Designing Novel Zn-Decorated Inorganic B$_{12}$P$_{12}$ Nanoclusters with Promising Electronic Properties: A Step Forward toward Efficient CO$_2$ Sensing Materials

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ABSTRACT: Gas sensing materials have been widely explored recently owing to their versatile environmental and agriculture monitoring applications. The present study advocates the electronic response of Zn-decorated inorganic B$_{12}$P$_{12}$ nanoclusters to CO$_2$ gas. Herein, a series of systems CO$_2$–Zn–B$_{12}$P$_{12}$ (E1–E4) are designed by adsorption of CO$_2$ on Zn-decorated B$_{12}$P$_{12}$ nanoclusters, and their electronic properties are explored by density functional theory. Initially, placement of Zn on B$_{12}$P$_{12}$ delivers four geometries named as D1–D4, with adsorption energy values of $-57.12$, $-22.94$, $-21.03$, and $-14.07$ kJ/mol, respectively, and CO$_2$ adsorption on a pure B$_{12}$P$_{12}$ nanocage delivers one geometry with an adsorption energy of $-4.88$ kJ/mol. However, the interaction of CO$_2$ with D1–D4 systems confers four geometries named as E1 ($E_{ad} = -75.12$ kJ/mol), E2 ($E_{ad} = -25.89$ kJ/mol), E3 ($E_{ad} = -42.43$ kJ/mol), and E4 ($E_{ad} = -28.73$ kJ/mol).

Various electronic parameters such as dipole moment, molecular electrostatic potential analysis, frontier molecular orbital analysis, $Q_{NBO}$, global descriptor of reactivity, and density of states are also estimated in order to understand the unique interaction mechanism. The results of these analyses suggested that Zn decoration on B$_{12}$P$_{12}$ significantly favors CO$_2$ gas adsorption, and a maximum charge separation is also noted when CO$_2$ is adsorbed on the Zn–B$_{12}$P$_{12}$ nanocages. Therefore, the Zn-decorated B$_{12}$P$_{12}$ nanocages are considered as potential candidates for application in CO$_2$ sensors.

1. INTRODUCTION

Nanoscience has developed a revolutionary trend in various fields of science. Functional nanomaterials are now attracting the modern research community because of their distinct structural and electronic properties. Recently, nanostructure semiconductors have gained significant interest from the scientific community because of their distinct physical and chemical properties. Nanostructures such as fullerenes, nanotubes, and nanoclusters have also received great interest from the modern research community because of their distinct physical and chemical properties. Functional nanomaterials are now attracting the modern research community because of their distinct physical and chemical properties.

Nanomaterials also find applications in transistors and adsorption because of their high surface/volume ratio. Metals adsorbed on the surface of nanocages enhance catalytic and adsorption properties. Group III–V semiconductors have gained importance because of their extensive use in light-emitting diodes, nonlinear optics, and in microelectronic devices. These are also used as adsorbents/sensors for various analytes. The small-sized solid-state adsorbents can easily be synthesized at low cost. These are also reproducible, which makes them excellent candidates for sensor applications.

Adsortion of gases on nanostructures, nanocages, and nanotubes are part of valuable literature. For example, Ahmadi et al. studied the adsorption energies of nitrogen oxide and carbon monoxide on MgO nanotubes. In addition, different reports specifically on the adsorption properties of different molecules on the surface of (AlP)$_x$ $(AlN)$_x$ $(BP)$_x$ and $(BN)$_x$ nanocages are also part of valuable literature. For example, Ayub studied the binding affinity of helium and neon atoms with X$_{12}$Y$_{12}$ $(X = B, Al, and Y = N, P)$ in exohedral and endohedral modes. Similarly, Rad et al. demonstrated the ability of Al$_{12}$N$_{12}$ nanoclusters for adsorption of BCl$_3$ by using density functional theory calculations. In another report, Rad and Ayub studied the geometries and electronic properties of Ni-doped Al$_{12}$N$_{12}$ nanocages. Baei et al. showed B$_{12}$N$_{12}$ nanoclusters as an outstanding adsorbent for aniline from groundwater to tackle the environmental issues. Significant

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literature is available for adsorption of various molecules such as pyridine, \textsuperscript{23} methylvamine, \textsuperscript{24} hydrogen cyanide, \textsuperscript{25} and fluorine\textsuperscript{26} on B\textsubscript{12}N\textsubscript{12} nanocages. Adsorption of biological molecules such as nitrogenous basis (uracil, cytosine, and adenine)\textsuperscript{27} and guanine\textsuperscript{28} on these nanocages are also part of valuable literature. In valuable literature, report on adsorption of pyrrole on Al\textsubscript{12}N\textsubscript{12}, Al\textsubscript{12}P\textsubscript{12}, B\textsubscript{12}P\textsubscript{12}, and B\textsubscript{12}N\textsubscript{12} nanocages is also present.\textsuperscript{29} Rad et al. studied the effective adsorption of O\textsubscript{3} on B\textsubscript{12}P\textsubscript{12}, Al\textsubscript{12}N\textsubscript{12}, and B\textsubscript{12}N\textsubscript{12} nanocages previously.\textsuperscript{25} Similarly, B\textsubscript{12}P\textsubscript{12} nanocages were also utilized for hydrogen gas adsorption.\textsuperscript{30}

Recently, metal decorations (dopants) have been launched to improve the adsorption, electronic,\textsuperscript{31−35} and nonlinear optical properties of nanostructures.\textsuperscript{36,37} Zhang et al.\textsuperscript{38} carried out DFT calculations to examine the hydrogen adsorption on pure and nickel metal-decorated aluminum nitride nanocages. They studied that in a pure AlN nanocage, a single Al atom avails only one H\textsubscript{2}, whereas the nickel atom in Ni−AlN has a tendency to adsorb three hydrogen molecules. Ayub et al.\textsuperscript{39} studied that nickel decoration on B\textsubscript{12}N\textsubscript{12} and B\textsubscript{12}P\textsubscript{12} significantly enhanced the adsorption of hydrogen gas. Nickel metal decoration on (XY)\textsubscript{12} was also proved useful for adsorption of SO\textsubscript{2}.\textsuperscript{40} Similarly, Shakerzadeh et al. investigated adsorption of phosphene gas on Al- and Ga-doped B\textsubscript{12}N\textsubscript{12} and B\textsubscript{10}N\textsubscript{16} nanoclusters.\textsuperscript{42} Decoration of metal is useful in order to enhance the effective role of these nanocages in NLO materials.\textsuperscript{43,44} In addition, these nanocages exhibit a variety of applications such as field-effective transistors,\textsuperscript{45} storage devices,\textsuperscript{46} and magnetic nanoparticles.\textsuperscript{47}

Because of the rapid increase in industrialization, population, and traffic, the percentage of CO\textsubscript{2} also increases in the atmosphere as a result of fossil fuel burning. Ultimately, the greenhouse effect is increasing and making the earth warmer. Oceans act as a sink of CO\textsubscript{2} and the dissolution of CO\textsubscript{2} affecting the system by lowering the pH. Therefore, it is important to monitor and control this pollutant to make the environment more safe and friendly. Recently, the research is devoted to develop some gas sensors for monitoring hazardous gas for its optimum level.\textsuperscript{48−50}

Carbon sequestration is a process through which atmospheric freely available carbon dioxide (CO\textsubscript{2}) is captured and stored through a natural process, so it has become a most important feature in environment protection. For better results, the sequestration material should be of large surface area for effective absorption and easy accessibility to atmospheric carbon dioxide.\textsuperscript{51,52} Therefore, it is important to capture this dangerous gas from the environment in order to make the environment green and clean. Recently, Cu-decorated B\textsubscript{12}N\textsubscript{12} has been used to detect the harmful phosgene gas.\textsuperscript{53} Similarly, Hussain et al. explored the remarkable response of Zn-doped B\textsubscript{12}P\textsubscript{12} to SO\textsubscript{2} gas.\textsuperscript{54}

In the literature, there is no detailed report on the adsorption of carbon dioxide on Zn-decorated nanocages. Analysis is performed for all promising relaxed structures of CO\textsubscript{2}-adsorbed nanocages on the above-mentioned surfaces. We discuss the result on adsorption through the net charge transfer, values of binding energy, molecular electrostatic potential (MEP) analysis, dipole moment, density of states (DOS), global descriptor of energy, and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) distribution on all possible forms of B\textsubscript{12}P\textsubscript{12} nanocages. Finally, we recommend a kind of novel systems with promising electronic properties for CO\textsubscript{2} sensing materials.

2. RESULTS AND DISCUSSION

The relaxed geometry of a B\textsubscript{12}P\textsubscript{12} nanocage at the B3LYP method with the 6-31G(d,p) level of DFT is shown in Figure 1. Two types of rings are present in the B\textsubscript{12}P\textsubscript{12} nanocage, one is tetragonal and the other is hexagonal. Both rings are interconnected in order to gain a three-dimensional nanocage. Similarly, two types of bonds are present in B\textsubscript{12}P\textsubscript{12}, one is b\textsubscript{64} (bond shared between tetragonal and hexagonal ring) and the other is b\textsubscript{66} (bond shared between two hexagonal rings). In an optimized geometry of B\textsubscript{12}P\textsubscript{12} nanocage, the b\textsubscript{64} and b\textsubscript{66} bond lengths are 1.93 and 1.91 Å, respectively.

![Figure 1. B12P12 DFT-based relaxed structure with the aid of the B3LYP method along with the 6-31G(dp) level of DFT.](https://dx.doi.org/10.1021/acsomega.0c01686)

2.1. Interaction Energies along with Bond Lengths.

Pure B\textsubscript{12}P\textsubscript{12} has equal number of electropositive and electronegative atoms. Six different sites are present for the decoration of a late transition metal (Zn). These sites are named as: (i) b\textsubscript{66} [decoration of Zn on a common bond present between two six-member (hexagonal) rings], (ii) b\textsubscript{64} [placement of Zn metal specifically on a bond shared between one four-member (tetragonal) and one six-member (hexagonal) ring], (iii) b\textsuperscript{top} (Zn metal installed on boron top), (iv) b\textsuperscript{top} (positing of Zn metal on phosphorus top), (v) r\textsubscript{6} (bringing Zn metal on the top center of the hexagonal ring), and (vi) r\textsubscript{6} (putting Zn metal on top of the tetragonal ring). We tried all the above-mentioned positions, but only four geometries could be optimized because some initial input geometries switched to other geometries. The obtained geometries are named as D\textsubscript{1} (Zn@b\textsubscript{66}), D\textsubscript{2} (Zn@b\textsuperscript{top}), D\textsubscript{3} (Zn@r\textsubscript{6}), and D\textsubscript{4} (Zn@b\textsuperscript{top}).

In the D\textsubscript{1} geometry, the positioning of the late transition metal (Zn) elongates the B−P bond length to 3.66 Å (as compared to 1.93 Å in pure BP) with an interaction energy value of −57.12 kJ/mol. In the D\textsubscript{2} geometry, the decoration of Zn metal on B\textsubscript{12}P\textsubscript{12} does not bring much change in the B−P bond length (bond length (B−P) = 1.98 Å), and the interaction energy value in this case is −22.94 kJ/mol. In the D\textsubscript{3} and D\textsubscript{4} geometries, the interaction of Zn metal with the B\textsubscript{12}P\textsubscript{12} nanocage executes a negligible alteration in the B−P bond length with interaction energy values of −21.03 and −14.07 kJ/mol, respectively. Similarly, the distances of Zn metal from the B\textsubscript{12}P\textsubscript{12} nanocage in D\textsubscript{1}, D\textsubscript{2}, D\textsubscript{3}, and D\textsubscript{4} geometries are 2.15, 2.15, 2.96, and 3.00 Å, respectively, as shown in Figure 2.

From the preceding discussion, it is cleared that D\textsubscript{1} is the most stable and D\textsubscript{4} is the least stable geometry among D\textsubscript{1}−D\textsubscript{4}. This might be due to the shape of the geometries; that is, in D\textsubscript{1}, adsorption of Zn metal changes the normal shape of B\textsubscript{12}P\textsubscript{12} to an open envelope shape, which ultimately reduces the strain of the tetragonal ring and becomes stable, whereas in...
D4, B12P12 does not provide enough room for adsorption of Zn metal, which decreases the stability of the Zn-doped system. Apart from this, the distance of Zn metal from the BP nanocage is very crucial, which suggests that large distance of Zn from BP in D4 causes weak adsorption and vice versa.

Further, adsorption of CO2 gas on pure and Zn-doped B12P12 nanocages is being analyzed. CO2 absorption on bare B12P12 exhibits the physisorption phenomenon. The large distance of gas from the nanocage (d_{CO2−BP} = 3.42 Å) and the low adsorption value (E_d = −4.88 kJ/mol) indicated that CO2 is not favorably adsorbed on bare B12P12. Besides this, CO2 is also adsorbed on Zn-doped B12P12 nanocages (D1–D4), which deliver four geometries named as E1, E2, E3, and E4.

We gained E1–E4 after CO2 adsorption on D1–D4, respectively, as shown in Figure 3. The adsorption energy values in E1 (E_{ad} = −75.12 kJ/mol), E2 (E_{ad} = −25.89 kJ/mol), E3 (E_{ad} = −42.43 kJ/mol), and E4 (E_{ad} = −28.73 kJ/mol) suggest that CO2 gas is favorably adsorbed on Zn-doped systems, which suggested potential utilization of these materials for CO2 gas sensing as compared to pure B12P12.

In all geometries (E1–E4), orientation of CO2 on Zn-decorated BP is different (Figure 3). Different orientations display different distances from the Zn−BP system. Among E1–E4, E1 and E3 disclosed high adsorption energy values, and these are due to the small distance of CO2 from the Zn–B12P12 nanocage [d_{CO2−Zn−BP} (E1 = 2.30 Å and E3 = 3.24 Å)]
Table 1. Distance of Zn Metal from the B12P12 Nanocage (Å), Distance between the Closest Atom of CO2 and Zn Metal (Å), Natural Bonding Orbital Charge (Q_NBO) on Metal and Gas (eV), Dipole Moment (Debye), and Adsorption Energy of All Systems (kJ/mol)

| systems       | \(d_{Zn-BP}\) (Å) | \(d_{CO2-Zn}\) (Å) \(^a\) | Q_{NBO} on CO2 (eV) | Q_{NBO} on Zn (eV) | \(\mu\) (D) | \(E_{ad}\) (kJ/mol) |
|---------------|-----------------|---------------------|------------------|------------------|--------|------------------|
| B12P12        | 0.00            |                     | 1.86             | 2.39             | 3.30   | 28.73            |
| B12P12−CO2    | 2.15            | 2.30                | −0.624           | 1.937            | 2.25   | −57.12           |
| Zn−BP (D1)    | 2.15            | 4.25                | −0.677           | 0.524            | 3.07   | −22.94           |
| Zn−BP−CO2 (E1)| 2.30            | 3.24                | −0.685           | 0.076            | 2.01   | −42.30           |
| Zn−BP (D2)    | 2.26            | 3.24                | −0.685           | 0.097            | 0.61   | −14.07           |
| Zn−BP−CO2 (E2)| 3.00            | 4.25                | −0.422           | 0.17             | 3.30   | −28.73           |

\(^a\)Distance between the nearest CO2 atom from the Zn metal. \(^b\)Adsorption energies of different systems.

as shown in Table 1. The closest distance of CO2 from Zn−B12P12 with high adsorption energy is found in the case of E1, where Zn metal effectively offers better adsorption because of the small distance of Zn from the B12P12 nanocage. Therefore, small distance allows favorable adsorption of CO2 on Zn-doped B12P12 nanocages. From the above discussion, it is concluded that adsorption of late transition metal (Zn) brings significantly enhance the adsorption rate of CO2 gas.

The literature is quite extensive on the utilization of different surfaces for CO2 detection and adsorption. We have now given comparison of our results with those available in the literature on different nanoclusters. Moreover, in valuable literature, reports related to CO2 adsorption on different nanocages are present. Baei et al.\(^5\) studied different orientations of CO2 on B12N_{12} nanocages with adsorption energies ranging from −14.99 to −15.45 kcal/mol. Similarly, Kaufman et al.\(^5\) studied the interaction of CO2 with the Au_{12} cluster with an adsorption energy value of 0.13 eV. Liang et al.\(^5\) studied the physisorption of CO2 on B12N_{12}, Li@B12N_{12}, Na@B12N_{12}, and K@B12N_{12} with adsorption energies of −1.86, −2.96, −3.18, and −2.66 kcal/mol, respectively. Based on DFT study, Jiang et al.\(^5\) reported that Al_{11}Mg_{5} nanoclusters had excellent capturing capacity of CO2 (\(E_{ad} = 0.114\) eV). Guo et al.\(^5\) reported the adsorption of CO2 on a hexagonal BN sheet, where the adsorption energies are as high as 0.42 eV (parallel orientation of CO2 on the h-BN sheet) and 0.44 eV (vertical orientation of CO2 on the h-BN sheet). The adsorption energies of Zn-doped boron phosphate nanocages (in our case) are much higher (−6.18 to −17.96 kcal/mol) than the reported values of adsorption energies of CO2 on different surfaces. These results illustrate the efficiency and potential of the Zn−B12P12 nanocluster for CO2 adsorption.

2.2. Dipole Moment. Dipole moment is another tool to explore the electronic change in the B12P12 nanocluster upon Zn decoration and CO2 adsorption. As we know, the electropositive and electronegative atoms are equal in number; therefore, a pure B12P12 nanocage is a symmetrical structure with zero dipole moment. However, decoration with late transition metal such as Zn brings significant change in the dipole moment as shown in Table 1. The dipole moments in D1−D4 geometries are noted as 2.25, 3.24, 0.94, and 0.61 D, respectively. All values of dipole moments revealed that the placement of Zn significantly disturbs the charge separation in the B12P12 nanocage. The disturbance in charge separation is high in the case of D1 and D2 systems, which might be due to

the small distance of Zn from BP. In addition, the disturbance in charge separation of B12P12 is also analyzed in CO2−B12P12 and E1−E4 geometries. Initially, when carbon dioxide is placed on top of B12P12, the dipole moment value is quite small (0.33 D), which indicates that adsorption of CO2 does not bring significant change in charge separation. However, when CO2 is positioned on Zn-decorated B12P12 nanocages (E1−E4), significant changes in the dipole moment value are noted. The dipole moment values for E1−E4 are 3.36, 3.07, 3.00, and 3.30 D, respectively. These values suggest that CO2 adsorption on D1−D4 geometries significantly affects the charge separation with dipole moment values as compared to the rest of the geometries. Large adsorption energies cause high charge separation (large dipole moment value) in E1−E4. The decreasing order of the dipole moment for all systems is E1 > E4 > D2 > E2 > E3 > D1 > D3 > D4 > CO2−B12P12. From the preceding discussion, it is cleared that CO2 adsorption on Zn-decorated B12P12 nanocages enhanced charge separation of B12P12 with large values of dipole moment.

2.3. Q_{NBO}. In support of dipole moment, Q_{NBO} analysis is performed in order to understand the strong interaction of Zn and CO2 with the B12P12 nanocage. In the case of D1−D4 geometries, the increase in Q_{NBO} is consistent with the increase in the dipole moment value. A highest Q_{NBO} value is noted in the D1 system with large dipole moment and \(E_{ad}\). The decreasing order of Q_{NBO} for D1−D4 is D1 > D2 > D3 > D4. This trend is consistent with the dipole moment trend of D1−D4 geometries. However, the Q_{NBO} analysis in CO2-adsorbed Zn-doped B12P12 systems (E1−E4) exhibited negative values. This might be due to shifting of charge from Zn−BP, which makes CO2 slightly negative in nature (Table 1). Therefore, from Q_{NBO} discussion, it is illustrated that Zn decoration on B12P12 nanocages shows a consistent trend with dipole moment, and CO2 adsorption on these metal-decorated Zn_{12}P_{12} nanocages makes carbon dioxide slightly negative in nature.

2.4. MEP Analysis. MEP analysis is another useful parameter to explore the extent of charge separation within a molecule. MEP analysis also correlates the geometry of a system with physiochemical properties such as dipole moment, chemical reactivity, and partial charges. MEP analysis is estimated at the B3LYP/6-31G(d,p) level of DFT. Figure 4 discloses the charge separation. Generally, blue area represents the electropositive end (boron in the present case), while yellow area represents the mean potential (the area
between the two extremes) in web version. Pure B12P12 being symmetrical shows equal charges. Fixing of CO2 on pure B12P12 does not bring significant charge separation as shown in Figure 4. However, placement of Zn on pure nanocage causes positive charge shifting on top of the Zn metal (blue color) because of the electropositive nature of late transition metal and the yellow area in the nanocage becomes less intense. However, in the case of E1–E4, major charge separation occurs as the blue area is shifted to Zn metal and the carbon center of CO2 while both oxygen atoms of CO2 exhibit extreme negative charge. All this charge shifting is attributed to an increase in dipole moment (D). For instance, pure B12P12 has zero dipole moment, whereas Zn-decorated B12P12 has some value of dipole moment.

Next, the correlation of the distribution of charges (in MEP) with the dipole moment is explored. In D1–D4 systems, an irregular trend of dipole moment is observed. A maximum dipole moment is noted in the D3 geometry; however, this value does not bring much change in the electrostatic potential plot, probably because of the large distance of metal and B-top adsorption of metal on BP. The second largest dipole moment value is obtained in the D1 geometry. In D1, some charge density is shifted toward the metal end upon Zn adsorption on BP, probably because of the incorporation of metal with the bond present between the tetragonal and hexagonal ring. The electrostatic potential plots of geometries D3 and D4 also exhibit a similar potential. Again, this is probably due to large distances and low values of dipole moment along with low adsorption energies values, which do not bring any change in charge distribution. Overall, the electrostatic potential (ESP) of D1–D4 is different from each other because of the difference in dipole moment values and orientation along with the distance of metal from the cage.

2.5. Electronic Properties. The frontier molecular orbitals (FMOs) (energies of HOMOs and LUMOs), Fermi level, and the HOMO–LUMO gap of systems are observed at the B3LYP/6-31G(d,p) level of density functional theory. The results of these key parameters are tabulated in Table 2. Pure B12P12 is viewed as semiconductor, which holds a HOMO–LUMO gap of 3.70 eV. The HOMO and LUMO orbitals of B12P12 are located at −5.92 and −5.61 eV, respectively. Generally, the Fermi level (EFL) of a molecule is observed at the midpoint of the HOMO–LUMO gap.59 The Fermi level is found at −4.98 eV for the B12P12 nanocage. When Zn is installed on the B12P12 nanocage (D1–D4), a remarkable change in the energies of HOMO and LUMO is observed. The energies of HOMO for D1–D4 are −5.92, −6.25, −6.27, and −6.44 eV, respectively. The energies of LUMO are decreased, which ultimately causes narrowing of the HOMO–LUMO gap. The HOMO–LUMO gap (Eg) is related to the conductivity of a material, and this direct relation is commonly measured with the aid of the following equation

\[
\sigma \propto \exp\left(-\frac{E_g}{kT}\right)
\]
The widths of H−L gaps for D1−D4 are 2.95, 3.09, 2.43, and 2.40 eV, respectively. These values disclosed the great conductivity of Zn-decorated B_{12}P_{12} nanocages. When CO\textsubscript{2} is adsorbed on pure B_{12}P_{12}, no such sifting of HOMO and LUMO orbital is observed. The difference in the energy gap of pure and CO\textsubscript{2}−B_{12}P_{12} is very minute as shown in Table 2. However, adsorption of CO\textsubscript{2} on Zn-decorated B_{12}P_{12} nanocages (E1−E4) appreciably destabilizes the HOMO orbitals and stabilizes the LUMO orbitals. The HOMO energies of E1−E4 geometries are −4.21, −4.73, −4.59, and −4.40 eV, whereas the LUMO energies are −2.77, −3.19, −3.02, and −3.19 eV, respectively. All these values indicated destabilization of HOMO orbital and stabilization of LUMO orbital (after CO\textsubscript{2} adsorption on D1−D4), which results in narrowing of the HOMO−LUMO energy gap. The HOMO−LUMO energy gap upon Zn decoration on B_{12}P_{12} decreases from 3.70 to 2.95 (D1), 3.09 (D2), 2.43 (D3), and 2.40 (D4). Therefore, Zn decoration significantly causes narrowing of the HOMO−LUMO energy gap with high conductivity as compared to pure and CO\textsubscript{2}−B_{12}P_{12} nanocages. The HOMO−LUMO energy gaps of E1−E4 are 2.88, 3.08, 3.41, and 2.42 eV, respectively. The values of HOMO−LUMO energy gap show that CO\textsubscript{2} adsorption on D1−D4 significantly reduces the HOMO−LUMO energy gap as compared to pure and CO\textsubscript{2}−B_{12}P_{12}, which suggest that Zn metal decoration favors CO\textsubscript{2} adsorption. However, the Fermi levels for E1−E4 are noted at −4.21, −4.73, −4.59, and −4.40 eV, respectively. The decreasing order of HOMO−LUMO energy gap for all systems including the pure B_{12}P_{12} nanocage is B_{12}P_{12} >CO\textsubscript{2}−B_{12}P_{12} >E_{3} >D_{2} >E_{2} >D_{1} >E_{1} >D_{3} >E_{4} >D_{4}. From this trend and the above-mentioned discussion, it is noted that Zn decoration on B_{12}P_{12} significantly enhances the conductivity of the B_{12}P_{12} nanocage, and Zn decoration also makes the BP nanocage an efficient material for CO\textsubscript{2} adsorption (Figure 5).

The distribution of HOMO and LUMO densities on all systems at B3LYP in conjunction with the 6-31G(d,p) level of DFT is shown in Figure 6. Generally, DOS is performed in support of FMOs. The DOS graphs are shown in Figure 6, which reveal that the HOMO and LUMO densities are equally shared within the whole B_{12}P_{12} nanocage. However, placement of Zn on B_{12}P_{12} shifted the HOMO and LUMO toward the Zn center in the D1 and
D2 geometries. However, in the case of D3 and D4 geometries, the position of Zn metal on BP causes shifting of a major part of HOMO on the metal center and LUMO on the cage end. This happens because of the presence of many electronegative atoms that make the metal atom electron-rich. A metal being electropositive cannot retain these electrons, and therefore, they are spread out as excess electrons causing high energy level of the newly formed HOMO. Moreover, in the E1–E4 geometries, a similar distribution pattern of HOMO and LUMO densities is observed as shown in Figure 6.

2.6. Global Descriptor of Reactivity. The global descriptor of reactivity of investigated systems is inspected at the B3LYP/6-31G(d,p) level of DFT. Various properties such as global hardness (\(\eta\)), global softness (\(S\)), global ionization potential (IP), global electron affinity (EA), electrophilic index (\(\omega\)), global chemical potential (\(\mu\)), and electronegativity (\(\chi\)) are carried out in order to illustrate the effect of Zn doping on the capturing of CO\(_2\). The conventional energy of LUMO expresses the electron accepting property, whereas the energy of HOMO represents the IP (according to the Koopmann theorem\(^{62}\)). The results in Table 3 reveal that all Zn-doped and CO\(_2\)-adsorbed Zn-decorated systems exhibit good affinity values with fine IP. The values of EA and IP suggested that our strategy of Zn decoration on pure B\(_{12}\)P\(_{12}\) is useful for CO\(_2\) adsorption. Similarly, the electrophilic index expresses the great chemical reactivity of a compound. The pure BP nanocage disclosed an electrophilic index of 6.703 eV. Fixing of Zn on B\(_{12}\)P\(_{12}\) (D1–D4) boosted the electrophilic index value to 7.951 from 6.703 eV for bare nanocage. Likewise, adsorption of CO\(_2\) on D1–D4 geometries improved the electrophilic index values in E1–E4 geometries, which recommended that Zn decoration is an effective way for CO\(_2\) adsorption. Global hardness and global softness parameters also point out that Zn-decorated and CO\(_2\)-adsorbed Zn–BP nanocages are hard in nature with low values of global softness. The great chemical stability of a system is directly related to the chemical potential of that system. A compound with large value of chemical potential is supposed to be least reactive and most stable in nature. The Pure B\(_{12}\)P\(_{12}\) nanocage exhibited a chemical potential value of \(-4.980\) eV, whereas the positioning of Zn metal on the B\(_{12}\)P\(_{12}\) nanocage increased the chemical potential in D1 (\(\mu(= -4.445\) eV)), D2 (\(\mu(= -4.705\) eV)), D3

Figure 6. DOS for all systems at the B3LYP/6-31G(d,p) level of DFT.

Table 3. IP, EA, X (Electronegativity), \(\mu\) (Chemical Potential), \(\eta\) (Global Hardness), \(S\) (Global Softness), and \(\omega\) (Global Electrophilicity) of All Systems

| system          | IP  (eV) | EA  (eV) | X   (eV) | \(\mu\) (eV) | \(H\) (eV) | \(S\) (eV\(^{-1}\)) | \(\Omega\) (eV) |
|-----------------|---------|---------|---------|-------------|-----------|----------------|------------|
| BP              | 6.830   | 3.130   | 4.980   | \(-4.980\)  | 1.850     | 0.270          | 6.703      |
| BP–CO\(_2\)     | 6.810   | 3.110   | 4.960   | \(-4.960\)  | 1.850     | 0.270          | 6.649      |
| Zn–BP (D1)      | 5.920   | 2.970   | 4.445   | \(-4.445\)  | 1.475     | 0.339          | 6.698      |
| Zn–BP–CO\(_2\) (E1) | 5.640  | 2.770   | 4.205   | \(-4.205\)  | 1.435     | 0.348          | 6.161      |
| Zn–BP (D2)      | 6.250   | 3.160   | 4.705   | \(-4.705\)  | 1.545     | 0.324          | 7.164      |
| Zn–BP–CO\(_2\) (E2) | 6.270  | 3.190   | 4.730   | \(-4.730\)  | 1.540     | 0.325          | 7.264      |
| Zn–BP (D3)      | 5.630   | 3.190   | 4.410   | \(-4.410\)  | 1.220     | 0.410          | 7.971      |
| Zn–BP–CO\(_2\) (E3) | 6.160  | 3.020   | 4.590   | \(-4.590\)  | 1.570     | 0.318          | 6.710      |
| Zn–BP (D4)      | 5.570   | 3.170   | 4.370   | \(-4.370\)  | 1.200     | 0.417          | 7.957      |
| Zn–BP–CO\(_2\) (E4) | 5.610  | 3.190   | 4.400   | \(-4.400\)  | 1.210     | 0.413          | 8.000      |
(μ = −4.410 eV), and D4 (μ = −4.370 eV)). Nonetheless, the adsorption of CO2 on Zn-doped B12P12 nanocages (E1–E4) significantly raised the chemical potential. The decreasing order of chemical potential among E1–E4 is |E1 (μ = −4.205 eV)| > |E4 (μ = −4.400 eV)| > |E3 (μ = −4.590 eV)| > |E2 (μ = −4.70 eV)|. Therefore, designed systems show good values of chemical potential and electronegativity. From the preceding discussion, it is concluded that all designed systems (Zn-decorated and CO2-adsorbed B12P12 nanocages) exhibited ordinary reactivity with remarkable stability and thus proved to be the best candidates for CO2 sensing materials.

3. CONCLUSIONS

In summary, the changes in the electronic behavior of B12P12 nanocage on Zn decoration and CO2 adsorption are studied. Zn decoration on B12P12 followed by CO2 adsorption on bare and Zn-decorated B12P12 causes narrowing of the HOMO–LUMO energy gap. The binding energy of CO2-adsorbed Zn–B12P12 nanocages [E1 (Ead = −75.12 kJ/mol), E2 (Ead = −25.89 kJ/mol), E3 (Ead = −42.43 kJ/mol), and E4 (Ead = −28.73 kJ/mol)] is remarkably higher than those of Zn–B12P12 [D1 (Ead = −57.12 kJ/mol), D2 (Ead = −22.94 kJ/mol), D3 (Ead = −21.03 kJ/mol), and D4 (Ead = −14.07 kJ/mol)] systems, which suggested the strong adsorption of CO2 on Zn-decorated BP systems. The dipole moment and Q_NBO analysis showed that maximum charge separation is observed for CO2–Zn–B12P12 geometries. MEP analysis confirmed the different charge zones on all systems. DOS analysis is also performed in support of FMO analysis, which explored the different distribution patterns of HOMO and LUMO orbitals on CO2-adsorbed and Zn-decorated B12P12 geometries. Finally, the global descriptors of reactivity are investigated, which demonstrated the great stability and least reactivity of our designed (Zn–B12P12 and CO2–Zn–B12P12) systems. The results of all analyses recommended our Zn-decorated B12P12 nanocages as potential candidates for application in CO2 sensors.

4. COMPUTATIONAL METHODS

The B3LYP method of DFT along with the 6-31G(d,p) basis set is utilized for performing all calculations through Gaussian 09.55 The same level of DFT is used in order to gain optimized geometries of all systems of interest. B3LYP66,67/6-31G(d,p)66,67 is a reliable level of DFT for computing the geometric and electronic properties of nanocages66,67 and other systems.66,67 Different parameters such as adsorption energy, Q_NBO, dipole moment, analysis of MEP, FMO distribution, and DOS are estimated at the B3LYP/6-31G(d,p) level of DFT. The HOMO–LUMO gap is directly related to the conductivity of a material and also plays a key role in evaluating the global descriptor of reactivity. Global hardness, global softness, electronegativity, chemical potential, IP, EA, and electrophilic index of all systems are calculated by using HOMO–LUMO gap values. Different equations are used to calculate the interaction energies of CO2 gas and Zn metal with B12P12 nanocages.

Equation 2 is useful for calculating the adsorption energy of the Zn–B12P12 system

\[ E_{ad} = E_{Zn-BP} - (E_{BP} + E_{Zn}) \]  

In this equation, \( E_{Zn-BP} \) stands for the zinc metal-decorated B12P12 nanocage. Similarly, \( E_{BP} \) expresses the energy of bare B12P12 nanocage and \( E_{Zn} \) points out the energy of Zn (metal). The adsorption energies in kJ/mol for CO2-adsorbed pure and Zn-decorated B12P12 are calculated with the aid of eqs 3 and 4.

\[ E_{ad(BP)} = E_{CO2-BP} - (E_{BP} + E_{CO2}) \]  

\[ E_{ad(Zn-BP)} = E_{CO2-Zn-BP} - (E_{Zn-BP} + E_{CO2}) \]  

The \( E_{ad(BP)} \) in eq 2 and the \( E_{ad(Zn-BP)} \) in eq 4 define the interaction energies of CO2 with pristine B12P12 and Zn-decorated B12P12, respectively. The \( E_{CO2-BP} \) and \( E_{CO2-Zn-BP} \) fragments highlight the total interaction energies of the CO2-adsorbed BP nanocage and CO2-adsorbed Zn–BP nanocages, respectively. Similarly, \( E_{CO2} \) indicates the single CO2 molecule energy in kJ/mol.

Valuable literature suggests that different equations were utilized for calculating different global indices of reactivity [electrophilicity index (\( \alpha \)), global softness (\( S \)), electronegativity (\( X \)), global hardness (\( \eta \)), and chemical potential (\( \mu \))], which are given below

\[ \mu = -1/2 \times (E_{HOMO} + E_{LUMO}) \]  

\[ \eta = (E_{LUMO} - E_{HOMO})/2 \]  

\[ S = 1/(2\eta) \]  

\[ \alpha = \mu^2/2\eta \]  

\[ X = -(E_{LUMO} + E_{HOMO})/2 \]

The visualization software utilized to study the different properties of investigated systems are GaussView 5.0 (used to manage the input files), Avogadro (for interpreting the HOMO and LUMO distribution), and Pymol (for DOS graphs).

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01686.
Cartesian coordinates of the optimized geometries (PDF)

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