| Imidazole | -141718.560 | -233178.107 | -236842.977 |
| Isoxazole | -154127.831 | -245607.196 | -249273.293 |
| Isothiazole | -356834.684 | -448312.137 | -451977.767 |
| Pyrazole | -141695.825 | -233160.38 | -236826.082 |
| Thiazole | -356847.053 | -448317.259 | -451982.693 |
| Oxazole-O | -154162.975 | -245607.435 | -249276.956 |
| Oxazole-N | -154162.975 | -245629.774 | -249297.404 |

**Table 5.** Energy of the different systems at different stages like bare ring, metal [Au(I)] decorated ring and $H_2$- trapped metal [Au(I)] decorated ring at optimized condition.

| Systems | Energy (kcal/mol) | | |
|---|---|---|---|
| | Bare ring (kcal/mol) | metal (Au) decorated ring (kcal/mol) | $H_2$ trapped metal (Au) decorated ring (kcal/mol) |
| Imidazole | -141718.560 | -226662.359 | -230334.146 |
| Isoxazole | -154127.831 | -239087.466 | -242760.075 |
| Isothiazole | -356834.684 | -441794.324 | -445466.233 |
| Pyrazole | -141695.825 | -226643.266 | -230316.299 |
| Thiazole | -356847.053 | -441800.578 | -445472.405 |
| Oxazole-O | -154162.975 | -239078.221 | -242751.230 |
| Oxazole-N | -154162.975 | -239113.840 | -242786.330 |

$H_2$trapped and with $H_2$-trapped system, the NBO charges on the metal center decreases (from Table 2 to 3) which clearly indicate that $H_2$ adsorption takes places at the metal center. The gravimetric weight percentages of the $H_2$-trapped metal-decorated AH systems ranged from 3.66 to 5.45 for the highest number of trapped $H_2$ molecules (Table S2). Although these values were considered moderate compared to the U.S. Department of Energy (DOE) goal, the studied systems were still considered promising for $H_2$ storage. Among all the investigated systems, imidazole and pyrazole exhibited better results. The graphical representation of gravimetric wt% of maximum $H_2$ trapped Ag(I)/Au(I)-AH systems have been shown in Fig. S3.

## 3.4 Binding nature

### 3.4.1 Adsorption of hydrogen in molecular form

Table S4 shows that the Ag(I)/Au(I) to $H_2$ molecule distances in all the maximum $H_2$ trapped systems fall within the favorable range of 1.895 Å to 3.944 Å, which is suitable for a $H_2$ storage system. The H-H distances in all the trapped $H_2$ molecules range from 0.801 Å to 0.741 Å, similar to the distance in isolated $H_2$ molecules (0.743 Å).[61] Details of other systems can be found in Table S3.

### 3.4.2 Electron localization function (ELF)

To understand the binding nature between the ring and metal as well as metal and $H_2$ molecules, a detailed investigation was conducted using shaded surface maps and electron localization function (ELF) of the $H_2$ trapped Ag(I)/Au(I)-decorated systems. Fig. S4, S5, S6, and S7 display the shaded surface maps and ELF of $H_2$ trapped metal decorated studied systems. From ELF study in Fig. 6, it is clearly established that a non-covalent type interaction occurred between ring nitrogen (N) and metal center, as well as between metal center and molecular $H_2$ because between metal to ring and ring to molecular $H_2$, there is approximately zero electron density.

### 3.4.3 Non-covalent interaction (NCI)

The non-covalent interaction (NCI) method, also known as the reduced density gradient (RDG) method, is widely used for the analysis of weak interactions. NCI analysis plays a crucial role in identifying different types of interactions. In the NCI plot, the reduced density gradient (RDG) and the sign $(\lambda_2)\rho$ are plotted to represent the precise areas of interaction. The sign $(\lambda_2)\rho$ is used to differentiate between strong and weak non-

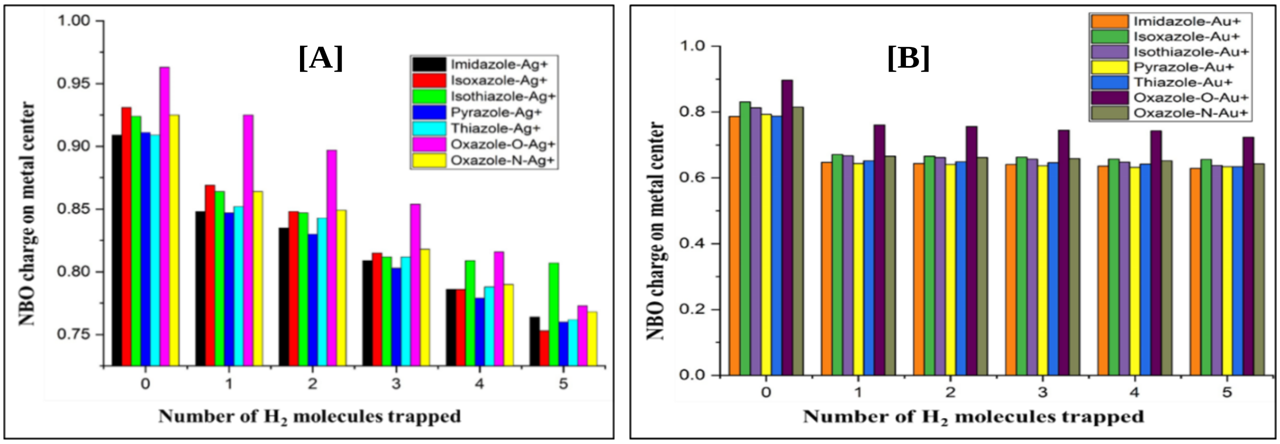
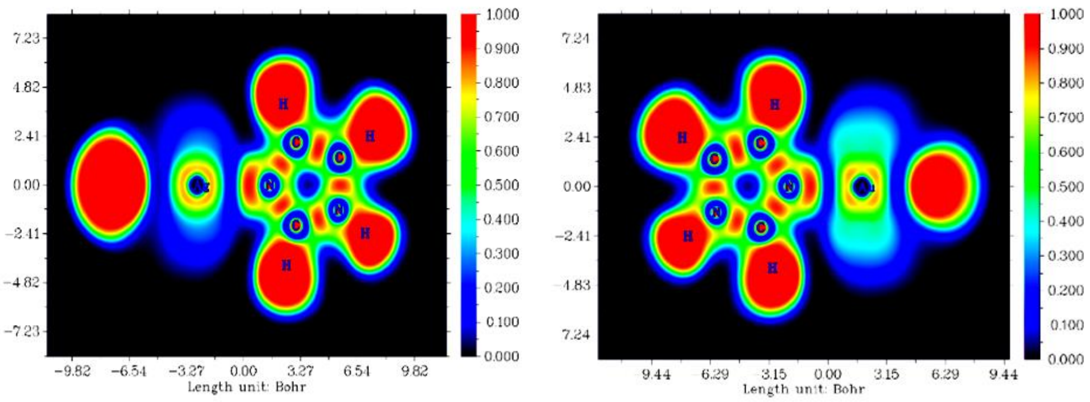


**Fig. 5** A plot of NBO charge on metal center Vs. no. of $H_2$ molecules trapped with $Ag^+$ [A]and $Au^+$[B]-decorated different five-membered aromatic heterocyclic systems.



[A] [B]

**Fig. 6** The plot of the ELF of the $H_2$ trapped Ag(I)[A]/Au(I)[B] decorated Imidazole systems.

covalent interactions. In the NCI plot, the sign $(\lambda_2)\rho$ is placed on the X-axis, while the RDGs are displayed on the Y-axis. By using the Multiwfn software package, an interaction chart can be generated (Fig. 7) to visualize the areas in the NCI plot, where weak interactions occur.

The NCI plot of the Imidazole-Ag(I) system have been generated. It is observed that spikes appear in the zone where sign $(\lambda_2)\rho$ is approximately equal to 0 after the adsorption of the $H_2$ molecule (Fig. 8[B]). However, in the system without $H_2$ molecule trapping, no spikes are observed in the sign $(\lambda_2)\rho \approx 0$ zone in the NCI plot (Fig. 8[A]), which is clearly explain by the color chart(Fig. 7) This indicates the presence of weak interactions between the metal and molecular $H_2$, which satisfy the weak adsorption between them and favors the quasi-sorption process. The NCI plot of the other studied systems is shown in Fig. S8.

### 3.4.4 Partial density of state (PDOS)

To obtain a detailed analysis of the contribution pattern of the hydrogen molecule, metal ion, and the different aromatic heterocyclic rings towards the formation of frontier molecular orbitals (FMOs), we performed density of state (DOS) and partial density of state (PDOS) calculations for all the studied systems, as shown in Fig. 9.

Figure 9 presents the DOS and PDOS of the hydrogen-trapped Imidazole-Ag(I)/Au(I)-AH systems, indicating the percentage contribution of H, metal ion, and aromatic heterocyclic systems towards the frontier molecular orbitals (FMOs). We divided the entire system into three different parts: trapped $H_2$, metal ion, and aromatic heterocyclic ring, and analyzed their respective contributions to the FMOs. From the DOS and PDOS values of the different systems, it can be concluded that all the fragments of the different systems significantly contribute to the formation of the frontier molecular orbitals (FMOs). The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of the complexes are formed from the contributions of the aromatic heterocyclic ring, metal ion, and trapped molecular hydrogen, respectively.[62,63] The PDOS plots for other systems can be found in the supporting information, Fig. S9.

### 3.5 Effect of temperature on $H_2$ adsorption

To investigate the spontaneity of the reversible hydrogen adsorption-desorption process, we calculated the gibbs free energy change ($\Delta G$) for the Imidazole system (with the highest gravimetric wt%). The results are shown in Fig. 10. It is found that at 298K, some systems exhibit a negative value of gibbs free energy, and we have wanted to investigate the specific temperature at which all the systems show a negative $\Delta G$ value.

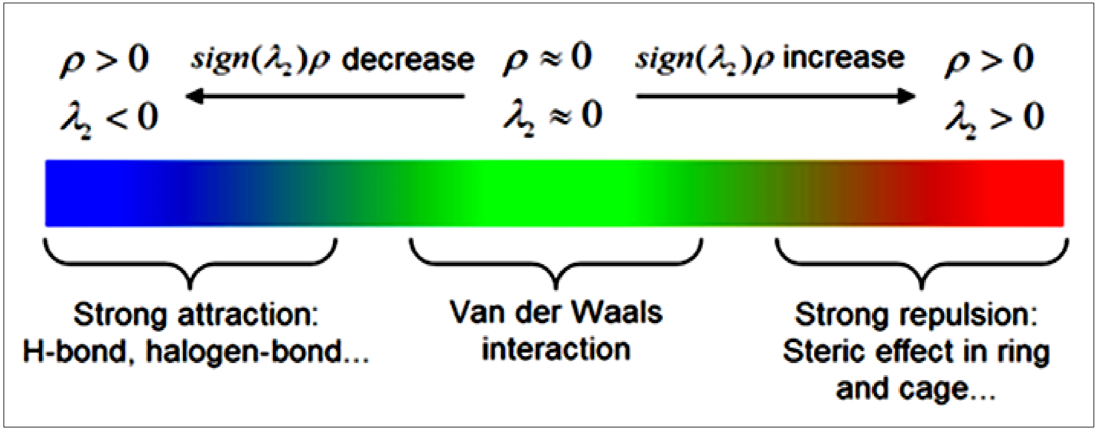


**Fig. 7** Chart for viewing different interaction zone correspond to sign $(\lambda_2)\rho$ value in NCI plot.

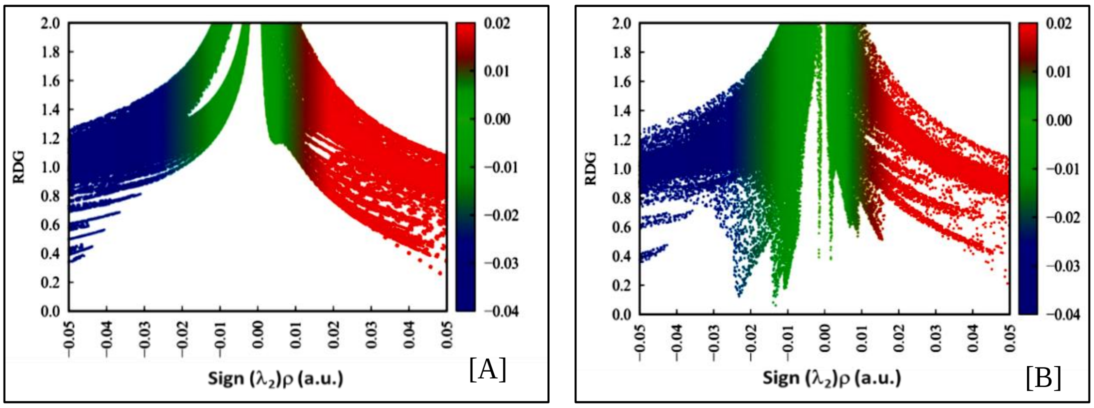
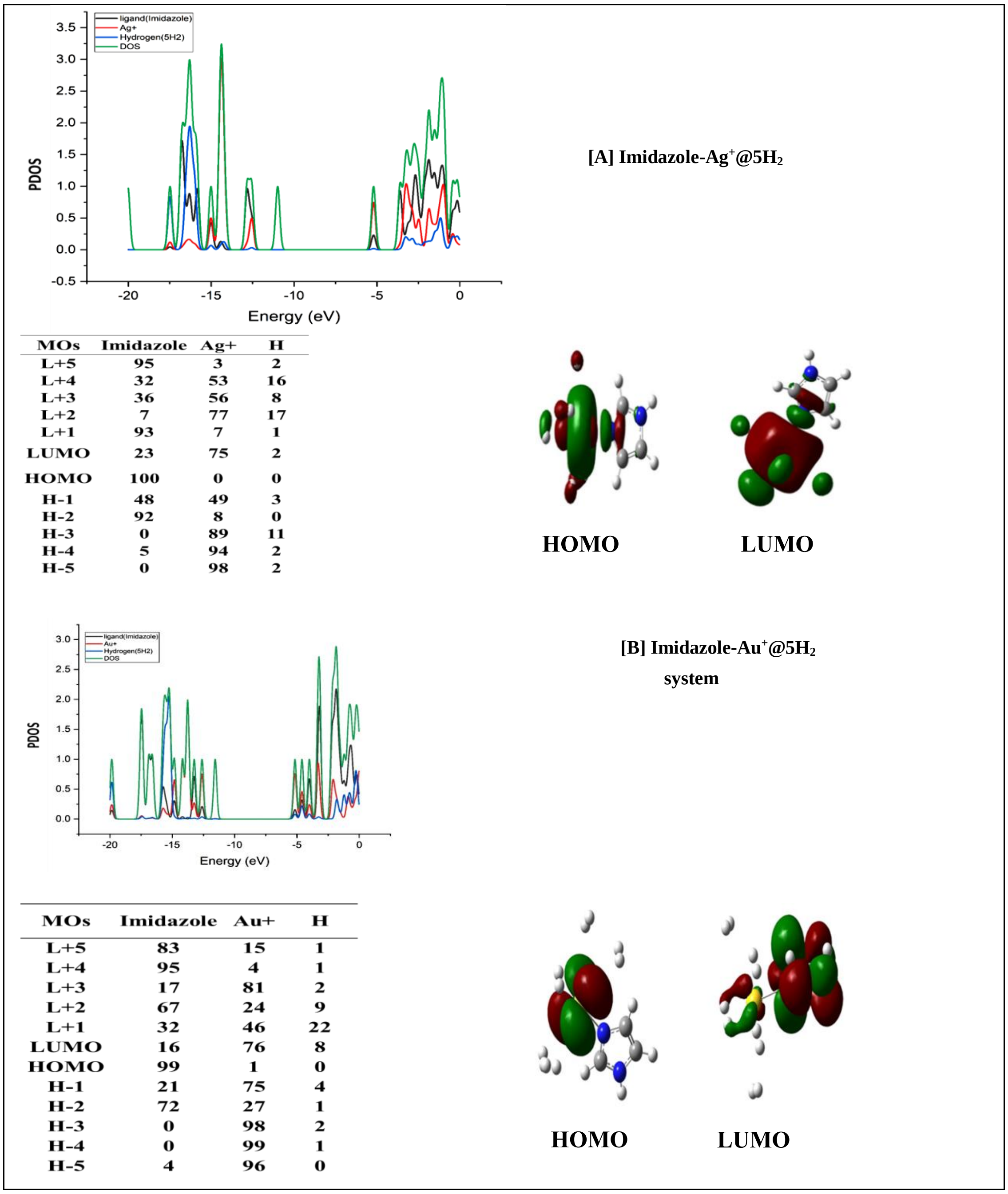


**Fig. 8** NCI plot of Imidazole-Ag$^+$system without trapping of molecular H$_2$[A] and trapped with molecular H$_2$ [B].



| MOs | Imidazole | Ag+ | H |
|---|---|---|---|
| L+5 | 95 | 3 | 2 |
| L+4 | 32 | 53 | 16 |
| L+3 | 36 | 56 | 8 |
| L+2 | 7 | 77 | 17 |
| L+1 | 93 | 7 | 1 |
| LUMO | 23 | 75 | 2 |
| HOMO | 100 | 0 | 0 |
| H-1 | 48 | 49 | 3 |
| H-2 | 92 | 8 | 0 |
| H-3 | 0 | 89 | 11 |
| H-4 | 5 | 94 | 2 |
| H-5 | 0 | 98 | 2 |

| MOs | Imidazole | Au+ | H |
|---|---|---|---|
| L+5 | 83 | 15 | 1 |
| L+4 | 95 | 4 | 1 |
| L+3 | 17 | 81 | 2 |
| L+2 | 67 | 24 | 9 |
| L+1 | 32 | 46 | 22 |
| LUMO | 16 | 76 | 8 |
| HOMO | 99 | 1 | 0 |
| H-1 | 21 | 75 | 4 |
| H-2 | 72 | 27 | 1 |
| H-3 | 0 | 98 | 2 |
| H-4 | 0 | 99 | 1 |
| H-5 | 4 | 96 | 0 |

**Fig. 9** DOS & PDOS of hydrogen trapped [A] Imidazole-Ag$^+$-AH and [B] Imidazole-Au$^+$-AH systems with % of contribution of trapped H$_2$, metal ion & aromatic heterocyclic systems towards FMOs with their HOMO & LUMO picture.

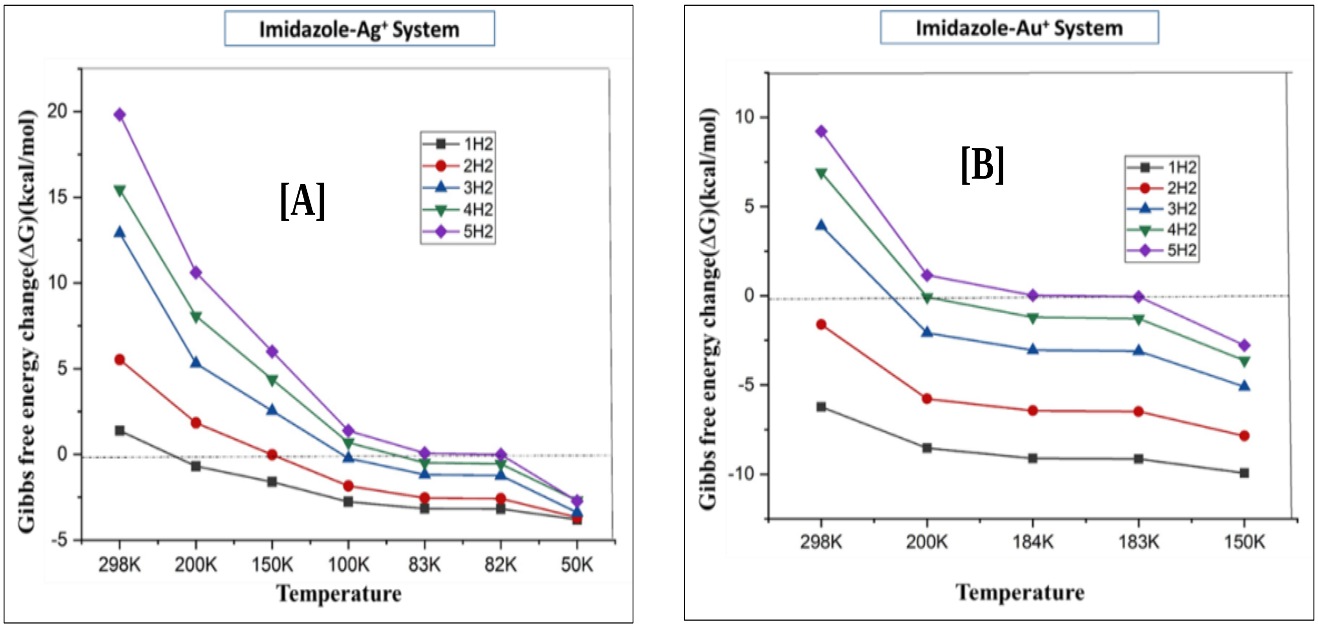


**Fig. 10** Gibbs free energy change (kcal/mol) Vs. the number of $H_2$ molecules trapped with the $Ag^+/Au^+$-decorated Imidazole systems at different temperature.

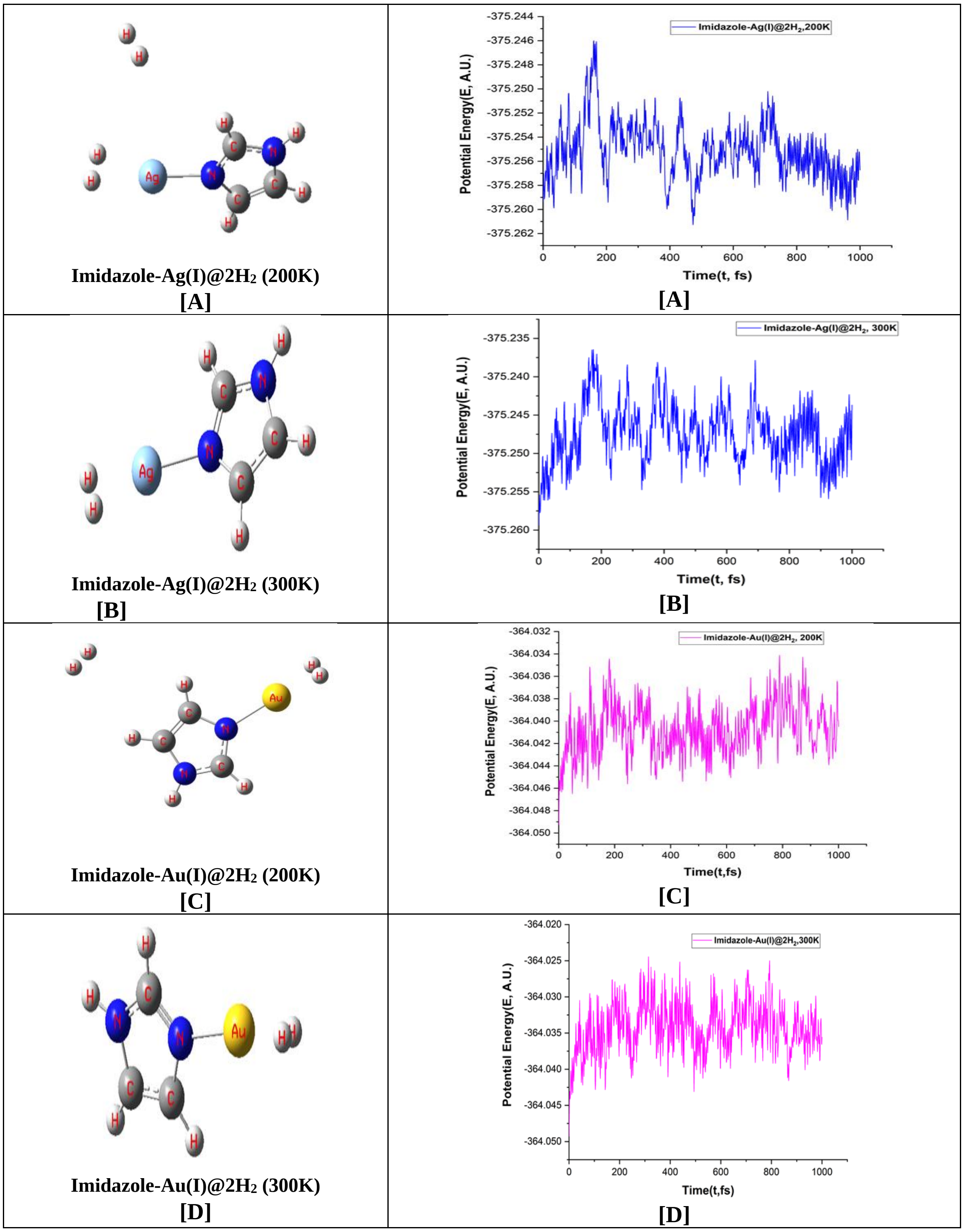
Therefore, we decreased the temperature from 298K to 200K and later to 150K. As we considered different AH systems decorated with Ag(I)/Au(I), an investigation has performed to identify the the temperature at which a particular system exhibits a negative ΔG value. It was observed that at 82K and 183K, the Imidazole-Ag(I)@5$H_2$ and Imidazole-Au(I)@5$H_2$ systems, respectively, displayed a negative value of gibbs free energy (Fig. 10). All the systems decorated with Au(I) show the higher temperature for negative ΔG value but on the other hand Ag(I)decorated systems show very lower temperature for this purpose. The results for other systems are shown in Fig. S10, and Table S5. This study has indicated that Au(I) decorated systems show the batter temperature than Ag(I)-decorated systems for reversible hydrogen adsorption-desorption process.

### 3.6 Atom centered density matrix propagation (ADMP) study

As we all know that Ag(I) compounds are easily reduced in $H_2$ occlusion, so we want to investigate the condition of Ag(I)-decorated model system upon $H_2$ adsorption. Due to this reason, atom centered density matrix propagation (ADMP) study has been carried out at two different temperatures (200 K & 300 K) to investigate the kinetic stability of the Ag(I)/Au(I)AH@n$H_2$ systems (AH = Imidazole) (n=2). Here we have selected imidazole complex due to highest gravimetric wt % among others. As a consequence, we used a 1 fs time interval and a velocity scaling thermostat to keep the temperature constant throughout the simulation. The graphs of potential energy (E, A.U.) vs. time (t, fs) have been given in Fig. 11. From Fig. 11, it is clear that; complexes can retain H2 molecules at lower temperature up to 1000 fs. But the desorption starts when the temperature is increased. Lastly at room temperature at least one molecular H2 is attached to the systems. From this it can be concluded that both metal decorated model systems survive upon H2 adsorption even at room temperature.

## 4. Conclusion

In this study, the hydrogen storage capacity of different heterocyclic aromatic systems (Imidazole, Isoxazole, Isothiazole, Pyrazole, Thiazole & Oxazole) decorated with Ag(I)/Au(I) were analyzed. The NICS values confirmed the aromatic nature of the studied systems prevail after the metal binding with AH and even after the hydrogen adsorption on the metal-AH system. The CDFT parameters provided insights into the stability and reactivity of the systems. The decreasing trends of the average adsorption energy and NBO charge on the Ag(I)/Au(I) site further supported the process of hydrogen adsorption. The negative Gibbs free energy change (ΔG) indicated the spontaneous nature of $H_2$ adsorption. The analysis of bonding nature revealed non-covalent interactions between the metal center and the molecular $H_2$. The H-H distance in the metal-decorated systems indicated that the $H_2$ were trapped in the metal-decorated systems in molecular form. Though Au(I)-decorated systems show lower gravimetric wt% than Ag(I)- decorated systems, interestingly it is observed that $H_2$-trapped Au(I)- decorated systems are more stable and indicate spontaneity of $H_2$adsorption-desorption process at higher temperature than Ag(I)-decorated systems. We designed and started our project two years back; to investigate the $H_2$ storage capacity of coinage metal (Cu/Ag/Au) decorated AH systems, and we recently reported the efficiency of Cu-decorated systems in the book 'Computational Studies: From Molecules to Materials', CRC Press/Tylor & Francis Group,[64] and very recently, Journal of the American chemical society (JACS) has published the synthetically established air-stable Cu(I) metal-organic framework (MOF) as hydrogen storage material.[43] It inspired



Imidazole-Ag(I)@2H$_2$ (200K) [A] [A]

Imidazole-Ag(I)@2H$_2$ (300K) [B] [B]

Imidazole-Au(I)@2H$_2$ (200K) [C] [C]

Imidazole-Au(I)@2H$_2$ (300K) [D] [D]

**Fig. 11** Simulated structures and Potential Energy (E, A.U.) vs Time (t, fs) of Ag(I)/Au(I) decorated AH system @2H$_2$ (AH = Imidazole) complexes at 300 K and 200 K and at 1000 fs obtained at the wb97xd/sdd level of theory.

us to investigate further the H$_2$ storage capacity of Ag(I)/Au(I)-AH systems, with the believe that our theoretical conclusion will help the synthetic laboratories to establish it in reality. The achieved results (gravimetric wt. %) of all the studied systems meet the target set by the US Department of Energy (2025) for coinage metal systems, and Ag(I)/Au(I)-imidazole and pyrazole systems showed highest gravimetric wt % among others. From the DOS and PDOS values, it can be concluded that all the fragments of the different systems (aromatic heterocyclic ring, metal ion, and molecular hydrogen respectively) significantly contribute to the formation of the FMOs. The ADMP analysis suggested the complexes can retain H$_2$ molecules at lower temperature up to 1000 fs, and desorption starts when the temperature is increased, and at the room temperature at least one molecular H$_2$ is attached to the systems. From this it can be concluded that both metal decorated Ag(I)/Au(I)-AH model systems survive upon H$_2$ adsorption even at room temperature.

Therefore, these metal-decorated Ag(I)/Au(I)-AH systems are the promising hydrogen storage systems, in designing of efficient storage material.

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## Conflict of Interest

There is no conflict of interest.

## Supporting Information

Applicable.

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# Development of a fluorescent scaffold by utilizing quercetin template for selective detection of $Hg^{2+}$: Experimental and theoretical studies along with live cell imaging

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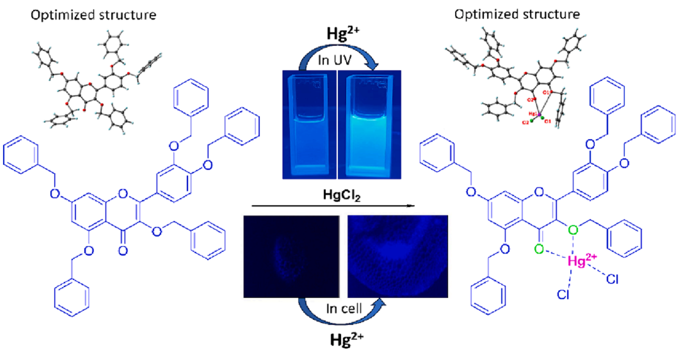
## HIGHLIGHTS

- We have developed a novel quercetin (a SARS-CoV-2 inhibitor) coupled benzyl ethers (QBE) chemosensor for selective detection of $Hg^{2+}$.
- To date, there are very few reports where quercetin itself have been used in sensing field (table 1) but the use of quercetin derivative in sensing field is almost nil.
- To the best of our knowledge our chemosensor QBE is the first chemosensor based on quercetin derivative for the selective detection of $Hg^{2+}$.
- The binding phenomenon of QBE with $Hg^{2+}$ has been proved by UV–vis, fluorescence, DFT and cyclic voltammograms study.
- Lower LOD (Limit of Detection) at 8.47 μM and high binding constant value as $2 \times 10^4$ $M^{-1}$ showed the strong binding affinity of $Hg^{2+}$ towards QBE.
- The intracellular activity of QBE with $Hg^{2+}$ binding has been examined by using living plant tissue by using green gram seeds.

## GRAPHICAL ABSTRACT



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## ABSTRACT

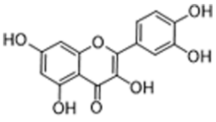
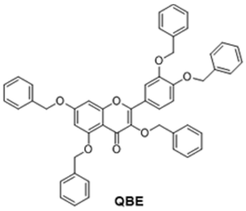
Quercetin is an important antioxidant with high bioactivity and it has been used as SARS-CoV-2 inhibitor significantly. Quercetin, one of the most abundant flavonoids in nature, has been in the spot of numerous experimental and theoretical studies in the past decade due to its great biological and medicinal importance. But there have been limited instances of employing quercetin and its derivatives as a fluorescent framework for specific detection of various cations and anions in the chemosensing field. Therefore, we have developed a novel chemosensor based on **q**uercetin coupled **b**enzyl **e**thers (**QBE**) for selective detection of $Hg^{2+}$ with “naked-eye” colorimetric and “turn-on” fluorometric response. Initially **QBE** itself exhibited very weak fluorescence with low quantum yield ($\Phi = 0.009$) due to operating photoinduced electron transfer (PET) and inhibition of excited state intramolecular proton transfer (ESIPT) as well as intramolecular charge transfer (ICT) within the molecule. But in presence of $Hg^{2+}$, **QBE** showed a sharp increase in fluorescence intensity by 18-fold at wavelength 444 nm with high quantum yield ($\Phi = 0.159$) for the chelation-enhanced fluorescence (CHEF) with coordination of $Hg^{2+}$, which hampers PET within the molecule. The strong binding affinity of **QBE** towards $Hg^{2+}$ has been proved by lower detection limit at 8.47 μM and high binding constant value as $2 \times 10^4\ M^{-1}$. The binding mechanism has been verified by DFT study, Cyclic voltammograms and Jobs plot analysis. For the practical application, the binding selectivity of **QBE** with $Hg^{2+}$ has been capitalized in physiological medium to detect intracellular $Hg^{2+}$ levels in living plant tissue by using green gram seeds. Thus, employing **QBE** as a fluorescent chemosensor for the specific identification of $Hg^{2+}$ will pave the way for a novel approach to simplifying the creation of various chemosensors based on quercetin backbone for the precise detection of various biologically significant analytes.

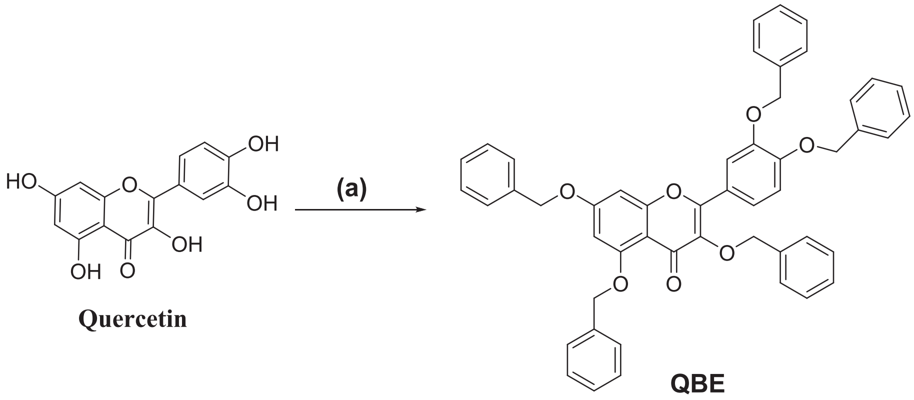
## 1. Introduction

Heavy metals are the primary contributors to contemporary environmental pollution, with mercury identified as the most detrimental among them. Its presence stems largely from coal combustion. Notably, mercury pollutants undergo transformation into methylmercury via assimilation by organisms at lower trophic levels, subsequently accumulating within the human body through the food chain [1]. Mercury is considered one among the few highly toxic metal ions, due to its detrimental effects to human beings over contamination [2]. Different type of anthropogenic and natural sources, like gold mining, solid waste incineration, fires from forest and fossils emit about 50 tonnes of mercury particulates annually into the atmosphere [3]. Based on the environment, the oxidation state of $Hg^{2+}$ can be converted to $Hg^0$ and also to highly toxic organomercury compounds (methylmercury) by several strains of aerobic bacteria [4]. Dental amalgam is also a source of mercury toxicity [5]. Mercury exposure causes digestive, kidney, and particularly neurological disorders, even at very low concentrations [6]. As the maximum permissible limit of mercury detection in food and drinking water is 2 ppb (10 nm), need for developing sensors for detection and monitoring mercury with its most stable form is of utmost importance as compared to any other toxic heavy metal ions [7]. As a result, numerous fluorescent sensors for the hazardous metal ion detection have been created over the past years. In spite of vast development of various fluorescent chemosensors, some common drawbacks for the sensors development are low sensitivity and selectivity at ppb level, poor solubility in aqueous environments, tedious and expensive preparative methods, unsatisfactory cell-permeability [8].

There has been a lot of interest in a supramolecular method involving binding between the mercury ion and a suitable ligand attached to a fluorophore; which produces a change in the fluorescence property. Moreover, the fluorometric detection of metal cations by emission spectroscopy is a highly sensitive and straightforward key method in this research area with relatively few demands on the equipment. In this regard, the significant enhancement of emission intensity of various fluorescent probes upon complex formation with metal ions are very

**Table 1**
Reported literatures based on quercetin moiety on comparison with **QBE.**

| Sl No. | Sensors | Type of sensor and analytes names | Detection Limit (LOD) | References |
|---|---|---|---|---|
| 1 |  **Quercetin** | Detection of tungsten species in water | 0.28 μg/L | 17a |
| 2 | Quercetin | $Fe^{3+}$ recognition in aqueous medium | 20.5 μM | 17b |
| 3 | Quercetin | Sensitive and selective detection of $Cu^{2+}$ | $1 \times 10^{-7}$ mol $L^{-1}$ | 17c |
| 4 | Quercetin | Detection of Yttrium ($Y^{3+}$) | 27 nM | 17d |
| 5 | Quercetin | Complexation and solvent extraction behaviour towards lanthanide ions | _ | 17e |
| 6 | Carbon dots-quercetin systems | Red emission ratiometric fluorescent nanoprobes towards $Zn^{2+}$ and ATP | 0.14 μM ($Zn^{2+}$)<br>0.55 μM (ATP) | 17f |
| 7 | Quercetin@ZIF-8composite | turn-on fluorescent sensor for detection of $Al^{3+}$ | 0.58 μM | 17 g |
| 8 | Carbon dot-Quercetin system | Visual and ratiometric fluorescent determination of $Al^{3+}$ | 90 nM | 17 h |
| 9 |  QBE | Detection of $Hg^{2+}$ employing DFT study and cell imaging with live green gram | 8.47 μM | **This work** |



**Scheme 1.** (a) quercetin, benzyl chloride, potassium carbonate, dimethyl formamide, 80–90 °C for 18 h.

useful and these probes are called "light-up probes". This significant fluorescence enhancement of various fluorescent probes upon metal binding is often applied in analytical biochemistry, biology, and also in medicine [9]. A wide range of fluorescent chemosensors for mercury ion have already been reported, however majority of them are obtained from various heterocycles like triazole, pyridine, thiazole, quinoline, pyrrole, or imidazole etc, and their derivatives are used as recognition units [10]. In the current work, a natural flavonoid source has been utilized as a fluorescent platform for selective detection of $Hg^{2+}$. Most of the plants contain flavonoids, a ubiquitous class of polyphenolic compounds that are concentrated in bark, flowers, seeds, fruit skin or peel etc [11] and the anti-inflammatory, anti-mutagenic, antiviral, anti-antineoplastic, antithrombotic and vasodilator properties of flavonoids have been demonstrated [12].

One of the most plentiful naturally occurring flavonoids in plants is quercetin. It is also the most significant flavonoid in the human diet, used as an active ingredient in various Chinese traditional treatments. It is known to have some anti-cancer characteristics and anti-inflammatory as well as antiviral actions [13]. Recently, it was demonstrated that flavonoids, including Quercetin, have a variety of inhibiting properties and can be employed as SARS-CoV inhibitory agents [14]. On the other hand, the photophysical characteristics of Quercetin, in particular the dual emission caused by excited state intramolecular proton transfer (ESIPT) intramolecular charge transfer (ICT) and its augmentation in aggregated state, known as aggregation-induced emission (AIE) have received a lot of interest [15]. Therefore, it is regarded to develop new quercetin based chemosensors for biological and chemical sensing of different important analytes. Moreover, quercetin has a significant chelating effect on metal ions and serves as a fluorescent unit in chemosensors due to its molecular structure containing one carbonyl oxygen and five hydroxyl oxygens, which provides lone electron pair and possess certain coordination abilities [16]. To date, there are very few reports where quercetin itself has been used as a fluorescent backbone for selective detection of different cations as metal ions and anions but the use of quercetin derivative in sensing filed is almost nil. We have summarized also a comparison table with previously reported quercetin based sensors (Table 1) [17]a–h. Herein, we have developed a fluorescent ligand **q**uercetin coupled **b**enzyl **e**thers (**QBE**) for selective detection of mercury in mixed aqueous media and to the best of our knowledge, **QBE** is the first quercetin based chemosensor for selective detection of $Hg^{2+}$. Ligand **QBE** has been synthesized by one step reaction of quercetin with benzyl chloride in presence of base potassium carbonate (Scheme 1) and **QBE** has been characterized by $^{1}H$ NMR, $^{13}C$ NMR and HRMS spectra (Fig.S5-Fig.S7).

## 2. Results and discussion

### 2.1. Synthesis and characterization

Anhydrous potassium carbonate was added (22.8 g, 165.2 mmol) to a solution of corresponding quercetin (5 g, 16.6 mmol) in dimethyl formamide (100 mL) under stirring condition for 6 h at room temperature. Followed by addition benzyl chloride (21 g, 165.5 mmol) to the reaction mixture, drop wise using dropping funnel. The reaction mass was later heated at 80—90 °C for 18 h. Reaction progress and completion of the reaction was monitored from TLC. Next the DMF solvent was distilled under reduce pressure. The resulting mixture was cooled at room temperature and followed by addition of dichloromethane (100 mL) washed the mixture with brine (2 × 50 mL) and the organic layer was dried over anhydrous sodium sulphate. The crude product was recrystallized with ethanol and isolated 7.8 g (yield 61 %). The chemical structures of the ligands were confirmed by NMR and mass spectrometry (ESI, Fig.S5 to S7).

**$^{1}$H NMR ($CDCl_3$, 500 MHz):** 7.71 (d, 1H, $J = 2$ Hz), 7.61 (d, 2H, $J = 9.5$ Hz), 7.53 (t, 1H, $J = 10$ Hz), 7.39 (m, 20H), 7.21 (m, 3H), 6.95 (d, 1H, $J = 11$ Hz), 6.49 (d, 2H, $J = 2.5$ Hz), 5.28 (s, 2H), 5.24 (s, 2H), 5.08 (s, 4H), 4.96 (s, 2H). **$^{13}$C NMR (DMSO-$d_6$, 100 MHz):** 172.83, 163.08, 159.58, 158.54, 152.51, 150.59, 148.09, 139.56, 137.44, 137.36, 137.28, 137.23, 136.52, 129.01, 128.91, 128.85, 128.83, 128.65, 128.60, 128.50, 128.41, 128.38, 128.33, 128.04, 128.00, 127.39, 123.38, 122.25, 114.55, 114.05, 109.36, 98.26, 94.63, 73.34, 70.63, 70.53, 70.43, 70.32. **HRMS (ESI-TOF):** ($m/z$, %): $M^{+}$ Calculated for $C_{50}H_{40}O_7$ is 752.2774; Found: 753.2861 $(M + H)^{+}$.

### 2.2. Uv–vis and fluorescence study

The photophysical behaviour of **QBE** ($c = 2 \times 10^{-5}$ M) was examined in $CH_3CN$-HEPES buffer solution (9:1, v/v, pH = 7.4). In the absorption spectra, **QBE** exhibited a sharp peak at 330 nm but on addition of $Hg^{2+}$, the absorption intensity gradually increased at 330 nm. Significantly, quercetin itself shows strong absorption peak appears at 372 nm but due to the protection of 5-hydroxy groups by benzyl ether moieties in **QBE**, bathochromic shift has been observed by appearing an absorption band at 330 nm ($\Delta\lambda = 42$ nm). This type of bathochromic shift in **QBE** is due to the inhibition of ESIPT (5-OH group with 4-carbonyl group) and ICT ($\pi$-electrons delocalization within molecule), which are generally active in quercetin itself exhibiting a strong absorption band at 372 nm [18].

The fluorescence properties of **QBE** ($c = 2 \times 10^{-5}$M) was analysed in $CH_3CN$-HEPES buffer (9:1, v/v, pH = 7.4) by addition of various cations such as $Hg^{2+}$, $Cr^{3+}$, $Na^{2+}$. $Al^{3+}$, $Mn^{2+}$, $Pb^{2+}$, $Mg^{2+}$, $Cd^{2+}$, $Fe^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ ($c = 2 \times 10^{-4}$ M). Particularly on addition of $Hg^{2+}$ to the receptor solution, the fluorometric behaviour was analysed. Upon excitation at 330 nm, initially the emission spectrum of **QBE** alone

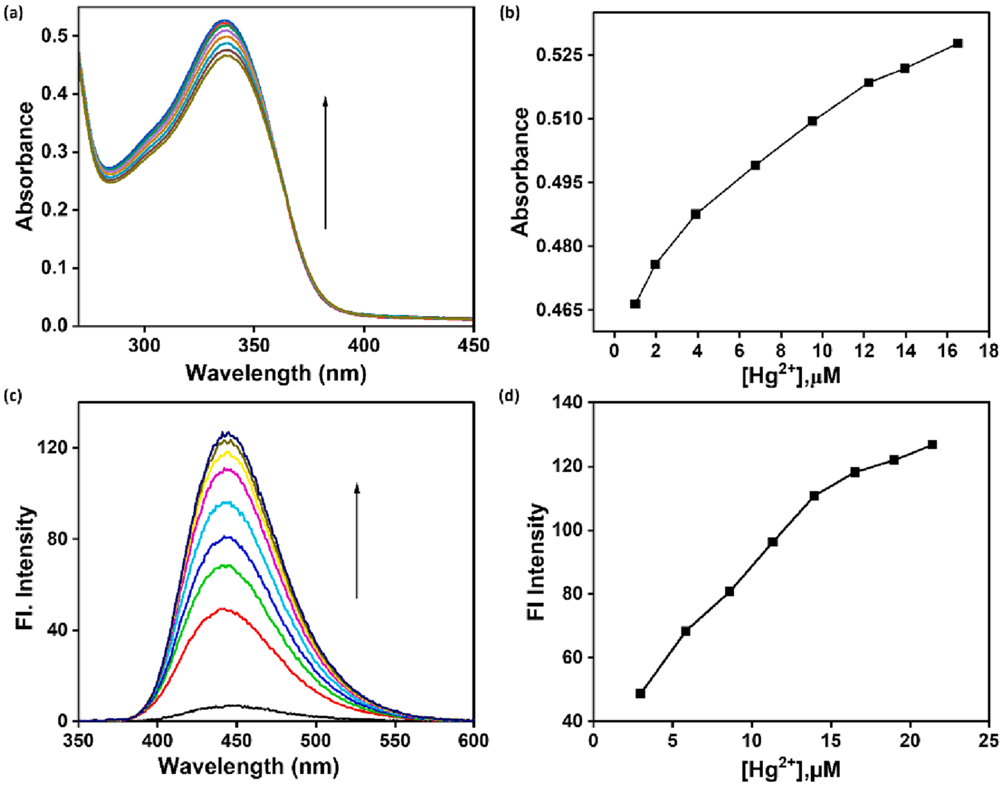
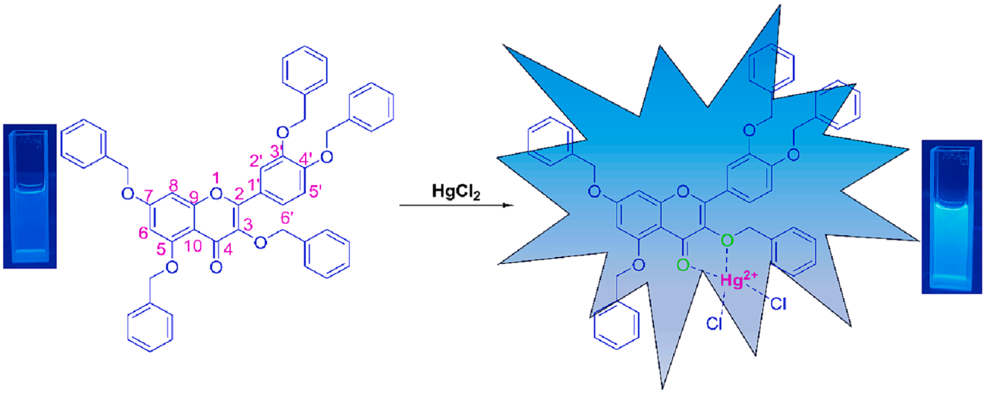


**Fig. 1.** (a) and (c) UV–*Vis* and Fluorescence titration spectra of **QBE** ($c = 2 \times 10^{-5}$ M) upon addition of $Hg^{2+}$ ($c = 2 \times 10^{-4}$M). (c) and (d) Changes of concentrations vs intensities of **QBE** for $Hg^{2+}$ in UV–*vis* and fluorescence spectra respectively.



**Scheme 2.** Probable binding mode of **QBE** with $Hg^{2+}$ in solution phase.

produced weak fluorescence signal at 444 nm with a relatively low quantum yield $\Phi = 0.0091$. Initial low fluorescence of **QBE** is due to near degeneracy of the π, π* and n, π* states of **QBE** forming a pseudo-Jahn-Teller distorted excited state [19]. Further increasing the concentration of $Hg^{2+}$, a strong emission band at 444 nm was observed with the increase of emission intensity as well as high quantum yield by 18-fold ($\Phi/\Phi_0 = 0.1595/0.0091 = 18$). In absorption and fluorescence spectra, on gradual addition of $Hg^{2+}$ to the receptor solution resulted enhancement of absorption and emission intensity at 330 nm and 444 nm respectively up to a saturation level as depicted in Fig. 1a and Fig. 1c. The variation of the absorbance and emission intensities with different concentrations of $Hg^{2+}$ has been shown in Fig. 1b and Fig. 1d respectively.

The detection limit (DL) of **QBE** for $Hg^{2+}$ has been calculated as 8.47 μM from emission titration results, using the equation $DL = K \times Sb_1/S$, where $K = 3$, $Sb_1$ is the standard deviation of the blank solution and S calibration curve slope [20] (Fig. S2). The molar absorptivity of the probe **QBE** and **QBE**–$Hg^{2+}$ are $2.6 \times 10^4$ $mol^{-1}$-liter-$cm^{-1}$ and $2.6 \times 10^4$ $mol^{-1}$-liter-$cm^{-1}$ at 337 nm. The 1:1 binding stoichiometry for **QBE**–$Hg^{2+}$ was established by Job plot analysis (Fig.S3). This implies that one mercury metal is incorporated into the cavity of **QBE** generated by carbonyl group and the benzylic ether moiety by four co-ordination binding patterns of the mercury ion (scheme 2). From the fluorescence titration experiment, the association constant (Ka) of **QBE** with $Hg^{2+}$ has been calculated as $2 \times 10^4$ $M^{-1}$ (error < 10 %) [21].

### 2.3. *Interference study*

To examine the binding of **QBE** towards various interfering metal ions ($Ni^{2+}$, $Mn^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Fe^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$, $Co^{2+}$, $Al^{3+}$, $Cr^{3+}$ as their chloride salts), the fluorescence experiment has been carried out in presence of each of these metal ions in $CH_3CN$–aqueous HEPES buffer (9/1, v/v, pH = 7.4). However, only treatment with $Hg^{2+}$ resulted in a

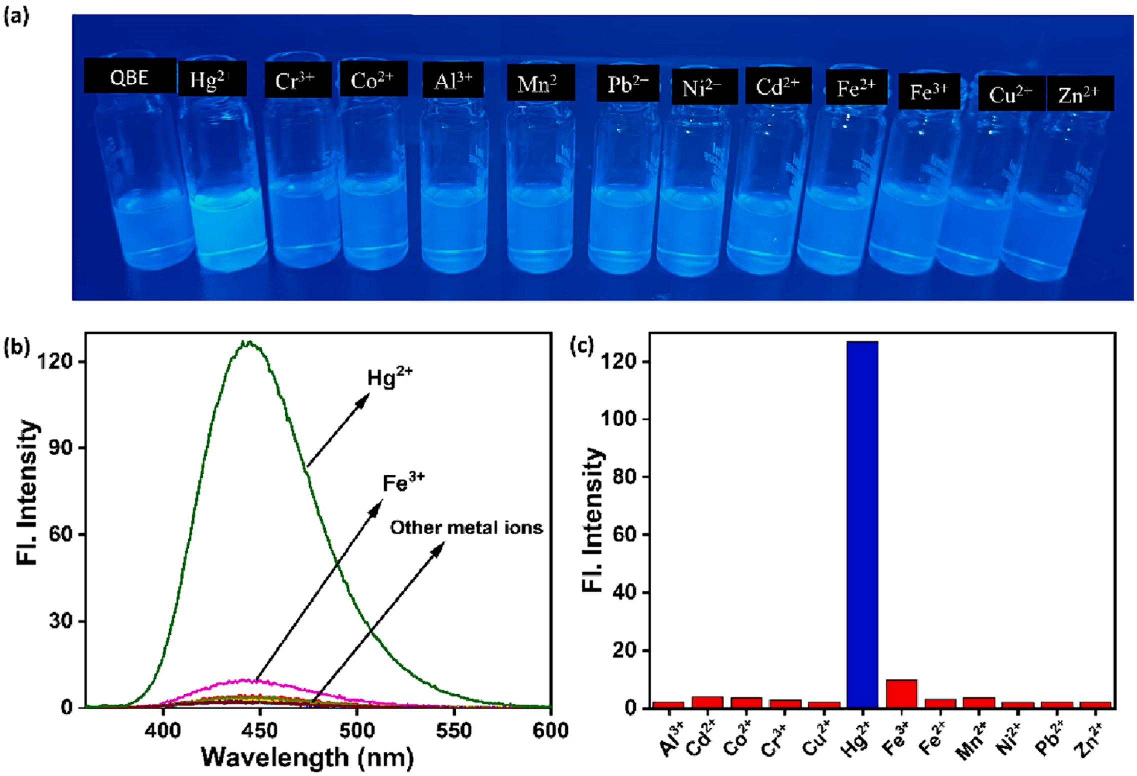


**Fig. 2.** (a) Emission color of ligand **QBE** with different metal ions. (b) The emission spectra of **QBE** ($c = 2 \times 10^{-5}$M) on addition of various metal ions (10 equiv.) in $CH_3CN$–aqueous HEPES buffer (9/1, v/v, pH = 7.4). (c) Change of emission intensity of **QBE** in bar diagram upon addition of 10 equiv. of each of interfering metal ions ($c = 2 \times 10^{-4}$M).

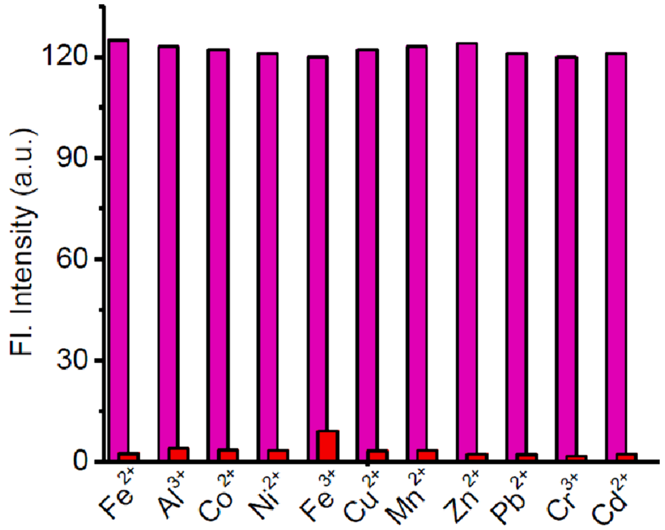


**Fig. 3.** Change in emission intensity of **QBE** ($c = 2 \times 10^{-5}$M) on addition of 10 equiv. different metal ions ($c = 2 \times 10^{-4}$M) (red bars); change in emission intensity with addition of 10 equiv. various other metal ions along with addition of 10 equiv. of $Hg^{2+}$ at 444 nm (pink bars). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

large enhancement of fluorescence intensity but significantly no emission enhancement has been observed even on introducing other interfering metal ions. The emission color changes of **QBE** in presence of all interfering metal ions have been shown in Fig. 2a. The relative change in the emission spectra of **QBE** in the presence of all metal ions has been shown in Fig. 2b and significantly only mercury induced fluorescence enhancement of **QBE** has been observed (green line). Similar observation has been depicted in the bar representation where blue bar indicates large emission enhancement in presence of $Hg^{2+}$ and other red bars represent no significant emission signal response in presence of other interfering metal ions (Fig. 2c).

### *2.4. Competition experiment*

To explore further selectivity of **QBE** for $Hg^{2+}$, the effect of competing metal ions on binding with **QBE** in the presence of $Hg^{2+}$ was studied by performing cross-contamination tests using 10 equiv. of $Hg^{2+}$ and other metal ions. As presented in Fig. 3, the results clearly depict the emission enhancement of **QBE** in presence of $Hg^{2+}$ (violet bars) remains uninterrupted with no remarkable variation in the emission signal at 444 nm in presence of other different interfering metal ions (red bars).

### *2.5. Reversibility Test*

The metal binding nature of **QBE** with $Hg^{2+}$ has been proved by the reversibility test experiment by addition of excess $Na_2EDTA$ (0–2.0 equiv.) to **QBE** + $Hg^{2+}$ complex solution. As represented in Fig. 4a, the fluorescence intensity was gradually decreased on increasing concentration of $Na_2EDTA$. The strong binding of $Na_2EDTA$ with $Hg^{2+}$ strips away the metal from the metal binding cavity of **QBE**. The concentration vs intensity changes of **QBE** on addition of $Hg^{2+}$ has been shown in Fig. 4b.

### *2.6. Probable binding mode in solution phase*

The interaction of **QBE** with $Hg^{2+}$ has been explained by various methods including UV–vis, fluorescence, cyclic voltammograms and theoretical study. In absence of $Hg^{2+}$, **QBE** itself showed very weak fluorescence since all the hydroxy groups of quercetin are protected by

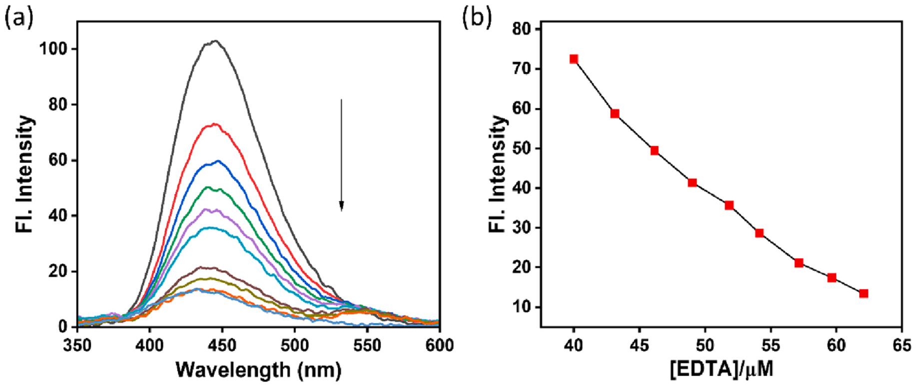


**Fig. 4.** (a) Fluorescence changes of **QBE** + $Hg^{2+}$ complex solution ($c = 2 \times 10^{-5}$M) upon addition EDTA ($c = 2 \times 10^{-4}$M). (b) Changes of the emission intensity of **QBE**-$Hg^{2+}$ complex as a function of concentration of EDTA.

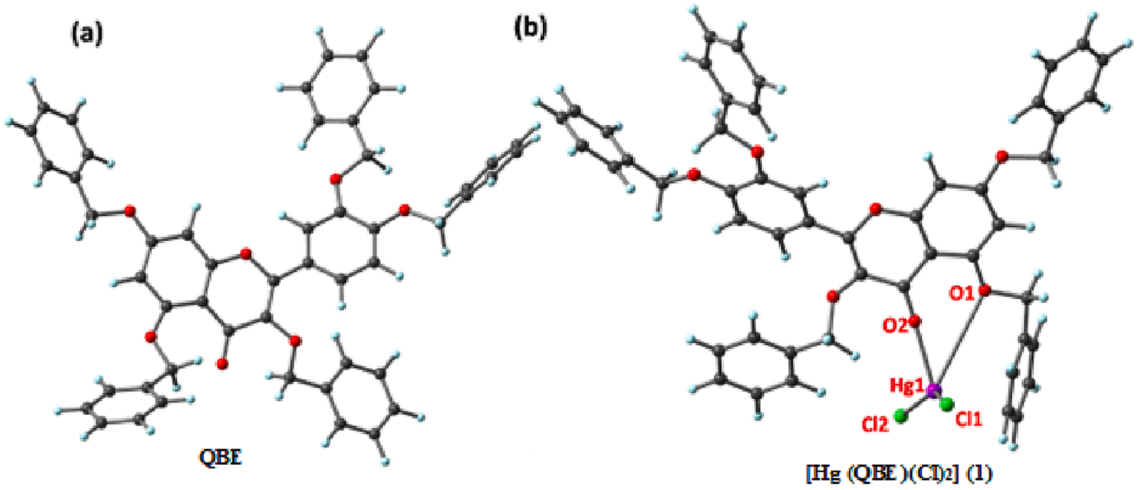


**Fig. 5.** Geometry optimized molecular structure of (a) **QBE** and (b) **1**.

benzyl groups, which results inhibition of ESIPT (5-OH group with 4-carbonyl group) and ICT (the delocalization of the π-electrons which is generally prompted in quercetin itself by five hydroxy groups throughout the molecule). The operating photoinduced electron transfer (PET) within **QBE** is also responsible for the weak emission. Moreover, weak fluorescence of **QBE** can be described by excited state degeneracy of π, π* and n, π* states which resulted the development of a pseudo-Jahn-Teller distorted excited state. The breakdown of the Born-Oppenheimer approximation in the higher energy state may stem from interactions occurring between the emitting state and adjacent excited states [18,22]. Therefore, on addition of $Hg^{2+}$, **QBE** showed high fluorescence for the chelation-induced enhanced fluorescence (CHEF) through the metal binding by multiple oxygen donor sites and inhibition of PET effect through ligand to metal charge transfer (LMCT) resulted for the generation of intense whitish blue fluorescence (Scheme 2). It has been reported that carbonyl oxygen atom and oxygens of 3-OH or 5-OH group (green coloured) of the quercetin are responsible to bind with metal ion and here the cavity formed by the flavone carbonyl group [17,23] and the oxygen of benzylic ether moiety of **QBE** fits for the binding with $Hg^{2+}$ with four co-ordination sites having two chlorine atoms of $HgCl_2$ (Scheme 2). Moreover, 1:1 binding stoichiometry of **QBE** with $Hg^{2+}$ has been proved by Jobs plot (Fig. S3) and theoretical analysis by DFT study (Fig. 8 and Fig. 9).

The sensing capability of **QBE** towards $Hg^{2+}$ has been explored across various pH levels ranging from pH 2 to pH 12. Generally, **QBE** exhibited negligible fluorescence within the pH range of 2 to 12. However, its fluorescence response remained notably high within the physiological pH range in the presence of $Hg^{2+}$ (Fig. S4). Significantly, **QBE** showed enhancement of fluorescence intensity in presence of $Hg^{2+}$ when the pH was increased from 4 to 12 with the highest fluorescence intensity at pH 7.4, indicating that the ligand **QBE** possesses high selectivity and sensitivity towards $Hg^{2+}$ within the physiological pH window (Fig. S4).

**Table 2**
Selective bond distances and bond angles for **1**.

| Bond distance(Å) | | Bond angles(°) | |
|---|---|---|---|
| Hg1-Cl1 | 2.335 | Cl1- Hg1-O1 | 97.66 |
| Hg1-O1 | 2.934 | Cl1- Hg1-O2 | 103.54 |
| Hg1-O2 | 2.388 | Cl1- Hg1-Cl2 | 142.44 |
| Hg1-Cl2 | 2.325 | O1- Hg1-Cl2 | 119.80 |
| | | O2– Hg1-Cl2 | 102.42 |
| | | O1- Hg1-O2 | 53.20 |

## 3. Structural optimization through DFT

The optimized geometry of **QBE** and complex **Hg (II)-QBE** (**1**) through DFT is shown in Fig. 5. The theoretical geometry related parameters of the complex are tabulated in Table 2.

The complex **1** having metal centre $Hg^{2+}$ are tetra-coordinated with neutral ligand (with $O_2$ donor system) and two mono negative chlorides counter anion, satisfy the tetrahedral geometry to form the mononuclear complex. The theoretical Hg–Cl bond distances are as 2.335 Å and 2.325

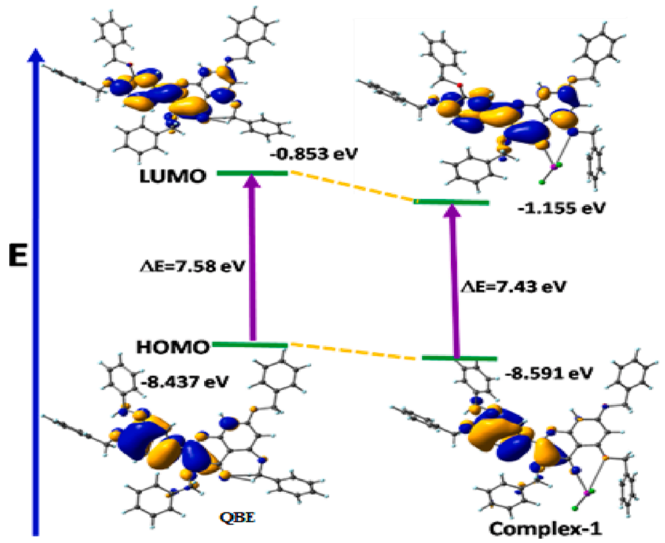


**Fig. 6.** Frontier molecular orbital with energy difference of **QBE** and complex **1**.

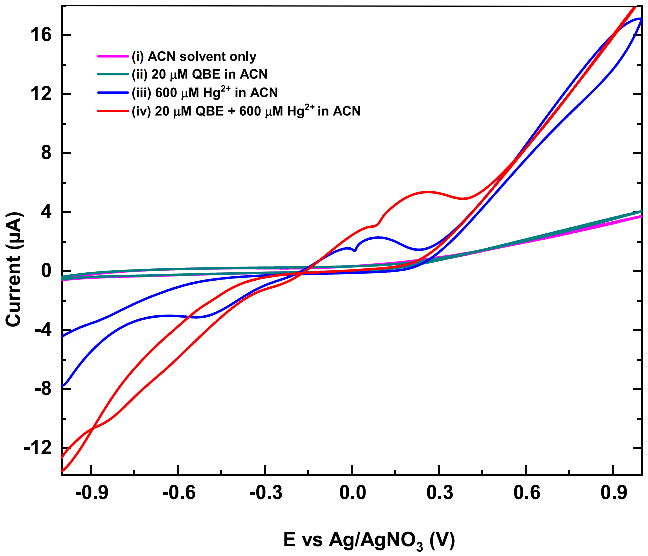


**Fig. 7.** Cyclic voltammograms recorded at a scan rate of 50 mV/s using glassy carbon electrodes (GCE) in (i) acetonitrile (ACN) solution as blank (ii) 20 μM of ligand in ACN solution (iii) mixture of 600 μM $Hg^{2+}$ and 20 μM ligand in ACN solution (iv) 600 μM $Hg^{2+}$ in ACN solution.

Å and Hg–O bond lengths are ranging as 2.388–2.934 Å for complex **1** respectively. Moreover, it is found that the HOMO-LUMO energy gap (Fig. 6) are $\Delta E = 7.58$ eV and 7.43 eV for **QBE** and complex **1** respectively which is responsible for the stabilization of the complex formation. Moreover, optical transition for the complex **1** with composition in terms of molecular orbital contribution of the transition, vertical excitation energies, and oscillator strength in acetonitrile has been calculated (Table S1).

Theoretical electronic spectra

The complex **1** shows one absorption band at 330 nm at room temperature and the corresponding calculated absorption band located at 325 nm which are in excellent agreement with experimental result. These spectral bands can be assigned to the $S_0 \rightarrow S_9$ transition for complex **1**.

## 4. Cyclic voltammograms study

The significant binding of QBE with $Hg^{2+}$ has been shown by Cyclic voltammograms analysis. Solution phase study was done for electrochemical analysis of the **QBE** where 3 electrode system was chosen for the analysis in which GCE acts as working electrode, platinum electrode as counter electrode and $Ag/AgNO_3$ in $CH_3CN$ as non-aqueous reference electrode. Firstly, a control cyclic voltammogram was obtained in 10 mL acetonitrile solution. Then 20 μM of **QBE** was added in $CH_3CN$ solution followed by cyclic voltammogram analysis. There was no significant peak was found in this analysis of **QBE**. After that a cyclic voltammogram was carried out in 600 μM of $HgCl_2$ in 10 mL of $CH_3CN$ without ligand addition and significant $Hg^{2+}$ oxidation peak current was observed. But once 600 μM of $HgCl_2$ was added in the presence of **QBE**, the $Hg^{2+}$ oxidation peak current was significantly decreased which strongly implied the binding of $Hg^{2+}$ with the **QBE** (Fig. 7).

## 5. Biological study

### 5.1. *In vitro cytotoxicity*

The trypan blue penetrates the damages membrane of the dead cells and, thereby stains it as blue [24]. In the present study, the LD50 of **QBE** was determined as 35.26 μM based on the linear equation $y = 1.5795x - 5.6982$, $R^2 = 0.8729$ by using the trypan blue cytotoxicity assay on the goat blood lymphocytes. The LD50 was found to be more than 3.5 times higher than the maximum concentration of the **QBE** (10 μM) used for this study. Hence **QBE** can be generally regarded as safe.

### 5.2. *Fluorescence imaging study*

For the practical application, we have utilized quercetin based fluorogenic potent chemosensor **QBE** for the detection of $Hg^{2+}$ accumulation in seedlings of green gram (*Vigna radiata*) cells. The plant green gram has been established as an economical, user-friendly, and easily accessible plant-based system for initial evaluation of lead compounds. We observed $\geq 90$ % germination of seeds, and no statistical differences in root lengths were noted for all the experimental conditions (Fig. 8). Finally, fluorescence microscope-based imaging study of the transverse sections of the root sample revealed strong fluorescence for 5 μM **QBE** + 50 μM $HgCl_2$ and 10 μM **QBE** + 50 μM $HgCl_2$ sets (Fig. 9).

## 6. Conclusion

Quercetin based a novel chemosensor (**QBE**) has been utilized for selective detection of $Hg^{2+}$. The interaction of **QBE** with $Hg^{2+}$ has been elucidated by various techniques like UV–*vis*, fluorescence, cyclic voltammograms and theoretical study. Strong binding affinity of **QBE** towards $Hg^{2+}$ has been shown by the strong increase in emission intensity as well as high quantum yield by 18-fold with a strong emission band at 444 nm due to inhibition of PET and chelation-enhanced fluorescence (CHEF) effect of **QBE** on binding with $Hg^{2+}$. Lower LOD (Limit of Detection) at 8.47 μM and high binding constant value as $2 \times 10^4$ $M^{-1}$ showed the strong binding affinity of $Hg^{2+}$ towards **QBE** with 1:1 binding stoichiometry. The intracellular activity of **QBE** towards $Hg^{2+}$ binding has been examined by using living plant tissue by using green gram seeds. In vitro cytotoxicity has been measured by using Trypan blue test and lymphocyte cells with the calculated LD50 (Lethal Dose 50) based on different concentrations of **QBE**. Since there have been limited instances of employing quercetin itself as a fluorescent framework for specific identification of various cations and anions, the utilization of **QBE** as fluorescent backbone for selective detection of $Hg^{2+}$ will open a new direction to simple design for the development of various chemosensors for selective detection of various biologically important analytes.

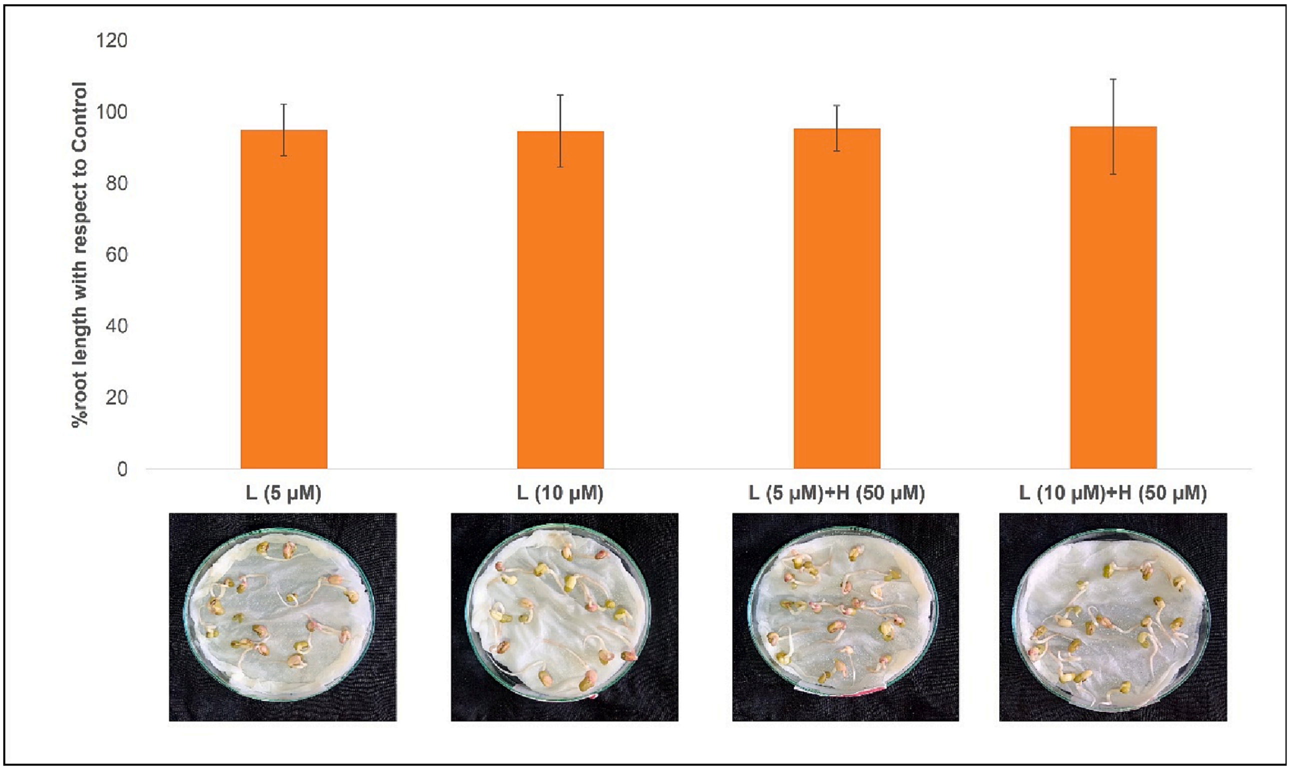
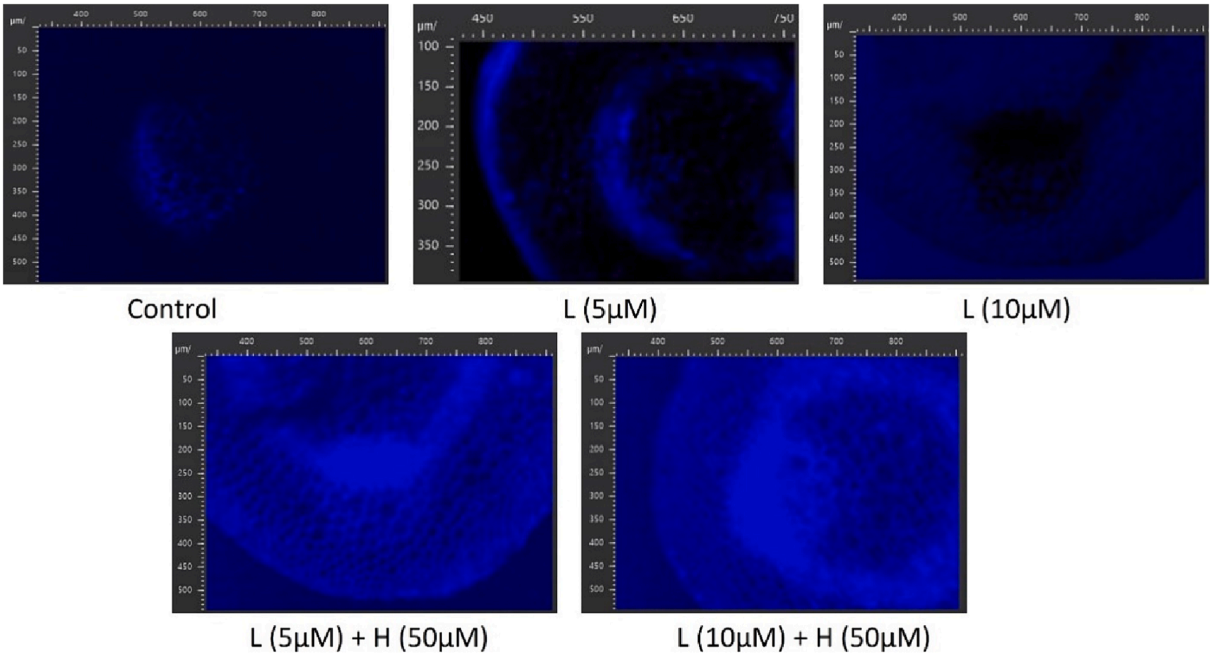


**Fig. 8.** Graphical representation of % root length (with respect to control) of green gram seeds from different experimental conditions; Photographs represent germinated seeds in Petri dishes, L: **QBE**, H: $HgCl_2$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)


Control

L (5µM)

L (10µM)

L (5µM) + H (50µM)

L (10µM) + H (50µM)

**Fig. 9.** T.S. of root samples visualized under fluorescence microscope (10X) at excitation wavelength of 325 nm; L: **QBE**, H: $HgCl_2$.

## CRediT authorship contribution statement

**Vishnu S.:** . **Sibaprasad Maity:** Investigation, Methodology, Project administration, Software, Supervision. **Annada C. Maity:** Data curation, Methodology, Resources. **Malavika S. Kumar:** Formal analysis, Investigation, Methodology, Writing – review & editing. **Malay Dolai:** Data curation, Formal analysis, Software. **Anish Nag:** Formal analysis, Investigation, Methodology, Visualization. **Yatheesharadhya bylappa:** Methodology, Formal analysis, Investigation. **Gorachand Dutta:** Resources, Methodology, Data curation. **Bimalendu Mukherjee:** Resources, Investigation, Data curation. **Avijit Kumar Das:** Funding acquisition, Conceptualization, Project administration, Resources, Supervision, Writing – review & editing.

## Declaration of competing interest

There are no conflicts of interest to declare.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.saa.2024.124249.

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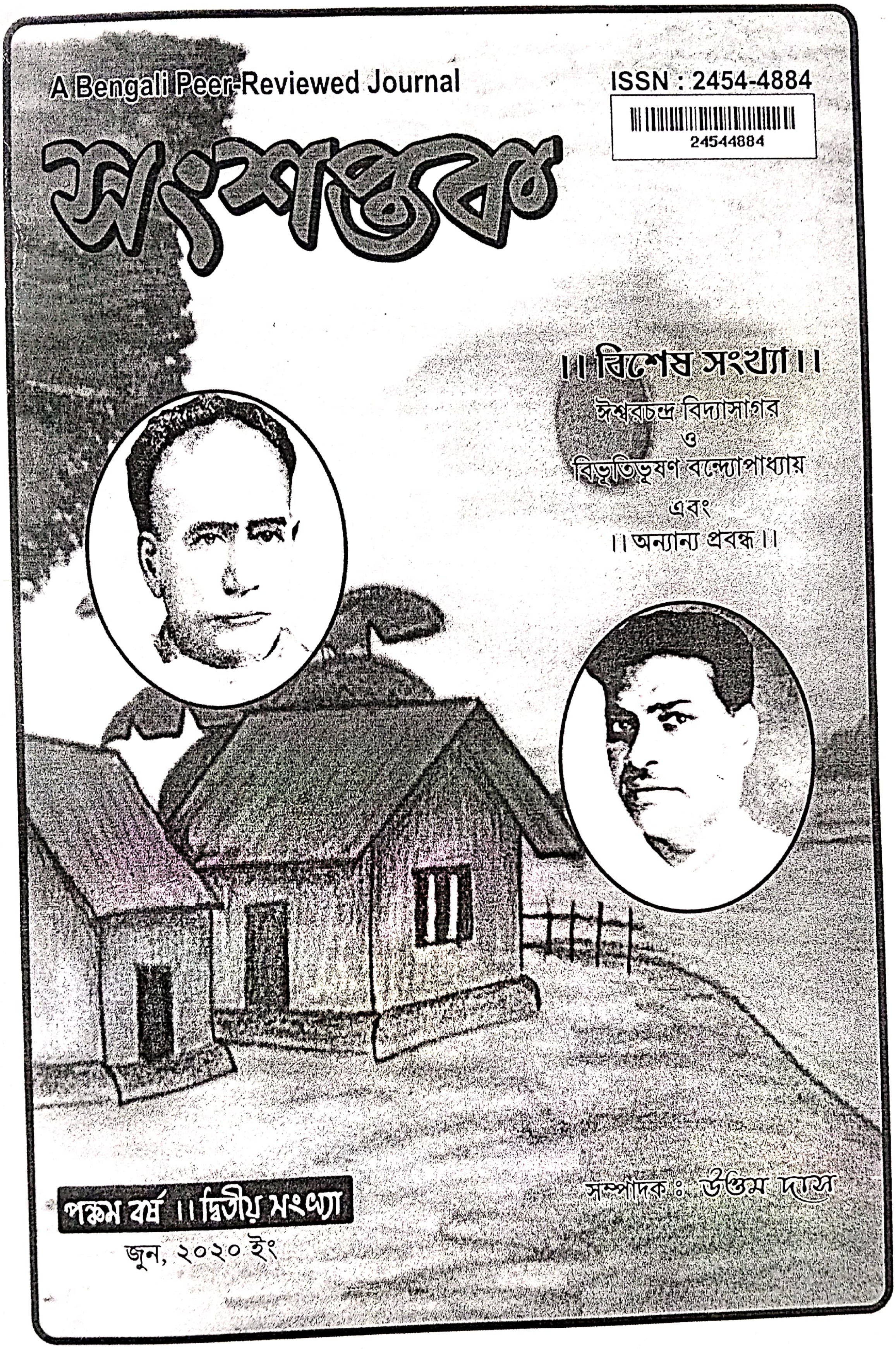

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## পরবর্তী সংখ্যার বিষয়

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# সাবিত্রী রায়ের ছোটগল্পে মৌলিকতা অনুসন্ধান

মণিকুন্তলা বসু

ছোটগল্প হল আধুনিককালের সাহিত্য প্রকরণ। এই কনিষ্ঠ সাহিত্যের শাখাটি বাংলা সাহিত্যে এসেছে পাশ্চাত্য সাহিত্য থেকে। এই সাহিত্য প্রকরণে মানুষকে বা স্রষ্টাকে অনেক বেশি কাছের থেকে নিবিড়ভাবে পাওয়া যায়। কথাসাহিত্যিক সাবিত্রী রায় ছোটগল্পে নিজের মনের কথাকে তুলে ধরেছেন, ছোটগল্পকে সমাজ পরিবর্তনের হাতিয়ার হিসাবে গণ্য করেছেন। বাংলা সাহিত্যে সমাজ-রাজনীতির নিখুঁত চিত্র সাবিত্রী রায়ের লেখনীতে পাঠক আস্বাদন করতে পারেন। তাঁর লেখনী যে বিশ্বস্ত এক দলিল। পাশাপাশি নারী আধুনিকতার পরশে নিজের মনের কথাকে অকপটে উচ্চারণ করতে চাইলেন, চাইলেন পুরুষের বেড়ি ভেঙে ভবিষ্যতের দিকে আত্মসম্মানের সঙ্গে এগিয়ে যেতে। এই দুইয়ের সংমিশ্রণে সাবিত্রী রায়ের চেতনার জগৎ গঠিত হল। ছোটগল্পকার সাবিত্রীর গল্পে সেই চেতনারই প্রতিফলন ঘটেছে।

সাবিত্রী রায় একজন রাজনৈতিক মনের মানুষ। সুনির্দিষ্ট একটি রাজনৈতিক মতাদর্শে তিনি বিশ্বাসী ছিলেন। নারীচেতনায় বিষয়টি আরও তাৎপর্যবহ হয়ে ওঠে। পুরুষের পাশে নারীর অবস্থানের তাৎপর্যকে, নারীর স্বাধীন চিন্তাধারাকে, তার সামাজিক, রাজনৈতিক ভাবনাকে সাবিত্রী রায় তাঁর গল্পে তুলে ধরলেন। রাজনৈতিক দায়বদ্ধতা তিনি কখনো ভোলেননি। এই বিষয়টি সেদিনের লেখিকাদের থেকে সাবিত্রী রায়কে এক অনন্য স্বাতন্ত্র্য দান করেছে। ১৯৩২ সালে সোভিয়েত লেখক সঙ্ঘের প্রতিষ্ঠা এবং সমাজতন্ত্রী বাস্তবতায় বিশ্বাসী রুশ দেশের সাহিত্যের অঙ্গনে পটপরিবর্তন ঘটল অনায়াসে। মানুষ যা নেই তার আকাঙ্খা করল, ফলে মানুষ হয়ে উঠল অসুখী - বিষয়টি সাহিত্যের বিষয়বস্তুকে বদলে দিল। সেক্ষেত্রে ব্যক্তি নয়, রাষ্ট্র ও সমাজ শক্তিকেই প্রাধান্য দেওয়া হচ্ছে। এই ধারাতেই পাশ্চাত্য সাহিত্যে পেলাম গোর্কি, শোলোখভকে, আলেক্সি তলস্তয় এবং অস্-ত্রোভস্কীকে । এঁদের সাহিত্যে দেখি, মানুষ প্রত্যয়ে ফিরছে, পায়ের তলার মাটি খোঁজার চেষ্টা করছে। সংগ্রাম, অধিকার আদায় অগ্রাধিকার পেল। প্রগতিশীল এই ভাবনায় অনুপ্রাণিত হওয়ায় এবং যুগের হাওয়াকে স্বীকার করায় সাবিত্রী রায়ের লেখায় পাই, বিশ্বযুদ্ধের ফ্যাসীবাদের রাজনীতি, বিশ্ববিপ্লবের সম্ভাবনার প্রত্যক্ষ বা বাস্তব আলেখ্য। সাবিত্রী রায় যখন গল্প লিখছেন তখন ব্রিটিশ শাসনের শেষ পর্যায়, যুদ্ধ মন্বন্তরের কালো ছায়া, দাঙ্গা, দেশভাগের অশনিসঙ্কেত। অন্যদিকে, গান্ধীবাদী, সন্ত্রাসবাদী ও বাম রাজনীতির পারস্পরিক দ্বন্দ্ব, হরতাল, কৃষক আন্দোলন এবং অবিভক্ত কমিউনিস্ট পার্টির প্রকাশ। এই বিষয়গুলিই তাঁর কথাসাহিত্যে এবং সেই সূত্রে গল্পের বিষয় এবং চরিত্রে উঠে আসে। তার গল্পের একদিকে যেমন আছে রাজনৈতিক বিশ্বাস তেমনি আছে মানুষের মনের প্রকৃত সত্য অন্বেষণের প্রচেষ্টা। সাবিত্রী রায়ের লেখা নারীমনের দাবীকে স্বাকীর করে। তাঁর লেখায় পাই নারী মনের না পাওয়ার বেদনা, পুরুষের বিশ্বাসঘাতকতায় নারীর মনের বিশ্বাসভঙ্গ ও আবার বিশ্বাস করা, বদ্ধ জীবন থেকে ছিটকে আসার জন্য নারী মনের প্রতিবাদ, পুরুষতন্ত্রের নগ্ন রূপ, নারীর জীবনে অবহেলা, বঞ্চনা, নারী-পুরুষের পারস্পরিক সম্পর্ক ও তার সূক্ষ্ম বিশ্লেষণ, সাম্রাজ্যবাদী ফ্যাসীবাদের প্রভাবে সমাজ ও পরিবার জীবনে নেমে আসা অন্ধকার ও তার পরিণাম। এখানে, একটি বিষয় লক্ষণীয়, লেখিকা তার সৃজনী সত্তাকে দুই ভাগে ভাগ করে দেখেছেন--ব্যক্তি এবং শিল্পীসত্তা - যা তার দেখার দৃষ্টিকে দিয়েছে এক সামগ্রিক সম্পূর্ণতা।

কথাসাহিত্যিক সাবিত্রী রায় প্রধানত ঔপন্যাসিক। তিনি স্বল্প সংখ্যক গল্প লেখেন। এই গল্পগুলির মধ্যে দিয়ে ছোটগল্পকার সাবিত্রী রায়ের জীবনদৃষ্টিকে সম্যকভাবে উপলব্ধি করা যায়। পারিপার্শ্বিকতা ও মানস বৈশিষ্ট্যের সমন্বয়ে সৃষ্টব্যক্তিত্ব সামাজিক-রাজনৈতিক-অর্থনৈতিক-মানবিক ঘাত-প্রতিঘাতের মধ্যে দিয়ে পৌঁছে যায় নির্দিষ্ট প্রত্যয়ে। ছোটগল্পে সেই প্রত্যয় প্রতিফলিত হয়। শারীরিক অসুস্থতা এবং মানসিক স্বাতন্ত্র্যবোধের কারণেও তিনি সক্রিয় রাজনীতিতে যুক্ত হতে পারলেন না। সুস্থ জীবনবোধ এবং প্রথাবিরোধী মনোভাবের জন্য সাবিত্রী রায়কে সাহিত্যের ইতিহাসে আলাদাভাবে চিহ্নিত করা যায়।

সাবিত্রী রায় যখন বাংলা সাহিত্যে আবির্ভূত হলেন তখন দেশে চলছে অস্থির অবস্থা। সময়টা হল বিগত শতকের চল্লিশের দশক। সুতরাং, সহজেই অনুমেয় হয় দেশের পরিস্থিতির চালচিত্র। সাবিত্রী রায় যে যুগ সন্ধিক্ষণে বাংলা সাহিত্যে আবির্ভূত তখন ফ্যাসীবাদ ভয়াল রূপ ধারণ করেছে। বিশ্ব রাজনীতি বা আন্তর্জাতিক রাজনীতির অবস্থা টালমাটাল। দুই দুটো বিশ্বযুদ্ধ সমগ্র পৃথিবীকে সঙ্কটের মুখে দাঁড় করিয়ে দিয়েছে।

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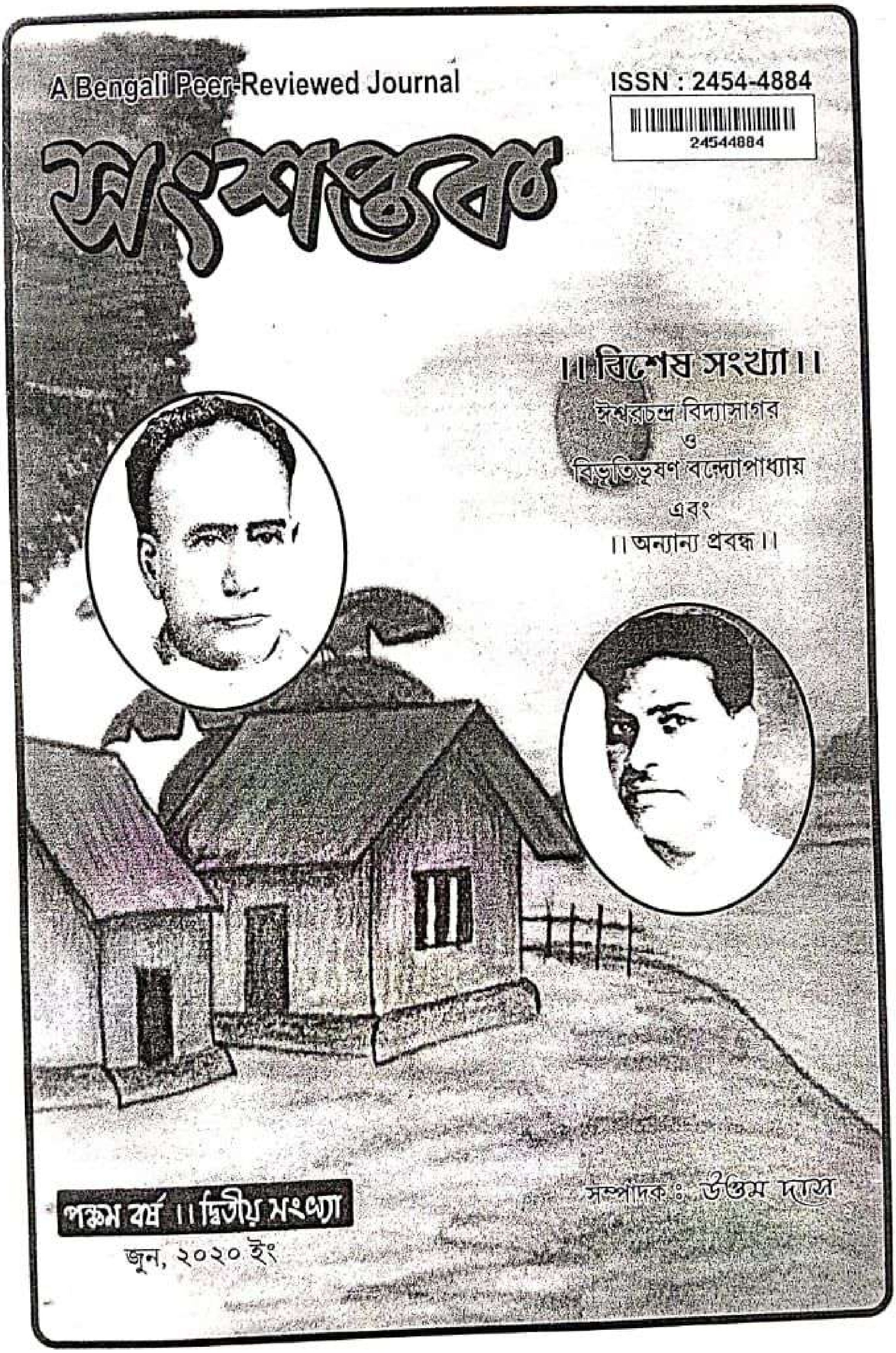
# সংশপ্তক



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ঈশ্বরচন্দ্র বিদ্যাসাগর
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'ছোটগল্প ও অন্যান্য প্রবন্ধ '

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# সাবিত্রী রায়ের ছোটগল্পে মৌলিকতা অনুসন্ধান

মণিকুন্তলা বসু

ছোটগল্প হল আধুনিককালের সাহিত্য প্রকরণ। এই কনিষ্ঠ সাহিত্যের শাখাটি বাংলা সাহিত্যে এসেছে পাশ্চাত্য সাহিত্য থেকে। এই সাহিত্য প্রকরণে মানুষকে বা স্রষ্টাকে অনেক বেশি কাছের থেকে নিবিড়ভাবে পাওয়া যায়। কথাসাহিত্যিক সাবিত্রী রায় ছোটগল্পে নিজের মনের কথাকে তুলে ধরেছেন, ছোটগল্পকে সমাজ পরিবর্তনের হাতিয়ার হিসাবে গণ্য করেছেন। বাংলা সাহিত্যে সমাজ-রাজনীতির নিখুঁত চিত্র সাবিত্রী রায়ের লেখনীতে পাঠক আস্বাদন করতে পারেন। তাঁর লেখনী যে বিশ্বস্ত এক দলিল। পাশাপাশি নারী আধুনিকতার পরশে নিজের মনের কথাকে অকপটে উচ্চারণ করতে চাইলেন, চাইলেন পুরুষের বেড়ি ভেঙে ভবিষ্যতের দিকে আত্মসম্মানের সঙ্গে এগিয়ে যেতে। এই দুইয়ের সংমিশ্রণে সাবিত্রী রায়ের চেতনার জগৎ গঠিত হল। ছোটগল্পকার সাবিত্রীর গল্পে সেই চেতনারই প্রতিফলন ঘটেছে।

সাবিত্রী রায় একজন রাজনৈতিক মনের মানুষ। সুনির্দিষ্ট একটি রাজনৈতিক মতাদর্শে তিনি বিশ্বাসী ছিলেন। নারীচেতনায় বিষয়টি আরও তাৎপর্যবহ হয়ে ওঠে। পুরুষের পাশে নারীর অবস্থানের তাৎপর্যকে, নারীর স্বাধীন চিন্তাধারাকে, তার সামাজিক, রাজনৈতিক ভাবনাকে সাবিত্রী রায় তাঁর গল্পে তুলে ধরলেন। রাজনৈতিক দায়বদ্ধতা তিনি কখনো ভোলেননি। এই বিষয়টি সেদিনের লেখিকাদের থেকে সাবিত্রী রায়কে এক অনন্য স্বাতন্ত্র্য দান করেছে। ১৯৩২ সালে সোভিয়েত লেখক সঙ্ঘের প্রতিষ্ঠা এবং সমাজতন্ত্রী বাস্তবতায় বিশ্বাসী রুশ দেশের সাহিত্যের অঙ্গনে পটপরিবর্তন ঘটল অনায়াসে। মানুষ যা নেই তার আকাঙ্খা করল, ফলে মানুষ হয়ে উঠল অসুখী – বিষয়টি সাহিত্যের বিষয়বস্তুকে বদলে দিল। সেক্ষেত্রে ব্যক্তি নয়, রাষ্ট্র ও সমাজ শক্তিকেই প্রাধান্য দেওয়া হচ্ছে। এই ধারাতেই পাশ্চাত্য সাহিত্যে পেলাম গোর্কি, শোলোখভকে, আলেক্সি তলস্তয় এবং অস্-ত্রোভস্কীকে । এঁদের সাহিত্যে দেখি, মানুষ প্রত্যয়ে ফিরছে, পায়ের তলার মাটি খোঁজার চেষ্টা করছে। সংগ্রাম, অধিকার আদায় অগ্রাধিকার পেল। প্রগতিশীল এই ভাবনায় অনুপ্রাণিত হওয়ায় এবং যুগের হাওয়াকে স্বীকার করায় সাবিত্রী রায়ের লেখায় পাই, বিশ্বযুদ্ধের ফ্যাসীবাদের রাজনীতি, বিশ্ববিপ্লবের সম্ভাবনার প্রত্যক্ষ বা বাস্তব আলেখ্য। সাবিত্রী রায় যখন গল্প লিখছেন তখন ব্রিটিশ শাসনের শেষ পর্যায়, যুদ্ধ মন্বন্তরের কালো ছায়া, দাঙ্গা, দেশভাগের অশনিসঙ্কেত। অন্যদিকে, গান্ধীবাদী, সন্ত্রাসবাদী ও বাম রাজনীতির পারস্পরিক দ্বন্দ্ব, হরতাল, কৃষক আন্দোলন এবং অবিভক্ত কমিউনিস্ট পার্টির প্রকাশ। এই বিষয়গুলিই তাঁর কথাসাহিত্যে এবং সেই সূত্রে গল্পের বিষয় এবং চরিত্রে উঠে আসে। তার গল্পের একদিকে যেমন আছে রাজনৈতিক বিশ্বাস তেমনি আছে মানুষের মনের প্রকৃত সত্য অন্বেষণের প্রচেষ্টা। সাবিত্রী রায়ের লেখা নারীমনের দাবীকে স্বাকীর করে। তাঁর লেখায় পাই নারী মনের না পাওয়ার বেদনা, পুরুষের বিশ্বাসঘাতকতায় নারীর মনের বিশ্বাসভঙ্গ ও আবার বিশ্বাস করা, বদ্ধ জীবন থেকে ছিটকে আসার জন্য নারী মনের প্রতিবাদ, পুরুষতন্ত্রের নগ্ন রূপ, নারীর জীবনে অবহেলা, বঞ্চনা, নারী-পুরুষের পারস্পরিক সম্পর্ক ও তার সূক্ষ্ম বিশ্লেষণ, সাম্রাজ্যবাদী ফ্যাসীবাদের প্রভাবে সমাজ ও পরিবার জীবনে নেমে আসা অন্ধকার ও তার পরিণাম। এখানে, একটি বিষয় লক্ষণীয়, লেখিকা তার সৃজনী সত্তাকে দুই ভাগে ভাগ করে দেখেছেন--ব্যক্তি এবং শিল্পীসত্তা – যা তার দেখার দৃষ্টিকে দিয়েছে এক সামগ্রিক সম্পূর্ণতা।

কথাসাহিত্যিক সাবিত্রী রায় প্রধানত ঔপন্যাসিক। তিনি স্বল্প সংখ্যক গল্প লেখেন। এই গল্পগুলির মধ্যে দিয়ে ছোটগল্পকার সাবিত্রী রায়ের জীবনদৃষ্টিকে সম্যকভাবে উপলব্ধি করা যায়। পারিপার্শ্বিকতা ও মানস বৈশিষ্ট্যের সমন্বয়ে সৃষ্টব্যক্তিত্ব সামাজিক-রাজনৈতিক-অর্থনৈতিক-মানবিক ঘাত-প্রতিঘাতের মধ্যে দিয়ে পৌঁছে যায় নির্দিষ্ট প্রত্যয়ে। ছোটগল্পে সেই প্রত্যয় প্রতিফলিত হয়। শারীরিক অসুস্থতা এবং মানসিক স্বাতন্ত্র্যবোধের কারণেও তিনি সক্রিয় রাজনীতিতে যুক্ত হতে পারলেন না। সুস্থ জীবনবোধ এবং প্রথাবিরোধী মনোভাবের জন্য সাবিত্রী রায়কে সাহিত্যের ইতিহাসে আলাদাভাবে চিহ্নিত করা যায়।

সাবিত্রী রায় যখন বাংলা সাহিত্যে আবির্ভূত হলেন তখন দেশে চলছে অস্থির অবস্থা। সময়টা হল বিগত শতকের চল্লিশের দশক। সুতরাং, সহজেই অনুমেয় হয় দেশের পরিস্থিতির চালচিত্র। সাবিত্রী রায় যে যুগ সন্ধিক্ষণে বাংলা সাহিত্যে আবির্ভূত তখন ফ্যাসীবাদ ভয়াল রূপ ধারণ করেছে। বিশ্ব রাজনীতি বা আন্তর্জাতিক রাজনীতির অবস্থা টালমাটাল। দুই দুটো বিশ্বযুদ্ধ সমগ্র পৃথিবীকে সঙ্কটের মুখে দাঁড় করিয়ে দিয়েছে।

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# বাংলা কথাসাহিত্যের সাম্প্রতিক প্রবণতার প্রেক্ষিতে নিরুপমা দেবী ও মহাশ্বেতা দেবীর গল্প : একটি তুলনামূলক সমীক্ষা

মণিকুন্তলা বসু

ভারতীয় সাহিত্য সময়ের গতির মতই প্রবহমান । সুদূর অতীতকাল থেকে বর্তমানকাল পর্যন্ত ভারতীয় সাহিত্য ভাঙা-গড়া, চড়াই-উৎরাই-এর মধ্যে দিয়ে, সমকালীন সামাজিক-রাজনৈতিক-অর্থনৈতিক-ধর্মনৈতিক-মনস্তাত্ত্বিক জীবনদর্শনকে আত্মীকরণ করে ভবিষ্যতের পথে এগিয়ে চলেছে । সাহিত্যের উদ্ভব ঘটে সমকালীন দেশকালের প্রেক্ষাপটে ও সাহিত্যিকের অভ্যন্তরীণ তাগিদে । ভারতীয় সাহিত্য যথার্থভাবে উপলব্ধি করতে হলে ভারতের মূল দর্শনটিকে জানা প্রয়োজন । ভারতবর্ষের চিন্তাচেতনার মূলে আছে বেদ ও উপনিষদের ভিত । উপনিষদ হল বেদেরই নির্যাস, এখানে ব্রহ্ম হল এক এবং অদ্বিতীয় ।

রবীন্দ্রনাথ যে সনাতন ভারতবর্ষকে আবিষ্কার করেছেন, সে ভারতবর্ষের সাধনাই বৈচিত্র্যের মধ্যে ঐক্যের সাধনা । বেদ-উপনিষদ শুধু নয়, বৌদ্ধদর্শন ও জৈন ধর্মের সংমিশ্রণও ঘটে ভারতীয় সাহিত্যে । ঐক্য ও মিলনের আদর্শ, সাম্য ও মৈত্রীর আদর্শ, বাধাশূন্য, হিংসাশূন্য মানসিকতাই হল মনুষ্যত্ব । ভারতীয় সাহিত্য এই ঐতিহ্যকে বহন করে চলেছে । পাশাপাশি সহাবস্থান করে চলেছে অন্ত্যজ সম্প্রদায়ের চিন্তাচেতনা এবং দার্শনিকতা । রবীন্দ্রনাথ, রামকৃষ্ণ পরমহংস, স্বামী বিবেকানন্দ ভারতীয় চেতনায় এই ঐতিহ্যকেই বহন করেছেন ও এক উদার ভাবনার জন্ম দিয়েছেন । এই উদারতা ও ত্যাগের মন্ত্রে ভারতীয় সাহিত্য আবহমানকাল থেকে সিক্ত ও সমৃদ্ধ ।

ভারতবর্ষে অস্পৃশ্যতা, জাতিভেদ প্রথা, কৌলিন্য, সাম্প্রদায়িকতা উন্নতির পথে বাধা সৃষ্টি করেছে । বিভেদকে ঐক্যের বাণীতে পরিণত করাই কবি-সাহিত্যিকের কাজ । দলিত, পতিত, অন্ত্যজ শ্রেণির মানুষের জীবন থেকে অভিশাপ দূর করাই হল মনুষ্যত্বের বড় ধর্ম । এই ধর্মবোধ থেকে পরাধীন ভারতবর্ষের শৃঙ্খলমোচনের উদ্দেশ্যে মানুষের সম্মেলনে মঙ্গল ঘট প্রতিষ্ঠিত হয়েছে ভারতবর্ষেই । ফলস্বরূপ নানা ভাষাভাষী ও সম্প্রদায়ের পাশাপাশি সহাবস্থান ঘটেছে । সৃষ্টি হয়েছে বিভিন্ন ভাষার সাহিত্যের । গুজরাটি, তামিল, তেলেগু, উর্দু, হিন্দী, অসমীয়া, ওড়িয়া, বাংলা বিভিন্ন ভাষার সাহিত্যের কয়েকটি দৃষ্টান্তমাত্র ।

বাংলা ভাষা ভারতীয় ভাষার একটি অঙ্গ । ভারতীয় সাহিত্যের প্রভাবে বাংলা সাহিত্যও একই উত্তরাধিকার বহন করে চলেছে । বাংলা সাহিত্য সংস্কৃতিতে অন্যের সংস্কৃতির প্রতি সম্মান প্রদর্শন করা হয় যথেষ্ট শ্রদ্ধার সঙ্গে । কারণ, বাংলাদেশে বিভিন্ন প্রদেশের মানুষের সহাবস্থান ঘটেছে ।

বাংলা সাহিত্য আবহমানকাল থেকে সমকালীন সামাজিক-অর্থনৈতিক-রাজনৈতিক-মনস্তাত্ত্বিক চিন্তাচেতনাকে বিশ্বস্তভাবে তুলে ধরেছে । ভারতীয় সাহিত্যের রূপান্তরের ধারায় বিশ শতকের প্রথম অর্ধের প্রতিনিধি স্থানীয় লেখিকা নিরুপমা দেবী এবং বিশ শতকের দ্বিতীয় অর্ধের ও একবিংশ শতকের প্রথম দশকের প্রতিনিধি স্থানীয় লেখিকা মহাশ্বেতা দেবীর গল্পের এক তুলনামূলক বিচার বিশ্লেষণ এই নিবন্ধে দেখানোর প্রচেষ্টা করা হবে, অনুসন্ধান করা হবে এই দুই লেখিকা তাঁদের সাহিত্যকর্মে কীভাবে সমকালীন ভাবনাকে রূপ দিয়েছিলেন । নারী ভাবনার বিবর্তনে এবং সময়কে সাক্ষী হিসাবে গ্রহণ করার ক্ষেত্রে দুই ভিন্ন সময়ের এই দুই লেখিকা কতখানি

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## পরবর্তী সংখ্যার বিষয়

সমাজ, সাহিত্য ও সংস্কৃতি বিষয়ক যে কোনো প্রবন্ধ

অভ্রতে কালপুরুষ ফন্ট এ লিখে সফট কপি uttamnbu@gmail.com এপাঠানফেব্রুয়ারি ২০২২
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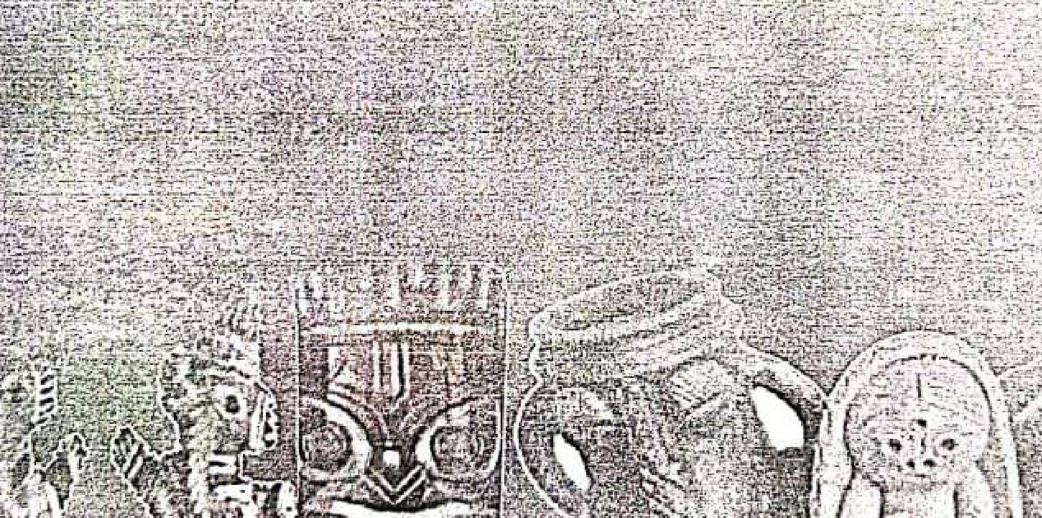
## বিশেষ সংখ্যা –
## লোকসংস্কৃতি
## ও
## অন্যান্য প্রবন্ধ



সম্পাদক : ড. উত্তম দাস

# নিম্নবর্গীয় চেতনার আলোকে আধুনিক বাংলা সাহিত্য

ড. মণিকুন্তলা বসু

## সারসংক্ষেপ (Abstract)

আলোচ্য প্রবন্ধে দেখানো হবে নানান রাজনৈতিক উত্থান পতনের মধ্যেও হাজার হাজার বছরের প্রাচীন বর্ণাশ্রমিক সমাজের বোঝা থেকে আমরা কেন মুক্ত হতে পারিনি। কোথাও স্থূলভাবে, কোথাও অতি সূক্ষ্ম আকারে সামন্তবাদ, উপনিবেশবাদ ও মনুবাদের মিশ্রণ সমাজের গভীর মনোজগতে চলমান থেকে যাচ্ছে। কিন্তু কেন? দীর্ঘদিন ধরে সমাজে যে অগণতান্ত্রিক সমাজ ব্যবস্থা চলে আসছিল তা থেকে মানুষের মুক্তির পথ ইতিহাসের প্রচ্ছন্ন উদ্দেশ্য বলে ভাবা হলে ইতিহাস চেতনার সঙ্গে গণতান্ত্রিক চেতনা গভীরভাবে সম্পর্কযুক্ত, একথাও বিশ্বাস করতে হবে। কিন্তু এতদিন ধরে আমরা সে চিন্তার পথে অগ্রসর হইনি। শুধু সাম্রাজ্যবাদের বিরোধিতা করে এত দিন আমরা যে ইতিহাস রচনা করেছি তা এলিটিস্টদের ইতিহাসে পরিণত হয়েছে। সেই ইতিহাসে সমাজের নারী, কৃষক-মজুর বা সমাজের নিপীড়িত মানুষদের কথা উঠে আসেনি।

মূল শব্দ – নিম্নবর্গ , সামন্তবাদ , সমাজ , ইতিহাস , উপন্যাস

## মূল প্রবন্ধ -

নিত্যপ্রসারণশীল মানুষের মন ও চেতনার জগতে একটা বিশেষ দেশ ও কালের গণ্ডী ছাড়িয়ে অতীত সময়ের স্রোতের মধ্যে সমাজকে বুঝতে চাওয়ার অনুসন্ধিৎসা মানুষের সহজাত প্রবৃত্তি। স্বাভাবিকভাবে সমাজকে বুঝতে হলে আমাদের অতীতচারী হতে হবে, অতি প্রাচীন কাল থেকে চলে আসা সামাজিক সমস্যাগুলিকে উপলব্ধি করে সমাজের প্রকৃত সমস্যা কোথায় তা বুঝে নিতে হবে এবং ইতিহাসের আশ্রয় নিয়েই তার সমাধান করতে হবে। মনে রাখতে হবে দীর্ঘদিন ধরে সমাজে যে অগণতান্ত্রিক সমাজ ব্যবস্থা চলে আসছিল তা থেকে মানুষের মুক্তির পথ ইতিহাসের প্রচ্ছন্ন উদ্দেশ্য বলে ভাবা হলে ইতিহাস চেতনার সঙ্গে গণতান্ত্রিক চেতনা গভীরভাবে সম্পর্কযুক্ত, একথাও বিশ্বাস করতে হবে। কিন্তু এতদিন ধরে আমরা সে চিন্তার পথে অগ্রসর হইনি। শুধু সাম্রাজ্যবাদের বিরোধিতা করে এত দিন আমরা যে ইতিহাস রচনা করেছি তা এলিটিস্টদের ইতিহাসে পরিণত হয়েছে। সেই ইতিহাসে সমাজের নারী, কৃষক-মজুর বা সমাজের নিপীড়িত মানুষদের কথা উঠে আসেনি। নিম্নবর্গের ইতিহাসচর্চার সাম্প্রতিক ধারায় ইতিহাস রচনা সমাজের নিম্নবর্গীয় সকল সম্প্রদায়ের ইতিহাসকে আলোচনায় তুলে এনে সাবলটার্ন স্টাডিজের একদল গবেষক আধুনিক ইতিহাসচর্চায় এক নতুন দিগন্তের উন্মেষ ঘটিয়েছেন এবং ইতিহাসচর্চাকে একটি গতিশীল বিজ্ঞানে পরিণত করেছেন। গতিশীল সমাজ, সংস্কৃতি, রাজনীতি, অর্থনীতি ইত্যাদি বিষয়ের উপর আলোকপাত করে ইতিহাসকে একটি ধারাবাহিক আন্দোলনে পরিণত করেছেন। এই আলোচনার উৎস হিসেবে যেমন সমাজ ও সভ্যতার উৎপত্তি, গঠন, প্রক্রিয়া, বিকাশ, স্বরূপ, বিস্তৃতি, জটিলতা প্রভৃতি বিষয়সমূহকে নানা ভাবে বিশ্লেষণের পরিধিতে আনতে হয়েছে তেমনি আমাদের সংস্কৃতি, রাজনীতি, শিল্প-সাহিত্য ইত্যাদি বিষয়সমূহকেও নিম্নবর্গীয় ইতিহাসচর্চার উপাদানে পরিণত করা হয়েছে।

ফলে সত্য অনুসন্ধানের জন্য ইতিহাসচর্চা যে শিল্প-সাহিত্যের মধ্য থেকে তার উপাদান সংগ্রহ করবে এটাই স্বাভাবিক। ইতিহাস সমাজবদ্ধ মানুষের জীবন বিশ্লেষণ করে। আর সমাজবদ্ধ মানুষকে জানতে যুগে যুগে লেখক-শিল্পীরা তাঁদের অন্তর্দৃষ্টি দিয়ে যে সাহিত্য ও শিল্প সৃষ্টি করে গেছেন তা বুঝতেও সাহায্য করে। রবীন্দ্রনাথ ঠাকুরের ভাষায়, "আমাদের অন্তঃকরণে যত কিছু বৃত্তি আছে সে কেবল

সূচীপত্র-

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অভ্রতে কালপুরুষ ফন্টে লিখে সফট কপি samsaptakuk12@gmail.com এ পাঠান ১৫ এপ্রিল ২০২৩ এর মধ্যে ।

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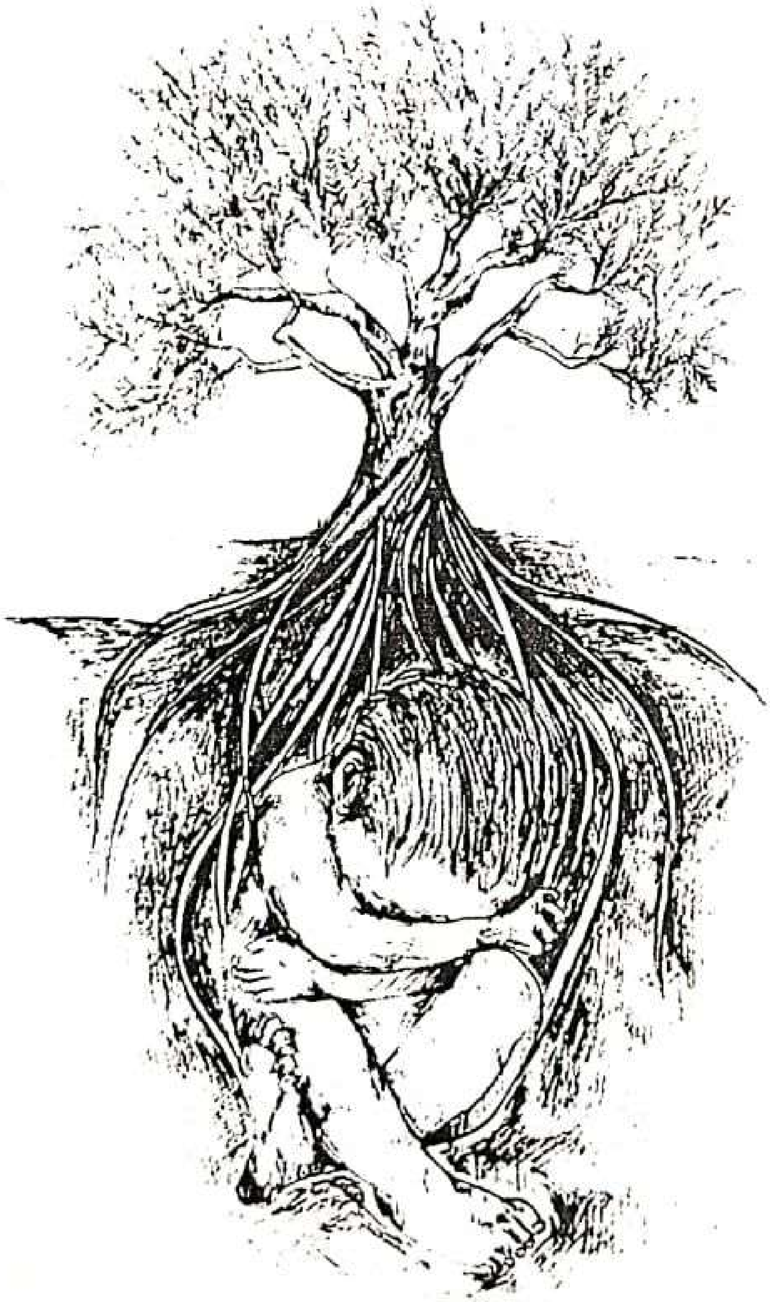
ডিসেম্বর - ২০২২



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সংশপ্তক II সপ্তম বর্ষ II প্রথম সংখ্যা

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# বাংলা কথাসাহিত্যের সাম্প্রতিক প্রবণতার প্রেক্ষিতে নিরুপমা দেবী ও মহাশ্বেতা দেবীর গল্প : একটি তুলনামূলক সমীক্ষা

মণিকুন্তলা বসু

ভারতীয় সাহিত্য সময়ের গতির মতই প্রবহমান । সুদূর অতীতকাল থেকে বর্তমানকাল পর্যন্ত ভারতীয় সাহিত্য ভাঙা-গড়া, চড়াই-উৎরাই-এর মধ্যে দিয়ে, সমকালীন সামাজিক-রাজনৈতিক-অর্থনৈতিক-ধর্মনৈতিক-মনস্তাত্ত্বিক জীবনদর্শনকে আত্মীকরণ করে ভবিষ্যতের পথে এগিয়ে চলেছে । সাহিত্যের উদ্ভব ঘটে সমকালীন দেশকালের প্রেক্ষাপটে ও সাহিত্যিকের অভ্যন্তরীণ তাগিদে । ভারতীয় সাহিত্য যথার্থভাবে উপলব্ধি করতে হলে ভারতের মূল দর্শনটিকে জানা প্রয়োজন । ভারতবর্ষের চিন্তাচেতনার মূলে আছে বেদ ও উপনিষদের ভিত । উপনিষদ হল বেদেরই নির্যাস, এখানে ব্রহ্ম হল এক এবং অদ্বিতীয় ।

রবীন্দ্রনাথ যে সনাতন ভারতবর্ষকে আবিষ্কার করেছেন, সে ভারতবর্ষের সাধনাই বৈচিত্র্যের মধ্যে ঐক্যের সাধনা । বেদ-উপনিষদ শুধু নয়, বৌদ্ধদর্শন ও জৈন ধর্মের সংমিশ্রণও ঘটে ভারতীয় সাহিত্যে । ঐক্য ও মিলনের আদর্শ, সাম্য ও মৈত্রীর আদর্শ, বাধাশূন্য, হিংসাশূন্য মানসিকতাই হল মনুষ্যত্ব । ভারতীয় সাহিত্য এই ঐতিহ্যকে বহন করে চলেছে । পাশাপাশি সহাবস্থান করে চলেছে অন্ত্যজ সম্প্রদায়ের চিন্তাচেতনা এবং দার্শনিকতা । রবীন্দ্রনাথ, রামকৃষ্ণ পরমহংস, স্বামী বিবেকানন্দ ভারতীয় চেতনায় এই ঐতিহ্যকেই বহন করেছেন ও এক উদার ভাবনার জন্ম দিয়েছেন । এই উদারতা ও ত্যাগের মন্ত্রে ভারতীয় সাহিত্য আবহমানকাল থেকে সিক্ত ও সমৃদ্ধ ।

ভারতবর্ষে অস্পৃশ্যতা, জাতিভেদ প্রথা, কৌলিন্য, সাম্প্রদায়িকতা উন্নতির পথে বাধা সৃষ্টি করেছে । বিভেদকে ঐক্যের বাণীতে পরিণত করাই কবি-সাহিত্যিকের কাজ । দলিত, পতিত, অন্ত্যজ শ্রেণির মানুষের জীবন থেকে অভিশাপ দূর করাই হল মনুষ্যত্বের বড় ধর্ম । এই ধর্মবোধ থেকে পরাধীন ভারতবর্ষের শৃঙ্খলমোচনের উদ্দেশ্যে মানুষের সম্মেলনে মঙ্গল ঘট প্রতিষ্ঠিত হয়েছে ভারতবর্ষেই । ফলস্বরূপ নানা ভাষাভাষী ও সম্প্রদায়ের পাশাপাশি সহাবস্থান ঘটেছে । সৃষ্টি হয়েছে বিভিন্ন ভাষার সাহিত্যের । গুজরাটি, তামিল, তেলেগু, উর্দু, হিন্দী, অসমীয়া, ওড়িয়া, বাংলা বিভিন্ন ভাষার সাহিত্যের কয়েকটি দৃষ্টান্তমাত্র ।

বাংলা ভাষা ভারতীয় ভাষার একটি অঙ্গ । ভারতীয় সাহিত্যের প্রভাবে বাংলা সাহিত্যও একই উত্তরাধিকার বহন করে চলেছে । বাংলা সাহিত্য সংস্কৃতিতে অন্যের সংস্কৃতির প্রতি সম্মান প্রদর্শন করা হয় যথেষ্ট শ্রদ্ধার সঙ্গে । কারণ, বাংলাদেশে বিভিন্ন প্রদেশের মানুষের সহাবস্থান ঘটেছে ।

বাংলা সাহিত্য আবহমানকাল থেকে সমকালীন সামাজিক-অর্থনৈতিক-রাজনৈতিক-মনস্তাত্ত্বিক চিন্তাচেতনাকে বিশ্বস্তভাবে তুলে ধরেছে । ভারতীয় সাহিত্যের রূপান্তরের ধারায় বিশ শতকের প্রথম অর্ধের প্রতিনিধি স্থানীয় লেখিকা নিরুপমা দেবী এবং বিশ শতকের দ্বিতীয় অর্ধের ও একবিংশ শতকের প্রথম দশকের প্রতিনিধি স্থানীয় লেখিকা মহাশ্বেতা দেবীর গল্পের এক তুলনামূলক বিচার বিশ্লেষণ এই নিবন্ধে দেখানোর প্রচেষ্টা করা হবে, অনুসন্ধান করা হবে এই দুই লেখিকা তাঁদের সাহিত্যকর্মে কীভাবে সমকালীন ভাবনাকে রূপ দিয়েছিলেন । নারী ভাবনার বিবর্তনে এবং সময়কে সাক্ষী হিসাবে গ্রহণ করার ক্ষেত্রে দুই ভিন্ন সময়ের এই দুই লেখিকা কতখানি

# সংশপ্তক, SAMSAPTAK

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## পরবর্তী সংখ্যার বিষয়

সমাজ, সাহিত্য ও সংস্কৃতি বিষয়ক যে কোনো প্রবন্ধ

অভ্রতে কালপুরুষ ফন্ট এ লিখে সফট কপি uttamnbu@gmail.com এপাঠানফেব্রুয়ারি ২০২২ এর মধ্যে।পিডিএফ করবেন না, 9734518427

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# সংশপ্তক

ISSN : 2454-4884

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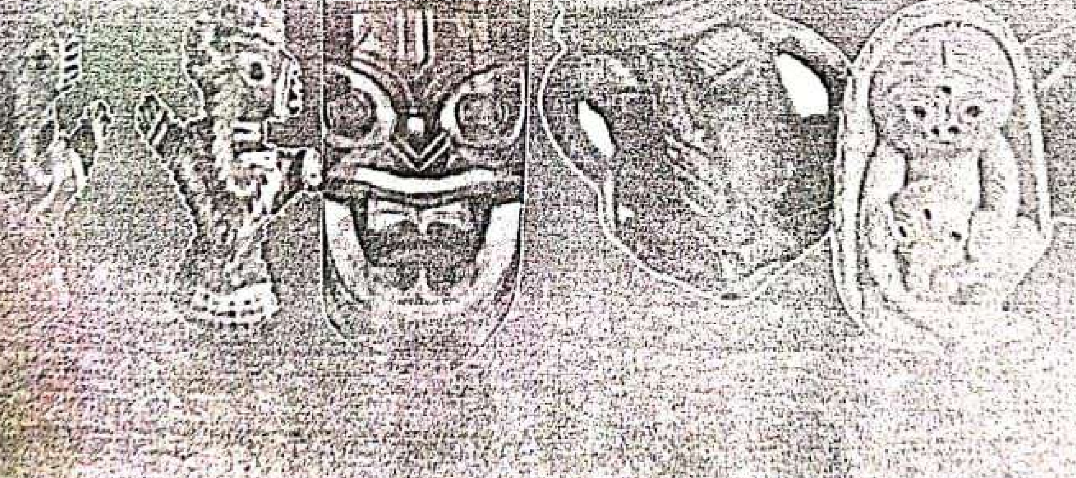
ডিসেম্বর-২০২১

## বিশেষ সংখ্যা – লোকসংস্কৃতি ও অন্যান্য প্রবন্ধ



সম্পাদক : ড. উত্তম দাস

| Journal Title | Publisher | ISSN | E-ISSN |
|---|---|---|---|
| सन्मति | Bahubali Vidyapeeth | 2395-5503 | NA |
| समकालीन भारतीय साहित्य | साहित्य अकादेमी | 0970-8367 | NA |
| समयांतर | Sweet Home Publication | 2249-0469 | NA |
| सर्वधारा | Sukhadev Dhanke | 2249-3034 | NA |
| Journal Title | Publisher | ISSN | E-ISSN |
| सहृदय | Nav Unnayan | 2230-8997 | NA |
| साहित्य अमृत | Sahitya Amrit | 2455-1171 | NA |
| हंस | Akshar Prakashan | 2454-4450 | NA |
| অন্তর্মুখ | Khokan Kumar Bag | 2249-3751 | NA |
| ইতিহাস | Bangiya Itihas Samiti Kolkata | 2320-3447 | NA |
| এবং মহুয়া ✓ | K. K. Prakashan | NA | NA |
| ঐতিহ্য- THE HERITAGE | Aitihya Samstha | 2229-5399 | NA |
| [illegible] চর্চা | Sisir Chatterjee | 2581-4788 | NA |
| [illegible] হিস্টোরিক্যাল স্টাডিজ | Department of History, Rabindra Bharati University | 0972-6756 | NA |
| [illegible] | Centre for Studies in Humanities | 2249-0612 | NA |

# List of UGC approved journals 2020

List from www.openacessjournal.com, or www.ugc-journal-list.website

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- ii) ii) Social Sciences
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- iv) iv) Multidisciplinary based on All Science Journal Classification (ASJC) codes, which are created and maintained by Scopus (Elsevier Science) Journals indexed in Web of Science as well as Scopus or discontinued are not included in the count.

| Journal Title | Publisher | ISSN | E-ISSN |
|---|---|---|---|
| Acta Fytotechnica et Zootechnica | Slovak University of Agriculture in Nitra | 1335-258X | 1336-9245 |
| Acta Geographica Debrecina, Landscape and Environment Series | Department of Landscape Protection and Environmental Geography, University of Debrecen | 1789-4921 | 1789-7556 |
| Acta Graphica | Faculty of Graphic Arts, University of Zagreb | 0353-4707 | 1848-3828 |
| Acta Universitatis Apulensis | Department of Mathematics and Informatics, University of Alba Iulia | 1582-5329 | NA |
| Acta Universitatis Matthiae Belii Series Mathematic | Department of Mathematics Faculty of Natural Sciences, Matej Bel University | 1338-712X | 1338-7111 |

# বিষয়-বৈচিত্র্যের দর্পণে আবুল বাশারের ছোটগল্প

## সমীরণ সরকার

বিংশ শতকের সাতের দশক থেকে বর্তমান সময় পর্যন্ত বাংলা কথাসাহিত্যের [illegible] নিরন্তরতা ও বিষয়-বৈচিত্র্যকে আশ্রয় করে আবুল বাশার সাহিত্য চর্চা করে চলেছেন প্রায় নিরবধি। বর্তমানে তিনি কলকাতা নগরের নাগরিক হলেও জন্মসূত্রে তিনি প্রত্যন্ত গ্রামীণ মানুষ। মুর্শিদাবাদ জেলার লালবাগ মহকুমার নতুন হাসানপুর নামক গ্রামে এক দরিদ্র কৃষক পরিবারে, ১৯৫১ খ্রিস্টাব্দে তাঁর জন্ম। তাঁর পিতার নাম কলিমুদ্দিন আহমেদ, মাতা জহরা খাতুন। আবুল বাশারের বয়স যখন মাত্র ৬ বছর তখনই কলিমুদ্দিন সপরিবারে টেঁকারাইপুর গ্রামে চলে আসেন। বাশারের পিতা একটা সময় ভারতীয় সেনাবাহিনীর অফিসে চাকরি করতেন, পরে গ্রামের বিদ্যালয়ে শিক্ষকতা করেন। অভাব-দারিদ্র্যের মধ্যে থেকেও পিতা কলিমুদ্দিন আবুল বাশারকে লেখা-পড়ায় উৎসাহ ও প্রেরণা দিয়েছেন অকৃপণ ভাবে।

মাত্র চৌদ্দ বছর বয়সে আবুল বাশারের কবিতা লেখায় হাতেখড়ি। তিনি ইসলামপুর হাইস্কুলে পড়তেন। পড়াশুনায় আগ্রহী ও মেধাবী বাশারকে স্কুলের সকল শিক্ষকই ভালোবাসতেন, স্নেহ করতেন। স্কুলের প্রধান শিক্ষক নিশিনাথ সেন তাকে কবিতা রচনায় উৎসাহ দিতেন, শেখাতেন নাটক অভিনয়ও। এই কৃতজ্ঞতায় বাশার "[illegible] সুন্দরী" উপন্যাসটি শিক্ষক নিশিনাথ সেনকে উৎসর্গ করেন। ১৯৭১ খ্রিস্টাব্দে তাঁর প্রথম কাব্যগ্রন্থ 'ঝড় উপড়ানো ডালপালা ভাঙা আর এক ঋতু' প্রকাশিত হয়। এর আগে "নবজাতক" পত্রিকায় তাঁর কবিতা প্রকাশিত হয়। ধীরে ধীরে তিনি মনীশ ঘটক, বীরেন্দ্র চট্টোপাধ্যায় প্রমুখ কবির সঙ্গে পরিচিত হয়ে ওঠেন।

স্কুলের পাঠ শেষ করে বহরমপুর কমার্স কলেজে ভর্তি হয়ে তিনি বাণিজ্য বিভাগে স্নাতক ডিগ্রি লাভ করেন। এই সময় তিনি বামপন্থী রাজনীতির সাথে যুক্ত হন। বাশারের বোন হেনা তখন গার্লস কলেজের ছাত্রী, এই বোনের হাত ধরেই তিনি বিপ্লবী দলের সঙ্গে যুক্ত হন, এস.ইউ.সি.আই. দলের কর্মী ও সংগঠক হয়ে ওঠেন তখন। তিনি নিজেকে সক্রিয়ভাবে রাজনীতির সঙ্গে জড়িয়ে ফেলার কারণে লেখার জগৎ থেকে এই সময়টায় দূরে সরে যান। দেশে জরুরি অবস্থা ও নকশাল আন্দোলনে [illegible] উত্তাল-বিক্ষুব্ধ। আবুল বাশার এই পার্টির অতি সক্রিয় কর্মী। বাশারের [illegible] তখন এই রাজনৈতিক উত্তাপে আরো তপ্ত হয়ে ওঠে। তাঁর রাজনৈতিক [illegible] পাব তাঁর 'অগ্নিবলাকা' উপন্যাসে। ১৯৭৭ সালে [illegible] হলে ধীরে ধীরে নকশাল আন্দোলনও স্তিমিত হয়, রাজনৈতিক

'এবং মহুয়া' -বিশ্ববিদ্যালয় মঞ্জুরী আয়োগ (UGC-CARE)
অনুমোদিত তালিকার অন্তর্ভুক্ত।
২০২০সালে প্রকাশিত ৮৬পৃ.তালিকার ৬০ পৃ.এবং ৮৪পৃ.উল্লেখিত।

# এবং মহুয়া

(বাংলা ভাষা, সাহিত্য ও গবেষণাধর্মী মাসিক পত্রিকা)

২৩ তম বর্ষ, ১২৯ সংখ্যা
জানুয়ারী ২০২১

সম্পাদক
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মো.-৯১৫৩১৭৭৬৫৩

কে.কে. প্রকাশন
গোলকুঁয়াচক, মেদিনীপুর, পশ্চিমবঙ্গ।

# An Ethical Excursion of Euthanasia

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## Abstract :

*Should an individual, in addition to the right to live, have a right to die? The debate of euthanasia has been a globally controversial and overheated issue for many decades. The word 'euthanasia' is derived from Greek 'euthanos' meaning 'a gentle and easy death'. However, it is now used to refer to the killing of patients who are incurably ill and in great pain and distress, in order to relieve them of their sufferings. Euthanasia can be of three types: voluntary euthanasia or assisted suicide or mercy killing (euthanasia performed with patient's consent), non-voluntary euthanasia (when the patient is unable to give consent) and involuntary euthanasia (which is performed on a patient against his will). Euthanasia can be carried out either by administering a lethal dose of a suitable drug (active euthanasia) or letting the patient die by withholding treatment (passive euthanasia). While passive euthanasia is considered legal in many countries (India, Australia, Germany, England, etc) active euthanasia is only legal in Netherlands and Belgium. The person seeking euthanasia often argues that in a civilized society giving everybody the right to a 'dignified death' without pain is ethically acceptable as a universal principle. However, there are many social, political and moral dilemmas legalizing euthanasia. In this dissertation few of them is highlighted.*

## Key words:

Euthanasia, dignified death, assisted suicide, mercy killing, active, passive, moral dilemma.

The ending of life is called death. But murder signifies the destruction of life. People die in regular flow of life in nature. But murder is always follow by a certain motive and a planning[1]. This motive might be both beneficial or fatal and sometimes it can be mighty. Now, question may arise - how can murder be mighty? In general, when a person takes life of another person for his vengeance to fulfilled. Again when a person destroys the life of his own, that is called suicide. There is no place for revenge behind suicide and there is no context of destruction of life against one's will. A person is the soul owner of his life and he possesses the right to destroy it. Hence, suicide, though no desired, but is not a crime at all[1].

There is another type of death which is called mercy killing or euthanasia. In this case, a person's life is put to an end out of mercy to relieve the person from his agony of incurable disease. Now the question is, should an individual, in addition to the right to live, have a right to die? Should he have a right to decide, how and when to end his life? The debate of Euthanasia has been a globally controversial and overheated issue for many decades. The debate cuts across complex and dynamic aspect such as legal, ethical, human rights, health, religious, economic, D.B

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# An Outline of Women's Empowerment

Dyutikana Bajani
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**Abstract:**

Women empowerment is an act of giving women the power or authority to do something. In our country 'women empowerment' is a very accessible topic. Few decades ago here women has no control over their own life or the situation they were in. In the post independence period the scenario has changed. This change took place due to the growth of female literacy. Educational knowledge makes them well known about their place in the outside world. They realize their ability or potentiality for the social development. This article discusses a formal description of the term 'empowerment' in the context of women empowerment. But there is not any well-defined explanation for this term 'empowerment'. Because the concept 'power' is itself unclear. So in understanding women empowerment, we need to look at the different meaning of the term 'power' and as well as 'empowerment'. This dissertation explains the term 'power' in different ways: 'power over', 'power to', 'power with', 'power within', 'social power', political power, psychological power etc. Like 'power' the term 'empowerment' is also used in various sense: empowerment at personal level, Empowerment at organization level and empowerment at community level. With all of these meaning of 'power' and 'empowerment' this article explains the basic concept of women empowerment.

**Keywords**: power over, power to, power with, power within, psychological power, empowerment, patriarchal.

Gender equality is, first and foremost, a human right. A woman is entitled to live in dignity and freedom. Empowering women is also an indispensable tool for advancing development and reducing poverty. Empowered women contribute to the health and productivity of whole families and communities and improved prospects for the next generation. Since the beginning of civilization, there has been bulk evidence of women being considered inferior to men. Almost every country, no matter how progressive has a history of ill-treating women. This has eventually nudged to women to retrospect their status in society and has even led women from all over the world to be rebellious to reach the status they have today. Since then, women have been vocal about gender equality and have continuously made efforts to empower themselves to achieve that equality. The empowerment and autonomy of women and the improvement of their political, social, economic, and health status is a highly important end in itself.

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Part -7

# মহারাজা নন্দকুমার ও একটি ফাঁসির ষড়যন্ত্র : মৌখিক তথ্যের পুনঃপর্যালোচনা

# Maharaja nanda kumar O Akti phansir sarajantra : Moukhik Tathyer punorparjalochona

**Ujjal mandal**
Assistant professor
Department of history
Sagardighi K.K.S. Mahavidyalaya

উজ্জ্বল মণ্ডল

**সহকারী অধ্যাপক, ইতিহাস বিভাগ**
**সাগরদিঘী কে. কে. এস. মহাবিদ্যালয়**

## Abstract:

*[Maharaja Nanda Kumar was the revenue collector of Alibardi Khan. Later disagreement broke out in between Sirajuddla and Nanda Kumar. Mirjafor, after becoming the Nawab of Bengal, failed to pay the demand of the E.I.C. and compelled to give up all responsibilities, regarding the collection of revenue in Nadia and Burdwan to E.I.C. From this time a conflict broke out in between Nanda Kumar and Waren Hastings, then the Governor General of Bengal. Nanda Kumar brought some precious wealth like string of pearls neckles and four diamond ring to Murshidabad when he was Dewan of Hooghly. Later he sold this wealth to Bulaki Das, a money lender and he lost it. As a result Bulaki Das failed to repay said money to Maharaja Nanda Kumar and gave him a deed by mentioning about the collection of said money from the British Treasury of Bangladesh. After death of Bulaki Das, Maharaja Nanda Kumar withdrawal the said money but Waren Hastings as a conspirator, tried to prove that this deed was duplicate one and Supreme Court declared hanging order to Nanda Kumar. Though oral sources says that Waren Hastings tried to export a precious Kali Idol from Bengal. But Maharaja Nanda Kumar wanted to setup this idol to his nearby village, I.E. Akalipur*

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১৫. ড: আদিত্য মুখোপাধ্যায় - 'পাথরের দেবতা', কলকাতা ২০১০ পৃষ্ঠা ৬৯।

১৬. বিনয় ঘোষ 'পশ্চিমবঙ্গের সংস্কৃতি', কলকাতা, ১৯৫৭, পৃষ্ঠা ২৯২।

১৭. বিনয় ঘোষ পূর্বোক্ত, পৃষ্ঠা ২৯২।

১৮. বামাক্ষ্যাপা ১৮৩৭ খ্রী: ১২ ফাল্গুন জন্মগ্রহণ করেন তারাপীঠের নিকটবর্তী আটলা গ্রামে। বজ্রবাসী কৈলাশপতি বাবার কাছে দীক্ষাগ্রহণ। 'জয় জয় তারা' মন্ত্র বলে তারামায়ের সিদ্ধিলাভ করেন; ১৯১২ খ্রী: তিরোধান।

১৯. কৈলাশপতি বাবার বাল্যনাম ভূবন মোহন মুখোপাধ্যায়। বাড়ী হুগলি জেলার উলু গুপ্তিপাড়া। প্রথমে ভৈরবী শুভঙ্করীর সান্নিধ্য লাভ করেন; তিনি বামাক্ষ্যাপার দীক্ষাগুরু ছিলেন; বেশ কিছুকাল তারাপীঠে কাটিয়েছিলেন।

২০. তারাক্ষেপা ছিলেন শ্রীশ্রী বামাক্ষ্যাপার মানস পুত্র এবং প্রধান শিষ্য। ভারতের মুক্তি সংগ্রামের সঙ্গে যুক্ত ছিলেন বলে কথিত আছেন।

২১. শঙ্করক্ষেপা ১৯২৬ খ্রী: তারাপীঠের নিকটবর্তী কবিচন্দ্রপুর গ্রামে জন্মগ্রহণ করেন। তিনি যে দোকানের খাবার চেয়ে খেতেন সেই দোকানের খাবার খুব দ্রুত বিক্রি হয়ে যেত। তিনি একবার জমিতে ফলিডল বিষ দেওয়া জল খেলেছিলেন কিন্তু তাতে তাঁর কোনো ক্ষতি হয়নি। এই সমস্ত অলৌকিক কর্মকান্ড মানুষ দেখেছেন।

২২. বিনয় ঘোষ তাঁর 'পশ্চিমবঙ্গের সংস্কৃতি' গ্রন্থে দেখিয়েছেন, ১৯৫৩ সালে তারাপীঠের রাস্তা ছিল অত্যন্ত দুর্গম কিন্তু ১৯৭৫ সালে তিনি রাস্তার যোগাযোগ সুগম হয়েছিল বলে উল্লেখ করেছেন।

২৩. গৌতম আচার্য (৫০), হস্তরেখাবিদ ও পুরোহিত, রামপুরহাট, ডাক্তারপাড়া।

২৪. সাধক বামাক্ষ্যাপা চলচিত্রটি মুক্তি পেলে তারাপীঠে বহু সংখ্যক পূন্যার্থী আসতে শুরু করে বাংলার বিভিন্ন জেলাগুলি থেকে।

২৫. বালুচিস্থানের মরুভূমিতে 'হিংলাচ' ৫১ সতীপীঠের একটি পীঠ। এই সতীপীঠকে কেন্দ্র করে একটি চলচিত্র মুক্তি পায় ফলে বাঙালী তথা ভারতীয়দের কাছে তীর্থক্ষেত্রটি জনপ্রিয় হয়ে ওঠে।

২৬. কলিকাতা যাবার পথে ট্রেনে অনেক তারামায়ের ভক্তদের সঙ্গে কথা বলে তারামায়ের অশেষ কৃপার কথা শুনেছি, অনেকে আবার বৎসরে দুই তিনবার বা তার থেকে বেশী তারাপীঠে পূজা দিতে আসেন।

২৭. বিপুল কুমার গঙ্গোপাধ্যায় 'মহাপীঠ তারাপীঠ', কলকাতা, ১৩৯২।

“তারাপীঠের তারামা” দীপ প্রকাশন, কলিকাতা- ২০০৮। এ প্রসঙ্গে উল্লেখযোগ্য ‘মরুতীর্থ হিংলাজ’ গ্রন্থটি তান্ত্রিক সাধক কালিকানন্দ রচনা করে বাঙালীদের কাছে পাকিস্তানের হিংলাজ সতীপীঠের জনপ্রিয়তা বাড়িয়ে তুলেছিলেন।৺

তথ্যসূত্র :

১. সাক্ষাৎকার – তারাময় মুখার্জী (৬০) স্থায়ী পান্ডা, তারাপীঠ ২৫/১১/১৪। প্রবোধ ব্যানার্জী (৪৫) তারাপীঠ মন্দির পরিচালনার সম্পাদক। প্রিয়রঞ্জন ব্যানার্জী (৪০) সহ পুরোহিত। সুখেন মুখার্জী (৩৭) সুমি পূজা ভান্ডারের মালিক। কার্তিক ধাড়া (৩৯) স্কুল শিক্ষক, স্থায়ী তারাপীঠের বাসিন্দা। তাপস দাস (৩৬) হোটেলের কর্মচারী। করিম্শা (৪১) চা দোকানের মালিক। প্রকাশ পাল (৪৭) শুভজিৎ টি স্টল এর মালিক। আশিস মণ্ডল (৪৭) লোকনাথ লজের মালিক। ইন্দ্রজিৎ মণ্ডল (৪৫) রামকৃষ্ণ হোটেলের মালিক।

২. ড: আদিত্য মুখাপাধ্যায়—‘রাঙামাটির গ্রাম’, বলাকা, কলকাতা ২০১৩, পৃষ্ঠা ১৫১।

৩. প্রবোধ কুমার বন্দ্যোপাধ্যায়—‘তীর্থভূমি তারাপীঠ’ মল্লারপুর প্রেস, ২০০৪ পৃষ্ঠা ৪০।

৪. বশিষ্ঠের সিদ্ধপীঠ হিসাবে খ্যাত তারাপীঠ। যে সব গ্রন্থে এর সমর্থন পাওয়া যায়ঃ গৌরিহর মিত্রের ‘বীরভূমের ইতিহাস’, পৃষ্ঠা - ৬২; ইংরেজি গ্রন্থ ডি সি. সরকার (সম্পাদিত) ‘দ্য শক্তি কাল্ট অ্যান্ড তারা’ এবং এন. এন. ভট্টাচার্যের রচিত ‘চাইনিজ অরিজিন অব দ্য কাল্ট অব তারা।’

৫. প্রবোধ কুমার বন্দ্যোপাধ্যায় - ‘তীর্থভূমি তারাপীঠ’ পৃষ্ঠা- ১৫।

৬. পার্থ শঙ্কর মজুমদার সম্পাদিত গৌরিহর মিত্রের – ‘বীরভূমের ইতিহাস’ থেকে জানা যায় ১২২৫ সালে মল্লারপুর নিবাসী জগন্নাথ রায় মহাশয় তারাদেবীর বর্তমান মন্দিরটি নির্মাণ করেন।

৭. এল. এস. এস. – বেঙ্গল ডিস্ট্রিক্ট গেজেটিয়ার : বীরভূম, পৃষ্ঠা - ১৪৬।

৮. ওম্যালীর মহিমা নিরঞ্জন চক্রবর্তী সম্পাদিত – বীরভূম বিবরণ (দ্বিতীয় খন্ড) ১৩২৬ বঙ্গাব্দ।

৯. গৌরহর মিত্রের ‘বীরভূমের ইতিহাস’ (প্রথম খন্ড), সিউড়ী, ১৯৪৩।

১০. বিনয় ঘোষ ‘পশ্চিমবঙ্গের সংস্কৃতি’, কলকাতা, ১৯৫৭।

১১. শ্রী সুশীল কুমার বন্দ্যোপাধ্যায় – - ‘তারাপীঠ ভৈরব’ কলকাতা, ১৯৬১।

১২. সুবোধ কুমার ব্যানার্জী – ইংরেজি গ্রন্থ ‘শ্রী শ্রী বামাক্ষ্যাপা’ কলকাতা ১৯৭১।

১৩. শ্রী সুশীল কুমার বন্দ্যোপাধ্যায় ‘ভৈরব শ্রী শ্রী বামাক্ষ্যাপা’ ১৩৭৩।

১৪. ড: আদিত্য মুখাপাধ্যায় ‘তারাপীঠের কথা’, তারাপীঠ ১৩৮৪।

সময় মানুষের কোলাহল ও 'জয় জয় তারা' কলরব। মেন রাস্তার বিপরীত দিকে রয়েছে মুন্ডমালিনী তলা, দ্বারকা নদীর তীরে বাঁধানো ঘাট। এই রাস্তার দুই ধারে রয়েছে অসংখ্য হোটেল, লজ, ভারত সেবা সংঘ ও আশ্রম। প্রতিদিন বিকেল থেকেই রঙিন আলোতে সেজে ওঠে তারাপীঠ। দর্শনার্থীরা বিকেল থেকে বেরিয়ে পড়ে তারাপীঠ ভ্রমণে। রাস্তার দুই ধারে অসংখ্য চা, মুড়ি ও অন্যান্য দোকানগুলিতে মানুষের আড্ডা ও মনোরম পরিবেশ তীর্থযাত্রীদের হৃদয়কে ছুঁয়ে ফেলে। তারাপীঠে সন্ধ্যার আলোকসজ্জা মহানগরীর আলোক সজ্জার থেকে কোন অংশে কম বলে মনে হয় না। আবার প্রতিদিন সন্ধ্যাবেলায় মূল মন্দিরের সামনে চাতালে দাঁড়িয়ে মায়ের সন্ধ্যা আরতি দর্শন তীর্থযাত্রীদের মনের অন্তস্থলে জায়গা করে নিয়েছে।

চিরকাল অজানাকে জানার এবং না পাওয়াকে পাওয়ার আকাঙ্ক্ষা মানুষের রয়েছে। বশিষ্ঠ আরাধিতা এই সাধন পীঠে বামাক্ষ্যাপা সিদ্ধি লাভ করেছে। কৈলাশপতি বাবা, শংকর ক্ষ্যাপা, নগেন পাণ্ডার মতো বহু মানুষ এখানে সিদ্ধি লাভের চেষ্টা করেছে। এই সিদ্ধি লাভের চেষ্টায় এখন বহু সাধু ফকির তান্ত্রিক তারাপীঠে এসে থাকেন। এখানে সিদ্ধিলাভের জন্য শুধু পশ্চিমবঙ্গ নয়, পার্শ্ববর্তী আসাম, ত্রিপুরা, ওড়িশ্যা, ঝাড়খণ্ড এবং অন্যান্য রাজ্য থেকেও সাধু, তান্ত্রিক ও অঘোরী সম্প্রদায়ের মানুষরা এখানে উপস্থিত হন। এই সব সাধু, তান্ত্রিকরা আবার মহাশ্মশানের বৃহৎ বৃহৎ যাগযজ্ঞের আয়োজন করেন। সঙ্গে আনেন অসংখ্য শিষ্য বর্গকে তারাই এই বৃহৎ যজ্ঞের ব্যায়ভার বহন করে।[২৩]

তারাপীঠ মন্দিরের জনপ্রিয়তা বৃদ্ধির অপর একটি গুরুত্বপূর্ণ কারণ হল 'সাধক বামাক্ষ্যাপা' চলচ্চিত্রটির মুক্তি লাভ।[২৪] এ প্রসঙ্গে উল্লেখযোগ্য বায়ুচিস্থানের 'হিংলাচ' সতীপটির উপর একটি চলচ্চিত্র মুক্তি পেলে ব্যাপক জনপ্রিয়তা অর্জন করে।[২৫] এগুলিই কি তারাপীঠে সাধন ক্ষেত্রের জনপ্রিয়তার কারণ, না অন্য কিছু? উত্তরে তারাপীঠে আগত বহু পুণ্যার্থীর কাছ থেকে জানা যায়, "তারাপীঠের তারামায়ের মহিমা বলে শেষ করা যাবে না"। তারা কমবেশি সকল পুণ্যার্থী জানান,[২৬] "তারাপীঠ আসার পূর্বে আমাদের সেরকম কিছুই ছিল না। কিন্তু তারা মায়ের কাছে পূজা দিয়ে ফিরে যাওয়ার পর তারা মায়ের কৃপায় সব পেয়েছি। অর্থাৎ ব্যবসা, বাড়ি, গাড়ি।" তারা আরও বলেন তারা মায়ের কাছে যা চাওয়া যায়, তাই পাওয়া যায়। তাই বলা যায় তারা মায়ের জনপ্রিয়তার মূল কারণ হলো তারা মায়ের মহিমা। তারা মায়ের সন্তানদের ওপর তারা মায়ের অশেষ কৃপা হাজার হাজার সন্তানকে তারাপীঠে টেনে আনে বলে আমার মনে হয়। বীরভূমে রয়েছে পাঁচটি সতীপীঠ। কিন্তু তারাপীঠে জনসমাগম অনেক বেশি।

স্বভাবতই মনে হয় তারা মায়ের মহিমা অতুলনীয়। পুণ্যার্থীদের বিশ্বাস তারা মায়ের মহিমা তারাপীঠ মন্দিরকে ধর্মীয় আকর্ষণের কেন্দ্রবিন্দু করে তুলেছে। বিংশ শতাব্দীর দ্বিতীয়ার্ধে তারাপীঠ মন্দির দারুণ জনপ্রিয়তা লাভ করলেও এই জনপ্রিয়তার প্রচেষ্টা শুরু হয়েছিল উনবিংশ শতকের শেষ লগ্নে বা বিংশ শতাব্দীর প্রথমার্ধে। এ প্রসঙ্গে উল্লেখ করা প্রয়োজন 'তারাপ্রেমী' কিছু মানুষ তারাপীঠ ভ্রমণের পর বেশ কিছু গ্রন্থ রচনা করেন। এই গ্রন্থে তারা তারামায়ের অলৌকিক ঘটনাকে তুলে ধরে। ফলে এই সব গ্রন্থগুলি পড়ে অনেকে তারামায়ের কৃপা লাভের জন্য তারাপিঠে ছুটে আসেন। এই গ্রন্থ গুলি হল শ্রী সুশীল কুমার বন্দোপাধ্যায়ের "তারাপীঠের ভৈরব" কলিকাতা- ১৯৬১, সুবোধ কুমার ব্যানার্জীর "শ্রী শ্রী বামাক্ষ্যাপা" কলিকাতা- ১৯৭১, ডঃ আদিত্য মুখোপাধ্যায়ের "তারাপীঠের কথা" তারাপীঠ- ১৩৮৪ সন, বিপুল গঙ্গোপাধ্যায়ের "মহাপীঠ তারাপীঠ" কলকাতা- ১৩৯২, প্রবোধকুমার মুখোপাধ্যায়ের "তীর্থভূমি তারাপীঠ" তারাপীঠ- ২০০৮, সুমন গুপ্তের

উনবিংশ শতাব্দীতে বেশ কিছু প্রসিদ্ধ তান্ত্রিক তথা সাধকের জন্ম হয়েছিল যাদের অলৌকিক কর্মকান্ডের ফলে বেশ কিছু তীর্থক্ষেত্র জনপ্রিয় হয়ে ওঠে, তাদের মধ্যে উল্লেখযোগ্য হলেন রাঢ়দেশের ব্রহ্মানন্দ, ময়মনসিংহের পূর্ণানন্দ গিরি, ত্রিপুরার মেহার কালীবাড়ির সর্বানন্দ ঠাকুর, দক্ষিণেশ্বরের রামকৃষ্ণ ঠাকুর।[১৭] ঠিক একইভাবে তারাপীঠকে জনপ্রিয় করে তুলেছিল সাধক বামাক্ষ্যাপা।[১৮] শুধু সাধক বামাক্ষ্যাপা নয়, তারাপীঠের বেশ কয়েকজন সাধকের কর্মকান্ড তারাপীঠকে বিশেষভাবে জনপ্রিয় করে তুলেছিল। এরা হলেন কৈলাসপতি বাবা[১৯], তারাক্ষেপা[২০], শঙ্করক্ষেপা[২১] প্রমুখ।

তারাপীঠের ভৌগোলিক অবস্থান এবং যোগাযোগ ব্যবস্থার সুন্দর বন্দোবস্ত তারাপীঠকে জনপ্রিয় করতে বিশেষভাবে সাহায্য করে। রামপুরহাট রেললাইনের সঙ্গে বিভিন্ন স্থানের সুন্দর যোগাযোগ ব্যবস্থা উনবিংশ শতাব্দী থেকে ছিল। তাছাড়া রেল স্টেশনের পাশেই ছিল বাসস্ট্যান্ড এখান থেকে সহজে বাসে করে তারাপীঠে যাওয়া যেত, তবে এই যোগাযোগ ব্যবস্থার উন্নয়নের গতি আসে দ্বারকা নদীর উপর সেতু নির্মানের পর থেকে।[২২] কলিকাতা থেকে রামপুরহাট এর দূরত্ব ২৩০ কিমি। হাওড়া ও শিয়ালদহ রেল স্টেশন থেকে খুব সহজে ট্রেন ধরে রামপুরহাটে পৌঁছানো যায়। বিশ্বভারতী ফাস্ট প্যাসেঞ্জার, হাওড়া ইন্টারসিটি এক্সপ্রেস, শিয়ালদহ ইন্টারসিটি এক্সপ্রেস, হাওড়া জয়নগর, কাঞ্চন এক্সপ্রেস, সরাইঘাট এক্সপ্রেস, মাতারা এক্সপ্রেস এর মত বহু সংখ্যক ট্রেন রামপুরহাট রেলস্টেশন এর উপর দিয়ে যাওয়ার ফলে তারাপীঠ পৌঁছানো খুব সহজ হয়েছে। এছাড়া পাশের রাজ্য ঝাড়খন্ডের দূরত্ব রামপুরহাট থেকে বাস বা ট্রেনে খুব বেশি নয়। তাছাড়া রেলস্টেশনের পাশেই ছিল বাসস্ট্যান্ড (বর্তমান বাসস্ট্যান্ডটি ১/২ কিলোমিটার দূরে অবস্থিত)। এখান থেকে সহজে বাস ধরে তারাপীঠে পৌঁছানো যেত। তবে এই যোগাযোগ ব্যবস্থার উন্নয়নের গতি আসে দ্বারকা নদীর উপর সেতু নির্মাণের পর থেকে। বর্তমানে রামপুরহাট রেল স্টেশন থেকে ট্রেকার, অটো ও টোটো মিলে হাজারের বেশি গাড়ি রয়েছে। মাত্র ২০ মিনিটের পথ তারাপীঠ।

সুন্দর যোগাযোগের পাশাপাশি বর্তমান তারাপীঠে রয়েছে সব মিলিয়ে আটশতের বেশি হোটেল, লজ বা ধর্মশালা। এখানে দর্শনার্থীরা তাদের পছন্দমত এবং সামর্থ্যমত মূল্যে ভাড়া নিতে পারেন। যদিও বিশেষ বিশেষ তিথিতে (অমাবস্যা, মঙ্গলবার, শনিবার) ভাড়া একটু বৃদ্ধি পায়। ফলে পশ্চিমবঙ্গের জেলাগুলি শুধু নয় পশ্চিমবঙ্গের বাইরের তীর্থযাত্রীরা খুব কম খরচে তীর্থ ভ্রমণ করতে পারে।

তারাপীঠের জনপ্রিয়তার অপর একটি কারণ হলো তারাপীঠ তীর্থক্ষেত্রকে কেন্দ্র করে বীরভূমের বেশ কয়েকটি জায়গা ভ্রমণ করা খুবই সহজসাধ্য। যেমন তারাপীঠের ঠিক পাশেই রয়েছে বামাক্ষ্যাপার বাড়ি, গৌড়ীয় বৈষ্ণব ধর্মের প্রচারক, নিত্যানন্দ মহাপ্রভুর জন্মস্থান। বীরচন্দ্রপুরে বাঁকারায়ের মন্দির। আবার মল্লারপুরে রয়েছে শিববাড়ী, এর পাশেই রয়েছে শিবপাহাড়ী মহাভারতের জয়রথ পূজিত শিব মন্দির। পাশেই নলহাটিতে রয়েছে নলহাটেশ্বরী মন্দির; বক্রেশ্বরের শিব মন্দির ও উষ্ণপ্রস্রবণ, সাঁইথিয়াতে নন্দকেশরী মন্দির। এখান থেকে রেলপথে আধঘন্টা দূরে রয়েছে বোলপুর শান্তিনিকেতন। ফলে তারাপীঠকে কেন্দ্র করে এই সব স্থানগুলি সহজে দর্শন করা যায়। মালুটি মন্দির খুব বেশি দূরে নয়।

তারাপীঠে তারা মায়ের মন্দির ছাড়াও রয়েছে জিবিৎকুণ্ড, বামা সংঘ, বামা মিশন, রাধাকৃষ্ণ মন্দির, দ্বারকা নদীর তীরে মহাশ্মশান যদিও বর্তমানে বিদ্যুৎ চালিত চুল্লি হয়েছে। মহাশ্মশানে রয়েছে বামাক্ষ্যাপার পঞ্চমুন্ডি আসন, বামাক্ষ্যাপার সমাধি, বর্তমানে এখানে প্রতিদিন সন্ধ্যাবেলায় বাউল, ফকির, কীর্তনীয়া সম্প্রদায়ের মানুষেরা ভজন সংগীতে মত্ত হয়ে ওঠে। মন্দিরের মূল প্রবেশদ্বারের বাইরে বেরোলে দেখা যায় রাস্তার দুই দিকে সজ্জিত পূজা সামগ্রীর দোকান, ফল, মিষ্টির দোকান, এছাড়াও মনোহারী হোটেল ও রেস্টুরেন্ট। এই রাস্তার মধ্যে সব

প্রাচীন শক্তিপীঠ তারাপীঠ বা চন্ডীপুর বর্তমানে 'তারাপীঠ' নামে জনমহলে সুপরিচিত হলেও তারাপীঠ সতীর ৫১ পীঠের কোন পীঠ নয়। তারাপীঠ বশিষ্ঠের আরাধিতা সিদ্ধপীঠ।[৪] কিংবদন্তী অনুযায়ী বশিষ্ঠ আরাধিতা তারামায়ের প্রথম মন্দির বনিক জয়দত্ত এবং দ্বিতীয় মন্দির তারাভক্ত সোমঘোষ নির্মান করেন যা আজও বর্তমান|[৫] তারাসাধক বামাক্ষ্যাপার অলৌকিক কর্মকান্ড মানুষকে তারামায়ের মন্দিরে টেনে এনেছিল ঠিকই, কিন্তু পুন্যার্থীর সংখ্যা ছিল খুব কম। ১৯১২ খ্রীষ্টাব্দে বামাক্ষ্যাপার মৃত্যু হয় এবং তারও অনেক পরে আনুমানিক বিংশ শতাব্দীর দ্বিতীয়ার্ধে এই মন্দির দারুণভাবে জনপ্রিয়তা অর্জন করতে থাকে।

আলোচ্য গবেষণা পত্রটির পূর্বে তারাপীঠ মন্দির এবং সাধক বামাক্ষ্যাপাকে কেন্দ্র করে বেশ কিছু গ্রন্থ রচিত হয়েছে। এই গ্রন্থগুলি হল ওম্যালির ডিস্ট্রিক্ট গেজেটিয়ার : বীরভূম[৬] মহিমা নিরঞ্জন চক্রবর্তী সম্পাদিত 'বীরভূম বিবরণ'[৭] (দ্বিতীয় খন্ড), গৌরিহরমিত্রের 'বীরভূমের ইতিহাস'[৮], বিনয় ঘোষের 'পশ্চিমবঙ্গের সংস্কৃতি'[৯], সুশীল কুমার বন্দ্যোপাধ্যায়ের 'তারাপীঠ ভৈরব'[১০], সুবোধ কুমার ব্যানার্জীর ইংরেজী - গ্রন্থ 'শ্রী শ্রী বামাক্ষেপা'[১১], সুশীল কুমার বন্দ্যোপাধ্যায়ের 'ভৈরব শ্রী শ্রী বামাক্ষ্যাপা'[১২], ড: আদিত্য মুখোপাধ্যায়ের 'তারাপীঠের কথা'[১৩], বিপুল কুমার বন্দ্যোপাধ্যায়ের 'মহাপীঠ তারাপীঠ'[১৪] প্রভৃতি গ্রন্থগুলি ধর্মবিশ্বাসী শিক্ষিত জ্ঞান পিপাসু মানুষদের তারামায়ের মন্দিরে টেনে এনেছিল। এই উপরিউক্ত গ্রন্থ গুলিতে তারাপীঠের অবস্থান, তারামায়ের উৎপত্তি, জয় দত্তের মন্দির প্রতিষ্ঠা, মায়ের পূজা ও ভোগ নিবেদন পদ্ধতি ইত্যাদির উপর আলোকপাত করা হয়েছে|

এই সমস্ত গ্রন্থ গুলির উল্লেখযোগ্য বৈশিষ্ট্য হল - গ্রন্থগুলিতে গুরুত্ব পেয়েছে বীরভূম, আর্থ-সামাজিক জীবন, তারাপীঠ মন্দির, তীর্থযাত্রীদের আগমন, তাদের মায়ের প্রতি শ্রদ্ধার্ঘ্য, মন্দির সংলগ্ন দোকানগুলিতে ক্রয় বিক্রয়, আর্থসামাজিক জীবনধারা, মন্দির সংশ্লিষ্ট কার্যাবলী, মানুষের সক্রিয় বা প্রত্যাক্ষ অংশগ্রহণ, নিষ্ক্রিয় বা পরোক্ষ অংশগ্রহণ ইত্যাদি| এই সকল গ্রন্থগুলির একটি উল্লেখযোগ্য সীমাবদ্ধতা হল তারাপীঠ মন্দির কেন্দ্রিক আর্থসামাজিক রূপান্তর ও পরিবর্তনের মূলে রয়েছে তারা মায়ের জনপ্রিয়তা| এই জনপ্রিয়তার মূলে ঠিক কোন কোন বিষয়গুলি গুরুত্বপূর্ণ ভূমিকা পালন করেছে সেই বিষয়ে এই গ্রন্থগুলিতে অনুচ্চারিত রয়ে গেছে|

তাই আলোচ্য প্রবন্ধের মূল উদ্দেশ্য হলো তারাপীঠ তীর্থক্ষেত্রটির জনপ্রিয়তার কারণগুলি তুলে ধরা| আলোচ্য প্রবন্ধ রচনার ক্ষেত্রে পর্যবেক্ষণলব্ধ জ্ঞান, অভিজ্ঞতালব্ধ জ্ঞান এবং বিভিন্ন গ্রন্থগুলিতে রচিত তারাপীঠ মন্দির সংক্রান্ত এক বা একাধিক প্রাথমিক ও গৌণ উপাদান|

'তারা' নামটি তারাপীঠের জনপ্রিয়তার অপর একটি কারণ বলে মনে হয়। তারার নামে তারাপীঠ। তারাপীঠের অনতিদূরে তারাপুর গ্রামেও তারা নাম জড়িত। 'তারা' যে কেবল বামাক্ষ্যাপার মুখের বুলি ছিল তাই নয়। বাংলাদেশের এমন কেউ আছেন কিনা জানিনা যিনি একবারও ঘটনাচক্রে অবলীলা ক্রমে 'তারা' নাম উচ্চারণ করেননি। 'তারা' নামের লোকপ্রিয়তা বোধহয় সমস্ত দেবদেবীকে ছাড়িয়ে যায়। রামপ্রসাদ, কমলাকান্ত, বাসুদেব প্রমুখ সাধক কবিদের কণ্ঠে 'তারা' নাম যেভাবে উৎসারিত হয়েছে এমন আর কোনো নাম হয়নি|[১৬] 'মা' ও তার সঙ্গে 'তারা' বাংলার শ্যামাসঙ্গীতের ছত্রে ছত্রে লোক কণ্ঠে ধ্বনিত হয়ে উঠেছে অত্যন্ত সহজে। সেই তারার নামে তারাপীঠ, তারাপুর। এছাড়াও মাতারা সুইট্স, মাতারা মুদি ভাণ্ডার, মাতারা মিট শপ, মাতারা বস্ত্রালয়, মাতারা স্পোর্টিং ক্লাব, মাতারা লটারি সেন্টার, মাতারা অটো মোবাইল, মাতারা ট্র্যাভেলস, মাতারা লজ, মাতারা এক্সপ্রেস, মাতারা টি স্টল এই সব নাম গুলি যেন মানুষের মনে বারাবার ধ্বনিত হতে থাকে| ফলে এই মাতারা নামটি মানুষের মনে জায়গা করে নিয়েছে| পশ্চিমবঙ্গের এমন কোন জেলা নেই যেখানে মাতারা নামটি উচ্চারিত হয় না| তাই মাতারা এই নামই বোধ হয় মানুষের আকর্ষণের কেন্দ্র|

# Tirtho Kendrer Janapriyatar Karon: Prosonga Tarapith Mandir

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**Abstract:** *Chandipur village in Birbhum is now known as Tarapith. Today the Tarapith temple has gained popularity like other pilgrimage sites like Tarkeswar, Kalighat or Dakshineshwar. As a result, a temple-centric tourism industry has developed around Tarapith. A large number of hotels have been built here due to the influx of pilgrims. Shops adjacent to the temple have seen a massive increase in buying and selling, resulting in a massive change in the socio-economic life style around the temple. In this article I have highlighted the reasons behind the popularity of Tarapith Temple. There are various reasons behind the popularity of temples located in different parts of India. Similarly the popularity of the Tarapith temple has increased. I have tried to highlight what other reasons are behind this. Discussion article includes miraculous Powers of 'Siddha Purusha' (man of religious austerity) like Bamakshyapa, Tarakshapa, Geographical location of Tarapith and the Improvement of communication System, facilities for the pilgrims, the opportunity to travel from here to other places or to the pilgrimage sites etc. have been highlighted. Side by side, the immense faith of the pilgrims towards 'Taramaa' (Tutelary deity) has also been highlighted as the main reason for the popularity of this pilgrimage site.*

**সূচক শব্দ :**

তারাপীঠ মন্দির, অর্থনৈতিক উন্নয়ন, তারামা, চণ্ডীপুর, বামাক্ষ্যাপা, ভারত সেবাসংঘ, শ্যামা সঙ্গীত, রামপ্রসাদ, মরুতীর্থ হিংলাচ, জয় জয় তারা, সতীপীঠ, রামপুরহাট, দ্বারকা নদী।

বীরভূমের চণ্ডীপুর গ্রাম এখন তারাপীঠ নামে প্রসিদ্ধ। ইতিহাসের পাতায় তারাপীঠ মন্দির, দক্ষিণেশ্বর, কালিঘাট, তারকেশ্বর, তথা ভারতবর্ষের অন্যান্য তীর্থক্ষেত্রের মত জনপ্রিয় একটি তীর্থক্ষেত্রে পরিণত হয়েছে। প্রতিদিনই তারাপীঠে এখন প্রায় ৫০০০ থেকে ২০০০০ পর্যন্ত পুন্যার্থী তাদের মনের বাসনা পূর্ণ করার জন্য মন্দিরে পূজো দিতে এসে থাকেন।[১] বিশেষ বিশেষ তিথিতে এর সংখ্যা বেড়ে গিয়ে এক লক্ষ ছাড়িয়ে যায়। শুধুমাত্র পশ্চিমবঙ্গের জেলাগুলি নয়, ভারতবর্ষের বিভিন্ন রাজ্য থেকে পূন্যার্থীরা এসে থাকেন।

তারাপীঠ বা চণ্ডীপুর গ্রামটি (জে. এল. নং - ১২৩) বীরভূম জেলার রামপুরহাট রেলস্টেশন থেকে ৫-৬ মাইল উত্তর-পূর্বে দ্বারকা নদীর তীরে অবস্থিত। বর্তমানে এটি তারাপীঠ থানার অধীন সাহাপুর পঞ্চায়েতের একটি গ্রাম।[২] বর্তমানে তারা মায়ের মন্দির ও অন্যান্য মন্দিরকে কেন্দ্র করে সর্বমোট ২.৯৮ একর জমি নিয়ে তীর্থ ভূমিটি বিকশিত হয়েছে।[৩] মন্দিরের নীচে দ্বারকা নদীর তীরে রয়েছে শ্মশান।

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Authors are requested to use standard system of transliteration and phonetic spellings when writing Sanskrit words in Roman letters. They are also requested to use Devanāgari letters for Sanskrit ślokas and prose passages.

# AN INFLUENCE OF R. N. TAGORE'S POETRY ON PARTITION LITERATURE

**Rajarshi Maity**
Research Scholar, Department of English, Sardar Patel University, Balaghat,
Madhya Pradesh, 481331.

## Abstract

Nearly two dozen plays and play lets are also among Tagore's many works and essays on subjects including philosophy, literature, religion, education, and society. Twenty of the 200 short stories that Tagore penned are among the finest gems. Fundamental societal issues are addressed in Tagore's books, including the deplorable circumstances of Hindu widows and the rise of a new type of woman seeking fulfillment. In general, Tagore's novels imply a pattern that aims to encompass his perception of Indian reality and his elaboration of concepts about the nature of Indian society and culture that have caught up with the theories of radical transformation. Rabindranath Tagore, India's Renaissance man was exposed to a wide range of concepts and ways of life from both the east and the west, which allowed tradition and culture to mingle and grow throughout the course of his lengthy life. We get to evaluate how these concepts were absorbed, modified, added to, and moulded in his magnificent consciousness. His subsequent compositions were heavily influenced by Vaishnava literature and philosophy. One may see how Bhanusimher Padaboli's literary ideas were influenced by lyrics from Vaishnava hymns. The explicit compilations are what present Tagore in relation to Bengal's Krishna-Chaitanya literary heritage. In his masterful plays, poetry, paintings, and musical works, he skillfully combined key Vaishnava themes like madhurya, viraha, abhisara, bhakti, lila, sadhana, and shakti, giving each one a mystical human appearance.

**Keywords:** R. N. Tagore's, Poetry on Partition, Tagore's families, Political Novels of Tagore, Emergence of New Women.

## Introduction

The systematic study of concepts and problems, the rational pursuit of fundamental truths, the search for a complete comprehension of reality, the investigation of moral principles, and a great deal more are all parts of philosophy. Additionally, philosophy makes a distinctive contribution to the comprehension of other academic disciplines and areas of research. One area of study that examines the moral relationships between people as well as the value and status of the environment and other living things is environmental philosophy. As we approach the third decade of this millennium, our globe faces fresh issues, notably those related to the environment and the economy. These issues have one thing in common: they affect everyone globally. The connection between people and nature is incredibly special and dynamic. The current perspective on this interface claims that our viewpoint is unsustainable and lacking in thoughtfulness. Therefore, reframing the relationship between humans and nature in a productive way can help us change our

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# CRITICAL REVIEW ON SELECTED NOVELS OF KHUSHWANT SINGH WITH SPECIAL REFERENCE TO SOCIAL REALISM

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## Abstract:

The goal of realism in art is to depict life as accurately as possible. The aim of social realism is to portray society as truthfully as possible. The social realism subgenre can be found in all forms of media, including film, literature, visual arts, television, and theatre. At best, Khushwant Singh represents this social genre. Indian contemporary literature served as a vehicle for the socio-political reality of that country during the British colonial administration. In this article, critical review on selected novels of Khushwant singh with special reference to social realism has been discussed.

**Keywords:** Khushwant Singh, Novels, Social, Realism

## INTRODUCTION:

An approach that stems from a study of reality in terms of natural forces, realism has focused primarily on the common places of everyday life among the middle and lower classes, where character is a product of social factors and environment is the integral element in the dramatic complications in literature. Although the two styles of realism are similar, social realism is a subgenre of realism. Realism is a literary genre that appears to faithfully "reflect" or record a true way of life. The phrase can be used to describe a literary technique that emphasizes accurate detail in description as well as a more general mindset that rejects romanticism's

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# A Message of Peace and brotherhood in the context of R N Tagore 'Poetry Rabindra Nath Tagore's Poetry: A source of Experiencing Peace and Harmony

RAJARSHI MAITY
Research Scholar

## Abstract

*A notable essayist Rabindranath Tagore, the entertainer of Mother India, possesses a front facing position in the universe of the prophets of Humanism. He turned into the very first Asian essayist to be granted a Nobel Prize in 1913 for deciphered variant of his pattern of melody sonnets, Gitanjali. It is imperative to realize that Rabindranath Tagore's manifestations and exercises has a typical having that is his affection toward Man at the end of the day his affection for humankind by upholding the upsides of mankind like harmony and concordance in the country at large. Tagore's verse Gitanjali mirrors his frantic endeavours to see the world to live in harmony and agreement truly. He endeavours hard and difficult to cultivate the upsides of humankind and get the satisfaction the land by empowering the majority to cherish each other, live in harmony and have an agreeable existence loaded with happiness. Tagore will probably channelize the floods of patriotism to the heading of universalism by liberating human spirit from all subjugation and insignificance of the world and in this way rising above itself into a quest for widespread love and fellowship that the Lord gives to the humankind.*

**Keywords:** *Brother Hood, Rabindranath Tagore, Harmony, Humanism*

## 1. Introduction

In his life, Rabindranath Tagore (1861-1941) is an incredible proportion of transcendental and groundbreaking figures, not only within his native Bengal and his beloved India. Was , yet to an impressive degree, all through the world. As a complex virtuoso and renaissance man second to none, he not just conveyed the writing and crafts of Bengal, essentially independently, to bewildering levels of imagination, yet, by his rousing words, his melodiously unmatched tunes,

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# AN ANALYSIS ON SOCIAL REALISM OF KHUSHWANT SINGH'S SELECTED NOVELS

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## Abstract:

A key and distinctive aspect of Khushwant Singh's writing is his use of literary realism. His depiction of Indian society and culture is rich and nuanced because of his attention to detail, concentration on the daily lives of common people, sensitivity to social and cultural distinctions, and refusal to romanticize or idealize Indian life. Because of his novel's sincerity, authenticity, and comprehension of the complexities of contemporary India, many people still read and value them. In this article, an analysis on social realism of Khushwant Singh's selected novels has been discussed.

**Keywords:** Social, Realism, Khushwant Singh, Novels

## INTRODUCTION:

Singh's novels express and uphold his positive, upbeat outlook on life as well as his unwavering belief in the virtues of humanity and love. As V.A. Shahane accurately notes, Khushwant Singh's realism promotes the idea that literature and society have an inextricable and enduring relationship. While significant, literature's reflexive value cannot serve as the exclusive benchmark for assessing works of literature. The artist's point of view during the experience

# Gandhi And Tagore`S Views Of 'Women Empowerment'

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## ABSTRACT

'Women empowerment' is burning and universal issue all over the world. Its refers to increasi and improving the social, economic, political and legal strength of the women to ensure equal- rig to women and to make them confident enough to claim their rights in community, society an workplaces. Here I discuss in this paper the views of Mahatma Gandhi, the father of nation an Rabindranath Tagore, proponent of Indian National Anthem. They had expressed their views an had written on numerous issues in particular and humanity in general. This article examines th important and relevance of their views on issues that directly impacts the status of women in Indi Gandhi is being considered the flowing issues of women like – equality of sexes, marriages, purda dowry system, widow remarriage, divorce, women`s honour, education and co-education, bir control, sterilization etc. Tagore also considered the women equality, education, poverty, imbalanc of income health and demographic change, education globalization, women environment etc. If w take these views in our life then it can change our society and motivate our humanity.

KEYWORDS: Empowerment, Rabindranath Tagore, Mahatma Gandhi, improving , Education,
Globalization

## DETAILS

'Women empowerment' is burning and universal issue all over the world. Its refers to increasing an improving the social, economic, political and legal strength of the women to ensure equal- right t women and to make them confident enough to claim their rights in community, society an workplaces. Here I discuss in this paper the views of Mahatma Gandhi, the father of nation an Rabindranath Tagore, proponent of Indian National Anthem. They had expressed their views and ha written on numerous issues in particular and humanity in general. This article examines the importa and relevance of their views on issues that directly impacts the status of women in India. Gandhi i being considered the flowing issues of women like – equality of sexes, marriages, purdah, dow system, widow remarriage, divorce, women`s honor, education and co-education, birth contro sterilization etc. Tagore also considered the women equality, education, poverty, imbalance of incom health and demographic change, education globalization, women environment etc.

### *Gandhi`s view of women empowerment:*

Equality of sexes: Women must not suffer any legal disability which is not suffered by men. Both a perfectly equal (Young India, 17th October, 1929). Sexual equality does not translate into occupation

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# Jibandebata, The Pursuit Of Rabindranath Tagore

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**Abstract-** The idea of God in our minds is not only important but also a matter of debate. For example, some of us think that God predetermines our fate or God can control our fate and it is happened accordingly our deeds in the previous birth. On the other hand, there are some people who completely believe in their works and they think that we can create our fate by our good deeds and most importantly we can control and manage ourselves. In this article we are going to discuss about Tagore's concept of 'that power 'by which we can make our lives. Accordingly to Tagore this 'power' is called 'Jibandebata' who is unseen but who's existence in our lives cannot be denied. Generally we think that Tagore's 'Jibandebata' is another name of God himself. But we come to know that Rabindranath Tagore never wants to mean God by his 'Jibandebata'. The religious texts always highlight that God who represents the world but Tagore's 'Jibandebata' is completely different from him. He says that 'Jibandebata' can be felt and he is special to everybody. He is the life and existence as well. Human beings have nothing else apart from him.

Keyword- 'Jibandebata', Nature, Atmaparachay, koutukmoyee, Viswaprakriti, Tagore, Anagoto.

It is thought that Tagore can first realize the presence of his 'Jibandebata' when in 1890 he has to go to Shilaidah from Kolkata to look after the zamindari. This 'Shilaidah days' is a very important part in Tagore's life because the environment he feels here, the people he comes across and the unceasing waves of river Padma help him to read the meaning of living more deeply. It can be easily said that if Tagore never gets opportunities to spend a long time in the bank of the river Padma then his 'Jibandebata' also remains elusive. Although the natural beauty of river Padma and the environment of Shilaidah take an important part in Tagore's realization of 'Jibandebata' but according to Tagore in his whole life he has faced the 'Jibandebata' in different ways at different times. In other words, he has felt his 'Jibandebata'(The God of life) in regular different forms.

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# आधुनिक परिप्रेक्ष्य में संस्कृत का आयुर्वेद में प्रभावः एक समीक्षा

**करिम सेख**
गवेषक
संस्कृत विभाग
ति.माँ. भा. विश्वविद्यालय
भागलपुर

**मूलशब्दः / कूट शब्दः**

आयुर्वेदः, वेद, संस्कृत, शल्यचिकित्सा, जीवन, विज्ञान आयुः, अष्टाङ्ग, प्राण, आयुः।

शोधसारः आधुनिक परिप्रेक्ष्य में संस्कृत (वेद) आयुर्वेद में एक विशेष महत्व रखता है। हम वेदों को भारतीय चित्राधारा के आदि स्त्रोत के मूल आधार मानते हैं। वेद और आयुर्वेद का सम्बन्ध अत्यन्त गंभीरता के रूप में निर्णय करते हैं। जब हम वेद और आयुर्वेद की चर्चा करते हैं तब चरक संहिता की इस श्लोक को स्मरण करते है।

जैसा कि –

हिताहित् सुखं दुःखमायुस्तस्य हिताहितम्।

मानं च तच्च यत्रोक्तमायुर्वेदः स उच्यते।। च.स.

(अर्थात् जिस ग्रन्थ आयु (जीवनानुकूल), अहितायुः (जीवन प्रतिकूल), सुखायुः (स्वस्थ आयु) एवं दुःखायुः (रोगावस्था) इनका वर्णन हो उसे आयुर्वेद कहते हैं।

संस्कृत एवं आयुर्वेद शब्दों का जब विश्लेषण करते है तब इसका अर्थ निकलता है इस प्रकार। संस्कृत शब्द सम्+कृ+क्त प्रत्यय से बनता है। अर्थात् संस्कृत शब्द का अर्थ शुद्ध, परिस्कृत, निर्मल एवं स्वच्छ है। संस्कृत का शाब्दिक अर्थ परिपूर्ण भाषा है। आयुर्वेद (आयुः+वेद) विश्व की प्राचीनतम चिकित्सा प्रणालियों में से एक है। आयुर्वेद का अर्थ है जीवन का अमृतरूपी ज्ञान। आयुर्वेद एवं वेद विश्व मे विद्यमान वह साहित्य है जिसके अध्ययन से ही हमारी जीवनशैली का विश्लेषण करते है–

1. आयुर्वेदयति बोधयीति। इति आयुर्वेदः।
   (अर्थात् जो शास्त्र (विज्ञान) आयु (जीवन) का ज्ञान कराता है, उसे आयुर्वेद कहलाता है।
2. स्वस्थ व्यक्ति एवं रोगी के लिए उत्तम मार्ग बताने वाला विज्ञान को आयुर्वेद कहलाते हैं। आधुनिक चित्राधारा, आधुनिकता के कारण आज मानवजाति विभिनन ध्वंसात्मक रोगों से ग्रसित है। आधुनिक उपकरण इत्यादि व्यक्तियों को मानसिक खाना–पीना, रहन–सहन, उठना–बैठना, वेश–भूषा, आधुनिक उपकरण इत्यादि व्यक्तियों को मानसिक चिन्ता एवं शारीरिक रोगों से ग्रसित रखता है। लेकिन हम आयुर्वेदिक चर्चा से स्वस्थ रह सकते हैं। आयुर्वेद को शाश्वत, अनत्र के रूप में माना जाता है क्योंकि इसका मूल सृष्टि वेदों से हैं। इस संसार में जो कुछ भी है सब कुछ संस्कृत निष्ट है। संस्कृत को हमारी देश की जननी मानते हैं। वेद ओर आयुर्वेद का सम्बन्ध सुदूर प्राचीन काल से ही प्राप्त होता है। आधुनिक समय मे विश्व के सभी मानवजाति आयुर्वेद से परिचित है। आयुर्वेद चिकित्सा प्रणालियों को समस्त ग्रन्थ संस्कृत में संग्रहीत है। आयुर्वेद के क्षेत्र में अध्ययन के लिए संस्कृत भाषा आवश्यक ही नहीं अपितु अनिवार्य भी है। यदा हम आयुर्वेद की बातें करते है तदा संस्कृत के महत्वपूर्ण ग्रन्थ चरक संहिता, सुश्रुत–संहिता एवं काश्यप संहिता का नाम पाया जाते हैं। आयुर्वेद एवं वेद दोनों एक ही उच्चकोटि में स्थान ग्रहण करता है जो कि चारों वेदों में चर्चित हैं। अतएव ऋग्वेद एंव अथर्ववेद से आयुर्वेद का उद्देश्य, वैद्य के गुण–कर्म,

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# जूनी ख्यात

इतिहास, कला एवं संस्कृति की शोध पत्रिका

मरु भूमि शोध संस्थान, श्री डूँगरगढ़ (राज.)

MARUBHUMI SHODH SANSTHAN, SRI DUNGARGARGH (RAJ.)

संपादक

**डॉ. बी.एल. भादानी**

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विभेत्यपश्रुताद्वेदो मामयं प्रहरिष्यति।।"[1]

पुराण शब्द का व्युत्पत्तिगत अर्थ है "पुरा भवं पुराणम्"। पुराण के पाँच लक्षण मत्स्य पुराण में बताया गया है। जैसे–

**"सर्गश्च प्रतिसर्गश्च वंशो मन्वन्तराणि च।**

**वंशानुचरितं चैव पुराणं पंचलक्षणम"[2]**

अर्थात् सर्ग (सृष्टि), प्रतिसर्ग (ध्वंस के बाद पुनः सृष्टि), वंश (देवता एवं ऋषिओं का वंश वर्णन), मन्वन्तर (एक एक मनु का शासन–काल), वंशानुचरितं (विभिन्न राजवंशों का इतिहास)। इसके अतिरिक छः गौण लक्षण प्राप्त है– (1) भुवन विस्तार (2) दानधर्म विधि (3) श्राद्धकल्प (4) वर्णाश्रम विभाग (5) इष्टापूर्त एवं (6) देवता प्रतिष्ठा। पुराण अष्टादश है। इसमें से भविष्यपुराण में आधुनिकता का विस्तार होने पर भी यह पुराण भी अत्यन्त प्राचनी है। भविष्य पुराण में भविष्य में घटित होने वाली घटनाओं का वर्णन है। समय समय पर विभिन्न ऋषियों द्वारा घटित होने वाली विषयों को जोड़ दिया गया है। इसलिए यह पुराण अब साम्प्रदायिक पुराण बन गया है। भविषय पुराण आज विभिन्न इतिहास का साक्षी स्वरूप है। अब यह प्रश्न मन में उठता है कि इसका नामकरण कैसे हुआ है। साहित्य नामकरण की विशेषता यह कि नामकरण यथार्थ होनी चाहिए। चाहे वह पृथिवी के कोई भी साहित्य हो। संस्कृत साहित्य भी इसका व्यतिक्रम नही है। वर्तमान घटना प्रवाहों के परिप्रेक्षित में काव्यकृति या साहित्यकृति का नामकरण होनी चाहिए। इस नामकरण के माध्यम से पाठकगण आलोच्य विषयों को हृदयड्गम कर पाता है। भविष्य पुराण नामकरण की सार्थकता विचार करते हुए भविष्य पुराण में वर्णित कुछ मुख्य विषयों का आलोकपात करनी चाहिए। जैसे कि यह पुराण अत्यन्त उच्चकोटि का ग्रन्थ माना जाता है क्योंकि इस पुराण का विषय वस्तु, वर्णनशैली, रचनाशैली साहित्यकृति तथा काव्य–रचना अत्यन्त रोचक एवं प्रभाव उत्पादक है। भविष्य पुराण में चार पर्व है– ब्राह्म, मध्यम, प्रतिसर्ग तथा उत्तर पर्व है। भविष्य पुराण के प्रतिसर्ग पर्व के वर्तमान घटना प्रवाहों के परिप्रेक्षित में भविष्य पुराण नामकरण सार्थक विचार किया जाता है।

### भविष्य पुराणः–

भारतीय संस्कृति का धारक एवं वाहक रूप में पुराण साहित्य को माना जाता है। इस पुराण में सामाजिक उपकार, आध्यात्मिक–ज्ञान, संस्कृति एवं धार्मिक विधान सम्यक रूप से प्राप्त होता है। इस कारण से पुराण साहित्य को भारत के अमूल्य निधिः माना गया है। कहा भी गया है कि – "पुरा नवं भवति इति पुराणम्।" अष्टादश पुराणों में से भविषय पुराण का स्थान अत्यन्त उच्चकोटि का है। भविष्य पुराण चार पर्व में विभाजित है। यह पुराण सूर्योपासना का महत्व को प्रतिपादित करता है। इसलिए इसे 'सोरग्रन्थ' भी कहा गया है। भविष्य पुराण को भारतवर्ष के समस्त आधुनिक इतिहास का मूलग्रन्थ माना गया है। इसलिए भविष्य पुराण के संज्ञा देते हुए कहा गया है कि भविष्य में घटित होने वाली घटनाओं का वर्णन जिसमें है उसे भविष्य पुराण कहा जाता है।

### अष्टादश पुराणों का संक्षिप्त वर्णनः–

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# प्राचीन भारत की परिवेश चिन्ता : एक विवेचन

करिम सेख

**शोध सार (Abstract) –**

प्राचीन भारत के परिवेश भावना में प्रकृति को कभी भी जीवनदर्शन के प्रतिपक्ष सोचा नहीं है। जीवन दर्पण में प्रकृति के साथ निगूढ़ सम्पर्क में विलीन होकर प्रकृति के साथ जिन सत्त्वा अत्यन्त गंभीर आत्मीयता का अनुभव करने के लिए कहा है, कठोपनिषद में उसका प्रतिफलन परिस्फुटन होता है। जैसे कि- ………

**"यदिदं किञ्चत् जगत् सर्वं प्राण एजतिनिःसृतम।**
**महद्भयम् वज्रमुद्यतं य एतद्विदुरमृतास्ते भवन्ति।"**

इस पृथ्वी में जो कुछ भी विद्यमान है वह सब कुछ प्राणरूप ब्रह्म निःसृत है। जहाँ पर प्राचीन ऋषि लोग निवास करते थे, वहाँ पर विश्वव्यापी प्रकृतिरूप विराट जीवन के साथ ऋषिओं के जीवन एक सूत्र में बाँधा हुआ था। उनके दैनन्दिन जीवन के कर्म के साथ प्रकृति का आदान-प्रदान सीमा-हीन था। प्राचीन भारत की परिवेश चिन्ता की वर्तमान प्रासङ्गिकता हमलोगों के जीवनदर्शन की अनुशीलन के बीच में खोज पाया जाता है।

**मूलशब्द/कूटशब्द** : नद-नदी, हरप्पा सभ्यता, सामाजिक अवस्था, स्त्रियों का अवस्थान, शिक्षा-व्यवस्था, शासन-व्यवस्था, कृषिकार्य, ज्योतिष-चर्चा।

**भूमिका** :- भारत के इतिहास हजारों साल पुराना है। पुरातात्त्विक की दृष्टि से मेहरगढ़ एक अत्यन्त महत्वपूर्ण स्थान है, जहाँ पर नव्य-प्रस्तर युग का अनेक अवशेष मिलता है। सिन्धु घाटी सभ्यता, जिनका आरम्भ 3300 साल ई० पू० माना गया है। सिन्धु घाटी सभ्यता वर्तमान पाकिस्तान एवं भारतीय प्रदेश में विस्तार लाभ किया है।

पुरातात्त्विक के प्रमाण से 1900ई० पूर्वाद्ध के आस-पास में सिन्धु सभ्यता का अचानक पतन हो गया था। प्राश्चात्य-विद्वान के प्रचलित दृष्टिकोण से कहा जा सकता है कि आर्य जाति के एक वर्ग भारतीय उप-महाद्वीप की सीमा में 200 ई० पू० में जाकर पहूँचा एवं पंजाब जाकर बसति स्थापन किया एवं वहाँ पर भी ऋग्वेद की 'ऋचा' का रचना किया। आर्य जाति के द्वारा उत्तर एवं मध्य भारत में एक विकसित सभ्यता का निर्माण किया, जिसको 'वैदिक सभ्यता' कहा जाता है। प्राचीन भारत के इतिहास में वैदिक सभ्यता प्रारम्भिक सभ्यता के नाम से जाना जाता है, जिसका सम्बन्ध आर्य जातिओं के आगमन के साथ सम्पर्क युक्त है। आर्य की भाषा था संस्कृत एवं धर्म था वैदिक धर्म अथवा सनातन धर्म। परवर्ती समय में विदेशोंओं के प्रभाव से इस धर्म का नाम हिन्दु धर्म हुआ। वैदिक सभ्यता सरस्वती नदी के तटीय क्षेत्र में विद्यमान है, जो आधुनिक भारत के पंजाब एवं हरियाणा में विकास लाभ किया है। साधारणतः अधिकतर विद्वान वैदिक सभ्यता का समय 2000-6000 ई० पू० के बीच मानते है। किन्तु कुछ पुरातात्त्विक के मतानुसार वैदिक सभ्यता का समयकाल 3000 ई० पू० माना गया है। इसका कारण यह है कि आर्य जाति का भारत में आने की कोई सठिक प्रमाण नहीं मिलता है, इसलिए वैदिक सभ्यता का भारत में ही शुरूआत हुआ था। वर्तमान में भारतीय पुरातत्त्व परिषद के द्वारा सरस्वती नदी का सन्धान से वैदिक सभ्यता हरप्पा सभ्यता एवं आर्य का सम्बन्ध में एक नया तथ्य सामने आया है, जिससे हरप्पा सभ्यता को सिन्धु सरस्वती नाम दिया गया है।

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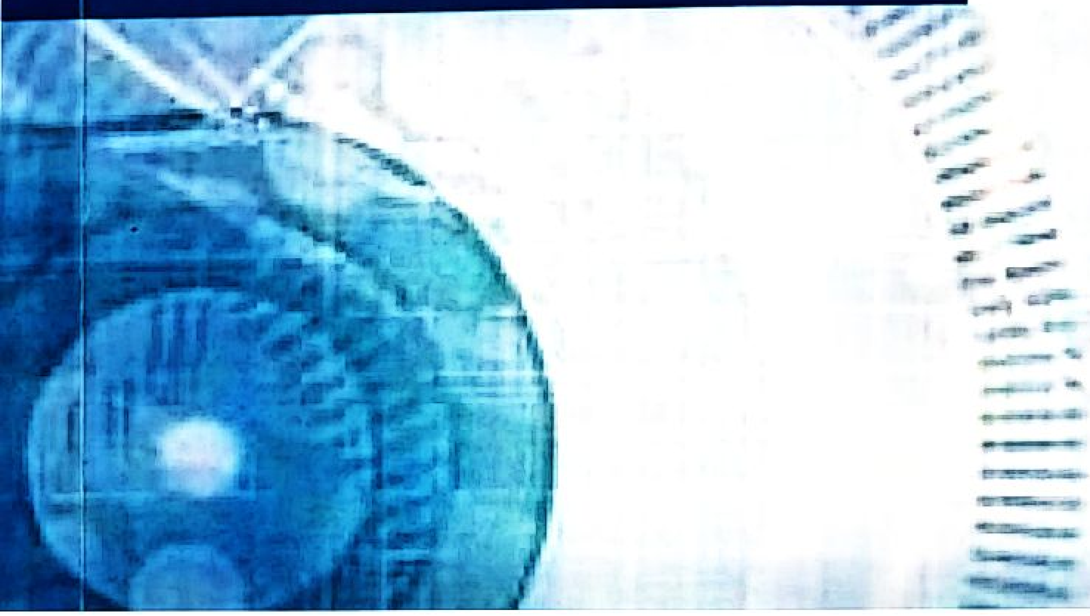

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# श्रीमदभगवत्गीता में कर्मयोग का महत्व : एक विवेचन

Karim SK, west bengal

## Abstract / शोधसारः

"तस्माद्योगाय युज्यस्व योगः कर्मसु कौशलम्"। गीता में द्वितीय अध्याय में पँचास संख्यक श्लोक में कर्मों में कुशलता को ही योग कहा गया है। कृष्णाभावनामृत ही योग है। गीता में सुकर्म, अकर्म व विकर्म के विषय में विचार किया गया है। कर्म में कुशलता लाने के लिए तीन सिढ़ियाँ पार करना पड़ता है। (1) कर्म को समझना (2) उचित कर्म को सटीक रूप देना (3) और उपरोक्त दोनों से कुशलता आएगी जो सफलता दिलाएगी, जब योजना को ही योग कहा जाता है तब कर्मवान व्यक्तियों में कुशलता आती है। कर्मबन्धन से मुक्त होना ही योग है। कर्म से मुक्त होने से योग नहीं मिलता है। वास्तव में योग और गीता हमें जीवन की सही दिशा दिखाते हैं। योग कहता है कि वर्तमान में जो कुछ भी है उस पर चलना है, और इसी से सजागता की जन्म होता है। यह सजागता ही हमारी कर्म को सही दिशा बतलाता है।

***मूलशद्र / कूटशब्दः–***

कर्म, योग, अकर्म, विकर्म, आत्मा, परमात्मा, कर्माधिकार, फललाभ।

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# भविष्यपुराण का प्रतिपाद्य विषयः एक विवेचन

## Abstract / शोधसारः

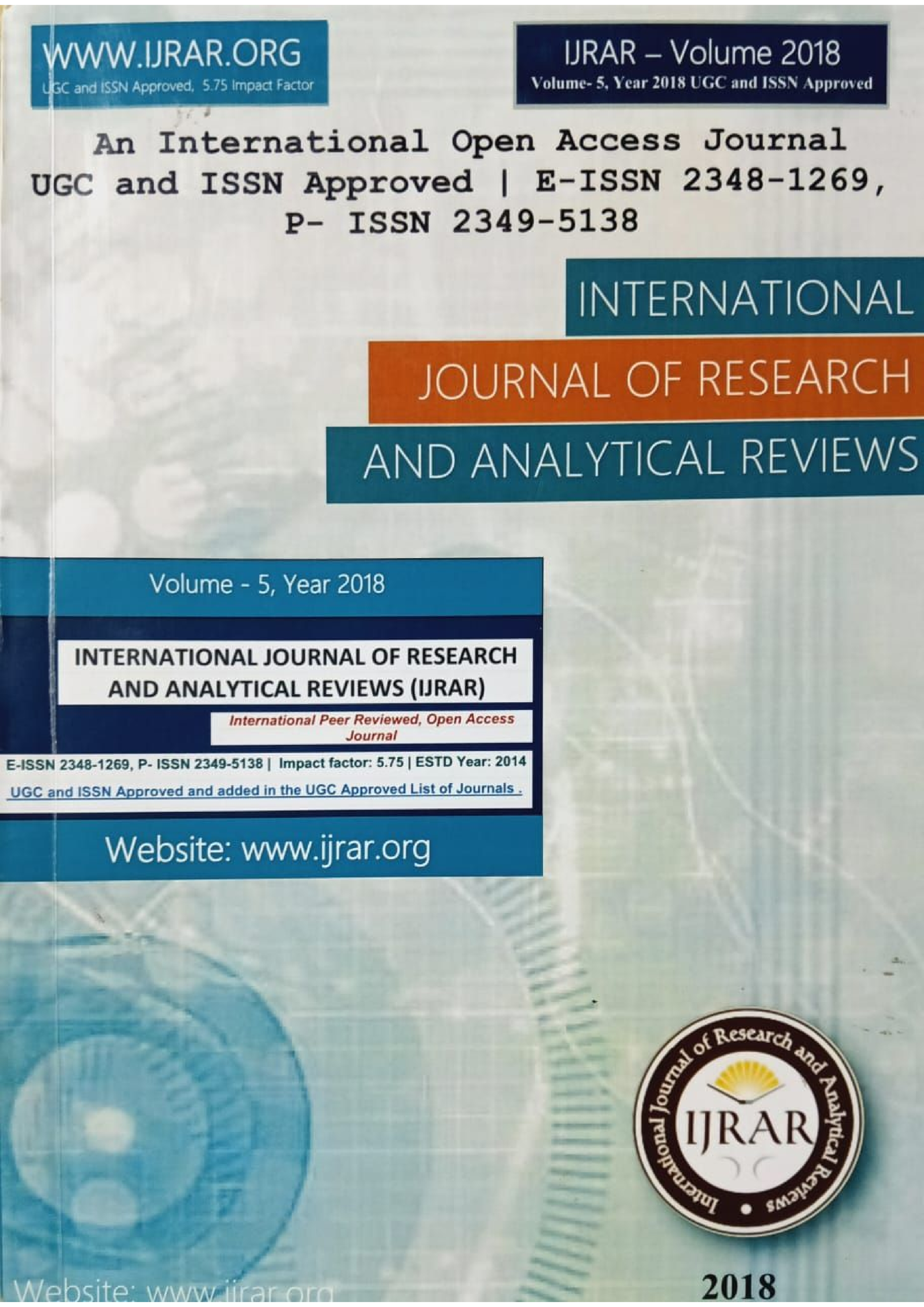
भारतीय संस्कृति में पुराण का एक विशिष्ट स्थान प्राप्त होता है। इसमें कर्म काण्ड, ज्ञानकर्म, उपासनाकाण्ड के माध्यम से वेद के अर्थ को स्पष्टीकरण करके साधारण मनुष्य को गूढ़ से गूढतम तत्व को हृदयड़्गम करा देता हैं भारतवर्ष में चारो वर्ण और चारों आश्रमों की रीति–नीति, आचार–व्यवहार की सामग्री अष्टादश पुराण ही है। इन आख्यानों से वेदार्थ सम्यक रूप से जाना जाता हैं जैसे कि–

*"इतिहास पुराणाभ्यां वेदं समुपवृंह्येत्।*
*विभेत्यिल्पश्रताद्वेदो मामयं प्रहरिष्पति।।"*

भविष्य पुराण एक सात्विक पुराण है एवं इसे सौर प्रधान ग्रन्थ भी कहा गया है। भविष्य पुराण में पंचलक्षण का भी वर्णन है। इस पुराण में चार पर्व हैं। भविष्य पुराण में मुख्य रूप से सूर्यापासना की बात कहीं गयी है। इसके अतिरिक्त ब्रह्मा, गणेश, कार्तिकेय तथा अग्नि आदि देवातों का वर्णन मिलता है।

## मूलशद्र / कूटशब्दः–

पुराण, उपपुराण, पंचलक्षण, सूर्योपासना, चारपर्व, भगवान विष्णु एवं शिव।



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# 'आधुनिक परिप्रेक्ष्य में योग की आवश्यकताः एक विवेचन'

**Abstract / शोधसारः "शरीरमाद्यं खलु धर्म साधनम्"** - इस कथन का निष्कर्ष है गीता में भगवान कहे हुए वाणी -योगः कर्मषु कौशलम्। शरीर को शुद्ध रखना, स्वस्थ रखने का महत्पूर्ण उपाय है योग। वर्तमान कल में स्वस्थ शरीर और स्वस्थ मन की परिचर्या का बिषय है योग। इस लिए पृथिवी के सर्वत्र योग को प्राधान्य दिया जा रहा है। इस सन्दर्भ में मेरी यह चिंतन समाज में योग की आवश्यकता को दर्शाता है।

**कूट शब्द / मूलशब्दः**- योग, समाधि, अष्टांग योग, चितभूमि

योग की धारणाः भारतीय आध्यात्मिक परम्परा में योगशास्तत्र का प्राधान्य सर्बोपोरी है। यद्यपि मोक्षप्राप्ति की बहुत मार्ग आचार्यों द्वारा व्याख्या किया गया है परन्तु मोक्ष प्राप्ति की एक ही उपाय है, वो है मन की संतुलन, शरीर की शुद्धता और मन के द्वारा परमात्मा के साथ लीन होना। प्राचीन युग में जितने वि शास्त्रों का रचना हुआ उसमें ज्यादातर शास्त्रियों आलोचना देखा जाता है। परन्तु प्रक्रिया के माध्यम से मन की स्वच्छता, एकाग्रता को प्राप्ति करना एक ही आचार्य की देन है और वो है महर्षि पतंजलि। संस्कृत युज् धातु से योग शब्द का उल्लेख मिलता है। संस्कृत योग शब्द का व्युत्पत्ति युज् धातु से जाना जाता है। युज् धातु का दो अर्थ- (१) यूजर एवं (२) युज् समाधि। **(1)** "योग" अर्थ से समिश्रण या योग के फल का आभास मिलता है। इससे उच्चतम समाधि का प्रतीत नहीं होता। अतः समाधि अर्थ से ही योग का सठीक अर्थ मिलता है। महर्षि पतंजलि ने समाधि के अर्थ में योग का लक्षण किये हैं-"योगश्चित्तवृत्ति निरोधः"। **(2)**

अर्थात मन सर्बदा चंचल है। मन की चंचलता के कारण शरीर का धैर्य निर्धारित होता है। और इस चंचल मन को नियंत्रण करने केलिए प्रयोजन अभ्यास और वैराग्य। "अभ्यास वैराग्याभ्यां तन्निरोधः"। **(3)**

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# Jibandebata, The Pursuit Of Rabindranath Tagore

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**Abstract-** The idea of God in our minds is not only important but also a matter of debate. For example, some of us think that God predetermines our fate or God can control our fate and it is happened accordingly our deeds in the previous birth. On the other hand, there are some people who completely believe in their works and they think that we can create our fate by our good deeds and most importantly we can control and manage ourselves. In this article we are going to discuss about Tagore's concept of 'that power 'by which we can make our lives. Accordingly to Tagore this 'power' is called 'Jibandebata' who is unseen but who's existence in our lives cannot be denied. Generally we think that Tagore's 'Jibandebata' is another name of God himself. But we come to know that Rabindranath Tagore never wants to mean God by his 'Jibandebata'. The religious texts always highlight that God who represents the world but Tagore's 'Jibandebata' is completely different from him. He says that 'Jibandebata' can be felt and he is special to everybody. He is the life and existence as well. Human beings have nothing else apart from him.

Keyword- 'Jibandebata', Nature, Atmaparachay, koutukmoyee, Viswaprakriti, Tagore, Anagoto.

It is thought that Tagore can first realize the presence of his 'Jibandebata' when in 1890 he has to go to Shilaidah from Kolkata to look after the zamindari. This 'Shilaidah days' is a very important part in Tagore's life because the environment he feels here, the people he comes across and the unceasing waves of river Padma help him to read the meaning of living more deeply. It can be easily said that if Tagore never gets opportunities to spend a long time in the bank of the river Padma then his 'Jibandebata' also remains elusive. Although the natural beauty of river Padma and the environment of Shilaidah take an important part in Tagore's realization of 'Jibandebata' but according to Tagore in his whole life he has faced the 'Jibandebata' in different ways at different times. In other words, he has felt his 'Jibandebata'(The God of life) in regular different forms.