Influence of Adsorption of Gold and Silver Nanoclusters on Structural, Electronic, and Nonlinear optical properties of Pentacene-5,12-dione: A DFT study

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Research Article

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Influence of Adsorption of Gold and Silver Nanoclusters on Structural, Electronic, and Nonlinear optical properties of Pentacene-5,12-dione: A DFT study

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Abstract

The present study deals with the investigation of the change in the hyperpolarizability of Pentacene-2,5-dione (PD) on the introduction of the gold (Au) and silver (Ag) nanoclusters using the density functional theory (DFT). The involvement of the nanoclusters induces the intramolecular interactions, which is confirmed by the electrostatic potential plot and Mulliken charge distribution. The process of adsorption of metal clusters on the surface of PD is investigated by absorption spectra and the Raman spectra analysis. The global reactivity parameters validate a hike in the reactivity of the PD after the adsorption of Ag₃ and Au₃ nanoclusters. The study reported extraordinary enhancement in the hyperpolarizability of the metal nanoclusters adsorbed complexes. The high value of hyperpolarizability for PD-Ag₃ (184.22×10⁻³⁰ esu) and PD-Au₃ (2057.26×10⁻³⁰ esu) validates their applications in highly efficient NLO devices. The statistical calculation of radiative lifetime and light-harvesting efficiency reveals that probe PD can fruitfully contribute to the development of photo luminescent material and photosensitizer dye in dye synthesized solar cells.

Keywords: Nanoclusters; Density functional theory; Nonlinear optics; Pentacene-2,5-dione; Luminescent material; Dye-synthesized solar cells

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1. Introduction

Aromatic hydrocarbon is a well-known category of reactive compounds having sigma bonds and delocalized π electrons between the carbon atoms [1]. These consist of multiple benzene rings clubbed together forming polycyclic hydrocarbons. Such molecules have considerable interest to theoretical and experimental researchers due to their versatile structure and high reactivity. Many studies have been reported to work on nonlinear optical (NLO) activity of different classes of aromatic hydrocarbons like anthracenes [2], quinacridone [3], naphthalene [4], pyrene [5], benzopyrenes [6], benzo-anthracene [7], ovalene [8], triphenylene [9], chrysene [10] and many more. The mentioned studies, thus, account for the high chemical reactivity of polycyclic hydrocarbons. Pentacene, on the other hand, is one of the classes of polycyclic aromatic hydrocarbons consisting of five linearly clubbed benzene rings. Pentacene and its derivatives have a number of applications in the development of organic thin-film transistors, organic NLO materials, solar cells, organic light-emitting diodes (OLEDs), etc. many studies have presented wide usage of Pentacene in the field of photovoltaics [11-14]. Due to having high mobility, the derivatives of Pentacene are also used as p-type organic semiconductors [15]. All the reported studies account for the high reactivity and applicability of the Pentacene and its derivatives in different branches of physical science. The major use of Pentacene and its derivatives was seen in the growth of the thin films [16]. A study on Pentacene based radio frequency circuits has been reported [17]. Pentacene and its compounds were also found to be used in the development of organic metal oxide semiconductor field-effect transistors [18]. Some studies that show the interactions of the Pentacene with metal atoms like gold are also found in the literature [19].

However, the adsorption of the organic compounds over the metal clusters has been of considerable interest to the researcher’s community as the introduction of the metal nanoclusters has reportedly given immense enhancement to the electro-optical and chemical properties of the organic compounds. Various studies have been reported for Pentacene from time to time. One such study targeting the enhanced hyperpolarizability of the Quinacridone after the adsorption of gold and silver nanoclusters has been reported and the results were highly appreciable [20]. The study based on the adsorption studies of benzene, aniline and naphthylamine on reduced graphene oxides was also reported using experiments and theoretical density functional theory (DFT) [21]. The development of photovoltaic cells with Pentacene adsorbed with fullerene (C\textsubscript{60}) had been reported to improve the power efficiency of the cell by enhancing the short circuit current density [22]. The bonding between the gold and
carbon atoms of Pentacene has been established using DFT and shed their applications in the second-order NLO applications [23]. Studies with the substitution of gold atoms to Pentacene making complex \( \text{Au}_2\text{C}_{22}\text{H}_{14} \) have also been reported to present the NLO responses of the complexes [24]. Thus, literature has a feast of kinds of studies reporting the NLO activity of Pentacene complexes with other metal atoms or clusters. Thus, one such derivative of pentacene namely Pentacene-2,5-dione (PD) has been considered for the present study. The study aims to establish the intensified NLO activity of the PD molecule after the adsorption of the silver (\( \text{Ag}_3 \)) and gold (\( \text{Au}_3 \)) metal nanoclusters. As the initial nucleation stage of silver and gold nanoparticle is the formation of the trimers (\( \text{Ag}_3 \) and \( \text{Au}_3 \)) [25,26] and numerous researches reporting adsorption studies of \( \text{Ag}_3 \) nanocluster has been accounted in the literature with tremendous rise in the NLO activities [27-28]. The NLO activities of inorganic complexes of group III phosphide nanoclusters were demonstrated using computational aids by Ullah and his team [29]. The development of anode materials by using \( \text{C}_{24}, \text{Si}_{12}\text{C}_{12}, \text{B}_{12}\text{N}_{12}, \text{B}_{12}\text{P}_{12}, \text{Al}_{12}\text{N}_{12}, \text{and Al}_{12}\text{P}_{12} \) for magnesium-ion batteries (MIBs) was also reported [30]. Thus, it is considered for the present study as the nanocluster. The chemical reactivity of the probe PD, PD-\( \text{Ag}_3 \), and PD-\( \text{Au}_3 \) complexes was established by molecular electrostatic potential (MEP) surface and frontier molecular orbital (FMO) parameters. Vibrational spectra also presented the adsorption site of the nanoclusters over the surface of the PD molecule and highlights the description of the adsorption. The intramolecular charge transfer (ICT) was also identified between the metal nanocluster and the PD molecule.

2. Computational Methods

The geometry optimization of probe PD, PD-\( \text{Ag}_3 \), and PD-\( \text{Au}_3 \) was performed using DFT with B3PW91/LANL2DZ (Los Alamos National Laboratory double zeta) level of theory in Gaussian 09 program [31]. The mentioned basis set is considered more accurate for quantum mechanical calculations of metal clusters and numerous studies have been reported to establish the metal-to-molecule interaction using the same pair of functions. The chemical reactivity of the probe PD, PD-\( \text{Ag}_3 \), and PD-\( \text{Au}_3 \) was established using MEP surface and global reactivity parameters. Different reactivity parameters like bandgap (\( \Delta E \)), ionization potential (\( IP \)), electron affinity (\( EA \)), chemical potential (\( CP \)), electronegativity (\( \chi \)), softness (\( S \)), and hardness (\( \eta \)) are calculated with the help of Koopman’s equations given below [32-35]:

\[
\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \quad \text{(1)}
\]

\[
IP = -E_{\text{HOMO}} \quad \text{(2)}
\]
\[ EA = -E_{LUMO} \] ............................. (3)

\[ CP = \frac{E_{HOMO} + E_{LUMO}}{2} \] ............................. (4)

\[ \chi = \frac{(IP + EA)}{2}, \] ............................. (5)

\[ \eta = \frac{E_{LUMO} - E_{HOMO}}{2}, \quad S = \frac{1}{\eta} \] ............................. (6)

The vibrational spectra was computed for the identification of the adsorption site of metal clusters on PD. The Raman intensity was calculated for high frequency modes using expression:

\[ I = \frac{f(v_o-v_i)^4 S_i}{v_i[1-\exp\left(-\frac{hc
\nu_i}{kT}\right)]} \] ............................. (7)

where \( I \) is Raman intensity of the vibrational mode, \( f \) is a constant with value \( 10^{-12} \), \( v_o \) has value 9398.5 cm\(^{-1} \). \( v_i \) and \( S_i \) is the vibrational wavenumber and Raman activity of selected mode respectively. \( h \) is Planck constant with value \( 4.1357 \times 10^{-15} \) eV K\(^{-1} \), \( c \) is speed of light having value \( 3 \times 10^8 \) m/s, \( K \) is Boltzmann constant with value \( 8.6173 \times 10^{-5} \) eV K\(^{-1} \), and \( T \) is temperature 293.5K.

The NLO activity of the probe and metal clusters adsorbed complexes was developed by polar frequency calculations. The tensor components were obtained for computing total isotropic polarizability (\( \alpha_{total} \)), and anisotropy of polarizability (\( \Delta \alpha \)) and first order hyperpolarizability (\( \beta_{total} \)) using finite field theory approach [37]. These parameters are computed using following expression:

\[ \alpha_{total} = \frac{1}{2}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \] ............................. (8)

\[ \Delta \alpha = \frac{1}{\sqrt{2}}[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2]^{\frac{1}{2}} \] ............................. (9)

\[ \beta_{total} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2\right]^{\frac{1}{2}} \] ............................. (10)

Where \( \alpha_{xx}, \alpha_{yy}, \) and, \( \alpha_{zz} \) are the tensor components of polarizability and \( \beta_{xxx}, \beta_{yyy}, \) and \( \beta_{zzz} \) are the tensor components of hyperpolarizability.
3. Results and Discussion

3.1 Structure and charge analysis

PD has planar geometry with C1 point group symmetry due to which the dipole moment vectors of the atoms cancel each other. The 2O and 1O attached to the opposite sides give rise to a low magnitude of the dipole moment of 0.0002 Debye for the PD molecule. After the adsorption of Ag and Au metal nanoclusters, a rise in the dipole moment of the adsorbed complexes was observed due to their unsymmetrical structures. The value of dipole moment for PD-Ag\(_3\) and PD-Au\(_3\) was observed as 8.71 Debye and 3.96 Debye respectively. The high value of dipole moment was probably due to the larger differences between electronegativities of the donor and acceptor moieties present in the complexes [38]. The rise in the dipole moment shows the enhanced chemical reactivity of the adsorbed complexes. The optimized geometries of the probe PD, and PD after adsorption of Ag\(_3\) and Au\(_3\) nanoclusters are illustrated in Figure 1. The computed ground state energies of PD, PD-Ag\(_3\), and PD-Au\(_3\) are -625175.27 kcal/mol, -899227.54 kcal/mol, and 879824.946 kcal/mol respectively. The significant decrease in the energy confirms the enhanced stability of the compounds. The bond lengths of the PD, PD-Ag\(_3\), and PD-Au\(_3\) are mentioned in SD 1. The bond length of 1O = 13C and 2O = 14C of the carbonyl group in PD has lower bond lengths than the C = C bonds associated with the PD molecule. The C – H bonds have lower bond lengths showing the stability of the C – H bonds. The shorter the bond length, the lower will be the chances of bond dissociation, and the longer the bond, the higher will be the chances of easy dissociating of the bond [39]. The bond dissociation will give rise to the charge cloud resulting in ICT. Similarly, the bond angles (SD 2) had a large variation in magnitudes between the C – H bonds and C = O bonds. High magnitudes of the bond angles lead to easier bond dissociation. After the adsorption of the metal clusters on the surface of the PD molecule, there seems a rise in the bond length of the C = O bonds of the carbonyl group. The bond lengths between the Ag and Au atoms of nanoclusters have larger magnitudes. This can be correlated with the easy dissociation of the bonds between nanoclusters and shows the involvement of these clusters in ICT [40]. The optimization parameters suggest that there is a possibility of ICT between the PD and the metal nanoclusters and validates the enhancement of electrostatic interaction after the adsorption of metal nanoclusters on the surface of PD. The Mulliken charge distribution of the optimized geometries of the PD, PD-Ag\(_3\), and PD-Au\(_3\) are illustrated in Figure 1. The color bar at the top of the Figure 1 indicates the positive and negative charge of the atoms. The red color indicates
the negative charge and the green color indicates the positive charges of the atoms [41]. The atoms of the optimized geometries were indicated by the charge color code. The charge distribution of the PD distributed in the range ±0.667 e shows the positive charge contribution of the hydrogen atoms of C–H bonds and the negative charge distribution of the oxygen atoms 1O and 2O (-0.225 e each) of carbonyl groups. The variation between the charges of the hydrogen atoms and carbonyl groups expresses the intramolecular interactions between these two parts of PD. After the introduction of Ag₃ and Au₃ nanoclusters, the involvement of the Ag and Au atoms in the ICT was noticed. The charge distribution of PD-Ag₃ and PD-Au₃ complex was distributed in ranges ±0.669 e and ±0.806 e respectively. The Ag atoms 37Ag (0.182 e), 38Ag (0.034 e), and 39Ag (0.064 e) contribute to the positive charge indicating the participation of the Ag₃ nanocluster as a donor moiety. The Au₃ atoms 37Au (0.154 e), 38Au (-0.143 e), and 39Au (-0.13 e) impart positive as well as negative to the overall charge distribution of the complex. The variation of the charges between the Au atoms and carbon and oxygen atoms of the carbonyl groups shows the ICT between the Au₃ nanocluster and the carbonyl groups. Thus, the charge distribution highlights the enhanced ICT in PD molecules after the adsorption of the Ag₃ and Au₃ nanoclusters.
Figure 1. Optimized geometries of PD, PD-Ag$_3$ and PD-Au$_3$ at B3PW91/LANL2DZ illustrating the Mulliken charge distribution.
3.2 MEP surface analysis

MEP surface is used to illustrate the ICT of molecules. These surfaces are used to locate the areas with electron excess and electron deficiency of the molecule which are responsible for inducing ICT within the molecule [32]. The moieties with donor properties are known as positive regions and are indicated by blue color while the acceptor moieties are called negative and are indicated by red color [43]. The potential range of the MEP surface is indicated by the color band at the top of the surface. The MEP surface of PD illustrated in Figure 2(a) validates the positive nature of C – H bonds of the benzene rings and the negative nature of 1O = 13C and 2O = 14C bonds of the carbonyl group. The electrostatic potential range for probe PD is ±5.004×10². The hydrogen atoms are highly electropositive and oxygen atoms are highly electronegative. The MEP map identifies the transportation of heavily accumulated charge from the C – H bonds towards the C = O bonds of the carbonyl groups. Adsorption of Ag and Au nanocages over the PD molecule induces a redistribution of electron density. The involvement of the Ag and Au nanocages in ICT within the PD-Ag₃ and PD-Au₃ complexes was identified by the MEP map of PD-Ag₃ and PD-Au₃ shown in Figures 2(b) and 2(c) respectively. It is observed that the blue region over the C – H bonds of the PD molecule is shifted over the Ag₃ nanocluster after the adsorption of the Ag₃ nanocluster. Thus, the Ag₃ nanocluster acts as a donor part of the PD-Ag₃ complex, and ICT is seen to act from Ag₃ towards the carbonyl groups. This supports the results analyzed from Mulliken charge variation. A similar kind of ICT is seen in the PD-Au₃ complex where the charge cloud dislocated from the Au₃ nanocluster to carbonyl groups. The availability of the donor and acceptor moieties within the PD, PD-Ag₃, and PD-Au₃ validates the enhanced ICT within the PD molecule after the introduction of the Ag₃ and Au₃ metal nanoclusters. This shows the high chemical reactivity of PD, PD-Ag₃, and PD-Au₃ as mentioned by structural parameters.
Figure 2. MEP surface of PD, PD-Ag$_3$ and PD-Au$_3$ computed by B3PW91/LANL2DZ. Red color regions indicates the electronegative part and blue color indicates the electropositive part of the title molecules.
3.3 Molecular orbital analysis

The FMO parameters are derived from the energies corresponding to the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO). These parameters are computed to confirm the chemical reactivity of the molecules [44]. All the computed FMO parameters are listed in Table 1. The energy gap or band gap ($\Delta E$) is the virtue that accounts for how easily electrons from the HOMO can transit to LUMO. Molecules having lower values of $\Delta E$ shows high reactivity [45]. It is seen that the $\Delta E$ for probe PD was 2.14 eV but a decrease in the $\Delta E$ was observed when the metal nanoclusters are adsorbed by the PD molecule. Thus, the low value of $\Delta E$ for PD-Ag$_3$ (1.00 eV) and PD-Au$_3$ (1.23 eV) shows that the electrons of PD can easily jump up to the higher energy state when combined with metal nanoclusters. The ionization potential ($IP$) of a molecule should be below to remove the electrons easily from the outermost shell of the donor atoms. PD-Ag$_3$ (5.23 eV) has the lowest value of $IP$ than the probe PD (5.75 eV) and PD-Au$_3$ (6.01 eV). The high value of electron affinity ($EA$) shows the greater tendency of the atoms to gain electrons. The $EA$ is highest for PD-Au$_3$ (4.78 eV). The chemical potential ($CP$) shows the high tendency of the molecules to undergo charge transfer and molecules having a high value of $CP$ are highly reactive. PD, PD-Ag$_3$ and PD-Au$_3$ have the value of $CP$ mutually close showing the high chemical reactivity of the three title molecules. The high value of electronegativity ($\chi$) for PD-Ag$_3$ shows how easily it attracts the shared electrons. The distribution of the HOMO-LUMO surface over the title molecules is illustrated in Figure 3 (a), (b), (c). The red surface indicates the positive and the green surface indicates the negative phases in molecular orbital wave function. The HOMO-LUMO surface is uniformly distributed over the geometry of PD. Larger positive and negative surfaces over the metal nanoclusters in HOMO are shifted over the benzene rings in LUMO. This shifting of surfaces shows that ICT exists from nanoclusters to PD molecules as stated by structural analysis. The chemical reactivity of PD undergo enhancement as the Ag$_3$ and Au$_3$ metal nanoclusters get adsorbed to the surface of the PD molecule. Thus, the analysis of the FMO parameters shows that the introduction of Ag$_3$ and Au$_3$ nanoclusters to PD intensify its chemical reactivity.

Table 1. Frontier molecular orbital parameters for the PD, PD-Ag$_3$ and PD-Au$_3$ molecule (all values are in eV and value of S is in eV$^{-1}$).

<table>
<thead>
<tr>
<th>S No.</th>
<th>Molecular property</th>
<th>PD</th>
<th>PD-Ag$_3$</th>
<th>PD-Au$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$E_{HOMO}$</td>
<td>-5.75</td>
<td>-5.23</td>
<td>-6.01</td>
</tr>
</tbody>
</table>
Figure 3. Molecular orbitals for the (a) PD, (b) PD-Ag$_3$ and (c) PD-Au$_3$. The lower structure shows HOMO and upper structure shows LUMO of the respective molecules and the band gap is represented by $\Delta E$.

3.4 Absorption analysis

The UV-Vis spectra for PD, PD-Ag$_3$, PD-Au$_3$ compounds are illustrated in Figure 4. The transition $S_0 \rightarrow S_1$ occurred at wavelength 561.5 nm was majorly responsible for the broad absorption band of PD. The oscillator strength ($f$) for this transition was observed as 0.719 and the excitation energy for this mode was computed as 2.2 eV. The high value of excitation energy and the $f$ reveals the high reactivity of the PD. It was observed that the introduction of metal nanoclusters to the PD shows the rise in the intensity of the transitions and bathochromic shift of wavelength. Broad spectra for PD-Ag$_3$ and PD-Au$_3$ was seen to range between 1000-5000 nm. The $S_0 \rightarrow S_1$ transition for PD-Ag$_3$ and PD-Au$_3$ occurred at high wavelength of 1823.64 and 2261.29 nm respectively. Although there seems a red shift in the intensity of the compounds. The rise in the wavelengths of the first transition was occurred mainly due to the interactions between the metal nanoclusters and the PD molecule. This creates a close relation.
between the ICT developed by the HOMO-LUMO surface distribution in molecular orbital analysis. The absorbance shifts in the wavelength and intensity was mainly due to the interference in the hyperconjugation of the bonds. This leads to the rise in the count of partial double bonds (π bonds) giving rise to lone pair of electrons. Thus, the hyperconjugation in the metal clusters results in absorbance shifts. Moreover, the rise in conjugation is proportional to the bond lengths. This also makes a good agreement with the higher bond lengths obtained for the metal clusters in structural analysis.

![Absorption spectra of PD, PD-Ag3 and PD-Au3 computed using B3PW91/LANL2DZ basis set.](image)

**Figure 4.** Absorption spectra of PD, PD-Ag3 and PD-Au3 computed using B3PW91/LANL2DZ basis set.

### 3.5 Vibrational analysis

The nature of adsorption of metal nanoclusters on the surface of the PD molecule was established by computing vibrational spectra using the B3PW91/LANL2DZ basis set. The important vibrational modes and the assignments are illustrated in Figure 5 and listed in SD 3. We have observed a rise in the intensities of different vibrational modes after the introduction of the metal nanoclusters. This rise seems to confirm the enhancement of the chemical reactivity of the PD after adsorption of the metal nanoclusters. The low frequency modes for the vibration of metal nanoclusters (113.8 cm⁻¹ for PD-Ag3 and 113.8 and 160.56 cm⁻¹ for PD-Au3) were observed showing adsorption interaction between the PD and metal nanoclusters.
The out of plane bending of the geometry of PD was observed at 541.8, 549.94, 620.81, and 698.17 cm⁻¹. Contrastingly, the out of plane vibrations for PD-Ag₃ are observed at comparatively higher frequencies 556.9, 628.86, 697.36, 740.99, and 793.26 cm⁻¹. Similar rise in the frequency was observed for the out of plane vibrational modes for PD-Au₃ at 535.59, 548.85, 629.21, 696.78, 739.27, 778.67 cm⁻¹. The carbonyl groups of the PD show ν_CO mode at 1695.05 cm⁻¹. The ν_CO mode for PD-Ag₃ and PD-Au₃ was identified at 1586.11 cm⁻¹ and 1584.77 cm⁻¹ respectively. Stretching of C = C bond of benzene ring for PD-Ag₃ (1412.14, and 1418.92 cm⁻¹) and PD-Au₃ (1414.98, and 1427.09 cm⁻¹) confirms the potential site for adsorption in each case.

![Vibrational spectra for the PD, PD-Ag₃ and PD-Au₃ molecule computed using B3PW91/LANL2DZ basis set (Symmetric stretching-ν, torsional bending in plane (scissoring)-δ, twisting-τ, rocking-ρ, and wagging-ω, stretching of C – C bonds in benzene- λ).](image-url)

**Figure 5.** Vibrational spectra for the PD, PD-Ag₃ and PD-Au₃ molecule computed using B3PW91/LANL2DZ basis set (Symmetric stretching-ν, torsional bending in plane (scissoring)-δ, twisting-τ, rocking-ρ, and wagging-ω, stretching of C – C bonds in benzene- λ).

### 3.5 NLO analysis

NLO materials interacting with electric field lines must have a high polarization density. When a material is kept in the homogeneous electric field, the energy possessed by the material is
expanded as Taylor’s series expansion where the $\alpha$ and $\beta$ are the coefficients of the Taylor series expansion [46]. These coefficients are correlated to NLO activity as the high value of the coefficient of high order derivatives leads to high NLO activity of the molecule. Thus, to predict the NLO activity, $\alpha_{\text{total}}$, $\Delta\alpha$ and $\beta_{\text{total}}$ are computed for the title molecules. All the computed tensor components of the $\alpha_{\text{total}}$, $\Delta\alpha$ and $\beta_{\text{total}}$ for PD, PD-Ag$_3$, and PD-Au$_3$ molecules are mentioned in SD 3, and 4 respectively and the values of polarizability parameters are mentioned in Table 2. The value of $\alpha_{\text{total}}$ is computed as $54.73 \times 10^{-24}$ esu for probe PD molecule but after the adsorption of Ag$_3$ and Au$_3$ nanoclusters, this value was increased to $129.79 \times 10^{-24}$ and $108.65 \times 10^{-24}$ esu respectively. These values are approximately twice the value of $\alpha_{\text{total}}$ for probe PD molecule. The values of $\Delta\alpha$ for PD-Ag$_3$ ($532.44 \times 10^{-24}$ esu) and PD-Au$_3$ ($436.42 \times 10^{-24}$ esu) are higher than the $\Delta\alpha$ for PD ($211.76 \times 10^{-24}$ esu). A very low value of $\beta_{\text{total}}$ for probe PD ($0.000181 \times 10^{-30}$ esu) was computed but an extraordinary rise in the values of the $\beta_{\text{total}}$ was observed after the adsorption of metal nanoclusters. The values of $\beta_{\text{total}}$ for PD-Ag$_3$ and PD-Au$_3$ were observed as $184.22 \times 10^{-30}$ esu and $2057.26 \times 10^{-30}$ esu. These values are 10117790 and 11427777 times higher than the $\beta_{\text{total}}$ for probe PD. In comparison with the generally used reference NLO material Urea ($0.781 \times 10^{-30}$ esu), the value of $\beta_{\text{total}}$ for PD-Ag$_3$ and PD-Au$_3$ are 236 and 2637 times higher [47]. Thus, this comparison is fairly enough to justify that the PD can act as an excellent NLO material when adsorbed with Ag$_3$ and Au$_3$ nanoclusters.

Table 2. Computed values of $\alpha_{\text{total}}$, $\Delta\alpha$ and $\beta_{\text{total}}$ for the PD, PD-Ag$_3$, and PD-Au$_3$ molecule

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\alpha_{\text{total}}$ (esu)</th>
<th>$\Delta\alpha$ (esu)</th>
<th>$\beta_{\text{total}}$ (esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PD</td>
<td>$54.73 \times 10^{-24}$</td>
<td>$211.76 \times 10^{-24}$</td>
<td>$0.000181 \times 10^{-30}$</td>
</tr>
<tr>
<td>PD-Ag$_3$</td>
<td>$129.79 \times 10^{-24}$</td>
<td>$532.44 \times 10^{-24}$</td>
<td>$184.22 \times 10^{-30}$</td>
</tr>
<tr>
<td>PD-Au$_3$</td>
<td>$108.65 \times 10^{-24}$</td>
<td>$436.42 \times 10^{-24}$</td>
<td>$2057.26 \times 10^{-30}$</td>
</tr>
</tbody>
</table>
Figure 6. Comparative plots of (a) polarizability ($\alpha_{total}$ and $\Delta\alpha$) and (b) $\beta_{total}$ for the PD, PD-Ag$_3$, and PD-Au$_3$ molecule illustrating the high value of polarizability parameters for PD after adsorbing Ag$_3$ and Au$_3$ nanoclusters.

3.6 Radiative and light harvesting properties

The absorption spectra were computed for the probe PD molecule to get an idea about the electronic transitions. The spectra comprised of a broad strong absorption band identified with its peak at 361.5 nm wavelength. The transition $S_0 \rightarrow S_1$ occurred at the peak wavelength with $f$ of 0.719 and excitation energy 2.20 eV. The other two transitions $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ occurred at wavelengths 246.16 and 246.34 nm respectively. The high excitation energy highlights the possibility of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ nature of the $S_0 \rightarrow S_1$ transition. Thus, the existence of such transitions shows the ICT in the PD molecule. The absorption spectra of PD was also used to establish the radiative and light-harvesting property of the probe molecule.

The computed absorption spectra of the PD was used for deriving the radiative property of the molecule. The radiative lifetime ($\tau$) was computed by below given formula [48]:

$$\tau = \frac{c^3}{2fE^2} \quad \text{.........................(11)}$$

where $c$ is the speed of light and $f$ and $E$ are the oscillator strength and the excitation energy obtained in the absorption spectra. The radiative lifetime accounts for the nature of transitions possessed by the molecules i.e., whether the molecules emit radiation during the transitions or the transitions are non-radiative [49]. The former is called emissive transition and the latter is called non-emissive transition. However, the transitions having lifetime values larger than 10 are non-radiative. The electronic transitions for which the $\tau$ value is less than 10 are known to be radiative and these transitions eject energy in the form of photons [50]. Thus, for the PD molecule, the value of $\tau$ is computed to be 5.9 nm–6nm. The $\tau<10$ for PD indicates that the
transition \( S_0 \rightarrow S_1 \) occurred between the HOMO-LUMO of PD was radiative and shows its nature to possess photoluminescence [51]. Thus, this establishes the potent applicability of PD molecules as an active luminescent material.

\( f \) is also used for calculating the light harvesting efficiency (LHE) for PD using the below mentioned formula [52]:

\[
\text{LHE} = 1 - 10^{f} \quad \text{......... (12)}
\]

LHE measures the efficiency of any material to increase the ability of any solar cell to convert light energy into electrical energy. Thus, the applicability of the molecule to be used as photosensitizer dye in Dye Sensitizer Solar Cells (DSSC) is statistically explained by LHE [53]. For PD, the LHE is computed to be 80.91. The adsorption of \( \text{Ag}_3 \) and \( \text{Au}_3 \) on the PD, gave a decrease in the LHE of the compounds PD-\( \text{Ag}_3 \) (27\%) and PD-\( \text{Au}_3 \) (20\%). This can be due to the reflective nature of the Ag and Au. These materials do not absorb light up to the extent that is required for solar cells, and therefore give a lustrous glare. Thus, PD can convert 80\% of the light incident on it into electrical energy. Hence, PD synthesized dye can lead to tremendous enhancement of the efficiency of solar cells.

4. Conclusion

A complete study of quantum mechanical properties of PD in probe state and adsorbed with \( \text{Ag}_3 \) and \( \text{Au}_3 \) nanoclusters were reported in the paper. The adsorption sites of the nanoclusters were identified by the high Raman intensity modes in vibrational spectra. The PD was found highly chemically reactive right after the adsorption of the \( \text{Ag}_3 \) and \( \text{Au}_3 \) nanoclusters and their chemical reactivity was verified using FMO parameters. The MEP surface over the nanoclusters also validated the electropositive character of nanoclusters and established their participation in inducing the ICT within the complex structures. In particular, the DFT calculations indicate the tremendous rise in the NLO activity of the PD after the adsorption of the \( \text{Ag}_3 \) and \( \text{Au}_3 \) nanoclusters. Thus, it can be concluded that the studied complexes hold considerable NLO activity and can be recommended for the high-tech applications of efficient NLO materials. Also, the experimental design of the studied complexes will be surely generative. The low value of \( \tau \) signifies the radiative emission of photons resulting in the application of PD as a potent photoluminescent molecule. Employment of PD as a photosensitizer dye was noted by its high LHE. Thus, the probe PD can better act as a photoluminescent material as well as a dye in DSSC.
Declarations

Ethical Approval
I give my consent for the publication of identifiable details, which include data and pictures to be published in the Journal “Optics and Quantum Electronics”.

Competing interests
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.

Authors' contributions
Shradha Lakhera: Data curation, Writing-Original draft preparation, Visualization, Investigation, Software, Validation.

Meenakshi Rana: Conceptualization, Methodology, Writing-Reviewing and Editing, Supervision

Kamal Devlal: Conceptualization, Writing- Reviewing and Editing

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Availability of data and materials

Extension conversion: http://openbabel.org/wiki/Main_Page

Optimization: https://gaussian.com/

Data analysis: https://gaussian.com/gaussview6/

Graph plotting: https://www.originlab.com/

References


[31] M. J. Frisch, Gaussian 09, Revision B.01, Gaussian Inc., Wallingford CT (2010).


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