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Fluorogenic Phenothiazine-Derivative as Radical Sensors

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This study investigates the use of 10-(4-butoxyphenyl)-10H-phenothiazine (PTZ), a phenothiazine-based molecule, for detecting chloroform and other chlorinated hydrocarbons (CHCs). Upon exposure to these compounds to the phenothiazine-dervitive in presence light, a significant change in emission occurs, enabling naked-eye detection. The visual detection range of this phenothiazine derivative extends down to concentrations as low as 5 ppm. We demonstrate the one-time use of thin-layer chromatography paper (TLC) sensors and glass-based sensors for on-site detection of chlorinated hydrocarbons using a light source such as sunlight, UV-lamp, or a solar box. Our findings suggest that this phenothiazine-derivative has potential as a simple, low-cost, and effective sensing platform for chlorinated solvents, with practical applications in environmental monitoring and industrial safety. Furthermore, our results provide insights into the development of molecular sensors for detecting chlorinated hydrocarbons.

Introduction

Numerous organic solvents have been utilized in scientific research and industrial manufacturing, and the choice of solvent is crucial to ensure optimal reaction efficiency for most organic reactions. Chlorinated hydrocarbons (CHCs) pose a current threat to the environment.[1,2] Chloroform ($CHCl_3$)[3] has been widely used in various industries as a solvent, pesticide, and refrigerant.[4] There has been a significant increase in the disposal of Chloroform into the environment in the form of aqueous waste. $CHCl_3$ and related chlorinated hydrocarbons (CHCs) can easily cause pollution of soil, sediments, and groundwater due to their solubility in water, which is 8.2 g/L at 25 °C.[4] These compounds have higher density than water and are known as dense nonaqueous phase liquids (DNAPLs) that can penetrate through the soil's surface and groundwater, causing DNAPL pools.[4–8] In general, most CHCs, including $CHCl_3$, present in low concentration in water or in air can cause damage to the kidneys, liver, and central nervous system. Majority of CHCs, including $CHCl_3$, have been suspected to be carcinogens.[9,10] Despite the hazards associated with the presence of residual organic solvents in finished products (e.g., drugs), it has been indicated that many of those currently employed in the production of active pharmaceutical ingredients (APIs) are not completely removed.[11–13] Consequently, APIs may contain traces of residual organic solvents. Referring to the International Conference on Harmonization (ICH), the level of $CHCl_3$ in pharmaceutical products should not exceed 60 ppm.[11–13] Thus, it is important to monitor the concentration of $CHCl_3$ in groundwater and in the pharmaceutical industry and environment.[11,14] Color and/or fluorescence change-based chemo-sensor technology is an effective tool that has been applied to detect molecules due to its simplicity, selectivity, and high sensitivity.[15,16] Various methods have been established to detect CHCl3, including GC-MS, mostly in tandem with preconcentration, such as trap and purge, headspace/SPME analysis, and solid-state microextraction (SPME).[17–23] Although these methods provide sufficient and sensitive detection limits, they usually require trained technicians and relatively expensive non-portable instruments. Additionally, they are difficult to be applied for site monitoring and are time-consuming methods. Therefore, the development of new methods and sensors for the chemical detection of CHCs on site is a hot subject of research. There is a need to develop a direct, simple, and low-cost method to detect chlorinated organic solvents, especially $CHCl_3$, in the environment and residues in pharmaceutical products. Fujiwara reactions have generally been used for the detection of CHCs in solution.[24–29] This reaction is used for the spectroscopic detection of $CHCl_3$, was first reported in 1916, and originally depended on a two-phase system containing and $NaOH_{aq}$ layer and pyridine layer to $CHCl_3$.[30] Then, this mixture was heated to obtain an intense red color that was monitored spectroscopically for chloroform identification and quantification. Later, pyridine is used in excess in many modified Fujiwara's procedures that are used for the detection and quantification of halogenated molecules.[24,26,27,29] Moreover, pyridine is known for its bad-smelling and toxicity.[31,32] Alternatively, CHCs can be detected using photoinduced electron transfer (PET) phenomena, which has been used in molecular sensors.[33–36] PET reactions are suitable for detecting CHCs due to the facile decomposition of organohalides in PET reactions due to the excellent electron-accepting behavior of halo-carbon bonds (C–X).[37,38] In a study by Lee et al. in 2018, it was demonstrated that compounds based on triphenylamine can serve as fluorescence sensors for chloroform and chlorinated solvents using photoinduced electron transfer.c Here, we introduce a green procedure based

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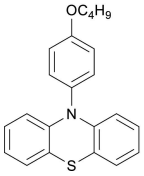
on a low-cost derivative of phenothiazine (PTZ) and light irradiation. Phenothiazine derivatives are extensively utilized as photocatalysts in various photochemical reactions.[39–42] Furthermore, phenothiazine is readily available at low cost and can be easily functionalized.[43]

Experimental Section

Reagents, materials, and Instruments

All the starting materials and solvents used in this experiment were commercially available reagents of analytically pure and were used as received without further purification. For Spectroscopic Measurements 1H NMR spectra were recorded on a JEOL ECZ-R 600, working at 600 MHz. Fluorescence spectra have been acquired with a Cary Eclipse Fluorescence spectrophotofluorimeter. The UV-Vis spectra were recorded in chloroform with an Agilent Technologies Cary60 UV-Vis spectrometer. The light irradiation was performed using a solar box (Solarbox 3000 e) of 1000 W power unless otherwise is indicated.

Synthesis of 10-(4-butoxyphenyl)-10H-phenothiazine (PTZ)



The reaction was performed in a 20 mL microwave vial that had been dried in an oven overnight, closed with a crimp, and purged with argon. Phenothiazine (5 g, 25.1 mmol, 1 eq), 1-bromo-4-n-butoxy-benzene (7.5 g, 32.6 mmol, 1.3 eq), Pd2(dba)3 [tris(dibenzylideneacetone)dipalladium(0)] (460 mg, 0.5 mmol, 0.02 eq), sodium t-butoxide (3.7 g, 38.4 mmol, 1.5 eq), and tri-t-butylphosphine (102 mg, 0.5 mmol, 0.02 eq) were dissolved in o-xylene (10 mL) and stirred under argon at 80 °C for 12 h. After completion of the reaction, the mixture was cooled down to room temperature and quenched with water. The mixture was extracted three times with dichloromethane and water. The organic layer was separated and dried with anhydrous sodium sulfate, and then the solvent was removed using a rotary evaporator. The crude product was precipitated from MeOH, giving white crystals (6.5 g, 75%).^{1}H NMR (600 MHz, Acetone-d_6) δ 7.33–7.27 (m, 2H), 7.21–7.15 (m, 2H), 7.01–6.95 (m, 2H), 6.87 (m, J = 8.3, 7.3, 1.6 Hz, 2H), 6.79 (m, 2H), 6.19 (dd, J = 8.2, 1.3 Hz, 2H), 4.08 (t, J = 6.4 Hz, 2H), 1.83–1.75 (m, 2H), 1.57–1.47 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 159.19, 144.74, 133.00, 132.20, 127.08, 126.50, 122.43, 119.55, 116.51, 115.82, 67.81, 31.27, 19.12, 13.32. MS/ESI^{+}: 347.08 a.m.u.

Fabrication of PTZ sensor film

TLC paper-based sensor

A solution of 5 mg PTZ was prepared by dissolving 5 mg of PTZ in 50 mL of acetone. This solution was then sprayed onto TLC paper measuring 25 mm × 50 mm and left to dry under argon.

Glass Based sensor film

The glass substrates were then coated evenly with the silica gel solution and left to dry overnight in air. After the silica gel-coated glasses were dried, they were placed in an oven and heated at 200 °C for 30 minutes to activate the silica gel. Meanwhile, 500 mg of polyvinyl alcohol (PVA) was dissolved in deionized water at 85 °C to create a PVA solution. Then, 3 mg of phenothiazine (PTZ), a fluorescent molecule, was dispersed in 10 mL of the PVA solution using ultrasound treatment for 1.5 hours to create a well-dispersed PTZ suspension. This PTZ/PVA suspension was then used to drop 300 μL of the mixture onto the activated silica gel sheet and dried at 60 °C for 3 hours to obtain the sensor film. This film was specifically designed to detect certain chlorinated hydrocarbons (CHCs), including chloroform.

Detection of Chlorinated compounds

Detection of volatile chloroform.

A homemade system was utilized for $CHCl_3$ detection, where 10 mL of chloroform was added to a 500 mL beaker. A PTZ-sprayed paper sensor was placed in an empty 100 mL beaker and then placed inside the 500 mL beaker. The entire system was covered with a watch glass and placed inside a solar box. Light was irradiated for 1 minute, and the system was used to detect 30 mM $CHCl_3$ in acetone and 30 mM $CHCl_3$ in deionized water.

Detection of liquid chloroform general method

The glass was immersed in liquid chloroform with different concentrations (30 mM $CHCl_3$ in acetone and 30 mM $CHCl_3$) and then was irradiated with light inside the solar box for 1 minute.

EPR Experiment

The PTZ was performed at a concentration of 10 mM in $CHCl_3$ and acetone without any photoexcitation sources, and light irradiation was carried out using a solar box as the light source.

UV-Vis Spectra

UV-Vis spectra in different solvents

A solution of 0.01 mM PTZ in different chlorinated and non-chlorinated solvents was prepared, and the UV-Vis spectra were measured before and after one minute of irradiation inside the solarbox.

Time-dependent UV-Vis spectra under light irradiation

A solution of 0.01 mM PTZ in chloroform was prepared, and the UV-Vis spectra were measured before irradiation of light and then after irradiation with light for 5 to 120 seconds.

Fluorescence

Fluorescence spectra in different solvents

A solution of 0.01 mM PTZ in different chlorinated and non-chlorinated solvents was prepared, and the fluorescence spectra were measured before and after one minute of irradiation inside the solar box.

Time-dependent fluorescence spectra under light irradiation

A solution of 0.01 mM PTZ in chloroform was prepared, and the fluorescence spectra were measured before irradiation of light and then after irradiation with light for 5 to 120 seconds.

LOD experiment

In the experimental section of the paper, the sensors for paper and glass were prepared using the procedures mentioned in sections 3.1 and 3.2. To test the sensors, drops of Chloroform with varying concentrations (ranging from 0 to 400 ppm) were added to the sensors using a pipette and then exposed to light irradiation. To prepare the Chloroform solutions, a stock solution of 0.05 mM PTZ in Acetonitrile was created, from which a 0.01 PTZ solution was made. Different concentrations of Chloroform (ranging from 0 to 400 ppm) were added to the 0.01 PTZ solution in transparent vials, and the final solution was made up to 2 mL using Acetonitrile. All solutions were then exposed to light irradiation for 2 minutes followed by performing the UV-Vis spectra.

Results and Discussion

As a proof of concept for the development of fluorogenic sensors for chloroform, we conducted EPR measurements for 10-(4-butoxyphenyl)-10H-phenothiazine (PTZ) (Figure 1). These measurements revealed spectra with a 3-line pattern attributable to the presence of an unpaired electron on the nitrogen atom of phenothiazine, in agreement with previous literature.[44,45] The intensity of the spectra decreased with increasing irradiation time. In the absence of light, no spectra were detected, indicating that radical formation is a photo-induced process in the presence of chloroform. Conversely, in the presence of acetone or non-chlorinated solvents, no spectra were observed. Further irradiation resulted in a decrease in the intensity of the spectra, which could be due to the transformation of PTZ into a new stable intermediate. Proton NMR spectra (Figure 2) after irradiation with light revealed that in acetone-d_6, the spectra of PTZ could still be recognized, whereas in $CDCl_3$, after irradiation with light we could no longer identify PTZ due to the formation of radical species over the aromatic ring. This observation confirms the formation of photoinduced radicals of PTZ in the presence of chloroform. These results suggest that our green procedure based on PTZ and light irradiation could be a promising approach for the development of simple and cost-effective fluorescence sensors for chloroform and other chlorinated solvents.

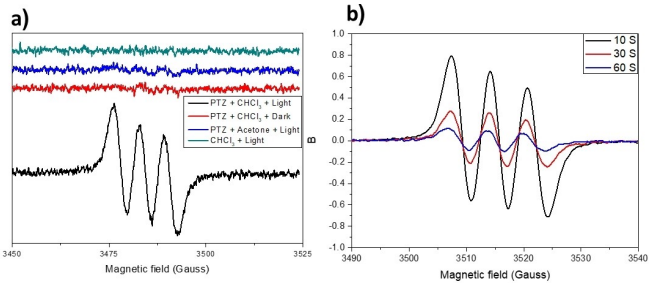


Figure 1. EPR spectra of PTZ a) In presence of acetone, $CHCl_3$ and light, b) In $CHCl_3$, with variation of irradiation time.

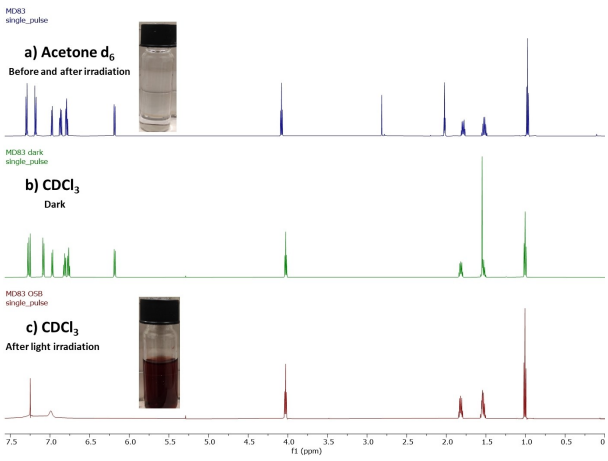
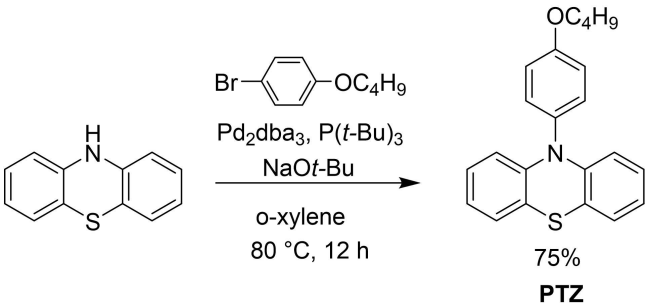


Figure 2. ^{1}H NMR spectra of PTZ a) In Acetone-d_6 before and after light irradiation, b) In $CDCl_3$ in dark conditions c) In $CDCl_3$ after light irradiation.

PTZ is obtained in good yield (75 %) in a one-step reaction via Buchwald amination between phenothiazine and 1-bromo-4-butoxybenzene (Scheme 1). The molecular structure was confirmed by 1H NMR, 13 C NMR, and mass spectra. The simplicity of the preparation, along with the low cost of phenothiazine (0.07 €/g), make it a perfect choice from an economic point of view.

The results of the study show that the TLC paper-based sensor prepared with PTZ can detect vapor $CHCl_3$ at room temperature upon light irradiation for one minute (Figure 3). The sensor changes its color from white to deep pink in the presence of pure $CHCl_3$ and to light pink in the case of low concentration of 30 mM of CHCl3 in acetone and water. This color change indicates that different concentrations of $CHCl_3$ can be differentiated by color. Based on these results, it can be concluded that the paper-based sensor is suitable for vapor detection of $CHCl_3$ due to its simplicity of preparation and cost effectiveness. However, when the paper-based sensor was immersed in pure $CHCl_3$ and irradiated in the solar box for one minute, the obtained color of the sensor was not clear due to the solubility of the active layer in $CHCl_3$. To overcome this



Scheme 1. Synthesis route of PTZ.

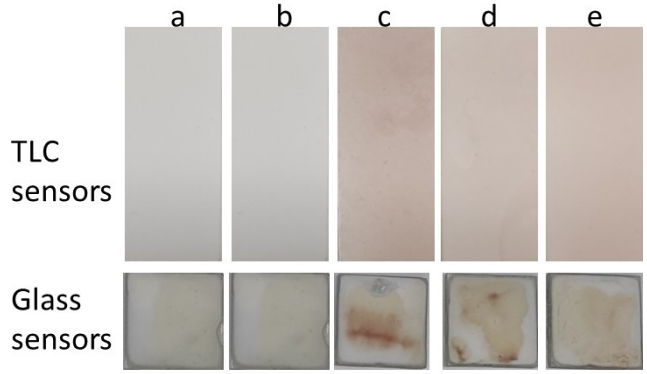


Figure 3. PTZ based sensors (down) after light irradiation a) Pristine, b) Only acetone, c) Only $CHCl_3$ d) 30 mM CHCl3 in acetone e) 30 mM $CHCl_3$ in water.

issue, a new PTZ film-protected sensor based on a glass substrate was developed. Sodium carboxymethyl cellulose was used to attach the silica gel onto the glass substrate, and PTZ was suspended in polyvinyl alcohol (PVA) solution and coated onto the silica layer. PVA was used as a protective layer for PTZ since it is not soluble in most organic solvents and can be solubilized in water at 60–90 °C, and is slightly soluble in ethanol.[46] The glass-based sensor provided stability for the sensor in both aqueous and organic solutions. The sensor's color changed from white to pink upon excitation in the solar box after the immersion in pure and 30 mM $CHCl_3$, indicating its suitability for in situ measurements for liquid samples. In conclusion, the paper-based sensor prepared with PTZ and the glass-based sensor developed with PTZ and PVA can detect vapor and liquid $CHCl_3$, respectively, with high sensitivity and selectivity, making them promising candidates for practical applications in the field of environmental monitoring.

In the time-dependent UV-Vis spectra of PTZ (0.01 mM) solution in $CHCl_3$ (Figure 4a), two absorption peaks of PTZ were observed. The maximum peak at 258 nm decreased gradually with the irradiation time and disappeared after 20 seconds, while the shoulder peak at 322 nm disappeared immediately after 5 seconds of light irradiation, even though the main peak was still diminishing, and the shoulder peak had already diminished. Three new bands emerged around 275 nm (λmax), 305 nm, and 340 nm, corresponding to the formation of PTZ/

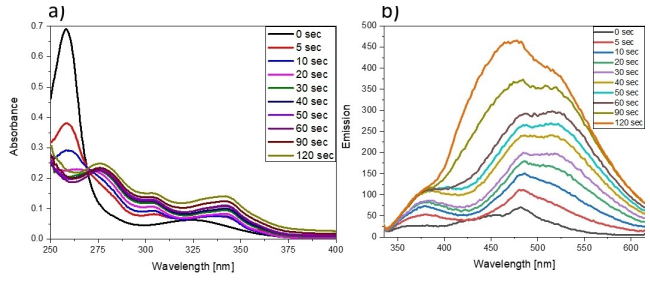


Figure 4. Irradiation time dependent a) UV-Vis and b)) spectra of 0.01 mM of PTZ in $CHCl_3$.

$CHCl_3$ radical intermediates. The peak at 275 nm appeared only after 30 seconds of irradiation, associated with the full disappearance of the peak at 285 nm. Along with this new absorption band, the absorption baseline at the longer wavelength also increased. Additionally, after the disappearance of the peak at 258 nm and the appearance of the new red shifted peak at 275 nm, only an increase in the baseline was observed while increasing the irradiation time, which indicates that light irradiation induced light scattering resulting in molecular aggregation, alongside the radical formation of PTZ in $CHCl_3$.[47] From the time-dependent fluorescence spectra (Figure 4b), an emission peak at 482 nm with very low emission intensity 70 a.u. was noticed before light irradiation. However, a very high intensity of 465 a.u. was detected after 120 seconds of irradiation, indicating that PTZ is a very suitable sensor for the rapid detection of chloroform under light irradiation as it transforms from a low emissive to a highly emissive form. At 482 nm, an emission peak appeared with low emission, which increased with the increase of the irradiation time. After 5 seconds of irradiation, a new peak was formed around 380 nm due to the formation of the radical species intermediates. By increasing the irradiation time, the emission intensities of the two peaks increased, indicating that the emission is dependent on the irradiation time. After 20 seconds of irradiation, another new peak around 514 nm was formed, referring to the formation of a new intermediate in the medium. After 30 seconds, the new peak formed around 514 nm was in equilibrium with the original peak, and then a new peak around 474 nm was forming at the same time the other 3 peaks around 380, 482, and 514 nm were disappearing, indicating the transformation of the starting materials and the intermediates to a new emissive product which can detect the presence of $CHCl_3$. This result is consistent with the EPR, ^{1}H NMR, UV-Vis, and visible eyes sensors that were prepared and tested.

It appears that for most chlorinated solvents as shown original spectra in (supporting information), the UV-Vis spectra were altered and new spectra were generated due to the light-induced PET between the chlorinated solvents and PTZ, except for Dichloromethane and 1,1,2 Trichloroethane, which showed an increase in the baseline and peak, likely due to light scattering induced aggregation.[47] Similarly, the Fluorescence spectra exhibited a significant difference between PTZ before and after one minute of light irradiation (Figure 5) and original spectra in (supporting information), except for Dichloromethane, and 1,1,2 Trichloroethane, which only showed a slight increase in emission spectra. It appears that Dichloromethane (CH_2Cl_2), Tetrachloroethylene (C_2Cl_4) and 1,1,2 Trichloroethane ($C_2H_3Cl_3$) did not undergo PET, which could be attributed to the mismatching of the LUMO energy levels of DCM and TCE with PTZ.[36] However, when non-chlorinated solvents were used (Figure 6), there was no noticeable alteration observed in the emission intensity of PTZ in different solvents after being exposed to light.Solvent-dependent studies were carried out to investigate the UV-Vis absorption and fluorescence spectra of PTZ (0.01 mM) without light irradiation in different halogenated (Table 1) and non-halogenated (Table 2) solvents. It was found

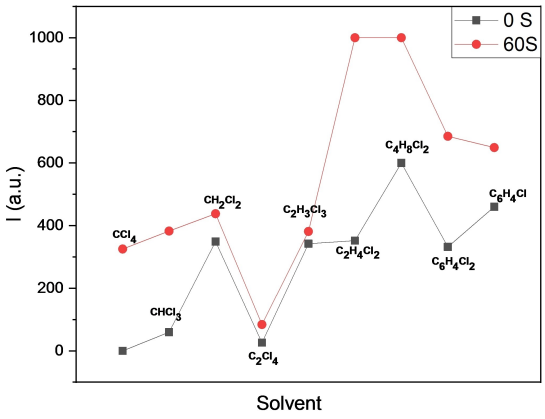


Figure 5. PL Intensity of 0.01 mM in different chlorinated solvents before light irradiation (0 S, black line) and after 60 seconds of light irradiation (60 S, red line).

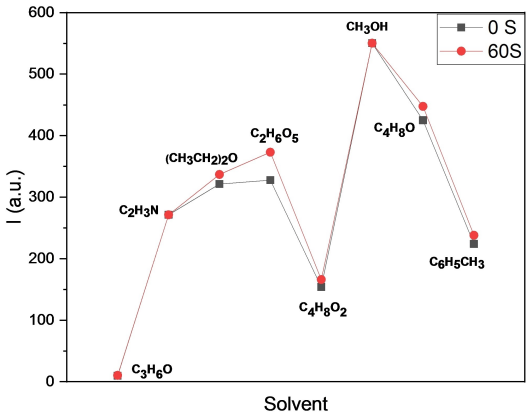


Figure 6. PL Intensity of 0.01 mM in different non-chlorinated solvents before light irradiation (0 S, black line) and after 60 seconds of light irradiation (60 S, red line).

Table 1. Solvent-dependent studies were carried out to investigate the UV-Vis absorption and fluorescence spectra of PTZ (0.01 mM) without light irradiation in different halogenated solvent.

Solvent[a]	$\lambda_{ab\ max}$ (nm)	$\lambda_{ab\ Shoulder}$ (nm)	λ_{em} (nm)	I (a.u.)
CCl_4	–	–	–	–
$CHCl_3$	258	325	480	59.7
CH_2Cl_2	258	325	446	349
C_2Cl_4	–	325	416	26
$C_2H_3Cl_3$	–	327	456	342
$C_2H_4Cl_2$	275	311	398	352
$C_4H_8Cl_2$	258	322	460	600.2
$C_6H_4Cl_2$	–	322	452	331.9
C_6H_5Cl	–	330	448	460

that PTZ exhibited a different maximum absorption band from 258 to 275 nm with varying absorbance values, indicating that the molar absorption coefficient of PTZ is dependent on the solvent used. In some solvents, the maximum absorption band could not be determined due to interference with solvent

Table 2. Solvent-dependent studies were carried out to investigate the UV-Vis absorption and fluorescence spectra of PTZ (0.01 mM) without light irradiation in different non-halogenated solvent.

Solvent	$\lambda_{abs\ max}$ (nm)	$\lambda_{ab\ Sholder}$ (nm)	λ_{em} (nm)	I (a.u.)
C_3H_6O	–	–	412	9.6
C_2H_3N	256	321	446.5	271.3
$(CH_3CH_2)2O$	256	322	444	321.3
$C_2H_6O_5$	–	–	350	327.7
$C_4H_8O_2$	275	301/331	450	154
CH_3OH	254	322	416	550.3
$C_4H_8O_2$	–	–	476	425
$C_6H_5CH_3$	–	324	448	224

cutoff. These maximum bands were accompanied by blue-shifted shoulder absorption bands from 311 to 330 nm, which could be attributed to the solvatochromic behavior of PTZ in different organic solvents. Regarding fluorescence emission, PTZ exhibited emission bands ranging from 350 to 476 nm in different chlorinated and non-chlorinated organic solvents. The highest emission peak at 550 a.u. was observed in solvents with higher polarity, such as methanol. However, carbon tetrachloride, which has zero polarity, did not exhibit any emission. These results suggest that PTZ can be utilized as an indicator to identify solvents with different polarity. These findings provide significant insights into the spectroscopic properties of PTZ and its potential applications in solvatochromic sensing.

The study found that the PTZ sensor is effective for detecting low concentrations of chloroform, with a limit of detection of 5 ppm. However, it takes more than two hours for the low concentrations of 5 ppm to 30 ppm to exhibit a colour change to red after irradiation of light. The UV/Vis spectra analysis revealed that the main absorption peak of PTZ at 256 nm decreased as the concentration of chloroform increased, while a new peak appeared at 274 nm when the concentration of chloroform reached 5 ppm (Figure 7).

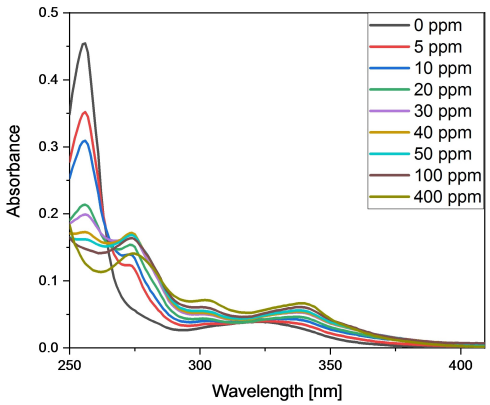


Figure 7. UV-Vis spectra of (0.01 mM) PTZ with $CHCl_3$ ranging from 0 to 400 ppm in acetonitrile after 120 s of light irradiation.

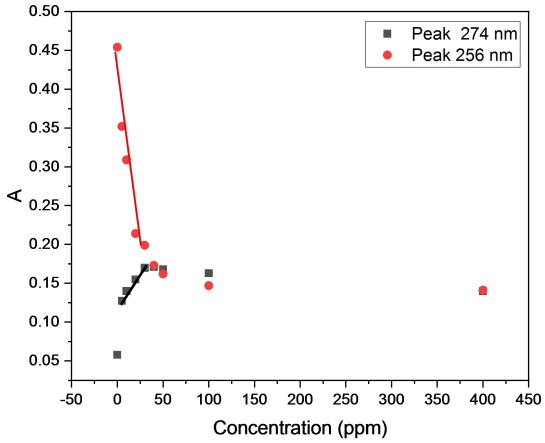


Figure 8. A calibration curve based on a correlation between the absorbance change at 254 nm (red) and 274 nm (black versus the concentration of CHCl3 at a fixed irradiation time of 120 s.

The linear relationship observed between the absorption peak at 256 nm in the UV-visible spectra of PTZ and the concentration of chloroform within the 0–30 ppm range indicates the PTZ sensor's good sensitivity to low concentrations of chloroform. However, the relationship became non-linear beyond 30 ppm (Figure 8), suggesting saturation of the sensing mechanism at higher concentrations of chloroform. Overall, the findings suggest that while the PTZ sensor is effective for detecting of low concentrations of chloroform.

Conclusion

In conclusion, this research has resulted in the development of a highly efficient and rapid photoinduced fluorescent sensor that utilizes PTZ and visible light to detect CHCs. This method is not limited to any specific light source and can be triggered by any source of light, including sunlight, making it a convenient option for on-site screening or field trips. Our technique is particularly useful for monitoring halocarbons, especially chloroform, with a limit of detection of 5 ppm. Furthermore, it provides quantitative detection of chloroform at very low concentrations ranging from 5 to 30 ppm. Overall, the simplicity and sensitivity of our method make it a promising candidate for the detection of chlorinated solvents.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Chloroform-detection · Organochloride-detection · Phenothiazine fluorogenic sensors · Photoinduced electron transfer · Radical reaction

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