



RECENT DEVELOPMENT OF HYDROGEN SULPHATE (HSO_4^-) TARGETING FLUORESCENT CHEMOSENSOR USING DIFFERENT APPROACHES

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ABSTRACT

Chemical sensors typically depend on fluorescent dyes, chromogenic compounds and metal complexes for analyte (HSO_4^-) induced signaling systems. These sensors involve binding or recognition event into a spectroscopic signals upon the introduction of hydrogen sulphate. There are some conventional methods for the detection of hydrogen sulphate but among these conventional methods, fluorescent chemosensors have become powerful tools for sensing of small samples due to their simplicity, sensitivity, low-toxicity, easiness of operation and working in pure aqueous media and which are applicable in both *in vitro* and *in vivo* use in recent years. Here we have tried to recapitulate the use of several organic molecules in the field of colorimetric and fluorescent HSO_4^- anion sensing that continues to be an important goal and is being pursued by a number of research groups worldwide. The present highlight provides an overview of different photophysical properties involved in the sensing of HSO_4^- ions leading to easy to observe naked eye colorimetric as well as fluorescence change. In addition to organic synthesized molecules, we have also shown here some metal complexes that are able to act as a superior HSO_4^- ions sensor. Some of the chemosensors are significantly capable to detect the distribution of hydrogen sulphate ions *in vitro* in living cells in aqueous medium at biological pH by fluorescence imaging studies.

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INTRODUCTION

The development of anion sensors has been an area attracting significant attention over the last 25 years, driven by the numerous fundamental roles in chemical, biological, environmental and industrial processes, for which the detection of such ions are of significant interest and imperative to many chemists, biologists and environmentalists [1,2]. Not only the scientific communities, but also increasingly the general populations are all becoming aware of the environmental and health problems associated with these ions. The negative ion gradients across lipid bilayer membranes originated by anion channels is equally important as the several critical physiological processes work due to the formation of these gradients [3]. Interestingly, the breakdown of this process leads to severe diseases, such as cystic fibrosis, nephrolithiasis, osteopetrosis, Angelman's syndrome and Bartter's syndrome type III [4], e.g. fluoride, a small inorganic anion is often added to toothpaste owing to its beneficial role in dental care. Some small ions that induce biological dysfunctions are of paramount research importance.

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Hydrogen sulfate is one of the important macronutrient in cell and is the fourth most abundant anion in human plasma (300 mM). They are required for proper cell growth and development of the organism. They are involved in a variety of important biological processes, including biosynthesis and detoxification *via* sulfation of many endogenous and exogenous compounds [5]. They also play appreciable role in radioactive waste remediation [6]. Amphiphilic hydrogen sulfate tends to dissociate at high pH to yield sulfate ions. Despite their importance in cellular activities, high levels of sulfate in rainwater, surface water and ground water correlated with emissions of sulfur dioxide from anthropogenic sources decreases the pH level of soil and water. Health concerns regarding contamination of sulfate in drinking water have been raised because of reports of diarrhea and it also causes irritation of skin and eyes and even respiratory paralysis [7]. Hydrogen sulfate anion has a large standard Gibbs energy of hydration ($-1080 \text{ kJ mol}^{-1}$), the recognition and separation of the hydrogen sulfate anion from an aqueous media is a challenging task [8].

Mechanisms of action of the anion sensors

Anions play many important roles in living organisms, being crucial to physiological function as well as various industrial

processes [9, 10]. As a result, in the environment, anionic species can be either essential to sustain growth or act as harmful pollutants. The supramolecular chemistry of anions is still one fertile area of research to explore the field of chemosensor [9,11,12]. A convenient and efficient strategy to design a colorimetric anion sensor is to combine an anion receptor with a chromogenic moiety, may be organic compounds or metal-organic complexes, which shows a color change that is visible to the naked eye when the binding event takes place. However, in case of design and syntheses of molecules with selective anionic receptor, several factors have to be considered like (i) anions are relatively large and therefore require receptors of considerably greater size of cations; (ii) even simple inorganic anions occur in a range of shapes and geometries, e.g. spherical (halides), linear (SCN^- , N_3^-), planar (PtCl_4^{2-} , NO_3^-), tetrahedral (PO_4^{3-} , SO_4^{2-}), octahedral (PF_6^-) as well as even more complicated examples; (iii) in comparison to cations of similar size, anions have high free energy of solvation and hence anion hosts must compete more effectively with the surrounding medium; (iv) many anions exist only in a relatively narrow pH window; (v) anions are usually saturated coordinatively and therefore bind *via* weak forces such as hydrogen bonding and Vander Waals interactions. As a result, generally design of chemosensors for anions follow one of the following three main approaches: (I) the “binding site-signaling subunit” protocol, (II) the “displacement” approach and (III) the “chemodosimeter” concept.

The binding site-signalling subunit approach

In the first approach, the interaction of the anion with the binding site in the system where “binding sites” and the optical “signaling subunit” are covalently bonded, provokes electronic modulations in the signaling unit to get a change in fluorescence colour [13-14]. Early systems from pioneers such as Paul Beer consisted of an anion-binding site formed from hydrogen bond donor groups that are arranged close to a redox-active ‘reporter’ group such ferrocene or a fluorescent group such as *ruthenium tris-bi-pyridyl*. When an anion bound to the hydrogen bond donor array, the electronic properties of the reporter group were perturbed resulting in a change in the redox or fluorescent properties of the receptor are perturbed so allowing the anion to be detected. Using these principles, many sensors for anions have been subsequently developed [2].

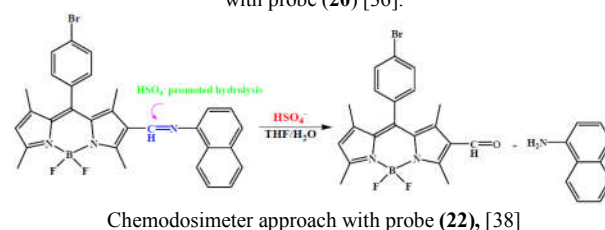
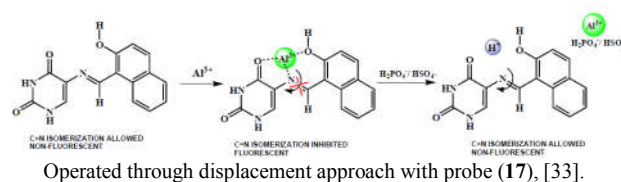
Displacement assay approach

This displacement protocol was pioneered by Eric Anslyn [15]. In the displacement protocol, the coordination of a certain anion to the binding site of a molecular ensemble results in the displacement of the signaling subunit along with a significant optical change [15-16]. In this strategy, the coordination of a certain anion to the binding site leads to the displacement of the signaling subunit and a drastic optical change is occurred as usual. Eric Anslyn [15] reported a complex derived from an indicator and a receptor *via* non-covalent interactions, where the target anionic guest binds to the receptor so firmly to displace the indicator. This change of the microenvironment around the indicator leads to the changing of its fluorescent properties and/or color, which enable to detect the target anion of interest.

Chemodosimeter approach

Finally, the “chemodosimeter” approach takes advantage of anion-induced irreversible chemical reactions resulting in changes in fluorescence or color [17-18]. So-called chemodosimeters can give very selective responses to particular anionic guest [2e]. Anion recognition with metal complexes has an advantage as they furnish electrostatic interactions that can authenticate anion binding even in semi-aqueous / aqueous medium. Moreover, those metal complexes which upon coordination with another analyte (usually anion), changes the fluorescence signal of metal complex in favor of sensing and recognition of the target analyte. Moreover, increasing interest is shown in the development of new sensing paradigms, most of which usually involve the use of nanomaterials. As interest in this area has grown, the selectivity of sensors has improved and sensors have moved out of the laboratory finding application in a number of areas including in sensing of these biologically active ions in the cellular environment i.e. both *in vivo* and *in-vitro* study.

Based on the above three processes there are several fluorogenic chemosensors for HSO_4^- ions have been reported [19-38]. In most of the cases, organic moieties have been reported as chemosensor by binding with the binding site-signalling subunit and most of them are lack of selectivity, low water solubility and less cell permeability, not practicable for intracellular imaging [19-27]. Only few are applicable for cellular study in aqueous solution [28-30]. Very few are metal complex operated through *turn-off* style [31-35] and one report of non-fluorescent coordination complex as HSO_4^- ion selective *turn-on* chemosensor is present in the literature [36], among which few are operated through displacement approach [31-33] and the others are binding with the binding site-signalling subunit [34-36]. There are also some reports are present in the literature where the fluorescent unit operated through chemodosimeter approach where the probes get hydrolyzed by the requisite anions (Table 1) [37-38].



Some chemosensor molecules for HSO_4^- ions sensing

J. S. Kim and co-workers has been designed and synthesized a coumarin-based derivative (**1**) highly selective and sensitive *turn-on* fluorogenic probe for the detection of HSO_4^- ions in aqueous solution. Various spectroscopic and DFT calculations revealed that H-bonding between the phenolic -OH and imine nitrogen of the probe played a crucial role in its high selectivity for HSO_4^- [19].

Mallick et al. provides Norharmine (**2**) as a simple unexplored class of anion receptor that allows for the selective ratiometric detection of F^- and HSO_4^- ions. HSO_4^- can easily protonate the basic H bond acceptor moiety (pyridinic N) and can modulate the optical response towards ratiometric enhancement in emission spectra [20].

A. T. Wu and co-workers reported a sugar-aza-crown ether-based cavitand (**3**) which can act as a selective *turn-on* fluorescence sensor for hydrogen sulfate ion in methanol among a series of tested anions. Several spectroscopic studies revealed that the C-H hydrogen bonding between 1,2,3-triazole ring of probe and hydrogen sulfate ion is crucial for the high selectivity of the receptor for hydrogen sulfate [21].

S. Shao and co-workers synthesized a new fluorescent receptor by the combination of BODIPY dye and indole moiety (**4**) that's binding and sensing abilities toward various anions have been studied by absorption, emission and ^1H NMR titration spectroscopy. The receptor could act as a highly selective "*Off-On*" fluorescent sensor for hydrogen sulfate anion in CH_3CN solvent and $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ medium. The fluorescence response of the receptor toward HSO_4^- in CH_3CN solvent could be due to the suppressed PET (photo-induced electron transfer) process induced by the multiple hydrogen bonding interactions between receptor and HSO_4^- and in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ medium, the HSO_4^- induced change is mainly the consequence of a simple protonation of the $\text{CH}=\text{N}-$ moiety of receptor, which inhibited the PET process and "turned on" the fluorescence [22].

Again, S. Shao et al. developed a BODIPY-based derivative containing hydrazone moiety (**5**) as a colorimetric and fluorometric sensor for fluoride and hydrogen sulfate anions. In the presence of fluoride anions, the sensor could act as an "*Off-On*" fluorescent sensor for hydrogen sulfate anions based on the reversible protonation process [23].

T. B. Wei and co-workers developed a novel and sensitive anion receptor, bearing Schiff base structure, nitrophenyl azobenzol and carboxyl groups (**6**) acts as chemosensor for the recognition of HSO_4^- anion. The different responses of UV-Vis spectra and color changes could be applied to the recognition for HSO_4^- over other anions by the naked eye. Furthermore, the anion binding interaction of receptor-anion was also studied using UV-Vis and ^1H NMR titration which revealed that the receptor displayed a remarkable binding ability for the HSO_4^- and the detection limitation of HSO_4^- with the receptor was very low in aqueous solution. Most importantly, the qualitative detection of HSO_4^- using receptor was attempted with test kit which was made from the receptor [24].

A. Wu and co-workers designed a class of novel heterocyclic compounds (**7**) which can effectively recognize HSO_4^- by the formation of hydrogen-bonded complexes in the $\text{CHCl}_3-\text{MeOH}$ [25].

X. Zeng and co-workers developed a novel fluorometric sensing strategy based on the anion-induced rotation-displaced H-aggregates of styryl-indolium dyes (**8-9**) were employed to enhance the selectivity of fluorescent chemosensors for HSO_4^- detection. The marvelous anion-induced H-aggregate strategy opens new routes to simple synthesis of receptors for tetrahedral anionic species [26].

S. Dey and co-workers synthesised an indole appended tetrapodal and hexapodal receptors (**10** and **11**) which exhibited a selective colorimetric on the spot response towards HSO_4^- ion in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (1:1). The receptors showed visually detectable colour changes on applying the HSO_4^- ion. Sharp fluorescence intensity quenching for **10** and fluorescence enhancement for **11** were observed with HSO_4^- [27].

P. Chattopadhyay et al. synthesised two new 2-(2-aminophenyl)benzimidazole based HSO_4^- ion selective receptors (**12**), which behave as highly selective chemosensor for HSO_4^- ions at biological pH in ethanol-water HEPES buffer (1/5) (v/v) medium over other anions. Fluorescence signal was tuned successfully through single point to ratiometric detection by employing the substituent effects present in these two probes [28]. In another work they synthesised a new cell permeable quinazoline based receptor (**13**) selectively senses HSO_4^- ions of nanomolar region in 0.1 M HEPES buffer (ethanol-water: 1/5, v/v) at biological pH over other competitive ions through the proton transfer followed by hydrogen bond formation and subsequent anion coordination to yield an ensemble, which has been crystallographically characterised to ensure the structure property relationship [29].

A newly designed water soluble organic moiety, 5*H*-5,7*a*,12-triaza-dibenzo[*a,e*]azulen-6-one (**14**) having a seven membered ring behaves as a cell permeable ratiometric chemosensor selectively for hydrogen sulphate ions of very low concentration of 5.5×10^{-7} M in aqueous solvent. Gradual additions of hydrogen sulphate ions to the probe (**14**), enhancement of a new fluorescent peak at 483 nm is obtained with the decrease of weak peak of free probe at 430 nm through an isoemissive point at 449 nm was observed in HEPES buffer (1 mM; water : ethanol (v/v), 98:2) at 25°C at biological pH. This probe is an efficient biomarker for the detection of the distribution of bisulphate ions in living cells under a fluorescence microscope [30].

N. Tang and co-workers designed a mononuclear magnesium complex of xanthone crown ether (**15**) which is a good colorimetric and fluorescent detector for HSO_4^- with high sensitivity and selectivity. Sensing phenomenon can nicely be explained as photo induced electron transfer is interrupted and the luminescence is switched on [31].

N. Singh and co workers synthesized Al^{3+} complex of imine linked chemosensor (**16**). The complex has offered an interesting opportunity for the ratiometric determination of HSO_4^- in $\text{DMF}/\text{H}_2\text{O}$ (7:3, v/v) solvent system. This is the first Al^{3+} complex used for the ratiometric determination of HSO_4^- in semi-aqueous medium [32].

K. K. Upadhyay and co-workers developed a Al^{3+} complex of pyrimidine-naphthalene anchored Schiff base (**17**) showed '*ON-OFF*' switching of the receptor by the analytes, HSO_4^- upto very low level (2.91×10^{-6} M) in aqueous solution, have

been explored through various spectroscopic studies along with theoretical calculations [33].

U. Fegade and co-workers developed a novel pyrrole-substituted salicylimine zinc (II) complex (**18**). The probe has high selectivity for HSO_4^- over other anions in $\text{CH}_3\text{OH} : \text{H}_2\text{O}$ (70 : 30, v/v) solvent system. The emission intensity of the probe was quenched upon addition of HSO_4^- . Photoinduced electron transfer (PET) is responsible for observed change [34].

In another work they developed a new chromogenic dipodal Zn^{2+} complex bearing an amide group (**19**) and the anion binding profile of this sensor was investigated with fluorescence and UV-Vis spectroscopy. The receptor has high affinity for HSO_4^- with and the binding ability was confirmed with spectroscopic methods and density functional theory calculation (DFT) [35].

A water soluble non-fluorescent structurally characterised distorted square planar copper(II) complex (**20**) selectively senses HSO_4^- ions as low as $3.18 \times 10^{-7} \text{ M}$ in water : DMSO (9 : 1, v/v) HEPES buffer at biological pH, which has been established by thorough experimental and theoretical studies. This biofriendly probe is also useful for the distribution of intracellular HSO_4^- ions under a fluorescence microscope [36].

K. K. Upadhyay and co-workers demonstrate for the first time for the compound **1** and **21** that the acidic nature of this HSO_4^- anion gives rise to hydrolysis of the Schiff base, which leads to the optical changes observed in this family of receptors in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (1 : 1, v/v) [37].

D. Cao and co-workers developed a novel colorimetric fluorescent chemosensor for HSO_4^- using BODIPY-based Schiff base (**22**) which is capable of showing high selectivity and sensitivity toward HSO_4^- over a wide range of other interfering anions. In presence of HSO_4^- the probe shows a significant blue-shift in the absorption spectra from 523 to 497 nm and an increase of the ratio of the absorbance at 497 and 523 nm over 150-fold, which induces colour changes from pink to yellow. The non-fluorescent probe upon interaction with HSO_4^- ions display a 114-fold fluorescence enhancement at 533 nm, resulting in strong green emission. In addition, the cell imaging experiments demonstrate that the probe can be successfully applied as a bio-imaging agent for monitoring HSO_4^- in HeLa cells [38].

A. Kuwar *et al* reported a 'turn-on' dual fluorescence sensor for selective detection of Zn^{2+} and HSO_4^- ions in 50 % aqueous CH_3CN having a lower sensing limit of 0.95 nM for the detection of HSO_4^- ions. The weakly fluorescent Chemosensor (**23**) showed highly selective enhancement in the emission wavelength at 470 nm and 425 nm for Zn^{2+} and HSO_4^- ions respectively upon excitation at 300 nm. They also carried out confocal microscopy experiments with the receptor for cell imaging of both the analyte, Zn^{2+} and HSO_4^- ions levels within living HeLa cells [39].

S.V. Bhosale and co-worker developed a sensitive and selective receptor (**24**) 3-cyano-4-imino-2-methylthio-4H-pyrimido [2,1-b] [1,3] benzothiazole, for the recognition of HSO_4^- ions in $\text{CH}_3\text{CN} : \text{H}_2\text{O}$ (2.5:7.5,v:v) operating through ICT off phenomenon resulted into quenching of the emission peak, showing a visual color change [40].

Y-M Zhang *et al* synthesized a dual-channel sensor (**25**) based on a phenazine derivative capable of successively detect CN^- and HSO_4^- ions. Upon the addition aqueous solution of CN^- , the sensor showed an immediate visible color change from yellow to orange, meanwhile, the yellow fluorescence of sensor get quenched in DMSO/ H_2O (7/3, v/v). The detection limits of (**26**) to CN^- and (**26**) + CN^- to HSO_4^- were estimated to be $8.90 \times 10^{-8} \text{ M}$ and $1.46 \times 10^{-10} \text{ M}$, respectively. The experimental result proved that this probe could be repeated use above 12 times [41].

S. Erdemir and co-workers designed a fluorescent sensor (**26**) based on calix[4]arene appended benzothiazole units for multianalytes namely Cu^{2+} , S^{2-} and HSO_4^- ions in aqueous solution. Probe served exclusive response towards HSO_4^- ions over competitive anions by "off-on" type fluorescent changes operate via hydrolysis process and with about 10-fold fluorescence enhancement at 542 nm. The fluorescence detection limit of (**26**) towards HSO_4^- was found to be 0.98 μM , making it applicable for detecting HSO_4^- levels in physiological and environmental media [42].

G. Das and co-workers synthesized a fluorogenic probe (**27**) able to show rapid and Turn-On responses by exhibiting a greenish-yellow fluorescence ($\lambda_{\text{em}} = 511 \text{ nm}$) for $\text{SO}_4^{2-}/\text{HSO}_4^-$ in 100% aqueous medium and live cells. The addition of $\text{SO}_4^{2-}/\text{HSO}_4^-$ to (**27**) resulted in the emergence of a new red shifted emission maximum at 511 nm accompanied by ~ 10 fold enhancement in the fluorescence intensity of probe. It has been argued that the presence of $\text{SO}_4^{2-}/\text{HSO}_4^-$ introduced the aggregation induced emission (AIE) behavior to the system to enable the TURN-ON fluorescence response [43].

J. Ren and co-workers prepared a new fluorescence turn-on chemosensor (**28**) having strong response toward HSO_4^- based on quinoline and naphthalimide. The sensing mechanism has been suggested to proceed via a hydrolysis process with an 8-fold fluorescence intensity enhancement in the presence of 10 equiv. of HSO_4^- in DMSO- H_2O (1/1, v/v) solution. The probe is also applied for the determination of hydrogen sulfate anion in biological and environmental science [44].

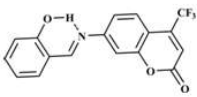
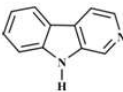
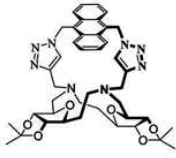
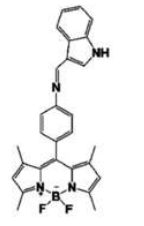
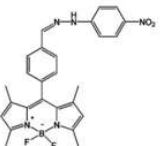
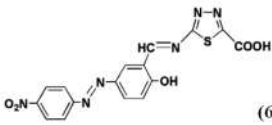
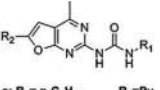
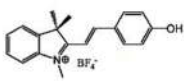
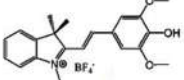
S. V. Bhosale and co-worker reported a new sensitive and selective HSO_4^- ion sensor (**29**) based on fused pyridopyrimidine. The detection of HSO_4^- over other anions such as Cl^- , F^- , Br^- , I^- , ClO_4^- , H_2PO_4^- , NO_3^- , and AcO^- was confirmed by fluorescent color changes, UV-vis and fluorescence spectroscopy. The HSO_4^- ion binding with the receptor was also investigated with a binding constant $1.09387 \times 10^5 \text{ M}^{-1}$, which revealed that the receptor showed a remarkable binding ability towards the HSO_4^- ion. The limit of detection was calculated to be $6.0378 \times 10^{-5} \text{ M}$ in $\text{CH}_3\text{CN} : \text{H}_2\text{O}$ (1:3, v:v) solvent mixture [45].


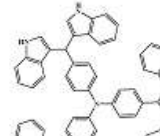
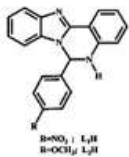
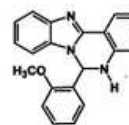
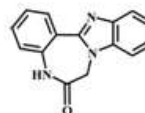
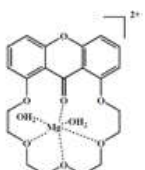
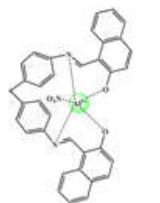

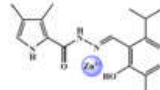
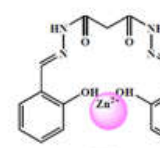
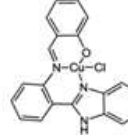
Y. Upadhyay *et al.* described rhodamine 6G hydrazide (**30**) for the selective colorimetric and turn-on fluorescent sensing in the application of hydrogen sulphate ions in aqueous medium. The ring opening of the colourless spirocyclic form of probe, was selectively triggered in the presence of HSO_4^- among the other tested anions (F^- , Cl^- , Br^- , I^- , AcO^- , H_2PO_4^- , NO_3^- , ClO_4^- , CN^- , HO^- , AsO_3^{3-} and SO_4^{2-}), which gives rise to a pink colour and strong fluorescence. The sensor showed a detection limit down to micromolar range without any interference from the other tested competitive anions [46].

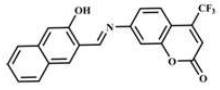
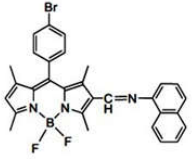
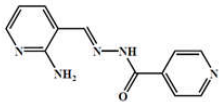
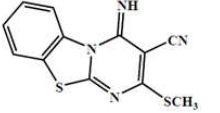
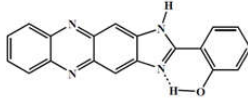
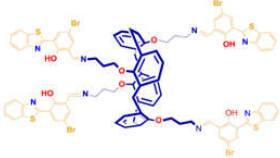
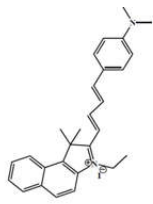
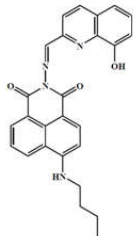
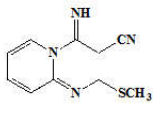
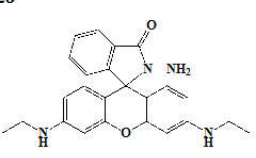
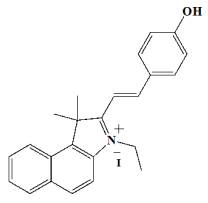
H. Chen and co-worker reported a novel fluorescent sensor, (*E*)-3-ethyl-2-(4-hydroxystyryl)-1,1-di-methyl-1H-benzo-[e]indolium iodide (**31**) based on benzo[e]indolium. It showed the simultaneous detection of $\text{SO}_3^{2-}/\text{HSO}_3^-$ and HSO_4^- ion with different emission channels. Based on the principle of ion-induced rotation-displaced H-aggregates, when treated with NaHSO_4 , a fluorescence enhancement at 580 nm was observed with the excitation wavelength at 420 nm.

While, in the advantage of the nucleophilic addition of SO_3^{2-} to the vinyl group, strong fluorescence was obtained at 455 nm when treated with Na_2SO_3 with the excitation wavelength at 320 nm, along with obvious color change by naked eyes. The sensor was also applicable for fluorescence imagings of bisulfite and hydrosulfate in living cells [47].

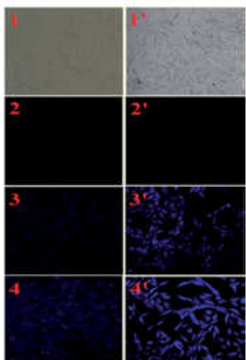
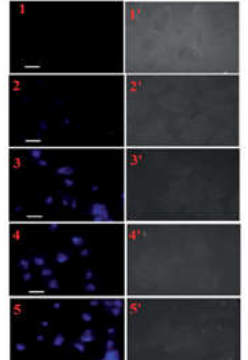
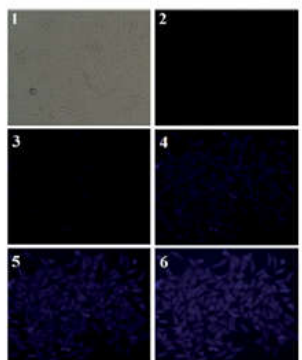
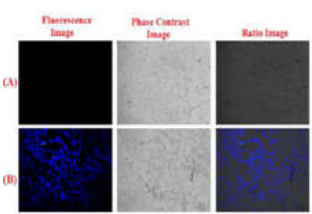
Table 1 Some selective chemosensors for hydrogen sulphate (HSO_4^-) ion:

Sl. No.	Probes (Compound Number)	Medium	Detection limit	Photo-physical process	Ref.
1	 (1)	$\text{CH}_3\text{CN} - \text{H}_2\text{O}$ (1 : 1, v/v)	$3.75 \times 10^{-6} \text{ M}$	H-bonding with the phenolic -OH and imine nitrogen	19
2	 (2)	$\text{CH}_3\text{CN} - \text{H}_2\text{O}$ (5 : 1, v/v)	---	Protonation of the pyridinic N- end	20
3	 (3)	MeOH	$1.39 \times 10^{-6} \text{ M}$	Interaction with the hydrogens of triazole and anthracene	21
4	 (4)	CH_3CN and $\text{CH}_3\text{CN} - \text{H}_2\text{O}$ medium.	---	CH_3CN : Suppression of PET process followed by hydrogen bond. $\text{CH}_3\text{CN} - \text{H}_2\text{O}$: suppression of PET process due to protonation	22
5	 (5)	CH_3CN	---	Due to reversible protonation process and inhibition of PET	23
6	 (6)	$\text{H}_2\text{O} / \text{DMSO}$, 3.8 : 6.2, v/v	$2 \times 10^{-6} \text{ mol L}^{-1}$	H-bonding interaction	24
7	 a: $\text{R}_1 = n\text{-C}_6\text{H}_{13}$ $\text{R}_2 = \text{Py}$ b: $\text{R}_1 = n\text{-C}_7\text{H}_{15}$ $\text{R}_2 = \text{Py}$ c: $\text{R}_1 = \text{isopropyl}$ $\text{R}_2 = \text{Py}$ (7)	$\text{CHCl}_3 - \text{MeOH}$ (9:1 v/v) solution	---	H-bonding interaction between host and guest	25
8	 (8)	$\text{H}_2\text{O} - \text{EtOH}$ (1 : 1, v/v)	For 8 $1 \times 10^{-6} \text{ M}$	(i) Hydrogen bonding	26
	 (9)		For 9 $1 \times 10^{-7} \text{ M}$	(ii) Electrostatic interactions	

9		CH ₃ CN - H ₂ O (1:1, v/v) (10)	10 ⁻⁴ M	TBET process (Fluorescence quenching for 10 and enhancement for 11)	27
		(11)			
10		HEPES buffer (C ₂ H ₅ OH: H ₂ O, 1/5, v/v) (12)	For L ₁ H: 18.08 nM For L ₂ H: 14.11 nM	Non covalent H- bonding interaction	28
11		HEPES buffer (C ₂ H ₅ OH: H ₂ O, 1/5, v/v) (13)	28.72 nM	Protonation followed by H- bond interaction	29
12		HEPES buffer (H ₂ O : C ₂ H ₅ OH (v/v), 98: 2) (14)	5.5 × 10 ⁻⁷ M	Intramolecular H-bonding assisted CHEF process	30
13		CH ₃ CN (15)		Photo-induced electron transfer is interrupted and the luminescence is switched on	31
14		DMF/H ₂ O (7:3, v/v) solvent (16)	1.99 μM	ESIPT	32
15		aqueous medium (17)	2.91 x 10 ⁻⁶ M	Fluorescence quenching occurs	33
16		CH ₃ OH : H ₂ O (7 : 3, v/v) (18)	40 nM	---	34
17		DMSO- H ₂ O (1 : 1, v/v) (19)	50 nM	---	35
18		DMSO- H ₂ O (1 : 9, v/v) (20)	3.18 × 10 ⁻⁷ M	Intramolecular H- bonding assisted CHEF process in <i>turn-on</i> style	36

19		CH ₃ CN- H ₂ O (1 : 1, v/v) (21)	---	Acidic nature of HSO ₄ ⁻ ions gives rise to hydrolysis of the Schiff base	37
20		THF-H ₂ O (8/1, v/v) (22)	6.45 × 10 ⁻⁷ M	The sensing mechanism is suggested to proceed via a hydrolysis process	38
21		CH ₃ CN- H ₂ O (1 : 1, v/v) (23)	0.95 nM		39
22		CH ₃ CN: H ₂ O (1:3,v/v) (24)	1.6067×10 ⁻⁷ M	Quenching through ICT off process	40
23		DMSO/H ₂ O (7/3, v/v) (25)	1.46 × 10 ⁻¹⁰ M	---	41
24		CH ₃ CN /H ₂ O (4/1, v/v) (26)	0.98 μM	Sensing mechanism was suggested to proceed via a hydrolysis process	42
25		Aqueous media (27)	---	Aggregation induced emission (AIE)	43
26		DMSO- H ₂ O (1 : 1, v/v) (28)	7.79 × 10 ⁻⁷ M	Sensing mechanism proceed via a hydrolysis process	44
27		CH ₃ CN- H ₂ O (1 : 3, v/v) (29)	6.03 × 10 ⁻⁵ M	Complex formation between the probe and HSO ₄ ⁻	45
28		Aqueous methanol (30)	3.72 × 10 ⁻⁵ M	Spirolactam ring opening due to the formation of hydrogen bonded complex between sensor and HSO ₄ ⁻	46
29		EtOH- H ₂ O (v/v, 8:2) (31)	2.82 × 10 ⁻⁹ M	Ion-induced H- aggregates	47

Biological study of some chemosensors for HSO_4^- ions distribution

Cell image	Chemosensor and reference	Cell image	Chemosensor and reference
	Probe (12) Ref. 28		Probe (13) Ref. 29
<p>Phase contrast (1 and 1') and fluorescence images of HeLa cells after incubation with (12) in presence of (2 and 2') 0 mM, (3 and 3') 5 mM and (4 and 4') 10 mM of HSO_4^- for 30 min at 37 °C.</p>		<p>Phase contrast (right) and fluorescence images (left) of HeLa cells after incubation with (13) in the presence of HSO_4^- ions (1,1') 0 mM, (2,2') 3mM, (3,3') 5mM, (4,4')7mM, and (5,5') 10 mM, respectively, for 30 min at 37°C</p>	
	Probe (14) Ref. 30		Probe (20) Ref. 36
<p>Fluorescence image of HeLa cells after incubation (14) in Presence of HSO_4^- ions (1) phase contrast, (2) 0 mM, (3) 3 mM, (4) 5 mM, (5) 7 mM, (6) 10 mM for 30 min at 37°C.</p>		<p>Fluorescence image of HeLa cells encumbered with (A) (20) (10.0 μM); (B) (20) (10.0 μM) with 10.0 μM HSO_4^- solution</p>	

SUMMARY AND OUTLOOK

Herein we have attempted to summaries the use of the several organic molecules in the field of colorimetric and fluorescent HSO_4^- anion sensing that continues to be an important goal and is being pursued by a number of research groups worldwide. The present highlight provides an overview of different photophysical properties involved in the sensing of HSO_4^- ions leading to easy to observe naked eye colorimetric as well as fluorescence change. Not only the organic ligand moieties alone but also we have also shown here some metal complexes, able to act as a superior HSO_4^- ions sensor. Some of the abovementioned chemosensor are significantly efficient to detect the distribution of hydrogen sulphate ions *in vitro* in living cells in aqueous medium at biological pH by developing the good image. It is clear from this short summary that the field of HSO_4^- ions sensing is rapidly growing and we optimistically believe that there is a way to combine the aforementioned approaches to fabricate new chromogenic sensor for HSO_4^- ions sensing, with high selectivity and sensitivity, pH independency, working in pure aqueous media and which are applicable in both *in vitro* and *in vivo* use.

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