

## Supporting Information

### High Capacity Hydrogen Storage in Porous Aromatic Frameworks with Diamond-like Structure

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The structure parameters of PAFs and partial computational details are available in the Supporting Information.

#### S1. The structure parameters of PAFs-301, -302, -303, 304

The structure parameters of PAFs-301, -302, -303, 304 are listed in **Table S1**

**Table S1** Unit cell parameters, mass, density and free volume of 3D PAFs

materials	a=b=c (Å)	chemical formula	mass (g/mol)	density (g/cm <sup>3</sup> )	free volume (%) <sup>a</sup>
PAF-301	13.7651	C <sub>104</sub> H <sub>64</sub>	1313.65	0.8364	40.92
PAF-302	23.7195	C <sub>200</sub> H <sub>128</sub>	2531.22	0.3150	77.60
PAF-303	33.8037	C <sub>296</sub> H <sub>191</sub>	3747.77	0.1611	87.50
PAF-304	43.5504	C <sub>392</sub> H <sub>256</sub>	4966.34	0.0998	92.10

<sup>a</sup> The free volume is the accessible volume of H<sub>2</sub> within one unit cell. It is accessible if the potential energy of the interaction between H<sub>2</sub> and the solid framework is less than 10<sup>4</sup> K

## S2. The computational details

### S2.1 The first-principles calculations

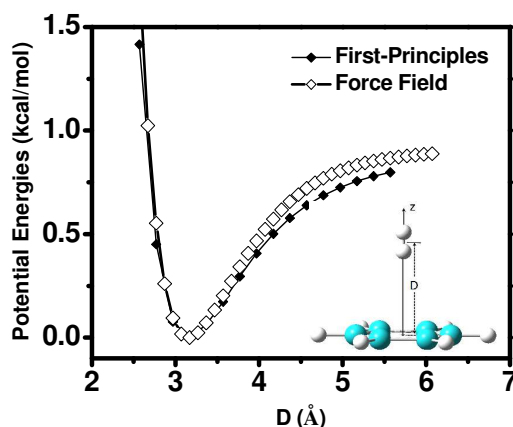
The four 3D frameworks studied here are mainly composed of the phenyls and carbon atoms which tetrahedrally bond together with another four carbon atoms. The potential energies between H<sub>2</sub> and the PAFs were calculated at the Møller–Plesset second-order perturbation (MP2) method with the Gaussian 03 program package,<sup>2</sup> and the cc-PVTZ (correlation consistent polarized Valence Double Zeta) basis set was chosen for all the atoms. Since the MP2 calculation is impractical for realistic PAFs systems, therefore, two clusters (i.e. C<sub>6</sub>H<sub>6</sub> and C<sub>5</sub>H<sub>12</sub> clusters) were adopted here to represent the atom types in the four 3D frameworks (see **Ref. 1** for details). These first-principles theoretical methods are expected to give reliable predictions at present. As an illustration, Figure S1 displays the calculated interaction energies between H<sub>2</sub> and the C<sub>6</sub>H<sub>6</sub> cluster. Using the calculated first-principles results, the non-bond interaction items can thus be determined in next section.

### S2. 2 Fitting and Parameterization of the Force Field

In this section, the interaction between H<sub>2</sub> and the PAFs were parameterized by the Morse potential as below,

$$U_{ij}(r_{ij}) = D[x^2 - 2x], x = \exp\left(-\frac{\gamma}{2}\left(\frac{r_{ij}}{r_e} - 1\right)\right) \quad (1)$$

Here,  $r_{ij}$  is the distance between atom i and atom j in Å.  $D$ ,  $\gamma$  and  $r_e$  are the required force field parameters, representing the well depth, stiffness (force constant) and equilibrium bond distance, respectively. The H<sub>2</sub> molecules are treated as diatomic ones. The achieved parameters are given in Table 1. It is found from Figure S1 that the fitted Morse force fields for the interaction between H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> cluster are in satisfying agreement with the potential energies derived from the first-principles calculations.



**Figure S1** Potential energies of H<sub>2</sub> on C<sub>6</sub>H<sub>6</sub> derived from the first-principles calculations and our force fields, respectively.

### S3. GCMC Simulation

The adsorption of H<sub>2</sub> in the designed PAFs was investigated by the GCMC simulations, in which the temperature, volume and chemical potential are specified previously. The periodic boundary conditions were applied in all three dimensions. The cutoff radius was set to 5 times the collision diameter. In our GCMC simulations, the 2×2×2 supercells were adopted as the simulation boxes. Moreover, the Widom's test particle insertion method in a NVT ensemble was used to bridge the relationship between chemical potential and pressure. The detailed description can be referred to in the literature.<sup>3</sup>

### References:

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