



Research article

Development of a smartphone-based real time cost-effective VOC sensor

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ABSTRACT

Air pollution by various volatile organic compounds (VOC) is a matter of concern for us. So in this regard, designing real-time VOC responsive materials is gaining attention across the scientific community. In this present work, we have developed an inexpensive VOC sensor based on a Meisenheimer complex derived from picric acid and *N,N'*-dicyclohexylcarbodiimide. The sensor coated TLC plate was used as a sensor of potentially harmful VOCs. The sensor coated TLC plate looks deep red colored and does not show any fluorescence emission under 366 nm UV light. But in the presence of harmful volatile organic compounds like benzene, toluene, xylene, etc the sensor coated TLC plate becomes orange colored and it also shows strong yellow emission under 366 nm UV light. This property was utilized to detect the VOCs by fluorescence spectroscopy. The detection limit for various VOCs was found to be in the range of 0.7–9 ppm. To make the sensor user friendly, we have demonstrated a method where VOCs can be detected using a smartphone in real-time and also the setup is portable.

1. Introduction

Increasing pollution levels around the world is a concern for us [1, 2]. Air pollution is the most severe one in the categories of pollution [3, 4, 5]. As a result, regular monitoring of air quality is very important in the urban and industrial areas. Various volatile organic compounds (VOCs) present in the air act as potential air pollutants [6]. So, the detection of VOCs has attracted interest in the scientific community in recent times due to the increasing air pollution [7]. Various aromatic volatile organic compounds such as benzene, toluene, xylene, ethylbenzene, etc. are health hazardous. Especially, benzene and ethylbenzene exposure is associated with an increased risk of leukemia and hematopoietic cancers [8, 9, 10, 11, 12, 13]. Toluene and xylene can lead to adverse reproductive effects when exposures are at high concentrations [14, 15]. All the four compounds may cause skin irritation, respiratory tract irritation, drying and dermatitis, dizziness upon prolonged exposure [16, 17, 18, 19]. Inhalation of toluene greater than 200 ppm can cause CNS encephalopathy, weakness, headache, depression, drowsiness, transient memory loss, etc. [17] A concentration of 800 ppm toluene can lead to the rapid irritation of nasal and mucous membranes, impaired balance, metallic taste, etc. [17] Similarly, non-aromatic volatile organic compounds are also harmful to us. For example, THF has also been found to be carcinogenic in some recent studies [20]. Other non-aromatic solvents like chloroform, acetone, dichloromethane (DCM), etc. can be

destructive for the tissues at higher concentrations. They can affect the central nervous system, create headache, eye irritation, lethargy, lack of communication, kidney and liver damage, cause irritation to the gastrointestinal tract, etc. [21, 22, 23] But on-site and real-time detection of VOCs using a simple cost-effective set up with high sensitivity is a challenging task for the scientific community [24, 25, 26]. Therefore, scientists around the world have been focusing to derive effective VOC sensors in the last two decades [27, 28, 29]. These sensors include electrochemical sensors [30, 31, 32, 33, 34], fluorescent sensors [35, 36, 37, 38, 39], and colorimetric sensors [40, 41, 42, 43], etc. Among them, colorimetric and fluorescent VOC sensors are highly convenient because of their naked eye detection.

In general, VOCs are detected using sophisticated and expensive instruments. Most of these instruments are somewhat complex to operate and also they are not portable [44, 45]. From that point of view, it is extremely important to develop simple and sensitive sensors for the detection of these VOCs. Among various developed VOC sensors, optical chemosensors, based on the change of emission and absorbance color, are extremely useful. In this category several optical chemosensors have been designed based on π -conjugated polymers [46, 47], immobilization of organic dyes on insoluble solid supports [35, 37], metal-organic frameworks/porous coordination polymers [48, 49, 50], metal complexes [51], porous organic crystals [52, 53], macrocycles [54], and cross-reactive sensor arrays [55], fluorescent sensors [56], colorimetric

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sensors [57], ionic chemiresistor skin sensor [58], nanomaterials [59, 60, 61, 62], etc. But still, the quest for new and highly efficient VOC sensors is continuing. Here in this present work, we have developed an extremely cost-effective fluorescent VOC sensor based on an inexpensive material derived from picric acid and *N,N'*-dicyclohexylcarbodiimide. Using this fluorescent sensor, 0.7–9 ppm of various VOCs can be detected. But the more interesting part of this sensor is its extremely simplified execution. In today's world, everyone is using multi-featured smartphones and these smartphones have various kinds of inbuilt sensors. So if we can utilize these smartphones for developing portable automatic sensors then that will save a huge amount of money as we shall not have to deal with sophisticated instruments. So here we have done the same. A smartphone has been utilized in association with this sensor to develop a portable VOC sensor. The detail of the sensor development and sensing process has been described below.

2. Experimental section, materials and methods

2.1. Synthesis of compound 1

Picric acid (1 g, 4.37 mmol) was taken in a 50 ml round bottom flask and it was dissolved in 30 ml acetonitrile. The solution was cooled in an ice-water bath. Then DCC (*N,N'*-dicyclohexylcarbodiimide) (3.59 g, 17.4 mmol) was added to the cold solution. Then 0.6 ml triethylamine (4.38 mmol) was added to the cold acetonitrile solution. The solution was allowed to be stirred for six hours. The progress of the reaction was monitored using TLC. Then the product was filtered off. The filtrate was evaporated using a rotary evaporator and the residue was dissolved in 100 ml ethyl acetate. The ethyl acetate solution was extracted with sodium bicarbonate solution in a separating funnel to remove the remaining picric acid. Then the ethyl acetate layer was dried over anhydrous sodium sulphate. After that, the solution was evaporated using a rotary evaporator. The crude product was purified by column chromatography. An ethyl acetate-hexane mixture was used as an eluent. The pure compound **1** was characterized using NMR spectroscopy, IR spectroscopy and mass spectrometry.

Yield: 1.4 g (2.19 mmol, 50 % for compound)

For compound **1**:

^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 154.82, 145.13, 130.99, 125.65, 120.28, 82.47, 67.43, 62.52, 61.85, 59.12, 34.53, 32.15, 31.75, 28.97, 27.41, 27.23, 26.73, 25.73, 25.42, 25.11, 25.06.

^1H NMR (400 MHz, CDCl_3 , δ in ppm): 9.02 (2H, s), 4.53 (1H, d, 9.2 Hz), 3.69–3.59 (1H, tt), 3.54–3.42 (1H, m), 2.69–2.58 (1H, tt), 2.56–2.41 (2H, q, $J = 10$ Hz), 2.32–2.17 (4H, m), 2.15–2.06 (2H, d, $J = 12$ Hz), 2.0–1.9 (4H, m), 1.9–1.81 (2H, d, $J = 14.6$ Hz), 1.79–1.61 (6H, m), 1.61–1.55 (4H, t), 1.54–1.47 (2H, m), 1.4–1.23 (6H, m), 1.23–1.09 (4H, m), 1.09–0.94 (4H, m).

IR: 3415, 1706, 1580, 1506, 1423, 1244, 1218, 1053 cm^{-1} .

HRMS (m/z): $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{32}\text{H}_{48}\text{N}_7\text{O}_7$, 642.3610; found, 642.3611 $[\text{M} + \text{H}]^+$.

2.2. Materials

Picric acid, *N,N'*-dicyclohexylcarbodiimide, and triethylamine were purchased from SRL Chemicals. 60 F₂₅₄ Merck silica gel TLC plates were used for performing the thin layer chromatography purpose. 60–120 mesh silica gel, ethyl acetate, hexane were used for the column chromatography purpose.

2.3. Mass spectrometry

Q-ToF Micro YA263 high-resolution (Waters Corporation) mass spectrometer was used in positive-mode electrospray ionization for recording the spectrum.

2.4. NMR experiments

The desired amount of sample was dissolved in 0.5 mL of CDCl_3 in an eppendorf. Then the solution was transferred inside the NMR tube. All NMR spectra were recorded on a JEOL 400 MHz spectrometer at 278 K.

2.5. FT-IR spectroscopy

A small amount of sample and 200 mg IR grade KBr were taken in a mortar. The mixture was grinded well using a pestle and a spatula. Then a pellet was prepared using a hydraulic press. Then FT-IR spectrum was recorded using a Perkin Elmer Spectrum RX1 spectrophotometer.

2.6. Fluorescence spectroscopy

The sensor plate was inserted inside the fluorescence cuvette diagonally. Then the VOC vapor was passed through the cuvette using an aquarium pump. All the fluorescence spectra were recorded using a JASCO FP8600 fluorometer with 1 cm quartz cell. 405 nm wavelength was used for the excitation purpose.

2.7. Field-emission scanning electron microscopy

At first 1 mM dichloromethane solution of compound **1** was prepared and the TLC plate was dipped inside the solution. After air-drying the sensor for 1 h, the TLC plate was subjected to a high vacuum for 1 h. Then the surface of the sensor plate was investigated using a ZEISS scanning electron microscope-ZSM-S 55 VP.

2.8. Optical microscopy

At first 1 mM dichloromethane solution of compound **1** was prepared and the TLC plate was dipped inside the solution. After air-drying the sensor for 1 h, the TLC plate was subjected to a high vacuum for 1 h. Then the surface of the sensor plate was also investigated using a KARL ZEISS optical microscope.

3. Results and discussion

We have synthesized compound **1** from picric acid and *N,N'*-dicyclohexylcarbodiimide using a solution-phase synthetic methodology (Figure 1). Out of these two reactants, picric acid has an explosion tendency and toxicity effect. But there are some points to be mentioned about picric acid. If we apply heat or pressurize perfectly dry picric acid, then only there is a chance of explosion. But in the case of wet picric acid or solution-phase picric acid, there is no chance of explosion at room temperature. During our synthesis of compound **1**, we used solution-phase methodology and cold condition. So in this way, we mitigated the chance of an accident. Regarding the biological toxicity, we kept the work up extract as well as the silica gel leftover during column chromatography containing picric acid separately for their safe disposal. The

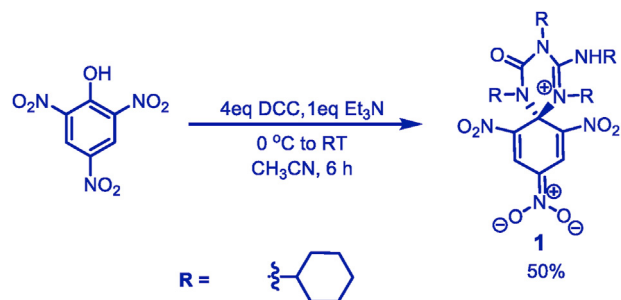


Figure 1. Synthesis of the VOC sensor **1** from picric acid and *N,N'*-dicyclohexylcarbodiimide.

solution of compound **1** is highly fluorescent with an emission maximum at 549 nm (Figure 2). The solution of compound **1** shows bright yellow emission under 366 nm UV light (Figure S1). The compound also shows emission in the solid-state (Figure 2). If we drop a benzene solution in an A4 paper and dry the paper then the paper will appear as orange-colored (Figure S2a) under the naked eye and 366 nm UV light it shows orange emission (Figure S2b). But interestingly if the same compound is coated over a TLC plate then the compound looks like deep red colored (Figure 3a) and it shows extremely faint emission under 366 nm UV light (Figure 3b). We have investigated the appearance of compound **1** coated TLC plate's surface through a microscope. At first 1 mM dichloromethane solution of compound **1** was prepared and the TLC plate was dipped inside the solution. After air-drying for 1 h, the TLC plate was subjected to a high vacuum for 1 h. FESEM and optical microscopic investigations were performed and both the microscopic study suggest the existence of spheres as well as aggregated spheres (Figure 4a and b). To understand this phenomenon we need to know compound **1** properly. Compound **1** is a zwitterionic spirocyclic Meisenheimer complex. It possesses a 2,4,6-trinitrocyclohexadienyl anion unit and a guanidinium cation unit. The bright emission by compound **1** is solely arising due to the 2,4,6-trinitrocyclohexadienyl anion unit. Silica gel is slightly acidic in nature. The negative charge of nitro oxygen of compound **1** interacts with the acidic silica over the TLC plate and becomes non-fluorescent. But upon exposure of volatile organic compounds like benzene, toluene, xylene, chloroform, dichloromethane, THF, acetone, etc. the compound **1** deposited over silica gel becomes solvated and in this way, the interaction between compound **1** and acidic silica surface gets disrupted. As a result, compound **1** regains its Meisenheimer complex nature. As a result, the orange color of compound **1** reappears (Figure 3c), and also it starts to show bright yellow fluorescence under 366 nm UV light (Figure 3d) in the presence of benzene vapor.

As long as the VOC vapor remains in touch with the compound **1** coated TLC plate, the yellow fluorescence remains on. But if we remove the compound **1** coated TLC plate out of the VOC chamber then with the passage of time, VOC vapor evaporates from the surface of the TLC plate and the yellow fluorescence vanishes gradually. Figure 5 and supplementary video 1 show the gradual diminish of fluorescence intensity of compound **1** coated TLC plate after soaking 1000 ppm benzene vapor with the progress of time.

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.heliyon.2020.e05167>

We tried to utilize this unique property for some practical application purposes. In the introduction, we have already discussed that VOCs are

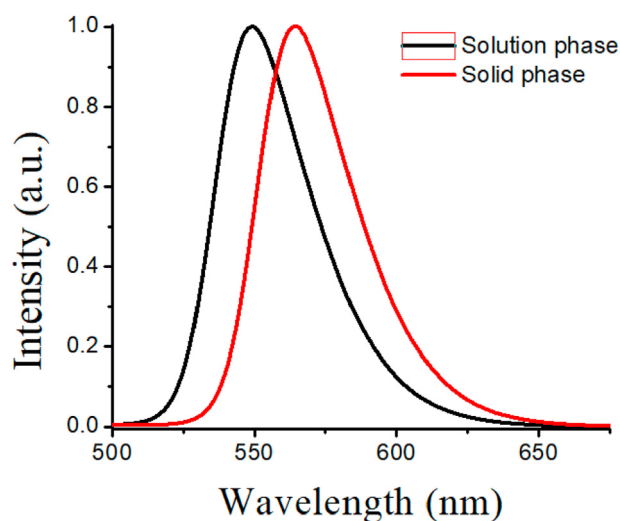


Figure 2. Comparison of fluorescence spectra of **1** between solution phase (benzene as a solvent) and solid phase. The excitation wavelength was 405 nm.

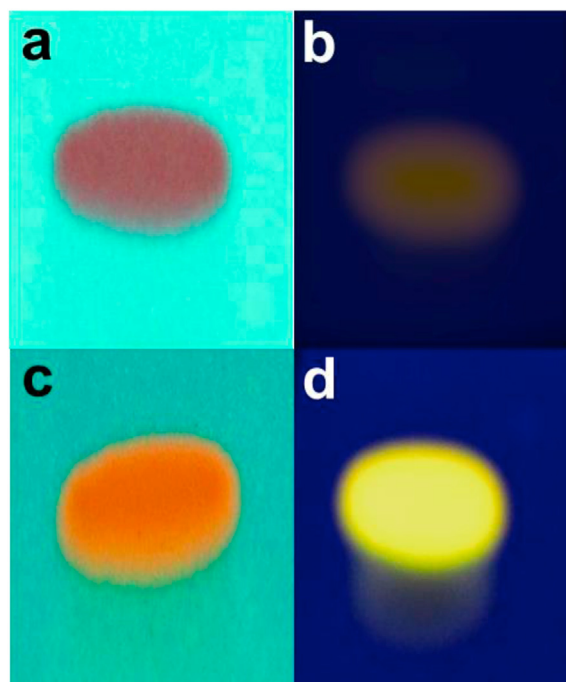


Figure 3. Coating of compound **1** over a TLC plate in perfectly dry condition under (a) natural light and (b) 366 nm UV light. Benzene vapor soaked compound **1** over a TLC plate under (c) natural light and (d) 366 nm UV light.

harmful to us. As our material is showing response in the presence of VOC as an external stimulus so we tried to utilize our material for VOC sensing purpose. We used fluorescence spectroscopy for detection purposes. We have taken various toxic VOCs like benzene, toluene, xylene, ethylbenzene, THF, CHCl_3 , CH_2Cl_2 , etc. for the study. The response of the TLC plate coated with compound **1** towards various VOCs was recorded using a fluorometer. We prepared different VOC chambers of known concentrations in the range 100 ppm–600 ppm. We used 25 L volume solvent drums for generating the solvent vapors. We considered 1 mg/L concentration as 1 ppm concentration. For example to prepare a 100 ppm VOC, 2.5 g of respective organic solvent was added inside the 25 L solvent drum. The drum was placed in a warm water bath kept at 80 °C to make the whole environment of the drum homogeneous. An aquarium pump was placed inside the drum to expel out the VOC containing air from the drum to the sensor surface. The TLC plate coated with compound **1** was placed diagonally inside the fluorescence cuvette (Figure S3). The ejected air was finally passed through a syringe and the air was contacted with the TLC plate coated with compound **1** inside a cuvette for ten minutes. Then the fluorescence intensity of compound **1** coated TLC plate was measured. Figures 6 and 7 show the enhancement in the fluorescence intensity after the exposure of 100–600 ppm VOCs. We have also tested the efficiency of the sensor in case of lower VOC concentration. We found that the sensor plate exhibited high sensitivity to various VOC vapors while having a wide linear range (Figure S4 and S5). Now we need to know the minimum lethal concentration of these VOCs and whether our designed sensor is capable of detecting them down to that limit. In this regard, the short-term exposure limit (STEL) is very useful. STEL is the acceptable exposure concentration over a short period of 15 min. It is very frequently used in occupational health, industrial hygiene, and toxicology. The short-term exposure limit for benzene, toluene, ethylbenzene, xylene, acetone, and THF, are respectively 2.5 ppm, 150 ppm, 125 ppm, 150 ppm, 750 ppm, and 250 ppm [63, 64]. We have investigated the minimum detection limit for each volatile organic compounds. For that, we prepared a series of chambers of different VOC concentrations. Then we placed an aquarium pump inside those chambers. Then the air coming out of those chambers via the

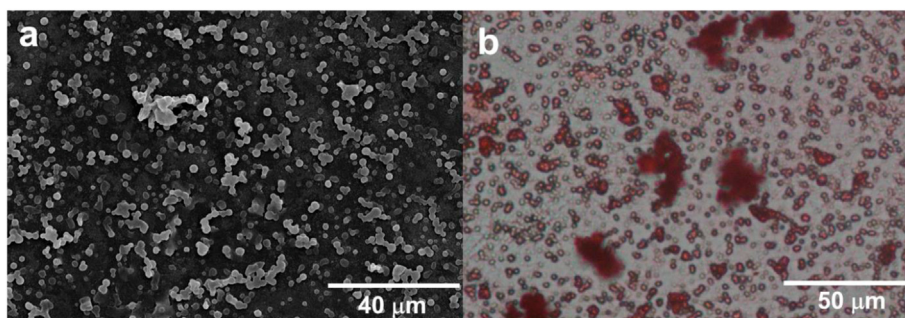


Figure 4. Microscopic investigations of the coating of compound 1 over a TLC plate. Sphere or aggregated sphere like assembly of compound 1 under a) FESEM image and b) optical microscope image of the coating of compound 1.

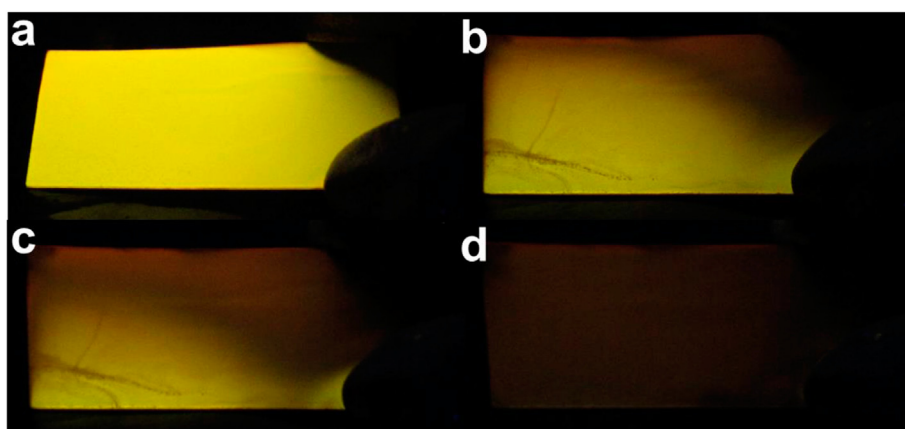


Figure 5. Change in the fluorescence emission of benzene vapor soaked TLC plate coated with compound 1 after (a) 0 s (fresh), (b) 20 s, (c) 40 s, and (d) 60 s.

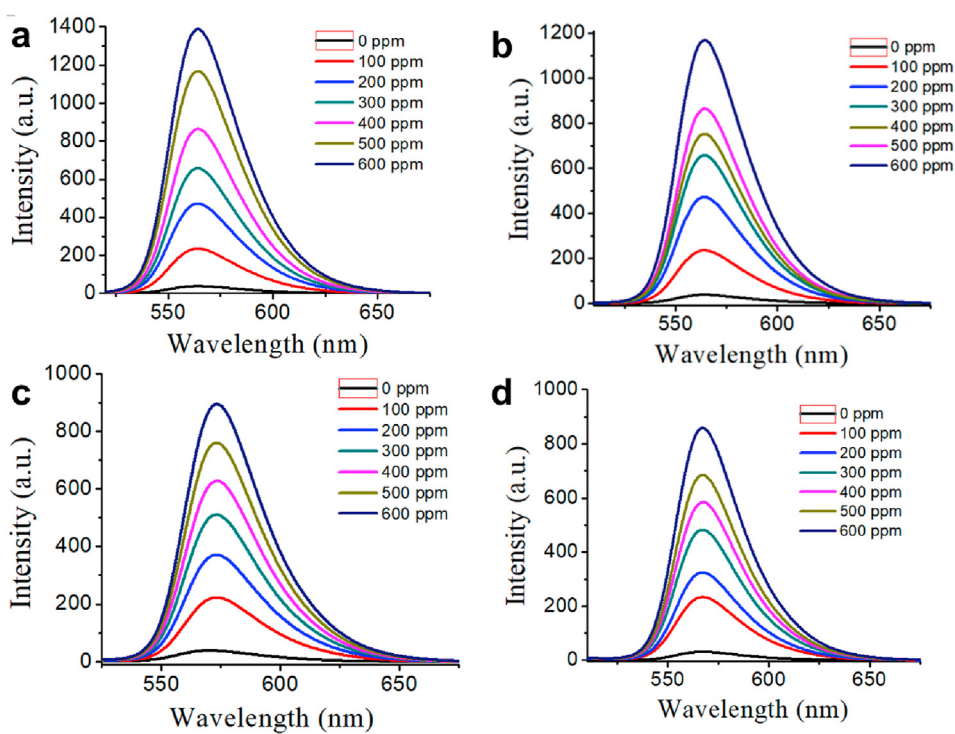


Figure 6. Change in the fluorescence intensity of compound 1 coated TLC plate after the exposure of 100–600 ppm VOC. The excitation wavelength was 405 nm. (a) Benzene vapor, (b) Toluene vapor, (c) Ethylbenzene vapor, and (d) Xylene vapor.

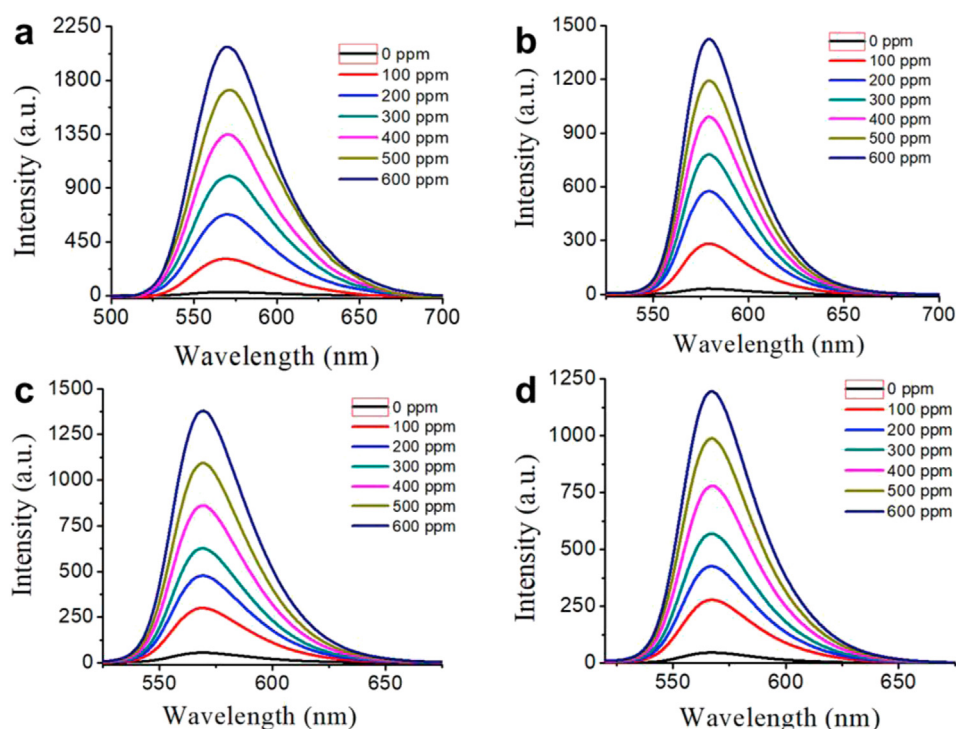


Figure 7. Change in the fluorescence intensity of compound 1 coated TLC plate after the exposure of 100–600 ppm VOC. The excitation wavelength was 405 nm. (a) THF vapor, (b) Acetone vapor, (c) DCM vapor, and (d) Chloroform vapor.

aquarium pump was interacted with the compound 1 coated TLC plate inside the cuvette. We have determined the LOD for various VOCs (Figures S6 and S7) following already existing literatures [65, 66] which is shown in Table S1 (Supporting Information). We plotted $(I-I_0)/(I_{max}-I_0)$ versus $\log[VOC]$ to get a straight line of formula $y = mx + c$. By putting $y = 0$, the value of x was obtained. I_0 and I_{max} is the fluorescence intensity without the VOC vapor and maximum fluorescence intensity after interacting with VOC. I is the fluorescence intensity in between I_0 and I_{max} . The corresponding VOC concentration value was obtained from x which is the LOD. The minimum detection limit of benzene, toluene, ethylbenzene, xylene, THF, $CHCl_3$, CH_2Cl_2 , acetone was found to be respectively 1.4 ppm, 3.9 ppm, 8.8 ppm, 9 ppm, 0.7 ppm, 0.7 ppm, 1.5 ppm, 1.6 ppm. So using the present sensor, we can detect all of these VOCs much below their respective STEL value and the detection limits of our designed sensor have been compared with other recently published research works (Table S2).

A gradual increase in the fluorescence intensity was observed in each case. Figure 8 shows the comparison of various VOC vapor's response towards the sensor using intensity versus concentration plot.

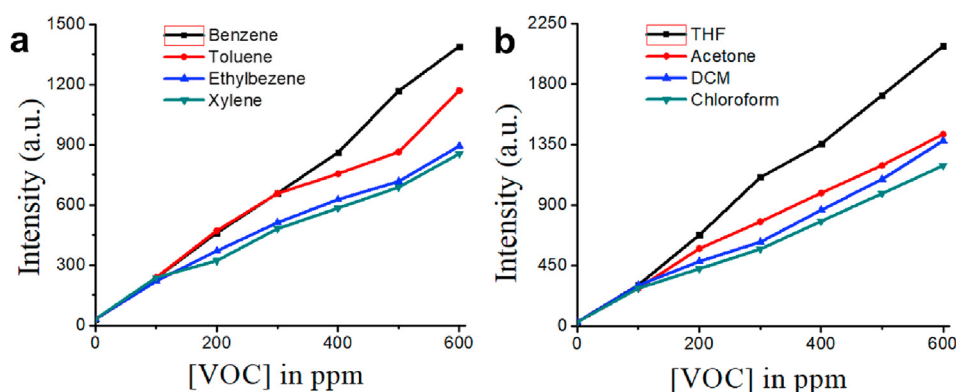


Figure 8. Comparison of fluorescence emission vs VOC concentration for (a) Aromatic VOCs and (b) Non-aromatic VOCs.

We have also compared the enhancement in the fluorescence intensity before and after the VOC exposure using a histogram representation (Figure 9). The maximum intensity enhancement was found to observe in the case of tetrahydrofuran. Significant emission enhancement was also observed for other VOCs like acetone, dichloromethane, chloroform, benzene, toluene, ethylbenzene, and xylene. We have also performed the same experiment with other common organic solvents like hexane, ethyl acetate, acetonitrile, methanol, isopropanol, and heptane. The sensor was exposed to 1000 ppm of these VOC concentrations and their fluorescence intensities were recorded (Figure S8). But only a negligible emission enhancement was observed in these cases (Figure S9). For other common organic solvents like DMSO and DMF, no enhancement was observed at all. In comparison to THF's 67.5 fold emission enhancement, methanol and isopropanol show only 1.4 and 1.3 fold emission enhancement respectively. Hexane, ethyl acetate, acetonitrile, and heptane show 4, 5, 3.5, and 2.2 fold emission enhancement respectively.

So far all the experiments of VOC detection are based on fluorescence spectroscopy. Later we tried to simplify the detection process. We have

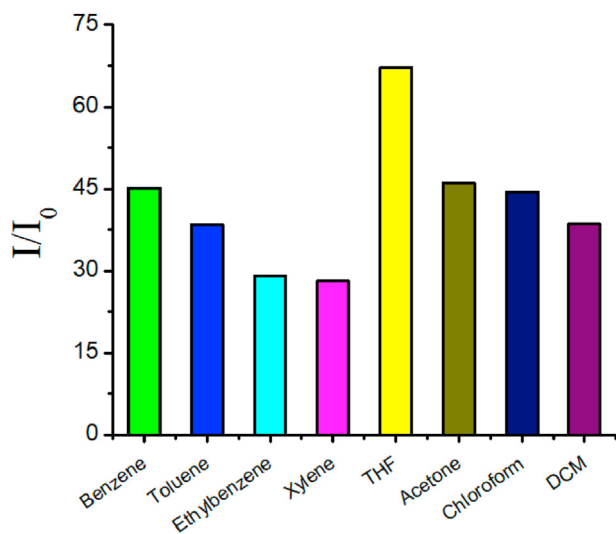


Figure 9. Ratio of fluorescence intensity after and before the VOC exposure.

designed an extremely simple detection method using a smartphone. We have utilized an android app Lux meter and 366 nm UV light for the easy execution of the sensor. Lux meter measures the intensity of the visible light. We have observed that compound 1 coated deep red colored TLC plate (Figure S10a) does not glow under the 366 nm UV light (Figure S10b). But upon exposure of VOC vapor, the same plate shows strong yellow emission (Figure S10c) and the intensity of this emission can be easily captured using a Lux meter. Here one can think why we are using two different exciting wavelengths i.e. 405 nm for fluorometer based detection and 366 nm for the Lux meter based VOC detection. First of all compound 1 can be excited in several wavelengths in UV as well as visible wavelengths like blue light in the presence of various VOCs. But the maximum emission intensity was obtained from compound 1 after exciting at 405 nm. So during our experiments involving a fluorometer, we used 405 nm as the excitation wavelength. But for our smartphone-based detection, we used 366 nm near UV light because of its ease of availability in the lab. Instead of this 366 nm UV light, we can also use blue light as a source of excitation. Both these 366 nm light and blue light are easily available in various e-Marketplaces. Now to measure the light intensity we have prepared a portable set up whose diagram is shown in figure S11 and S12. For mimicking the real sample, here also we prepared different VOC chambers of known concentration in the range of 100 ppm–500 ppm. Then we placed aquarium pumps inside those chambers and the VOC containing air was passed through that pump. During our experiment, we observed fluorescence enhancement from the very first minute of VOC exposure. With the progress of time, the fluorescence value increases, and saturation is obtained within 7–8 min. But we kept the exposure time 10 min to eliminate any chance of underexposure. So the ejected air was finally passed through a syringe and the air was contacted with the TLC plate coated with compound 1 for 10 min. After that, the intensity of the yellow light emitted from that surface was detected using the Lux meter under 366 nm UV light (Table S3 and table S4). For a TLC plate coated with compound 1 (Figure 10a), the Lux meter value is equal to 2 under 366 nm UV light (Figure 10c and supplementary video 2) when there is no VOC. But in the presence of VOC the Lux meter value increased in the case of each VOC vapor. Figure 10b shows the image of compound 1 coated TLC plate after exposure of 200 ppm benzene vapor. The Lux meter value of this benzene vapor soaked TLC plate is 20 under 366 nm UV light (Figure 10d and supplementary video 2).

We have plotted the Lux meter value versus the VOC concentration for all the eight VOCs. Straight-line relationships were obtained for all the cases (Figure 11 and Figure 12). So these lines can be considered as a standard curve and an unknown VOC concentration can be determined from the standard curve. We tried to detect the VOC below 100 ppm level

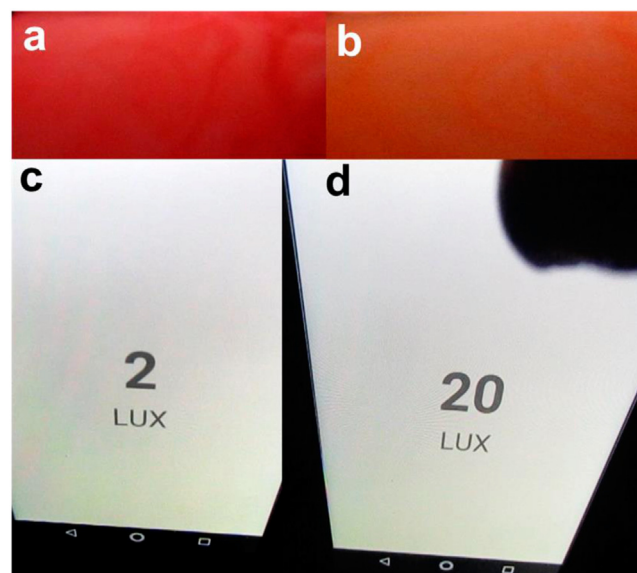


Figure 10. (a) Compound 1 coated TLC plate and (b) Compound 1 coated TLC plate after the exposure of 200 ppm benzene vapor. Lux meter value of compound 1 coated TLC plate (c) before VOC exposure and (d) after VOC exposure.

for all these VOCs. But down to 50 ppm, the detection was found to be reliable. So we can easily detect most of the VOCs below their STEL concentrations using the smartphone which makes the method highly interesting and promising for real-life applications.

The entire Lux meter based experiment was performed using a Moto G5S smartphone. We used the 5 MP f/2.0 inbuilt front camera for the detection process. We downloaded a free android app named 'illumometer lux meter free' made by Shigeto Takagi for the smartphone-based VOC sensing application. To check whether there is any deviation in the Lux meter value after changing the camera we arranged a few more smartphones namely Samsung M30, Oppo F15, and Redmi Note 8 Pro. The detected Lux meter values of a dim light source by these phones were respectively 25, 28, and 24. While the same Lux meter value was 22 for Moto G5S smartphone. So there is a little bit of variation in the detected Lux meter value if we change the camera. So if we want to marketize this sensor along with a camera as a product, then we have to use a camera of the same configuration for the entire batch to ensure the reliability and accuracy of the result. Here one can think whether our sensor can be applied for widespread use. Currently, each one of us is using smartphones for our various daily life activities. From this point of view, we can say that the main component of the sensor is already in our hands. The extra thing that we need is a sensor coated TLC plate and a 366 nm light or a blue LED light source for the detection of VOC. The cost of the sensor compound 1 is around 10 rupees per gram and a few mg samples is sufficient enough for sensor fabrication. That is why the presented method will be extremely cost-effective as compared to the sophisticated VOC sensors available in the market. Yes, the Lux meter value will be a little bit different for different smartphones. So for marketizing only the sensor plate along with blue or 366 nm UV light source as a product, we have to prepare a list of smartphones available in the market and their standard detection values have to be mentioned on that list.

Later we checked the effect of distance between the camera and sensor surface on the value of Lux meter. The distance between the smartphone camera and compound 1 coated TLC plate affects the detection process. The principle of Lux meter is based on the intensity of the light reaching the smartphone camera. With increasing distance from the light source the intensity of the light decreases. With reducing the light intensity, the Lux meter value decreases. During our experiment, we maintained a distance of 1 cm between compound 1 coated surface and the smartphone camera. Then we investigated the effect of intensity of

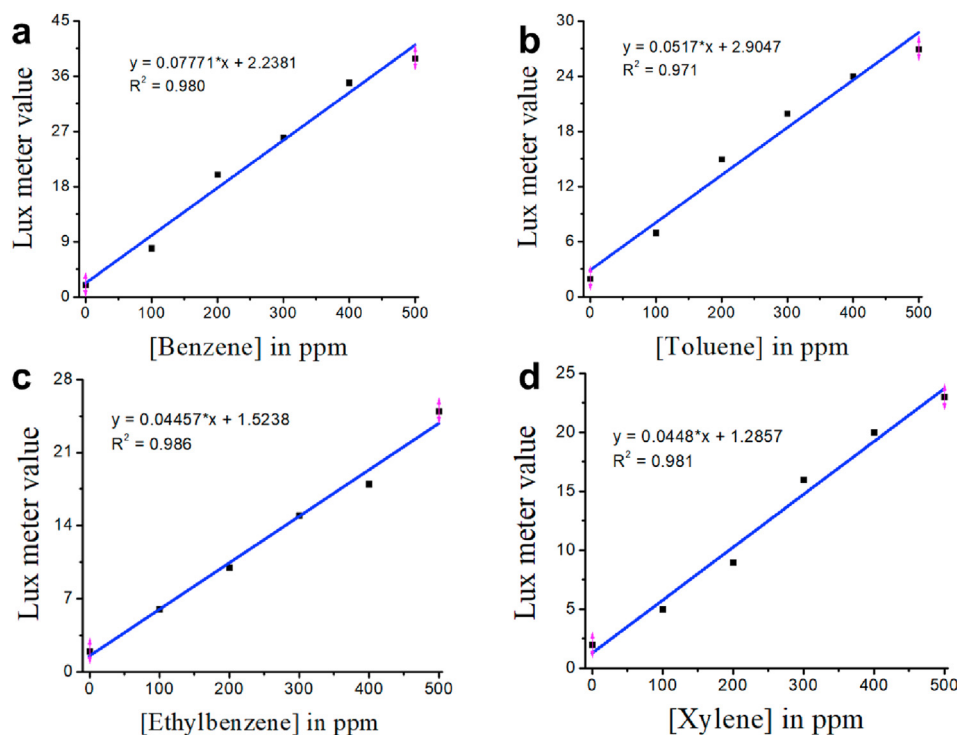


Figure 11. Plot of Lux meter value of compound 1 coated TLC plate vs VOC concentration in the range of 100–500 ppm. (a) Benzene vapor, (b) Toluene vapor, (c) Ethylbenzene vapor, and (d) Xylene vapor.

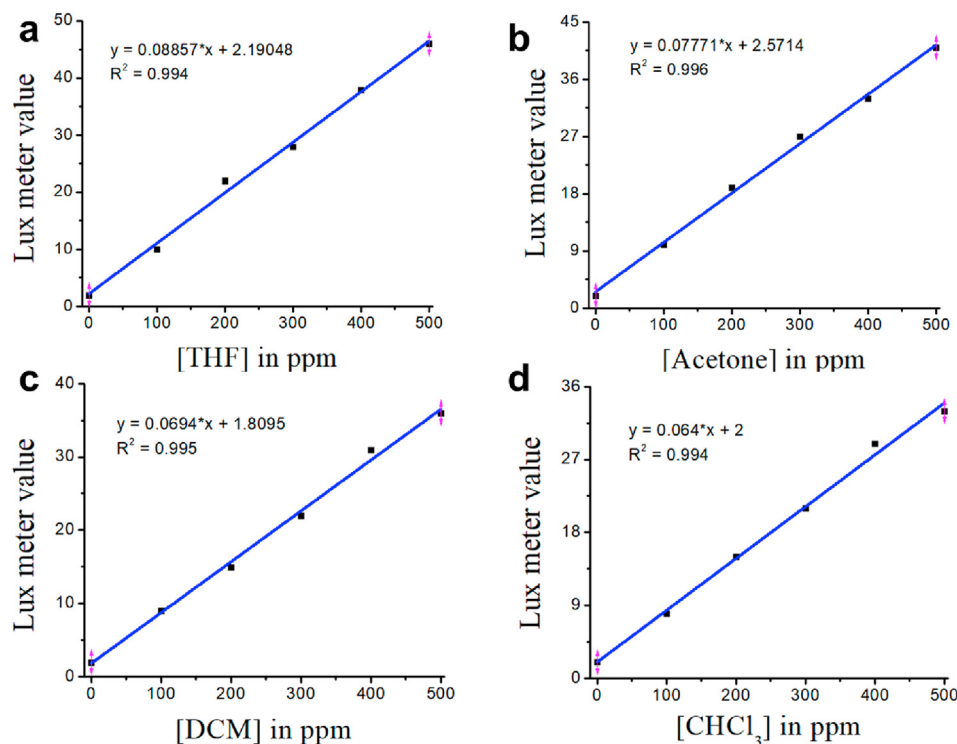


Figure 12. Plot of Lux meter value of compound 1 coated TLC plate vs VOC concentration in the range of 100–500 ppm. (a) THF vapor, (b) Acetone vapor, (c) DCM vapor, and (d) Chloroform vapor.

exciting light during the VOC measurement. We observed that the increase in the exciting light's intensity increases the fluorescence emission from the coated surface and so does the Lux meter value. But for an intense exciting light, we have to make sure that the exciting light is not reaching the camera of the smartphone. So we placed the sensor plate

and smartphone camera parallel to each other. The light source was guarded using a mirror film in such a way that it can only illuminate the surface of the sensor plate. No exciting light was allowed to enter the camera. Otherwise erroneous results will be obtained. During our entire experiment, we have taken enough precautions to avoid such kind of

error. During the use of the Lux meter if an erroneous result is obtained then we have to perform a step in the smartphone to rectify the problem. In the Lux meter app, there is a reset button. By pressing this button, we can reset the settings. By doing this we can avoid any chances of error due to the Lux meter.

Now for the real-life application of a VOC sensor, the sensor material must be highly stable under adverse atmospheric conditions. Luckily compound **1** is robust. The melting point of this compound is 180 °C and we did not observe any color fading phenomenon of the sensor coated TLC plate with time. After using the sensor for one month, we retrieved the sensor compound from the surface and it was checked using thin layer chromatography taking pure compound **1** as a reference. The study reveals that there is no degradation of compound **1** during continuous use. We have tested the equal efficacy of this sensor in artificially prepared dry as well as humid conditions. So regarding the chemical and thermal stability, there is no problem with compound **1**.

We have also checked the efficiency of the reported sensor against a mixture of VOCs. Like the individual VOC, here also we observed enhanced fluorescence intensity. The enhanced fluorescence intensity was found to be almost additive (Table S5). This indicates that there is no competition of one VOC over the other VOC towards the sensor plate. For example, we have prepared various mixtures of VOCs like 100 ppm THF & 100 ppm xylene, 100 ppm benzene & 100 ppm CHCl₃, 100 ppm acetone & 100 ppm DCM, 100 ppm acetone & 100 ppm ethylbenzene, 100 ppm xylene & 100 ppm ethylbenzene, 100 ppm DCM & 100 ppm CHCl₃, etc. Their Lux meter response value was recorded (Table S5). From this study, we can say if we are fully aware of the leakage of any particular VOC then we can detect the VOC concentration exactly. But in the case of unknown VOC mixtures, we have to report the result in the form of a range. We have considered the highest and lowest emission out of the eight VOCs to guess a range of VOCs. For example, THF exhibits the maximum emission and xylene exhibits the minimum emission in the entire set. A 100 ppm THF atmosphere shows 10 Lux value while 100 ppm xylene shows 5 Lux value. So if an unknown air sample exhibits a Lux value of 10 then the expected unknown VOC concentration must be in the range of 100–200 ppm i.e. 100 ppm THF or 200 ppm xylene or other VOCs in between 100–200 ppm range. We have made the calculation simpler. For an unknown air sample, we have to project the fluorescence intensity or Lux meter value in the standard curve of THF. If the corresponding VOC concentration is found to be x ppm then we have to publish the report in the range of x to 2x ppm. The VOC concentration will definitely lie in this range. But this can be considered as a limitation of this sensor.

Then we were curious to compare our designed sensor with an already existing sensor available in the market. Alvens digital gas detector alarm, which works based on the change of resistance, was utilized for the comparison. It is not a selective sensor and it can detect wide varieties VOCs. So inside a fume hood chamber, we spread a few ml benzene. After closing the fume hood and waiting for one hour, the benzene vapor concentration was detected by both the methods. The result from our designed sensor was found to be 929 ppm. On the other hand, the Alvens gas detector showed a value of 1000 ppm. Though these two values are not exactly the same, they are close enough and this experiment reinforces the chance of practical applicability of our designed sensor.

4. Conclusion

We have developed a cost-effective VOC sensor using Meisenheimer complex **1** produced from picric acid and N,N'-dicyclohexylcarbodiimide. The actual VOC sensor was fabricated by coating compound **1** over the silica gel TLC plate. The sensor i.e. compound **1** coated TLC plate showed only a negligible fluorescence under 366 nm UV light. But in the presence of some of the VOCs, compound **1** coated TLC plate starts to show a yellow glow. We utilized this property to detect the VOCs by fluorescence spectroscopy. Only in case of a limited VOCs such as benzene, toluene, ethylbenzene, xylene, THF, CHCl₃, CH₂Cl₂, and

acetone significant fluorescence enhancement was observed. For other VOCs like hexane, methanol, ethyl acetate, acetonitrile, heptane, and isopropanol negligible response was observed. The detection limit was found to be 0.7 ppm for THF and 1.6 ppm for benzene. To make the sensor user friendly, we have designed a set up where VOCs can be detected using a smartphone if the VOC concentration is above 50 ppm. This method can be utilized for the detection of VOCs in real-time and portable basis.

Declarations

Author contribution statement

Statement Tanmay Das: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mrityika Mohar: Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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The authors declare no conflict of interest.

Additional information

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