Title: Methyllithium Doped Naphthyl Containing Conjugated Microporous Polymer with Enhanced Hydrogen Storage Performance

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Methyllithium Doped Naphthyl Containing Conjugated Microporous Polymer with Enhanced Hydrogen Storage Performance

Dan Xu,[a] Lei Sun,[a] Gang Li,[b] Jin Shang,[c] Rui-Xia Yang,[a] and Wei-Qiao Deng*[a]

Abstract: Hydrogen storage is a primary challenge for using hydrogen as a fuel. With ideal hydrogen storage kinetics, the weak binding strength of hydrogen to sorbents is the key barrier to obtain decent hydrogen storage performance. Here, we reported the rational synthesis of a methyllithium doped naphthyl containing conjugated microporous polymer with exceptional binding strength of hydrogen to the polymer guided by theoretical simulations. Meanwhile, the experimental results showed that isosteric heat can reach up to 8.4 kJ/mol and the methyllithium doped naphthyl containing conjugated microporous polymer exhibited an enhanced hydrogen storage performance with 150% enhancement comparing with its counterpart naphthyl containing conjugated microporous polymer. These results indicated that this strategy provided a direction for design and synthesis of new materials to meet the DOE hydrogen storage target.

Introduction

Hydrogen is considered as an ideal clean energy due to its high energy density and zero emission after combustion.[1] Accordingly, design and synthesis of materials with high performance should be fully developed at first for further on board hydrogen storage.[2] Among all the potential materials for hydrogen storage, microporous materials are promising systems for the advancement of hydrogen technologies because of their remarkable thermodynamics and kinetics of hydrogen absorption/desorption.[3] These microporous materials including metal organic frameworks, covalent organic frameworks and conjugated microporous polymers, etc have received considerable attention in hydrogen storage applications owing to their large surface areas and fine-tunable pore structures.[4-6] However, experimental results are yet to meet comparable capacity to the theoretical values.[7]

concluded that the binding strength of hydrogen to a material is the most important factor once this material reaches certain free volume.[8] Enlightened by this theoretical work, we aimed to design new materials through increasing their binding strengths to hydrogen.

In the previous work, we demonstrated that lithium doped porous materials can dramatically enhance the hydrogen storage capacities[9] as confirmed by other groups.[10, 11] However, two main problems still exist that limits the further application of these materials. One is that Li atoms were prone to agglomeration during lithiation process due to the lack of effective active sites in the host materials. The triple bonds built in such porous organic polymers can act as active sites for fixing lithium, but Li atoms still tended to form cluster with increasing Li contents and severely reduced specific surface areas and total pore volumes of the host materials, and hence, H_2 uptake decrease. The other is that, generally tedious process was needed to reach the right balance between doping amount and improved capacity, which is time-consuming and redundancy. Therefore, in order to rational and efficient design and synthesize lithium doped hydrogen storage materials, more in depth studies about location of doped lithium, the optimum doping amount, and their binding affinity toward hydrogen are highly desirable.

In this work, under the guidance of theoretical simulation, methyllithium (**MeLi**) was selected as a novel and ideal dopant alternative to traditional lithium atom because MeLi itself was a positive charge cluster providing a more readily accessible binding environment for H_2. Meanwhile, naphthyl containing conjugated microporous polymer (**N-CMP**) was selected as the host material which suppressed the clustering effect of lithium with its loading amount increasing. More importantly, one time doping can achieve optimum doping amount with remarkably enhanced hydrogen storage capacity in that MeLi selectively anchored on the predesigned active sites through strong interaction. Experimental results also showed that MeLi doped N-CMP had a promising H_2 uptake not only under cryogenic condition, but near room temperature. The synergy between theoretical simulation and experiment made it more efficient and facile to prepare new hydrogen storage materials meeting the 2017 U.S.Department of Energy (**DOE**) target.[12]

Results and Discussion

We used quantum chemistry second-order Møller-Passet (**MP2**) calculations to investigate the location of doped lithium and their existing forms. In addition, conjugated microporous polymers (**CMPs**) were initially selected as host material because of their high design flexibility, diverse types of synthetic methods, and outstanding physical stability.[13]I nitially, triethynylbenzene based CMP and N-CMP were used as substrates. Triple bonds can act as active sites for binding of lithium at low lithium

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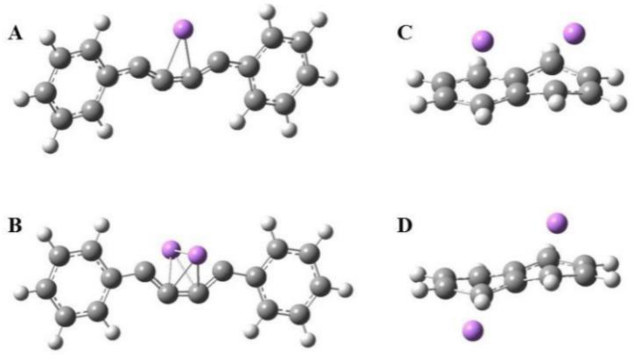

Figure 1. Optimized structures for the adsorptive binding of lithium atom when triple bonds act as active sites, A and B; Optimized structures for the adsorptive binding of lithium atom when naphthyl act as active sites, C and D.

loadings with a binding energy of 3.08 kcal/mol (**Figure 1A**). But, optimized structures at higher Li content showed clustering of Li (**Figure 1B**). In contrast, the isolated form of Li atoms was preferred over clustering while naphthyl was built into the microporous polymers because Li atoms can dispersed on both sides of naphthyl plane. Optimized structures for the binding of Li atoms when naphthyl acted as active sites were shown in **Figure 1C** and **D** with a binding energy of 9.66 kcal/mol. That is to say, lithium can disperse in the polymer in the form of single atoms if naphthyl building block was used in the microporous polymers. At the same time, each localized lithium atom can function as binding core for hydrogen, and thus providing lithium doped N-CMP an enhanced hydrogen storage capacity. Furthermore, extensive studies on the interactions between doped lithium and hydrogen molecules have also been carried out.[14] The presence of charge transfer from lithium atom to naphthyl planes leads to partially positively charged lithium ions which can polarize the surrounding H_2 molecules.

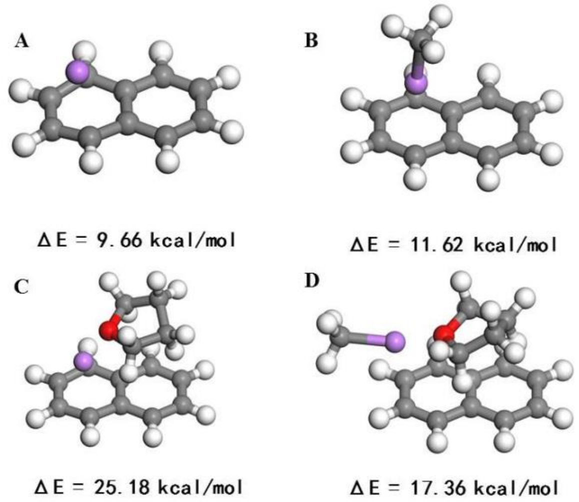

Figure 2. Optimized structures and binding energies for lithium atom to naphthyl (A), MeLi to naphthyl (B), THF to naphthyl bonded lithium (C), and THF to naphthyl bonded MeLi (D).

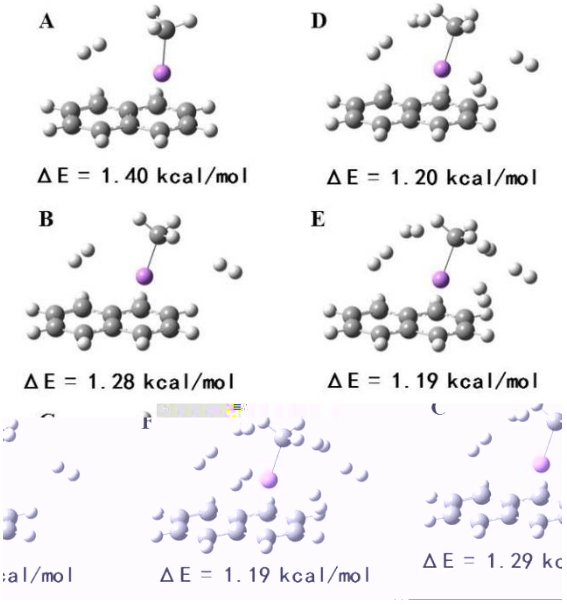

Figure 3. Optimized structures of nH_2 adsorbed to MeLi@N-CMP and average binding energies of nH_2 on MeLi.

This dipole-induced dipole interaction is stronger than that by typical van der Waals interactions between nanostructured materials and hydrogen molecules, which could considerably enhance the adsorption enthalpy.

Theoretically, six hydrogen molecules can adsorb onto one Li cation based on the charge polarization mechanism.[15] However, the adsorption sites of the doped Li was frequently preoccupied by solvent molecules which could reduce the hydrogen storage capacities. A commonly used solvent to disperse the precursor of Li atoms is tetrahydrofuran (THF). The calculated binding energy for attaching the first THF to a Li cation was 48.37 kcal/mol, and this gradually dropped to 17.70 kcal/mol till the attachment of the fifth THF.[16] The removal of such strongly bonded THFs needed excessively high temperature which led to cohesion of lithium atoms making it not an effective binding core to hydrogen.[17] THF decorated lithium atom also displayed weakened binding strength to hydrogen (0.32 kcal/mol) compared with that of naked lithium atom (3.20 kcal/mol) (**Figure S1A and1B**). Therefore, there remains a challenge to find a dopant capable of simultaneously meeting two conflicting criteria-favorable H_2 adsorption, but weakly enough to release residue solvent under low degas temperature.

Our MP2 calculations predicted that MeLi was an ideal dopant alternative to lithium atom. As shown in **Figure 2A** and **B**, naphthyl can also act as active site for MeLi with a binding energy of 11.62 kcal/mol slightly higher than that of lithium atom to naphthyl. While, the energy of THF binding to MeLi was significantly lower than that to naked lithium indicating that THF can be easily removed (**Figure 2C and D**). Although hydrogen adsorption onto MeLi exhibited a relatively low binding energy (1.40 kcal/mol) compared with that on lithium cation (3.20 kcal/mol), we found that the favourable number of H_2

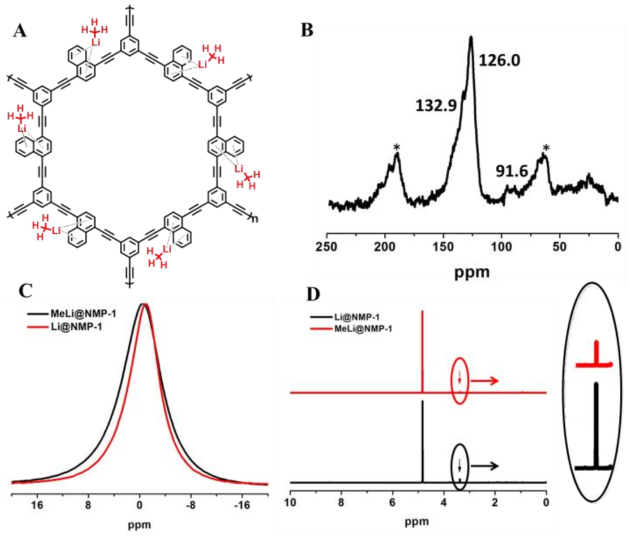

Figure 4. Chemical structure of MeLi@N-CMP (A), ^{13}C MAS NMR spectra of the MeLi@N-CMP (Asterisks denote spinning side bands) (B), ^{7}Li NMR spectra of MeLi@N-CMP and Li@N-CMP (C), ^{1}H NMR spectra of MeLi@N-CMP and Li@N-CMP dissolved in D_2O (D).

molecules bond per MeLi (positively charged cluster) was six (**Figure 3 and Figure S2**). While the maximum number of H_2 molecules adsorbed on naked lithium cation (a point charge) was four (**Figure S3 and S4**). The larger radii of the binding core, the more number of H_2 molecules able to be adsorbed.[18]The corresponding average binding energies ranged from 1.4 to 1.2 kcal/mol permolecule on MeLi. The distances between H_2 molecule and MeLi varied from 3.179 to 3.400 Å. Calculated

elongated $_2$ molecule(0.738 Å) demonstrated the charge polarization interaction between H_2 molecule and MeLi resulting in an enhanced interaction stronger than typical van der Waals interaction.[19] Theoretical calculations also predicted that THF decorated MeLi was not an effective binding core (**Figure S1C and 1D**). Fortunately, THF can be easily removed. It is expected that MeLi doped N-CMPs has a promising H_2 storage capacity.

On the basis of above theoretical predications, we synthesized N-CMP as Li hosting materials via Sonogashira reaction from 1,3,5-triethynylbenzene and 1,4-dibromonaphthalene.[20] The morphology of the polymer was examined by SEM and HRTEM showing porous structures (**Figure S5A**) and nanometer-scale cavities (**Figure S5B**), respectively. The Brunauer Emmett Teller (BET) surface area of N-CMP was 755 m^2/g with a total pore volume of 1.0 cm^3/g and micropore volume of 0.33 cm^3/g. The main pore size of N-CMP was distributed at 0.5 nm and 4 nm (**Figure S7**). These data indicated that N-CMP have both micropore and mesopores. Type IV N_2 gas sorption isotherms of N-CMP further illustrated the existence of mesopores (**Figure S6**). The presence of mesopores may attribute to the interparticle voids and porogenic solvent medium.Two types of naphthyl containing conjugated microporous polymers namely, MeLi doped N-CMP (labeled as MeLi@N-CMP) and lithium doped N-CMP (labeled as Li@N-CMP) were both prepared for comparison study. To prepare these materials, we immersed the N-CMP in solution of MeLi in diethyl ether and lithium naphthalenide in THF, respectively. The mixture was stirred for three days under an argon atmosphere to allow for sufficient interaction between dopants and active binding sites. Then the mixture was filtered and rinsed by anhydrous THF several times. The solid product was dried under high vacuum at 120℃ to remove the residual solvent and naphthalene. The structure of MeLi@N-CMP (**Figure 4A**) was confirmed by solid-state ^{13}CMAS NMR measurement. As shown in **Figure 4B**, the signals of chemical shift

ppm suggested the presence of phenyl and naphthyl group.[21] The signal located at 91.6 ppm is indicative of the acetylene group.[10b] The ^{7}Li NMR spectra of MeLi@N-CMP and Li@N-CMP (**Figure 4C**) were characterized by signals located at δ -0.49 and -0.94 ppm, respectively, the typical region of lithium alkyls and lithium cations, indicating the different chemical environment and average electronic density.[22]

Experiments to check the residue of THF have also been carried out. MeLi@N-CMP (5 mg) and Li@N-CMP (5 mg) were dispersed in D_2O (1 ml) to make all lithium convert to LiOD. The upper clear solutions were characterized by ^{1}H NMR. One set

observed from NMR spectra demonstrating the existence of residual THF. The signal of THF in Li@N-CMP was more discernible than that in MeLi@N-CMP which agreed well with the theoretical simulation (**Figure 4D**).

MeLi@N-CMP and Li@N-CMP were studied for their high-pressure hydrogen ads

Figure 5. 80 bar excess H_2 uptake of N-CMP, MeLi@N-CMP, and Li@N-CMP measured at 77 K(A), 80 bar excess H_2 uptake of N-CMP and MeLi@N-CMP at 273K (B), 80 bar excess H_2 uptake of MeLi@N-CMP and Li@N-CMP measured at 87 K(C), and isosteric heats of hydrogen adsorption to 3 wt%Li_MeLi@N-CMP and 9 wt%Li_Li@N-CMP (D).

much higher than MeLi, hydrogen uptake of 9 wt%Li_Li@N-CMP was less than that of 3 wt%Li_MeLi@N-CMP. Theoretically, two Li atoms can locate at the same side or both sides of the naphthyl plane, but Li was not an effective binding core due to the residue of THF on one hand, and high density of Li in Li@N-CMP may cause agglomeration during degas process limitting the available adsorption sites on the other hand. With regard to MeLi@N-CMP, the high degree of desolvation facilitated the adsorption toward H_2. Moreover, the highly dispersed MeLi and its positive charge cluster provided a more readily accessible binding environment. In fact, it was difficult to fine tune the doping amount of lithium. In this work, guided by theoretical simulations, dopants selectively anchored on the predesigned active sites through strong interaction and one time saturated sorption have achieved optimum doping amount and remarkably enhanced hydrogen storage capacity.

H_2 adsorption isotherms for MeLi@N-CMP and Li@N-CMP were also collected at 87K (**Figure 5C**). Data collected at 77K and 87 K were fitted to virial-type equation, and isosteric heat of adsorption (Q_{st}) was calculated by using Clausius-Clapeyron equation.[12] **Figure 5D** showed that initial Q_{st} value of 3 wt%Li_MeLi@N-CMP (8.4 kJ/mol) was greater than that of 9 wt%Li_Li@N-CMP (5.9 kJ/mol) with 2.5 kJ/mol enhancement. MeLi@N-CMP displayed a slightly reduced isosteric heat with the increase of hydrogen uptake demonstrating a consistently high affinity of charged MeLi cluster toward H_2. This initial Q_{st} value was a little higher than Li-CMP (8.1 kJ/mol),[9] Li doped MOFs,[10a] and close to potassium-intercalated graphite.[23] For Li@N-CMP, the rapid decrease of isosteric heat can be attributed to the weaker interactions of hydrogen molecules with the lithium. More importantly, materials demonstrate high storage capacity at room temperature is crucial for the real-world application and commonly is quite a hard issue. A H_2 uptake of 1.0 wt% was achieved with 3 wt%Li_MeLi@N-CMP, still with 100% increase over the N-CMP at 273 K and 80 bar (**Figure 5B**) .

Lithium dopants decorated with other groups, such as n-BuLi and MeOLi were also tested. However, their H_2 adsorption capacities were not as good as MeLi (**Figure S9**). Compared with methyl, butyl is more bulky, making binding site adjacent to Li inaccessible. Although it has been reported that alkoxy Li can act as binding core for hydrogen uptake,[11b] MeOLi was not an effective dopant in our system.

Screening a promising dopant that can be strongly anchored in the microporous polymers and function as effective charge-dense binding core offering enhanced interaction between H_2 molecule and adsorbentis crucial in the design of new hydrogen storage materials that satisfy the 2017 DOE target. Aforementioned results clearly showed that MeLi doped N-CMP was an ideal material for hydrogen storage under high pressure. One difficulty in broadly using lithium doped microporous polymers as hydrogen storage materials lies in their low stability against air and water. In this case, a more stable dopant that can strongly polarize the H_2 molecule will be a better choice. Our future work will move towards prudently screening the dopant under the guidance of computational modeling, and then experimentally design and synthesis of the novel type hydrogen storage materials.

Conclusions

In summary, we have developed a strategy to significantly enhance the hydrogen storage performance of conjugated microporous polymers under the guidance of theoretical simulation. Experimentally, MeLi@N-CMP maintained a 150 % increase over the undoped N-CMP at 77 K and 80 bar, and a 100% increase over the undoped N-CMP at 273 K and 80 bar. In view of the distinct performance of MeLi@N-CMP for hydrogen storage, it is anticipated that this method opens a new way for efficient design and synthesis of naphthyl containing conjugated microporous materials with large specific surface areas and total pore volumes in order to meet the hydrogen storage target proposed by DOE.

Experimental Section

Theoretical simulation: Quantum chemistry second-order Møller-Passet (MP2) method with 6-311++G(d,p) basis set was used to optimize structures for adsorptive binding of lithium atom to triple bond and

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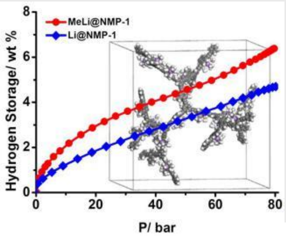
Based on a combined theoretical and experimental approach, a new strategy was developed to enhance hydrogen uptake of naphthyl containing conjugated microporous polymers through methyllithium doping.



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Supporting Information

Methyllithium Doped Naphthyl Containing Conjugated Microporous Polymer with Enhanced Hydrogen Storage Performance

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1. Theoretical simulation

The calculations in this paper were performed with the Gaussian 09 program package.[S1]

2. Experimental Section

2.1 Chemicals

1,3,5-Triethynylbenzene, 1,4-Dibromonaphthalene, Lithium methoxide, tert-Butyllithium (1.3 M solution in pentane) and Methyllithium (1.6 M solution in diethyl ether) were purchased from J&K Scientific. ZIF-8 was purchased from BASF. DMF, THF, and other affiliated chemicals were all from local suppliers. All solvents and chemicals were of reagent quality and were used after purification.

2.2 Characterization

Morphology and microstructure of microporous polymer was observed by a JEM-2100 scanning electron microscope and JSM-7800F field emission high resolution transmission electron microscopy. Surface area (Brunauer-Emmett-Teller (BET)) calculated from nitrogen adsorption isotherms and argon adsorption isotherms measured by Quadrasorb Adsorption Instrument at 77.3 K and 87K, respectively. The total pore volume was calculated at a relative pressure P/P_0 = 0.99. The micropore volume was calculated by the Saito Foley (SF) model. Pore-size distributions were calculated by Barret, Joyner and Halenda (BJH) method for mesopore and Saito Foley (SF) method for micropore, using a carbon slit pore model. ^{13}C MAS NMR spectra ($C_2H_5NO_2$ as reference) and ^{7}Li NMR ($LiNO_3$ as reference) were obtained by a Bruker 500NMR spectrometer. ^{1}H NMR was recorded by a Bruker AVANCE III 400 MHz spectrometer. ICP was carried out using PerkinElmer NexION 300D.

2.3 *Volumetric high-pressure hydrogen adsorption measurements*

In order to verify the accuracy of our instrument, commercially available ZIF-8 (BET= 1300 cm^2/g) was tested for comparison. The amount of ZIF-8 used was about 200 mg to fully fill the sample vessel. For the samples we prepared, the sample mass used was about 110 mg because this amount has already made the sample vessel full.

Hydrogen storage capacity of ZIF-8 is 3.3 wt% at 80 bar and 77K, close to the results reported in other reference （3.1 wt% (excess adsorption capacity) obtained at 77 K and 80 bar.[S2] This result indicates that excess adsorption capacity provided by our instrument is relatively reliable.

2.4 *Calculation of Volumetric H_2 capacity*[S3]

Volumetric H_2 capacity = Mass H_2 adsorbed/Sample Volume

= Mass H_2 adsorbed/(Mass sample*V_{bulk})

$V_{bulk} = V_{skeletal} + V_{pore}$

$V_{skeletal}$ (the volume of MeLi@N-CMP skeleton) was determined from the helium expansion (<5 bar) at 298 K using the same Hy-Energy Scientific Instruments. V_{pore} was measured by Quadrasorb Adsorption Instrument.

$V_{skeletal} = 0.84\ cm^3/g$, $V_{pore} = 1.0\ cm^3/g$, $V_{bulk} = 1.84\ cm^3/g$

Mass H_2 adsorbed/(Mass sample + Mass H_2) = 6.5% (77K)

Mass H_2 adsorbed = 0.07 Mass sample (Mass sample expressed in g)

Volumetric H_2 capacity = 0.07 Mass sample/(Mass sample *1.84 cm^3/g) = 38 g/L

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3. Additional Material Characterizations

Figure S1 Optimized structures and binding energies for hydrogen to lithium atom (A), hydrogen to THF decorated lithium atom (B), hydrogen to methyllithium (C), and hydrogen to THF decorated methyllithium (D).

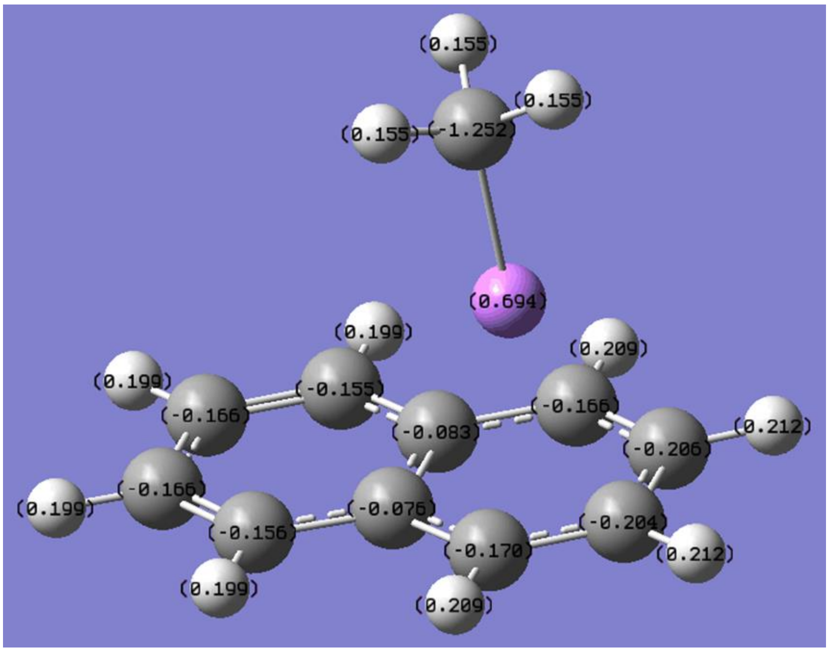

Figure S2 Charge distribution of methyllithium decorated naphthyl showing positively charged methyllithium cluster.

Figure S3 Optimized structures of nH_2 adsorbed to Li@N-CMP and average binding energies of nH_2 on Li.

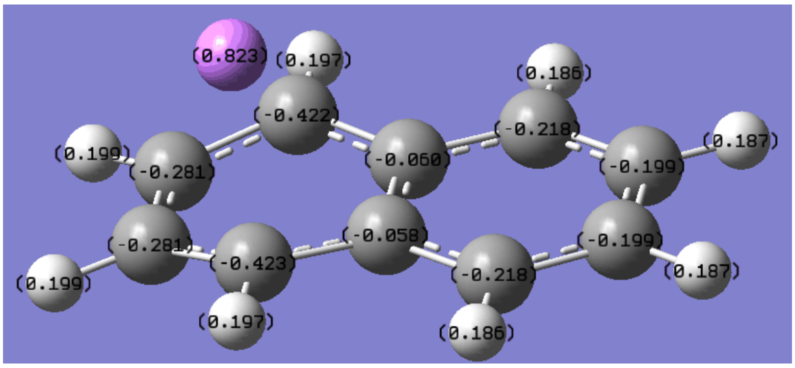

Figure S4 Charge distribution of lithium decorated naphthyl showing positively charged lithium.

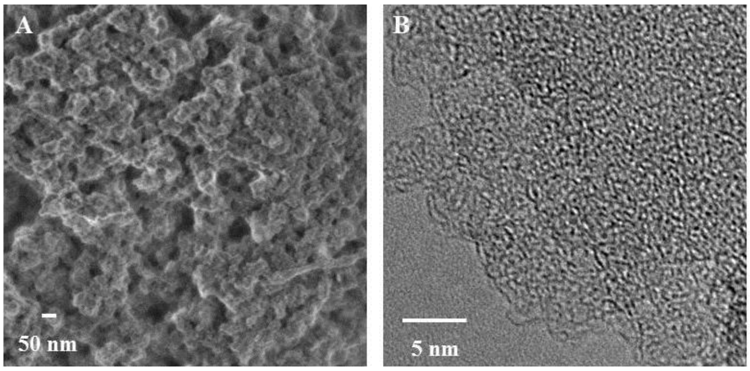

Figure S5 SEM image of N-CMP (A) and HRTEM image of N-CMP (B).

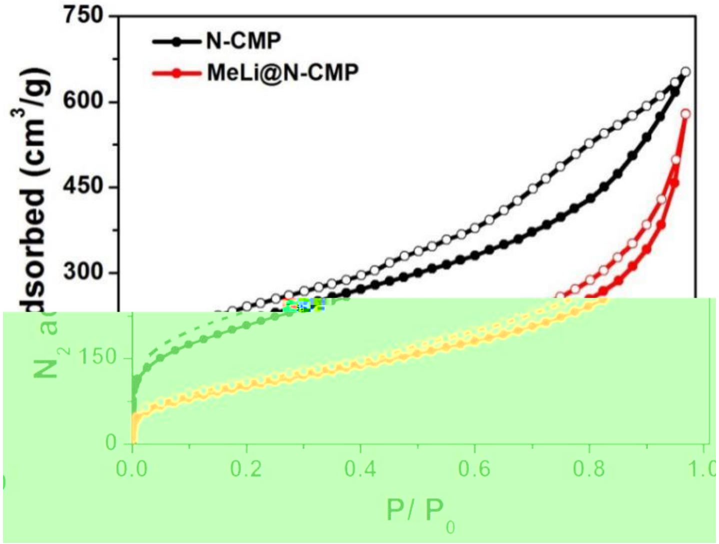

Figure S6 N_2 adsorption/desorption isotherms of N-CMP and MeLi@N-CMP at 77.3 K.

[redacted]

Figure S7 Pore size distribution of micropore of N-CMP and MeLi@N-CMP calculated using SF method (A) and pore size distribution of mesopore of N-CMP and MeLi@N-CMP calculated using BJH method (B).

Figure S8 Argon adsorption/desorption isotherms of Li@N-CMP at 77.3 K (A) and pore size distribution of mesopore Li@N-CMP calculated using BJH method (B).

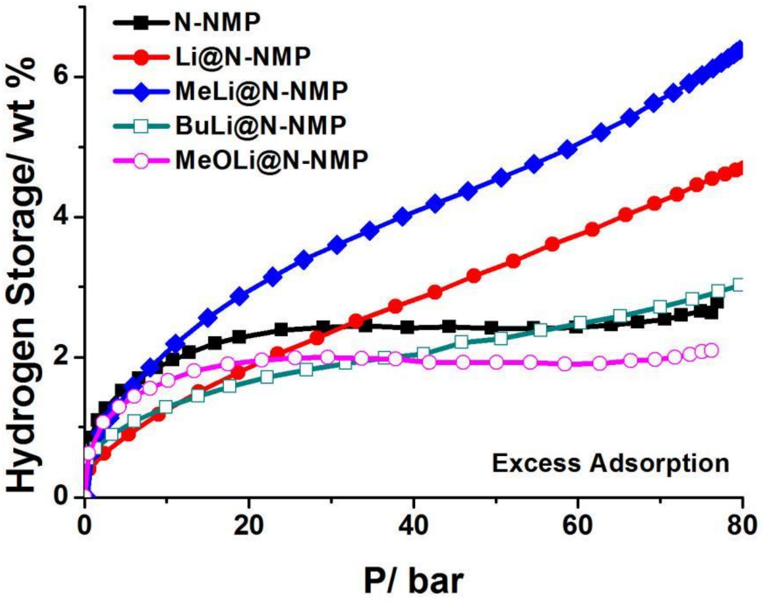

Figure S9 80 bar, 77K excess H_2 uptake of MeLi@ N-CMP, Li@ N-CMP, BuLi@ N-CMP, and MeOLi@N-CMP.