NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

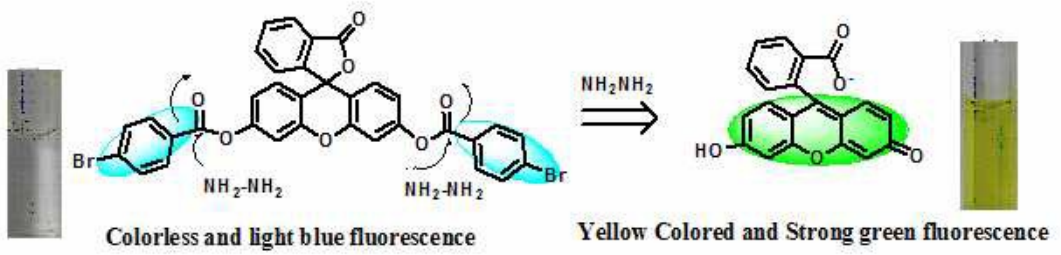
Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc



Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Fast and ratiometric " Naked eye" detection of hydrazine both solid and vapour phase sensing

Shyamaprosad Goswami*, Sima Paul and Abhishek Manna

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A new ''naked-eye'' ratiometric colorimetric and fluorescence chemodosimeter (PBF) was constructed to enable trace vapor detection of hydrazine. This probe utilizes an irreversible and fast hydrazine -promoted cleavage of ester linkage in PBF. This probe was shown to be highly selective for hydrazine, and showed real time response as well as a positive linear relationship to hydrazine concentration. The probe also shows an excellent performance in the ''dip stick'' method.

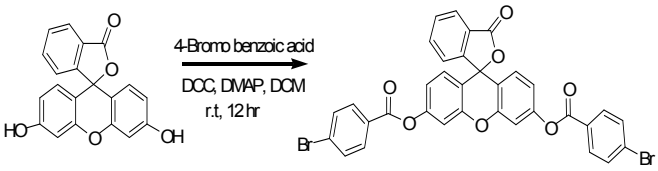
Introduction :

In the past decade, efficient and reaction specific synthetic probes with better sensitivity for the detection of small molecule has been a subject of intense research interest, because they play important roles in biological systems and also constitute some pollutants in our environment.[1] As a significant industrial chemical, hydrazine exhibits various applications in chemical, pharmaceutical, and agricultural industries involving catalysts, corrosion inhibitors, and pesticides.[2] Hydrazine is a well-known high-energy fuel in rocket propulsion and missile systems due to its improved detonable properties.[3]

But due to its toxicity to human beings, hydrazine has been classified as a probable human carcinogen by the U.S. Environmental Protection Agency (EPA) with a low threshold limit value (TLV) of 10 ppb.[4] Hydrazine is a neurotoxin and has severe mutagenic effects causing serious damage to the liver, lungs, kidneys, and the human central nervous system.[5] Therefore, reliable analytical approaches for hydrazine detection with satisfactory sensitivity and selectivity are of great interest and importance.

To date, a variety of analytical techniques, including chromatography- mass spectrometric,[6] titrimetric,[7] spectrophotometry[8] and electrochemical methods[9] have been exploited for the purpose of hydrazine analysis. But those methods are complicated and time consuming for real-time and on-site analysis.[10] So, simple but reliable detection methods for the rapid and sensitive detection of hydrazine both qualitatively and quantitatively are in great need. However, that complication can be removed by the use of simple chemodosimeter fluorescence probes for hydrazine because those probes are highly sensitive, easy-to-operate and of low cost. However, up to now, only a limited number of fluorescence probes for hydrazine have been reported in the literature.[11] Chemodosimeters appended with specific protection groups for selective detections via target specific deprotection for various analytes have often been utilized effectively.[12] Ratiometric and reaction specific fluorescent chemodosimeters are exceptionally useful due to their specificity and they allow the measurement of emission intensities at two different wavelengths which permit the correction for environmental effects. Thus, we have designed a ratiometric "naked eye" as well as fluorescent probe for the detection of hydrazine.

Our hydrazine sensor discussed herein, is synthetically simple and based on the photoinduced electron transfer (PET) principles where a fluorophore is connected to a receptor by a short spacer. Initially the probe becomes non fluorescent due to the PET effect. In this type of chemodosimeter, the fluorescence intensity can be enhanced by breaking the linkage of the electron withdrawing and electron donating groups through a chemical reaction promoted by special analytes. In our chemodosimeter, two hydroxyl groups in fluorescein were protected by para bromo benzoic acid. The fluorescence of the probe was partly suppressed due to photoinduced electron transfer (PET) from electron-donating fluorescein moiety to electron deficient bromo benzoic moiety. Now, hydrazine could readily break the ester linkage of the fluorochrome to yield a deprotected analogue and regenerate the phenolic moiety of fluorochromes of fluorescein. In the later case the yield of the receptor is also higher than the former. The target compound para bromobenzoic acid protected fluorescein probe (PBF) was synthesized through the following reaction detailed in Scheme 1. The structure of the receptor was confirmed using ^{1}H NMR, ^{13}C NMR and HR MS spectra (ESI†).



Scheme 1: Synthetic route of the receptor (PBF).

Experimental section

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 in an open-mouth capillary and were uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Brucker 400 MHz instruments respectively. For NMR spectra, 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. UV-vis titration experiments were performed on a JASCO UV-V530 spectrophotometer and fluorescence experiment was done using PTI fluorescence spectrophotometer with a fluorescence cell of 10 mm path. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer, using KBr discs.

Methods for the preparation of receptor :

Synthesis of receptor (PBF): Fluorescein (700 mg, 2.1 mmol) and DMAP (100 mg, 0.82 mmol), were added to 4-bromobenzoic acid (1 gm, 4.9 mmol). The mixture was dissolved in dry dicholoromethane (20 mL) and chilled at 0°C followed by the addition of a solution of DCC (900 mg, 4.36 mmol) in dry dichloromethane. The reaction mixture was stirred under nitrogen atmosphere at 0°C for 15 minutes and at room temperature for 12 hrs. The precipitate of urea was removed by filtration and the filtrate was concentrated in high vacuum to give an oily residue. This residue was purified by column chromatography using silica gel (100-200 mesh size) and 10% ethyl acetate in pet ether as eluent to give a colorless gummy liquid, which solidifies on cooling (1.5 gm, 88%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.02 (m, 4H), 7.65 (m, 6H), 7.16 (m, 3H), 6.88 (m, 3H), 6.66 (m, 1H), 6.57 (m, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm): 84.9, 107.3, 113.4, 116.9, 121.0, 121.3, 123.3, 124.8,125.2, 127.2, 127.8, 129.0, 129.4, 134.8, 134.9, 151.4, 159.5, 164.9, 171.5.
MS (ESI MS): (m/z, %): 698.0076 [(M^+, 100 %]

Synthesis of hydrazine product of PBF: PBF is mixed with two equivalents of hydrazine in acetonitrile at room temperature to give a yellow solution. On removing the solvent, a solid product was obtained which was used for ^{1}H-NMR and MASS spectroscopy.
^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 9.99 (s, 1H), 9.80 (s, 1H), 8.30(s, 1H), 7.96 (d, 2H, J=7.5 Hz), 7.84 (m, 2H), 7.65 (m, 2H), 7.46 (t, 1H, J=7.5 Hz), 7.35 (d, 1H, J= 7.5 Hz), 7.19 (d, 1 H, J= 7.5 Hz), 7.09 (m, 1H)
MS (ESI MS): (m/z, %): 331.1101 [(M^+, 100 %]

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%).
The quantum yield of **PBF** itself is 0.003 which is remarkably changed into 0.28, an enhancement around 93 fold is observed.

General method of UV-vis and fluorescence titrations:

By UV-vis and fluoescence method:

For UV-vis and fluorescence titrations, stock solution of the sensor was prepared (c = 2 x 10^{-5} ML^{-1}) in CH_3CN: H_2O (6:4, v/v). The solution of the guest cations and anions were prepared (2 x 10^{-4} ML^{-1}) in CH_3CN: H_2O (6:4, 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 amine containing compounds were prepared separately. The spectra of these solutions were recorded by means of UV-vis and fluorescence methods.

Results and discussion

UV-vis and Fluorescence study :

The colorimetric sensing abilities of PBF was primarily investigated in a CH_3CN–H_2O solution (6 : 4, v/v, 10 mM HEPES, pH 7.4) with various metal ions and anions (Ag^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Pd^{2+}, Cl^-, Br^-, I^-, SO_4^{2-}, SO_3^-, ClO_4^-, HPO_4^-). The probe PBF without hydrazine exhibited a moderate UV-vis absorption band at 438 nm which was attributed to the photoinduced electron transfer (PET) transition in the molecule. Addition of hydrazine to a solution of PBF led to an obvious absorption enhancement at 508 nm, along with a color change from colorless to yellow which allows the detection of hydrazine with the naked eye (Figure 1). Upon increasing the concentration of hydrazine, the absorbance of PBF is also increased and it reaches saturation when 2 equiv. hydrazine is added. Thus, this hydrazinolysis reaction by hydrazine generated fluorescein, which exhibited its characteristic chromogenic behavior. In contrast, the addition of other metal ions and anions resulted in a negligible response (Figure 2). This indicates that under signaling conditions, the possible interference of ester hydrolysis assisted by common metal ions or anions is not a practical problem in hydrazine sensing by PBF. The absorbance at 508 nm changed almost 64-fold (from 0.031 to 1.974) in the presence of hydrazine (Figure 1b). To our pleasure, the detection limit of PBF for hydrazine was found to be 0.41μM

(Figure 1b), which lies below the safe hydrazine level (10 ppb), indicating that the probe PBF may further be developed for the detection of hydrazine in practical applications.

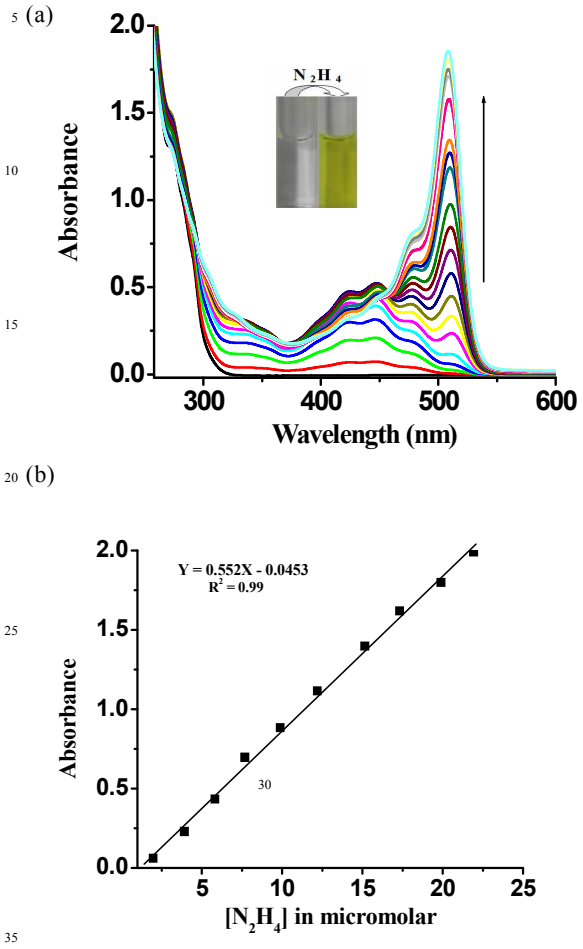


Figure 1: (a) UV absorption spectra of sensor PBF in the presence of an increased concentration of hydrazine (0–200 μM) in CH_3CN–H_2O solution (6 : 4, v/v, 10 mM HEPES, pH 7.4); the inset shows the color change detectable by the naked eye of sensor PBF with the addition of hydrazine (b) Absorbance change at 508 nm of PBF upon gradual addition of hydrazine.

The fluorescence detection of hydrazine by PBF was also pronounced. As shown in Figure 3, PBF exhibited an extremely weak blue fluorescence under the fluorescence excitation at 380 nm (Q = 0.003). Upon addition of hydrazine, the fluorescence intensity at 418 nm diminished and the band at 530 nm (Q = 0.28) increased due to the ring-opened fluorescein structure. Concomitantly, the fluorescence color of the solution changed from blue to green under UV illumination (inset of Figure 3). These changes in the fluorescence spectra stopped when the amount of added hydrazine reached 2 equiv. The probe induced a nearly 43-fold variation in the fluorescence ratio (F_{530}/F_{418}) (Figure S2). From this figure, we also concluded that (F_{530}/F_{418}) varies almost linearly vs. the concentration of hydrazine in the range of 0.56–28.0 μM, with the coefficient R^2 = 0.99. This phenomenon implied that PBF was potentially useful for the quantitative determination of hydrazine concentration.

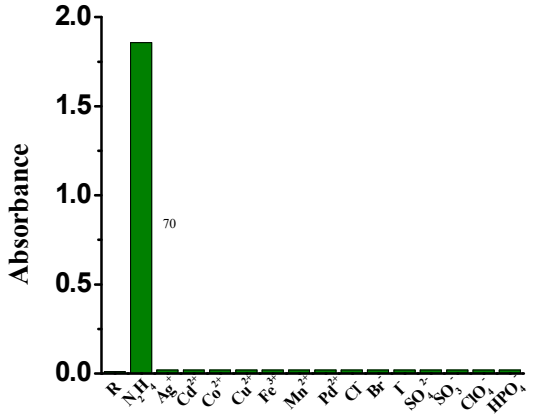


Figure 2: The variation of absorbance for probe PBF in a CH_3CN–H_2O solution (6 : 4, v/v, 10 mM HEPES, pH 7.4) in presence of various metal ions and anions.

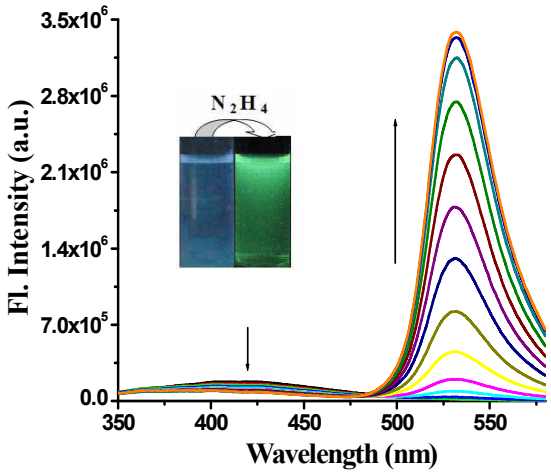


Figure 3: (a) Fluorescence emission spectra of PBF (2.0 X 10^{-5} M) with hydrazine (2.0 X 10^{-4} M) at pH 7.4 in CH_3CN–H_2O (6: 4, v/v), λex = 380 nm. The inset shows the naked eye fluorescence change of PBF with addition of hydrazine.

The receptor is inert towards all cations and anions except hydrazine (Figure 4a). Next, ion interference experiments were carried out both in buffered aqueous solution for evaluation of the sensing ability of the PBF chemosensor (1 mM) towards hydrazine and in the presence of 10 equiv. of a series of background metal ions and anions by means of fluorescence spectra (Figure 4b). Clearly, the presence of background metal ions and anions did not cause any significant fluorescence change of PBF. This showed that the PBF probe could selectively detect hydrazine in the presence of other metal ions and anions. The chemosensor PBF was also treated with some amine containing compounds. It was found that these compounds had no obvious interference to

probe PBF in the aqueous CH_3CN solution (Figure S1).

In the time dependent fluorescence spectra, it is seen that the reaction is completed within 1 min, with a rate constant of 15.43 × 10^{-2} s^{-1}, which strongly supports the high reactivity of the probe (Figure 5).

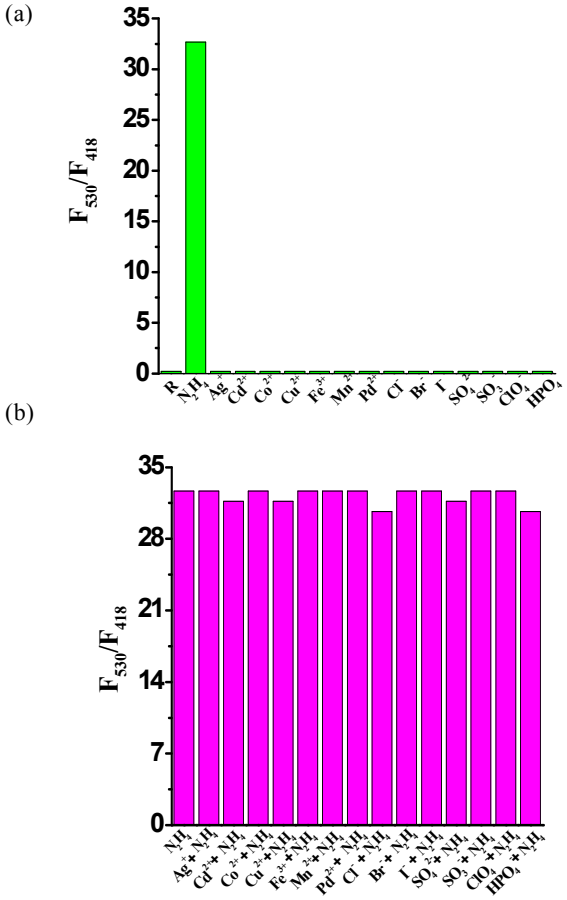
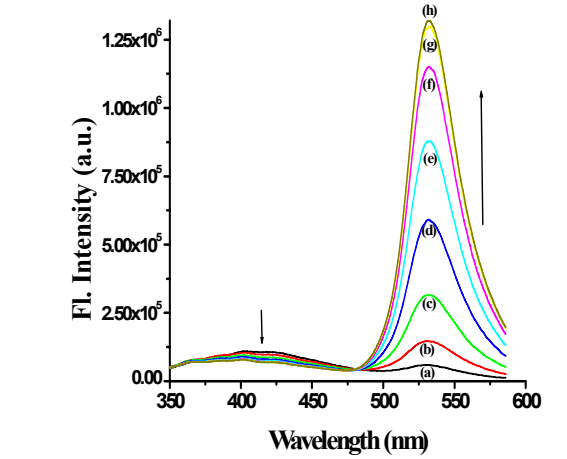


Figure 4: (a) The variation of fluorescence intensity ratio (F_{530}/F_{418}) for probe PBF in a CH_3CN–H_2O solution (6: 4, v/v, 10 mM HEPES, pH 7.4) in presence of various metal ions and anions (b) Fluorescence intensity ratio (F_{530}/F_{418}) of PBF (2.0 X 10-5 M) to hydrazine (2 equiv.) containing 10 equiv. of various metal ions and anions (λex = 380 nm).



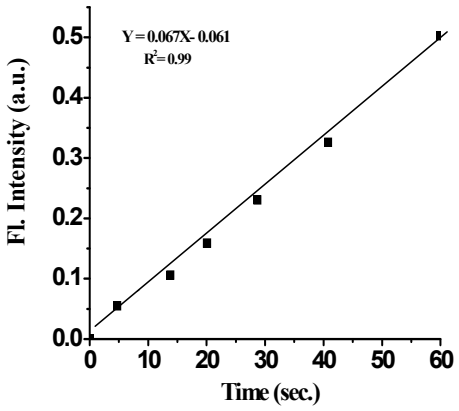
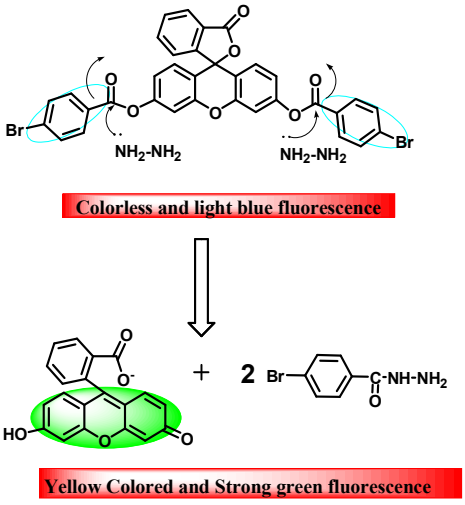


Figure 5: The time vs. fluorescence spectra of (a) PBF (c = 2.0 x 10^{-5} M) in presence of 2 equiv. hydrazine (c = 2.0 x 10^{-4} M) at pH 7.4 in CH_3CN:H_2O (6:4, V/V) at different time [(b) 5 (c) 10 (d) 20 (e) 30 (f) 40 (g) 50 (h) 60 sec] (left) and the time vs. fluorescence at fixed wavelength (530 nm) plot using first order rate equation (right). λex = 380 nm.

^{1}HNMR and HR MS study of receptor and adduct :

Furthermore, we investigated the ^{1}H-NMR spectra of PBF in the presence of hydrazine and compared with that of the sensor itself. The protons of benzene ring in PBF dramatically shifted upfield upon hydrazine addition, indicating that hydrazine functions as a nucleophile. Most interestingly, a new peak is generated at 9.994 ppm which is due to generation of hydroxyl group, breakage of ester linkage in receptor PBF when hydrazine is added to it. In high resolution HR MS specta, there is a peak at m/z 698.0076 corresponding to PBF. Hydrazine adduct give a peak at m/z 331.1101 which indicates regeneration of fluorescein moiety. All of these results are consistent with our proposed mechanism (supporting information)

Sensing Mechanism of receptor towards hydrazine:



Scheme 2: Signaling of hydrazine by chemodosimeter (PBF)

Based on these experimental observations we outlined the plausible signalling mechanism. Deprotection of the hydroxyl group of probe PBF proceeds first at the carbonyl position by the nucleophilic addition of hydrazine. The subsequent nucleophile attacked on the carbonyl group to generate fluorescein and 4- bromobenzohydrazine, which possessed a unique colorimetric and ratiometric response (Scheme 2).

Applications with Water and TLC plates:

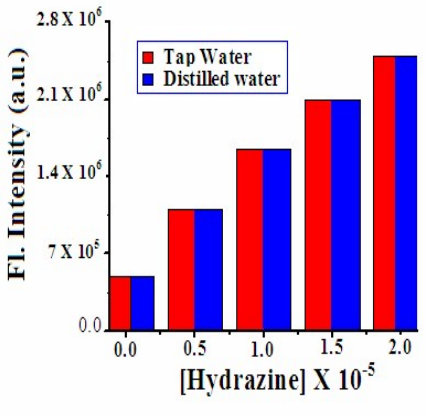


Figure 6: Fluorescence detection of hydrazine in distilled water and tap water by PBF. [PBF] = 2.0 X 10^{-6} M, [hydrazine] = from 0 to 2.0 X 10^{-5} M at pH 7.4 in $CH_3CN:H_2O$ (6:4, V/V). λex = 380 nm.

We also explored opportunities for PBF in practical applications because hydrazine is a suspected carcinogen and is widely used in various industrial processes and thus hydrazine detection in aqueous samples is of interest. We analyzed hydrazine in and distilled water and tap water. An aliquot of hydrazine was added in both types of water and and the pH was adjusted to 7.4. Then the results of the recovery of hydrazine by PBF from these two water samples were compared (Figure 6). The analysis of hydrazine in both solutions agreed well at hydrazine concentrations up to 2.0 X 10^{-5} M. We also prepared the TLC plates were prepared to detect hydrazine both in its liquid (Figure 7) and in its vapour phase (Figure 8)

(i) (ii)

Figure 7: Color changes on test paper (a) PBF (b) PBF in presence of hydrazine.

The fluorescence response of PBF solutions before and after exposure to saturated hydrazine vapor for various time intervals is illustrated in Figure 8. PBF solutions were kept being stirred during the overall absorbing process. Emission intensity at 530 nm of the solutions was enhanced after exposing to hydrazine vapor for 60 s. Further work on determination of hydrazine in practical vapor samples is still in progress.

Figure 8: Change in the TLC plate (coated with PBF) in the presence of hydrazine vapour

Conclusions

We have developed a smart fluorescence turn-on sensor that easily detect trace amount of hydrazine vapor. The sensor mechanism is based on hydrazine mediated cleavage of ester linkage in PBF moiety which turns to be strongly fluorescent upon conversion into the fluorescein state. The recognition events of the sensor toward hydrazine are demonstrated nicely by absorbance and fluorescence spectroscopy and explained by other spectroscopic data with NMR and mass. This fluorescence turn on reaction is extremely selective towards hydrazine. In addition, the probe could serve as a practical colorimetric sensor for ‘‘in-the-field’’ measurement, which does not require any additional equipment, just using a ‘‘dip-stick’’ approach.

Acknowledgements

Authors thank the DST and CSIR (Govt. of India) for financial supports. S.P. and A.M. acknowledge the UGC and CSIR respectively for providing fellowships.

Notes and references

Bengal Engineering And Science University, Shibpur, Howrah 711103, India. Fax: +91-3326682916; E-mail: spgoswamical@yahoo.com

† Electronic Supplementary Information (ESI) available: [details of charectarisation and spectral data are avialable]. See DOI: 10.1039/b000000x/

1. W.Rettig, B.Strehmel, S.Schrader, H.Seifert Applied fluorescence in chemistry, biology and medicine. New York: Springer; 1999; D.Diamond, S.Coyle, S.Scarmagnani, J. Hayes Wireless sensor networks and chemo-/biosensing. Chem Rev 2008;108:652e79; A.Shapira, YD.Livney, HJ.Broxterman, YG. Assaraf. Nanomedicine for targeted cancer therapy: towards the overcoming of drug resistance. Drug Resist Updat 2011;14:150e63;J.Buffle, G.Horvai. In situ monitoring of aquatic systems; chemical analysis and speciation. New York: Wiley; 2001.

2. C.A. Reilly, S.D. Aust, *Chem. Res.Toxicol*. 1997, **10**, 328; U. Ragnarsson, *Chem. Soc. Rev*. 2001, **30**, 205; S. Garrod, M.E. Bollard, A.W. Nicholls, S.C. Connor, J. Connelly, J.K. Nicholson, E. Holmes, *Chem. Res. Toxicol*. 2005, **18**, 115; J. Wang, L. Chen, *Anal. Chem.* 1995, **67**,824.

3. JAE Hannum, *Chemical Propulsion Information Agency; June* 1982. CPTR 82e15; EW Schmidt, *Hydrazine and its derivatives: preparation, properties, applications. New York: Wiley;* 1984; J.Wang, *Hydrazine detection using a tyrosinase-based inhibition biosensor*, Anal Chem 1995;67:3824e7; SD Zelnick, DR Mattie, PC Stepaniak, *Occupational exposure to hydrazines: treatment of acute central nervous system toxicity. Aviat Space Environ Med* 2003; 74:1285.

4. B. Toth, *Cancer Res.,* 1975, **35**, 3693; S. Garrod, M. E. Bollard, A. W. Nicholls, S. C. Connor, J. Connelly, J. K. Nicholson and E. Holmes, *Chem. Res. Toxicol.,* 2005, **18**, 115; C. A. Reilly and S. D. Aust, *Chem. Res. Toxicol*., 1997, **10**, 328.

5. *International Agency for Research on Cancer: Re-evaluation of some organic chemicals, hydrazine, and hydrogen peroxide. IARC monographs on the evaluation of carcinogenic risk of chemicals to humans. Lyon, IARC,* 1999, **71**, 991.

6. Y.-Y. Liu, I. Schmeltz and D. Hoffmann, *Anal. Chem.,* 1974, **46**, 885; J.-W. Mo, B. Ogorevc, X. Zhang and B. Pihlar, *Electroanalysis,* 2000, **12**, 48; S. D. Zelnick, D. R. Mattie and P. C. *Stepaniak, Aviat., Space Environ. Med.,* 2003, **74**, 1285; U. Ragnarsson, *Chem. Soc. Rev.,* 2001, 30, 205.

7. Z. K. He, B. Fuhrmann and U. Spohn, *Anal. Chim. Acta,* 2000, **409**, 83; J. S. Budkuley, *Microchim. Acta,* 1992, **108**, 103.

8. A. Safavi, F. Abbasitabar and M. R. H. Nezhad, *Chem. Anal*., 2007, **52**, 835.

9. A. Benvidi, P. Kakoolaki, H. R. Zare and R. Vafazadeh, *Electrochim. Acta,* 2011, **56**, 2045; N. Maleki, A. Safavi, E. Farjami and F. Tajabadi, *Anal. Chim. Acta,* 2008, **611**, 151.

10. A. Umar, M. M. Rahman, S. H. Kim and Y.-B. Hahn, *Chem. Commun.,* 2008, **166**; J. Liu, Y. Li, J. Jiang and X. Huang, *Dalton Trans.,* 2010, **39**, 8693.

11. J. Liu, Y. Li, J. Jiang and X. Huang, *Dalton Trans*., 2010, **39**, 8693; Z. Zhao, G. Zhang, Y. Gao, X. Yang and Y. Li, *Chem. Commun*., 2011, **47**, 12816; M. G. Choi, J. Hwang, J. O. Moon, J. Sung and S.-K. Chang, *Org. Lett*., 2011, **13**, 5260; M. G. Choi, J. O. Moon, J. Bae, J. W. Lee and S. K. Chang, *Org. Biomol. Chem*., 2013, **11**, 2961; G. E. Collins and S. L. Rose-Pehrsson, *Anal. Chim. Acta*, 1993, **284**, 207; G. E. Collins and S. L. Rose-Pehrsson, *Analyst*, 1994, **119**, 1907; A. B. Brown, T. L. Gibson, J. C. Baum, T. Ren and T. M. Smith, *Sens. Actuators, B,* 2005, **110**, 8; S. W. Thomas and T. M. Swager, *Adv. Mater*., 2006, **18**, 1047; X. Chen, Y. Xiang, Z. Li, A. Tong, *Analytica chimica acta*, 2008, **625**, 41; S. Goswami, S. Paul and A. Manna, *RSC Adv*., 2013, **3**, 18872; M. V. R. Raju, E. C. Prakash, H. C. Chang, H. C. Lin, *Dyes and Pigments* 2014, **103**, 9; M. Sun, J. Guo, Q. Yang, N. Xiao and Y. Li, *J. Mater. Chem. B,* 2014, **2**, 1846; C. Hu, W. Sun, J. Cao, P. Gao, J. Wang, J. Fan, F. Song, S. Sun, and X. Peng, *Org. Lett.,* 2013, **15**, 4022; S. Goswami, S. Das, K. Aich, B. Pakhira, S. Panja, S. K. Mukherjee, and S. Sarkar, *Org. Lett.,* 2013, **15**, 5412; B. Chena, X. Suna, X. Li, H. Ågren, and Y. Xie, *Sensors and Actuators B,* 2014, **199**, 93; S. Goswami, S. Das , K. Aich, D. Sarkar and T. K. Mondal, *Tetrahedron Letters*, 2014, **55**, 2695; K. Li, H. R. Xu, K. K. Yu, J. T. Hou and X. Q. Yu, *Anal. Methods*, 2013, **5**, 2653; M. H. Lee, B. Yoon, J. S. Kim and J. L. Sessler, *Chem. Sci.,* 2013, **4**, 4121; S. Zhu, W. Lin and L. Yuan, *Anal. Methods*, 2013, **5**, 3450.

12. S. Goswami, S. Paul and A. Manna, *Dalton Trans*., 2013, **42**, 10097; S. Goswami, A. Manna, S. Paul, A. K. Das, K. Aich and P. K. Nandi, *Chem. Commun*., 2013, **49**, 2912; Jiang J, Liu W, Cheng J, Yang L, Jiang H, Bai D, *Chem Commun* 2012; **48**, 8371; S. Goswami , A. Manna, S. Paul, K. Aich, A. K. Das, and S. Chakraborty, Tetrahedron Letters 2013, **54**, 1785; S. Goswami, S. Paul and A. Manna, *Dalton Trans.*, 2013, **42**, 10682; S. Goswami, A. Manna, A. K. Maity, S. Paul, A. K. Das, M. K. Das, P. Saha, C. K. Quah and H. K. Fun, *Dalton Trans*., 2013, **42**, 12844; P.Das, AK Mandal, NB Chandar, M Baidya, HB Bhatt, B Ganguly, *Chem Eur J* 2012, **18**, 15382; S. Goswami, A. Manna, S. Paul, C. K. Quah and H. K. Fun, *Chem. Commun.*, 2013, **49**, 11656; ZQ Hu, WM Zhuang, M Li, MD Liu, LR Wen and CX Li, *Dyes Pigmen,* 2013, 98, 286; S. Goswami, A. Manna, S. Paul, A. K. Das, P. K. Nandi, A. K. Maity, P. Saha, *Tetrahedron Letters* 2014, **55**, 490.