Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

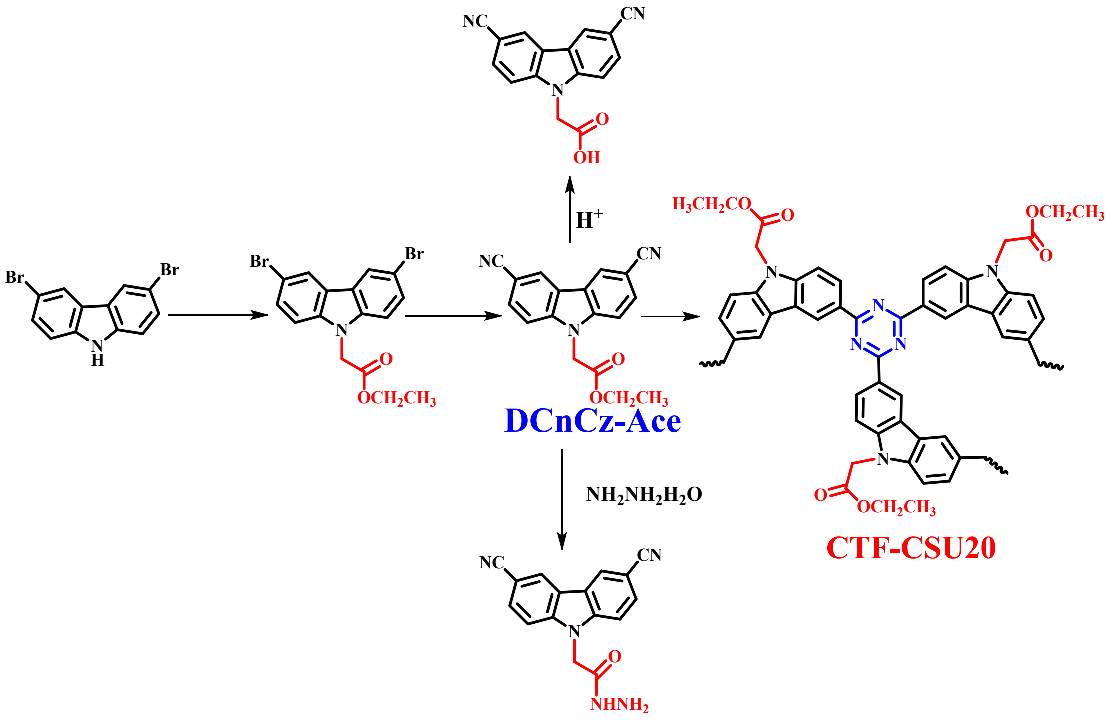
Electronic Supplementary Information (ESI)

Pore-surface Engineering in Covalent Triazine Frameworks for Low-pressure CO_2 Capture: *Pre*-designable Strategy or *Post*-synthesis Modification

Yu Fu,[a] Zhiqiang Wang,[a] Xianbiao Fu,[a,b] Jun Yan, [a] Cheng Liu[c], Chunyue Pan,[a] Guipeng Yu*[a,c]

Table of content

1. The synthetic process



Scheme S1 the synthetic routes of monomers and polymers

Ethyl-2-(3,6-dibromo-9H-carbazol-9-yl)acetate (EDCA):

3,6-Dibromo-9H-carbazole (3.25 g, 10 mmol), dry K_2CO_3 (3.73 g, 27 mmol) and tetrabutyl ammonium bromide (322 mg, 1mmol) were dissolved in dry DMF (50 mL). The mixture was stirred for 30min at 50 °C before ethyl bromoacetate (3.3 mL, 30 mmol) was added. The mixture was stirred at 90°C for 12 h. After cooling to room temperature the mixture was poured into ice water (200mL) and extracted with $CHCl_3$. The organic layer was washed with water and dried with $MgSO_4$. Afterward, the solvent was removed by reduced pressure and the crude product was purified by silica column chromatography to give a white crystal (3.45 g, 84%). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ = 8.18 (s, 2 H), 7.60-7.58 (d, *J*=8.0 Hz, 2 H), 7.24-7.23 (d, *J*=8.0 Hz, 2 H), 4.97 (s, 2 H), 4.24-4.20 (q, *J*=8.0 Hz, 2 H), 1.26-1.32(t, *J*=4.0 Hz, 3 H)

Ethyl-2-(3,6-Dicyano-9H-carbazol-9-yl)acetate:

Amixtureof ethyl-2-(3,6-dibromo-9H-carbazol-9-yl) acetate (8.22 g, 20 mmol), cuprous cyanide(8.95 g, 100 mmol) and 18-Crown-6 (180 mg) was stirred for 48 hin dry DMF(100 mL) at 150 °C under N_2 atmosphere, and then the mixture was poured into 1L hartshorn(ammonia/distilled water = 1:1 (V/V)) and stirred for another 1 h. The brown solid was collected by filtration, washed with water (10 mL*3) and ethanol(10 mL*3), and then dried. The crude product was purified by silica column chromatography (dichloromethane/petroleum ether = 1:2) to give a white solid (3.3 g, 82 %).^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 8.45 (s, 2 H), 7.84-7.82 (d, *J*=10.0 Hz, 2 H), 7.45-7.48 (d, *J*=10.0 Hz, 2 H), 5.09 (s, 2 H), 4.29-4.25 (q, *J*=10.0 Hz, 2 H), 1.30-1.27 (t, *J*=5.0 Hz, 3 H).

2-(3,6-Dicyano-9H-carbazol-9-yl) acetic acid:

Ethyl-2-(3,6-dicyano-9H-carbazol-9-yl) acetate (3.05 g, 10 mmol) was dissolved in tetrahydrofuran (60 mL) and distilled water (60 mL). The mixture was stirred for 2 h at 25 °C, and then the aqueous LiOH (15 mL, 1 $molL^{-1}$) solution was added dropwise and stirredfor 3 h and then the pH of the solution was adjusted to 7 with the aqueous hydrochloric acid (10 mL, 1$molL^{-1}$).The residue was concentrated remove a majority of organic solvents, after filtrated and washed with water (10 mL*3) and ethanol (10 mL*3),and then dried(2.75 g, 74 %).^{1}H NMR (400 MHz, DMSO): δ (ppm) 8.851 (s, 2 H), 7.947-7.969 (d, *J*=8.8 Hz, 2 H), 7.813-7.834 (m, *J*=8.8 Hz, 2 H), 5.165 (s, 2 H), 9.594 (s, 1 H).

2-(3,6-Dicyano-9H-carbazol-9-yl)acetohydrazide:

Ethyl-2-(3,6-dibromo-9H-carbazol-9-yl) acetate (3.03 g, 10 mmol) was dissolved in ethanol (100 mL), The mixture was stirred for 30 min at 80 °Cunder N_2 atmosphere, and stirred for another 24 h after the addition of hydrazine hydrate (8 mL). The maple solid was collected by filtration, washed with distilledwater(10 mL*3) and hot ethanol(10 mL*3), and then dried. The crude product was purified by silica column chromatography (dichloromethane/petroleum ether = 1:2) to give a maple solid(2.51 g, 87 %).^{1}H NMR (400 MHz, DMSO): δ (ppm) 8.837 (s, 2 H), 7.890-7.912 (d, *J*=8.8 Hz, 2 H), 7.736-7.757 (d, *J*=8.4 Hz, 2 H), 4.973 (s, 2 H), 7.956 (s, 1 H) ,1.390-1.398 (d, *J*=3.2 Hz, 2 H).

CTF-CSU20:

CTF-CSU20 was synthesized by heating a mixture of the ethyl-2-(3,6-dicyano-9H-carbazol- 9-yl)acetate (1.0 g, 3.3 mmol) and $ZnCl_2$ (4.5 g, 33 mmol) in a quartz ampule (3×10 cm). The tube was evacuated to a high vacuum and then sealed rapidly. Following by a temperature program (350/10h, 400^{o}C/80 h), the quartz tube was cooled down to 25 °C. After cooling, the homogenously brown-black block of salt and product was ground and was stirred for overnight in boiled distilled water to dissolve the salt. The product was washed successively with water (15 mL*3) and methyl alcohol(15 mL*3), followed by Soxhlet extraction overnight using acetone, methyl alcohol and hexane as eluting solvent sequentially and then dried. Yield: 90%.

CTF-CSU36@post:

CTF-CSU20 (1 g) was dispersed in100 mL hydrochloric acid (1 $mmolL^{-1}$) stirred for 24 h at 100 °C. The resulting black powder was filtered, washed successively with water(15 mL*3) and ethanol(15 mL*3)and dried. Yield: 90 %.

CTF-CSU37@post:

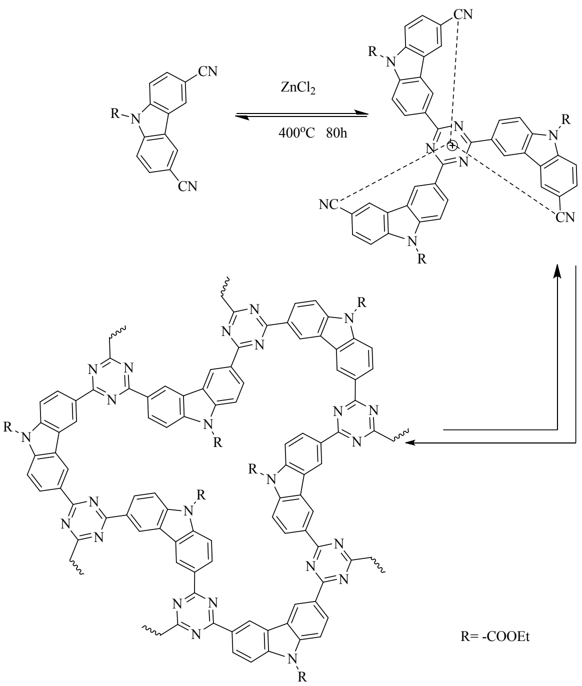
CTF-CSU20 (1 g) was dispersed in ethanol (120 mL) and stirredtheCTF-CSU20for 30min at 80 °Cunder N2 atmosphere, and then hydrazine hydrate (3 mL) was added and stirred for another 12 h. The reaction mixture was filtered, and washed successively with water(15 mL*3) and ethanol(15 mL*3)and dried. Yield: 92 %.

CTF-CSU36@pre:

The synthesis method ofCTF-CSU36@pre was almost the same as that for CTF-CSU20. Yield: 92 %.

CTF-CSU37@pre:

The synthesis method of CTF-CSU37@pre was almost the same as that for CTF-CSU20. Yield: 91 %.



Scheme S2 Proposed schematic illustration of the trimerization of carbazole based nitriles in molten ZnCl2

2. Materials and Method

3,6-Dibromo-9H-carbazole, ethyl bromoacetate and Copper(I) cyanidewas purchased from Alfa Aesar Chemical Inc. and used as received. 18-crown-6 and tetrabutyl ammonium bromide was purchased fromAladdin Chemical Inc. and used as received. $ZnCl_2$ was refluxed over $SOCl_2$ and filtered justbefore use. Unless otherwise specified, all other solvents and reagents were purchased fromEnergy Inc. and used as received.

Fourier transform infrared spectroscopy (FTIR) was collected with a VARIAN 1000 FTIR(scimitar series) spectrometer in the 400-4000 cm^{-1} region.Samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks. Samples were mounted on a sample holder and measured using Cu Kα radiation with a theta range of 5-80. Thermo-gravimetric analysis (TGA) was performed at a heating rate of 10K/min under N_2 atmosphere using a PERKIN ELMER TGA7. NMR data were collected on a Bruker 400MHz spectrometer at 25°C, using tetramethylsilane as an internal reference.For scanning electron microscopy (SEM) imaging, samples were prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The samples were then coated with gold at a pressure of 1x10^{-5}mbar under a nitrogen atmosphere for 120 seconds before imaging. Images were taken on a Quanta-200 Scanning Electron Microscope. High-resolution Transmission electron microscopy (HRTEM) was performed on a Phillips CM 200 FEG electron micro-scope equipped with a field emission gun. Powder X-ray diffraction data were collected on a PanalyticalX'pert pro multipurpose diffractometeroperated at 40 kV and 40 mA with Cu Kradiation (step size 0.017S, step time:10.34 s). The gas adsorption-desorption isotherms were performed on a Micromeritics ASAP 2020 analyzer. N_2 adsorption–desorption measurements were carried out at 77K and 273 K, CO_2 adsorption–desorption isotherms were collected at 273K and 298 K, respectively. High purity gas (99.999 %) was used for the adsorption experiments. Prior to measurements, the samples were degassed at 180°C under high vacuum for 12 h. Liquid nitrogen bath and an ice-water bath equipped with a temperature sensor were utilized to control the temperature at 77K, 273K, and 298K, respectively. The apparent surfaces areas (BET) for N_2 were calculated using the Brunauer-Emmett-Teller (BET) model range from 0.01 to 0.1 bar for three samples. Microporous volumes were calculated using single-point measurements at $P/P_0=$ 0.1, while the total porous volumes were obtained at $P/P_0=$ 0.99. Pore size distributions were derived from the N_2 adsorption isotherms using the Non-local density functional theory (NLDFT). CO_2 adsorption isotherms were measured at 273 and 298 K up to 1 bar.

Tab. S1. Reaction Conditions and Porosity of CTF-CSU20 samples

Entry	Sample name	$ZnCl_2$ (mol equiv)	Time (h)	Temp. (°C)	S_{BET}[a] ($m^2\ g^{-1}$)	CO_2 uptake[b] (wt%)
1	CTF-CSU20@1	1	10/20	350/400	251	n.m.[c]
2	CTF-CSU20@2	1	10/40	350/400	476	4.5
3	CTF-CSU20@3	1.5	10/40	350/400	569	4.9
4	CTF-CSU20@4	1	10/80	350/400	952	11.8
5	CTF-CSU20@5	1	10/20/20	350/400/600	1124	12.1

[a] Surface area determined by the BET method; [b] CO_2 uptake measured at 273 K and 1 bar. [c] not measured.

3. Infrared spectroscopy

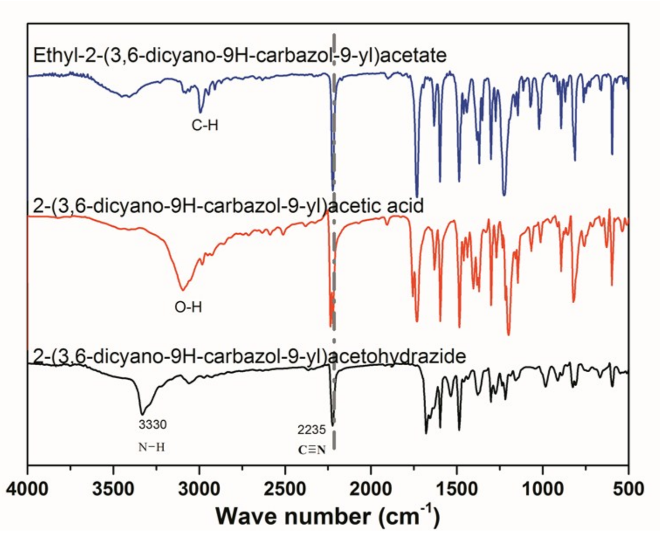


Fig.S1 FT-IR spectra of monomers

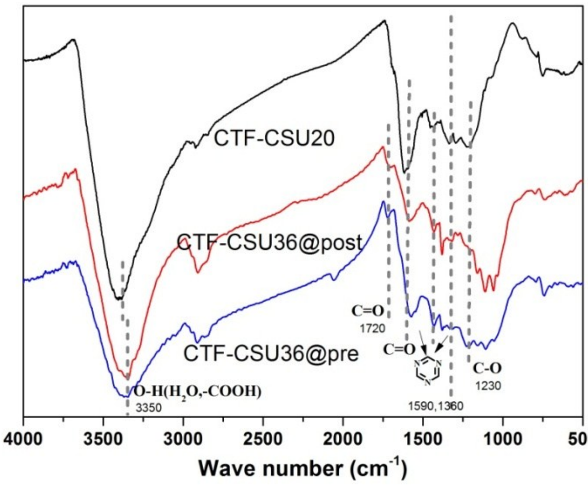


Fig.S2 FT-IR spectra of CTF-CSU20, CTF-CSU36@post and CTF-CSU36@pre

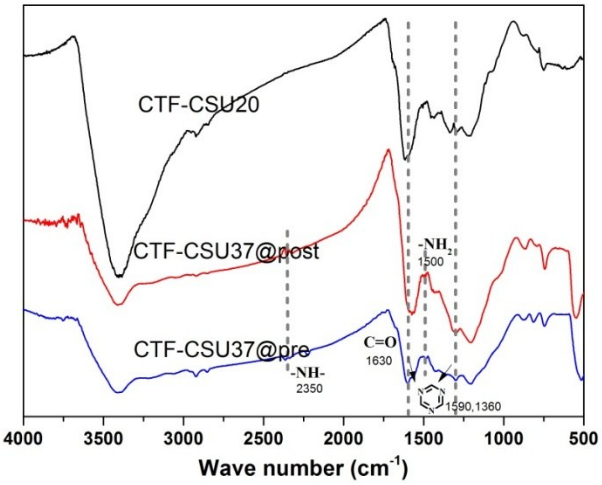


Fig.S3 FT-IR spectra of CTF-CSU20, CTF-CSU37@post and CTF-CSU37@pre

4. Analysis of FTIR integration for appended functional groups

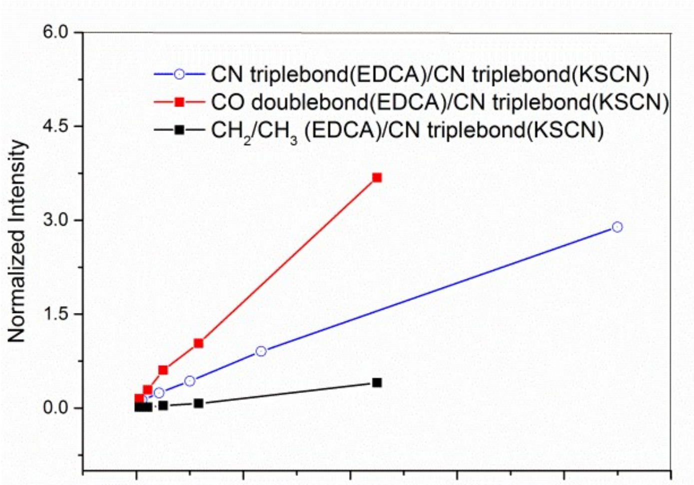


Fig.S4 Standard curves of FT-IR spectra using KSCN as an external reference (EDCA: Ethyl-2-(3,6-dibromo-9H-carbazol-9-yl)acetate)

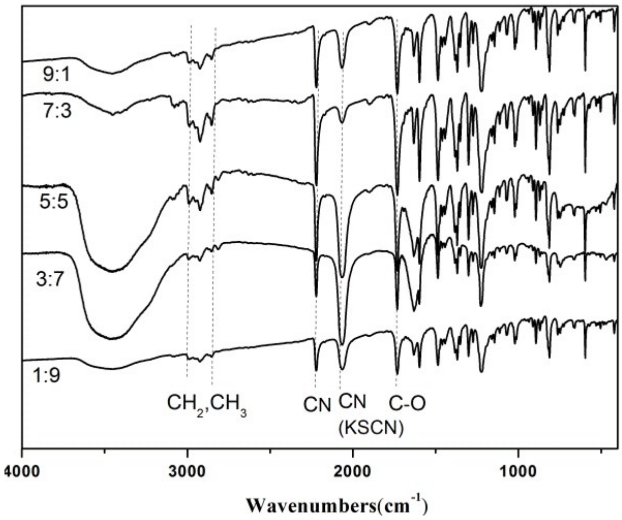


Fig.S5 FT-IR spectra ofethyl-2-(3,6-dibromo-9H-carbazol-9-yl)acetate (EDCA) with different content of KSCN

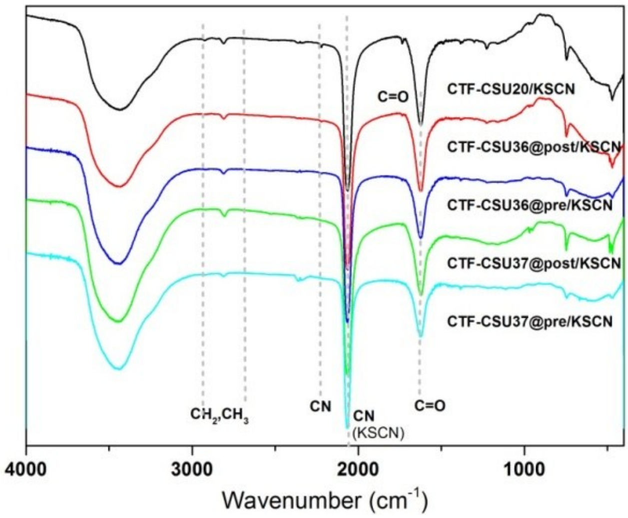


Fig.S6 FT-IR spectra of CTF-CSU20, CTF-CSU36@post, CTF-CSU36@preCTF-CSU36@post and CTF-CSU36@pre mixing with KSCN

Tab. S2 Analysis of FTIR integration for residual appended functional groups after polymerization utilizing pre-designable strategy or post-synthesis modification

Sample	CN conversion[a] (mol%)	C=O[b] (mol%)	-CH$_2$, -CH$_3$[c] (mol %)	-COOH (mol %)	-CONHNH$_2$ (mol %)
EDCA	0	100	100	0	0
CTF-CSU20	99.3	75.5	74.9	0	0
CTF-CSU36@pre	97.4	65.1	0	65.6	0
CTF-CSU36@post	99.3	73.2	2.1	71.8[d]	0
CTF-CSU37@pre	98.9	54.8	0	0	54.1
CTF-CSU37@post	99.3	69.3	4.4	0	68.8[e]

[a] CN conversion was calculated by the following equation, [CN conversion]=100*A [CN$_{EDCA}$]

A'[CN_{SCN-}]/A'[CN] A[CN_{SCN-}], where A[CN_{EDCA}] refers to the CN band intensity of EDCA in a mixture of EDCA/KSCN ,A[CN_{SCN-}] refers the CN band intensity of SCN^-in the mixture of EDCA/KSCN. Where A'[CN] refers to the CN band intensity of a certain polymer in a mixture of polymer/KSCN, A'[CN_{SCN-}] refers to the CN band intensity of SCN^-in a mixture of polymer/KSCN.

[b]where residual C=O was calculated in a similar way with those of CN conversion

[c]where residual CH_2, CH3wascalculated in a similar way with those of CN conversion

[d]where the content of -COOH was calculated assuming no other decomposition of -$COOCH_2CH_3$during the post-modification process.

[e]where the content of -$CONHNH_2$ was calculated assuming no other decomposition of -$COOCH_2CH_3$during the post-modification process.

5. Raman scattering.

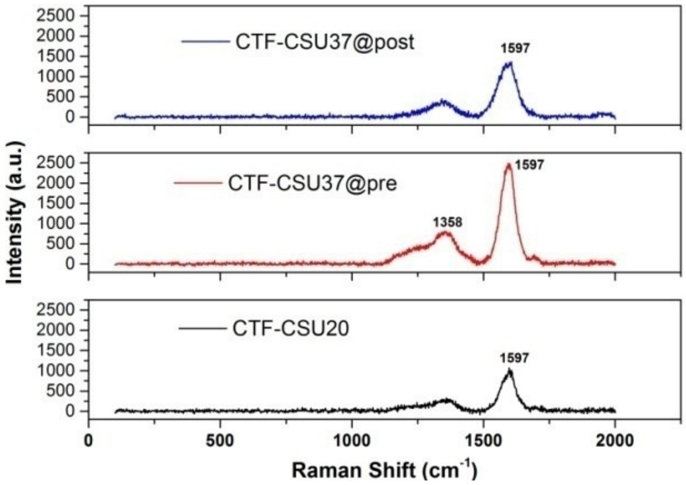
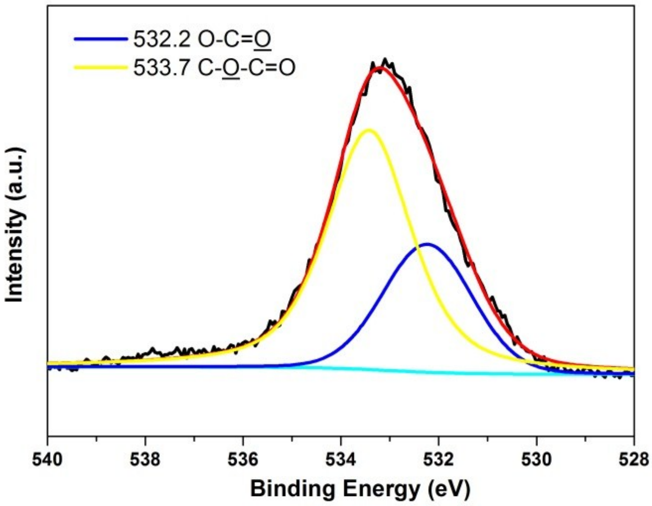


Fig.S7 Raman scattering of CTF-CSUs

6. XPS analysis



F**ig.S8** XPS spectrum of CTF-CSU20 (Calculated integrated area of C-O:C=O = 2:1)

7. Elemental analysis

Tab. S3 Elemental analysis date of the polymers

Sample	Found (%)				Calculated (%)			
	C	H	O	N	C	H	O	N
CTF-CSU20	66.28	4.22	21.04	8.06	71.28	4.29	10.56	13.86
CTF-CSU36@post	60.76	3.37	17.71	18.01	69.82	3.27	11.63	15.27
CTF-CSU37@post	60.73	3.09	15.41	19.52	66.43	3.81	5.53	24.22
CTF-CSU36@pre	67.63	3.60	13.85	14.39	69.82	3.27	11.63	15.27
CTF-CSU37@pre	70.00	3.46	14.47	11.87	66.43	3.81	5.53	24.22

8. ^{1}H NMR of monomers

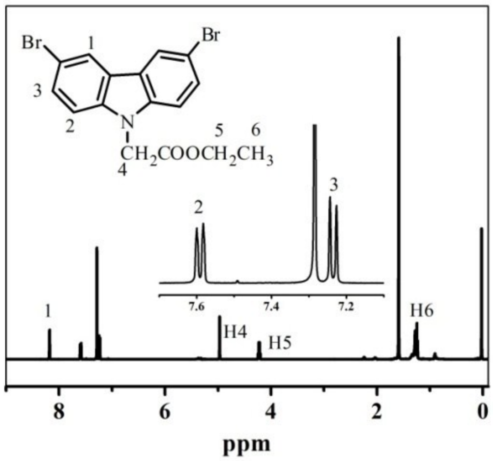


Fig.S9 ^{1}H NMR spectrum of Ethyl-2-(3,6-dibromo-9H-carbazol-9-yl)acetate

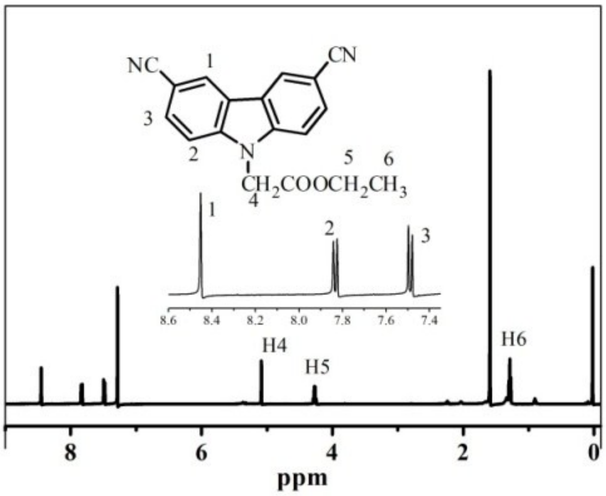


Fig.S10 ^{1}H NMR spectrum of Ethyl-2-(3,6-dicyano-9H-carbazol-9-yl)acetate

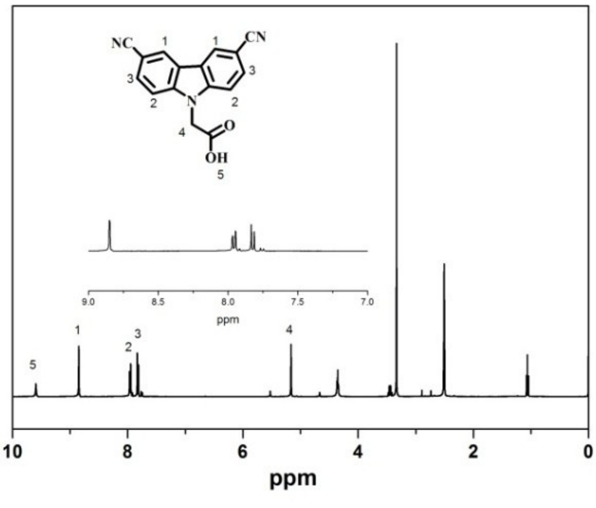


Fig.S11 ^{1}H NMR spectrum of 2-(3,6-dicyano-9H-carbazol-9-yl)acetic acid

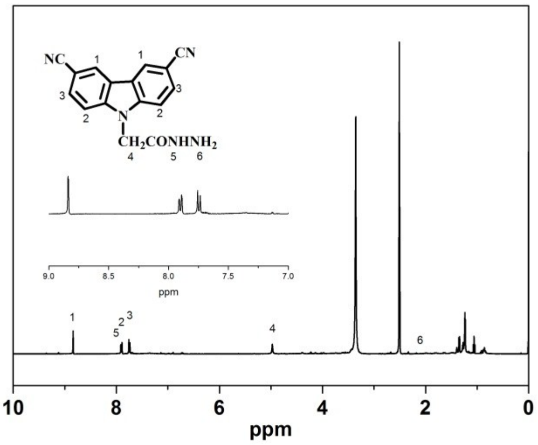


Fig.S12 ^{1}H NMR spectrum of 2-(3,6-dicyano-9H-carbazol-9-yl)acetohydrazide

9. ^{13}C NMR of monomers

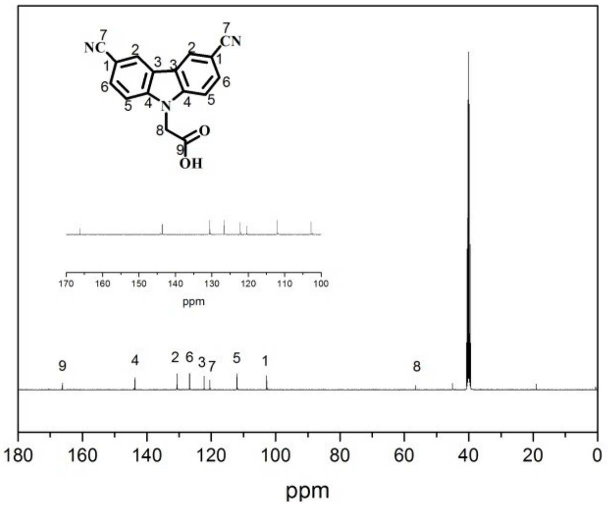


Fig.S13 ^{13}C NMR spectrum of 2-(3,6-dicyano-9H-carbazol-9-yl)acetic acid

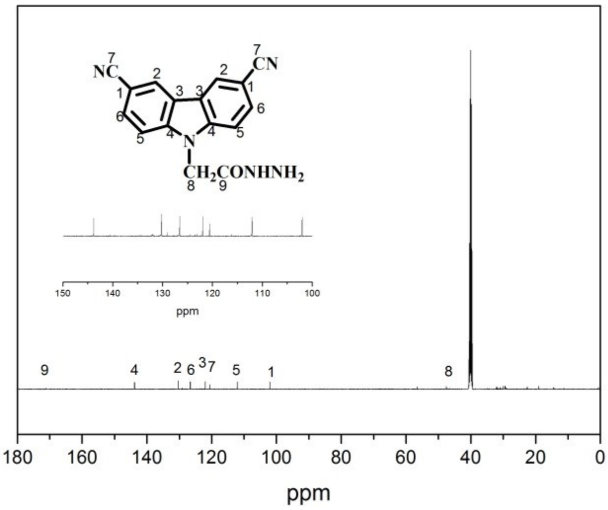


Fig.S14 ^{13}C NMR spectrum of 2-(3,6-dicyano-9H-carbazol-9-yl)acetohydrazide

10.XRD analysis

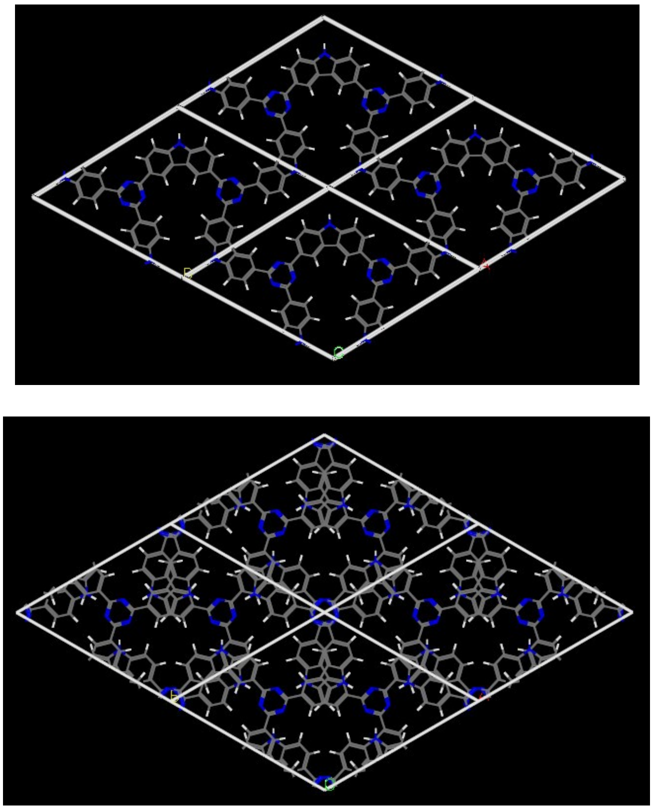


Fig.S15 Stacking of the AA (top, a = b = 17.05 Ǻ, and c = 3.5 Ǻ, P6 2M) and AB (down, a = b = 16.98 Ǻ, and c = 6.7 Ǻ, P6 2C) of CTF-CSU20 framework with P-6 hexagonal unit cell.

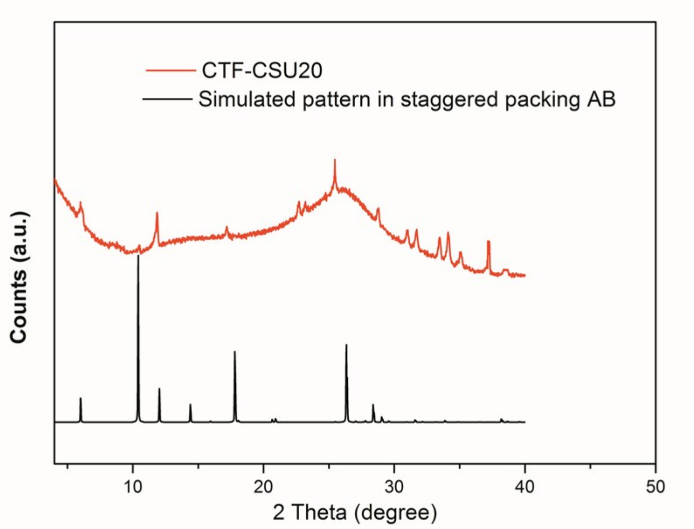


Fig.S16 Experimental PXRD pattern and the simulated patterns for CTF-CSU20 framework in staggered packing AB (down, a = b = 16.98 Ǻ, and c = 6.7 Ǻ, P6 2C) of with P-6 hexagonal unit cell.

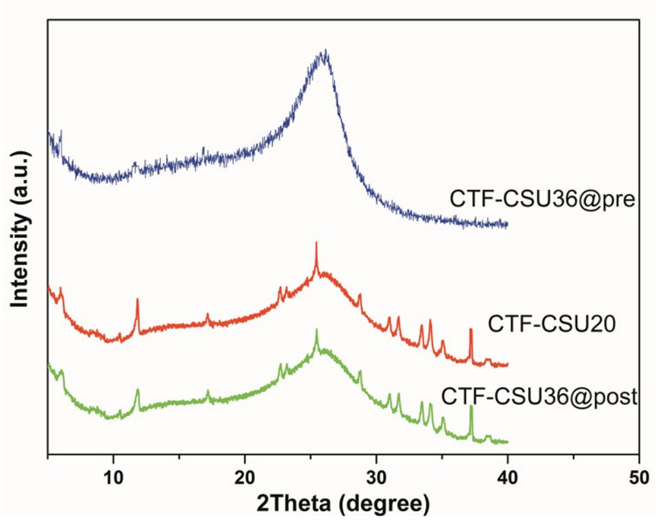


Fig.S17 PXRD patterns of CTF-CSU36@pre and CTF-CSU36@post

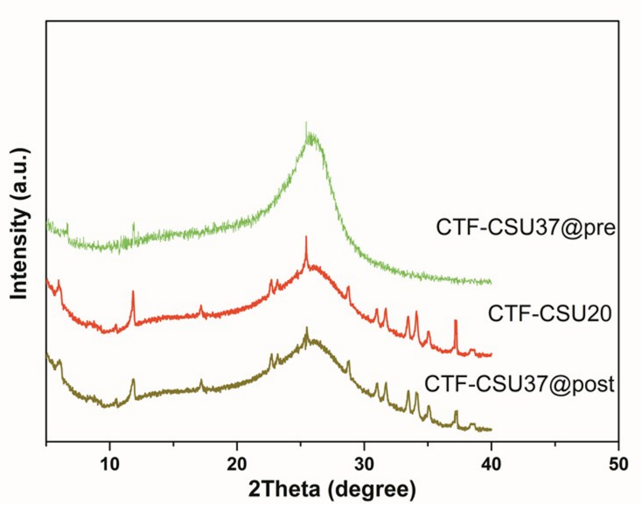


Fig.S18 PXRD patterns of CTF-CSU37@pre and CTF-CSU37@post

11.Thermo-gravimetric analysis

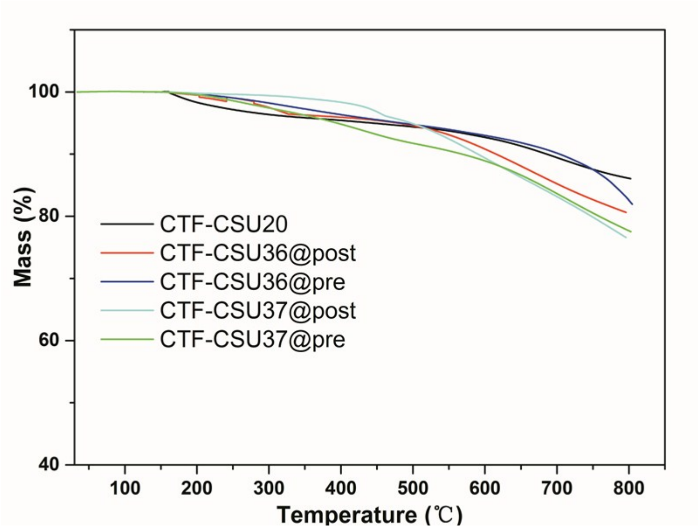


Fig. S19 Thermo-gravimetric traces (TGA) for CTF-CSUs

12.Morphology analysis by SEM and TEM

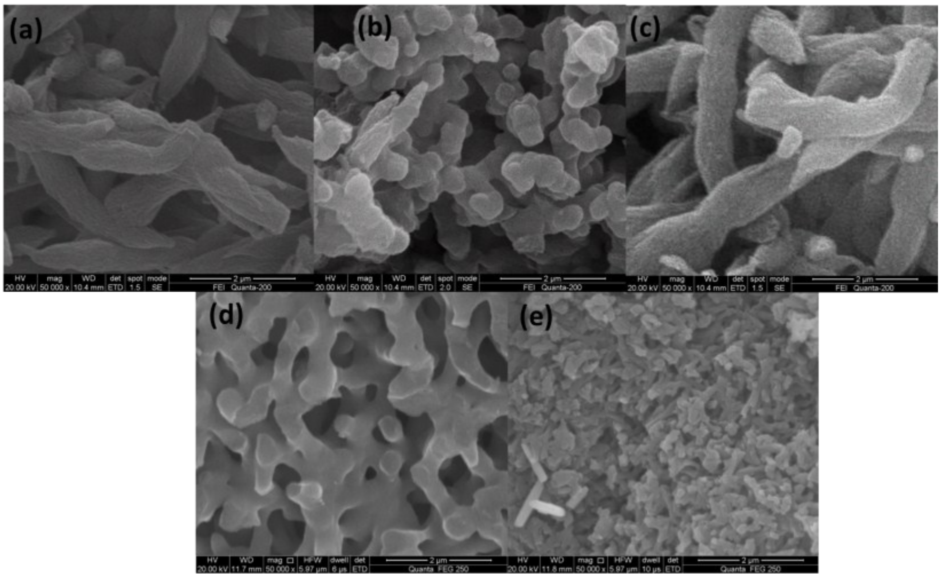


Fig.S20 Scanning electron micrographs (SEM) for (a) CTF-CSU20; (b) CTF-CSU37@post; (c) CTF-CSU36@post;(d) CTF-CSU36@pre; (e) CTF-CSU37@pre

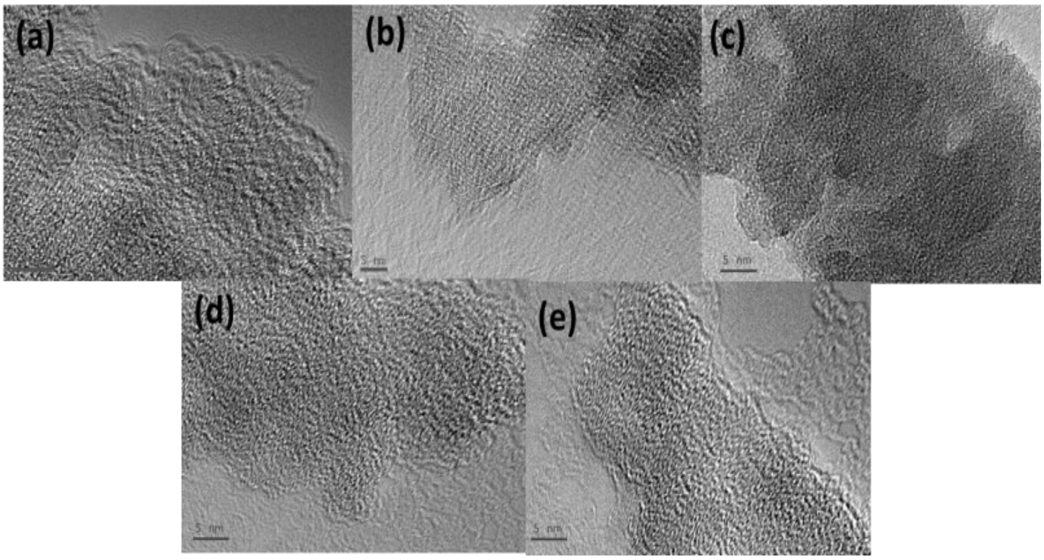


Fig.S21 Transmission electronmicrographs (TEM) for (a) CTF-CSU20; (b) CTF-CSU37@post; (c) CTF-CSU36@post; (d) CTF-CSU36@pre; (e) CTF-CSU37@pre

13.Gas CO_2 sorption isotherms of CTF-CSUs at 273K and 298K

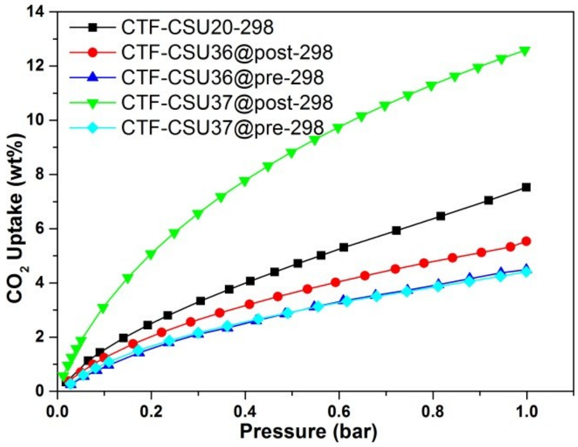


Fig.S22 CO_2 adsorption isotherms of CTF-CSUs at 298K

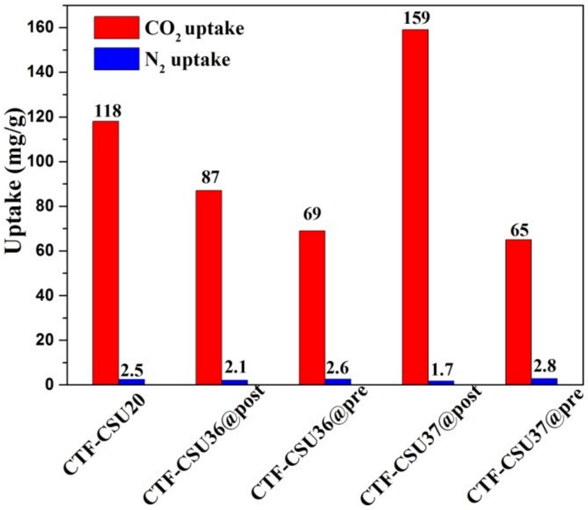


Fig.S23 CO_2 and N2 uptake of CTF-CSUs at 273 K

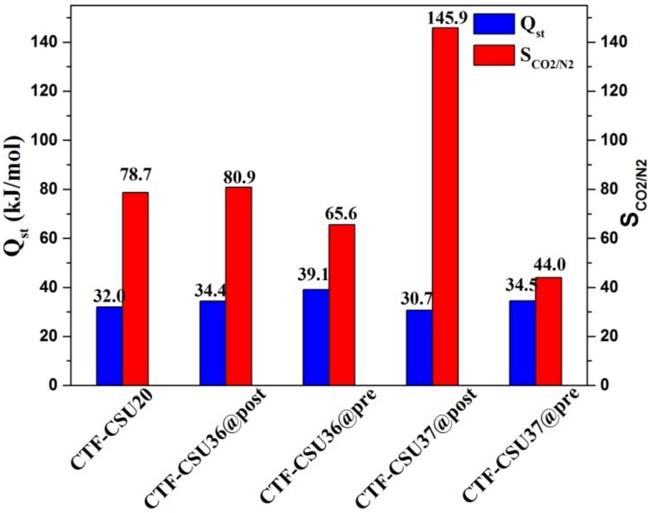


Fig.S24 Comparison of isosteric heat of adsorption and IAST selectivities.
blue: Plots of Q_{st} for CO_2 versus CO_2 uptake; red: IAST selectivities of CO_2 over N_2 for binary gas mixtures of 15/85 molar composition at 273 K.

14.Gas adsorption selectivity study

Adsorption selectivity of CO_2 over N_2 for CTF-CSUs at 273 K imitated by ideal adsorbed solution theory (IAST) model.

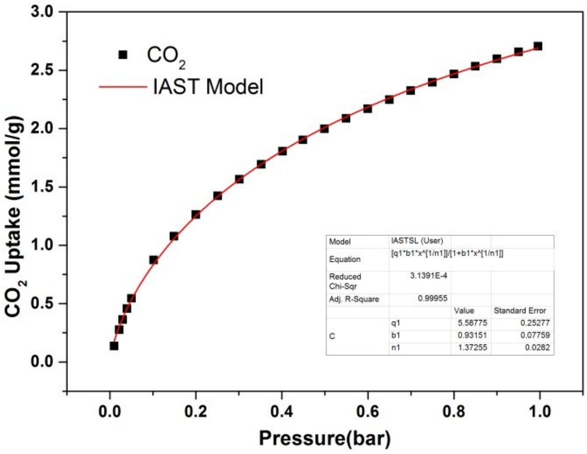


Fig.S25 CO_2 isotherm of CTF-CSU20 fitted by single-site Langmuir equation

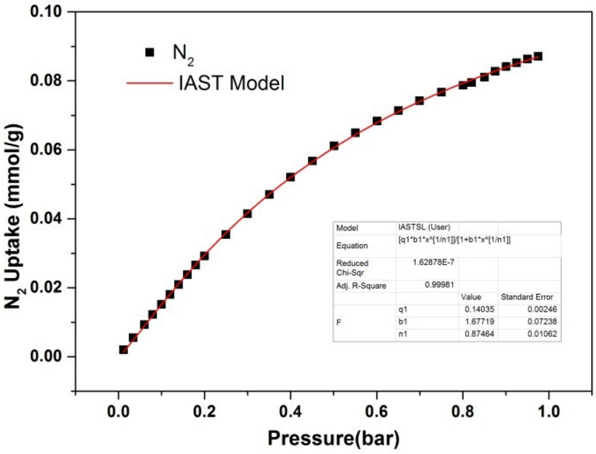
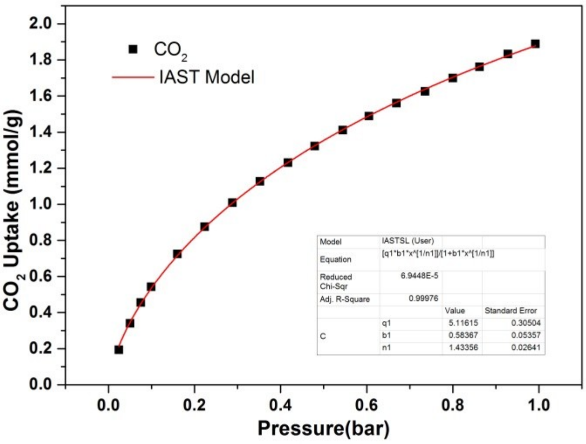
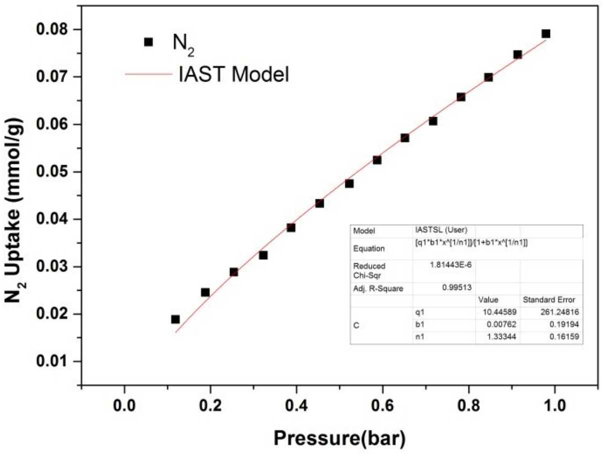


Fig.S26 N_2 isotherm of CTF-CSU20 fitted by single-site Langmuir equation



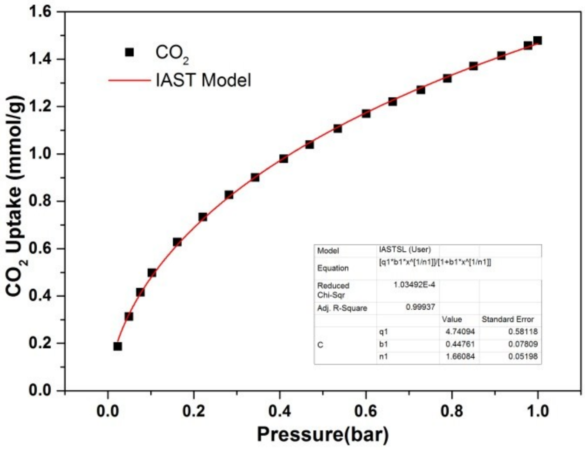
Model	IASTSL (User)		
Equation	[q1*b1*x^[1/n1]]/[1+b1*x^[1/n1]]		
Reduced Chi-Sqr	6.9448E-5		
Adj. R-Square	0.99976		
		Value	Standard Error
C	q1	5.11615	0.30504
	b1	0.58367	0.05357
	n1	1.43356	0.02641

Fig.S27 CO_2 isotherm of CTF-CSU36@pre fitted by single-site Langmuir equation



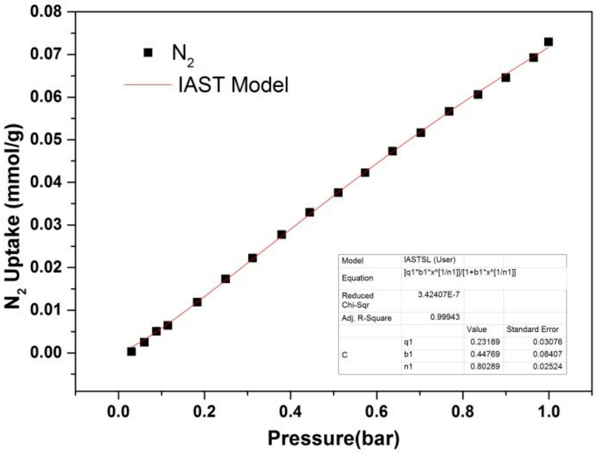
Model	IASTSL (User)		
Equation	[q1*b1*x^[1/n1]]/[1+b1*x^[1/n1]]		
Reduced Chi-Sqr	1.81443E-6		
Adj. R-Square	0.99513		
		Value	Standard Error
C	q1	10.44589	261.24816
	b1	0.00762	0.19194
	n1	1.33344	0.16159

Fig.S28 N_2 isotherm of CTF-CSU36@pre fitted by single-site Langmuir equation



Model	IASTSL (User)		
Equation	[q1*b1*x^[1/n1]]/[1+b1*x^[1/n1]]		
Reduced Chi-Sqr	1.03492E-4		
Adj. R-Square	0.99937		
		Value	Standard Error
C	q1	4.74094	0.58118
	b1	0.44761	0.07809
	n1	1.66084	0.05198

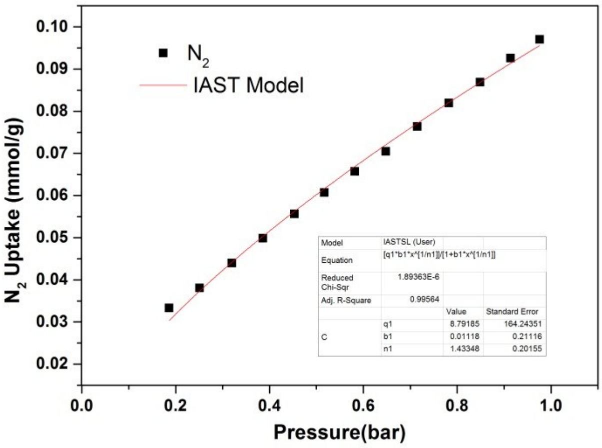
Fig.S29 CO_2 isotherm of CTF-CSU36@post fitted by single-site Langmuir equation



Model	IASTSL (User)		
Equation	[q1*b1*x^[1/n1]]/[1+b1*x^[1/n1]]		
Reduced Chi-Sqr	3.42407E-7		
Adj. R-Square	0.99943		
		Value	Standard Error
C	q1	0.23189	0.03076
	b1	0.44769	0.08407
	n1	0.80289	0.02524

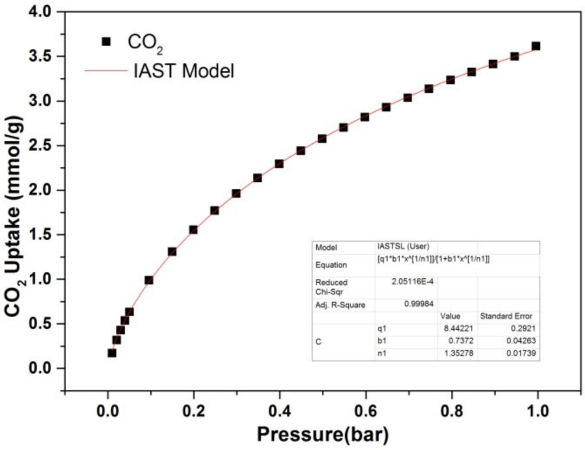
Fig.S30 N$_2$ isotherm of CTF-CSU36@post fitted by single-site Langmuir equation

Fig.S31 CO$_2$ isotherm of CTF-CSU37@pre fitted by single-site Langmuir equation



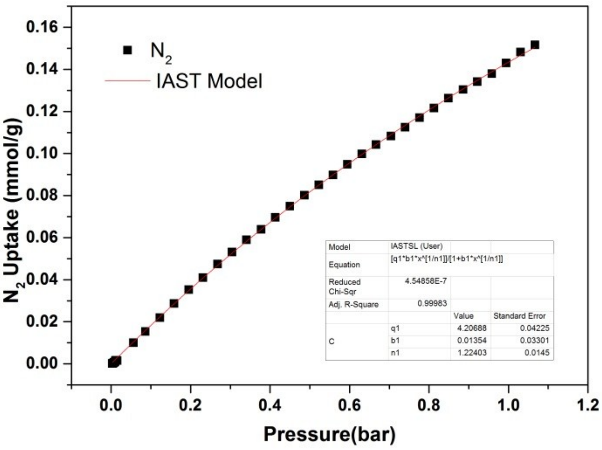
Model	IASTSL (User)		
Equation	[q1*b1*x^[1/n1]]/[1+b1*x^[1/n1]]		
Reduced Chi-Sqr	1.89363E-6		
Adj. R-Square	0.99564		
		Value	Standard Error
C	q1	8.79185	164.24351
	b1	0.01118	0.21116
	n1	1.43348	0.20155

Fig.S32 N$_2$ isotherm of CTF-CSU37@pre fitted by single-site Langmuir equation



Model	IASTSL (User)		
Equation	[q1*b1*x^[1/n1]]/[1+b1*x^[1/n1]]		
Reduced Chi-Sqr	2.05116E-4		
Adj. R-Square	0.99984		
		Value	Standard Error
C	q1	8.44221	0.2921
	b1	0.7372	0.04263
	n1	1.35278	0.01739

Fig.S33 CO_2 isotherm of CTF-CSU37@post fitted by single-site Langmuir equation



Model	IASTSL (User)		
Equation	[q1*b1*x^[1/n1]]/[1+b1*x^[1/n1]]		
Reduced Chi-Sqr	4.54858E-7		
Adj. R-Square	0.99983		
		Value	Standard Error
C	q1	4.20688	0.04225
	b1	0.01354	0.03301
	n1	1.22403	0.0145

Fig.S34 N_2 isotherm of CTF-CSU37@post fitted by single-site Langmuir equation

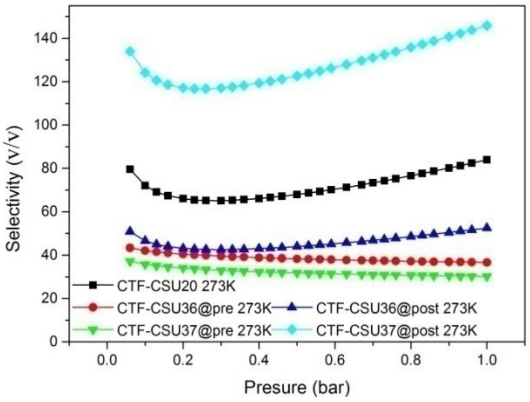


Fig.S35 IAST selectivities of CO_2 over N_2 for binary gas mixtures of 15/85 molar composition in CTF-CSUs at 273 K.

15.References

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