# Supporting information (SI)

## Improved Ethanol Adsorption Capacity and Coefficient of Performance for adsorption chillers of Cu-BTC@GO Composite Prepared by Rapid room temperature Synthesis

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**S1. Fourier Transform Infrared (FTIR) Analysis**

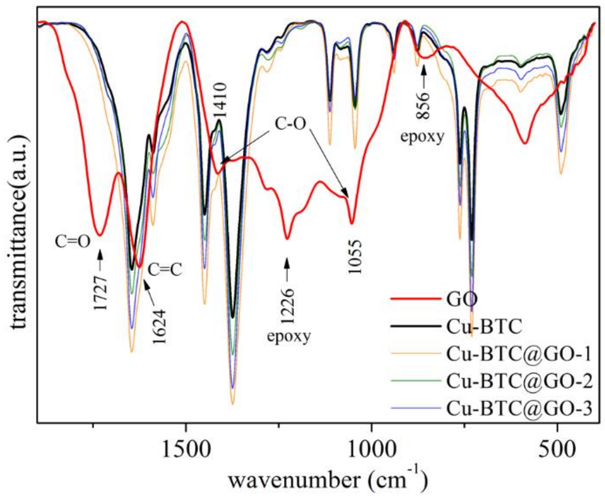


**Fig. S1.** FTIR spectra of Cu-BTC, and the Cu-BTC@GO composites with different GO content.

**S2. Isotherms/Isobars of Ethanol on Cu-BTC@GO and Cu-BTC and Selected MOFs**

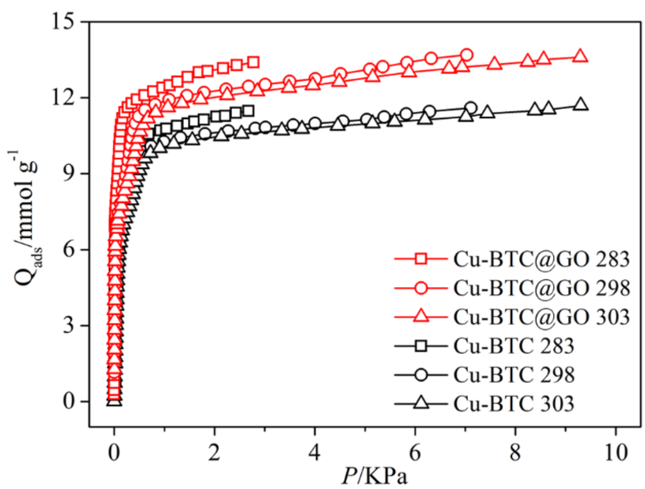


**Fig. S2.** Ethanol adsorption isotherms for the materials at 283 K, 298 K and 303 K.

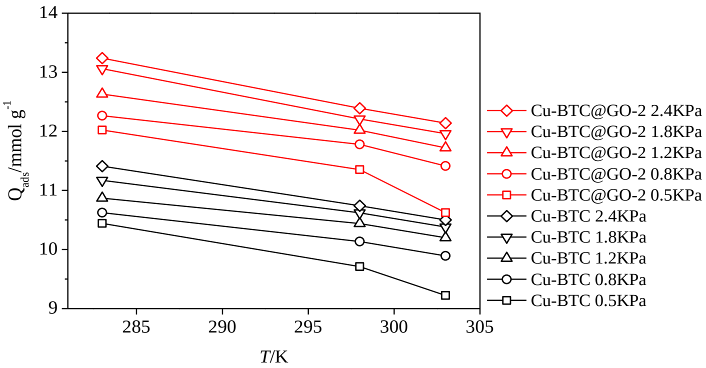


**Fig. S3.** Ethanol adsorption isobars for the materials at 0.5−2.4 KPa.

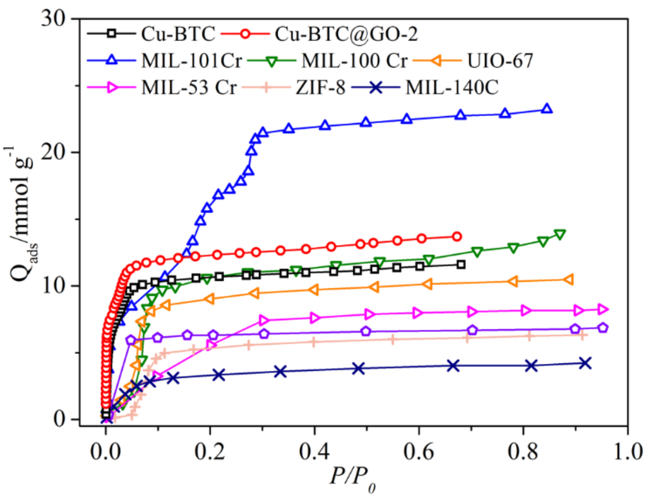


**Fig. S4.** Ethanol adsorption isotherms of different MOFs. (MIL-101 (Cr) [1], MIL-100(Fe) [2], MIL-53[1], ZIF-67[3], ZIF-8[3] and MIL-140c[3] were taken from the literature.

It was clearly visible that at low pressure $P/P_0 < 0.15$, ethanol adsorption capacity of Cu-BTC@GO was higher than those of MIL-101 (Cr), MIL-100(Fe), MIL-53, ZIF-67, ZIF-8 and MIL-140c.

## S3. Employed Operational Temperatures in This Work for the Two Different Applications

Table S1 presents the employed operational temperatures for adsorption refrigeration and ice making. It was noted that in most cases it is chosen to equate $T_{ads}$

to the condenser temperature, $T_{con}$ [4,5]. In this work, the simulation model was based on a basic cycle, and has considered the whole process of heating-desorption-condensing and cooling-adsorption-evaporation. The isosteric cycle diagram of ideal refrigeration cycle was shown in Figure S5, the solid or dashed lines refers the desorption and adsorption process, respectively. The whole process consisted of 4 steps: the first step (*I-II*) of the cycle is isosteric heating, the second step (*II-III*) is isobaric desorption, accompanied by condensing, the third step (*III-IV*) is isosteric cooling, and the final step (*IV-I*) is isobaric adsorption, along with evaporation.

**Table S1**. Applied Operation Temperatures for Adsorption Refrigeration

| | $T_{ev}$/K | $T_{ads}$/K | $T_{con}$/K |
|---|---|---|---|
| Refrigeration | 278 | 303 | 303 |
| Ice making | 268 | 298 | 298 |

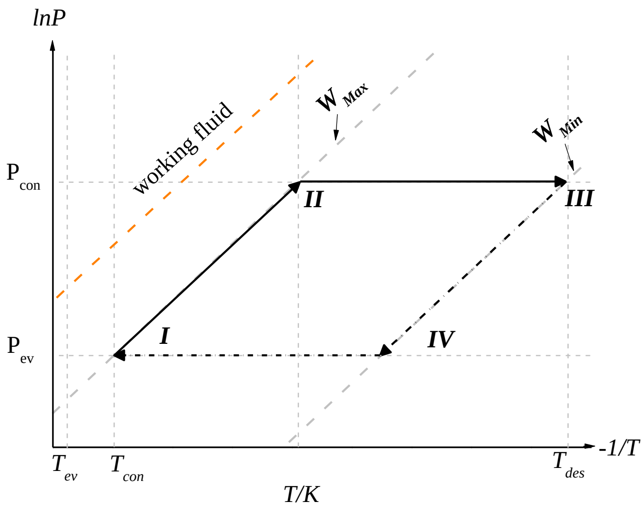


**Fig. S5.** Isosteric cycle diagram of ideal refrigeration cycle and AHP cycle

## S4. Calculation of the Coefficients of Performance (COP)

To calculation of the coefficients of Performance (COP), a so-called characteristic curve needs to be constructed to transfer the loading from two dependent variables ($p$, $T$) to one, the adsorption potential, A, which is the molar Gibbs free energy of adsorption with opposite sign, defined as: [6]

$$A = RT\ln\left(\frac{p_0(T)}{P}\right) \quad \text{(S1)}$$

Here $p_o$ is the temperature-dependent vapor pressure of the adsorbate of choice. The equation means that each combination of pressure ($p$,$T$) can be converted to a single adsorption potential, $A$.

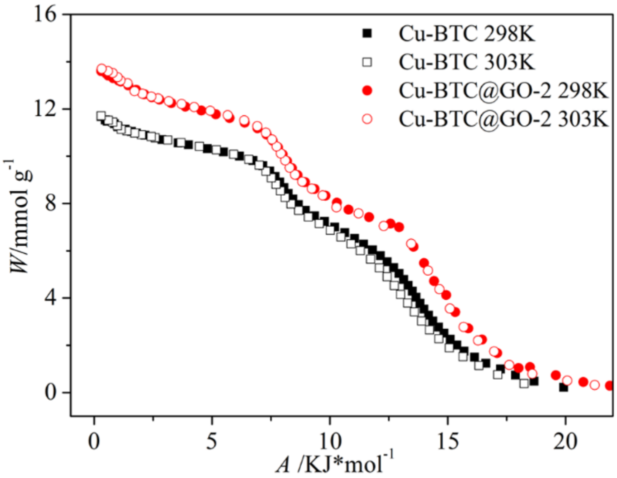


**Fig. S5.** Characteristic curve for ethanol on Cu-BTC@GO and Cu-BTC (298 K and 303 K.)

The COP is defined as the useful energy output divided by the energy required as input. For cooling application, the coefficient of performance becomes:

$$COP_c = \frac{Q_{ev}}{Q_{regen}} \quad \text{(S2)}$$

Here, $Q_{ev}$ is the energy released by evaporator, $Q_{regen}$ is the energy required for regeneration of adsorbent. Simply, $Q_{regen}$ was calculated mainly from the $T_d$, $C_p^{sorbent}$, $W_{max}$, $W_{min}$ and $\Delta H_s$. The specifics on how to exactly calculation these energetic contributions are explained in detail in the reference [3, 5, 6]. It was noted that the specific heat capacity ($C_p^{sorbent}$) was assumed to be 1 J $g^{-1}$ $K^{-1}$ independent of temperature, which is an average value for a variety of MOF materials [5-7]. In fact the effect of actual value of $C_p^{sorbent}$ on calculated COP was negligible [3].

## Reference


(1) Rezk, A.; Al-Dadah, R.; Mahmoud, S.; Elsayed, A., Investigation of Ethanol/metal organic frameworks for low temperature adsorption cooling applications. *Appl. Energy* **2013,** *112*, 1025-1031.

(2) Seo, Y.-K.; Yoon, J. W.; Lee, J. S.; Lee, U. H.; Hwang, Y. K.; Jun, C.-H.; Horcajada, P.; Serre, C.; Chang, J.-S., Large scale fluorine-free synthesis of hierarchically porous iron(III) trimesate MIL-100(Fe) with a zeolite MTN topology. *Microporous Mesoporous Mater.* **2012,** *157*, 137-145.

(3) de Lange, M. F.; Verouden, K. J. F. M.; Vlugt, T. J. H.; Gascon, J.; Kapteijn, F., Metal−Organic Frameworks in Adsorption-Driven Heat Pumps: The Potential of Alcohols as Working Fluids. *Langmuir* **2015,** *31*, 12783-12796.

(4) Van Assche, T. R. C.; Duerinck, T.; Gutiérrez Sevillano, J. J.; Calero, S.; Baron, G. V.; Denayer, J. F. M., High Adsorption Capacities and Two-Step Adsorption of Polar Adsorbates on Copper–Benzene-1,3,5-tricarboxylate Metal–Organic Framework. *J. Phys. Chem. C* **2013,** *117*, 18100-18111.

(5) Cadiau, A.; Lee, J. S.; Damasceno Borges, D.; Fabry, P.; Devic, T.; Wharmby, M. T.; Martineau, C.; Foucher, D.; Taulelle, F.; Jun, C. H.; Hwang, Y. K.; Stock, N.; De Lange, M. F.; Kapteijn, F.; Gascon, J.; Maurin, G.; Chang, J. S.; Serre, C., Design of Hydrophilic Metal Organic Framework Water Adsorbents for Heat Reallocation. *Adv. Mater.* **2015,** *27*, 4775-80.

(6) de Lange, M. F.; Verouden, K. J. F. M.; Vlugt, T. J. H.; Gascon, J.; Kapteijn, F., Adsorption-Driven Heat Pumps: The Potential of Metal–Organic Frameworks. *Chem. Rev.* **2015,** *115*, 12205-12250.

(7) Bae, Y.-S.; Yazaydın, A. Ö.; Snurr, R. Q., Evaluation of the BET Method for Determining Surface Areas of MOFs and Zeolites that Contain Ultra-Micropores. *Langmuir* **2010,** *26*, 5475-5483.