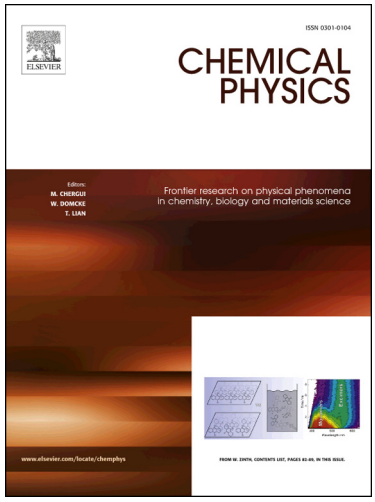

Fate of protected HBT based chemodosimeters after undergoing deprotection: restoration of ESIPT or generation of emissive phenoxide?

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Fate of protected HBT based chemodosimeters after undergoing deprotection: restoration of ESIPT or generation of emissive phenoxide?

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Abstract

-OH protected 2-(hydroxyphenyl) benzothiazole (**HBT**) based ratiometric chemodosimeters have previously been reported to undergo regeneration of excited state intramolecular proton transfer (**ESIPT**) process upon deprotection. In the current work it is demonstrated for the first time that generation of anion of **HBT** leads to the optical changes in these types of chemodosimeters rather than regeneration of **HBT** by using a Hydrazine specific chemodosimeter based on substituted **HBT**.

Keywords

HBT; ESIPT; chemodosimeter; ratiometric; anion

1. Introduction

Since the epoch making work by Weller, excited state intramolecular proton transfer [1] (ESIPT) process has gained tremendous attention from chemists due to dual emission and large Stokes' shift. The difference in the nature of ESIPT in various systems also provide excellent opportunities for theoretical chemists to propose newer models which aid in uncovering the mechanism behind ESIPT processes [2-4]. However, due to easy synthetic route, 2-(2'-hydroxyphenyl) benzothiazole (**HBT**) backbone can be tailored at will to provide a number of ESIPT derivatives and hence **HBT** is widely used by analytical, organic as well as inorganic chemists to design many beautiful sensors. Dual emission with appreciably distant bands [5-8] observed in bare **HBT** has prompted chemists to design brilliant optical chemosensors for detecting large range of analytes. These are of two types, non-chemodosimetric [9] and chemodosimetric [10]. While the former type undergoes complexation/acid-base type reaction with analyte(s); the latter undergoes reaction with analyte(s) to furnish optical signal. Judicious protection of the phenolic –OH moiety in HBT results in generation of protected form (**PF**) of the former. Analyte(s) undergoes chemical reaction with **PF** to generate the HBT in free form (**FF**). Using this approach many receptors have been designed for detecting analytes ranging from cations, anions as well as neutral analytes [11-23]. Interestingly, almost all reports have shown that generation of **FF** is associated with a typical 'blue-fluorescence' when observed under the UV-light and a ratiometric response is also observed during this reaction with the emission maxima at ~450-470 nm (Table 1). This new peak in emission profile as well as the colour observed under the UV-light is assigned to be due to the regeneration of ESIPT. In addition, two perturbing factors are also pertinent: a) no spectral comparison between **FF** and the parent **HBT** molecule from which the **PF**s were generated. Thus, instead of a 'point-by-point'

correlation of the peak representing the so-called '**ESIPT**' form, the entire assignment was done by assuming that cleavage of **PF** leads to **ESIPT**. b) All the studies were carried out in polar protic/mixture of polar protic and aprotic solvent systems where **ESIPT** from **HBT**-based probes are reported to be disfavoured [6]. At this juncture, an interesting self-contradicting report further increased our confusion. Goswami et al. reported the **ESIPT** regaining of a probe in presence of amino acids homocysteine and cysteine by increment of a band at ~520 nm [24]. The same group reported the regeneration of ESIPT at an emission maxima of 462nm [17] associated with a blue luminescence in presence of H_2S/S^{2-}. In both cases, the parent skeleton was **HBT**. In order to verify the claim of **ESIPT** restoration, a similar model compound 2-(benzo[d]thiazol-2-yl)-4-bromophenyl benzoate (**PHBT**) was hence designed from to detect Hydrazine in aqueous methanol as there is increasing need for selective detection of hydrazine owing to its many beneficial and detrimental aspects [25-27]. **PHBT** shows a ratiometric response in presence of Hydrazine and can successfully detect Hydrazine in real water samples. The color change observed under UV-light was blue as previous reports. However, by careful spectroscopic comparison of **PHBT**-Hydrazine ensemble with the parent compound 2-(benzo[d]thiazol-2-yl)-4-bromophenol (**UHBT**) revealed that the anionic form of **UHBT** (**AUHBT**) was responsible for the spectral results instead of regeneration of **ESIPT** as claimed by previous works. To remove any possible ambiguity due to presence of bromine substitution in **PHBT**, a thorough literature survey was done which revealed that for unsubstituted **HBT** also, anion is generated. Thus, the present work finds its own merit for establishing the true reason behind the optic response of protected **HBT** derivatives upon deprotection.

Table 1. Reported λ^{em}_{max} of protected **HBT** based chemodosimeters

Receptor(reference)	**Analyte detected**	λ^{em}_{max}**(nm)**
BTB(10)	Hydrazine	458
APBT(9)	BO_3^-	455
FBBP(11)	H_2S/S^{2-}	462
CS1(8)	Cu^{2+}	460
PHBT(current work)	Hydrazine	470

2. Experimental

2.1. Reagents

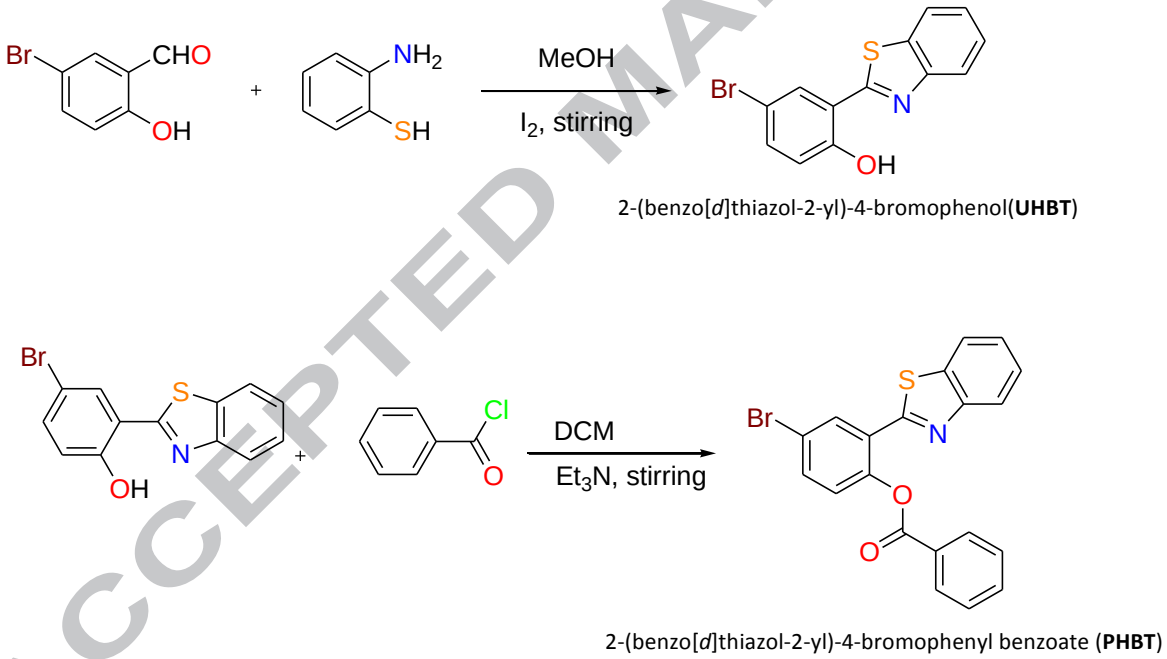
5-bromosalicylaldehyde, 2-aminothiophenol, benzoyl chloride, metal perchlorate salts and Tetrabutylammonium salts of anions were purchased from Merck and used as received. All solvents were of spectroscopic grade purchased from Spectrochem.

2.2. Apparatus

Steady state electronic absorption and fluorescence spectra were recorded on a Hitachi UV-Vis (Model U-3501) spectrophotometer and Perkin Elmer LS55 Fluorimeter respectively. ^{1}H NMR spectra were recorded on a Bruker Advance 300 spectrometer, where chemical shifts (δ in ppm) were determined with respect to Tetramethyl silane (TMS) as the internal standard. Mass spectrum was recorded on Waters Xevo G2-S Q TOF mass spectrometer.

2.3. Synthetic Scheme

In short, **UHBT** was synthesized (Scheme 1) by reacting 5-bromosalicyladehyde (2.0 mmol), 2-aminothiphenol (2.0 mmol) and molecular iodine (1.0 mmol) in 20 mL methanol and filtering the greenish white solid obtained after 5 hr stirring at room temperature. The NMR spectra of **UHBT** are provided in Fig. S1. In the next step, 1.0 mmol of benzoyl chloride was added to a solution of **UHBT** (1.0 mmol) in dry DCM followed by adding equivalent amount of triethylamine. The entire reaction mixture was stirred overnight and then filtered, followed by acidic work-up of the filtrate. Subsequent evaporation of DCM layer provided **PHBT** as a grey solid in 59% yield (Scheme S1). The NMR and ESI-MS spectra are provided in Fig.S2-S5.



Scheme 1. Synthetic outline for **PHBT**.

3. Results and discussions

Receptor **PHBT** was synthesized by a two step reaction starting from 5- bromosalicylaldehyde. The detailed synthesis and characterization has been provided in the supplementary information (Fig. S2-S5) and the purity was hence verified.

3.1. Response of PHBT as a probe for Hydrazine

To a 30 μM solution of **PHBT** in aqueous methanol (3: 7, v/v), 100 equivalents of various amines (Fig. 1) were added. Addition of only Hydrazine and 2, 4-DNP resulted in color changes. However, when observed under UV-light, the vial containing Hydrazine only showed a strong blue emission. When the UV-spectrum was recorded for all the amines utilized for naked eye color change along with various metals and anions, no interference was observed, even from 2, 4-DNP. Only Hydrazine addition resulted in a new profile with bands at 290, 345 and 400 nm respectively (Fig. 2).Thus, the color change in case of addition of 2, 4-DNP was due to the yellow color in itself and it could be stated that **PHBT** is selective towards Hydrazine. When excited at 300 nm, a 5 μM solution of **PHBT** itself shows an emission maxima centered at ~380 nm. Upon addition of Hydrazine, the aforesaid profile diminished and a new peak of much higher intensity appeared at 475 nm. Such a response was not obtained upon addition of other amines as well as metals or anions (ESI, Fig. S6).

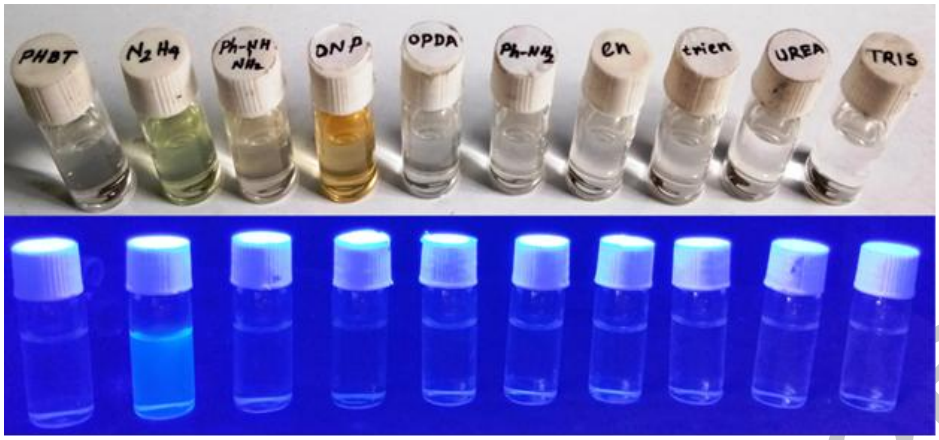


Fig. 1. Color Change of **PHBT** (far left; 30µM) under ambient light (top) and UV-light (bottom). Analytes added (from left) hydrazine, phenyl hydrazine, 2, 4-dinitrophenyl hydrazine, orthophenylene diamine, aniline, ethylene diamine, diethylenetriamine, urea and tris (each 100 equivalent)

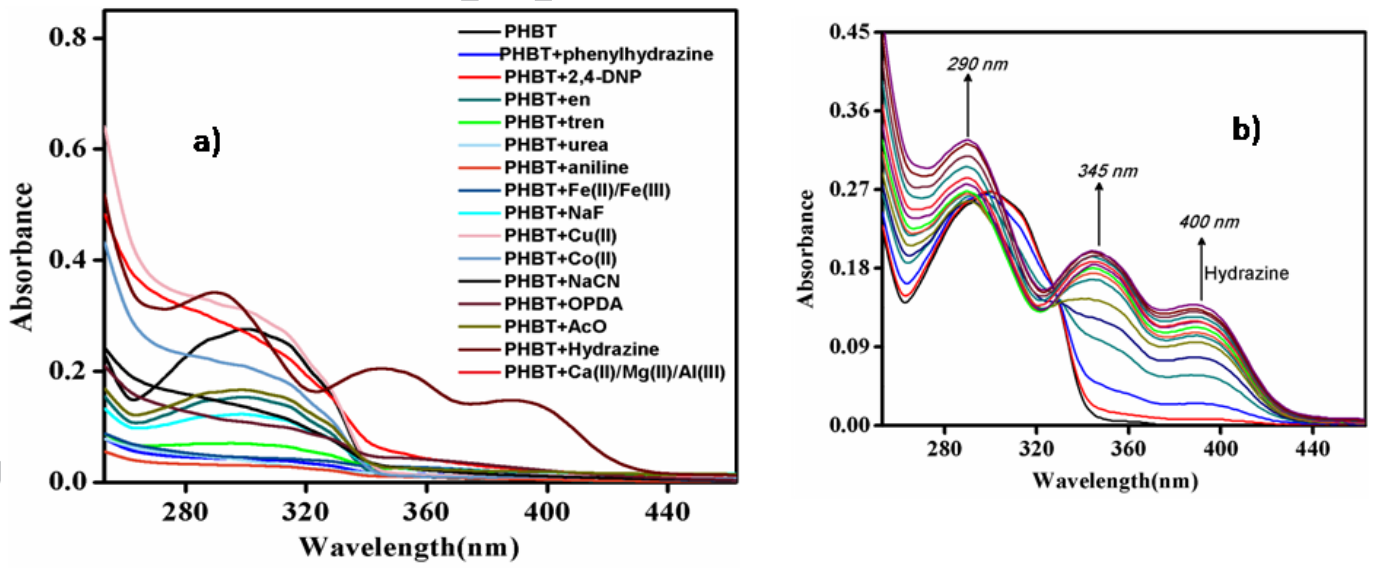


Fig. 2. a) UV-Vis response of **PHBT** (10 µM) towards various amines including Hydrazine, cations and anions; b) UV-Vis titration of **PHBT** (10 µM) with Hydrazine (0-20 equivalent).

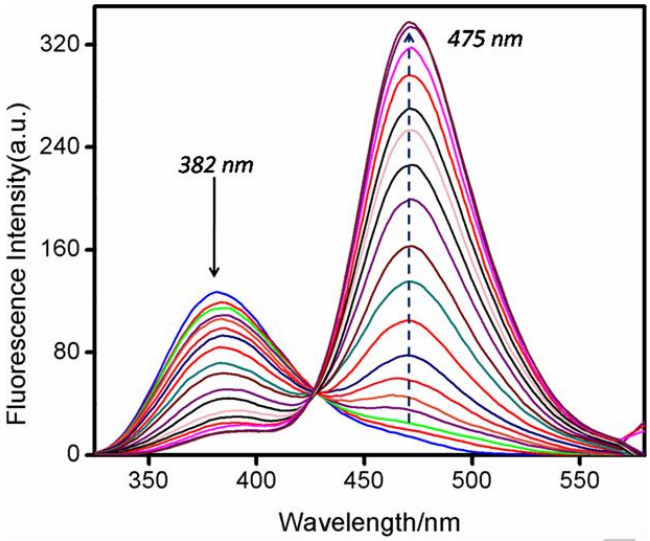


Fig. 3. Fluorimetric titration of **PHBT** (5 µM) with Hydrazine (0-10 equivalents).

The above obtained results proved the potential of **PHBT** to be a selective ratiometric probe for Hydrazine. To find out the mechanism of Hydrazine detection, ESI-MS experiments were conducted. A suspension of **PHBT** in methanol was treated with hydrazine and stirred overnight. The mixture thus obtained was subjected to ESI-MS. The prominent signal appeared for **UHBT** ([M+H^+] calc. 305.9588 and 307.9588; obtained 305.9484 and 307.9482) (Fig. 4). In another experiment, Hydrazine was added instantly to a solution of **PHBT** and was subjected to ESI-MS. Two peaks were found corresponding to masses of **PHBT** as well as **UHBT** which clearly prove that **UHBT** is formed as a result of reaction of **PHBT** with Hydrazine. A very small signal was obtained having a mass corresponding to that of **PHBT**+N_2H_4. The small intensity proves that this is the intermediate of the reaction of **PHBT** with Hydrazine (Fig. 5).

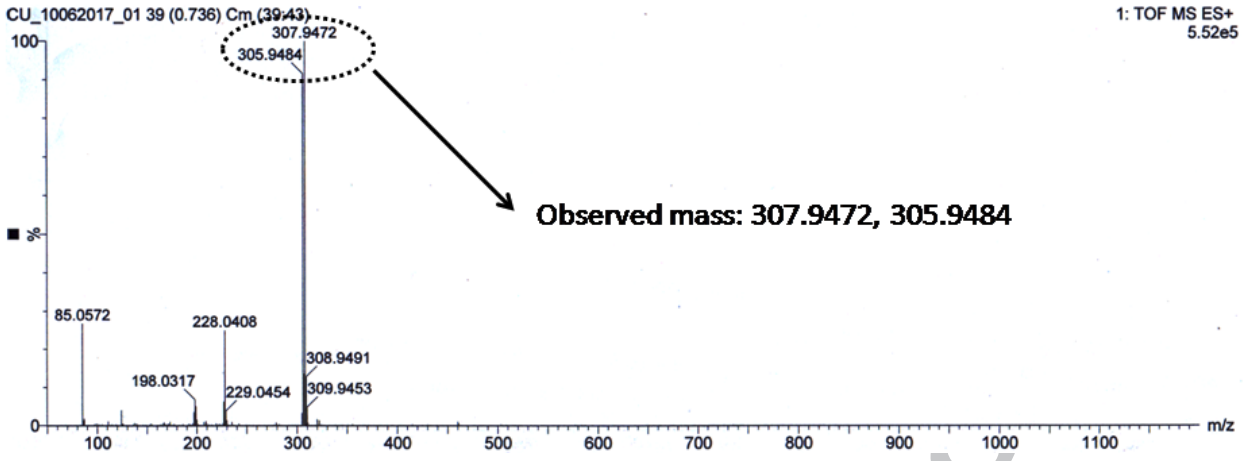


Fig. 4. ESI-MS of **PHBT**-Hydrazine adduct.

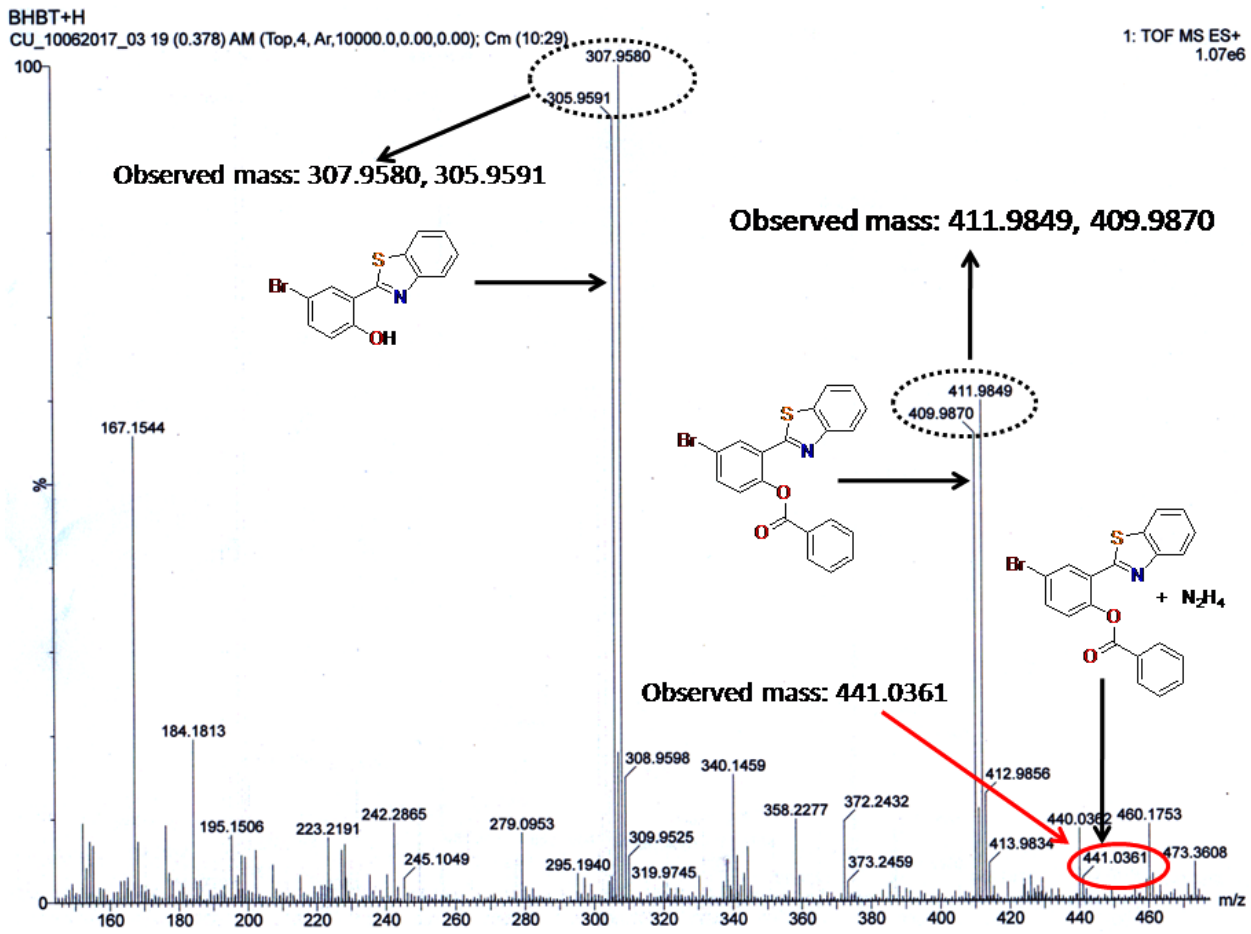


Fig. 5. ESI-MS of an instantly prepared mixture of **PHBT** and Hydrazine.

Furthermore, NMR spectra were recorded for **PHBT-N_2H_4** ensemble (ESI, Fig. S7, S8). Hence it could be concluded that parent compound 2-(benzo[d]thiazol-2-yl)-4-bromophenol (**UHBT**) was generated from **PHBT** upon addition of Hydrazine and the latter is thus a chemodosimeter for Hydrazine.

3.2. Practical application of PHBT

At this stage, we sought out to find a practical application of **PHBT** for Hydrazine detection. We prepared a drinking water sample spiked with Hydrazine (20 μM) and added the same to an aqueous methanolic solution of **PHBT**. Although no naked eye color change was observed, a blue luminescence was observed under UV-light; ensuring the practical utility of **PHBT** (Fig. 6).

Fig. 6. Detection of Hydrazine in drinking water by **PHBT** observed under UV-light (right).

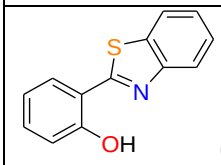
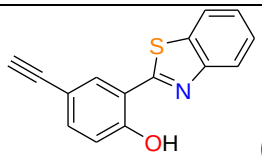
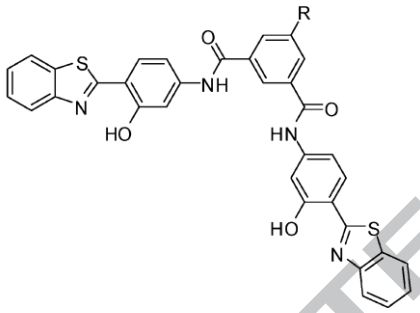
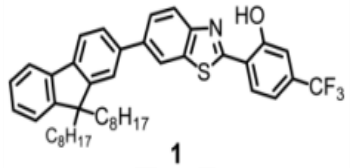
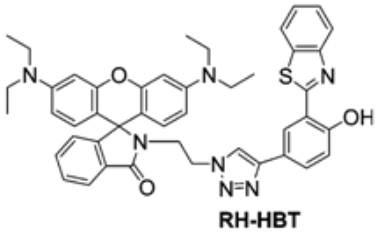
3.3. Comparison of PHBT-N_2H_4 ensemble with UHBT

Our observations were consistent with other existing reports up to this point. Instead of concluding that **ESIPT** is restored upon deprotection of **PHBT**, we conducted a comparative spectral study of **PHBT**-Hydrazine ensemble with the parent compound **UHBT**. A thorough spectral investigation of the parent compound **UHBT** was first conducted (Fig.7, 8) for that purpose. The UV-Vis profile of **UHBT** furnished two bands at 290 nm and 340 nm; the latter corresponded to the coupling between benzothiazole and the hydroxyphenyl ring [28]. In DMSO an additional band appeared at 415 nm (Fig. 7). To ascertain the nature of this band, base was

added to a solution of **UHBT** in acetonitrile, as in acetonitrile no major contribution is present apart from the two strong absorbing bands. Upon addition of base, a band was generated at 403 nm, indicating anion formation upon base addition. Hence, the third band in DMSO was attributed to anion generation of **UHBT**. The red shift in the anionic band in DMSO compared to acetonitrile could be attributed to its high stabilisation in DMSO (dielectric constant value of ~47). The basic nature of DMSO also contributes to the easy formation of anion in the said solvent. **UHBT** showed single emission band only in non-polar solvents (only **ESIPT** operative; λ^{em}_{max}~520 nm) whereas dual emission was observed for polar protic as well as aprotic solvents ((λ^{em}_{max}=390 and 470 (DMSO)/515(ACN) nm). For methanol a triple emission was observed with an additional band at ~470 nm. The peak at ~520 nm was hence due to **ESIPT** and local emission of **UHBT** was responsible for the band at 390 nm by comparing similar bands reported in literature for **HBT** [5]. The band at ~470 nm was also observed upon addition of base to **UHBT** in acetonitrile (Fig. 9). Hence, the band at ~470 nm was attributed to the anionic form of **UHBT** [6]. In polar protic solvent like methanol, the phenolic proton undergoes efficient intermolecular hydrogen bonding with methanol. Due to the aforementioned intermolecular hydrogen bond formation, the intramolecular hydrogen bond between the phenolic –OH proton and the N atom of benzothiazole moiety is ruptured. Consequently, the proton in **UHBT** becomes labile and thus the emission spectrum contains three bands. The hindrance in occurrence of ESIPT in polar solvents due to intermolecular hydrogen bonding has also been reported previously by theoretical chemists also by the aid of meticulous computational methods [2-5]. Had **ESIPT** been restored after adding Hydrazine to **PHBT**, a band at ~520 nm would naturally be expected to appear. But from Fig. 3 it was obvious that no peak or even a shoulder was generated at 520 nm. The peak at 470 nm was assigned to be the anionic form of **UHBT**

(**AUHBT**). A comparison of the UV-Vis and Fluorescence profiles in Fig. 9 gives a clear idea of the generation of **AUHBT** from **PHBT** after addition of Hydrazine. A less rigorous experiment provided an easy to apprehend yet solid reasoning behind formation of **AUHBT**. The colours of **UHBT** solutions in various solvents were observed under UV-light (Fig. 10). The colour appeared to be yellowish green in almost all solvents except DMSO where it changes to blue due to anion generation. A similar blue colour was observed when base was added to **UHBT** (Fig.3). Recalling that addition of Hydrazine to **PHBT** furnishes a similar blue colour (Fig. 1), it could be stated that this colour was typical of the anion of the **HBT** concerned. Thus, the deprotection of **PHBT** affords **AUHBT** than **UHBT** itself. Emission maxima for **ESIPT** and anionic emission of a series of **HBT** based derivatives have been tabulated in Table 2. A perusal of the data given in Table 2 indicates that substitution effect has little influence on the positions of bands corresponding to anionic and proton transferred form of **HBT** derivatives. At this juncture, the report by Potter et al. proved to crucial [8] where it was clearly stated that the 460 nm band observed in unsubstituted **HBT** is due to formation of anion in polar solvents. In short, in **HBT** derivatives the **ESIPT** emission corresponds to a wavelength greater than 500 nm and the anionic form has emission maxima between ~450-480 nm. The bromine substitution in our synthesized model **PHBT** hence does not affect the generality of our conclusions. Thus, we confirmed that the claim of **ESIPT** restoration from cleavage of **PF** were consequences of correct observation but improper explanation and it could be stated in general that deprotection of protected **HBT** based compounds affords the anion of the **HBT** concerned.

Table 2. Tabulated representation of λ_{max} for ESIPT and anionic form in various HBT derivatives.

Structure of ESIPT active compound(reference number)	**λ^{em}_{max} of ESIPT form**	**λ^{em}_{max} of anionic form**
 (5)	~500 nm	~460 nm
 (4)	~ 530 nm	~465 nm
 (4)	~509 nm	Not Provided
 (3)	~515 nm	~470 nm
 (4)	~540 nm	~480 nm

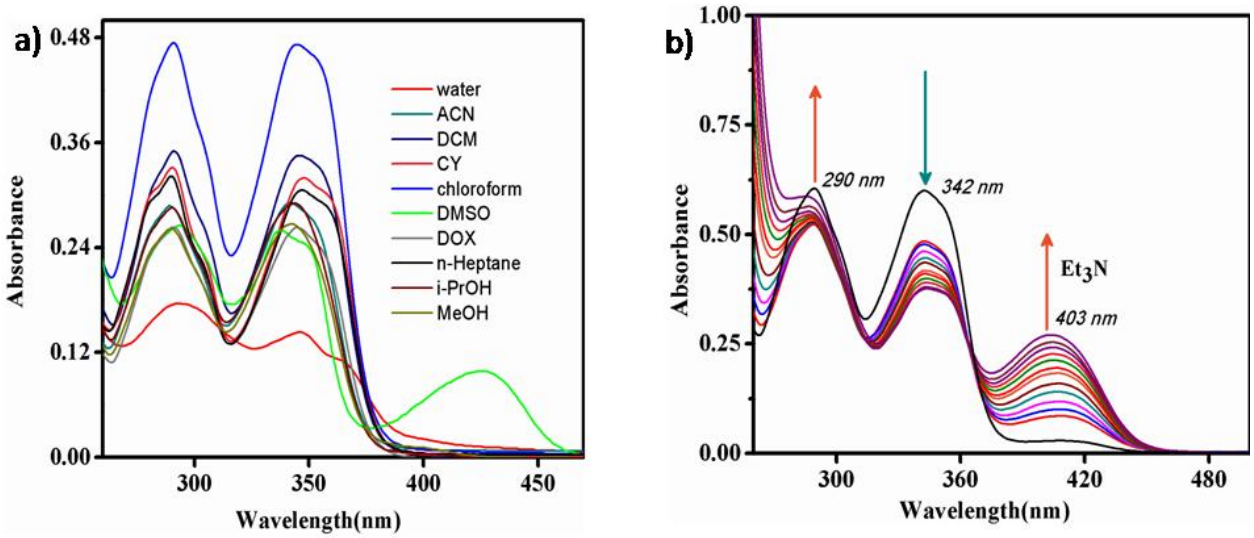


Fig. 7. a) UV-Vis spectra of **UHBT** in various solvents. b) Base effect observed in acetonitrile.

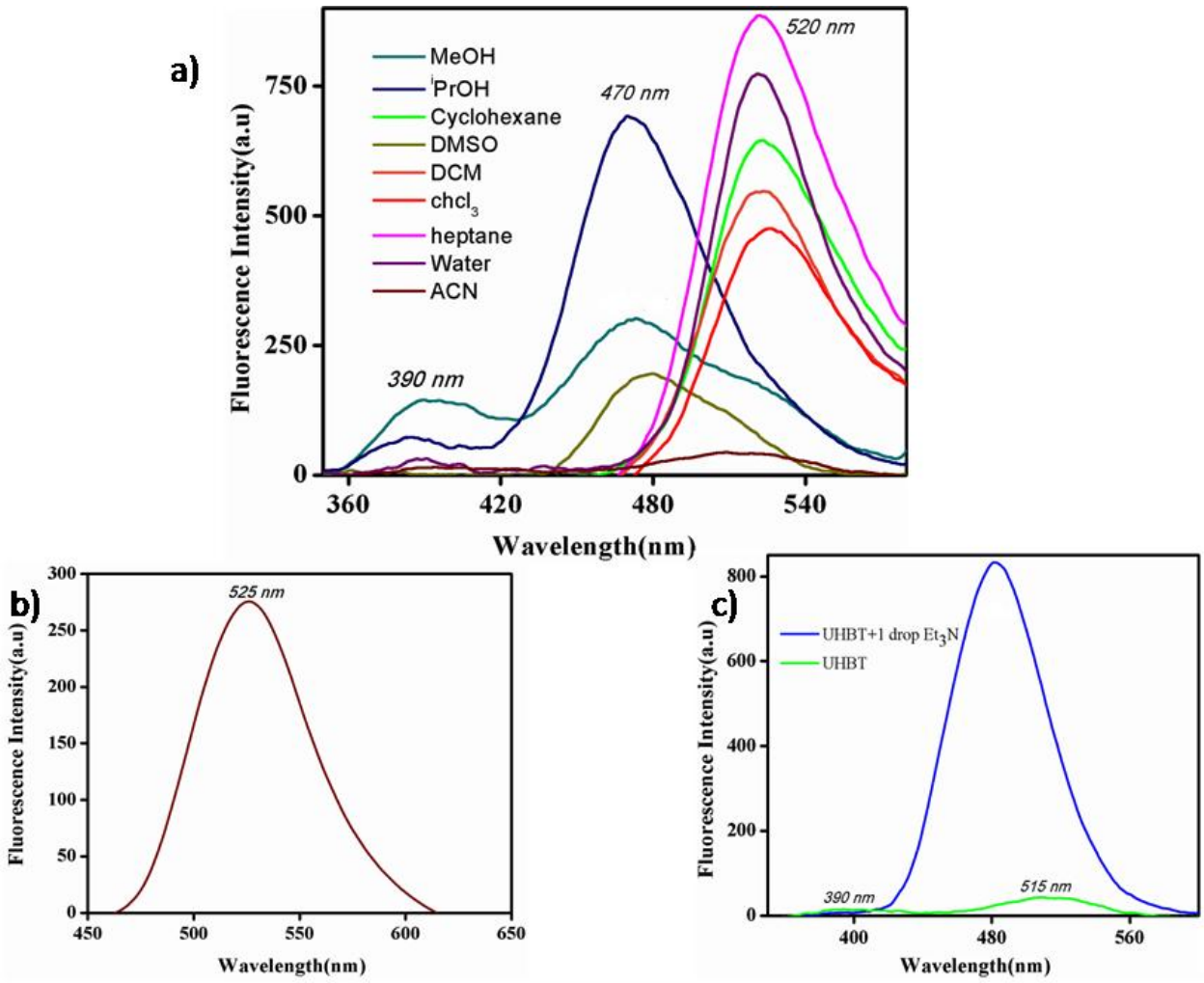


Fig. 8. a) Fluorescence Spectrum of **UHBT** in various solvents (λ_{ex}=340 nm); b) Solid state Fluorescence spectrum of **UHBT** (λ_{ex}=340 nm); c) **UHBT**+1 drop acetonitrile in acetonitrile.

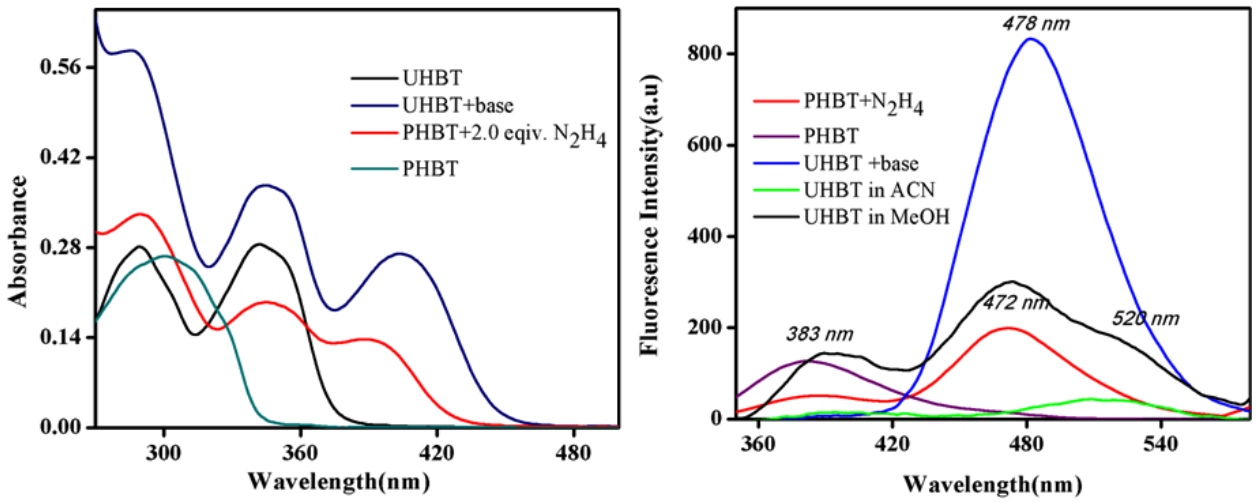


Fig. 9. Comparative a) UV-Vis and b) Fluorescence profiles of **UHBT, UHBT**+base, **PHBT** and **PHBT**+hydrazine ensembles.

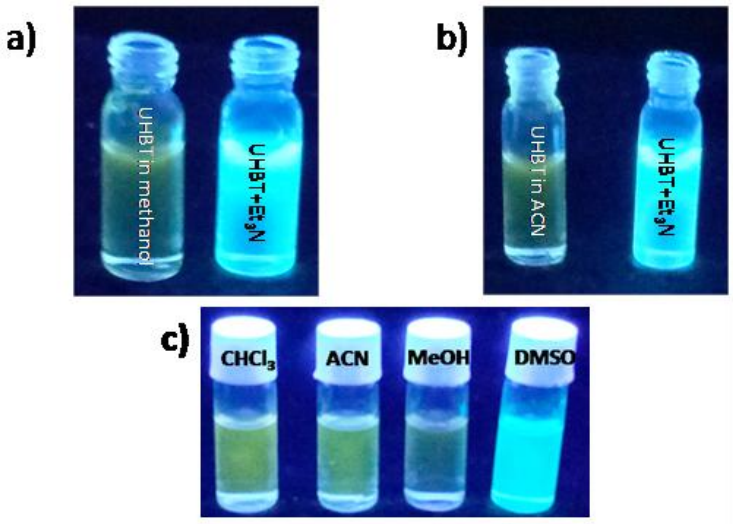


Fig. 10. Base effect of **UHBT** under UV-light for a) methanol; b) acetonitrile and c) colour of **UHBT** observed under UV light in solvents of varying polarity.

4. Conclusions

In conclusion, the present study negates a long existing misleading explanation behind the ratiometric response of protected **HBT** based chemodosimeters upon deprotection. The observed blue emission observed during the ratiometric response is not due to **ESIPT** generation but due to anion formation in polar solvent(s). We supported our claim by synthesizing a novel protected bromo substituted HBT derivative (**PHBT**) and conducted thorough spectroscopic comparison with its unprotected analogue (**UHBT**). In addition, **PHBT** can be utilised for detecting Hydrazine in drinking water.

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Appendix A. Supplementary Information.

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Supplementary Information

Fate of protected HBT based chemodosimeters after undergoing deprotection: restoration of ESIPT or generation of emissive phenoxide?

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8. CMR spectrum of PHBT-N_2H_4 adduct in DMSO-d_6.

1. PMR and CMR spectra of UHBT in $CDCl_3$.

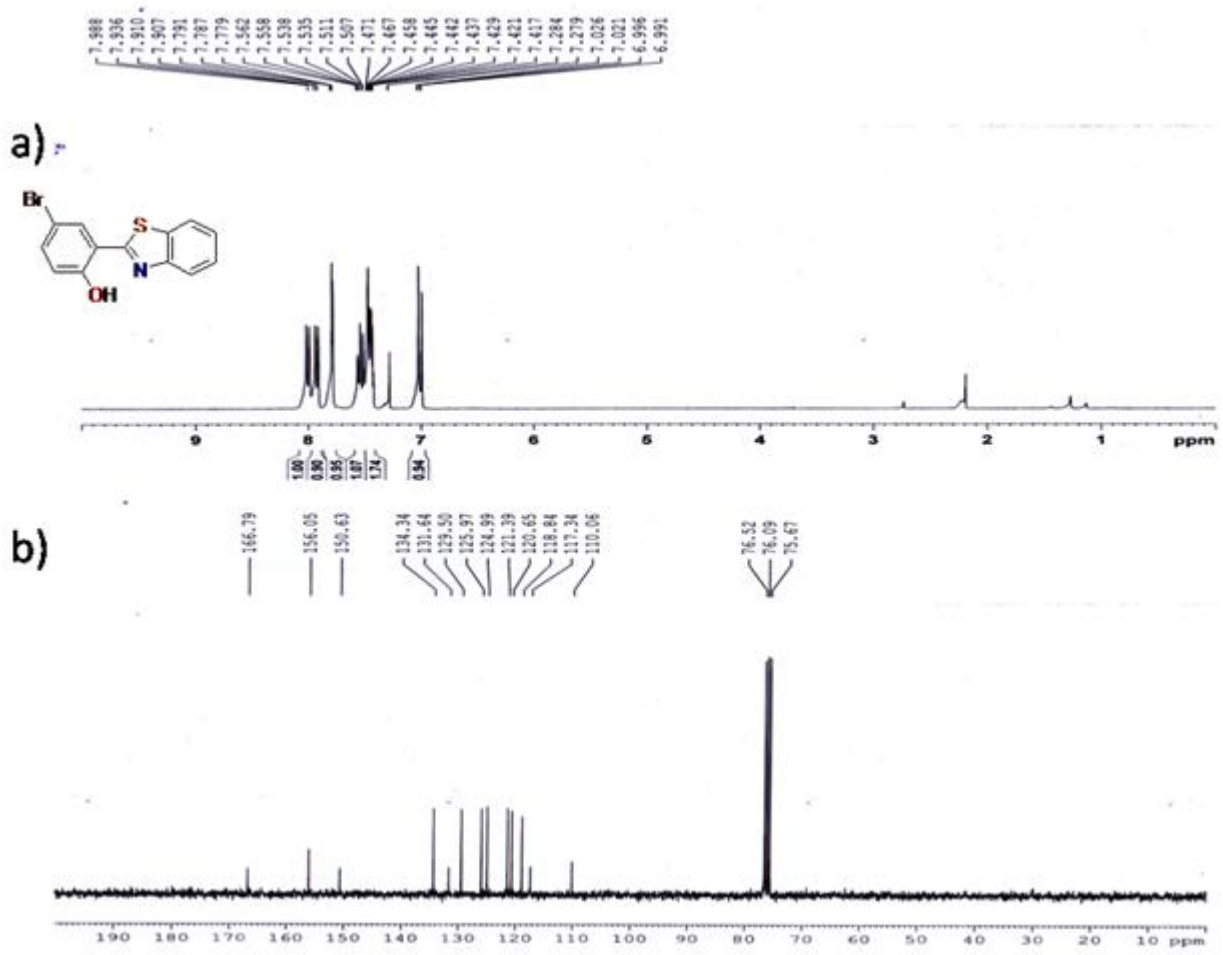

Fig.S1 a) PMR and b) CMR spectra of **UHBT** in $CDCl_3$.

2. PMR spectrum of PHBT in $CDCl_3$.

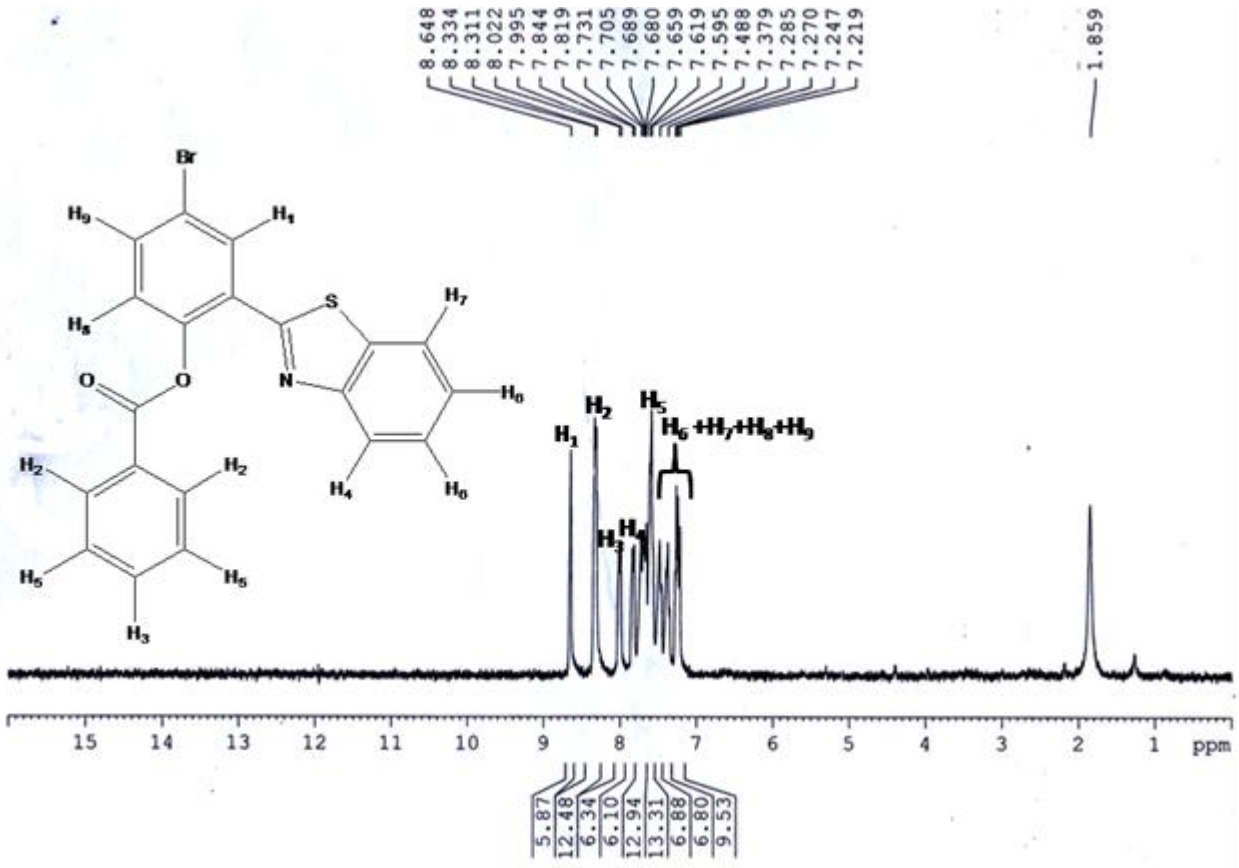

Fig.S2 PMR spectrum of **PHBT** in $CDCl_3$.

3. CMR spectrum of PHBT in $CDCl_3$.

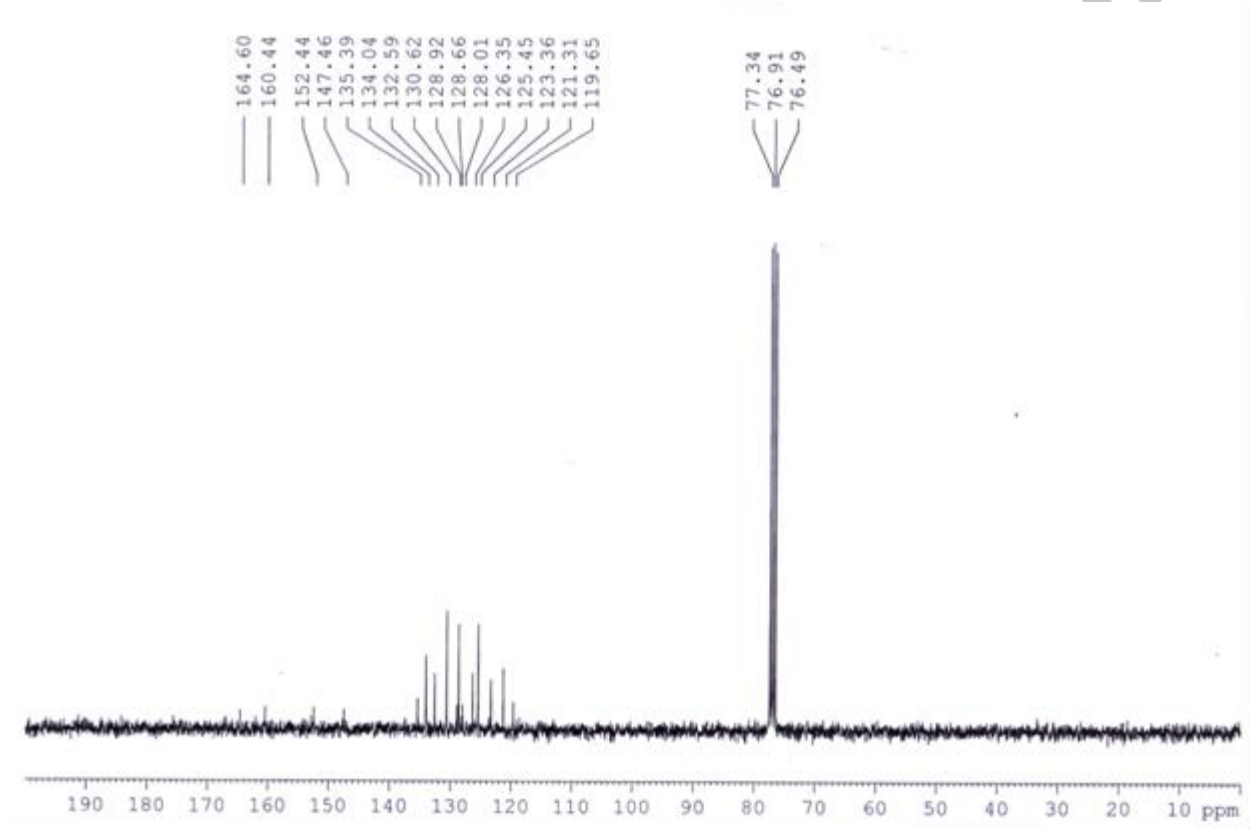

Fig. S3 CMR spectrum of **PHBT** in $CDCl_3$.

4. FTIR spectrum of PHBT.

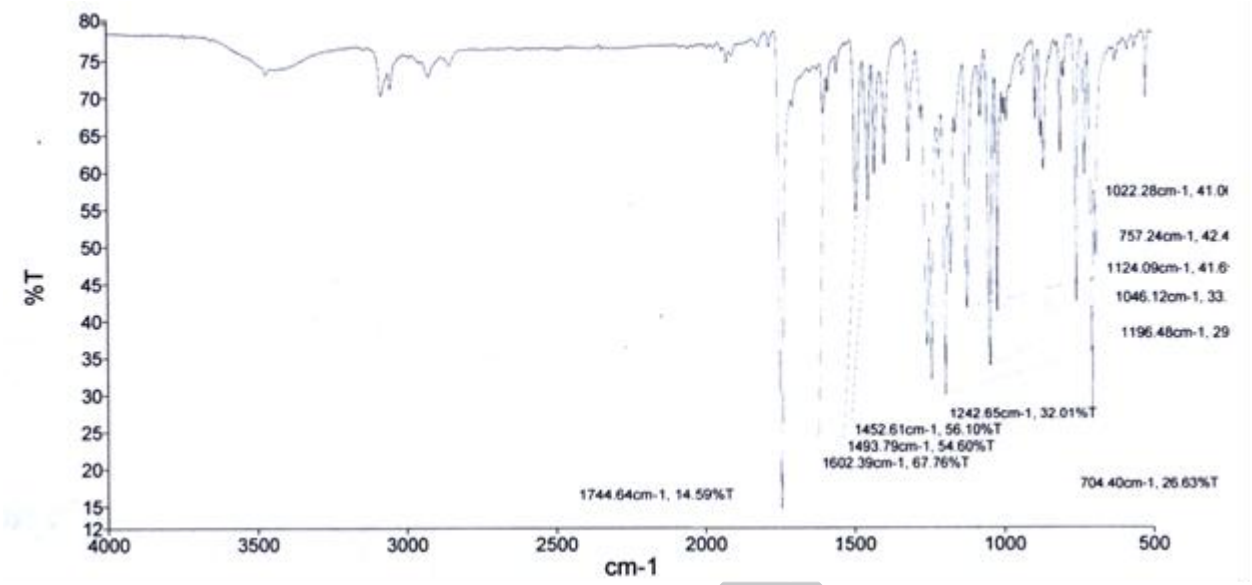

Fig. S4 FTIR spectrum of **PHBT**.

5. ESIMS of PHBT

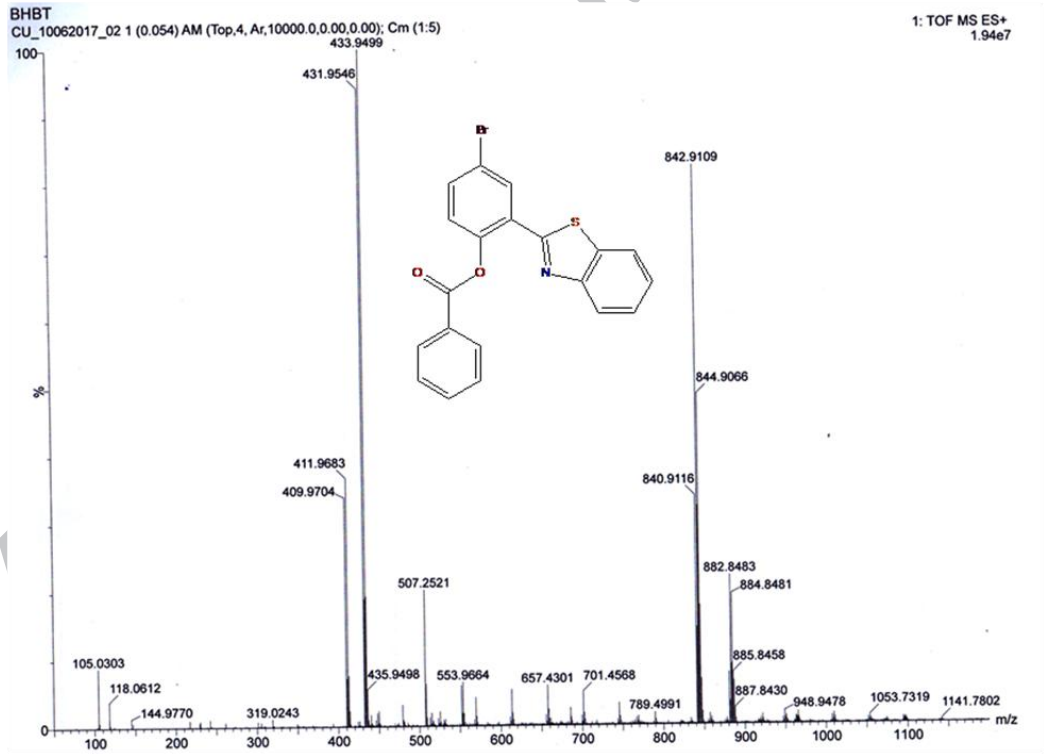

Fig. S5 ESIMS of **PHBT;** calculated for [M+Na^+] =431.9560 and 433.9549.

6. Fluorimetric response of PHBT (10 µM) in presence of various amines, hydrazine, cations and anions

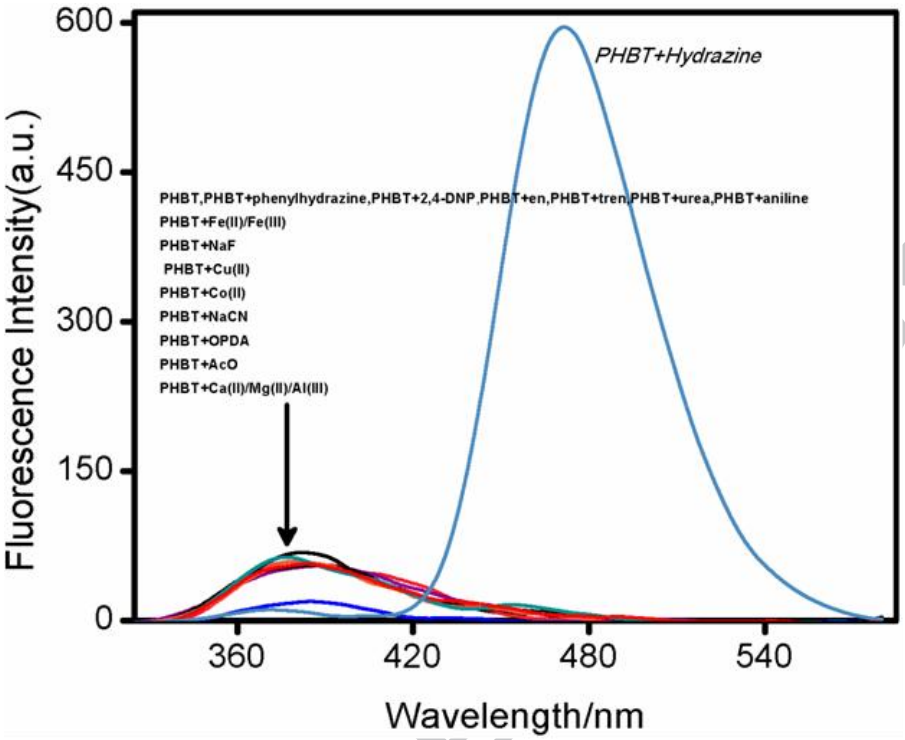

Fig. S6 Fluorimetric response of **PHBT** (10 µM) in presence of various amines, hydrazine, cations and anions.

7. PMR spectrum of PHBT-N_2H_4 adduct

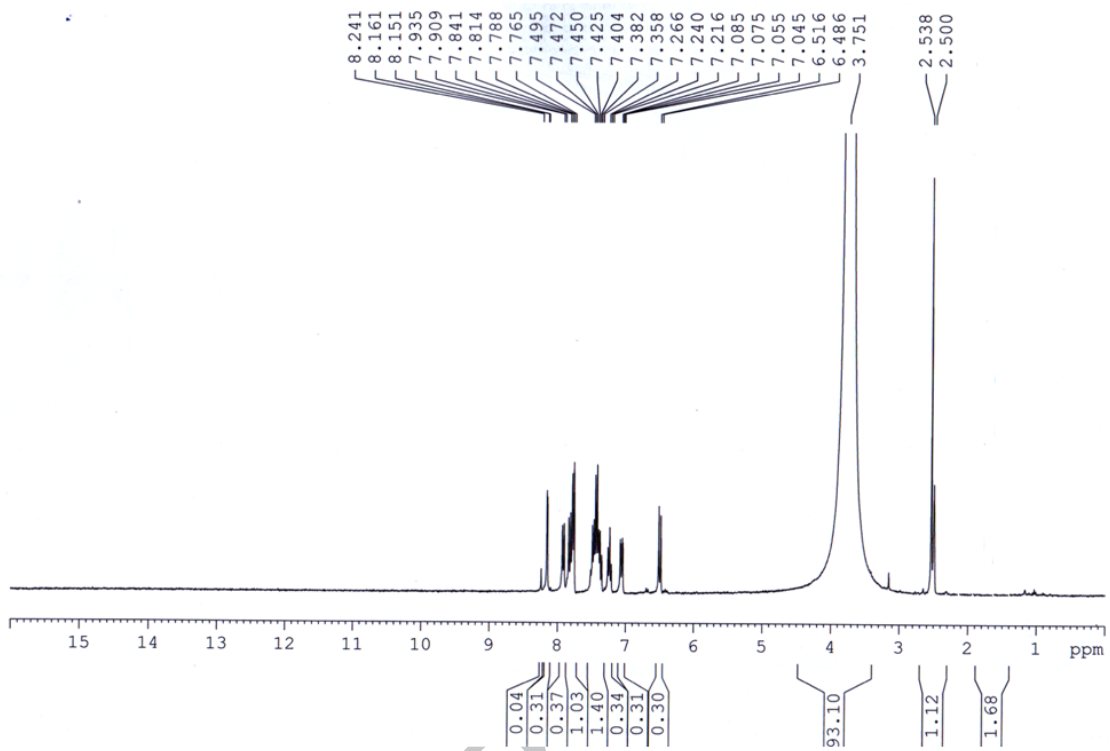

Fig. S7 PMR spectrum of **PHBT**-N_2H_4 adduct in DMSO-d_6.

8. CMR spectrum of PHBT-N_2H_4 adduct

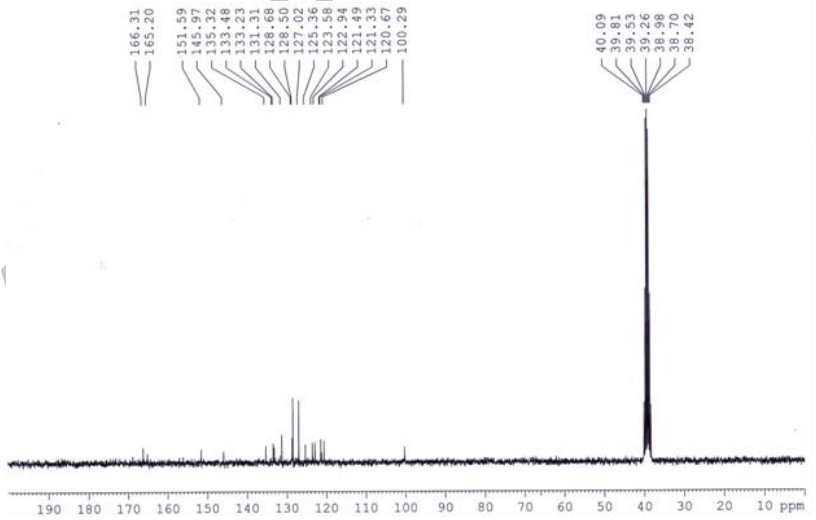

Fig.S8 CMR spectrum of **PHBT**-N_2H_4 adduct in d_6-DMSO.

Graphical abstract

Fate of protected HBT based chemodosimeters after undergoing deprotection: restoration of ESIPT or generation of emissive phenoxide?

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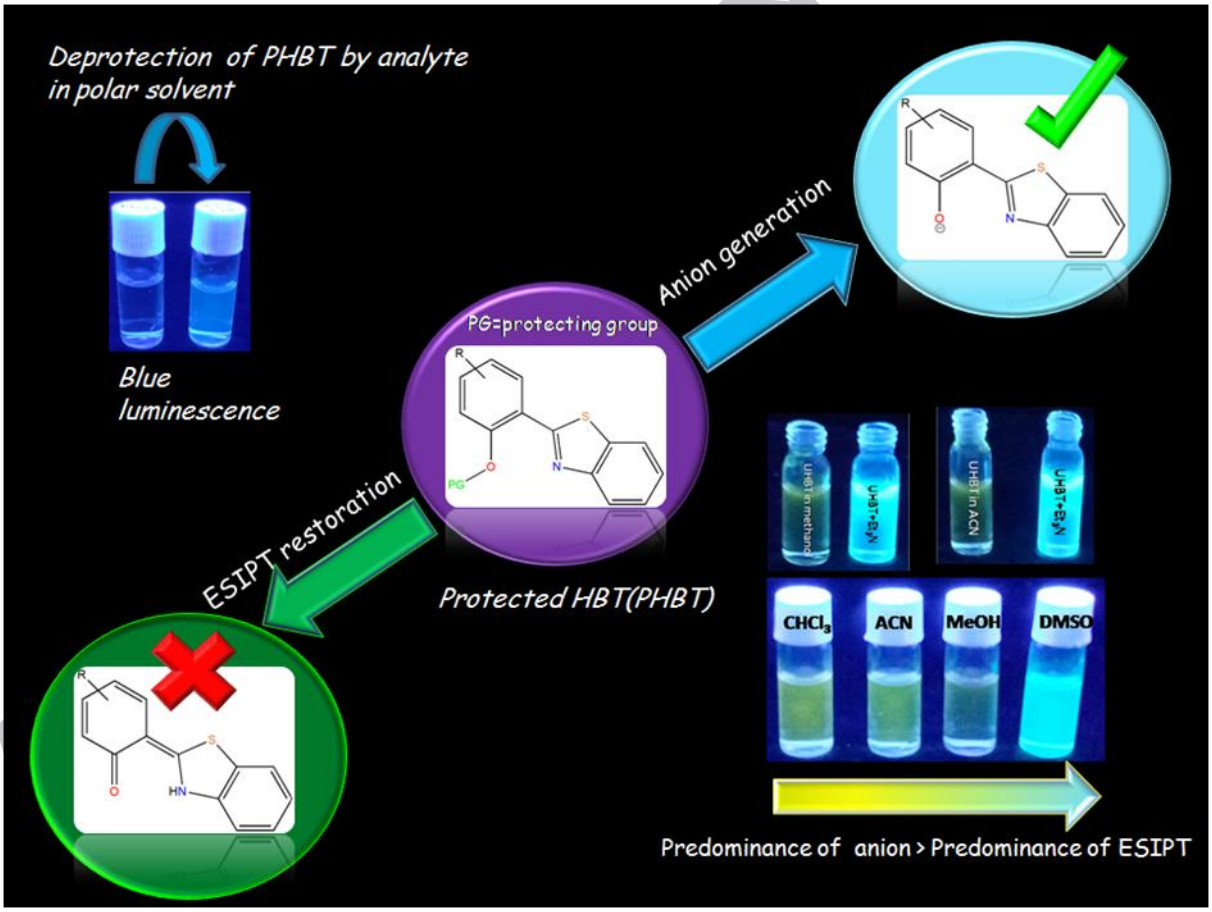

Research highlights

► A model chemodosimeter specific to Hydrazine was synthesized.

►Re-assignment of Red shifted emission in deprotected **HBT** and protected **HBT**.

► Ratiometry observed from **HBT** based chemodosimeters are reported to be due to **ESIPT** reappearance.

► Spectroscopic analysis revealed anion of **HBT** is formed rather than returning of **ESIPT**.