Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

SI

Fabrication of morphology-preserved microporous carbon from a zeolitic-like porous coordination polymer for CH_4 purification

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Sample activation. The solvent-exchanged sample was prepared by immersing the HCl (concentrated) treated samples in EtOH for 2 days to remove the nonvolatile solvates, and the extract was decanted every 8 hours and fresh EtOH was replaced. The completely activated sample was obtained by heating the solvent-exchanged sample at 180 °C under a dynamic high vacuum for 24 hours.

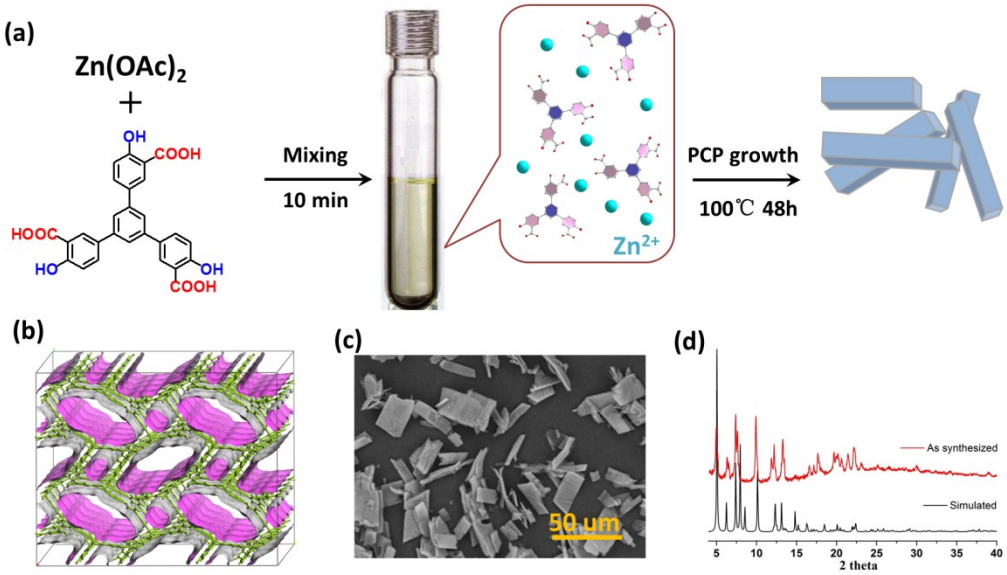
Adsorption experiments. In the gas sorption measurement, Ultra-high-purity grade, N_2, CH_4, C_2H_4, C_2H_6 and CO_2 gases (99.995% purity) were used throughout the adsorption experiments. All of the measured sorption isotherms have been repeated several times to confirm the reproducibility within experimental error. Low-pressure N_2, CO_2, CH_4 and H_2 adsorption measurements (up to 1 bar) were performed on BEL mini analyzer. Helium was used for the estimation of the dead volume, assuming that it is not adsorbed at any of the studied temperatures. To provide high accuracy and precision in determining P/P_0, the saturation pressure P_0 was measured throughout the N_2 analyses by means of a dedicated saturation pressure transducer, which allowed us to monitor the vapor pressure for each data point. The pore size distribution was obtained from the GCMC method in the BEL mini software package based on the N_2 sorption at 77K.

Table S1. Crystal data and structure refinement for **NTU-17** at 173 K

	NTU-17
Empirical formula	$C_{27}H_{18}Zn_2O_{11}$
Formula weight	649.19
Crystal system	monoclinic
Space group	*P21/c*
Unit cell dimensions	*a* = 7.3800(15) Å *b* = 28.290(6) Å *c* = 22.470(5) Å *β* = 99.13(3) °
Volume	4631.9(18) $Å^3$
Z	4
Density (calculated)	0.931 g/cm^3
Mu(MoKa)	1.071 mm^{-1}
$F_{(000)}$	1312
Theta min-max	1.7, 25.1
Index ranges	-8<=h<=8 -33<=k<=24 -26<=l<=26
Tot., Uniq. Data, R(int)	29923, 8233, 0.078
Observed data [I > 2σ (I)]	5418
*N*ref, *N*par	8233, 363
R_1, wR_2, S	0.0719, 0.2264, 1.04
Max Shift	0

$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^4)]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (0.1452P)^2]$ where $P = (F_o^2+2F_c^2)/3$

Structure of **NTU-17**



Scheme S1. Synthesis and characterization of **NTU-17**: (a) involved ligands and metal source for preparing rod shaped **NTU-17**; (b) packing view of accessible inner pore surface of **NTU-17**; (c) SEM image of crystals of **NTU-17**; (d) PXRD of simulated and as-synthesized **NTU-17**.

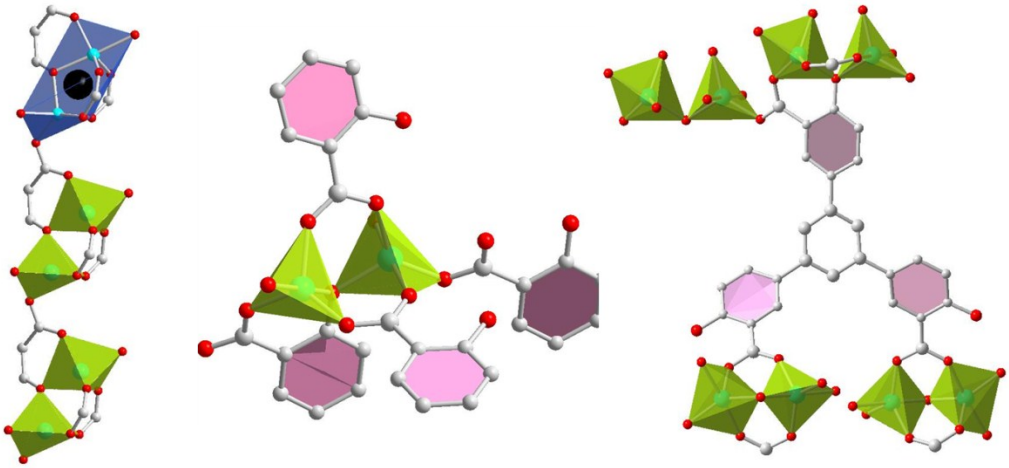


Fig. S1 Structural information of **NTU-17**: infinite metal oxygen chain (left), connection of Zn dimer (middle) and ligand connection (right) of **NTU-17**.

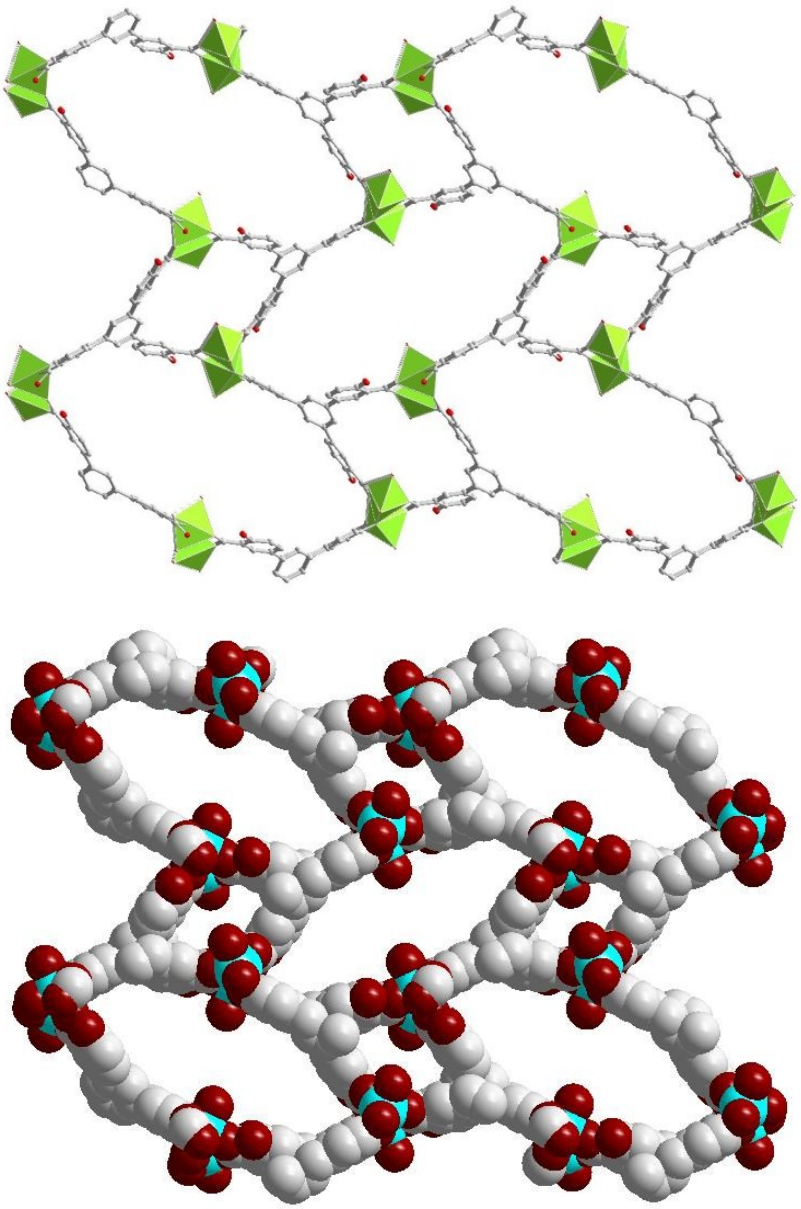


Fig. S2 Packing view of **NTU-17** along a-axis: two kinds of channel with significant window aperture.

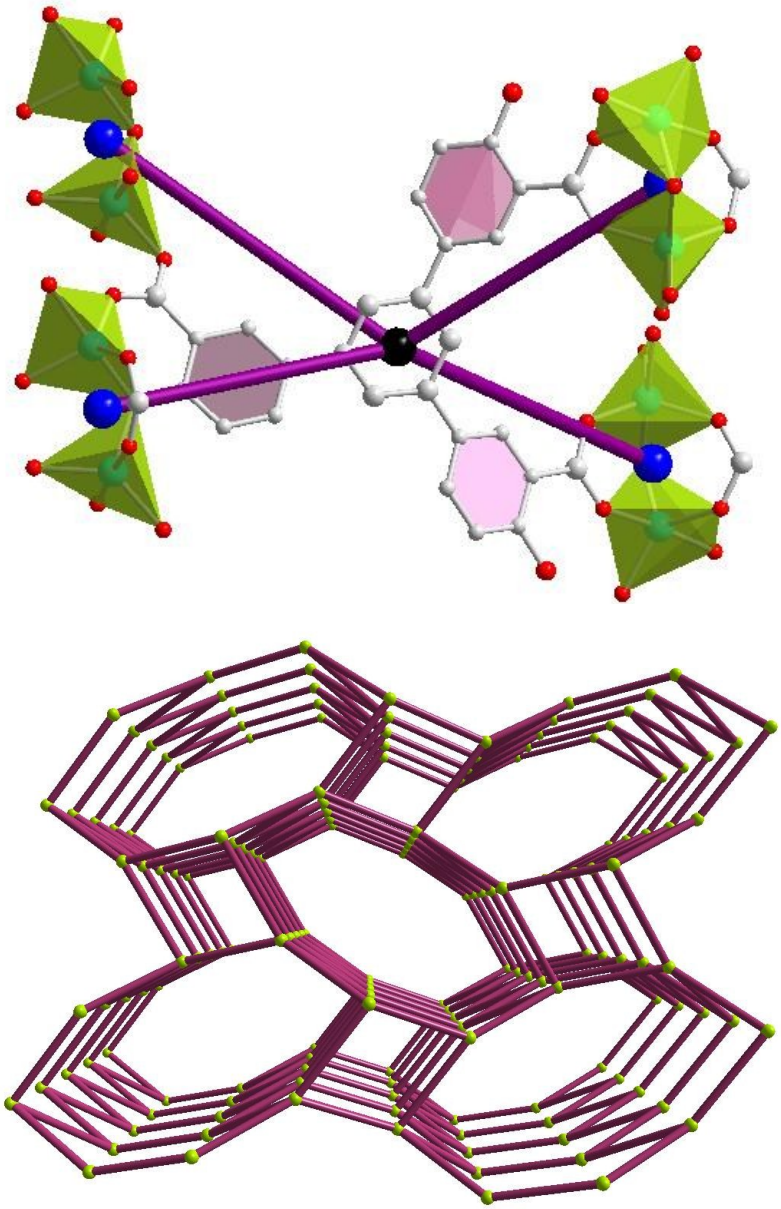


Fig. S3 4-c connected **crb/BCT** topology of **NTU-17**.

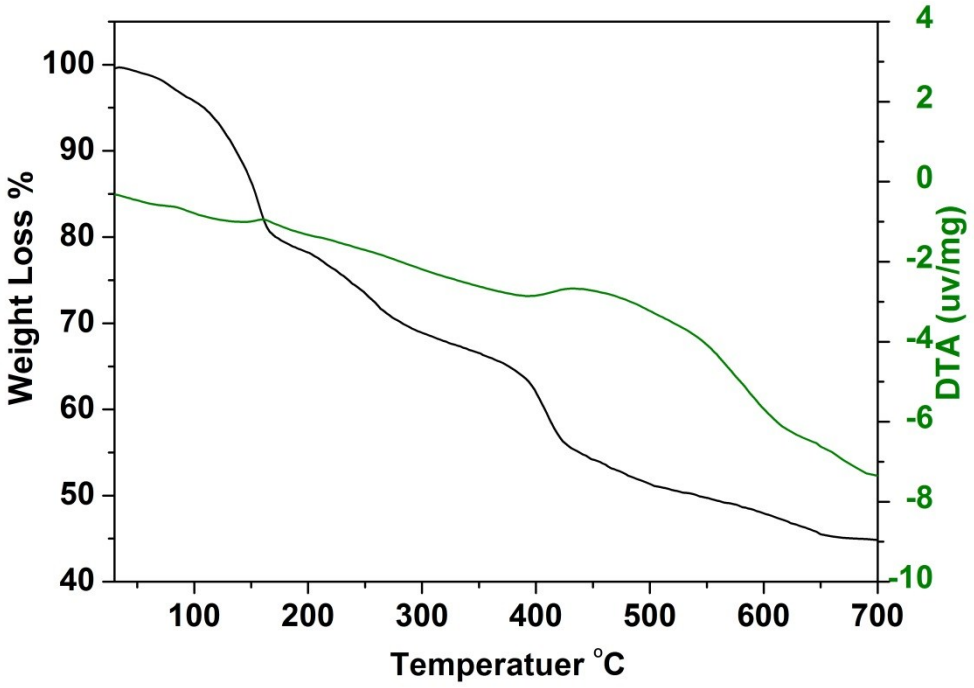


Fig. S4 TG of as-synthesized **NTU-17**.

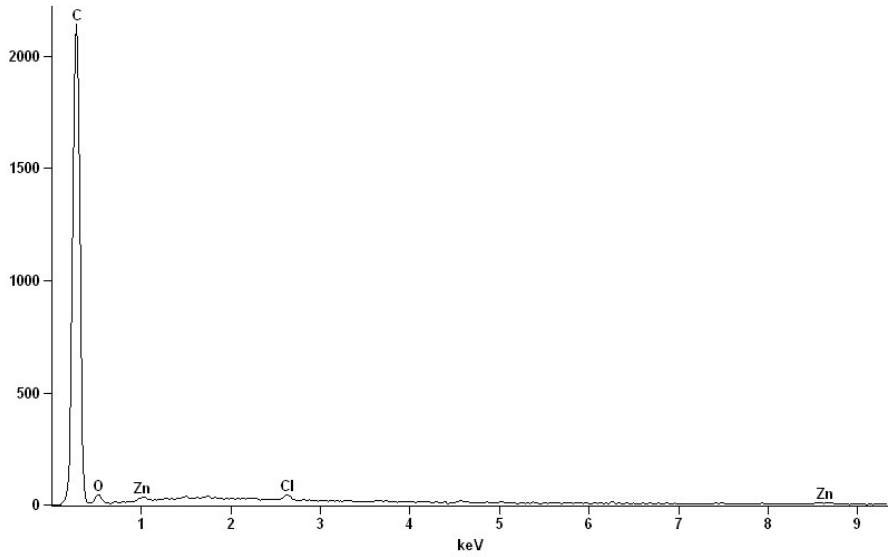


Fig. S5 EDX analysis of **C-600**.

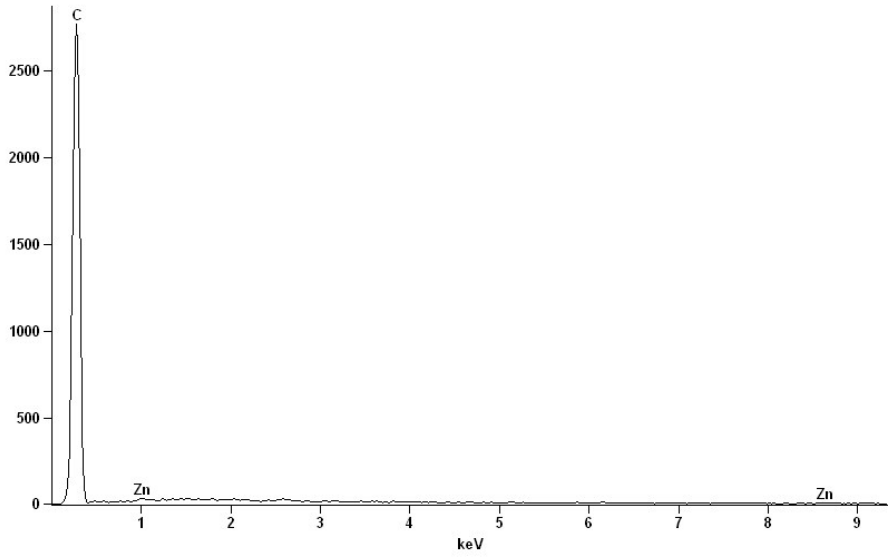


Fig. S6 EDX analysis of **C-650.**

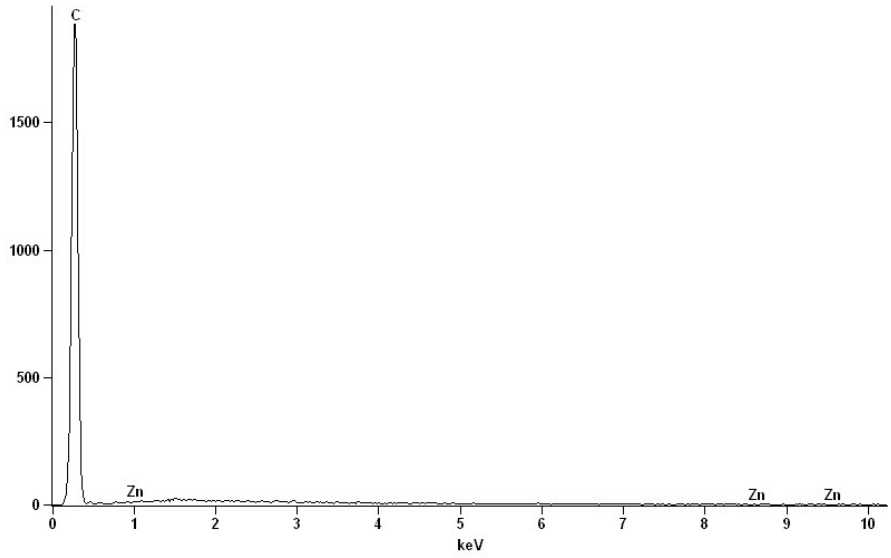


Fig. S7 EDX analysis of **C-700**.

Table S2 EDS and EA results of C and N in **C-600**, **C-650** and **C-700**

	EDS analysis				EA analysis	
	C(%)	O(%)	Cl(%)	Zn(%)	C(%)	N(%)
C-600	98.22	0.54	0.44	0.8	97.82	-
C-650	99.73	-	-	0.27	98.25	-
C-700	99.95	-	-	0.05	98.64	-

- : no data

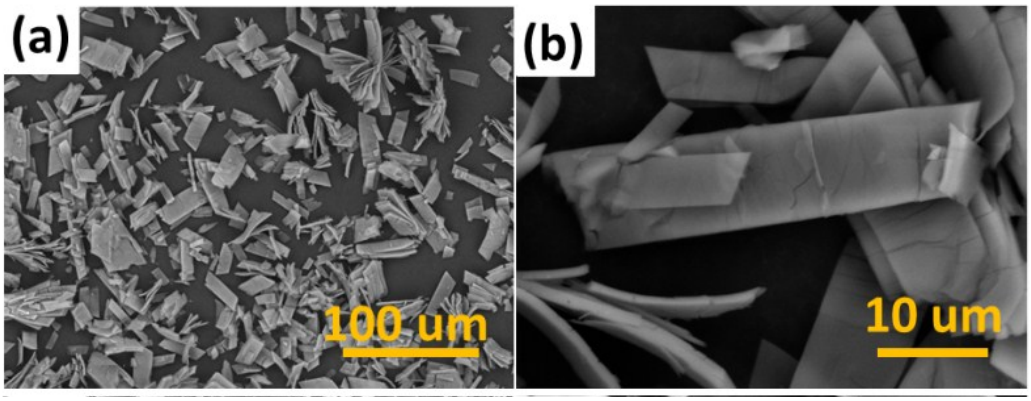


Fig. S8 SEM of as-synthesized **NTU-17** crystals.

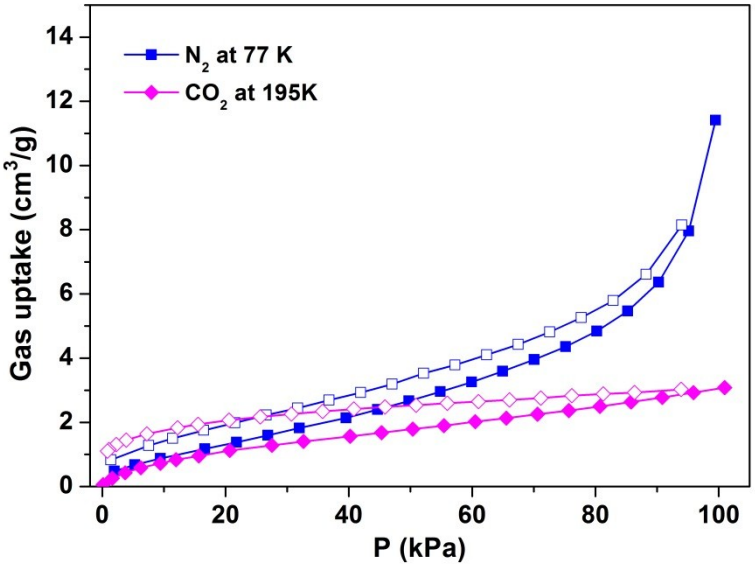


Fig. S9 Gas uptakes of **NTU-17**.

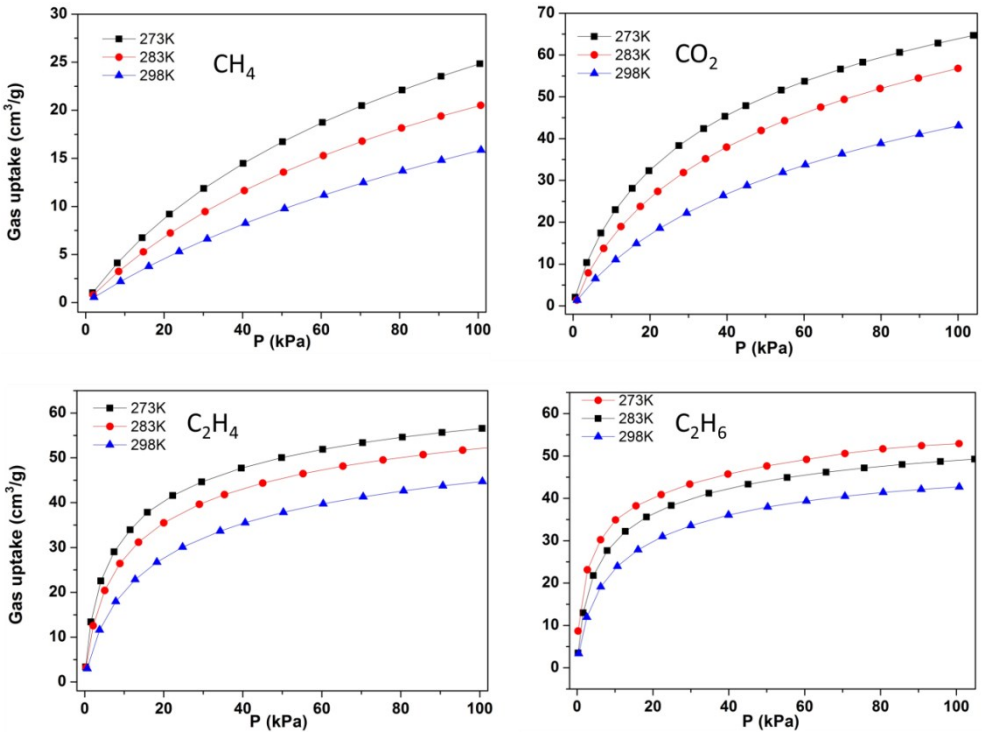


Fig. S10 Gas uptakes of **C-600** at 273, 283 and 298K.

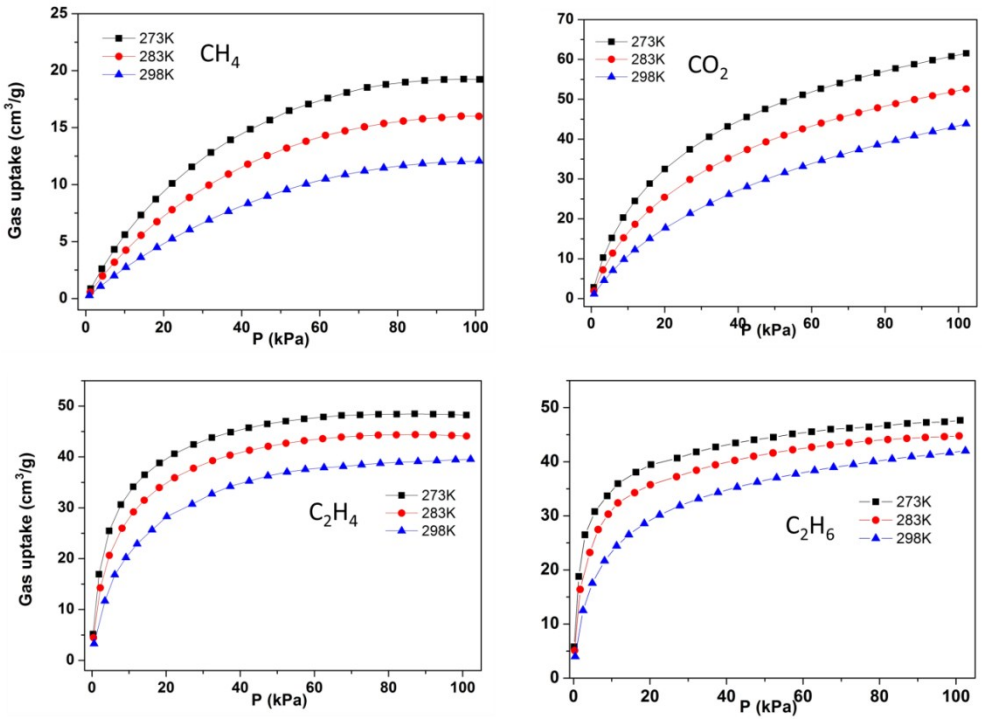


Fig. S11 Gas uptakes of **C-650** at 273, 283 and 298K.

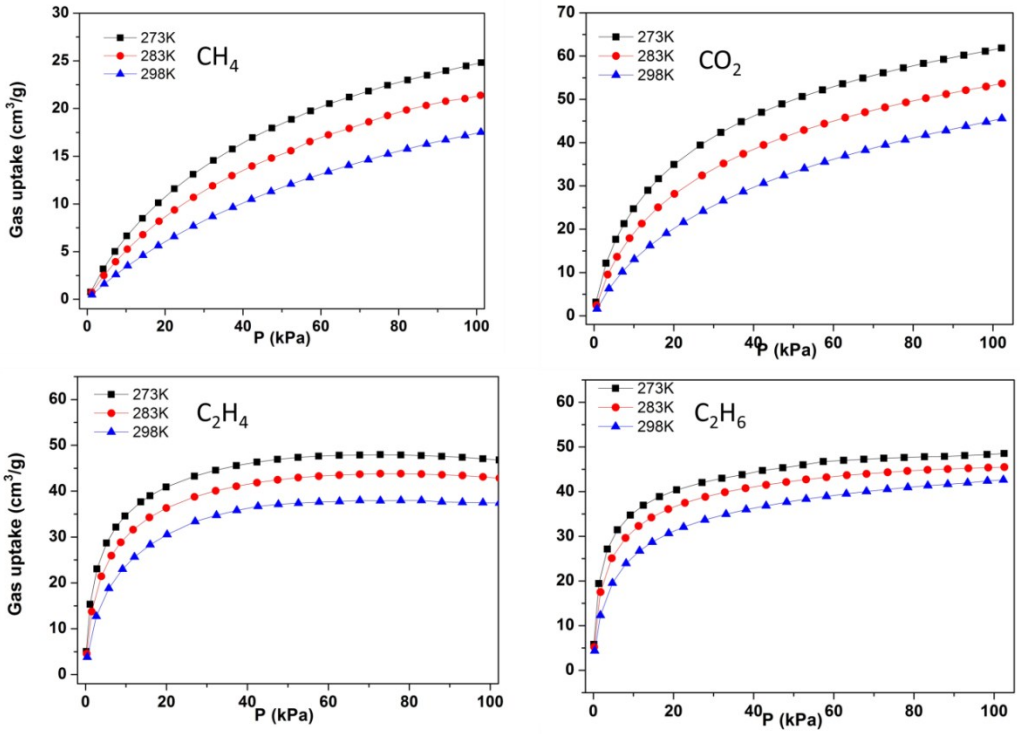


Fig. S12 Gas uptakes of **C-700** at 273, 283 and 298K.

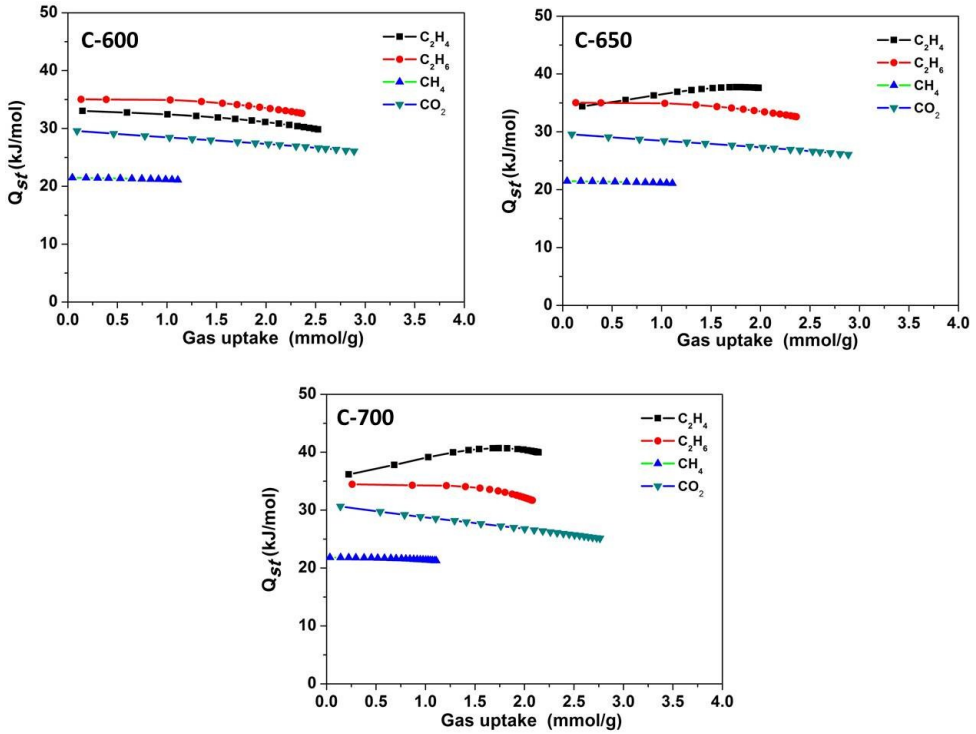


Fig. S13 Adsorption heats of series carbon materials.

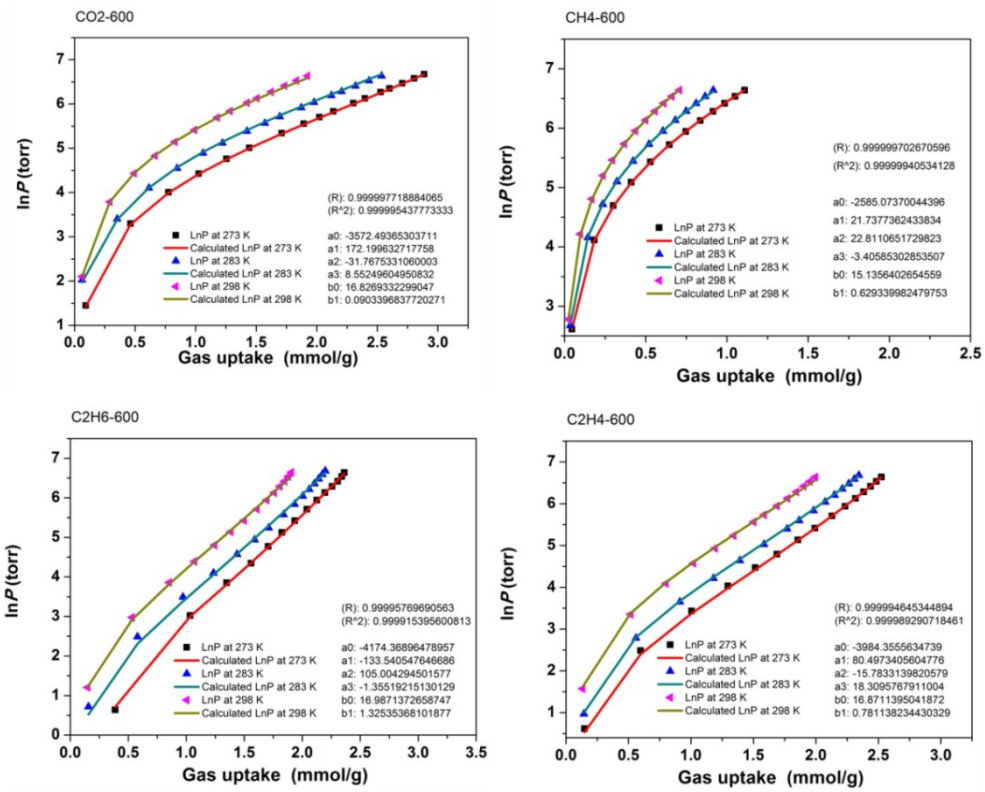


Fig. S14 The calculated virial equation isotherms parameters fit to the experimental data of **C-600**.

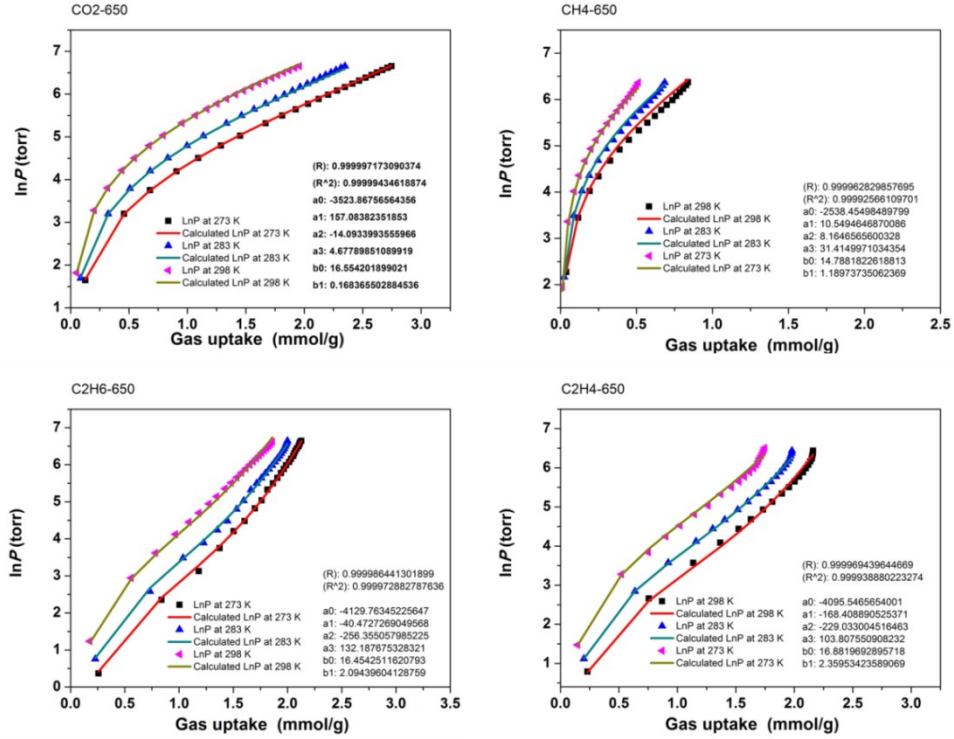


Fig. S15 The calculated virial equation isotherms parameters fit to the experimental data of **C-650**.

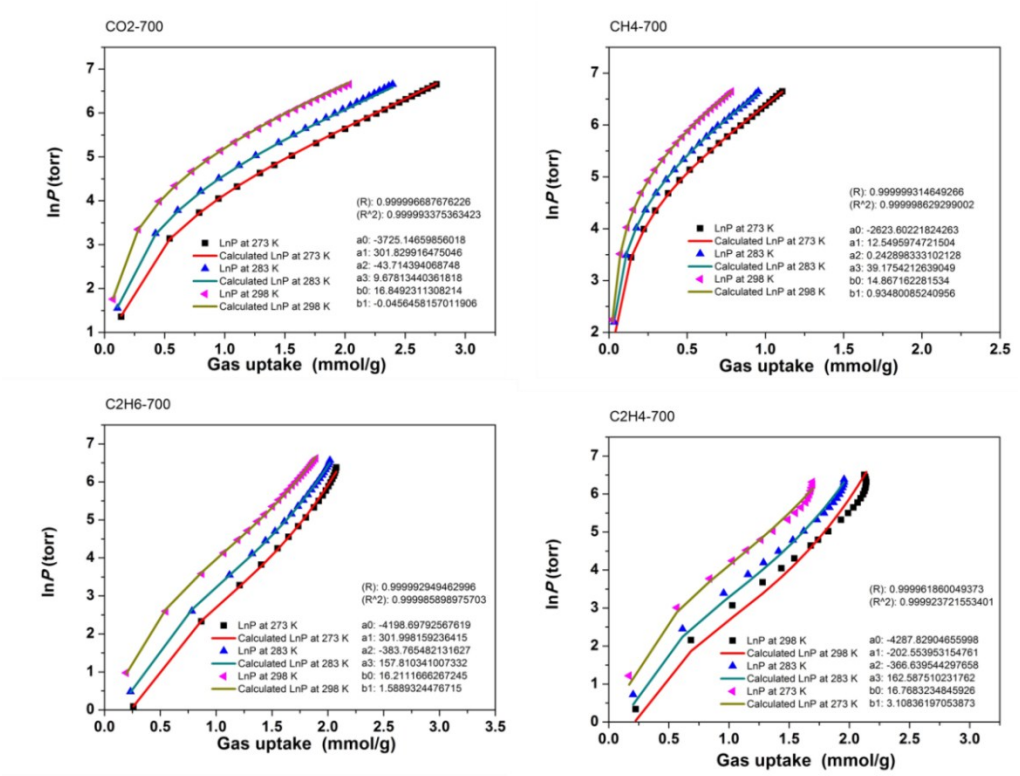


Fig. S16 The calculated virial equation isotherms parameters fit to the experimental data of **C-700**.

Table S3 Fitting parameters for IAST simulation

C-600			
CH_4-298K	**C_2H_4-298K**	**C_2H_6-298K**	**CO_2- 298K**
(R): 0.999997690231	(R): 0.999999725913265	(R): 0.999997183222678	(R): 0.999999787296525
(R^2): 0.999995380467335	(R^2): 0.999999451826606	(R^2): 0.99999436645329	(R^2): 0.999999574593094
a1:2.08988820130398	a1:1.92257626294582	a1:2.22053162265302	a1: 0.607243829000806
a2:1.23754998249685E-16	a2:0.783160628148363	a2:0.136079606220517	a2: 3.16079250854806
b1:0.00602249039434644	b1:0.041467455847789	b1:0.124949465596855	b1: 0.0493772391267279
b2:0.997080392082391	b2:0.176282327734726	b2:0.298895880255514	b2: 0.00948089228019574
c1:0.963229066852609	c1:0.829844264589429	c1:0.749391540609093	c1: 0.998060791009544
c2:4.94817954492443	c2:0.970735067139434	c2:1.78046533311894	c2: 0.966733452269509
CH_4-273K	**C_2H_4-273K**	**C_2H_6-273K**	**CO_2- 273K**
(R): 0.999991260976647	(R): 0.999993300366406	(R): 0.999917780482295	(R): 0.999962913688925
(R^2): 0.999982522029665	(R^2): 0.999986600777697	(R^2): 0.999835567724639	(R^2): 0.999925828753245
a1:2.35899547882683	a1:2.13688506696019	a1:0.384859819509356	a1:0.0184117293097664
a2:1.33707670685992E-16	a2:1.0850080582125	a2:3.52013888768585	a2:4.36845748067681
b1:0.0122321933826171	b1:0.0737652538115886	b1:0.265766887780471	b1:17.1922064681629
b2:175.793192190558	b2:0.372952704187628	b2:0.207043105349749	b2:0.0409352701546699
c1:0.928505110115257	c1:0.738614079656138	c1:1.43419660507792	c1:63.9919222295221
c2:14.0460791158412	c2:0.949769397159319	c2:0.398887991299829	c2:0.825430786984331

Continue Table S3			
C-650			
CH_4-298K	**C_2H_4-298K**	**C_2H_6-298K**	**CO_2- 298K**
(R): 0.99893845159471	(R): 0.999864002283489	(R): 0.999997901355323	(R): 0.999997343975968
(R^2): 0.997878030074437	(R^2): 0.999728023062357	(R^2): 0.99999580271505	(R^2): 0.999994687958991
a1:0.803789683480824	a1:0.246544468167174	a1:1.33923162726014	a1:1.19771014930387
a2:1.41038800737144E-16	a2:1.65672855898846	a2:1.24156270010237	a2:3.27001435451067
b1:0.0142407397018956	b1:1.72871010472352E-5	b1:0.0308059900930132	b1:0.0414381852089713
b2:4.03860679120099	b2:0.145520683857082	b2:0.284269766415117	b2:0.00565554627314712
c1:1.047855855555088	c1:3.2631707423852	c1:0.776696432674971	c1:0.946473128685303
c2:1.02340543411818	c2:0.948904754177187	c2:0.862880513534958	c2:0.95207215282671
CH_4-273K	**C_2H_4-273K**	**C_2H_6-273K**	**CO_2- 273K**
(R): 0.999822562411871	(R): 0.999760636159039	(R): 0.999919827192959	(R): 0.999998284619766
(R^2): 0.999645156307839	(R^2): 0.999521329613127	(R^2): 0.999839660813597	(R^2): 0.999996569242475
a1:3.14915870263107E-16	a1:0.373728499049345	a1:2.16673983925511	a1:2.76077428347419
a2:1.13280179388078	a2:1.8982671004686	a2:0.391949694267807	a2:1.65936743811639
b1:1.47939833102894	b1:0.000814642261317146	b1:0.330471764733788	b1:0.0167761393752145
b2:0.0227536737665319	b2:0.385425869188062	b2:0.485342978440942	b2:0.0870791474171067
c1:0.978480337679016	c1:2.33557372386242	c1:0.541251149810369	c1:0.86813457337547
c2:1.000895642458882	c2:0.87653483483006	c2:3.16304473385424	c2:0.90549274023867
C-700			
CH_4-298K	**C_2H_4-298K**	**C_2H_6-298K**	**CO_2- 298K**
(R): 0.99999743045041	(R): 0.999262300309574	(R): 0.999995438242696	(R): 0.999997990259185
(R^2): 0.999994860907422	(R^2): 0.998525144819981	(R^2): 0.999990876506201	(R^2): 0.99999598052241
a1: 1.4837683064654	a1: 0.514161929110793	a1: 1.17957137519422	a1: 0.983388555500943
a2: 0.0883269914798796	a2: 1.21864981681207	a2: 1.31925747363562	a2:3.23059097240004
b1: 0.00839206385176629	b1:0.000383675637725286	b1: 0.364209177378394	b1:0.0665768709434871
b2: 0.055074034279636	b2: 0.324451408784486	b2: 0.0627519562968484	b2:0.00963016420617445
c1: 1.01458906404605	c1: 2.72793643029148	c1: 0.824080159098974	c1: 0.922415520198292
c2: 1.0327453066347	c2: 1.06015917803629	c2: 0.684266755162972	c2: 0.895009078179171
CH_4-273K	**C_2H_4-273K**	**C_2H_6-273K**	**CO_2- 273K**
(R): 0.999997036824732	(R): 0.999106785541577	(R): 0.999917003161533	(R): 0.999997816985744
(R^2): 0.999994073658245	(R^2): 0.998214368915223	(R^2): 0.999834013211542	(R^2): 0.999995633976253
a1: 0.423667303998799	a1: 1.72053217023449	a1: 2.19300934936023	a1: 3.00949928328448
a2: 1.16650271159966	a2:0.472859201003888	a2: 0.135453336435367	a2: 1.30926578372934
b1: 0.0775455888368812	b1: 0.600376913774541	b1: 0.52159668150433	b1: 0.0280983877409228
b2: 0.00655492508087461	b2: 0.00144085097416454	b2: 1.60093068532868E-5	b2: 0.137665502133905
c1: 0.985889616797554	c1: 0.896013511438587	c1: 0.690893571028121	c1: 0.800374254877338
c2: 1.203019850133	c2: 2.3665559664558	c2: 3.07585423387694	c2: 0.863752276799497