Construction of microporous covalent organic frameworks for high gas uptake capacities

Experimental

Materials

Acetic acid, tetrahydrofuran, n-butanol, o-DCB, DMF, iodine, and other chemicals were obtained from J&K Scientific company, TCI, Wako, and Sigma-Aldrich. Tris(4-aminophenyl)amine, 1,3,5-benzenetrialdehyde, 2,4-dihydroxybenzene-1,3,5-tricarbaldehyde were obtained from Yanshen Technology Co., Ltd.

Material Characterization

Recording Fourier Transform Infrared (FT-IR) Spectrum with FT-IR Frontier Infrared Spectrometer with Perkin-Elmer Model. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, compressed, Photoluminescence spectra were recorded on JASCO model FP-8600 spectrofluorometer. Elemental analysis (C, H, and N) was performed on a Euro Vector EA3000 elemental analyzer. Solid-state ^{13}C CP/MAS NMR measurements were recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The samples were prepared for SEM by drop-casting a tetrahydrofuran suspension onto mica substrate and then coated with gold. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to $30°$ with $0.02°$ increment. TGA analysis was carried out using a Q5000IR analyser (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of 5 °C min^{-1} under a nitrogen atmosphere. Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer. Before measurement, the samples were degassed in vacuum at 60 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution. All gas adsorption measurements (CO_2 and CH_4) were performed on Micromeritics instruments (Models ASAP 2420 and ASAP 2020). Before gas adsorption measurements, samples were activated by drying under a dynamic vacuum at 60 °C for

1 hour. Prior to obtained gas measurements, samples were dried again using the 'outgas' function of the surface area analyzer for 10 h at 100 °C.
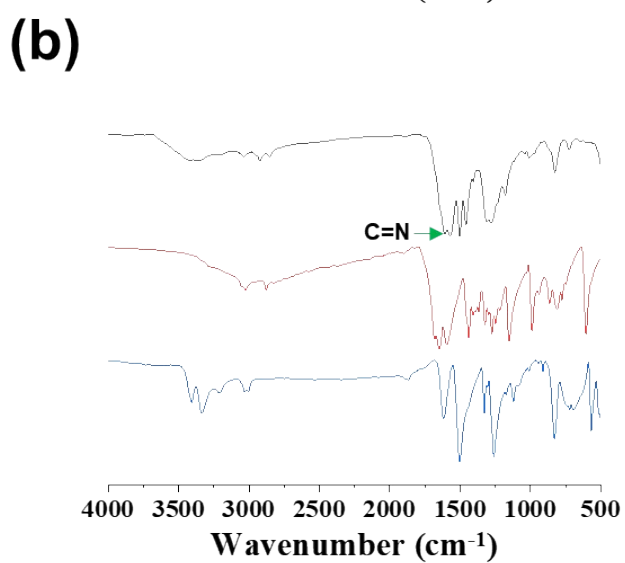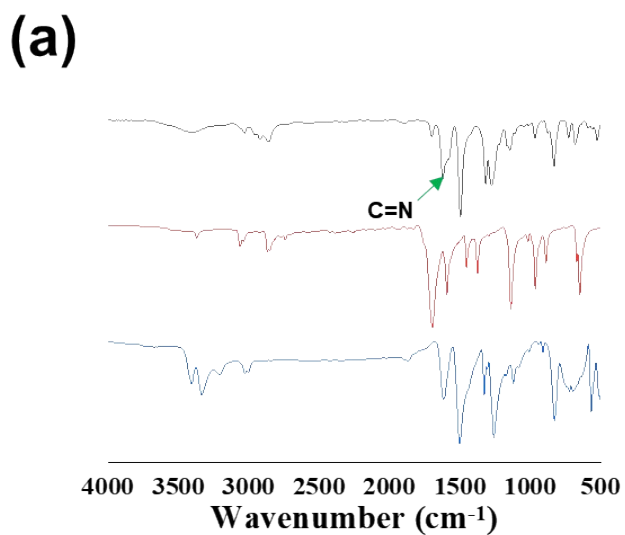
Synthesis of M-COF-1

Tris(4-aminophenyl)amine (58.1 mg, 0.2 mmol) and 1,3,5-benzenetrialdehyde (32.4 mg, 0.2 mmol), o-DCB (1.0 mL), n-butanol (1.0 mL), acetic acid (6 M, 0.4 mL) were added into the system. The mixture was degassed through three freeze–pump–thaw cycles, sealed under vacuum, and was heated about 120 °C for 72 h. After cooling down to room temperature, the sample was filtered, washed by DMF, acetone, and ethanol, Soxhleted by THF for 6 h, and dried in vacuum at 80 °C for 6 h to afford a yellow powder (M-COF-1, Yield: 97%).

Synthesis of M -COF-2

Tris(4-aminophenyl)amine (58.1 mg, 0.2 mmol) and 2,4-dihydroxybenzene-1,3,5-tricarbaldehyde (38.8 mg, 0.2 mmol), o-DCB (1.0 mL), n-butanol (1.0 mL), acetic acid (6 M, 0.4 mL) were added into the system. The mixture was degassed through three freeze–pump–thaw cycles, sealed under vacuum, and heated about 120 °C for three days. After cooling down to room temperature, the sample was filtered, washed by DMF, acetone, and ethanol, Soxhleted by THF for 6 h, and dried in vacuum at 80 °C for 6 h to afford a modena powder (M-COF-2, Yield: 91%).

Iodine sorption

Three open vials (5 mL) with M-COFs samples were kept in a large bottle (70 mL) containing iodine (3.0 g). The large bottle was sealed and stored at 350 K. Three open vials were cooled down to room temperature and weighted to observe iodine capture value by the selected time. The large vial was restored at 350 K to observe iodine capture.

(a)

C=N

4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm^{-1})

(b)

C=N

4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm^{-1})

Fig. S1. FT-IR spectra of (a) tris(4-aminophenyl)amine (blue), 1,3,5-benzenetrialdehyde (red), M-COF-1 (black); (b) tris(4-aminophenyl)amine (blue), 2,4-dihydroxybenzene-1,3,5-tricarbaldehyde (red), M-COF-2 (black).
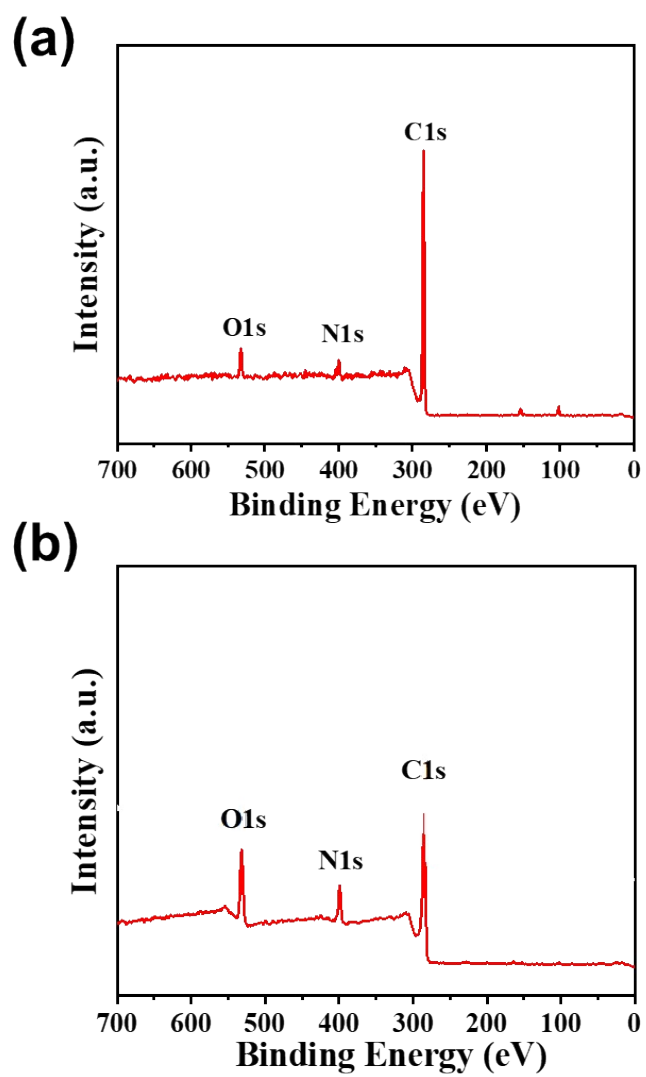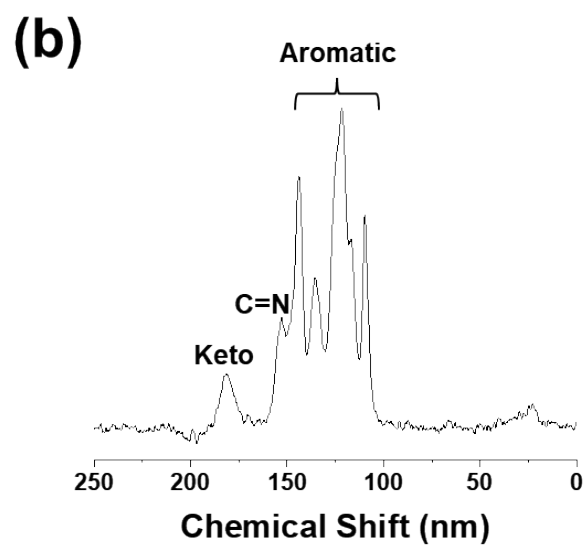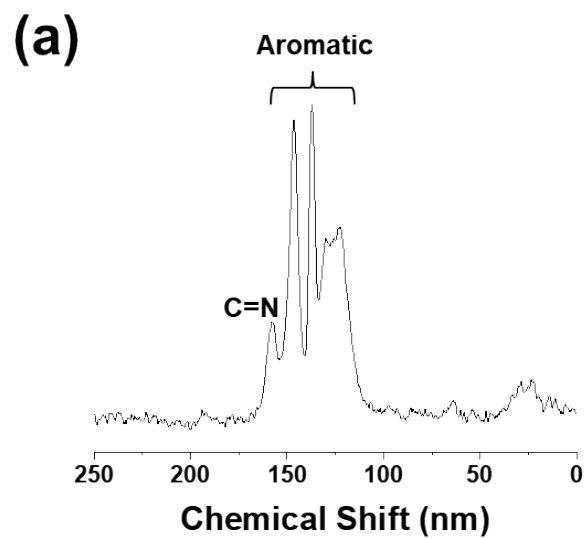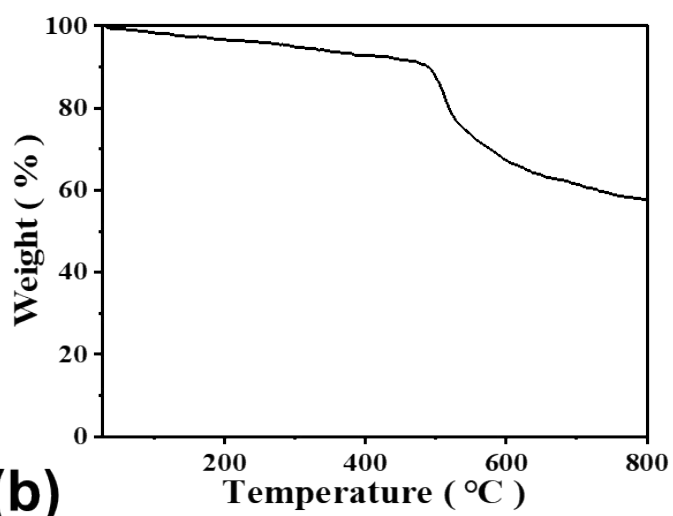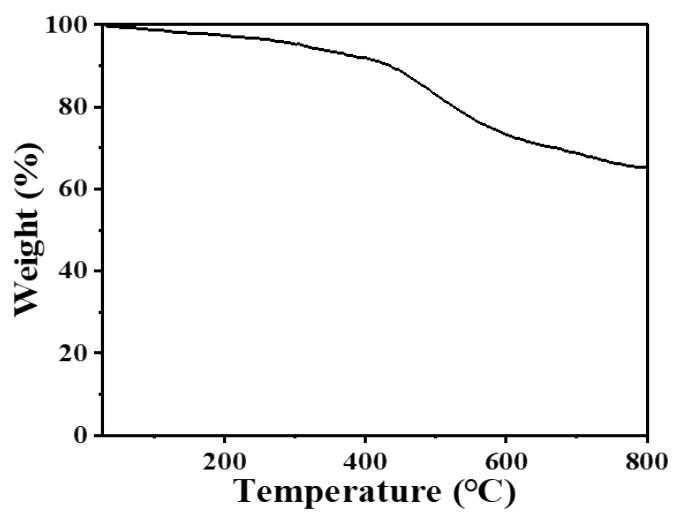
Fig. S2. XPS spectra of (a) M-COF-1 and (b) M-COF-2.

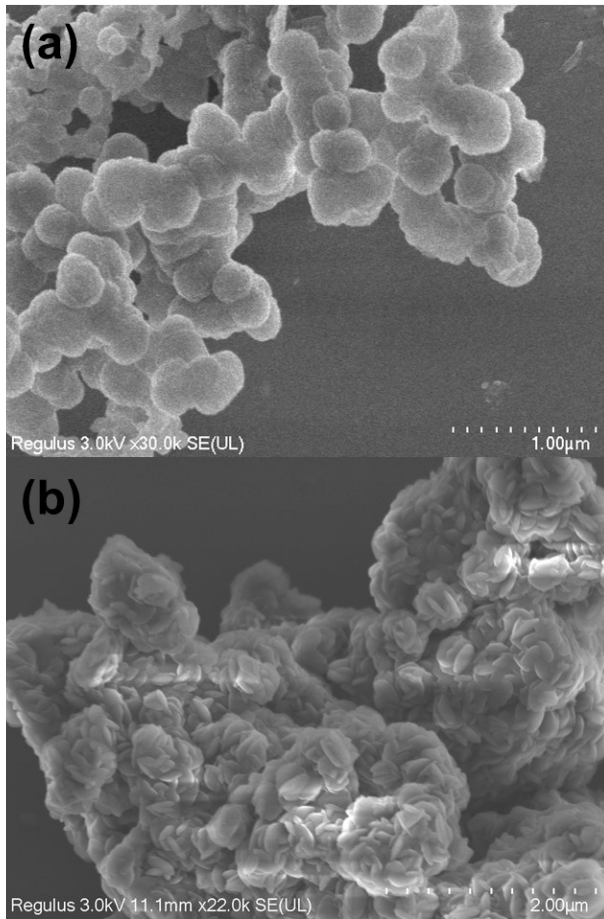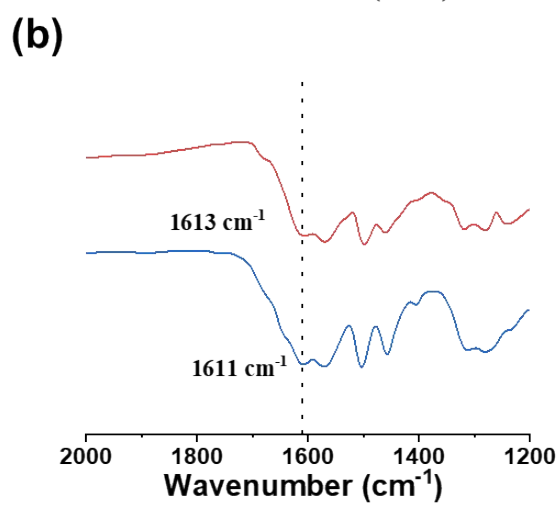**Fig. S3**. [13] C NMR spectra of (a) M-COF-1 and (b) M-COF-2.

(a)

(b)

Fig. S4. TGA curves of (a) M-COF-1 and (b) M-COF-2.

(a)

Regulus 3.0kV ×30.0k SE(UL)   1.00µm

(b)

Regulus 3.0kV 11.1mm x22.0k SE(UL)   2.00µm
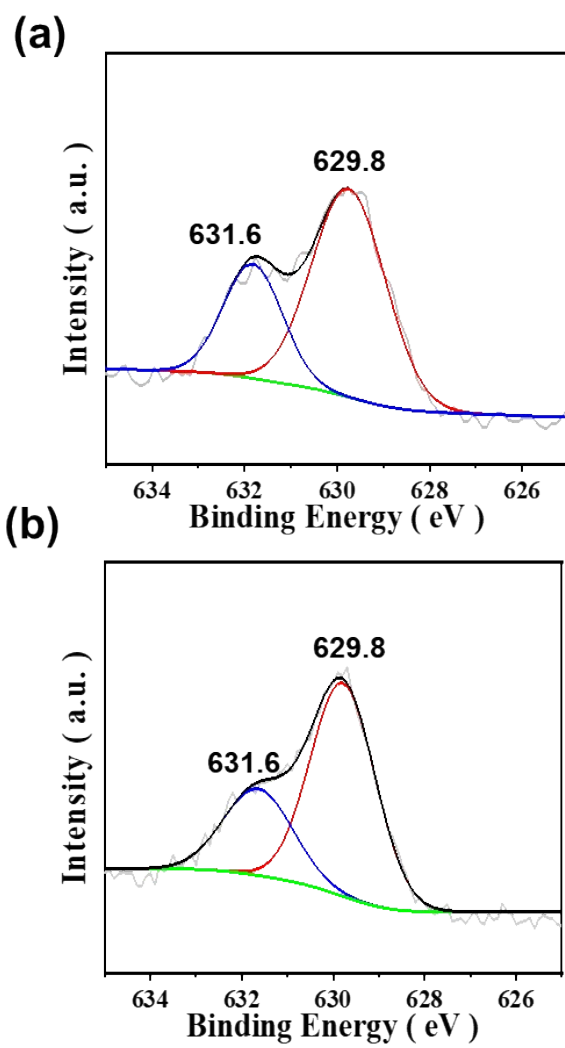
Fig. S5. FE SEM images of (a) M-COF-1 and (b) M-COF-2.
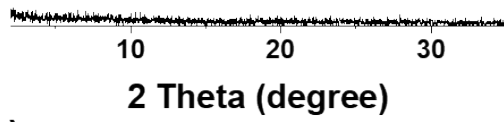
(a)

(b)
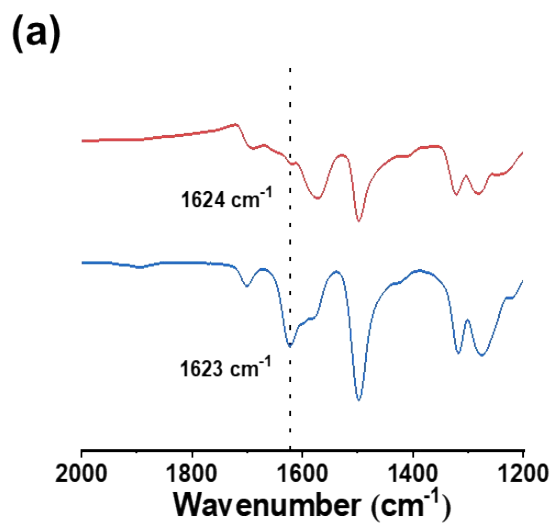
Fig. S6. FT-IR spectra of (a) M-COF-1 (blue), M-COF-1 loading iodine (black) and (b) (a) M-COF-2 (blue), M-COF-2 loading iodine (black).

Fig. S7. I$_{3d}$ XPS spectra of (a) M-COF-1 and (b) M-COF-2.

(a)

10   20   30
2 Theta (degree)
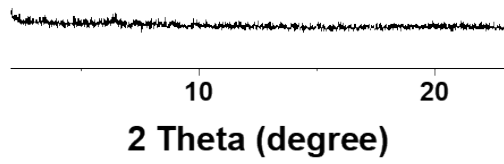
(b)

10   20
2 Theta (degree)

Fig. S8. PXRD patterns of (a) M-COF-1 loading iodine and (b) M-COF-2 loading iodine.

Table S1. Pore size of typical 2D C=N based COFs.

	Pore size (nm)	Reference
M-COF-1	0.87	*This work*
M-COF-2	0.85	
ILCOF-1	2.3	*Chem. Eur. J.* 2013, 19, 3324.
ACOF-1	0.91	*Chem. Commun.* 2014, 50, 13825.
N-COF	1.1	*Chin. J. Chem.* 2015, 33, 90.
iPrTAPB-TFP	3.4	*J. Mater. Chem. C* 2015, 3, 7159.
COF-JLU2	0.96	*Chem. Eur. J.* 2015, 21,12079.
AB-COF	1.3	*Chem. Mater.* 2015, 27, 7874.
$[C=C]_{50}$-H_2P-COF	2.1	*J. Am. Chem. Soc.* 2015, 137, 7079.
$[EtNH_2]_{75}$-H_2P-COF	1.6	
$[HO]_{100\%}H_2$P-COFs	2.5	*Angew. Chem. Int. Ed.* 2015, 54, 2986.
$[HO_2C]100\% H_2$P-COFs	1.4	
TH-COF-1	1.5	*Microporous Mesoporous Mater.* 2016, 224, 95.
HEX-COF 1	1.1	*Chem. Commun.* 2016, 52, 2843.
$[EOH]_{50\%}$Py-COF	2.2	*Chem. Commun.* 2016, 52, 7082.
$[Et_4NBr]_{50\%}$-Py-COF	1.6	
BTMA–TAPA–COF	1.59	*Chem. Commun.* 2017, 53, 4242-4245
PyTTA-BFBIm-iCOF	2.3	*Angew. Chem. Int. Ed.* 2017, 56, 4982.
AT-DHBD	2.61 and 3.79	*ChemPlusChem* 2017, 82, 1253.
TAT-TFP(2)	1.17	
TPE-COF-II	1.19	Chem. Mater. 2018, 30, 5, 1762.
Car-TPA COF	2.3	*ACS Appl. Mater. Interfaces* 2019, 11, 9343.
H_2P-DHPh COF	2.0	*Chin. J. Catal.* 2020, 41, 4850.
AMIMBr@H_2P-DHPh COF	1.3	
M−COF	1.4	*Mater. Lett.* 2021, 304, 130657
ESM-COF-1	0.85	*Microporous and Mesoporous Mater.* 2013, 349, 112419