Electronic Supplementary Information

Gas adsorption properties of highly porous metal-organic frameworks containing functionalized naphthalene dicarboxylate linkers

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Section S1 ^{1}H-NMR Spectra

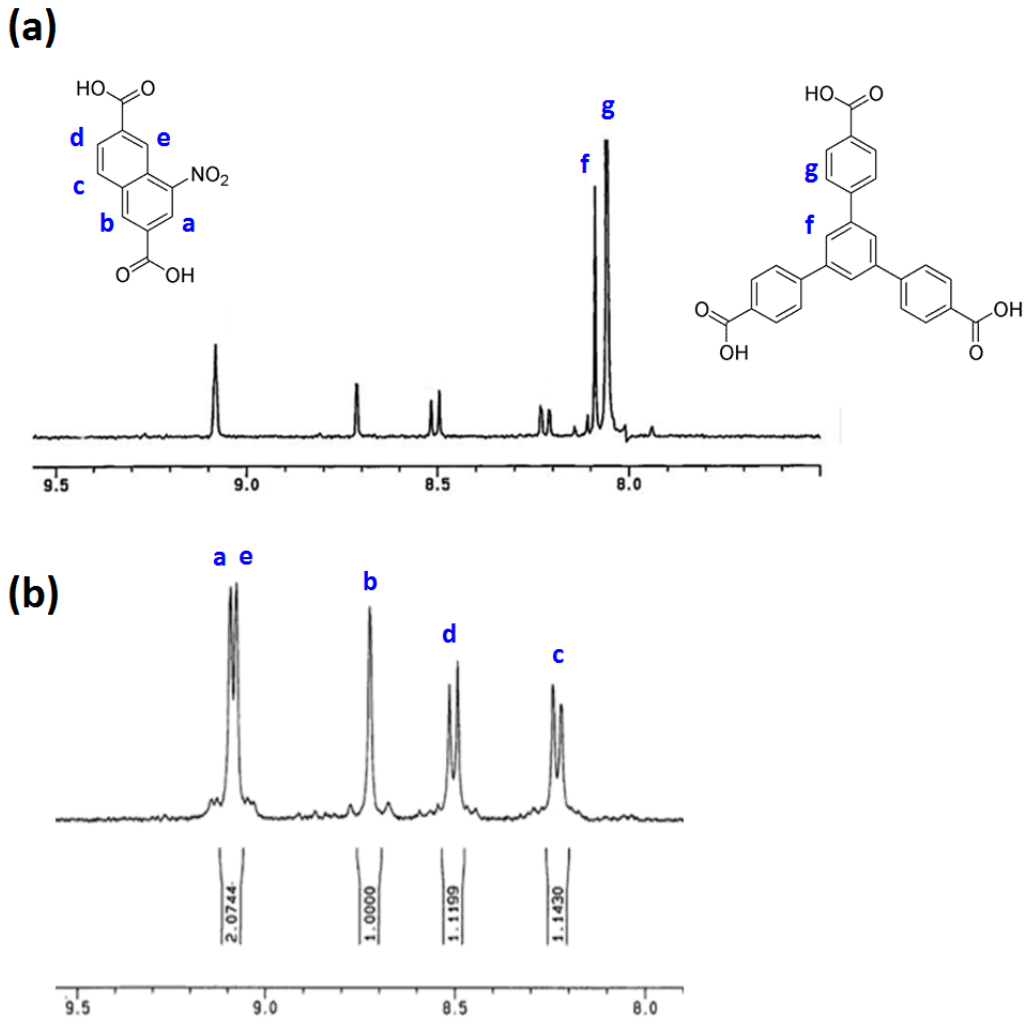

Figure S1. ^{1}H-NMR spectra for **(a)** the evacuated MOF-205-NO_2 crystals dissolved in DCl/DMSO-d_6 solution, and **(b)** H_2NDC-NO_2 in DMSO-d_6.

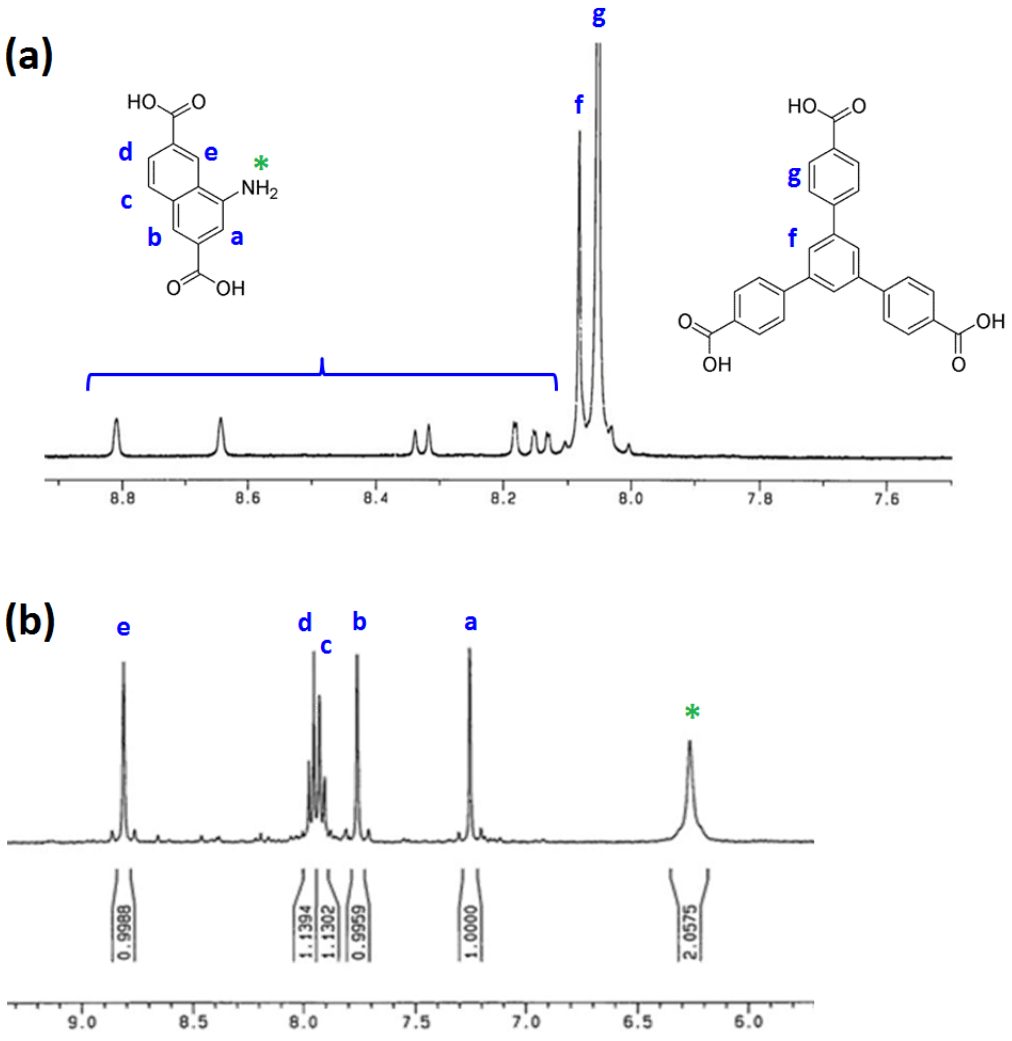

Figure S2. ^{1}H-NMR spectra for **(a)** the evacuated MOF-205-NH_2 crystals dissolved in DCl/DMSO-d_6 solution, and **(b)** H_2NDC-NH_2 in DMSO-d_6.

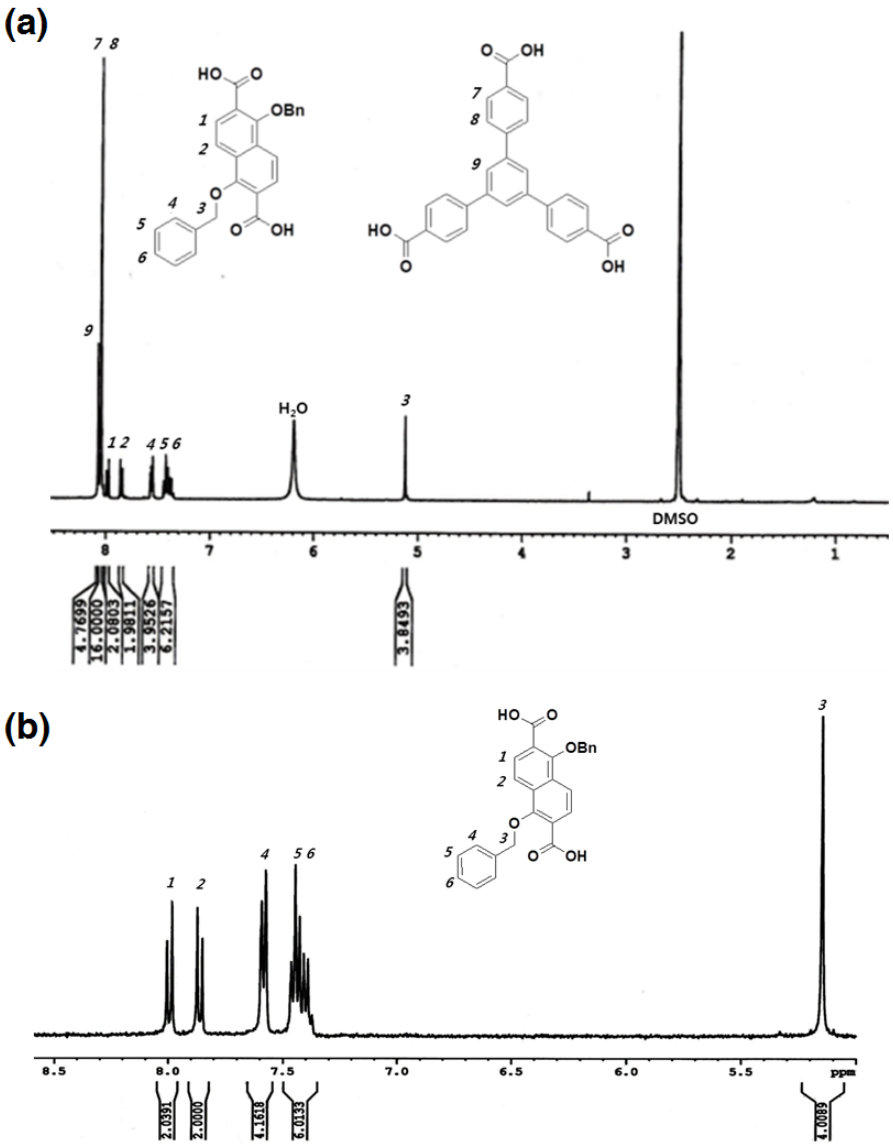

Figure S3. ^{1}H-NMR spectra for **(a)** the evacuated MOF-205-OBn crystals dissolved in DCl/DMSO-d_6 solution, and **(b)** H_2NDC-$(OBn)_2$ in DMSO-d_6.

Section S2 Thermogravimetric Analysis (TGA) Traces

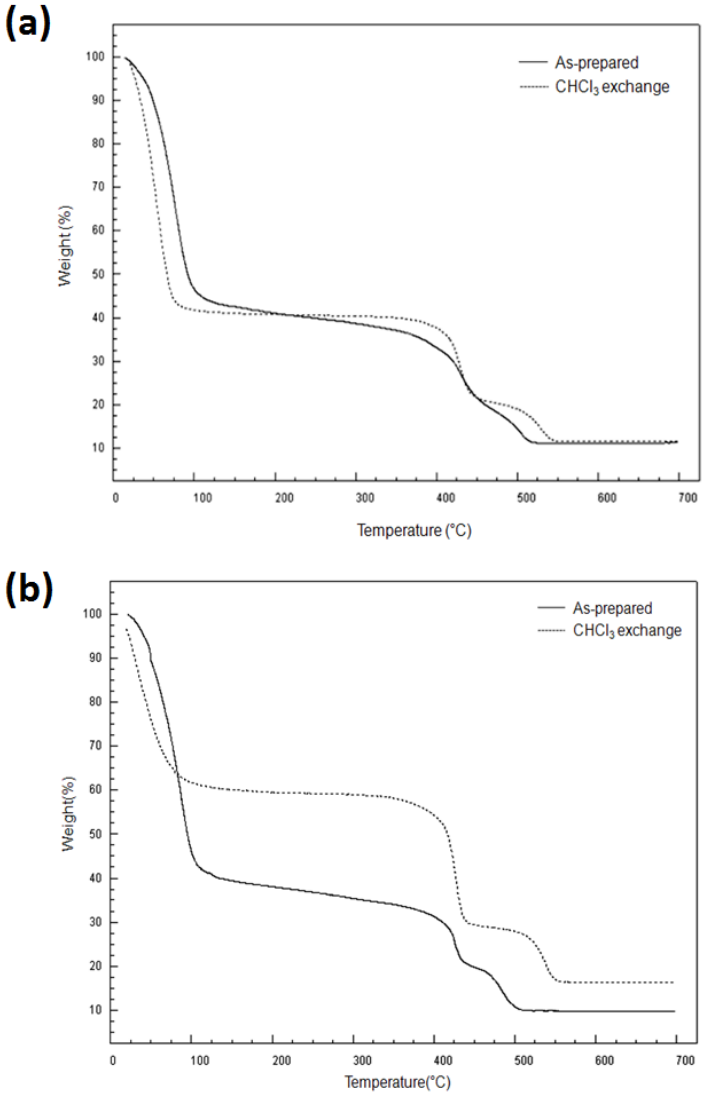

Figure S4. The TGA thermograms of the as-prepared (solid) and chloroform-exchanged (dash) (a) MOF-205-NO_2 and (b) MOF-205-NH_2 samples.

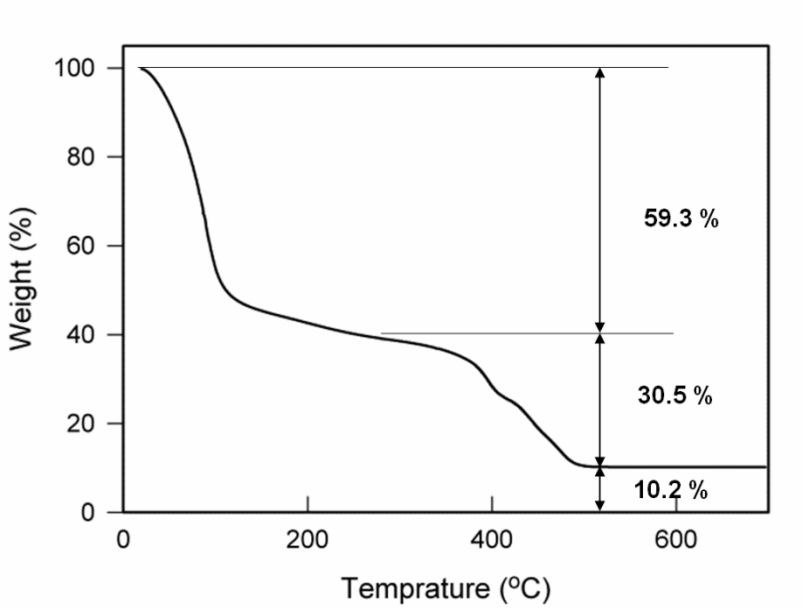

Figure S5. The TGA trace for the as-prepared MOF-205-OBn.

Section S3 X-ray Crystallography Analyses

The X-ray data for H_2NDC-NH_2 was collected on a Bruker APEX CCD diffractometer, and those for H_2NDC-NO_2, MOF-205-NH_2, and MOF-205-NO_2 were collected on on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea.

Two MOF crystals were respectively evacuated under vacuum in order to prevent the unidentified electron densities at the last stages of structure refinement processes. Therefore, SQUEEZE treatments were not applied for the refinement processes.

Direct methods were applied for obtaining initial structures using SHELXS-97. The preliminary model structures were refined by subsequent refinement processes using SHELXL-97. Except for H_2NDC-NO_2 (Figure S6), all other crystals showed disorders. H_2NDC-NH_2 sits on an inversion center, which required the -NH_2 group bonded to C2 was refined with a half occupancy factor. In turn, the H2 atom bonded to C2 was also refined with a half occupancy factor (Figure S7).

In the crystal structures of MOF-205-NH_2 and MOF-205-NO_2, the organic linkers, BTB and NDC-R showed same disorders. In detail, the BTB sitting on a special position with a 32 site symmetry has a disordered benzoate group at general positions. As the phenylene ring adopted two conformations, and their site occupancy factors were refined. The BTB peripheral phenylene ring is also disordered over two sites at general positions: (C3, C4) and (C3' and C4').

In contrast that the BTB disorder was treated clearly, the disorder model for the NDC-R could be obtained with some approximation. While the NDC-R linkers has only a mirror plane at the molecular plane due to the asymmetric functional group, the site symmetry (*mmm*) where the NDC-R is located in the crystal is too high to describe the NDC structure with a simple disorder model. This symmetry condition also requires that the terminal –COO group should be disordered in order to form a reasonable NDC structure. However, this suggestion also requires the disorder of the Zn atoms in order to exhibit same Zn-O bond distances. Therefore, for simplicity, further analyses were not applied, and instead an ordered model was built using modeling software as described in the main text and the Section 4 in the ESI.

In the case of MOF-205-NH_2, the –NH_2 group bonded to C11 must be disordered over four sites (Figure S8). During the refinement processes, the positions of the N atoms approached to the position where two perpendicular mirror planes meet. Therefore, it was modeled such that two N atom was shared by four disordered NDCs. A same treatment was applied to MOF-205-NO_2 for the refinement of the disordered structure (Figure S9).

All non-H atoms were refined anisotropically. All H atoms were generated in ideal positions and refined with a riding model.

Final crystal and refinement results are listed in Table S1-S4.

Table S1. Crystal data and structure refinement for $H_2NDC\text{-}NO_2$.

Empirical formula	C15 H14 N2 O7	
Formula weight	334.28	
Temperature	100(2) K	
Wavelength	0.70000 Å	
Crystal system	Monoclinic	
Space group	*C* 2/*c*	
Unit cell dimensions	*a* = 23.991(5) Å	α = 90°.
	b = 5.7460(11) Å	β = 106.07(3)°.
	c = 21.791(4) Å	γ = 90°.
Volume	2886.5(10) $Å^3$	
Z	8	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	0.120 mm^{-1}	
F(000)	1392	
Crystal size	0.30 x 0.10 x 0.05 mm^3	
Theta range for data collection	3.48 to 30.00°.	
Index ranges	-34<=h<=33, 0<=k<=8, -30<=l<=30	
Reflections collected	7410	
Independent reflections	4283 [R(int) = 0.0899]	
Completeness to theta = 30.00°	97.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4283 / 0 / 222	
Goodness-of-fit on F^2	1.234	
Final R indices [I>2sigma(I)]	R1 = 0.0679, wR2 = 0.1770	
R indices (all data)	R1 = 0.1032, wR2 = 0.2108	
Extinction coefficient	0.212(15)	
Largest diff. peak and hole	0.778 and -0.929 $e.Å^{-3}$	

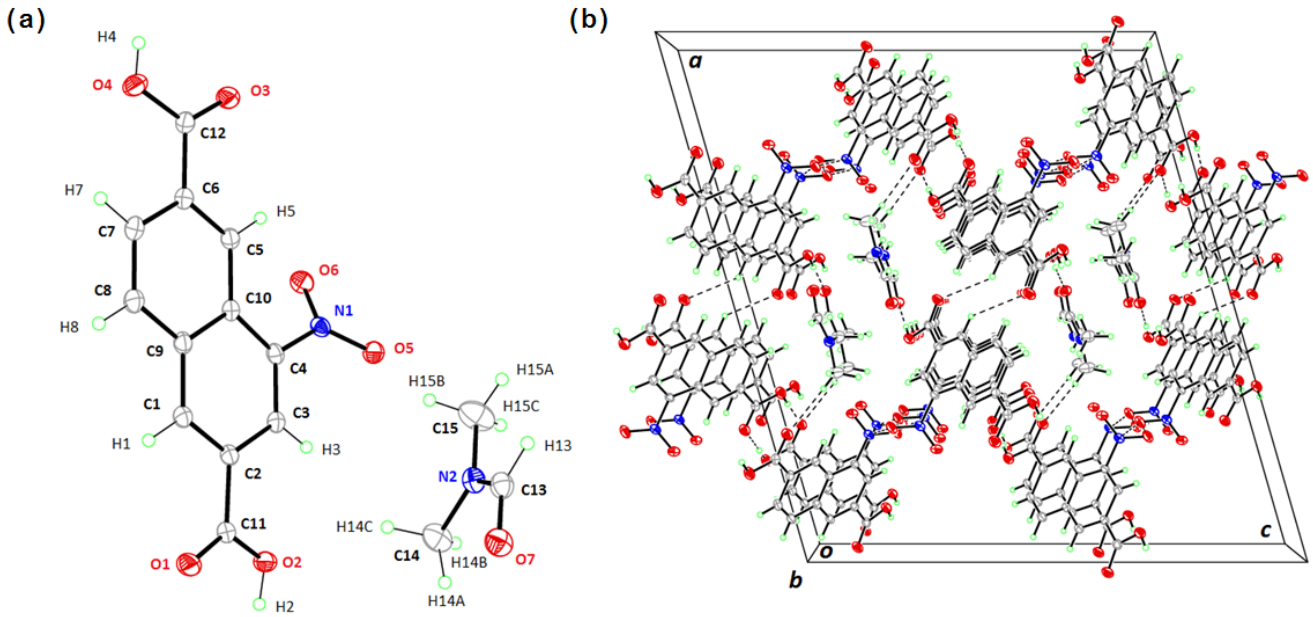

Figure S6. The ORTEP drawings of $H_2NDC\text{-}NO_2$ are shown with 50% thermal ellipsoids for (a) the asymmetric unit and (b) a unit-cell packing.

Table S2. Crystal data and structure refinement for $H_2NDC\text{-}NH_2$.

Empirical formula	C22 H27 N3 O6	
Formula weight	429.47	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P\,2_1/n$	
Unit cell dimensions	a = 7.3194(7) Å	α = 90°.
	b = 10.4461(11) Å	β = 98.358(3)°.
	c = 14.5397(15) Å	γ = 90°.
Volume	1099.89(19) $Å^3$	
Z	2	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	456	
Crystal size	0.20 × 0.17 × 0.08 mm^3	
Theta range for data collection	2.41 to 24.73°.	
Index ranges	-8<=h<=6, -12<=k<=11, -17<=l<=16	
Reflections collected	5872	
Independent reflections	1876 [R(int) = 0.0614]	
Completeness to theta = 24.73°	99.8 %	
Max. and min. transmission	0.9924 and 0.9812	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1876 / 0 / 146	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0886, wR2 = 0.2015	
R indices (all data)	R1 = 0.1321, wR2 = 0.2264	
Largest diff. peak and hole	0.577 and -0.279 e.$Å^{-3}$	

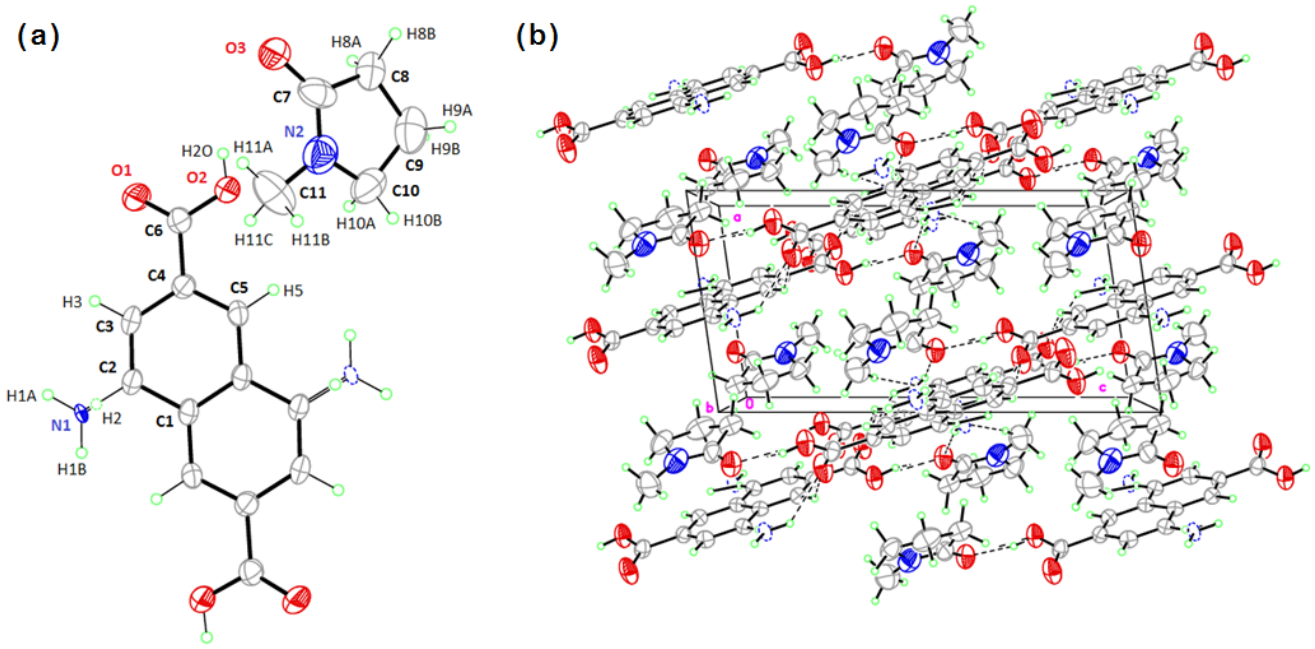

Figure S7. The ORTEP drawings of $H_2NDC\text{-}NH_2$ are shown with 50% thermal ellipsoids for (a) the asymmetric unit and (b) a unit-cell packing.

Table S3. Crystal data and structure refinement for MOF-205-NH_2.

Empirical formula	C48 H27 N O13 Zn4	
Formula weight	1087.19	
Temperature	223(2) K	
Wavelength	0.70000 Å	
Crystal system	Cubic	
Space group	*P m* -3 *n*	
Unit cell dimensions	*a* = 30.310(4) Å	α = 90°.
	b = 30.310(4) Å	β = 90°.
	c = 30.310(4) Å	γ = 90°.
Volume	27847(6) $Å^3$	
Z	6	
Density (calculated)	0.389 Mg/m^3	
Absorption coefficient	0.507 mm^{-1}	
F(000)	3276	
Crystal size	0.40 × 0.30 × 0.20 mm^3	
Theta range for data collection	2.48 to 29.99°.	
Index ranges	-43<=h<=43, -43<=k<=43, -43<=l<=43	
Reflections collected	295560	
Independent reflections	7452 [R(int) = 0.0487]	
Completeness to theta = 29.99°	99.7 %	
Max. and min. transmission	0.9054 and 0.8230	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7452 / 66 / 125	
Goodness-of-fit on F^2	1.093	
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1471	
R indices (all data)	R1 = 0.0613, wR2 = 0.1520	
Extinction coefficient	0.0119(5)	
Largest diff. peak and hole	0.435 and -0.604 $e.Å^{-3}$	

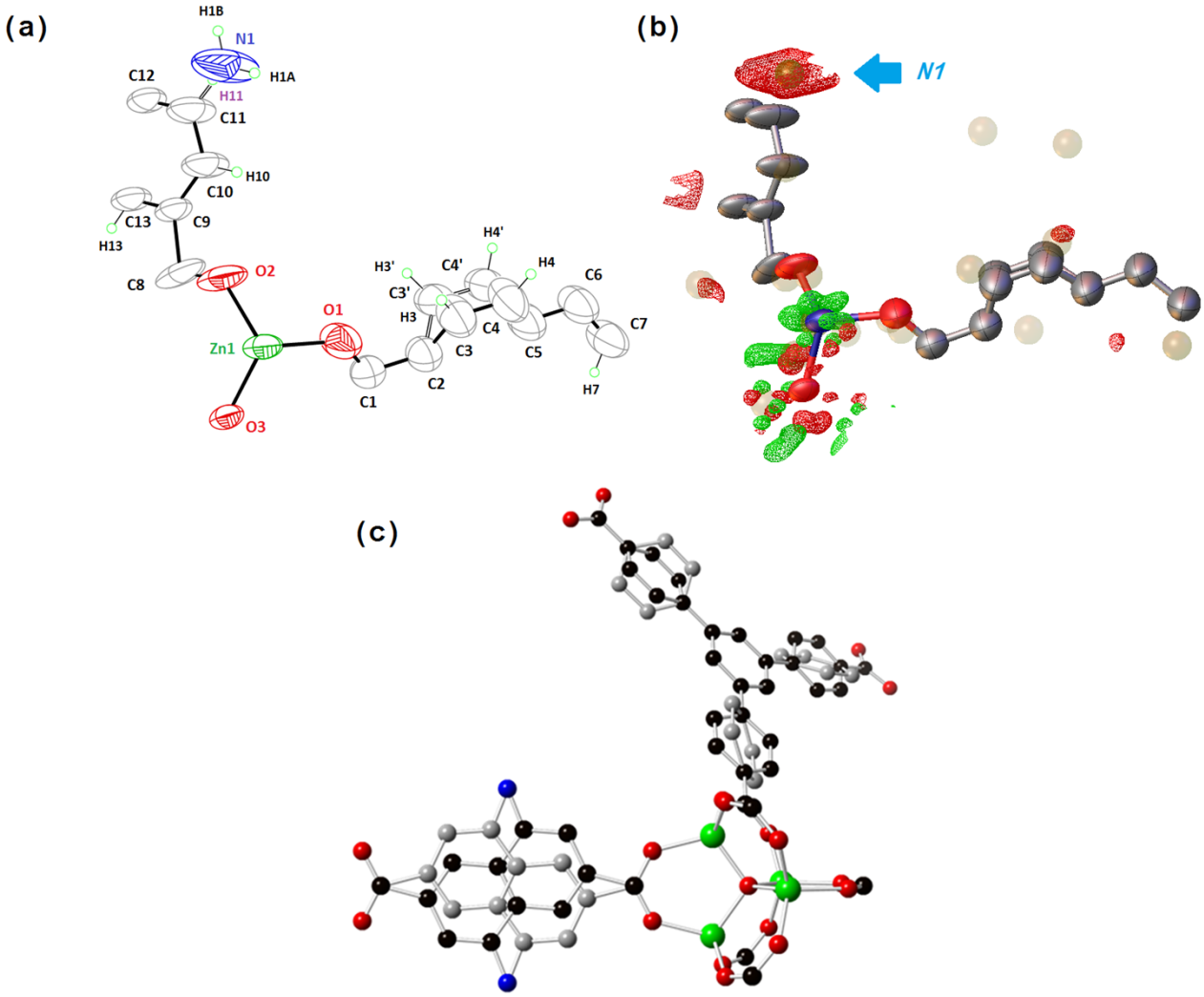

Figure S8. (a) ORTEP drawing of **MOF-205-NH$_2$** with 50% thermal ellipsoids is shown for the asymmetric unit. (b) The electron density corresponding to the N1 atom is displayed with other atoms. (b) The disorder model is shown with a fragment structure.

Table S4. Crystal data and structure refinement for MOF-205-NO_2.

Empirical formula	C48 H25 N O15 Zn4	
Formula weight	1117.17	
Temperature	223(2) K	
Wavelength	0.70000 Å	
Crystal system	cubic	
Space group	*P m* -3 *n*	
Unit cell dimensions	*a* = 30.312(4) Å	α = 90°.
	b = 30.312(4) Å	β = 90°.
	c = 30.312(4) Å	γ = 90°.
Volume	27851(6) $Å^3$	
Z	6	
Density (calculated)	0.400 Mg/m^3	
Absorption coefficient	0.508 mm^{-1}	
F(000)	3360	
Crystal size	0.50 × 0.40 × 0.30 mm^3	
Theta range for data collection	2.48 to 30.00°.	
Index ranges	-43<=h<=43, -42<=k<=42, -42<=l<=42	
Reflections collected	291703	
Independent reflections	7451 [R(int) = 0.0624]	
Completeness to theta = 30.00°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7451 / 28 / 131	
Goodness-of-fit on F^2	1.124	
Final R indices [I>2sigma(I)]	R1 = 0.0623, wR2 = 0.1695	
R indices (all data)	R1 = 0.0682, wR2 = 0.1738	
Extinction coefficient	0.0203(8)	
Largest diff. peak and hole	0.528 and -0.556 e.$Å^{-3}$	

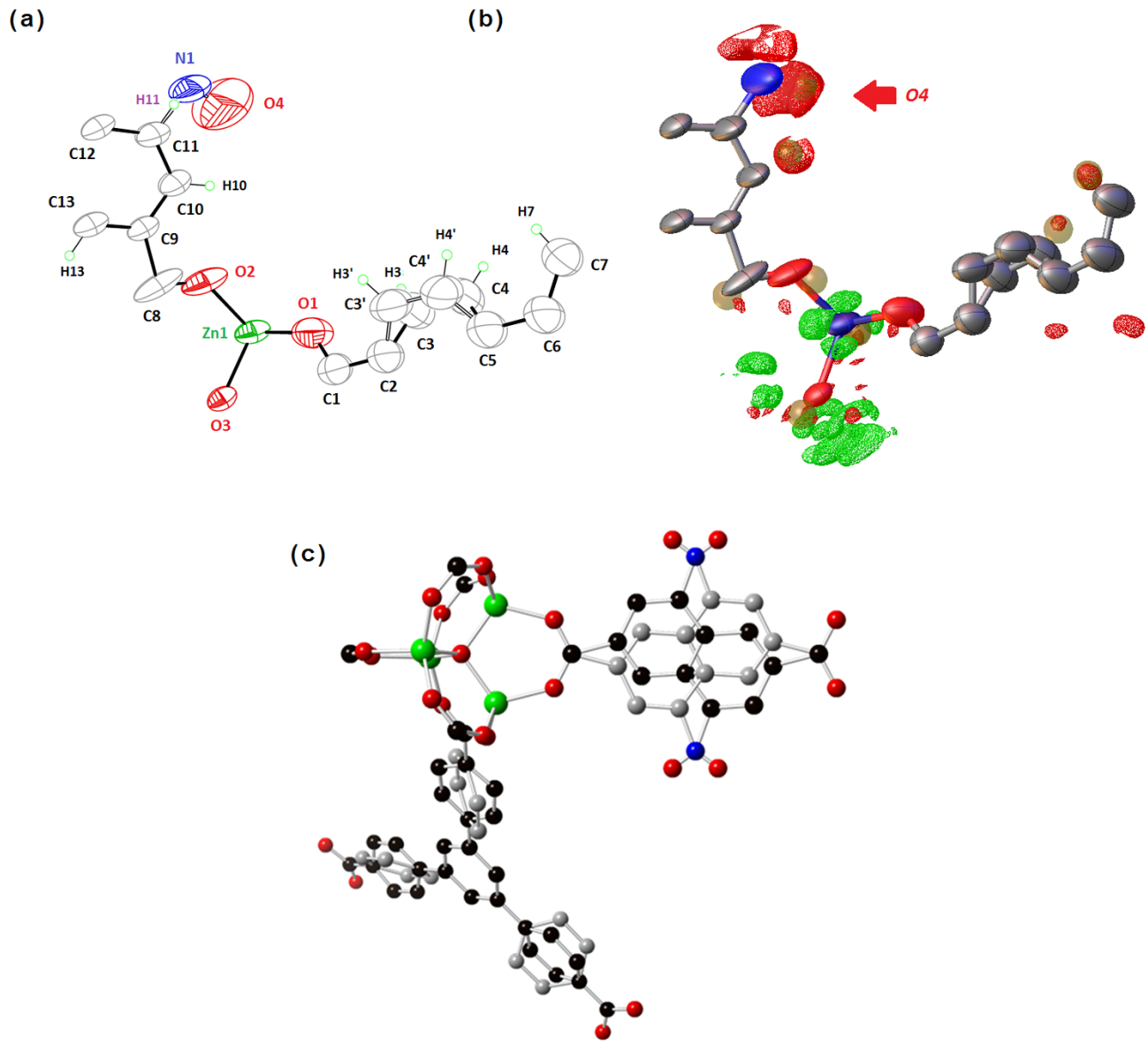

Figure S9. (a) ORTEP drawing of MOF-205-NO_2 with 50% thermal ellipsoids is shown for the asymmetric unit. (b) The electron density corresponding to the O4 atom is displayed with other atoms. (b) The disorder model is shown with a fragment structure.

Section S4 Modelling of the Ordered MOF Structures

The X-ray data for MOF-205-OBn were collected on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. An initial model for MOF-205-OBn with a cubic space group ($Pm\bar{3}$) with a = 30.173(4) Å at 100 K was obtained by direct methods, and improved by subsequent refinements. However, as the NDC-$(OBn)_2$ groups severely disordered around the crystallographic special positions, and due to the insufficient and weak reflections, the pendant and flexible –OBn groups could not be located. Thus, a possible model structure was built by aid of *Materials Studio* 6.1.0™ (Accelrys Software Inc.). Using the model structure, the crystal structure of MOF-205-OBn has been refined. However, due to the severe disorder of the –OBn groups, the refined structure has bad some contacts between the –OBn groups and the main framework with a high R_1 value as in Table S5. Thus, the crystal data (a CIF file) for MOF-205-OBn has not been deposited. The possible ordered structures for MOF-205, MOF-205-NH_2 and MOF-205-NO_2 were also obtained similarly. For comparison of the porosity with the same volume, the unit cell parameters of all MOFs were changed to those of MOF-205 with a = 30.353 Å. The final space groups were $P1$ for MOF-205-NH_2 and MOF-205-NO_2, and $P\bar{1}$ for MOF-205. The ordered model structures are displayed in Figure 1. Using these models, their van der Waals and accessible solvent surface areas (SA_{vdW}, SA_{acc}) and pore volumes (V_{vdw}) were calculated using a probe radius of 1.82 Å by the "Atom Volumes & Surfaces" utility in the Materials Studio (Table 1). The pore volumes were also calculated using PLATON with a "CALC SOLV probe 1.82" command.

S4. 1. Preliminary Crystal and Refinement Data for MOF-205-OBn

The ordered model structure of MOF-205-OBn was built based on the disordered structure obtained by single-crystal X-ray diffraction analysis. Table S5 contains the unit cell parameters and space group information, and refinement data for a disordered model structure. In fact, the final R1 value is not suitable for publication, and thus, its CIF file has not been reported. The current structure model has severely disordered –OBn groups that show several bad contacts not fixed with the current X-ray data.

Table S5. Crystal data and structure refinement for **MOF-205-OBn**: **d**ue to the severe disorder, the structural model was used only for building an ordered structural model, and not deposited.

Empirical formula	C62 H38 O15 Zn4
Formula weight	1284.40
Temperature	95(2) K
Wavelength	0.90000 Å

Crystal system	Cubic	
Space group	*P m* -3	
Unit cell dimensions	*a* = 30.173(4) Å	α = 90°
	b = 30.173(4) Å	β = 90°
	c = 30.173(4) Å	γ = 90°
Volume	27470(6) $Å^3$	
Z	6	
Density (calculated)	0.466 Mg/m^3	
Absorption coefficient	1.003 mm^{-1}	
F(000)	3900	
Crystal size	0.20 × 0.20 × 0.20 mm^3	
Theta range for data collection	2.84 to 32.15°.	
Index ranges	-35<=h<=34, -23<=k<=22, -23<=l<=22	
Reflections collected	5279	
Independent reflections	4164 [R(int) = 0.1045]	
Completeness to theta = 32.15°	49.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4164 / 59 / 177	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.1686, wR2 = 0.4048	
R indices (all data)	R1 = 0.2531, wR2 = 0.4289	
Extinction coefficient	0.036(4)	
Largest diff. peak and hole	0.323 and -0.311 $e.Å^{-3}$	

S4. 2. Model Building of an Ordered MOF-205-OBn Using Forcite Geometry Optimization

The framework structure with Zn_4O, BTB, and NDC units was loaded, and using the Visualizer utility of *Materials Studio* 6.1.0™ (Accelrys Software Inc.) the –OBn model fragments were positioned at the NDC units. Then, the space group of the structural model was made to *P*1, and the disordered parts were carefully removed to generate an ordered framework structure. After generating H atoms at the BTB and NDC carbon atoms, and setting the aromatic C–C and carboxylate C–O bonds to delocalized double bonds, the crystal structure was optimized using a Forcite routine that conducts Molecular Mechanics calculations with the Universal force-fields. During the geometry optimization, the positions of the Zn_4O clusters were fixed and the unit cell parameters were not allowed to be changed. The space group of the optimized structure was changed to $P\bar{1}$, and the same optimization calculation was again carried out to

produce the final ordered structure of MOF-205-OBn. For comparison of the porosity with the same volume, the unit cell parameters of all MOFs were changed to those of MOF-205 with a = 30.353 Å. The final space groups were $P1$ for MOF-205-NH_2 and MOF-205-NO_2, and $P\bar{1}$ for MOF-205. The ordered model structures are displayed in Figure 1. The followings are the results for the Forcite calculations.

```
---- Geometry optimization parameters ----

Algorithm           : Smart
Convergence tolerance:
  Energy                      : 0.001 kcal/mol
  Force                       : 0.5 kcal/mol/A
Maximum number of iterations  : 500
External pressure             : 0 GPa
Motion groups rigid           : NO
Optimize cell                 : NO

---- Energy parameters ----
Forcefield                    : Universal
Electrostatic terms:
  Summation method            : Ewald
  Accuracy                    : 0.001 kcal/mol
  Buffer width                : 0.5 A

van der Waals terms:
  Summation method            : Ewald
  Accuracy                    : 0.001 kcal/mol
  Repulsive cutoff            : 6 A
  Buffer width                : 0.5 A

---- Initial structure ----

Total enthalpy                : 4592.256666 kcal/mol
  External pressure term      : 0.000000 kcal/mol

Total energy                  :      4592.256666 kcal/mol

Contributions to total energy (kcal/mol):
  Valence energy (diag. terms) :      1983.804
    Bond                      :       932.691
    Angle                     :       803.498
    Torsion                   :       243.691
    Inversion                 :         3.925
  Non-bond energy             :      2608.453
    van der Waals             :      2608.453
    Electrostatic             :         0.000

rms force  : 3.097E+002 kcal/mol/A
max force  : 6.490E+003 kcal/mol/A

Cell parameters:   a:  30.353000 A   b:  30.353000 A   c:  30.353000 A
             alpha:  90.000 deg  beta:  90.000 deg gamma:  90.000 deg

---- Final structure ----
Total enthalpy                : 1294.054513 kcal/mol
  External pressure term      : 0.000000 kcal/mol

Total energy                  :      1294.054513 kcal/mol
```

```
Contributions to total energy (kcal/mol):
  Valence energy (diag. terms)  :       800.461
    Bond                        :       160.402
    Angle                       :       396.953
    Torsion                     :       241.895
    Inversion                   :         1.212
  Non-bond energy               :       493.593
    van der Waals               :       493.593
    Electrostatic               :         0.000

rms force  : 1.702E-001 kcal/mol/A
max force  : 1.669E+000 kcal/mol/A

Cell parameters:    a:  30.353000 A    b:  30.353000 A    c:  30.353000 A
              alpha:  90.000 deg  beta:  90.000 deg gamma:  90.000 deg
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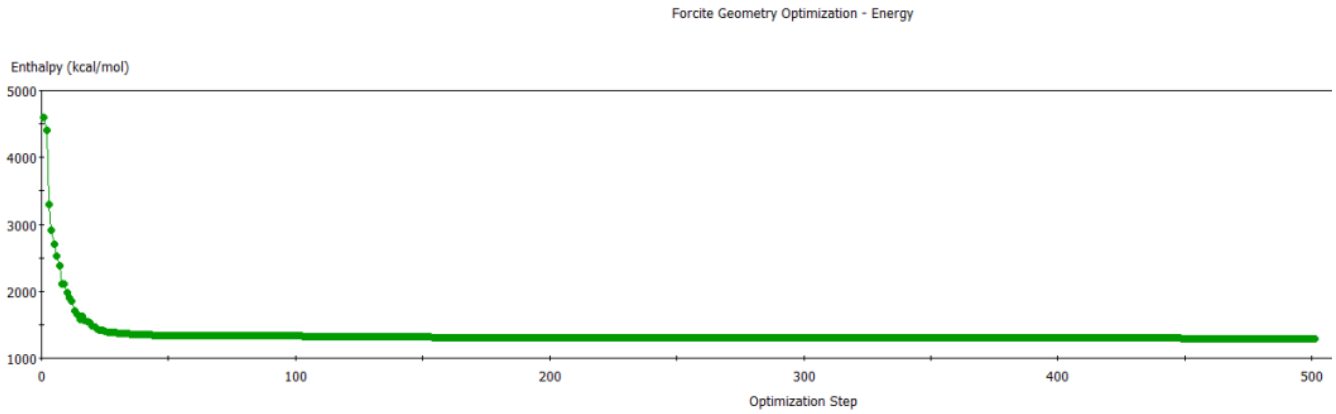


S4. 3. Ordered Model Structure of MOF-205-OBn

The calculated porosity values in Table 1 were calculated using the geometry-optimized models.

MOF	*f.w.*	d_{calc} (cm^3/g)	SA_{vdW} (m^2/g)	SA_{acc} (m^2/g)	V_{vdW} (cm^3/cm^3)
MOF-205	1072.17	0.382	4220	4640	0.850
MOF-205-NH_2	1087.19	0.387	4230	4680	0.847
MOF-205-NO_2	1117.17	0.398	4190	4660	0.845
MOF-205-OBn	1284.40	0.458	4530	3770	0.808

For a representative example, the SA_{vdW}, SA_{acc}, and V_{vdW} values of **MOF-205-OBn** were obtained as follows. The unit-cell volume used was V = 27964 $Å^3$ (See Table 1).

- Parameters for the 'Atom Volumes & Surface' tool

  Grid resolution: Fine; Grid interval: 0.25 Å; vdW scale factor: 1.0000

  Max solvent radius: 1.82 Å; Initial solvent radius: 1.82 Å

• Results

vdW Surface

Occupied Volume: 5376.26 Å^3; Free Volume: 22588.10 Å^3; Surface Area: 5797.50 Å^2

V_{vdw} = (Free Volume)/V = (22588 Å^3) / (27964 Å^3) = 0.808 (cm^3/cm^3)

SA_{vdW} = (Surface Area)/f.w.

= (5797.5 × 10^{-20} m^2)/(Z × f.w. / N_A), (N_A, Avogadro's number)

= (5797.5 × 10^{-20} m^2 × 6.022 × 10^{23}) / (6 × 1284.4 g)

= 4530 m^2/g

Solvent Surface @1.82

Occupied Volume: 15889.12 Å^3; Free Volume: 12075.24 Å^3; Surface Area: 4818.95 Å^2

Accessible Solvent Surface @1.82

Occupied Volume: 15889.58 Å^3; Free Volume: 12074.78 Å^3; Surface Area: 4817.98 Å^2

SA_{acc} = (Surface Area)/f.w.

= (4817.98 × 10^{-20} m^2)/(Z × f.w. / N_A), (N_A, Avogadro's number)

= (4817.98× 10^{-20} m^2 × 6.022 × 10^{23}) / (6 × 1284.4 g)

= 3770 m^2/g

MOF-205:

vdW Surface

Free Volume: 23760.05 Å^3

V_{vdw} = (Free Volume)/V = 0.850 (cm^3/cm^3)

Surface Area: 4505.71 Å^2

SA_{vdW} = (4505.71× 10^{-20} m^2 × 6.022 × 10^{23}) / (6 × 1072.17g) = 4220 m^2/g

Accessible Solvent Surface @1.82

Free Volume: 14788.04 Å^3

Surface Area: 4957.92 Å^3

SA_{acc} = (4957.92 × 10^{-20} m^2 × 6.022 × 10^{23}) / (6 × 1072.17g) = 4640 m^2/g

MOF-205-NH_2

vdW Surface

Occupied Volume: 4277.30 Å^3

Free Volume: 23687.06 Å^3/ 27964 = 0.847

Surface Area: 4586.84 Å^2

SA_{vdW} = (4586.84 × 10^{-20} m^2 × 6.022 × 10^{23}) / (6 × 1087.19) = 4230 m^2/g

Accessible Solvent Surface @1.82

Occupied Volume: 13416.28 Å^3

Free Volume: 14548.07 Å^3

Surface Area: 5070.33 Å^2

SA_{acc} = (5070.33 × 10^{-20} m^2 × 6.022 × 10^{23}) / (6 × 1087.19) = 4680 m^2/g

MOF-205-NO_2

vdW Surface

Occupied Volume: 4348.28 Å^3

Free Volume: 23616.08 Å^3/ 27964 = 0.845

Surface Area: 4668.50 Å^2

SA_{vdW} = (4668.50 × 10^{-20} m^2 × 6.022 × 10^{23}) / (6 × 1117.17) = 4190 m^2/g

Accessible Solvent Surface @1.82

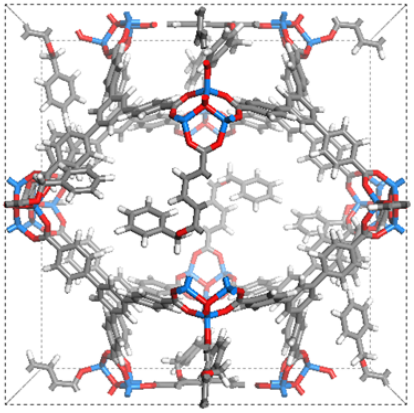
Occupied Volume: 13686.62 Å^3

Free Volume: 14277.74 Å^3

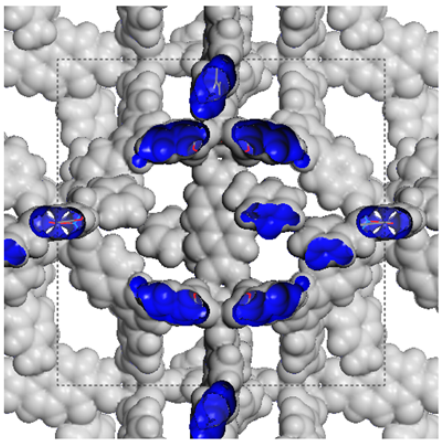
Surface Area: 5188.72 Å^2

SA_{acc} = (5188.72 × 10^{-20} m^2 × 6.022 × 10^{23}) / (6 × 1117.17) = 4660 m^2/g

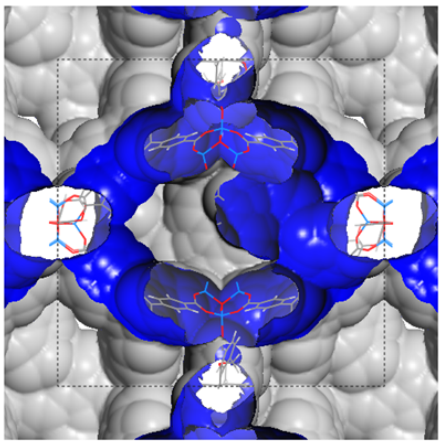
MOF-205-OBn



geometry optimized structure



van der Waals surface



solvent accessible surface

Section S5 Electrostatic Potential Maps

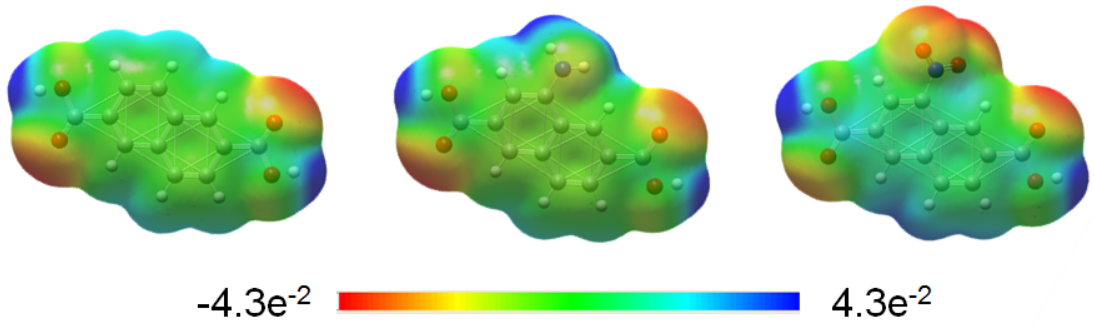


Figure S10. Electrostatic potential maps for $H_2NDC\text{-}NH_2$ and $H_2NDC\text{-}NO_2$. After molecular structure optimization by using the three-parameter hybrid functional of Becke (B3LYP) with a 6-31+G(d,p) basis set and energy calculations using B3LYP/6-311++G(d,p) DFT methods, the dipole moments for H_2NDC, $H_2NDC\text{-}NH_2$, and $H_2NDC\text{-}NO_2$ were obtained as 0, 1.70, and 4.54 Debye, respectively.

Section S6 Powder X-ray Diffraction (PXRD) Patterns

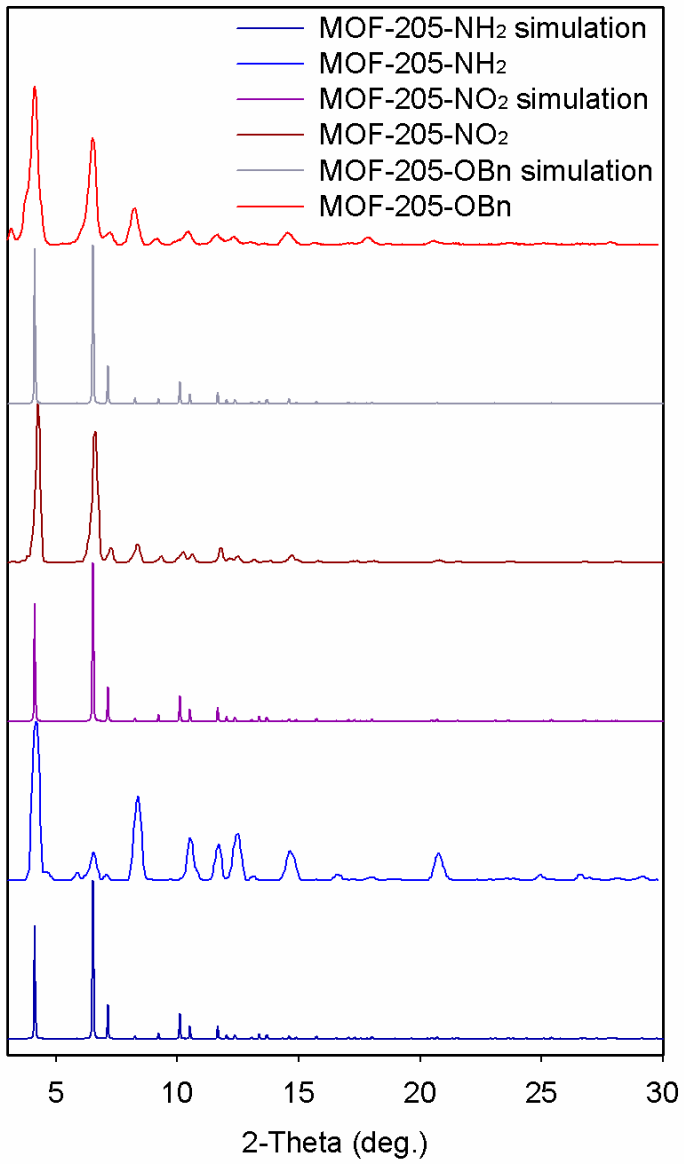


Figure S11. The PXRD patterns of MOF-205-NO_2, MOF-205-NH_2, and MOF-205-OBn. The simulated patterns were produced from the crystal structures. In the case of MOF-205-OBn, the measured pattern was compared with the simulation generated by the crystal structure of MOF-205.

Section S7 Gas Adsorption Analyses

Adsorption isotherms of N_2, H_2, CO_2, and CH_4 at pressures up to 1 bar were measured by standard volumetric procedures on a BELSORP-mini apparatus (BEL-Japan, INC.). The measurement temperature was maintained using a liquid nitrogen bath (77 K) or a circulator (253, 273, and 298 K). Adsorption isotherms of CO_2 and CH_4 at pressures respectively up to 48 and 85 bar at 298 K were measured by standard volumetric procedures on a BELSORP-HP apparatus (BEL-Japan, INC.). Before the measurements, the MOF samples were activated typically as follows. The as-prepared MOF crystals were immersed in anhydrous dichloromethane or chloroform for 3 days to replace the occluded solvent (mostly DMF); during the exchange period the solvent was refreshed three times. After transferring the collected sample as a suspension to a quartz cell, the solvent was decanted. The wet sample was evacuated (1.0×10^{-3} Torr) at room temperature for 10 h before heating at 160 °C for 6 h.

S7. 1. Hydrogen Adsorption at 77 K and under 1 bar

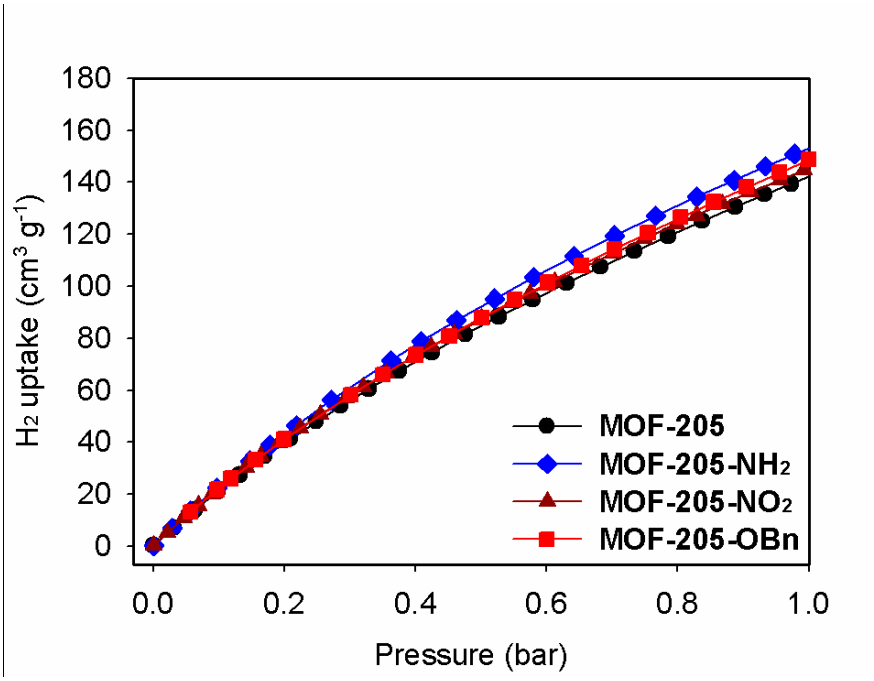


Figure S12. H_2 adsorption isotherms at 77 K for MOF-205, MOF-205-NH_2, MOF-205-NO_2, and MOF-205-OBn. Note that the y-axis unit is represented as the gravimetric hydrogen uptake amounts whereas the capacity comparison is described based on the volumetric capacity (cm^3/cm^3) in the main text.

S7. 2. Isosteric Heats of CO_2 Adsorption

The isosteric heat of adsorption, Q_{st}, defined as

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i$$

was determined by fitting the CO_2 adsorption isotherms at 253, 273, and 298 K to the following virial-type expression, which is composed of parameters a_i and b_i that are independent of temperature.

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$

P is pressure (atm), N is the amount adsorbed H_2 gas (mg g^{-1}), T is temperature (K), and m and n represent the number of coefficients required to adequately describe the isotherms.

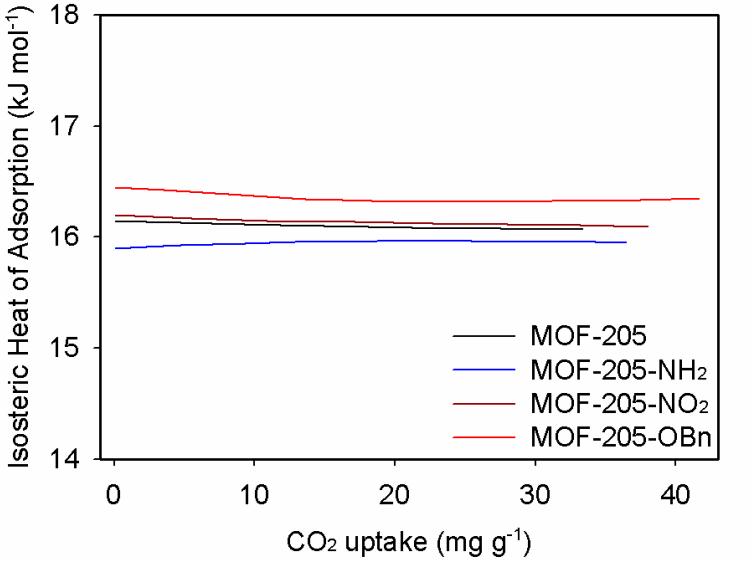


Figure S13. Isosteric heats of CO_2 Adsorption for MOF-205, MOF-205-NH_2, MOF-205-NO_2 and MOF-205-OBn.

The isosteric heat of CO_2 adsorption was also calculated by applying these fits to the van't Hoff equation.

$$\frac{\partial(\ln P)}{\partial(1/T)} = -\frac{Q_{st}}{R}$$

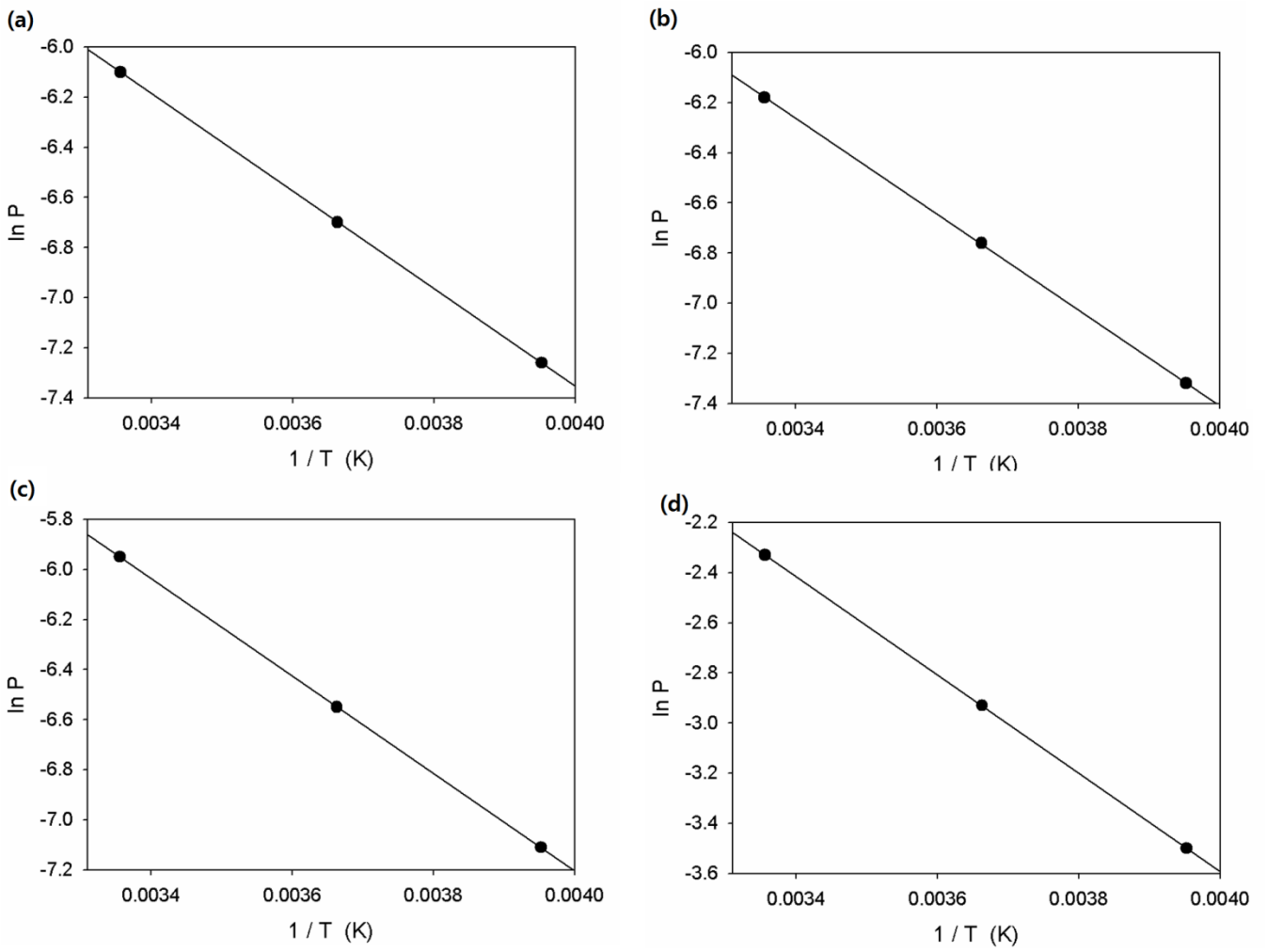


Figure S14. The van't Hoff plots for (a) MOF-205, (b) MOF-205-NH_2, (c) MOF-205-NO_2 and (d) MOF-205-OBn.

Table S7. Isosteric heats of CO_2 Adsorption calculated from van't Hoff equation for MOFs.

	1/T (K)			slope : lnP vs 1/T	Q_{st} (kJ mol^{-1})	
	253 K	273 K	298 K		virial	van't Hoff
MOF-205	3.95E-3	3.66E-3	3.36E-3	-1943.58	16.14	16.16
MOF-205-NH_2				-1909.75	15.89	15.88
MOF-205-NO_2				-1943.58	16.19	16.16
MOF-205-OBn				-1977.08	16.42	16.30

S7. 3. IAST Calculations of Gas Adsorption Selectivity

The pure component isotherms for CO_2, N_2, and CH_4 gases were fitted to single-site Langmuir-Freundlich equation**.**

$$q_i = q_{i,sat}\frac{b_i P_i^{V_i}}{1 + b_i P_i^{V_i}}$$

The saturation capacities $q_{i,sat}$, Langmuir-Freundlich parameters b_i, along with the exponents v_i, are provided in Table S6.

Table S8. Langmuir-Freundlich parameters for CO_2, N_2, CH_4 isotherms in MOF-205 / MOF-205-OBn at 298 K.

MOF-205				**MOF-205-OBn**			
	$q_{i,sat}$ mol / kg	b_i Pa^{-vi}	v_i		$q_{i,sat}$ mol / kg	b_i Pa^{-vi}	v_i
CO_2	64.299	0.012	1.012	CO_2	16.070	0.062	0.957
N_2	2.420	0.074	0.957	N_2	0.684	0.273	0.819
CH_4	84.758	0.004	1.005	CH_4	31.600	0.011	1.006

Using the pure component isotherm fits, the adsorption selectivities defined by

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

can be determined using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.[S1]

Reference

S1. A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121-127.