Inclusive DFT insight into sensing mechanism of cyclotetrapyrole

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 cyclotetrapyrole (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 analytes 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 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 $\lambda_{\text{max}}$ 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. Moreover, the competing role of naturally occurring atmospheric water is also investigated. 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

- The highest QNBO 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.
- The orbital overlap results in a 41% red shifting of $\lambda_{\text{max}}$ in chlorine@CTPy.
- Cyclotetrapyrole is highly sensitive for chlorine.

Keywords DFT Study · Sensors · Cyclotetrapyrole · Lung irritants

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 nineteenth century [7, 8]. In 1995, more than 6000 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]. Lung 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 [22–26]. 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, MOFs, BN, and AlN sheets have been theoretically investigated for the adsorption of CWAs [23–25, 27–30].

Conducting polymers due to their remarkable properties are widely used in solar cells, batteries, electronic and sensing devices [31–33]. 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 [34, 35]. There are a handful of reports available in the literature on conducting polymers for the detection of hydrazine, methanol, ethanol, halogens, hydrogen halides, H$_2$O, CO$_2$, CH$_4$, NH$_3$, HCN, etc. [36–40].

Although linear conducting polymers exhibit reasonable sensing properties, their sensitivity and selectivity are still less satisfactory [38]. The cyclic conducting polymers such as cyclic tetrapyrole (CTPy), cyclic tetrathiophene, and cyclic tetratfuran 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 tetrapyrole (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 tetrapyrole is studied for the detection of NH$_3$, NF$_3$, NCl$_3$, and NBr$_3$ [38].

Keeping in mind the toxic effects of CWAs and outstanding sensing properties of cyclic conducting polymers, in the DFT framework we herein presented cyclotetrapyrole (CTPy) as a sensing platform for the detection of lethal lungs irritants or pulmonary agents (Fig. 1). 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 methods**

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) simulations were performed at the B3LYP-D3/6–31 + G (d, p) level with Gaussian 09 software and the results were visualized by GaussView 5.0 package [41, 42]. The B3LYP is a reliable functional for electronic properties [43]. The van der Waals (vdW) corrections proposed by Grimme (DFT-D3) were used to describe long-range noncovalent interactions in the complexes [44–46]. The Interaction energies ($E_{int}$) of the complexes were calculated by using Eq. 1.

$$E_{int} = E_{complex} - (E_{cyclotetrapyrole} + E_{analyte})$$  (1)

Literature shows that the B3LYP functional with the 6–31 + G (d, p) basis set is an optimal method for electronic properties [47–51]. Hence, the electronic properties

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**Fig. 1** Structures of lung irritants

![Fig. 1 Structures of lung irritants](image-url)

chlorine  
phosgene  
diphosgene  
chloropicrin
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 pairs are elaborated through NBO and CDA analyses. FMO analysis is carried out to understand the variation in conductivity upon complexation. Excited state calculations at 20 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 [52]. The TDOS, NCI and CDA analyses are performed with the Multiwfn 3.7 program to acquire an understanding of several energy states existing in occupied and virtual orbitals besides the nature of various interactions during complexation [53, 54].

Results and discussion

The outcome of frequency simulations established that optimized geometries are exact minima with no imaginary frequency. 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 the geometries, see supporting information (Table S1–S5).

Optimized geometry and stability of the complexes

The interaction mechanism of phosgene, diphosgene, chloropicrin, chlorine, and water 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 Fig. 2. The interaction mechanism in the complexes is authenticated via the strength of H-bonding beside van der Waals dispersion interactions. The attachment of phosgene with CTPy results in an E_int of −36.98 kJ mol−1. The distance between closest interacting atoms (H…O) in phosgene@CTPy complex is 2.08 Å. The interaction of phosgene with CTPy results from hydrogen bonding along with dispersion interactions (vide infra). The electronic cloud is transported from the highly electronegative oxygen atom of the analyte towards the electron-deficient hydrogen atom of the substrate which results in H-bonding interactions. Phosgene interacts with CTPy surface more firmly than with graphdiyne surface reported in the literature which can be depicted from higher E_int of the phosgene@CTPy complex [20]. Likewise the E_int of phosgen@CTPy is also higher than the reported E_int of phosgene over cyclic analogue of cyclotetrapyrrole, cyclotetrafuran and cyclotetrathio- phene calculated at ωB97XD/with 6–31+G (d,p) level [23]. The E_int of diphosgene@CTPy complex is −47.70 kJ mol−1 along with 2.05 Å 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 of CTPy with lung irritants. The high E_int of the complexes determines the dominating hydrogen bonding beside weak van der Waals interactions (vide infra). The adsorption of chloropicrin over CTPy results in E_int of −38.82 kJ mol−1 beside distance between closest interacting atoms (H…O) of 2.51 Å. In chloropicrin@CTPy complex, the oxygen atom of analyte interacts with hydrogens atom of substrate because the electronic cloud is centered on its oxygen atoms. In contrast to an analyte, a 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 kJ mol−1 and 2.42 Å, 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 beside weak van der Waals dispersion forces. The order of stability is diphosgene@CTPy > chloropicrin@CTPy > chlorine@CTPy > phosgene@CTPy. Moreover, the adsorption of lung irritants over cyclotetrapyrrole results in higher E_int than the reported E_int of NH3, NF3, NCl3, and NBr3 over cyclotetrapyrrole surface [55]. The CTPy surface is also used to understand its sensibility for naturally competing for atmospheric water. The interaction of water results in E_int of −56.65 kJ mol−1, which is as a result of strong hydrogen bonding interactions in the complex and is higher than

| Complex            | E_int (kJ/mol) | E_def (kJ/mol) | Closest interacting atoms | Bond length (Å) | Q_NBO(e) on analyte |
|--------------------|---------------|---------------|--------------------------|----------------|---------------------|
| Phosgene@CTPy      | −36.98        | 1.13          | H…O                     | 2.08           | 0.029               |
| Diphosgene@CTPy    | −47.70        | 3.27          | H…O                     | 2.05           | 0.027               |
| Chloropicrin@CTPy  | −38.82        | 1.22          | H…O                     | 2.51           | 0.012               |
| Chlorine@CTPy      | −37.24        | 3.77          | H…Cl                    | 2.42           | −0.121              |
| Water@CTPy         | −56.65        | 3.92          | H…O                     | 1.94           | 0.034               |
previously reported $E_{\text{int}} (42.25 \text{kJ/mol})$ of polypyrrole–H$_2$O complex calculated at B3LYP/6-31G(d) level of DFT [56]. The higher $E_{\text{int}}$ of water@CTPy in all studied analytes is also depicted from its shortest H…O distance of 1.94 Å. As water acts as a ligand and shows strong influence on the interaction with CTPy surface, hence some other medium should be used for the detection process. Furthermore, the extent of interaction in the complexes is also validated from deformation energy ($E_{\text{def}}$) of CTPy surface upon complexation. Various factors such as mode of interaction, interaction
distances, nature, and number of interacting atoms of analytes cause the deformation of base substrate. The highest $E_{\text{def}}$ is calculated for water@CTPy whereas least for Phosgene@CTPy complex that agree well with their $E_{\text{int}}$. Furthermore, the results of $E_{\text{int}}$ reveal that these analytes physically adsorbed over CTPy surface.

**QNBO analysis**

The charge transfer is a remarkable parameter to get a deeper evaluation of the interaction mechanism in the complexes. NBO analysis permits examining the amount and direction of charge transfer between donor and acceptor components upon complexation. The outcome of $Q_{\text{NBO}}$ is illustrated in Table 1. The $Q_{\text{NBO}}$ transferred illustrate that 0.029 $e$ amount of charge is transferred from phosgene to CTPy surface contrary to the reported NBO charge transferred from graphdiyne surface to phosgene [23]. The electronic cloud is transferred from electron rich oxygen and nitrogen atoms of phosgene towards electropositive hydrogen atoms of the CTPy which results in charge transfer H-bonding interactions (vide supra). In the diphosgene@CTPy complex, 0.027 $e$ charges are 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 hydrogen bonding and dispersion 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 from substrate towards analyte during complexation.

An appreciable amount of charge is reversed back during complexation which results in charge transfer dispersion interactions. In water@CTPy complex, 0.034 $e$ charge is transferred from analyte to substrate as a result of H-bonding interactions which is slightly higher than reported 0.025 $e$ of charge transfer in 3PPy–H2O (vide supra) [56]. The following order of $Q_{\text{NBO}}$ transfer is observed in the complexes, i.e., chlorine@CTPy > water@CTPy > phosgene@CTPy > diphosgene@CTPy > chloropicrin@CTPy.

**Orbital analysis**

Energies variations in HOMO or occupied and LUMO or virtual orbitals are important parameters of electronic properties. The adsorption of analytes over substrate causes a substantial drop in the H–L energy gap ($E_{\text{g}}$). The outcome of the FMO analysis is displayed in Table 2. The picturing of densities of occupied and LUMO of the complexes are displayed in Fig. 3. The HOMO and LUMO of isolated phosgene appeared at −9.08 and −2.09 eV, beside the H–L gap of 6.99 eV. The HOMO and LUMO of diphosgene appeared at somewhat at higher energy than phosgene. The HOMO of diphosgene is located at −9.02 eV while LUMO is at −2.06 eV along with an H–L gap of 6.96 eV. The HOMO of chloropicrin is present at −8.99 eV whereas its LUMO is at −3.26 eV beside the H–L energy gap of 5.73 eV. The presence of various electronegative atoms makes chloropicrin an electrophile. The reported energy of HOMO and LUMO of chloropicrin are −7.38 and −3.68 eV, beside H–Lgap of 3.7 eV calculated at GGA-PBE/6-31G** level [24]. HOMO of isolated chlorine appeared at an energy of −8.65 eV and its LUMO at −4.04 eV. The H–L gap in chlorine is 4.61 eV, which is the least among studied analytes. The HOMO and LUMO of isolated water are present at −8.73 and 0.68 eV, respectively beside Eg of 9.41 which matched well with its reported energy gap (9.62 eV) at B3LYP/6-31G(d) level [56].

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 interaction 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. Reduction in H–Lgap for the adsorption of phosgene over CTPy is much greater as compared to the reported decrease in the H–L gap of phosgene over graphdiyne surface. The prominent decrease in $E_g$ authenticates the enhanced sensitivity of CTPy surface for phosgene compared to graphdiyne surface [20].

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 interaction 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 interaction which is also depicted from its highest shifting of absorption maximum (vide infra). The HOMO and LUMO of water@CTPy are situated at $-5.53$ and $-1.23$ eV, respectively. The H–L energy gap of 4.30 eV is present in water@CTPy which is similar to the reported energy gap of 3PPy-H$_2$O (4.34 eV) [56]. The $E_g$ of water@CTPy is slightly increased compared to $E_g$ of an isolated water molecule. This insignificant change in H-L gap shows that the electronic character of CTPy is not influenced by the interaction of H$_2$O.

**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 Fig. 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 (Fig. 4). DOS spectra reflect that numerous new energy states are produced in both occupied and virtual orbitals upon complexation compared to the bare CTPy (Fig. 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 interaction 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). The interaction of water with CTPy results in the origination of new energy states at various new energy states in the HOMO side at $-5.80$, $-6.21$, and $-6.34$ eV while on the LUMO side at $-0.78$, $-6.34$, and $-0.16$ eV. Moreover, the densities of both HOMO and LUMO are present at the CTPy substrate. PDOS spectra of water@CTPy complex indicate that CTPy shows sole contribution in HOMO energy of the complex.

**UV–Visible analysis**

UV–Visible spectroscopic study shows a 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 $\lambda_{\text{max}}$ of CTPy upon interactions with upcoming analytes is graphically presented in Fig. 5. For an excited state we have one or more transitions, and the dominant transition is selected from relative contributions of each transition (see supporting information). The results of isolated CTPy surface reveal that the maximum absorbance ($\lambda_{\text{max}}$) appear at 253 nm which is in quite good agreement with its previously reported absorption maxima ($\lambda_{\text{max}} = 226$ nm) [55]. The excitation energy ($E_{\text{exc}}$) required for critical HOMO → LUMO + 5 transition is 4.89 eV. The interaction of CTPy with phosgene results in the shifting of $\lambda_{\text{max}}$ 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 $\lambda_{\text{max}}$ towards longer wavelength in the complex is 6% which reflects increased conductivity upon complexation. A larger shift of absorption maxima is observed for the interaction of phosgene with CTPy surface than the previously reported value of $\lambda_{\text{max}}$ in phosgene@GDY complex [20]. The observed $\lambda_{\text{max}}$ in diphosgene@CTPy is 293 nm beside 4.23 eV excitation energy. The red shifting 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 $E_{\text{exc}}$ of 4.20 eV, associated with dominant HOMO − 1 → LUMO + 2 transition.
**Fig. 4** PDOS spectra of the complexes

**Table 3** UV–Visible results of analytes@CTPy complexes

| Complex        | Excitation energy (eV) | λ<sub>max</sub> (nm) | λ<sub>max</sub> (% shift) | Oscillator strength (a.u) | Dominant transition (relative probability) | Result         |
|----------------|------------------------|----------------------|---------------------------|----------------------------|---------------------------------------------|----------------|
| CTPy           | 4.89                   | 253                  | 0%                        | 0.00                       | HOMO→LUMO + 5 (97%)                       | Reference      |
| Phosgene@CTPy  | 4.64                   | 267                  | 6%                        | 0.02                       | HOMO→LUMO + 4 (80%)                       | Red shift      |
| Diphosgene@CTPy| 4.23                   | 293                  | 16%                       | 0.00                       | HOMO – 5→LUMO (68%)                       | Red shift      |
| Chloropicrin@CTPy| 4.20                  | 295                  | 17%                       | 0.01                       | HOMO – 1→LUMO + 2(77%)                     | Red shift      |
| Chlorine@CTPy  | 3.48                   | 356                  | 41%                       | 0.27                       | HOMO – 7→LUMO (85%)                       | Red shift      |
| Water@CTPy     | 4.17                   | 296                  | 17%                       | 0.00                       | HOMO→LUMO + 1 (70%)                       | Red shift      |
Fig. 5 UV–Visible spectra of analyte@CTPy complexes

The highest shifting of \( \lambda_{\text{max}} \) (41\%) towards a longer wavelength is observed in chlorine@CTPy which is quite consistent with its highest reduction in \( E_{\text{exc}} \) between occupied and virtual orbitals (vide supra). The \( E_{\text{exc}} \) required for dominant HOMO → LUMO transition of electron significantly drop to 3.48 eV. The lowering of \( E_{\text{exc}} \) indicates an increase in electronic transition (\( \pi \rightarrow \pi^* \)) and hence enhanced conductivity upon complexation. The interaction of water with CTPy cause shifting of absorption maxima towards a longer wavelength of 296 nm. The red-shifted values as mentioned earlier illustrate the sensing aptitude of CTPy surface toward studied analytes. The visual changes in UV–Visible spectra of the complexes indicate that cyclotetrapyrole also act as chemical sensors for studied analytes.

NCI analysis

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

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

where \( \rho \) and \( \nabla \rho \) represent electronic density and electronic density gradient, respectively. 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; 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, \( \lambda_2 \) eigenvalue is vital and therefore \( \lambda_2 < 0 \) and \( \lambda_2 > 0 \), respectively. Moreover, RDG iso-surface is constructed on color codes, i.e., red, blue, and green colors represents the steric clashes, hydrogen bonding, and non-covalent interaction, respectively. Characteristics spikes either towards positive or negative of \( \lambda_2 \rho \) can be recognized from RDG-2D scatter map. NCI-RDG 2D scatter maps and 3D color-filled RDG iso-surfaces of analyte@CTPy are shown in Fig. 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 hydrogen bonding, noncovalent forces, and steric clashes, respectively. The anchoring of chloropicrin with CTPy results in three different spikes in the RDG map. Spikes that 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 H-bonding, van der Waals dispersion interaction and steric repulsions, respectively. The interaction of water with the CTPy surface results in the origination of distinct spikes at \( \lambda_2 \rho = -0.01 \) a.u. and between \( -0.02 \) to 0.02 a.u. related to van der Waals and H-bonding interactions. The spike at the positive side of the RDG map indicates repulsion in the complex.

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 emphasize 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 phosgen@CTPy complex is \( -0.0047 \) e. The negative charge shows that charge transference by \( \pi \)-backdonation leads to a donation during the interaction. The value of repulsive polarization between phosgene-CTPy fragments is \( -0.001 \) e which advocates the moving aside of charge density from the 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. Interaction of 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 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 $-0.071$ and $-0.084 \, e$, respectively. Transfer of charge via backdonation mechanism leads in chlorine-CTPy pair. Moreover, during interaction moving aside of charge density from the binding zone is observed in chlorine-CTPy pair. The relative donation of charges in the water@CTPy complex indicate that charge transfer via back donation dominates while repulsive polarization show moving away of charge density as of interaction region during complexation.

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

| System         | Donation (d) | Backdonation (b) | $d - b$ | Repulsion ($r$) |
|----------------|--------------|------------------|--------|-----------------|
| Phosgene@CTPy  | $-0.023$     | $0.025$          | $-0.047$ | $-0.001$        |
| Diphosgene@CTPy| $0.009$      | $0.001$          | $0.007$ | $-0.081$        |
| Chloropicrin@CTPy| $-0.011$    | $-0.009$         | $-0.002$ | $0.053$         |
| Chlorine@CTPy  | $-0.017$     | $0.054$          | $-0.071$ | $-0.085$        |
| Water@CTPy     | $-0.019$     | $0.036$          | $-0.055$ | $-0.167$        |
Conclusions

Herein, in the DFT framework, we presented cyclotetrapyrole as a promising sensor for the detection of highly toxic lung irritants. The stability order of complexes in terms of $E_{\text{int}}$ of diphosgene@CTPy $>$ chloropicrin@CTPy $>$ chlorine@CTPy $>$ phosgene@CTPy. Furthermore, the competing role of naturally occurring atmospheric water is noticed in chlorine@CTPy. Furthermore, interaction in another medium should be used for the detection process. The highest $Q_{\text{sub}}$ 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, interaction results in a 41% red shifting of $\lambda_{\text{max}}$ in chlorine@CTPy. Batohromic 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 expose a new path for the exploration of smart sensors constructed on CTPy for the detection of toxic analytes.

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Authors’ contributions Saif Ullah and Haleema Bibi: calculations and data curation. Faizan Ullah: software, visualization, investigation. Tabish Jadoon: conceptualization, investigation, supervision, authentication, and draft preparation. All authors read and approved the final manuscript.

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Data availability The corresponding author declares that the data associated with the current manuscript will be provided on demand.

Code availability Gaussian 09 software, GaussView 5.0 package

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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