Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.


# Highly Efficient Hydrogen Storage of Sc Decorated Biphenylene Monolayer near Ambient-temperature: An Ab-initio Simulations

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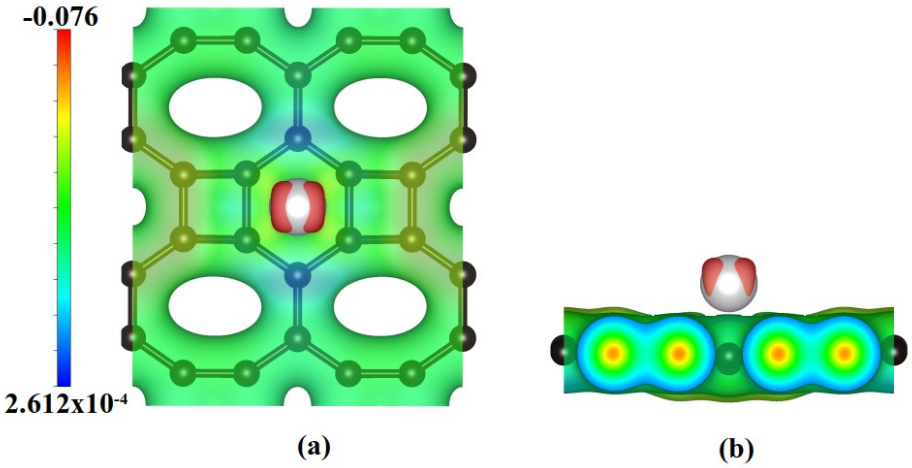



**Fig. S 1:** Difference of charge density of BPh+Sc and BPh sheet, ρ(BPh+Sc@C2)-ρ(BPh) with isovalue $4.54 \times 10^{-2}$ (a) top view (b) side view.

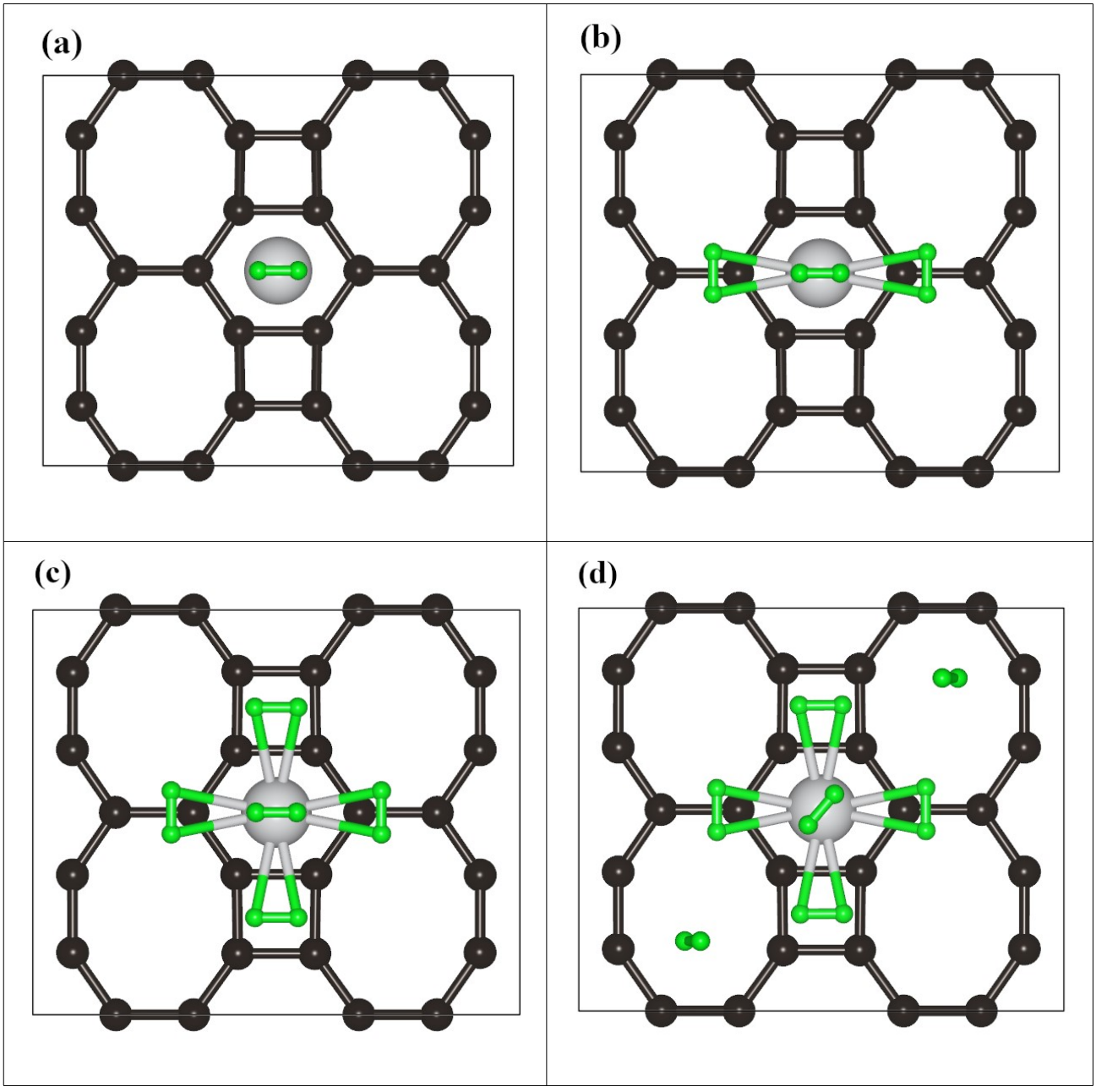



**Fig. S2:** DFT+Grimme-D2 optimized structure of $nH_2$ adsorbed on BPh+Sc(@C2).
(a) BPh+Sc+$1H_2$ (b) BPh+Sc+$3H_2$ (c) Bph+Sc+$5H_2$ (d) BPh+Sc+$7H_2$.

**Table S1:** The adsorption energy of $nH_2$ molecules on BPh+Sc(@C2) using GGA (PBE) and GGA+ Grimme-D2 corrected functional:

| S.N. | System | GGA(eV) | GGA+DFT-D2(eV) |
|---|---|---|---|
| 1. | BPh+Sc | -3.563 | -3.811 |
| 2. | BPh+Sc+1$H_2$ | -0.353 | -0.399 |
| 3. | BPh+Sc+3$H_2$ | -0.379 | -0.492 |
| 4. | BPh+Sc+5$H_2$ | -0.314 | -0.453 |
| 5. | BPh+Sc+7$H_2$ | -0.125 | -0.143 |
| Average binding energy per $H_2$ (up to 5$H_2$) | | -0.293 eV | -0.448 eV |

Since 7$^{th}$ $H_2$ molecule binding energy is not in the range of DoE range (0.2-0.7), we consider only five doped hydrogen molecules adsorbed on Sc+BPh(@C2), and their corresponding gravimetric weight percentage turns out to be:

**one side** (24C+4Sc+20$H_2$) : **7.93 wt%**

**both side (24C+8Sc+40$H_2$)** : **11.07 wt%**

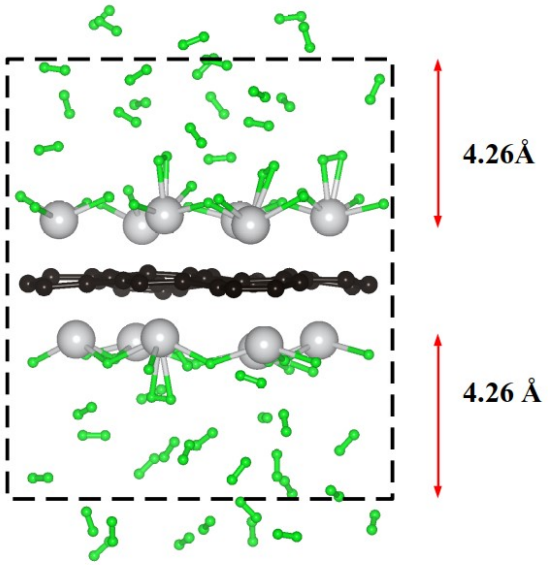



**Fig. S3:** Side view of BPh+8Sc+40$H_2$ after 5ps AIMD simulations performed at room temperature.

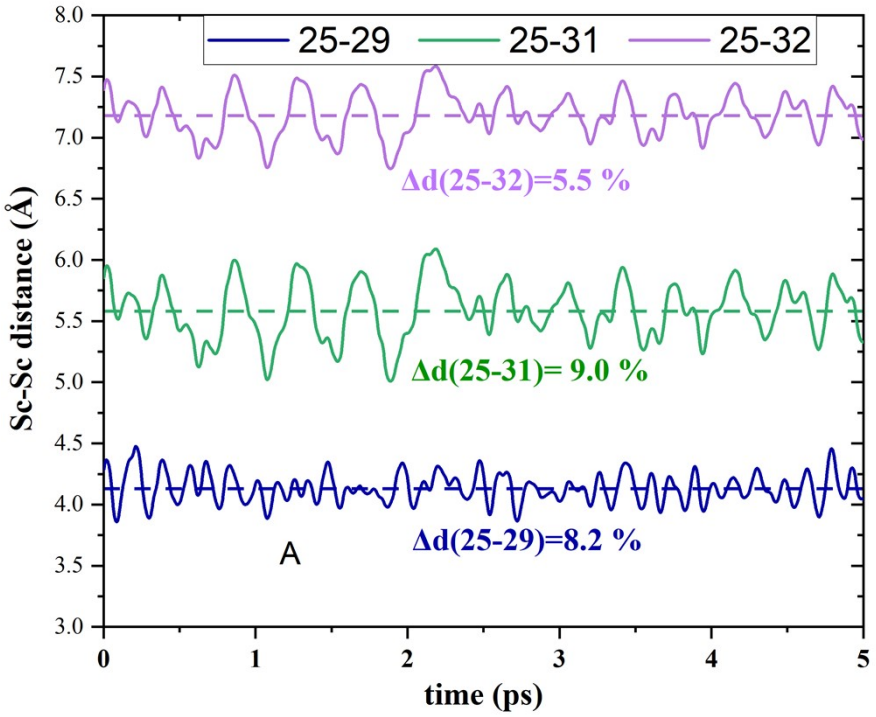
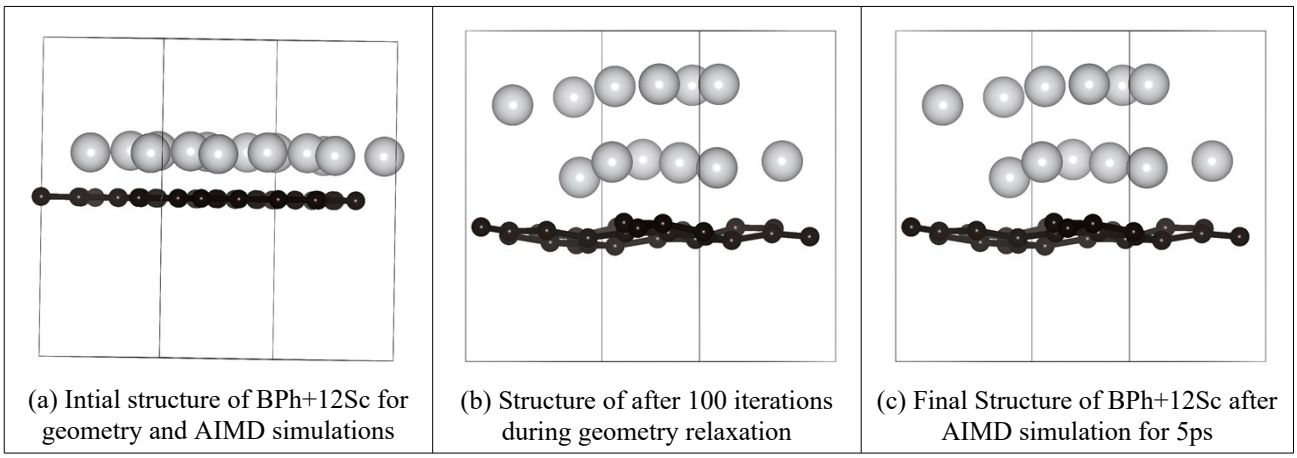



**Fig. S4:** The variation of distance between two Sc of BPh+8Sc(@B2') at 300K. Δd(N1, N2) denotes the maximum percentage deviation w.r.t. mean values between two $N_1$, $N_2^{th}$ Sc atoms. Dotted lines show the average of distance.

## Doping of Sc atoms at different sites simultaneously on BPh sheet

**1-** After decorating Sc atoms at all porous positions i.e. at the center of square, hexagon and octagon, we performed geometry relaxation, MD-simulations and plotted the final structures in Figs. S4(b) and S4(c) respectively.



(a) Intial structure of BPh+12Sc for geometry and AIMD simulations

(b) Structure of after 100 iterations during geometry relaxation

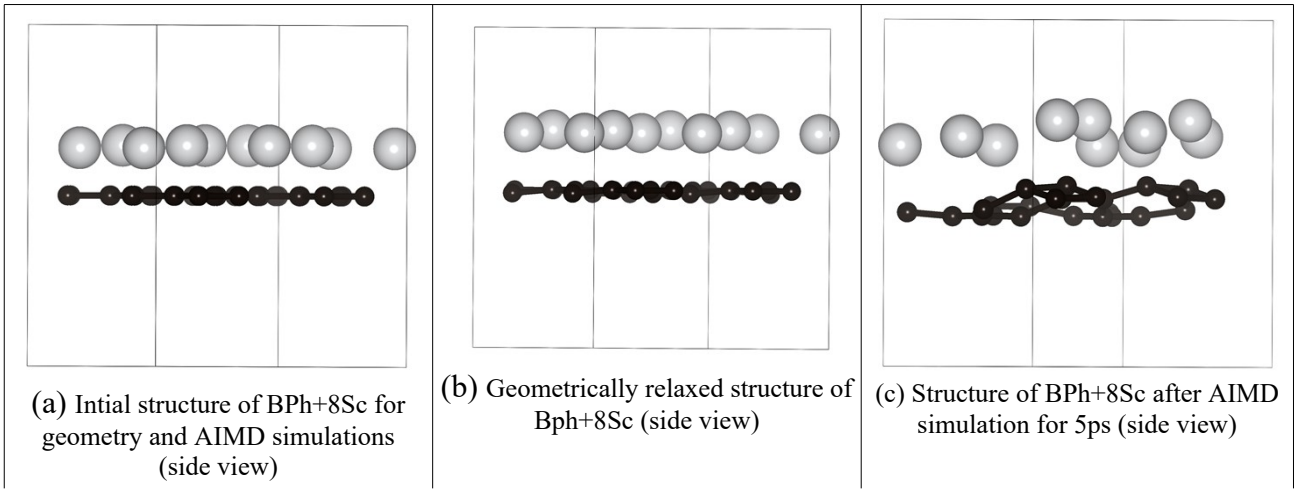
(c) Final Structure of BPh+12Sc after AIMD simulation for 5ps

**Fig S5:** (a) Plotting of structure when Sc atoms are decorated at all porous sites i.e., square, hexagon, and octagon. (b) Geometrically relaxed structure up to ~100 iterations. Since the structure seemed disturbed, relaxation is terminated. (c) AIMD simulation of structure for 5ps with steps of 1fs at 300K.

From both the geometrical relaxation and MD-simulation, it is clear that doping of Sc atoms on all porous sites are not possible.

**2-** After the finding unstability of Sc atoms doping on at all porous positions (hexagon, octagon and square), we explored the possibility of stability on decoration of Sc at hexagon and octagon positions. We plotted the geometry relaxation S5(b) and MD-simulations results in Figs. S6(b) and (c), respectively.

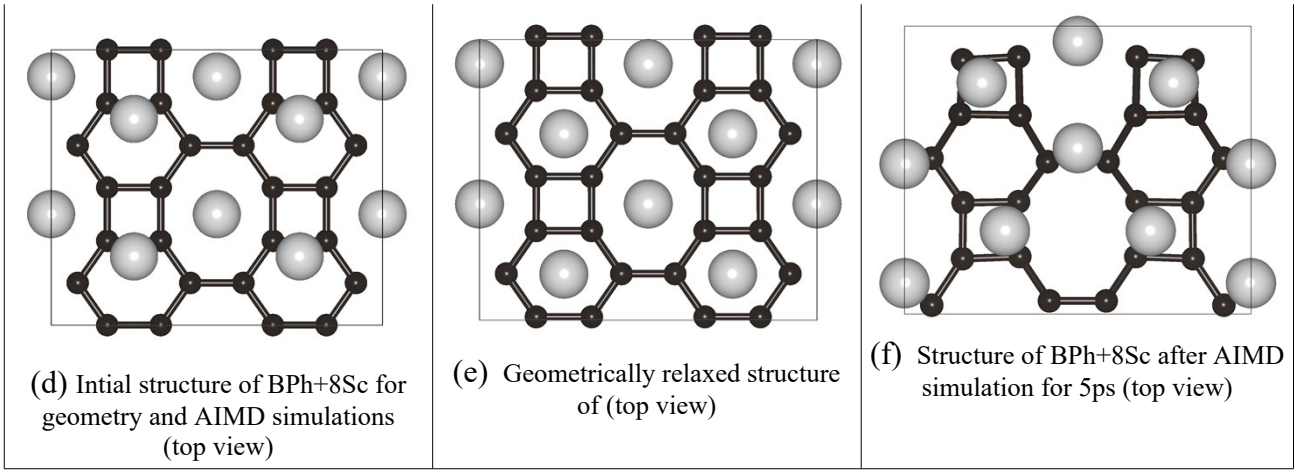
**Geometrical relaxation and MD-simulations:**



(a) Intial structure of BPh+8Sc for geometry and AIMD simulations (side view)

(b) Geometrically relaxed structure of Bph+8Sc (side view)

(c) Structure of BPh+8Sc after AIMD simulation for 5ps (side view)



(d) Intial structure of BPh+8Sc for geometry and AIMD simulations (top view)

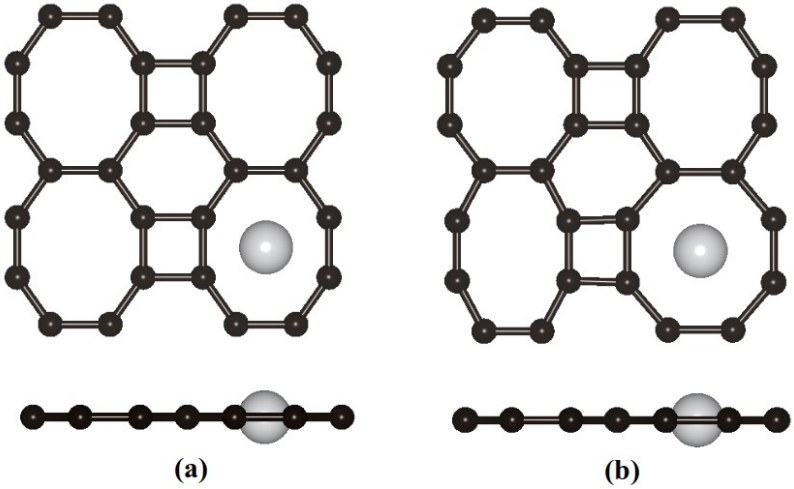
(e) Geometrically relaxed structure of (top view)

(f) Structure of BPh+8Sc after AIMD simulation for 5ps (top view)

**Fig S6:** (a,d) side and top view of BPh+8Sc when Sc atoms are decorated at hexagon and octagon sites (b,e) side and top view of the geometrically relaxed structure of BPh+8Sc. (c) AIMD simulation of structure for 5ps with steps of 1fs at 300K.

In geometrical relaxation of the system, all the Sc atoms are remain at the center of the hexagon and octagon. However, in AIMD-simulation, Sc atoms are displaced from the center to bond sites, i.e., AIMD-simulations exclude the possibility of simultaneous doping of Sc atoms at hexagon and octagon.

**3-** Being the octagon as the largest pore BPh sheet, one can think of doping Sc atoms at the center of octagon of BPh sheet. We have checked the binding energy of Sc atom by putting it at the center of octagons Fig. S6 and found the binding energy is positive (+3.89 eV), hence the Sc atom at the center of octagon is weakly bounded. To verify the weak strength of Sc at the center of octagon, we displaced Sc atom by 0.5 Å Fig. S7 (a) and after optimizaton, it moved over the center of octagon with negative binding energy (-2.9 eV) Fig. S7 (b) as in our previous manuscript for over center of octagon. We have repeated calculations with doping an Sc on each octagon and found similar results. Hence we conclude that the Sc doping at center of octagon is the local minima for BPh+Sc while over the center of octagon is stable.



(a) (b)

**Fig. S7:** Top and side view of initial (a) and final (b) optimized structure of Sc decorated BPh sheet.

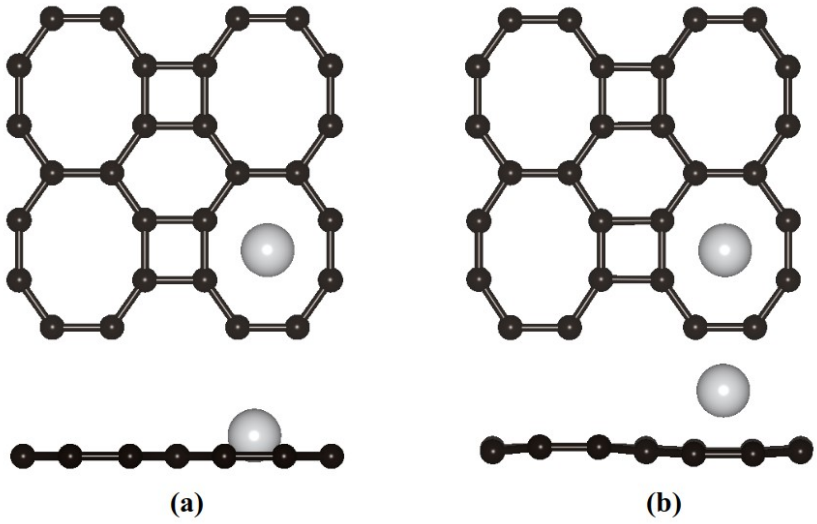



**Fig. S8:** Top and side view of initial strcuture (a) displaced by 0.5 Å from center of octagon and final (b) optimized structure of Sc decorated BPh sheet.

**H-H bond length of $H_2$ molecule:**

We have used the experimental bond length (0.74 Å) of the hydrogen molecule in our simulations for hydrogen storage. We have performed ground state energy calculations for different H-H separations starting from 0.70 Å to 0.80 Å as plotted below, which indicates that simulated H-H separation distance with PBE functional is 0.75Å.

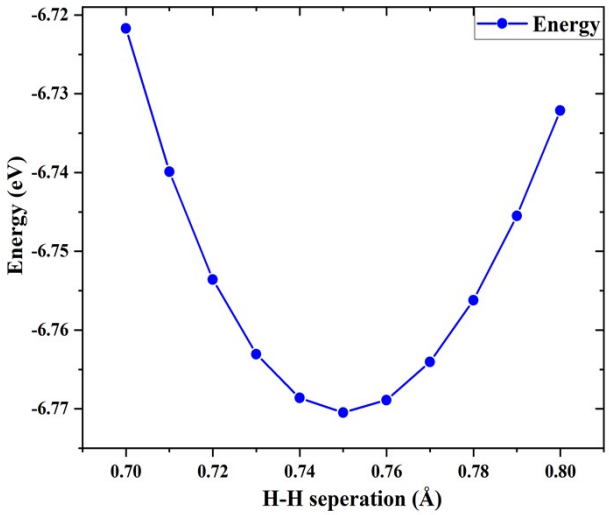



**Fig. S9:** DFT ground state energy with respect to H-H separation for $H_2$ molecules.