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A highly reactive (<1 min) ratiometric chemodosimeter for selective ''naked eye'' and fluorogenic detection of hydrazine†

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Hydrazine is an important industrial chemical but also very toxic. Thus rapid detection of hydrazine is very important. We have judiciously designed and constructed a novel ICT-based ratiometric ''naked eye'' and fluorescence smart probe, carbazole based malononitrile (CBM), that rapidly (<1 min) and selectively detects hydrazine in the presence of different metal ions, anions and other amines in aqueous medium. As a possible application of the probe, hydrazine sensing in tap water was tested. The probe also shows an excellent performance in the ''dip stick'' method.

Introduction

The design and synthesis of new molecular sensors towards biologically and environmentally important species are always essential for practical research in various fields of science.[1] Fluorescent chemosensors are used as powerful tools to detect neutral and ionic species owing to high selectivity, sensibility, versatility and relatively simple handling.[2] In these regards, the design and synthesis of chemosensors is currently of great interest.[3] Hydrazine is a highly reactive base and reducing agent[4] and is used as an important reactant in the preparation of pharmaceuticals, pesticides, corrosion inhibitors, photography chemicals, emulsifiers and textile dyes in various chemical industries.[5] It is famous as a high-energy fuel in rocket propulsion systems due to its flammable and detonable characteristics.[6] In industry it is often applied as a chemical blowing agent. Hydrazine and its water solutions, however, are highly toxic to humans and animals and can potentially lead to serious environmental contamination during their manufacture, use, transport and disposal.[7] It is readily absorbed by oral, dermal, or inhalation routes of exposure. Indeed, it has been classified as a probable human carcinogen by the U.S. Environmental Protection Agency (EPA) and has a low threshold limit value (TLV) of 10 ppb.[8] In contrast to its usefulness, the carcinogenic and toxic effects of hydrazine potentially lead to serious environmental contamination.[9] In this regard, the design and synthesis of hydrazine probes have attracted much attention in recent years and are still in high demand.

Many different methods have been developed for the detection of hydrazine. Traditional methods, including electrochemical analysis,[10] chromatography,[11] gas chromatography,[12] HPLC,[13] and capillary electrophoresis,[14] require long procedure times and the involvement of intelligent instruments, whereas chemical sensors provide another approach which is simple, inexpensive, and rapid allowing real-time monitoring. Spectrophotometry using colored derivatives, such as *p*-dimethylaminobenzaldehyde[15] and chlorosalicylaldehyde,[16] and other colorimetric systems[17] have also been reported as analytical methods to detect hydrazine. The ''naked eye'' colorimetric sensors are especially promising because the color change can easily be observed with the naked-eye, thus requiring less labor and no equipment. On the other hand, ratiometric colorimetric probes can enable the measurement of absorption intensities at two different wavelengths, providing a built-in correction for environmental effects and increasing the dynamic range of absorption measurements. This was considered as a good approach to overcome the major limitation of intensity based probes, in which variations in the environmental sample and probe distribution were problematic for quantitative estimation. Therefore, the design of ratiometric probes is currently of great interest. In general, ratiometric probes can be designed to function *via* two mechanisms: intramolecular charge transfer (ICT) and fluorescence resonance energy transfer (FRET). Although good ratiometric responses could be frequently achieved in some FRET-based probes, generally they need long pathways for their synthesis as well as strong spectral overlap between the emission of the donor and the absorption of the acceptor. On the other hand, ICT-based ratiometric probes are structurally simple and have the advantages that they are easy-to-make and have large emission

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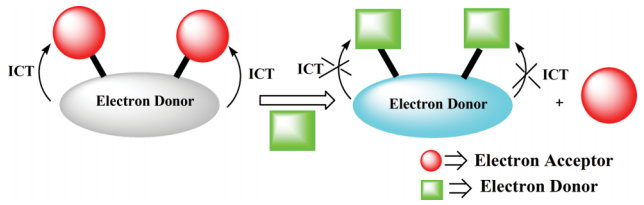
† Electronic supplementary information (ESI) available: details of the synthetic procedure with characterisation and spectral data are available. See DOI: 10.1039/c3ra42771d

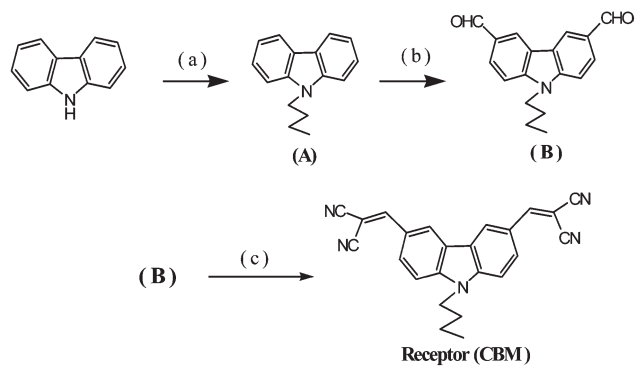


Scheme 1 Schematic approach in this work for the detection of hydrazine.

shifts *etc*. However, to date, small-molecule fluorescent probes for hydrazine detection are still very limited.[18]

Recently, Fan *et al.* reported interesting results of hydrazine detection using a ratiometric turn-on type coumarin-based fluorescent sensor.[19] Now, considering all the above facts, we report a "naked eye" ratiometric, colorimetric and fluorescent probe based on a carbazole fluorescence moiety with a dicyano-vinyl group as the reaction site containing multiple binding groups. We introduced a dicyano vinyl group (electron acceptor) into carbazole dialdehyde to get the carbazole based malononitrile (CBM) probe, which can construct an ICT system with charge from a carbazole moiety (electron donor) from the donor proceeding to the acceptor upon excitation. The specific reaction between arylidenemalononitrile and hydrazine yielded the product hydrazone, which has also been reported.[20] Due to formation of hydrazone, the ICT process in the CBM stopped and thus the molecule becomes fluorescent, which helped us to detect hydrazine by using the CBM probe (Scheme 1).

A convenient synthetic route to chemodosimeter CBM was developed as shown in Scheme 2. Intermediate compounds **A**[21] and **B**[22] were synthesized according to the reported procedures and condensation of compound **B** with excess malononitrile under refluxing conditions in ethanol using Et_3N as a catalyst afforded the desired designed target receptor CBM. The detailed procedure of its preparation is discussed in the ESI†. The structure of the CBM probe was confirmed by ^1H NMR, ^{13}C NMR, ESI MS and elemental analysis (ESI†).



Scheme 2 Synthetic route of the receptor (CBM). Reagents and conditions: (a) butylbromide, K_2CO_3, KI, CH_3CN, heated to 80 °C, 4 h; (b) $POCl_3$, DMF, 100 °C, 20 h; (c) excess malononitrile, ethanol, Et_3N (catalyst), reflux, N_2 atmosphere, overnight.

Experimental section

General

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Brucker 400 MHz instruments. For NMR spectra, d_6-DMSO was used as the solvent with TMS as an internal standard. Chemical shifts are expressed in d units and ^1H–^1H Hz. UV-vis titration experiments were performed on a JASCO UV-V530 spectrophotometer and fluorescence experiments were done using a PTI (Photon Technology International) fluorescence spectrophotometer with a fluorescence cell of 10 mm path.

Methods for the preparation of the receptor

Synthesis of the receptor (CBM). Under an atmosphere of dry nitrogen, carbazoledialdehyde (compound **B**, 300 mg, 1.07 mmol) and malononitrile (140 mg, 2.12 mmol) were refluxed in absolute ethanol (15 mL) overnight with a trace of Et_3N as a catalyst. 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 petroleum ether–dichloromethane (1 : 7, v/v) as eluent to afford carbazole based malononitrile (CBM) as a deep yellow solid (299 mg, 80%).

^1H NMR ($CDCl_3$, 400 MHz): δ (ppm): 8.032 (s, 1H), 7.852 (s, 1H), 7.527 (m, 2H), 7.376 (m, 2H), 4.364 (t, 2H, J = 9.6 Hz), 1.882 (m, 2H), 1.395 (m, 2H), 0.978 (t, 3H, J = 4.8 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm): 156.55, 137.05, 130.57, 119.42, 118.15, 113.05, 111.51, 110.17, 69.09, 60.60, 32.14, 20.52, 13.82.

MS (ESI MS): (m/z, %): 375.24 [M^+, 100%].

Elemental analysis: C = 76.74%, H = 4.55%, N = 18.71% (calculated values: C = 76.78%, H = 4.56%, N = 18.65%).

Synthesis of hydrazine adducted CBM. CBM is mixed with two equivalents hydrazine in acetonitrile at room temperature to give a colorless solution. On removing the solvent, a solid product was obtained, which was used for ^1H NMR, elemental analysis and mass spectroscopy.

^1H NMR ($CDCl_3$, 400 MHz): δ (ppm): 8.622 (s, 1H), 8.150 (s, 1H), 7.540 (m, 2H), 7.376 (m, 2H), 4.364 (t, 2H, J = 9.6 Hz), 2.052 (s, 4H), 1.882 (m, 2H), 1.395 (m, 2H), 0.979 (t, 3H, J = 4.8 Hz).

MS (ESI MS): (m/z, %): 307.52 [M^+, 100%].

Elemental analysis: C = 70.35%, H = 6.87%, N = 22.78% (calculated values: C = 70.33%, H = 6.89%, N = 22.78%).

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 wavelength and n = index of

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

Calculation of the detection limit

The detection limit (DL) of CBM for hydrazine was determined from the following equation:[23]

$$DL = K \times Sb1/S$$

where K = 2 or 3 (we take 2 in this case), Sb1 is the standard deviation of the blank solution and S is the slope of the calibration curve. Using the formula we get DL = 1.02 μM and details of calculation of the detection limit is given in the supporting information (Fig. S4, ESI†).

Method for the preparation of TLC plate sticks

Thin layer chromatography (TLC) plate sticks were easily prepared by immersing a TLC plate into a solution of CBM (2×10^{-4} M) in CH_3CN (1 mM) and then exposing it to air to evaporate the solvent. The detection of hydrazine was carried out by inserting the TLC plate into different concentrations of hydrazine solution (Fig. 7a and Fig. S5, ESI†) and evaporating the solvent to dryness.

General method of UV-vis and fluorescence titrations

UV-vis and fluorescence method. For UV-vis and fluorescence titrations, a stock solution of the sensor was prepared (2×10^{-5} M) in CH_3CN–H_2O (8 : 2, v/v). The solution of the guest cation was prepared (2×10^{-4} M) in CH_3CN–H_2O (8 : 2, v/v) at pH 7.4 by using 10 mM HEPES buffer. The original volume of the receptor solution was 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.

Theoretical and computational methods. All the calculations were performed using the Gaussian 03[24] program using the B3LYP[25] exchange correlation functional with a cc-pvTZ basis set (triple ζ quality for diffused orbital electrons and lone pairs).

Results and discussion

UV-vis and fluorescence study

The chromogenic and fluorogenic signaling behavior of CBM was investigated in a CH_3CN–H_2O solution (8 : 2, v/v, 10 mM HEPES, pH 7.4). As shown in Fig. 1, without hydrazine the CBM probe showed absorption bands centered at 405, 324 and 258 nm. Upon addition of hydrazine, the absorption bands at 405 and 324 nm diminished and the band at 258 nm increased. The presence of well-defined isosbestic points at 313 nm indicates the formation of the hydrazone product. The color of the solution changes from yellow to colorless upon addition of hydrazine, as shown in Fig. 1a (inset) which allows the detection of hydrazine with the naked eye.

In contrast, the addition of other metal ions and anions, namely Ag^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Na^+, Pd^{2+}, Zn^{2+}, Cl^-, Br^-, I^-, ClO_4^-, SO_3^{2-}, SO_4^{2-} and HPO_4^{2-} resulted in a negligible response. These results suggest that CBM can serve as a highly selective chemodosimeter for hydrazine (Fig. S2a, ESI†). Under the same conditions, the ratio change of the two absorption peaks (A_{258}/A_{405}) produced an excellent linear function with the concentration of hydrazine between 0.995 and 20.224 μM (R^2 = 0.989, Fig. S1a, ESI†).

The detection limit for hydrazine was 1.02 μM based on the equation[23] DL = $K \times Sb1/S$, where Sb1 is the standard deviation of blank measurements and S is the slope of the calibration curve (ESI†), which is much lower than the TLV (10 ppb) set by the EPA. This indicated that the CBM smart probe could be used to quantitatively detect hydrazine concentration in a relatively wide range. Because the optical signal changes relied on the chemical reaction between the CBM probe and hydrazine, the reaction rate might affect the experimental results. We therefore investigated the influence of the reaction time on the probing results (Fig. 1b). From the reaction curve

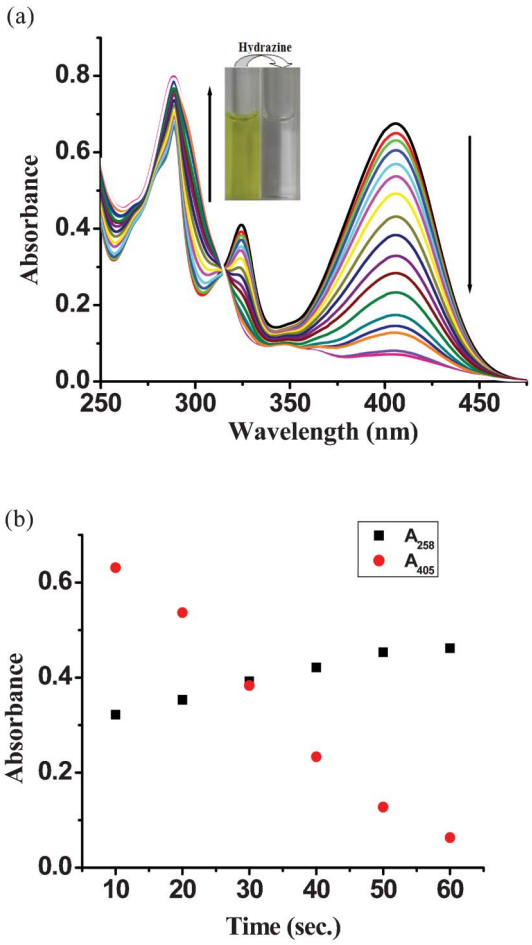


Fig. 1 (a) UV-vis absorption titration spectra of CBM (2.0×10^{-5} M) in the presence of hydrazine (2.0×10^{-4} M) at pH 7.4 in CH_3CN–H_2O (8 : 2, v/v) [gradual addition of 0, 10, 10, 10, 10, 10, 10, 10, 10, 10, 10, 20, 20, 20, 20 and 20 μL hydrazine, respectively]. The inset shows the naked eye colour change of CBM with addition of hydrazine. (b) Time-dependent absorption intensity of CBM at 405 nm (in red) and 258 nm (in black) in the presence of hydrazine (2 equiv.).

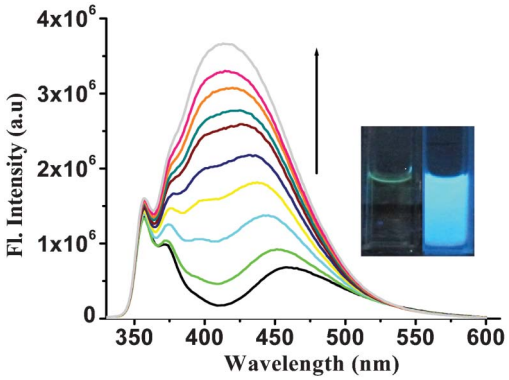


Fig. 2 Fluorescence emission spectra of CBM (2.0×10^{-5} M) with hydrazine (2.0×10^{-4} M) at pH 7.4 in CH_3CN–H_2O (8 : 2, v/v) [gradual addition of 0, 10, 10, 20, 20, 20, 20, 20, 30 and 50 μl hydrazine, respectively]. The inset shows the naked eye fluorescence change of CBM with addition of hydrazine.

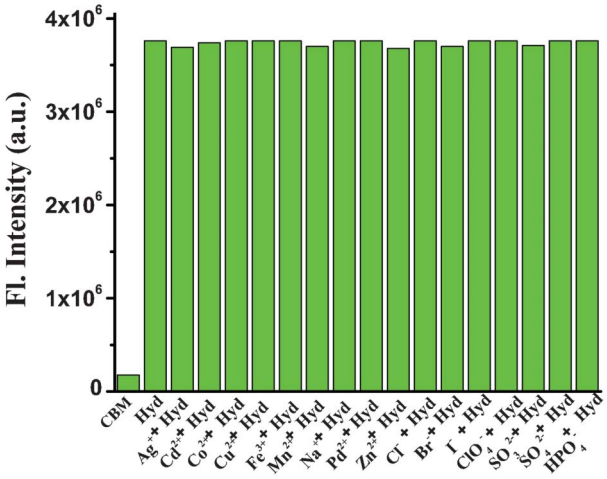


Fig. 3 Fluorescence responses of CBM (2.0×10^{-5} M) to hydrazine (2 equiv.) containing 10 equiv. of various metal ions and anions at 413 nm (λ_{ex} = 313 nm).

we can figure out that a plateau of ratiometric absorption intensity changes is achieved within 1 min, indicating that the sensor can achieve real-time detection of hydrazine.

As shown in Fig. 2a, the CBM chemodosimeter exhibited very weak fluorescence bands centered at 356 and 458 nm (φ = 0.123) upon excitation at 313 nm in the absence of hydrazine or in the presence of other metal ions and anions, namely Ag^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Na^+, Pd^{2+}, Zn^{2+}, Cl^-, Br^-, I^-, ClO_4^-, SO_3^{2-}, SO_4^{2-} and HPO_4^{2-}. Only the solution containing hydrazine showed remarkable change. The peak at 458 nm shifted to 413 nm (φ = 0.466) accompanied by a color change from light yellow to sky blue. This peak gradually increased in intensity with gradual addition of hydrazine (2×10^{-4} M). A linear relationship was observed between the fluorescence intensity and concentration of hydrazine in the range of 1.98–18.18 μM (Fig. S1b, ESI†).

Next, ion interference experiments were carried out both in buffered aqueous solution for evaluation of the sensing ability of the CBM 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 (Fig. 3). Clearly, the presence of background metal ions and anions did not cause any significant fluorescence change of CBM. This showed that the CBM probe could selectively detect hydrazine in the presence of other metal ions and anions.

Spectral study

The CBM chemosensor was also treated with some amine containing compounds. It was found that these compounds caused no obvious interference of probe CBM in aqueous CH_3CN solution (Fig. S3, ESI†). In the time dependent absorption spectra, we see the reaction is complete within 60 s with a rate constant of 5.2×10^{-2} s^{-1}, which strongly supports a high reactivity of the probe (Fig. 4).

The ability of CBM to detect hydrazine was studied by ^1H NMR, ^{13}C NMR and ESI TOF mass spectra. The ^1H NMR titration experiment confirms the corresponding hydrazone product formation by the reaction between CBM and hydrazine, by following the progressive shift of the protons at 8.032 and 7.852 ppm (in CBM) towards 8.622 and 8.150 ppm (in CBM + Hyd), respectively, and a new resonance signal at δ = 2.052 ppm appeared corresponding to amine hydrogen (Fig. 5). Comparing the ^{13}C NMR spectra of CBM and corresponding product, we found that two peaks at 110.17 and 69.09 corresponding to malononitrilic carbon disappeared and the peaks at 156.55, 137.05 and 130.57 shifted to 143.35, 132.05 and 124.42, respectively. The CBM sensor displayed a characteristic *m*/*z* peak at 375.24. However, after the addition of an excess amount of hydrazine this peak totally disappeared. At the same time, a new *m*/*z* peak at 307.52 assigned to the corresponding hydrazone compound appeared. All these results strongly demonstrated that the probe is highly effective for hydrazine.

DFT calculation. Meanwhile, the calculation based on density functional theory (DFT) using the cc-pvTZ basis set (triple ζ quality for diffused orbital electrons and lone pairs) and the B3LYP hybrid functional method for CBM and the corresponding hydrazone product was performed to get

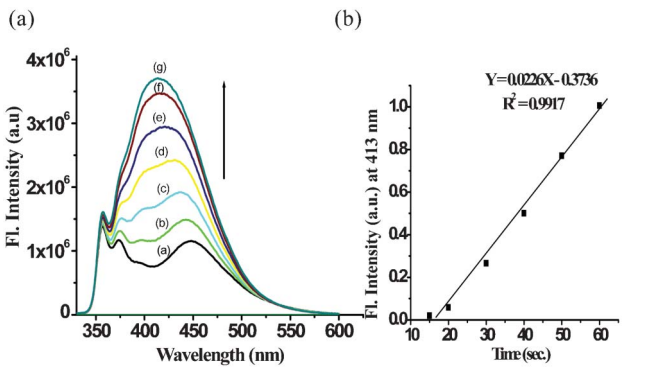


Fig. 4 (a) The time *vs.* fluorescence spectra of CBM (2.0×10^{-5} M) in the presence of hydrazine (2.0×10^{-4} M) at pH 7.4 in CH_3CN–H_2O (8 : 2, v/v) at different times: (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, (g) 60 s. (b) The fluorescence intensity *vs.* time at a fixed wavelength (413 nm) plotted using the first order rate equation.

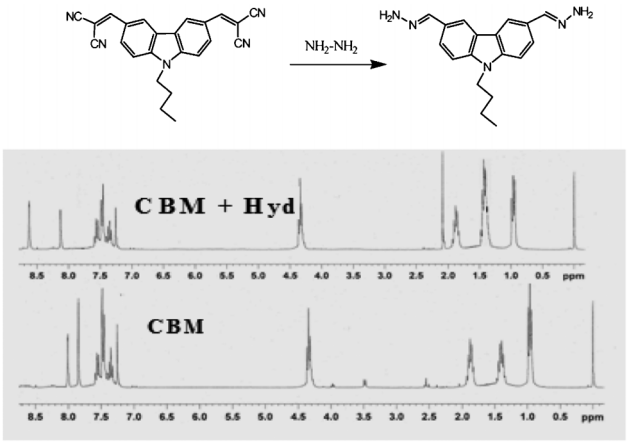


Fig. 5 Partial ^{1}H NMR spectra of CBM and CBM + Hyd in $CDCl_3$.

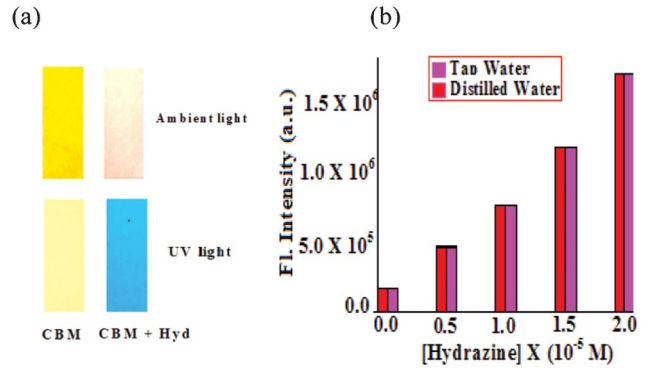


Fig. 7 (a) Color changes of CBM on test paper in the absence and presence of hydrazine under ambient and UV light. (b) Fluorescence detection of hydrazine in distilled water and tap water by CBM. [CBM] = 2.0 × 10^{-6} M, [hydrazine] = from 0 to 2.0 × 10^{-5} M at pH 7.4 in CH_3CN–H_2O (8 : 2, v/v). λ_{ex} = 313 nm.

insight into the optical response. Comparing the level changes of the HOMO (the highest occupied molecular orbitals) and LUMO (the lowest unoccupied molecular orbitals) in CBM and the corresponding hydrazone product, respectively, due to the ICT effect, after reaction with hydrazine both of them increased (Fig. 6). The LUMOs increased much more. The HOMO–LUMO energy gaps were calculated as 2.9617 eV and 3.016 eV for CBM and the corresponding hydrazone product, respectively; *i.e.* the energy gap between the HOMO and LUMO of the corresponding product was larger than that of CBM. This is in good agreement with the remarkable blue shift in the absorption spectra.

Applications

We also explored opportunities for CBM 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 tap water and distilled water. An aliquot of hydrazine was added to tap and distilled water and the pH was adjusted to 7.4. The results of the recovery of hydrazine by CBM from these two water samples were compared (Fig. 7b). The analysis of hydrazine in both solutions agreed well at hydrazine concentrations up to 2.0 × 10^{-5} M. We also prepared the TLC plates of CBM to determine the suitability of a ''dip-stick'' method for the detection of hydrazine (Fig. 7a).

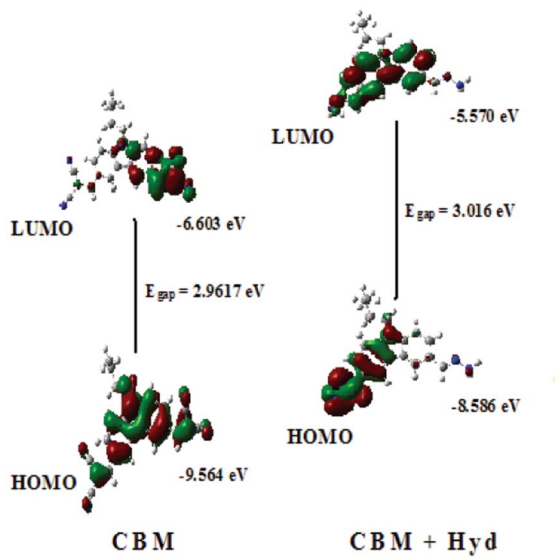


Fig. 6 HOMO–LUMO energy levels and interfacial plots of the orbitals for CBM and the corresponding hydrazone product (CBM + Hyd).

Conclusions

A new ''naked-eye'' ratiometric colorimetric and fluorescence chemodosimeter (CBM) was constructed by taking advantage of the formation of the specific product hydrazone by the reaction between arylidenemalononitrile and hydrazine. CBM displayed high sensitivity and selectivity for hydrazine with respect to other metal ions and anions. The probe demonstrated some advantages such as good sensitivity and high selectivity for hydrazine, relatively good solubility in aqueous media and good ratiometric response, as well as the successful application in real water samples. The sensing event is explained by spectroscopy along with the DFT calculation. 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

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