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

Supporting Information

Microporous covalent triazine polymers: efficient Friedel-Crafts synthesis and adsorption/storage of CO_2 and CH_4

Pillaiyar Puthiaraj, Sung-Min Cho, Yu-Ri Lee and Wha-Seung Ahn*

Department of Chemistry and Chemical Engineering, Inha University,

Incheon 402-751, South Korea

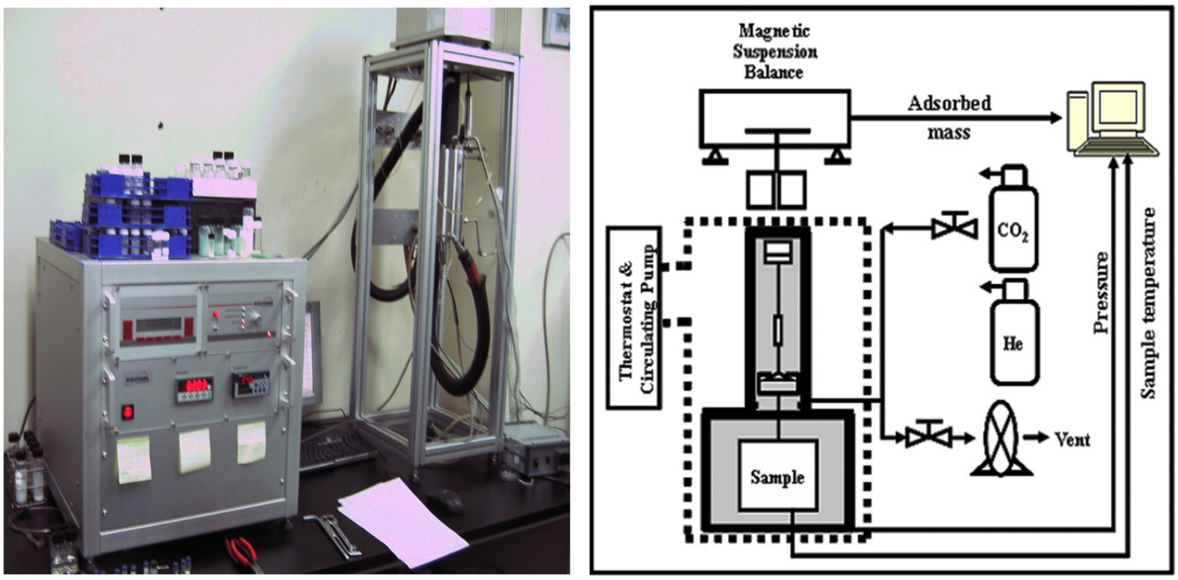
E-mail: whasahn@inha.ac.kr

CONTENTS

1. Experimental section

1.1 General methods

All chemicals were purchased from commercial suppliers and used as received unless specified otherwise. The powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku diffractometer using CuKα (λ=1.54 Å) with 0.5° min^{-1}. The N_2 adsorption- desorption isotherms were measured in a BELsorp-Max (BEL, JAPAN) at 77K. The specific surface areas and pore sizes of the samples were calculated using the Brunauer–Emmett–Teller (BET) and nonlocal density functional theory (NL-DFT) model with slit pore geometry method, respectively. The surface morphology and size of the materials were analyzed by scanning electron microscopy-energy dispersive X-ray (SEM, Hitachi S-4300). The aluminium content was measured by inductively coupled plasma spectrometry (ICP-OES, Optima 7300DV). The thermal stability of the samples was evaluated by thermogravimetric analysis (TGA, SCINCO thermal gravimeter S-1000) under an Argon (Ar) atmosphere over the temperature range, 30–700 °C, in flowing argon at a heating rate of 5 °C min^{-1}. The FT-IR spectra were obtained on a VERTEX 80V FT-IR spectrometer (Bruker) under ambient conditions. CO_2, N_2 and CH_4 adsorption isotherms under static conditions were obtained using a BELsorp(II)-mini (BEL, Japan) at 273, 293, 298, 303, and 308 K from 0-1 bar. High-pressure CO_2 adsorption isotherms were obtained using a magnetic suspension balance (Rubotherm, Germany) with in situ density measurements in a closed system. High-pressure adsorption was carried out using ultra-high-purity CO_2, N_2 and CH_4 (99.999%) over the pressure range, 0–35 bar at 300 K. The adsorption equilibrium was assumed when no further weight change in the sample under the given pressure condition was detected in 30 min. Before measuring the CO_2, N_2 and CH_4 adsorption capacity, the buoyancy effect was corrected in ultra-high-purity He (99.999%).



Scheme S1. Schematic diagram of the Rubotherm experimental unit

1.2 CO_2 adsorption/desorption recycling study

The same TGA unit (SCINCO thermal gravimeter S-1000) connected to a flow panel was used for the CO_2 adsorption/desorption measurements. A sample weight of ca. 10 mg was loaded into an alumina sample pan and subjected to the CO_2 adsorption studies. Ar (ultrahigh purity, U-Sung) was used as a purge gas in this study. The adsorption run was carried out using high purity CO_2 (99.999%). A feed flow rate to the sample chamber of 30 mL/min was controlled using a MFC. Initially, the sample was pretreated at 130 ^{o}C to remove the moisture using argon (99.999%) as a purge gas. When there was no weight loss, the temperature was decreased to the adsorption temperature and CO_2 was flowed into the chamber. After the CO_2 adsorption run, the desorption step was followed by a purge with Ar (99.999%).

1.3 Isosteric heats of adsorption

The isosteric heats of adsorption (Q_{st}) were derived from the adsorption data using the Clausius-Clapeyron equation,

$$\Delta H = R[\,\partial\, lnP/\,\partial\,(1/T)]_{\theta}$$

where, R is the universal gas constant [$kJmol^{-1}K^{-1}$], θ is the fraction of the adsorbed sites at a pressure P and temperature T.

1.4 Synthesis of MCTP-1 network

A 250 mL round bottom flask was charged with a measured amounts of cyanuric chloride (1.48 g, 8 mmol) and 1,3,5-triphenylbenzene (2.45 g, 8 mmol) in dichloromethane (DCM; 100 mL). The solution was kept at 20 ^{o}C and anhydrous aluminium chloride (3.00 g, 24 mmol) was added slowly. The reaction mixture was fitted with a condenser and heated to 70 ^{o}C under reflux for 16 h. After the reaction was complete, the resulting mixture was cooled to room temperature and a solid brownish black precipitate was collected by simple filtration, washed with DCM, methanol and water several times to completely remove the unreacted starting precursors. Finally, the brownish black solid was dried in a vacuum for 6 h to obtain the solvent free material in 88% yield.

1.5 Synthesis of MCTP-2 network

The synthesis of MCTP-2 was similar to that of MCTP-1 except that *trans*-stilbene (2.16 g, 12 mmol) was used instead of 1,3,5-triphenylbenzene. A brown color solid powder was obtained in 92% yield.

2. Characterization data

Table S1. Elemental analysis data of MCTP-1 and MCTP-2 networks

Polymers	**Found (%)**			**Calculated (%)**		
	C	**H**	**N**	**C**	**H**	**N**
CTP-1	77.78	4.53	9.92	85.02	3.96	11.02
CTP-2	76.93	4.87	10.28	83.46	4.38	12.17

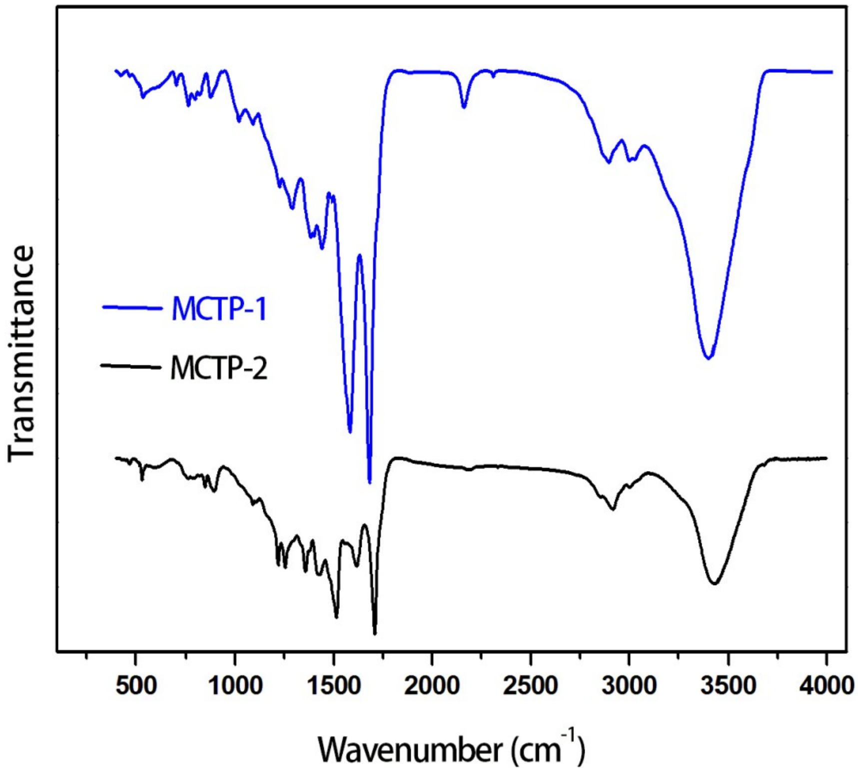


Fig. S1. FT-IR spectra of MCTP-1 and MCTP-2

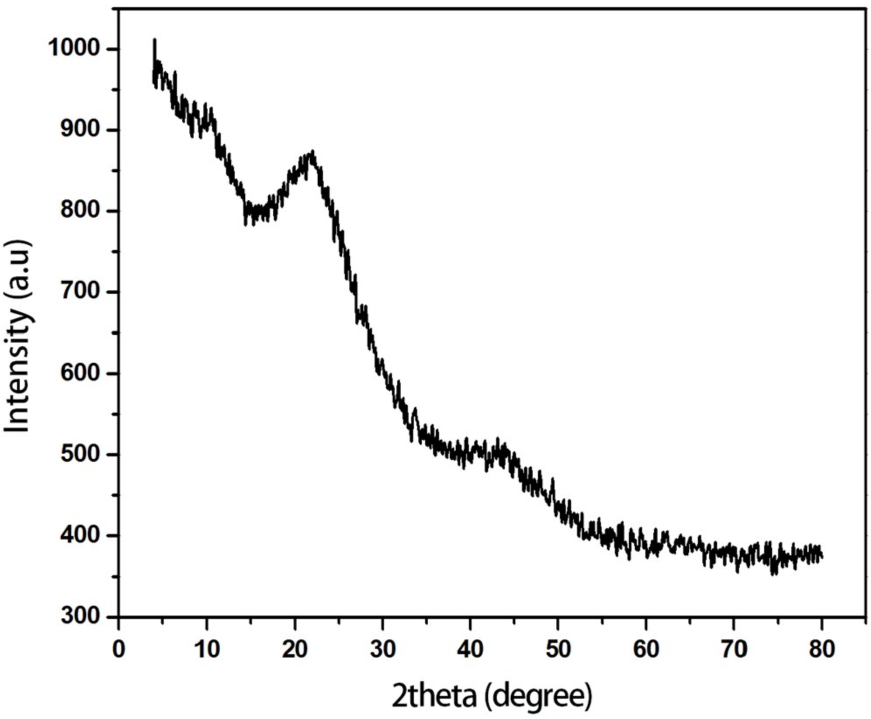


Fig. S2. Powder XRD pattern of MCTP-1

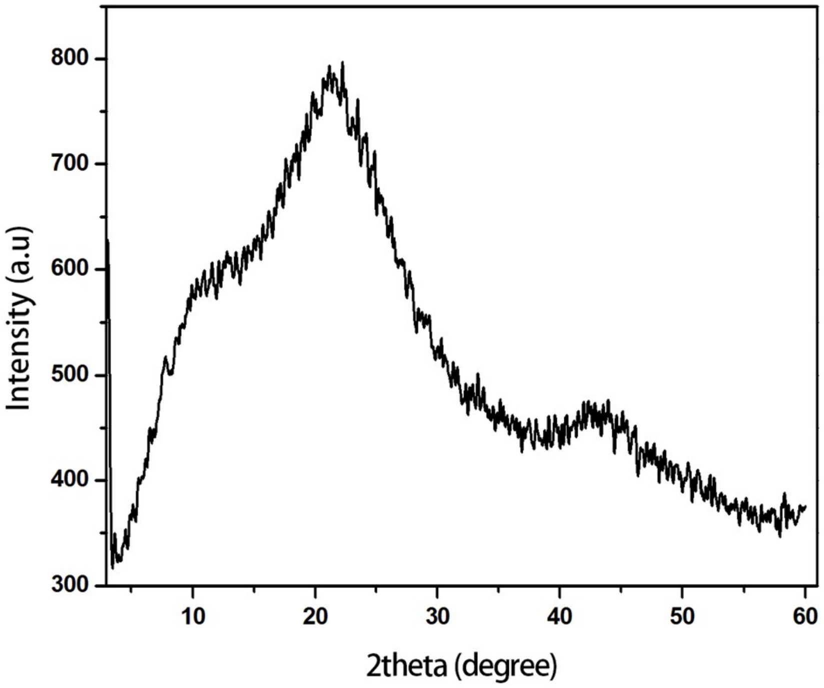


Fig. S3. Powder XRD pattern of MCTP-2

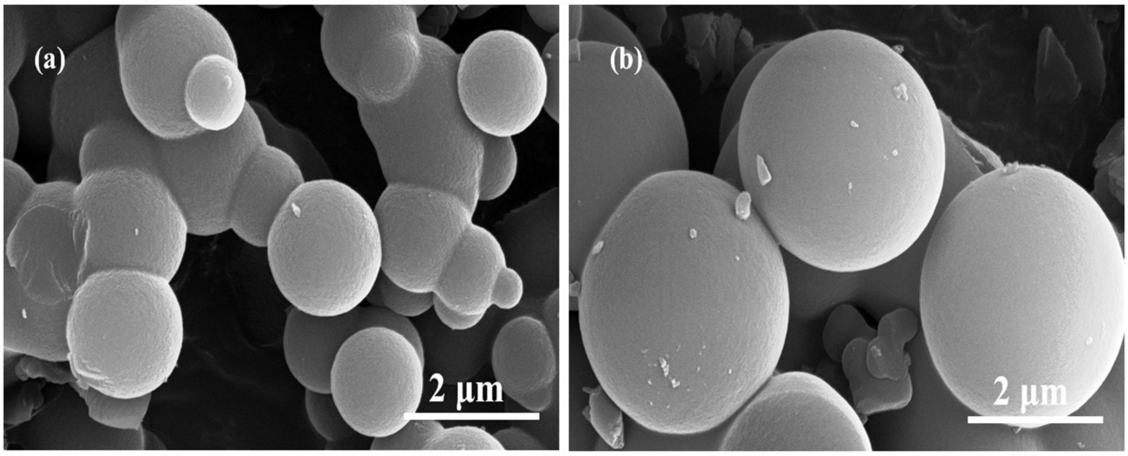


Fig. S4. SEM image of MCTP-1 (a) and MCTP-2 (b)

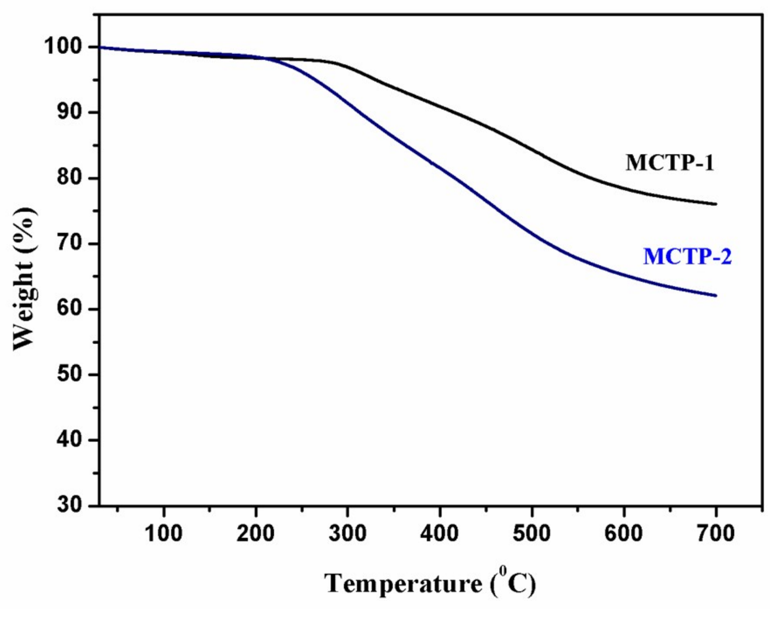


Fig. S5. TGA spectra of MCTP-1 and MCTP-2

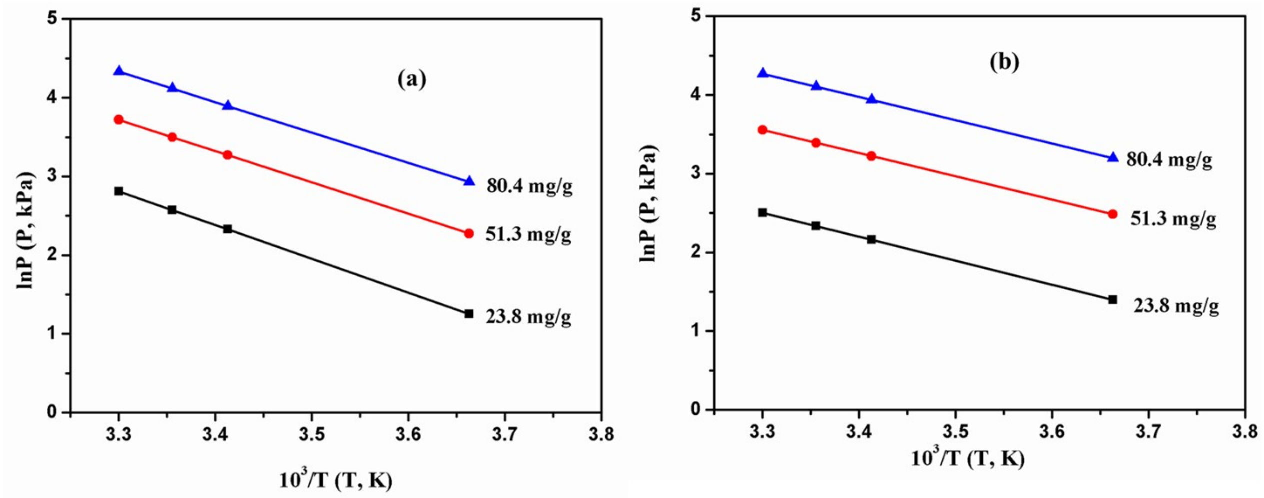


Fig. S6. CO_2 adsorption isosteres at temperature ranging from 273 K to 303 K on (a) MCTP-1 and (b) MCTP-2 with the corresponding amount adsorbed

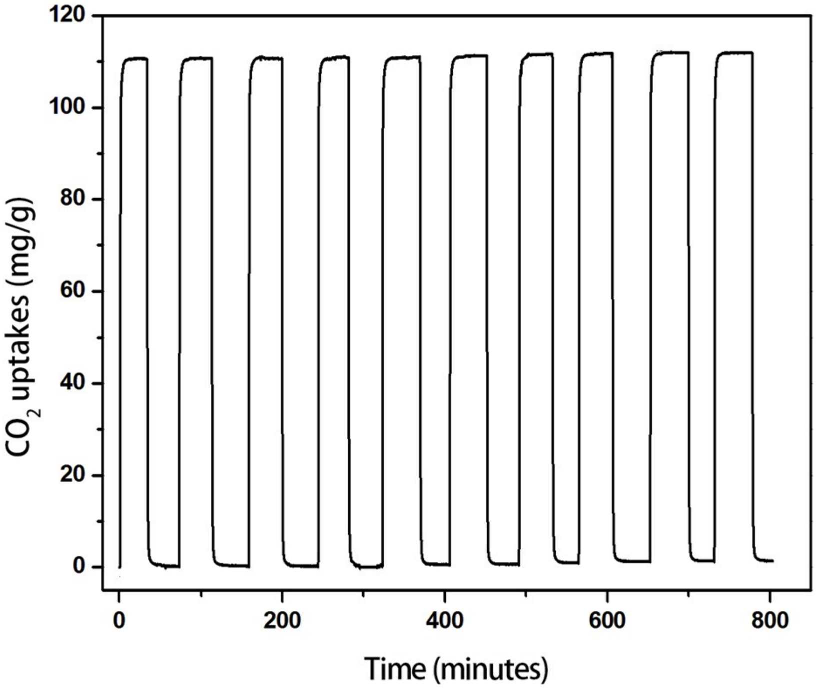


Fig. S7. CO_2 adsorption-desorption cycles obtained for the MCTP-1 at 27 °C

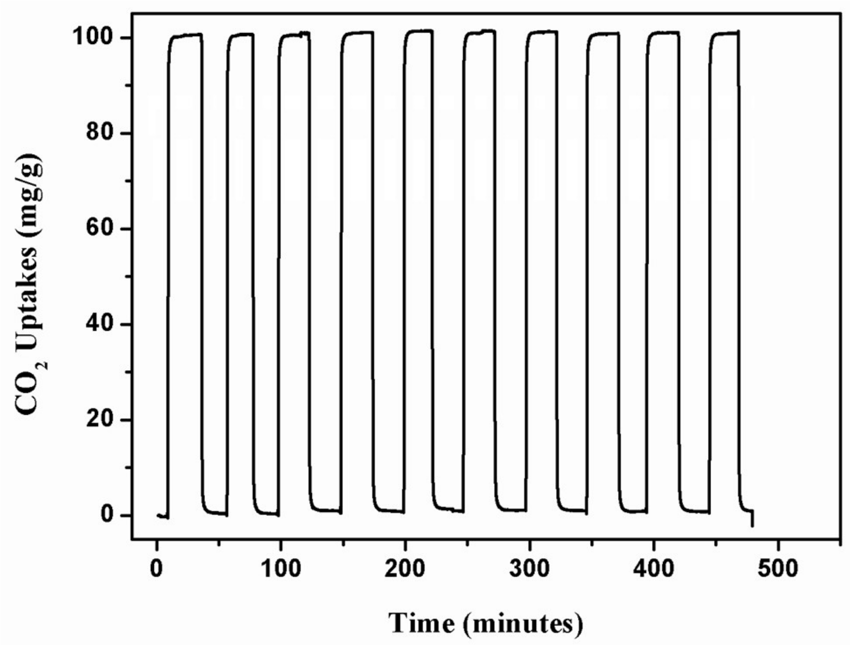


Fig. S8. CO$_2$ adsorption-desorption cycles obtained for the MCTP-2 at 27 °C

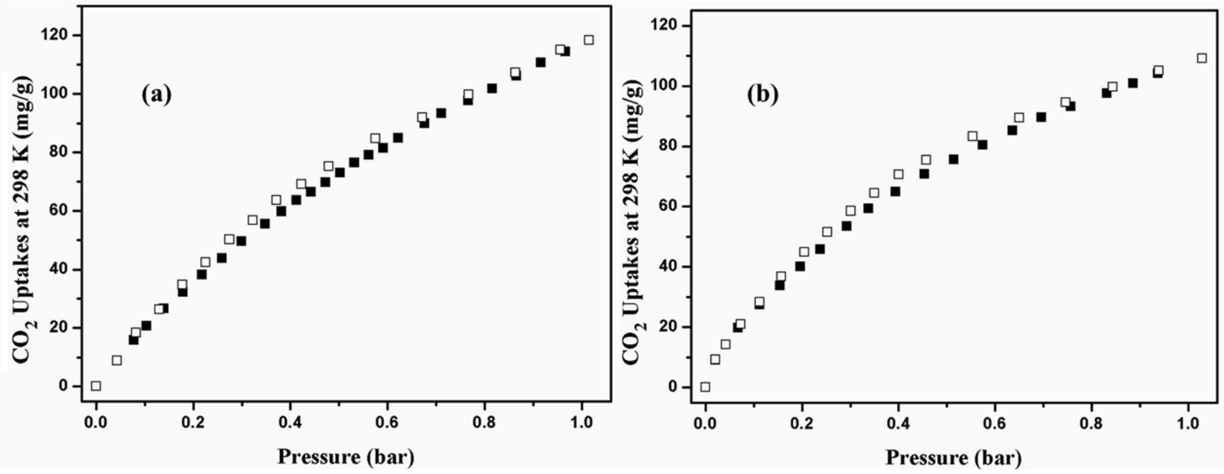


Fig. S9. CO$_2$ adsorption (solid square) - desorption (empty square) isotherm of MCTP-1 (a) and MCTP-2 (b) at 298 K/1 bar

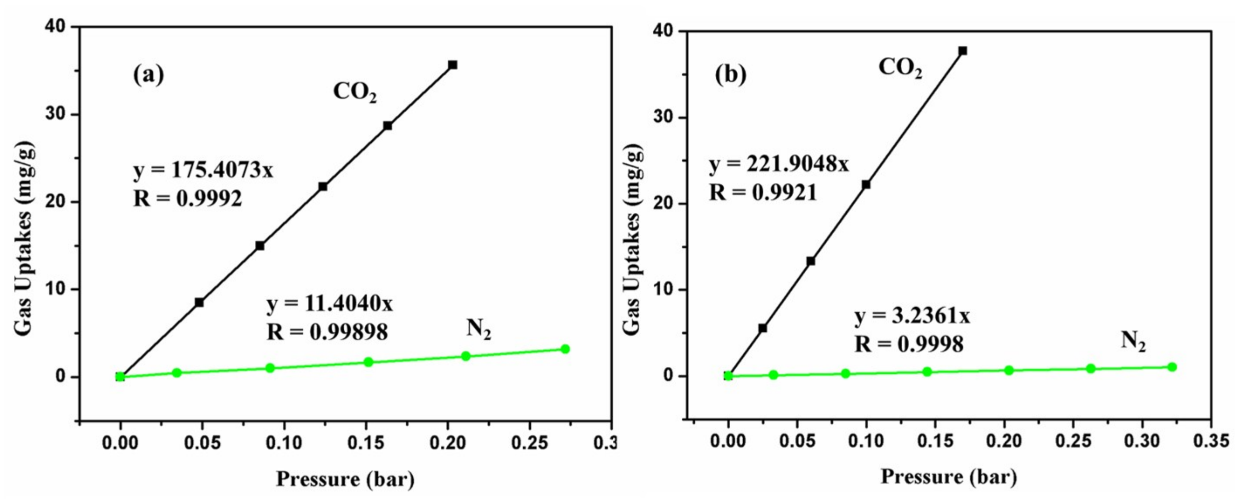


Fig. S10. Initial slope calculation of the CO_2/N_2 adsorption selectivity for MCTP-1 (a) and MCTP-2 (b) at 298 K/1 bar

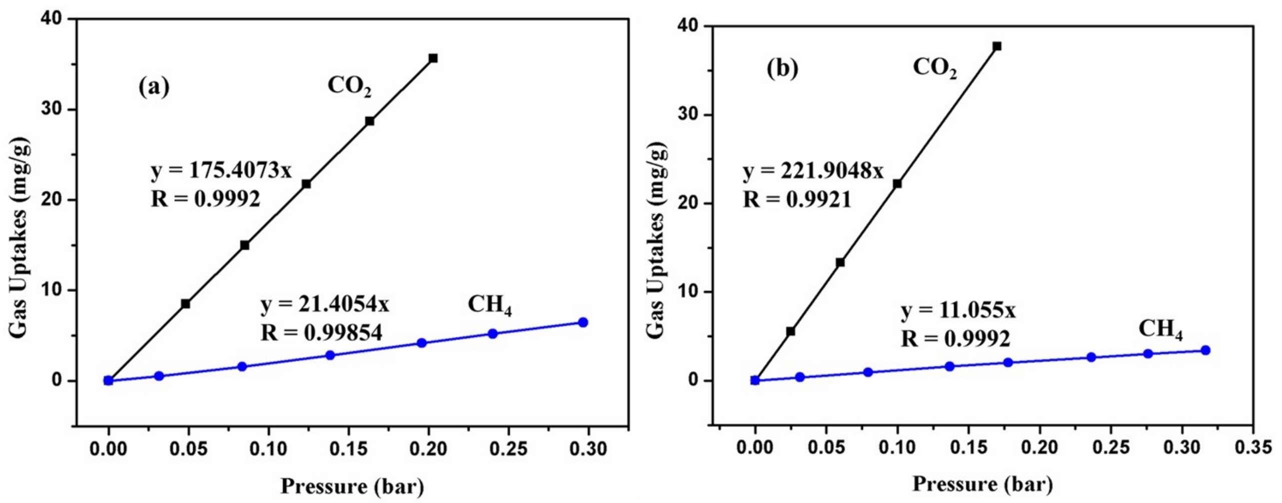


Fig. S11. Initial slope calculation of the CO_2/CH_4 adsorption selectivity for MCTP-1 (a) and MCTP-2 (b) at 298 K/1 bar

Table S2. Comparison of the CO_2 uptakes capacities of some previously reported POPs at 1 bar

POPs	BET surface area ($m^2\,g^{-1}$)	CO_2 uptakes at 1 bar (mg/g)		References
		273K	298K	
POF-1B	773	~186	~90	1
POF-2B	917	~155	~75	
POF-3B	608	~125	~65	
MPN-P1	99	82.1	63	2
MPN-P2	56	57.6	41	

MPN-P3	50	56.2	38	
NPAF	1790	152	102	3
NPC-700	1876	189	108	4
NPC-750	3195	187	95	
CMP-1	837	~90	52	5
CMP-1-NH_2	710	~72	~43	
CMP-1-COOH	522	70	~43	
CMP-1-$(CH_3)_2$	899	~72	41	
CMP-1-$(OH)_2$	1043	~80	47	
BLP-1H	1360	~74	~41	6
BLP-12H	2244	~128	~79	
MOP-A	4077	117	64	7
MOP-B	1847	145	72	
MOP-C	1237	170	97	
MOP-D	1213	106	59	
MOP-E	1470	130	78	
MOP-F	653	79	48	
MOP-G	1056	95	55	
FOF-1	830	77	-	8
FOF-2	96	17		
FOF-3	307	21		
FOF-4	571	64		
ACMP-C	629	68.8	48	9
ACMP-C6	380	36	25	
ACMP-N	46	52	36	
MPI-1	1454	~165	~97	10
MPI-2	814	~138	~95	
MPI-3	586	~100	~74	
POP-diimide	960	177	88	11
APOP-1	1298	187	118	12
APOP-1-OH	875	131	82	
APOP-1-ONa	760	131	75	
APOP-1-F	724	135	89	
APOP-2	906	100	57	
APOP-3	1402	196	113	
APOP-4	833	119	72	
BILP-1	1172	188	131	13
azo-COP-1	635	107	65	14
azo-COP-2	729	112	67	
azo-COP-3	493	85	54	
PPN-6	4023	87	66	15
HCP-1	1646	132	75	16
HCP-2	1684	145	75	

HCP-3	1531	143	71	
HCP-4	1642	172	71	
MOP A-B1	378	117	88	17
MOP A-B2	614	119	84	
MOP A-B3	589	99	75	
HMP Th-1	726	127	75	18
HMP Py-1	437	119	75	
HMP Fu-1	514	97	62	
JUC-Z2	2034	141	70	19
PAF-1	5460	91	48	20
PAF-3	2932	154	81	
PAF-4	2246	107	51	
NPOF-4	1249	110	62	21
NPOF-4-NO_2	337	106	69	
NPOF-4-NH_2	554	128	83	
BLP-10-Cl	924	119	62	22
PI-1	506	88	62	23
PI-2	568	66	44	
SMPI-0	574	111	63	24
SMPI-10	112	139	82	
SMPI-50	44	130	71	
SMPI-100	23	124	82	
MCTP-1	**1452**	**204**	**119**	**Present work**
MCTP-2	**859**	**161**	**108**	
Porous organic frameworks (POFs); microporous polymers networks (MPN); nitrogen rich porus aromatic framework (NPAF); nitrogen doped porous carbons (NPCs); conjugated microporous polymer (CMP); borazine-linked polymers (BLPs); micorporous organic polymers (MOPs); Furan-based imine-linkage porous organic frameworks (FOFs); acetylene gas mediated conjugated microporous polymers (ACMPs); microporous polyimides (MPI); aminal-linked porous organic polymers (APOPs); Benzimidazole-Linked Polymer (BILPs); covalent organic polymers (COPs); porous polymer networks (PPN); hyper cross-linked polyemrs (HCPs); hypercrosslinked aromatic heterocyclic microporous polymers (HMPs); porous aromatic frameworks (PAFs); nanoporous organic frameworks (NPOF); series of novel microporous polyimides (SMPI).				

Table S3. Comparison of the CH_4/CO_2 uptakes capacities of some previously reported MOFs at 298 K/35 bar

Chemical Formula	**Common name**	**CH_4 Uptakes (mg/g)**	**CO_2 Uptakes (mg/g)**	**Pressure (bar)**	**Ref.**
Cd(bpydb)		61.4	-	35	25
$Cd(azpy)_3(NO_3)_4$		30.7	-	36.5	26

CO_2(4,4'-bpy)$_3$(NO_3)$_4$		38.6	-	35	27
Co_2(ndc)$_2$(dabco)	DUT-8 (Co)	55.7	-	35	28
Zn_2(ndc)$_2$(dabco)	DUT-8 (Zn)	42.1	-	35	28
Cu_2(PF6)(NO_3)(4,4'-bpy)$_4$.1.4PF_6.0.6NO_3		22.1	-	36.5	29
Zn_2(tcpbda)	SNU-30	50.7	-	35	30
Co(azpy)$_2$(NCS)$_2$		10.7	-	35.5	31
Co_2(azpy)$_3$(NO_3)$_4$		9.3	-	36.5	
Zn_2(tcpbda)(bpta)	SNU-31	26.4	-	35	30
Cu($C_4H_2O_4$)(ted)$_{0.5}$		73.6	-	35	32
Cu(dhbc)$_2$(4,4' -bpy)	AX-21 activated	50.0	-	35	33
$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]$	Zeolite NaX	52.9	-	35.5	34
$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$	Zeolite 5A	50.0	-	35.5	
$Zn_2(BDC)_2$	MOF-2	-	141	36.2	35
	Norit RB2	-	421	36.2	
[Cu_2(bptc)(H_2O)$_2$(dmf)$_3$(H_2O)]	MOF-505	-	449	34	
$Zn_2(C_8H_2O_6)$	MOF-74	-	455	34.1	
$Cu_3(BTC)_2$		-	470	34.1	
$Cu_3(C_9H_6O_6)_2$	MOF-199	-	404	25.8	36
$Na_{86}(AlO_2)_{86}(SiO_2)_{106}$	NaX	-	~286	35	37
$Zr_6O_4(OH)_4(BDC)_6(DMF)_2(H_2O)_2$	UiO-66(Zr)	-	~308	35	
$Zr_6O_4(OH)_4(NH_2\text{-}BDC)_6(DMF)_2(H_2O)_2$	UiO-66(Zr)-NH_2	-	~352	35	
	Takeda 5A	-	~440	35	
$Ti_8O_8(OH)_4(C_6H_3C_2O_4NH_2)_6$	MIL-125(Ti)-NH_2	-	~440	35	
MCTP-1		85	497	35	**Present work**
MCTP-2		50	333		
(EBTC = 1,1' -ethynebenzene-3,3',5,5' -tetracarboxylate; G = guest molecule); azpy = 4,4'-azopyridine; 4,4'-bpy = 4,4'-bipyridine; bpydb = 4,4'-(4,4'-bipyridine-2,6-diyl)dibenzoate; bte = 4,4',4''-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tribenzoate; dabco = 1,4-diazabicyclo-[2.2.2]octane; dhbc = 2,5-dihydroxybenzoate; ndc = 2,6-naphthalenedicarboxylate; cpbda = *N, N, N', N'* -tetrakis(4-carboxylphenyl)biphenyl-4,4'-diamine; ted = triethylenediamine; BDC = 1,4-benzenedicarboxylate; BTC = 1,3,5-tribenzene carboxylate; bptc = biphenyl-3,3',5,5'-tetracarboxylic acid.					

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