Supporting Information

New Li-doped fullerene-intercalated phthalocyanine covalent organic frameworks designed for hydrogen storage

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The supporting file describes the Li-H force field parameters derived from the first-principles calculations.

To determine the interactions between the doped Li ions and hydrogen molecules, we considered a fullerene (C_{30}, C_{36}, C_{60} or C_{70}) doped with one Li atom to which one H_2 molecule was bonded (as seen in Fig. S1). Then the interaction between the Li cation and H_2 was derived from high quality first-principles calculation, PW91/6-311g** (implemented by Gaussian 03 code[1]), with the basis set superposition error correction. Finally, the force field parameters for the Li-H_2 interaction were obtained by fitting the interaction energies between H_2 and the doped Li atom to the Lennard-Jones (LJ) potential :

$$V_{LJ}(r_{ij}) = 4\varepsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^{6}] \qquad \text{(S1)}$$

here, r_{ij} is the distance between atoms i and j. The parameters ε_{ij} and σ_{ij} are the energy well depth and vdW radius, respectively.

The fitted force field parameters for H_2 interaction with Li cations are σ = 1.81 Å; ε = 1.85 Kcal/mol. Fig. S2 displays the Li-H_2 interaction energies obtained from both the first-principles calculation and the fitted force field. Apparently, the potential energies from our force fields are in good agreement with those from first-principles calculations. According to our results, the binding energy between H_2 and a Li cation is about 3.70 kcal/mol, which is comparable to the previously reported 4.15 kcal/mol calculated at the MP4/6-311g** level for the average binding energy of one Li^+ binds seven H_2 molecules.[2]

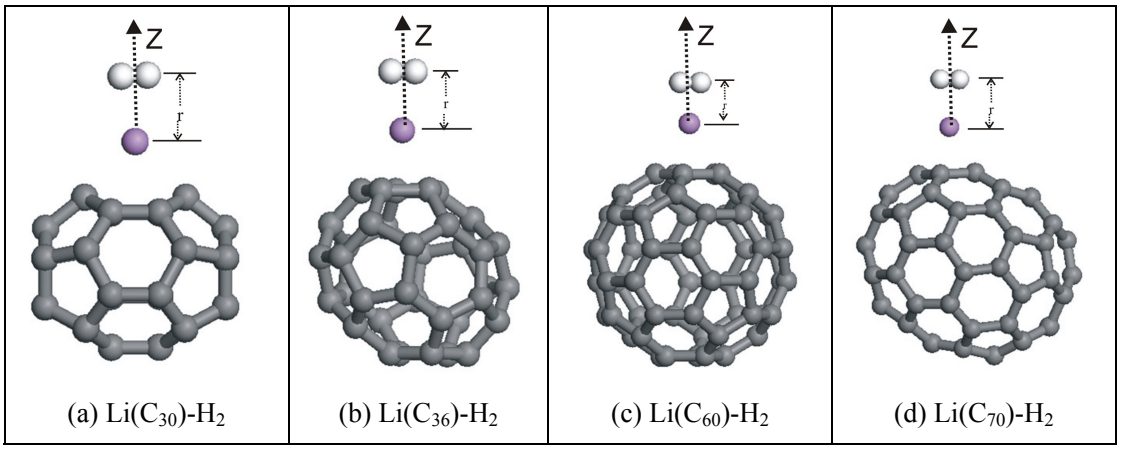

Fig. S1. The models of a fullerene (C_{30}, C_{36}, C_{60} or C_{70}) doped with one Li atom to which one H_2 molecule was bonded. The r denotes the distance between Li dopant and the center of mass of H_2.

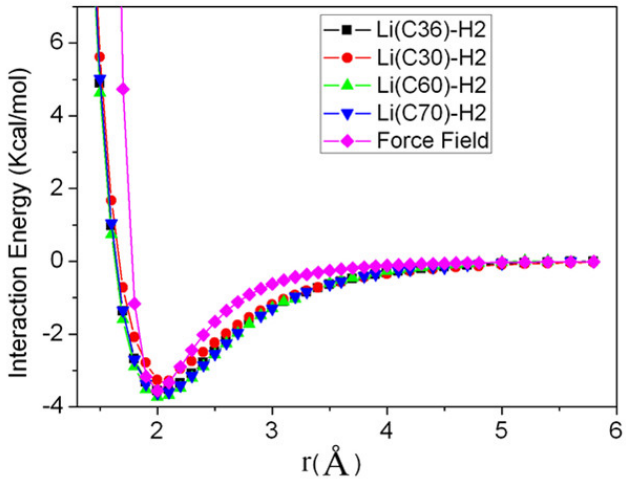

Fig. S2. The interaction energies between H_2 molecule and Li dopant on fullerenes (C_{30}, C_{36}, C_{60} or C_{70}) as a function of the distance (r) between Li and the mass center of H_2 derived from our first-principles calculations and force-field fitting, respectively.

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2 M. Barbatti, G. Jalbert and M. A. C. Nascimento, *J. Chem. Phys.*, 2001, **114**, 2213-2218.