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Hydrogen-bond acidic polymers coated SAW sensors for 2,4-dinitrotoluene detection

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Abstract

Two strong hydrogen-bond acidic (HBA) polymers DKAP and PLF, including fluorinated phenol and fluorinated alcohol functional group respectively in the siloxane-based polymer structures, were coated onto 434 MHz surface acoustic wave (SAW) devices for rapid detection of an explosive compound 2,4-dinitrotoluene (2,4-DNT). Sensitivity and selectivity of the polymer-coated sensors were studied by exposing to 2,4-DNT in the concentration range of 200 ppb to 1 ppm, as well as some common interferences at higher concentrations. The results showed that DKAP sensor has a 4.6 times higher sensitivity to 2,4-DNT than the PLF one at the concentration of 1 ppm, while a further comparison indicated that their sensitivities to dimethyl methylphosphonate (DMMP) are essentially identical. The superior sensitive performance of DKAP to nitroaromatics as compared to PLF can be attributed to the dipolarity induced by the aromatic ring segments, which promotes π-π interaction between the explosive vapor and the polymer coating. In addition, the DKAP sensor exhibits a high response of 4.6 kHz to 200 ppb 2,4-DNT, with an extrapolated limit of detection (LOD) of 0.1 ppb, which is comparable to most sensitive polymer-coated sensors previously reported. Furthermore, both adsorption and recovery time of the DKAP sensor is much shorter than other related sensors. And sensor responses to possible common interferences are found to be 11-35 fold lower than that to 2,4-DNT. In-situ infrared spectroscopy studies were performed to demonstrate the hydrogen bonding between nitroaromatic compounds and the chemoselective polymers.

Keywords: 2,4-Dinitrotoluene; Chemical Sensor; Explosive Detection; HBA Polymer

1. Introduction

Detection of nitroaromatic explosive compounds has become an urgent issue due to increasing threat of terrorist attacks, safety concern of mining, long-term devastation caused by landmines [1, 2]. Explosives are remarkably difficult to detect, methods that rely on sampling of air spaces need very large volumes due to low vapor pressure [3]. Many techniques like chromatographic techniques [4], ion-mobility spectrometry [5], neutron analysis [6], X-ray backscattering [7] and nuclear magnetic resonance (NMR) spectroscopy [8, 9] have been studied for explosives detection. However, these techniques are quite expensive and require sophisticated instruments that are not easy for on-site application. Therefore, the development of inexpensive, sensitive, selective, rapid, reusable and on-site detection technology has long been a worldwide necessity.

Detection of explosives can base on the detection of 2,4-dinitrotoluene (2,4-DNT), since 2,4-DNT is a major impurity as well as a decomposition product of TNT, and the saturated concentration of 2,4-DNT in air at 20 ℃ is approximately 25-fold larger than TNT (148 ppb compared to 6 ppb) [10]. In recent years, surface acoustic wave (SAW) sensors with a variety of selective materials have been utilized for detection of explosive compounds, chemical warfare agents, and other trace level vapors [11-19]. These SAW sensors have attracted much attention for offering improved dynamic frequency responses compared to other sensors. The frequency responses can be detected with extremely high sensitivity, enabling very low detection limits. The response of a SAW sensor as well as other gravimetric based chemical sensors including quartz crystal microbalance (QCM), microcantilever and so on, primarily depends on the interaction between the analyte and the chemoselective coating [20]. The interactions are categorized into polarizability, dipolarity, hydrogen-bond acidity/basicity and dispersion in terms of the linear solvation energy relationships (LSERs). Carbowax-1000, the first chemoselective coating for nitroaromatic explosive detection, was introduced on a 9 MHz QCM sensor for mononitrotoluene [21] and later on a 150 MHz SAW delay line sensor for 2,4-DNT [11]. Carbowax-1000 has a terminal hydroxyl group, offering moderate hydrogen-bond acidity, thus can interact with the hydrogen-bond basic (HBB) nitroaromatics through hydrogen bonding. The HBA property of a hydroxyl can be greatly increased by the fluorination at its neighboring sites, resulting in strong HBA polymers such as FPOL, SXFA, and etc [12-15]. These polymers are fluorinated polysiloxane, polycarbosiloxane, or even hyperbranched polymers, initially designed for strong HBB analytes (e.g., nerve agents), thus are not the best candidate for nitroaromatic explosives due to the nitrobenzene has a relatively lower hydrogen-bond basicity while a higher dipolarity as compared to nerve agents. To complement both requirements, modified strong HBA polymers with enhanced dipolarity were synthesized, such as SXPHFA and CS6P2 [16-19] shown in Fig. 1, while they provide no further comparison to demonstrate the effect of π-π interaction. By another approach, polymers with even higher dipolarity but weaker HBA property were prepared, alternatively. The polymers are polypropylene glycol (PPG) based, with p-nitroazobenzene segments to provide the strong dipole moment [22] and were tested against nitrobenzene, o-nitrotoluene and 2,4-DNT using a 10 MHz QCM. Among these polymers, CS6P2 and PPG-AN-NT are extremely sensitive to nitroaromatics, however, both adsorption and desorption processes of these polymers-coated sensors toward 2,4-DNT are quite slow. Therefore, a better sorbent is in need.

In our previous works, HBA siloxane polymers such as DKAP [23] and PLF [24], were synthesized in our laboratory and used for nerve agents detection. In this paper, the same polymers were coated onto 434 MHz SAW devices and employed for the detection of 2,4-DNT vapor. It was found that the DKAP sensor is very sensitive to 2,4-DNT with a limit of detection (LOD) of 0.1 ppb and has fast response (21-35 s) and quick recovery (<120 s) performance.

2. Experimental

2.1 Materials and Apparatus

N,N-dimethyl formamide (DMF), ethanol, toluene, 1,2-dichloroethane (DCE), and 1,5-dichloropentane (DCP) were of analytical reagent grade, obtained from Kelong, China. Dimethyl methylphosphonate (DMMP) (97%) was purchased from Sigma-Aldrich. The 434 MHz SAW two-port resonators were obtained from Shenzhen Luguang electronics, China. The network analyzer E5070B was purchased from Agilent Technologies. Four mass flow controllers (MFC) were obtained from Beijing Sevenstar Electronics CO. LTD. The printed circuit board for SAW sensors oscillating and the corresponding data acquisition equipment were designed and made by our laboratory. The permeation tube was purchased from VICI Metronics. Frequency counter SS7200A was obtained from Suin Digital Instruments, China.

FT-IR spectrum was measured by a Shimadzu 8400S instrument system. MF-3C dynamic vapor generator was purchased from China National Metrology Technology Development CO.

2.2 SAW sensor system

The 434 MHz SAW device was coated by spray coating method from a diluted DKAP solution in chloroform. The frequency was monitored during deposition, until a frequency shift of 295 kHz was reached, corresponding to a film thickness of about 10.6 nm. The DKAP-coated SAW device had a Q value of 3982 and an insertion loss of -12 dB, monitored by the network analyzer, which ensuring the compatibility with the oscillating circuit. The DKAP-coated SAW device, as well as a bare SAW device, was mounted onto the printed circuit board. Each sensor was excited in an independent oscillating loop and exposed to the vapor stream in a line. Their outputs were mixed, low pass filtered and recorded by the frequency counter. By the same way, another 434 MHz PLF sensor was fabricated and tested, with a Q value of 3500, an insertion loss of -14 dB and a thickness of 21 nm.

2.3 2,4-DNT vapor detection

A permeation-tube method based on diffusive limitation was used to generate 2,4-DNT vapor. The test platform is shown in Fig. 2. The pure nitrogen passed through the permeation tube in an airtight container at 80 ℃. The flow rate of the carrier N_2 stream was fixed to 50 ml/min by a mass flow controller (MFC-1), generating a 2,4-DNT stream at a standard concentration of 1 ppm at the first stage. Then the original stream was then diluted by another N_2 stream adjusted by the

MFC-2 to generate various test concentrations. The diluted vapor was then delivered to a small test chamber made up of aluminum alloy and mounted gas tightly on the sensor printed circuit board. To minimize the fluctuation of the gas pressure, a constant flow rate of 50 ml/min was delivered into the test chamber by the MFC-4. The excessive vapor stream was exhausted through a by-pass and the flow rate at the exit was monitored by MFC-3 to verify there was no leakage. The 2,4-DNT vapor exposures detailed here were performed with vapor concentrations from 200 ppb up to 1 ppm. After each vapor exposure, the test chamber was thoroughly flushed by N_2. The frequency of the sensor was automatically measured by the frequency counter and collected real-timely by a PC with corresponding data acquisition hardware and software. All the vapor tests were performed at room temperature.

2.4 VOCs tests

Besides 2,4-DNT, the DKAP sensor was also tested against several common volatile organic compounds (VOCs, including N,N-dimethylformamide (DMF), 1,2-dichloroethane (DCE), 1,5-dichloropentane (DCP), ethanol and toluene) and deionized water at 10 mg/m^3, as well as DMMP at a range of 1 to 49 mg/m^3. Vapors were generated by the MF-3C dynamic vapor generator. The vapor generator has two digital mass flow controllers and one vaporizing chamber into which small amount of the analyte was injected by a micro syringe. The vaporized analyte was fluxed by pure N_2 and stored in a standard gas bag and subsequently diluted by another pure N_2 stream to obtain the required concentration. The diluted vapor was then delivered to the device and the frequency was recorded by the frequency counter.

3. Results and discussions

The real-time response (defined as the change of the frequency shift as a function of time) of DKAP sensor to 2,4-DNT vapor ranging from 200 ppb to 1 ppm is shown in Fig. 3. It can be seen that the frequency changes immediately with the injection of the 2,4-DNT vapor into the test chamber and rapidly reaches a steady value which represents an equilibrium state of the adsorption process. The response time T_{80}, defining as the time interval between the vapor on and the frequency shift Δf reaches to 80% maximum, is 21-35 s, increases slightly with the decrease of the vapor concentration. When pure N_2 is purged into the test chamber, desorption takes place also immediately and the frequency can return to its initial value within 120 s, resulting a negligible baseline drift. More than 4.6 kHz value is recorded at a concentration of 200 ppb, and the responses are 8.6 kHz, 12.4 kHz, 15.7 kHz, 18.7 kHz at the concentrations of 400 ppb, 600 ppb, 800 ppb and 1 ppm respectively. The inset of Fig. 3 shows the response of the sensor as a function of the vapor concentration. DKAP is a viscous liquid at room temperature and the responses will be influenced by the viscoelastic effect of the polymer. Thus a parabolic fitting was chosen instead of the linear fit, which is more suitable for pure gravimetric devices like quartz crystal microbalance (QCM). After polynomial fittings, an expression of $\Delta f = 13.6 + 25.0165C - 0.00714C^2$ is obtained where Δf is in Hz and vapor concentration C is in ppb. According to this expression, the response of the sensor at 0.1 ppb is estimated to be 16 Hz. Thus, the LOD of the sensor, taking into account the signal-to-noise ratio of 3:1, is deducted to be 0.1 ppb since the noise level of the coated SAW sensor is around 5 Hz. The results indicate that the sensor exhibits high sensitivity, fast response, negligible baseline drift and rapid recovery to baseline when exposes to 2,4-DNT vapor.

As a comparison, the response of the PLF sensor to 2,4-DNT vapor is considerably slow. The real-time response curve of the PLF sensor to 1 ppm 2,4-DNT is shown in Fig. 4. It is clearly that the response of the sensor increases continuously during the exposure time, showing a turning point in the real-time response curve while doesn't reach an equilibrium response at the end of the 3 min duration. Later then, the chamber is purged into pure N_2, desorption takes place and the frequency can return to almost the initial value in 3 min. The whole adsorption-desorption cycle shows a smooth, steady and repeatable signal, while a much weaker signal (8.2 kHz) relative to DKAP sensor (18.7 kHz) at the same concentration, giving a direct result that the DKAP sensor is nearly 2.3 times sensitive than PLF sensor. Considering the response is roughly proportional to the film thickness [25, 26], DKAP coating has a 4.6-fold higher sensitivity than PLF coating.

However, when the two sensors were used to detect DMMP in the range of 1-49 mg/m^3, as shown in Fig. 5, the PLF sensor is evidently twice sensitive with regard to the DKAP sensor. Taking the film thickness into account, the sensitivity of the two materials towards DMMP are almost the same.

The diverse sensitive performances of the two chemoselective polymers towards DMMP and 2,4-DNT can be attributed to their different chemical properties. According to the LSERs, the chemical properties of an analyte/coating pair should match as highly as possible in terms of polarizability, dipolarity, hydrogen-bond acidity/basicity and dispersion interaction. On one hand, the hydrogen-bond basicity of DMMP is very strong (1.05) while other solvation parameters are relatively low. Hence, strong HBA polymers are suitable for the detection of DMMP as well as nerve agents. On the other hand, the hydrogen-bond basicity of 2,4-DNT is not very strong (0.47), whereas the parameter related to dipolarity is relatively higher. Thus, for nitroaromatics detection, the chemoselective polymer should be both strongly dipolar and hydrogen-bond acidic to complement the dipolar and HBB properties of the nitroaromatics. Based on this theoretical consideration, the strong HBA functional group, fluorinated phenol, was incorporated into the siloxane backbone to form the designed DKAP molecule, thus offering the desired HBA and dipolar properties. On the contrary, the polymer PLF doesn't contain aromatic rings to promote the π-π interactions. Thus we believe, this multiple interact mechanism would account for the much higher sensitivity of DKAP sensor than the PLF one towards 2,4-DNT vapor.

The suggested mechanism was confirmed by the vapor exposure tests of the two sensors toward toluene at a concentration of 10 mg/m^3. As shown in Figure 7, the sensitivity of the DKAP senor to toluene is almost 10-fold higher than the PLF sensor when taking the film thicknesss into consideration. According to the theoretical calculation made by M.O. Sinnokrot and C.D. Sherrill [27], the π-π interaction between benzene dimmers with a face-to-face configuration will bind stronger when substituents exist (substituted dimers bind more strongly than benzene dimer), regardless whether the substituents are considered electron donating (OH, CH_3) or electron withdrawing (CN, F). The specific influence of subsituents to binding strength is far more complex and details will not be discussed here. In the experiments made by A.S. Ogunlaja et al [28], strong absorption was observed for several sulfone-containing organo-sulfur compounds on the polybenzimidazole (PBI) nanofiber, demonstrating the coexistence of hydrogen bondings between suflone oxygen groups and NH groups of PBI, as well as the π-π interactions between the benzimidazole rings and the aromatic rings of sulfone compounds. Thus, our research results are in good agreement with the above theoretical and experimental results. It confirms that π-π interactions exist between DKAP polymer coating and toluene/2,4-DNT vapors, demonstrating that π-π interaction does affect the absorption process between the coating and the analyte.

Our DKAP, PLF sensors are further compared with other polymer-coated SAW sensors previously reported in the literatures for 2,4-DNT detection. It can be seen in Table 1, all the sensors were tested against 2,4-DNT at a different exposure time, e.g., 60s, 180s, 250s and 300s. Except for DKAP sensor, other sensors couldn't reach the equilibrium state at the end of the exposure tests. Thus, the response Δf is taken as the frequency shift between the 2,4-DNT vapor on and off. From Table 1, it is clearly that the CS6P2 sensor has the highest sensitivity toward nitroaromatic explosives. At a much lower concentration of 31 ppb, the 250 MHz sensor has a response as high as 9.5 kHz. Since the response of a SAW sensor has a square relationship with the working frequency (f_0) [25] and a linear relationship with the coating thickness [26, 29], these predominating factors must be normalized to facilitate the inter comparison.

Consequently, the CS6P2 coating is 7.75-fold higher sensitive to 2,4-DNT than our DKAP coating.

Although the CS6P2 was more sensitive, the kinetic behavior of the CS6P2 sensor was much more inferior. The sensor couldn’t reach the saturated state after 250 s exposure at a stream flux of 250 ml/min, which was 5 times higher than the flux used in our tests. The signal increased with the exposure time in a linear manner, no turning point was evident, thus, the CS6P2 coating responded to the explosive vapor more slowly as a comparison to our PLF sensor, let alone our fastest DKAP sensor. Besides the adsorption process, the desorption process of the CS6P2 coated sensor was also remarkably slower than our two sensors. It took 15 min for the CS6P2 sensor to recover to its baseline. The test was performed at a chamber temperature of 30 ℃, which was even slightly higher than ours. Therefore, the much slower desorption process of the CS6P2 sensor could not be attributed to the temperature (30℃ VS ~25℃), since an elevated temperature will decrease desorption time significantly [30]. We believe that the steric effect plays a dominant role in the kinetic behavior of these polymer-coated sensors. For a HBA polymer, the acidic site is on the oxygen atom of the hydroxyl group. Thus, the polymer CS6P2 will suffer stronger steric effect since two CF_3 groups are closer to the active site, while they are much far away in the DKAP polymer. During the adsorption process, the access of the analyte to its bonding site is blocked, resulting in longer response time. Meanwhile in the desorption process, the strike of the flux gas (N_2) on the existed hydrogen bonding is also shielded, giving a prolonged desorption time as well.

SXPHFA was the first HBA polymer specially designed for the nitroaromatic vapor detection. After the same calculation, this polymer shows a 0.631-fold sensitivity to 2,4-DNT with regard to our DKAP coating. As for the other materials listed in Table 1, their sensitivities are further lower, especially Carbowax-1000, since its hydrogen-bond acidity is much lower (1.98) when compared to other strong HBA polymers such as SXFA (4.25) [31]. Hence, DKAP is demonstrated to be a very good candidate for 2,4-DNT vapor detection.

FTIR tests were carried out to further confirm nitroaromatics-polymer interactions. KBr tablet was coated with the DKAP polymer and then exposed to 2,4-DNT vapor to observe the interaction between the vapor and the polymer film. Sequential IR absorbance spectra were collected about every 1 min until no further change was observed, tests of “during” and “before” all used the same coated tablet and were repeated for three times. The final spectra are shown in Fig. 6. It was clear that when DKAP coated KBr tablet was exposed to 2,4-DNT vapor, the bonded OH peak around 3500-3100 cm^{-1} shifted to lower wave number (3419 to 3325 cm^{-1}). The inset is the difference spectrum, showing a loss of free OH (3612 cm^{-1}) as a negative signal while an increase in hydrogen-bonded OH as a shoulder near 3300 cm^{-1}. When the tablet was purged with N_2, the spectrum could return to the initial value. The results indicate that the interaction between nitroaromatics and DKAP can interact via hydrogen bonding.

Explosive detection based on chemical vapor sensing will encounter difficulties due to a wide diversity of interferences present in the environment. Since these vapors most likely exist in much higher concentrations than those of explosives, it is crucial for the polymer to distinguish interferences from explosives. In this study, several common VOCs at higher concentrations of 10 mg/m^3 were tested by the DKAP and PLF sensors, as shown in Fig. 7. These interferences can be categorized by functional groups of their structures. Among them, toluene is aromatic compound, ethanol is polar hydrocarbon, DMF is nitric hydrocarbon, and DCP and DCE are halogenated hydrocarbons. It is clearly found from this figure that the DKAP sensor has a 11-35-fold stronger response to 2,4-DNT than to other interferences, indicating good selectivity of the DKAP sensor for nitroaromatic explosives detection.

4. Conclusion

DKAP and PLF, two strong HBA siloxane polymers for SAW sensor application, were coated onto 434 MHz SAW sensors to investigate the sensitivity to 2,4-DNT at room temperature. The selectivity of DKAP sensor to six interference vapors was also investigated. DKAP based SAW sensor exhibits fairly fast response, excellent reversibility, high sensitivity and pretty good selectivity on detection of 2,4-DNT vapor. Comparing with PLF and other high sensitive HBA polymers, DKAP shows the fastest response and recovery ability. Interaction mechanism between DKAP and 2,4-DNT is confirmed by a sensitivity comparison with PLF to toluene and FT-IR testing. Therefore, DKAP polymer is demonstrated a very promising sensitive polymer material for explosives detection. Additional research to improve sensitivity of SAW sensor to chemical vapors, and promote the electronic applications in the specific practical targets is underway at present.

Acknowledgement

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Figure captions

Figure 1: Some related HBA polymers.

Figure 2: A schematic diagram of a home-made 2,4-DNT test system.

Figure 3: The response of DKAP-coated sensor to different concentrations of 2,4-DNT (The inset is the polynomial fitting of the response against concentration).

Figure 4: The response of PLF-coated sensor to 1 ppm 2,4-DNT.

Figure 5: Real-time responses of DKAP and PLF sensors to different concentrations of DMMP.

Figure 6: FT-IR spectrum of DKAP in the OH stretching region before (blue line) and during (red line) exposure to 2,4-DNT (The inset is the absorbance difference spectrum).

Figure 7: The sensitivity of DKAP and PLF sensors to various vapors.

Table 1: Comparison of HBA polymers coated SAW sensors to 2,4-DNT

Material	f_0 (MHz)	C (ppb)	△f (Hz)	Film thickness (nm)	Response time (s)	Recovery time (s)	Flux (sccm)	Relative sensitivity	T(℃)	Refer.
Carbowax-1000	150	253	156	~2750[a]	>60	100	50	0.00855	50	[11]
FPOL-POSS	500	50	~1980	25	>300	600	250	0.508	90	[13]
SXPHFA	250	400	8.5k	50	NA	reversible	NA	0.631	NA	[16]
CS6P2	250	31	9.5k	50	>250	~900	250	7.75	30	[17]
PLF	434	100	1.5 k	21	>180	180	50	0.22	25	This work
DKAP	434	200	4.6 k	10.6	28	110	50	1	25	This work

a: corrected value, the thickness in the original literature was 10 µm.

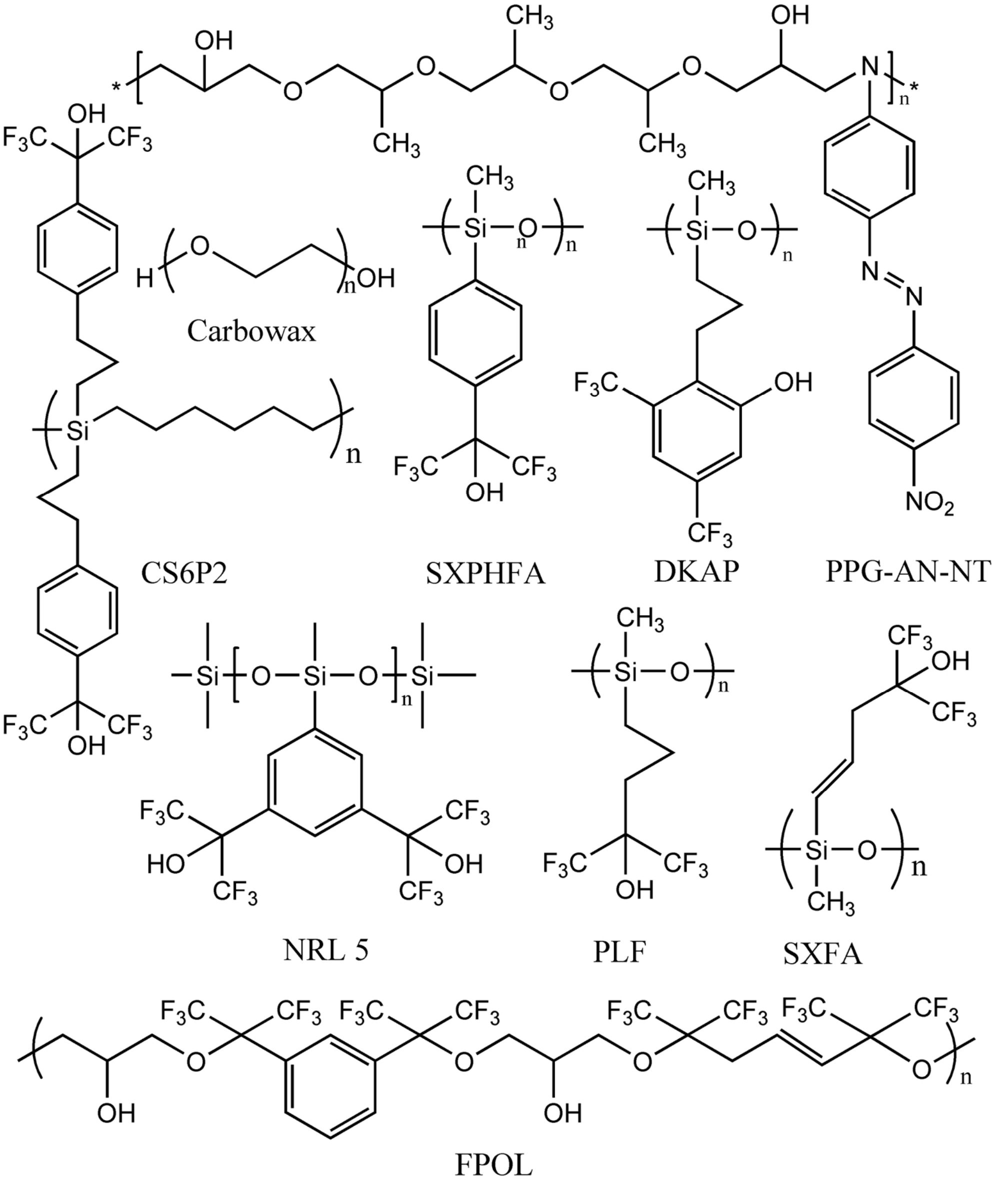

Figure 1. Some related HBA polymers.
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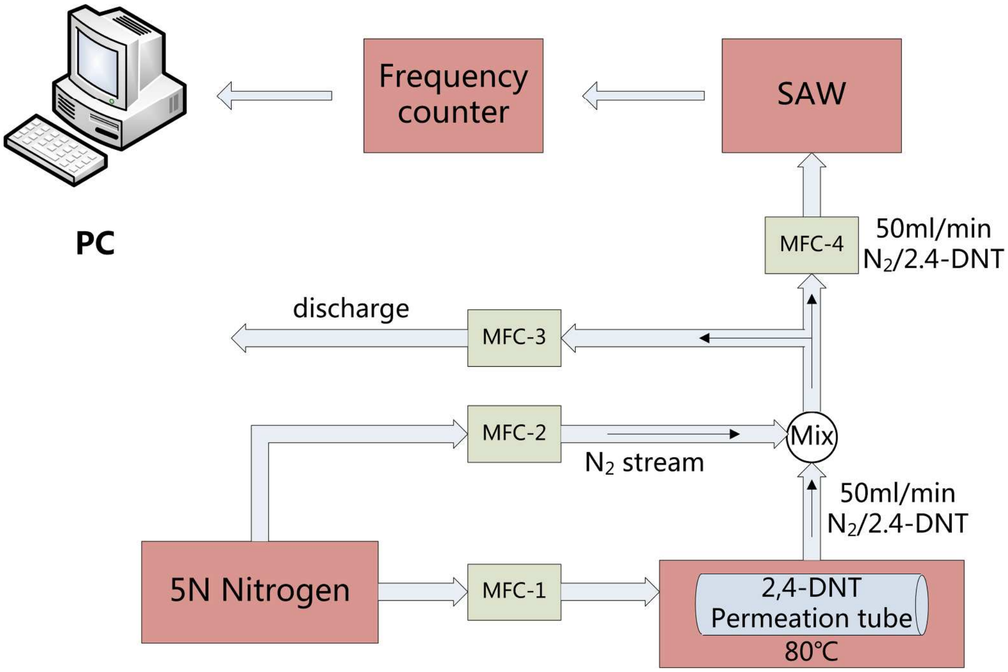

Figure 2. A schematic diagram of a home-made 2,4-DNT test system
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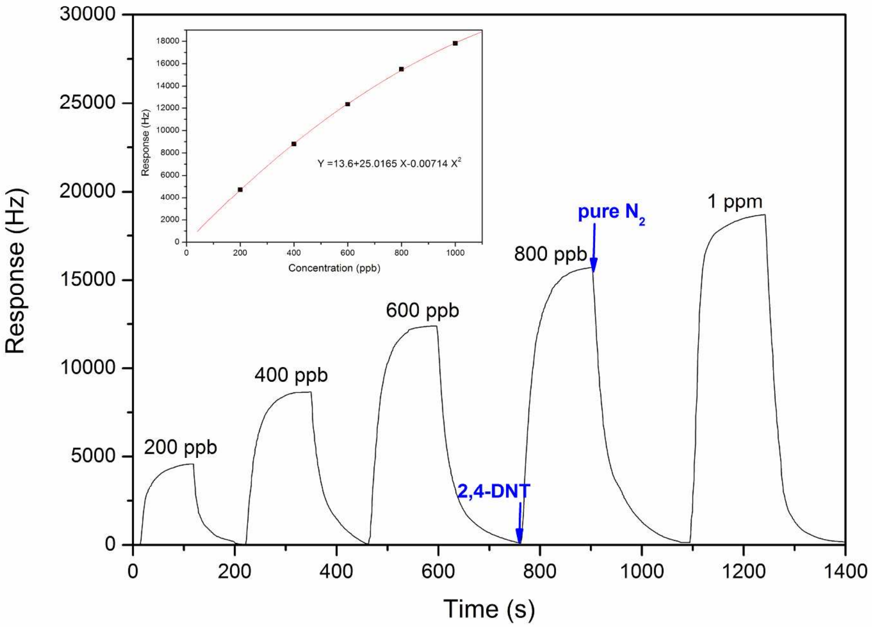

Figure 3. The response of DKAP-coated sensor to different concentrations of 2,4-DNT (The inset is the polynomial fitting of the response against concentration)
128x98mm (600 x 600 DPI)

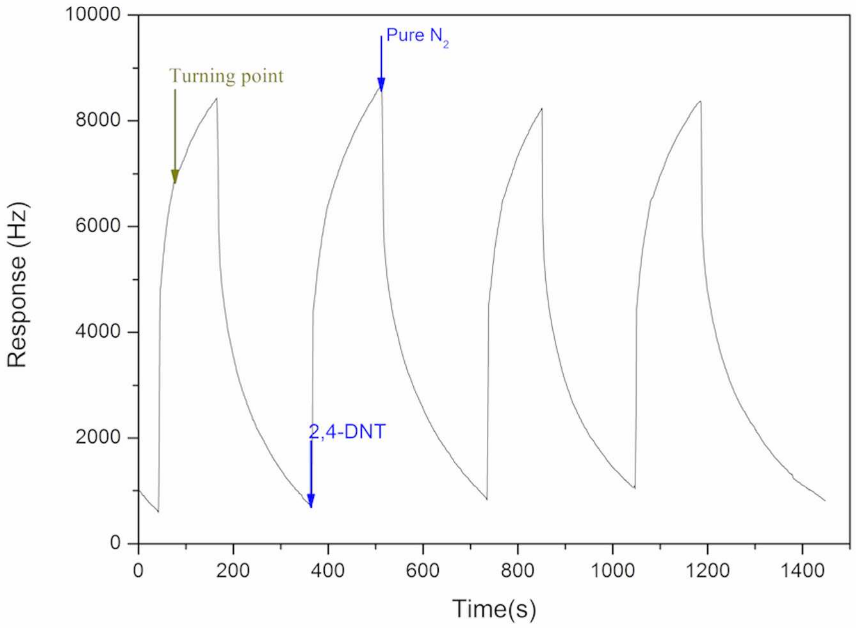

Figure 4. The response of PLF-coated sensor to 1 ppm 2,4-DNT
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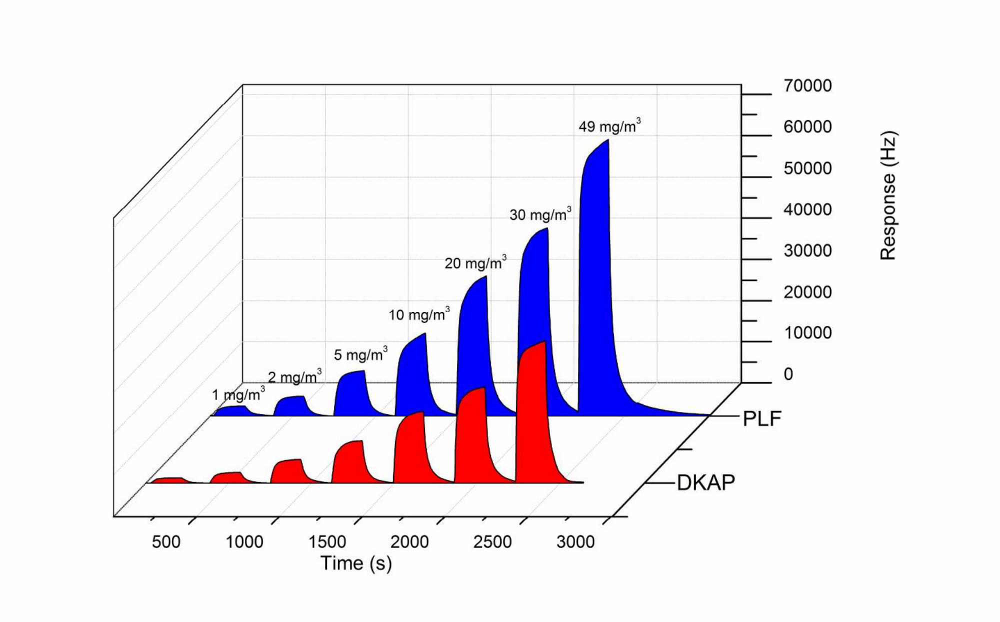

Figure 5. Real-time responses of DKAP and PLF sensors to different concentrations of DMMP
101x63mm (600 x 600 DPI)

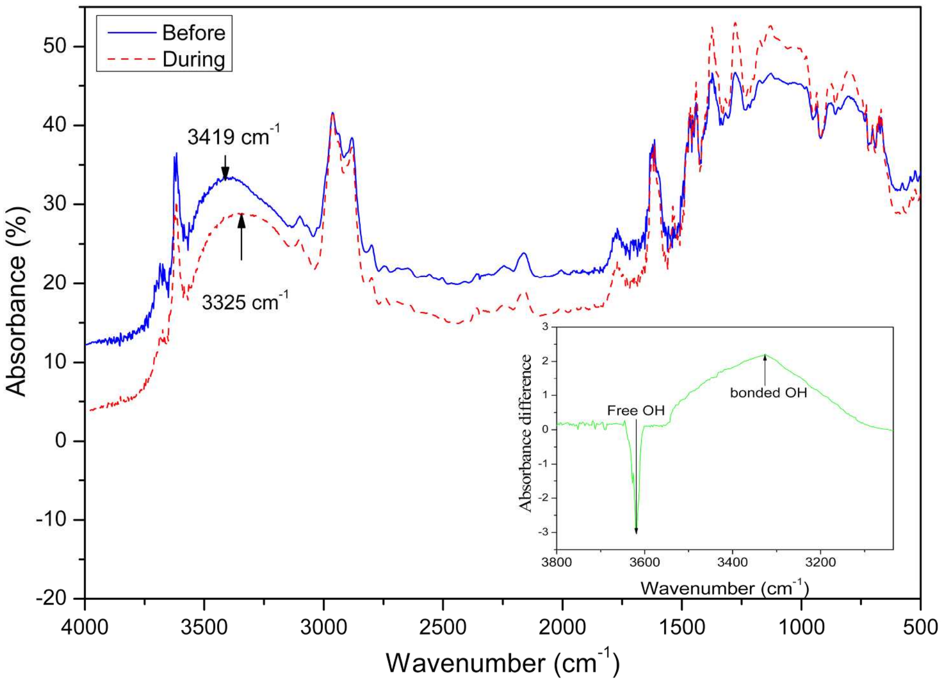

Figure 6. FT-IR spectrum of DKAP in the OH stretching region before (blue line) and during (red line) exposure to 2,4-DNT (The inset is the absorbance difference spectrum).
118x83mm (600 x 600 DPI)

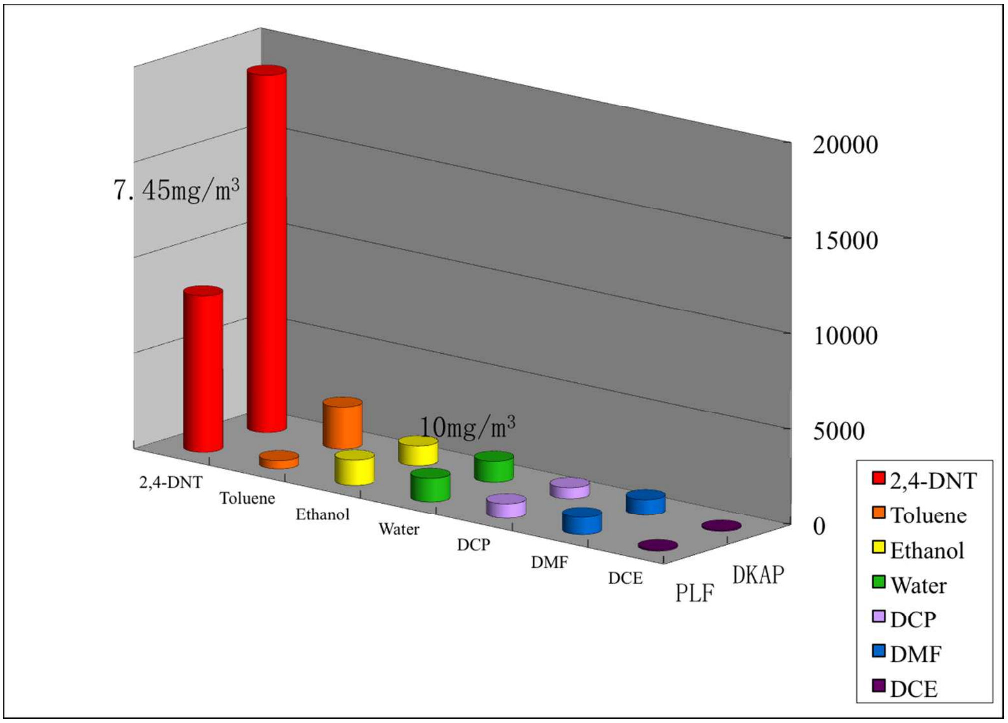

Figure 7. The sensitivity of DKAP and PLF sensors to various vapors.
215x153mm (150 x 150 DPI)