Electronic Supplementary Information

Lithium-doped MOF impregnated with lithium-coated fullerenes: A hydrogen storage route for high gravimetric and volumetric uptakes at ambient temperatures

Dewei Rao,[a] *Ruifeng Lu,**[a,b] *Chuanyun Xiao,*[a,b] *Erjun Kan*[a,b] *and Kaiming Deng**[a,b,c]

[a] *Department of Applied Physics, Nanjing University of Science and Technology, Nanjing 210094, P R China; E-mail: rflu@mail.njust.edu.cn*
[b] *Key Laboratory of Soft Chemistry and Functional Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, P R China*
[c] *Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208, USA; E-mail: kmdeng@mail.njust.edu.cn*

S1. Model Structure

In this work, the organic linker of the IRMOF-10 structure[1] is 4,4'-biphenyldicarboxylate (BPDC), see Figure S1. Four lithium atoms are doped on one linker of BPDC. For the $Li_{12}C_{60}$, twelve lithium atoms site above each of the twelve pentagonal faces of the C_{60}. The geometric structures as well as the chemical composition of pristine IRMOF-10 and IRMOF-10-based materials are given in Figure S2.

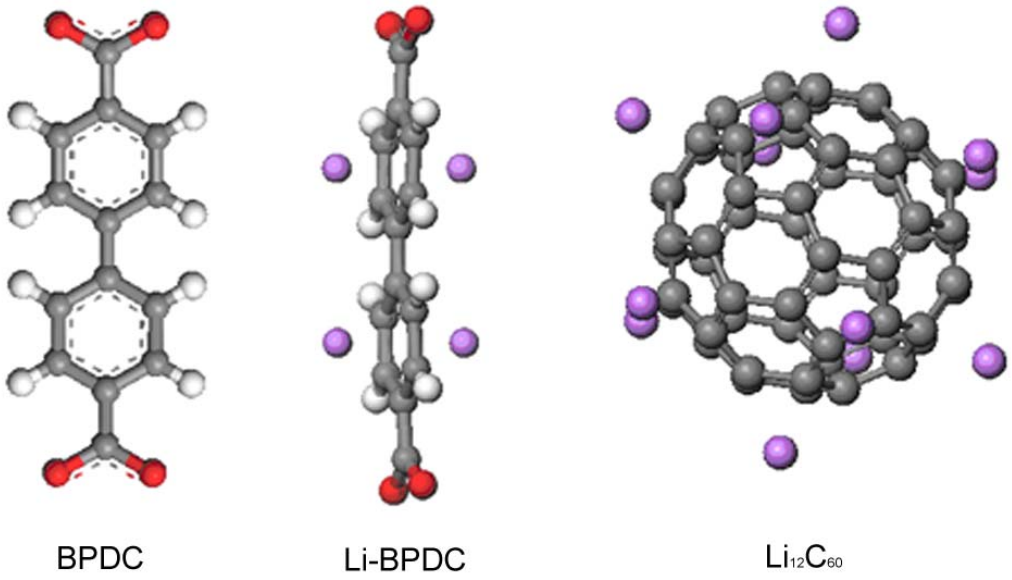

Figure S1. The structures of BPDC, Li-BPDC and $Li_{12}C_{60}$.

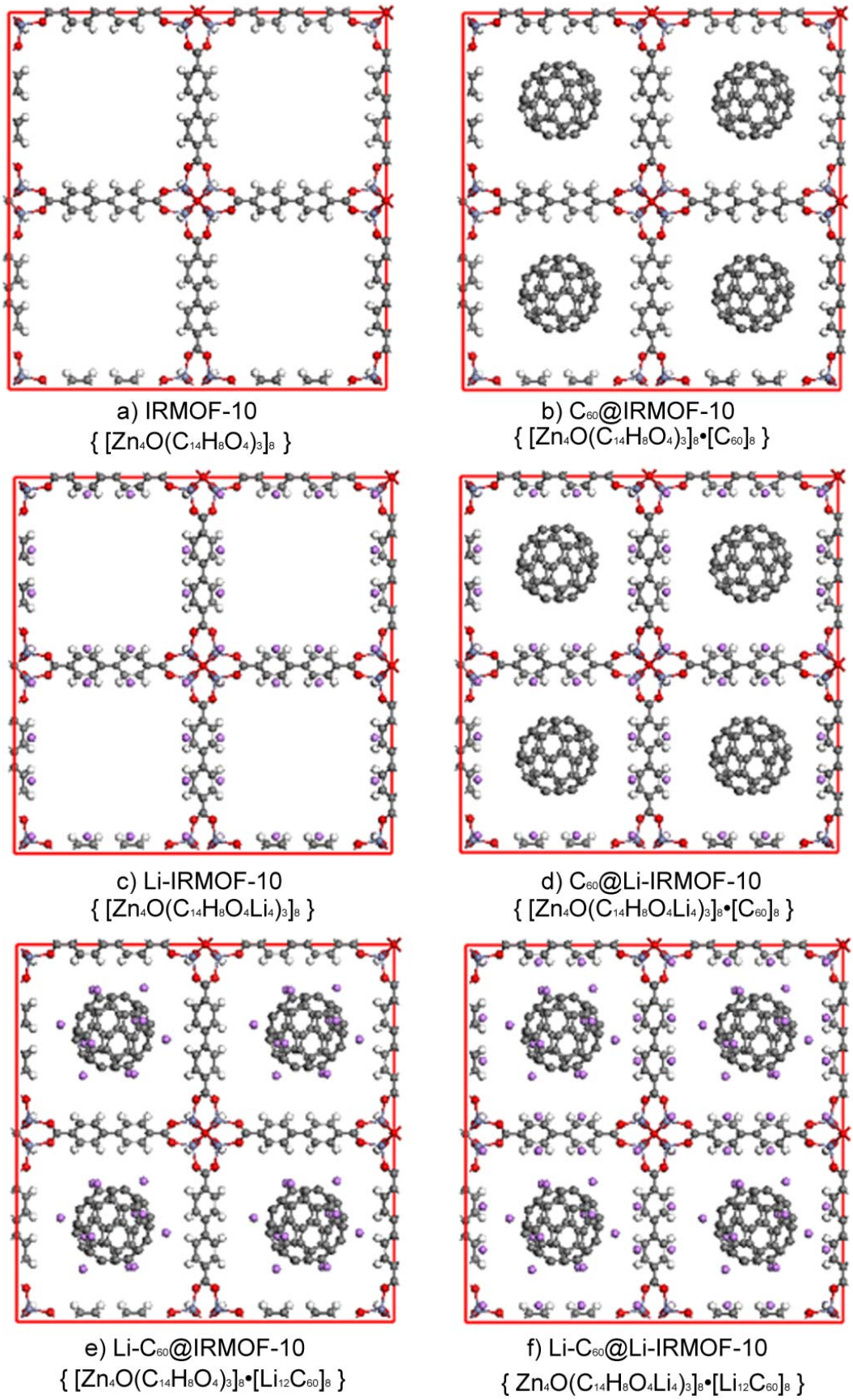

Figure S2. The structures and the chemical composition of all the sorbents under study.

S2. Molecular force field

Classical force field plays an important role in molecular simulations. We carried out DFT calculations with Gaussian 03[2] at the level of X3LYP/6-311G** to determine the interaction potential between H_2 and Li-coated-fullerene as shown in Figure S3.

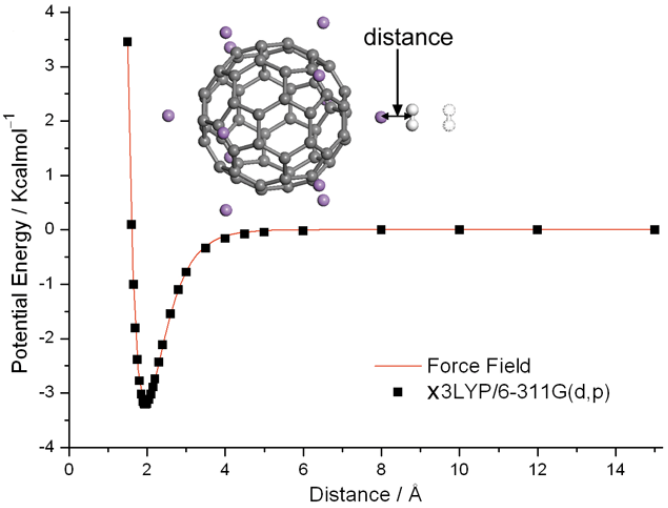

Figure S3. Comparison of the DFT calculations and fitted force field. Lithium atom was oriented vertically to the bond of hydrogen molecule. The abscissa is the distance between Li and the center of mass of H_2.

Such a computational method is expected to yield an accurate description of van der Waals interaction.[3] It should be noted from our calculations that the binding energy for Li adsorbed on the five-member ring is larger than that for Li on the six-member ring, which is consistent with previous theoretical[4] and experimental studies.[5] The Morse pair potentials Eq. (S1) were used to fit the results.

$$U_{ij}(r_{ij}) = D\left\{\exp\left[\alpha(1-\frac{r_{ij}}{r_o})\right] - 2\cdot\exp\left[\frac{\alpha}{2}(1-\frac{r_{ij}}{r_o})\right]\right\}, \qquad \text{Eq. (S1)}$$

where the parameter D is the well depth, r_0 is the equilibrium bond distance, and α is the force constant.

All the force field parameters are given in Table S1.

Table S1: Force field parameters employed in present work. Li_ indicates the atom type of lithium coated on fullerenes and C_C60 means the carbon atom of fullerenes.

Term	D (kcal/mol)	r_0 (Å)	α
C---H_A[a]	0.10082	3.12022	12.00625
H_---H_A[a]	0.00087	3.24722	12.00625

H_A---H_A[a]	0.01815	3.56980	10.70940
O---H_A[a]	0.02515	3.32249	12.00187
Zn---H_A[a]	0.12447	2.76130	13.41420
Li---H_A[a]	2.15752	2.01844	7.12510
Li_--- H_A	1.59671	1.99390	7.94047
Li_--- C_C60	11.00832	2.11431	6.36085

[a]Data from ref. 6.

S3. Mechanism of hydrogen sorption

The binding energies of H_2 with the Li atoms decorated on both C_{60} and the organic linkers (investigated representatively by $C_{12}H_{10}$ molecule) of IRMOF-10 were calculated at the level of X3LYP/6-311G** as well (see Table S2).

Table S2: Binding energy per *A* (H_2 molecule or Li atom)

A…*B*	Binding energy (eV)	ref. 7 (eV)
H_2…$Li_{12}C_{60}$	0.117	0.06~0.18
H_2…$Li_4C_{12}H_{10}$	0.126	-
Li…C_{60}	1.632	1.78

For Li doping on the five-member ring of C_{60} and on the aromatic ring of $C_{12}H_{10}$, we have found significant charge transfer from Li atoms to the nearest C atoms (Table S3).

Table S3: Charge transfer per atom for Li doping

Atom type	Charge Transfer	
	this work	ref. 4
Li ($Li_{12}C_{60}$)	+0.37 e	+0.38 e
C ($Li_{12}C_{60}$)	-0.073 e	-0.077 e
Li ($Li_4C_{12}H_{10}$)	+0.32 e	-
C ($Li_4C_{12}H_{10}$)	-0.106 e	-

Moreover, charge distribution is important to understand the mechanism of hydrogen sorption. Figure S4 and S5 display the charge density redistributions of hydrogen adsorbed on $Li_{12}C_{60}$ and organic linkers of Li-IRMOF-10 ($Li_4C_{12}H_{10}$), respectively. It is clear that the adsorbed H_2 molecules are polarized, which can be

attributed to the positive point charge of Li atoms (Table S3)

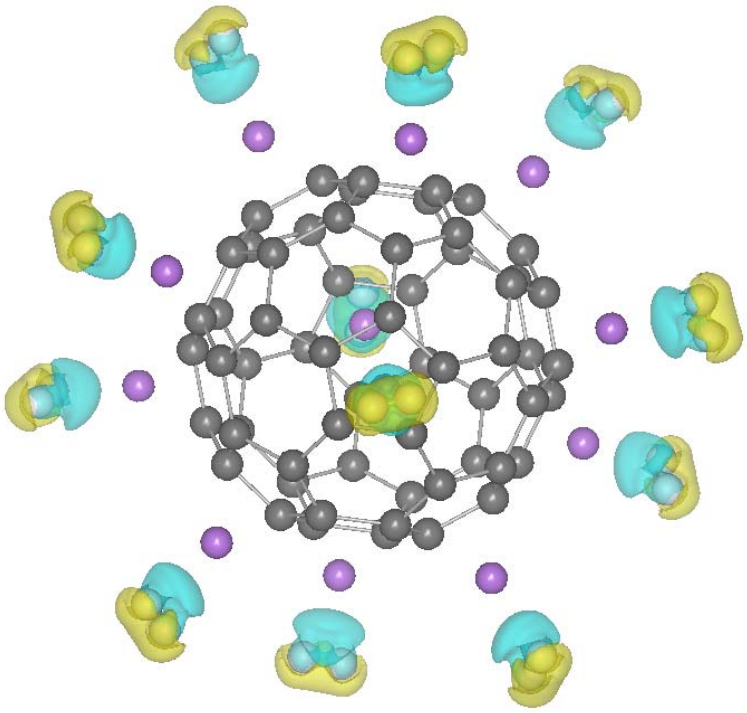

Figure S4. Charge density difference for the interaction of H_2 with $Li_{12}C_{60}$. Blue represent charge gain distribution, yellow is for charge loss.

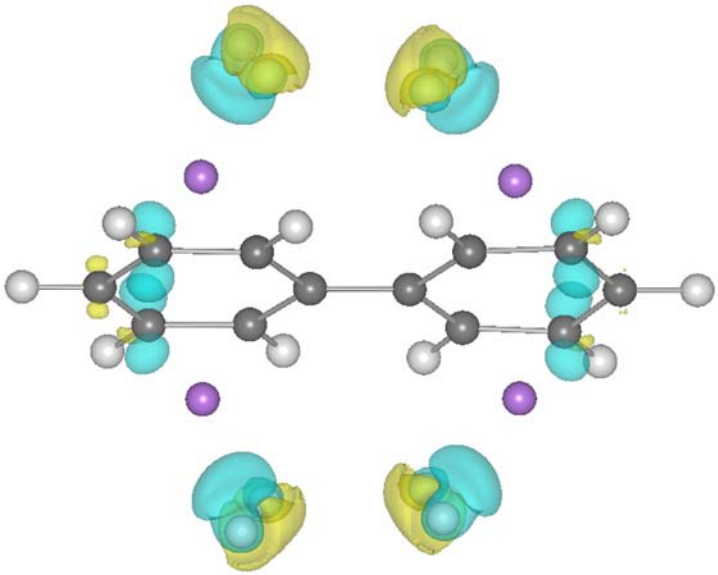

Figure S5. Similar to figure S4 but for the interaction of H_2 with Li modified organic linker (representatively $Li_4C_{12}H_{10}$) of IRMOF-10.

S4. Simulation details

We used Materials Studio Modeling 5.5[8] to calculate the properties of the materials under investigation. The lattice parameters of IR-MOF10 took the

experiment date.[1] The structural stability was examined through geometric optimization with Forcite module.[7] The Connolly surface area and free volume were calculated using the "Atom, Volumes and Surface" module with the grid interval of 0.25 Å and radius of 1.82 Å (Table S4). The Connolly surface[9] is generated by rolling a spherical probe of a specified radius over the van der Waals surface.

Table S4: The density, Connolly surface area and free volume of materials.

	Density (gcm^{-3})	Surface area (m^2cm^{-3})	Free volume (cm^3cm^{-3})
IRMOF-10	0.329	1216	0.860
C_{60}@ IRMOF-10	0.567	1928	0.762
Li-C_{60}@ IRMOF-10	0.594	2210	0.728
Li-IRMOF-10	0.357	1516	0.807
C_{60}@Li-IRMOF-10	0.594	2229	0.707
Li-C_{60}@Li-IRMOF-10	0.622	2582	0.668

Grand Canonical Monte Carlo (GCMC) was employed to study the performance of H_2 storage capacity. For hydrogen adsorption simulation, we used DREIDING force field[10] and force field parameters derived from our DFT calculations. 6000000 Monte Carle steps were constructed to simulate each point on the isotherm, in which the first 3000000 steps were for equilibration and the remains were production steps. The simulation data are the absolute amount of the gas molecules adsorbed, while the experimental results are the excess amount of the gas molecules adsorbed; however, the latter can be transformed as follows:[11]

$$N_{ex} = N_{abs} - V_g \rho_g . \qquad \text{Eq. (S2)}$$

Figure S6-S11 shows the sorption snapshots of Li-C_{60}@Li-IRMOF-10 at different temperatures and pressures.

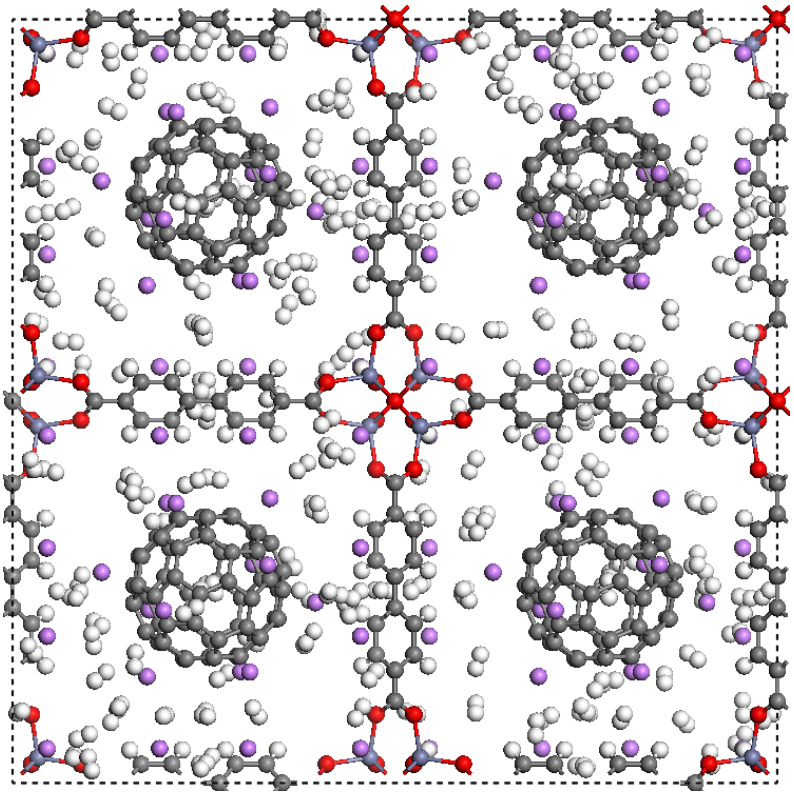

Figure S6. The hydrogen sorption snapshots of Li-C_{60}@Li-IRMOF-10 at 243 K and 2 bar. (Zn purple, O red, C gray, Li pink, H atoms of IRMOF-10 white, density of adsorbed H_2 red dots)

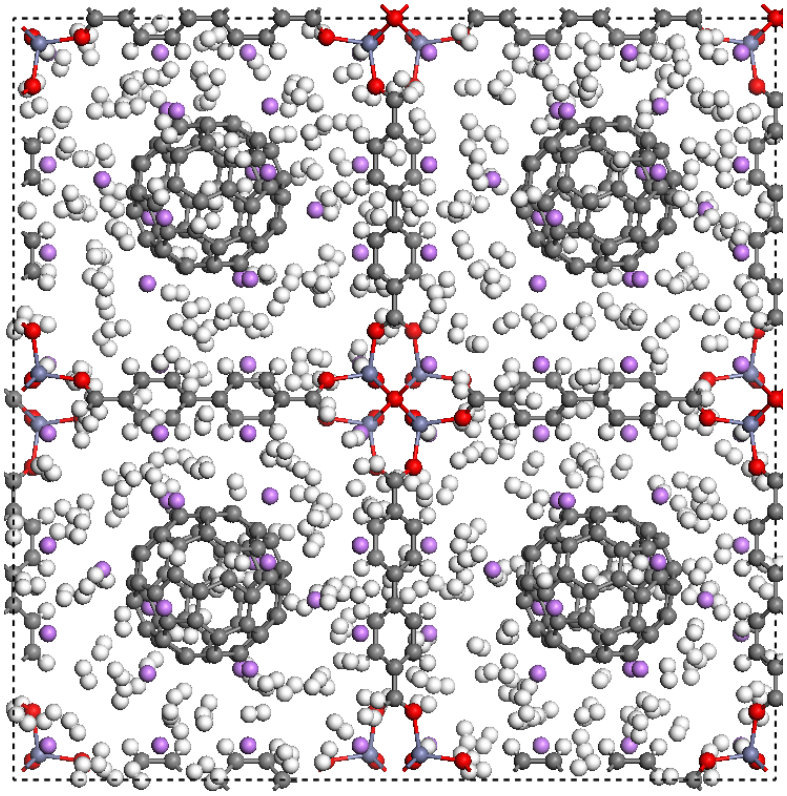

Figure S7. The hydrogen sorption snapshots of Li-C_{60}@Li-IRMOF-10 at 243 K and 20 bar.

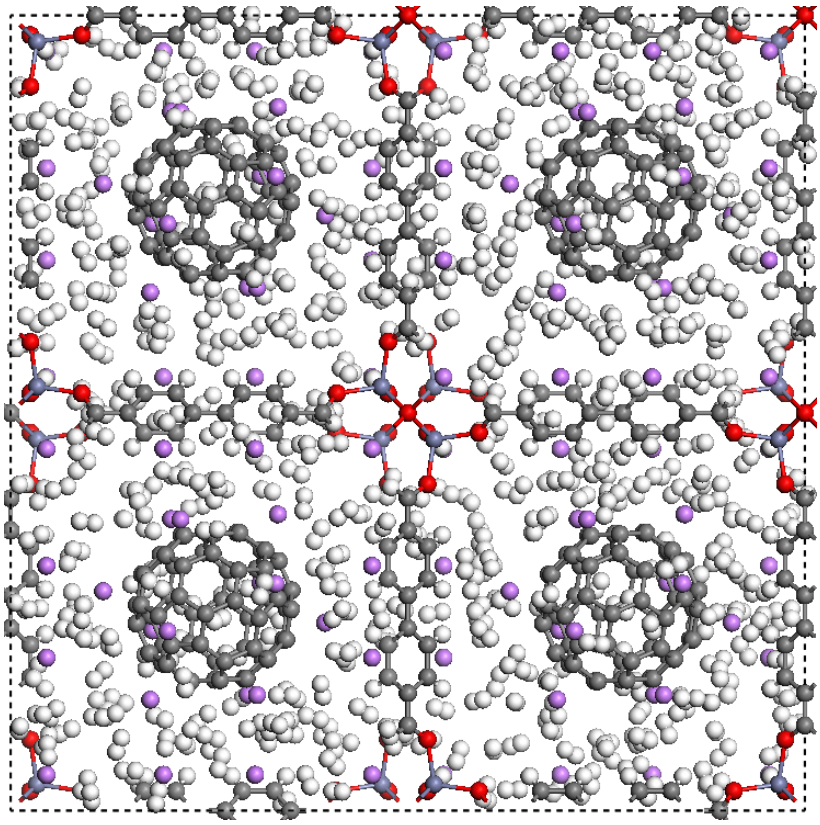

Figure S8. The hydrogen sorption snapshots of Li-C_{60}@Li-IRMOF-10 at 243 K and 100 bar.

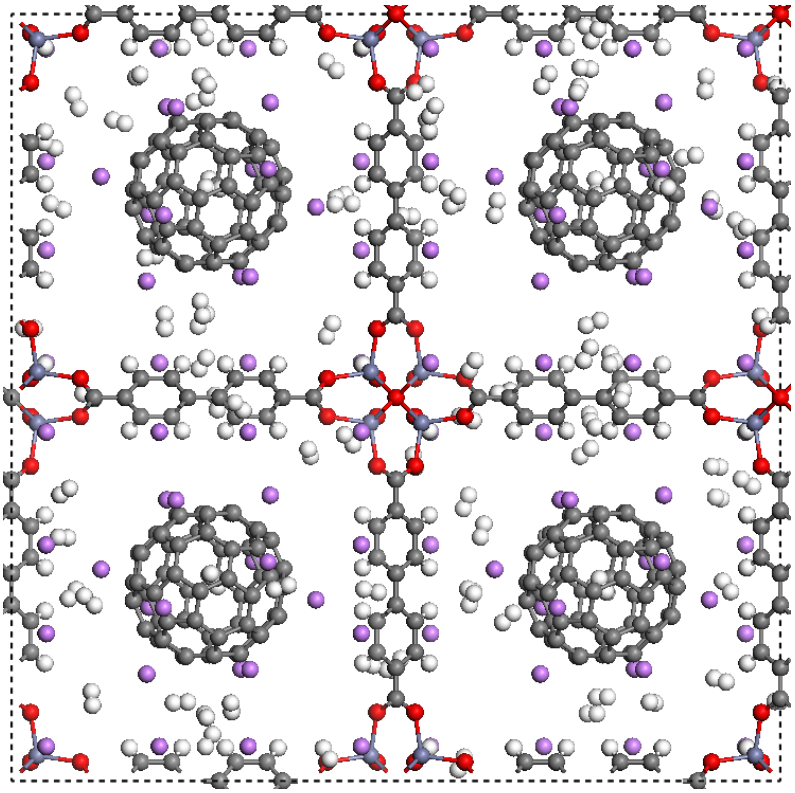

Figure S9. The hydrogen sorption snapshots of Li-C_{60}@Li-IRMOF-10 at 298 K and 2 bar.

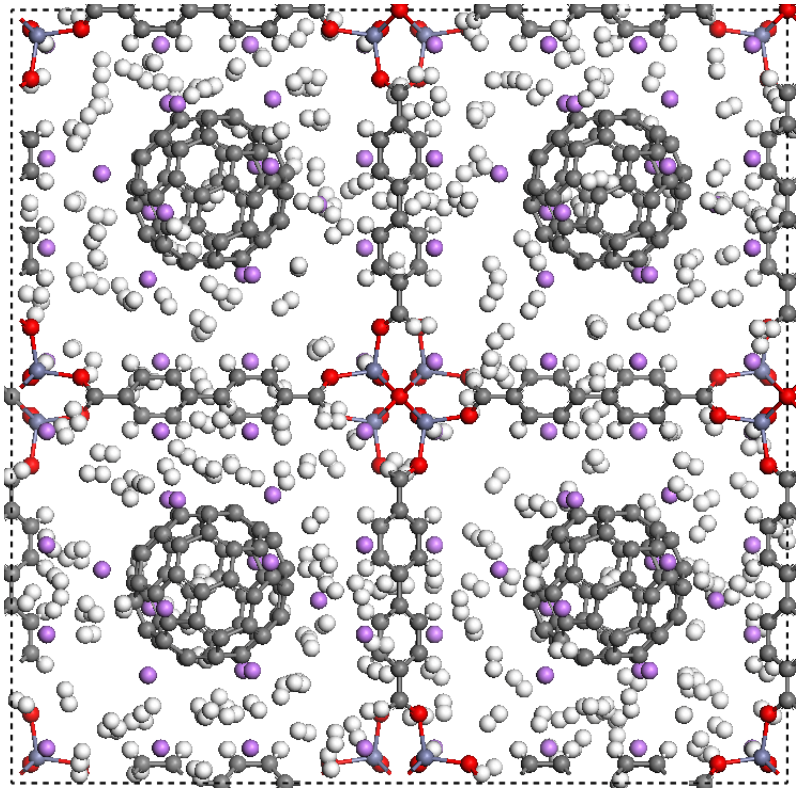

Figure S10. The hydrogen sorption snapshots of Li-C_{60}@Li-IRMOF-10 at 298 K and 20 bar.

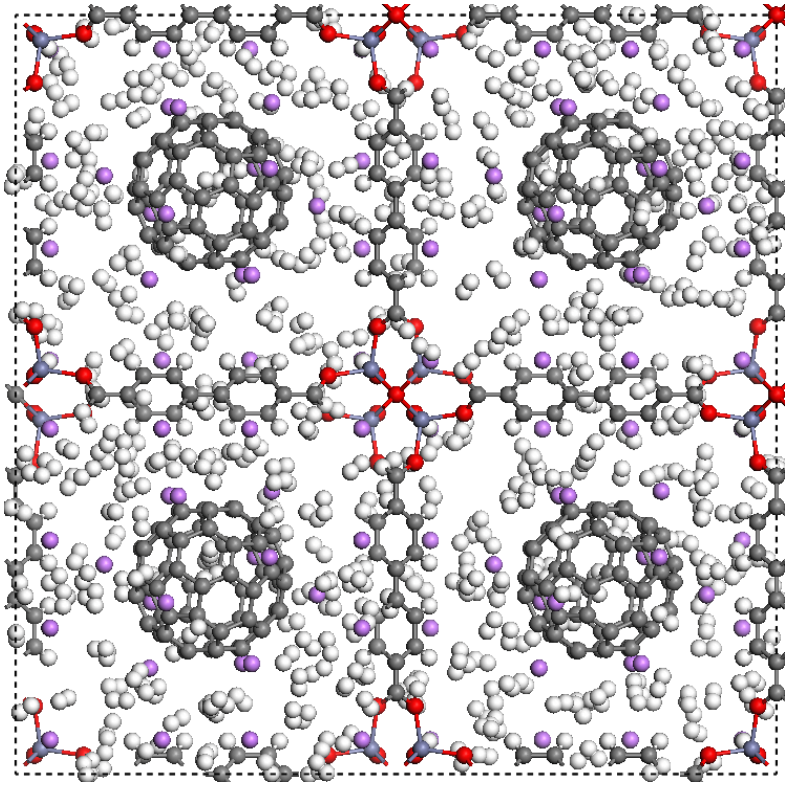

Figure S11. The hydrogen sorption snapshots of Li-C_{60}@Li-IRMOF-10 at 298 K and 100 bar.

References

[1]. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.

[2]. Gaussian 03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N.Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford, CT, 2004.

[3]. X.Xu and W. A. Goddard, *Proc. Nat. Acad. Sci. U.S.A.*, 2004, **101**, 2673.

[4]. D. Ö stling and A. Rosén, *Chem. Phys. Lett.*, 1996, **256**, 109.

[5]. U. Zimmermann, N. Malinowski, A. Burkhardt and T. P. Martin, *Carbon*, 1995, **33,** 995.

[6]. S. S. Han and W. A. Goddard, *J. Am. Chem. Soc.*, 2007, **129,** 8422.

[7]. Q. Sun, P. Jena, Q. Wang and M. Marquez, *J. Am. Chem. Soc*., 2006, **128**, 9741.

[8]. The Materials Studio 5.5 program (Accelrys, San Diego).

[9]. M. L. Connolly, *J. Appl. Cryst.*, 1983, **16**, 548.

[10]. S. L. Mayo, B. D. Olafson and W. A. Goddard, *J. Phys. Chem.*, 1990, **94**, 8897.

[11]. H. Frost, T. Düren and R. Q. Snurr, *J. Phys. Chem. B*, 2006, **110**, 9565.