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ARTICLE

Instant Detection of Picric Acid Vapour by Developing Layer by Layer Polymer Detectors and an Electronic Prototype†

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Detection of ultra-trace amount of picric acid have attracted substantial efforts from the perspective of health, safety and environment. Due to very low vapour pressure, the detection of picric acid vapour is quite challenging in comparison to that of the liquid phase. In this work, we have overcome this problem by developing layer by layer polymer detectors and an electronic prototype for instant detection of ppm level concentration of picric acid vapour via impedance spectroscopy. The detectors constitute of mainly two polymer layers with poly-cholesteryl methacrylate sulfonated hexene as the two outer layers and copolymer of 2-vinyl pyridine with acrylonitrile as the middle layer. In presence of the analyte, the detectors undergo steep decrease in impedance within few seconds. The thickness of the individual polymer layers play a vital role and it was observed that the detector with thinner outer layers (0.25 mm) is more efficient as it shows about 99 % decrease in the impedance for 0.334 ppm of picric acid vapour within 10 seconds. The method is selective, the effect of varying humidity is negligible and the detection limit was found to be 0.006 ppm. Moreover, the detectors show reproducible results and are also consistent for a long period. Using these detectors, we have designed an electronic prototype for visual detection of picric acid at room temperature. Unlike other sophisticated techniques the prototype is simple, portable, cost effective and can be used for detection of such higher explosives due to various implications such as homeland security, forensic and criminal investigations and remediation of explosive manufacturing sites.

1. Introduction

Chemical warfare agents and explosives are considered as the two of the most rigorous threats used in terrorist and warfare activities.¹ Nerve gas attacks on civilians in Syria in 2013 and Boston Marathon bombing are the burning examples of such activities. Instant and selective detection of ultra-trace amount of explosives has been found to be one of the most demanding topic in research due to its implications in various important aspects such as homeland security, remediation of explosive manufacturing sites, tactical and humanitarian demining, forensic and criminal investigations, and so on.²⁻⁴ Various techniques are also available for such purposes. The most common techniques are the metal detectors and train dogs; however, these techniques have their own limitations. The metal detectors cannot trace the explosive kept in plastic casing. Use of trained dogs are difficult to maintain, very expensive and also easily fatigued.⁵

Nitroaromatic chemicals (NACs) are being used to prepare explosives worldwide since world war-I. Among all other NACs, 2, 4, 6-trinitrophenol, commonly known as picric acid (PA) has been

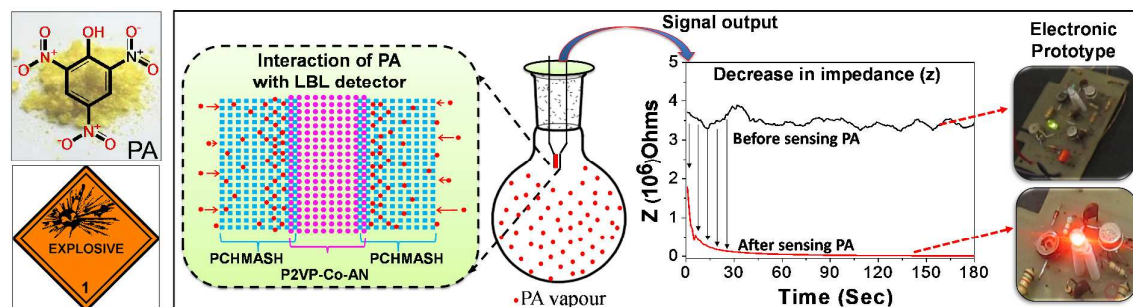
demanding social concern because of its highly explosive nature. It is employed in lethal weapons and its explosive power is reported to be higher than 2, 4, 6-trinitrotoluene.⁶ Its explosive nature develops from the chemical composition, very low vapour pressure and high volatility.⁷ PA is being used along with other explosives which upon initiation undergo very high exothermic reactions and releases toxic gaseous products.⁸ In addition, PA is water soluble and its extensive use in large scale industries such as pharmaceuticals, dyes, matches etc. may increase the probability to be released to the environment which further causes adverse health conditions, soil and water pollution.^{9,10} According to the material safety data sheet, over exposure to PA causes anaemia, liver function disorder, cataract, skin and eye irritation, unconsciousness or death.¹¹ Therefore, in recent years development of methods for detection of PA from the suspected sites have attracted a substantial research efforts. But practically, the detection process takes place in very complex environments such as blast sites, mine fields, wastewater treatment plants etc.¹² In such sites, the presence of other contaminants along with PA and their amounts are undefined. Under such circumstance, selective and sensitive detection of PA becomes a very challenging task. Different methods and analytical techniques have been developing for the selective detection of NACs such as fluorescence,¹³⁻¹⁷ gas chromatography and electron capture,¹⁸ voltametric,¹⁹ cyclic voltammetry,²⁰ surface enhanced raman spectroscopy,^{21, 22} fibre optic detection,²³ energy dispersive X-ray diffraction,²⁴ nuclear

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quadrupole resonance,²⁵ amperometry,²⁶ gas chromatography coupled with a mass spectrometer²⁷ etc. Although,



Scheme-1: Schematic representation of the chemical structure of PA and the protocol for the detection of PA vapour using LBL detectors via impedance (Z) measurements with time and the electronic prototype for visual detection of such chemicals.

most of the processes suffer different issues like portability, very expensive, low selectivity, sensitivity etc. which makes them impracticable to be applied on real sites.

The vapour phase detection of NACs is quite challenging in contrast to solution phase detection. Sensing systems cannot produce measurable signal output with fast response in presence of very low concentrated analyte vapour in real time. In this work, we have overcome such disadvantages by developing layer by layer (LBL) polymer detectors of two organic polymers viz. poly-2-vinyl pyridine with acrylonitrile (P2VP-Co-AN) and copolysulfone of cholesterol methacrylate with hexane (PCHMASH) which undergo drastic change in impedance in presence of very low concentration of NACs vapour within few seconds. Here, PA was chosen as the model NAC. Using the LBL detector we have successfully developed a very simple, efficient and cost effective electronic prototype for visual detection of PA. The method developed in this work for the detection of PA vapour is demonstrated in Scheme-1.

2. Experimental Section

2.1 Materials: Cholesterol (LOBA-Chem), Acrylonitrile (Ranbaxy), 2-vinyl pyridine, Ethyl Methyl Ketone, Triethyl amine, Azobisisobutyronitrile-AIBN (Sigma), Methanol, 2, 5-dinitrosalisyllic acid (DNSA), nitrobenzene (NB), 1,4-dinitrophenol (DNP), o-nitrophenol (ONP), p-nitrophenol (PNP) were purchased from Merck and used without further purification. PA was purchased from SIGMA.

Caution! PA should be handled with extreme caution and also should be used in small quantities. Personal protective equipment must be worn while handling such chemicals. PA is stored in 50 % of water as recommended by the chemical company and vacuum dried before the sensing experiments.

2.2 Preparation of methacryloyl chloride: Preparation of methacryloyl chloride is previously reported elsewhere.²⁸

2.3 Synthesis of PCHMASH: Synthesis and characterization of PCHMASH is already reported elsewhere.²⁹ Very briefly, cholesterol methacrylate (CHMA) and n-hexene (1:1 mole ratio) was dissolved

in chloroform and transferred into a vacuum tube. A mixture of t-butylhydroperoxide and methanol was then added to the reaction mixture. The reaction tube was inserted into a 1.5 litre liquid N₂ canister at below 0 °C and the tube is evacuated by rotary vacuum pump. In a separate set-up, SO₂ gas was prepared in Kipp's apparatus and passed through the reaction mixture and the reaction tube was sealed for about 3 hours at below 0 °C. Finally, the reaction mixture was poured in acidified methanol to recrystallize white polysulfones of CHMA. The residue was washed with hot water for several times. We named it as poly-cholesteryl methacrylate sulfonated hexene (PCHMASH). The synthesized polymer was previously characterized with the help of FT-IR, NMR, GPC, TGA, DSC and hot stage optical microscope. It is a liquid crystalline polymer and possesses typically temperature sensing properties based on which we have already designed thermistor type safety devices. Its electrical, thermal and liquid crystalline properties were also well studied.

2.4 Synthesis of P2VP-Co-AN: 2-vinyl pyridine (2-VP) and acrylonitrile (AN) were mixed into 1:1 molar ratios and stirred for about half an hour. To this mixture solution very small amount of AIBN was added as initiator and connected to a vacuum pump for about 1 hour to remove the dissolved gases. After complete removal of the dissolved gas molecules the temperature of the reaction mixture was maintained at 60 °C for about 24 hours. The product so obtained was dissolved in chloroform and re-precipitated in distilled water. This final product was repeatedly washed with distilled water and stored in vacuum desiccator over fused CaCl₂. The polymer so obtained was well characterized in our previous work.³⁰

2.5 Physical Measurements: FT-IR spectra were recorded using Nicolet 6700 FT-IR in the range of 650-4000 cm⁻¹. The spectra were collected in ATR mode with a resolution of 4 cm⁻¹ over 32 scans. Impedance (Z) measurements of the LBL detectors in presence of NACs were performed in HIOKI 3532-50, LCR HI-TESTER.

3. Results and discussion

3.1 Fabrication of the detectors and working mechanism: To fabricate the monolayer polymer detectors, the polymers P2VP-Co-

AN and PCHMASH were finely grinded and then separately inserted in between two stainless steel (SS) mesh with 1 cm^2 area with pore size of $200 \mu\text{m}$ and thickness of 0.23 mm by gentle pressing. Both the SS mesh were previously soldered with Cu-wire which are further to be connected with the two probes of impedance analyser for sensing experiments. After deposition of the polymer layers the meshes were hold together by strong solid binder and kept under vacuum desiccator. To fabricate the LBL detectors, firstly, a known amount of PCHMASH was deposited on two SS mesh separately and gently pressed. The thickness of these layer were determined with the help of a screw gauge. Secondly, the middle layer, i.e. P2VP-Co-AN was deposited on one of the PCHMASH layers and pressed gently to form a double layer of P2VP-Co-AN and PCHMASH. The thickness of this second layer was calculated by deducting the thickness of the SS mesh and the PCHMASH layer from the total thickness. Finally, the remaining PCHMASH layer with the SS mesh was placed above the P2VP-Co-AN and PCHMASH double layer and the whole LBL polymer matrix with SS meshes were strongly hold together with solid binder. The thickness of the individual polymer layers were alternately changed to investigate the effect of thickness toward the sensitivity for NACs as shown in Table-1. Here, two sets of detectors were fabricated.

Table-1: LBL detectors and the thickness of the individual polymer layers

| Detectors | | Thickness in mm | |
|---------------------|------------|-----------------|--------------|
| | | Outer layers | Middle layer |
| 1 st set | Detector-1 | 0.25 | 0.40 |
| | Detector-2 | 0.35 | 0.40 |
| | Detector-3 | 0.45 | 0.40 |
| 2 nd set | Detector-4 | 0.25 | 0.50 |
| | Detector-5 | 0.25 | 0.60 |

In reference to Scheme-1, the LBL detectors were exposed to the vapour of NACs and the change in the Z values were recorded with respect to time in seconds. For the impedance measurements, an external bias of 0.1 V was applied to the detectors and the corresponding Z values were recorded for 180 seconds. Within this period, all the detectors show steady Z in the semiconducting range (10^6 Ohms). During the sensing experiments, the analyte molecules instantly interacts with the LBL detectors which causes a remarkable decrease in Z of the detectors with time to the conductor range. The concentration of the vapour was maintained by heating a definite amount of the dry solid analyte. The vapour concentration at different temperatures are given in Table S1[†]. The selectivity, reversibility and stability of the detectors were checked and at the final stage, we have used the LBL detectors to fabricate an electronic prototype for detection of the analyte. This prototype is based on instant decrease in the Z of the detectors from semiconducting range to the conducting range in presence of the analyte which helps in visual detection with the help of light emitting diode (LED) connected to the circuit of the prototype.

3.2 Sensing studies: Fig. 1 depicts the Z versus time plot of Detector-1 in presence of PA vapour. The detector showed an instant and very steep decrease in the Z in presence of the analyte vapour. It was observed that the sensitivity of the detectors increases with increase in the vapour concentration of the analyte. A comparative study of the results of all the LBL detectors was carried out and it was found that the sensitivity of the Detector-1, i.e. with thinner outer layer is higher than that of the other LBL detectors. The sensitivity of the remaining detectors are presented in Fig. S1-S4[†]. The sensitivity of the monolayer polymer detectors was also monitored and it was observed that these detectors are not efficient in sensing PA vapour, a brief discussion is given in Fig. S5[†]. Interestingly, combination of the two polymers in LBL detectors with PCHMASH as the outer layers showed a significant change in Z with time in presence of PA. But the LBL detector with P2VP-Co-AN as the outer layers is inactive towards PA vapour detection as demonstrated in Fig. S6[†]. The probable reason is that PCHMASH being an electron rich polymer with high negative surface zeta potential (ζ) of about -37.9 mV enhances the interaction of the LBL detector with the electron withdrawing analyte. On the other hand, P2VP-Co-AN is almost a neutral copolymer with ζ only about -2.42 mV . The ζ distribution of these two polymers are given in Fig. S7[†].

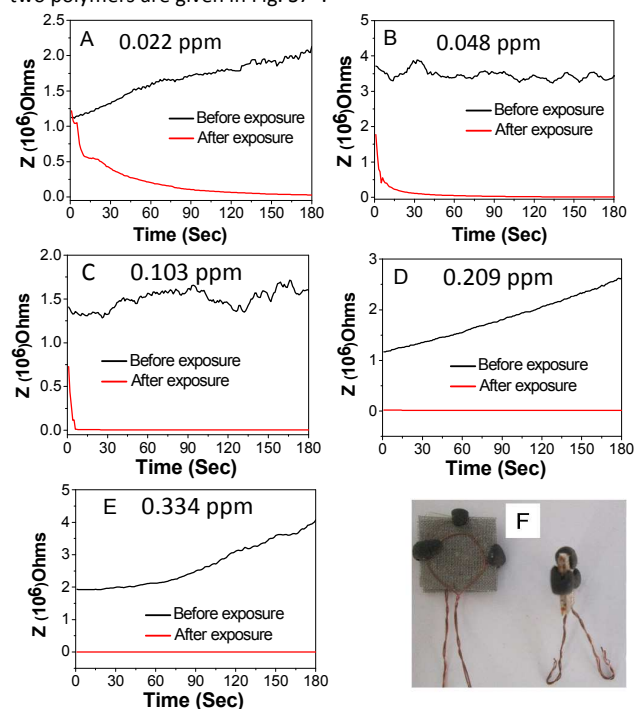


Fig. 1: Impedance (Z) versus time (sec) plot for the Detector-1 in presence of A. 0.022, B. 0.048, C. 0.103, D. 0.209, and D. 0.334 ppm of PA. F. Photograph of the Detector-1.

From the above results as evident from Fig. 1, it is clear that the Z values of Detector-1 steeply decreases within 10 seconds in presence of PA. Therefore, it was assumed that the response time of the Detector-1 toward NACs is about 10 seconds. Similarly, for the remaining detectors the change in the Z values with 10 seconds can be clearly observed in Fig. S1-S4[†]. Compared to the previously

reported works, such small response time is fair enough to carry out experiments for the sensing of NACs. A comparative study of the results of the present methods is given in section 3.6. From the Z versus time plots of all the detectors we have calculated the % Z values for the first 10 seconds of interaction with PA and then plotted in Fig. 2. From these plots it is evident that each detector shows lower value of Z for higher concentration of the analyte vapour. It was observed that, all the detectors show increasing sensitivity at higher concentration of the analyte vapour and depending on the thickness of the individual layers their sensitivities are different. In this regard, Detector-1 (with 0.25 mm outer layers) shows highest sensitivity as its % Z values almost reaches to its saturation point (minimum value) at 0.103 ppm of PA. At 0.209 ppm and 0.334 ppm, the % Z values are negligibly small. But when the thickness of the outer layers were increased to 0.35 mm and 0.45 mm in Detector-2 and 3, the % Z values did not reach the saturation point and hence their sensitivity towards PA decreases. This indicates that, greater is the thickness of outer layer lesser is the efficiency of the detector for sensing the analyte. For farther analysis of these results, the % decrease in Z within 10 seconds were calculated. For Detector-1, at lower concentration of PA vapour, i.e. 0.022 ppm, the % decrease in Z is 18.28 % and it steeply drops to 80.25 % when the concentration of PA is 0.048 ppm. At higher concentration of PA i.e. at 0.209 and 0.334 ppm, the values are almost 99 %. Therefore, the sensitivity of Detector-1 increases with the increase in the analyte concentration. But for Detector-2 and 3, the % decrease in the Z values is not as efficient as the Detector-1. For Detector-4 and 5 (where the thickness of the outer polymer layers are 0.25 mm), the results do not vary significantly. Both the detectors are almost equally efficient in sensing PA vapour and also shows a linear relationship with increasing concentration of the analyte (discussed later) which indicates that the thickness of the middle layer has minimal effect toward the sensitivity for PA.

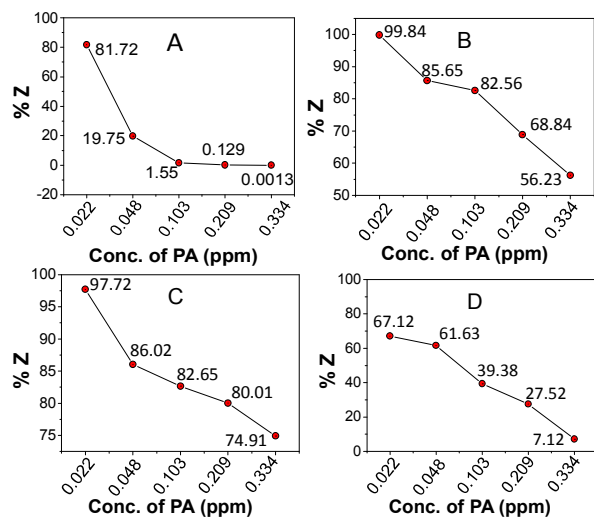


Fig. 2: % Z versus picric acid (PA) vapour concentration (conc.) plot of A. Detector-1, B. Detector-2, C. Detector-3, D. Detector-4 and E. Detector-5.

We have constructed the calibration curves for Detector-4 and Detector-5 as depicted in the Fig. 3. Here, the error bars indicates ± 3 standard deviations (SD). The limit of detection (LOD) are determined with the help of the equation $3.3 \times \text{SD}/\text{slope}$.³¹ Considering the data points of 0 ppm and 0.022 ppm, LOD are calculated to be 0.006 and 0.007 ppm for Detector-4 and -5 respectively. The corresponding limit of quantification (LOQ= $10 \times \text{SD}/\text{slope}$) are 0.022 and 0.024 ppm respectively. Interestingly, for Detector-1, 2 and 3, the decrease in the Z values with increasing concentration of PA is very steep and hence the calibration curves do not meet the statistical criteria of linearity.

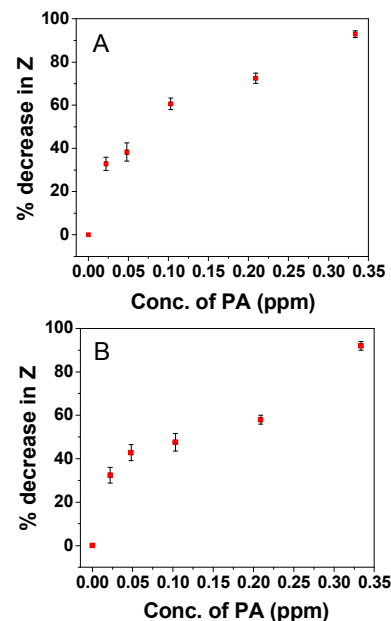


Fig. 3: Calibration curves for A. Detector-4 and B. Detector-5 for calculation of limit of detection.

To assess the selectivity of the LBL detector toward PA vapour, we have carried out sensing experiments for other NACs vapours viz. NB, DNSA, DNB, ONP, PNP and some other common laboratory chemicals like phenol, benzene, ethanol, acetone, ammonia, nitric acid and sulphuric acid. As shown in the Fig. 4, the Z values of the Detector-1 gradually decreases in presence of NB w.r.t time. However, unlike PA vapour it was found that the detector undergoes only about 7.44 % decrease in impedance within 10 seconds. For the remaining NACs and the common laboratory

chemicals and strong acid vapours, the sensitivity is very negligible. Such high selectivity for a particular analyte, negligible sensitivity for common laboratory chemicals, low response time (less than 10 seconds) are very important for an efficient sensing process. We have also investigated the effect of varying humidity conditions toward the sensitivity for PA. Fig. 5A, B depicts that, the sensitivity Detector-1 for PA vapour is almost same in all the experimental humidity conditions. This is a great advantage of this method that the LBL sensors are capable of detecting the analyte vapour at any humidity condition. In general, varying humidity has an adverse effect on sensor systems and their efficiency. In our case, it can be said that there is no interaction in between the vapour phase water molecules with the materials of the LBL detector and thus the sensitivity of the detectors are same at different humidity.

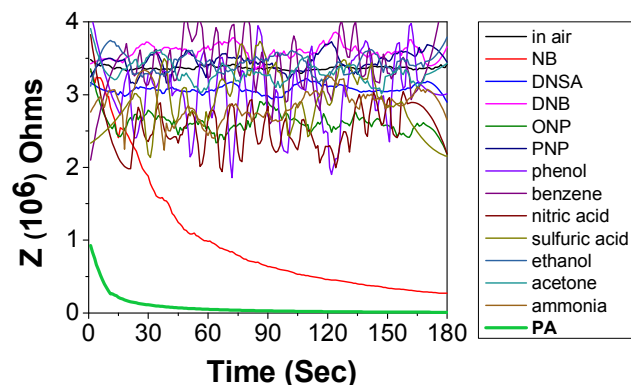


Fig. 4: Z versus time (sec) plot of the LBL detector in presence of different NACs and common laboratory chemicals at room temperature.

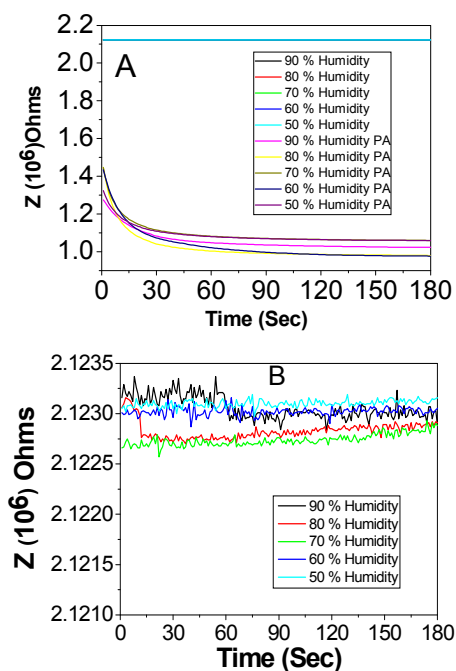


Fig. 5: A. Z versus time (sec) plot of the LBL Detector-1 in presence of PA vapour at varying humidity conditions at room temperature, B. Z values of the detector with time at different humidity.

3.3 Reproducibility and stability of the LBL detector:

Reproducibility of results is very important for any sensor system from the viewpoint of practical use. Sensors which are unable to reproduce experimental data are not generally preferable. In this present context, the results of the LBL detectors are reproducible as its original state is very easily achieved after each sensing experiment. We have carried out 20 consecutive sensing experiments using the Detector-1 at PA concentration of 0.01 ppm. In Fig.6 the plots for 1st, 4th, 8th, 12th, 16th and 20th consecutive measurement are shown. Here, after each sensing experiment hot air stream (about 70 °C) was blown on the detector for about a minute with the help of a conventional drier and then the detector was kept under ambient air for about two minutes to reach its original Z. The detector is remain connected to the impedance analyser during this recovery process and the measurements were constantly carried out with time. The blue lines in the plots of Fig. 6 represents the reproducibility of the detectors for the consecutive measurements. This line clearly indicates that, the detector regains its original values within 180 seconds. Since the concentration of PA vapour is very low, the analyte molecules present in the detector can be removed just by employing such an easy process which helps regain its original Z.

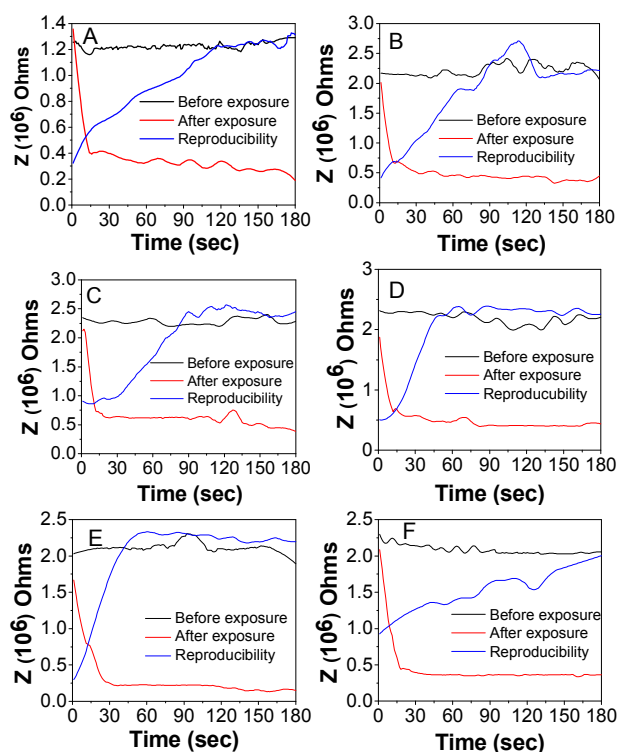


Fig. 6: Reproducibility: Impedance (Z) versus time (sec) plot for Detector-1 during A. 1st, B. 4th, C. 8th, D. 12th, E. 16th and F. 20th

consecutive measurements with PA concentration of 0.01 ppm at 25°C.

The stability of the LBL detector was determined by performing the sensing experiment with a single detector for seven consecutive days and the results are plotted in Fig. 7. It shows that the sensitivity of the LBL detector for PA vapour is consistent with about 1.86 % standard deviation. From this study, it can be said that the LBL detectors are stable i.e. the results do not vary with time scale and hence the same detector can be used to perform sensing experiments for several days. Varying humidity conditions are directly related to the stability of any chemical sensor. It was previously mentioned that the sensing efficiency of LBL detector do not alter with varying humidity which indicates that humidity do not change the materials properties of the LBL detectors. Negligible effect of humidity could be the main reason behind the good stability of the LBL detectors.

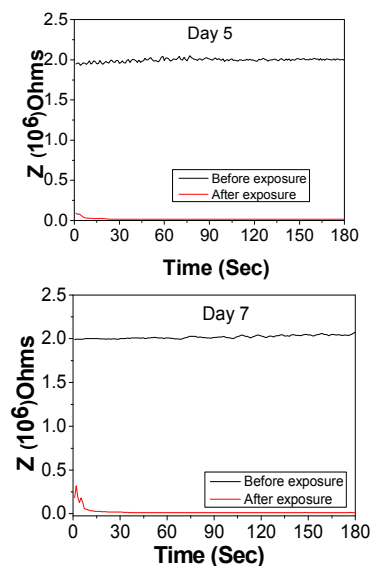
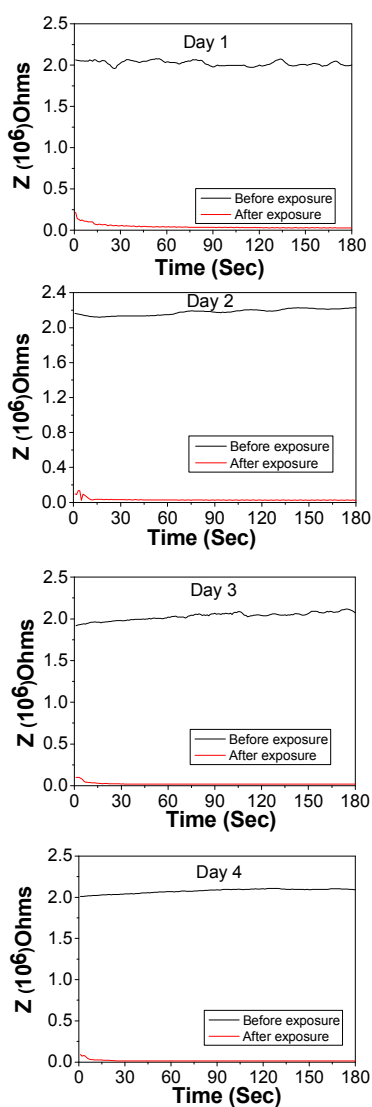
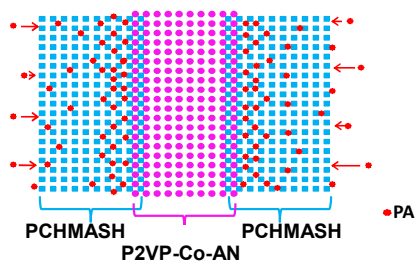


Fig. 7: Stability measurements: Z versus time (sec) plot for the detector in presence of PA vapour for seven consecutive days.

3.4 Mechanism: The change in the Z values of the LBL detector results from the electronic movements within the system. With three $-\text{NO}_2$ groups, the electron withdrawing nature of PA is higher than the other NACs used in the experiments and hence it preferably interact with the electron rich outer layers (PCHMASH) of the LBL detectors. This interaction is facilitated by the external bias voltage of 0.1 V applied on the LBL detector to carry out the measurements. The key role of the external bias is that, it stimulates the electron density of the outer layers and hence the LBL detector act as electron donor towards the electron withdrawing analyte. By withdrawing the electrons from the outer layers, the analyte molecules get physically adsorbed at the interface between PCHMASH and the neutral polymer P2VP-Co-AN (Scheme 2) which further enhances the electronic migration within the system and hence decreases its Z values. For the detector with thinner outer layers, the physisorption of the analyte is easier compared to the remaining LBL detectors with higher thickness, which is the probable reason for very steep decrease in impedance of the former. Since physisorption is a reversible process, the analyte molecules can be easily removed from the LBL detector by blowing hot air stream as mentioned in section 3.3. We have observed that the oxidation-reduction behaviour of the materials remains unchanged (Fig. S8†) after the interaction with PA, which would have been changed if the process involved permanent oxidation of the material. This is also very important for the reversibility of the system. Unlike chemical adsorption processes, physical adsorption doesn't alter the original chemical structure of the sensing materials which is confirmed with the help of FT-IR spectral analysis of the polymers after exposure to PA vapour with increasing time scale as discussed below.



Scheme 2: Pictorial representation for the interaction of the PA molecules with the LBL detector.

Fig. 8 A, B depicts the FT-IR spectra of the polymers scaled out from the detectors that has been exposed to PA vapour for 1, 3, 5, 10 and 24 hours. The spectra of both the polymers are exactly the same before and after sensing PA even after 24 hours exposure time which indicates that there is no change in the chemical structures of the polymers after interaction with PA. The FT-IR peak analysis of the polymers is given in Table S2[†] and Table S3[†]. It is assumed that PA molecules get loosely bound to the interfaces of the LBL detectors causing drastic changes in its electrical properties. It is easily removable from the detectors by blowing hot air and thus the original state of the detectors can be regained.

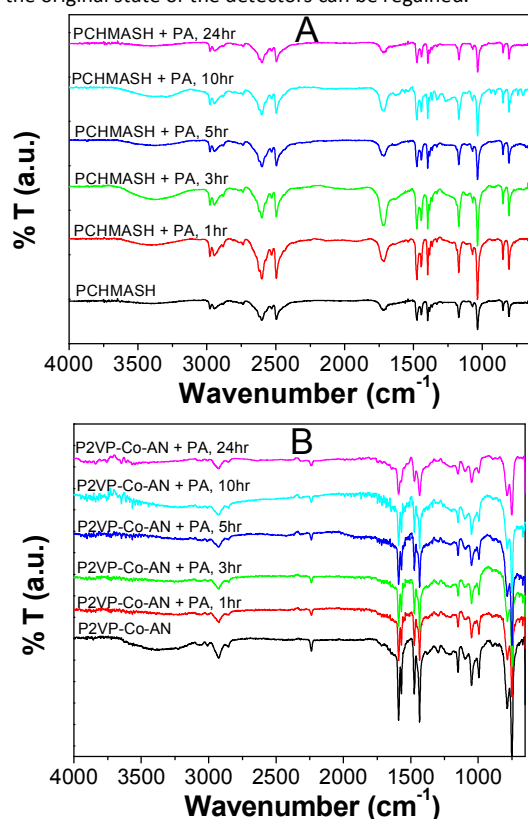


Fig. 8: Comparison of the FT-IR spectra of A. PCHMASH and B. P2VP-Co-AN after exposure to PA vapour at different time scale.

3.5 Fabrication of the electronic prototype for sensing NACs based on the LBL detectors: After the laboratory tests for sensing PA vapour, we have designed a prototype sensor device using the LBL detector to explore its potential use for practical application. To do

this, firstly we have checked the frequency used in the impedance analyser where we get maximum sensitivity for the detector. After thorough examination the optimum frequency was found to be 10 KHz and therefore the oscillator circuit designed for the prototype uses a sinusoidal oscillation frequency of 10 KHz. The circuit basically is a Wien-Bridge Oscillator using LM741 operational amplifier (op-amp) followed by CA3140 op-amp which act as a comparator. A dual power supply is used to power up the circuit which develops a sinusoidal wave above and below 0 volt. Initially at the beginning of the experiment due to absence of any analyte, the detector remains at a very high impedance and therefore, a very little current is able to pass through it. Since, the voltage developed at the output of the detector is rectified, filtered and then fed to the non-inverting input of the op-amp, the output of the op-amp remains in 'off' state. When the detector absorbs analytes, its impedance falls. This cause an increase of the flow of current to the comparator op-amp. When a sufficient voltage is developed at the non-inverting input of the op-amp and crosses the threshold point, it turns the output from 'off' state to 'on' state and the bicolour flickering LED connected to the output start glowing. Red part of the bicolour LED glows first because it require less current compare to the blue one. The change in the colour of the diode at different time of exposure is shown in the Fig. 9. The circuit diagram of the electronic prototype is shown in Fig. 10. The final wave front generated from this prototype as seen in the oscilloscope is shown in Fig. S9[†].

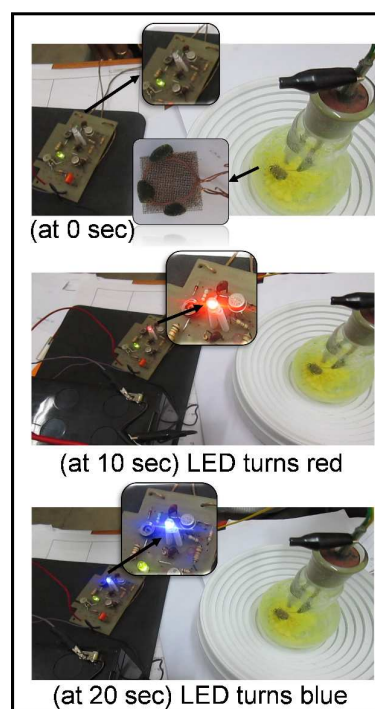


Fig. 9: The change in the colour of LED at different exposure time to PA vapour.



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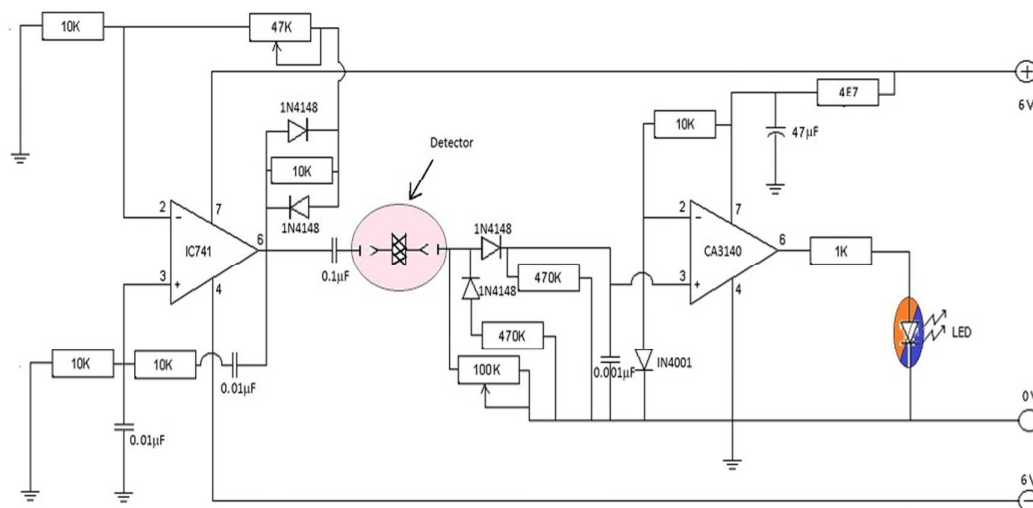


Fig. 10: Circuit diagram of the prototype for sensing nitroaromatic chemicals.

3.6 Comparative study: In our previous reported works, we have found that biological compounds like curcumin can be polymerized for NACs detection. The response time of such polymers toward NACs vapour at room temperature was about 10 minutes.²⁸ But for practical applications, the detectors should show quick response within few seconds which has been achieved in the present work. Curcumin-glycerol solution and curcumin-amino acid conjugates are also efficient in sensing nitroaromatic chemicals as their fluorescence activity remarkably changes in presence of NACs.^{32, 33}

However, detection of such explosives in vapour phase is quite challenging in comparison to that of liquid state. Extensive literature study has been done to perform a comparative study of the results of our method with the previously reported works. In this study, it has been found that the response time for the NACs vapour gained in our method is much smaller compared to the previous works reported by Menga *et al.*,³⁴ Pochekailov *et al.*³⁵ and Chen *et al.*³⁶ Also the change in the electrical properties of the sensors are less compared to our detectors. Patil *et al.*³⁷ has reported a very sophisticated technique using piezo-resistive microcantilever for the detection of TNT, RDX and PETN under ambient conditions. Here, the response time is about 20 seconds (10 seconds for our method), the efficiency starts decreasing after 10th exposure cycle (about 20 exposure cycle for our method), and again unlike our method the effect of humidity is not completely negligible. Quartz Crystal Microbalance method has been recently reported for NAC vapour detection where response time mentioned was about five minutes.³⁸ In another patented work, Eric C. Nallon

has reported a photovoltaic sensor for dinitrobenzene operable under UV-excitation.³⁹ The response time of the method is almost same to our method though the selectivity, stability terms are not mentioned therein. Edmiston *et al.* reported waveguide interferometry to ppt level detection of TNT where the response time is comparable but the process is partially reversible as the presence of TNT was observed in the FT-IR spectral analysis.⁴⁰ Moreover, the method shows less selectivity.

4. Conclusion:

In conclusion, our study revealed the simple fabrication of layer by layer polymer detectors for selective detection of picric acid vapour. The interaction of the analyte vapour causes a remarkable change in the electrical properties of the detectors within few seconds. This change in the electrical properties was monitored in terms of the decrease in the impedance with respect to time. We have found that the thickness of the individual polymer layers plays an important role in tuning the sensitivity of the detectors toward nitroaromatic chemicals and thinner outer layered detectors are most efficient. The interaction of the analyte do not alter the original chemical structure of the polymers used in the detectors as evident from FT-IR measurements. For this reason, the results are reproducible and the layer by layer detectors can be repeatedly used for sensing picric acid vapour. At the final stage of this work, we have employed these layer by layer detectors to facilitate design a portable, low costs electronic prototype for visual detection of nitroaromatic chemicals. Development of such prototypes for

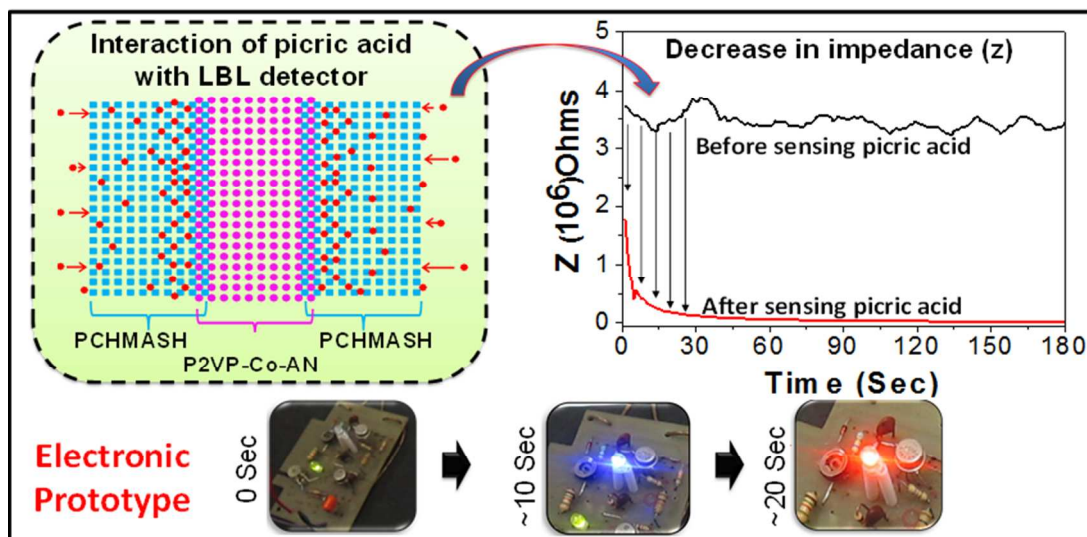
explosive sensing is of great importance for safety concerns worldwide and our further study will comprise of practical applications of sensing such explosives in real samples using the developed prototype.

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Layer by layer polymer detectors and an electronic prototype efficiently used in sensing picric acid vapour via impedance measurements.