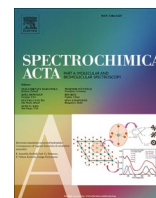




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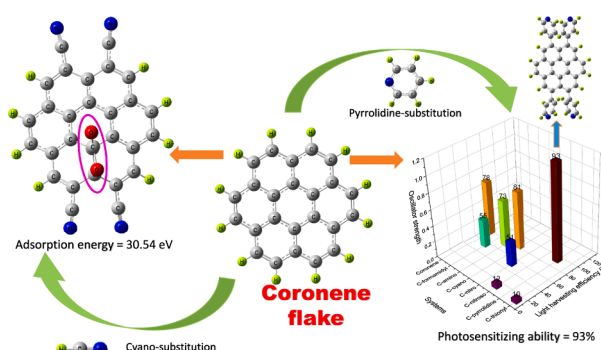
Influence of the substitution of different functional groups on the gas sensing and light harvesting efficiency of zero-dimensional coronene quantum dot: A first principle DFT study

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HIGHLIGHTS

- Investigation of sensing nature of functionalized coronene quantum dot.
- Frontier molecular orbitals and molecular electrostatic potential surface validates their chemical stability.
- Higher adsorption energy was observed for gas molecules on quantum dot.
- Light harvesting efficiency of functionalized quantum dots was elevated.
- The designed quantum dots have potential applications in gas sensing and photosensitivity.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study accounts for the structural and electronic properties of a zero-dimensional coronene quantum dot (QD) and its substituted structures with seven different functional groups. The substitution of functional groups lead to the alteration of the centrosymmetric geometry of the coronene flake and thus, incredible properties were observed for the functionalized QDs. The increment in the band gap after the substitution of the functional groups was responsible for the increase in the chemical stability. The cohesive energy however decreased for the functional QDs. Fourier transform Infrared spectra were traced for all the QDs to confirm the availability of the functional groups and their participation in the chemical reactivity. After the substitution of functional groups, the extremely enhanced light harvesting efficiency of functionalized QDs was obtained. Furthermore, the sensing capability of the functionalized QDs for CO, CO₂, and NH₃ was also calculated and it was found that C-cyano, C-nitro, C-nitroso, C-pyrrolidine, and C-thionyl QDs have better sensing capabilities for CO₂ molecules. C-pyrrolidine had the highest value of light harvesting efficiency of about 96%. This reflects the potential photosensitive candidature of C-pyrrolidine. Therefore, the present study sets a perfect benchmark for designing and fabricating efficient photosensitive materials and gas-sensing devices using the introduced QDs in the near future.

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1. Introduction

Quantum dots (QDs) are a class of compounds with the most tunable properties. Yet they are expensive and working with them directly without having any pre-evaluation of the desired properties can be financially striking. QDs are the materials of the future and every possible domain of research and technology has its embedded applications. Generally, large polycyclic aromatic hydrocarbons are graphene structures with remarkable physical properties and wide applicability in physical as well as material science [1–3]. Their planer structures and extended π -conjugation of benzene rings are the reason for them being strong donors and acceptors in the presence of acceptors and donors respectively. They are often unreactive but the substitution of the reactive moieties results in the increment of the reactivity [4]. Coronene ($C_{24}H_{12}$) is one such polycyclic aromatic hydrocarbon also called superbenzene and cyclobenzene that consists of seven *peri*-fused benzene rings [5]. Its structure is similar to pyrene. It is a carbon flake that is the zero-dimensional dot i.e., QD with finite nanostructures and small sizes ranging from 2 to 10 nm [6]. The centrosymmetric structure of coronene is the reason for its low dipole moment and chemical reactivity. Generally, aromatic hydrocarbons do not have an active tendency toward chemical reactions [7]. It's their bond conjugation that helps in creating an environment for the hydrocarbon to experience the charge transfer. Moreover, the substitution of chemically reactive moieties like functional groups might enhance the chemical importance of such QD structures. These QD structures have immense physio-chemical properties and have applications in quantum confinement, imaging, Quantum computing, photovoltaics, light-emitting diodes, single-photon sources, cell biology, chromatography, microscopy, and many more [8–10]. There are a lot of studies reported on the different applications of the mono-layered QD structures and aromatic hydrocarbons. Polycyclic aromatic hydrocarbons like phenanthrene, anthracene, naphthalene, etc., have been studied and successfully employed for different optoelectronic applications so far [11–13]. Motivated by this fact, we look forward to establishing such utility of coronene flake in the present study. On the other hand, the reported ionization potential (IP) of coronene (IP = 7.29 eV) is lower than those of naphthalene (IP = 8.14 eV), phenanthrene (7.89 eV), and anthracene (7.44 eV) [14–17]. This reveals that coronene has to show stronger electron donor properties upon the electron donor–acceptor interaction and is ideal for charge transport applications.

Boron-nitrogen decorated coronene and hexabenzocoronene were employed for charge transport applications by Tonshoff and Shanyal in their respective studies [18,19]. These studies are favorable in developing the tunable optoelectronic properties of boron-nitrogen functionalized coronene QD and reveal significant shifts of absorption spectra if compared to those of coronene. Borazine is sometimes also called “inorganic benzene” due to its similarities with benzene and is also used as a dopant or additive agent to the graphene nanosheet for optoelectronic applications. The strong polarity of borazine induces significant transformations of physical and structural properties to functionalized graphene sheets [20]. The enhanced electronic properties and biological activity of the aromatic QDs make them a potential candidate for various exotic applications as gas sensors [21,22] and as anti-HIV protease inhibitors [23]. The sensing capabilities of QDs were reported in a lot of studies. The sensing capability of graphene and silicene concerning some gas molecules such as NH_3 , NO, and CO was previously reported [24–27]. Recently, an experimental and computational study was performed for some nanoribbons with complex shapes of edges, such as zigzag-shaped ribbons for enhanced sensitivity towards gas molecules [28]. It was observed that the QDs have good responsivity towards the sensing property. The reported study is motivated by the literature.

The present study accounts for the structural and electronic properties of the coronene QD (CQD) flake and functionalized coronene QD after the substitution of formamide, amino, cyano, nitro, nitroso,

pyrrolidine, and thionyl groups on the coronene flake. The density functional theory (DFT) tools were used for the quantum chemical calculations of all the functionalized QDs. The electronic properties of the functionalized QDs were examined using the computed absorption spectra. The vibrational modes of the bonds related to the substituted functional groups were studied using the computed Fourier-transform infrared (FT-IR) spectra. The present study will account for the ability of the functionalized QDs to sense the gas molecules.

2. Materials and methods

DFT along with suitable hybrid functionals was used for the structural optimizations to the true local minima. All the quantum chemical calculations were carried out by Gaussian software (<https://gaussian.com/>). The PDB structure of coronene flake was downloaded from the PubChem database (<https://pubchem.ncbi.nlm.nih.gov/>) with PDB ID:9115. The structure optimization was done using the B3LYP/6–311++G(d,p) set of functionals. The structural relaxation was successfully achieved to the true local minima as there are no imaginary frequencies found. The substitution of the functional groups in the coronene flake was done using the Gauss view program (<https://gaussian.com/gaussview6/>). The stability of the functionalized QDs was calculated using the expression (1) [29]:

$$E_{\text{cohesive}} = \frac{\sum [N_{\text{element}} \times E_{\text{element}}] - E_{\text{QD}}}{\sum N_{\text{element}}} \quad (1)$$

where E_{cohesive} is the cohesive energy that is the measure of interaction of the gas molecule and the QD. E_{QD} is the optimization energy of the functionalized QDs, N_{element} is the number of atoms of specific elements present in the gas molecule and E_{element} is the energy corresponding to each element.

Koopman's set of equations along with the energies of highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO) was adopted for calculating the global reactivity descriptors. Koopman's equations were previously used in reference papers [30,31]. The band gap of the functionalized QDs obtained from the reactivity descriptors was further verified from the density of states (DOS) analysis. The DOS spectra were plotted using the Gauss sum software (<https://gausssum.sourceforge.net/>). The molecular electrostatic potential (MEP) surface was traced for all the considered QD structures for locating the nucleophilic and electrophilic sites within the functionalized QDs. The polar calculations were done to obtain the vibrational spectra and account for the vibrational details of the substituted functional groups. The excited state calculations were studied using the time-dependent-density functional theory (TD-DFT) with self-consistent field theory (SCF). The oscillator strength (f) obtained for the electronic transitions was further employed for calculating the light-harvesting efficiency (LHE). LHE of the CQDs was calculated using the below-mentioned formula [32,33]:

$$\text{LHE} = 1 - 10^{-f} \quad (2)$$

The sensing capability of the functionalized QDs was also analyzed computationally. The gas molecules of carbon dioxide (CO_2), carbon monoxide (CO), and ammonia (NH_3) were drawn by the builder tool, and the geometries were optimized to check the influence of the gas molecules in the functionalized QDs. The interaction between the gas molecules and the QD structures was reported by calculating the adsorption energy using the below-given expression [34,35]:

$$E_{\text{adsorption}} = |E_{(\text{gas}+\text{QD})} - (E_{\text{gas}} + E_{\text{QD}})| \quad (3)$$

$E_{\text{adsorption}}$ and $E_{(\text{gas}+\text{QD})}$ are the adsorption energy and optimization energy of the complex formed after the adsorption of the gas molecule on the QD surface. E_{gas} and E_{QD} are the optimization energy of the gas molecule and QD respectively.

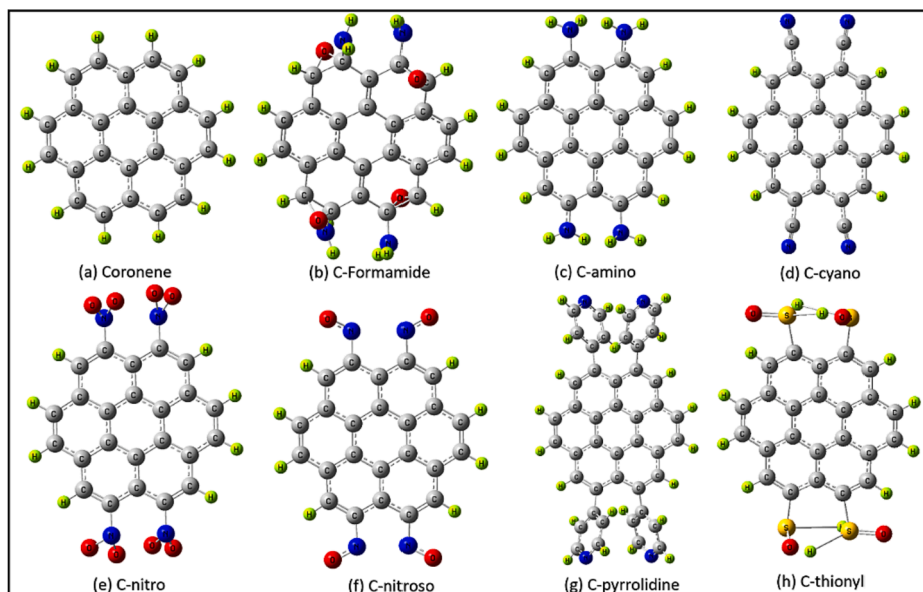


Fig. 1. Relaxed structures of the optimized geometries of coronene QD and other functionalized QDs.

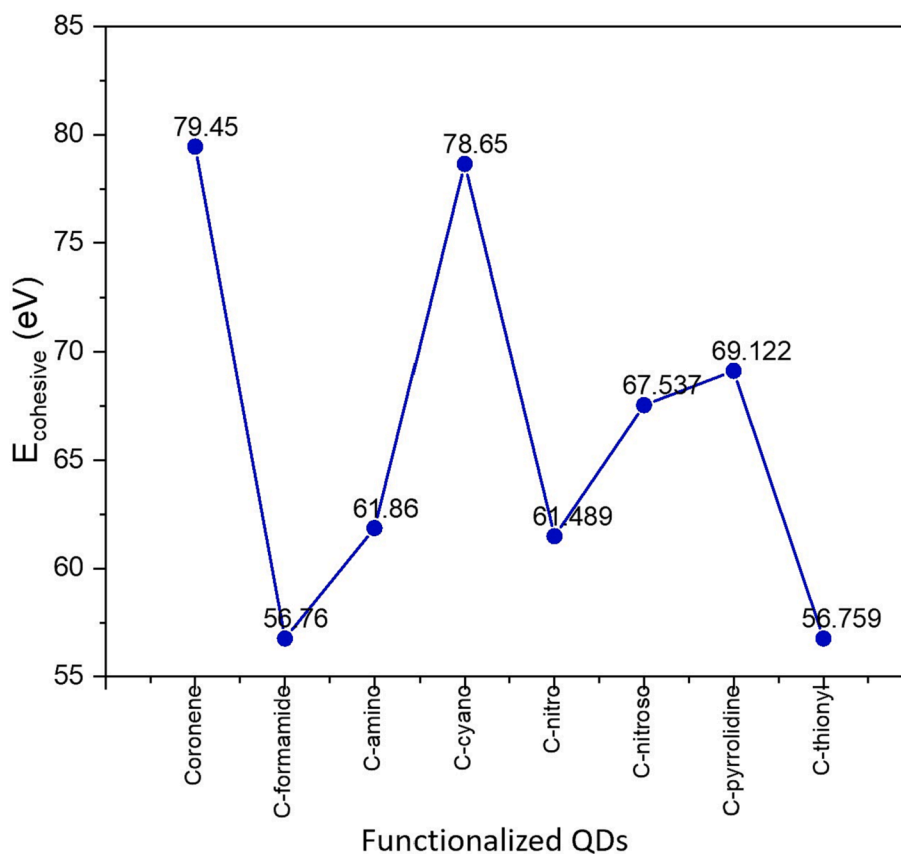


Fig. 2. Comparison of the cohesive energy of the functionalized QDs.

3. Results and discussion

3.1. Structural and Charge Analysis

In the present study, seven different functionalized QDs were designed by substituting the functional groups in coronene flake (Fig. 1 (a)). By substituting different functional groups at the two opposite sides

of the coronene flake like formamide (Fig. 1(b)), amino (Fig. 1(c)), cyano (Fig. 1(d)), nitro (Fig. 1(e)), nitroso (Fig. 1(f)), pyrrolidine (Fig. 1 (g)), and thionyl (Fig. 1(h)), the symmetrical functionalized QD structures were obtained. Except for C-formamide and C-cyano which have D_2 and D_{2h} symmetry respectively, all the other considered QDs have $C1$ point group symmetry. The D_2 symmetry of C-formamide is due to the involvement of the unsymmetrical multi-atomic functional groups. The

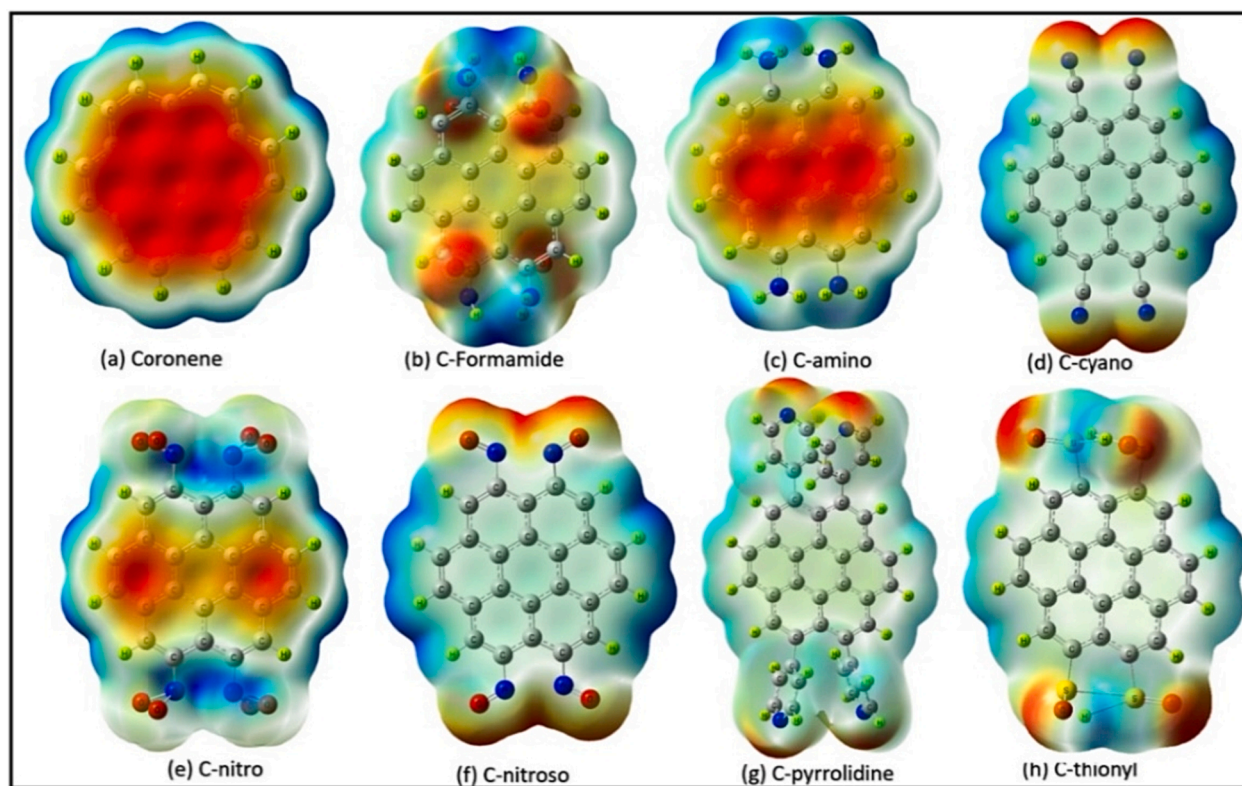


Fig. 3. Molecular electrostatic potential surfaces of the functionalized QDs.

C = N bonds in the cyano group form the carbon chain and thus result in the D_{2h} symmetry. The symmetrical structures of the designed QDs show the isotropic behavior of the structures and this leads to low polarity of the structures [36]. The low polarity leads to a low dipole moment. The bond length was also analyzed and is listed in SD 1. The bond length corresponding to the functional groups and the position of substitution were majorly monitored. The C–H bonds in the coronene flake were observed to be 1.08 Å. These bonds have less length as compared to the other C = C (1.37 Å) and C–C (1.42 Å) bonds. The substitution of the functional groups was done on the 13C, 15C, 24C, and 28C. As the designed QDs must be stable in order to undergo practical fabrication and experimentation. The cohesive energy or the binding energy was calculated for all the functionalized QDs (Fig. 2). The cohesive energy is the measure of the stability of the functionalized QD [37]. The positive value of cohesive energy reveals the stable configuration of the functionalized QDs. The larger the value of cohesive energy, the higher will be the stability of the structures. The cohesive energy for coronene flake was calculated as 79.45 eV. This value was observed to decrease after the substitution of the functional groups. All the functionalized QDs have lowered the value of cohesive energy compared to coronene flake. The centrosymmetric structure of coronene flake has higher stability but the substitution of the functional groups made the QD structures symmetrical yet chemically reactive. Due to the rise in the chemical reactivity, there observed decrement in the cohesive energies of the functionalized QDs. C-formamide has the lowest cohesive energy of 56.76 eV. C-amino, C-cyano, C-nitro, C-nitroso, C-pyrrolidine, and C-thionyl have cohesive energy equal to 61.86, 78.65, 61.48, 67.53, 69.12, and 66.75 eV respectively. Thus, the functionalized QDs have cohesive energy in decreasing order of C-cyano > C-pyrrolidine > C-nitroso > C-amino > C-nitro > C-formamide > C-thionyl. In this context, C-cyano was observed as the most stable functionalized QD followed by C-pyrrolidine.

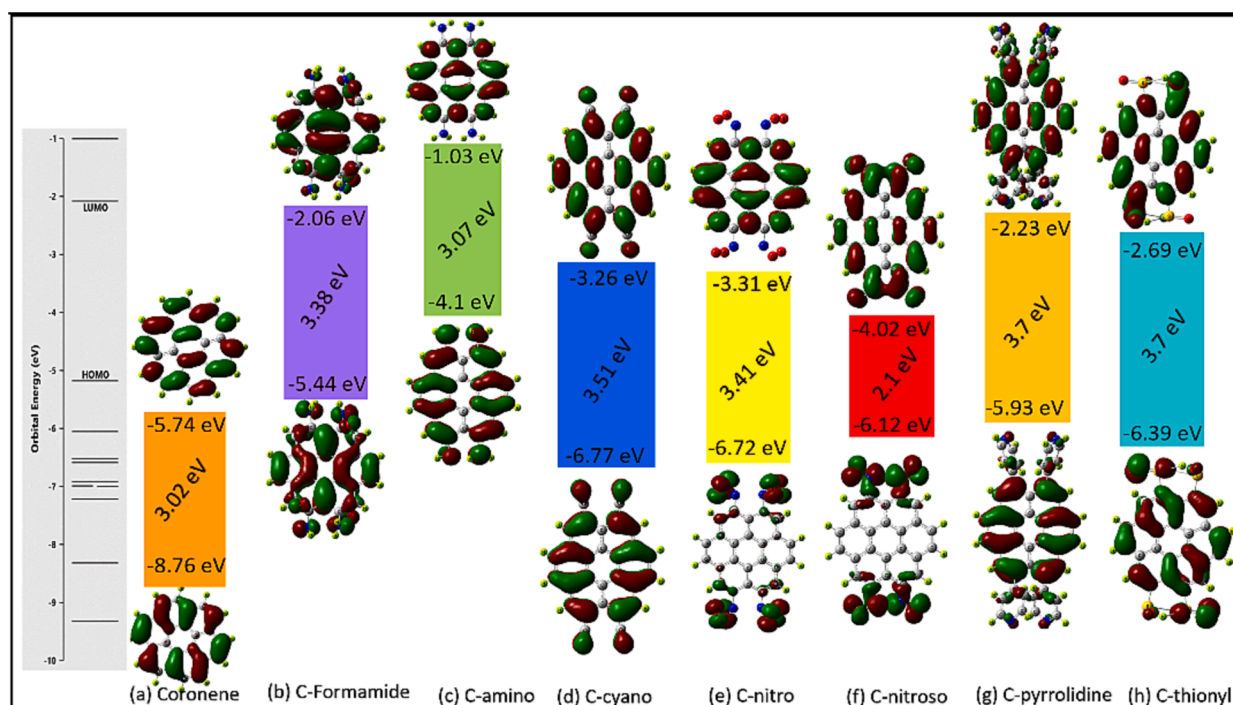
3.2. Molecular electrostatic potential surface analysis

MEP surface is the hypothetical surface mapping over the molecular geometries. These surfaces allow us to visualize variably charged regions of a molecule. These surfaces majorly comprise red and blue colors indicating the electron-withdrawing and electron-donating moieties, respectively [38]. The coronene flake gave a beautiful symmetrical MEP shape (Fig. 3 (a)). The centrosymmetric structure of coronene flake results in the centrosymmetric distribution of the charge throughout the geometry. The boundary hydrogen atoms in coronene flake act as strong electron-donating due to the positive Mulliken charge distribution. The carbon atoms of the benzene act as strong electron-withdrawing groups. This was due to the availability of the conjugated C–C bonds in the coronene flake. Thus, the MEP surface of the coronene flake indicates the involvement of the overall geometry in charge interactions. These reactive surfaces were seen to get shifted toward the substituted functional groups in the functionalized QDs. The benzene ring in C-amino (Fig. 3(c)) and C-nitro (Fig. 3(e)) QD showed the negative electrostatic potential that suggests the active participation of the benzene rings as nucleophiles in intramolecular interactions. However, the amino hydrogen and the nitrogen atoms of the nitro groups acted as electrophilic moieties. The electropositive character of the nitrogen molecules of the amino and nitro groups results in the electropositive character of the respective functional groups. The boundary hydrogen atoms in C-cyano and C-nitroso QDs act as strong electropositive moieties (Fig. 3(d), and (f)). The red surface in C-cyano and C-nitroso was settled over the functional groups. In C-formamide there seen absence of involvement of the C–C bonds in the intramolecular interactions. Despite this, intramolecular interactions were observed between the nitrogen and oxygen atoms of the formamide group (Fig. 3(b)). The nitrogen atom acts as the donating and the oxygen atom acts as the withdrawing atom. Similar kind of interactions within the functional group was observed in C-thionyl (Fig. 3(h)). Due to the availability of the sulfur atom which is strong electron-donating in the thionyl group, it acts as positive and the oxygen

Table 1

Values of the global reactivity parameters of all the functionalized QDs (all values are in eV).

Parameters	HOMO	LUMO	ΔE	IP	EA	CP	χ	η
Coronene	-8.76	-5.74	3.02	8.76	5.74	-7.25	7.25	1.51
C-formamide	-5.44	-2.06	3.38	5.44	2.06	-3.75	3.75	1.69
C-amino	-4.1	-1.03	3.07	4.1	1.03	-2.56	2.56	1.53
C-cyano	-6.77	-3.26	3.51	6.77	3.26	-5.01	5.01	1.75
C-nitro	-6.72	-3.31	3.41	6.72	3.31	-5.05	5.05	1.7
C-nitroso	-6.122	-4.02	2.1	6.122	4.02	-5.07	5.07	1.05
C-pyrrolidine	-5.93	-2.23	3.7	5.93	2.23	-4.08	4.08	1.85
C-thionyl	-6.39	-2.69	3.7	6.39	2.69	-4.54	4.54	1.85

**Fig. 4.** Molecular orbitals and orbital surfaces distribution of HOMO-LUMO surfaces and the respective band gap of all the CQDs.

atoms act as negative moieties. The pyrrolidine ring being strong charge withdrawing was seen to be under the influence of red surface and the boundary hydrogen atoms impart in the electron donation. Therefore, the charge interactions in C-pyrrolidine were observed between the pyrrolidine ring and the boundary hydrogens of the benzene rings (Fig. 3 (g)). The MEP surface reports strong intramolecular interactions within all the functionalized QD structures. This shows the immense high structural stability and strong chemical reactivity of all the functionalized QDs.

3.3. Molecular orbitals and reactivity descriptors analysis

The molecular orbital energies and the global reactivity descriptors were studied to establish the strong stability and occurrence of intramolecular charge transfer within the functionalized QD structures [39]. The HOMO-LUMO energies were employed for the calculations of the reactivity descriptors. All the calculated parameters are listed in Table 1. The band gap (ΔE) of 3.02 eV was observed for the probe coronene flake. The substitution of the active functional groups in the coronene flake was seen to increase the ΔE (except C-nitroso) of the functionalized QD structures. The availability of single nitrogen and oxygen atoms with nearly equal electronegativities result in the perfect occurrence of the sharing of electrons and makes the QD stable. The non-polar interactions thus take place between the nitrogen and oxygen atoms making the geometry of the C-nitroso group of nonpolar nature. The nonpolar

nature thus, fails to hinder the dipole moment of the system, that's why the reduction in the dipole moment of the C-nitroso QD was stated in the earlier discussion. The ΔE for all the considered functionalized QDs were obtained in sequence C-pyrrolidine = C-thionyl > C-cyano > C-nitro > C-formamide > C-amino > C-nitroso. A comparison of the band gap of all the functionalized QDs is illustrated in Fig. 4. IP is the potential that is required by any system to eject the electrons from the outermost shells for charge interactions. The low value of IP denotes the ease of electron donation. The IP of coronene flake was obtained as 8.76 eV. The effect of the substitution of the functional groups was observed by the decrement in the values of IP . C-amino was the QD with the lowest value of IP followed by C-formamide and C-pyrrolidine. The EA of the functionalized QDs was in sequence coronene > C-nitroso > C-nitro > C-cyano > C-thionyl > C-pyrrolidine > C-formamide > C-amino. The electron affinity (EA) values represent the active nature of the molecules in withdrawing the charge cloud from the donating moiety. In this context, the C-amino was the best QD with withdrawing ability followed by the C-pyrrolidine and C-formamide. The CP denotes the chemical reactivity of the molecules towards the intramolecular bond formation and charge transfer. The CP of the QDs was in sequence coronene > C-nitroso > C-nitro > C-cyano > C-thionyl > C-pyrrolidine > C-formamide > C-amino. The tendency of the functional groups and the reactive sites of the molecule to attract shared electrons for forming a chemical bond is explained using electronegativity (χ). The χ of coronene flake was obtained as 7.25 eV and was seen to decrease for the functionalized QDs.

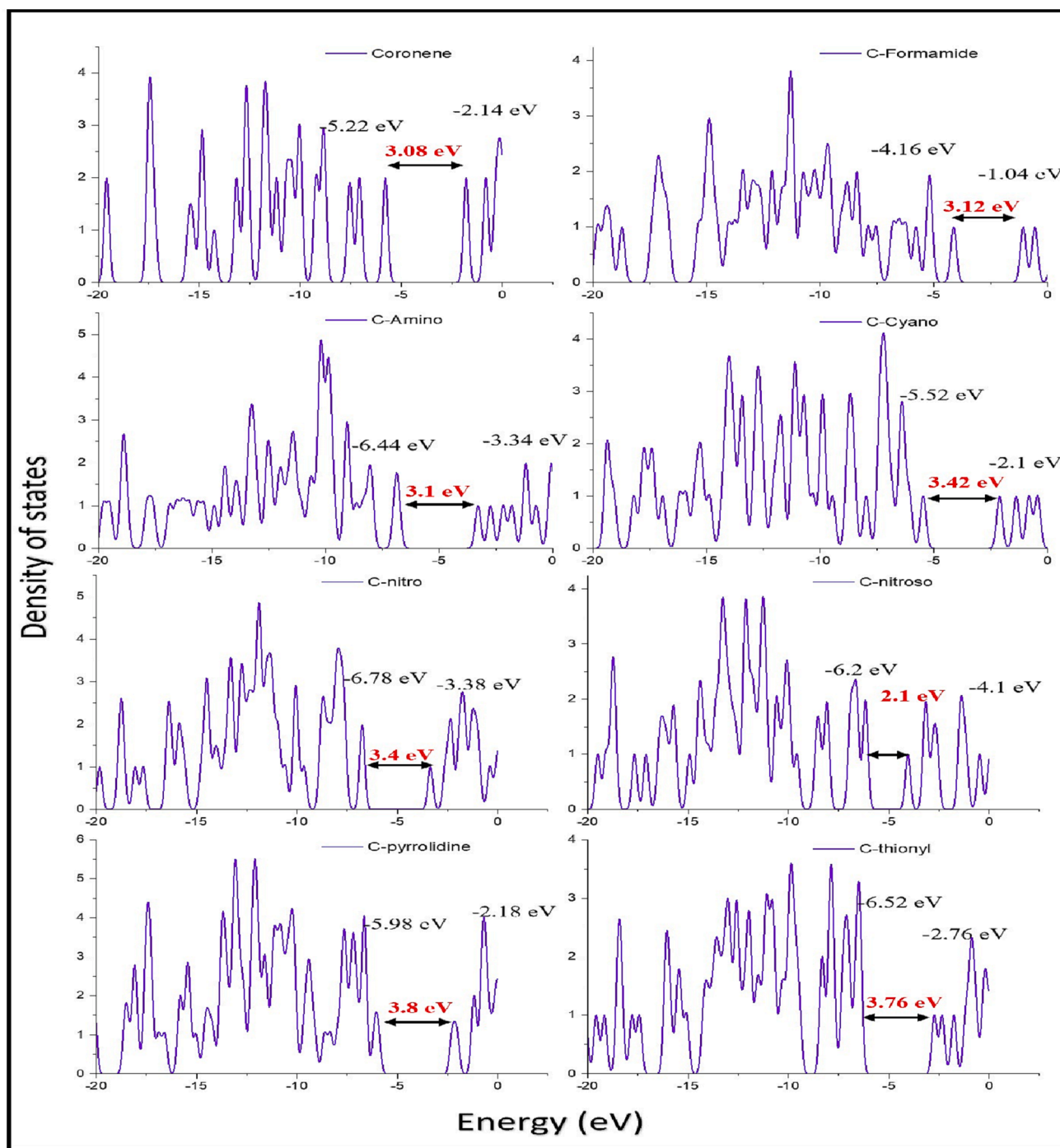


Fig. 5. The density of state maps for all the functionalized QDs illustrates the band gap between the molecular orbitals.

The decrement in the χ represents the overall electropositive character and stability of the functionalized QDs. The chemical hardness (η) is the extent of the hardness and rigidity of any compound. This simply explains the stiffness of any compound when involved in a chemical reaction. The unstable molecules often dissociate during the chemical reaction and thus have low η . However, the value of η seen to increase after the substitution of the functional groups. C-pyrrolidine and C-thionyl were the QDs with the highest η . For a better understanding of charge transfer, the molecular orbital surfaces have been studied. The pictorial representation of the FMO surfaces is represented in Fig. 4. Red color represents the positive phase of molecular orbitals while green color indicates the negative phase respectively. The molecular surfaces were seen to surround the complete geometries of all the QDs except C-

nitro and C-nitroso where the clear transferring of the charge cloud was observed from nitro and nitroso groups to the benzene rings of the coronene respectively. This might be due to the involvement of the nitrogen atoms which are highly electropositive and act as perfect strong electron-donating parts. In all the functionalized QDs, the HOMO-LUMO surfaces reveal the extreme involvement of the substituted functional groups in the occurrence of ICT. The overall FMO analysis reveals that all the functionalized QDs have undergone significant chemical reactivity and C-pyrrolidine was the QD with intermediate values for all the FMO parameters. Therefore, C-pyrrolidine was found to be the best QD with promising chemical reactivity and good responses in further computational parameters can be expected from C-pyrrolidine.

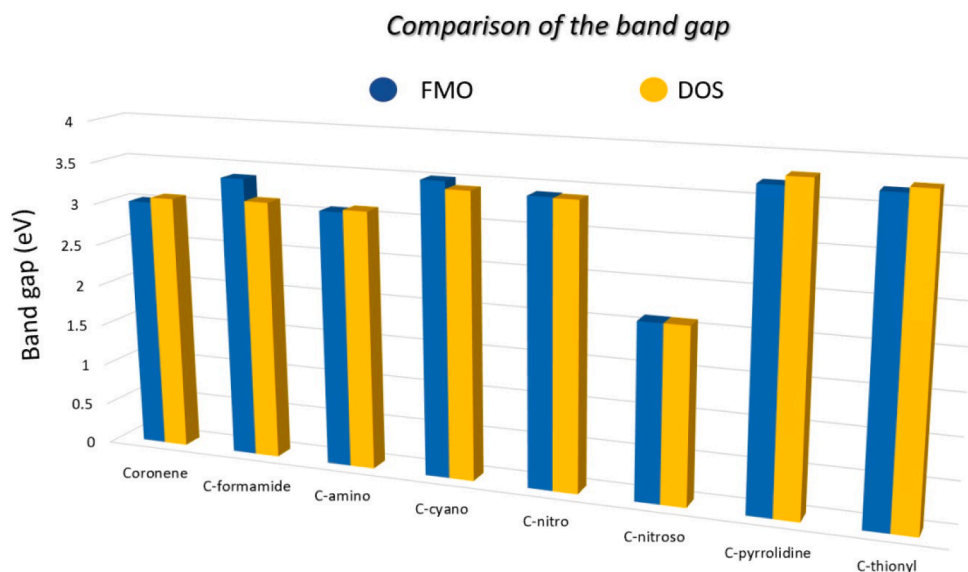


Fig. 6. Comparison between the band gap of all the QDs obtained from the frontier molecular orbitals and density of states.

3.4. Density of states analysis

DOS spectra reveal the accumulation of the HOMO and LUMO corresponding to the energy. The peaks located in the left side of the DOS spectra indicate the HOMO and the peaks in the right side of the DOS spectra indicate the LUMO. The energy gap between the last peak of HOMO and the first peak of LUMO (from left to right) is expressed as the band gap of the respective geometry [40]. Fig. 5 indicates the DOS spectra of all the functionalized QDs and their corresponding band gap. The comparison between the band gap of the functionalized QDs obtained from Koopman's equation and DOS spectra was found comparable and is shown in Fig. 6. The band gap obtained from Koopman's equation was in sequence C-pyrrolidine = C-thionyl > C-cyano > C-nitro > C-formamide > C-amino > C-nitroso. The band gap obtained from the DOS spectra was in the decreasing sequence of C-pyrrolidine > C-thionyl > C-cyano > C-nitro > C-formamide > C-amino > coronene > C-nitroso. A huge similarity in the band gaps was observed. Thus, the DOS analysis justifies the calculation of the band gap and better supports the results obtained by Koopman's calculations.

3.5. Vibrational modes analysis

The vibrations of the substituted functional groups in QDs were reported using the FT-IR spectra. Fig. 7 illustrates the FT-IR spectra for coronene flake and all the functionalized QDs. In the present study, there were observed numerous vibrational assignments corresponding to each considered functionalized QDs but only modes corresponding to the substituted functional groups were mentioned in the paper. To show the proper comparison, the same range of wavenumber from 0 to 4000 cm^{-1} is taken. The vibrational modes with major IR peaks were shown in Figure and the vibrational details were listed in SD 2. The modes corresponding to the substituted functional groups were observed to give most of the prominent peaks in the IR spectra. The coronene flake has only C-H bonds that give a standard rocking peak at 561 cm^{-1} , a torsional peak at 871 cm^{-1} , and an asymmetric stretching peak at 3176 cm^{-1} . The C-formamide was observed to give higher peaks for the wagging of the C-H bonds at 210, 260, and 543 cm^{-1} . The out-of-plane torsional bending of N-H bonds in C-formamide was observed to give a peak at 1668 cm^{-1} . After this peak, two other prominent peaks were obtained for symmetric and asymmetric stretching of the N-H bond at 3490 and 3607 cm^{-1} respectively. Similar to C-formamide, the N-H bonds of the C-amino were seen to give major IR peaks for N-H

stretching at 3420 and 3608 cm^{-1} . The peaks at the start of the IR spectra of C-amino were observed for the twisting of the N-H bonds at 193, 467, and 721 cm^{-1} . The out-of-plane bending of the N-H bond gave a sharp peak at 885 cm^{-1} . Therefore, the amino group in C-amino majorly contributed to the formation of the peaks of the IR spectra. In C-cyano, the C-N bond has a rocking vibration at 553 cm^{-1} . The other bending modes of C-H bonds are also seen to give sharp peaks at 842, 961, 1238, and 1410 cm^{-1} . The symmetric stretching of the C-N bond in C-cyano was obtained at 2336 cm^{-1} . Thus, in C-cyano, not only C-N, but other C-H bonds also constituted the IR spectra. In IR spectra of C-nitro, the N-O bond gave rocking at 637 and bending of C-N at 1134 cm^{-1} . The rest of the peaks were observed for the bending and stretching of C-H bonds. Similar to C-nitro, the only mode observed for the substituted-nitroso group in C-nitroso was obtained as rocking of C-N bonds at 642 and 799 cm^{-1} . The IR spectra of C-pyrrolidine gave multiple peaks in the starting range from 0 to 1500 cm^{-1} . Multiple major modes in this region were observed for the rocking and bending of the 63C-15C, 13C-53C, 43C-22C, and 33C-25C bonds. These bonds attach the pyrrolidine ring to the coronene flake. These modes were observed at 143, 253, 498, 513, 529, 542, 551, 590, 594, and 633 cm^{-1} . Therefore, all the bonds of the pyrrolidine ring were involved in the vibrations of the C-pyrrolidine structure. In C-thionyl, stretching modes of S-C with high IR intensity were observed at 864 cm^{-1} and stretching of S-H at 2097 cm^{-1} . Thus, the FT-IR study of all the functionalized QDs showed that in most of the structures like C-formamide, C-amino, C-cyano, C-pyrrolidine, and C-thionyl, the substituted functional groups were found to give the major peaks and thus imparts in the formation of the FT-IR spectra. Additionally, it can be mentioned that the IR peaks in the designated regions of the vibrations of the functional groups gave a practical verification of the presented study. In other words, the practical synthesis of such QDs will give the desired results and the presented study can be experimentally followed. The modes obtained for the vibrations of the functional groups showed the active participation of the substituted functional groups in the formation of the IR spectra.

3.6. Electronic transitions analysis

QDs are technologically important structures that have fabulous tunable properties of the UV-Vis spectra and that can be used for numerous optoelectronic applications. The absorption spectra of all the functionalized QDs were computed for fifteen states and are shown in Fig. 8. The absorption spectra suggests that all the functionalized QDs

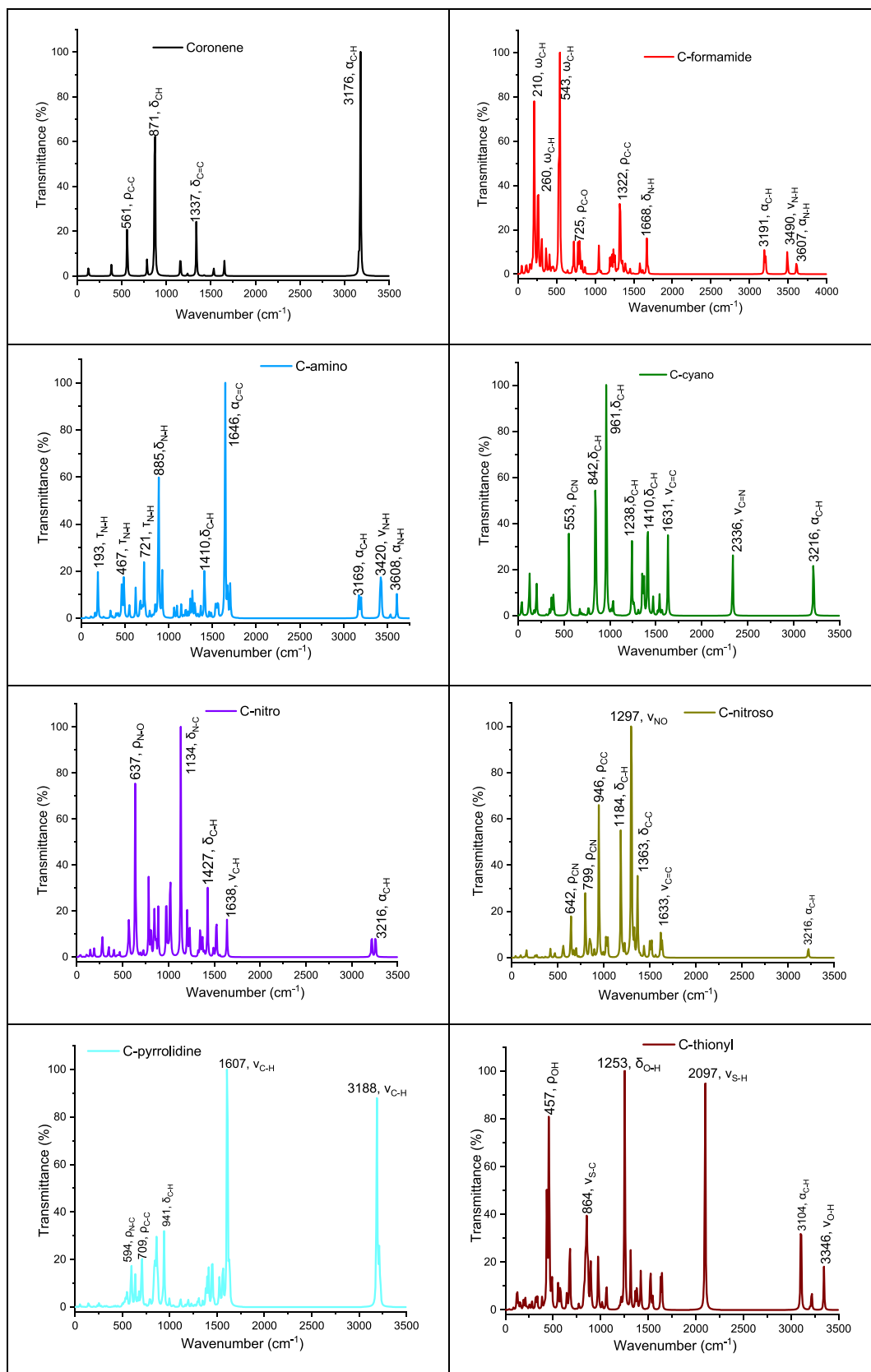


Fig. 7. FT-IR spectra of all the functionalized QDs with labelled vibrational modes for the substituted functional groups (Symmetric stretching- ν , asymmetric stretching- α , torsional bending in plane (scissoring)- δ , twisting- τ , rocking- ρ).

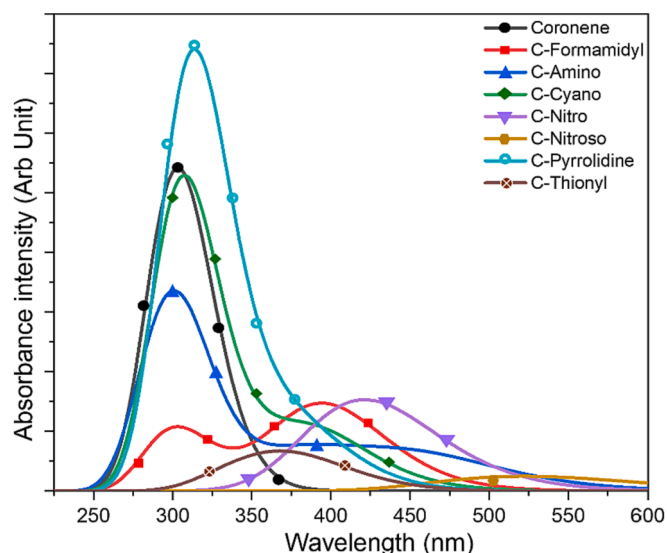


Fig. 8. Computed absorbance spectra of all the functionalized QDs.

Table 2

Details of the crucial transitions of the absorption spectra for all the functionalized QDs.

Systems	Excitation energy	Wavelength	Oscillator strength
Coronene	4.08 eV	303 nm	0.6689
C-formamide	4.06 eV	305 nm	0.1296
C-amino	4.04 eV	306 nm	0.5831
C-cyano	4.06 eV	304 nm	0.7222
C-nitro	2.96 eV	417 nm	0.3119
C-nitroso	2.38 eV	520 nm	0.0594
C-pyrrolidine	3.96 eV	312 nm	1.1961
C-thionyl	3.42 eV	362 nm	0.0476

have strong absorption in the UV range along with the weak or strong absorption in the visible region. The crucial transitions (transitions with the highest oscillator strength) were selected from each absorption data for analyzing the absorption properties of all the functionalized QDs (Table 2). The probe coronene flake gave a sharp absorption spectrum between 250 and 400 nm with the crucial transition at 303 nm wavelength. This is the $S_0 \rightarrow S_4$ transition that leads to the peak of the coronene flake absorption spectra. The substitution of the functional groups in the coronene flake results in the broadening of the range of the absorption band. Two broad and attached gaussian bands were observed for C-formamide with crucial transition $S_0 \rightarrow S_1$ at 305 nm with low absorbance intensity. The absorption band of C-amino was primarily between 250 and 350 with a broad shoulder band between 350 and 600 nm. Transition $S_0 \rightarrow S_6$ was observed as the crucial transition for C-amino at 306 nm. A similar kind of more intensified spectra was obtained for C-cyano with one gaussian and one shoulder band between 250 and 500 nm. $S_0 \rightarrow S_5$ transition of C-cyano was the crucial transition and resulted in the peak of the absorption spectra at 304 nm. C-nitro has a broad absorption band between 350 and 550 nm with a shifted peak at 417 nm. A similar shift of peak was observed for C-nitroso at 520 nm. C-nitro and C-nitroso were the structures with the highest wavelength of the absorption spectra. C-pyrrolidine was the QD with the highest absorbance intensity of the absorbance peak at 312 nm wavelength. Due to the highest intensity, the highest peak was observed for C-pyrrolidine. Moreover, the crucial transition of C-pyrrolidine was found to have the highest oscillator strength of 1.1961. C-thionyl gave a broad absorption with low intensity and peak wavelength at 362 nm. There was a significant behavior in the modification of wavelength and excitation energy observed after the substitution of the functional groups in the coronene flake. The peak wavelength for all the functionalized QDs was seen to increase and the excitation energy was observed to be decreased. Therefore, it can be said that bathochromic shift was observed in the absorbance spectra of all the functional QDs. Such behavior of the functionalized QDs reveals the existence of the transitions that involve moving an electron from a bonding π orbital to an antibonding π^* orbital. Thus, the introduced QDs possess $\pi \rightarrow \pi^*$ transitions. Bond conjugation in the benzene rings of the coronene after the substitution of

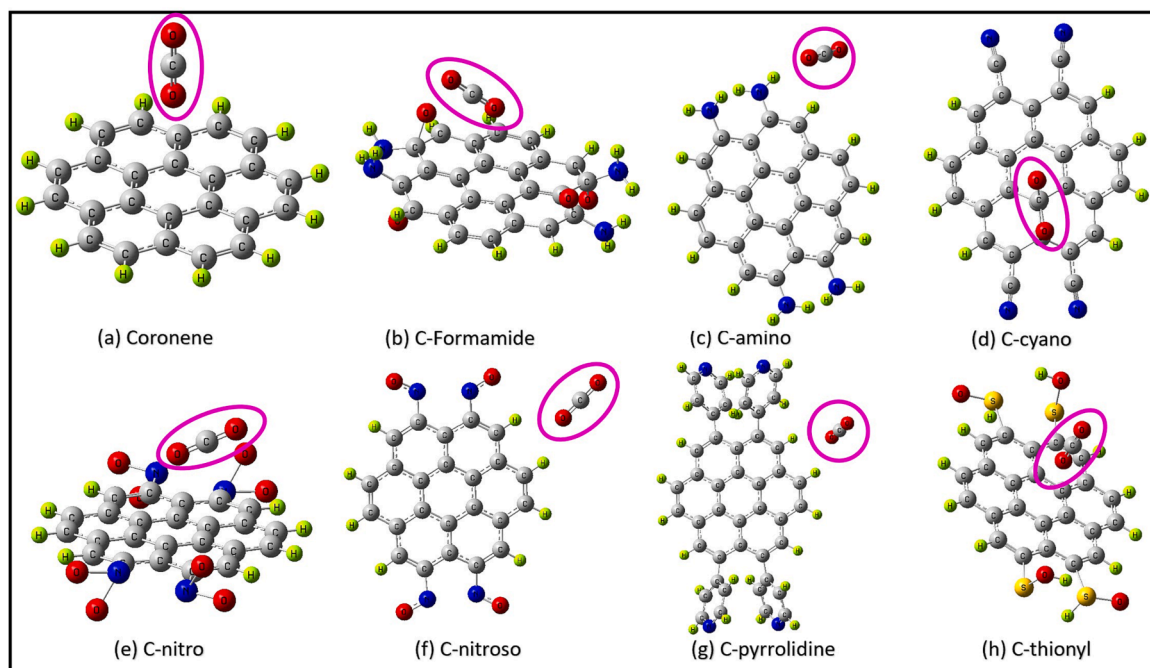


Fig. 9a. Position of CO₂ molecule (highlighted by a magenta circle) on the edge and above the surface of all the functionalized QDs after the adsorption. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

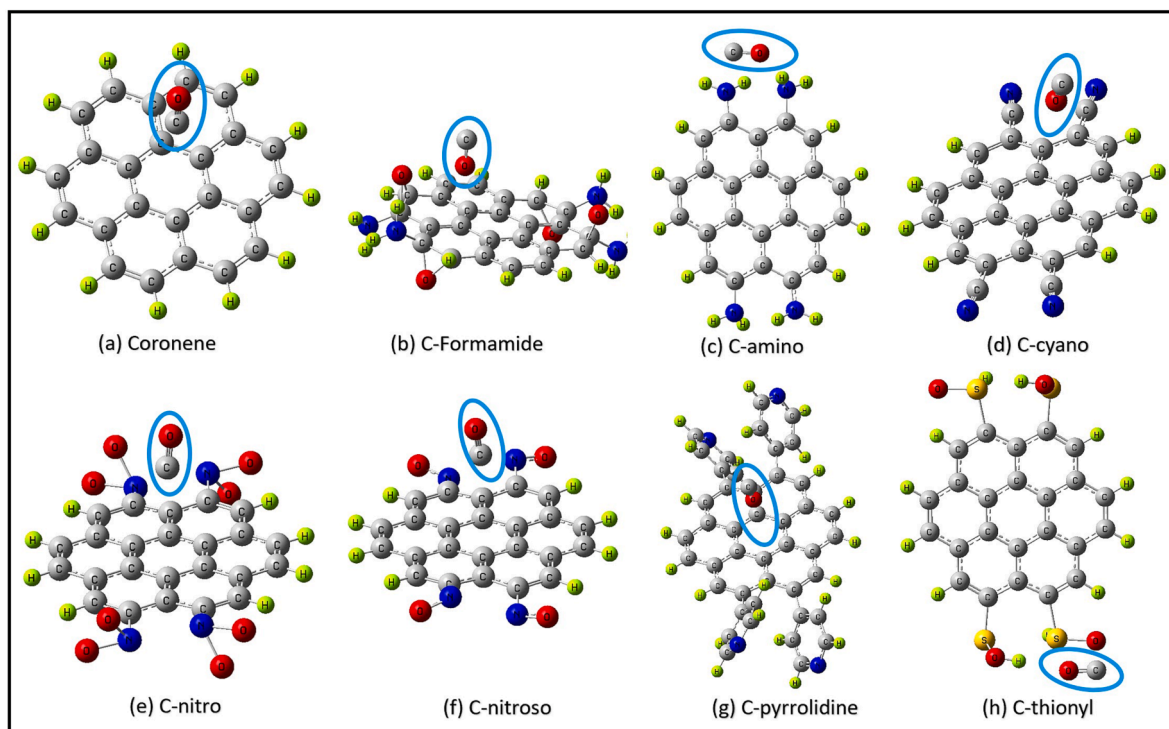


Fig. 9b. Position of CO (highlighted by blue circle) on the edge and above the surface of all the functionalized QDs after adsorption. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

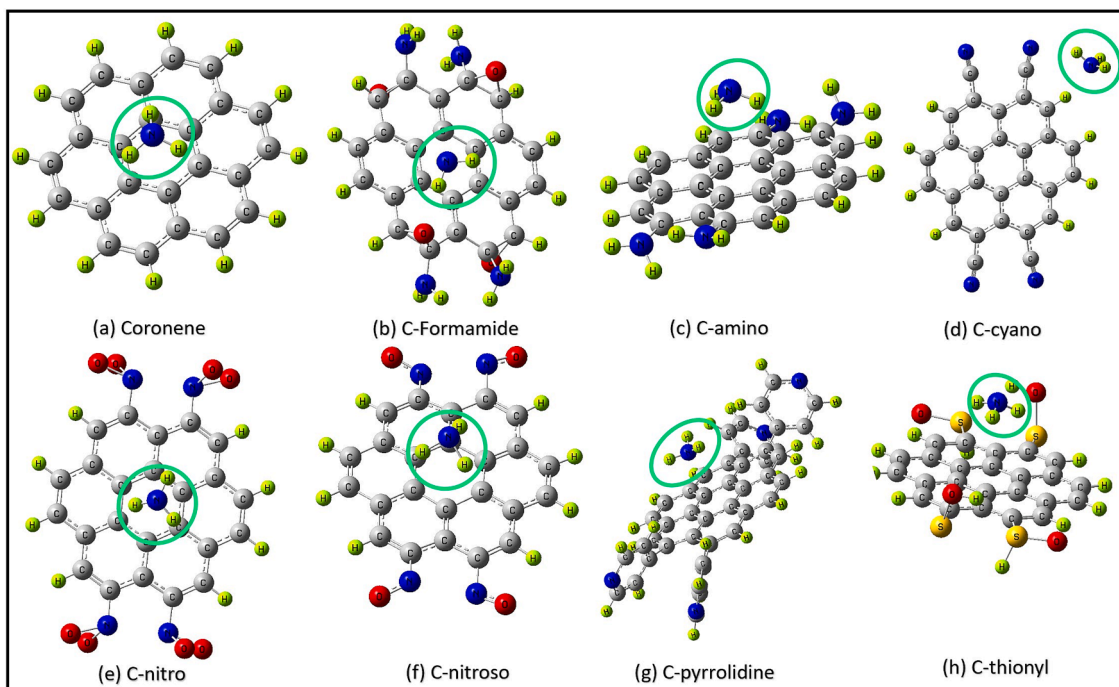


Fig. 9c. Position of NH_3 (highlighted by the green circle) on the edge and above the surface of all the functionalized QDs after adsorption.

the functional groups can be considered as a reason for the occurrence of these transitions. Thus, the involvement of benzene can lead to higher conjugation and thus high oscillator strengths in the transitions [41]. Therefore, among all the functionalized QDs, C-pyrrolidine is the one comprising the highest degree of conjugation and therefore, has the most stable $\pi \rightarrow \pi^*$ transitions.

3.7. Sensing capability of CQDs

The sensing capability of all the functionalized QDs was determined by calculating the adsorption energy between the gas molecule and the functionalized QDs. The gases considered were CO_2 , CO, and NH_3 . Initially, the gas molecules were drawn at a 3 Å distance from the surface of all the functionalized QDs following the reference [15]. The geometry

Table 3

Adsorption distance, adsorption energy, and band gap of all the gases adsorbed functionalized QDs.

Gas	QD structures	Distance (Å)	Position	E _{adsorption} (eV)	E _g (eV)
CO ₂	Coronene	3.19	surface	2.66	3.42
	C-formamide	3.59	surface	24.41	1.08
	C-amino	2.10	edge	4.725	2.05
	C-cyano	1.59	surface	30.54	3.45
	C-nitro	2.91	edge	27.64	3.70
	C-nitroso	2.30	edge	27.67	2.14
	C-pyrrolidine	2.42	edge	27.5	3.70
	C-thionyl	2.63	surface	27.87	3.71
	Coronene	3.56	surface	18.20	1.10
CO	C-formamide	2.65	surface	3.22	2.08
	C-amino	2.13	edge	0.501	3.10
	C-cyano	2.65	edge	0.061	3.51
	C-nitro	3.46	surface	0.292	3.69
	C-nitroso	3.45	surface	0.049	2.10
	C-pyrrolidine	2.99	surface	0.26	3.69
	C-thionyl	2.69	edge	0.325	3.72
	Coronene	1.22	surface	9.63	2.59
	C-formamide	2.30	surface	3.40	3.54
NH ₃	C-amino	3.30	surface	4.725	3.05
	C-cyano	2.09	edge	0.585	3.52
	C-nitro	3.38	surface	0.288	2.25
	C-nitroso	2.32	surface	4.62	1.95
	C-pyrrolidine	3.00	surface	0.23	3.59
	C-thionyl	3.27	surface	0.079	2.67

optimizations were carried out for all the systems to check the stability of the systems. The same set of hybrid basis functionals was used for the calculations of the designed QD in the availability of the gas molecule. The geometry obtained after the optimization was with zero imaginary frequency. The sensing characteristics were studied using the obtained geometries. The positions of the gas molecules CO₂, CO, and NH₃ after

the geometry optimization were illustrated in Figs. 9(a), 9(b), and 9(c) respectively. After the optimization, the gas molecules were observed at varying distances. The atoms around which the gas molecule is observed after the structure optimization are the preferred adsorption sites for the gas [42,43] and are illustrated in Fig. 9. All the calculated parameters like band gap, adsorption energy, interatomic distance, and location of the gas molecule have been mentioned in Table 3. The adsorption energy explains the adsorption of the gas molecules over the surface of the functionalized QDs. As per the definition, the positive value of E_{adsorption} ensures the stability of the adsorption [45]. The stronger the adsorption, the larger will be the value of the adsorption energy. CO₂ molecule got adsorbed on the surface of the coronene, C-formamide, C-cyano, and C-thionyl QD with a adsorption energy of 2.66, 24.41, 30.54, and 27.87 eV respectively. For the rest of the QDs (say C-amino, C-nitro, C-nitroso, and C-pyrrolidine), CO₂ got adsorbed on the edge of the QDs with energy 4.72, 27.64, 27.67, and 27.5 eV respectively. The adsorption energy of the CO₂ molecule with all the functionalized QDs was in the pattern C-cyano > C-thionyl > C-nitroso > C-nitro > C-pyrrolidine > C-formamide > C-amino > coronene. Thus, C-cyano has the highest adsorption energy for CO₂ molecules with the lowest distance between the QD and gas molecule of 1.59 Å. The rest of the QDs have intermolecular distance (suppose the distance between the QD and gas molecule in this case) greater than that of the C-cyano. For gases CO and NH₃, probe coronene flake has higher adsorption energy than the rest of the functionalized QDs. The adsorption energy for the CO molecule was in sequence coronene > C-formamide > C-amino > C-thionyl > C-nitro > C-pyrrolidine > C-nitroso. The adsorption energy for CO and NH₃ for all the systems was significantly less than that for the CO₂ gas molecule. The adsorption energy for NH₃ was observed as coronene > C-amino > C-nitroso > C-formamide > C-cyano > C-nitro > C-pyrrolidine > C-thionyl. On the contrary, the adsorption energy computed in the present study was huge

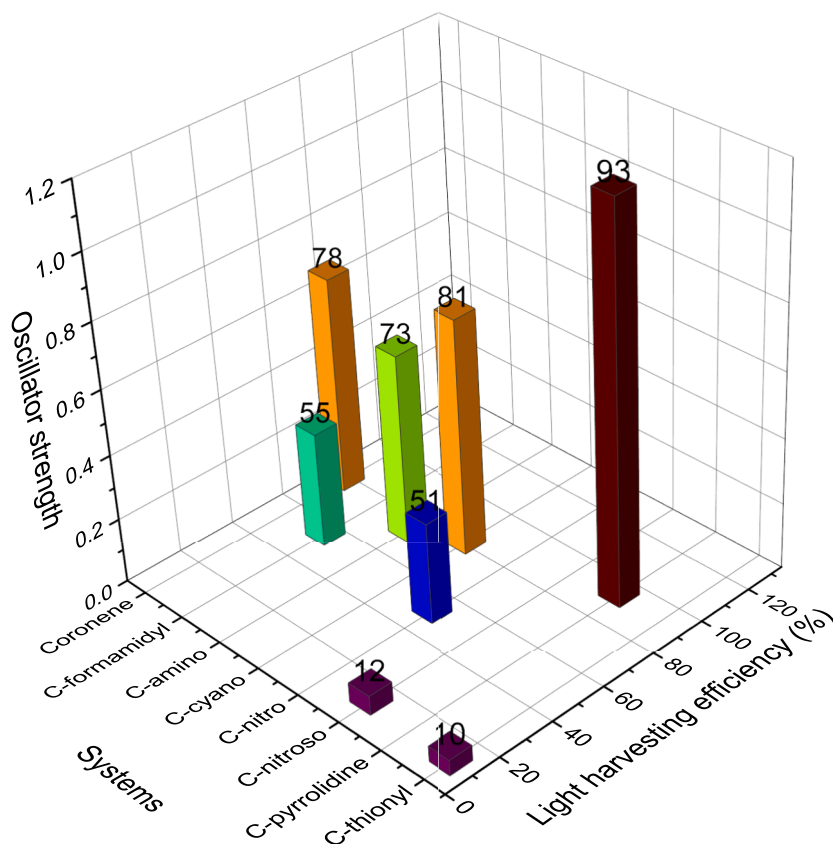


Fig. 10. Comparison of the light-harvesting efficiency of all the functionalized QDs.

as compared to the adsorption energy of gas over QD that is obtained in the referenced articles [15,42,43]. The adsorption energy of considered gases (H_2S , CH_4 , CO , and NH_3) in [15] were all in the range of 0.04 to 0.69 eV. Moreover, the intermolecular distance in our study was also comparable to that presented in [15]. From the adsorption energy analysis, the higher values of the adsorption energies were obtained for the QDs complexed with CO_2 as compared to the rest of the gases. The reason might be the nonpolar nature of CO_2 and the availability of two oxygen atoms which impart in the increment in the interactive behavior of the QD with the substitute functional group. Therefore, the discussion done so far on adsorption energy says that the designed QDs have good sensing ability towards the CO_2 molecule as compared to CO and NH_3 . These extreme values of adsorption energy well support the strong nature of the functionalized QDs in the making of the gas sensing devices. Additionally, the geometry optimizations of all the functionalized QDs with gas molecules were done at standard thermodynamic conditions of 298.15 K temperature and 1 atm pressure that supports the working of the designed gas sensing devices at room temperature.

3.8. Light harvesting efficiency analysis

The oscillator strength of the crucial transition obtained in the computed absorption spectra was employed to calculate the LHE of the considered CQDs. The LHE of any compound is the extent to which a compound can absorb light and compounds having a high LHE are considered as the perfect light absorber in photovoltaic devices [44]. The oscillator strength obtained corresponding to the crucial transitions from the absorption spectra was employed in the calculation of the LHE. As the LHE is exponentially proportional to the negative of the oscillator strength, the higher value of oscillator strength leads to the higher LHE [46]. The oscillator strength of C-pyrrolidine (1.1961) was the highest among all the other QDs resulting in highest LHE. After C-pyrrolidine, the C-cyano, coronene, C-amino, C-nitro, and C-formamide have oscillator strengths in decreasing order equal to 0.7222, 0.6689, 0.5831, 0.3119, and 0.1296 respectively. These functionalized QDs have LHE equal to 0.81, 0.78, 0.73, 0.55 and 0.51 respectively. The C-nitroso and C-thionyl were the functionalized QDs with minimum LHE. The comparison of the calculated LHE of all the considered CQDs is illustrated in Fig. 10. The LHE of CQDs were in sequence C-pyrrolidine > C-cyano > Coronene > C-amino > C-formamide > C-nitro > C-nitroso > C-thionyl. From the comparison, the maximum LHE was obtained for C-pyrrolidine. The LHE of C-pyrrolidine was found comparable to that of the molecule reported by Y. S. Mary in reference [32]. This reveals the potential characteristics of C-pyrrolidine as an efficient light absorber and its applications as a photosensitizer in photovoltaic devices.

4. Conclusion

The present article accounts for the computational study performed for coronene flake and seven different functional groups substituted coronene QDs to investigate the gas sensing ability and light harvesting efficiency of these functionalized QDs. The substitution of the functional groups results in the decrement of the cohesive energy of functionalized QDs. The traced MEP surfaces over the functionalized QDs indicated the active participation of the substituted functional groups in the intramolecular interactions. Moreover, the substitution of the functional groups results in the broadening of the band gap of all functionalized QDs. This might be due to the unsymmetrical and anisotropy of the functionalized QDs. The availability of functional groups makes space for the large charge cloud that was visualized using the HOMO-LUMO surfaces. The charge surfaces were seen to dislocate from the conjugated bonds of the benzene rings over the substituted functional groups. The chemical reactivity descriptors were of favorable values to justify the chemical reactivity of functionalized QDs well. Moreover, the band gap obtained from DOS spectra for all the functionalized QDs was nearly equal to the band gap obtained from Koopman's calculations. The

functional groups associated with functionalized QDs gave strong prominent infrared vibrational peaks. The electronic transitions with higher oscillator strengths were seen for the functionalized QDs and were favorable for most stable $\pi \rightarrow \pi^*$ transitions. The sensing capabilities of all these functionalized QDs were established using adsorption energy. Among the considered gases, the functionalized QDs were found favorable for sensing the CO_2 molecules. Moreover, the calculations found that among all the functionalized QDs and gas molecules, C-cyano had the highest adsorption energy of 30.54 eV with the lowest intermolecular distance of 1.59 Å. Rest, C-nitro, C-nitroso, C-pyrrolidine, and C-thionyl also have adsorption energy high enough to favor the sensing capabilities of these functionalized QDs. LHE is another possible application of the functionalized QDs that have been reported in this article. C-pyrrolidine was found to have the highest LHE of 93 %. Therefore, the introduced QDs with high tunability of adsorption are highly favorable in designing superior coronene gas sensors and photosensitizing materials as well. Experimental fabrication and characterizations of sensing and photosensitizing devices can be confidently performed based on the reported study.

Availability of data and materials

All data generated or analyzed during this study, which support the plots within this paper and the other findings of this study, are included in this article and its [Supplementary Information](#). Source data are provided in this paper.

Ethical approval

This material is the authors' original work, which has not been previously published elsewhere. All authors have been personally and actively involved in substantial work leading to the paper and will take public responsibility for its content. The paper properly credits the meaningful contributions of all the co-authors.

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CRediT authorship contribution statement

Shradha Lakhera: Data curation, Investigation, Software, Validation, Visualization, Writing – original draft. **Kamal Devlal:** Conceptualization, Writing – review & editing. **Meenakshi Rana:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Vivek Dhuliya:** Investigation, Software, Validation, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.saa.2023.123737>.

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