Electronic Supplementary Information (ESI)

A Novel Polyhedron-Based Metal-Organic Framework with High Performance for Gas Uptake and Light Hydrocarbon Separation

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Calculation procedures of selectivity from IAST

The measured experimental data is excess loadings (q^{ex}) of the pure components CO_2, CH_4, C_2H_6 and C_3H_8 for **JLU-Liu40**, which should be converted to absolute loadings (q) firstly.

$$q = q^{ex} + \frac{pV_{pore}}{ZRT}$$

Here *Z* is the compressibility factor. The Peng-Robinson equation was used to estimate the value of compressibility factor to obtain the absolute loading, while the measure pore volume 0.86 cm^3 g^{-1} is also necessary.

The dual-site Langmuir-Freundlich equation is used for fitting the isotherm data at 298K.

$$q = q_{m_1} \times \frac{b_1 \times p^{1/n_1}}{1 + b_1 \times p^{1/n_1}} + q_{m_2} \times \frac{b_2 \times p^{1/n_2}}{1 + b_2 \times p^{1/n_2}}$$

Here p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol kg^{-1}), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol kg^{-1}), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), n_1 and n_2 are the deviations from an ideal homogeneous surface.

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as

$$S = \frac{q_1/q_2}{p_1/p_2}$$

q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

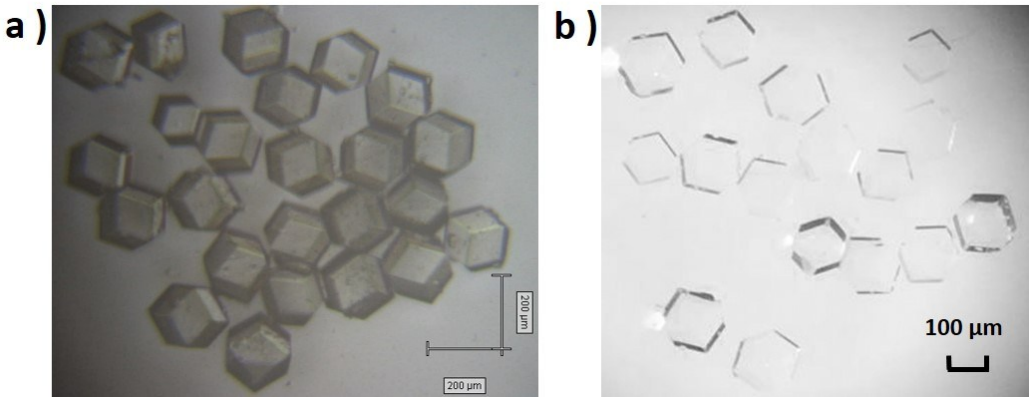

Figure S1. Optical images (a) without light and (b) with light of **JLU-Liu40**.

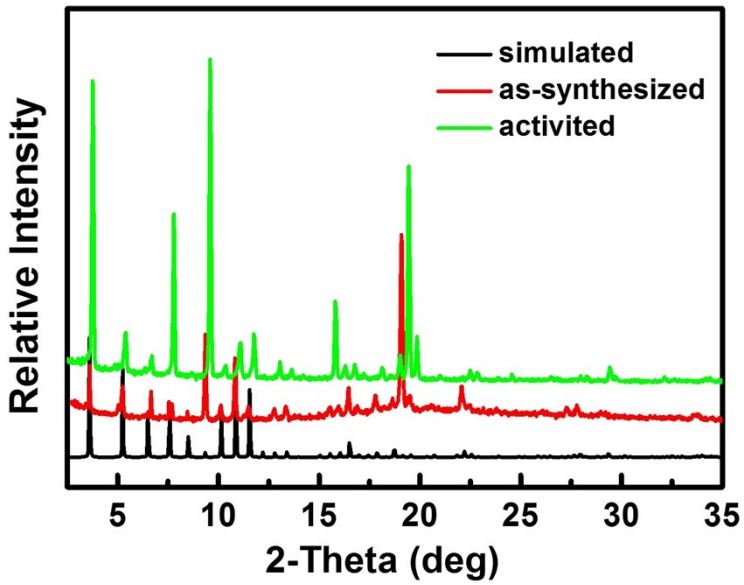

Figure S2. Simulated, as-synthesized and activated PXRD patterns for **JLU-Liu40** samples.

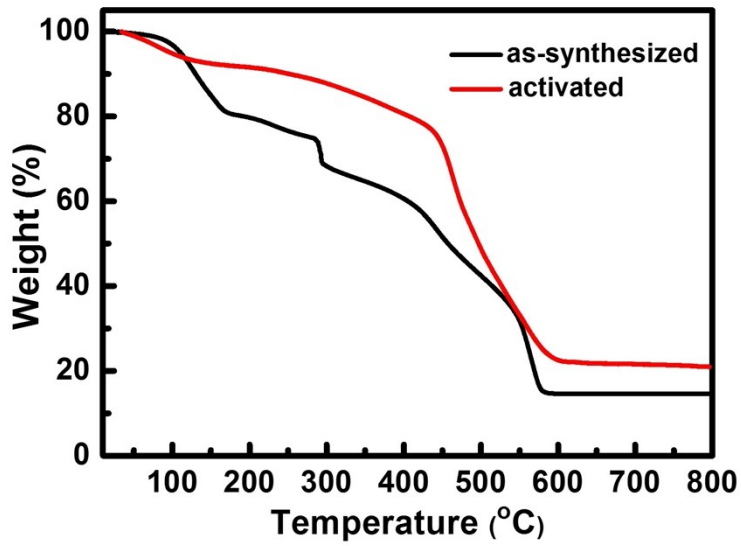

Figure S3. TGA curves of **JLU-Liu40** for the as-synthesized and activated samples.

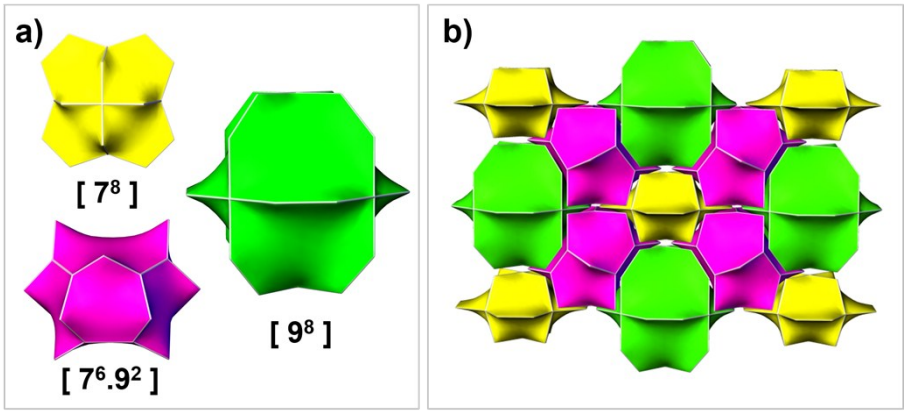

Figure S4. (a) Three types of tiles with face symbol; (b) Natural tiling of **JLU-Liu40**.

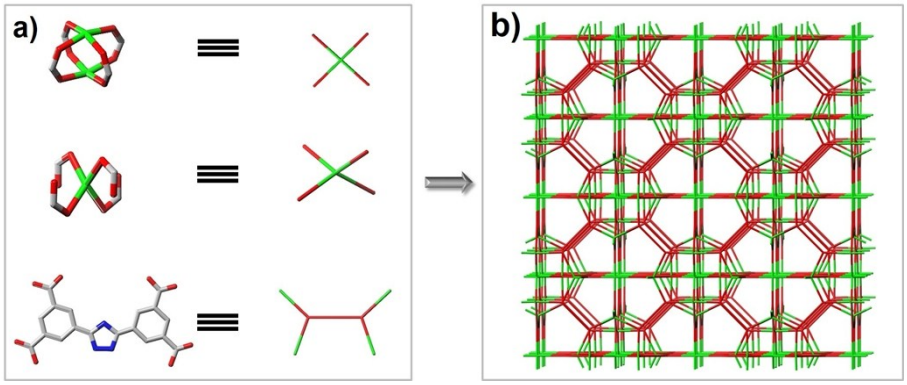

Figure S5. Illustration of topology of **JLU-Liu40**.

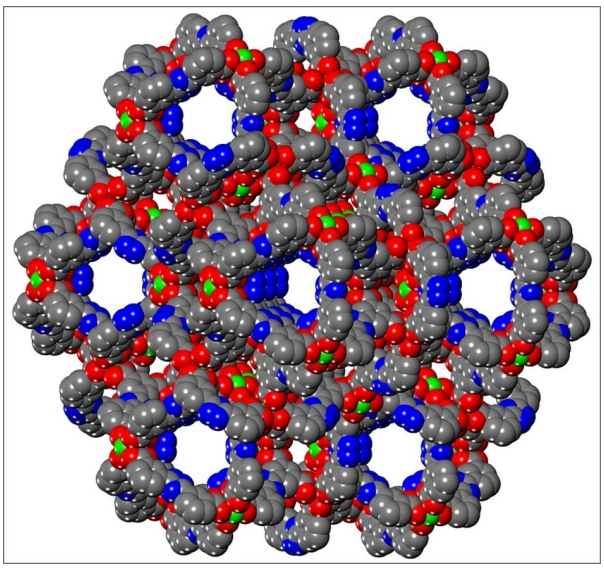

Figure S6. Space-filling view of the structure of **JLU-Liu40** along the (111) directions.

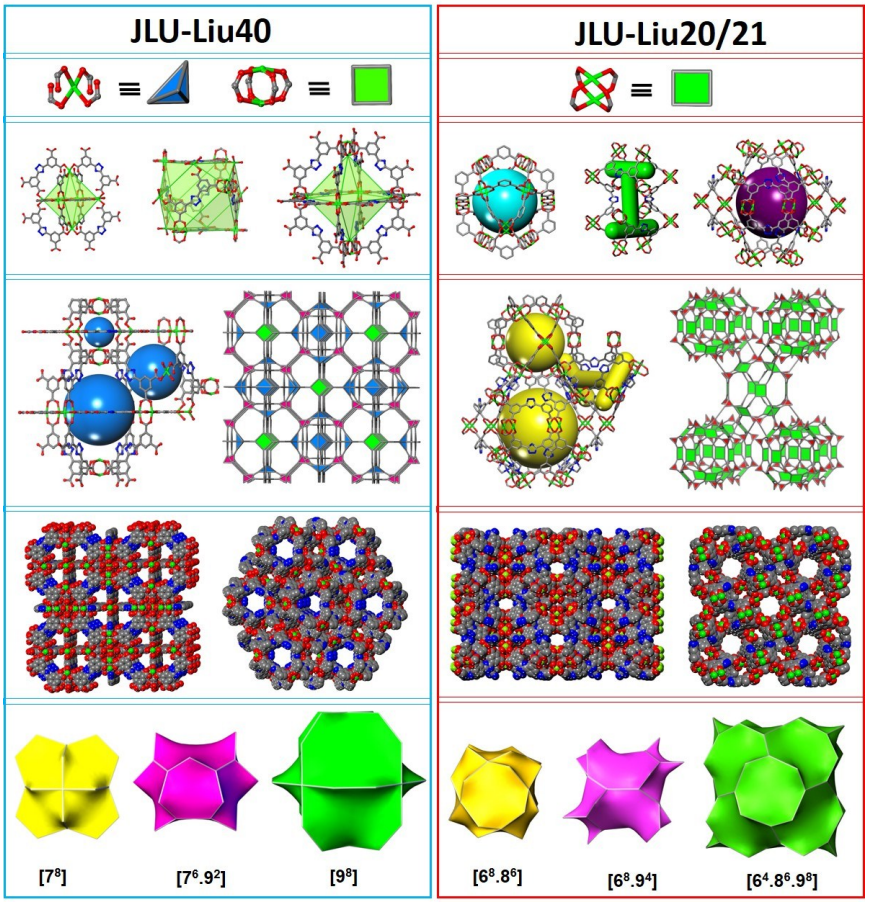

Figure S7. The structure differences between **JLU-Liu40** and the previously reported **JLU-Liu20/21**.

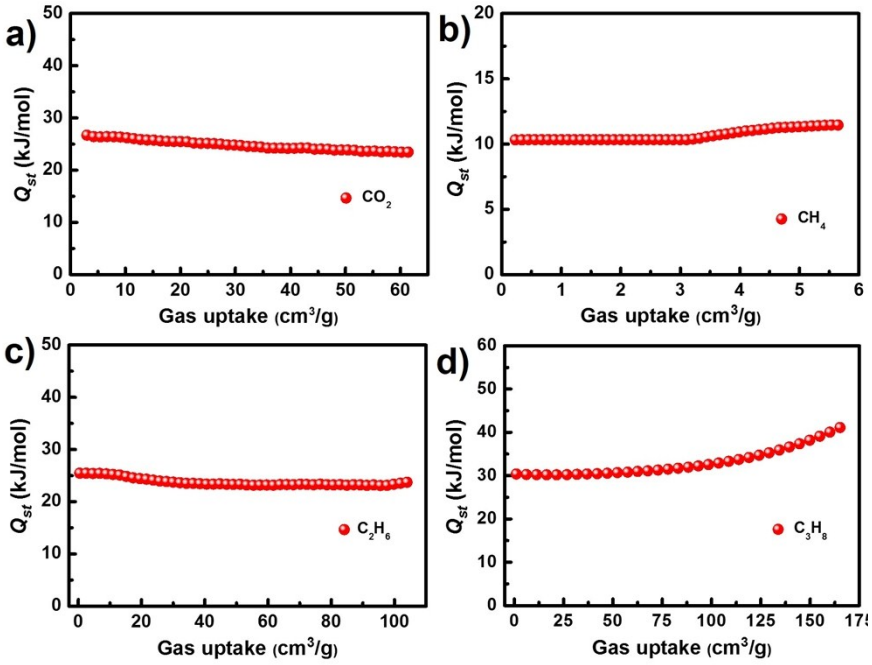

Figure S8. Isosteric heat of CO_2 (a), CH_4 (b), C_2H_6 (c) and C_3H_8 (d) for **JLU-Liu40**.

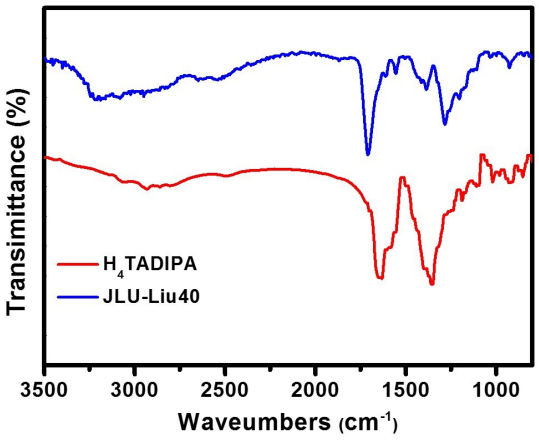

Figure S9. The infrared spectra for the ligand (red) and **JLU-Liu40** (blue).

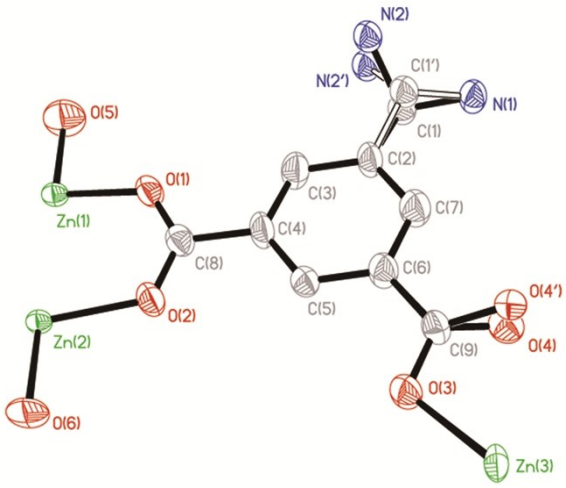

Figure S10. ORTEP drawing of the asymmetric unit of **JLU-Liu40**.

Table S1. The companies and reactants purities of chemicals used for the synthesis of **JLU-Liu40.**

Materials	Companies	Purities
$Zn(NO_3)_2{\cdot}6H_2O$	Sinopharm Chemical Reagent Co., Ltd.	99%
H_4TADIPA	Jinan Henghua Sci. & Tec. Co., Ltd.	95%
DMF	Sinopharm Chemical Reagent Co., Ltd.	99%
DABCO	Aladdin Industrial Corporation	98%
CH_3CN	Sinopharm Chemical Reagent Co., Ltd.	99%

HNO_3	Sinopharm Chemical Reagent Co., Ltd.	99%

Table S2. Crystal data and structure refinements for **JLU-Liu40**.

compound	**JLU-Liu40**
Formula	$C_{58}H_{72}N_{14}O_{22}Zn_3$
Formula weight	1162.85
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Cubic
Space group	*Im-3m*
a (Å)	31.289(4)
b (Å)	31.289(4)
c (Å)	31.289(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	30631(11)
Z, D_c (Mg/m^3)	12, 0.985
F(000)	9408
ϑ range (deg)	2.255-25.014
reflns collected/unique	44862/2556
R_{int}	0.0848
data/restraints/params	2556/143/88
GOF on F^2	1.068
R_1, wR_2 (I>2σ(I))	0.0598, 0.1591
R_1, wR_2 (all data)	0.0808, 0.1712

Table S3. Summary of CO_2 uptake for materials based on Zn or Cu units reported in the literature.

Compounds	CO_2 Ads (wt%)		Ref.
	273K	298K	
CPM-231	**45.6**	**N. A.**	**1**
Cu-TDPAT	**44.7**	**25.8**	**2**
Cu-TPBTM	**44.5**	**23.3**	**3**
JLU-Liu21	**42.3**	**23.2**	**4**
SUN-5	**38.5**	**N. A.**	**5**
JLU-Liu20	**31.8**	**17.3**	**4**
SIFXIX-2-Cu-i	**28.6**	**23.8**	**6**
$Cu_2(EBTC)(H_2O)_2$	**25.9**	**N. A.**	**7**
JLU-Liu40	**20.7**	**10.2**	**This work**
$[Zn_2(abtc)(DMF)_2]_3$	**20.6**	**N. A.**	**8**
$Zn_2(BTetB)$	**19.7**	**N. A.**	**9**
$[Cu_2(abtc)(DMF)_2]_3$	**19.2**	**N. A.**	**8**
$Cu_2(TCM)$ (SNU-21S)	**18.4**	**11.1**	**10**
$Cu_2(TCM)$ (SNU-21H)	**17.1**	**9.65**	**10**

N.A.: Not Available. The article do not list the data.

Table S4. The refined parameters for the Dual-site Langmuir-Freundlich equations fit for the pure isotherms of CO_2, CH_4, C_2H_6 and C_3H_8 for **JLU-Liu40** at 298 K.

	q_{m1}	b_1	n_1	q_{m2}	b_2	n_2	R^2
CO_2	7.92137	2.1407	1.55526E-4	0.02062	1.56943	0.94179	0.99995
CH_4	2.88752	0.03673	0.00168	1.72543E-13	1.03069	6.56259	0.99999
C_2H_6	1.25107	8.42528	9.28115E-7	0.01066	3.11838	0.95015	0.99996
C_3H_8	1.99721	6.15838	0.00336	0.10724	2.2914	0.87292	0.99992

Table S5. N_2 adsorption data and structure information for **JLU-Liu40**.

Compounds	SA_{BET} ($m^2\ g^{-1}$)	$SA_{Langmuir}$ ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$) (Experimental/Theoretical)	OMSs (nm^{-3})	LBSs (nm^{-3})
JLU-Liu40	1455	2084	0.86/1.16	0.76	1.59

Table S6 Topological information for **JLU-Liu40**.

	Coordination Sequence										
Vertex	**CS1**	**CS2**	**CS3**	**CS4**	**CS5**	**CS6**	**CS7**	**CS8**	**CS9**	**CS10**	**Cum10**
V_1 (4-c)	5	13	33	63	111	195	303	441	605	815	**2584**
V_2 (4-c)	5	13	33	70	126	203	303	457	633	854	**2697**
V_3 (3-c)	4	12	30	61	111	188	292	420	601	813	**2532**
Vertex	**Extended point symbols**										
V_1 (4-c)	**[7(2).7(2).7(2).7(2).8(3).8(3)]**										
V_2 (4-c)	**[7.7.7.7.8.8]**										
V_3 (3-c)	**[7(2).7(2).9(2)]**										

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