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ARTICLE TYPE

Ratiometric detection of hypochlorite applying the restriction to 2-way-ESIPT: Simple design for “naked-eye” tap water analysis

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We have designed a ESIPT based ratiometric sensor (3-(benzo[d]thiazol-2-yl)-2-hydroxybenzylidene)thiosemicarbazide (BTHT) for OCl^- with high selectivity and sensitivity with “naked-eye” colour change (from orange to blue under UV light). Here strong H-bonding mediated inhibition of 2-way-excited-state intramolecular proton transfer (ESIPT) of BTHT is observed over other anions and oxidants in aqueous solution. The sensor is remarkably efficient for the sensitive recognition of hypochlorites present in differentially treated tap water.

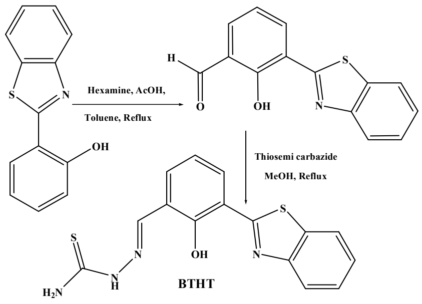
Introduction:

Ozone, chlorine dioxide, H_2O_2 and chlorine are used as oxidants for remediation of drinking water for decades.[1] The most predominant disinfection method used for water and waste water treatment is chlorination due to its low cost and capability to disable a broad range of pathogenic microorganisms.[2] Hypochlorites are easy alternatives to chlorine gas which is difficult to handle in many contexts. Sodium hypochlorite is the most commonly used chlorinated substance and extensively used as a household cleaning agent.[3] Household bleach is, in general, a solution containing 3-8% sodium hypochlorite and 0.01-0.05% sodium hydroxide; sodium hydroxide is used to slow the decomposition of sodium hypochlorite into sodium chloride and sodium chlorate. Usually 50 to 250 mL of bleach per load is recommended for a standard-size washer. Sodium hypochlorite solutions have been used to treat dilute cyanide wastewater, such as electroplating wastes. In drinking water systems, swimming pools, etc., sodium hypochlorite are widely used for chlorination.[4] Dilute HOCl baths (0.005% v/v) are used for decades to treat human atopic dermatitis[5] but recently Kim et. al. has shown that a very dilute (0.005%) solution of sodium hypochlorite was doing well in treating skin-damage with an inflammatory constituent caused by radiation therapy, excess sun exposure or aging in laboratory mice.[6] Banned drugs such as cocaine can also be tracked by sodium hypochlorite.[7] In its protonated form (hypochlorous acid, HClO), it is a biologically important reactive oxygen species (ROS)[8] and functions as an antimicrobial agent in organisms. It is known that hypochlorite anion is synthesized from hydrogen peroxide and chloride ions in a biosystem catalyzed by the enzyme myeloperoxidase (MPO). In living organisms, hypochlorite can damage various bio molecules (i.e., DNA, RNA, fatty acids, cholesterol and proteins),[9] thus an abnormal level of hypochlorite can lead to tissue damage and diseases such as hepatic ischemia-reperfusion injury,[10] atherosclerosis,[11] lung injury,[12] rheumatoid[13] cardiovascular diseases,[14] neuron degeneration,[15] arthritis,[16] cancer,[17] Alzheimer[18] and organ transplant rejection.[19]

These significant findings also encourage us to build up reactive and specific probes for detecting hypochlorite used in our day to day life. Thus, there is a requirement for a fast and responsive method for the detection of hypochlorite in real tap water samples which is used as drinking water also. Compared to other detection methods, fluorescent probes have natural advantages including superior sensitivity, rapid response time and straightforwardness of implementation, offering various types of application methods. On the other hand, ratiometric fluorescent probes are able to allow the measurement of fluorescence intensities at two dissimilar wavelengths, considered as a good move toward to defeat the most important limitation of intensity based probes, in which variations in the environmental model and probe sharing were difficult for quantitative measurements.

In recent times, a number of organic fluorescent probes for HOCl/ OCl^- sensing have been reported through conversion of general fluorophores, for example napthalene,[20] cyanine,[21] rhodamine,[22] fluorescein,[23] BODIPY,[24] quinoline,[25] triphenylamine,[26] coumarin,[27] phenanthroline,[28] anthraquinone,[29] imidazoline-2-thione,[30] and carbazole[31] with HOCl/OCl^- reactive groups. Though, there are some ratiometric fluorescent probes for OCl^- reported in recent times, but ratiometric ‘naked-eye’ detection of ‘tap water hypochlorite’ is still unknown.

Scheme 1: Synthetic scheme of BTHT:



Motivated by all these approaches, we herein report a new Exited State Intramolecular Proton Transfer (ESIPT) based ratiometric fluorogenic sensor, (3-(benzo[d]thiazol-2-yl)-2-hydroxybenzylidene)thiosemicarbazide (BTHT) for hypochlorite recognition with a rapid response. The structure of the receptor BTHT (Scheme 1) was confirmed by ^{1}H NMR, ^{13}C NMR and ESI TOF mass spectra (supporting information†).

Experimental Section:

General

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. ^{1}H-NMR and ^{13}C NMR spectra were recorded on a Brucker 400 MHz. For NMR spectra, $CDCl_3$ and d_6-DMSO was used as solvent with TMS as an internal standard. Chemical shifts are expressed in δ units and ^{1}H–^{1}H coupling constants in Hz. Fluorescence experiment was done using PTI fluorescence spectrophotometer with a fluorescence cell of 10 mm path.

General method of fluorescence titrations

For fluorescence titrations, stock solution of the sensor was prepared (c = 2×10^{-5} ML^{-1}) in CH_3CN: H_2O (1:1, v/v). The solution of the guest anion was prepared (2×10^{-5} ML^{-1}) in CH_3CN: H_2O (1:1, v/v) at pH 7.4 by using 10 mM HEPES buffer. The original volume of the receptor solution is 2 ml. Solutions of the sensor of various concentrations and increasing concentrations of cations, anions and another species containing compounds were prepared separately. The spectra of these solutions were recorded by means of fluorescence methods.

Calculation of the detection limit

The detection limit (LOD) was determined from the following equation:

DL = K* Sb1/S

Where K = 2 or 3 (we take 2 in this case); Sb1 is the standard deviation of the masurement and S is the slope of the calibration curve.

Determination of fluorescence quantum yield

Here, the quantum yield φ was measured by using the following equation,

$$\varphi_x = \varphi_s \,(F_x / F_s)(A_s / A_x)(n_x^2/ n_s^2)$$

Where,

X & S indicate the unknown and standard solution respectively, φ = quantum yield,

F = area under the emission curve, A = absorbance at the excitation wave length,

n = index of refraction of the solvent. Here φ measurements were performed using anthracene in ethanol as standard [φ = 0.27] (error ~ 10%).

Method for the preparation of TLC plate sticks

It was easily prepared by immersing a TLC plate into the solution of BTHT (2×10^{-3} M) in CH_3CN and then exposing it to air to evaporate the solvent. The detection of hypochlorite was carried out by inserting the TLC plate to the solution of NaOCl in water and evaporating solvent to dryness. Finally, under ambient light and UV light the naked eye color and fluorescence were checked respectively.

Synthetic procedure (scheme 1)

Synthesis of receptor (3-(benzo[d]thiazol-2-yl)-2-hydroxybenzylidene) thiosemicarbazide (BTHT): 3-(benzo[d]thiazol-2-yl)-2-hydroxybenzaldehyde is reproduced in the basis of our previous reported literature method.[32] Under an atmosphere of dry nitrogen, 3-(benzo[d]thiazol-2-yl)-2-hydroxybenzaldehyde 1 (500 mg, 1.52 mmol) and thiosemicarbazide (170 mg, 1.86 mmol) are refluxed overnight to produce the receptor, BTHT in absolute ethanol (20 mL). Then, the resultant mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography using dichloromethane to 3% methanol in dichloromethane as eluent to afford the product as a yellow solid (402 mg, 60%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 12.96 (s, 1H), 9.05 (s, 1H), 8.36 (s, 1H), 8.05 (d, 1H, *J* = 8.08 Hz), 7.92 (t, 2H, *J* = 7.96 Hz), 7.75 (m, 1H), 7.54 (t, 1H, *J* = 7.32 Hz), 7.45 (t, 1H, *J* = 7.44Hz), 7.15 (d, 1H, *J* = 8.68 Hz), 6.10 (m, 1H), 6.29 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 178.74, 159.09, 154.12, 151.89, 147.74, 133.08, 130.59, 128.38, 128.24, 124.01, 123.14, 118.34, 105.42, 96.80.

MS (ESI MS): (m/z, %): 329.05 [(BTHT+H$^+$), 100 %].

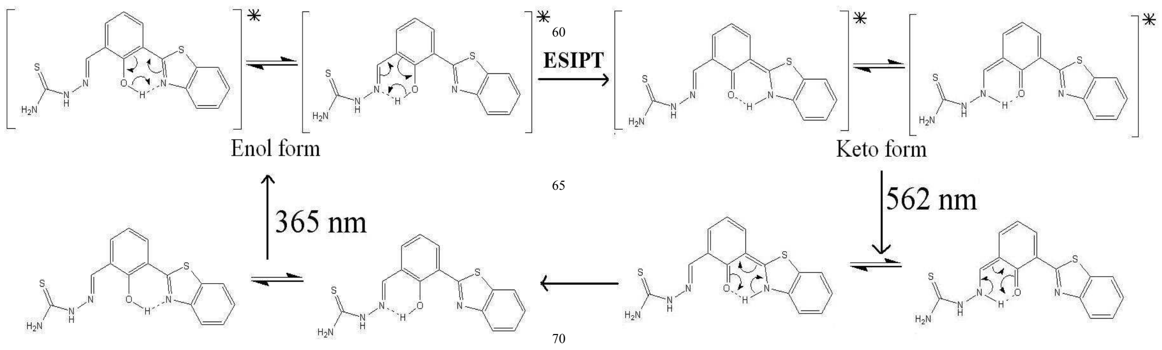
Results and discussion:

Excited-state intramolecular proton transfer (ESIPT) of HBT and its derivatives

2-(2'-hydroxyphenyl)benzothiazole (HBT) and its derivatives, upon irradiation, generate the excited-state intramolecular proton transfer (ESIPT) tautomers (the keto forms), which show fluorescence more strongly at longer wavelength compared to the phenol forms. Scheme 2 shows a representative molecule BTHT exhibiting ESIPT along with the general 4-level reaction scheme with the two possibilities of ESIPT in equilibrium. The enol isomer, which is lower in energy than the keto isomer in the electronic ground state, undergoes the proton transfer reaction upon excitation to the excited state. Though in the earlier reports it was thought that the movement of the hydrogen atom was a reaction coordinate, modern experimental and theoretical findings show that low frequency skeletal vibrations are directly coupled to the reaction, while the proton itself participates in the reaction quite inactively.[33]

Fluorescence studies

The fluorescence properties of chemosensor BTHT was studied in CH_3CN–H_2O solution (1: 1, v/v, 10 mM HEPES, pH 7.4). BTHT exhibits emission band at 476 nm and 562 nm in absence of OCl^-. However, an increasing emission around 476 nm emerged gradually and the emission around 562 nm decreased



Scheme 2: 4 level 2-way-ESIPT diagram of BTHT:

simultaneously with a clear isosemissive point at 538 nm, when OCl^- was added to the BTHT (Fig. 1). In this case, a ratiometric shift was apparently attributed from 562 nm and 476 nm because no more ESIPT is possible when OCl^- strongly bounded to the hydrogen of hydroxyl group in BTHT. The orange coloured fluorescent solution showed sky blue colored fluorescence, when OCl- is gradually added to the solution of BTHT (Figure 1, inset). The selectivity and sensitivity of probe BTHT towards OCl^- in the presence of various analytes were examined. In each case, probe BTHT (20 µM) was treated separately with 200 µM of each analyte (Cu^{2+}, Co^{2+}, Hg^{2+}, Fe^{3+}, F^-, I^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, IBX,H_2O_2, OH^-, O_2^-, MCPBA, CH_3CO_3H) in HEPES buffer (10 mM, pH = 7.4). However, no significant fluorescence enhancements were observed for all analytes (Figure. 2).

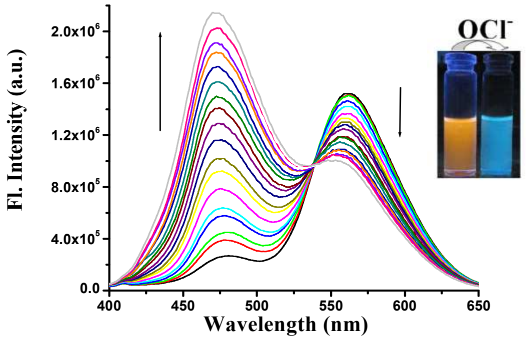


Figure 1: Fluorescence emission spectra of BTHT (c = 2.0 x 10^{-5} M) with OCl^- (c = 2.0 x10^{-5} M) at pH 7.4 in CH_3CN:H_2O (1:1, V/V) with the naked eye fluorescence change (inset).

These results confirm that BTHT shows a good sensitivity and selectivity towards OCl^- over other competitive ions. However in these condition, fluoride and superoxide anion shows some interference making a weak H- bond with the phenolic proton of HTBT due to presence of their high electronegativity. But in the light of ratiometric response the interference becomes very minor when it stands in front of the ratiometric response of hypochlorite (Figure 2).

In fact, in the presence of 1 equiv. of OCl^-, a 12.7 fold enhancement in the ratiometric value of F_{476}/F_{562} (0.17 to 2.19) was achieved with respect to the hypochlorite free solution (Figure 2). In the time dependent fluorescent spectra, we see the reaction is completed within 8 min, which strongly supports the high reactivity of the probe which is a essential criteria for real application of the sensor (Figure 3a).

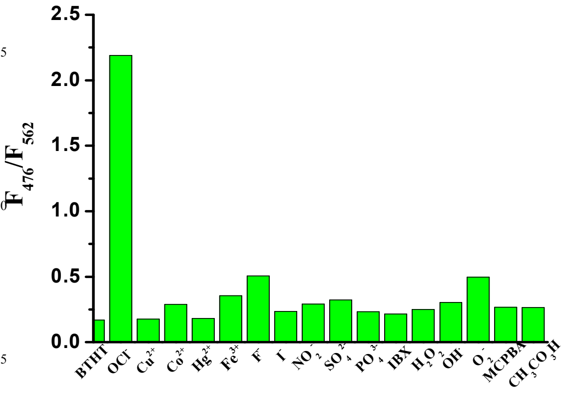


Figure 2: Ratiometric response of BTHT (c = 2.0 x 10^{-5} M) towards different oxidizing agent (1 eqiv.) with the proposed reaction scheme of BTHT with OCl^-.

(a) (b)

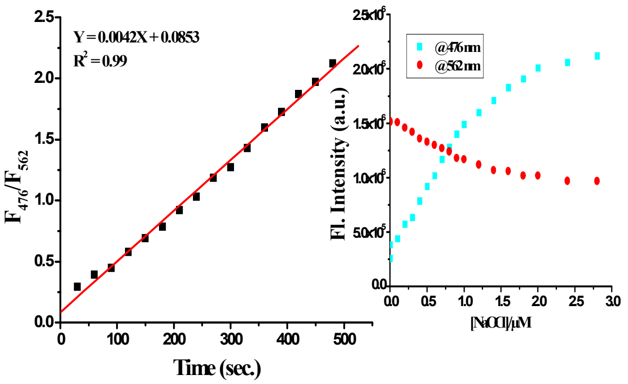


Figure 3: (a) The linearity response of ratiometric Fl. Intensity vs. time at 476 nm/ 562 nm. (b) Plot of [OCl^-] vs. Fl. Intensity at two different wave lengths (i.e. at 476 nm and 562 nm λ_{ex}=365 nm).

The detection limit was found to be 0.14 μM based on K* Sb1/S,[32] where Sb 1 is the standard deviation and S is the slope of the calibration curve (Figure S1: Supporting information†). From Figure 3b, it is clear that only 10 μM hypochlorite solution is enough for the naked eye color change of the mixed aqueous solution of HTBT (i.e. from orange to blue).

Fortunately, the sensor (BTHT) showed a full fluorescence response to OCl^- in the presence of 10 equiv. of all other oxidizing agents. The competition experiment showed that SO_4^{2-}, OH^- and CH_3CO_3H have a slight interference and other oxidizing agents have a negligible influence on the sensing of OCl^- (Figure S3: supporting information†).

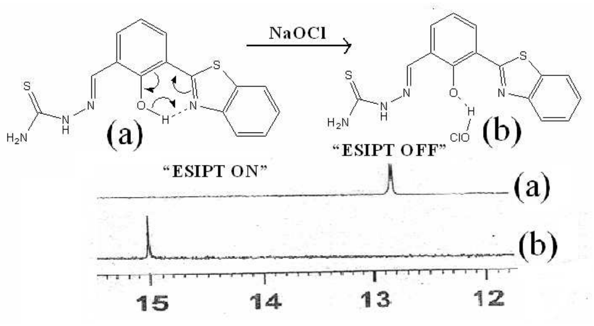


Figure 4: The probable binding mode of hypochlorite with BTHT with their partial ^{1}H-NMR spectra.

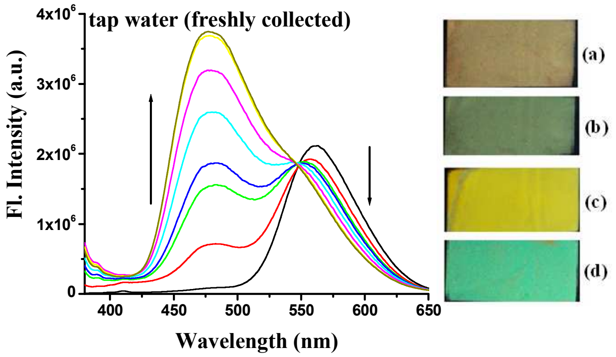


Figure 5: Intensity change of BTHT in addition with tap water (freshly collected, 0 to 1.5 ml) (left) and color changes visualized on TLC plate strips of (a) and (c) BTHT (c = 2.0 x 10^{-3} M) and during addition of NaOCl at (b) and (d) 2.0 x 10^{-5} M. (a and b: under ambient light) (c and d: under hand held UV lamp) (right).

Predicted chemical mechanism for OCl^- detection

To explore the sensing mechanism of probe BTHT to OCl–, the ^{1}H-NMR of BTHT with 1 equiv. NaOCl was carried out in d*6*-DMSO solution. From the ^{1}H-NMR spectra (the phenolic proton is downfield shifted from δ 12.70 ppm to δ 14.99 ppm), it is clear that when NaOCl solution is added to the solution, the OCl^- anion can strongly bind the phenolic proton of HTBT. The probable scheme with the partial ^{1}H-NMR spectra are shown in Figure 4.

Applications

Due to its excellent spectroscopic response, we tested the probe BTHT for detecting OCl^- in various types of water samples i.e., tap water, distilled water, tube well water etc.. Shockingly we can see that in presence of tap water which is a main source of drinking water in India, the BTHT solution becomes blue from orange. The titration data of BTHT solution with increasing the volume of freshly collected tap water give a similar ratiometric response (Figure 5) like addition of hypochlorite solution in BTHT solution in Figure 1. Only the addition of 500 micro litre of tap water result a remarkable ratiometric result of fluorescence. This result indicates that the probe BTHT can detect the OCl^- in significantly more complex compositions as compared to laboratory conditions (Figure 5).

Interestingly no significant fluorescence response was found in case of other water samples like distilled water, millipore water or tube well water. Only river water (water sample collected from the river of Ganges, India, collection place Botanical Garden ghat, Shibpur, Howrah) can make a significant interference probably due to the presence of various types of pollutants (Figure 6).

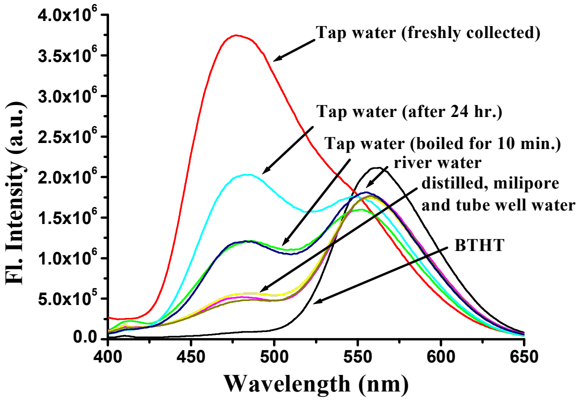


Figure 6: Intensity change of BTHT in addition with tap water (just collected, after 24 hour and after boiling for 10 min.), river water, distilled water, millipore water and tube well water.

The results become more surprising when we add the boiled tap water (boiled for 10 min.) to the solution of HTBT. It can cause only about one third response (fluorescence intensity) with respect to raw tap water which concludes that the use of boiled tap water as a drinking water is safe enough from the raw tap water. Even tap water left alone for 24 hours is better (for the reduced content of OCl^-) for drinking than the freshly collected tap water (Figure 6).

Test strips were also prepared to detect OCl^- in solid phase. These test strips demonstrated apparent color changes under ambient light or a hand held UV lamp with shorter wavelength (color changes from bright yellow to bright blue under UV lamp: Figure 5). Importantly, these strips could be conveniently used for the detection of OCl^-.

Conclusions

In summary, we have achieved a ratiometric fluorescence chemo sensor, 3-(benzo[d]thiazol-2-yl)-2-hydroxybenzylidene) thiosemicarbazide (BTHT) for detection of OCl^- via strong H-bonding mediated inhibition of excited-state intramolecular proton transfer (ESIPT) of BTHT over other anions and oxidants in aqueous solution. Thus we have proved here that even increased strength of hydrogen bonding can exceptionally enable a sensor to efficiently discriminate even differential treatment of tap water. The usual practice of using bleaching powder or dilute hypochlorite solution for water purification also hints its presence of some excess may also be dangerous to human health. Our sensor is sensitive enough to prove that boiling of tap water for ten minutes is safer and a good habit for drinking water.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of spectroscopic data available in ESI]. See DOI: 10.1039/b000000x/

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