***SUPPORTING INFORMATION*:**

Highly Selective Adsorption of *p*-Xylene over other C_8 Aromatic Hydrocarbons by Co-CUK-1: A Combined Experimental and Theoretical Assessment

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Contents

Fitting of pure component isotherms in Co-CUK-1

The measured pure component isotherm data for each aromatic molecule was fitted with the single-site Langmuir-Freundlich model:

$$q = q_{sat} \frac{bp^{\nu}}{1 + bp^{\nu}} \tag{1}$$

The saturation capacities q_{sat}, Langmuir- constants b, and the Freundlich exponent ν, are provided in Table S5. It provides a comparison of the experimental isotherm data with the Langmuir-Freundlich fits. The fits are excellent for all four guest molecules.

Let us define, $q_{\mathrm{i,sat}}$, as the saturation capacity of species *i*. The saturation capacities are determined to be:

p-xylene(1), $q_{\mathrm{1,sat}}$ = 2.53 mol kg^{-1}
m-xylene(2), $q_{\mathrm{2,sat}}$ = 1.33 mol kg^{-1}
o-xylene(3), $q_{\mathrm{3,sat}}$ = 1.25 mol kg^{-1}
ethylbenzene(4), $q_{\mathrm{4,sat}}$ = 1.73 mol kg^{-1}

IAST calculations of mixture adsorption equilibrium in Co-CUK-1

We use the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz[1] to determine the adsorption equilibrium for equimolar gas phase 4-component equimolar *p*-xylene(1)/*m*-xylene(2)/*o*-xylene(3)/ethylbenzene(4) mixtures; see Figure 4(a) With increasing total gas pressure, the *p*-xylene loading increases at the expense of its partner molecules. We note that at a total pressure of 100 kPa, the adsorbed phase is rich in *p*-xylene.

Let us define the fractional occupancy within the pores, θ_{t}

$$\theta_t = \sum_{i=1}^{n} \frac{q_i}{q_{i,sat}} \tag{2}$$

where q_{i} is the molar loading of species *i* in the mixture, and $q_{\mathrm{i,sat}}$ is the saturation capacity of species *i*.

Figure S6 shows the calculations of the fractional occupancy, θ_{t}, within the pores of Co-CUK-1 as a function of the total gas phase pressure, p_{t}. We note that the pores are saturated, i.e. $\theta_{\mathrm{t}} \to 1$, when the total pressure p_{t} reaches 100 kPa.

For separation of 4-component equimolar *p*-xylene(1)/*m*-xylene(2)/*o*-xylene(3) /ethylbenzene(4) mixtures we adopt the following definition of selectivity that was used in the recent paper of Torres-Knoop et al.[2]

$$S_{ads} = \frac{(q_3)/(q_1 + q_2 + q_4)}{(p_3)/(p_1 + p_2 + p_4)} = 3\frac{(q_3)}{(q_1 + q_2 + q_4)} \tag{3}$$

Figure S7 shows that the S_{ads} value as a function of the fractional pore occupancy, θ_t. We note that the selectivity value approaches a value of about 50 as $\theta_t \to 1$. The selectivity is strongly in favor of *p*-xylene because of molecular packing effects; this principle has been elucidated in detail in earlier work.[3] The strong, near-exponential increase in the selectivity in favor of *p*-xylene selectivity is a typical characteristic of separations due to molecular packing or entropy effects.

Transient breakthrough simulations

The separation performance of a fixed-bed adsorber is dictated by both adsorption selectivity and capacity. A higher capacity to adsorb p-xylene is a desirable characteristic of SMB adsorbers. Using the pure component isotherm fits of experimental data, we carried out transient breakthrough simulations for Co-CUK-1(MW) using the methodology described in in earlier works.[4,5]

The breakthrough characteristics for any component are essentially dictated primarily by the characteristic contact time $\frac{L}{v} = \frac{L\varepsilon}{u}$ between the crystallites and the surrounding fluid phase. It is common to use the dimensionless time, $\tau = \frac{tu}{L\varepsilon}$, obtained by dividing the actual time, *t*, by the characteristic time, $\frac{L\varepsilon}{u}$ when plotting simulated breakthrough curves. For the breakthrough simulations reported here we use the parameter values: L = 0.3 m; voidage of bed, ε = 0.4; interstitial gas velocity, v = 0.1 m/s; superficial gas velocity, u = 0.04 m/s.

Notation

b	Langmuir-Freundlich constant, $\mathrm{Pa}^{-\nu}$
c_i	molar concentration of species *i* in gas mixture, mol m^{-3}
c_{i0}	molar concentration of species *i* in gas mixture at inlet to adsorber, mol m^{-3}
L	length of packed bed adsorber, m
n	number of components in the mixture, dimensionless
p_i	partial pressure of species *i* in mixture, Pa
p_t	total system pressure, Pa
q_i	component molar loading of species *i*, mol kg^{-1}
q_t	total molar loading for mixture adsorption, mol kg^{-1}
$q_{i,sat}$	molar loading of species *i* at saturation, mol kg^{-1}
Q_i	volumetric loading of species *i* at saturation, mol L^{-1}
ΔQ_i	volumetric separation capacity of species *i* from a mixture, mol L^{-1}
S_{ads}	adsorption selectivity, dimensionless

t	time, s
T	absolute temperature, K
u	superficial gas velocity in packed bed, m s^{-1}
v	interstitial gas velocity in packed bed, m s^{-1}
y_{i}	mole fraction of species *i* in a mixture of species, dimensionless

Greek letters

ε	voidage of packed bed, dimensionless
θ_{t}	fractional occupancy for mixture adsorption, dimensionless
ν	exponent in dual-Langmuir-Freundlich isotherm, dimensionless
τ	time, dimensionless

Subscripts

i	referring to component *i*
t	referring to total mixture

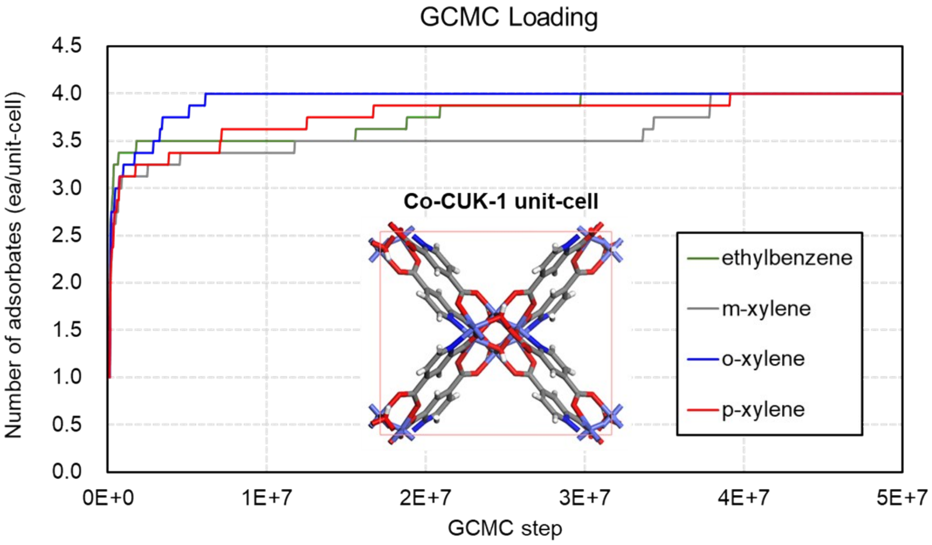

Figure S1. GCMC loading trajectory for each adsorbate molecule in Co-CUK-1 unit-cell.

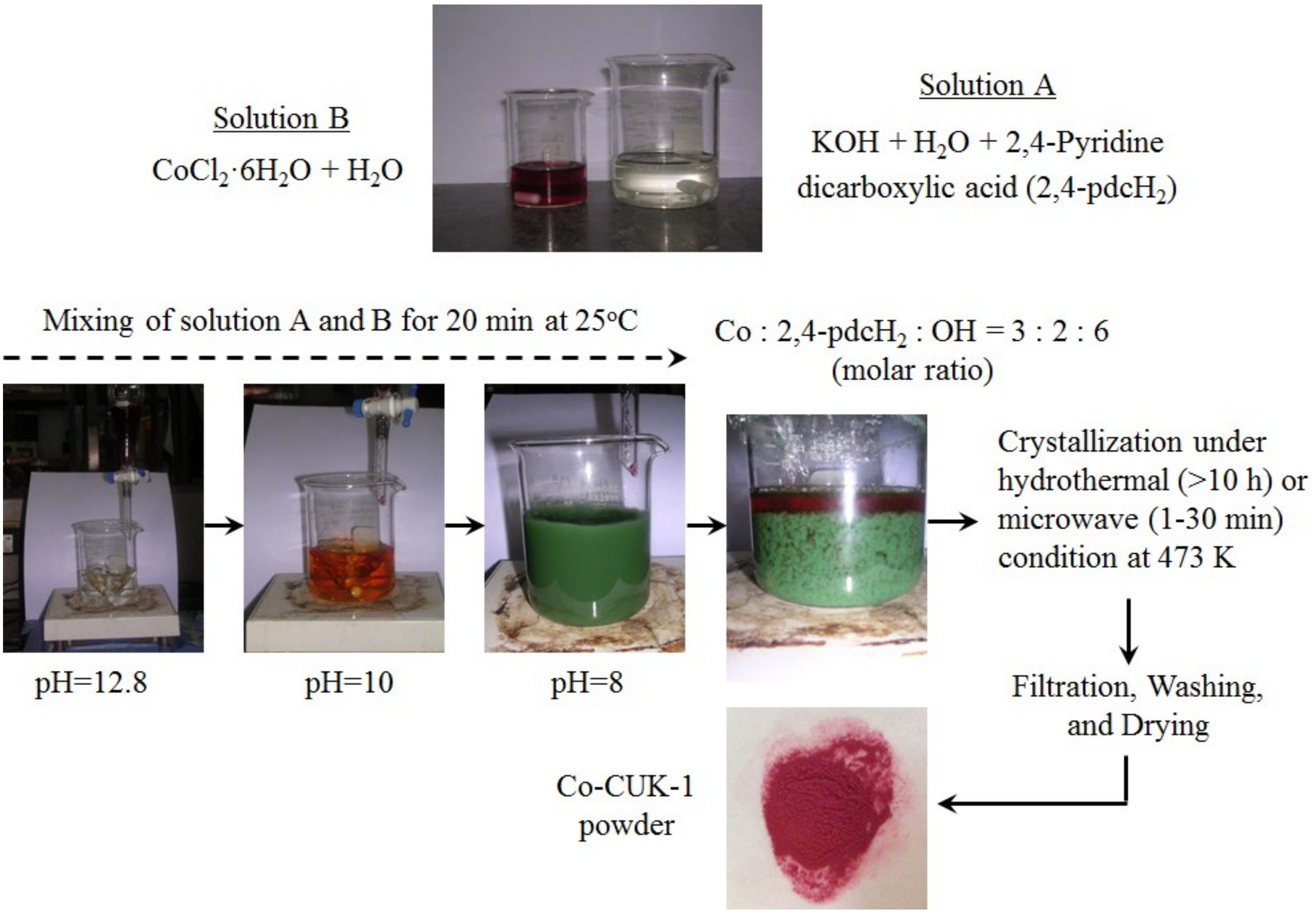

Figure S2. Stepwise pictures according to synthesis steps of Co-CUK-1.

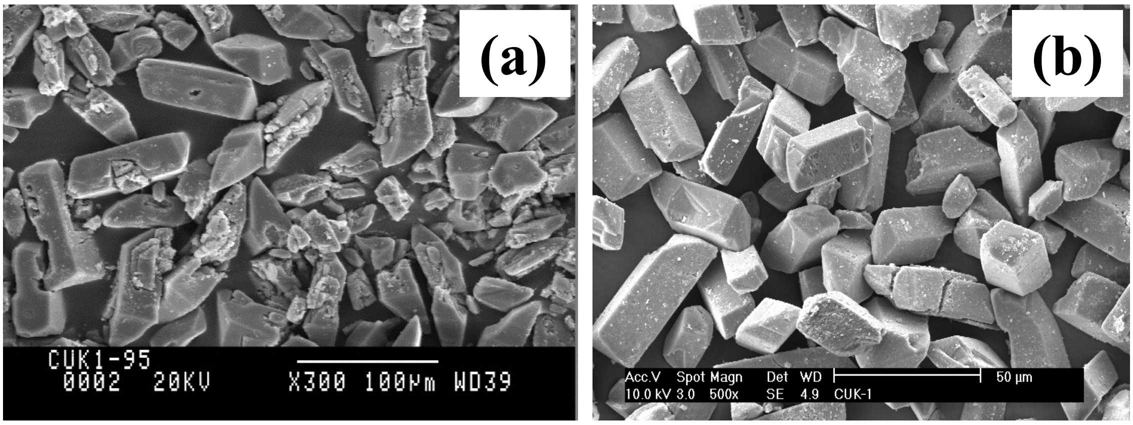

Figure S3. SEM images of (a) Co-CUK-1(HT) and Co-CUK-1(MW).

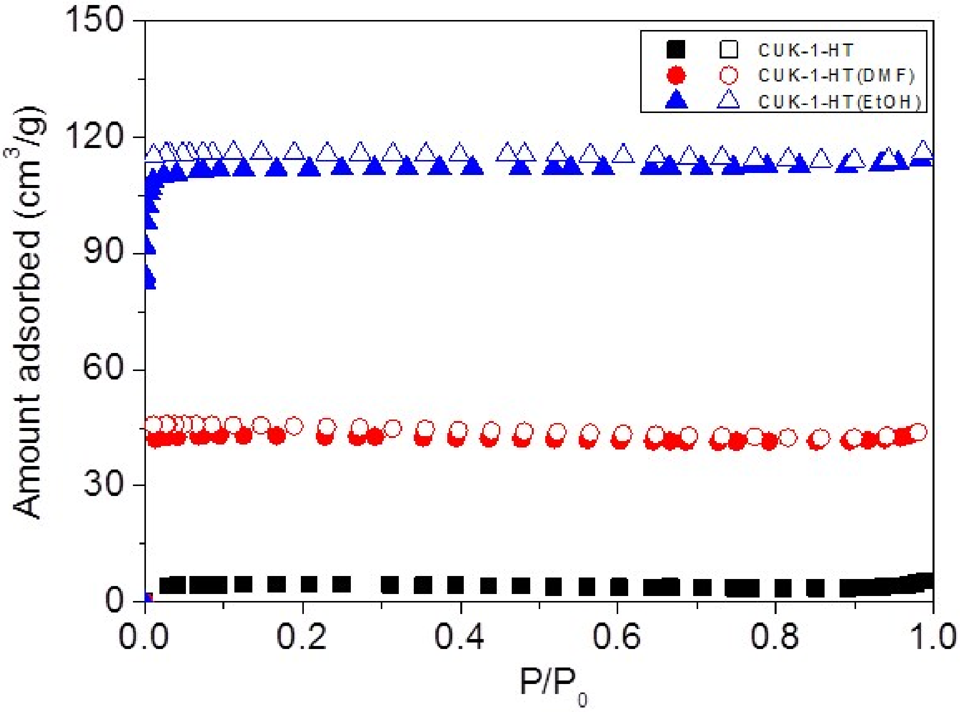

Figure S4. N_2 adsorption isotherms of Co-CUK-1(HT) at 77 K depending on purification with solvents.

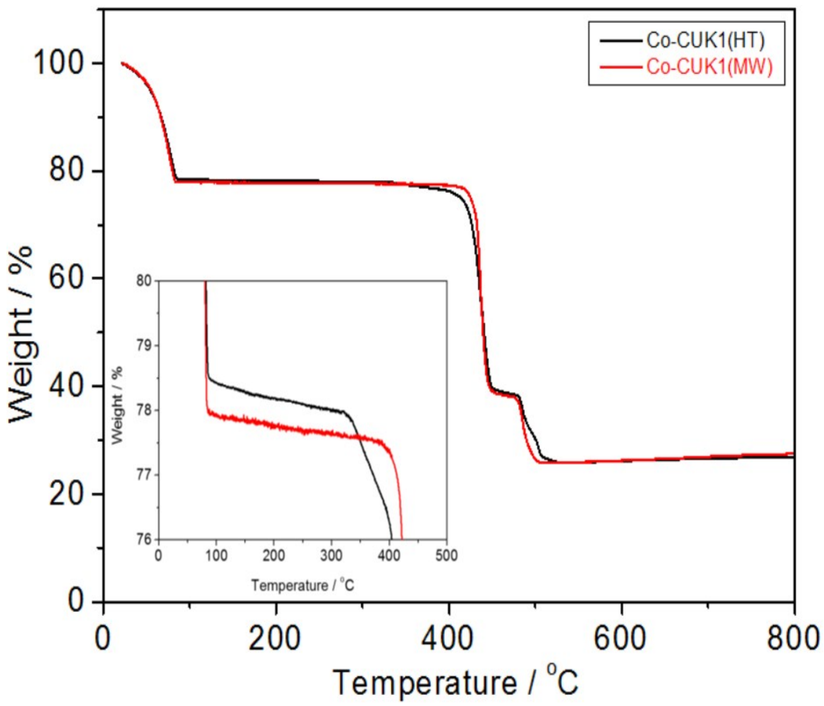

Figure S5. Thermogravimetric profiles of two Co-CUK-1 samples. An inset figure displays a larger weight loss (0.5 wt%) in Co-CUK-1(MW) than that in Co-CUK-1(HT) below 673 K.

	q_{sat} mol kg^{-1}	b Pa^{-v}	v_i dimensionless
p-xylene	2.53	5.74×10^{-2}	0.54
m-xylene	1.33	2.32×10^{-2}	0.72
o-xylene	1.25	1.79×10^{-2}	0.72
ethylbenzene	1.73	5.71×10^{-3}	1

Table S1. Langmuir-Freundlich parameters for C_8 aromatic hydrocarbons at 323 K in Co-CUK-1(MW).

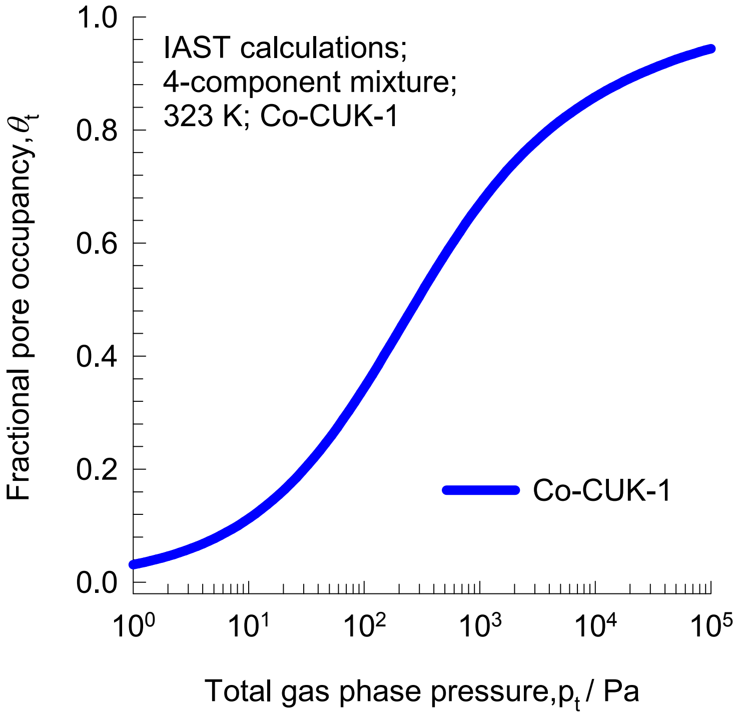

Figure S6. Calculations of the fractional occupancy, θ_t, within the pores of Co-CUK-1(MW) at 323 K as a function of the total gas phase pressure, p_t.

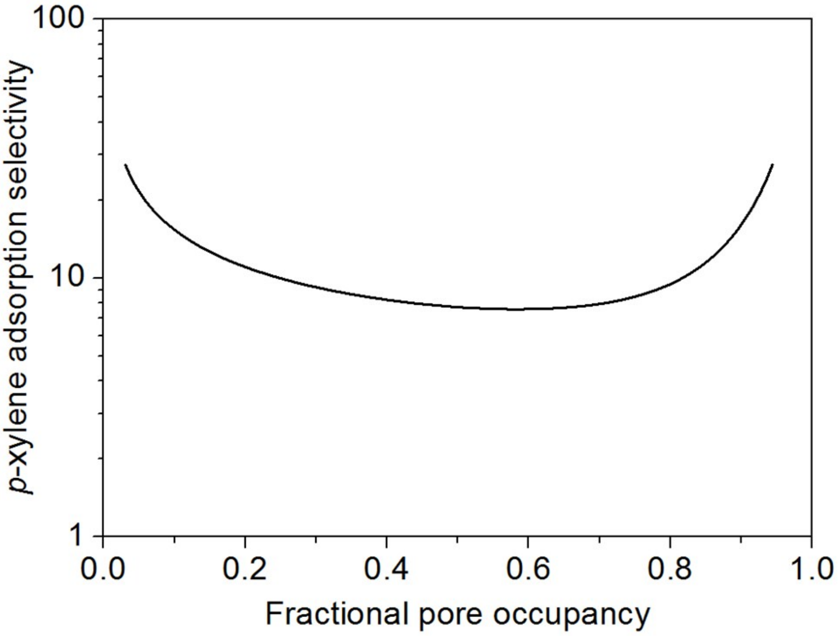

Figure S7. IAST calculations for *p*-xylene adsorption selectivity for 4-component *p*-xylene/*m*-xylene/*o*-xylene/ethylbenzene mixture in Co-CUK-1(MW) at 323 K. The *x*-axis is fractional occupancy, θ_t, within the pores of the MOFs.

Adsorbate	Average Interaction Energy (kcal/mol/molecule) Total / Electrostatic / VdW
p-Xylene	-22.13 / -20.71 / -1.42
m-Xylene	-20.63 / -19.37 / -1.26
o-Xylene	-20.60 / -19.70 / -0.91
ethylbenzene	-20.58 / -19.51 / -1.07

Table S2. Average interaction energy between adsorbate and framework.

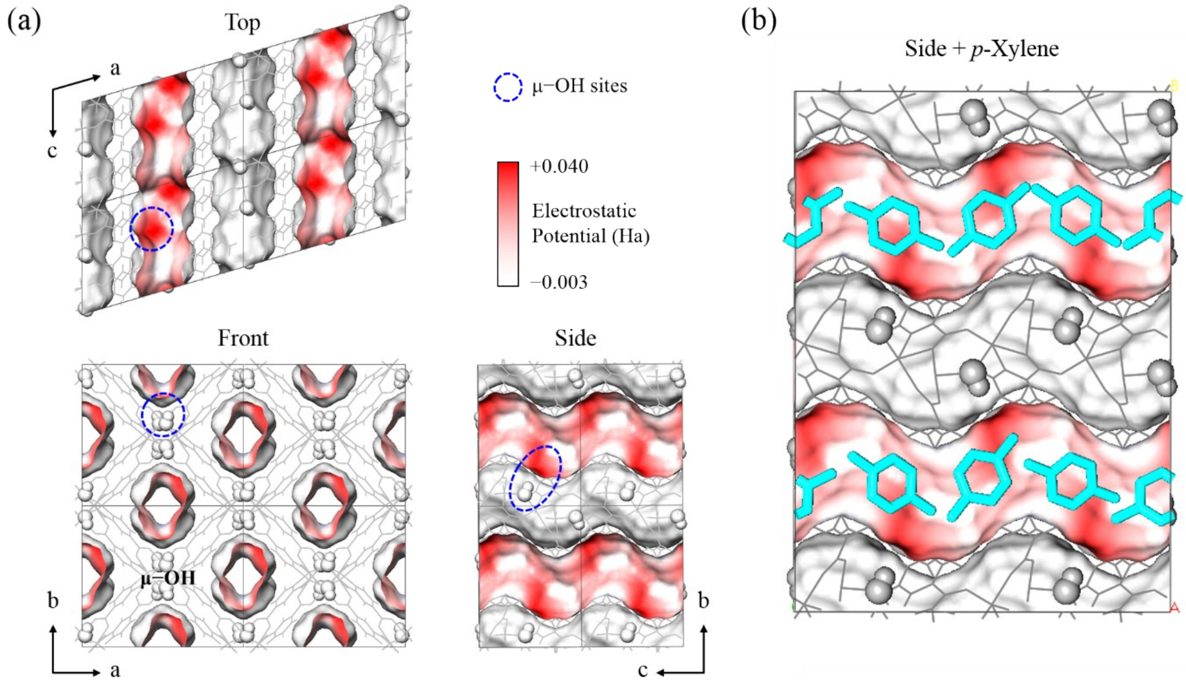

Figure S8. (a) Electrostatic potential map due to the electron density of the Co-CUK-1 framework, which shows highly polarized region due to μ-OH functional groups and (b) Chemical topology of *p*-xylene and its packing structure are suitable for developing adsorbate-framework interaction with highly polarized region.

References

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