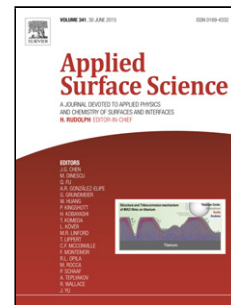


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Functionalized Carbon Nitride (g-CN) Monolayer as a Promising Energy Storage Material: A Density Functional Theory Study

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Highlights:

- DFT study of the binding mechanism of two polyolithiated molecules, CLi_2 and OLi_2 , on g-CN.
- It was observed that CLi_2 (OLi_2) bind to g-CN with an average binding energy of -3.19 eV/ CLi_2 (-2.55 eV/ OLi_2)
- The H_2 adsorption energies for both the systems lie ideally between 0.20-0.40 eV/ H_2 ,
- Both CN-2CLi_2 and CN-2OLi_2 monolayers could be considered as efficient H_2 storage materials.

Abstract:

Two-dimensional graphitic carbon nitride (g-CN) sheet, functionalized with polyolithiated molecules (CLi_2 , OLi_2), has been investigated to study their structural, electronic and hydrogen (H_2) storage properties by van der Waals corrected first principles calculation. A strong binding of both $\text{CLi}_2/\text{OLi}_2$ with two-sided coverage and large enough molecular distance ensures their uniform dispersion over the g-CN monolayer without forming clusters. Each Li in g-CN@ 2CLi_2 (g-CN@ 2OLi_2) adsorbs 3H_2 , due to its cationic nature through transferring a portion of its charge, resulting into a high H_2 storage capacity of 10.34 % (9.76%). The calculated H_2 adsorption energies are well suited for practical applications.

Introduction:

Decreasing reserves of fossil fuels and their overwhelming effects on the environment has made it necessary to look for sustainable and clean energy sources for the future. Among several available options, hydrogen (H_2) stands out as a clean and renewable energy carrier having the highest energy density among all known sources to date. [1-3] Hydrogen could be considered

as a perfect alternative to the existing energy sources would it not be for its difficult storage requirements. [4, 5] Despite extensive research in the last couple of decades, a promising option for effective H₂ storage has yet to be achieved. However, a material based storage approach sounds practicable, provided a suitable material could hold a large amount of H₂ and release it on demand under reasonable operating conditions. [6, 7] Cost effective and lightweight materials with large surface area and having equitable interaction with H₂ can be stimulating in this regard.

Carbaceous nanostructures possessing extremely large surface area and with several modes of synthesis can be regarded as perfect absorbing materials, however in pure form, their interaction with H₂ is an issue of concern. [8-10] For an ideal storage material with adsorption/desorption occurring at a feasible temperature/pressure range, the H₂ binding energy with the host material should lie within 0.2-0.6 eV. [11, 12] Thus to achieve a suitable H₂ binding with carbaceous nanostructures, researchers have considered defects, metal binding and the application of mechanical strain in the recent past. [8, 13-15] In this regard graphene-like carbon nitride (g-CN), which is an important member of CN-family, could be a potential candidate for clean energy storage. Although two of its sister structures triazine C₃N₄ and heptazine C₆N₇ have already been studied for various applications including energy storage, not many studies have been carried out for g-CN. [16-20]

In this study, we have performed a systematic study to investigate the structural analysis and binding mechanism of polyolithiated molecules (CLi₂, OLi₂) functionalized g-CN monolayer. Electronic structure and the H₂ storage properties of the functionalized systems, CN-2CLi₂ and CN-2OLi₂, have also been explored.

Computational methodology:

In order to study the structural, electronic and hydrogen properties of polyolithiated functionalized g-CN, we performed the calculations by means of density functional theory (DFT) using the VASP code. [21] Generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) was employed for the exchange and correlation functional. [22] We used projector augmented wave (PAW) method with an energy cutoff of 500 eV throughout the calculations. [23] The Brillouin-zone (BZ) sampling was done by k-point mesh of 5×5×1 for structural optimization and 9×9×1 for plotting density of states (DOS) under Monkhorst-Pack scheme. [24] Based on our previous experience, the underestimation of using GGA in calculating the H₂ adsorption energies could be rectified by including van der Waals correction

of Grimme (D2). [25] The charge transfer mechanism was studied by using Bader analysis. [26] A unit cell of g-CN was used with a vacuum space of 20 Å perpendicular to the sheet to decouple an unwanted interaction between the layers.

The binding energies of polyolithiated molecules CLi_2 and OLi_2 were calculated by

$$E_b = E(\text{CN-}n\text{CLi}_n/\text{OLi}_n) - E(\text{CN}) - n E(\text{CLi}_n/\text{OLi}_n) \quad (1)$$

Here 1st, 2nd and 3rd term represent the total energies of CN doped with polyolithiated molecules, pristine CN and isolated polyolithiated molecules, respectively.

The van der Waals corrected adsorption energies of H_2 has been calculated by the following relation

$$E_{\text{ads}} = E\{n H_2 @\text{CN-}2\text{CLi}_2/\text{CN-}2\text{OLi}_2 - E(n-1) \text{CN-}2\text{CLi}_2/\text{CN-}2\text{OLi}_2 - E(H_2)\} \quad (2)$$

Here 1st and 2nd terms represent the total energies of $\text{CN-}2\text{CLi}_2/\text{CN-}2\text{OLi}_2$ sheets with n and $(n-1)$ H_2 molecules, respectively. $E(H_2)$ represents the total energy of H_2 molecule in the gas phase.

Results and discussion:

Before discussing the binding mechanism of polyolithiated molecules (CLi_2 , OLi_2) over g-CN, we give a brief description of its structural and electronic properties. Despite being an isostructure to g- C_3N_4 and C_4N_3 , the g-CN membrane has an equal C to N ratio unlike the other two membranes and it also has a big central round pore with six N as shown in Fig. 1. Upon structural relaxation, C-N and C-C bonds are found to be 1.35 Å and 1.55 Å, respectively. The two types of angles present in the small hexagons are $\angle\text{NCN} = 125^\circ$ and $\angle\text{CNC} = 115.4^\circ$.

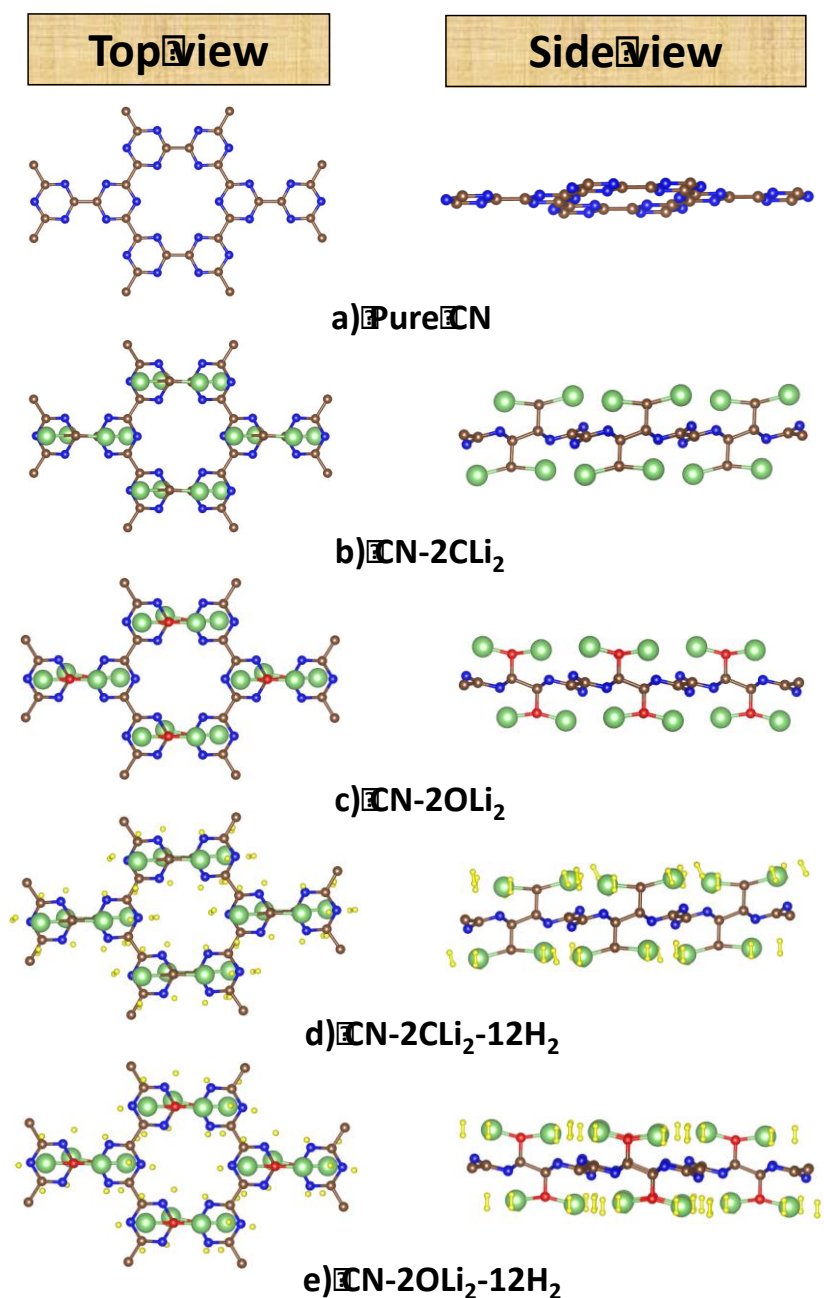


Figure 1: Top and side views of extended structures of CN, CN-2Cl₂, CN-OLi₂, CN-2Cl₂-12H₂ and CN-2OLi₂-12H₂, Brown, blue, red, green and yellow balls represent C, N, O, Li and H atoms respectively.

Now, we report the binding configurations of both the polyliothiated molecules, CLi₂ and OLi₂, to the g-CN monolayer. In order to achieve the most stable configurations, each molecule is introduced to all the available binding sites, i. e. top of C/N atoms, bridge (C-N and C-C) and hollow (small hexagon and big pore). Both, CLi₂ and OLi₂ prefer to bind on C-top of g-CN with binding energies of -5.15 eV and -3.83 eV, respectively, which are strong enough to avoid clustering among the periodically repeating structures. Strong interaction between a single CLi₂/OLi₂ molecule and g-CN encourages us to explore the possibility of adding another

molecule. However, in order to achieve uniform distribution of polyolithiated molecules over g-CN, a reasonably large distance between the molecules is equally important as strong binding energies. Thus, the second $\text{CLi}_2/\text{OLi}_2$ was introduced on the other side of the g-CN sheet that yielded $\text{CLi}_2\text{-CLi}_2$ and $\text{OLi}_2\text{-OLi}_2$ distances of 3.94 Å and 3.72 Å, respectively as shown in Fig. 1 (b, c). Even with two molecular dopants, we still find strong binding energies of -3.19 eV/ CLi_2 and -2.55 eV/ OLi_2 and isolated existence of both the polyolithiated molecules. This is similar to previous findings where polyolithated molecules were also adsorbed on either side of a 2D monolayer with strong adsorption energies and well dispersed distribution. [27-30]

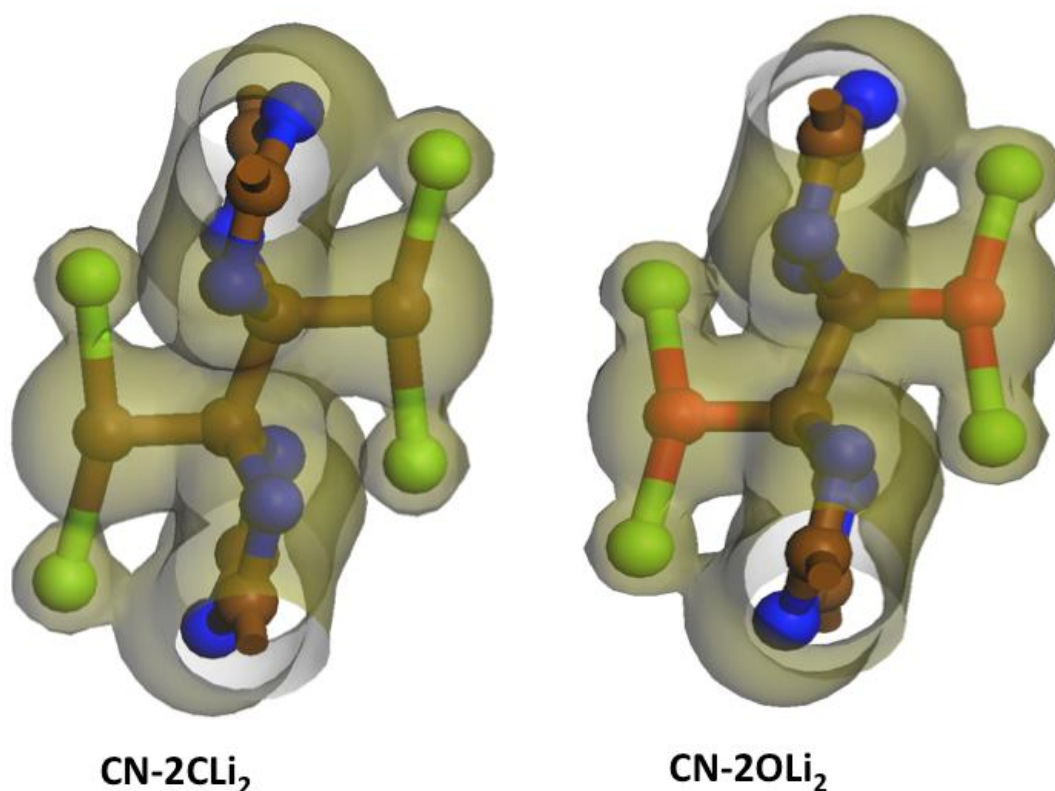


Figure 2: Electron density of CN-2CLi_2 and CN-2OLi_2 . Brown, blue, red and green balls represent C, N, O, and Li atoms respectively. The grey clouds represent the electron density, which is plotted at $0.3 \text{ e}^-/\text{\AA}^3$.

Attachment of both CLi_2 and OLi_2 on either side of the g-CN through covalent bonds, as evident from electron density plots in Fig. 2, alter the planer structure of g-CN slightly. The C-N and C-C and bonds change to 1.49 Å (1.485 Å) and 1.59 Å (1.60 Å) respectively in case of g-CN- 2CLi_2 (g-CN- 2OLi_2) binding. The considerable elongation of C-N bonds compared with those in pure CN can simply be described by the fact that CN has become buckled upon CLi_2 and CLi_2 adsorption. The charge states of $\text{CN-CLi}_2/\text{CN-OLi}_2$ also change with each Li donating a fraction of its charge and attain a partial positive state.

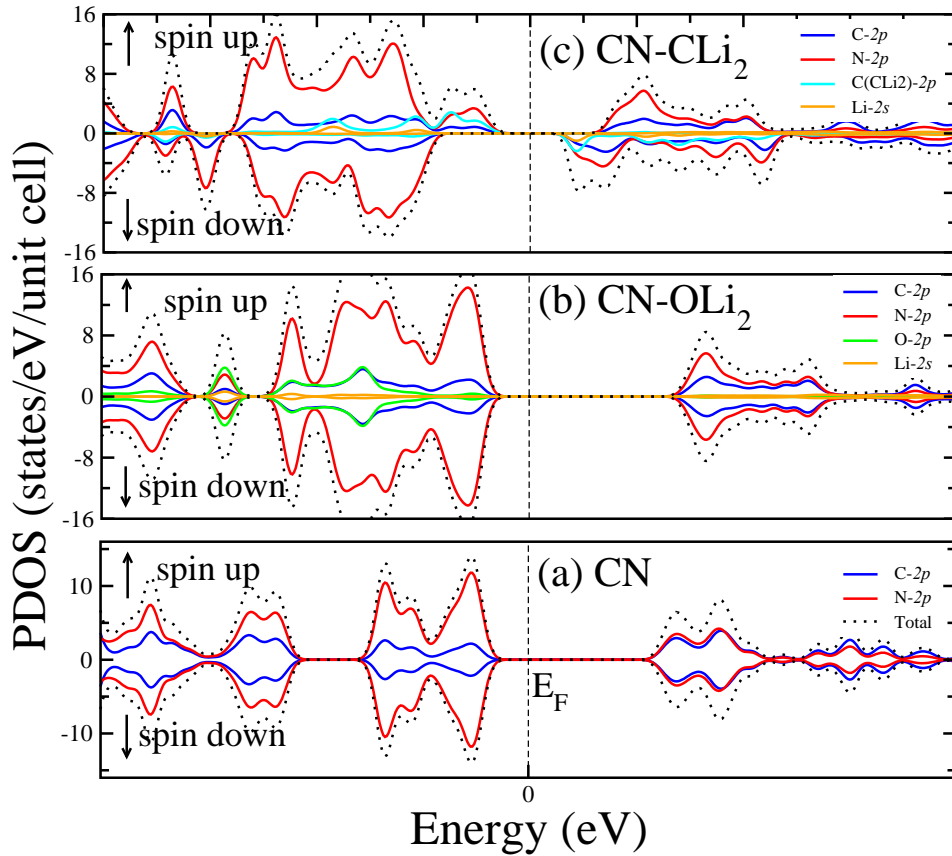


Figure 3: Orbital-resolved density of states (PDOS) of (a) pure CN and (b) CN-2OLi₂ and (c) CN-2CLi₂. Here, the valence band maximum has been shifted to zero. The total density of states (DOS) is indicated by the dotted line in all three cases.

Interactions between pure CN and polyolithiated molecules can be elucidated by the analysis of orbital-resolved density of states (PDOS) as depicted in Fig. 3. It is evident from the DOS in Fig. 3 (a) that CN is a semiconductor and its band edges are predominantly formed by C-2*p* and N-2*p* states. The adsorption of OLi₂ molecules on CN results in a slight change in the band gap. Like pure CN, C-2*p* and N-2*p* states still dominate near the band edges. Meanwhile, O-2*p* and Li-2*s* states from the OLi₂ molecules play an insignificant role. However, there is considerable hybridization of C-2*p* and O-2*p* positioned between -2.5 eV and -1.0 eV, which accounts for the strong C-O covalent bonds. Unlike the adsorption of OLi₂ molecules to CN, the presence of CLi₂ molecules consequently turns the system to be magnetic as characterized by the asymmetric DOS between the spin-up and spin-down channels. There is the strong hybridization of N-2*p* and C-2*p* (from CLi₂ molecules) close to the valence band maximum (VBM) of spin-up channel and the conduction band minimum (CBM) of spin-down channel. This intensive hybridization originates from the covalent C-C bonds between the C atoms of the monolayer and the C atoms of the CLi₂ molecule and it is responsible for the stronger adsorption energy of the CLi₂ molecules compared to the OLi₂ molecule. It is important to emphasize that some electronic charge is transferred from Li to the O (C) atoms of polyolithiated

molecules and also to N atoms of CN because Li has a lower electronegativity than O, C and N (0.98 compared to 3.44 for O, 2.55 for C and 3.04 for N). Therefore, the Li atoms bind to O, C and N atoms via ionic interactions where the Li atoms have become positively charged, i. e., Li^+ , to be ready for H_2 adsorption via electrostatic and weak van der Waals forces. The charge donation of Li can be also explained by PDOS of CN-OLi₂ and CN-CLi₂ where there is noticeable hybridization of Li-2s with O-2p, C-2p and N-2p located between -2.5 eV to -1.0 eV. Furthermore, the plot of electron density in Fig. 2 indicates that there is overlapping of electron cloud between Li and C, O and N atoms. Thus, Li-(O,C,N) bonds are not purely ionic where there is a contribution of covalent bonding.

As discussed earlier, in the case of each of doped systems CN-CLi₂/CN-2OLi₂ there are four Li cations available to adsorb H_2 molecules because of the local electric field of Li^+ . [27] Due to the charged Li dopants, the incident H_2 molecule gets polarized and sticks to the Li through electrostatic interaction. It is also observed that in addition to electrostatic interactions, van der Waals interactions also play an important role in H_2 adsorption to CN-2CLi₂/CN-2OLi₂ systems. While introducing H_2 to each Li in both functionalized sheets, different H_2 orientations have been considered, which includes vertical, horizontal and tilted configurations. We have found that the vertical H_2 adsorption strategy seems to be the most viable one, as it ensures a maximum number of H_2 adsorptions. We introduced one H_2 on each of four Li dopants simultaneously and allowed both, CN-2CLi₂/CN-2OLi₂, systems to attain their ground states. Once the hydrogenated systems have undergone complete structural relaxation, another H_2 on each of the four Li has been introduced and we performed the optimization again. While adding the second H_2 , it was made sure that both H_2 (on each Li) maintained a reasonable distance not only with the Li but also between themselves to avoid steric repulsion, due to their polarizability caused by Li^+ . This process of adding H_2 to each Li continued until the CN-2CLi₂/CN-2OLi₂ systems get saturated with hydrogen and further H_2 are getting repelled by the existing ones. We have observed that both CN-2CLi₂ and CN-2OLi₂ systems could adsorb 12 H_2 each, reaching H_2 storage capacities of 10.34 % and 9.76% respectively. The H_2 capacities obtained are almost twice as large as the target of 5.5 wt% set by the DOE to be achieved by the year 2017. Apart from high H_2 contents, its adsorption energies also fall within the desired range of 0.20-0.40 V per H_2 . The complete set of H_2 adsorption energies, H-H bonds lengths and H_2 storage capacities are given in Table 1.

CN-2CLi ₂				CN-2OLi ₂		
No. of H_2	E_{ads} (eV)	$D_{\text{H-H}}$ (Å)	wt%	E_{ads} (eV)	$D_{\text{H-H}}$ (Å)	wt%
4 H_2	-0.311	0.781	3.70	-0.324	0.782	3.48

8H ₂	-0.251	0.773	7.14	-0.281	0.779	6.72
12H ₂	-0.222	0.771	10.34	-0.242	0.771	9.76

Table 1: Adsorption energies (E_{ads}), H-H distance ($D_{\text{H-H}}$) and H₂ storage capacity (wt%) of CN-2CLi₂ and CN-2OLi₂ under varied hydrogenation.

The storage capacities found are in a similar range to those previously found for polyolithiated molecule functionalized 2D monolayer membranes. For a BC₃ 2D membrane our previous studies found 9.83 wt% for 2CLi₃, 11.88 wt% for 2CLi₄ and 8.70 wt% for 2OLi functionalization of the monolayer. [28, 29] For graphane (CH) we found a capacity of 12.90 wt% for 2OLi₂, 13.87 wt% for 2CLi₃ and 13.33 wt% for 2CLi₄. [30, 31] The results for BC₃ show that one can achieve a significant increase in storage capacity by increasing the lithium content of the functionalizing molecule. However, the results for CH show that one needs to take care that the resulting increase in molecular weight and also decrease in available space due to the larger size of the molecule are not counting against this, resulting in smaller capacities. The results from the current study emphasize that lighter functionalizing molecules are preferred as a significant higher capacity can be achieved with the same number of adsorbed hydrogen molecules.

Conclusion:

Here we employed first principles calculations based on DFT to study the binding mechanism of two polyolithiated molecules, CLi₂ and OLi₂, on g-CN and further explore their promise as potential high capacity H₂ storage material. It was observed that CLi₂ (OLi₂) bind to g-CN with an average binding energy of -3.19 eV/CLi₂ (-2.55 eV/OLi₂) and an average distance of 1.52Å (1.42Å). Reasonably high binding energies and large enough distances between themselves guaranteed a uniform spreading of both CLi₂ and OLi₂ over g-CN, which is necessary for a reversible H₂ storage medium. Each Li in CN-2CLi₂ (CN-2OLi₂), having a partial positive charge, could anchor a maximum of three H₂ molecules through electrostatic and van der Waals interaction reaching a significantly high H₂ storage capacity of 10.34 wt% (9.76 wt%). The H₂ adsorption energies for both the systems lie between 0.20-0.40 eV/H₂, which fall within the preferred range for the operation at reasonable condition of temperature and pressure. Thus, both CN-2CLi₂ and CN-2OLi₂ monolayers could be considered as efficient H₂ storage materials.

Acknowledgments

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Figure Caption

Fig-1

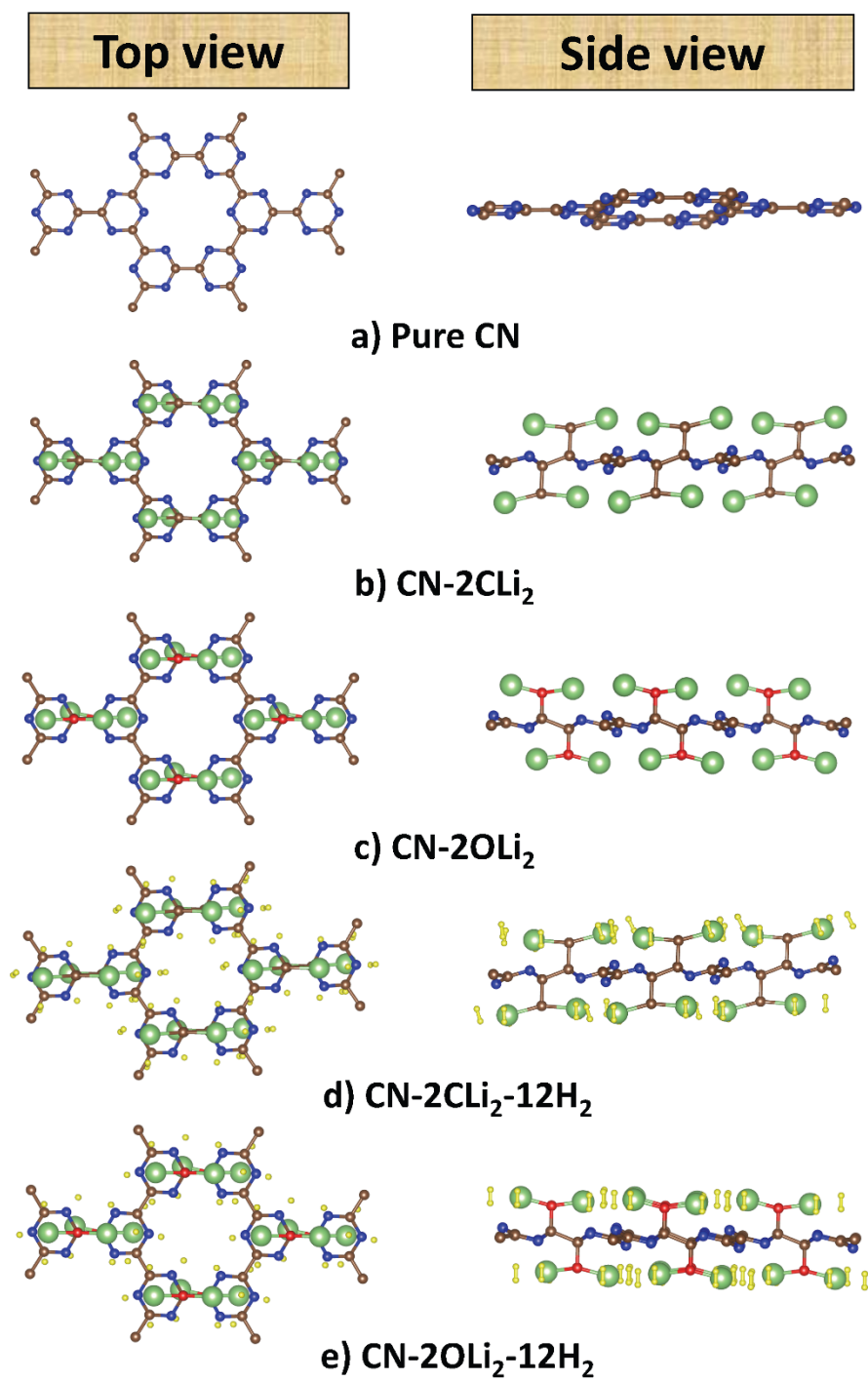


Fig-2

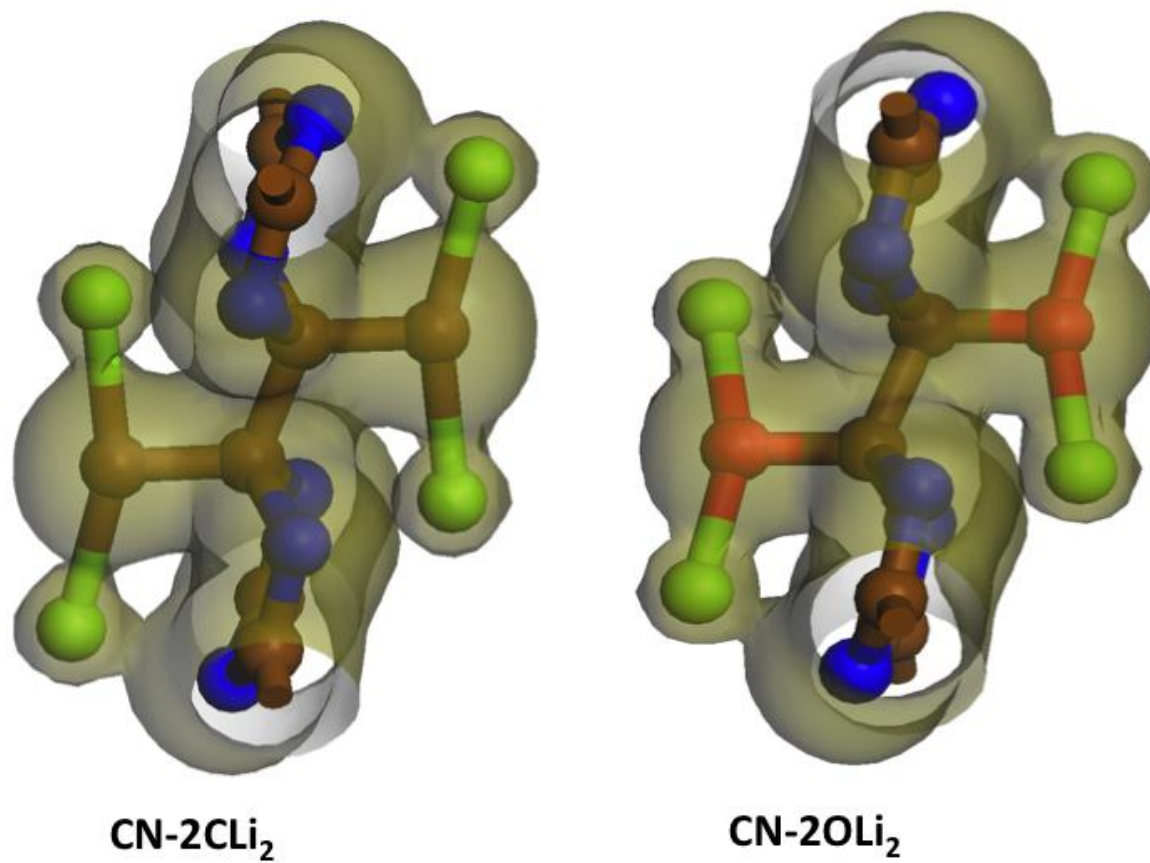


Fig-3

