Electronic supplementary information

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

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Experimental

Chemicals

4-Aminobenzophenone and benzophenone were purchased from Sigma Aldrich (India). $TiCl_4$ was purchased from Spectrochem Pvt. Ltd. Mumbai (India). All other common chemicals and solvents of LR grade were obtained from different commercial suppliers and were used without further purification.

Instrumentation

NMR spectra were recorded on Bruker Avance (300 or 400 MHz, respectively) NMR spectrometer. Mass spectra were obtained from Waters Q-TOF micro mass spectrometer (ESI^+) and Agilent 6400B LC-MS (ESI^+). Fluorescence spectra were taken on a JASCO FP-6300 spectrofuorometer, the slit width was 5 nm for both excitation and emission. Absorption spectra were recorded on a JASCO V570 UV/Vis/NIR spectrophotometer at room temperature. IR spectra were recorded on IR Affinity-1 FTIR Spectrophotometer Shimadzu. Elemental analysis was carried out on Elementar vario MICRO cube.

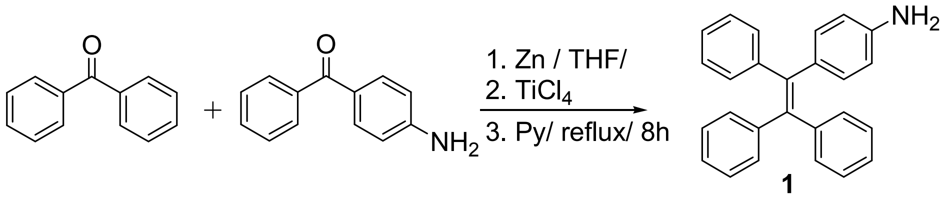
General Procedure

THF was dried over sodium and freshly distilled before use. The reactions were monitored by thin layer chromatography (TLC) carried out on 0.25-mm silica gel plates (60F-254) using UV light (254 or 365 nm) or naked eye for visualization. Stock solutions of compound **1** (1 mM) was prepared in THF. The solutions of sodium nitrite and β-Naphthol in 10% aqueous NaOH (1 mM) were prepared in deionized water (MilliQ, 18Ω). Deionized water was used for dilution purpose. For study of the effect of different anions stock solutions were prepared by dissolving sodium salts of anions in deionized water. The real sample study was done using water samples collected from different places. All solutions were subjected to filtration through 0.22 μm syringe filter in order to avoid any interference by any particulate matter in fluorescence measurement.

Procedure for fluoremetric studies

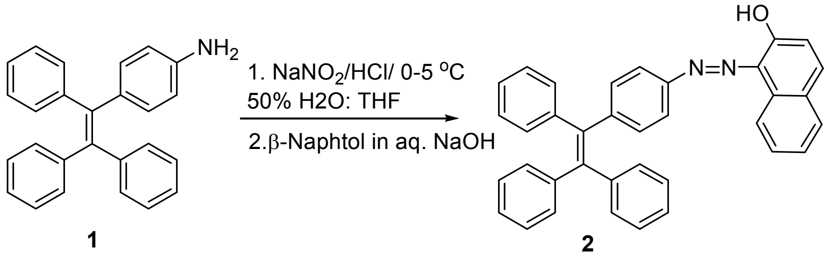
All the reactions were carried out in 3% THF in 0.1 N HCl at 0–5 °C. The fluorescence study was completed by adding 90 μL (1 mM) of probe **1** in THF was added to 0.1 N HCl (2.5 mL). To this solution required volume of NO_2^- (1 mM) was added followed by addition of 90 μL (1 mM) of β-Naphthol in 10% NaOH solution after 5 min. The final volume of the solution was made 3 mL of 3% THF in 0.1 N HCl by addition of required volume of THF and 0.1 N HCl. The solution was incubated for further 5 min. Then, the solution was taken in 3 mL cuvette and fluorescence response was measured. For equivalent study the concentration of nitrite was changed from 0.01–2.0 equivalent. For each reaction mixture the fluorescence spectrum was recorded separately. The same procedure was followed for the other anions.

Synthesis of the probe 4-aminotetraphenylethylene (1):[1]



In a three-necked flask zinc powder (0.8 g, 12 mmol) in 20 mL anhydrous THF was taken and the reaction vessel was kept under nitrogen atmosphere. The mixture was cooled to 0 °C and $TiCl_4$ (0.65 mL, 6 mmol) was slowly added by a syringe. The suspension was warmed to room temperature and stirred for 30 min, then heated at reflux for 2.5 h. The mixture was again cooled to 0 °C, charged with pyridine (0.25 mL, 3 mmol) and stirred for 10 min at cold condition. An equimolar solution of 4-aminobezophenone and benzophenone (2.4 mmol each) in 20 mL of THF was added slowly. After complete addition, the reaction mixture was heated at reflux for 8 h. The reaction was quenched by addition of 10% aqueous K_2CO_3 solution and extracted with CH_2Cl_2. The organic layer was collected and concentrated. The crude product was purified by column chromatography to give the desired product, **1** (320 mg, yield: 72%) as yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.58 (2H, s, exchangeable), 6.46 (2H, d, J = 8.0 Hz), 6.89 (2H, d, J = 8.0 Hz), 7.03-7.26 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 114.4, 126.2, 126.3, 127.6, 127.8, 131.45, 131.49, 131.6, 132.6, 134.0, 139.4, 141.1, 144.27, 144.30, 144.5, 144.9; ESI-MS: *m/z* 348 $[M + H]^+$; Anal. Calc. for $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03; Found: C, 89.75; H, 6.03; N, 4.19.

Synthesis of TPE azo-dye (2):



To a solution of probe **1** (100 mg, 0.29 mmol) in 50% aqueous THF (1.5 mL) was added 0.1 mL of conc. HCl at 0-5 °C. A cold aqueous $NaNO_2$ (21 mg, 0.31 mmol, in 0.3 ml of water) was added next and the reaction mixture was allowed to stand for 5 min with occasional gentle shaking. The above reaction mixture was then added to an alkaline solution of β-Naphthol (41.7 mg, 0.29 mmol; this was dissolved in 0.2 ml of 10% NaOH) at 0-5 °C with occasional gentle shaking. The reaction mixture was allowed to stand for 5 min. The solid precipitate was filtered, thoroughly washed with 10% NaOH followed by distilled water, and air dried and crystallized from ethanol as red crystals (107 mg, yield: 74%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.28 (1H exchangeable), 6.84 (1H, d, J = 9.3 Hz), 7.03-7.16 (17H, m), 7.36 (1H, dd, J = 7.6, 0.8 Hz), 7.37-7.49 (1H, m), 7.48 (2H, d, J = 8.4 Hz) 7.57 (1H, d, J = 7.6 Hz), 7.67 (1H, d, J = 9.3 Hz), 8.47 (1H, d J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 118.1 (2C), 121.7, 124.6, 125.6, 126.6, 126.7, 126.8, 127.7 (2C), 127.85 (2C), 127.94 (2C), 128.0 (2C), 128.6, 128.8, 130.1, 131.36 (2C), 131.40 (2C), 131.44 (2C), 132.7 (2C), 133.5, 139.8, 140.1, 141.8, 143.0, 143.4, 143.5, 143.6, 171.1; ESI-MS: 503.2 $[M + H]^+$; Anal. Calc. for $C_{36}H_{26}N_2O$: C, 86.03; H, 5.21; N, 5.57; O, 3.18; Found: C, 85.86; H, 5.25; N, 5.26; O, 3.34.

pH dependant florescence response of probe 1

The stability of the probe (**1**) within a pH range 1-7 was studied. The fluorescence response of the probe in THF-water (3:97) at different pH was measured. The probe was found to be stable and highly fluorescent within the pH range under consideration. The ideal pH for the diazotization reaction was also determined by adding $NaNO_2$ (and alkaline β-naphthol) to a probe solution at various pH and pH 1 was found to be most suitable in this regard.

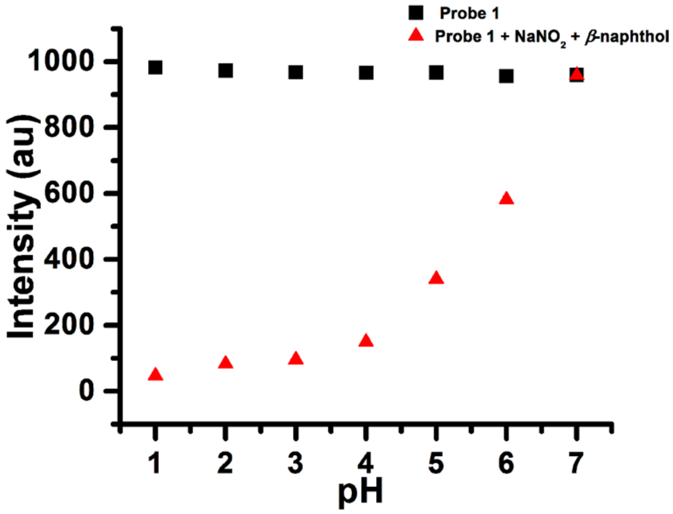


Figure S1. The fluorescence output of probe (**1**) in the absence and presence of nitrite ions within a pH range 1-7 in THF-water (3:97).

Quantum mechanical studies of probe 1 and azo-dye 2

Quantum mechanical studies have been carried out at the density functional theory (DFT)[2] and time-dependent density functional theory (TD-DFT)[3-5] level using Gaussian 09 program.[6] Becke's three parameter exchange function (B3)[7] with Lee-Yang-Parr correlation[8] function (LYP) have been employed using 6-311G basis set for the geometry optimization calculations.

The ground state structures of TPE-amine (**1**) and azo-dye (**2**) are optimized at the B3LYP/6-311G level (Figure S2A, S4A). 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 (optimized at the TD-B3LYP/6-311G level, Fig. S2B) while its adjacent C-C single bond lengths were found to decrease by 0.02 to 0.05 Å. Therefore, an alternation of single and double bond characters of the C-C bonds happen in the excited state. 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. S3A). 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. 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 the 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. S5A). 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 optimized singlet excited state of this species (Figure S4B) is almost having a similar geometry as the ground state. The energy gap between the excited state at its optimized geometry and the ground state at this geometry was found to be very small (~0.78 eV). According to the energy gap law[9] this indicates a possibility of non-radiative decay of the singlet excited state. 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.

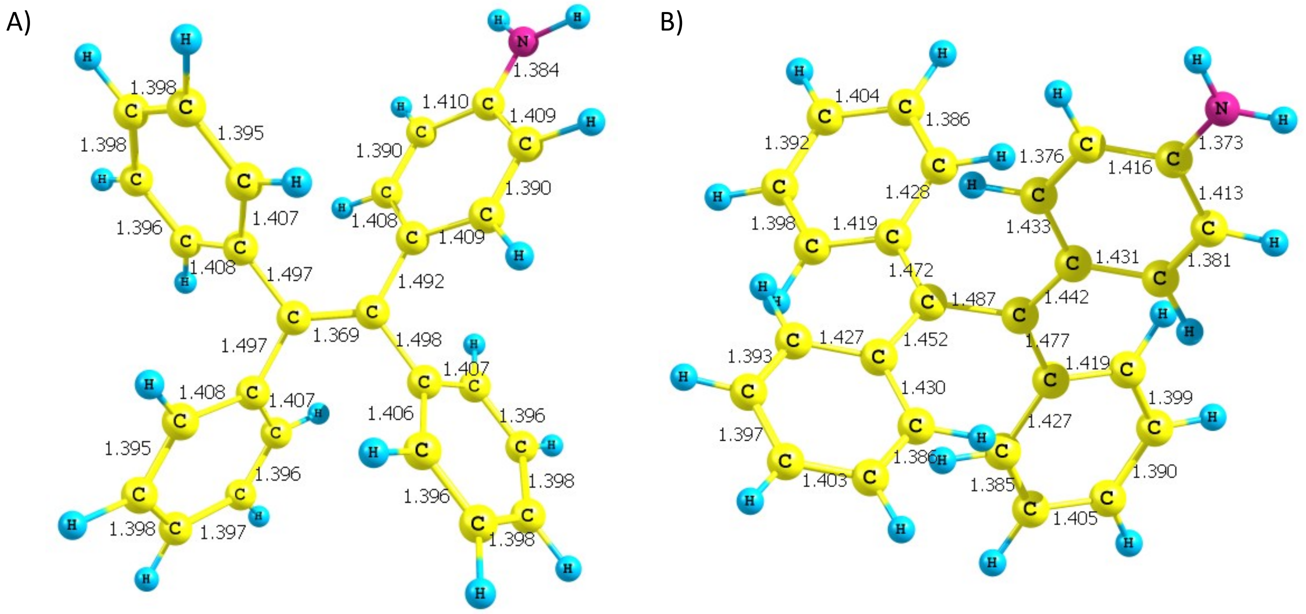
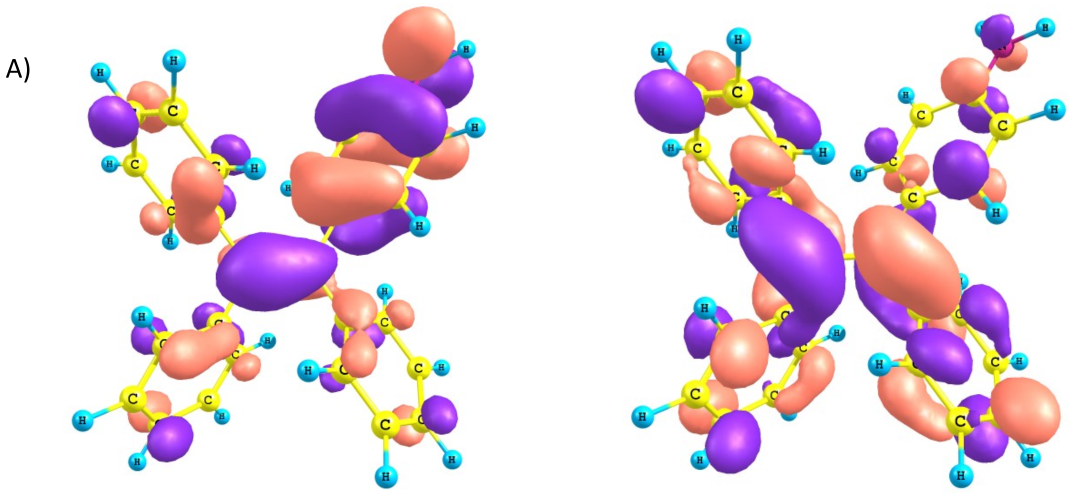
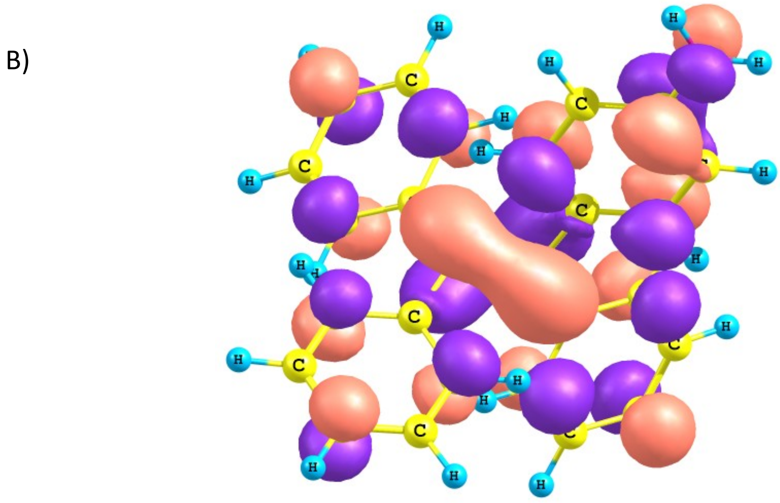


Figure S2. (A) Ground state geometry (optimized at the B3LYP/6-311G level) and (B) excited state geometry (optimized at the Td-B3LYP/6-311G level) of probe **1**.



HOMO LUMO



LUMO

Figure S3. Figures of frontier molecular orbitals of the probe (**1**) at the optimized (A) ground state and (B) excited state geometries.

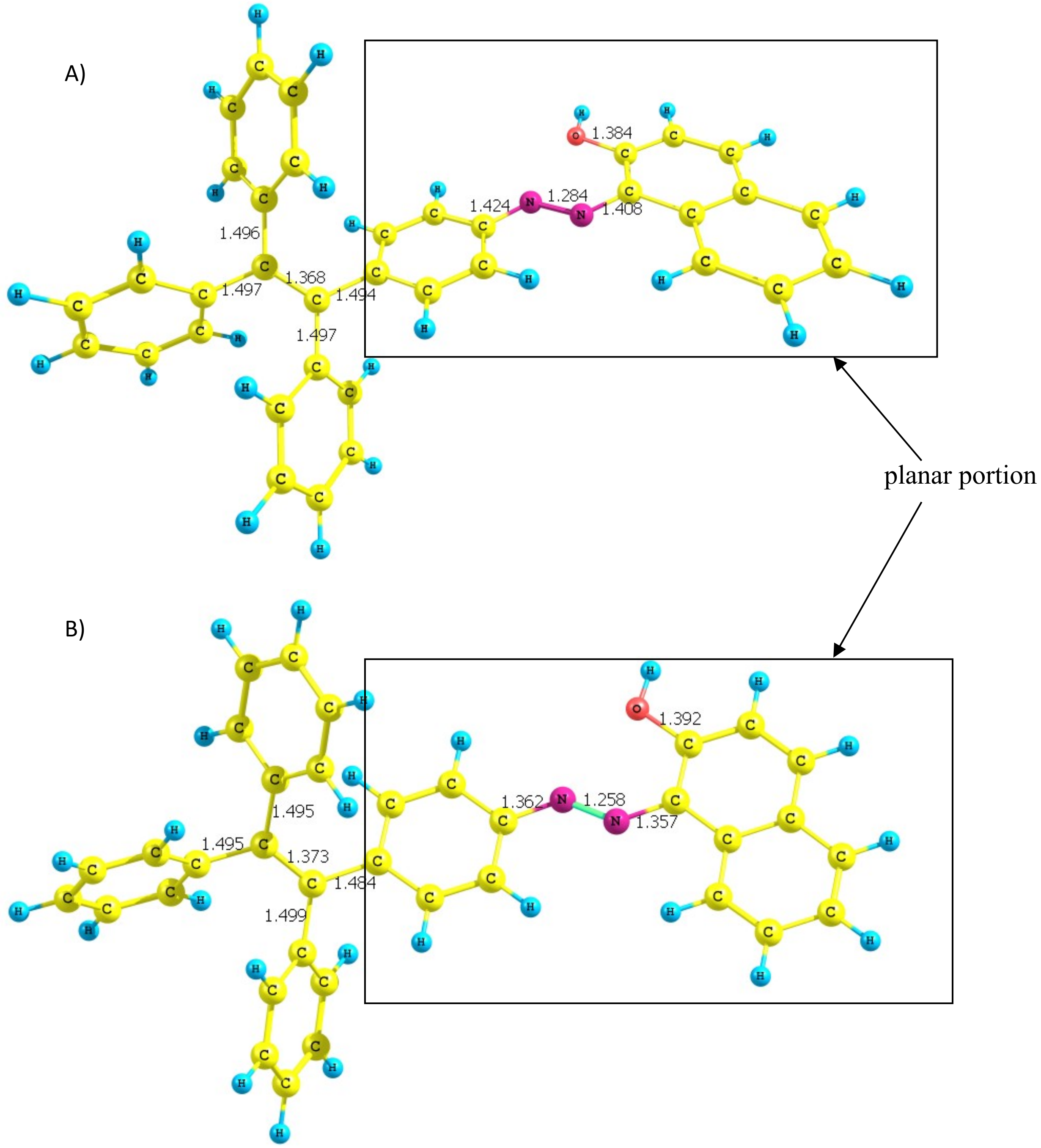


Figure S4. (A) Ground state geometry (optimized at the B3LYP/6-311G level) and (B) excited state geometry (optimized at the Td-B3LYP/6-311G level) of the azo-dye (**2**).

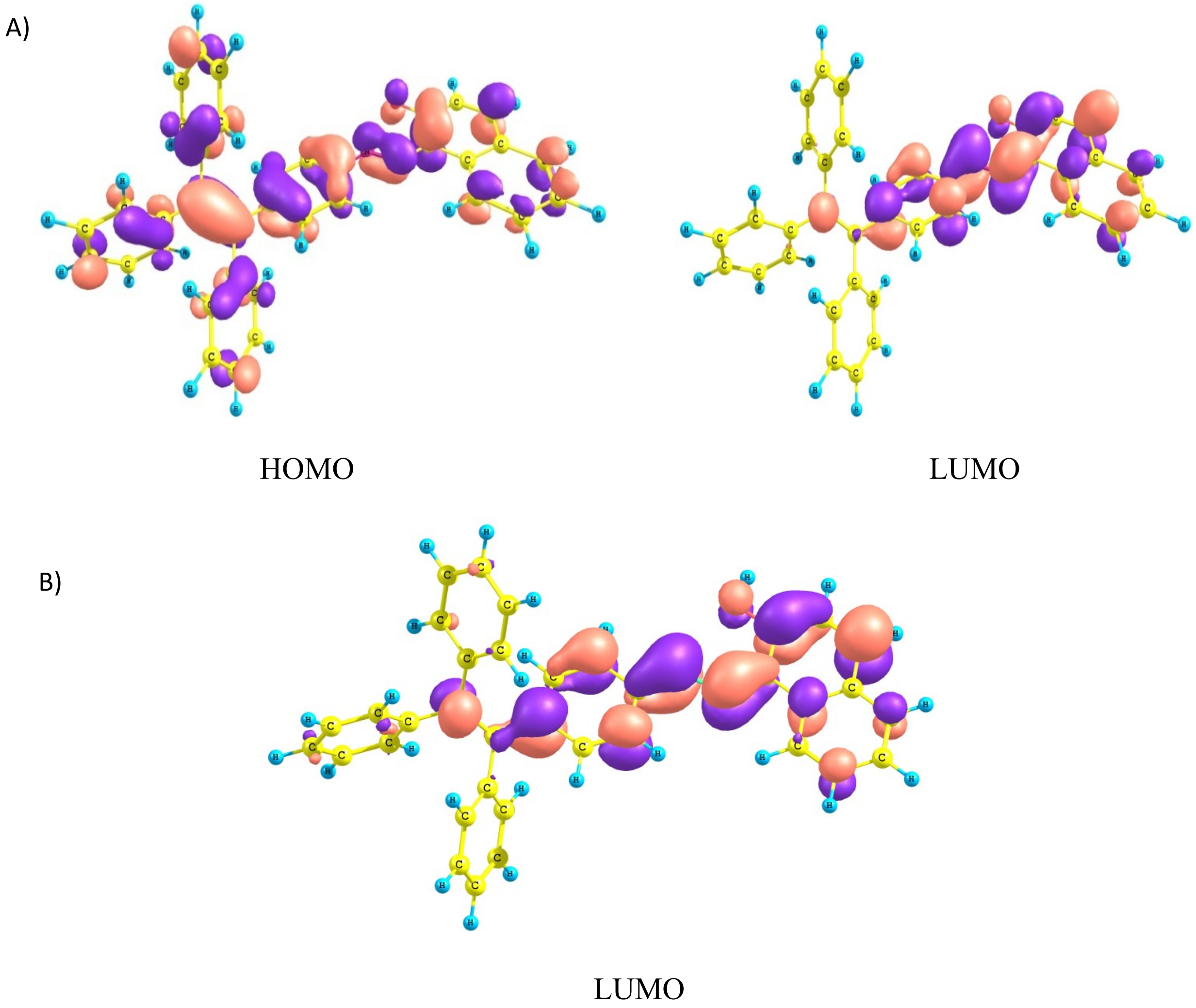


Figure S5. Figures of frontier molecular orbitals of the azo-dye (**2**) at the optimized (A) ground state and (B) excited state geometries.

Fluorimetric response of probe 1 and azo-dye 2 in THF-water

The non-fluorescent nature of azo-dye **2** in solution was verified by measuring its fluorescence response in various proportions of THF in water. As reveled in Fig. S6, azo-dye **2** hardly showed any fluorescence up to 99% of H_2O-THF mixture.

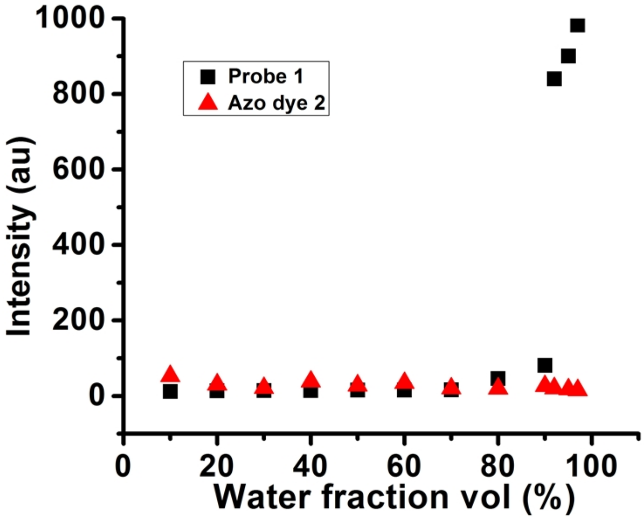


Figure S6. Plot of fluorescence intensity of azo dye **2** (30 µM) against various proportions of Waterl–THF mixture (λ_{ex} 345 nm, λ_{em} 447 nm). The fluorescence response of azo-dye **2** is merged with that of probe **1**.

Fluorometric response of probe 1 in the presence of nitric oxide (NO):

We were interested to know the fluorescence response of probe **1** in the presence of NO under the prevailing condition of diazotization reaction to get an insight of the fact that the presence of oxidizable anions has minimum interference in the detection of nitrite ions. Nitric oxide was freshly generated by addition of a solution of $FeSO_4$ in sulphuric acid to solid $NaNO_2$ and purified by successively passing through 1 M NaOH solution, KOH column and P_2O_5 column. The study was done by bubbling excess NO gas into an acidic solution of probe **1** at pH 1 and 0-5 °C for 5 min and by measuring its fluorescence response after 5 min of incubation. As depicted in Figure S7, the probe solution showed negligible fluorescence response in the presence of NO at pH 1. The drop in fluorescence response in the presence of NO is presumably because of the availability of effective diazotizing agent, NO^+ in the solution via formation of nitrite ions at pH 1. This ensures that NO can be spontaneously converted to nitrite ions in acidic solution.

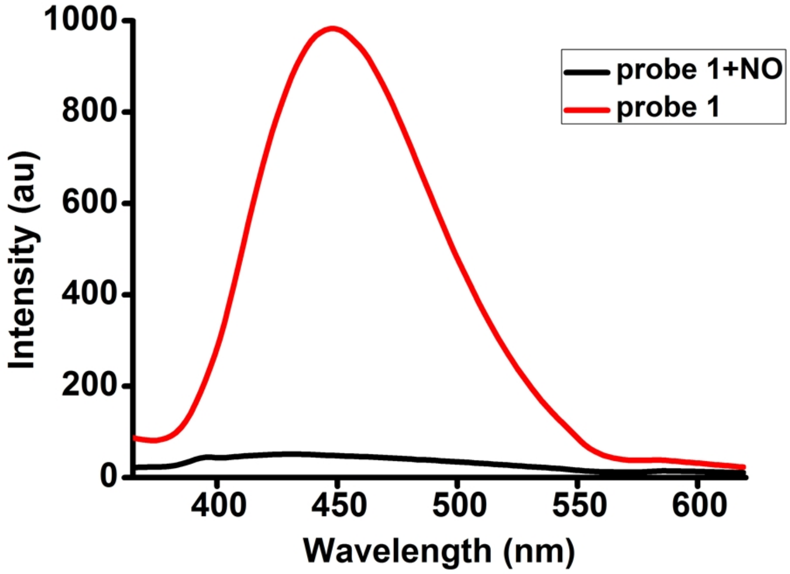


Figure S7. The above figure shows that the fluorescence intensity of probe **1** drops drastically upon passing NO gas through an aqueous solution of the probe containing 3% THF in 0.1 N aqueous HCl.

Determination of limit of detection (LOD) of probe 1:

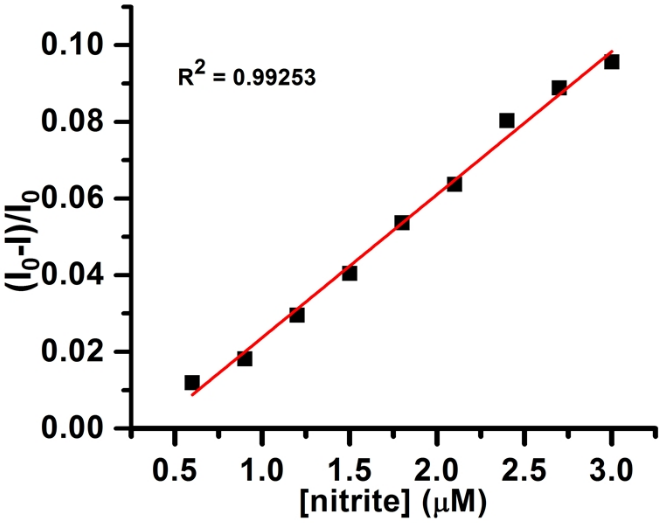


Figure S8. A fluorescence intensity plot of probe **1** against the low concentration range of NO_2^- (0.3-3.0 μM) in 3% THF in 0.1 N HCl showing an excellent linear fit ($R^2 = 0.994$)

which ensures that probe **1** can detect nitrite level as low as 0.6 μM or 27.6 ppb [λ_{ex} 345 nm, λ_{em} 447 nm].

Absorbance spectra of probe 1 and azo-dye 2

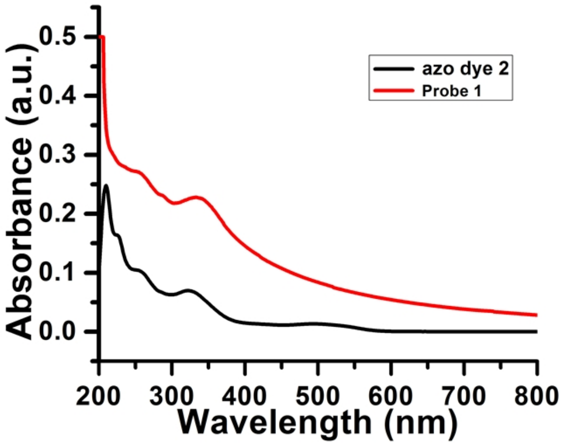


Figure S9. Absorbance spectra of probe **1** (30 μM) (red) and the azo-dye (i.e. probe **1** + NO_2^- + β-naphthol) (black). All the spectra were recorded in 3% THF in 0.1 N aqueous HCl.

IR study

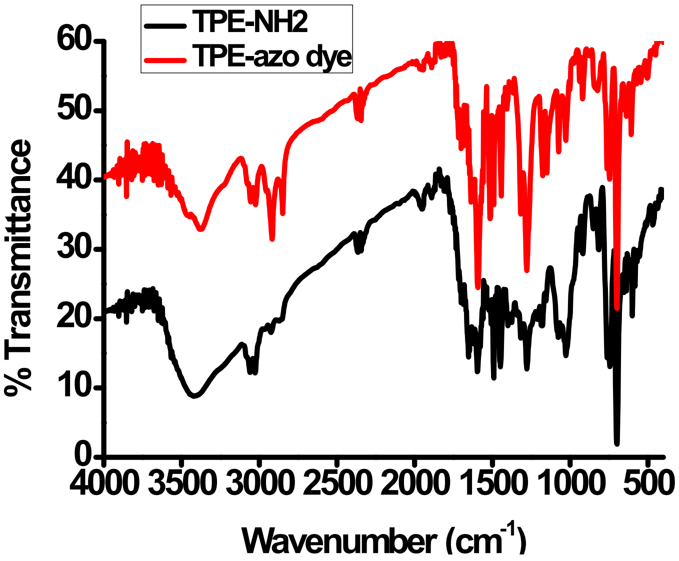


Figure S10. Merged IR spectrum of probe **1** (black) and azo-dye, **2** (red).

References

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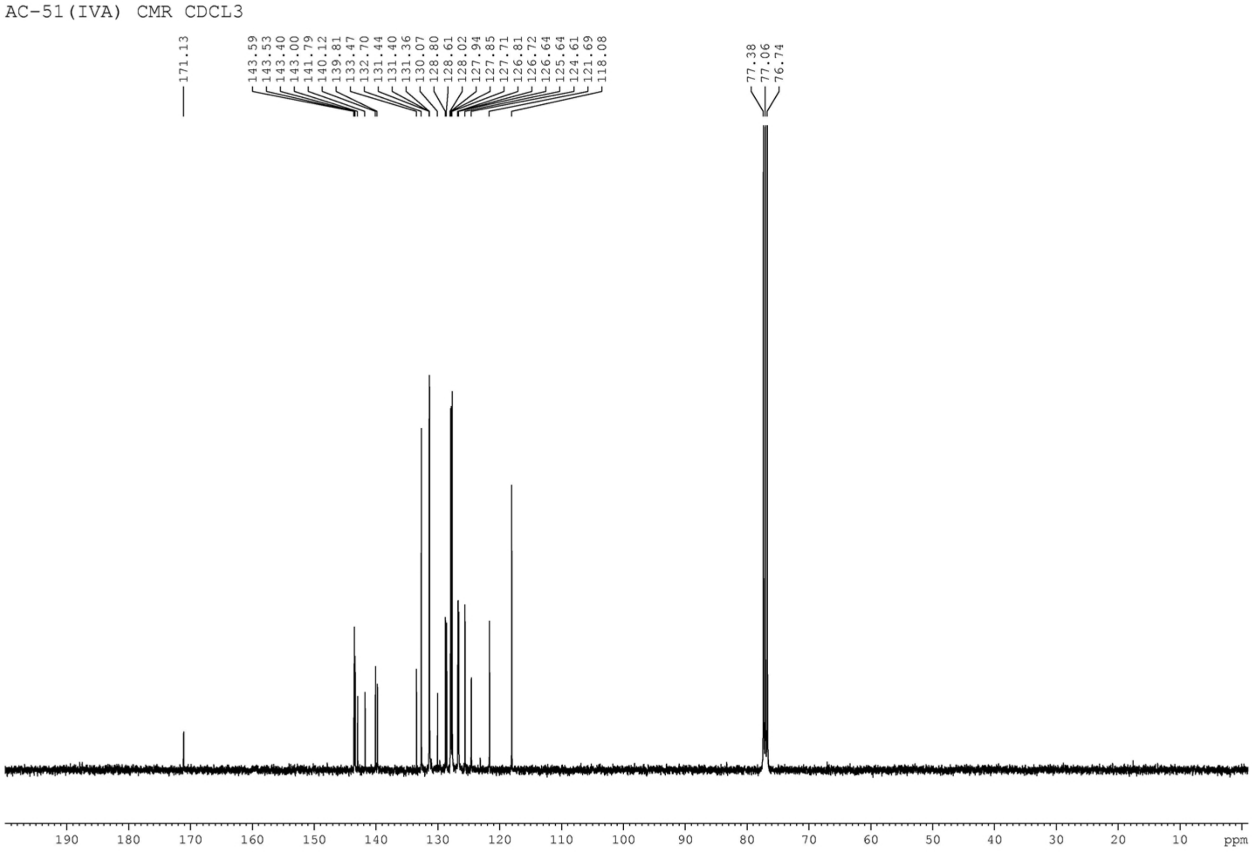
^{1}H NMR of probe **1**

^{13}C NMR of probe **1**

^{1}H NMR of azo dye **2**

^{13}C NMR of azo dye **2**



DEPT of azo dye 2