

## Finned hierarchical MOFs supported on cellulose for the selective adsorption of n-hexane and 1-hexene

Xinyang Yin,<sup>a</sup> Jie Zha,<sup>a</sup> Skyler Gregor,<sup>ab†</sup> Shengzhe Ding,<sup>a</sup> Ahmad Alsuwaidi,<sup>a</sup> and Xueyi Zhang<sup>a\*</sup>

a. Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16801.

b. Chemical Engineering Program, Century College, White Bear Lake, MN 55110.

† Current Address: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455.

### Electronic Supplementary Information (ESI)

- Chemicals

Sodium hydroxide and methanol were purchased from EMD Millipore Corporation. (3-aminopropyl) triethoxysilane (APTES) (99%), hexane, 1-hexene, cyclohexane were purchased from Sigma-Aldrich.  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Fisher Science Education, reagent grade), terephthalic acid (BDC, TCI Chemicals, >99.0%), N,N-dimethylformamide (DMF, VWR BDH Chemicals, HPLC grade), Acetonitrile (ACN, VWR BDH Chemicals) were purchased and used without further purification.

- Cellulose acetate hydrolysis and surface modification

Cellulose acetate was purchased from ADVANTEC (C020A025A) and hydrolyzed based on a previous report<sup>[1]</sup> implemented as the following. The cellulose acetate was immersed in 2.0ml 2.0M NaOH solution (in methanol) for 3 hours. After the 3 hours hydrolysis, the cellulose was washed with methanol 3 times and then washed with DI water 3 times until the final pH is approximately 7. Cellulose was stored in DI water for further use.

The cellulose after hydrolysis was then washed with DMF before APTES treatment. Afterwards, cellulose was placed into stagnant 2% APTES DMF solution at 120°C for 18 hours. After the reaction, the modified cellulose was washed thoroughly with DMF to remove unreacted APTES and stored in DMF for further use.

- Primary MOF  $\text{Ni}_2(\text{BDC})_2(\text{DABCO})$  on cellulose/APTES synthesis

In the primary MOF growth procedure,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.0100g) was dissolved in DMF (3.51 g). Acid Linker BDC (0.0085 g) was dissolved in DMF (4.00 g). Once linkers and metal salt were completely dissolved, base linker DABCO (0.0019 g) was added into acid linker solution. Once all metal salt and linkers were dissolved, the two solutions were mixed together. The final mixture has a molar ratio of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : \text{BDC} : \text{DABCO} : \text{DMF} = 2 : 3 : 1 : 6000$  and was kept in an oven at 70°C for 24 hours. After the heating, the composite  $\text{Ni}_2(\text{BDC})_2(\text{DABCO})$  on cellulose/APTES was sonicated for 1 minute before taken out of the liquid. The coating was then washed with DMF 3 times and stored in DMF for further use.

- Secondary MOF  $\text{Cu}(\text{BDC})$  on Primary MOF  $\text{Ni}_2(\text{BDC})_2(\text{DABCO})$  on cellulose/APTES synthesis

In the secondary MOF synthesis procedure,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.0083g) was dissolved in DMF (15.02 g). Acid Linker BDC (0.0085 g) was dissolved in DMF (15.02 g). Once linkers and metal salt were completely

dissolved, the two solutions were mixed together. The final mixture has a molar ratio of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  : BDC : DMF = 2 : 3 : 24000 and was kept at room temperature (22°C) for 12 hours. The composite (Cu(BDC) on  $\text{Ni}_2(\text{BDC})_2(\text{DABCO})$  on cellulose/APTES) was sonicated for 1 minute before taken out of the liquid. The composite was then washed with ethanol 3 times and kept in ethanol for 12 hours to remove residual DMF. After 12 hours, the composite was dried in a 30°C oven for 12 hours to remove ethanol while keeping cellulose flat.

- Primary MOF Cu(BDC) on cellulose/APTES synthesis

In the primary MOF growth procedure,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.0083g) was dissolved in DMF (15.02 g). Acid Linker BDC (0.0085 g) was dissolved in DMF (15.02 g). Once linkers and metal salt were completely dissolved, two solutions were mixed together. The final mixture has a molar ratio of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  : BDC : DMF = 2 : 3 : 24000 and was kept at room temperature (22°C) for 12 hours. The composite (Cu(BDC) on cellulose/APTES) was sonicated for 1 minute before taken out of the liquid. The composite washed with ethanol 3 times and kept in ethanol for 12 hours to remove residual DMF. After 12 hours, the composite was dried in a 30°C oven for 12 hours to remove ethanol while keeping cellulose flat.

- Characterization

Powder XRD patterns were obtained using PANalytical Empyrean diffractometer (40 mA, 45 kV) with Cu K $\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ).

SEM images were taken using Thermo Fisher Apreo at 1.25 - 2.0 kV.

The Fourier-transform infrared (FT-IR) spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer. A background spectrum of air was subtracted to produce the sample's percent transmittance spectrum. The spectrometer's calibration was regularly checked using a film of polystyrene.

Thermogravimetric analysis (TGA) was performed in a PerkinElmer Pyris 1 analyzer. Samples weighing 1.5-2.0 mg were added to a platinum sample pan for analysis. A nitrogen atmosphere was used for the analysis. The mass of the sample was recorded while the temperature of the sample was increased from 30°C to 500°C at 20°C/min.

$\text{CO}_2$  physical adsorption was measured using a Micromeritics ASAP 2420 analyzer. The samples were evacuated at 70°C for 12 hours before testing. Samples were placed in an ice bath (0 °C) for  $\text{CO}_2$  adsorption measurements.

Solid-state NMR were carried out on a Bruker Avance-III-HD ss500 spectrometer.  $^{13}\text{C}$  MAS spectra were collected at a frequency of 125.69 MHz, a spinning rate of 12 kHz and 25 °C using direct excitation without power  $^1\text{H}$ -decoupling. In order to study the interaction between 1-hexene and the MOF material, 1-hexene was added to the MOF material and let dry naturally. The sample containing 1-hexene was evacuated at 22 °C under dynamic vacuum ( $6 \times 10^{-7}$  mBar) before testing to remove physically adsorbed 1-hexene. The MOF material without adsorbing 1-hexene was also evacuated at 22 °C before testing.

Elemental analysis was carried out using Inductively Coupled Plasma Emission Spectrometry (ICP-AES) on a Thermo iCAP 7400 spectrometer.

- Batch adsorption experiments

5% n-hexane (by mass) in cyclohexane and 5% 1-hexene (by mass) in cyclohexane were prepared for the batch adsorption experiments. All batch adsorption experiments were performed at room temperature (22°C). The composite samples (adsorbents) were weighed and added into 20 ml glass vials containing 1 g of the 5% hydrocarbon solution. The vials were sealed with parafilm and placed on an orbital shaker at 200 rpm for 24 hours. The before adsorption and equilibrated n-hexane and 1-hexene concentrations were evaluated using gas chromatography (Agilent Technology 7890B, HP-5 column, FID, oven at 100°C constantly, 2 µL of hydrocarbon solution was injected each time), where cyclohexane was used as an internal standard. Each concentration after-adsorption solution was repeated for 3 times. The

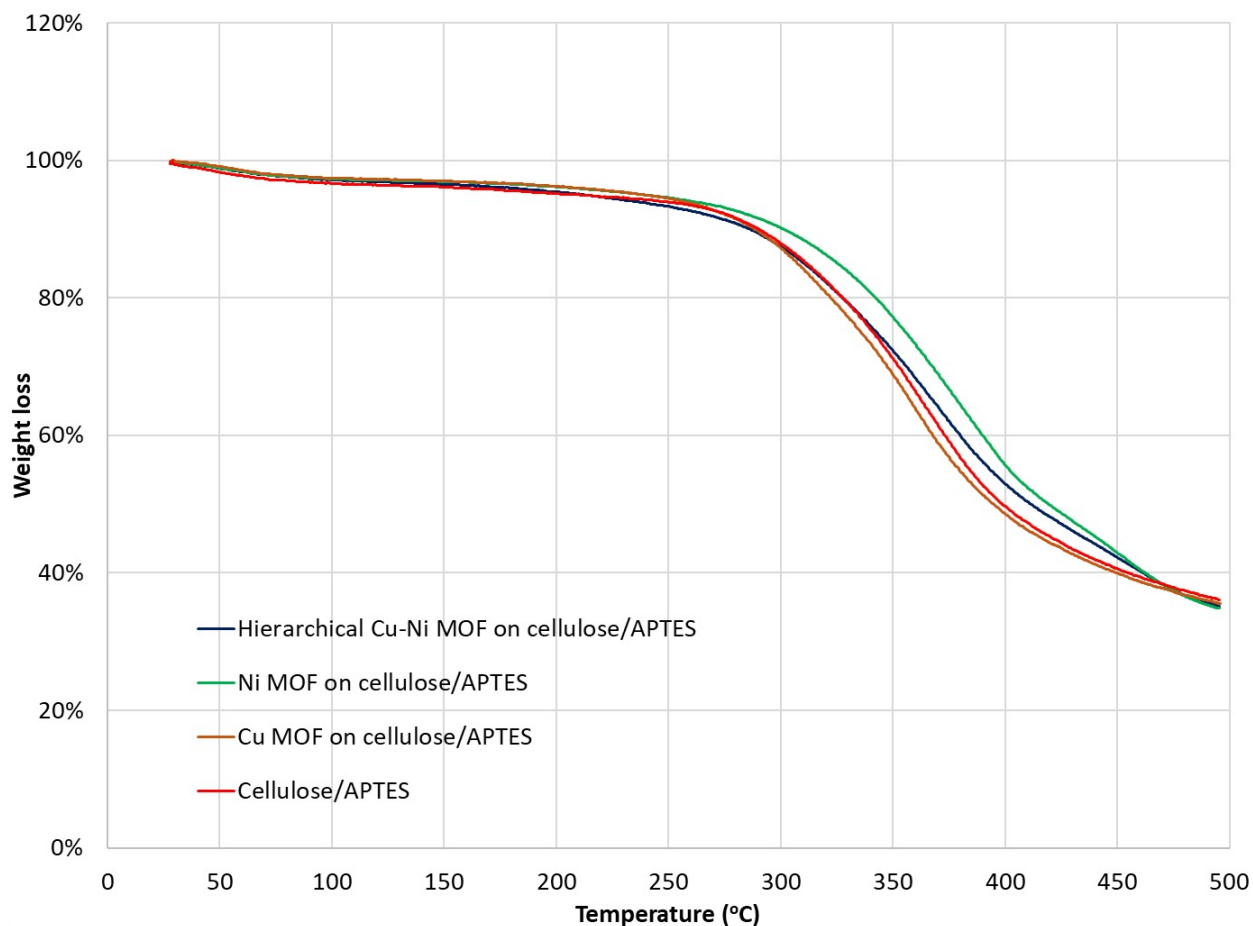
adsorption capacity of the composites  $Q$  (mg/g) can be calculated based on  $Q = \frac{m_1}{m_2} \times (C_0 - C)$ , where  $m_1$  (g) is solution mass,  $m_2$  (g) is composite (adsorbent) mass,  $C_0$  (%) is the n-hexane or 1-hexene mass percentage before adsorption,  $C$  (%) is the n-hexane or 1-hexene equilibrated mass percentage after adsorption. Ideal selectivity was calculated by Ideal selectivity = (1-hexene adsorption amount) / (n-hexane adsorption amount).

- Liquid adsorption

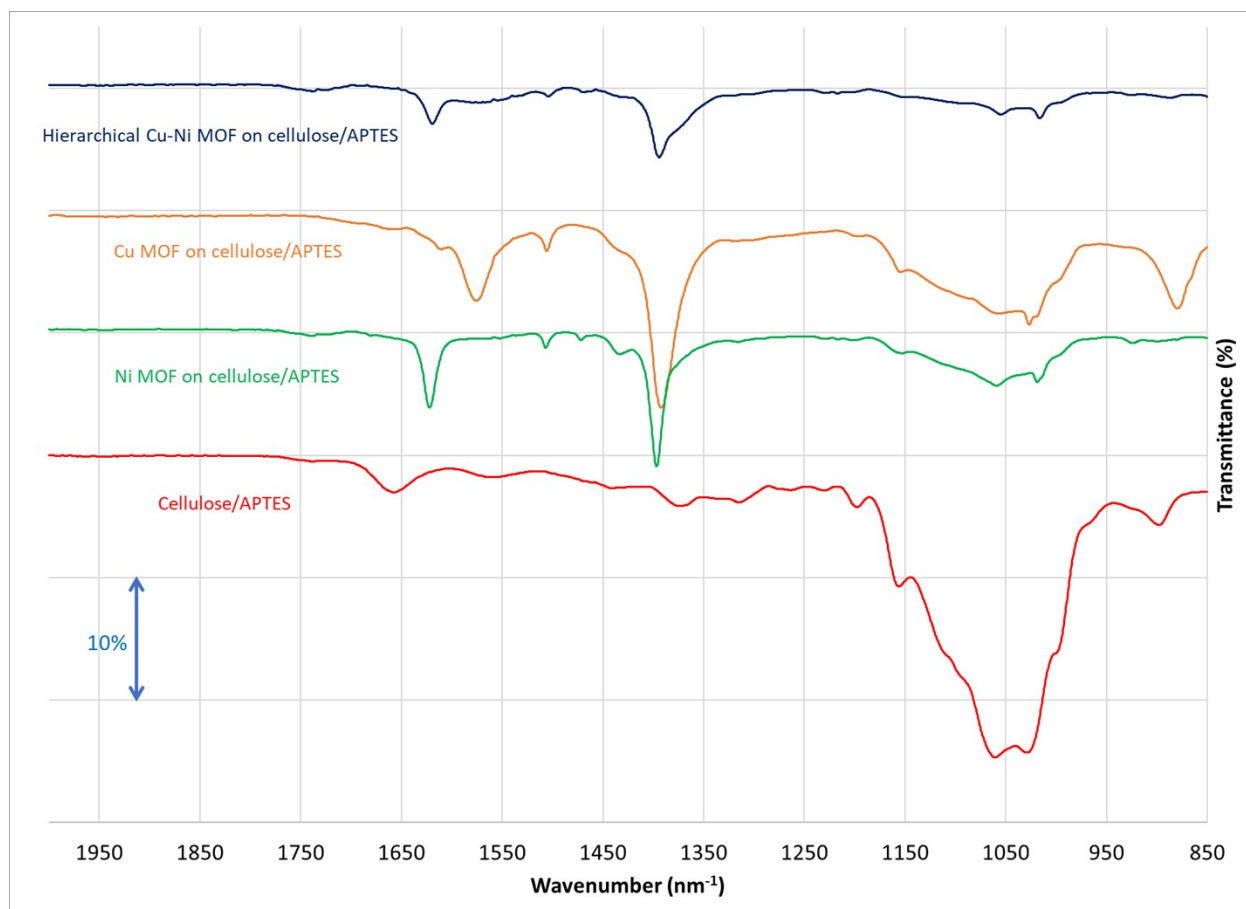
Liquid (pure species) adsorption amount measurements were performed at 22°C gravimetrically as described by Wang et al.<sup>2</sup> Pure C<sub>6</sub> hydrocarbons (n-hexane, 1-hexene, cyclohexane as described in the Chemicals section in this ESI) were used for liquid adsorption. A PerkinElmer Pyris 1 TGA was used as the microbalance. Other procedures were the same as described in Wang et al.

- Vapor phase column breakthrough

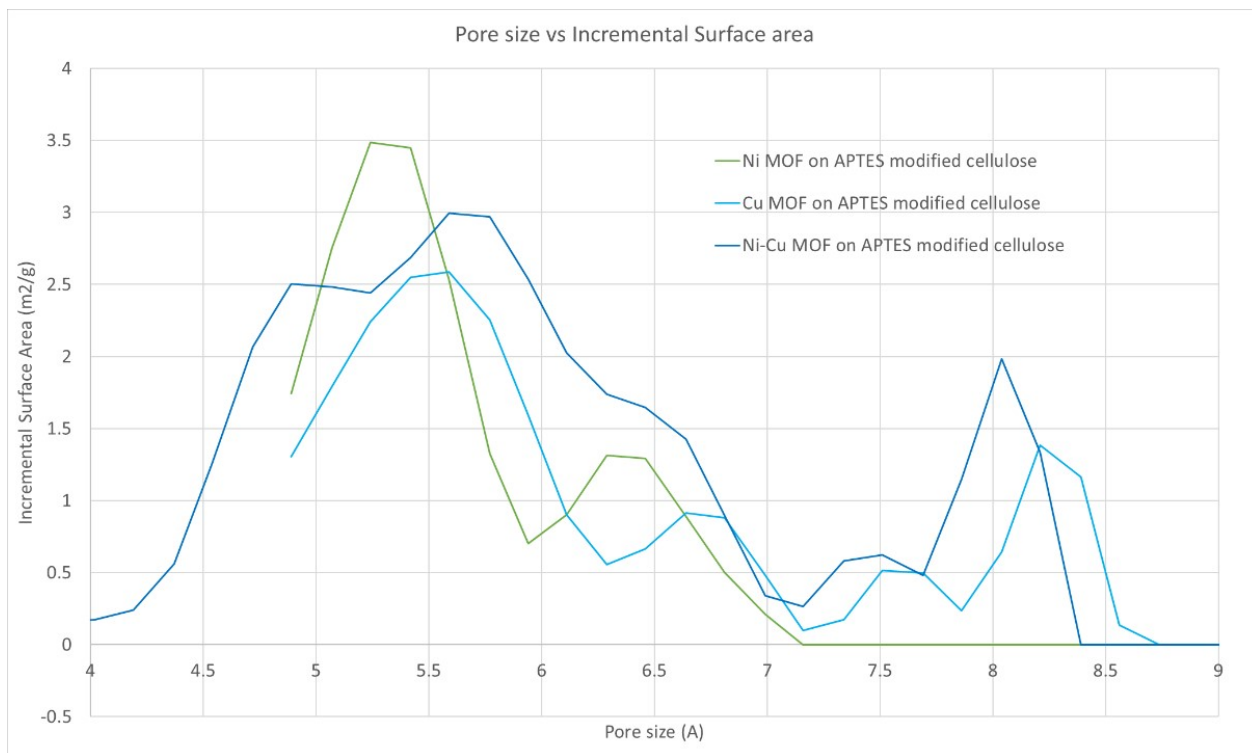
0.300 g hierarchical Ni-Cu MOF supported on cellulose was packed into a 314 stainless steel column with an inner diameter of 0.165 cm and a length of approximately 6 cm. Before the experiment, the content of the column was heated at 70°C under vacuum for 12 hours. The breakthrough experiment was done at 22°C and a total pressure of 1 atm. During the experiment, an equimolar 1-hexene and n-hexene mixture was flowed through the column in a helium atmosphere. The helium flow rate (controlled by a Parker mass flow controller) was 50 cm<sup>3</sup>/min at 22°C. The 1-hexene and n-hexene mixture flow rate (controlled by a KD Scientific LEGATO 100 syringe pump) was 0.0020 mL/min, resulting in 0.38 kPa of partial pressure for each C<sub>6</sub> at 22°C. The product composition was analyzed online using an Agilent 7890B GC with a HP-5 column (30 m) and FID.



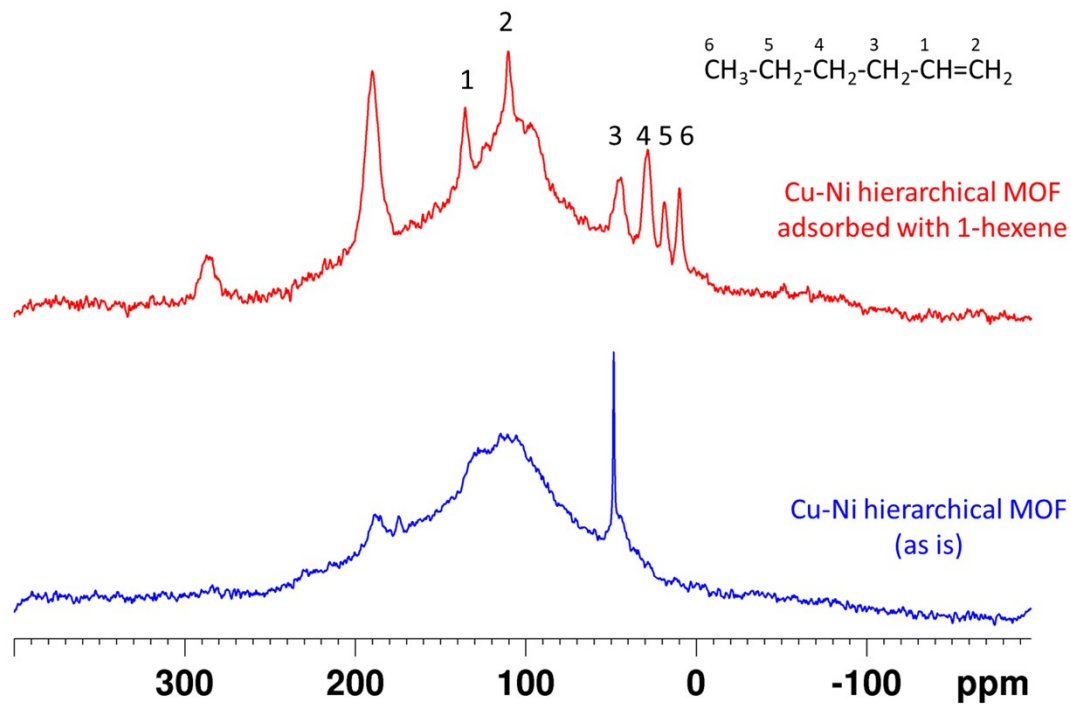
**Figure S1** Thermogravimetric analysis curves of cellulose/APTES (the support), Cu(BDC) MOF on cellulose/APTES, Ni(BDC)<sub>2</sub>(DABCO) MOF on cellulose/APTES, and Cu(BDC) on Ni(BDC)<sub>2</sub>(DABCO) MOF on cellulose/APTES. The similar gravimetric behaviors suggested that the composite materials are not more unstable than the cellulose support. The weight loss of all samples is negligible below the normal boiling points of n-hexane (69°C) or 1-hexene (63°C).



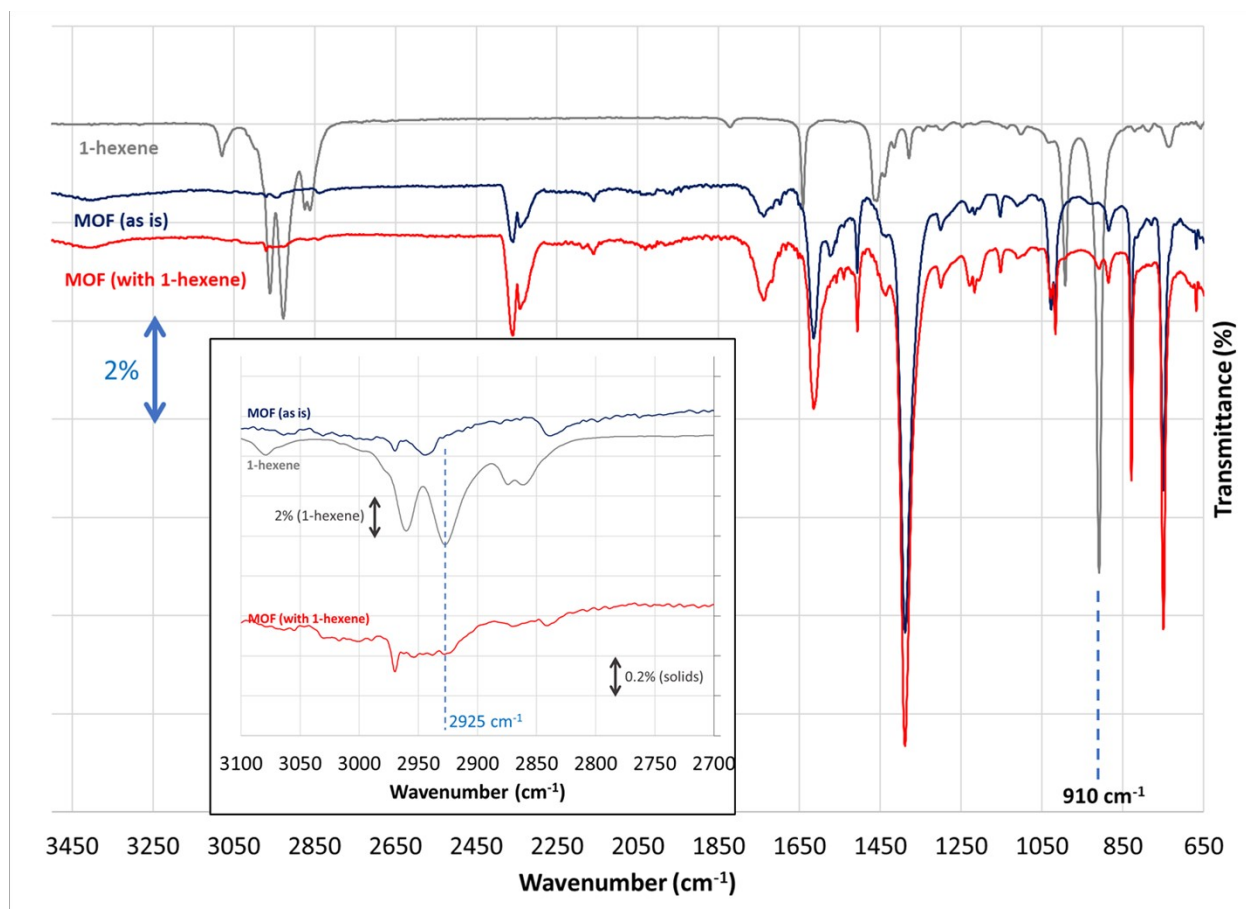
**Figure S2** IR spectra of cellulose/APTES (the support), Cu(BDC) MOF on cellulose/APTES, Ni(BDC)<sub>2</sub>(DABCO) MOF on cellulose/APTES, and Cu(BDC) on Ni(BDC)<sub>2</sub>(DABCO) MOF on cellulose/APTES. Absorption bands between 1650  $\text{cm}^{-1}$  and 1350  $\text{cm}^{-1}$  and absence of absorption near 1700  $\text{cm}^{-1}$  indicate complete coordination of aromatic carboxylic acid linkers.



**Figure S3** Pore size distribution from CO<sub>2</sub> adsorption of the MOF-containing materials showing the micropores characteristic of the respective MOFs. The micropores in the hierarchical MOF contain those of both Ni(bdc)<sub>2</sub>(dabco) and Cu (bdc).

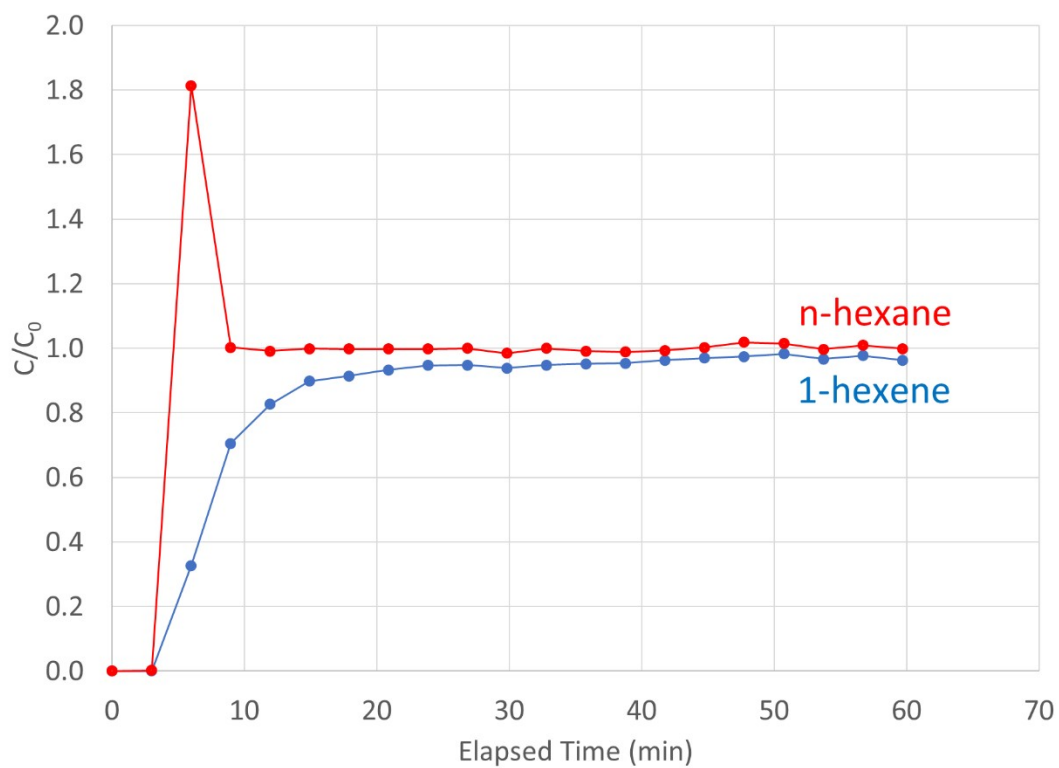


**Figure S4**  $^{13}\text{C}$  NMR spectra of MOF (mechanically separated from Cu-Ni MOF on cellulose/APTES) adsorbed with 1-hexene, compared with the MOF material without 1-hexene. Samples were evacuated under high vacuum before testing. The peaks from 1-hexene are marked in the spectra.



**Figure S5** IR spectra of pure 1-hexene, Cu-Ni hierarchical MOF (mechanically separated from Cu-Ni MOF on cellulose/APTES, evacuated under high vacuum before testing), and 1-hexene-adsorbed Cu-Ni hierarchical MOF (mechanically separated from Cu-Ni MOF on cellulose/APTES, evacuated under high vacuum before testing). The spectra show the presence of 1-hexene features (910 cm<sup>-1</sup> in the figure and 2925 cm<sup>-1</sup> in the inset) on the 1-hexene-adsorbed Cu-Ni hierarchical MOF.





**Figure S6** Column breakthrough curves of 1-hexene and n-hexane (dead volume subtracted; partial pressure was 0.38 kPa for each  $C_6$  hydrocarbon in 50  $\text{cm}^3/\text{min}$  helium flow at 22  $^\circ\text{C}$ ).

**Table S1** Comparison of common n-hexane/1-hexene separation methods using adsorbents

Material	Ideal Selectivity	Source
Zeolite NaX	2.36	Eberly et al. <sup>3</sup>
Zeolite 5A	8	Yang et al. <sup>4</sup>
Phosphine coordination material	5	Nuñez et al. <sup>5</sup>
Cu <sub>3</sub> (btc) <sub>2</sub>	5	Bentley et al. <sup>6</sup>
Co/Mg-MOF-74	9.74	Sun et al. <sup>7</sup>
Hierarchical MOF	11.4	(this study)

**Table S2** Elemental composition (from ICP-OES) of the materials studied in this manuscript

	Ni Mass Percentage (%)	Cu Mass Percentage (%)
Cellulose/APTES	(<0.001)	(<0.001)
Ni MOF on cellulose/APTES	1.54	(<0.001)
Cu MOF on cellulose/APTES	(<0.001)	0.43
Cu/Ni MOF on cellulose/APTES	0.96	0.41

**Table S3** Total liquid adsorbed at 295 K on the materials studied in this manuscript

	Amount Adsorbed (mg liquid/g solid)	
	n-Hexane	1-Hexene
Cellulose/APTES	56.81	612.4
Ni MOF on cellulose/APTES	285.8	1411
Cu MOF on cellulose/APTES	160.6	942.7
Cu/Ni MOF on cellulose/APTES	183.5	2291

## References for ESI:

---

- <sup>1</sup> Xin, Y., Xiong, Q., Bai, Q., Miyamoto, M., Li, C., Shen, Y., & Uyama, H. (2017). A hierarchically porous cellulose monolith: A template-free fabricated, morphology-tunable, and easily functionalizable platform. *Carbohydrate Polymers*, *157*, 429-437.
- <sup>2</sup> Wang, D., McLaughlin, E., Pfeffer, R., & Lin, Y. S. (2011). Adsorption of organic compounds in vapor, liquid, and aqueous solution phases on hydrophobic aerogels. *Industrial & Engineering Chemistry Research*, *50*(21), 12177-12185.
- <sup>3</sup> Eberly, P. E., Kimberlin, C. N., & Baker, L. E. (1967). Vapour phase adsorption measurements of C<sub>6</sub> hydrocarbon mixtures on synthetic faujasite. *Journal of Applied Chemistry*, *17*(2), 44-47.
- <sup>4</sup> Yang, R., Gao, R., Wang, Y., Qian, Z., & Luo, G. (2020). Selective adsorption of C<sub>6</sub>, C<sub>8</sub>, and C<sub>10</sub> linear  $\alpha$ -olefins from binary liquid-phase olefin/paraffin mixtures using zeolite adsorbents: experiment and simulations. *Langmuir*, *36*(29), 8597-8609.
- <sup>5</sup> Nuñez, A. J., Shear, L. N., Dahal, N., Ibarra, I. A., Yoon, J., Hwang, Y. K., Chang, J.-S. & Humphrey, S. M. (2011). A coordination polymer of (Ph<sub>3</sub>P)AuCl prepared by post-synthetic modification and its application in 1-hexene/n-hexane separation. *Chemical Communications*, *47*(43), 11855-11857.
- <sup>6</sup> Bentley, J., Foo, G. S., Rungta, M., Sangar, N., Sievers, C., Sholl, D. S., & Nair, S. (2016). Effects of open metal site availability on adsorption capacity and olefin/paraffin selectivity in the metal-organic framework Cu<sub>3</sub>(BTC)<sub>2</sub>. *Industrial & Engineering Chemistry Research*, *55*(17), 5043-5053.
- <sup>7</sup> Sun, H., Ren, D., Kong, R., Wang, D., Jiang, H., Tan, J., Wu, D., Chen, S., & Shen, B. (2019). Tuning 1-hexene/n-hexane adsorption on MOF-74 via constructing Co-Mg bimetallic frameworks. *Microporous and Mesoporous Materials*, *284*, 151-160.