Electronic Supplementary Information for

Lithium Doping on 2D Squaraine-Bridged Covalent Organic Polymers for Enhancing Adsorption Property: A Theoretical Study

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Computational Details

DFT calculations.
We computed Li-modified formation energies ($\Delta E$) via equation (1),

$$\Delta E = E_{SQ\cdot COP\cdot Li} - E_{SQ\cdot COP} - nE_{Li}$$

and Li-O bond energy $\Delta E_{Li-O}$ via equation (2),

$$\Delta E_{Li-O} = \frac{E_{SQ\cdot COP\cdot Li} - E_{SQ\cdot COP\cdot Li\_remove} - E_{nLi}}{n}$$

where $E_{SQ\cdot COP\cdot Li}$ is the energy of the SQ-COP-Li, $E_{SQ\cdot COP}$ is the energy of the SQ-COP, $E_{SQ\cdot COP\cdot Li\_remove}$ is the energy of SQ-COP-Li with Li removed, $E_{Li}$ is the energy of Li atom in a 20×20×20 Å box, $E_{nLi}$ is the energy of SQ-COP-Li without SQ-COP, $n$ is the number of Li in SQ-COP-Li.

To reproduce atomic chemical states and the electrostatic potential surrounding of SQ-COP and SQ-COP-Li materials, we used well-suited Density Derived Electrostatic and Chemical (DDEC) charges for constructing force fields, which are used in investigating electrostatic interaction of Monte Carlo simulations and bond order of the Li-O bond.1-2

GCMC simulation.
The non-bonded interatomic interaction is modeled as the combination of Lennard-Jones (LJ) and Coulomb potentials between atoms in the framework and the adsorbates

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\frac{\sigma_{ij}}{r_{ij}}\right]^{12} - \left[\frac{\sigma_{ij}}{r_{ij}}\right]^{6} + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}$$

Here, $i$ and $j$ index the interacting atoms, $r_{ij}$ is the distance between atoms $i$ and $j$, $q_i$ and $q_j$ are the partial atomic charges on atoms $i$ and $j$, $\varepsilon$ and $\sigma$ are the LJ parameters, and $\varepsilon_0$ is the vacuum permittivity constant. The $\varepsilon$ and $\sigma$ parameters for the framework atoms were taken from the Dreiding force field,3 except that for lithium, which was taken from universal force field (UFF),4 which has been validated for other Li-doped systems.5 Note that lithium of modification on SQ-COPs materials were seen as the atoms and hold fixed, otherwise lithium ion and dissociative, like traditional doped methods, thus there is not necessary to fit the force field parameters between Li and others atoms. CH$_4$ was represented by the spherical united-atom model,6 while CO$_2$,7 CO$_8$ and H$_2$$_9$ were model as the three-site model, the detailed parameters were listed in Table S1. Note that electrostatic interaction is important on Li-modified system, except CH$_4$, all molecular models use in this work all considers charges. Moreover, the used CO model in this work not only reproduces the vapor-liquid equilibrium curve, the vapor pressure curve, and the bulk density for a wide range of temperatures, but also can provide an experimental dipole moment of 0.112 D. LJ parameters between different atom types were calculated using the Lorentz-Berthelot mixing rules. The long-range electrostatic interactions arising from the presence of atomic partial charges were summed using the method of Ewald. All atoms in the COFs were held fixed during the simulations. Note that electrostatic interaction between adsorbents and adsorbates are not considered in the calculated adsorption isotherm of SQ-COPs,10 but electrostatic interaction of Li-doped system is extremely
important, and the adsorption isotherms of CO\textsubscript{2} and H\textsubscript{2} in SQ-COP were recalculated for comparison with SQ-COP-Li.

Here, we reported the single component adsorption uptakes of CO\textsubscript{2}, CO, H\textsubscript{2} and CH\textsubscript{4} mainly for storage applications at high pressure, it is the total amount adsorbed ($N_{\text{abs}}$) that is of main importance. Besides, the excess amounts ($N_{\text{ex}}$) were used to compare with experimental results

$$N_{\text{ex}} = N_{\text{abs}} - V_p\rho_g$$

(4)

where $V_p$ is the pore volume of material, that helium atom was used as the probe molecules to calculate it.

The selectivity ($S_{A/B}$) for species A relative to B is calculated by equation (5)

$$S_{A/B} = \left(\frac{x_A}{x_B}\right)\left(\frac{y_B}{y_A}\right)$$

(5)

where $x_A$ and $x_B$ are the mole fractions of A and B in the adsorbed phase, respectively, while $y_A$ and $y_B$ are the mole fractions of A and B in the bulk phase, respectively.
Table S1. Non-bonded interaction parameters of adsorbates and adsorbents.

<table>
<thead>
<tr>
<th>Term</th>
<th>$\varepsilon$</th>
<th>$\sigma$</th>
<th>Term</th>
<th>$\varepsilon$</th>
<th>$\sigma$</th>
<th>q</th>
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<tr>
<td>O_adsorbent</td>
<td>48.158</td>
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<td>C_adsorbent</td>
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<td>H_adsorbent</td>
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<tr>
<td>N_adsorbent</td>
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<td>C_CO</td>
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<td>3.636</td>
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<td>0.5168</td>
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<td>Li_adsorbent</td>
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<td>COM_H$_2$$^b$</td>
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<td>CH$_4$</td>
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<td>H_H$_2$</td>
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<td></td>
<td>0.4829</td>
</tr>
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$^a$Pseudo atom in CO, $^b$Center of H$_2$ molecule, $^c$Zero potential.
Figure S1. The electronic density of state (DOS) for (a) SQ-COP1 and (b) SQ-COP3 system with preferred configuration. $E_F$ is the Fermi level.
Figure S2. Adsorption isotherms comparison of SQ-COP and SQ-COP-Li, (a) CO$_2$, (b) CH$_4$, CO and H$_2$ at 298K, and (c) H$_2$ at 77K.
Figure S3. The CO$_2$ adsorption structures on SQ-COP and SQ-COP-Li frameworks.
References


