Reversible hydrogen storage capacity of Sc and Y functionalized [1,1]paracyclophane: Insights from density functional study

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Abstract

This work reports the hydrogen storage, and delivery capacities of Sc and Y functionalized [1,1]paracyclophane using dispersion corrected density functional theory calculations. The Sc and Y atoms are bind strongly with benzene rings of [1,1]paracyclophane. Each Sc and Y atom functionalized over [1,1]paracyclophane adsorb up to 6 H₂ molecules via Kubas interaction achieving maximum gravimetric density up to 8.22 wt% and 6.33 wt%, respectively. The calculated average hydrogen adsorption energy (0.36 eV) is lower than the chemisorption but higher than the physisorption process. The kinetic stabilities are verified through the HOMO-LUMO gap and different global reactive descriptors. ADMP molecular dynamics simulations reveal the reversibility of adsorbed H₂ molecules at sufficiently above the room temperature and the solidity of host material at 500 K. Average Van't Hoff desorption temperature for Sc and Y decorated system was calculated to be 439 K and 412 K respectively at 1 atm of pressure. The estimated thermodynamically usable hydrogen capacities are found to be 5.92 wt% and 5.87 wt% of hydrogen which fulfil the hydrogen energy criteria (by 2025) of US-DOE. Hence, we believe that Sc and Y functionalized [1,1]paracyclophane can be considered as a thermodynamically viable, and potential reversible hydrogen storage materials at ambient environment.

Keywords: Hydrogen storage, DFT, Van’t-Hoff equation, ADMP, [1,1]paracyclophane, ESP

1. INTRODUCTION

The excessive demand on fossil fuels for vehicular and industrial purposes has not only caused depletion of the limited fossil fuels but also triggered alarming global warming and environmental pollution [1]. Therefore, international organizations such as United Nation Environment Program (UNEP) has been urging for alternative and clean energy resources. In this regard, hydrogen is considered as an ideal, environment-friendly, and sustainable energy carrier, which, in addition, has higher energy per unit mass (120 MJ/kg) than the fossil fuels
(44 MJ/kg for gasoline) [2,3] However, efficient storing and delivering hydrogen energy as fuel under ambient conditions, has been a major challenge for the commercial developments. [4,5]. To store hydrogen in compressed gaseous form, voluminous tanks are required that can withstand high pressure (~70 MPa), and which is quite difficult and expensive [6]. Storing liquid hydrogen requires the cryogenic temperature about -253°C under high pressure (~ 250-350 atm) which makes the process highly expensive [7]. Therefore, solid-state material-based hydrogen storage systems have been proposed to be the selective method which is supposed to efficient and cost-effective as well. The basic criteria that an efficient solid-state storage system should follow, according to the US department of energy (DOE-US) are; a) intermediate adsorption energy in the range of 0.2-0.6 eV/H 2 b) minimum gravimetric density up to 5.5 wt%, c) volumetric density above 40 kg/m 3 d) refuelling time of less than 3 minutes over the lifetime, and d) fast kinetic with ambient thermodynamics (T ~40-85 °C and under P ~100 atm) [8,9]

Since last few decades, researchers have extensively studied different substrates such as carbon nanostructures [10,11,12], metal hydrides [13,14], graphene [15,16], zeolites [17], metal-organic frameworks [18,19], as hydrogen storage materials. However, these storage systems are reported have several drawbacks such as low storage capacity, high desorption temperature, instability at high temperature. So, these issues must be addressed while developing viable hydrogen storage substrates for commercial applications. Organometallic compounds functionalized with transition metals (TM) such as TM-decorated organometallic buckyballs [20], TM-ethylene [21], can be highly potential hydrogen storage substrates as compared to many other materials reported in literature. It was reported that TM bonded strongly with π -electron delocalized compound via Dewar coordination and trap hydrogen molecules through Kubas interaction [22, 23]. Many authors have reported TM atoms like Ti, Sc and Y functionalized carbon-based nanostructures for efficient hydrogen storage [24, 25, 26, 27, 28, 29]. For example Modak et al. made a comparative study of the hydrogen uptake capacity of single-wall carbon nanotubes functionalized with Y, Zr, Nb, and Mo. Their study suggested that, TM having lowest number of d electron in their outer shell showed better hydrogen storage capacity [30]. Mananghaya et al. studied hydrogen storage in Sc and Ti coating single walled carbon nanotubes using thermodynamic simulations and reported a gravimetric capacity of 5.85 wt% at 300K [31]. Recently, the hydrogen storage capacity of scandium and yttrium decorated C 24 fullerene was studied by Shukla et al. [32, 33]. They found that, each Sc and Y atom could capture six hydrogen molecules leading to maximum gravimetric density up to 13.02 wt% at high temperature of 500 K. Many researchers have studied the hydrogen storage properties and capacities of MOF impregnated with fullerenes [34,35]. For example, Rao et al. investigated H 2 storage capacity of Li doped MOF impregnated with Li-coated fullerenes and reported a gravimetric capacity of 6.3 wt% at 100 bar and 243 K [36]. Yu et al. studied the hydrogen gravimetric and volumetric capacity of fullerene impregnated with IRMOFs and reported C 60 in IRMOF had a capacity of 7.4 wt% at 77K and 18 bar [37]. Mehrabi et al. experimentally showed that Pd doped multi-walled carbon nanotubes are potential hydrogen storage system with nearly 6wt% hydrogen capacity [38]. Chakraborty et al. investigated the H 2 storage capabilities of yttrium coated carbon nanotube and reported 6.1 Wt% of storage capacity with 100 % desorption of H 2 at 612 K
Zhang et al. studied yttrium doped B$_{40}$ and reported that each Y atom could adsorb 5H$_2$ molecules leading to 5.8 wt% with an adsorption energy of -0.211 eV/H$_2$ [40]. Sathe et al. studied the hydrogen storage in Li and Sc functionalized [4,4]paracyclophane and reported that each Sc atom can adsorb via physisorption of 5H$_2$ leading to 11.8 wt% of storage capacity [41]. They showed that Sc atoms are bound with PCP44 via Dewar mechanism, and the hydrogen molecules are attached to the sorption center via Kubas interaction. Kumar et al. reported the hydrogen storage capacity up to 10.3 wt% of paracyclophane decorated with Sc and Li [42].

In this report, we have explored the hydrogen uptake and delivery capacity of [1,1]paracyclophane (PCP11) functionalized with Sc and Y transition metal atoms. The preceding square bracket number, “[1,1]” in [1,1]paracyclophane, indicates that the consecutive benzene rings (2 benzene rings) in paracyclophane are linked with one (-CH$_2$-) moiety [43]. The linking bridges are relatively short; thus, the separation between consecutive benzene rings is small which develops a strain in the aromatic rings. This strain in the rings can be utilized for Sc and Y functionalization over the aromatic benzene ring. Due to the strain and metal functionalization, the aromatic benzene rings loses their inherent planarity [44]. Since, aromatic benzene rings are there in the PCP, these are easy for experimental synthesis and functionalization of metal atoms [45]. From the previous reports it is evident that metal functionalized with aromatic benzene rings could be treated as a viable hydrogen storage material [46, 47]. Recently, Sathe et al. investigated the hydrogen adsorption properties of Li functionalized [1,1]paracyclophane, and reported that each Li atom on PCP11 could hold 4H$_2$ molecules with a gravimetric density of 13.42 wt% [48]. We choose to functionalize Sc and Y transition metal atoms over the PCP11, as both are TM atom possess minimum number of electrons in d- block which can be beneficial for the reversible hydrogen adsorption. Our estimation reveals that each Sc and Y atoms on PCP11 can adsorb 6H$_2$ molecules via Kubas interaction. We verified the solidity of host materials and theoretically predicted hydrogen storage capacities of these materials by using molecular dynamics simulations. We believe that our work on Sc and Y functionalized [1,1]paracyclophane as potential hydrogen storage material can contribute substantially to the research and development of new materials for hydrogen energy.

2. THEORY AND COMPUTATION

The important mathematical parameters to quantify the characteristics of the hydrogen storage systems are the average binding energy of the host clusters, adsorption and successive desorption of hydrogen molecules from the host substrates.

The binding strength of the transition metal atom (Sc and Y) on the PCP11 is calculated using the following equation.

\[ E_b = \frac{1}{m} [E_{PCP11} + mE_{TM} - E_{mTM+PCP11}] \] (1)

Where $E_{PCP11}$, $E_{TM}$, and $E_{mTM+PCP11}$ are the total energy of PCP11, metal atom and TM-decorated PCP11 respectively. $m$ is the number of metal atoms added over PCP11 substrate.
Then the average adsorption energy per hydrogen molecule of the system can be calculated as:

\[ E_{ads} = \frac{1}{n} \left[ E_{PCP11+TM} + nE_{H_2} - E_{mTM+PCP11+nH_2} \right] \]  

(2)

Where \( E_{PCP11+TM} \), \( E_{H_2} \), and \( E_{mTM+PCP11+nH_2} \) is the total energy of host material, hydrogen molecule and hydrogen trapped complexes respectively. \( n \) is the number of \( H_2 \) molecules adsorbed over each complex.

Now, at a particular thermodynamic condition, the successive desorption energy of adsorbed \( H_2 \) molecules is calculated using the following equation.

\[ E_{des} = \frac{1}{n} \left[ 2E_{H_2} + E_{Host+(n-2)H_2} - E_{Host+nH_2} \right] \]  

(3)

Here, \( n \cdot 2 \) factor in the above formula arises because of successive desorption of one \( H_2 \) molecule each from the two TM adsorbents. The above energetic calculations have been performed incorporating the basis set superposition error (BSSE).

Moreover, computations of gravimetric density and thermodynamics of the studied storage systems are also important in view of their practical usability.

To obtained the hydrogen uptake capacity, gravimetric density (wt\%) of hydrogen can be calculated using the following equation:

\[ H_2(\text{wt}\%) = \frac{M_{H_2}}{M_{H_2}+M_{Host}} \times 100 \]  

(4)

Here \( M_{H_2} \) represent the mass of the total number of \( H_2 \) molecules adsorbed and \( M_{Host} \) represent the mass of metal-doped PCP11.

To depict a quantitative picture of \( H_2 \) adsorption and desorption at different temperature (T) and pressure (P), the number of \( H_2 \) molecules adsorbed on each sorption center (occupation number) “N” in TM decorated PCP11 is calculated by [49, 50].

\[ N = \frac{\sum_{n=0}^{n_{\text{max}}} n g_n e^{[n(\mu-E_{ads})/K_BT]} \sum_{n=0}^{n_{\text{max}}} g_n e^{[n(\mu-E_{ads})/K_BT]}} \]  

(5)

Here \( n_{\text{max}} \) is the maximum number of \( H_2 \) molecules adsorbed in each TM on PCP11, \( n \) and \( g_n \) represent the number of \( H_2 \) molecules adsorbed and configurational degeneracy (taken \( g_n = 1 \) by avoiding phonon contribution to entropy) for a \( n \). \( K_B \) is the Boltzmann constant and \( E_{ads} (<0) \) indicates the adsorption energy of \( H_2 \) molecules to TM-PCP11. \( \mu \) is the chemical potential of \( H_2 \) at specific T and P, obtained by using the following expression [51].

\[ \mu = H^0(T) - H^0(0) - TS^0(T) + K_BT \ln \left( \frac{P}{P_0} \right) \]  

(6)

Here \( H^0(T) \), \( S^0(T) \) are the enthalpy and entropy of \( H_2 \) at pressure \( P^0(1 \text{ bar}) \).
The bare and hydrogenated TM-decorated [1,1]paracyclophane (PCP11) complexes are optimized using hybrid ωB97Xd functional along with 6-311+G(d,p) basis sets within the framework of density functional theory. ωB97Xd is a range separated version of Becke's 97 functional and includes the long-range and Grimme's D2 dispersion correction [52, 53]. It is worth mentioning that ω B97Xd approach is a reliable method for investigating non-covalent interaction, organometallic systems, and its thermochemistry. During the geometry optimization of metal functionalized PCP11, all electron triple-split valence basis set 6-311+G(d,p) is used for carbon, hydrogen and scandium atom, whereas, for the yttrium atom, an effective core potential (ECP) based LanL2DZ basis set is used [54]. The harmonic frequencies of all the studied systems are calculated to ensure the systems are in true ground state on the potential surface.

The atomistic molecular dynamic (AMD) simulations are then performed employing the extended Lagrangian technique, atom-centered density matrix propagation (ADMP), to explore the solidity of host materials and the reversibility of hydrogen molecules from the substrate. The time step for ADMP molecular dynamics simulations is set at 1 fs, and using the velocity scaling method, the temperature is maintained throughout the simulations. All the calculations are performed with gaussian 09 computational program [55].

3. RESULTS AND DISCUSSION

Optimized structure of PCP11 is shown in Figure 1(a). There are two benzene rings in PCP11, connecting with single -CH₂- moiety as bridge. The distance between carbon atoms of -CH₂- and benzene is 1.55 Å, which corresponds to the findings of Sathe et al. [48]. The attached benzene rings lose their inherent planarity and bend slightly inwards due to the short connecting bridges and the strain induced by it. The induced strain also has a vital role in transition metal (TM) functionalization. Before functionalizing the TM atom, we have calculated the Nucleus Independent Chemical Shift (NICS) in order to check the aromaticity of the benzene rings. NICS value is calculated from the center to 3 Å above benzene ring with an increment of 1 Å. At a distance of 1 Å above the benzene ring, NICS is found negative maximum (−8.66 ppm), indicating the high aromaticity [56, 57]. The optimization of TM-functionalized PCP11 is then initialized for NICS(1) of the benzene rings.
3.1. Functionalization of Sc and Y
Optimized structures of Sc and Y functionalized over PCP11 (PCP11-2Sc, and PCP11-2Y) are shown in Figure 1(a) and 1(b) respectively. The Sc and Y atoms are grafted over the benzene ring of PCP11 with average binding energy of 1.43 eV and 1.66 eV, respectively. These high binding energy value reveals the strong bonding of Sc and Y with PCP11 and averts the possibility of metal clustering. The Sc and Y atoms are supposed to bind with the delocalised π-electrons of the benzene ring of PCP11 via Dewar coordination. In Dewar coordination, the benzene ring of the system donates its π-electrons density from the bonding orbital to empty d-orbital of Sc and Y atoms. Further, the electrons from filled d-orbital are back donated to empty π*-antibonding orbital of the benzene ring of PCP11. The average distance of Sc from the center of benzene ring (R_c) is found as 1.814 Å and the C-C bridge distance reduced to 1.52 Å after metal functionalization, which matches with earlier reports [41, 59]. Similarly, the average distance between Y and R_c is found to be 2.047 Å and C-C bridge bond length reduced to 1.525 Å. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gap (E_g) of PCP11 is found to be 7.26 eV. This energy gap is lowered to 3.02 eV and 2.45 eV after functionalization of Sc and Y atoms, respectively. Reduction in the energy gap of the substrate may be due to the contribution of d orbital of TM atoms [58, 59]. The high energy gap of these systems reveals their kinetic stabilities. The electrostatic potential (ESP) map of bare and TM functionalized PCP11 has been plotted and depicted in Figure S1 (in supporting information). In ESP plot,
the red region over benzene ring shows the accumulation of electron density and the blue region over Sc and Y region indicates the deficiency of electron density. The calculated average Hirshfeld charge on the benzene ring of PCP11 is -0.034 e.u. The Hirshfeld charge on Sc and Y atom after functionalization is +0.423 e.u and +0.399 e.u, respectively, which makes TM atoms ionic. These ionic open metal sites can adsorb the guest H$_2$ molecules.

**Table 1**: Average distance between carbon bridge (C-C), center of PCP11 benzene ring ($R_c$) and Sc atom ($R_c$-Sc), Sc and adsorbed hydrogen molecules (Sc-H), and the intermolecular hydrogen distances (H-H).

| Name of complex | Bridge c-c (Å) | $R_c$-Sc (Å) | Sc-H (Å) | H-H (Å) |
|-----------------|----------------|--------------|----------|---------|
| PCP11-2Sc       | 1.520          | 1.814        |          |         |
| PCP11-2Sc-2H$_2$| 1.522          | 1.855        | 1.982    | 0.807   |
| PCP11-2Sc-4H$_2$| 1.527          | 1.937        | 1.963    | 0.821   |
| PCP11-2Sc-6H$_2$| 1.532          | 1.966        | 2.091    | 0.805   |
| PCP11-2Sc-8H$_2$| 1.526          | 2.039        | 2.004    | 0.806   |
| PCP11-2Sc-10H$_2$| 1.525         | 2.055        | 2.020    | 0.795   |
| PCP11-2Sc-12H$_2$| 1.525         | 2.050        | 2.473    | 0.786   |

**Table 2**: Average distance between carbon bridge (C-C), center of PCP11 benzene ring ($R_c$) and Y atom ($R_c$-Y), Y and adsorbed hydrogen molecules (Y-H), and the intermolecular hydrogen distances (H-H).

| Name of complex | Bridge c-c (Å) | $R_c$-Y (Å) | Y-H$_2$ (Å) | H-H (Å) |
|-----------------|----------------|-------------|-------------|---------|
| PCP11-2Y        | 1.525          | 2.047       |             |         |
| PCP11-2Y-2H$_2$ | 1.523          | 2.067       | 2.178       | 0.796   |
| PCP11-2Y-4H$_2$ | 1.528          | 2.143       | 2.136       | 0.818   |
| PCP11-2Y-6H$_2$ | 1.532          | 2.180       | 2.184       | 0.804   |
| PCP11-2Y-8H$_2$ | 1.528          | 2.226       | 2.194       | 0.799   |
| PCP11-2Y-10H$_2$| 1.527          | 2.236       | 2.284       | 0.789   |
| PCP11-2Y-12H$_2$| 1.525          | 2.270       | 2.372       | 0.781   |

### 3.2. Geometry and stability after H$_2$ adsorption

After functionalization of Sc and Y atoms on PCP11, hydrogen molecules are introduced to each TM atom sequentially. Sequential addition of H$_2$ atoms to each sorption center which
lowers the intricacy of steric hindrance due to H₂ crowded, urges to investigate the stability of each hydrogenated complex as well as the pattern of adsorption and desorption energy.

The successive addition of H₂ molecules in PCP11-2Sc reveals that each Sc atom can hold up to six H₂ molecules. The hydrogenated complexes PCP11-2Sc-2nH₂ (n= 1-6) are depicted in Figure 2. The average distance between Sc atom and R_c, Sc and adsorbed H₂ molecules (Sc-H₂), and inter-molecular hydrogen distance (H-H) are provided in Table 1. It is found that the Sc-R_c and Sc-H₂ distances increases with the number of hydrogen molecule in the complexes. On introduction of first H₂ to PCP11-2Sc the Sc-R_c bond distance increase by 2 %, while on addition of sixth hydrogen this distance increases by almost 13%. This increase in bond distance is due to small charge transfer from the benzene ring of PCP11 to Sc atoms. Further the average Sc-H₂distances also increases from 1.98 Å to 2.47 Å after adsorption of sixth hydrogen to each Sc which may be attributed to the steric hindrance due to hydrogen crowded around the Sc atom. The H-H bond length (0.82 Å) is found to be elongated by 10% from experimental value of isolated H₂ (0.74 Å) which indicate hydrogen undergoes molecular adsorption on PCP11-2Sc. Similarly, Sequential adsorption of hydrogen on PCP11-2Y show that each Y atoms can bind up-to 6H₂ molecules, and the optimized structures of H₂ adsorbed systems PCP11-2Y-2nH₂ (n= 1-6,) are depicted in Figure 3. The geometrical bond length of Y-R_c and Y-H₂ and H-H are presented in Table 2. The distance between adsorbed H₂ molecules and the sorption center increases with increase in hydrogen molecules in the system. The inter-atomic hydrogen distance is found in the range of 0.78 Å to 0.81 Å.

In order to investigate the stability of bare and hydrogenated systems, we have estimated various reactivity parameters such as the energy gap between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) (E_g), hardness (η), electrophilicity index (ω), using the Koopman's theorem [60]. A larger E_g corresponds to a higher energy required for an electron jump from HOMO to LUMO. In other words, a smaller E_g gap suggests greater chemical reactivity, whereas a larger E_g gap indicates decreased chemical reactivity. The variation of HOMO-LUMO gap with the number of hydrogen molecules in PCP11-2Sc(2Y) are depicted in Figure 4. It is seen that the E_g shows an increasing tendency with increase in number of hydrogen molecules on the host, which reveals the kinetic stability of the studied systems with successive addition of H₂ molecules (Figure 4). It has been observed that, the value of η is decreases with increase in number of H₂ molecules in the system. Similarly, ω value decreases with the rise in value of H₂ in the system (Figure: S2 and Table: S1). This assures the stabilities of the studied systems by following the maximum hardness and minimum electrophilicity principle [61].
Figure 2: Optimized geometry of bare and hydrogenated Sc functionalized PCP11
(a) PCP11-2Sc, (b) PCP11-2Sc-2H2, (c) PCP11-2Sc-4H2, (d) PCP11-2Sc-6H2, (e) PCP11-2Sc-8H2, (f) PCP11-2Sc-10H2, (g) PCP11-2Sc-12H2

Figure 3: Optimized geometry of bare and hydrogenated Sc functionalized PCP11
(a) PCP11-2Y, (b) PCP11-2Y-2H2, (c) PCP11-2Y-4H2, (d) PCP11-2Y-6H2, (e) PCP11-2Y-8H2, (f) PCP11-2Y-10H2, (g) PCP11-2Y-12H2
Figure 4: Variation of HOMO-LUMO gap with number of hydrogen molecules adsorbed on Sc/Y functionalized PCP11

3.3. Energetic parameters

To understand the hydrogen molecules interaction with TM atoms decorated PCP11, the average H$_2$ adsorption energy and successive H$_2$ desorption energy of studied systems are calculated using Equations 2 and 3 respectively. Figure 5 shows that, the average adsorption energy decreases with increase in number of H$_2$ adsorption. For first 2H$_2$ adsorption on PCP11-2Sc, the E$_{ads}$ is found to be 0.39 eV, which decreases to 0.29 eV after attaining H$_2$ saturation (12H$_2$). This is attributed to the steric hindrance caused by H$_2$ crowded. The adsorption process involved in our study indicates that, the hydrogen molecules are adsorbed via Kubas-type of interaction with Sc atoms in which there is small charge donation from σ (HOMO) orbitals of hydrogen molecules to vacant 3d orbital of scandium atom occurs followed by back donation of charge from partial filled d orbitals of scandium to unfilled σ * (LUMO) orbitals of hydrogen molecules takes place [22, 62]. In this process, H$_2$ molecules gain a fraction of charge resulting in elongation of H-H bond lengths. The bonding of the last two H$_2$ molecules on Sc atoms is due to the charge polarization mechanism proposed by Niu-Rao-Jena [63, 64]. In this mechanism the positively charged Sc ion produces electric field which polarize the H$_2$ molecules and binds them in quasi-molecular manner. The average energy of hydrogen adsorption (0.36 eV) appears to be lower than the chemisorption but higher than the physisorption process which is a desired requirement for effective hydrogen storage as proposed by US-DOE. Similarly, For Y functionalized PCP11, the 1$^{st}$ 2H$_2$ molecules adsorbed with an average E$_{ads}$ of 0.35 eV, subsequently, the 2$^{nd}$, 3$^{rd}$, 4$^{th}$, 5$^{th}$ and 6$^{th}$ H$_2$ adsorbed with E$_{ads}$ of 0.35, 0.34, 0.34, 0.33, and 0.28 eV respectively. The Y atoms also bind the H$_2$ molecules through Kubas-type interaction. Successive desorption energy (Figure: 5) decreases with increase in H$_2$ number which implies the fact that the outermost H$_2$
molecules require less energy to desorb than \( \text{H}_2 \) molecules close to TM centres and this is obvious due to weak polarization bonds.

![Figure 5](image)

**Figure 5**: Average adsorption and successive desorption energy of (a) PCP11-2Sc-nH\(_2\) (b) PCP11-2Y-nH\(_2\)

3.4. Electrostatic potential and Hirshfeld charges

To get an insight into the distribution of electron density over the system during the process of metal functionalization and hydrogen adsorption, electrostatic potential map on the total electron density have been plotted and depicted in Figure 6 and 7. The distribution of electron density is used to determine the active adsorption sites of the Sc and Y functionalized PCP11. In the ESP plot the region with red colour represents the accumulation of electron density (highest negative potential zone) whereas blue region represents the depletion of electron density (highest positive potential zone). The colour variation in ESP maps implies the transfer of electronic charge density during the adsorption of hydrogen [65]. The red region
over the benzene ring represents the accumulation of electron density and with the functionalization of Sc and Y atoms over the benzene ring, the red regions disappear and a blue region appears over the metal atoms which indicate the depletion of electron density implying that the metal atom become somewhat ionic. It is observed from the ESP map of PCP11-2Sc and PCP11-2Y that the sorption centres (Sc and Y) are marked by dark blues surfaces indicating their electron deficiency as compared to PCP11. Upon addition of H₂ molecules to each sorption atoms, the colour map turns from dark blue to light blues implying the fact that the positive charges get transferred from the TM atoms to H₂ molecules. Successive addition of H₂ molecules to PCP11- 2Sc(2Y) changes the colour of TM atoms from blue to light blue and then to blueish-green indicating further transfer of charge density. From the figures, it is evident that the hydrogen saturated systems, PCP11-2Y(2Sc)-12H₂, have low accumulation of electron density over the top of H₂ and mild density of electron near benzene ring. This implies that more hydrogen molecules are unlikely to be adsorbed on the host material.

**Figure 6**: Electrostatics potential map of (a) PCP11-2Sc (b) PCP11-2Sc-2H₂ (c) PCP11-2Sc-4H₂ (d) PCP11-2Sc-6H₂ (e) PCP11-2Sc-8H₂ (f) PCP11-2Sc-10H₂ (g) PCP11-2Sc-12H₂

**Figure 7**: Electrostatics potential map of (a) PCP11-2Y (b) PCP11-2Y-2H₂ (c) PCP11-2Y-4H₂ (d) PCP11-2Y-6H₂ (e) PCP11-2Y-8H₂ (f) PCP11-2Y-10H₂ (g) PCP11-2Y-12H₂

To get a quantitative picture of the charge distribution of SC/Y functionalized PCP11 and H₂ stored system, the hirshfeld charge analysis has been performed. Figure 8 depicts the average hirshfeld charges on adsorbed H₂ molecules, transitions metal atoms (Sc, Y) and benzene ring carbon atoms as a function of adsorbed number of H₂ molecules. The hirshfeld charge on benzene ring C atoms of PCP11 is found to be -0.034 e which increases to -0.097 e after Sc functionalization. The charges on Sc in PCP11-2Sc(Y) is +0.42 e (+0.399 e) which infers that Sc (Y) atoms get more ionic during the PCP11 functionalization making them suitable adsorption centres. The average electronic charges on the benzene ring of PCP11-2Sc-2H₂ and PCP11-2Y-2H₂ is found to be 0.092 e and 0.095 e respectively, which reduces by 26% (for Sc) and 27% for hydrogen saturated Y functionalized PCP11. With successive adsorption of H₂ molecules on the systems, the average electronic charges on Sc and Y atoms increases by 38 % and 20% respectively. The average charges on adsorbed hydrogen
molecules found in the range of -0.019 e to 0 e, this net charge gain by the H₂ molecules subject to a small elongation of H-H bond length.

**Figure 8:** Hirshfeld charges before and after hydrogen adsorption on (a) PCP11-2Sc, (b)PCP11-2Y and adsorbed hydrogen

### 3.5. ADMP molecular dynamics simulations

To verify the hydrogen adsorption and desorption predicted by the DFT calculation, we have performed atomistic density matrix propagation (ADMP) simulations. ADMP belongs to the extended Lagrangian approach to molecular dynamics using gaussian basis functions and propagating the density matrix. Our calculation was performed with a canonical (NVT) ensemble by adding thermostat into ADMP. The nuclear kinetic energy thermostat is introduced by velocity scaling method and the temperature is checked and scaled at every 10-fs time step. For ADMP simulations, the maximum gravimetric density hydrogenated systems are kept at a pressure of 1 atm and three different temperatures above room temperature viz, 300 K, 375 K, and 475 K, for 1ps. The trajectory of potential energy and time evolution of bond length between sorption center and H₂ molecules are shown in Figure
ADMP simulations at 300 K illustrate that each Sc atom in PCP11-2Sc system, hold at least 4H\textsubscript{2} molecules just above room temperature, and the remaining 2H\textsubscript{2} desorbed from the host with the progress of time (Figure 10(a)). Similarly, in PCP11-2Y system, the last H\textsubscript{2} molecules get desorbed and at least 5H\textsubscript{2} molecules retains with each Y atoms at 300 K (Figure 10(b)). The adsorbed hydrogen molecules are oscillating near the sorption center within a distance of 1.9-2.5 Å for Sc and 2.1-3.3 Å Y functionalized system. As the temperature raised to 375 K and then to all hydrogen molecules from the vicinity of TM begins to increase movement after 500 fs (for Sc) and 350 fs (for Y). Since studied TM interacts strongly with hydrogen, the system needs higher temperature to desorb all H\textsubscript{2} molecules. At a temperature of 475 K, overall H\textsubscript{2} molecules began to move away from the sorption centers. The ADMP snapshots of both the studied system are shown in Figure S5.

![Figure 9: Potential energy trajectories of (a) Sc and (b) Y decorated PCP11 at 300K, 375K, and 475 K temperatures.](image)

![Figure 10: Time evolution trajectories of distance between TM and H\textsubscript{2} in (a) Sc and (b) Y functionalised PCP11 system at 300 K. (Each coloured line represents the distance of each adsorbed hydrogen molecules from sorption center)](image)

For practical hydrogen storage substrate, we have examined the stabilities of Sc and Y decorated PCP11, at much above the room temperature (500 K) by performing the atomistic molecular dynamics simulations. It is recommended that for the realistic hydrogen storage, the H\textsubscript{2} molecules should be adsorbed on the substrates at room temperature and desorbed at a
higher temperature. Secondly, the geometry of functionalized PCP11 should remain almost intact during the adsorption-desorption process. The atomistic molecular dynamics simulations for the above calculation have been performed for 1 ps with time step of 1 fs at a temperature of 500 K and 1 atm pressure. We observe that the Sc and Y decorated PCP11 structures are remain stable in the varied thermodynamic conditions, and negligible changes in C-C, C-Sc, and C-Y bond length after simulations are noted. The time evolution of C-Sc and C-Y bond lengths along with their potential energy trajectory are depicted in Figure S4 and S3 respectively. It is noticed that, the C-Sc and C-Y bond length oscillates around the mean value (for Sc: 2.20 Å and for Y: 2.42 Å) with negligible shift indicating the structural integrity above room temperature. Since these simulations ensure the solidity of host material, we believe that, studied materials can be proposed as feasible hydrogen storage system.

To avoid the metal-metal clustering, the diffusion energy barrier should be significantly greater than the thermal energy of transition metal (TM) atom (Sc and Y) at the highest desorption temperature. The thermal energy gained by the Sc and Y atoms at highest desorption temperature (500 K) is calculated using the following equation [1].

\[ E = \frac{3}{2} K_B T \]

Here, \( E \) is the thermal energy of TM atoms, \( K_B \) is the Boltzmann constant and \( T \) is the temperature of 500 K (higher than desorption temperature). We have calculated diffusion energy barrier for TM atoms by displacing the TM atoms from its stable position to next position. The calculated diffusion energy barrier (2.04 eV for Sc, and 1.83 For Y) is much higher than the obtained thermal energy of TM atoms (0.065 eV) at 500 K. These results prevent the possibility of metal clustering in the studied system.

### 3.6. Practical hydrogen capacity and gravimetric density

For a realistic hydrogen storage model, it is essential to estimate the adsorption and desorption of \( \text{H}_2 \) at a wide range of temperature (T) and pressure (P). Thus, it is more practical to calculate the number of hydrogen molecules available to use in an adsorption -desorption cycle. To get a quantitative picture of hydrogen storage (adsorption) and delivery (desorption) at different T and P, we calculated the number of hydrogen molecules adsorbed to each metal atom (occupation number) ( using equation 5 and 6) with the help of the empirical value of \( \text{H}_2 \) gas chemical potential ( \( \mu \) ). Figure 11 depicts the plot of occupation number (\( N \)) for Sc/Y functionalized PCP11, using various value of \( \mu \) at a range of temperature and pressure.
Figure 11: Hydrogen occupation number for (a) PCP11-2Sc and (b) PCP11-2Y at various T and P

Figure 11 shows that each Sc and Y atoms on PCP11 can hold 6H₂ molecules under temperature of 100K and a pressure range of 0-60 bar. At this condition the maximum gravimetric densities of Sc and Y decorated PCP11 system are calculated as 8.22 wt % and 6.33 wt % which is comparable with the experimentally reported value for Pd [38]. As the temperature increases beyond 100 K, H₂ molecules begin to desorb, while each Sc and Y atom has a maximum capacity to hold 5H₂ molecules throughout a temperature range of 100-300 K and pressure range of 0-60 bar. At a temperature of 400K under pressure range of 1-3 bar, almost all H₂ molecules from Y atoms are desorbed and PCP11-2Sc finally carries ~1H₂.

while plotting the of occupation number, we considered two thermodynamic conditions viz: ideal storage condition (300 K under 30 bar) and ideal delivery condition (400K under 3 bar). For PCP11-2Sc system, at 300 K and 30 bar, $N$ is calculated to be 9.50. This N value signifies that, each Sc atom carries around 5H₂ molecules resulting in the gravimetric density of 6.62 wt %. At 400 K under 3 bar, $N$ is found to be 1.06which implies that only one H₂ molecule is retained by the host at this condition. For PCP11-2Y system, each Y atom carries 5H₂ molecules at storage condition giving rise to 5.26 wt% and desorb all H₂ molecules at the delivery condition. The number of usable hydrogen molecules for Sc and Y functionalized PCP11 are thus found to be around 8H₂ and 10H₂ respectively giving rise to the gravimetric densities higher than the US-DOE target. This makes us propose our materials suitable for practical hydrogen storage.

| System     | $N_{theory}$ | $N_{ads}$ | $N_{des}$ | $N_{use}$ | $G_{theory}$ | $G_{practical}$ | $G_{usable}$ |
|------------|--------------|-----------|-----------|-----------|--------------|-----------------|---------------|
| PCP11-2Sc-2H₂ | 2            | 1.99      | 0.70      | 1.29      | 1.47         | 1.46            | 0.95          |
| PCP11-2Sc-4H₂ | 4            | 3.99      | 1.02      | 2.97      | 2.9          | 2.89            | 2.17          |
| PCP11-2Sc-6H₂ | 6            | 5.96      | 1.06      | 4.9       | 4.28         | 4.26            | 3.52          |
| System          | N<sub>theory</sub> | N<sub>ads</sub> | N<sub>des</sub> | G<sub>theory</sub> | G<sub>practical</sub> | G<sub>usable</sub> |
|-----------------|-------------------|----------------|--------------|-------------------|---------------------|-----------------|
| PCP11-2Sc-8H<sub>2</sub> | 8                 | 7.95          | 1.06         | 6.89              | 5.63                | 5.60            |
| PCP11-2Sc-10H<sub>2</sub> | 10                | 9.48          | 1.06         | 8.42              | 6.94                | 6.61            |
| PCP11-2Sc-12H<sub>2</sub> | 12                | 9.50          | 1.06         | 8.44              | 8.22                | 6.62            |
| PCP11-2Y-2H<sub>2</sub>   | 2                 | 1.98          | 0.26         | 1.72              | 1.11                | 1.10            |
| PCP11-2Y-4H<sub>2</sub>   | 4                 | 3.98          | 0.33         | 3.65              | 2.20                | 2.19            |
| PCP11-2Y-6H<sub>2</sub>   | 6                 | 5.96          | 0.33         | 5.63              | 3.27                | 3.25            |
| PCP11-2Y-8H<sub>2</sub>   | 8                 | 7.96          | 0.34         | 7.62              | 4.31                | 4.29            |
| PCP11-2Y-10H<sub>2</sub>  | 10                | 9.86          | 0.34         | 9.52              | 5.33                | 5.26            |
| PCP11-2Y-12H<sub>2</sub>  | 12                | 9.86          | 0.34         | 9.52              | 6.33                | 5.26            |

* N<sub>theory</sub> is the number of theoretically adsorbed H<sub>2</sub> molecules in DFT. N<sub>ads</sub> and N<sub>des</sub> are the number of H<sub>2</sub> molecules adsorbed at storage (300 K - 60 bar) and delivery (400 K - 3 bar) conditions respectively. N<sub>use</sub> is the difference between N<sub>ads</sub> and N<sub>des</sub> represent the usable number of H<sub>2</sub> molecules. G<sub>theory</sub> and G<sub>practical</sub> are theoretical and practical hydrogen wt% at storage-delivery conditions respectively. G<sub>usable</sub> is the wt% of hydrogen that can be use practically.

Now, while considering the hydrogen storage systems for practical use such as vehicular purposes, characterization of the desorption temperature plays an important role. We calculated the prevailing desorption temperatures of the studied systems by using Van't Hoff equation as described below,

\[
T_D = \left( \frac{E_{ads}}{K_B} \right) \left( \frac{\Delta S}{R} - \ln p \right)^{-1}
\]  

(7)

Here E<sub>ads</sub> is the calculated hydrogen adsorption energy with Sc and Y decorated PCP11. K<sub>B</sub> is the Boltzmann constant, R is the gas constant, P is the equilibrium pressure (in our calculation we use 1 to 5 atm with increment of 0.5 atm) and \( \Delta S \) is the change in entropy of hydrogen from gas to liquid phase [66]. The maximum desorption temperature (T<sub>D(max)</sub>) is calculated by using the adsorption energy of first 2H<sub>2</sub> molecules adsorbed by the host materials. This is essential to understand the complete delivery of hydrogen from the studied system. By using the adsorption energy of sixth H<sub>2</sub> molecules adsorbed by each Sc and Y atom on PCP11, the minimum desorption temperature (T<sub>D(min)</sub>) is calculated, which is necessary to activate the desorption process of H<sub>2</sub> from the host. Figure 12 shows the Van't Hoff desorption temperature with a range of equilibrium pressure of 1-5 atm. At a pressure of 1 atm the calculated minimum desorption temperature for Sc and Y doped PCP11 are 372 K and 370 K respectively. The desorption temperature for hydrogenated systems are increases with the increase in equilibrium pressure. The estimated value of average desorption temperature confirms that, all the adsorbed H<sub>2</sub> molecules are not dissociate at room temperature and even in small thermal fluctuation.
4. CONCLUSION

We investigated the hydrogen storage capacity of scandium and yttrium functionalized [1,1]paracyclophane using density functional theory calculations. Transition metal atoms (Scandium and yttrium) are found to strongly bind with PCP11 through Dewar mechanism. Each of Sc and Y atoms on PCP11 were found to adsorb up to 6H₂ molecules via Kubas-type interaction with an average adsorption energy of 0.36 eV and 0.34 eV respectively which was intermediate between chemisorption and physisorption. Average desorption temperature for Sc and Y decorated system was calculated to be 439 K and 412 K respectively at 1 atm of pressure. For Sc and Y functionalized PCP11, the calculated hydrogen storage capacities are 8.22 wt% and 6.33 wt% respectively, however at the adsorption thermodynamics of 300 K and 30 bar the 6.62 wt% and 5.26 wt% respectively. At desorption condition of 400 K and 3 bar, the practical usable hydrogen became 5.92% and 5.09 wt% which is good enough as per US-DOE target. ADMP molecular dynamics simulations showed that the desorption of hydrogen was sufficiently above room temperature (500K) which is quite essential for practical use of hydrogen storage. Scandium and yttrium functionalized PCP11 have suitable adsorption energy and desorption temperature for H₂ molecules, the host structure is stable above desorption temperature and good hydrogen storage capacity. Therefore, the Sc and Y functionalized PCP11 can be proposed as practically viable systems for reversible hydrogen storage at ambient environment. We hope that our work can contribute substantially to the research and development of new materials for hydrogen energy and help experimental synthesis of the material.

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References

1. Hoel, M., Kverndokk, S. Depletion of fossil fuels and the impacts of global warming. Resource and energy economics. 1996;18(2):115-136. https://www.sciencedirect.com/science/article/pii/092876559600005X

2. Jena, P. Materials for hydrogen storage: past, present, and future. The Journal of Physical Chemistry Letters. 2011;2(3):206-211. https://pubs.acs.org/doi/abs/10.1021/jz1015372

3. Das GP, Bhattacharya S. Simulation, modelling and design of hydrogen storage materials. Proc Indian Natn Sci Acad. 2015;8:939–951. http://scinet.science.ph/union/Downloads/Vol81_2015_4_Art18_336317.pdf

4. Preuster, P., Alekseev, A., Wasserscheid, P. Hydrogen storage technologies for future energy systems. Annual review of chemical and biomolecular engineering. 2017;8:445-471. https://www.annualreviews.org/doi/10.1146/annurev-chembioeng-060816-101334

5. Sinigaglia, T., Lewiski, F., Martins, M. E. S., Siluk, J. C. M. Production, storage, fuel stations of hydrogen and its utilization in automotive applications-a review. International journal of hydrogen energy. 2017;42(39):24597-24611. https://www.sciencedirect.com/science/article/pii/S0360319917332895

6. Jorgensen, S. W. Hydrogen storage tanks for vehicles: Recent progress and current status. Current Opinion in Solid State and Materials Science. 2011;15(2):39-43. https://www.sciencedirect.com/science/article/pii/S1359028610000483

7. Schlapbach, L., Züttel, A. Hydrogen-storage materials for mobile applications. Materials for sustainable energy: a collection of peer-reviewed research and review articles from nature publishing group. 2011;265-270. https://www.worldscientific.com/doi/abs/10.1142/9789814317665_0038

8. DOE technical system targets for onboard hydrogen storage for light-duty fuel cell vehicles. https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogenstorage-light-duty-vehicles.

9. Hassan, I. A., Ramadan, H. S., Saleh, M. A., Hissel, D. Hydrogen storage technologies for stationary and mobile applications: Review, analysis and perspectives. Renewable and Sustainable Energy Reviews. 2021;149:111311. https://www.sciencedirect.com/science/article/pii/S1364032121005980

10. Sahoo, R. K., Chakraborty, B., Sahu, S. Reversible hydrogen storage on alkali metal (Li and Na) decorated C_{20} fullerene: A density functional study. International Journal of Hydrogen Energy. 2021;46(80):40251-40261. https://www.sciencedirect.com/science/article/pii/S0360319921038349

11. Gaboardi, M., Amade, N. S., Aramini, M., Milanese, C., Magnani, G., Sanna, S., Pontiroli, D. Extending the hydrogen storage limit in fullerene. Carbon. 2017;120:77-82. https://www.sciencedirect.com/science/article/pii/S0008622317304712.

12. Woo, Y., Kim, B. S., Lee, J. W., Park, J., Cha, M., Takeya, S., Yoon, J. H. Enhanced hydrogen-storage capacity and structural stability of an organic clathrate structure with fullerene (C60) guests and lithium doping. Chemistry of Materials. 2018;30(9):3028-3039. https://pubs.acs.org/doi/abs/10.1021/acs.chemmater.8b00749.

13. Von Colbe, J. B., Ares, J. R., Barale, J., Baricco, M., Buckley, C., Capurso, G., Dornheim, M. Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives. International journal of hydrogen energy.
2019;44(15):7780-7808. https://www.sciencedirect.com/science/article/pii/S0360319919302368

14. Sakintuna, B., Lamari-Darkrim, F., Hirscher, M. Metal hydride materials for solid hydrogen storage: a review. *International journal of hydrogen energy*. 2007;32(9):1121-1140. https://www.sciencedirect.com/science/article/pii/S0360319906005866.

15. Shiraz, H. G., Tavakoli, O. Investigation of graphene-based systems for hydrogen storage. *Renewable and Sustainable Energy Reviews*, 2017;74:104-109. https://www.sciencedirect.com/science/article/pii/S136403211730271X

16. Nagar, R., Vinayan, B. P., Samantaray, S. S., Ramaprabhu, S. Recent advances in hydrogen storage using catalytically and chemically modified graphene nanocomposites. *Journal of Materials Chemistry A*. 2017;5(4):22897-22912. https://pubs.rsc.org/en/content/articlelanding/2017/ta/c7ta05068b

17. Nishihara, H., Hou, P. X., Li, L. X., Ito, M., Uchiyama, M., Kaburagi, T., Kyotani, T. High-pressure hydrogen storage in zeolite-templated carbon. *The Journal of Physical Chemistry C*. 2009;113(8):3189-3196. https://pubs.acs.org/doi/abs/10.1021/jp808890x

18. Murray, L. J., Dincă, M., Long, J. R. Hydrogen storage in metal–organic frameworks. *Chemical Society Reviews*. 2009;38(5):1294-1314. https://pubs.rsc.org/en/content/articlelanding/2009/CS/b802256a

19. Sathe, R. Y., Ussama, M., Bae, H., Lee, H., Dhillip Kumar, T. J. Density Functional Theory Study of Li-Functionalized Nanoporous R-Graphyne–Metal–Organic Frameworks for Reversible Hydrogen Storage. *ACS Applied Nano Materials*. 2021 4(4), 3949-3957. https://pubs.acs.org/doi/abs/10.1021/acsannm.1c00325.

20. Zhao, Y., Kim, Y. H., Dillon, A. C., Heben, M. J., Zhang, S. B. Hydrogen storage in novel organometallic buckyballs. *Physical review letters*. 2005;94(15):155504. https://journals.aps.org/pra/abstract/10.1103/PhysRevLett.94.155504.

21. Durgun, E., Ciraci, S., Zhou, W., Yildirim, T. Transition-metal-ethylene complexes as high-capacity hydrogen-storage media. *Physical review letters*. 2006;97(22):226102. https://journals.aps.org/pra/abstract/10.1103/PhysRevLett.97.226102

22. Kubas, G. J. Metal–dihydrogen and σ-bond coordination: the consummate extension of the Dewar–Chatt–Duncanson model for metal–olefin π bonding. *Journal of Organometallic Chemistry*. 2001;635(1-2):37-68. https://www.sciencedirect.com/science/article/pii/S0022328X0101066X

23. Kalamse, V., Wadnerkar, N., Chaudhari, A. Multi-functionalized naphthalene complexes for hydrogen storage. *Energy*. 2013;49:469-474. https://www.sciencedirect.com/science/article/pii/S0360544212008791.

24. Sahoo, R. K., Ray, S. S., Sahu, S. A first principle study of hydrogen storage in titanium-doped small carbon clusters (C<sub>n</sub>Ti<sub>n</sub>, n= 2–6). *Structural Chemistry*. 2021;32:1673–1683. https://link.springer.com/article/10.1007/s11224-020-01692-9.

25. Wang, T., Tian, Z. Yttrium-decorated C<sub>48</sub>B<sub>12</sub> as hydrogen storage media: A DFT study. *International Journal of Hydrogen Energy*. 2020;45(46):24895-24901. https://www.sciencedirect.com/science/article/pii/S0360319920305061.

26. Ma, L. J., Hao, W., Han, T., Rong, Y., Jia, J., Wu, H. S. Sc/Ti decorated novel C<sub>24</sub>N<sub>24</sub> cage: Promising hydrogen storage materials. *International Journal of Hydrogen Energy*. 2021;46(10):7390-7401. https://www.sciencedirect.com/science/article/pii/S0360319920345055.
27. Chen, Y., Wang, J., Yuan, L., Zhang, M., Zhang, C. Sc-decorated porous graphene for high-capacity hydrogen storage: first-principles calculations. Materials. 2017;10(8):894. https://doi.org/10.3390/ma10080894

28. Yuan, L., Chen, Y., Kang, L., Zhang, C., Wang, D., Wang, C., Wu, X. First-principles investigation of hydrogen storage capacity of Y-decorated porous graphene. Applied Surface Science. 2017; 399:463-468. https://www.sciencedirect.com/science/article/pii/S0169433216327714.

29. Ray, S. S., Sahoo, S. R., Sahu, S. Hydrogen storage in scandium doped small boron clusters (BnSc2, n= 3–10): A density functional study. International Journal of Hydrogen Energy. 2019;44(12):6019-6030. https://www.sciencedirect.com/science/article/pii/S0360319918340771.

30. Modak, P., Chakraborty, B., Banerjee, S. Study on the electronic structure and hydrogen adsorption by transition metal decorated single wall carbon nanotubes. Journal of Physics: Condensed Matter. 2012;24(18):185505. https://iopscience.iop.org/article/10.1088/0953-8984/24/18/185505/meta.

31. Mananghaya, M., Yu, D., Santos, G. N., Rodulfo, E. Scandium and titanium containing single-walled carbon nanotubes for hydrogen storage: a thermodynamic and first principle calculation. Scientific reports. 2016;6(1):1-9. https://www.nature.com/articles/srep27370?sf107980192=1.

32. Mahamiya, V., Shukla, A., Chakraborty, B. Scandium decorated C24 fullerene as high capacity reversible hydrogen storage material: Insights from density functional theory simulations. Applied Surface Science. 2022; 573:151389. https://www.sciencedirect.com/science/article/pii/S0169433221024417.

33. Mahamiya, V., Shukla, A., Chakraborty, B. Exploring yttrium doped C24 fullerene as a high-capacity reversible hydrogen storage material: DFT investigations. Journal of Alloys and Compounds, 2021; 162797. https://www.sciencedirect.com/science/article/pii/S0925838821042079.

34. Thornton, A. W., Nairn, K. M., Hill, J. M., Hill, A. J., Hill, M. R. Metal–organic frameworks impregnated with magnesium-decorated fullerenes for methane and hydrogen storage. Journal of the American Chemical Society, 2009; 131(30), 10662-10669. https://pubs.acs.org/doi/abs/10.1021/ja9036302.

35. Xu, G., Meng, Z., Liu, Y., Guo, X., Deng, K., Lu, R. Heterofullerene-linked metal–organic framework with lithium decoration for storing hydrogen and methane gases. International Journal of Hydrogen Energy, 2019; 44(13), 6702-6708. https://www.sciencedirect.com/science/article/pii/S0360319919302666.

36. Rao, D., Lu, R., Xiao, C., Kan, E., & Deng, K. Lithium-doped MOF impregnated with lithium-coated fullerenes: A hydrogen storage route for high gravimetric and volumetric uptakes at ambient temperatures. Chemical Communications, 2011; 47(27):7698-7700. https://pubs.rsc.org/en/content/articlelanding/2011/CC/c1cc11832c.

37. Yu, S., Jing, G., Zhou, X., Li, Z., Zhang, W., Ju, X. Fullerene-impregnated IRMOFs for balanced gravimetric and volumetric H2 densities: A combined DFT and GCMC simulations study. International Journal of Hydrogen Energy. 2021;46(80):40294-40300. https://www.sciencedirect.com/science/article/pii/S0360319921038623.

38. Mehrabi, M., Parvin, P., Reyhani, A., & Mortazavi, S. Z. Hydrogen storage in multi-walled carbon nanotubes decorated with palladium nanoparticles using laser
39. Chakraborty, B., Modak, P., Banerjee, S. Hydrogen storage in yttrium-decorated single walled carbon nanotube. *The Journal of Physical Chemistry C*. 2012;116(42):22502-22508. https://pubs.acs.org/doi/abs/10.1021/jp3036296.

40. Zhang, Y., Han, X., Cheng, X. The high-capacity hydrogen storage material of Y-doped B_{40}: A theoretical study. *Chemical Physics Letters*, 2020;739:136961. https://www.sciencedirect.com/science/article/pii/S000926141930942X

41. Sathe, R. Y., Kumar, S., Kumar, T. J. D. First-principles study of hydrogen storage in metal functionalized [4, 4] paracyclophane. *International Journal of Hydrogen Energy*. 2018;43(11):5680-5689. https://www.sciencedirect.com/science/article/pii/S0360319918303021.

42. Sathe, R. Y., Kumar, T. D. Paracyclophane functionalized with Sc and Li for hydrogen storage. *Chemical Physics Letters*. 2018; 692:253-257. https://www.sciencedirect.com/science/article/pii/S0009261417311065.

43. Tobe, Y., Ueda, K., Kaneda, T., Kakiuchi, K., Odaira, Y., Kai, Y., Kasai, N. Synthesis and molecular structure of (Z)-[6] Paracycloph-3-enes. *Journal of the American Chemical Society*. 1987;109(4):1136-1144. https://pubs.acs.org/doi/abs/10.1021/ja00238a024.

44. Demissie, T. B., Dodziuk, H., Waluk, J., Ruud, K., Pietrzak, M., Vetokhina, V., Hopf, H. Structure, NMR and electronic spectra of [m,n] paracyclophanes with varying bridges lengths (m, n= 2–4). *The Journal of Physical Chemistry A*. 2016;120(5):724-736. https://pubs.acs.org/doi/abs/10.1021/acs.jpca.5b12168.

45. Kotha, S., Shirbhate, M. E., Waghule, G. T. Selected synthetic strategies to cyclophanes. *Beilstein Journal of Organic Chemistry*. 2015;11(1):1274-1331. https://doi.org/10.3762/bjoc.11.142.

46. Seenithurai, S., Chai, J. D. Effect of Li adsorption on the electronic and hydrogen storage properties of acenes: a dispersion-corrected TAO-DFT study. *Scientific reports*. 2016;6(1):1-10. https://doi.org/10.1038/srep33081.

47. Tavhare, P., Titus, E., Chaudhari, A. Hydrogen adsorption on metal-functionalized benzene and B-substituted benzene. *International Journal of Energy Research*. 2021; 45(13):18810-18826. https://doi.org/10.1002/er.6986.

48. Sathe, R. Y., Kumar, T. D. Reversible hydrogen adsorption in Li functionalized [1, 1] paracyclophane. *International Journal of Hydrogen Energy*. 2020;45(23):12940-12948. https://doi.org/10.1016/j.ijhydene.2020.03.009.

49. Lee, H., Nguyen, M. C., Ihm, J. Titanium-functional group complexes for high-capacity hydrogen storage materials. *Solid state communications*. 2008;146(9-10):431-434. https://doi.org/10.1016/j.ssc.2008.03.018.

50. Lee, H., Choi, W. I., Nguyen, M. C., Cha, M. H., Moon, E., Ihm, J. Ab initio study of dihydrogen binding in metal-decorated polyacetylene for hydrogen storage. *Physical Review B*. 2007;76(19):195110. https://doi.org/10.1103/PhysRevB.76.195110.

51. Wassmann, T., Seitsonen, A. P., Saiutta, A. M., Lazzeri, M., Mauri, F. Structure, stability, edge states, and aromaticity of graphene ribbons. *Physical review letters*. 2008;101(9):096402. https://doi.org/10.1103/PhysRevLett.101.096402.
52. Chai, J. D., Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Physical Chemistry Chemical Physics*, 2008;10(44):6615-6620. https://doi.org/10.1039/B810189B.

53. Halsey-Moore, C., Jena, P., McLeskey Jr, J. T. Tuning range-separated DFT functionals for modeling the peak absorption of MEH-PPV polymer in various solvents. *Computational and Theoretical Chemistry*, 2019;1162:112506. https://doi.org/10.1016/j.comptc.2019.112506.

54. Yang, Y., Weaver, M. N., Merz Jr, K. M. Assessment of the “6-31+ G**+ LANL2DZ” mixed basis set coupled with density functional theory methods and the effective core potential: prediction of heats of formation and ionization potentials for first-row-transition-metal complexes. *The Journal of Physical Chemistry A*. 2009;113(36):9843-9851. https://doi.org/10.1021/jp807643p.

55. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. *Gaussian 09*, revision E.01. Wallingford CT: Gaussian, Inc; 2013.

56. Grimme, S. On the Importance of Electron Correlation Effects for the π-π Interactions in Cyclophanes. *Chemistry–A European Journal*. 2004;10(14):3423-3429. https://doi.org/10.1002/chem.200400091.

57. Schleyer, P. V. R., Maerker, C., Dransfeld, A., Jiao, H., van Eikema Hommes, N. J. Nucleus-independent chemical shifts: a simple and efficient aromaticity probe. *Journal of the American Chemical Society*. 1996;118(26):6317-6318. https://doi.org/10.1021/ja960582d.

58. Rehman, S. U., Majid, A., Hassan, N., Shakoor, A., Murtaza, G., Khan, S. D. A DFT study of the effects of Sc doping on electronic and optical properties of CdS nanoparticles. *Materials Science Poland*. 2015;33(4):782-791. https://doi.org/10.1515/msp-2015-0110.

59. Kumar, S., Sathe, R. Y., Kumar, T. D. First principle study of reversible hydrogen storage in Sc grafted Calix [4] arene and Octamethylcalix [4] arene. *International Journal of Hydrogen Energy*. 2019;44(10):4889-4896. https://doi.org/10.1016/j.ijhydene.2018.12.188.

60. Koopmans, T. Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den einzelnen Elektronen eines Atoms. *Physica*. 1934;1(1-6):104-113. https://doi.org/10.1016/S0031-8914(34)90011-2.

61. Pan, S., Solà, M., Chattaraj, P. K. On the validity of the maximum hardness principle and the minimum electrophilicity principle during chemical reactions. *The Journal of Physical Chemistry A*. 2013;117(8):1843-1852. https://doi.org/10.1021/jp312750n.

62. Kubas, G. J. Hydrogen activation on organometallic complexes and H2 production, utilization, and storage for future energy. *Journal of Organometallic Chemistry*. 2009;694(17):2648-2653. https://doi.org/10.1016/j.jorganchem.2009.05.027.

63. Niu, J., Rao, B. K., Jena, P. Binding of hydrogen molecules by a transition-metal ion. *Physical review letters*. 1992;68(15):2277. https://doi.org/10.1103/PhysRevLett.68.2277

64. Niu, J., Rao, B. K., Jena, P., Manninen, M. Interaction of H2 and He with metal atoms, clusters, and ions. *Physical Review B*. 1995;51(7):4475. https://journals.aps.org/prb/abstract/10.1103/PhysRevB.51.4475

65. Jaiswal, A., Sahoo, R. K., Ray, S. S., & Sahu, S. (2021). Alkali metals decorated silicon clusters (SinMn, n= 6, 10; M= Li, Na) as potential hydrogen storage materials.
A DFT study. *International Journal of Hydrogen Energy*. 2021;47(3):1775-1789. https://doi.org/10.1016/j.ijhydene.2021.10.228

66. D.R. Lide CRC handbook of chemistry and physics, vol. 85, *CRC press*. 2004.