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Supporting Information

Amino-functionalized Cu-MOF for efficient purification methane from light hydrocarbons and excellent catalytic performance

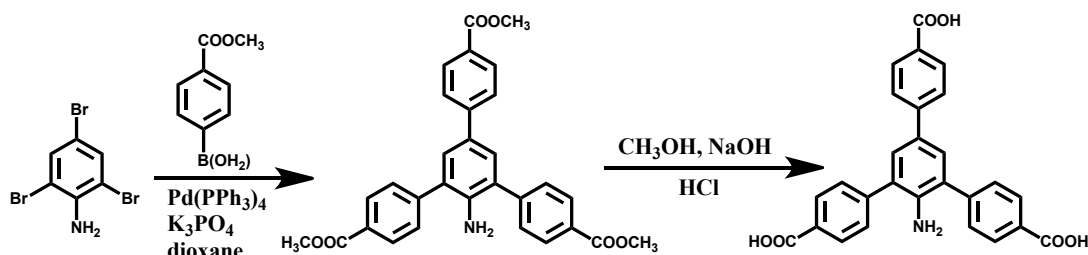
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1. Synthesis of H₃BTB-NH₂ ligandScheme S1. Synthetic procedures of the H₃BTB-NH₂ ligand.**(1) Dimethyl 2'-amino-5'-(4-(methoxycarbonyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate**

2,4,6-tribromoaniline (1.6 g, 4 mmol), Methyl 4-boronobenzoate (1.57 g, 14.4 mmol), Pd(PPh₃)₄ (0.15 g, 0.13 mmol) and K₃PO₄ (3.82 g, 18.0 mmol) were placed in a 500 mL two-necked round bottom flask under a N₂ gas atmosphere. The flask was further charged with a 200 mL of dry 1,4-dioxane, and the contents were heated for 48 h. After the mixture was cooled to room temperature, the solvent was removed, water was added. The water phase was washed with CH₂Cl₂. The mixed organic phases were dried with MgSO₄. After the solvent was removed, the crude product was purified by column chromatography with CH₂Cl₂ as the eluent. ¹H NMR (400 MHz, CDCl₃) 3.87(s, 3H), 3.96(s, 6H), 7.59(d, 4H), 7.84(s, 2H), 8.16(d, 4H). Anal. Calcd. for C₂₄H₂₁NO₆ (mw 419): C, 68.73; N, 3.34; H, 5.05. Found: C, 68.80; N, 3.29; H, 5.10.

(2) 2'-amino-5'-(4-carboxyphenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid

Dimethyl 2'-amino-5'-(4-(methoxycarbonyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (2.0 g, 4.8 mmol) was dissolved in 50 mL MeOH, 50 mL 2 M NaOH aqueous solution was added. The mixture was stirred at 50°C overnight. The organic phase was removed, the aqueous phase was acidified with diluted hydrochloric acid to give yellow precipitate, which was filtered and washed with water several times. ¹H NMR (400 MHz, CDCl₃) 5.10 (s, 2H), 7.62(d, 6H), 8.07(d, 4H), 12.78(s, 3H). Anal. Calcd. for C₂₁H₁₅NO₆ (mw 377): C, 66.84; N, 3.71; H, 4.01. Found: C, 66.78; N, 3.73; H, 4.00.

2. Materials and Instruments

All the chemical reagents were purchased from chemical vendors and without further purification. The powder XRD diffractograms were obtained on a Panalytical X-Pert PRO diffractometer with Cu-K α radiation. Elemental analyses (C, H, N) were performed using a CE instruments EA 1110 elemental analyzer. Infrared spectroscopy (IR) were collected on a Nicolet 330 FTIR Spectromete within the 4000-400 cm⁻¹ region. Thermo-gravimetric analysis (TGA) measurements were carried out on a Mettler Toledo TGA instrument under a N₂ atmosphere with a heating rate 10°C /min at the range of 40-900°C. Gas adsorption experiments containing low-pressure H₂, N₂ gas sorption experiments at 77 K, 87 K, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ light hydrocarbons experiments at 273 K and 298 K were carried out on the surface area analyzer ASAP-2020.

Catalytic experiment studies: The reactions catalytic cycloaddition of CO₂ and epoxides were implemented under solvent free environment at a certain temperature, pressure and reaction time. Epoxides (15.0 mmol), **UPC-99** as catalyst (0.01 mmol), TBAB (n-Bu₄NBr) (1 mmol) in a 10 mL Schlenk tube. At the end of the reaction, the product is centrifuged and the supernatant is collected for further testing. **UPC-99** was centrifuged by DMA and methanol many times for the next cycle catalytic test. Conversion of products was determined by gas chromatography(GC-MS). (DB-1 column, L×I.D. × T.H. 30.0 m × 0.25 mm × 0.25 μ m; injector temperature 300 °C). Heating rate: 15 °C /min

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3. Synthesis, Crystal data, structure and characterization of UPC-99.

3.1 Synthesis of UPC-99

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.035 g, 0.15 mmol), $\text{H}_3\text{BTB-NH}_2$ (0.003g, 0.05 mmol) in 2 mL DMA- H_2O (v/v = 1:1) were sealed in a 10 mL Teflon reactor, and heated to 75 °C in 60 min, kept 75 °C for 1200 min, then the reaction system was cooled to room temperature slowly at a rate of 0.1 °C/min. The blue, block-shaped crystals were obtained and washed with DMA and dried in the air (yield: 82%. based on Copper). Elemental analysis calcd (%) for **UPC-99**: C 55.70; H 3.44; N 2.41. Found: C 55.63; H 3.49; N 2.37. IR (KBr, cm^{-1}): 3393 (s), 1608 (s), 1399 (s), 1259 (w), 1182(w), 1020(m), 788 (w), 592(w).

3.2 Crystal data, structure and characterization of UPC-99.

Table S1. Crystal data and structure refinement of UPC-99 with CCDC 1872997.

Identification code	UPC-99
Empirical formula	C ₅₄ H ₄₀ Cu ₃ N ₂ O ₁₆
Formula weight	1163.53
Temperature/K	150.01(10)
Crystal system	Cmce
Space group	orthorhombic
a/Å	59.7742(15)
b/Å	29.1040(6)
c/Å	13.6375(5)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	23724.7(12)
Z	2
ρ_{calc} mg/mm ³	0.651
μ /mm ⁻¹	0.894
F(000)	4744.0
2 Θ range for data collection	6.756 to 132.99
Reflections collected	26580
Independent reflections	10550 [R _{int} = 0.12410, R _{sigma}
Data/restraints/parameters	10550/978/343
Goodness-of-fit on F ²	0.953
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0930, wR ₂ = 0.2668
Final R indexes [all data]	R ₁ = 0.1219, wR ₂ = 0.2955
Largest diff. peak/hole /e Å ⁻³	1.23/-0.80

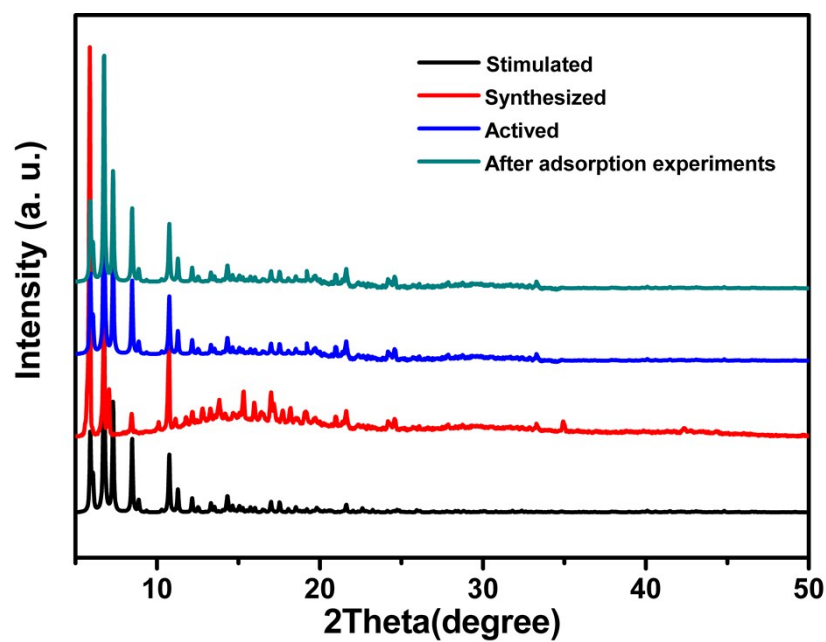


Figure S1. Powder X-ray diffraction PXRD data of UPC-99.

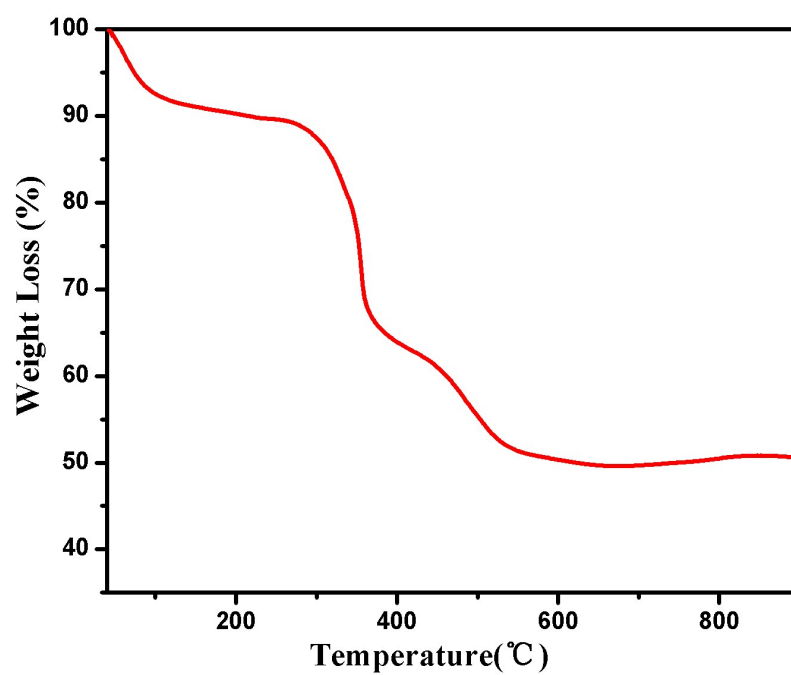


Figure S2. The TGA of UPC-99.

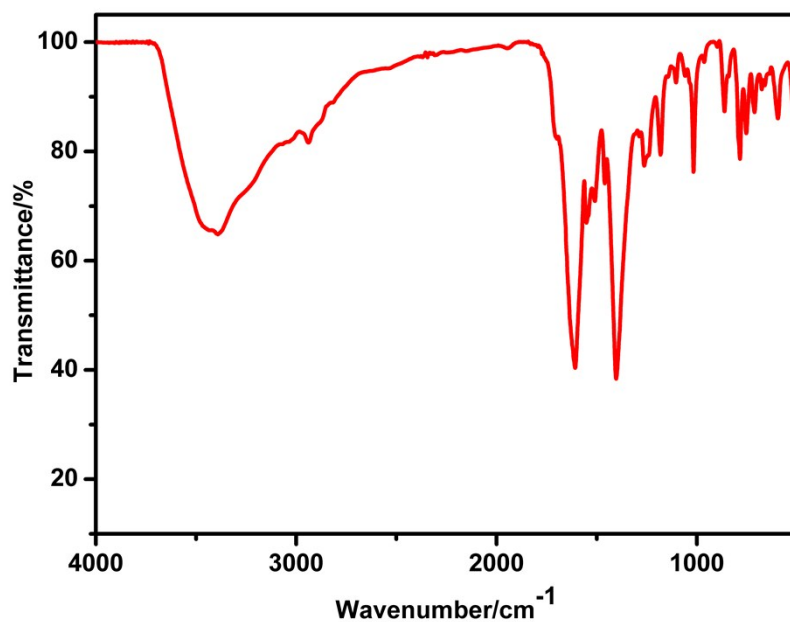
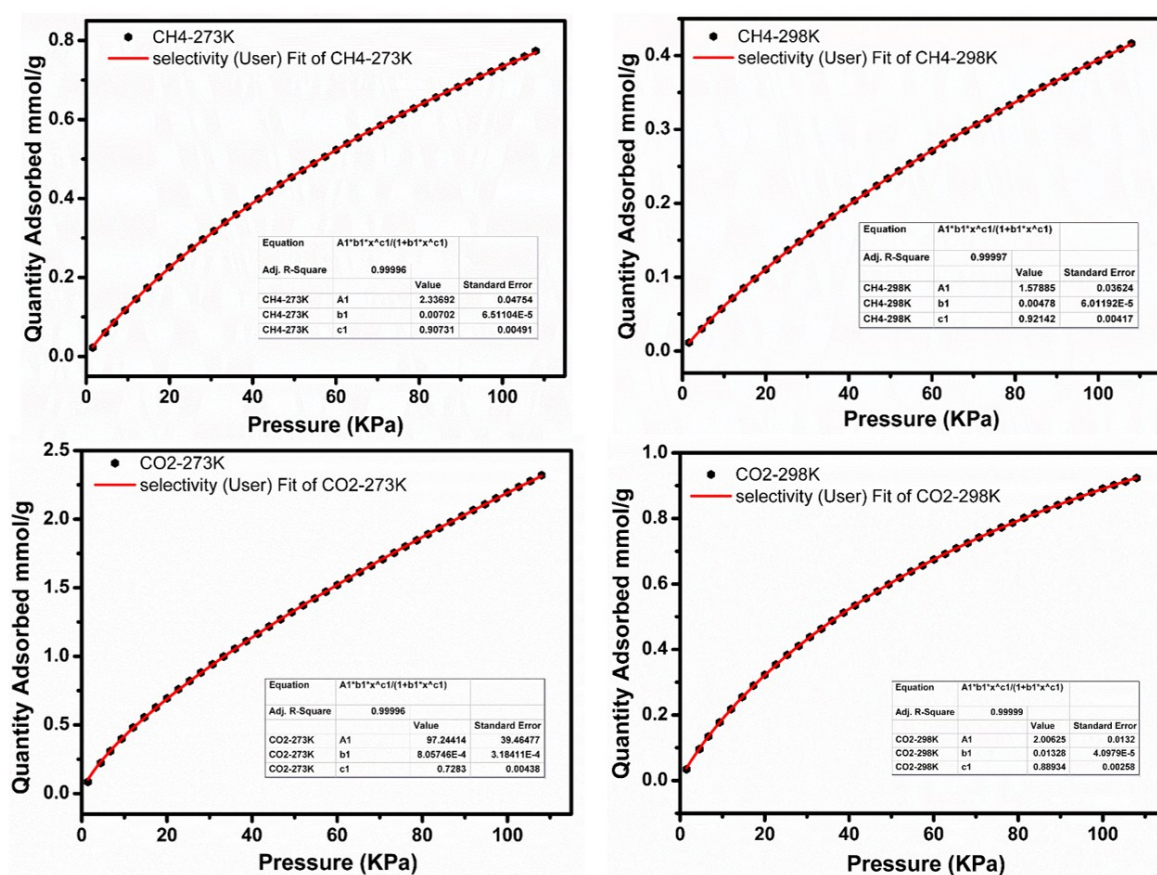
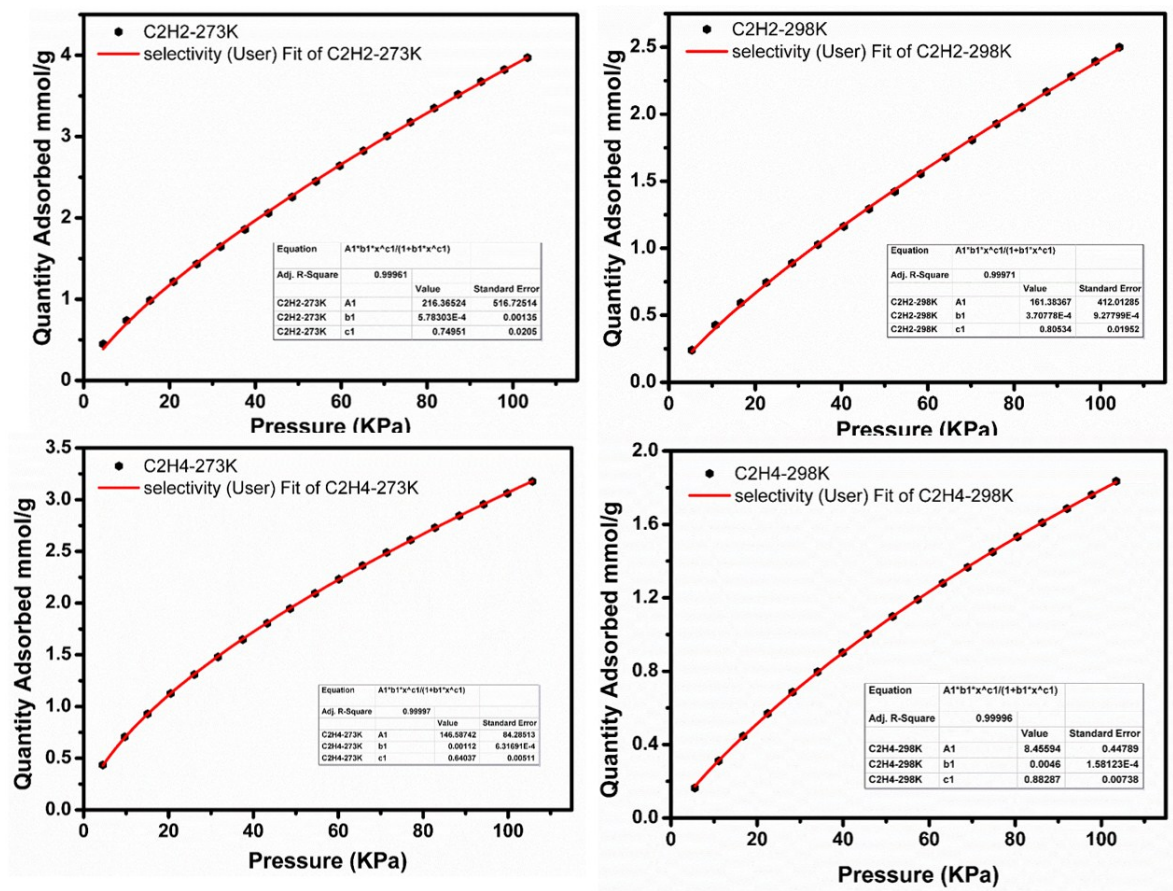


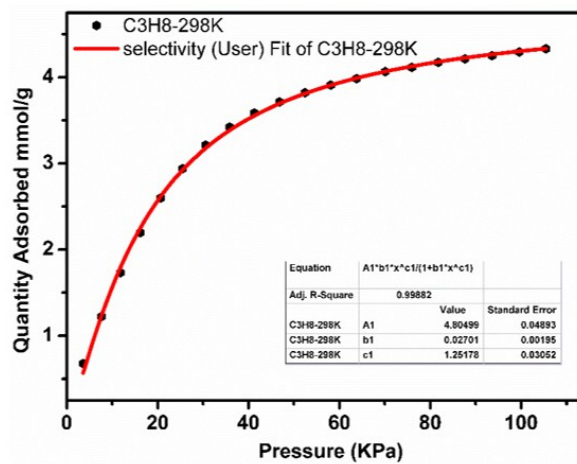
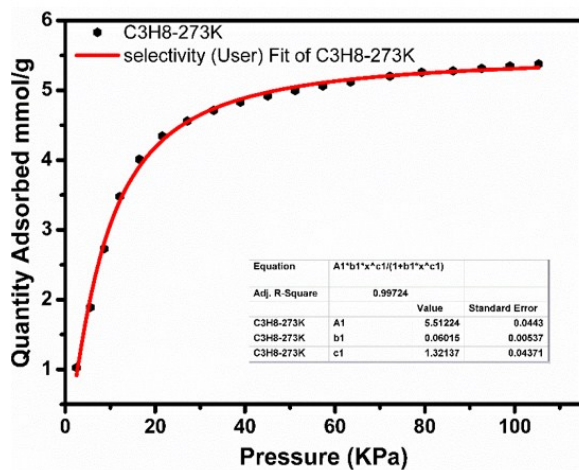
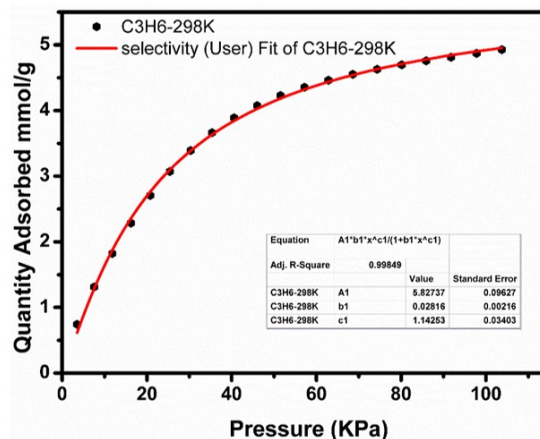
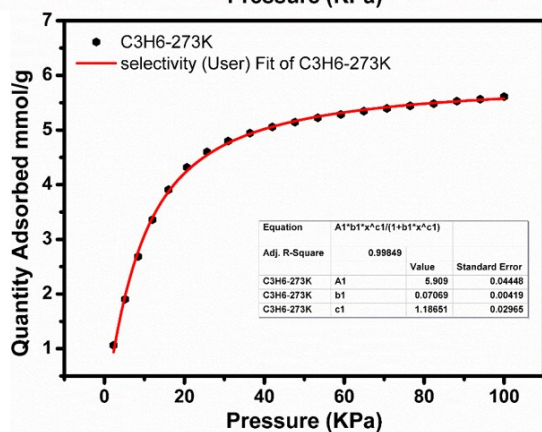
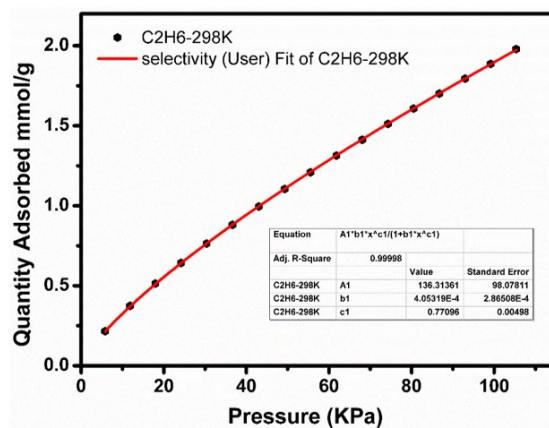
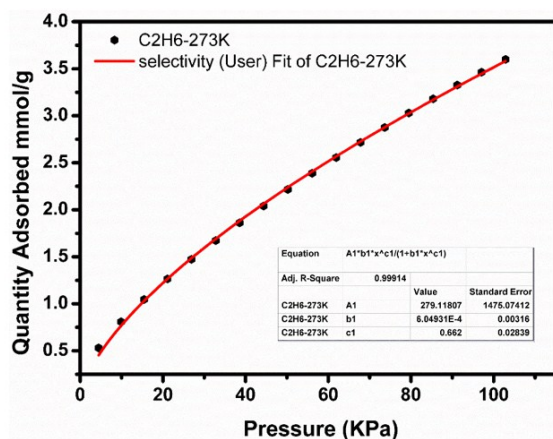
Figure. S3 The IR of UPC-99.

4. Simulation and calculation for gas selectivity by IAST methods.





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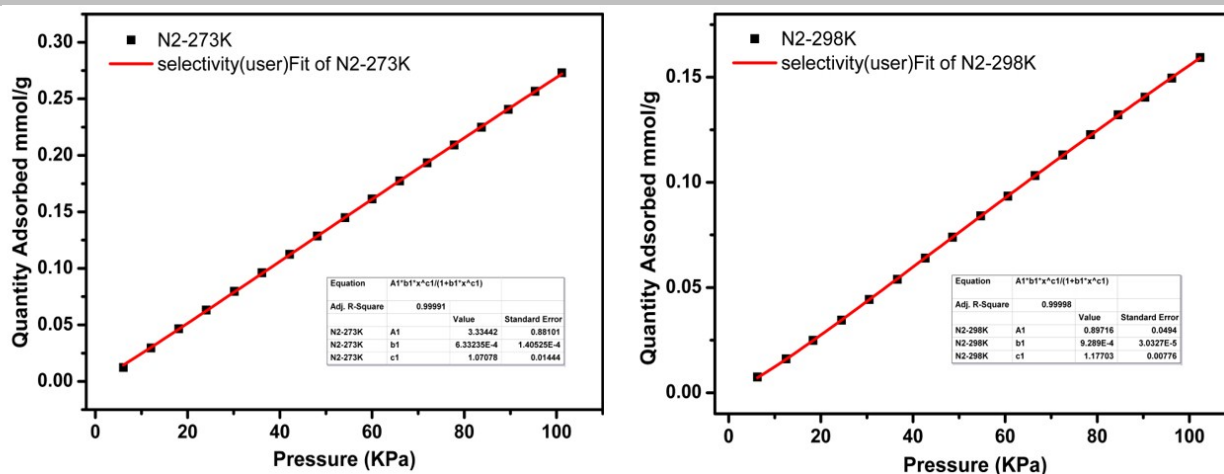


Figure. S4 The detail of virial equation (solid lines) fitting to the experimental gases adsorption data for **UPC-99** by IAST methods.

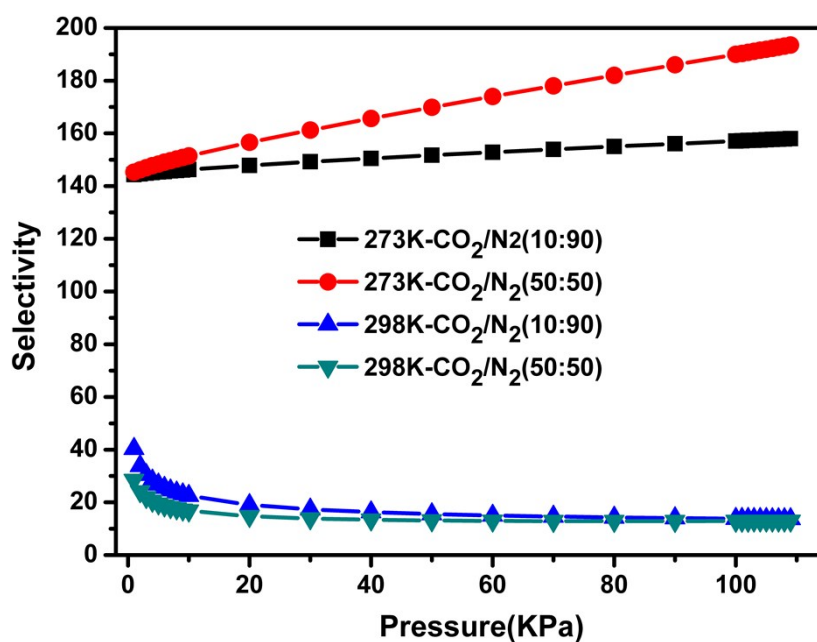


Figure. S5 The selectivity for CO₂ over N₂ at 273 K and 298K.

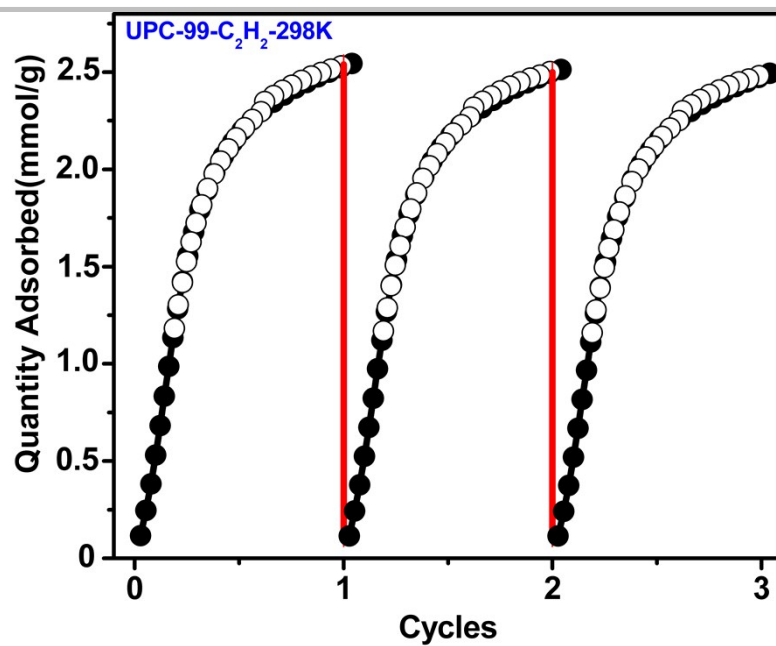


Figure. S6 The cyclic adsorption stability curves of C_2H_2 at 298K for UPC-99.

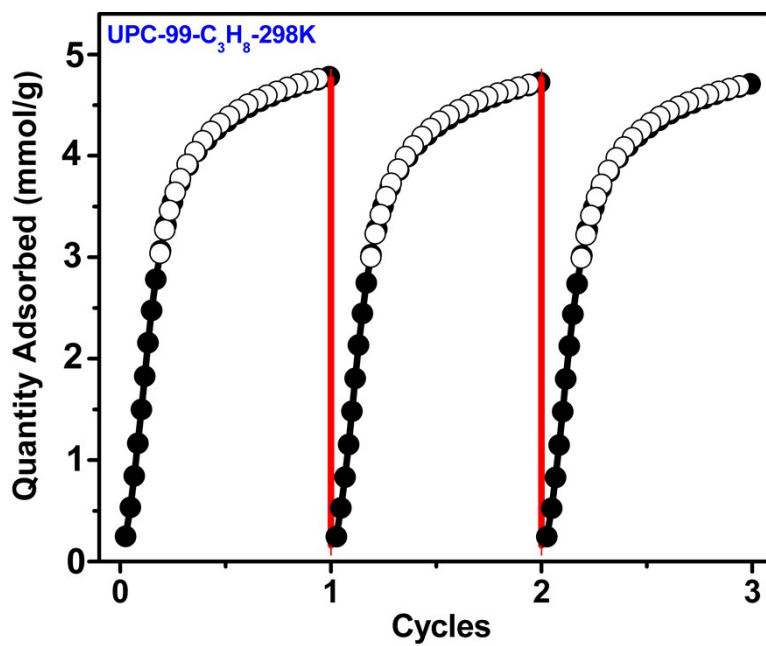


Figure. S7 The cyclic adsorption stability curves of C_3H_8 at 298K for UPC-99.

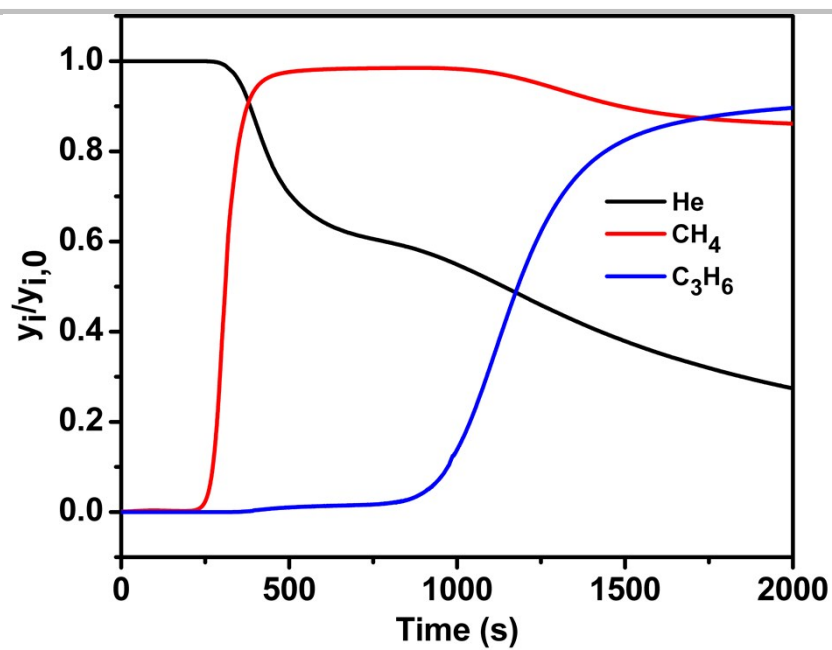
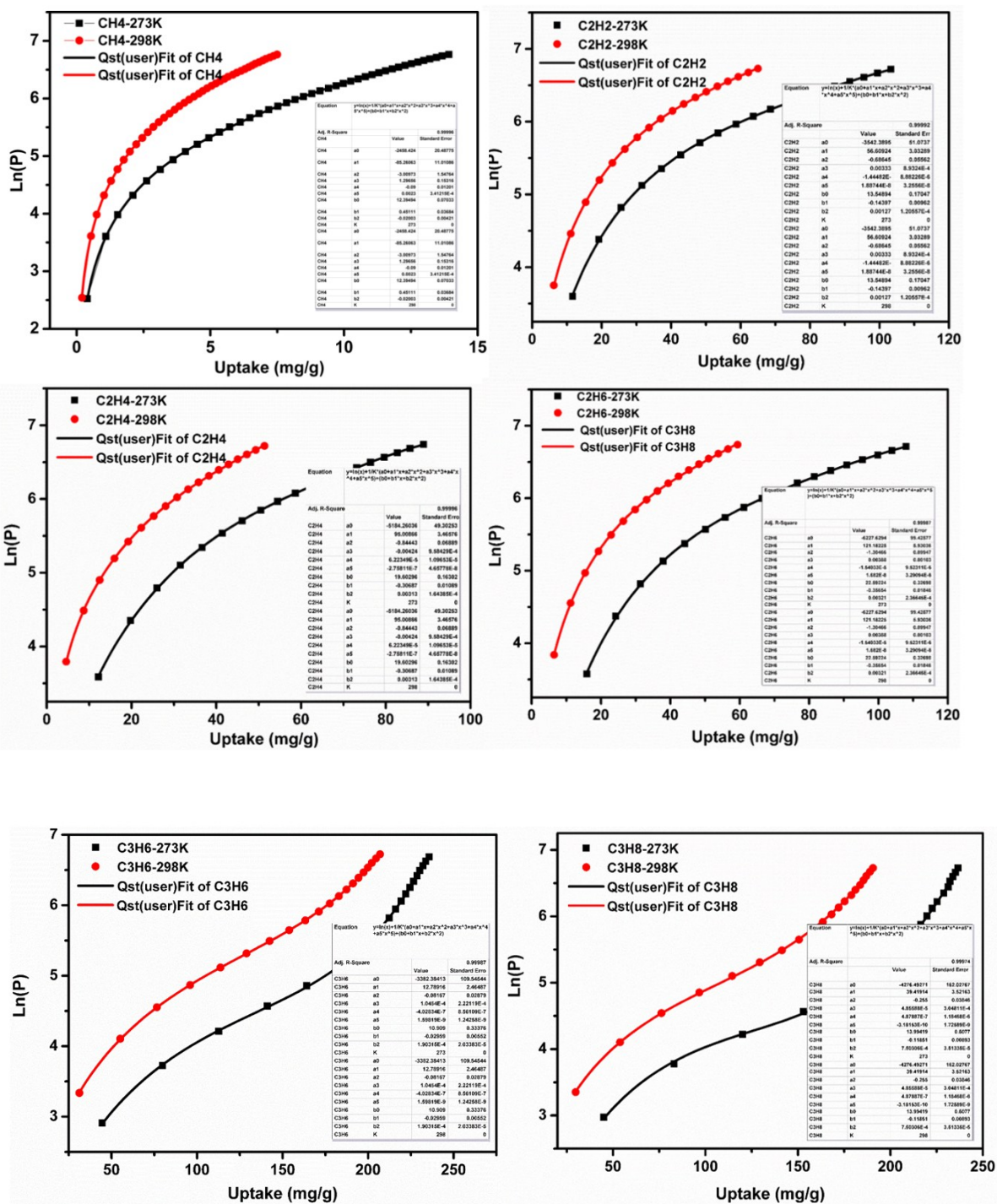


Figure. S8 The breakthrough curves of C₃H₆ and CH₄ gas mixtures (50:50) at 298K for UPC-99.

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5. Simulation and calculation for Q_{st} by Clausius-Clapeyron equation.



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Table S2. Comparison of Light Hydrocarbon Adsorption Data for Selected MOFs

MOFs	T	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	ref
UPC-99	273	18.9	75.1	87.4	92.7	127.5	122.3	This work
	298	9.8	43.1	44.3	61.0	119.5	108.7	
UPC-33	273	9.7	65.1	43.6	51.8	114.2	111.8	1
	298	7.0	44.3	31.1	35.0	94.3	93.6	
FJI-C1	273		135.9	85.2	123.6		160.9	2
	298	9.7	93.8	64.0	87.4		141.9	
FJI-C4	273	32.7	82.8	70.1	73.4		74.7	3
	298	18.4	72.5	61.4	66.3		71.5	
UTSA-33a	296	9.2mg/g	97.1	76.2	83.0			4
1-mim	273	14.65	119.42	92.37	101.03		102.92	5
	297	10.64	76.26	64.95	79.91		96.87	
1-eim	273	19.32	117.84	87.30	99.348		97.36	5
	297	11.48	73.70	61.29	75.38		86.60	
1-pim	273	16.24	101.42	84.54	93.78		97.31	5
	297	9.70	65.00	53.72	71.65		83.29	
1-buim	273	14.08	93.54	73.16	81.77		83.46	5
	297	8.86	56.14	48.70	63.00		75.22	
UPC-21	273	43.2	196.5	123.1	137.6	124.1	116.2	6
	295	25.7	139.5	98.4	104.3	110.1	103.0	
M'MOF-20	195	70	268	81	77		39	7
	273		95.0	53.0			43.0	
	298	8.0	81.0	44.0	49.0		47.0	
UPC-35	273	11.0	72.5	56.4	70.1	138.1	128.7	8
	298	4.8	44.4	35.9	40.9	118.3	111.3	

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6. Catalytic Cycloaddition of CO₂ with Epoxides of UPC-99.

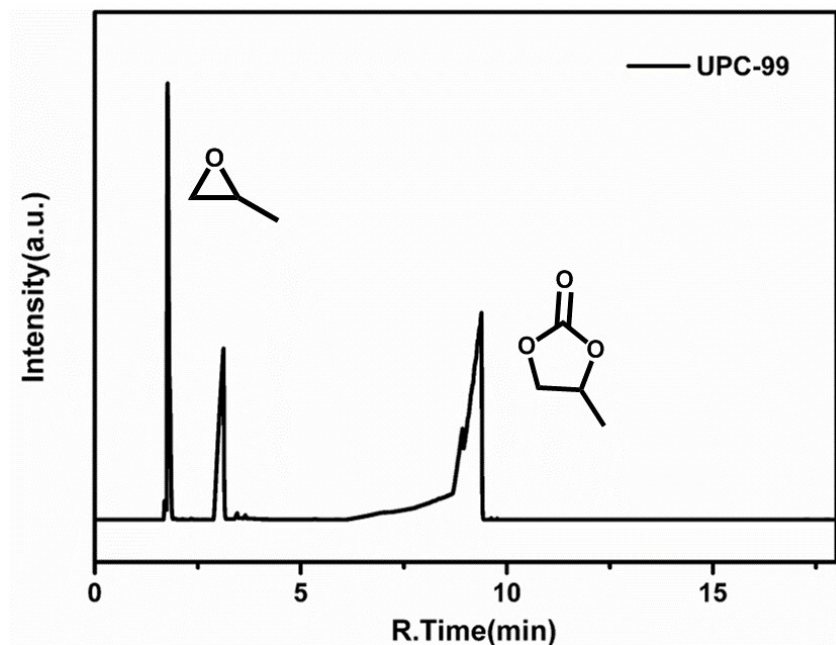


Figure. S10 The GC spectrum for heterogeneous nature of catalysis in reaction of Propylene carbonate at room temperature and 1 bar. **MS** $[M+H]^+$: 102.0317.

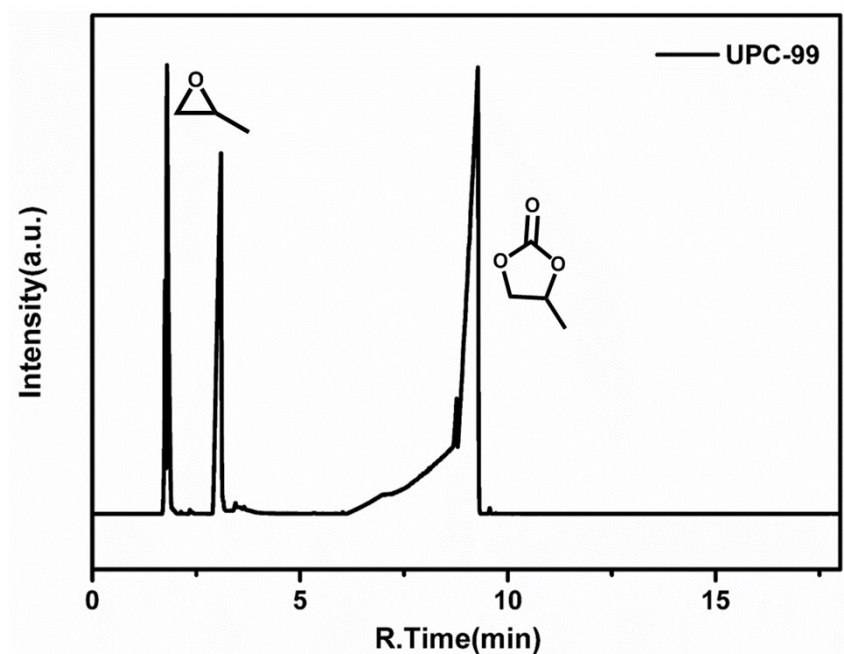


Figure. S11 The GC spectrum for heterogeneous nature of catalysis in reaction of Propylene carbonate at 50°C and 6 bar. **MS** $[M+H]^+$: 102.0317.

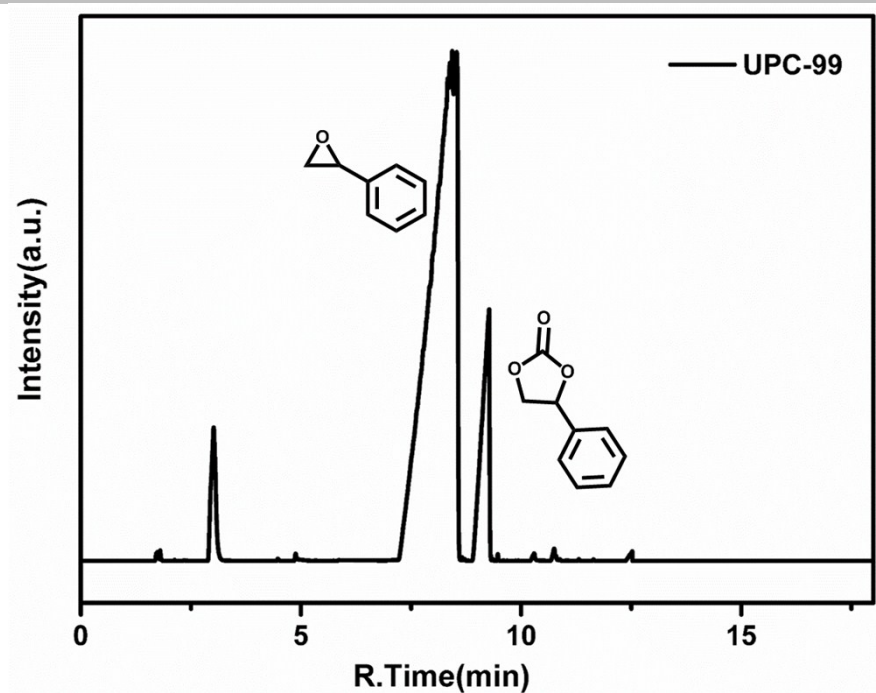


Figure. S12 The GC spectrum for heterogeneous nature of catalysis in reaction of 4-phenyl-1,3-dioxolan-2-one at 50°C and 6 bar. MS $[M+H]^+$: 164.0473.

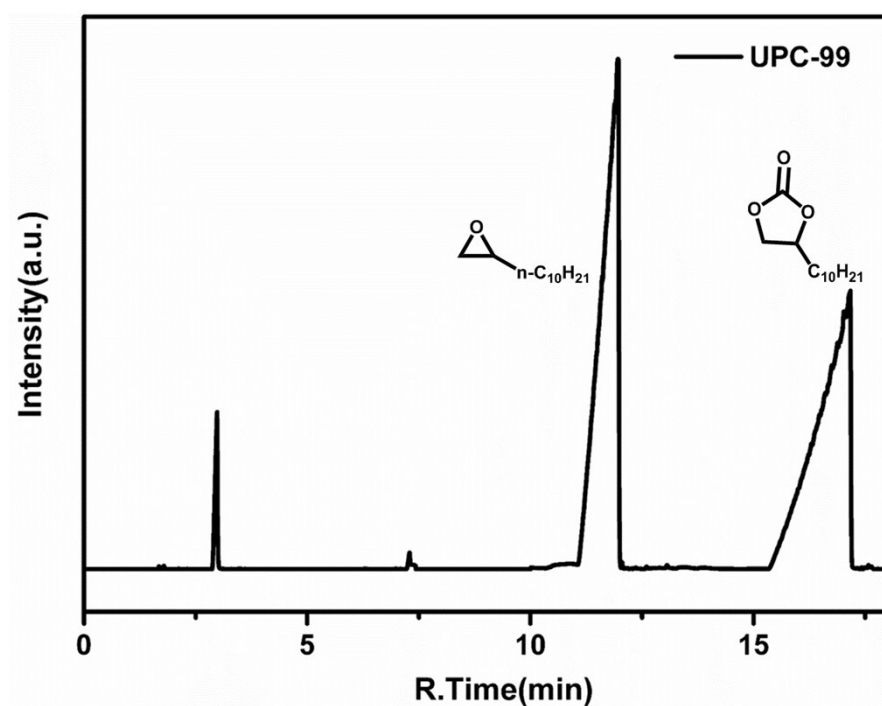


Figure. S13 The GC spectrum for heterogeneous nature of catalysis in reaction of 4-decyl -1,3-dioxolan-2-one at 50°C and 6 bar. MS $[M+H]^+$: 228.1725.

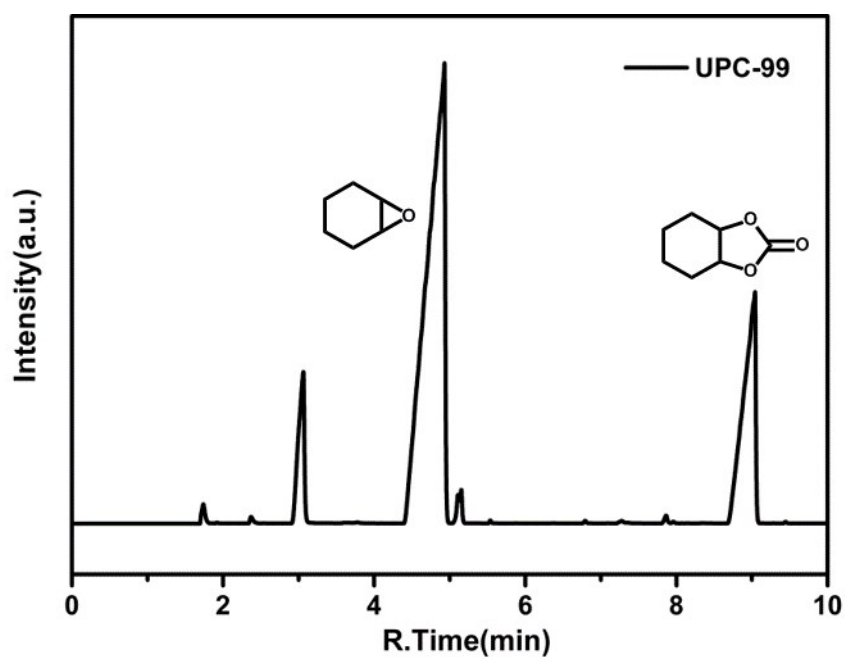


Figure. S14 The GC spectrum for heterogeneous nature of catalysis in reaction of hexahydrobenzo[d][1,3]dioxol-2-one at 50°C and 6 bar after two recycle. **MS** $[M+H]^+$: 142.0630.

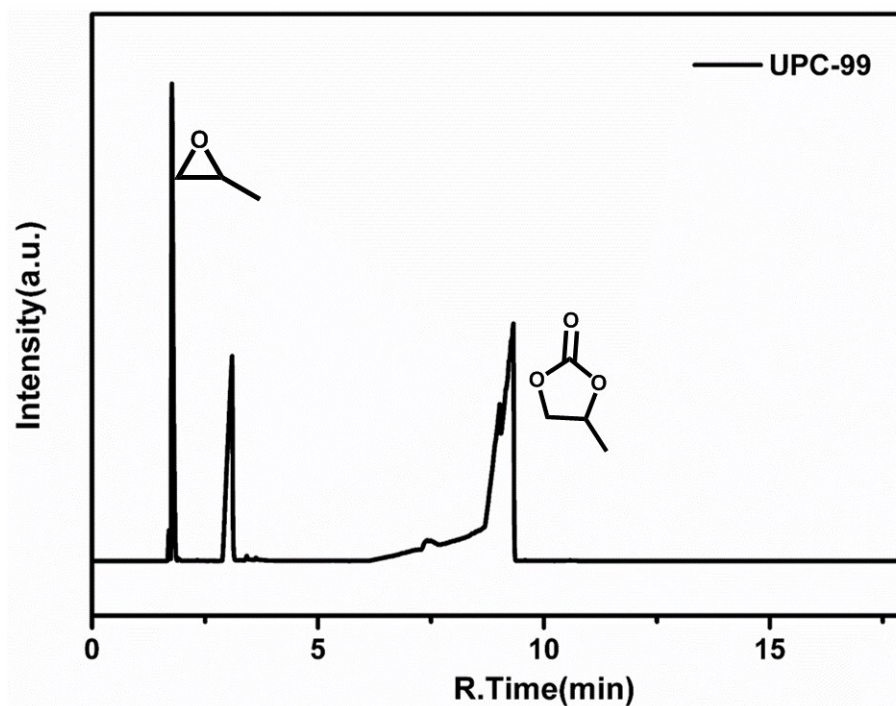


Figure. S15 The GC spectrum for heterogeneous nature of catalysis in reaction of Propylene carbonate at 50°C and 6 bar after one recycle. **MS** $[M+H]^+$: 102.017.

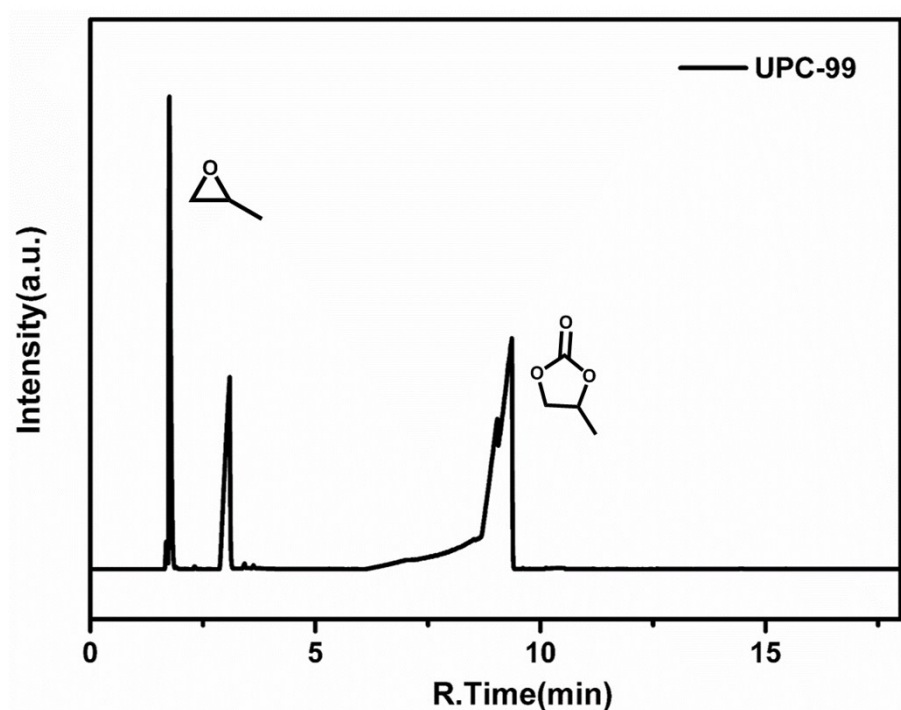


Figure. S16 The GC spectrum for heterogeneous nature of catalysis in reaction of Propylene carbonate at 50°C and 6 bar after two recycle. MS $[M+H]^+$: 102.0317.

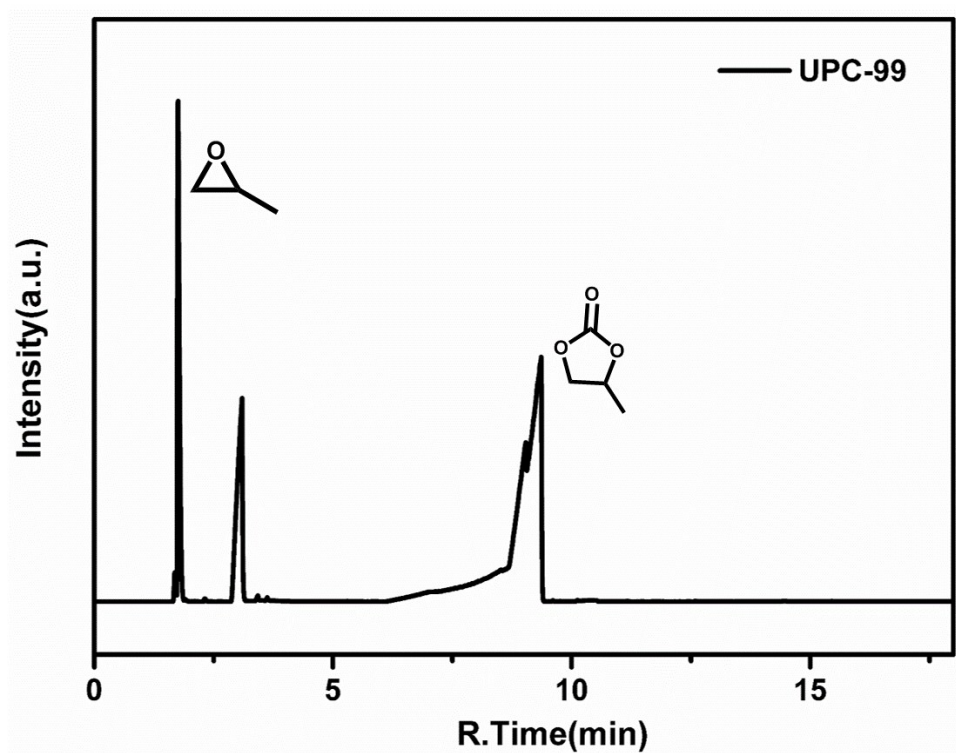


Figure. S17 The GC spectrum for heterogeneous nature of catalysis in reaction of Propylene carbonate at 50°C and 6 bar after three recycle. MS $[M+H]^+$: 102.0317.

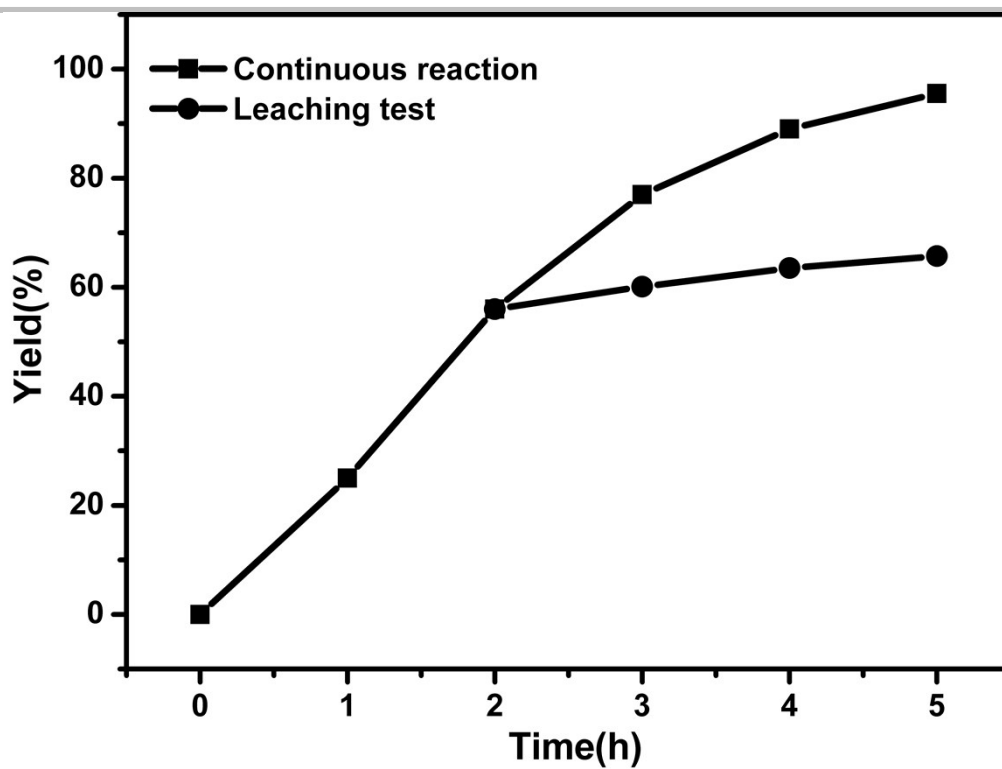


Figure. S18 The leaching test for catalysis in reaction of Propylene carbonate at 50°C and 6 bar
(●) catalyst was removed after 2 hour.

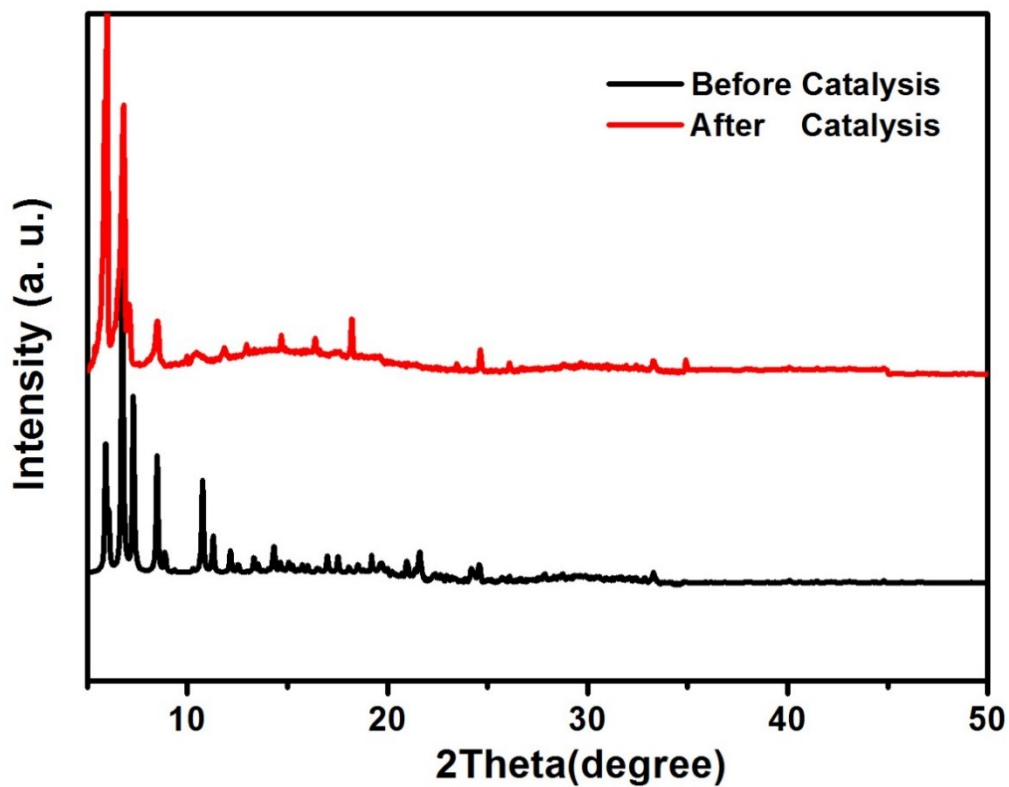


Figure. S19 The PXRD of UPC-99 before and after catalysis.

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Table S3. Comparison of catalysts performances in the cycloaddition of CO₂ with different epoxides for selected MOFs.

MOF	Catalytic type	T(°C)	P(bar)	Time(h)	Yields(%)	ref
UPC-99	1(R=CH ₃)	25	1	48	80.21	This work
	1(R=CH ₃)	50	6	5	95.50	This work
	2(R=Ph)	50	6	5	49.86	This work
	3(R=C ₁₀ H ₂₁)	50	6	5	60.64	This work
MOF-505	1	25	1	48	48.0	9
HKUST-1	1	25	1	48	49.2	9
(I-)Meim-UiO-66	2	120	2	24	46	10
PCN-900(Eu)- CoTCPP-CoBPYDC	1	50	1	20	93	11
	2	50	1	20	81	11
MMPF-9	1	25	1	48	87.4	12
Zn-MOF	1	100	1	16	99	13
	2	100	1	16	89	13
gea-MOF-1	1	120	20	6	88	14
Co-MOF	1	25	1	48	57.1	15
UIO-67-IL	2	90	1	3	51	16
ZIF-8	2	100	7	5	54	17

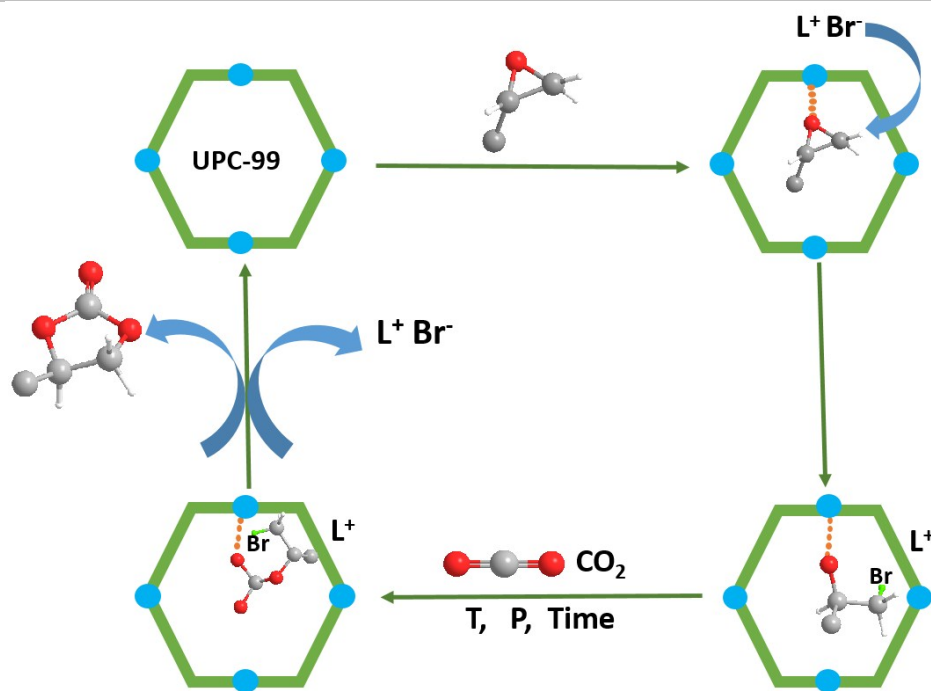


Figure. S20 The catalytic mechanism for the cycloaddition of CO₂ with epoxides into cyclic carbonates catalyzed by **UPC-99**. (The blue ball represents the open Cu(II) sites; L⁺ =tetra-n-tertbutylammonium).

References

1. W.D. Fan, Y.T. Wang, Q. Zhang, Angelo Kirchon, Z.Y. Xiao, L.L. Zhang, F.N. Dai, R.M. Wang, and D.F. Sun. *Chem. Eur. J.* 2017, 23, 1-8.
2. Y. B. Huang, Z.J. Lin, H. R. Fu, F. Wang, M. Shen, X. S. Wang, and R. Cao. *ChemSusChem*. 2014, 7, 2647-2653.
3. L. Li, X. S. Wang, J. Liang, Y. B. Huang, H. F. Li, Z. J. Lin, and R. Cao. *ACS Appl. Mater. Interfaces*. 2016, 8, 9777-9781.
4. Y. B. He, Z. J. Zhang, S. C. Xiang, F. R. Fronczek, R. Krishna, and B. L. Chen. *Chem. Eur. J.* 2012, 18, 613-619.
5. H. R. Fu and J. Zhang. *Inorg. Chem.* 2016, 55, 3928-3932.
6. M. H. Zhang, X. L. Xin, Z. Y. Xiao, R. M. Wang, L. L. Zhang and D. F. Sun. *J. Mater. Chem. A*, 2017, 5, 1168-1175.
7. N. Sikdar, S. Bonakala, R. Haldar, S. Balasubramanian, and T. K. Maji. *Chem. Eur. J.* 2016, 22, 6059-6070.
8. Y.T. Wang, W.D. Fan, X. Wang, Y.F. Han, L.L. Zhang, D. Liu, F.N. Dai, and D.F. Sun. *Inorg, Chem. Front.*, 2018, 5, 2408-2412.
9. W.Y. Gao, Y. Chen, Y. H. Niu, K. Williams, L. Cash, S. Q. Ma. et al., *Angew. Chem. Int. Ed.* 2014, 53, 2615-2619.

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10. J. Liang, R.P. Chen, X.Y. Wang, T.T. Liu, X.S. Wang, Y.B. Huang, and R. Cao. *Chem. Sci.*, 2017, 8, 1570-1575.
11. L.L. Zhang, S. Yuan, L. Feng, B.B. Guo, J.S. Qin, B. Xu, C. Lollar, D.F. Sun, H.C. Zhou. *Angew. Chem. Int. Ed.* 2018, 57, 5095-5099.
12. W.Y. Gao, L. Wojtas, S.S. Ma. *Chem. Commun.*, 2014, 50, 5316-5318
13. Y.H. Han, Z.Y. Zhou, C.B. Tiana and S.W. Du. *Green Chem.*, 2016, 18, 4086-4091.
14. V. Guillermin, Ł.J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D'Elia, Ł. Wojtas, K. Adil and M. Eddaoudi. *NATURE CHEMISTRY*. 2014, 6, 673-680.
15. H.H. Wang, L. Hou, Y.Z. Li, C.Y. Jiang, Y.Y. Wang, Z.H. Zhu. *ACS Appl. Mater. Interfaces*. 2017, 9, 17969-17976.
16. L.G. Ding, B.J. Yao, W.L. Jiang, J.T. Li, Q.J. Fu, Y.A. Li, Z.H. Liu, J.P. Ma, Y.B. Dong. *Inorg. Chem.* 2017, 56, 2337-2344.
17. M.Q. Zhu, D. Srinivas, S. Bhogeswararao, P. Ratnasamy, M. A. Carreon. *Catalysis Communications*. 2013, 32, 36-4.