Polydiacetylene and imidazole mixed self-standing films for colorimetric detection of various volatile organic analytes

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Abstract. Polydiacetylens (PDAs) have attracted great attention for application in sensing field due to their unique fluorescence and colorimetric properties. Polydiacetylens (PDAs) are important class of polymer that exists in two distinct phases namely metastable, non-fluorescent blue phase and stable, auto-fluorescent red phase under specific conditions. PDA is obtained through polymerization of diacetylene (DA) monomers, typically using UV irradiation that leads to photopolymerization of the diacetylene lipids. Herein, the diacetylene monomer 10, 12-tricosadiynoic acid (TCDA) and N-1-hexadecyl Imidazole have been used to prepare mixed films onto a filter paper surface using the self-standing technique and then polymerizes the mixed films to get blue phase by UV irradiation. The PDA and N-1-hexadecyl Imidazole mixed films in the blue phase exhibit rapid colorimetric/fluorescence response upon exposure to various volatile organic analytes. The colorimetric and fluorogenic responses of TCDA and N-1-hexadecyl Imidazole mixed films were investigated by UV-vis absorption spectroscopy, inverting fluorescence microscopy and RGB analysis. This study demonstrates that PDA and N-1-hexadecyl Imidazole mixed films can be a used for detection of various volatile organic analytes even in naked eye.

1. Introduction
During last few decades effort on assaying/monitoring of the volatile organic compounds (VOCs) has gained enormous interest in the environmental society due to the strong health hazards gestured by exposure to these substances. This can be overcome by development of efficient, sensitive and selective VOCs sensors. Among various VOCs sensor reported so far, electrical, optical, colorimetric change of the sensing materials upon exposure to VOCs has become great research interests for their excellent sensing performances [1–4]. From literature survey it has been found that small organic compounds, metal complexes and conjugated polymers have been used extensively as sensing materials for colorimetric detection of VOCs [5–8]. Among these sensing materials, polydiacetylenes (PDAs) are one of the most promising smart material due to their unique optical and naked eye colorimetric (blue to red transformation) properties. PDAs exhibits colour change from blue to red upon conformational alternations in its backbone induced by external micro environmental stimuli, such as pH change, temperature, sorption, ligand-receptor interaction, solvents and mechanical stress etc [9–19]. The change in colour is mainly due to change in absorption profile and in fluorescence intensity. Maximum absorption wavelength ($\lambda_{\text{max}}$) was found to be at 640 nm (blue phase) and it changes towards lower wavelength to 540 nm (red phase) on increasing the UV irradiation time or
exposure to different analytes [9,20]. However, almost no fluorescence was observed in their blue phase, interestingly the emission peak reveals at 560 nm in red phase. Herein, we report on VOC detection system composed of pure TCDA and TCDA/Imidazole mixed film coated on filter paper using self-standing method which is very convenient and economical to fabricate TCDA sensor array. However, literature survey revealed that there exist few reports that demonstrated visible colorimetric transformations of PDA assemblies, induced by various external stimuli and analytes. However, most of the PDA-based assemblies for VOC detection are synthetically complex and/or exhibit limited sensing parameters, e.g., slow response time and low sensitivity [7,21–24]. In our present work we have prepared the self-standing film by an easy and low time consuming process. Overall, the TCDA/Imidazole mixed self-standing film may be used as a sensing platform for detection, visualization and specification of various VOCs.

2. Experimental Section

2.1. Materials

Diacetylene monomer 10, 12-TCDA was purchased from Sigma Chemical Company. The clay minerals hectorite in this study was obtained from the Source Clays Repository of the Clay Minerals Society. Chloroform (99.9%; SRL, India) used as a solvent, was of spectroscopic grade and its purity were checked by fluorescence spectroscopy. N-1-hexadecyl Imidazole was synthesised and provided by our collaborator [25]. The molecular structure of TCDA and N-1-hexadecyl Imidazole is shown in figure 1. Active solutions were prepared by dissolving the diacetylene monomer (DA) in spectroscopic grade chloroform (SRL) and filtered through a 0.2 μm (PTFE) nylon filter and purity of the same was also checked by UV–Vis absorption and fluorescence spectroscopic techniques and was used without further purification. Ultrapure water, emanated in our lab by a Millipore Milli-Q unit, having resistivity 18.2 MΩ cm was also used as solvent.

Figure 1. Molecular structures of (a) TCDA and (b) N-1-hexadecyl Imidazole.
2.2. Methodology
Stock chloroform solution of diacetylene monomer (3 ml) of concentration $10^{-3}$ M were added into a 10 ml vial and allowing it to dry in the dark at room temperature. After removal of solvent, 3 ml water dispersion of clay (hectorite) was added into vial and subsequently the sample was sonicated for 1 hour which gives a clear, colorless solution. Same procedure was followed for mixture. TCDA and TCDA/Imidazole coated paper films were prepared by filtering the aqueous dispersion of TCDA and DA/Imidazole mixture through suction technique (shown in the figure 2). Before using the as prepared TCDA and TCDA/Imidazole mixed paper film as VOCs sensor, the films were exposed to UV-irradiation for 30 second so that the TCDA molecules convert to its blue phase in the film [9,20]. The blue phase of TCDA and TCDA/Imidazole prepared by this method was found to be very stable.

For UV-Vis absorption spectroscopy and inverting fluorescence microscopy studies, we have deposited the films onto quartz/glass substrate. UV-vis absorption and inverting fluorescence microscopy images of pure as well as those of mixed films were recorded by using absorption spectrophotometer (PerkinElmer, Lambda 25) and Immunofluorescence Microscope (Carl Zeiss).

3. Result and discussion
In order to investigate the colorimetric response, the paper film of TCDA and TCDA/Imidazole mixture were exposed to six chosen VOCs i.e. benzene, acetone, ethanol, methanol, propanol and chloroform. Photographs showing corresponding colour change have been shown in figure 3. Upon exposure to VOCs vapor for 5 min, pure TCDA and TCDA/Imidazole mixed coated filter paper (self-standing film) shows different degrees of colorimetric responses. This colorimetric transformation is mainly due to photopolymerization of TCDA from blue phase to red phase owing to the deformation of TCDA backbone [26–28]. However, the colorimetric responses of pure TCDA self-standing film towards the most VOC vapours are less sensitive compared to the TCDA/Imidazole mixed films. The TCDA and N-1-hexadecyl Imidazole mixed films exhibited significant colorimetric/fluorescence response upon exposure to various volatile organic analytes compared to pure TCDA. Among the various VOCs benzene and chloroform shows higher sensitivity than others. Thus, we have an array of different colour patterns of mixed film upon exposure to six VOCs. To evaluate the colorimetric response of pure TCDA and TCDA/Imidazole mixed self-standing film towards six VOCs vapours, we have calculated the red, green and blue (RGB) values of the scanned colour images using Matlab scientific software after and before exposure to VOCs vapours. Noticeably, the RGB colour change profile (as shown in figure 4) is in good agreement with scanned images (shown in figure 3).
Figure 3. Scanned images of paper-based PDA sensor array.

Figure 4. RGB colour change profile of paper-based TCDA sensor.
In order to have information about the affects of various VOCs vapor on the phase behaviour of TCDA and TCDA/Imidazole mixed films we have investigated UV-Vis absorption spectra of pure TCDA and TCDA/Imidazole mixed (blue phase shows prominent band at 645 nm along with a weak hump at 590 nm [9]. These two bands are the characteristics of blue phase of TCDA film. After exposure to various VOCs these two bands vanishes and new band appeared at around 510 nm and 557 nm which are the characteristics of TCDA red phase [9,20]. Interestingly, significant variations in absorption intensities were observed for pure and mixed films as well as for various VOCs. Accordingly, variations in the extent of colour change were observed.

![Figure 5. UV-Vis absorption spectra of TCDA and TCDA/imidazole films before (curve 1) and after (curve 2) exposure to various VOCs.](image)

In order to have visual information about the unique colorimetric responses due to deformation of TCDA backbone upon exposure to various VOCs vapor, we have carried out fluorescence imaging analysis by observing inverting fluorescence microscopy images (as shown in figure 6). Inverting fluorescence microscopy images of pure as well as mixed films did not show any distinct organized structure before exposure, whereas after exposure to various VOCs vapor both films show distinct organized structure with different texture. It is well known that pure TCDA shows fluorescence only in the red phase, no fluorescence was observed in blue phase [9,20]. Inverting fluorescence microscopy images of the TCDA and TCDA/Imidazole mixed films presented in Figure 6 complement the fluorescence spectroscopy measurements and displayed the distinct VOC-induced fluorescence transformations. Figure 6 shows different structures depending on the extent of deformation of TCDA backbone upon VOCs exposure and hence the sensitivity of TCDA and TCDA/Imidazole films towards various VOCs vapours.
4. Conclusion

We have demonstrated the preparation and characterization of paper-based TCDA and TCDA/imidazole film towards applications of six various VOCs sensors. It has been observed that incorporation of imidazole enhances the sensitivity of the system. Significant colorimetric response has been observed for chloroform and benzene. This type of paper sensor is very cost effective and easy to use without the requirement of any costly sophisticated equipment.

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