Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Pyridinium Linkers and Mixing Anions in Cationic Metal-Organic Frameworks

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Experiment Section

Materials and Methods. All commercially available reagents were used as received without further purification. H_2ipqPF_6 and H_2ipqBF_4 (H_2ipq^+ for 1-(3,5-dicarboxyphenyl)-4-(pyridin-4-yl) pyridinium) were prepared according to a reported method.[1] ^{19}F NMR spectra was collected using a Bruker Advance II 400 MHz NMR spectrometer. All materials were dissolved in DCl/DMSO-*d*6 solvents. TGA was collected using a Netzsch STA 409 PC, using an Al pan at a heating rate of 2°C min^{-1}. Elemental analysis was performed using a Perkin Elmer Model 2400 series II. Powder x-ray diffraction patterns were collected using a Rigaku Miniflex II bench top PXRD equipped with a CuKα x-ray source. Gas sorption isotherms were measured on ASAP 2020. Before the measurement, the samples were all activated under a dynamic vacuum up to 10^{-2} Pa in two stages, initially at 25 °C for 6 hrs then to 150 °C at 0.5 °C min^{-1} for 5 hrs until the outgas rate less than 0.2 Pa min^{-1}. All compounds were measured with the same equilibrium criterion.

Synthesis of [Cu(ipq)]NO_3·2DMF·2H_2O (CALF-32(NO_3)·g): A mixture of $Cu(NO_3)_2·4H_2O$ (20 mg, 0.1 mmol), H_2ipqPF_6 (47 mg, 0.1 mmol), *N*,*N*-diethylformamide (DMF) (2 mL) and ethanol (0.5 mL) was ultrasonically dissolved and sealed in a 20-mL Pyrex vial and heated at 80 °C for 12 hours, and then cooled by 5 °C/hr to room temperature to give blue crystals of [Cu(ipq)]NO_3·2DMF·H_2O in ca. 60% yield. Anal. calcd (%) for $C_{24}H_{29}CuN_5O_{11}$: C, 45.97; H, 4.66; N, 11.17;. Found: C, 44.79; H, 4.42; N, 11.12.

Synthesis of [Cu(ipq)]BF_4·2DMF·3H_2O (CALF-32(BF_4)·g): A mixture of $Cu(BF_4)_2$ (24 mg, 0.1 mmol), H_2ipqBF_4 (41 mg, 0.1 mmol), DMF (2 mL) and ethanol (0.5 mL) was ultrasonically dissolved and sealed in a 20-mL Pyrex vial and heated at 80 °C for 12 hours, and then cooled by 5 °C/hr to room temperature to give blue crystals of [Cu(ipq)]BF_4·2DMF·3H_2O in ca. 32% yield. ^{19}F NMR (400 MHz, DCl and DMSO-*d*6; Fig. S1c): δ = -148.5, -149.8 (BF_4^-); Anal. calcd (%) for $C_{24}H_{31}BCuF_4N_4O_9$: C, 43.03; H, 4.66; N, 8.36;. Found: C, 38.94; H, 3.82; N, 8.11.

Synthesis of [Cu(ipq)]$(BF_4)_{0.8}$$(PF6)_{0.2}$·2DMF·3$H_2O$ (CALF-32$(BF_4)_{0.8}$ $(PF_6)_{0.2}$·g): A mixture of $Cu(BF_4)_2$ (24 mg, 0.1 mmol), H_2ipqPF_6 (47 mg, 0.1 mmol), DMF (2 mL) and ethanol (0.5 mL) was ultrasonically dissolved and sealed in a 20-mL Pyrex vial and heated at 80 °C for 12 hours, and then cooled by 5 °C/hr to room temperature to give blue crystals of [Cu(ipq)]$(BF_4)_{0.8}$ $(PF6)_{0.2}$·2DMF·3H_2O in ca. 70% yield. ^{19}F NMR (400 MHz, DCl and DMSO-*d*6; Fig. S1d): δ = -71.1, -73.0 (PF_6^-); -148.7, -150.0 (BF_4^-); Anal. calcd (%) for $C_{24}H_{31}B_{0.8}CuF_{4.4}N_4O_9P_{0.2}$: C, 42.30; H, 4.58; N, 8.22;. Found: C, 43.96; H, 3.80; N, 7.74.

Synthesis of [Cu(ipq)]$(BF_4)_{0.6}$$(PF6)_{0.4}$·3DMF·2$H_2O$ (CALF-32$(BF_4)_{0.6}$ $(PF_6)_{0.4}$·g): A mixture of $Cu(BF_4)_2$ (24 mg, 0.1 mmol), H_2ipqPF_6 (70 mg, 0.15 mmol), DMF (2 mL) and ethanol (0.5 mL) was ultrasonically dissolved and sealed in a 20-mL Pyrex vial and heated at 80 °C for 12 hours, and then cooled by 5 °C/hr to room temperature to give blue crystals of [Cu(ipq)]$(BF_4)_{0.6}$$(PF6)_{0.4}$· 3DMF·2$H_2O$ in ca. 28% yield. ^{19}F NMR (400 MHz, DCl and DMSO-*d*6; Fig. S1e): δ = -70.5, -72.4 (PF_6^-); -147.9, -149.3 (BF_4^-); Anal. calcd (%) for $C_{27}H_{36}B_{0.6}CuF_{4.8}N_5O_9P_{0.4}$: C, 43.34; H, 4.85; N, 9.36;. Found: C,43.96; H, 4.03; N, 8.89.

Crystal Structure Determination. Intensity data were collected on a Nonius CCD diffractometer equipped with an Apex II CCD area-detector diffractometer (Mo-Kα). The diffraction spots were measured in full, scaled with SCALEPACK, corrected for Lorentz-polarization correction, and integrated using DENZO.[2] The structures were solved with direct method and refined with a full-matrix least-squares technique with the SHELXTL program package.[3] Anisotropic thermal parameters were applied to all non-hydrogen atoms except the guest molecules. The organic hydrogen atoms were generated geometrically.

1 D. Bongard, M. Möller, S. N. Rao, D. Corr and L. Walder, *Helv. Chim. Acta*, 2005, **88**, 3200.

2 Z. Otwinowski and W. Minor, In Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A; C. W. Carter Jr and R. M. Sweet, Eds.; Academic Press: New York, NY, *1997*; pp 307-326.

3 Bruker Analytical Instrumentation: Madison, WI *2000*.

Table S1. Crystallographic data.

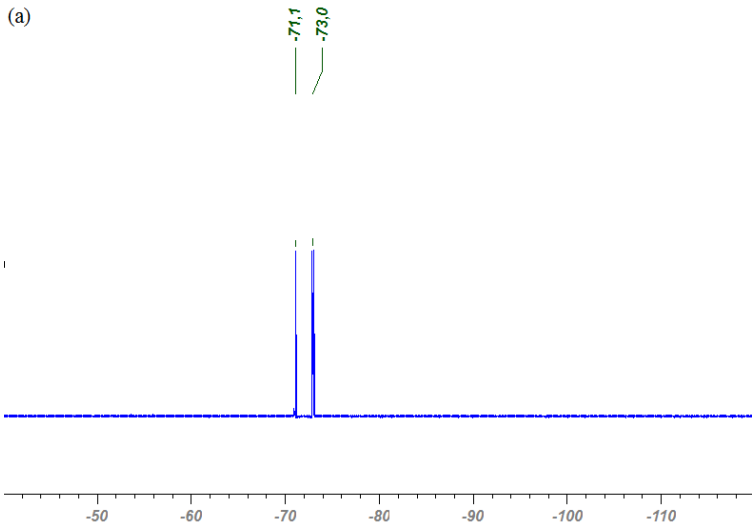
Complex	CALF-32(NO_3)
Formula	$C_{24}H_{29}CuN_5O_{11}$
Formula weight	627.06
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.6530(5)
b/Å	13.5330(5)
c/Å	13.6150(5)
β/°	103.918(2)
V/Å ^{3}	2799.42(17)
Z	4
D_c /g cm^{-3}	1.488
μ/mm^{-1}	0.847
reflns coll.	20078
unique reflns	5507
R_{int}	0.1194
R_1 [$I > 2\sigma$][a]	0.0928
wR_2 [$I > 2\sigma$][b]	0.2650
R_1 (all data)	0.1287
wR_2 (all data)	0.3027
GOF	1.008

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

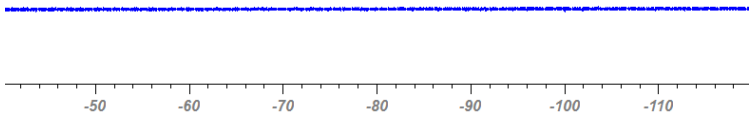
Table S2. Gas adsorption and selectivity.

	CALF-32 (NO_3)	CALF-32 (BF_4)	CALF-32 $(BF_4)_{0.8}(PF_6)_{0.2}$	CALF-32 $(BF_4)_{0.6}(PF_6)_{0.4}$
Langmuir surface area from N_2 (77 K)/CO_2 (195 K) (m^2 g^{-1})	2.5/118	248/430	317/600	955/1186
Q_{st} for CO_2 at low CO_2 loading (kJ mol^{-1})	32	35	35	31
CO_2 uptake at 273 K/298 K at 1 bar (w.t.%)	3.4/2.5	6.6/4.6	8.8/6.1	21/15
CO_2 uptake at 273 K/298 K at 1 bar (mmol g^{-1})	0.8/0.6	1.5/1.0	2.0/1.4	4.8/3.4
N_2 uptake at 273 K at 1 bar (w.t.%)	0.1	0.2	0.2	0.8
CH_4 uptake at 273 K at 1 bar (w.t.%)	0.2	0.5	0.5	2.1
IAST Selectivity at 273 K and 1 bar in CO_2/N_2:13/87 mixture	63	85	157	98
IAST Selectivity at 273 K and 1 bar in CO_2/ CH_4:50/50 mixture	19	18	47	14

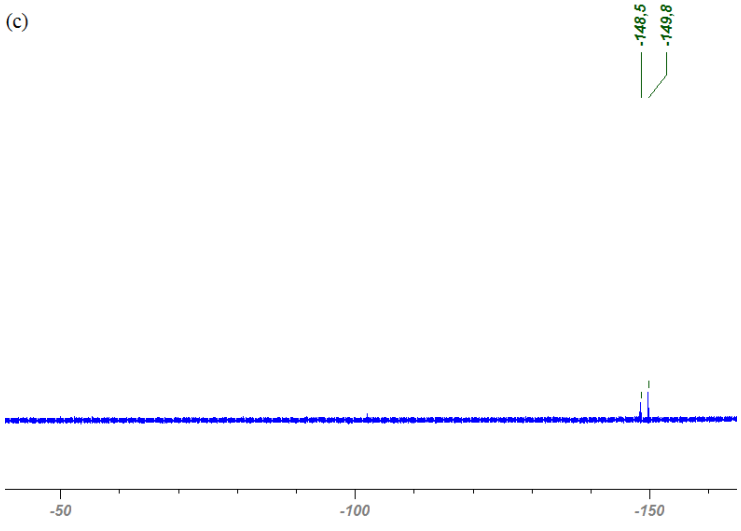
(a)


-71,1
-73,0
-50
-60
-70
-80
-90
-100
-110

(b)


-50
-60
-70
-80
-90
-100
-110

(c)


-148,5
-149,8
-50
-100
-150

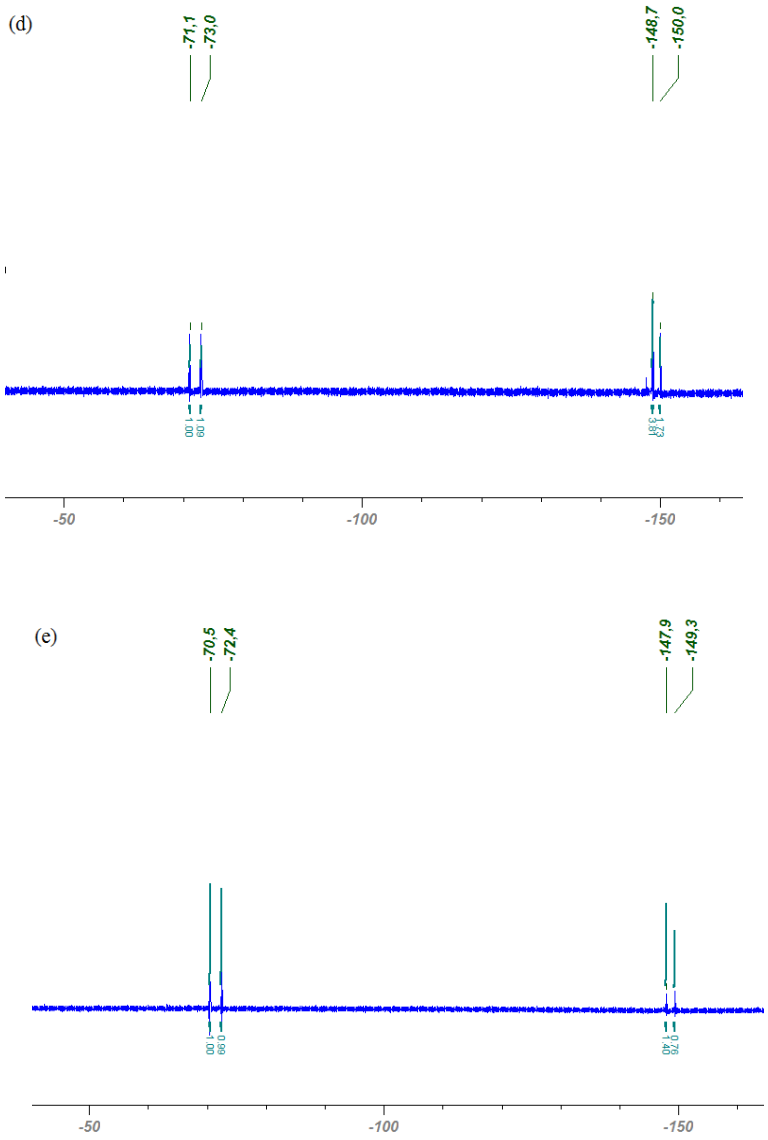
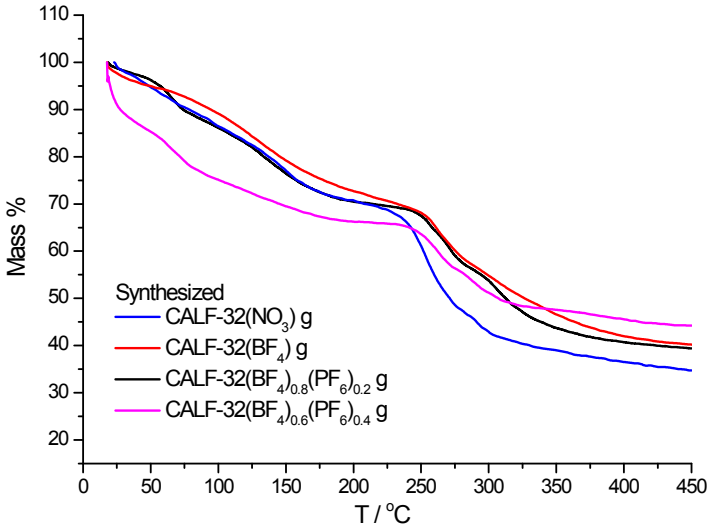


Fig. S1 ^{19}F NMR spectra for compounds (a) H_2ipqPF_6, (b) CALF-32(NO_3), (c) CALF-32(BF_4), (d) CALF-32$(BF_4)_{0.8}(PF6)_{0.2}$ and (e) CALF-32$(BF_4)_{0.6}(PF6)_{0.4}$



. **Fig. S2** TGA of synthesized CALF-32(A).

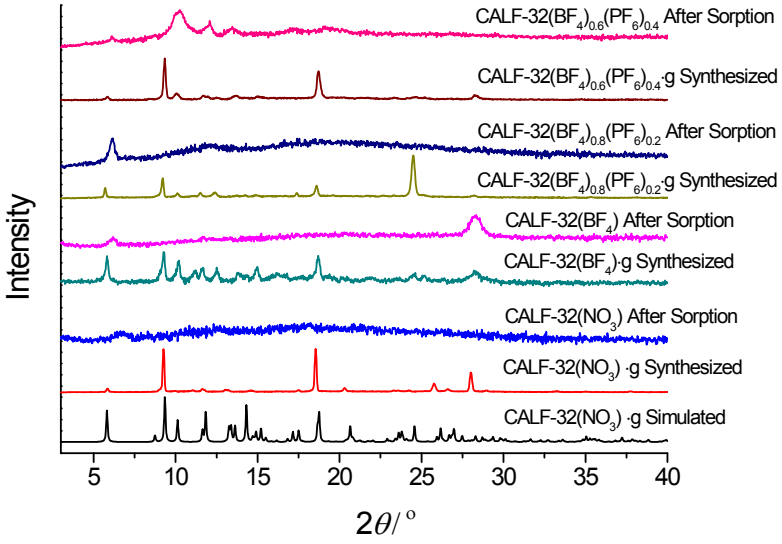
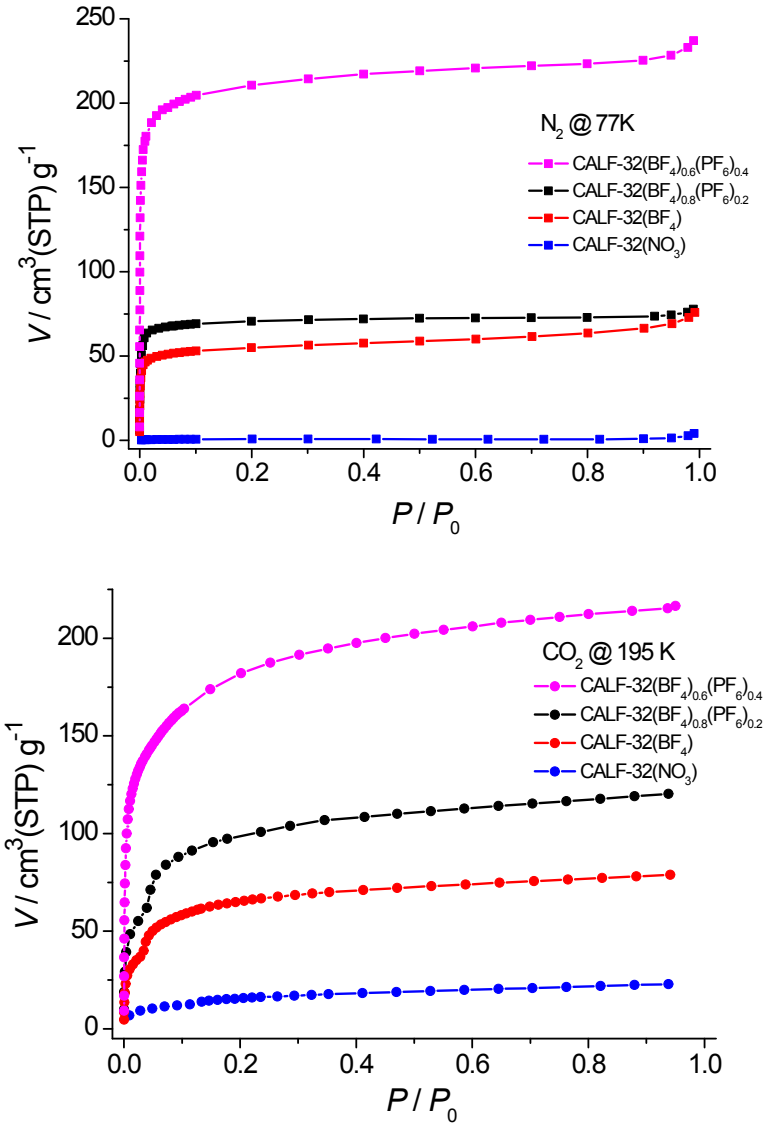
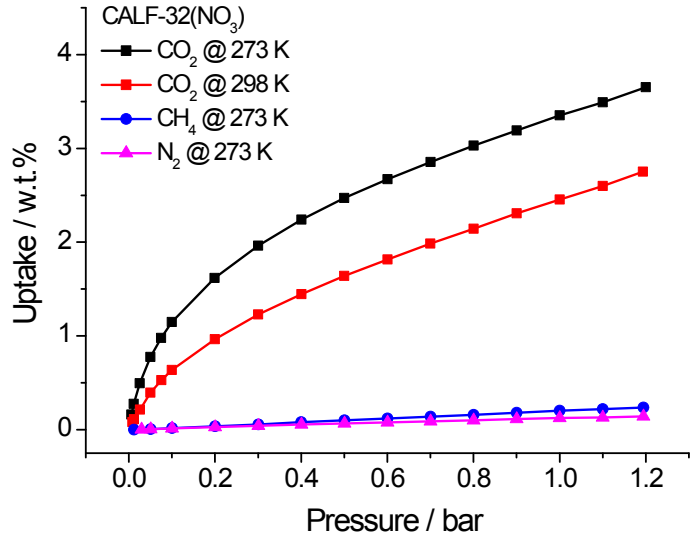
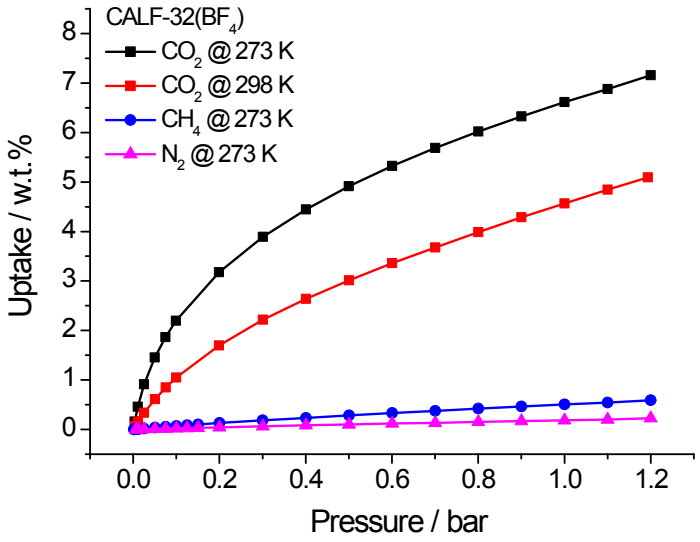


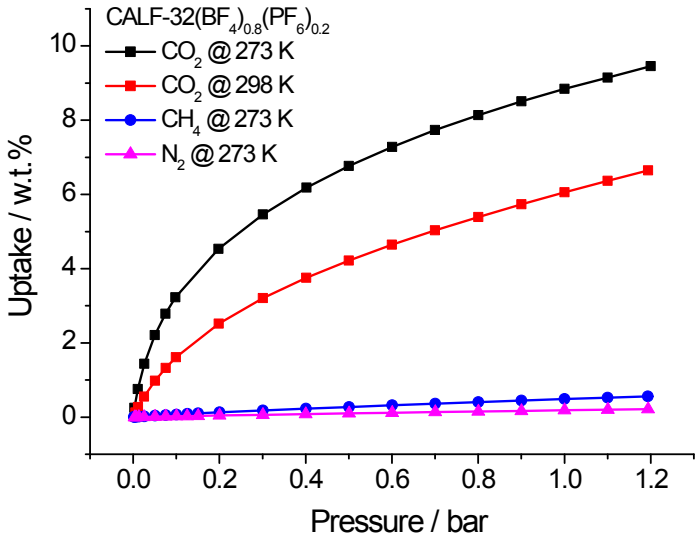
Fig. S3 PXRD patterns of the simulated CALF-32(NO_3), synthesized and activated CALF-32(A).

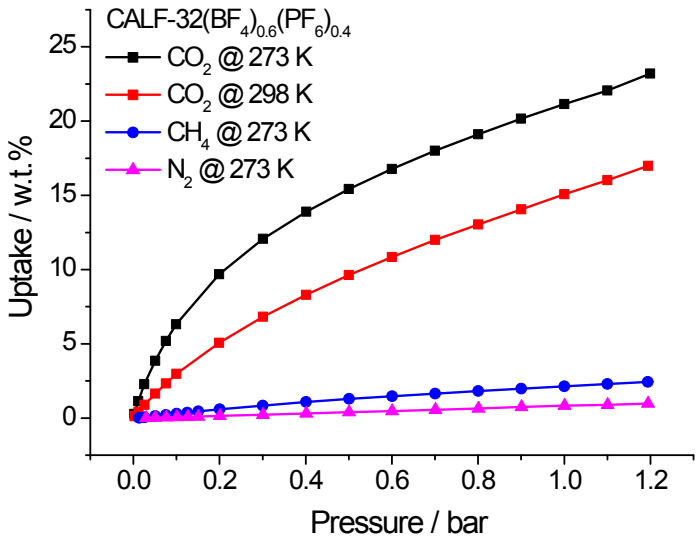


. **Fig. S4** N_2 and CO_2 sorption isotherms of activated CALF-32(A) measured at 77 and 195 K, respectively.


CALF-32(NO3)
CO2 @ 273 K
CO2 @ 298 K
CH4 @ 273 K
N2 @ 273 K
Uptake / w.t.%
Pressure / bar


CALF-32(BF4)
CO2 @ 273 K
CO2 @ 298 K
CH4 @ 273 K
N2 @ 273 K
Uptake / w.t.%
Pressure / bar


CALF-32(BF4)0.8(PF6)0.2
CO2 @ 273 K
CO2 @ 298 K
CH4 @ 273 K
N2 @ 273 K
Uptake / w.t.%
Pressure / bar



. **Fig. S5** CO_2, CH_4 and N_2 sorption isotherms of activated CALF-32(A) measured at 273 and 298 K.

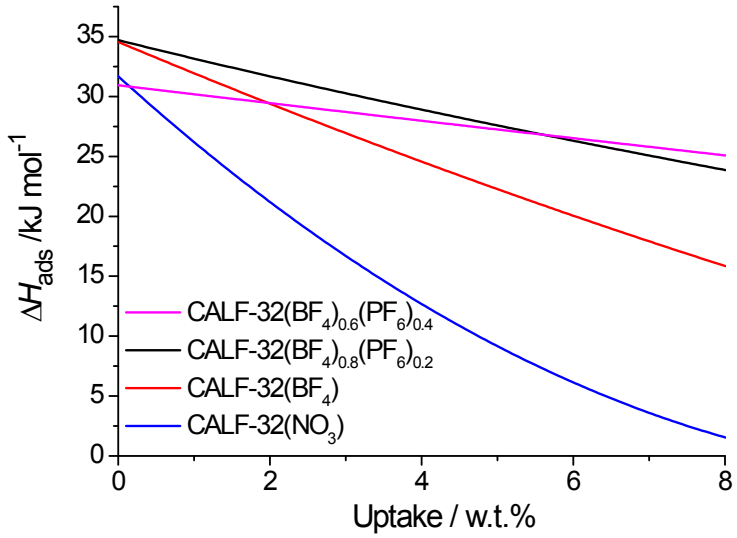
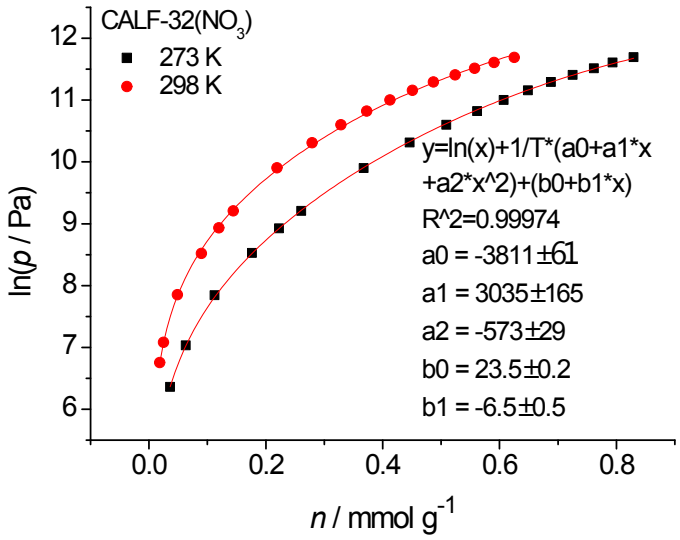
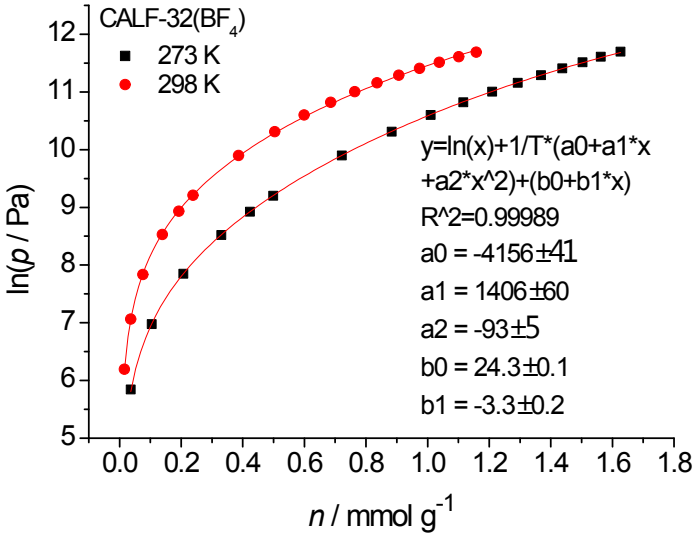


Fig. S6 Adsorption enthalpies of CO_2 calculated by isotherms at 273 and 298 K in CALF-32(A).


CALF-32(NO3)
273 K
298 K
y=ln(x)+1/T*(a0+a1*x
+a2*x^2)+(b0+b1*x)
R^2=0.99974
a0 = -3811±61
a1 = 3035±165
a2 = -573±29
b0 = 23.5±0.2
b1 = -6.5±0.5
ln(p / Pa)
n / mmol g-1


CALF-32(BF4)
273 K
298 K
y=ln(x)+1/T*(a0+a1*x
+a2*x^2)+(b0+b1*x)
R^2=0.99989
a0 = -4156±41
a1 = 1406±60
a2 = -93±5
b0 = 24.3±0.1
b1 = -3.3±0.2
ln(p / Pa)
n / mmol g-1

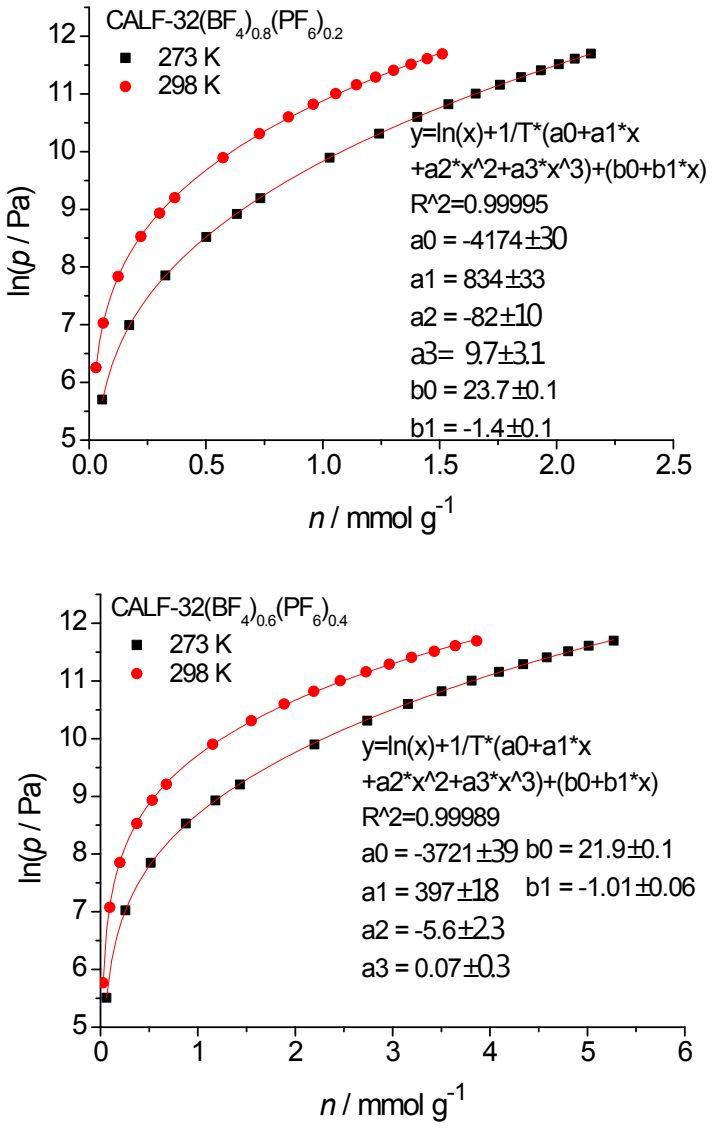
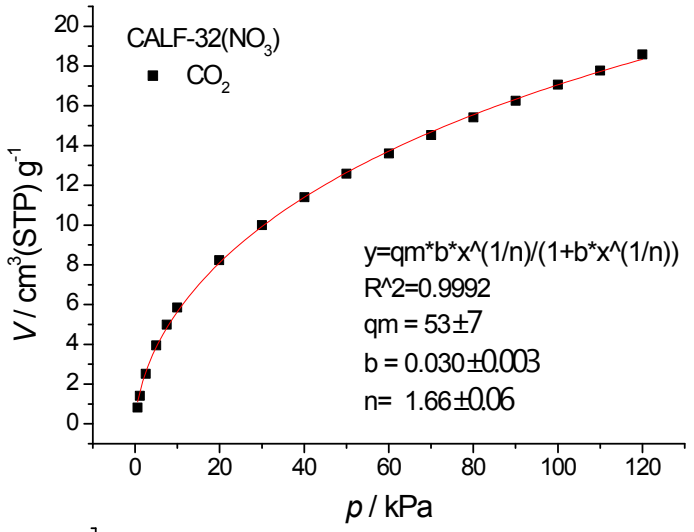
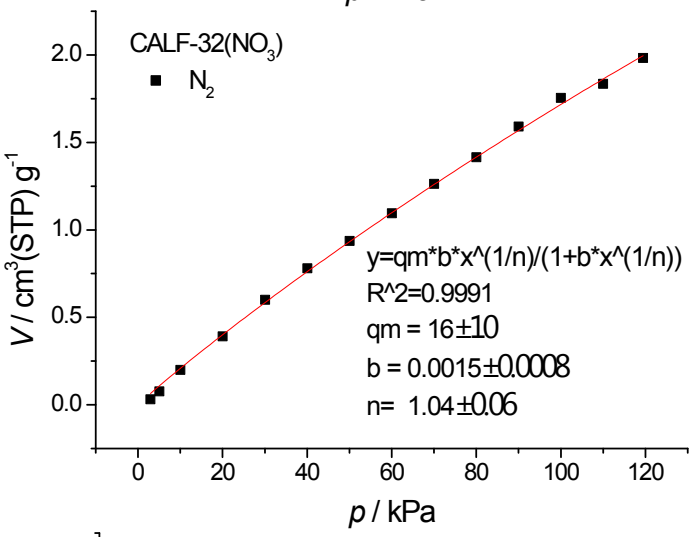
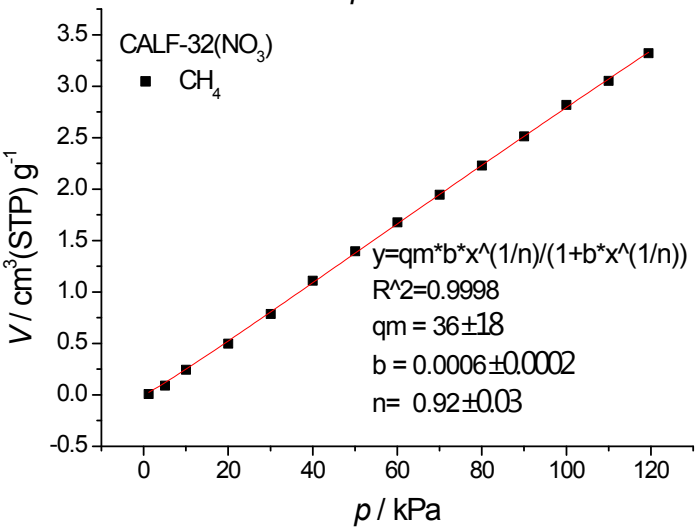
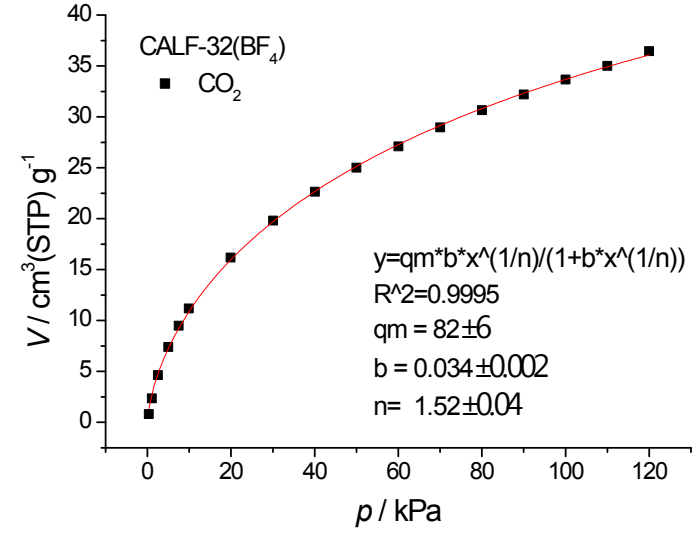


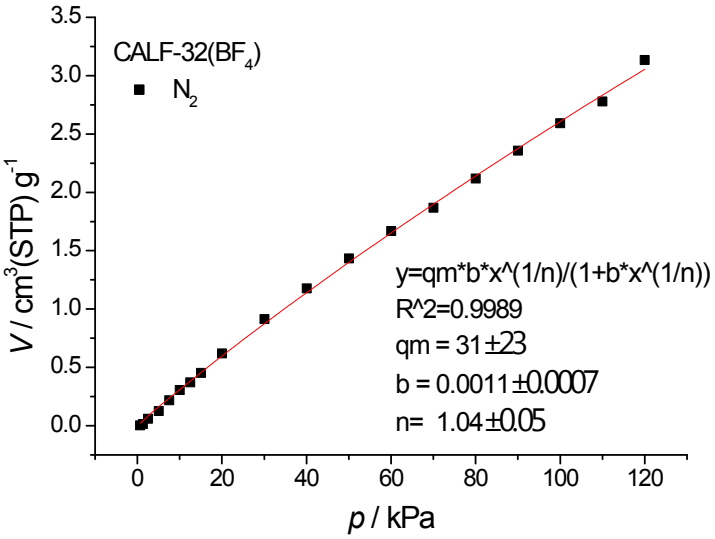
Fig. S7 CO_2 adsorption isotherms for CALF-32(A) with fitting by virial method.

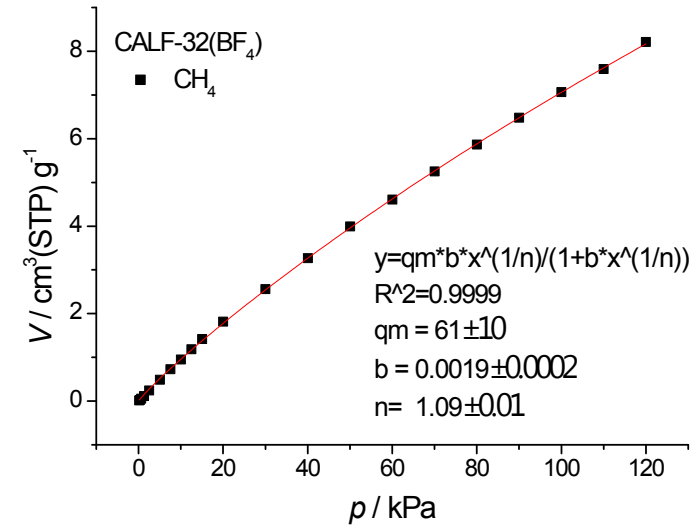

CALF-32(NO3)
CO2
y=qm*b*x^(1/n)/(1+b*x^(1/n))
R^2=0.9992
qm = 53±7
b = 0.030±0.003
n= 1.66±0.06
V / cm3(STP) g-1
p / kPa

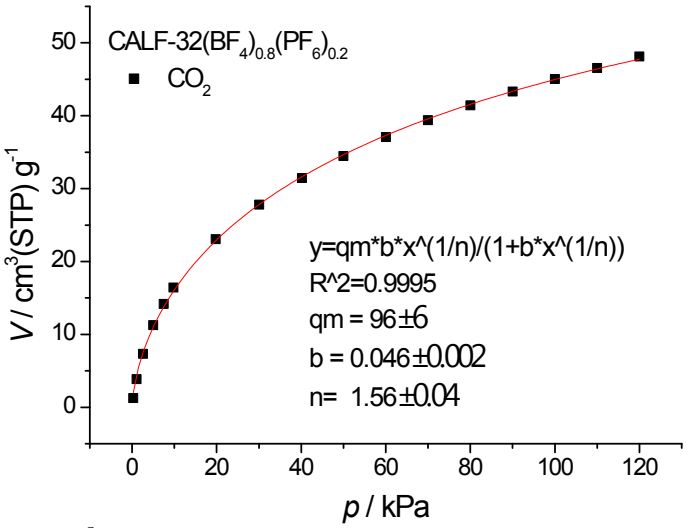

CALF-32(NO3)
N2
y=qm*b*x^(1/n)/(1+b*x^(1/n))
R^2=0.9991
qm = 16±10
b = 0.0015±0.0008
n= 1.04±0.06
V / cm3(STP) g-1
p / kPa

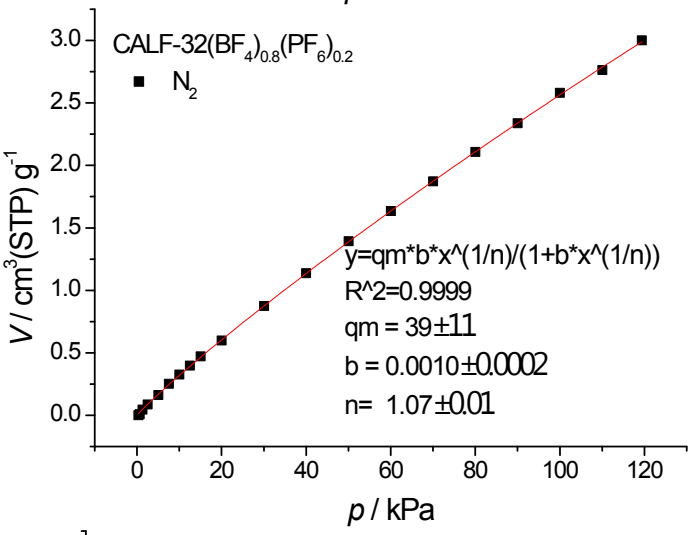

CALF-32(NO3)
CH4
y=qm*b*x^(1/n)/(1+b*x^(1/n))
R^2=0.9998
qm = 36±18
b = 0.0006±0.0002
n= 0.92±0.03
V / cm3(STP) g-1
p / kPa

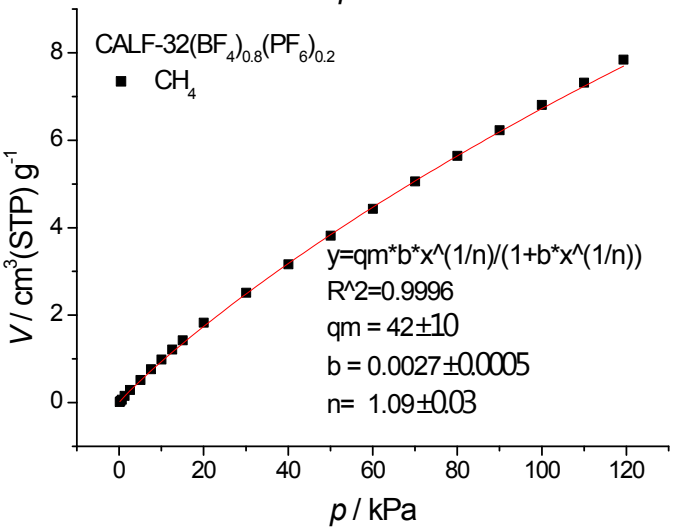

CALF-32(BF4)
CO2
y=qm*b*x^(1/n)/(1+b*x^(1/n))
R^2=0.9995
qm = 82±6
b = 0.034±0.002
n= 1.52±0.04
V / cm3(STP) g-1
p / kPa


CALF-32(BF4)
N2
y=qm*b*x^(1/n)/(1+b*x^(1/n))
R^2=0.9989
qm = 31±23
b = 0.0011±0.0007
n= 1.04±0.05
V / cm3(STP) g-1
p / kPa


CALF-32(BF4)
CH4
y=qm*b*x^(1/n)/(1+b*x^(1/n))
R^2=0.9999
qm = 61±10
b = 0.0019±0.0002
n= 1.09±0.01
V / cm3(STP) g-1
p / kPa


CALF-32(BF4)0.8(PF6)0.2
CO2
y=qm*b*x^(1/n)/(1+b*x^(1/n))
R^2=0.9995
qm = 96±6
b = 0.046±0.002
n= 1.56±0.04
V / cm3(STP) g-1
p / kPa


CALF-32(BF4)0.8(PF6)0.2
N2
y=qm*b*x^(1/n)/(1+b*x^(1/n))
R^2=0.9999
qm = 39±11
b = 0.0010±0.0002
n= 1.07±0.01
V / cm3(STP) g-1
p / kPa


CALF-32(BF4)0.8(PF6)0.2
CH4
y=qm*b*x^(1/n)/(1+b*x^(1/n))
R^2=0.9996
qm = 42±10
b = 0.0027±0.0005
n= 1.09±0.03
V / cm3(STP) g-1
p / kPa

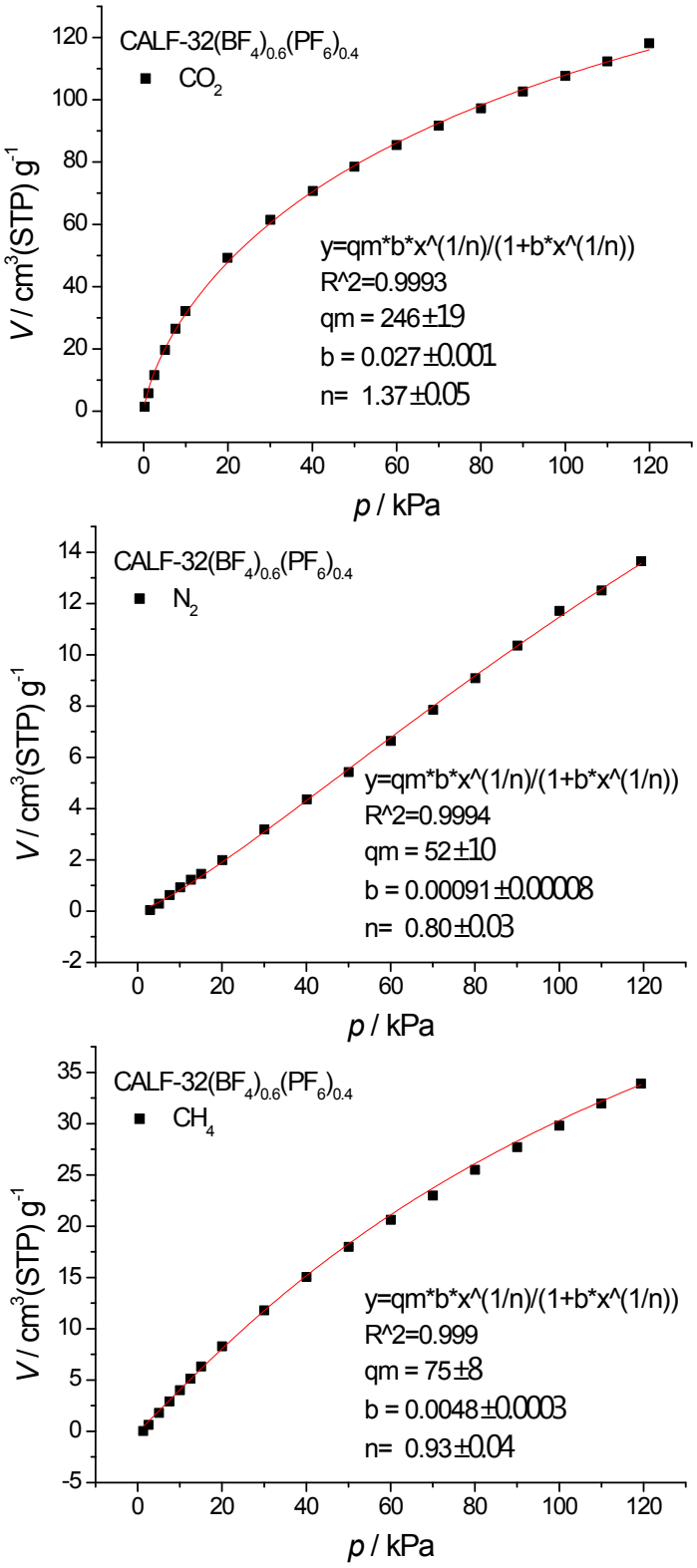


Fig. S8 CO_2, N_2 and CH_4 adsorption isotherms for CALF-32(A) with fitting by Langmuir-Freundlich method.