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\textsubscript{2} molecule was bonded (as seen in Fig. S1). Then the interaction between the Li cation and H\textsubscript{2} was derived from high quality first-principles calculation, PW91/6-311g** (implemented by Gaussian 03 code\textsuperscript{1}), with the basis set superposition error correction. Finally, the force field parameters for the Li-H\textsubscript{2} interaction were obtained by fitting the interaction energies between H\textsubscript{2} and the doped Li atom to the Lennard-Jones (LJ) potential:

\[ V_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \]  

where, \( r_{ij} \) is the distance between atoms \( i \) and \( j \). The parameters \( \varepsilon_{ij} \) and \( \sigma_{ij} \) are the energy well depth and vdW radius, respectively.

The fitted force field parameters for H\textsubscript{2} interaction with Li cations are \( \sigma = 1.81 \) Å; \( \varepsilon = 1.85 \) Kcal/mol. Fig. S2 displays the Li-H\textsubscript{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\textsubscript{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\textsuperscript{+} binds seven H\textsubscript{2} molecules.\textsuperscript{2}
Fig. S1. The models of a fullerene (C₃₀, C₃₆, C₆₀ or C₇₀) doped with one Li atom to which one H₂ molecule was bonded. The r denotes the distance between Li dopant and the center of mass of H₂.

Fig. S2. The interaction energies between H₂ molecule and Li dopant on fullerenes (C₃₀, C₃₆, C₆₀ or C₇₀) as a function of the distance (r) between Li and the mass center of H₂ derived from our first-principles calculations and force-field fitting, respectively.
