1. Experiments

UiO-66: A mixture of zirconium tetrachloride $ZrCl_4$, 1,4-benzenedicarboxylate (BDC), hydrochloric acid and dimethylformamide in the 25 mmol/50 mmol/50 mmol/ 150 mL ratio. The slurry was then introduced in a 750 mL Teflon liner and further introduced in a metallic PAAR bomb. The system was heated 16 h at 220 C. The resulting white product was filtered off, washed with DMF to remove the excess of unreacted terephthalic acid, then washed again with acetone and dried at room temperature.

Zr-NDC: $ZrCl_4$ (4.08 g) and 2,6-naphthalenedicarboxylic acid (NDC) (3.78 g) in DMF (200 mL) at room temperature, then 5 mL hydrochloric acid (the molarity is 12 mol/L) was added to get more crystal nucleus. The slurry was then introduced in a 500 mL single-necked flask, then the fiask was placed in oil bath and heated 403 K for 24 h. Then, the solution was cooled to room temperature. The resulting white product was filtered off, and washed with DMF and acetone to remove the excess of unreacted NDC, then washed again with methanol and dried under vacuum at 423 K for 8 h.

UiO-67: A solution of 4,4'-biphenyldicarboxylate acid (BPDC) (0.25 mmol), $ZrCl_4$ (0.25 mmol), 1.3g benzoic acid and 10 mL DMF was sealed in a 20 mL glass vial and heated at 120 °C for 48 h. The resulting colorless crystals were collected and washed with DMF and acetone and then dried in air.

Zr-bipy: Ligand 2,2'-bipyridine-5,5'-dicarboxylate acid (bipy) (0.4 mmol) and ZrOCl2 (0.4 mmol) were mixed in DMA (12 ml), with 1.8 g benzoic acid was added as the modulate agent. After 30 minutes of stirring at ambient conditions, the mixture was transferred into a 20 mL glass vial and heated at 413 K for 72 hours. A pure phase of octahedral shaped colorless crystals was obtained by filtration and washed with DMA.

BUT-11: A solution of dibenzo [b, d] thiophene-3,7-dicarbox-ylic acid 5,5-dioxide (DTDAO) (61mg, 0.2 mmol), $ZrCl_4$(47 mg, 0.2 mmol), and 1.7 mL of acetic acid in 18 mL of DMF was sealed in a 20 mL glass vial and heated at 120 °C for 48 h. The resulting colorless crystals were collected and washed with DMF and acetone and then dried in air.

2. Thermogravimetric analysis (TGA)

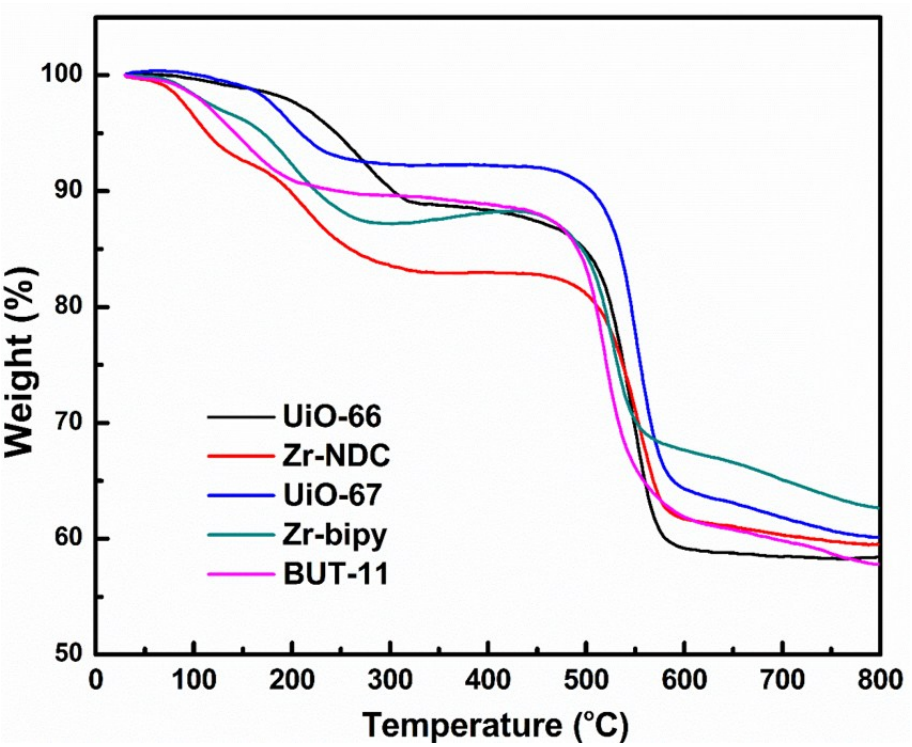
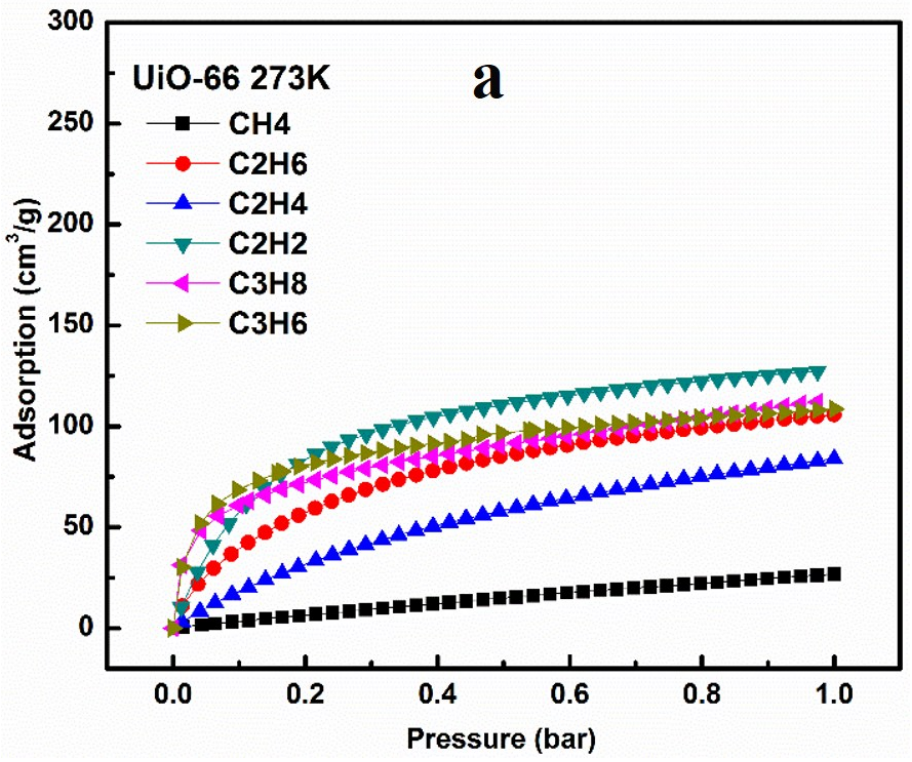
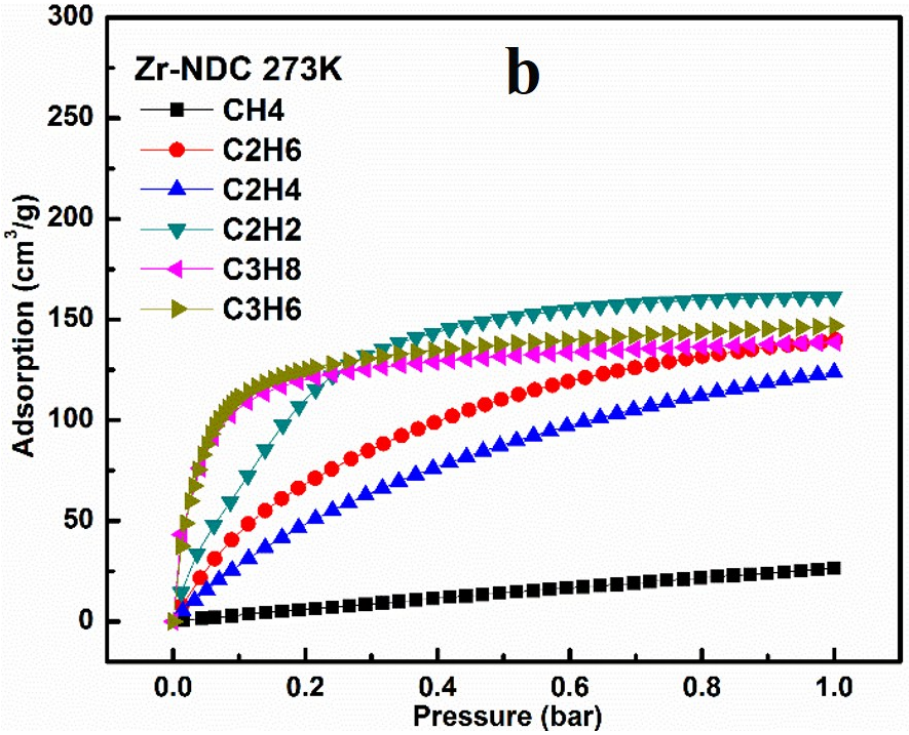
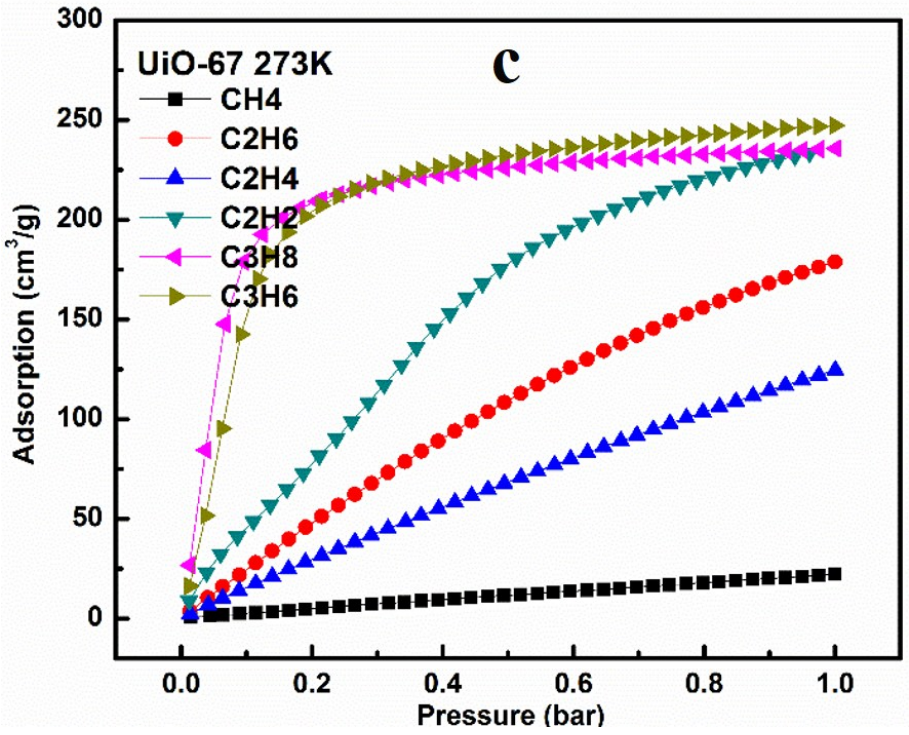


Fig. S1 The TGA of UiO-66, Zr-NDC, UiO-67, Zr-bipy and BUT-11

3. Single-component adsorption measurements at 273 K




Zr-NDC 273K
b
CH4
C2H6
C2H4
C2H2
C3H8
C3H6
Adsorption (cm3/g)
Pressure (bar)
0
50
100
150
200
250
300
0.0
0.2
0.4
0.6
0.8
1.0


UiO-67 273K
c
CH4
C2H6
C2H4
C2H2
C3H8
C3H6
Adsorption (cm3/g)
Pressure (bar)
0
50
100
150
200
250
300
0.0
0.2
0.4
0.6
0.8
1.0

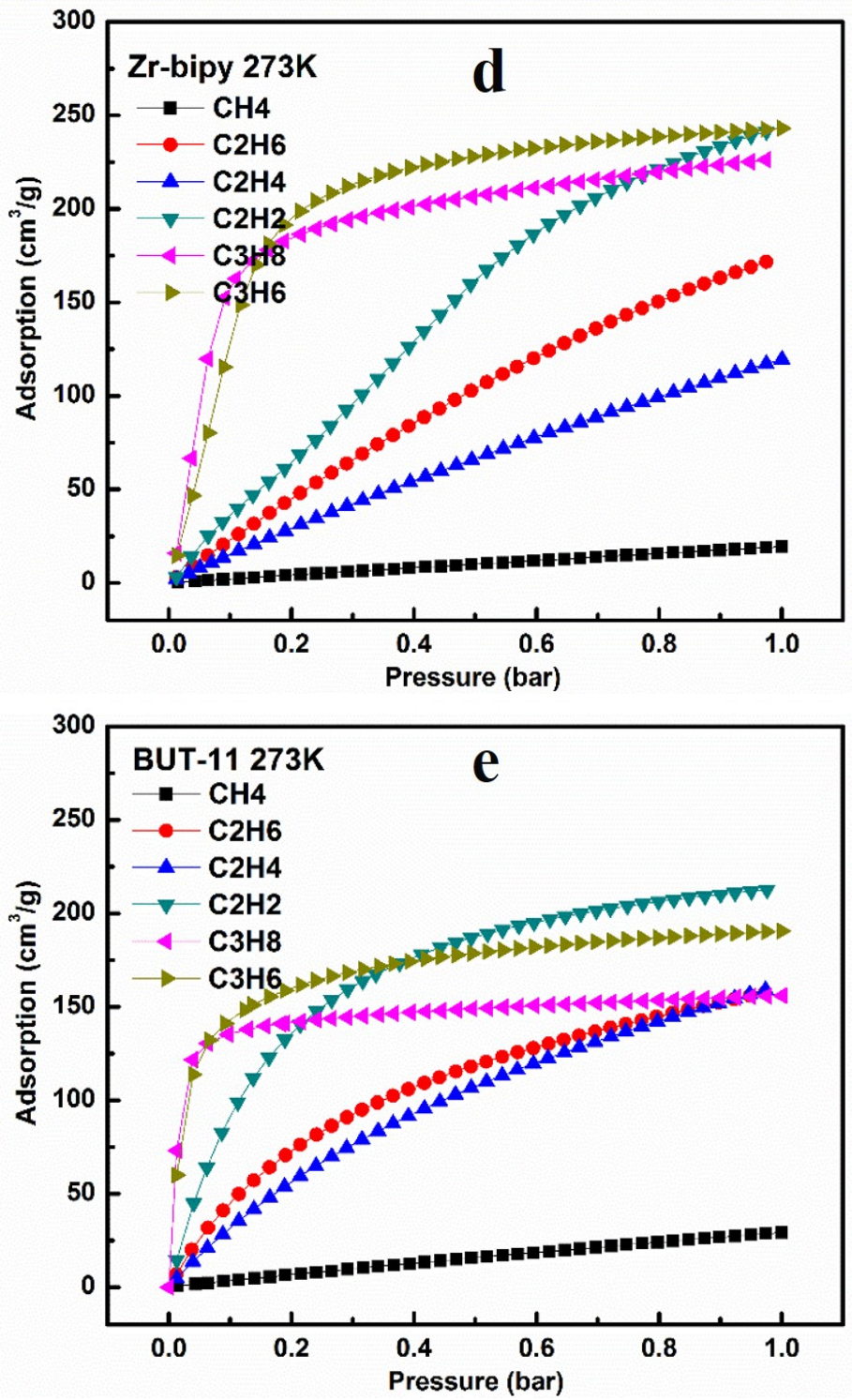
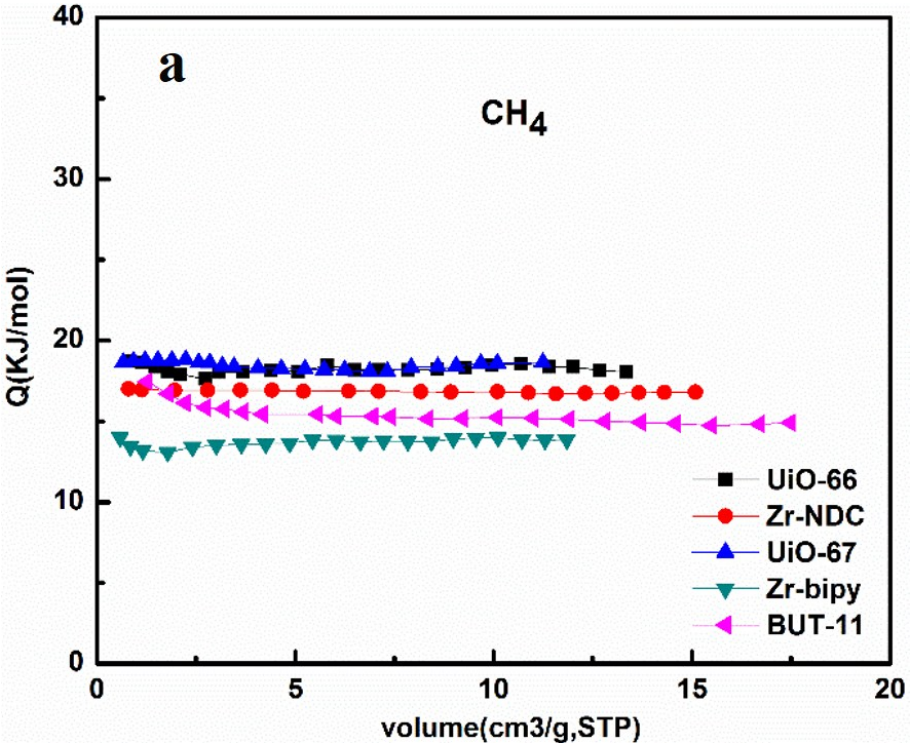
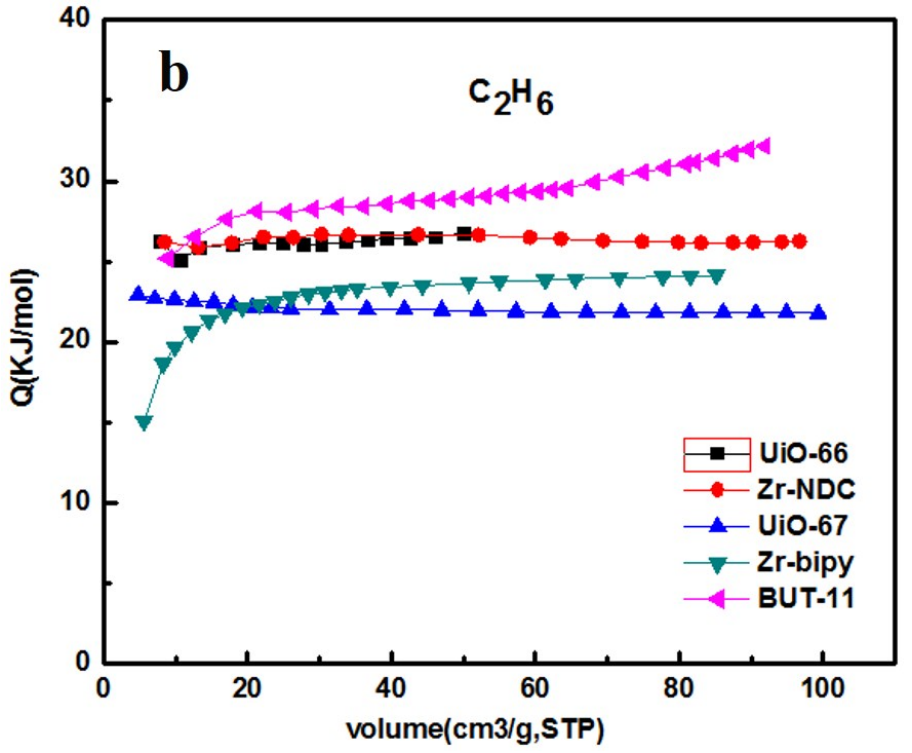
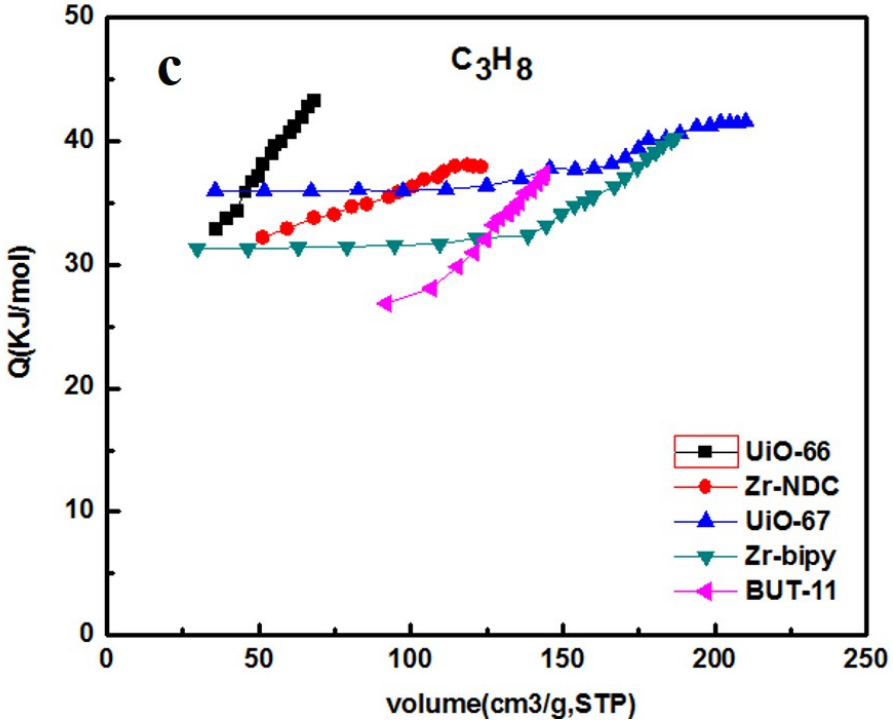


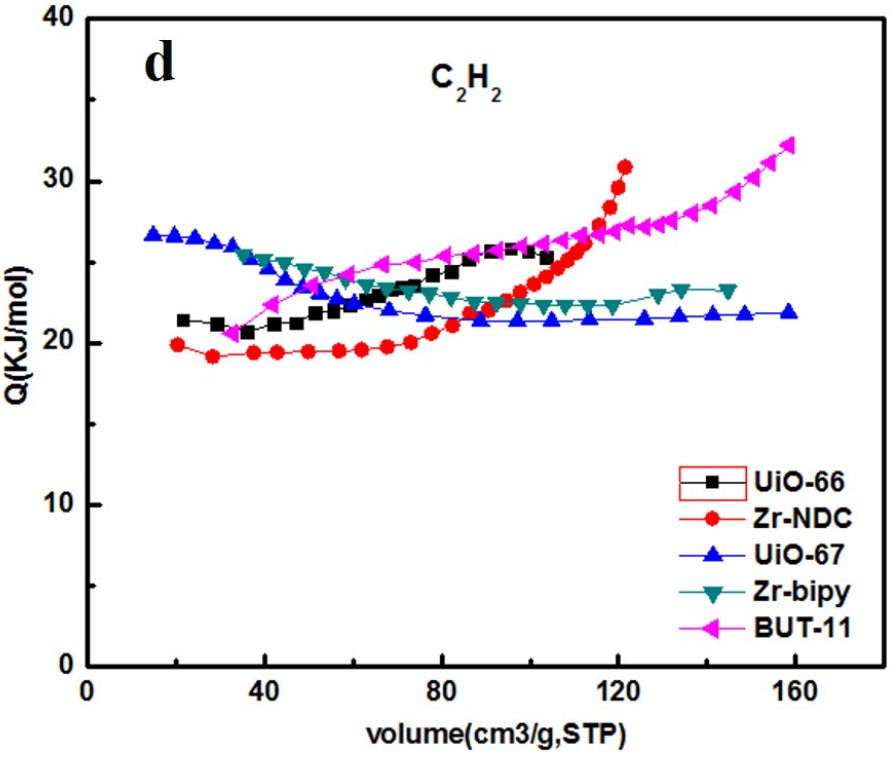
Fig. S2 UiO-66 (a), Zr-NDC (b), UiO-67 (c), Zr-bipy (d) and BUT-11 (e) of light hydrocarbons adsorption isotherms at 273 K.

4. Isosteric Heat of Adsorption


a
CH4
Q(KJ/mol)
volume(cm3/g,STP)
UiO-66
Zr-NDC
UiO-67
Zr-bipy
BUT-11


b
C2H6
Q(KJ/mol)
volume(cm3/g,STP)
UiO-66
Zr-NDC
UiO-67
Zr-bipy
BUT-11


c
C3H8
Q(KJ/mol)
volume(cm3/g,STP)
UiO-66
Zr-NDC
UiO-67
Zr-bipy
BUT-11
0
10
20
30
40
50
0
50
100
150
200
250


d
C2H2
Q(KJ/mol)
volume(cm3/g,STP)
UiO-66
Zr-NDC
UiO-67
Zr-bipy
BUT-11
0
10
20
30
40
0
40
80
120
160

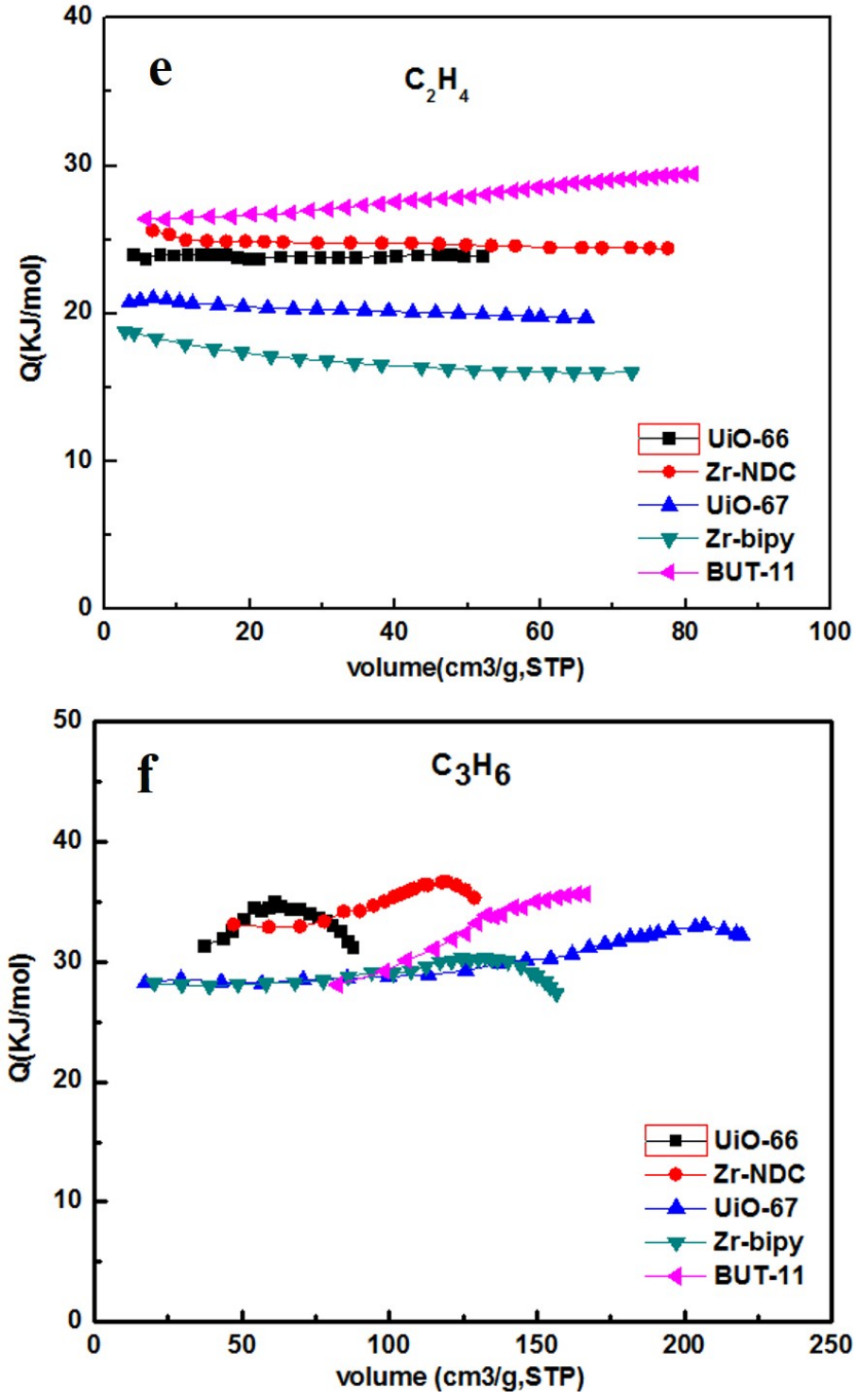
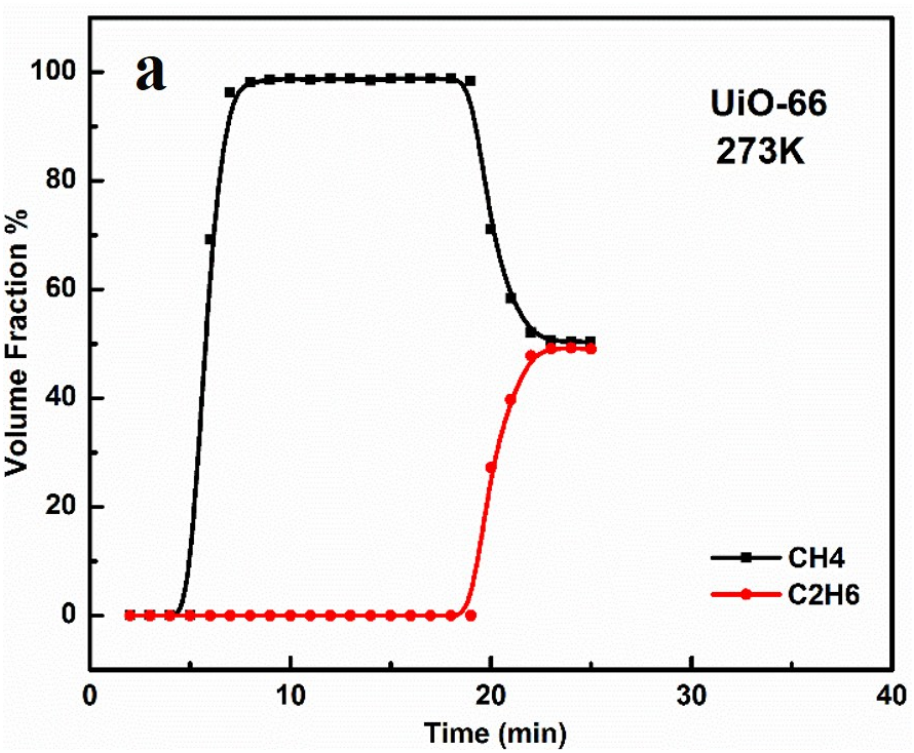
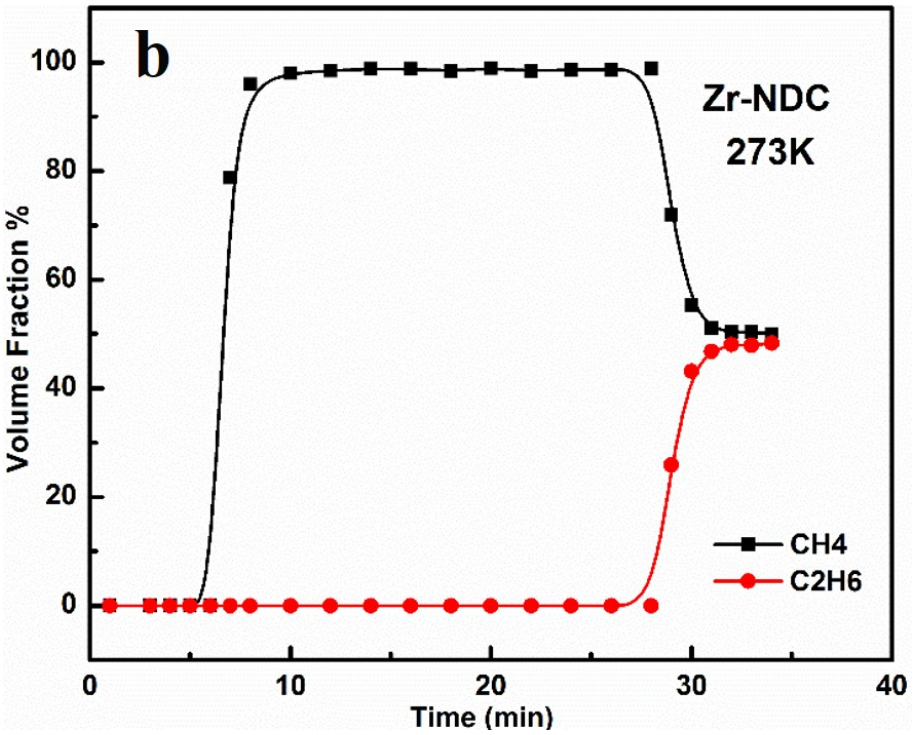


Fig. S3 Adsorption heats for CH_4, C_2H_6, C_3H_8, C_2H_2, C_2H_4 and C_3H_6 on UiO-66 (black), Zr-NDC (red), UiO-67 (blue), Zr-bipy (olive) and BUT-11(magenta).

5. Breakthrough Experiments


a
UiO-66
273K
Volume Fraction %
Time (min)
CH4
C2H6
0
20
40
60
80
100
0
10
20
30
40


b
Zr-NDC
273K
Volume Fraction %
Time (min)
CH4
C2H6
0
20
40
60
80
100
0
10
20
30
40

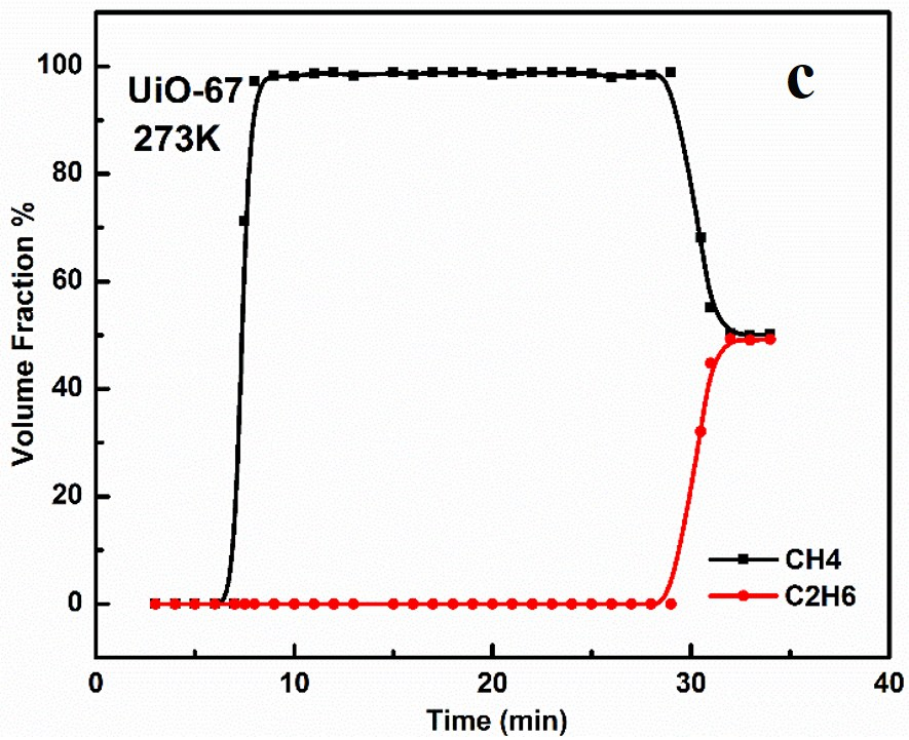
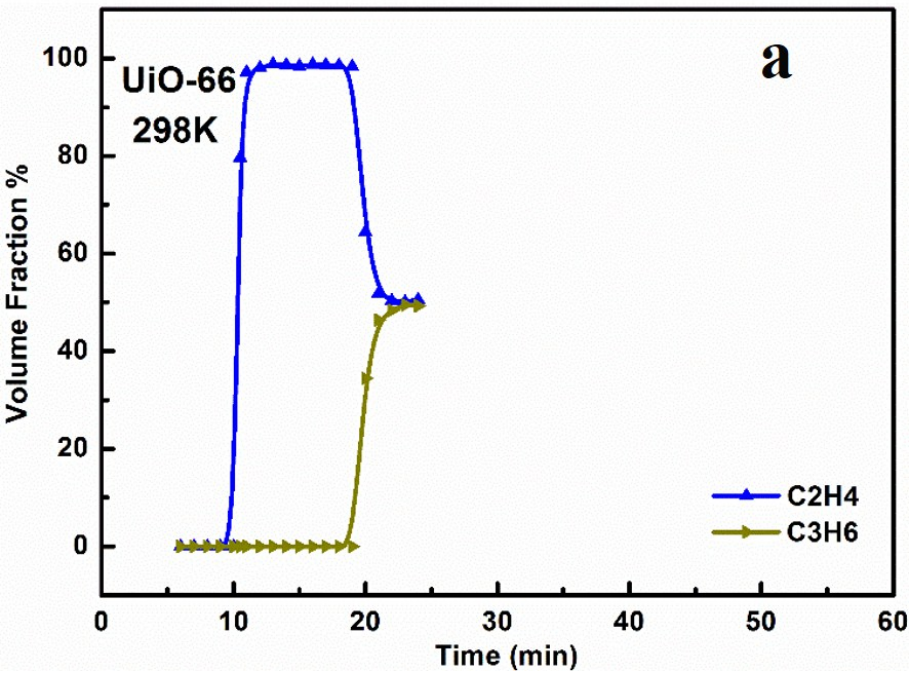


Fig. S4 Breakthrough experiments of UiO-66 (a), Zr-NDC (b) and UiO-67 (c) for separation of equimolar 2-component CH_4/C_2H_6 mixtures in a fixed bed of adsorbent at 273 K.



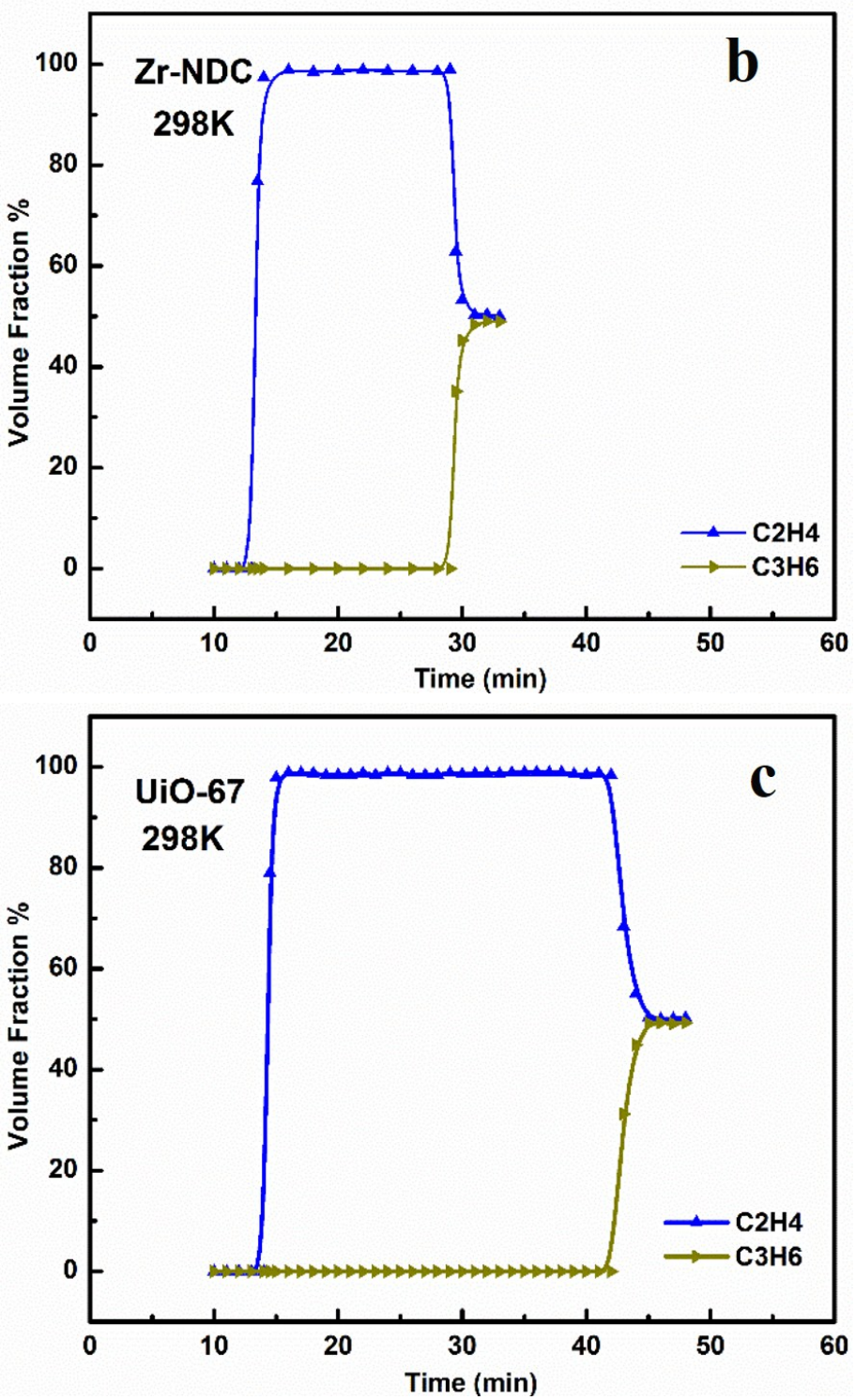
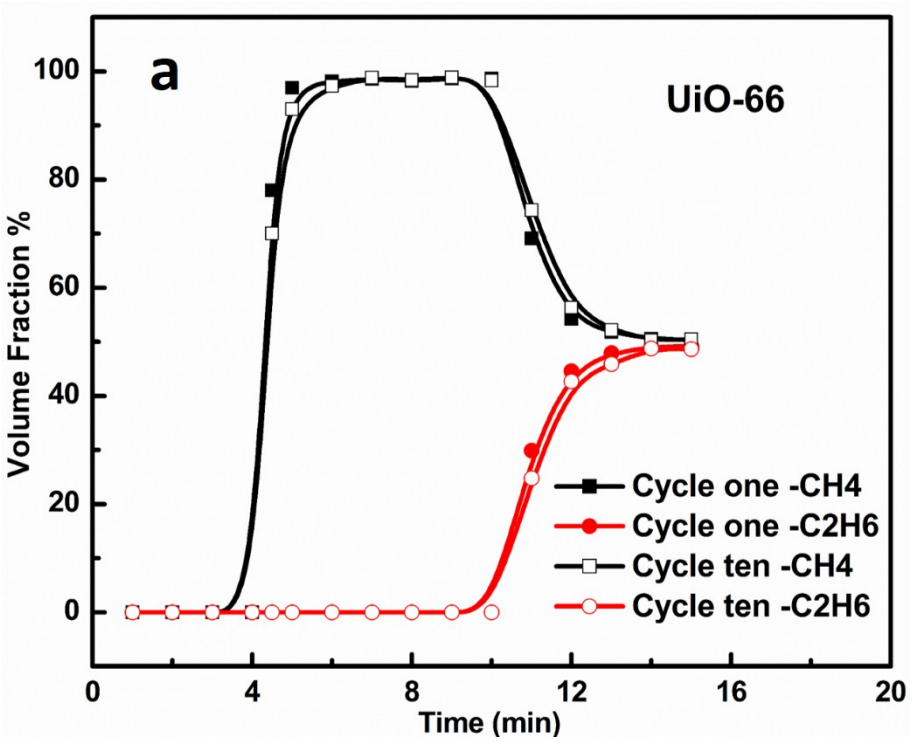
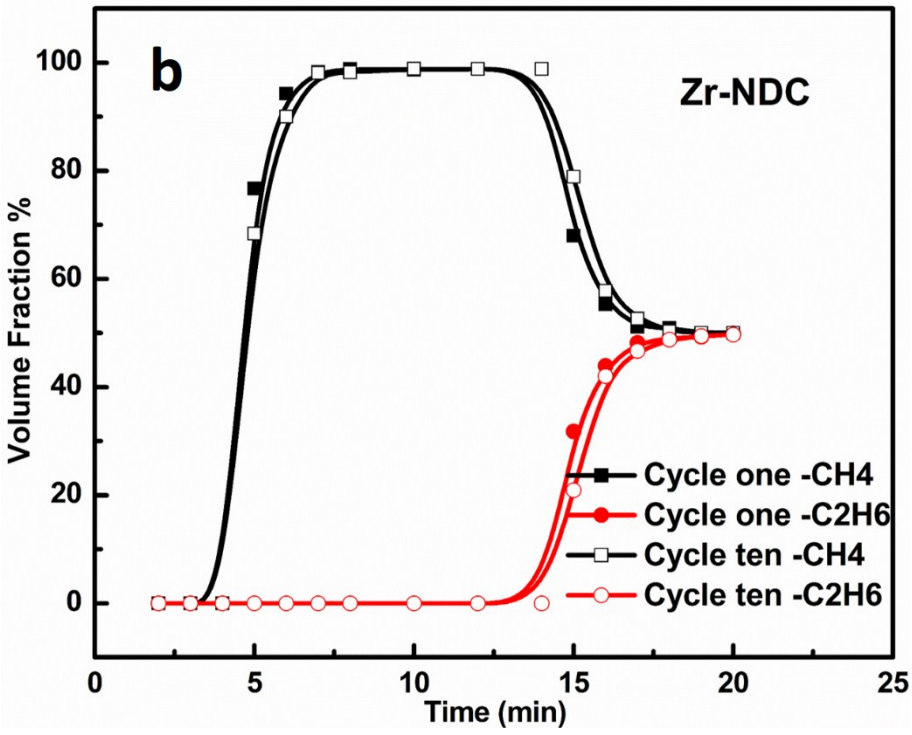


Fig. S5 Breakthrough experiments of UiO-66 (a), Zr-NDC (b) and UiO-67 (c) for separation of equimolar 2-component C_2H_4/C_3H_6 mixtures in a fixed bed of adsorbent at 298 K.


a
UiO-66
Volume Fraction %
Time (min)
Cycle one -CH4
Cycle one -C2H6
Cycle ten -CH4
Cycle ten -C2H6


b
Zr-NDC
Volume Fraction %
Time (min)
Cycle one -CH4
Cycle one -C2H6
Cycle ten -CH4
Cycle ten -C2H6

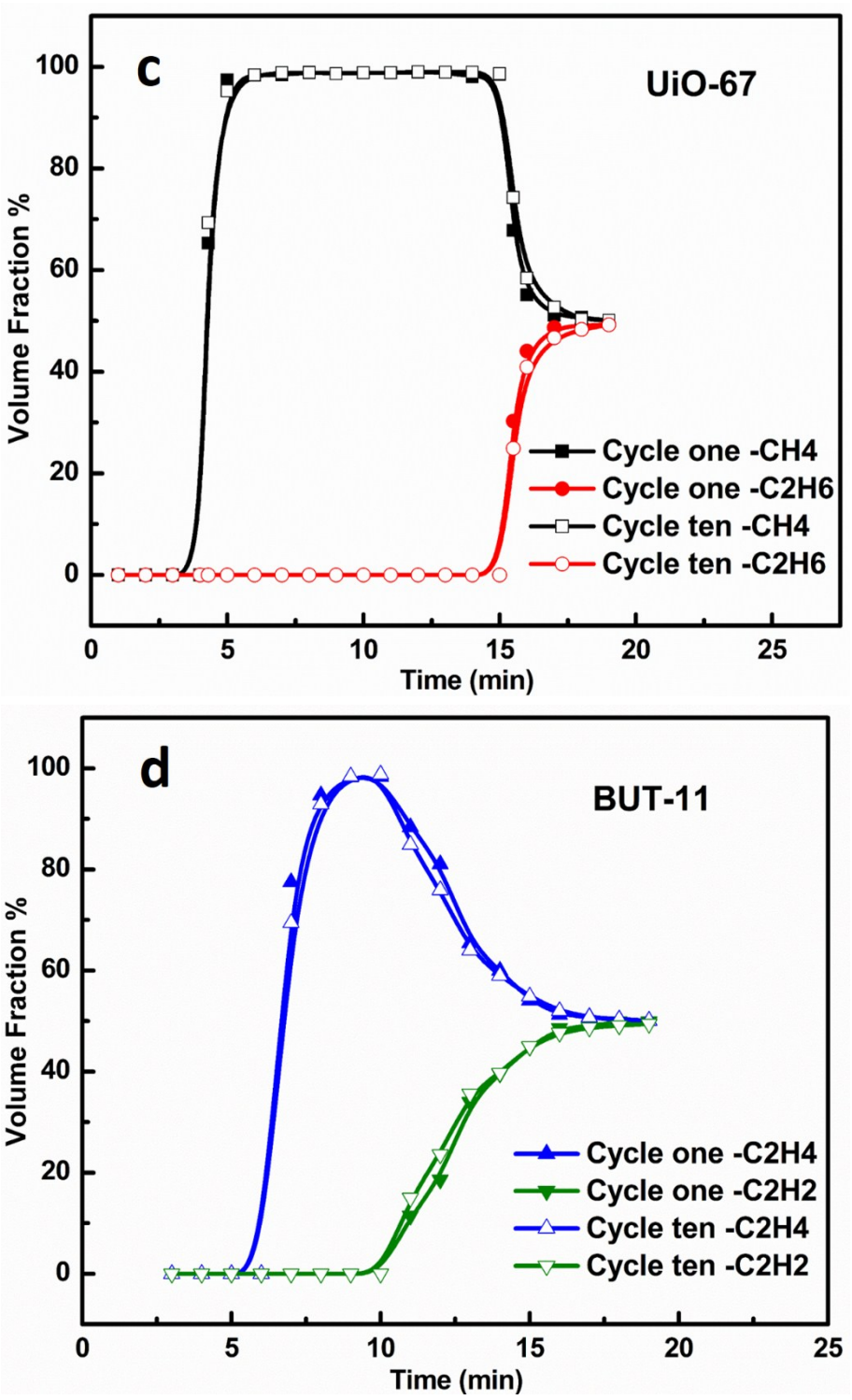


Fig. S6 Separation cycling experiments for CH_4/C_2H_6 (50%/50%) mixtures on UiO-66 (a), Zr-NDC(b), UiO-67(c) and C_2H_4/C_2H_2 (50%/50%) mixtures on BUT-11(d) at 298 K and 1 bar.

Samples	The breakthrough time (min)		
	CH_4	C_2H_6	C_2H_6-CH_4
UiO-66	4.5	11.0	6.5
Zr-NDC	5.0	15.0	10.0
UiO-67	4.3	15.5	11.2
	C_2H_6	C_3H_8	C_3H_8-C_2H_6
UiO-66	11.0	20.0	9.0
Zr-NDC	15.0	27.0	12.0
UiO-67	15.5	44.0	28.5
	C_2H_4	C_3H_6	C_3H_6-C_2H_4
UiO-66	10.5	20.0	9.5
Zr-NDC	13.5	29.5	16.0
UiO-67	14.5	43.0	28.5
Raw gas ratio	C_2H_4	C_2H_2	C_2H_2-C_2H_4
BUT-11 (50%:50%)	7.0	11.0	4
BUT-11 (99%:1%)	6.3	16.5	10.2

Table.S1 Breakthrough times for gas separation experiments using light hydrocarbons mixtures at 298 K and 1 bar.

6. SEM of the studied MOFs

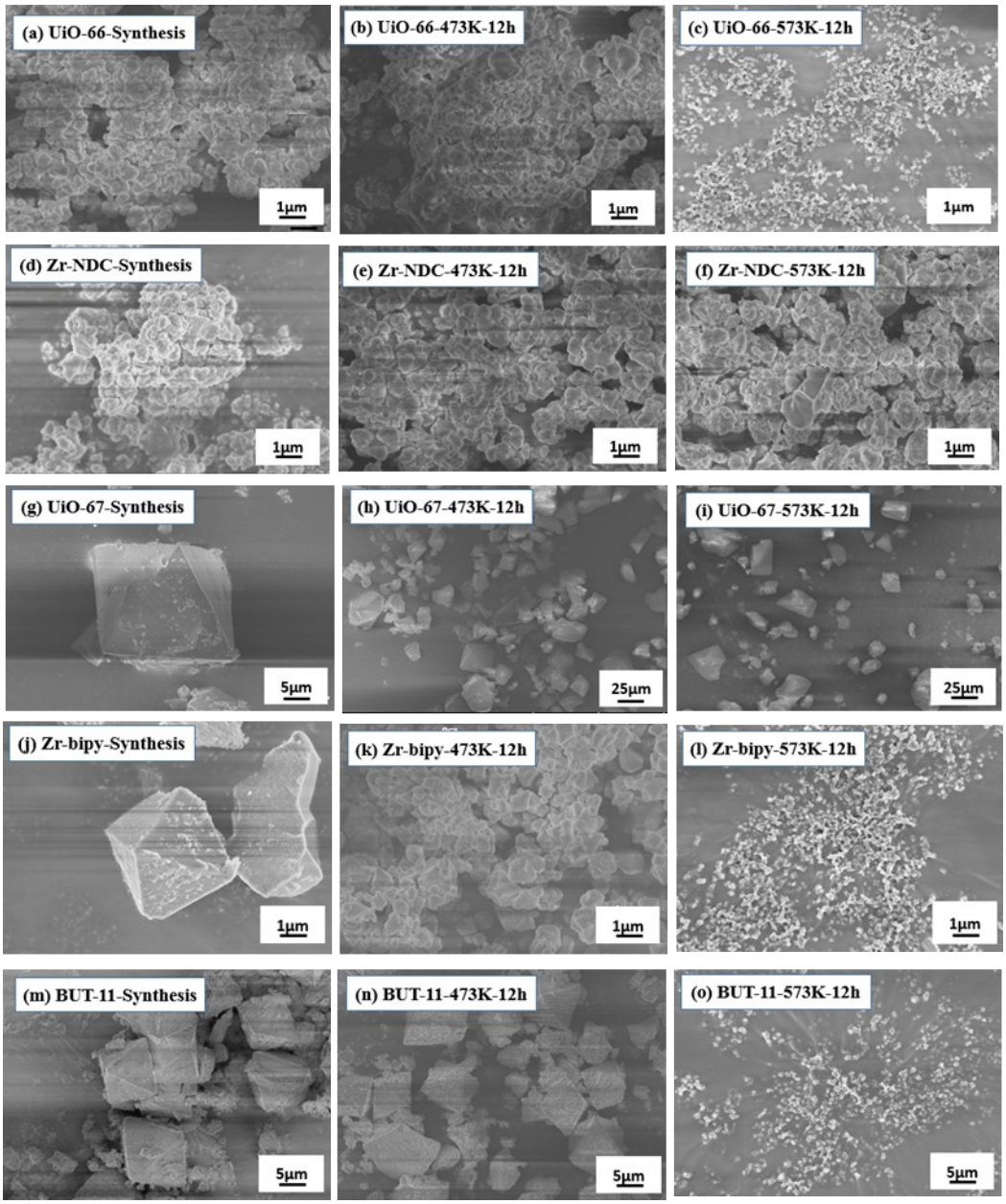


Fig. S7 SEM of the UiO-66, Zr-NDC, UiO-67, Zr-bipy and BUT-11. (left: synthesis; middle: Vacuum 12h at 473K; right: Vacuum 12h at 573K)