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Study of charge transfer mechanism of PEDOT polymer for detection of solid TEX and CL-20 explosives using pulsed photoacoustic technique



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ABSTRACT

We report the use of PEDOT polymer (poly (2, 3-dihydrothieno [3,4-b] dioxane-5,7-diyl) as a sensing medium for the detection of solid secondary explosives like TEX and CL-20 in solid form using pulsed photoacoustic (PA) technique under visible 532 nm wavelength. The PEDOT polymer (poly (2, 3-dihydrothieno [3,4-b] dioxane-5,7-diyl) plays the role of an optode or an effective sensing medium for the detection of explosives when mixed in equal proportion and subjected to 532 nm wavelength obtained from Q-switched Nd: YAG laser without any chemical treatment. The study reveals that one milligram of PEDOT is sufficient to initiate the charge transfer mechanism between the positive charge on the oxidized PEDOT and the lone pairs of electrons on the oxygen atoms of the nitro group of the explosives. The strength of the enhanced PA signal for TEX and CL-20 was of the order of 65.38 and 1.77 times, respectively. However, the same experiment was repeated with nonexplosive samples such as NaNO2 and NaNO3, separately mixed with PEDOT. The obtained peaks of PA spectra were very weak, broaden and distorted in nature and occupies less than 3 kHz frequency rage and 3.5 times less than the PA signal of pure PEDOT. The estimated minimum detection limit of the solid explosives, CL-20 and TEX were of the order of 0.33 ng and 1.03 ng, respectively.

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1. Introduction

In recent years, nitramine class of caged molecules has attracted the interest of the High Energy materials community due to high detonation performance. Among them, 4,10-dinitro-2,6,8,12-tetraoxide-4,10diazaisowurtzitane (TEX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12hexaazaisowurtzitane (CL-20) are widely used explosives in military and civilian applications [1]. Also, it is well known fact that plastic explosives pose a challenge in detection because of their low volatility and weak electron-withdrawing ability as they do not have an absorption band in the visible region. In this report, we have utilized the redox nature of poly(3,4-ethylenedioxythiophene) (PEDOT) as a tool for the detection of these high energy materials in the visible region using a specially designed PA cell made of aluminium. Continous wave and pulsed photoacoustic spectroscopy of solid samples and its use in measurements of absorption parametres and detection of explosives are reported by many groups [2–5]. Incident laser energy of visible photons is utilized in transferring the electrons from the electron-rich oxygen atom of the nitro group to the electron-deficient oxidized PEDOT. On gaining electrons, the oxidized state of PEDOT converts into a reduced state and responsible for absorption in the visible region. The reduced state of PEDOT makes charge-transfer possible, which leads to the enhancement of the generated photoacoustic signal. The present technique makes an advantage over the conventional optical detector over chemical treatment or pre-concentration strategy.

4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane, which is most commonly and conveniently abbreviated as TEX is a high energy material having a density of 1.985 g cm^{-3} . The molecular structure of TEX is closely related to the cage structure of CL-20 but is differentiated by the replacement of bridged nitramine groups with ether linkage (Fig. 1). The absence of nitramine groups diminishes its sensitivity significantly and establishes it as an interesting explosive with excellent thermal stability as well as high detonation velocity (8665 m/s) and detonation pressure. Most of the reports on optical detection of these explosives are based on photoluminescence (PL) or fluorescence techniques that arise due to radiative decay [6]. A.K. Chaudhary et al and Akhgari et al have shown the use of solid graphite powder and carbon nano tubes as a sensing medium to detect TNT in the visible region [7,8].

Furthermore, the production cost of CL-20 restricts its use for large scale applications. Unlike the CL-20, the production cost of TEX is very less. It can be synthesized in two easy steps with the commercially available starting materials reported by Talwar et al. as shown in Scheme 1. In the first step, DFTHP has been prepared by the reaction of glyoxal (40% in water) and formamide in 57% yield. Further reaction of DFTHP with HNO₃ and H₂SO₄ obtained TEX in 20% yield [9].

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Fig. 1. Chemical structures of TEX and CL-20.

Explosives like CL-20 and TEX do not show any absorption in visible region, but they can either be detected in UV or near-infrared region using conjugated polymer matrix as a sensor [10–13]. Most of these reports of detection of these explosives are based on photoluminescence (PL) or fluorescence techniques, which are caused due to radiative decay. Along with radiative decay, the process of non-radiative decay also occurs in the intra-band energy level of the excited state of the analyte, and provides valuable information about the transition of electrons in the visible region. Non-radiative decay emits localized heat which produces thermal pressure wave which can be recorded as acoustic signals in photoacoustic spectroscopy. In the present report, efforts have been focused on sensing of two well known secondary explosives; CL-20 and TEX mixing with PEDOT, a conjugated polymer matrix, using the photoacoustic spectroscopic technique and are discussed in detail.

2. Experimental details

2.1. Synthesis of samples

2.1.1. Synthesis of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine(DFTHP)

To a stirred mixture of aqueous glyoxalsolution (40%, 50 g, 0.86 mol), formamide (58.18 g, 1.29 mol) was added drop-wise over a period of 20 min. The pH of the reaction mixture was adjusted to 8 by adding 20 mg sodium hydrogen carbonate at 25 °C. After 6 h, the precipitated solid was filtered, washed with cold water, and methanol was added to obtain DFTHP as white solid (52 g, yield 57%); mp:185–190 °C (decomposition).

2.1.2. Synthesis of 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-Diazaisowurtzitane (TEX)

To a cooled solution of sulphuric acid (620 mL), a homogeneous mixture of glyoxal(40% in water, 55.68 g, 0.96 mol) and DFTHP (100 g, 0.48 mol) was added at 5-10°Cwith constant mechanical stirring over 20 min (slightly exothermic). Then the reaction mixture was stirred for 5 h at 15 °C, then cooled to 5-10 °C, and fuming nitric acid (650 mL) was added dropwise over 60 min. During this period, the viscous light brown solution was converted into a less viscous, colorless solution with separation of a small quantity of TEX. The reaction mixture was allowed to stand for 35 h at room temperature with occasional stirring. The reaction mixture was poured in crushed ice with stirring and filtered the solid to afford TEX as white solid (19 g, yield 20%); mp: >250 °C [14–19].

2.1.3. Synthesis of CL-20:

During a 1-h period, glyoxal (72.5 g, 40% aqueous solution, 0.50 mol) was added drop wise to a solution of benzylamine (117.9 g, 1.10 mol), water (100 mL), and formic acid (88%, 5.76 g, 0.110 mol) in acetonitrile (1100 mL) while keeping the temperature below 20 °C. The addition funnel was rinsed with 10 mL of water. After standing at 25 °C overnight (16–18h), the precipitated product was removed by filtration and washed with cold acetonitrile. The crude product is resuspended twice in cold acetonitrile with stirring and filtered. The yield is 94.8 g (80%) of hexabenzylhexaazaisowurtzitane; mp 150–152 °C [20]

2.1.4. Synthesis of PEDOT

EDOT and 2,5-dibromo EDOT (DBEDOT) were synthesized and characterized in the lab using reported procedure. Before polymerization, DBEDOT was recrystallized in petroleum ether.In the next step, 5 mg of DBDOT crystals(16.67 mmoles) were taken in a round bottom flask equipped with an open gas inlet and heated to 65C for 24 h. The Bromine vapor was continuously released during the period of heating. Consequently, the white crystals of DBEDOT started turning black. The whole mixture was stirred periodically with a glass rod to acquire homogeneous heating. The heat was stopped after 24 h, and the mixture was allowed to cool to room temperature. The polymer was isolated by precipitating the reaction mixture in acetonitrile. The resulting polymer was centrifuged and washed three times with fresh methanol. The resulting isolated polymer is a dark blue-black color powder that is insoluble in all common organic solvents, and identified as PEDOT.

2.2. Experimental setup

Fig. 2 shows the experimental setup of PA spectroscopy. Experiments were performed in the time domain mode by varying the incident laser energies and data acquisition time. The samples were placed in aluminium cubic shaped $(5 \times 5 \times 6 \text{ cm}^3)$ cell. A Q-switched Nd: YAG laser of wavelength 532 nm was used as a source to excite the samples for recording the PA signals. The generated PA signals were recorded using a pre-polarized microphone (BSW, China), which



Reagents and conditions: i) Formamide, Glyoxal, NEt₃, 40-45 °C, 3h, 57%; ii) HNO₃, H₂SO₄, RT, 6h, 20%



Fig. 3. (a and b) The experimental layout for PA spectroscopy and nonradiative transition mechanism.

was housed in a Teflon jacket and placed at a distance of 1.0 cm from the sample cavity. The explosive and PEDOT sample were mixed in 1:1 ratio. Two milligrams of sample was uniformly adjusted in the circular shaped sample cavity of the PA cell. The distance between the centers of the sample to the microphone head was 2.2 cm. An aluminium plate along with a neoprene washer was used to cover the cavity. The plate has a one-inch diameter guartz window for irradiating the sample placed in the cavity. The pre-amplified PA signal is fed to the digital storage oscilloscope (Tektronix, 200 MHz) to record the time domain signal. The output of the oscilloscope was connected to a personal computer for the recording Fast Fourier Transform spectra using a data acquisition program developed LabView based software. The experimental setup for the measurement of PA spectroscopy was first optimized by graphite powder since graphite has good absorption in all the wavelength range. Then, the experiments were carried out in four steps: in the first step, the polymer PEDOT was synthesized. In the second step, the PA spectra of PEDOT, TEX, and CL-20 were recorded at different data acquisition time and varying incident laser energies. The schematic diagram, which was used for the recording the data, is shown in Fig. 3(a).

When a sample is irradiated with incident laser pulses, it absorbs energy in the form of photon, and that leads to initiate the electron transition from the ground state to an excited state. While returning to its ground state from excited state, it can follow two possible paths: (i) radiative decay and (ii) non-radiative decay, as shown in Fig. 3(b). The non-radiative decay produces thermal pressure waves, also known as acoustic waves, and detected by the pressure sensor which works as a detector in case of PA spectroscopy. In the present report, we have explored the detection of these plastic explosives in the visible region using PEDOT as a sensing matrix. The thermal pressure waves generated in the PA cell are then transformed in the time domain or frequency domain using a specially developed data acquisition program in LABVIEW software for analyzing the data.

3. Results and discussion

This section is divided into seven numbers of subsections. Part 3.1; deals with Q factor of the PA cell while 3.2; discuss the measurement of cell responsivity. Part3.3; deals with time domain PA spectra for pure and PEDOT mixed explosives, part 3.4; discuss the PA spectra and data acquisition time. Part 3.5; deals with charge transfer mechanism between PEDOT and explosive molecules and part 3.6 and 3.7 cover the effect of PEDOT on FTIR spectra of explosives and Non explosive samples, respectively .

3.1. The quality factor "Q" of the PA cell

The quality factor 'Q' is defined as the ratio of the energy stored in the PA cavity to the energy lost by the explosive molecules per cycle. The mathematical expression for the quality factor is given as follows:

$$Q = \frac{\omega}{\Delta \omega} \tag{1}$$

Where ω and $\Delta \omega$ are the central frequency and full width at half maximum (FWHM) of the exciting acoustic modes. Fig. 4 shows the Lorentz fits of one of the sharp, intense peak and for laser wavelength of 532 nm. Here, t = 5 ms, and it is fixed in the case of 532 nm spectra. The approximate central frequency of the acoustic mode is shown on the X-axis of the respective figures. Fig. 4 clearly shows that the central frequency of the acoustic modes vary due to the selection of excitation



Fig. 4. Quality factor of the photoacoustic cell used in the experiment.

wavelength and is also associated with the change in concentration of samples used in the photoacoustic cell.

The quality factor 'Q' is directly proportional to ω of the acoustic mode. Therefore, high-frequency acoustic modes of PA spectra give a higher quality factor. In addition, higher data acquisition time leads to high-quality factor because the gap between the two adjacent data points of PA spectra is lower (i.e., provides low $\Delta\omega$). From the above mathematical expression of the quality factor, it is clear that lower $\Delta\omega$ value provides high-quality factor. Therefore, for evaluation of the quality factor of the PA cavity, it is necessary to select the fixed data acquisition time and consider the standard approximate acoustic mode at different concentrations. Here, the data acquisition time, t = 5 ms, and it is fixed in the case of 532 nm PA spectra.

3.2. PA cell responsivity

The PA cell responsivity is calculated at 10 kHz mode, where the excitation laser wavelength is 532 nm. The incident energy with respect to the PA signal is plotted to calculate the cell responsivity. The PA cell responsivity for PEDOT is 7.5 (V/J), whereas, for the mixture with high Energy material (TEX, CL20), is 25 (V/J). Therefore, the cell responsivity for explosive mixed with PEDOT is 3.3 times higher than the pure PEDOT.

3.3. The PA spectra of pure PEDOT, CL-20 and TEX and their mixtures: this section show the time domain spectra of pure explosives and their mixture with PEDOT

Fig. 6(a-d) shows the frequency domain PA spectra of pure CL-20 and CL-20 mixed with PEDOT polymer. The PA spectra of Pure sample, shows excited modes at 2, 4.5, 7.2, 9.2, 11, 15.8 and 19 kHz whereas $CL-20 \pm PEDOT$ shows enhancement of amplitude of only three modes located at 2, 4.5 and 15.8 kHz range out which only mode present at 4.5 kHz is strongest for the mixture while other modes at 7.2 and 9.2 kHz are reduced between 82 and 50% range. Similarly, Fig. 6(c-d) shows the PA spectra of pure TEX sample and its mixture with PEDOT. The amplitude of all modes of pure TEX are lower as compared to TEX+PEDOT. The modes at 0.5, 1.3, 1.9 and 4.1 kHz frequency range are enhanced between 72.9 and 6438.46% range, respectively. It also shows some additional peaks at 14, 19.8 and 32.5 kHz. Finally, Fig. 6 (e) shows the PA spectra of pure PEDOT, CL20 and TEX samples. Here, we notice a significant increase in the signal strength in the lower frequency range as compared to higher frequency range. All data of above figures are comprised in Tables 1 and 2, respectively.

3.4. PA spectra for data acquisition time and energy

Fig. 7 (a and b) shows the decay behaviour of acoustic modes of TEX and CL-20 along with their mixture with PEDOT. The above graphs clearly show the exponential decay behaviour of acoustic modes. It shows a normalized intensity of one of the predominant acoustic modes (PA mode = 30 kHz) for the compounds as a function of data acquisition time, whereas the behaviour of PA Signal to the incident

Table 1	
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CL-20 and CL-20 +	- PEDOT.
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Major Photoacoustic Modes (kUr)	PA signal of Pure	PA signal of CL-20+	Increase/decrease in peak value (%)
WOULDS (KI12)	CL-20 III (IIIV)	FEDOT III (IIIV)	
2	270	480	77.77
4.5	1000	1050	5
7.2	1650	300	-81.81 (reduced)
9.2	300	150	-50 (reduced)
11	200	200	0
15.8	100	190	90
19	230	50	-78.26 (reduced)

Tabl	e 2		
TEX.	TEX+	-PEDO	Г.

Major Photoacoustic Modes (kHz)	PA signal of Pure TEX in (mV)	PA signal of TEX + PEDOT in(mV)	Increase in peak value (%)
0.5 1.3 1.9	290 210 110	500 1250 600 2400	72.41 495.23 445.45
4.1	52	3400	6438.46

energy is shown in the next graph. It is observed that the PA Signal is enhanced when PEDOT is mixed with the premium explosives used.

3.5. Charge transfer mechanism between PEDOT and explosive molecules

The role PEDOT as a sensing medium can be explained based on the charge transfer mechanism. The positive charge on the sulphur atom of the prepared oxidized PEDOT permits coordination of negative charge on the oxygen atom of the nitro- group of the explosives providing an efficient acid-base interaction between PEDOT and the analyte of interest. Since the Lewis acid-base interaction is weak. Therefore, efficient detection is best in the solid phases of samples. A part of this mechanism of charge transfer has been discussed by the group Chaudhary et al. in the 20th International Conference on Photoacoustic and Photothermal phenomena [21] PEDOT in its pure form, is insoluble, i.e., infusible at reasonable temperatures and exhibits excellent redox properties. The process ability of PEDOT was achieved by preparing aqueous dispersion in the presence of poly styrenesulfonate (PSS), as the charge-balancing counter ion surfactant to form PEDOT:PSS which is commercially available by the trade name CLEVIOS P. In PEDOT: PSS, PEDOT is in the oxidized state which bears a positive charge on the sulphur atom along the polymer chain. These positive charges interact with the negative charge on the oxygen atom of the polystyrene sulphonate (PSS) to form a stable aqueous dispersion. When it is irradiated with visible 532 nm laser light, as shown in Fig. 8, the free electron (exciton) as produced from the explosive present in the mixture of PEDOT+ explosive interacts with the positive charge present on the sulphur. This can also be termed as optode interaction, and this interaction leads to non-radiative thermal pressure waves, which are nothing but a photoacoustic signal, which can be recorded using indigenously developed data acquisition program in LABVIEW software.

3.6. Effect of PEDOT on FTIR spectra of pure and mixed explosives

From the above FTIR spectra of pure CL-20 and Tex along with these samples mixed with PEDOT between 2500 cm^{-1} to 500 cm^{-1} range clearly shows the interaction of the explosive samples; CL-20 and TEX with PEDOT (Fig. 9). We have focused our study between 1000 and 1300 cm^{-1} these samples as the Nitrogen group stretch occurs in the range of $1290-1360 \text{ cm}^{-1}$. The pure sample shows sharp absorption peaks at 1260 cm^{-1} and 1600 cm^{-1} , whereas the same peaks get reduced when the pure high energy materials are mixed with PEDOT. It confirms the process of the photo-excitation mechanism, which takes place in the visible region. On one side, it provides a strong PA signal due to nonradiative decay, whereas on the other hand, it affects all types of vibrational modes of the molecules. Raman Spectroscopy further validates this interaction between the lone pairs of oxygen present in the explosive samples (TEX and CL20) and the positive charge present on the sulphur atom present in the PEDOT matrix.

3.7. PA spectra of pure and PEDOT mixed with non explosive molecules

We have repeated same experiment with some non-explosive samples such as $NaNO_2$ and $NaNO_3$, and the graph is shown in Fig. 10. One can easily differentiate the PA spectra of explosives and nonexplosives. It also confirms that PA spectroscopy in the presence of PEDOT optode

provides very strong and sharp spectrum lines of explosive as compared to nonexplosive samples. The obtained peaks of PA spectra of pure samples are weak, but their mixture with PEDOT provides broad and distorted peaks as well as 20 times enhancement with respect to the pure sample. However, the intensity of the signature peak is almost 3.5 times less than the PA signal of pure PEDOT.

Sherif et.al have examined the explosive nature of energy-rich bonds such as nitrates (NO_3^-) and perchlorates to identify and differentiate between explosive and non-explosive materials using photoacoustic phase-shift spectroscopy which is mainly based on thermal relaxation process [22]. Further the technique was extended for hyperspectral imaging and pattern recognition for remote sensing of explosive materials. Common explosive materials, including TNT, RDX, and HMX using multi-spectral line sources at 457, 488, and 514 nm wavelengths for standoff imaging of all concealed explosive materials [23]. However, in present case, we have utilized the redox nature of a conducting polymer PEDOT which works as an optode and help to enhance the absorption properties of test samples at visible 532 nm wavelength range. Consequently, there is a significant enhancement of characteristic cavity modes of the PA cell. These modes are well defined and sharp and very strong in nature. However, in case of non-explosive samples these modes are very weak and broaden and occupy the lower than 3 kHz frequency range. The cluster of modes are concentrated between 1 and 3 kHz frequency range and provide clear cut distinction on false detection. The use of PEDOT optode provides an effective sensing medium for the detection of explosives in the visible region using 532 nm wavelength. It also indicates the futuristic use of PEDOT in form of spray to detect solid explosive samples directly in standoff mode.

4. Minimum detection limit

This part is divided into two sub parts. Part (a) deals with CL-20 while part (b) covers the Tex sample analysis.

4.1. CL-20 and TEX

The experiments for different quantities of pure CL-20 and TEX samples were repeated to estimate the minimum level of detection. The selection of mode frequency for determination of Minimum level of detection based on the highest response of the explosives as shown in Fig. 6(a-d).

4.2. Minimum level of detection (D_{min}) of CL-20

Fig. 5 shows the typical strength of the PA signal of CL 20, where the amount of sample used for the experiment was 0.5 mg at 0.5 mJ of incident laser energy. The maximum recorded intensity of the PA signal at 7.2 kHz was of the order of 1650 mV. Therefore, the estimated value of SNR of our PA system is:

$$SNR = 10 \log \left(\frac{S}{N}\right)$$

Where S is the value of the primary signal, and N is the value of the noise. The measured maximum Noise value for the above system was 1.0μ V, and the measured maximum signal value was 1650 mV. Hence,

$$SNR = 10 \log \left(\frac{1.65}{0.000001} \right)$$

= 62.17dB

The SNR is of the order of $165^{*}10^{4}$, and the corresponding minimum detection limit (D_{min}) of CL 20 is:

$$Dmin = \frac{0.5*10 - 3}{165*104} = 0.33*10(-9)g$$

4.3. Minimum level of detection (D_{min}) of TEX

The minimum level of TEX was calculated in a similar manner that was followed for finding out the minimum level detection of CL 20. The signal to noise ratio, SNR, is calculated as follows:

$$SNR = 10 \log\left(\frac{S}{N}\right)$$

The measured maximum Noise value for the above system is $1.5 \,\mu$ V, and the measured maximum signal value at 0.5 kHz mode was 290 mV. Hence,

$$SNR = 10 \log \left(\frac{0.29}{0.0000015} \right) = 17.13 \text{dB}$$



Fig. 5. This figure shows the cell responsivity of the PA cell.



Fig. 6. (a-e) The frequency domain PA spectra of pure high energy sample and their mixture with the organic polymer PEDOT for CL-20 and TEX.

The SNR is of the order of $19.33^{*}10^{4}$, and the corresponding minimum detection limit (D_{min}) of TEX is:

$$Dmin = \frac{0.2*10^{-3}}{19.33*10^{4}} = 1.03.0*10^{-9} \text{g}$$

5. Conclusions

The time-resolved pulsed photoacoustic spectroscopic technique has been carried out for the detection and sensing of high energy materials such as CL20 and TEX using poly (2, 3-dihydrothieno [3,4-b] dioxane-5,7-diyl as a sensor. These explosive shows good absorption PA spectra when it is mixed with PEDOT matrix due to charge transfer mechanism from PEDOT to $-NO_2$ functional group of HEMs under visible 532 nm wavelength. In addition, the effect of PEDOT on detection of non explosive samples such as NaNO₂ and NaNO₃ were also carried out and observed that PA response of non explosives are very weak and broaden in nature. Moreover, total response was always much more smaller then the Pure PEDOT and over ruled the possibility of false detection. The minimum detection limits of CL-20 and TEX were of the order of 0.33×10^{-9} g and 1.03×10^{-9} g, respectively.



Fig. 7. The exponential decay behaviour of acoustic modes of TEX and CL-20 along with their mixture with PEDOT.



Fig. 8. Schematic diagrams showing the mechanism of charge transfer between CL 20 and PEDOT.

Authors Credit statement

The first author Ms. Archana Kumari is a research scholar and pursuing her doctrate work on selected topic. She has carried out entire experimental work and did curation and formal analysis of experimnetal data and calculations. She coauthored in writing – original draft. Second and corresponding author Prof. A.K. Chaudhary, has conceived and conceptualized the idea of using PEDOT as a sensing medium in solid explosive samples without any chemical reaction. Secondly, designed the PA cell and entire experimental setup and methodology used in the experiment. He has also written the major portion of manuscript as well as checked and corrected the experimental and theoretical



Fig. 9. (a, b) This figure shows the FTIR Spectra of CL-20, TEX and their respective mixtures with PEDOT along with highlighting the shift in the absorption peak of explosives when added with PEDOT.



Fig. 10. The PA spectra of pure NaNO₂ and NaNO₃ and their mixtures with PEDOT.

data. In addition, he was involved in funding acquisition, project adminsitation supervison and finally preparing the referees comments and final proof reading.

Third author Dr. K. Rajasekhar has synthesized the new explosive molecules TEX and well known CL-20 samples. His is a resouce person for synthesising pure explosive samples .In addition, he has completed the chemistry part of the manuscript and provided the detailed chemical structure of the samples.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.saa.2020.118597.

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