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First-principles study of hydrogen storage in metal functionalized [4,4]paracyclophane

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ABSTRACT

Storing hydrogen for commercial purpose with high gravimetric density is a major task. Li and Sc are functionalized over delocalized π electrons of [4,4]paracyclophane to explore reversible hydrogen storing capacity. Electronic structure calculations are performed with Minnesota 06 hybrid functional and 6-311G(d,p) basis set. [4,4]paracyclophane binds strongly to Sc showing Dewar coordination. Sc functionalized [4,4]paracyclophane complex has a capacity of holding 10 H₂ molecules while Li functionalized complex holds 8 H₂ molecules with hydrogen weight percentage of 11.8% and 13.7% respectively. Conceptual DFT parameters namely hardness and electrophilicity confirm the high stability of the complexes. Atom Density Matrix Propagation simulations at various temperatures and their desorption pattern indicate reversibility of adsorbed hydrogens. The study confirms the potential of Sc functionalized [4,4]paracyclophanes as a hydrogen storage material.

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Introduction

The Twenty-first century is an era of rapidly growing technology. Amongst many booming technologies, transportation is one of them. It is primarily dependent on the fossil fuels. Increasing rates of fuel consumption for transportation is an issue of concern all over the globe [1,2]. An alternative to the fossil fuels is to use hydrogen as an energy carrier [3] since it is the simplest and the most abundant element in the universe. Additionally, hydrogen is eco-friendly, renewable, and economical [1,4].

There are broadly two modes of storing hydrogen; system based and material based [1,5]. System based modes like compressed H₂ gas, cryogenic storage, and cryo-compressed storage involve high processing cost and require expensive materials like Carbon Fibre Reinforced Plastic (CFRP) which

makes use of these techniques costly [6]. In recent days, material based techniques are widely followed in energy applications. A tremendous research focused on energy applications based on π -complex containing carbon-based materials is going on due to the ease of modification within their structures [7–11]. An important factor to be considered while storing hydrogen is gravimetric density. Finding a storage material which shows high gravimetric density under favorable thermodynamic conditions and exhibits fast kinetics is a difficult task [12–14]. The aim is to achieve high gravimetric density i.e. load maximum amount of hydrogen with the least modifications in original structure of the targeted complex [5,14,15]. Metal-coated or metal-functionalized materials are widely used in renewable energy technologies [16,17]. Transition metals, for example, Sc and Ti show stronger Kubas interaction with π -complexes and hence are easy to functionalize. Many experimental evidences prove the

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enhanced activity of materials after metal functionalization in wide range of applications [18–22]. Decorating a targeted molecular complex with elements such as Li, B, Be, Ca, Na, Al, Mg, Sc, Ti has proved to have better gravimetric density [15,23–25]. Storing hydrogen in molecular form has better kinetics over storing it in atomic form due to its reversible sorption nature [15,26]. Storage material should also desorb hydrogens in the temperature range of –40 to 85 °C and under moderate pressure below 100 atm [27]. Many molecular systems such as conjugated microporous polymers [28], porous polymer networks [29], triazine-based organic frameworks [30,31], covalent boron oxide-based frameworks [32], porous aromatic frameworks [33], and hyper-cross-linked polymers [34], are under trial to be used as hydrogen storage material, yet none of them are able to pass the standards set by Department of Energy, US (DOE) with ultimate target of 7.5% by year 2020 [35].

Paracyclophanes have aromatic benzene rings which on functionalization with metals can act as a good candidate for hydrogen storage [5,14]. Subgroup paracyclophane is a derivative of cyclophanes and its nomenclature is based on arene substitution patterns. The preceding numbers in square brackets refer to the number of carbon atoms linking consecutive benzene rings [36]. Strain between two aromatic rings due to bent bridges can be utilized for metal functionalization. Due to this strain aromatic rings in paracyclophanes do not exhibit inherent planarity [37]. Paracyclophanes are easy to synthesize and can be functionalized with metal atoms easily due the presence of benzene rings in their structures [38]. In this work, properties of Li and Sc metal functionalized [4,4]paracyclophanes [38] (PCP44) are studied to investigate their reversible hydrogen storage capacity. Li and Sc are chosen because both are lightweight *s*- and *d*-block metals, respectively, known to physisorb H₂ molecules reversibly. All computational details are presented in Section [Computational details](#), in Section [Results and discussion](#) results are discussed and complete work is summarized and concluded in Section [Conclusion](#).

Computational details

The DFT calculations are performed on [4,4]paracyclophane (PCP44) system using Minnesota-06 (M06) exchange-correlation energy functional [39] along with 6-311G(d,p) basis set. M06 functional is specifically modelled for metals, non-metals, and best suited for studying non-covalent interactions [39]. The calculations are carried out in Gaussian 09 [40]. GaussView 5.0 [41] is used to create 3D molecular complexes. Optimization of PCP44, metal functionalized PCP44 along with its H₂ adsorbed derivatives is performed. Vibrational frequencies of PCP44, metal functionalized PCP44 along with its H₂ adsorbed derivative complexes are calculated and all are found to be positive, which indicates that these complexes are stable structures. Values for Nucleus-Independent Chemical Shifts [42] (NICS) are obtained with respect to both benzene rings to study aromaticity [40]. Energy of adsorption and desorption of each complex is calculated for hydrogen adsorption using the following formula [43–47];

$$E_{\text{ad}} = \frac{[nE_{(\text{H}_2)} + E_{(\text{PCP44-2M})} - E_{(\text{PCP44-2M-nH}_2)}]}{n} \quad (1)$$

where E_{ad} is adsorption energy, n is the number of H₂ molecules, M is the metal atom (Li or Sc), $E_{\text{PCP44-2M}}$ is total energy of the metal functionalized PCP44 complex, $E_{(\text{H}_2)}$ is energy of the H₂ molecule, $E_{(\text{PCP44-2M-nH}_2)}$ is the total energy of the maximum number of hydrogens adsorbed on the PCP44 molecule functionalized by metals.

The sequential desorption energy is calculated using following formula; [43,44]

$$E_{\text{d}} = \frac{[nE_{(\text{H}_2)} + E_{[\text{PCP44-2M-(nH}_2-2)]} - E_{(\text{PCP44-2M-nH}_2)}]}{2} \quad (2)$$

where E_{d} is desorption energy, $E_{[\text{PCP44-2M-(nH}_2-2)]}$ is the total energy of a complex preceding to $E_{(\text{PCP44-2M-nH}_2)}$ complex.

Saturated complexes are subjected to the Atom-centered Density Matrix Propagation (ADMP) simulations [40] to study the stability at different time steps when a particular complex exposed to various temperatures. Temperature range 100–300 K is considered with a difference of 100 K in successive simulations. H₂ adsorbed derivative of Sc functionalized complex is also subjected to a higher temperature of 373 K. Maximum 1000 steps are specified for each trajectory along with the time interval of 1 fs in each step. An ultrafine grid is utilized (pruned; 99, 590) [40] for all the ADMP simulations while they are carried under the temperature for nuclear kinetic energy thermostat using internal option (IOp) [40] 1/82. Global reactivity descriptors are calculated for conceptual DFT [48–51] study to identify the stability and reactivity of metal functionalized complexes and their H₂ adsorbed derivatives. Electronegativity(χ) is calculated by following formula;

$$\chi = \frac{I + A}{2} \quad (3)$$

where vertical ionization potential (I) and electron affinity (A) are calculated based on the principle of Koopmans's theorem [48].

Hardness (η) is given as;

$$\eta = I - A \quad (4)$$

Electrophilicity (ω) is expressed as;

$$\omega = \frac{\chi^2}{2\eta} \quad (5)$$

Results and discussion

Optimization of PCP44 and aromaticity

Optimized structure of PCP44 is shown in [Fig. 1](#). In the optimized structure of PCP44, the diagonal distance between two carbon atoms at the corners is found to be 6.811 Å. This distance makes up the pore size of the single PCP44 molecule. The distance between adjacent carbon atoms in ring-connecting bridges stays in the range of 1.504 Å to 1.544 Å which indicates a slight strain in the molecule. This strain is the reason that both the benzene rings in the structure are not perfectly planar. These structural properties due to strain are

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