

REGULAR ARTICLE

First-Principles Investigation of Li⁺-doped Conjugated Microporous Polymer as a Potential Hydrogen Storage Medium

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Abstract: We used first-principles calculations to investigate the adsorptive binding of hydrogen molecule with lithium doped triethynylbenzene. The prior binding site of Li⁺ is above the C≡C triple bond rather than the aromatic ring at the computational level of UM06-L/6-311G(d,p), which could provide an accurate description of cation- π interaction. For single, double, and multiple dihydrogen interaction with a formula unit of Li⁺-doped triethynylbenzene, the average binding energies per H₂ are found to be in the range of $-5.08 \sim -4.58$ kcal/mol. The strong binding affinity is promising for hydrogen storage, since it will play a crucial role in physisorption at ambient condition. Further, with a saturated 4-5-5 adsorption, a reversible hydrogen storage capacity of 14.0 wt% is attained. Based on the calculated results, we designed Li cation doped conjugated microporous polymer as hydrogen storage medium and obtained excellent hydrogen uptake performance.

AMS subject classifications: 65D18, 68U05, 68U07

Key words: Density functional theory, conjugated microporous polymer, Li doping, hydrogen storage, physisorption

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1 Introduction

The non-renewable fossil fuel resources are fast diminishing and the combustion of them always leads to not only environmental pollution but also global warming, nowadays it is imperative to exploit new sources of energy. Molecular hydrogen is thought to be an ideal replacement, because it is clean and renewable, and also abundant on earth. While considerable challenges exist in hydrogen economy, enormous efforts have been focused on developing viable hydrogen storage materials [1]. Previous studies have been devoted to complex light metal hydrides [2] as well as carbon [3–8] or BN [9, 10] based nanostructures, metal-organic frameworks (MOF) [11–16], covalent organic frameworks (COF) [17–21], zeolites [22–24], and even organic chemical hydrides [25–28]. Although many of them exhibit interesting characteristics, the problems still remain due to that they all have poor thermodynamics or kinetics, and actually none in experiment yet meet the new 2017 US Department of Energy target of 5.5 wt% reversible hydrogen storage at ambient condition. The current stage prompts us to expedite the hydrogen energy research that demands safe, efficient, and economic hydrogen storage materials.

Of the existing materials, porous polymer would be a kind of appropriate candidate for hydrogen storage as relatively simple and economic synthesis, for example, Ti-coated polymers, particularly polyacetylene [29] and ethylene [30] complexes have been suggested to possess good gravimetric densities, but Ti atoms tend to cluster and severely undermine the hydrogen storage capacity [31]. Through numerous studies of porous solid structures, such as MOF and COF, porosity and accessible surface area are prerequisite factors for gas uptake. So far, there are lack of pertinent investigations on polymer systems, partially because of their amorphism in nature and low thermal stability. Very interestingly, a new family of rigid conjugated microporous polymer (CMP) using triethynylbenzene as building block were synthesized by Cooper et al. [32, 33], who claimed that the CMP has very good chemical and thermal stability and retention of microporosity under a variety of conditions, moreover, the physical properties like micropore size and surface area can be fine tuned by varying the monomer strut.

Various *ab initio* calculations, grand canonical Monte Carlo and molecular dynamics simulations have recently shown that doping with alkali metals can enhance the fundamental interaction of H₂ with the host structures in a desired range of magnitude [5, 34–42]. The mechanism can be generally attributed to electrostatic charge–quadrupole and charge induced dipole interactions, which is further related to the localization and

polarizability between hydrogen and charged metal sites [43–45]. Intriguingly, substantial enhancement of hydrogen uptake has been experimentally realized by doping a mixed-ligand MOF with Li^+ [46, 47].

On the basis of all of these investigations and followed by our pioneering work [5] about a Li-pillared graphene sheet system fulfilling the 6.0 wt% target theoretically, herein we used density functional theory (DFT) calculations to investigate hydrogen binding with Li-doped triethynylbenzene (representing Li-doped CMP). Lithium is favorably chosen, not only because it is the lightest metal, but also due to that it binds more strongly to C than to itself (shown in Section 3) and the cohesive energy of bulk Li is smaller than those of transition metals, which discounts the likelihood of clustering [8, 34]. Schematic diagram, **Figure 1**, displays the CMP under research; the polymer network is chosen the same as the homocoupled conjugated microporous polymer produced from 1,3,5-triethynylbenzene (HCMP-1) reported in Ref. 32. The ultrahigh porosity and amorphous property are clearly illustrated, and the Brunauer-Emmet-Teller (BET) surface area was assessed to be as high as about $842 \text{ m}^2/\text{g}$ [32]. It should be note that the advantage of alkali metals over other metal elements is that the isolated form is preferred over clustering, and lithium selected in this work has accessional superiority as it is the lightest metal element.

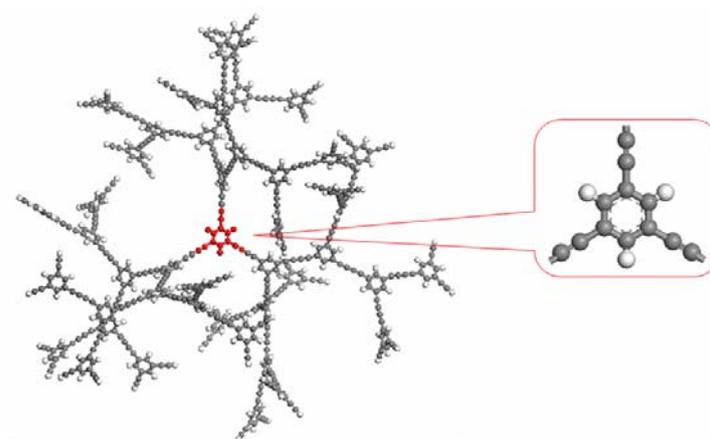


Figure 1: Schematic diagram of the HCMP-1 network structure (Ref. 32).

2 Computational methods

Owing to the amorphous property and consisting of huge number of atoms in CMP, we have to run computation on smaller fragment, which is similar to the treatment of microporous crystalline materials [40]. The representative molecular model by terminating the formula

unit with H atom is indicated in **Figure 2**. Several theoretical studies have been conducted on simple systems both at DFT and MP2 levels with large basis sets, in some sense MP2 method is more rigorous than the common DFT for treating electronic correlation [38, 40, 48], nevertheless, the results show qualitative agreement with each other in acceptable discrepancies. The metal cation- π interaction is recognized as a strong noncovalent binding force that plays a dominant role in present hydrogen storage case [49, 50], new density functional M06-L has been recently developed and validated to include medium-range correlation energy [51]. We balanced the computational accuracy and CPU time by employing electronic-spin-unrestricted UM06-L/6-311G** level for both optimization and single-point energy. All binding energies were corrected for the basis set superposition error by means of the counterpoise scheme [52]. All calculations were performed with the Jaguar program package [53].

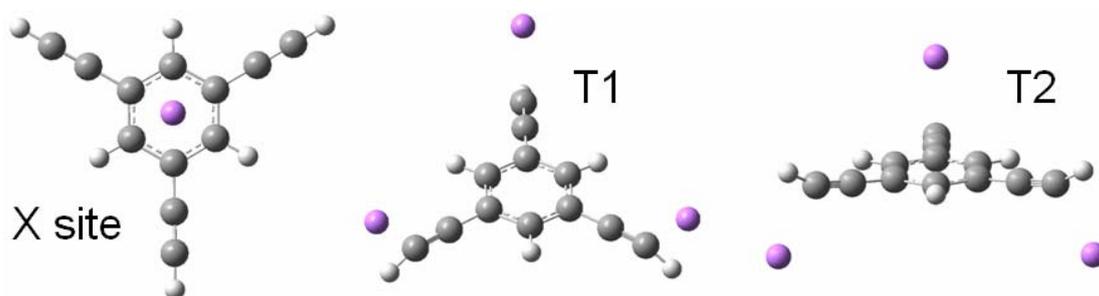


Figure 2: Optimized structures for the adsorptive binding of Li^+ on the representative formula unit by terminating with H atom (atom colors: gray, carbon; white, hydrogen; purple, lithium).

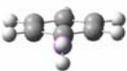
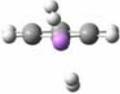
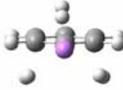
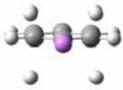
Table 1: Ab initio geometries (distances in angstrom and angles in degree) and binding energies (BE, in kcal/mol) of Li^+ -ACE and Li^+ -MAC.

Li^+ -ACE	r_1	r_2	R	θ	BE			
Exp ^a	1.080	1.210	—	180.0	—			
B3LYP/TZV ^a	1.070	1.202	2.311	175.2	21.3			
UM06-L/6-311G**	1.070	1.205	2.266	175.1	20.1			
Li^+ -MAC	r_1'	r_2'	r_3'	θ_1'	θ_2'	R_1'	R_2'	BE
Exp ^a	1.460	1.210	1.060	180.0	180.0	—	—	—
B3LYP/TZV ^a	1.456	1.208	1.070	177.3	173.5	2.385	2.184	26.7
UM06-L/6-311G**	1.442	1.212	1.069	178.4	174.3	2.419	2.180	26.0

^a Data obtained from Ref. 50

In order to evaluate the accuracy of UM06-L/6-311G** level compared with other computational level, we have performed test calculations of some typical systems. **Table 1** and **Figure 3** show the results for acetylene (ACE) and methylacetylene (MAC) adducted with lithium cation, while **Table 2** presents the comparison among DFT (UM06-L), MP2, and more accurate CCSD (T) methods [38]. All tests indicate that the absolute energy differences estimated among different theoretical methods are comparatively small (no more than 10%) with respect to the binding energies, so UM06-L/6-311G** is accurate enough to describe the interaction between lithium cation and carbon-carbon triple bond as well as the multiple dihydrogen interaction with lithium containing organic molecules, and it is not necessary to interpret with considerable caution for our proposed system.

Table 2: Optimized structures and binding energies for H₂ molecules adsorbed over lithium benzide among DFT (UM06-L), MP2, and CCSD(T) methods^a (atom colors: gray, carbon; white, hydrogen; purple, lithium).

	1 H ₂	2 H ₂	3 H ₂	4 H ₂
Geometry				
UM06-L/ 6-311G**	-2.39	-2.84	-2.87	-2.93
MP2/def2-TZVPP ^b	-2.55	-2.68	-2.76	-2.67
CCSD(T)/ CBS ^b	-2.54	-2.71	-2.82	-2.71

^a All BE values are in kcal/mol. ^bCalculated from Turbomole (Ref. 38).

3 Results and discussion

To determine the adsorption of Li⁺ on CMP network, two active sites are examined: (a) Li⁺ above the center of hexagon (X site in **Figure 2**); (b) Li⁺ above the C≡C triple bond (T site). For the latter binding site, two different structures labeled as T1 and T2 are shown in **Figure 2**. The optimized distance for X site between metal cation to the center of aromatic ring is 1.91 Å, and the calculated binding energy is -1.28 eV. With regard to T site, when we place Li⁺ on the same side of the representative CMP unit (T1 structure), each Li⁺ is bound to two carbon atoms in C≡C triple bond at two distances, i.e., 2.36 and 3.14 Å, the corresponding binding energy per Li⁺ is -2.81 eV. While for T2 structure, both Li cations on the same side of aromatic ring plane are bound to the neighboring C atoms at distances of 2.37 and 3.11 Å,

the binding energies are both -2.80 eV, the other Li cation is 2.39 and 3.09 Å away from its adjacent C atoms with a binding energy of -2.76 eV. To make discussion convenient, we define these two different Li⁺ positions: One denoted as P2Li is that two cations on the same side of aromatic ring, P1Li is named to be that single Li cation on the other side of that plane. For all optimized geometries of T site, tilt angles between C≡C and terminal CH bonds are observed as the terminal H atoms are tilted outward Li⁺.

Obviously, the binding energy of Li⁺ above T site is almost twice larger than that above X site, so T structure is the preferred one. A careful survey indicates T2 is stable than T1 (total energy $E_{T2} - E_{T1} = 0.1$ eV), while the average binding energy per Li⁺ (-2.79 eV) of T2 is slightly smaller than that of T1 structure (-2.81 eV). The favorite T2 structure preserves in the following situation of H₂ adsorption. If network were extended, the tilting would result in Li⁺ clustering at first glance, however, in a realistic system, the linked units cross each other with certain dihedral angles to allow enough space for Li⁺ separation. It should be noted here that the additional Li⁺ can be bound symmetrically to X and T sites, but from the experimental aspect, excessive penetration of lithium ions into the CMP network will result in stacking and hence decreasing of the BET surface areas as well as the cumulative pore volume, which would block gas uptake. This phenomenon has been confirmed by optimal substoichiometric amounts of Li at about 5 mol% for facilitating gas adsorption [46].

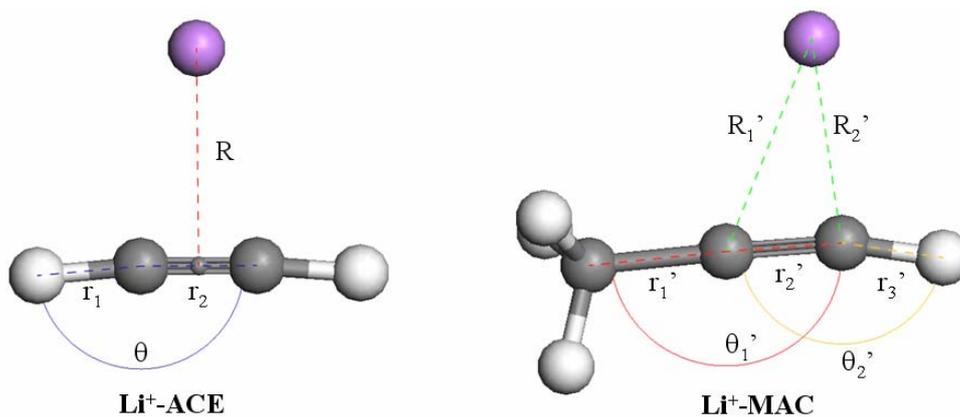


Figure 3: Optimized structures of acetylene (ACE) and methylacetylene (MAC) adducted with lithium cation (atom colors: same as **Figure 2**).

Next, to discuss the hydrogen adsorption, only preferred T site is our research prototype. In fact, no matter what the initial geometry for successively adding H₂ molecules would be, it is relaxed to the same final geometry as T2 framework. **Figure 4** indicates the optimized geometries of adsorbed H₂ on Li⁺-decorated CMP and **Table 3** summarizes the

calculated results, the number of hydrogen molecules per Li^+ under current investigation is up to five. The first dihydrogen is adsorbed over the Li^+ in an asymmetric manner, which means one of two H atoms becomes a little bit closer to the lithium cation. The Li^+ places almost on the top of the benzene plane along the $\text{C}\equiv\text{C-H}$ line, which is similar to the situation without hydrogen adsorption. All the distances from the centers of mass (c.m.) of dihydrogens to Li cations are approximately 1.96 Å, while the distances between Li^+ and its closest C atom are slightly shortened, and the tilt angles increase a few degrees. The relatively large binding energies of H_2 for P1Li suggest that H_2 is adsorbed more strongly over P1Li position than P2Li. Note that the molecular H-H bond lengths are 0.75 Å for both positions, a little larger than the experimental value of 0.74 Å [54] for the free H_2 molecule, which means that the polarization leads to a slight stretching of hydrogen molecule. When the second dihydrogen is added, the distances between Li^+ and its closest C atom and the tilt angles change little, and the H_2 molecules take side-on placements with respect to Li^+ . H_2 molecule is still bound strongly to Li^+ of P1Li. The average binding energy per H_2 of -4.69 kcal/mol is smaller than that of -5.08 kcal/mol for the first H_2 interaction with Li^+ .

Table 3: Average binding energies for two different adsorption positions of H_2 on lithium cation and the corresponding total average values. The values for P1Li and total average in the last column indicate the mean binding energies excluding the external dihydrogen. The value in brackets is for the external dihydrogen. All values are in kcal/mol

	1 H_2	2 H_2	3 H_2	4 H_2	5 H_2
P1Li	-5.10	-4.72	-4.80	-4.63	-4.65 (-1.33)
P2Li	-5.07	-4.68	-4.69	-4.58	-4.55
Average	-5.08	-4.69	-4.73	-4.59	-4.58

In the presence of three or four adsorbed hydrogen molecules, the c.m. of dihydrogens distribute as a triangular or square pattern with Li^+ located at the center of them to minimize the repulsive $\text{H}_2\text{-H}_2$ interaction and maximize the attractive charge-quadrupole coupling. Similar to one hydrogen adsorption, all the dihydrogens (two or more H_2 adsorptions) are found to be adsorbed asymmetrically over the Li^+ for both P1Li and P2Li positions. The corresponding average binding energies for 3 and 4 H_2 adsorption are estimated at -4.73 and -4.59 kcal/mol, respectively. The last case presented here is 5- H_2 adsorption, it is noticeable that one dihydrogen is in equilibrium at about 4.05 Å from the Li cation for P1Li position. The particular binding energy of this dihydrogen is -1.33 kcal/mol. The external position of the weakly binding hydrogen is analogous to the scenario found by studying the clusters $\text{Li}_3^+(\text{H}_2)_n$, and can be called as outer (second) shell as well [43]. By excluding the outer shell

dihydrogen, the average binding energy for 4-H₂ adsorption at P1Li and 5-H₂ adsorption per Li⁺ at P2Li is still large with the value of - 4.58 kcal/mol. An additional sixth H₂ molecule (not shown) causes at least one dihydrogen to be far away from each Li⁺ with Li-H distances elongated and binding energies decreased. In fact, it also leads to strong binding for 4-H₂ adsorption at P1Li and 5-H₂ adsorption per Li⁺ at P2Li. We could nominate this saturated phenomenon to be 4-5-5 adsorption. Incorporating the factor of spatial alignment, now we can deduce that six or more dihydrogens adsorption per Li⁺ is not as stable as less dihydrogens adsorption and it will not be beneficial to reversible hydrogen storage.

By comparing the average binding energies in **Table 3**, we found impressive adsorption energy of hydrogen (0 K), the absolute values are much higher than that of the optimal adsorption enthalpy (3.57 kcal/mol) at ambient condition [55]. The favorable H₂ adsorption number per Li can be up to four, thus the gravimetric density of Li⁺-decorated CMP becomes 12.4 wt% accordingly. It is even higher that the hydrogen storage capacity can amount to 14.0 wt% with saturated 4-5-5 adsorption. This is a remarkable result taking the relatively easy and economic synthesis of CMP into account. The electrostatic charge-quadrupole and charge-induced dipole interactions which is inherently stronger than the weak van der Waals interactions are responsible for the medium magnitude of binding affinities [45]. Besides the electrostatic interactions, another contribution to the hydrogen molecules adsorption is the charge transfer from H₂ molecules to the positive charged Li⁺. Through Mulliken population analysis, it is well understood that when a dihydrogen is adsorbed over the Li⁺, electron density is transferred from the H atom toward the positive Li⁺, however, the magnitude of the charge transfer is very small and will decrease when additional H₂ is adsorbed onto the Li⁺-doped CMP. So the underlying mechanism is predominant with the polarization-induced electrostatic effect rather than van der Waals interactions and orbital interaction (i.e., donor-acceptor bonding by charge transfer).

Based on the calculated results, lithium cation doped CMP has a great potential to store up to 14wt% hydrogen. We have carried out the experimental effort to synthesize Li doped CMP [56]. Although first attempt with 0.5wt% Li-doped CMP demonstrated only 6.1wt% hydrogen storage amount at 77K and 1bar, this hydrogen storage capacity is superior to any reported physisorption hydrogen storage material such as carbon nanostructure (3.0wt%) [57] and MOF (2.59wt%) [16] at same condition.

4 Conclusion

As a conclusion, accurate quantum mechanical calculations have been carried out with a Li⁺-containing HCMP-1 unit model. The prior binding placement of Li⁺ is above C≡C triple

bond rather than aromatic fragment. Single, double, and multiple H_2 interactions demonstrate a strong binding affinity for dihydrogen physisorption with a mean value of at least -4.5 kcal/mol, thus Li cation doped CMP has a prospective H_2 storage capacity of 14.0 wt%. With the development of polymer synthesis method from fine-tunable monomer strut and alkali metal doping technique, this computational-based scheme will be hopeful to achieve efficient hydrogen storage materials.

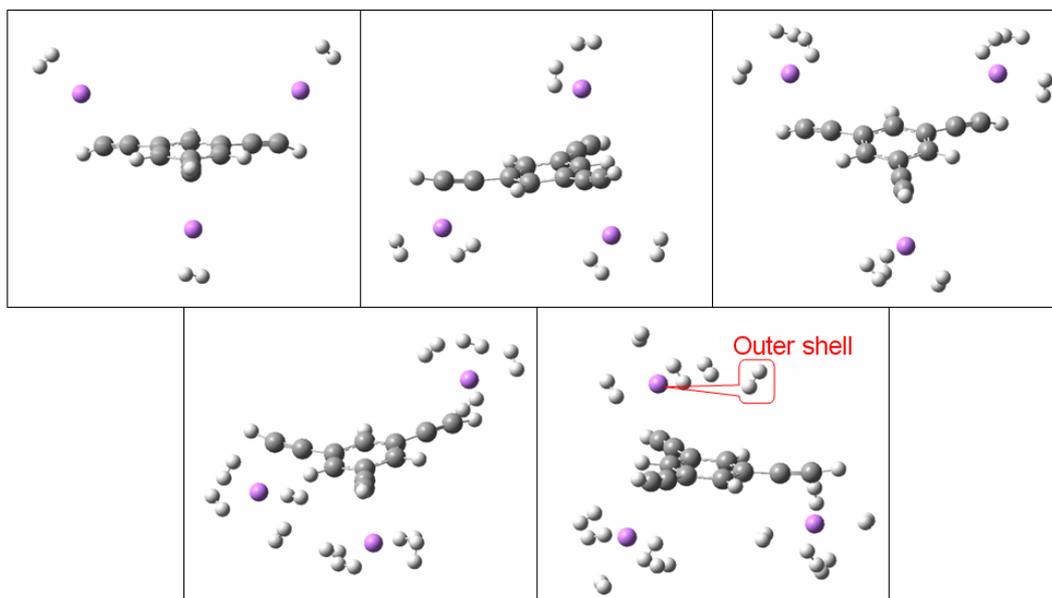


Figure 4: Optimized structures of 1, 2, 3, 4, and 5 H_2 molecules adsorbed over Li^+ -decorated CMP formula unit (atom colors: same as **Figure 2**).

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References

- [1] See U.S. DOE website: <http://www1.eere.energy.gov/hydrogenandfuelcells/storage/>.
- [2] P. Chen, Z. T. Xiong, J. Z. Luo and K. L. Tan, Interaction of hydrogen with metal nitrides and imides, *Nature*, 420 (2002), 302–304.

- [3] C. Ataca, E. Aktürk, S. Ciraci and H. Ustunel, High-capacity hydrogen storage by metalized graphene, *Appl. Phys. Lett.*, 93 (2008), 043123.
- [4] Y. Ye, C. C. Ahn, C. Witham, B. Fultz, J. Liu, A. G. Rinzler, D. Colbert, K. A. Smith and R. E. Smalley, Hydrogen adsorption and phase transitions in fullerite, *Appl. Phys. Lett.*, 74 (1999), 2307.
- [5] W. Q. Deng, X. Xu and W. A. Goddard, New Alkali doped pillared carbon materials designed to achieve practical reversible hydrogen storage for transportation, *Phys. Rev. Lett.*, 92 (2004), 166103.
- [6] S. S. Han and H. M. Lee, Adsorption properties of hydrogen on (10,0) single-walled carbon nanotube through density functional theory, *Carbon*, 42 (2004), 2169–2177.
- [7] S. S. Han, H. S. Kim, K. S. Han, J. Y. Lee, H. M. Lee, J. K. Kang, S. I. Woo, A. C. T. van Duin and W. A. Goddard, Nanopores of carbon nanotubes as practical hydrogen storage media, *Appl. Phys. Lett.*, 87 (2005), 213113.
- [8] A. J. Du, Z. H. Zhu and S. C. Smith, Multifunctional porous graphene for nanoelectronics and hydrogen storage: new properties revealed by first principle calculations, *J. Am. Chem. Soc.*, 132 (2010), 2876–2877.
- [9] C. C. Tang, Y. Bando, X. Ding, S. Qi and D. Golberg, Catalyzed collapse and enhanced hydrogen storage of BN nanotubes, *J. Am. Chem. Soc.*, 124 (2002), 14550–14551.
- [10] S. S. Han, J. K. Kang, H. M. Lee, S. I. Woo, A. C. T. van Duin and W. A. Goddard, Theoretical study on interaction of hydrogen with single-walled boron nitride nanotubes. II. Collision, storage, and adsorption, *J. Chem. Phys.*, 123 (2005), 114704.
- [11] M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, Hydrogen storage in a microporous metal-organic framework with exposed Mn^{2+} coordination sites, *J. Am. Chem. Soc.*, 128 (2006), 16876–16883.
- [12] J. L. C. Rowsell, A. R. Millward, K. S. Park and O. M. Yaghi, Hydrogen sorption in functionalized metal-organic frameworks, *J. Am. Chem. Soc.*, 126 (2004), 5666–5667.
- [13] A. G. Wong-Foy, A. J. Matzger and O. M. Yaghi, Exceptional H_2 saturation uptake in microporous metal-organic frameworks, *J. Am. Chem. Soc.*, 128 (2006), 3494–3495.
- [14] J. L. C. Rowsell and O. M. Yaghi, Effects of functionalization, catenation, and variation of the metal oxide and organic linking units on the low-pressure hydrogen adsorption properties of metal-organic frameworks, *J. Am. Chem. Soc.*, 128 (2006), 1304–1315.
- [15] M. Dincă, A. F. Yu and J. R. Long, Microporous metal-organic frameworks incorporating 1,4-benzeneditetrazolate: Syntheses, structures, and hydrogen storage properties, *J. Am. Chem. Soc.*, 128 (2006), 8904–8913.
- [16] X. Lin, J. H. Jia, X. B. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey and M. Schröder, High H_2 adsorption by coordination-framework materials, *Angew. Chem. Int. Ed.*, 45 (2006), 7358–7364.
- [17] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger and O. M. Yaghi, Porous, crystalline,

- covalent organic frameworks, *Science*, 310 (2005), 1166–1170.
- [18] R. W. Tilford, W. R. Gemmil, H. zur Loye and J. L. Lavigne, Facile synthesis of a highly crystalline, covalently linked porous boronate network, *Chem. Mater.*, 18 (2006), 5296–5301.
- [19] A. P. Côté, H. M. El-Kaderi, H. Furukawa, J. R. Hunt and O. M. Yaghi, Reticular synthesis of microporous and mesoporous 2D covalent organic frameworks, *J. Am. Chem. Soc.*, 129 (2007), 12914–12915.
- [20] H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O’Keeffe, O. M. Yaghi, Designed synthesis of 3D covalent organic frameworks, *Science*, 316 (2007), 268–272.
- [21] S. S. Han, H. Furukawa, O. M. Yaghi and W. A. Goddard, Covalent organic frameworks as exceptional hydrogen storage materials, *J. Am. Chem. Soc.*, 130 (2008), 11580–11581.
- [22] V. B. Kazansky, V. Y. Borovkov, A. I. Serykh, R. A. van Santen and P. J. Stobbelaar, On the role of zinc oxide nanometric clusters in preparation of ZnNaY zeolite by ion exchange, *Phys. Chem. Chem. Phys.*, 1 (1999), 2881–2886.
- [23] H. W. Langmi, A. Walton, M. M. Al-Mamouri, S. R. Johnson, D. Book, J. D. Speight, P. P. Edwards, I. Gameson, P. A. Anderson and I. R. Harris, Hydrogen adsorption in zeolites A, X, Y and RHO, *J. Alloys Compd.*, 356 (2003), 710–715.
- [24] J. Weitkamp, M. Fritz and S. Ernst, Zeolites as media for hydrogen storage, *Int. J. Hydrogen Energy*, 20 (1995), 967–970.
- [25] D. E. Schwarz, T. M. Cameron, P. J. Hay, B. L. Scott, W. Tumas and D. L. Thorn, Hydrogen evolution from organic "hydrides", *Chem. Commun.*, 47 (2005), 5919–5921.
- [26] E. Clot, O. Eisenstein and R. H. Crabtree, Computational structure-activity relationships in H₂ storage: how placement of N atoms affects release temperatures in organic liquid storage materials, *Chem. Commun.*, 22 (2007), 2231–2233.
- [27] R. B. Biniwale, S. Rayalu, S. Devotta and M. Ichikawa, Chemical hydrides: A solution to high capacity hydrogen storage and supply, *Int. J. Hydrogen Energy*, 33 (2008), 360–365.
- [28] R. F. Lu, G. Boëthius, S. H. Wen, Y. Su and W. Q. Deng, Improved organic hydrogen carriers with superior thermodynamic properties, *Chem. Commun.*, 13 (2009), 1751–1753.
- [29] H. Lee, W. I. Choi and J. Ihm, Combinatorial search for optimal hydrogen-storage nanomaterials based on polymers, *Phys. Rev. Lett.*, 97 (2006), 056104.
- [30] E. Durgun, S. Ciraci, W. Zhou and T. Yildirim, Transition-metal-ethylene complexes as high-capacity hydrogen-storage media, *Phys. Rev. Lett.*, 97 (2006), 226102.
- [31] S. Li and P. Jena, Comment on "combinatorial search for optimal hydrogen-storage nanomaterials based on polymers", *Phys. Rev. Lett.*, 97 (2006), 209601.
- [32] J. X. Jiang, F. Su, H. J. Niu, C. D. Wood, N. L. Campbell, Y. Z. Khimyak and A. I. Cooper, Conjugated microporous poly(phenylene butadiynylene)s, *Chem. Commun.*, 4 (2008), 486–488.
- [33] J. X. Jiang, F. Su, A. Trewin, C. D. Wood, H. J. Niu, J. T. A. Jones, Y. Z. Khimyak and A. I. Cooper,

- Synthetic control of the pore dimension and surface area in conjugated microporous polymer and copolymer networks, *J. Am. Chem. Soc.*, 130 (2008), 7710–7720.
- [34] Q. Sun, P. Jena, Q. Wang and M. Marquez, First-principles study of hydrogen storage on $\text{Li}_{12}\text{C}_{60}$, *J. Am. Chem. Soc.*, 128 (2006), 9741–9745.
- [35] R. F. Lu, Z. S. Meng, E. J. Kan, F. Li, D. W. Rao, Z. L. Lu, J. C. Qian, C. Y. Xiao, H. P. Wu and K. M. Deng, Tunable band gap and hydrogen adsorption property of a two-dimensional porous polymer by nitrogen substitution, *Phys. Chem. Chem. Phys.*, 15 (2013), 666–670.
- [36] R. F. Lu, D. W. Rao, Z. L. Lu, J. C. Qian, F. Li, H. P. Wu, Y. Q. Wang, C. Y. Xiao, K. M. Deng, E. J. Kan and W. Q. Deng, Prominently improved hydrogen purification and dispersive metal binding for hydrogen storage by substitutional doping in porous graphene, *J. Phys. Chem. C*, 116 (2012), 21291–21296.
- [37] D. W. Rao, R. F. Lu, C. Y. Xiao, E. J. Kan and K. M. Deng, Lithium-doped MOF impregnated with lithium-coated fullerenes: A hydrogen storage route for high gravimetric and volumetric uptakes at ambient temperatures, *Chem. Commun.*, 47 (2011), 7698–7700.
- [38] A. Mavrandonakis and W. Klopper, First-principles study of single and multiple dihydrogen interaction with lithium containing benzene molecules, *J. Phys. Chem. C*, 112 (2008), 11580–11585.
- [39] E. Klontzas, A. Mavrandonakis, E. Tylianakis and G. E. Froudakis, Improving hydrogen storage capacity of MOF by functionalization of the organic linker with lithium atoms, *Nano Lett.*, 6 (2008), 1572–1576.
- [40] P. Dalach, H. Frost, R. Q. Snurr and D. E. Ellis, Enhanced hydrogen uptake and the electronic structure of lithium-doped metal-organic frameworks, *J. Phys. Chem. C*, 112 (2008), 9278–9284.
- [41] A. Blomqvist, C. M. Araújo, P. Srepusharawoot and R. Ahuja, Li-decorated metal-organic framework 5: A route to achieving a suitable hydrogen storage medium, *Proc. Nat. Acad. Sci. U.S.A.*, 104 (2007), 20173–20176.
- [42] S. S. Han and W. A. Goddard, Lithium-doped metal-organic frameworks for reversible H_2 storage at ambient temperature, *J. Am. Chem. Soc.*, 129 (2007), 8422–8423.
- [43] B. K. Rao and P. Jena, Hydrogen uptake by an alkali metal ion, *Europhys. Lett.*, 20 (1992), 307–312.
- [44] M. Barbatti, G. Jalbert and M. A. C. Nascimento, Clustering of hydrogen molecules around a molecular cation: The $\text{Li}^{3+}(\text{H}_2)_n$ clusters ($n=1-6$), *J. Phys. Chem. A*, 106 (2002), 551–555.
- [45] R. C. Lochan and M. Head-Gordon, Computational studies of molecular hydrogen binding affinities: The role of dispersion forces, electrostatics, and orbital interactions, *Phys. Chem. Chem. Phys.*, 8 (2006), 1357–1370.
- [46] K. L. Mulfort and J. T. Hupp, Chemical reduction of metal-organic framework materials as a method to enhance gas uptake and binding, *J. Am. Chem. Soc.*, 129 (2007), 9604–9605.
- [47] K. L. Mulfort and J. T. Hupp, Alkali metal cation effects on hydrogen uptake and binding in metal-organic frameworks, *Inorg. Chem.*, 47 (2008), 7936–7938.

- [48] J. G. Vitillo, A. Damin, A. Zecchina and G. Ricchiardi, Theoretical characterization of dihydrogen adducts with alkaline cations, *J. Chem. Phys.*, 122 (2005), 114311.
- [49] T. Kar, R. Ponc and A. B. Sannigrahi, Electronic structure, stability, and nature of bonding of the complexes of C_2H_2 and C_2H_4 with H^+ , Li^+ , and Na^+ ions. Extensive ab Initio and density functional study *J. Phys. Chem. A*, 105 (2001), 7737–7744.
- [50] B. Bonelli, B. Civalleri, P. Ugliengo, Z. Gabelica and E Garrone, Adducts of alkali-metal ions with the C equivalent to C triple bond: an experimental and ab initio study, *Phys. Chem. Chem. Phys.*, 4 (2002), 1658–1664.
- [51] Y. Zhao and D. G. Truhlar, A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions, *J. Chem. Phys.*, 125 (2006), 194101.
- [52] S. F. Boys and F. Bernardi, The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors, *Mol. Phys.*, 19 (1970), 553–566.
- [53] Jaguar 7.5; Schrodinger Inc.: Portland, OR, 2008.
- [54] D. R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 84th ed. (CRC Press LLC, 2003-2004).
- [55] S. K. Bhatia and A. L. Myers, Optimum conditions for adsorptive storage, *Langmuir*, 22 (2006), 1688–1700.
- [56] A. Li, R. F. Lu, Y. Wang, X. Wang, K. L. Han and W. Q. Deng, Lithium-doped conjugated microporous polymers for reversible hydrogen storage, *Angew. Chem. Int. Ed.*, 49 (2010), 3330–3333.
- [57] Y. Gogotsi, R. K. Dash, G. Yushin, T. Yildirim, G. Laudisio and J. E. Fischer, Tailoring of nanoscale porosity in carbide-derived carbons for hydrogen storage, *J. Am. Chem. Soc.*, 127 (2005), 16006–16007.