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# A Pair of Polymorphous Metal-Organic Frameworks Based on an Angular Diisophthalate Linker: Synthesis, Characterization and Gas Adsorption Property

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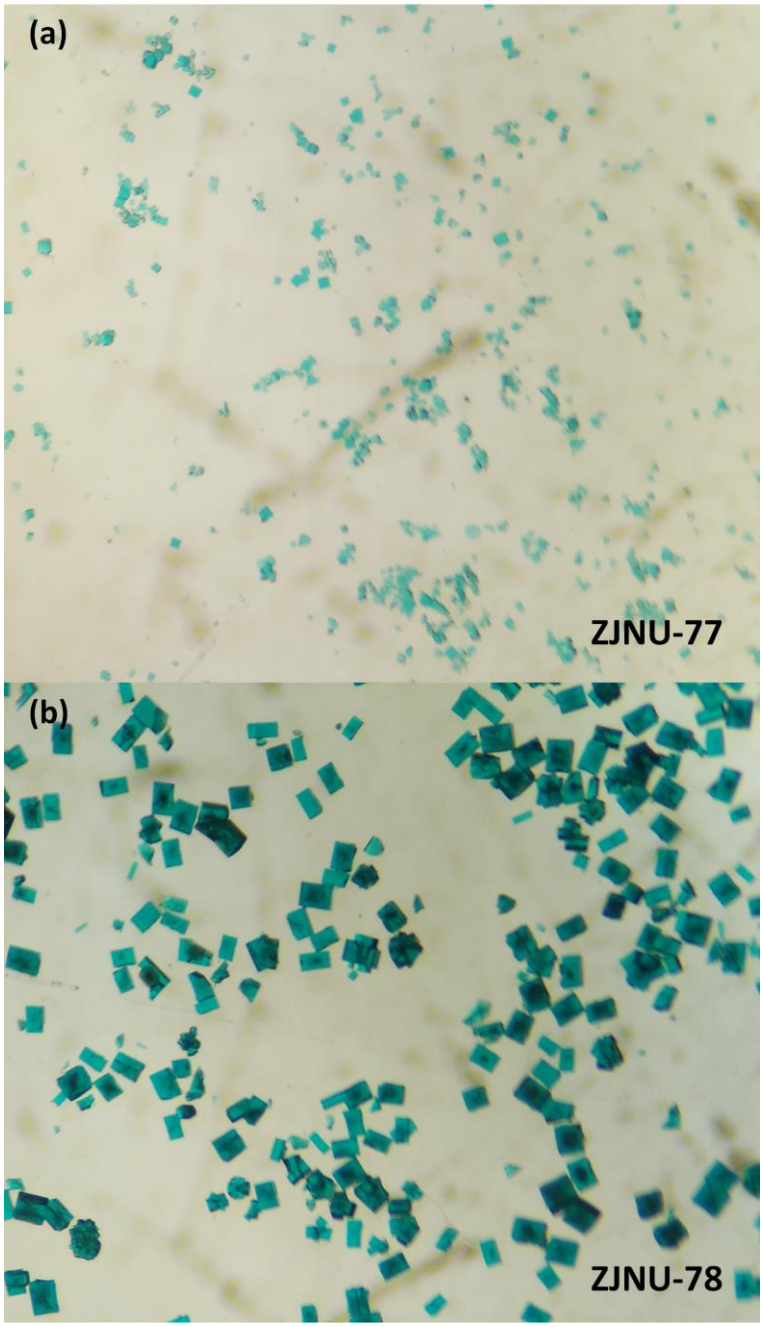



**Fig. S1** The photographs of the as-synthesized (a) **ZJNU-77** and (b) **ZJNU-78**.

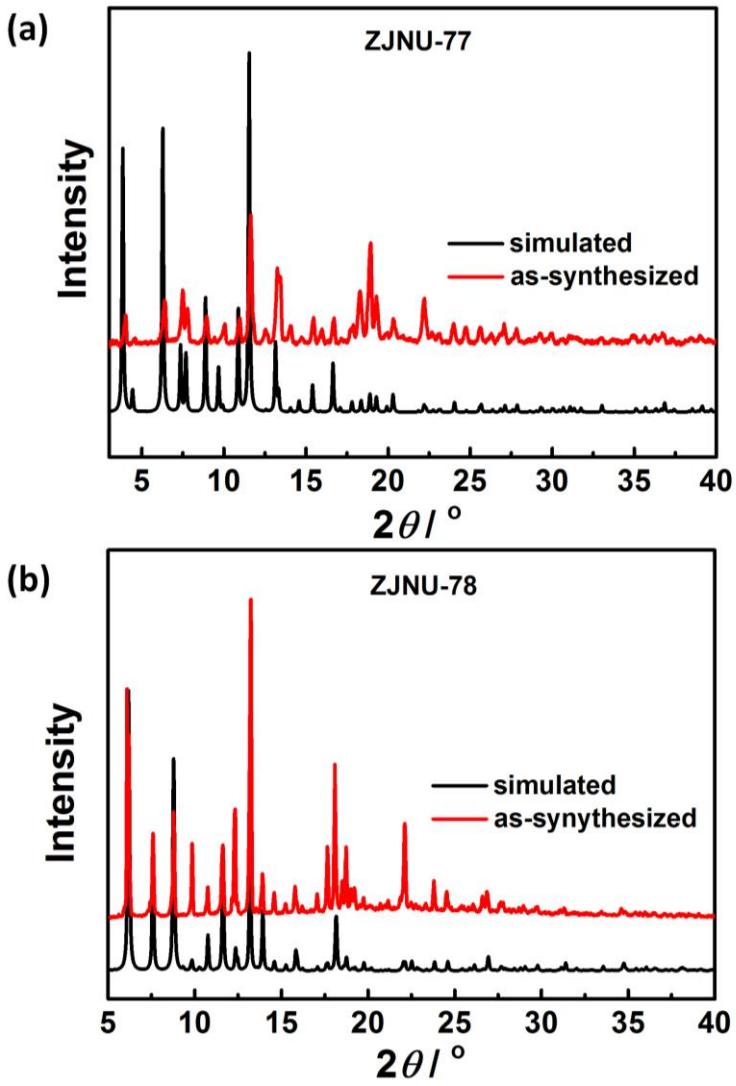



**Fig. S2** Comparison of the experimental (red) and simulated (black) PXRD patterns for (a) **ZJNU-77** and (b) **ZJNU-78**.

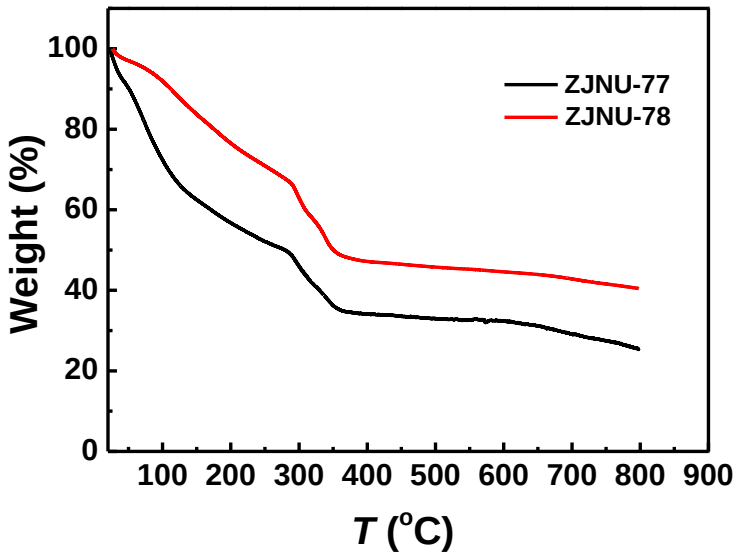



**Fig. S3** TGA curves of the as-synthesized (a) **ZJNU-77** and (c) **ZJNU-78** under nitrogen atmosphere.

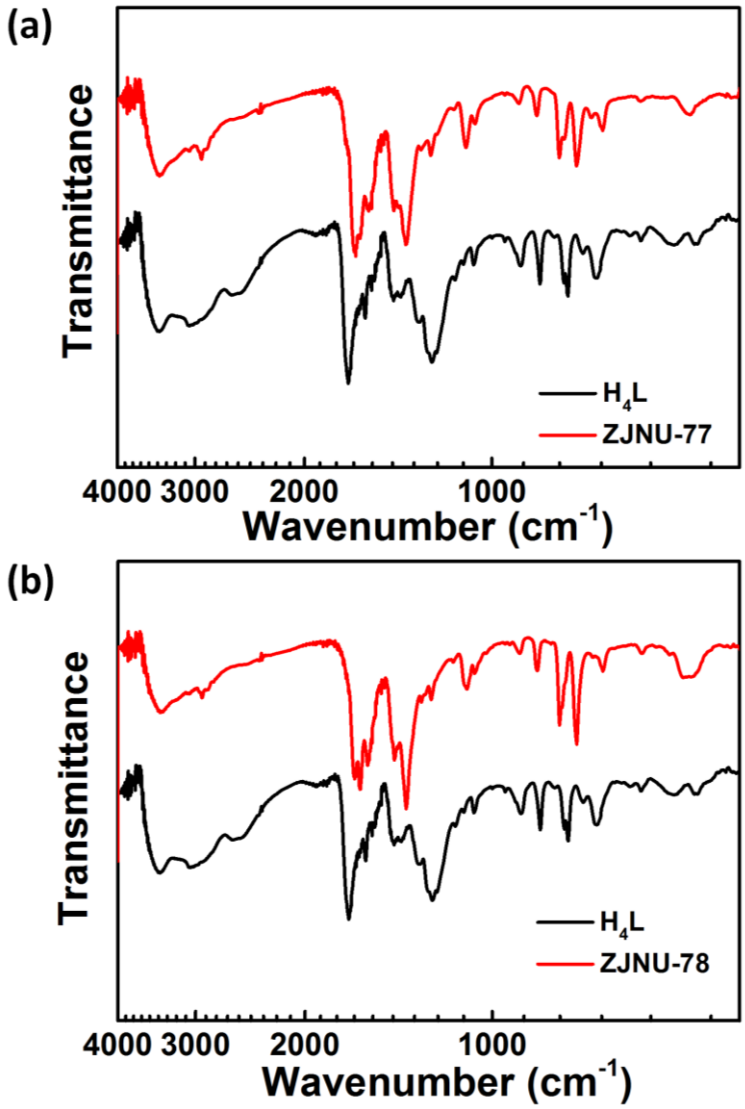
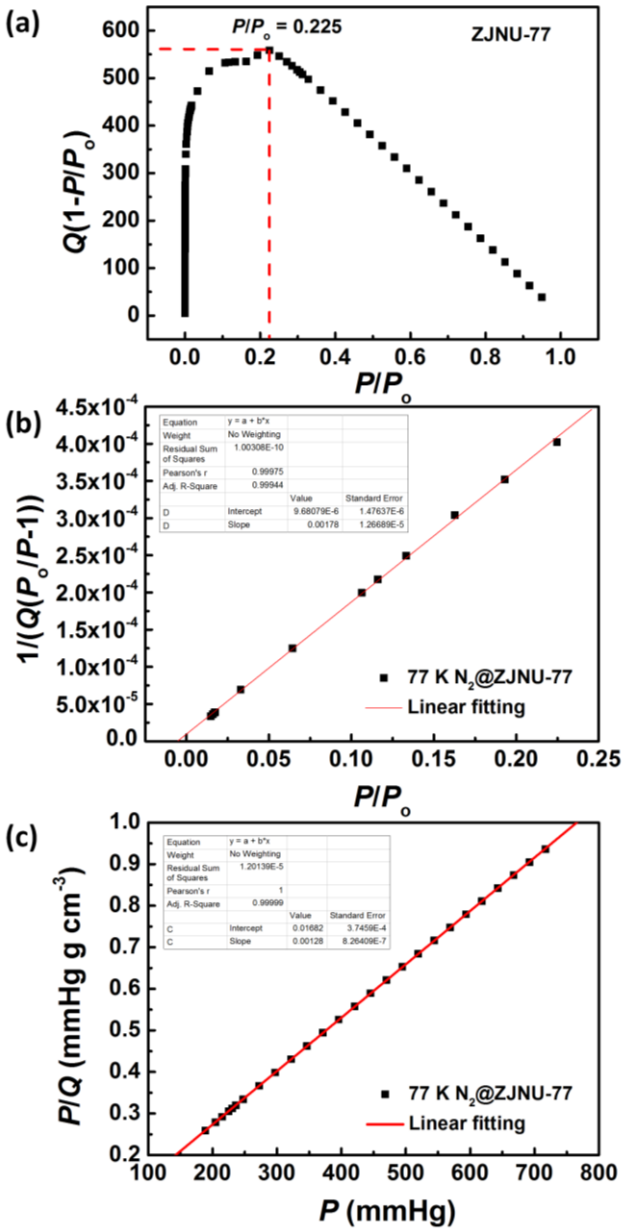



**Fig. S4** Comparison of FTIR spectra of the organic linker and its corresponding MOFs




$S_{BET}$ = 1/(9.68079 ×$10^{-6}$+0.00178)/22414 × 6.023 × $10^{23}$ × 0.162 × $10^{-18}$ = 2432 $m^2$ $g^{-1}$

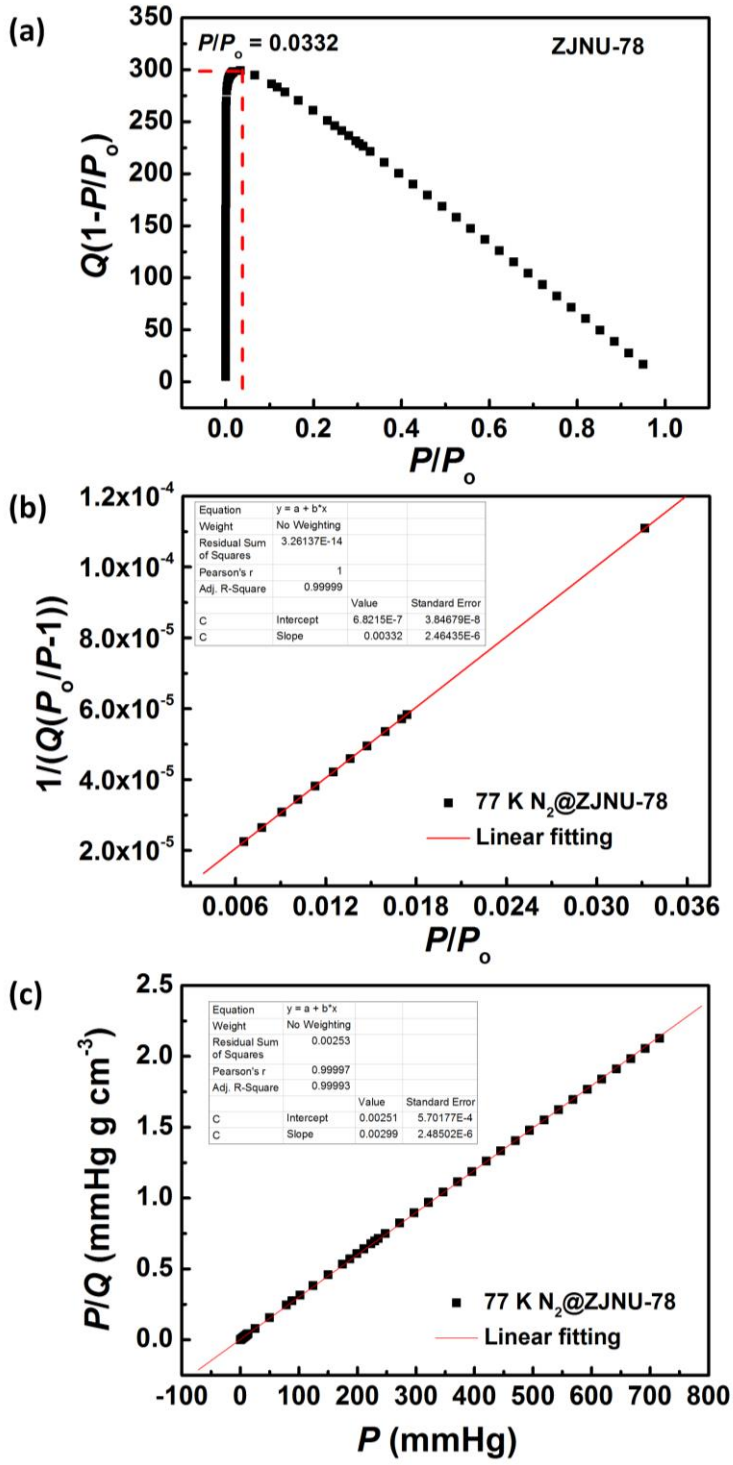
$S_{Langmuir}$= (1/0.00128)/22414 × 6.023 × $10^{23}$ × 0.162 × $10^{-18}$ = 3401 $m^2$ $g^{-1}$

BET constant $C$ = 1 + 0.00178/9.68079 ×$10^{-6}$ = 185

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.0685$$

**Fig. S5** The consistency plot (a), BET plot (b) and Langmuir plot (c) for **ZJNU-77**.

*NOTE*: For BET surface area calculation, a set of consistency criteria should comply with: (a) $V_{ads}(1-P/P_o)$ increases continuously as a function of $P/P_o$; (2) the value of the BET constant $C$ should be positive and have a value of at least 10; (3) the relative pressure corresponding to a given monolayer should be located within the chosen relative pressure range.




$S_{BET}$ = 1/(6.8215 ×10$^{-7}$ + 0.00332)/22414 × 6.023 × 10$^{23}$ × 0.162 × 10$^{-18}$ = 1311 m$^2$ g$^{-1}$

$S_{Langmuir}$= (1/0.00299)/22414 × 6.023 × 10$^{23}$ × 0.162 × 10$^{-18}$ = 1456 m$^2$ g$^{-1}$

BET constant = 1 + 0.00332/6.8215 ×10$^{-7}$ = 4868

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.01413$$

**Fig. S6** The consistency plot (a), BET plot (b) and Langmuir plot (c) for **ZJNU-78**.

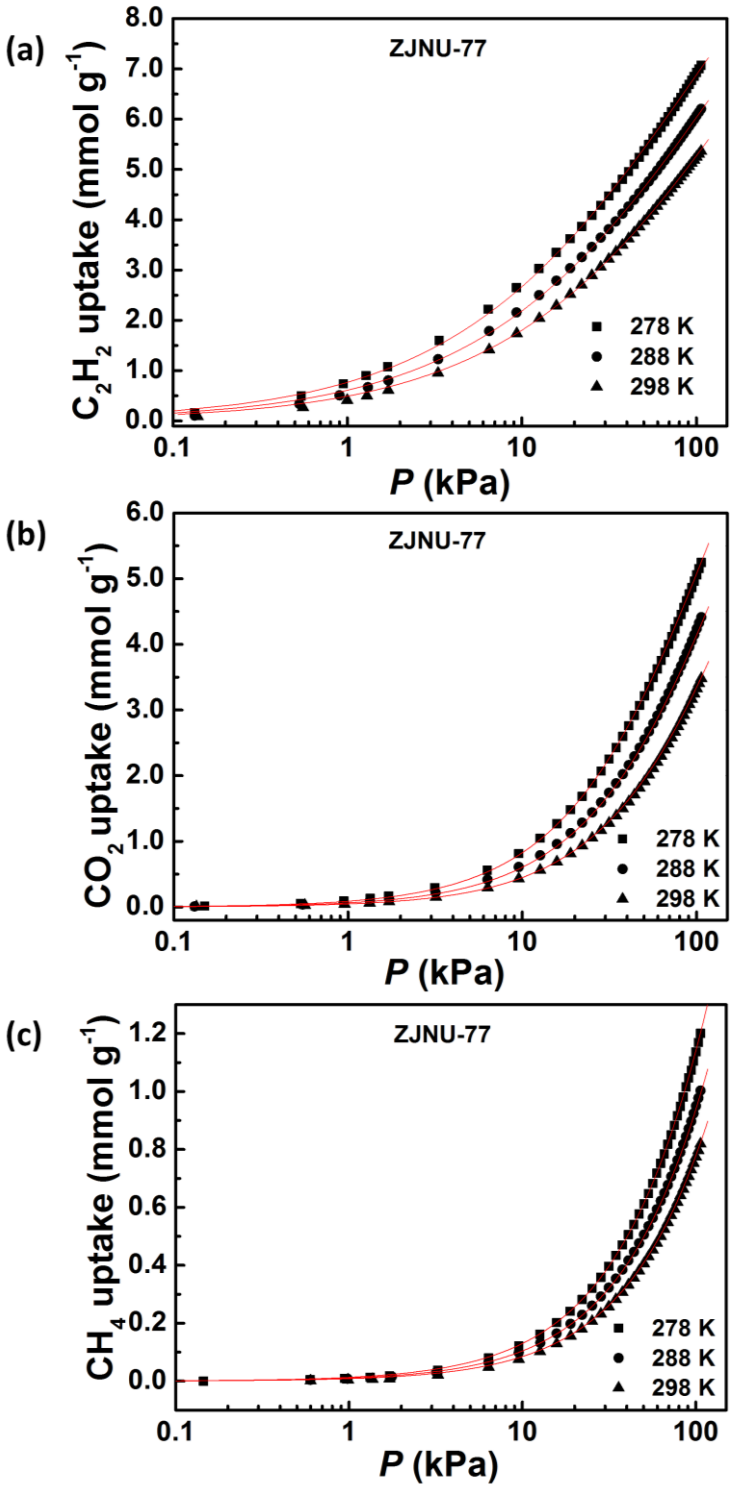



**Fig. S7** Comparison of the pure-component isotherm data for (a) $C_2H_2$, (b) $CO_2$, and (c) $CH_4$ in **ZJNU-77** with the fitted isotherms (shown by continuous solid lines) at 278 K, 288 K and 298 K.

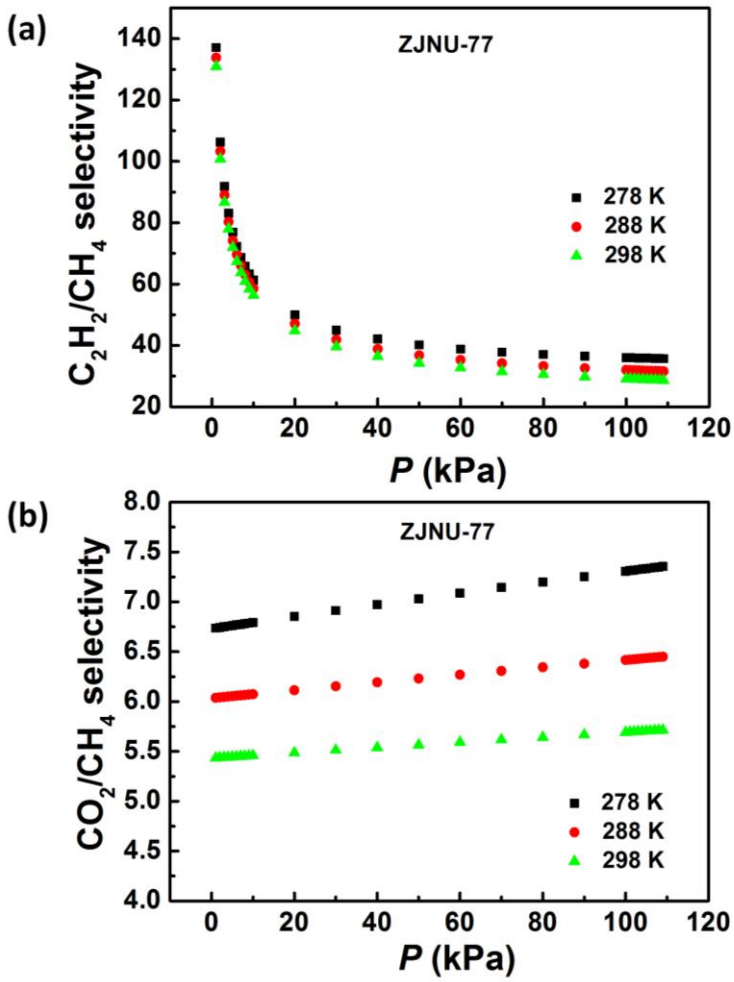



**Fig. S8** IAST selectivities for the equimolar (a) $C_2H_2/CH_4$ and (b) $CO_2/CH_4$ gas mixtures in **ZJNU-77** at three different temperatures of 278 K, 288 K and 298 K.

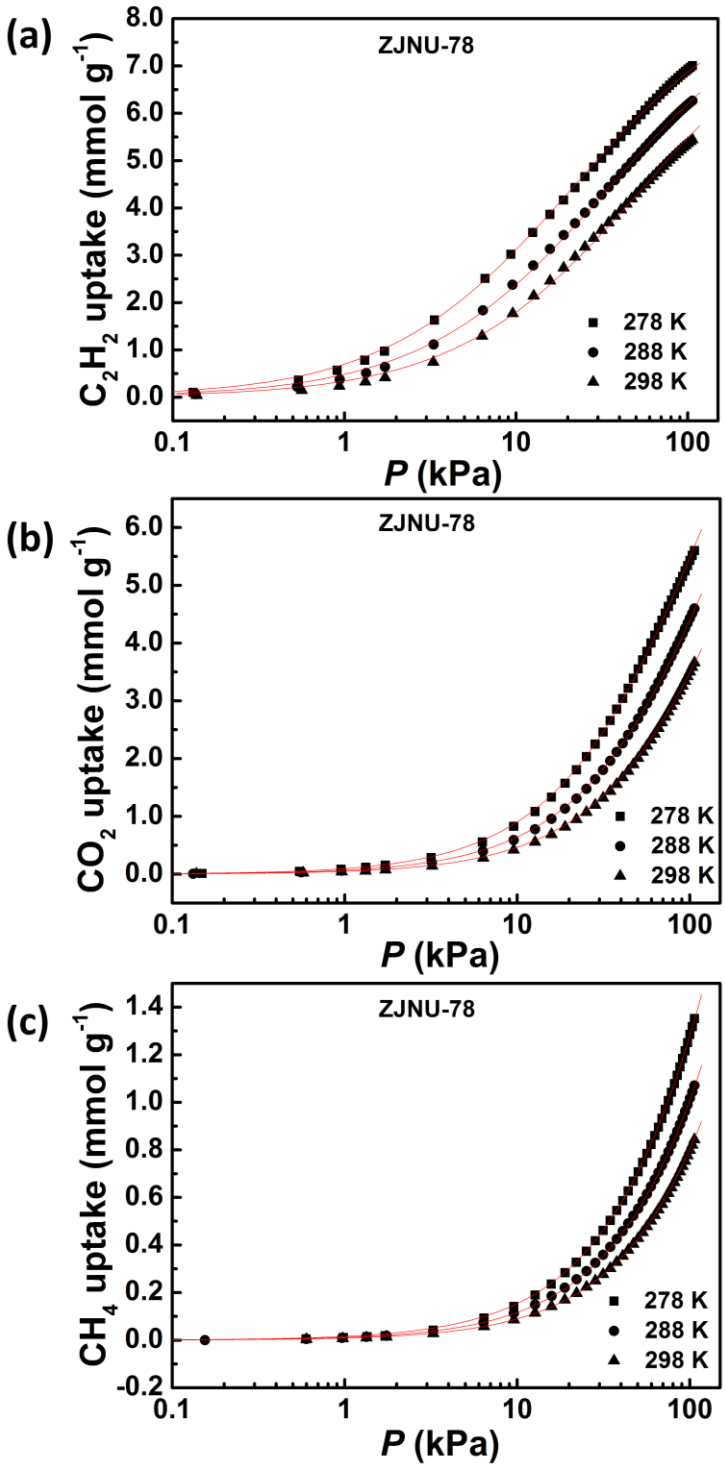



**Fig. S9** Comparison of the pure-component isotherm data for (a) $C_2H_2$, (b) $CO_2$, and (c) $CH_4$ in **ZJNU-78** with the fitted isotherms (shown by continuous solid lines) at 278 K, 288 K and 298 K.

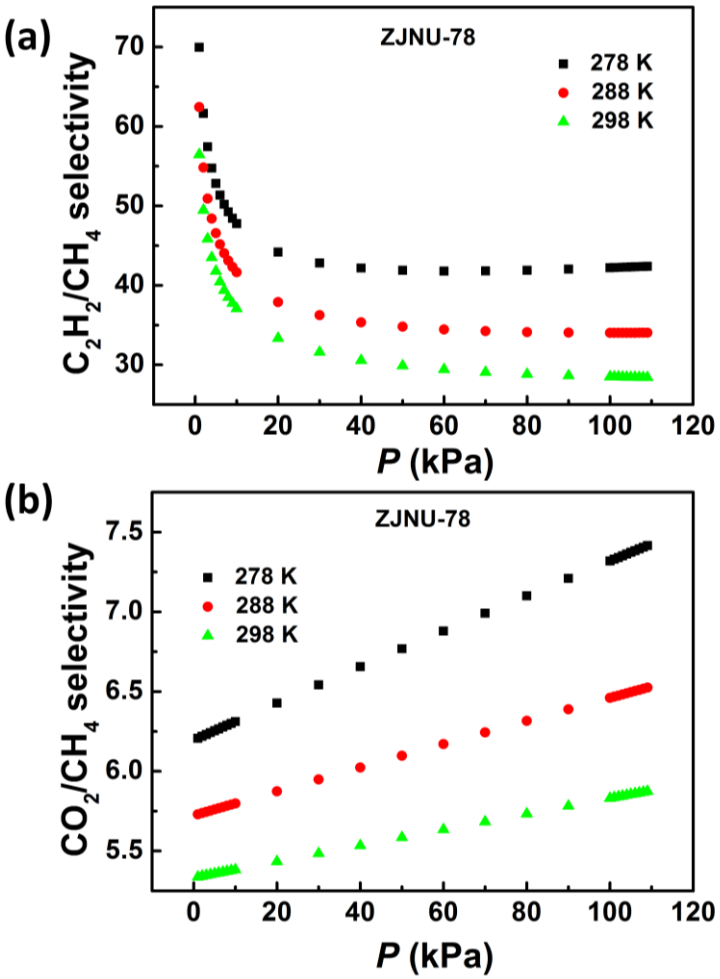



**Fig. S10** IAST selectivities for the equimolar (a) $C_2H_2/CH_4$ and (b) $CO_2/CH_4$ gas mixtures in **ZJNU-78** at three different temperatures of 278 K, 288 K and 298 K.

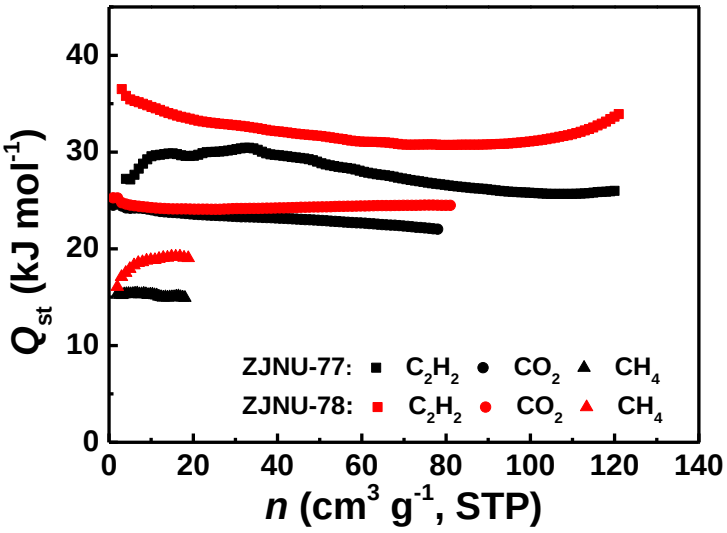
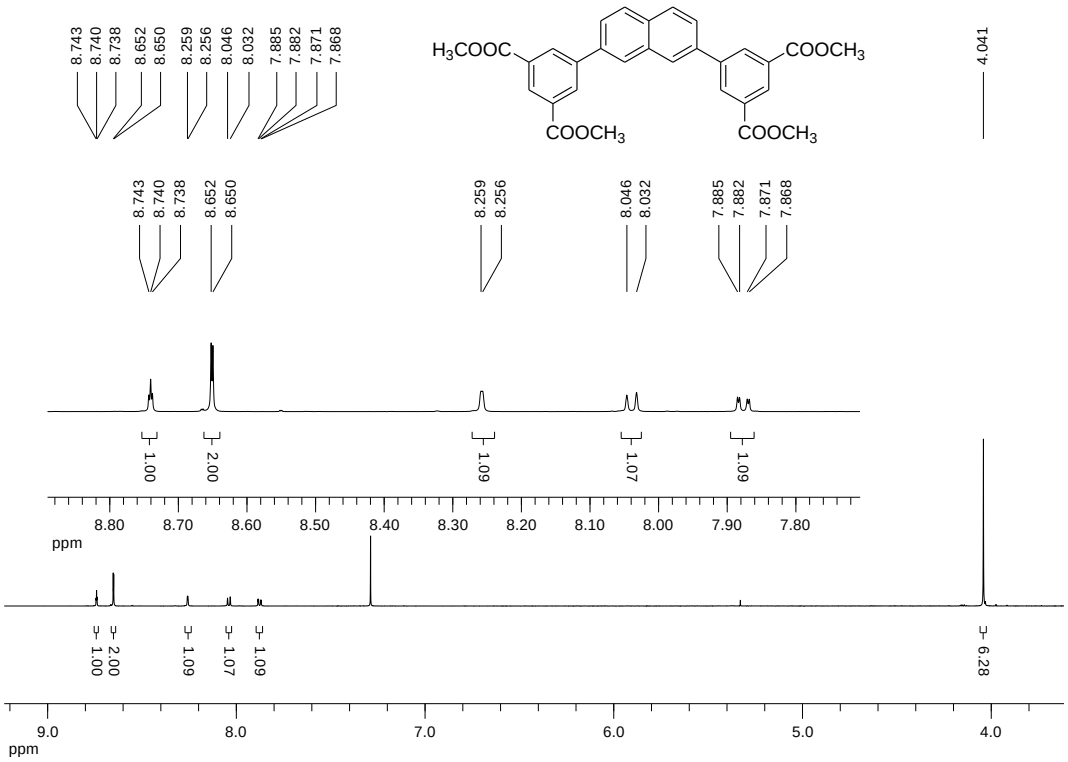
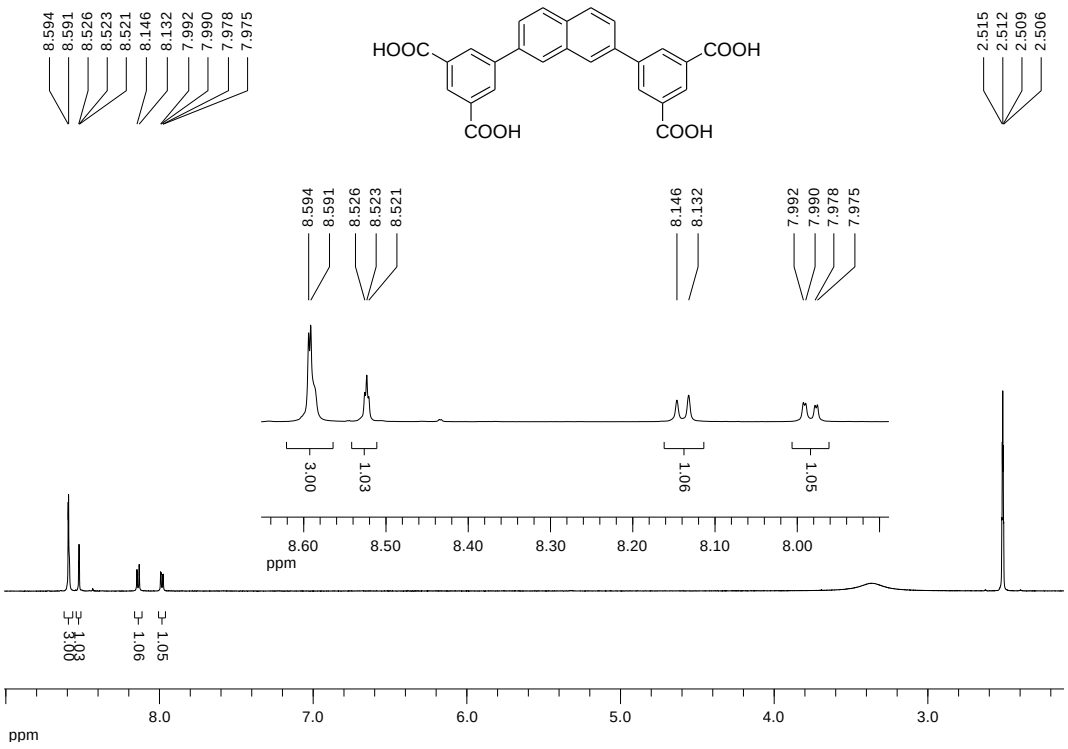



**Fig. S11** The isosteric heat of $C_2H_2$, $CO_2$ and $CH_4$ adsorption in **ZJNU-77** (black) and **ZJNU-78** (red) as a function of gas loadings.


8.743
8.740
8.738
8.652
8.650
8.259
8.256
8.046
8.032
7.885
7.882
7.871
7.868
4.041
H3COOC
COOCH3
COOCH3
COOCH3
1.00
2.00
1.09
1.07
1.09
6.28
ppm


8.594
8.591
8.526
8.523
8.521
8.146
8.132
7.992
7.990
7.978
7.975
2.515
2.512
2.509
2.506
HOOC
COOH
COOH
COOH
3.00
1.03
1.06
1.05
ppm

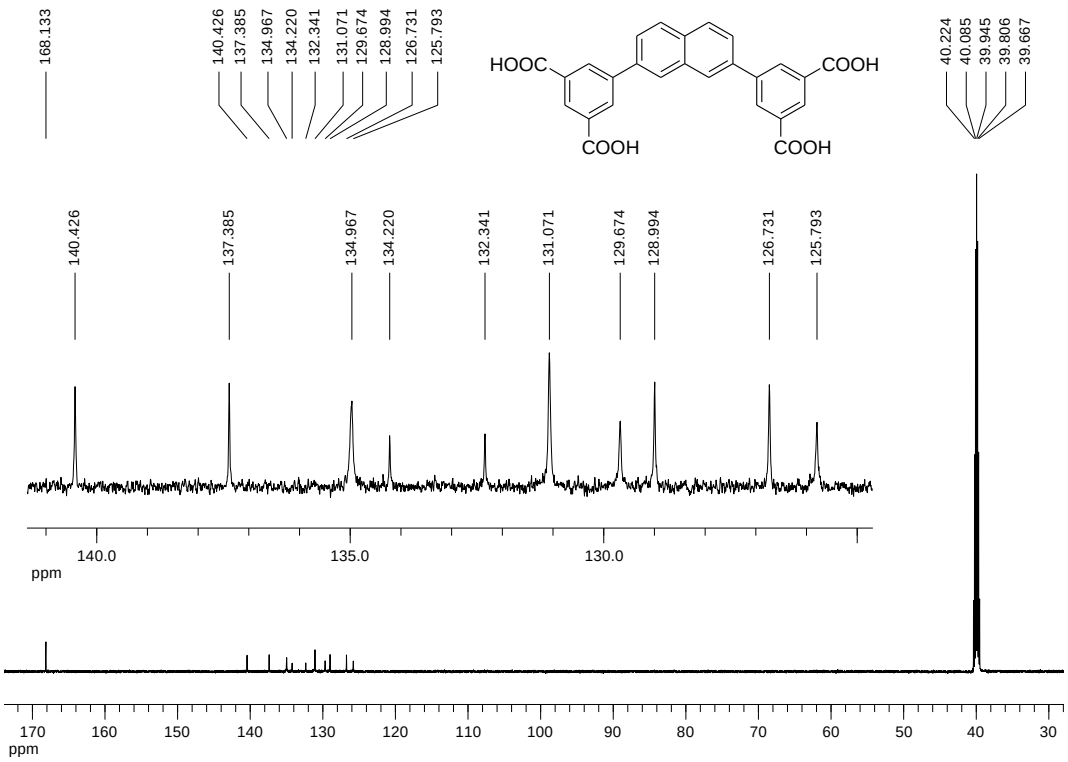



**Fig. S12** $^{1}$H NMR and $^{13}$C NMR spectra

**Table S1** Crystal data and structure refinement for **ZJNU-77-78**.

| MOFs | **ZJNU-77** | **ZJNU-78** |
|---|---|---|
| Empirical formula | $C_{26}H_{16}O_{10}Cu_2$ | $C_{78}H_{48}O_{30}Cu_6$ |
| Formula weight | 615.47 | 1846.40 |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| Crystal system | Cubic | Tetragonal |
| Space group | *F*m-3m | $P4_2$/mnm |
| Unit cell dimensions | $a$ = 39.8231(14) Å<br>$b$ = 39.8231(14) Å<br>$c$ = 39.8231(14)Å<br>$\alpha$ = 90°<br>$\beta$ = 90°<br>$\gamma$ = 90° | $a$ = 28.36750(10) Å<br>$b$ = 28.36750(10) Å<br>$c$ = 28.6376(2) Å<br>$\alpha$ = 90°<br>$\beta$ = 90°<br>$\gamma$ = 90° |
| $V$ (Å$^3$) | 63155(4) | 23045.1(2) |
| $Z$ | 48 | 8 |
| $D_c$ (g cm$^{-3}$) | 0.777 | 1.064 |
| $\mu$ (mm$^{-1}$) | 0.836 | 1.145 |
| $F$(000) | 14880 | 7440 |
| Crystal size (mm) | 0.13 × 0.12 × 0.09 | 0.23 × 0.18 × 0.12 |
| $\theta$ range for data collection (°) | 1.70 to 25.01 | 1.61 to 26.40 |
| Limiting indices | $-45 \le h \le 37$<br>$-47 \le k \le 37$<br>$-46 \le l \le 43$ | $-24 \le h \le 35$<br>$-35 \le k \le 33$<br>$-35 \le l \le 35$ |
| Reflections collected / unique | 39677 / 2759 | 202235 / 12372 |
| $R_{int}$ | 0.0839 | 0.0218 |
| Max. and min. transmission | 0.9286 and 0.8991 | 0.8748 and 0.7787 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2759 / 30 / 118 | 12372 / 0 / 535 |
| Goodness-of-fit on $F^2$ | 1.426 | 1.080 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0783<br>$wR_2$ = 0.2182 | $R_1$ = 0.0511<br>$wR_2$ = 0.1654 |
| $R$ indices (all data) | $R_1$ = 0.1098<br>$wR_2$ = 0.2296 | $R_1$ = 0.0524<br>$wR_2$ = 0.1677 |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.598 and -0.704 | 2.959 and -0.553 |
| CCDC | 1582889 | 1582890 |

**Table S2** Langmuir-Freundich parameters for adsorption of $C_2H_2$, $CO_2$, and $CH_4$ in **ZJNU-77**

| | $q_{sat}$ (mmol $g^{-1}$) | $b_0$ $(kPa)^{-v}$ | $E$ (kJ $mol^{-1}$) | $v$ |
|---|---|---|---|---|
| $C_2H_2$ | 14.24915 | $5.66836\times10^{-5}$ | 15.976 | 0.60723 |
| $CO_2$ | 11.80214 | $5.05081\times10^{-7}$ | 22.211 | 1 |
| $CH_4$ | 8.25222 | $2.59306\times10^{-6}$ | 14.850 | 1 |

**Table S3** Langmuir-Freundich parameters for adsorption of $C_2H_2$, $CO_2$, and $CH_4$ in **ZJNU-78**

| | $q_{sat}$ (mmol $g^{-1}$) | $b_0$ $(kPa)^{-v}$ | $E$ (kJ $mol^{-1}$) | $v$ |
|---|---|---|---|---|
| $C_2H_2$ | 8.85937 | $1.07128\times10^{-6}$ | 26.094 | 0.80202 |
| $CO_2$ | 12.50058 | $2.24056\times10^{-7}$ | 24.169 | 1 |
| $CH_4$ | 6.80442 | $6.33649\times10^{-7}$ | 18.960 | 1 |