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ARTICLE TYPE

Amine functionalized tetraphenylethylene: A novel aggregation–induced emission based fluorescent chemodosimeter for nitrite and nitrate ions

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A novel AIE-based fluorescent probe for the detection of trace amount of nitrite and nitrate ions in water has been developed. The probe, a monoamine of tetraphenylethylene, spontaneously detects nitrites (or nitrates) by fluorescence "turn-off" method via diazotization followed by formation of a non fluorescent TPE-azodye. The salient features of this method is high sensitivity and selectivity, cost effective synthesis, fast detection process and low detection limit.

The hysterical increase in the concentration of nitrite and nitrate ions in groundwater, rivers and lakes by chemical fertilizers, livestock waste etc. is a growing threat to public health and the environment.[1] Nitrite is well-known to take part in key physiological roles in blood flow regulation, signaling and hypoxic nitric oxide homeostasis.[2] It reacts with the dietary components in the stomach to generate carcinogenic nitrosamine.[3] Another latent hazard with the nitrite ions is its capability to adapt oxyhemoglobin into methemoglobin when present in the bloodstream and thereby, prying with oxygen transport in the blood.[4] Nitrate, though less toxic, is converted to nitrite by microbial reduction under physiological conditions.[4] High concentration of nitrate and nitrite ions in drinking water results in a number of medical issues, such as premature birth, intrauterine growth restriction and birth defects of the central nervous system.[4] Therefore, monitoring of nitrite (and nitrate) level in drinking water and food stuffs is of great importance.

Till date, a large number of techniques have been developed for the detection of nitrite ions, based on organic chromophores,[5] electrochemical detection,[6] ion chromatography,[7] and others.[8] Many of these available methods require use of sophisticated instruments and thus, not cost-effective. In addition, some of these are not passably sensitive or selective for the determination of trace amount of nitrite ions, hence, cannot be used for real-time application. Recently, a few sensitive chromogenic sensors have been reported for nitrite ions as well.[9] However, over the last decade, fluorimetric probes have brought revolution to the sensing technology because of their operational simplicity and cost-effectiveness, in addition to the high sensitivity and selectivity.[10] Surprisingly, molecular probes for nitrite ions based on fluorimetric technique are rare.[11] Therefore, it is highly desirable to develop new and sensitive methods for the determination of trace level of nitrite ions in water and other bodies. However, conventional organic fluorophores have a major inadequacy among several advantages. Although, they are highly emissive in dilute solutions, the tarnished aggregation-caused quenching effect (ACQ) in the condensed phase confines their real world applications.[12] Recently, advancement of luminogen molecules, which emits more effectively in aggregated form than in the solution by aggregation-induced emission (AIE) mechanism, has stimulated great research interests for various applications.[13-17] Using this novel phenomenon great variety of AIE active molecules were designed for cell imaging,[16a,d,e,17i] optical devices,[17h,j] electroluminescent materials,[15f,16e] chemo/biosensor[13,15,17a,b,d,g,k] etc. Tetraphenylethylene (TPE), due to their easy synthesis and also for simple functionalization strategies, is one of the most studied luminophore and its manifestation for practical applications for the detection of analytes[15] and for other purposes[16] has been investigated in recent times. However, to the best of our knowledge, aggregation-induced emission property has not been exploited to develop a sensor for the detection of nitrite ions till date. In this regard, we envisioned, a TPE-amine may serve as an efficient sensor for nitrite ions by making use of simple "diazotization" reaction. As a part of our continued effort for the development of fluorescent sensors for biologically / environmentally important analytes,[11a,15l,m,18] we report, herein, an AIE-active TPE-based fluorescent chemodosimeter for selective and sensitive detection of nitrite (and nitrate) ions in contaminated water.

For the sensing purpose probe **1** (Fig. 1) was synthesized by McMurry cross-coupling reaction from benzophenone and 4-aminobenzophenone in a single-step adopting a reported procedure (see Supporting Information (SI) for details),[19] which undergoes ready "diazotization" by reaction with the nitrite ions present in acidic water at 0–5 °C. Upon addition of alkaline *β*-

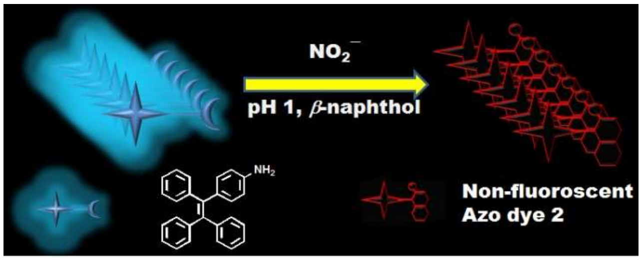

Fig. 1 The sensing mechanism for the detection of nitrite ions.

naphthol solution, it results in a TPE-azodye congener (**2**), which is non-fluorescent in either solid state or in solution phase (Fig. 1).

As anticipated, probe **1** was non-emissive in THF solution and since its solubility is very poor in water addition of large volume of water or mild acid (viz. 0.1 N HCl) preserves intense fluorescence response under identical condition manifesting AIE behaviour. As the diazotization process requires acidic condition, the solvent dependent AIE behaviour of the probe was examined in THF and aqueous HCl. The fluorescence signal from the solution of probe **1** was started appearing once the volume of THF in 0.1 N aqueous HCl (pH 1) was reduced to only 10% and approached to maximum at and below 3% of THF in 0.1 N aqueous HCl (Fig. 2). As a preliminary study, we checked the ability of probe **1** for the detection of nitrite ions in 20% THF in water at pH 1. We expected a turn-on type fluorescence response from the probe in the presence of nitrite ions due to anticipated poor solubility of the resultant azo-dye (**2**) in the same solvent system. To our surprise, a non-fluorescent solution of **1** did not show any fluorescence response even addition of one equiv of nitrite. Moreover, the solid dye was settled down at the bottom and as an added surprise, the dye was found non-fluorescent in the solid state as well. This unexpected outcome indulged us to carry out thorough investigation on the theoretical aspects of the electronic ground and excited states of both **1** and **2**. We also established the optimum condition for diazotization reaction by measuring fluorescence intensity of various solutions at different pH containing 1 equiv of nitrite ions at 0−5 °C. A pH range 1−7 was studied and pH 1 was found to be most suitable in terms of time required for completion of the reaction (Fig. S1 of SI). The rate of diazotization gets slower and slower up to pH 4.

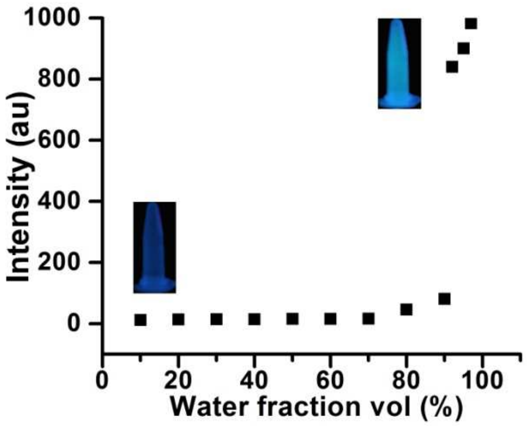

Fig. 2 Plot of fluorescence intensity of probe **1** (30 μM) against various proportions of 0.1 N HCl−THF mixture (λ_{ex} 345 nm, λ_{em} 447 nm).

As expected, the probe does not work at or near to neutral pH. Low temperature, a requirement of conventional diazotization reaction, was maintained for all fluorimetric studies to avoid any side reaction.

To understand the ground and excited state behaviour, quantum mechanical studies were carried out at the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) level using Gaussian 09 program (see SI for details). The optimized structures showed that the ethylenic C=C bond (1.37 Å) of probe **1** almost became a single bond (1.48 Å) in the photo-excited singlet state while its adjacent C-C single bond lengths were found to decrease by 0.02 to 0.05 Å. The S_0-S_1 transition arises due to the HOMO→LUMO excitation and this was characterized by a movement of the π-cloud from the aniline moiety towards the central ethylenic part (Fig. S3 of SI). However, the non-coplanarity of the phenyl rings and the central C-C bond are likely to hinder the extensive π-delocalization in both ground and excited states. A better co-planarity resulting in improved delocalization can be expected in the aggregated form and might be the reason behind the fluorescent nature of TPE-amine **1** in this state. However, the azo dye **2** was found to be non-fluorescent in nature both in the solution and in the solid state. A major fraction of the π-cloud from its HOMO was found to be shifted away from the TPE-moiety and resided close to the azo bond and naphthalene moiety in the LUMO. The π electronic cloud was found to disappear from the three phenyl rings and the central ethylene part of the TPE moiety on HOMO → LUMO excitation (Fig. 3). The phenyl ring of the TPE moiety connected to the electron withdrawing azo bond and the naphthalene moiety situated on the other side of this bond are co-planar, and creates a channel for shifting of this π-cloud from TPE to this part during the S_0-S_1 transition. Disappearance of π electronic cloud on the major portion of the TPE moiety during the HOMO → LUMO excitation is probably related to the observed nonfluorescent nature of the azo-dye (**2**). This photo-induced intramolecular charge transfer process is subsequently followed by a non-radiative decay path from this charge separated excited state. The energy gap between the excited state at its optimized geometry and the ground state at this geometry was found to be negligibly small, which indicates a possibility of strong vibronic coupling between the states leading to a non-radiative decay of the singlet excited state (see SI). Moreover, the aggregated state is also not expected to have a better π-delocalization (even if it becomes completely planar) as the electron withdrawing part of the dye will still inhibit any π-electronic cloud over the TPE part.

For sensing study, we selected 3% THF in 0.1 N HCl as the most suitable solvent system in which probe **1** fluoresces with highest intensity. In a typical experiment the fluorescence response of highly fluorescent TPE-amine **1** gradually turned off upon addition of 0−2 equiv of nitrite ions followed by addition of alkaline *β*-naphthol after an interval of 5 min at 0−5 °C and incubation of the resultant mixture for further 5 min (Fig. 4). Initially, the solution showed an intense blue fluorescence at λ_{max} 447 nm and upon the addition of nitrite the fluorescence intensity reduced slowly with almost no change in the absorption maxima. It is expected that probe **1** would be quickly diazotized in the

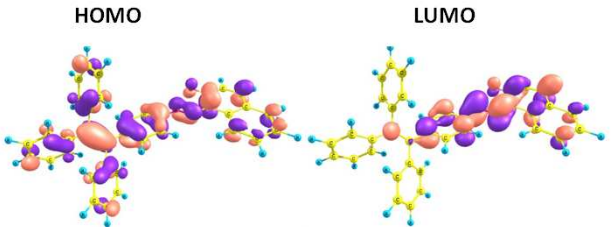

Fig. 3 Frontier molecular orbital diagrams of HOMO and LUMO of azo-dye **2** at optimized ground state geometry.

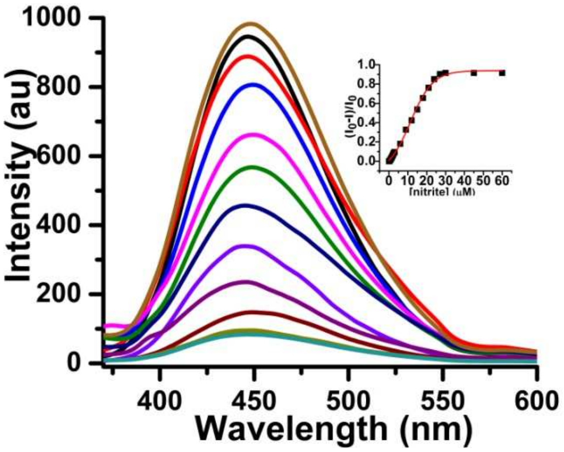

Fig. 4 Fluorescence response of probe **1** (30 μM) upon addition of different concentration of nitrite (0-60 μM) and alkaline *β*-naphthol solution [solvent system: 3% THF in 0.1 N aqueous HCl; λ_{ex} 345 nm]. Inset: Plots of relative emission intensity against no. of equiv of nitrite ions.

presence of nitrite ions under acidic condition at low temperature and react with alkaline *β*-naphthol to form corresponding azo-dye **2**. Since the dye is non-fluorescent in solution as well as in the solid state the fluorescence response is slashed down gradually. About 15-fold drop in the fluorescence intensity was observed indicating the probe could efficiently detect trace level of nitrite ions in solution. The azo-dye **2** was subsequently isolated in good quantity by keeping a relatively large scale reaction and its structure was confirmed by ^{1}H NMR, ^{13}C NMR and ESI-MS spectrum (see SI for details). In a separate experiment, the non-fluorescent nature of azo-dye **2** in solution was verified by measuring its fluorescence response in various proportions of THF in water (Fig. S6 of SI).

The selectivity of probe **1** was assessed by challenging it with several other environmentally relevant anions such as I^-, Br^-, CH_3COO^-, N_3^-, SO_4^-, NO_3^- and they do not educe any change in fluorescence intensity relative to the blank, even at relatively higher concentration, showing evidence of its high selectivity to nitrite ions (Fig. 5).

The specificity is an outcome of the fact that diazotization of the amine group of probe **1** is only possible when nitrite ions are present in the system. However, expected drop in the fluorescence intensity was not observed in case of oxidizable anions like I^-, $S_2O_3^{2-}$ and Br^-. Oxidizable anions, mainly iodide, are expected to impede in the detection of nitrite ions by instinctively reacting with them under acidic condition to produce NO gas.[20] On the other hand, reactive radical species, NO does not last in aqueous solution for long time but undergoes oxidation to generate mainly nitrite ions.[21] Making an allowance for these facts, we presume that both the reactions take place in a successive manner, at different extents depending on the kind of oxidizable anion present in the solution for the competition experiments, to uphold similar level of nitrite ions in solution rendering minor drop in the fluorescence intensity. Our conjecture was supported by the fact that fluorescence emission of probe 1 is negligible in the presence of NO under the established diazotization condition at pH 1 (Figure S7 of SI).

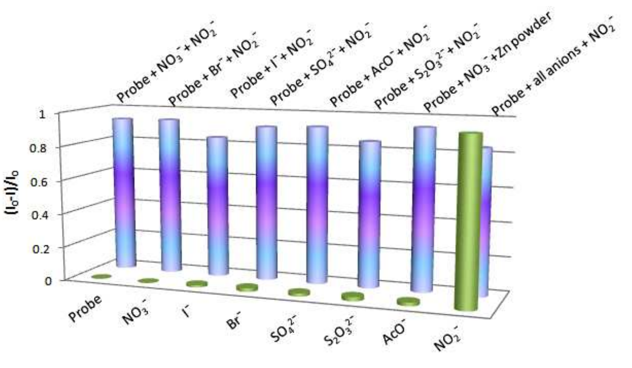

Fig. 5 Maximum fluorescence response of probe **1** (30 μM) upon addition of different anions (30 μM) in 3% THF–0.1 N aqueous HCl.

Our sensing system is well verge to detect nitrite ions well below 1 ppm, the MCL set by EPA for drinking water. Probe **1** responds to NO_2^- ions linearly below micro molar concentration range and from that the detection limit of probe **1** was estimated to be 6 x 10^{-7} M of $NaNO_2$ or 27.6 ppb (Figure S8 of SI).

Notably, we extended the capability of this probe for the detection of nitrate ion by performing an in-situ Zn powder facilitated reduction step. The reduction was carried out by adding a small amount of zinc (a toothpick full), which spontaneously catalyzes the reduction of nitrate to nitrite ions in quick time. Therefore, similar fluoremetric response was obtained as that of nitrite ions when 0−2 equiv of nitrate ions was added to probe **1** in 3% THF in 0.1N HCl at 0−5 °C and dipping a toothpick full of Zn-dust and shaking the resultant mixture for 5 min followed by addition of alkaline *β*-naphthol solution and incubation of the resultant mixture for further 5 min (Fig. 6).

The applicability of probe **1** was verified by detecting the nitrite level in several real samples. The samples were collected from various sources like river, paddy field, and aquarium water. For the determination of nitrite level in each real sample, it was made appropriately acidic by addition of conc. HCl, then probe **1** was added at 0−5 °C followed by the addition of *β*-naphthol and fluorescence intensity was measured. The level of nitrite in real samples was obtained by plotting the intensity values in a

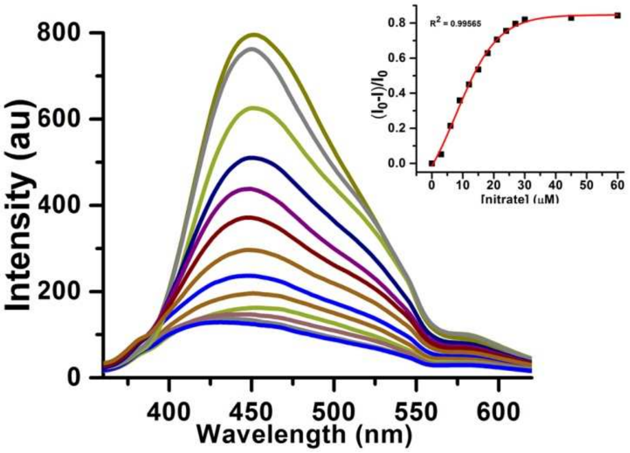

Fig. 6 Fluorescence response of probe **1** (30 μM) upon addition of different concentration of nitrate (0-60 μM) and small amount of Zn powder followed by alkaline *β*-naphthol solution [solvent system: 3% THF in 0.1 N aqueous HCl; λ_{ex} 345 nm]. Inset: Plots of relative emission intensity against no. of equiv of nitrate ions.

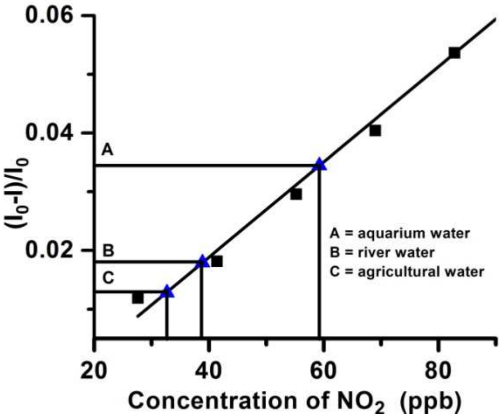

Fig. 7 A plot of the relative intensities of different real samples onto standard fluorescence curve to quantify the level of nitrite ions in those samples.

standard fluorescence intensity curve and found in the range of 30−60 ppb (Fig. 7).

Conclusions

In conclusion, we have developed a novel AIE-based fluorescent probe for the detection of trace amount of nitrite ions in water. The function of probe **1**, which is an amine derivative of tetraphenylethylene, depends on diazotization of its amino group in the presence of dissolved nitrite followed by coupling with β-naphthol to produce an azo-dye (**2**). Although the probe is highly fluorescent in 3% THF–0.1N HCl solution, the resultant azo-dye is nonfluorescent in solution as well as in the solid sate and thereby, the probe acts as a turn-off type molecular sensor for nitrite ions in the presence of many other interfering anionic species. The probe works equally well for the detection of nitrate ions under reducing condition (in the presence of Zn-dust). High sensitivity and selectivity, low detection limit, fast reaction coupled with cost effective synthesis make this probe highly considerable for practical purpose.

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Notes and references

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† Electronic Supplementary Information (ESI) available: general information, synthetic procedures, experimental procedures, pH study, limit of detection, details of theoritical calculations and spectral data; spectra of probe **1** and azo dye **2**. See DOI: 10.1039/b000000x/

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Graphical abstract

A novel AIE-based fluorescent probe for the detection of trace amount of nitrite and nitrate ions in water has been developed. The probe, a monoamine of tetraphenylethylene, spontaneously detects nitrites (or nitrates) by fluorescence “turn-off” method via diazotization followed by formation of a non fluorescent TPE-azodye. The salient features of this method is high sensitivity and selectivity, cost effective synthesis, fast detection process and low detection limit.