Inclusive DFT Insight into Sensing Mechanism of Cyclotetrapyrrole Towards Lung Irritants

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Abstract

The development of smart sensing devices for toxic analytes detection especially lung irritants is much essential. The cyclic conducting polymers having infinite π -conjugation are proved to be highly sensitive for toxic analytes. Herein, by using the DFT approach, we investigated the sensing mechanism of cyclotetrapyrrole (CTPy) for accurate detection of phosgene, diphosgene, chloropicrin and chlorine at the B3LYP-D3/6-31+ G (d, p) level. The calculated interaction energies show the physisorption of lungs irritants over the CTPy surface. Natural bond orbital (NBO) and charge decomposition (CDA) analyses predict charge transfer interactions in the complexes. The reduced density gradient (RDG) approach reveals that charge transfer electrostatic hydrogen bonding interactions dominate in the complexes. The sensitivity of CTPy towards lung irritants is further illustrated by the reduction in HOMO-LUMO energy gaps, red shifting of $\lambda_{\max}$ in UV–Visible spectra. Density of state (DOS) analysis affirm that enhanced conductivity upon complexation is due to the origination of new energy states in occupied and virtual orbitals nearer to the Fermi level. Moreover, PDOS spectra show that CTPy primarily contributes to the energy of HOMO. The outcome of the current study depicts appreciable sensitivity of CTPy towards lung irritants. We believe that the upshot of the current findings and their forecasts will provide useful guidelines for an experimentalist to design highly sensitive sensors for toxic analytes using CTPy.

Highlights

1. The highest Q_{NBO} transfer towards the analyte (-0.121) is seen in the chlorine@CTPy complex.
2. The highest reduction in E_g (61 %) between occupied and virtual orbitals is noticed in chlorine@CTPy.
3. The orbital overlap results in a 41 % red shifting of $\lambda_{\max}$ in chlorine@CTPy.
4. Cyclotetrapyrrole is highly sensitive for chlorine.

Introduction

Life on this planet is facing a continuous threat from chemical warfare agents (CWAs), explosives and toxins [1–6]. CWAs have been used in World War I and II due to their detrimental effects. CWAs due to their highly toxic nature are frequently been used in terrorist activities worldwide since the 19th century [7, 8]. In 1995, more than six thousand people in Tokyo have been badly affected by CWAs used in a terrorist attack. In 2016, a variety of CWAs is used as chemical weapons in Malaysia and Syria [9].

Chemical warfare agents can be divided into pulmonary agents or lung irritants (damage lung tissue), vesicants (damage cells), respiratory poisons (stops use of O_2), nerve agents (block nerve impulses) and hallucinogens (mimic neurotransmitter, serotonin involved in dreaming), depending upon their action mechanism and structural dissimilarities [10–13]. Lungs irritants are the derivatives of halogenated nitroalkanes, halogenated carbonic acid and interhalogen compounds [11]. Among toxic warfare agents, the exposure of lungs irritants may cause a severe threat to public health. Lungs irritants include chlorine, phosgene, diphosgene, and chloropicrin [14, 15]. The first CWA used in World War I was chlorine [16].

Exposure to chlorine causes bronchospasm, dyspnea and acute lung injury depending upon the time of exposure and concentration which ultimately results in death and signs of pulmonary fibrosis and reactive airway disease in the survivors [17]. Literature reveals that phosgene caused more than 80% of death in world war I and II among all CWAs. Exposure to phosgene (0.1 ppm) causes severe lungs damage which often results in death [18–20]. Phosgene and diphosgene enter the pulmonary system entirely through inhalation. The most serious toxic effect of phosgene and diphosgene is pulmonary edema. The continuous exposure to phosgene and diphosgene is mostly fatal. Chloropicrin was also used extensively as a lachrymatory agent and lethal gas in World War I [11, 21]. The inhalation of chloropicrin results in vomiting which forced soldiers to remove face masks and expose themselves to the severe action of toxic gases. The lethal effects of chloropicrin are enhanced when mixed with other toxic agents, particularly phosgene and diphosgene. The chloropicrin between 0.8 and 2 ppm concentration is very toxic for mammals and possibly cause lethal pulmonary edema. Due to large scale industrial usage of chloropicrin, it is included in schedule 3 of chemical weapons conventions like phosgene.

Owing to the toxic effect of CWAs, particularly lungs irritants, the development of a sensor for their selective and accurate detection is of great curiosity to the scientific community [22–24]. Various materials have been used as sensors for CWAs experimentally besides theoretical studies which assist to describe the adsorption mechanism of CWAs on highly sensitive novel materials. literature reveals that various surfaces such as C_{24} , $Al_{12}P_{12}$, $B_{12}N_{12}$ and $Be_{12}O_{12}$ nanocages, carbon nanotubes, graphene, graphdiyne, BN and AlN sheets have been theoretically investigated for the adsorption of CWAs [23–27].

Conducting polymers due to their remarkable properties are widely used in solar cells, batteries, electronic and sensing devices [28–30]. Conducting polymers have gained the substantial interest of the scientific community due to outstanding sensing properties. The π -conjugated electron system in conducting polymers provide outstanding electronic and sensing properties. The sensing properties of conducting polymers such as polypyrrole (PPy), polyaniline (PANI), polyfuran (PF) and polythiophene (PTh) have been studied both theoretically and experimentally [31, 32]. There are a handful of reports available in the literature on conducting polymers for the detection of hydrazine, methanol, ethanol, halogens, hydrogen halides, H_2O , CO_2 , CH_4 , NH_3 and HCN etc.

Although linear conducting polymers exhibit reasonable sensing properties, their sensitivity and selectivity are still less satisfactory [33]. The cyclic conducting polymers such as cyclic tetrapyrrole (CTPy), cyclic tetrathiophene and cyclic tetra furan exhibit high sensitivity as compared to the linear analogues owing to their infinite conjugation and highly active porous cavity [23]. Moreover, as per the literature study, cyclic tetrapyrrole (CTPy) is highly sensitive and selective for the adsorption of analytes as compared to its cyclic tetra thiophene or tetra furan counterparts. In recent DFT work, the sensing properties of cyclic tetrapyrrole is studied for the detection of NH_3 , NF_3 , NCl_3 and NBr_3 [33].

Keeping in mind the toxic effects of CWAs and outstanding sensing properties of cyclic conducting polymers, in the DFT framework we herein presented cyclotetrapyrrole (CTPy) as a sensing platform for

the detection of lethal lungs irritants or pulmonary agents. The current study to the best of our understanding has certainly not been described in the literature. This theoretical study will hopefully provide a guideline to experimentalists in developing CTPy based smart sensors for the accurate determination of pulmonary agents.

Computational Methodology

Density functional theory (DFT) and time dependent density functional theory (TD-DFT) simulations are performed at the B3LYP-D3/6-31+ G (d, p) level with Gaussian 09 software and the results are visualized by GaussView 5.0 package [34, 35]. The B3LYP is a reliable functional for geometric and electronic properties of complexes [36]. The van der Waals (vdW) corrections proposed by Grimme (DFT-D3) is used to describe long-range noncovalent interactions in the complexes [37–39]. The Interaction energies (E_{int}) of the complexes is calculated by using equation 1.

$$E_{int} = E_{complex} - (E_{cyclotetrapyrrole} + E_{analyte}) \quad (1)$$

Literature shows that the B3LYP functional with the 6-31+ G (d, p) basis set is an optimal method for electronic properties. Hence, the electronic properties including natural bond orbitals (NBO), frontier molecular orbitals (FMO), energy gap (H-Lgap) between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), total density of states (TDOS), noncovalent interactions (NCI) and charge decomposition analysis (CDA) are also calculated at B3LYP/6-31+G (d, P) level.

The amount of charge transfer and its direction between donor-acceptor pair are elaborated through NBO and CDA analyses. FMO analysis is carried out to understand the variation in conductivity upon complexation. Excited state calculations at twenty excitation states are done with TD-DFT to inspect a change in λ_{max} during interactions. These excitations are considered enough because they brought spectra within the UV-Visible range. The TDOS, NCI and CDA analyses are performed with the Multiwfn 3.7 program to acquire understanding about number of energy states existing in occupied and virtual orbitals beside nature of various interaction during complexation [40, 41].

Results And Discussion

The out come of frequency simulations established that optimized geometries are exact minima (products) with no imaginary frequency (transition state). Moreover, the results of geometry optimization of most stable configurations of each complex are quoted in the manuscript (Table 1) while for the rest of geometries, see supporting information (Table S1-S4).

Optimized Geometry And Stability Of The Complexes

The interaction mechanism of phosgene, diphosgene, chloropicrin and chlorine is investigated over CTPy. E_{int} besides interaction distances (D_{int}) play an important role to get an insight into the sensitivity of substrate towards analytes. The most stable geometries of the complexes are displayed in Figure 2. The interaction mechanism in the complexes is authenticated via strength of H-bonding beside van der Waals and electrostatic interactions. The attachment of phosgene with CTPy results in an E_{int} of $-36.98 \text{ kJ mol}^{-1}$. The distance between closest interacting atoms (H...O) in phosgene@CTPy complex is $2.51 \text{ \AA}$. The interaction of phosgene with CTPy results from hydrogen bonding along with noncovalent interactions (*vide infra*). The electronic cloud is transported from the highly electronegative oxygen atom of analyte towards the electron-deficient hydrogen atom of the substrate which results in charge transfer interactions. The E_{int} of diphosgene@CTPy complex is $-47.70 \text{ kJ mol}^{-1}$ along with $2.05 \text{ \AA}$ of D_{int} between closest interacting H...O atoms. The value of E_{int} of diphosgene@CTPy complex is the highest while D_{int} is the shortest among all studied complexes. The high E_{int} of the complexes determines the strong hydrogen bonding and van der Waals charge transfer interactions because of efficient orbitals overlap (*vide infra*). The adsorption of chloropicrin over CTPy results in E_{int} of $-38.82 \text{ kJ mol}^{-1}$ beside distance between closest interacting atoms (H...O) of $2.51 \text{ \AA}$. In chloropicrin@CTPy complex, the oxygen atom of analyte interacts with hydrogens atom of substrate because the electronic cloud is centred on its oxygen atoms. In contrast substrate (CTPy) exhibits a highly electrophilic cavity which is the most attractive site for the interacting nucleophilic analyte. The E_{int} and D_{int} (H...O) in chlorine@CTPy complex are $-37.24 \text{ kJ mol}^{-1}$ and $2.42 \text{ \AA}$, respectively. In this complex, the chlorine interacts with the CTPy surface because of charge transfer dispersion interactions. The E_{int} values of the complexes attribute that the interaction of phosgene, diphosgene and chloropicrin with CTPy results from dominating hydrogen bonding (electrostatics) beside weak non-covalent forces. The order of stability is diphosgene@CTPy > chloropicrin@CTPy > chlorine@CTPy > phosgene@CTPy.

Table 1
Results of E_{int} , D_{int} and Q_{NBO} of complexes.

Complex	E_{int} (kJ/mol)	Closest interacting atoms	Bond length ($\text{\AA}$)	Q_{NBO} (e) on analyte
Phosgene@CTPy	-36.98	H...O	2.51	0.029
Diphosgene@CTPy	-47.70	H...O	2.05	0.027
Chloropicrin@CTPy	-38.82	H...O	2.51	0.012
Chlorine@CTPy	-37.24	H...Cl	2.42	-0.121

Q Analysis

The charge transfer is a remarkable parameter to get a deeper evaluation of the interaction mechanism in the complexes. NBO analysis permits the amount and direction of charge transfer between donor-acceptor components upon complexation. The outcome of Q_{NBO} is illustrated in Table 1. The Q_{NBO} transferred illustrate that 0.029 e amount of charge is transferred from analytes in phosgene@CTPy complex. The electronic cloud is transferred from electron rich oxygen and nitrogen atoms of phosgene towards electropositive hydron atoms of the CTPy which results in charge transfer H-bonding interactions (*vide supra*). In the diphosgene@CTPy complex, 0.027 e charges is transferred towards the substrate which results in H-bonding interactions. The amount of charge transference from analyte to substrate in chloropicrin@CTPy complex is 0.012 e . The charge transference between donor-acceptor fragments of the complex results in electrostatic hydrogen bonding interaction. Among all studied complexes the highest amount of charge transference ($-0.121 e$) is noticed in chlorine@CTPy. Moreover, contrary to the other complexes, the direction of charge transfer in chlorine@CTPy is

Orbital Analysis

Energies variations in HOMO or occupied and LUMO or virtual orbitals during orbital hybridization in complex formation is an important parameter of electronic properties. The adsorption of analytes over substrate cause a substantial drop in H-L energy gap (E_g). The outcome of FMO analysis are displayed in Table 2. The picturing of densities of occupied and LUMO of the complexes are displayed in Figure 3. The energies of occupied and virtual orbitals of bare CTPy are situated at -5.63 and -1.35 eV, respectively beside E_g of 4.27 eV. The anchoring of phosgene with CTPy altered the energies of HOMO and LUMO to -5.52 and -2.71 eV, respectively in the resultant complex. The orbital hybridization causes a significant reduction of E_g to 2.80 eV in phosgene@CTPy. The percent reduction in E_g is 34% compared to the E_g in bare CTPy. The decrease in E_g authenticates the enhanced conductivity upon complexation.

In the diphosgene@CTPy complex, the HOMO and LUMO are present at -5.49 and -2.30 eV, respectively beside E_g of 3.18 eV. The interaction of diphosgene with CTPy lowers the energy of LUMO, which therefore decreases the E_g to 3.18 eV. The percent reduction in E_g in diphosgene@CTPy is 26% which reveal the sensitivity of CTPy towards analyte. The adsorption of chloropicrin over CTPy results in shifting of energies of HOMO and LUMO orbitals closer to the Fermi level. The HOMO and LUMO of chloropicrin@CTPy are located at -5.66 and -3.50 eV, respectively beside E_g of 2.15 eV. The reduction in E_g compared to the E_g of bare CTPy is 49%. The considerable variations in the energies of both occupied and virtual orbitals are noticed in the chlorine@CTPy complex. The HOMO and LUMO are present at -5.75 and -4.09 eV, respectively. The orbital hybridization of chlorine with CTPy results in its noteworthy decrease of E_g (61%). The highest reduction in E_g is observed in chlorine@CTPy which is quite consistent with the highest Q_{NBO} transfer in the complex. So the highest conductivity is expected in the

chlorine@CTPy complex because of efficient orbital hybridization which is also depicted from its highest shifting of absorption maximum (*vide infra*).

Dos Analysis

DOS analysis is made to further explore the interaction mechanism in complexes through the creation of new energy states besides variations in peaks intensities in spectra. The variation in peaks demonstrates the electronic transport which may either increase or decrease the conductivity. The DOS spectra with HOMO and LUMO visualization are shown in Figure 3. Partial density of states (PDOS) is also made to recognize the contribution of various components of the system towards occupied and virtual energy states (Figure 4). DOS spectra reflect that numerous new energy states are produced in both occupied and virtual orbitals upon complexation compared to the bare CTPy (Figure 3). In phosgene@CTPy complex, new energy states are produced such as at -5.62, -6.20, and -6.40 eV in HOMO while at -2.90, -2.05, and -0.76 eV in LUMO. The generation of new energy states nearer to the Fermi level in both occupied and virtual orbitals results in a reduction in E_g and hence results in an increased conductivity of the complex. The orbital hybridization of diphosgene with CTPy results in the creation of new energy states nearer to the Fermi level at -5.92, -6.10, and -6.12 eV in HOMO whereas at -2.30, -2.25, and -1.74 eV on the LUMO side. The origination of new energy states in DOS spectra affirms the enhanced conductivity of diphosgene@CTPy. Numerous new energy states also arise in the HOMO side such as at -5.80, -6.18, and -6.56 eV, while on the LUMO side at -2.15, -1.78, and -1.02 eV in chloropicrin@CTPy complex. The densities of both HOMO and LUMO are located at the substrate in phosgene@CTPy, diphosgene@CTPy and chloropicrin@CTPy complexes. Moreover, PDOS spectra display that CTPy mainly contributes to HOMO energies in these complexes. For chlorine@CTPy, various new energy states in HOMO have appeared at -5.82, -6.34 and -6.36 eV. Also on the LUMO side, new energy states arise at -4.02, -4.01 and -1.76 eV. The origination of new energy states nearer to the Fermi level eventually causes the reduction in E_g which thus reflects the improved sensitivity of CTPy towards chlorine. The HOMO density is located at CTPy whereas LUMO at chlorine affirms the transferring of electronic cloud from substrate towards analyte which is quite consistent with Q_{NBO} transfer in the complex (*vide supra*).

Uv-visible Analysis

UV-Visible spectroscopic study shows an crucial role in the accurate investigation of sensing and conducting properties of a system towards approaching analytes. UV-Visible spectroscopic studies are performed with TD-DFT and outcomes are tabulated in Table 3. The variation in λ_{max} of CTPy upon interactions with upcoming analytes is graphically presented in Figure 5.

The results of isolated CTPy reveal that the maximum absorbance (λ_{max}) appear at 253 nm. The excitation energy (E_{exc}) required for critical HOMO→LUMO+5 transition is 4.89 eV. The interaction of CTPy with phosgene results in the shifting of λ_{max} to a longer wavelength of 267 nm (bathochromic

shift). The excitation energy of CTPy drops from 4.89 to 4.64 eV upon complexation with phosgene. The lower excitation energy facilitates dominant HOMO→LUMO+4 transition in phosgene@CTPy. The shifting of $\lambda_{\max}$ towards longer wavelength in the complex is 6 % which reflects increased conductivity upon complexation. The observed $\lambda_{\max}$ in diphosgene@CTPy is 293 nm beside 4.23 eV excitation energy. The red shifting

Table 2
FMO analysis of analytes@CTPy complexes.

Complex	E_H (eV)	E_L (eV)	E_g (eV)	H-Lgap (% reduction)
CTPy	-5.63	-1.35	4.27	0%
Phosgene@CTPy	-5.52	-2.71	2.80	34%
Diphosgene@CTPy	-5.49	-2.30	3.18	26%
Chloropicrin@CTPy	-5.66	-3.50	2.15	49%
Chlorine@CTPy	-5.75	-4.09	1.65	61%

Table 3
UV-Visible results of analytes@CTPy complexes.

Complex	Excitation energy (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (% shift)	Oscillator strength (a.u)	Dominant transition
CTPy	4.8960	253	0%	0.0000	HOMO→LUMO+5
Phosgene@CTPy	4.6438	267	6%	0.0179	HOMO→LUMO+4
Diphosgene@CTPy	4.2354	293	16%	0.0040	HOMO-5→LUMO
Chloropicrin@CTPy	4.2037	295	17%	0.0106	HOMO-1→LUMO+2
Chlorine@CTPy	3.4834	356	41%	0.2740	HOMO-7→LUMO

of maximum absorbance in the complex is 16% compared with bare CTPy. The Decrease in excitation energy of electrons is linked to crucial HOMO-5→LUMO transition. The absorption maxima of

chloropicrin@CTPy are red-shifted to 295 nm (17%) besides E_{exc} of 4.20 eV, associated with dominant HOMO – 1→LUMO+2 transition. The highest shifting of λ_{max} (41%) towards a longer wavelength is observed in chlorine@CTPy which is quite consistent with its highest reduction in E_g between occupied and virtual orbitals (*vide supra*). The E_{exc} required for dominant HOMO–7→LUMO transition of electron significantly drop to 3.48 eV. The lowering of E_{exc} indicates an increase in electronic transition ($\pi \rightarrow \pi^*$) and hence enhanced conductivity upon complexation.

Nci Analysis

NCI is formulated on density and reduced density gradient (RDG). The RDG scattering graph is based on the following equation.

$$RDG = \frac{1}{2 \left(3\pi^2 \right)^{1/3} \rho \cdot (r)^{4/3}} |\nabla \rho(r)|$$

Where, ρ and $\nabla \rho$ represents electronic density and electronic density gradient, respectively. So as to recognize the nature of interactions, three eigenvalues ($\lambda_1 \leq \lambda_2 \leq \lambda_3$) of Hessian are measured. The maximum electronic density is located at nuclei and hence all the eigenvalues are negative. For covalent interactions, two eigenvalues are negative whereas the third one is positive. For bonded and non-bonded interactions, λ_2 eigenvalue is vital and therefore $\lambda_2 < 0$ and $\lambda_2 > 0$, respectively. Moreover, RDG iso-surface is constructed on colour codes i.e. red, blue and green colours represents the steric clashes, hydrogen bonding and non-covalent interaction, respectively. Characteristics spikes either towards positive or negative of $\lambda_2 \rho$ can be recognize from RDG-2D scatter map. NCI-RDG 2D scatter maps and 3D colour-filled RDG iso-surfaces of analyte@CTPy are shown in Figure 6.

RDG map of phosgene@CTPy indicates characteristic spikes originated at the low-density side. The low-density spikes at $\lambda_2 \rho = -0.01$ and $\lambda_2 \rho = -0.02$ a.u. indicate noncovalent and hydrogen bonding interactions, respectively. Spikes at $\lambda_2 \rho = 0.01$ corresponds to steric clashes in the complex. The presence of NCI are also depicted from a green disc in a 3D-isosurface map. For diphosgene@CTPy bunch of three characteristic spikes appeared at $\lambda_2 \rho = -0.02$, -0.01 and 0.01 a.u. corresponds to hydrogen bonding, noncovalent forces and steric clashes, respectively. The anchoring of chloropicrin with CTPy results in three different spikes in the RDG map. Spikes appeared at $\lambda_2 \rho = -0.02$ a.u. are due to hydrogen bonding interactions whereas spikes at $\lambda_2 \rho = -0.01$ to 0.01 a.u. are due to vdW interactions. The peaks linked with steric clashes appear at $\lambda_2 \rho = 0.02$ a.u. The outcome of NCI clarified that in chlorine@CTPy three distinct spikes appeared at $\lambda_2 \rho = -0.02$, -0.01 to 0.01 and $\lambda_2 \rho = 0.02$ a.u., related to electrostatic interactions, van der Waals dispersion and steric repulsions, respectively.

Cda Analysis

CDA is an imperative procedure to investigate the charge transfer between donor-acceptor fragments pairs. The results of CDA are displayed in Table 4. Here, we primarily emphasis on the relative extent of charge transfer through donation or backdonation (d-b) and repulsive polarization (r) between fragment pairs of complexes.

The d-b via donation between phosgene and CTPy fragments pair of phosgene@CTPy complex is $-0.0047 e$. The negative charge shows that charge transference by π -backdonation leads over a donation during orbital overlap. The value of repulsive polarization between phosgene-CTPy fragments is $-0.001 e$ which advocates the moving aside of charge density from binding region upon complexation. The d-b in the diphosgene-CTPy is $0.007 e$ beside $-0.081 e$ repulsion. In diphosgene@CTPy charge transfer via donation dominates. Orbital hybridization in diphosgene and CTPy cause moving away of charge density from the interaction zone. The d-b and r in chloropicrin-CTPy pair of chloropicrin@CTPy are -0.002 and $0.053 e$, respectively. This complex transference of charge via backdonation leads over the donation and also charge density concentrate in the binding region during complexation. In chlorine@CTPy complex, the values of the relative amount of charge transference and repulsions in the fragments pair are -0.071 , $-0.084 e$, respectively. Transfer of charge via backdonation mechanism leads in chlorine-CTPy pair. Moreover, during orbitals overlap moving aside of charge density from the binding zone is observed in chlorine-CTPy pair.

Table 4
CDA of analytes@CTPy complexes (in units of e).

System	Donation (d)	Backdonation (b)	$d - b$	Repulsion (r)
Phosgene@CTPy	-0.022678	0.024781	-0.047459	-0.001064
Diphosgene@CTPy	0.009009	0.001926	0.007083	-0.081533
Chloropicrin@CTPy	-0.011629	-0.008904	-0.002725	0.053176
Chlorine@CTPy	-0.017413	0.053694	-0.071107	-0.084644

Conclusions

Herein, in the DFT framework, we presented cyclotetrapyrrole as a promising sensor for the detection of highly toxic lung irritants. The stability order of complexes in terms of E_{int} of diphosgene@CTPy > chloropicrin@CTPy > chlorine@CTPy > phosgene@CTPy. The highest Q_{NBO} transfer towards the analyte (-0.121) is seen in the chlorine@CTPy complex. The highest reduction in E_g (61%) between occupied and virtual orbitals is noticed in chlorine@CTPy. Furthermore, orbital overlap results in a 41% red shifting of λ_{max} in chlorine@CTPy. Bathochromic or red shifting of absorption maxima in UV-Visible spectra is due to increased $\pi \rightarrow \pi^*$ electronic transitions. The creation of new energy levels in HOMO and LUMO sides

closer to Fermi level in DOS spectra and origination of distinct peaks in RDG map authenticate greater sensitivity of CTPy towards lung irritants. CDA results show that transference of charge through backdonation leads over the donation in phosgene@CTPy, chloropicrin@CTPy and chlorine@CTPy complexes. The current comprehensive theoretical work will exposed a new path for the exploration of smart sensors constructed on CTPy for the detection of toxic analytes.

Declarations

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Credit author statement

Saif Ullah: Calculations, Data curation. **Haleema Bibi:** Calculations, Data curation. **Faizan Ullah:** Software, Visualization, Investigation. **Tabish Jadoon:** Conceptualization, Investigation, Supervision, Authentication, Draft preparation.

Conflict of interest

The authors have no known opposing financial or personal interests that could have seemed to effect the work described in this manuscript.

Code availability

Gaussian 09 software, GaussView 5.0 package

Data availability

Corresponding author declare that the data associated with current manuscript will be provided on demand.

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Figures

Figure 1

Structures of lung irritants

Phosgene@CTPy

Diphosgene@CTPy

Chloropicrin@CTPy

Chlorine@CTPy

Figure 2

Most stable optimized geometries of analyte@CTPy complexes.

Figure 3

DOS spectra with HOMO and LUMO visualization.

Phosgene@CTPy

Diphosgene@CTPy

Chloropicrin@CTPy

Chlorine@CTPy

Figure 4

PDOS spectra of the complexes.

Figure 5

UV-Visible spectra of analyte@CTPy complexes.

Figure 6

RDG-2D scatter map (Right) and 3D colour isosurface (Left).

Supplementary Files

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