Supporting Information

Controlling of Metal Composition in Bimetallic Mg/Zn(dobpdc) Constructed from a One-Dimensional Zn-based Template

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Preparation.

All chemicals and solvents in the synthesis were reagent grade and used without further purification. 4,4′-Dihydroxy-(1,1′-biphenyl)-3,3′-dicarboxylic acid (H_4dobpdc) was synthesized according to the literature procedure.[1, 2]

Synthesis of [Zn(H_2dobpdc)(H_2O)$_2$]·0.2H_2O (1): H_4dobpdc (0.55 g, 2 mmol) was treated with 1 M NaOH (4 mL). Sonication of the mixture at room temperature afforded a transparent solution. The solution was maintained in the range of pH 8~9. An aqueous solution (3 mL) of $ZnSO_4 \cdot 7H_2O$ (0.60 g, 2.1 mmol) was added to the resulting solution and crystals were immediately precipitated. The crude product was washed with acetic acid and water, dried at room temperature under high vacuum condition to produce the 1D Zn polymer. Single crystals were obtained via slow evaporation of the filtrate of the solution after the initial precipitationYield: 0.45 g (64%). Elemental analysis (%) calcd for $C_{14}H_{12.4}O_{8.2}Zn$: C 44.58, H 3.31; found: C 44.38, H 3.35.

Synthesis of M_2(dobpdc):

[Mg_2(dobpdc)(DMF)$_2$]·1.6DMF·1.3H_2O [Mg_2(dobpdc)]: H_4dobpdc (86 mg, 0.36 mmol), $Mg(NO_3)_2 \cdot 6H_2O$ (185 mg, 0.73 mmol), and 12 mL of solvent (DMF:EtOH = 1:1, v/v) were loaded into a 24mL Pyrex cell and sealed with a PTFE cap. The resulting mixture was then placed in a convection oven pre-heated to 130 ^oC and kept at this temperature for 4 h. Colorless powders were formed, collected by filtration, and washed with DMF and MeOH. Yield: 130 mg (78%). Elemental analysis (%) calcd for $C_{24.8}H_{33.86}Mg_2N_{3.6}O_{10.9}$: C 49.21, H 5.63, N 8.33; found: C 48.86, H 5.64, N 8.59.

[Zn_2(dobpdc)(DMF)$_2$]·1.6DMF·1.3H_2O [Zn_2(dobpdc)]: H_4dobpdc (86 mg, 0.36 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (214 mg, 0.72 mmol), and 12 mL of solvent (DMF:EtOH = 1 : 1, v/v) were loaded into a 24mL Pyrex cell and sealed with a PTFE cap. The resulting mixture was then placed in a convection oven pre-heated to 130 ^oC and kept at this temperature for 4 h, and colorless powders formed. The powders were collected by filtration, washed with DMF and MeOH. Yield: 90 mg (93%). Elemental analysis (%) calcd for $C_{24.8}H_{33.8}Zn_2N_{3.6}O_{10.9}$: C 43.33, H 4.96, N 7.33; found: C 43.71, H 4.64, N 7.03.

Synthesis of bimetallic $[Mg_{1.08}Zn_{0.92}(dobpdc)(DMF)_2]\cdot 1.1H_2O$: H_4dobpdc (43 mg, 0.16 mmol), $Mg(NO_3)_2\cdot 6H_2O$ (140 mg, 0.56 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (46 mg, 0.16 mmol), and 12 mL of solvent (DMF:EtOH = 1 : 1, v/v) were loaded into a 24mL Pyrex cell and sealed with a PTFE cap. The resulting mixture was then placed in a convection oven which was pre-heated to 130 ^oC and kept at this temperature for 4 h. The powders were collected by filtration and washed with DMF and MeOH. Yield: 80 mg (83%). Elemental analysis (%) calcd for $C_{20}H_{22.2}Mg_{1.08}N_2O_{9.1}Zn_{0.92}$: C 45.97, H 4.28, N 5.36; found: C 45.88, H 4.14, N 5.22. The metal composition was checked by ICP-AES.

Synthesis of bimetallic M/Zn(dobpdc) constructed from polymer 1:

$[Mg_{1.02}Zn_{0.98}(dobpdc)(DMF)_2]\cdot 1DMF0.5H_2O$ [Mg/Zn(dobpdc)]: Polymer **1** (66.5 mg, 0.178 mmol), $Mg(NO_3)_2\cdot 6H_2O$ (185 mg, 0.73 mmol), and 12 mL of solvent (DMF:EtOH = 1 : 1, v/v) were loaded into a 24mL Pyrex cell and sealed with a PTFE cap. The resulting mixture was then placed in a convection oven pre-heated to 130 ^oC and kept at this temperature for 4 h, and colorless powders formed. The powders were collected by filtration, washed with DMF and MeOH. Yield: 82 mg (91%). Elemental analysis (%) calcd for $C_{23}H_{28}Mg_{1.02}Zn_{0.98}N_3O_{9.5}$: C 47.03, H 4.81, N 7.15; found: C 46.96, H 4.89, N 7.42. The metal composition was checked by ICP-AES.

$[Mg_{1.2}Zn_{0.8}(dobpdc)(DMF)_2]\cdot 2.3DMF\cdot 1H_2O$: This compound was prepared according to the synthetic procedure similar to Mg/Zn(dobpdc) except for the reaction time for 12 h. Elemental analysis (%) calcd for $C_{26.9}H_{38.1}Mg_{1.2}Zn_{0.8}N_{4.3}O_{11.3}$: C 47.24, H 5.61, N 8.81; found: C 47.00, H 5.62, N 9.00. The metal composition was checked by ICP-AES.

Mn/Zn phase [Mn/Zn(dobpdc)]: This compound was prepared according to the synthetic procedure similar to **Mg/Zn(dobpdc)** except for the use of $MnCl_2\cdot 4H_2O$. The metal composition was checked by XPS.

Co/Zn phase [Co/Zn(dobpdc)]: This compound was prepared according to the synthetic procedure similar to **Mg/Zn(dobpdc)** except for the use of $Co(NO_3)_2\cdot 6H_2O$. The metal composition was checked by XPS.

Ni/Zn phase [Ni/Zn(dobpdc)]: This compound was prepared according to the synthetic procedure similar to **Mg/Zn(dobpdc)** except for the use of $Ni(NO_3)_2 \cdot 6H_2O$. The metal composition was checked by XPS.

Synthesis of mmen-M_2(dobpdc) and of mmen-Mg/Zn(dobpdc):

[Mg_2(dobpdc)(mmen)$_{1.58}$(H_2O)$_{0.42}$]·2.98H_2O [mmen-Mg_2(dobpdc)]: The solid **Mg_2(dobpdc)** was soaked in MeOH for 1 d. The MeOH-exchanged sample (100 mg, 0.36 mmol) was dried for 1 h at an oven preheated at 70 °C and put into a 250 mL one-neck round-bottom flask. *N,N'*-Dimethylethylenediamine (mmen) (1.89 mL, 18 mmol) and toluene (100 mL) were transferred to the flask and the mixture was sonicated over 6 h at 50 °C. The solid was separated by centrifugation, washed several times with toluene and hexane in order, and dried under Ar for 30 min. Yield: 170 mg (98.2%). Elemental analysis (%) calcd for $C_{20.32}H_{31.76}Mg_2N_{3.16}O_{9.4}$: C 46.99, H 6.16, N 8.52; found: C 47.31, H 6.14, N 8.13. The solid was evacuated at 110 °C for 3 h to obtain the activated sample.

[Zn_2(dobpdc)(mmen)$_{1.5}$(H_2O)$_{0.5}$]·0.7H_2O [mmen-Zn_2(dobpdc)]: This compound was prepared according to the synthetic procedure similar to mmen-Mg_2(dobpdc) except for the use of **Zn_2(dobpdc)**. Yield: 183 mg (98.3%). Elemental analysis (%) calcd for $C_{20}H_{26.4}Zn_2N_3O_{7.2}$: C 43.30, H 4.80, N 7.57; found: C 43.09, H 5.03, N 7.79. The solid was evacuated at 110 °C for 3 h to obtain the activated sample.

[$Mg_{1.02}Zn_{0.98}$(dobpdc)(mmen)$_{1.7}$(H_2O)$_{0.3}$]·1.2H_2O (mmen-Mg/Zn(dobpdc)]: This compound was prepared according to the synthetic procedure similar to mmen-Mg_2(dobpdc) except for the use of **Mg/Zn(dobpdc)** synthesized by polymer **1**. Yield: 173 mg (98.1%). Elemental analysis (%) calcd for $C_{20.8}H_{29.4}Mg_{1.02}Zn_{0.98}N_{3.4}O_{7.5}$: C 46.61, H 5.53, N 8.89; found: C 46.42, H 5.24, N 8.92. The solid was evacuated at 110 °C for 3 h to obtain the activated sample.

Physical Measurements. IR spectra were obtained with an ATR module using a Nicolet iS10 FT-IR spectrometer. Powder XRD patterns were recorded using Cu Kα radiation (λ = 1.5406 Å) on a Rigaku Ultima III diffractometer with a scan speed of 2° min^{-1} and a step size of 0.02°. SEM images were acquired using a JSM-7001F scanning electron microscope. Elemental analyses for C, H, and, N were performed at the Elemental Analysis Service Center of Sogang University. XPS data were collected at the Semiconductor & Display Green Manufacturing

Research Center at Korea University using X-tool. EDS-SEM analysis was performed was performed at the Korea Basic Science Institute using SU-70. EDS-TEM analysis was performed at the Korea Basic Science Institute using TECNAI G2 F30 S-Twin. NMR data were obtained from a 500 MHz Magnet System 500'54 Ascend Bruker NMR.

Gas Sorption Measurements. Highly pure N_2 (99.999%) and CO_2 (99.999%) were used in the sorption experiments. The N_2 and CO_2 isotherms for the samples were measured by using a Micromeritics 3-FLEX instrument.

Crystallographic Structure Determination. Single crystal of **1** was mounted on a cryoloop under a cooling stream of dinitrogen. Diffraction data were collected with synchrotron radiation by using a 2D-SMC ADSC Quantum-210 detector with a Pt-coated Si double crystal under a cooling stream of N_2 at the Pohang Accelerator Laboratory. The ADSC Quantum-210 ADX program was used for data collection and HKL3000 was used for cell refinement, data reduction, and absorption corrections. The structure was solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program.[3] All hydrogen atoms except for hydrogens bound to water oxygens were calculated at idealized positions and refined with the riding models. Crystal data for **1**: empirical formula= $C_{14}H_{12}O_8Zn$, M_r = 373.61, T = 100(2) K, space group = $P2/c$, a = 8.4040(17) Å, b = 5.2320(10) Å, c = 15.513(3) Å, β = 103.76(3)°, V = 662.5(2) Å^3, Z = 2, D_{calc} = 1.873 g cm^{-3}, μ = 1.898 mm^{-1}, 3067 reflections collected, 1790 unique (R_{int} = 0.0218), $R1$ = 0.0426, $wR2$ = 0.1187 [$I > 2\sigma(I)$]. CCDC 1850759 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

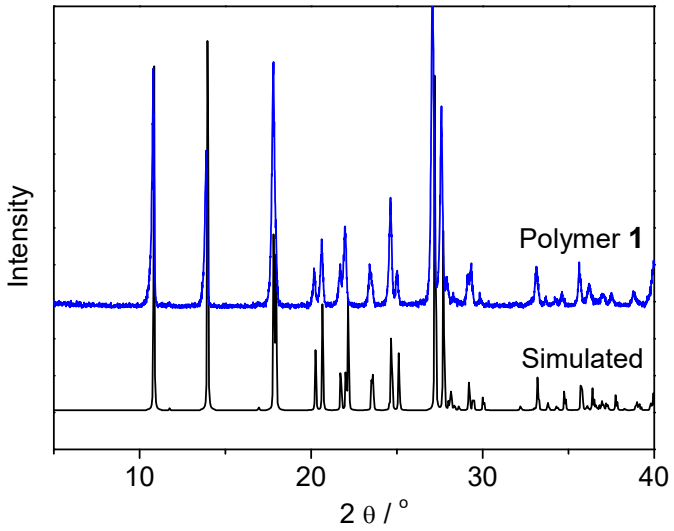
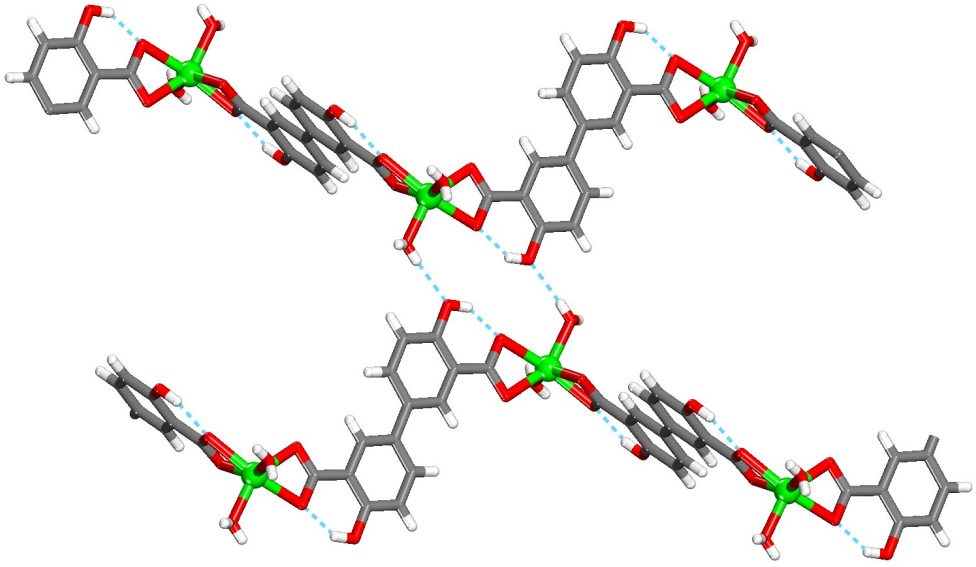
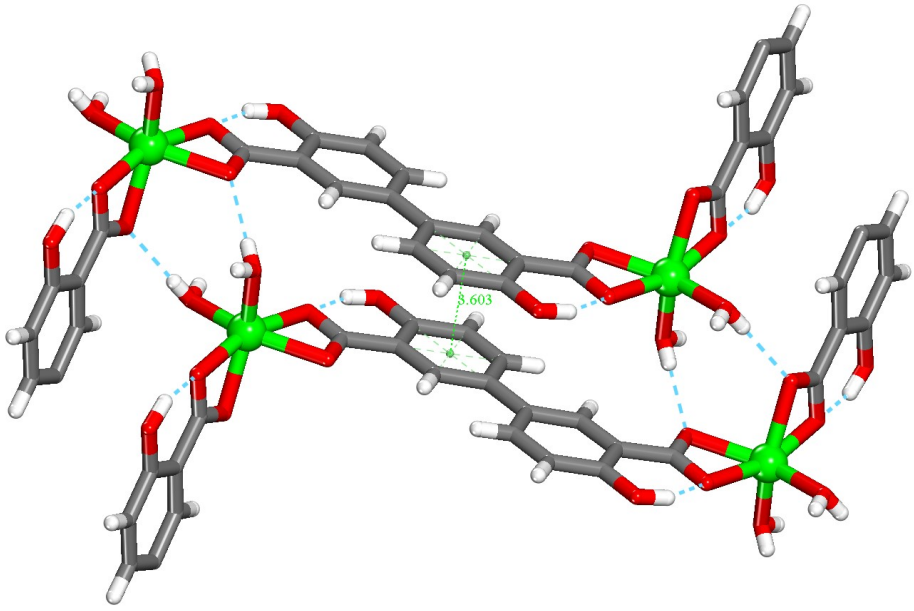


Figure S1. PXRD profiles of simulated and **1**.



(a)



(b)

Figure S2. Two types of extended structures of **1** (a) showing two neighboring chains entangled by hydrogen bonds among hydroxyl groups, carboxylate oxygens, and water molecules (sky blue lines), and (b) showing hydrogen bonds and π-π stacking interaction between benzene rings (green line).

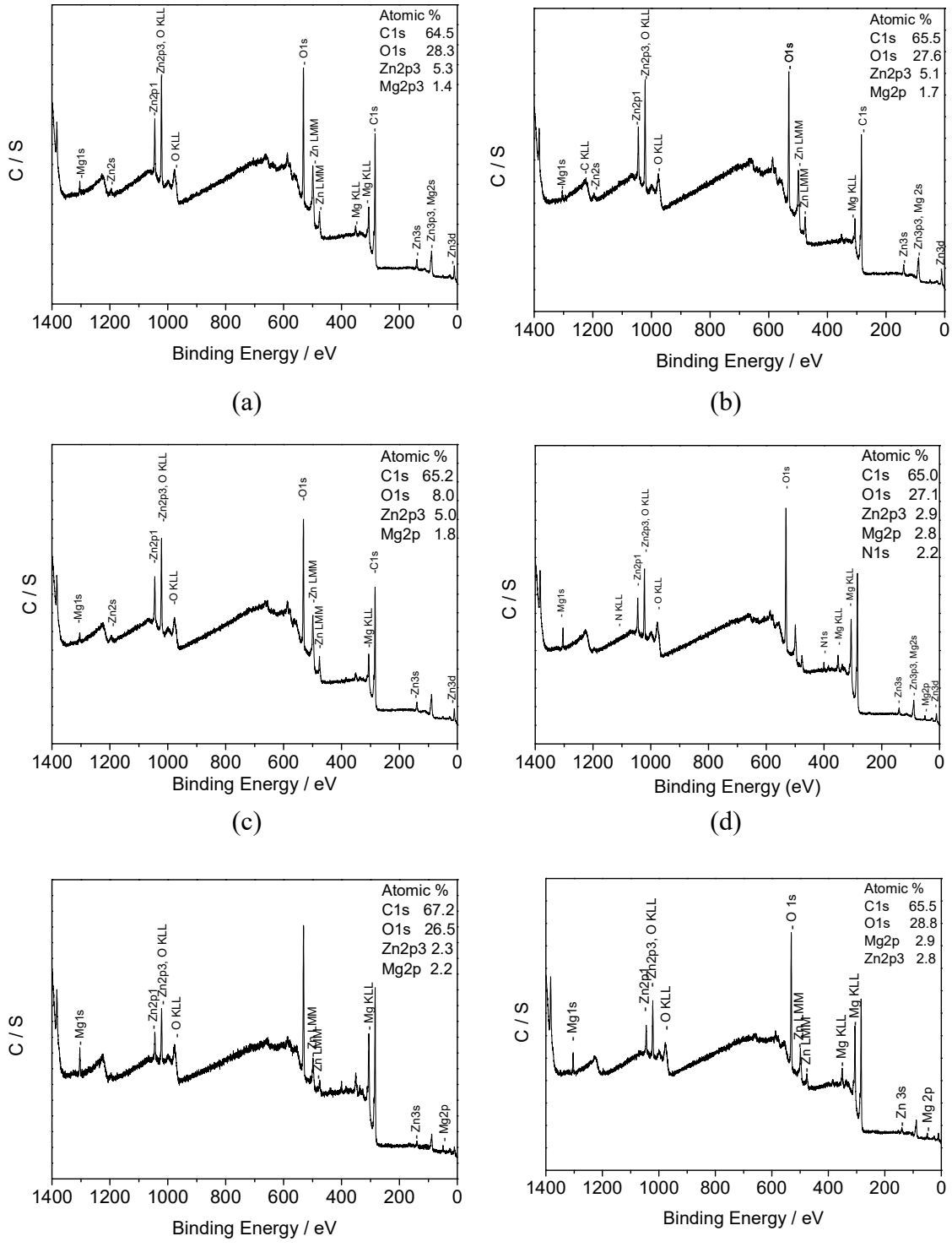


Figure S3. XPS data of the phases prepared in Mg:Zn ratio of (a) 1:1, (b) 2:1, (c) 3:1, (d) 3.5:1, (e) 6:1, and (f) 10:1. The solvothermal reaction of **1** with Mg^{2+} in DMF/EtOH was carried out at 130 ^{o}C for 3 h.

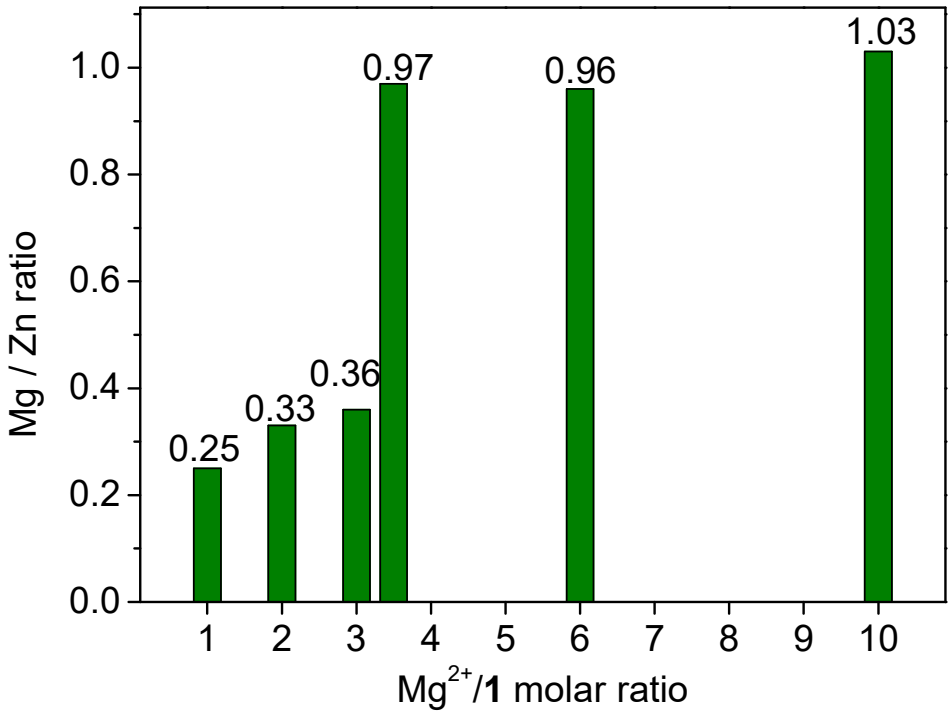
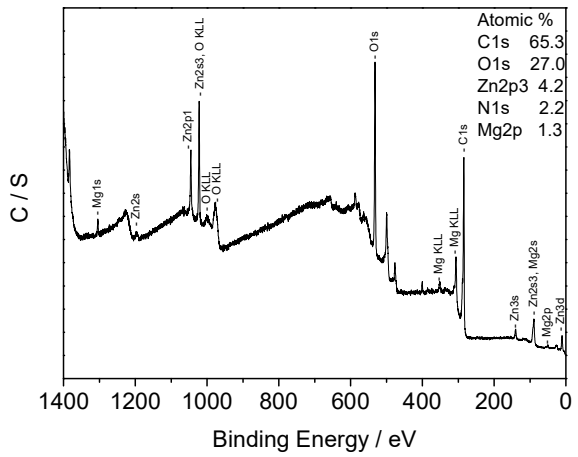


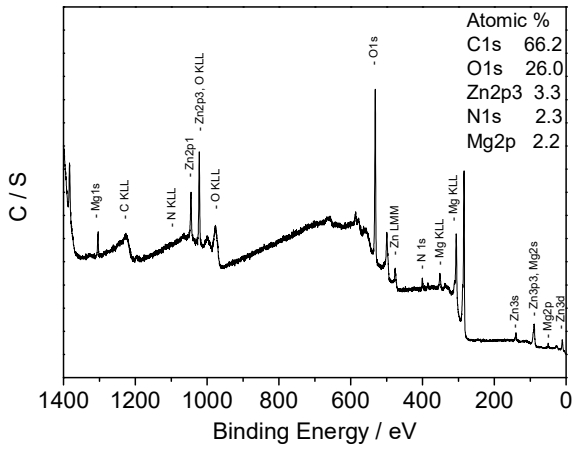
Figure S4. Ratio of Mg/Zn as a function of Mg^{2+}/**1** molar ratio. The compositional ratio was obtained by XPS data in Figure S3.

Table S1. ICP-AES results of Mg/Zn(dobpdc) for different reaction times.

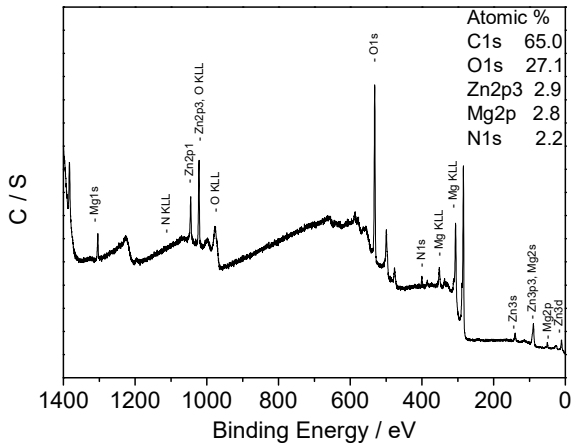
Reaction time	Mg (mmol L^{-1})	Zn (mmol L^{-1})	Mg/Zn
3 h	1806.8	2422.8	0.75
4 h	1554.8	1500.1	1.04
12 h	1642.7	1096.6	1.50



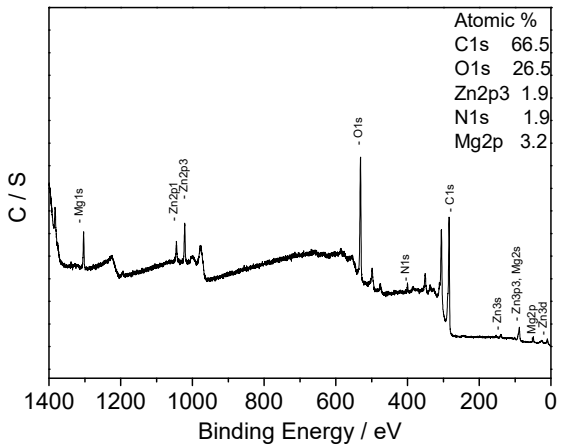
(a)



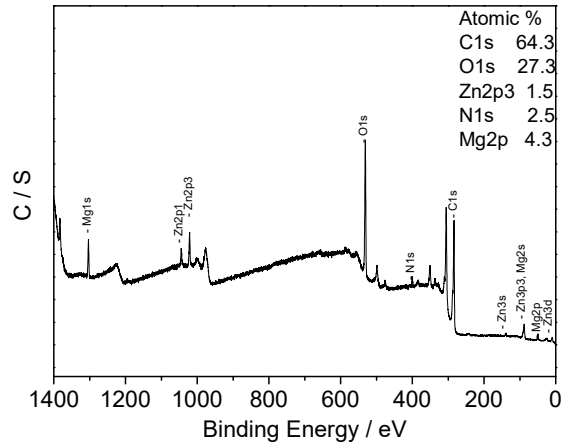
(b)



(c)



(d)



(e)

Figure S5. XPS data of the phases prepared by a solvothermal reaction of **1** with 3.5 equiv of Mg^{2+} for different reaction times: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, and (e) 12 h.

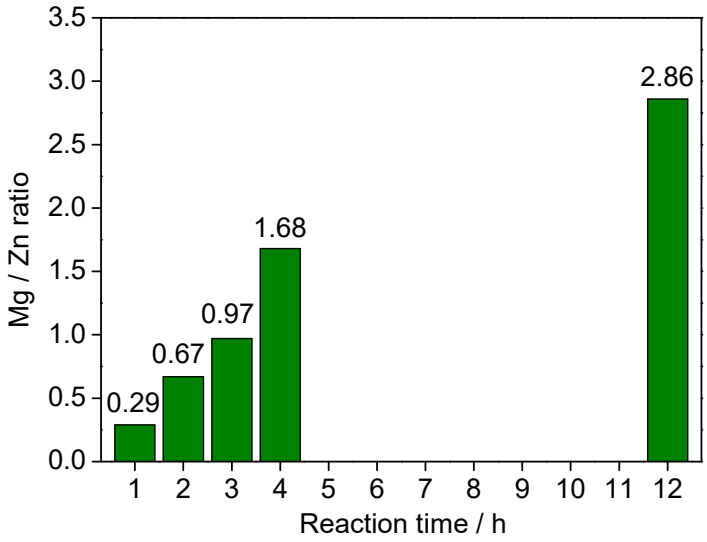


Figure S6. Mg/Zn ratio as a fucntion of reaction time. A 3.5 equiv of Mg^{2+} was reacted with compound **1** at 130 ^{o}C. The ratio was obtained using XPS data in Figure S5

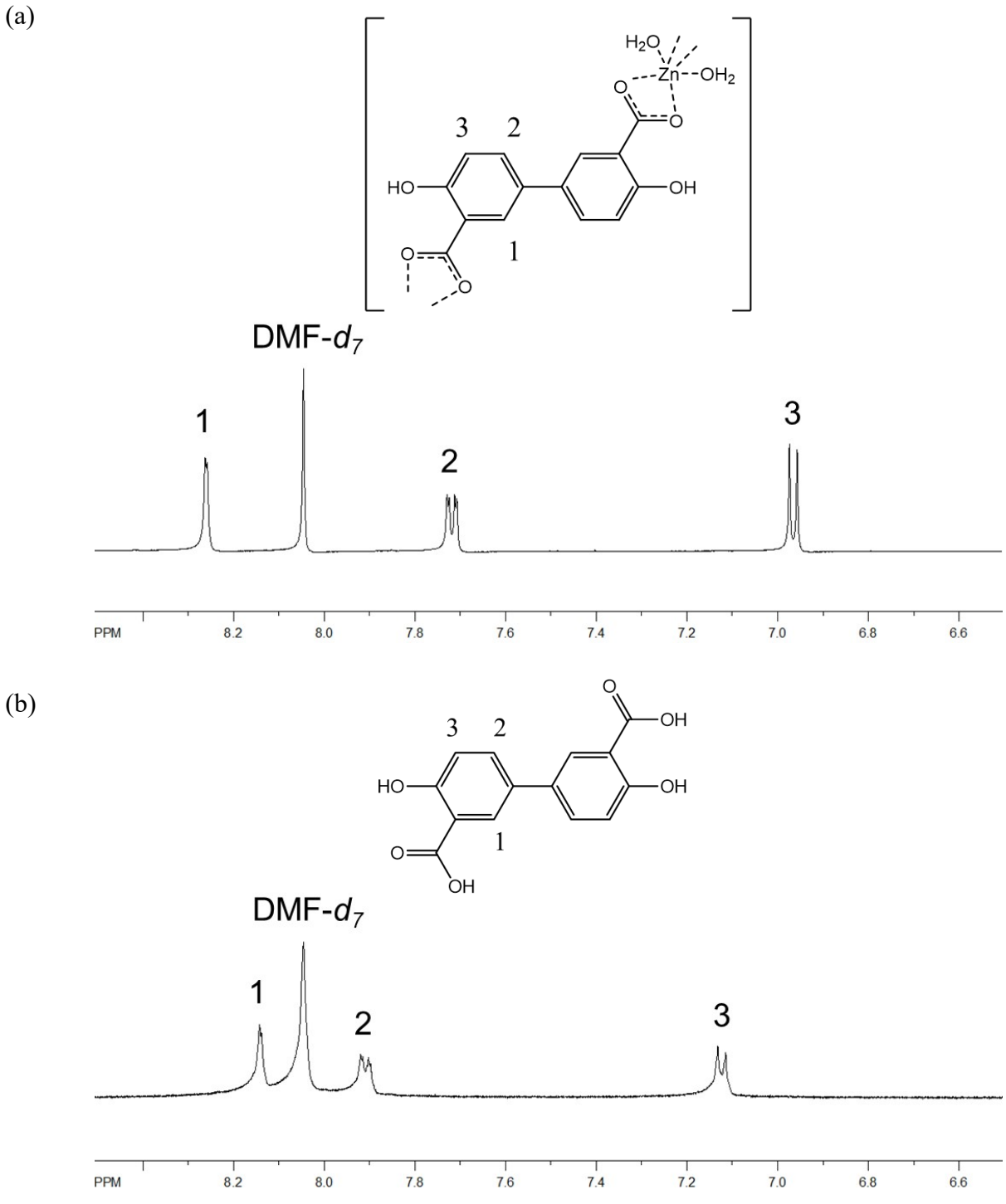
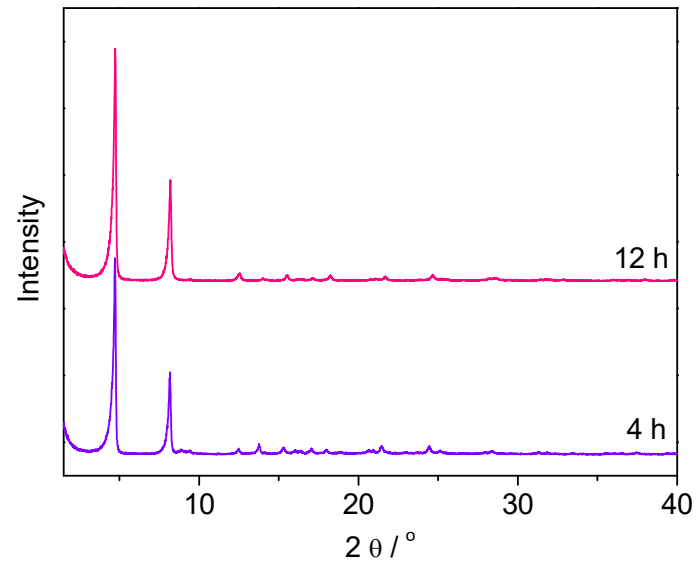
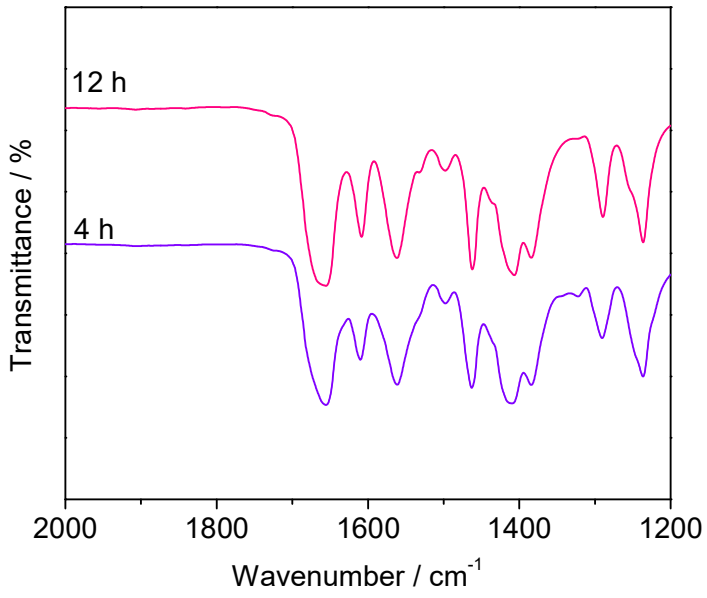


Figure S7. ^{1}H NMR of (a) **1** and (b) H_4dobpdc (NMR solvent: DMF-d_7).



(a)



(b)

Figure S8. (a) PXRD profiles and (b) IR spectra of Mg/Zn(dobpdc) after 4 and 12 h, formed by 1D precursor **1**.

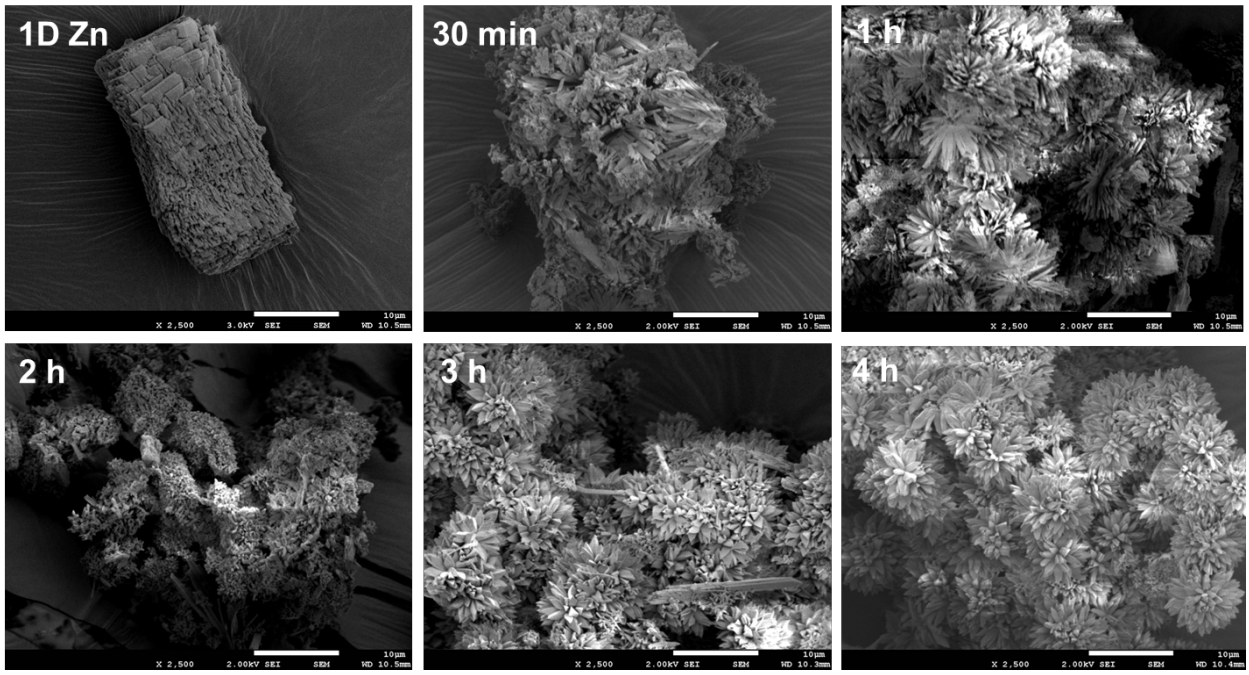


Figure S9. SEM images of intermidate phases during 1D-to-3D phase transformation. The images were collected at indicated reaction time.

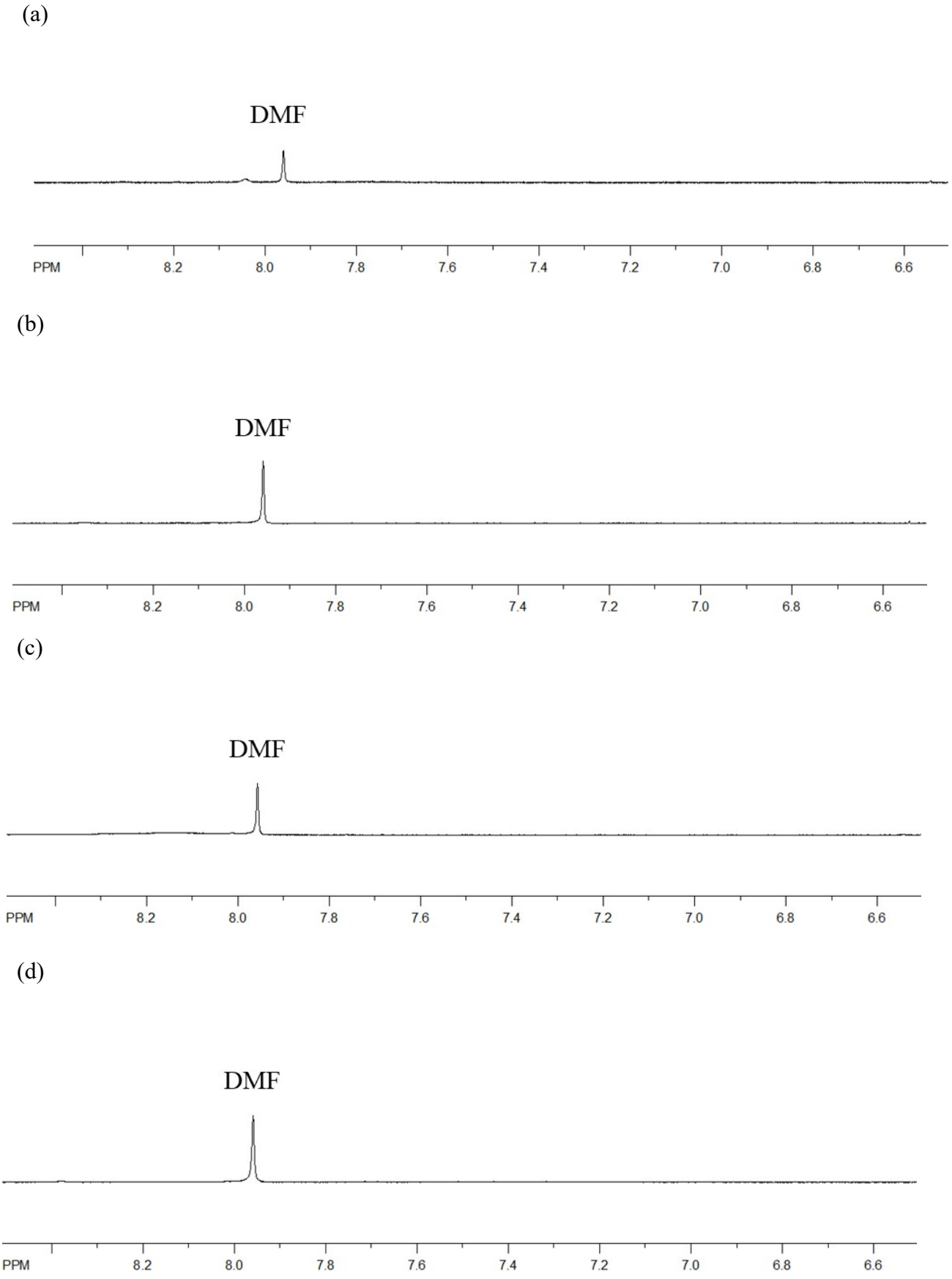
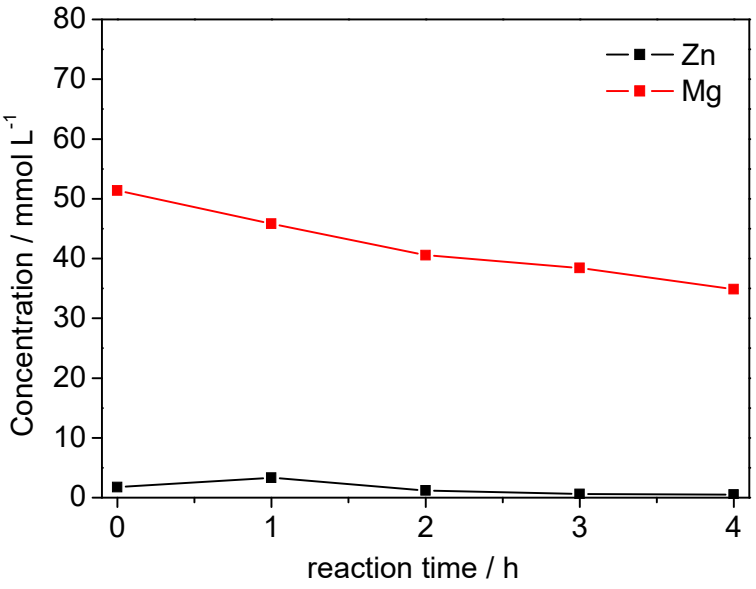
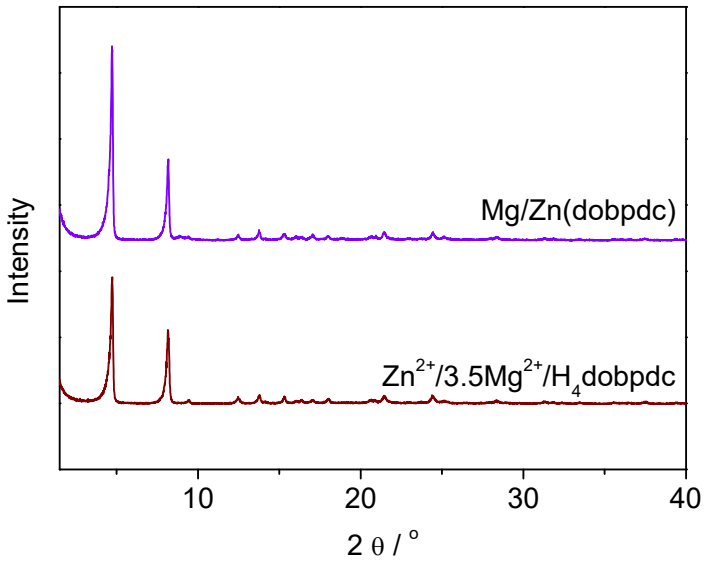


Figure S10. ^{1}H NMR of the reaction filtrates at different times: (a) 1 h, (b) 2 h, (c) 3 h, and (d) 4 h (NMR solvent: DMSO-d_6).

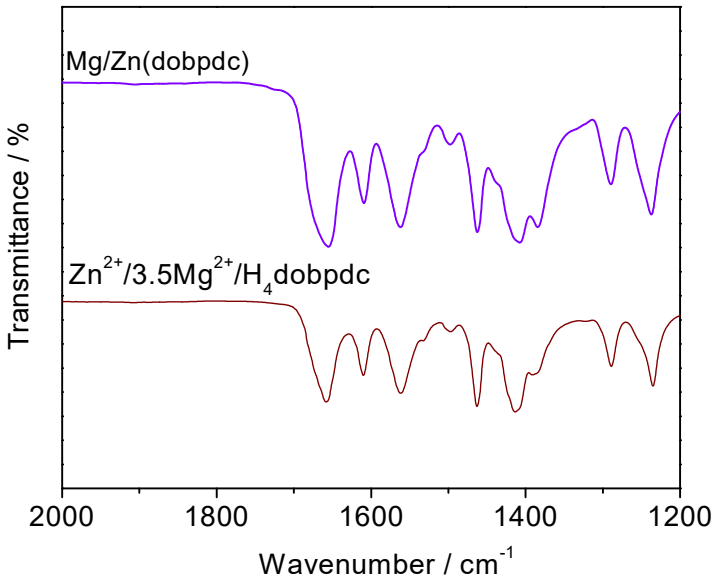


Reaction time	Mg (mmol L^{-1})	Zn (mmol L^{-1})
0 h	51.36	1.77
1 h	45.85	3.31
2 h	40.58	1.18
3 h	38.42	0.58
4 h	34.85	0.53

Figure S11. ICP-AES analysis of concentrations of Mg^{2+} and Zn^{2+} ions in the filtrate of Mg/Zn(dobpdc) after the reaction at different reaction times.

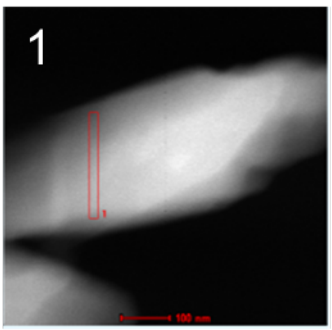


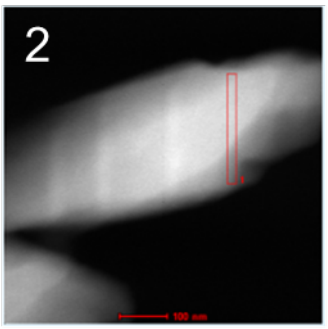
(a)

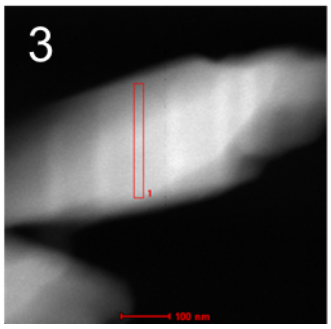


(b)

Figure S12. (a) PXRD profiles of Mg/Zn(dobpdc), and Zn^{2+}/3.5Mg^{2+}/H_4dobpdc for the solvothermal reaction of Mg^{2+} (3.5 equiv), Zn^{2+}(1 equiv), and H_4dobpdc (1 equiv) in DMF/EtOH at 130 ^{o}C for 4 h. (b) IR spectra of the corresponding samples.







Area	Mg/Zn
1	1.07
2	1.58
3	0.79

Figure S13. TEM-EDS images of Zn^{2+}/3.5Mg^{2+}/H_4dobpdc formed by the solvothermal reaction of Mg^{2+} (3.5 equiv), Zn^{2+} (1 equiv), and H_4dobpdc (1 equiv) in DMF/EtOH after 4 h

Table S2. ICP-AES results of Mg/Zn(dobpdc) and Zn^{2+}/3.5Mg^{2+}/H_4dobpdc .

	Reaction time	**Mg (mmol L^{-1})**	**Zn (mmol L^{-1})**	**Mg/Zn**
Mg/Zn(dobpdc)	4 h	1554.8	1500.1	1.04
Zn^{2+}/3.5Mg^{2+}/H_4dobpdc	4 h	2362.9	2004.6	1.18

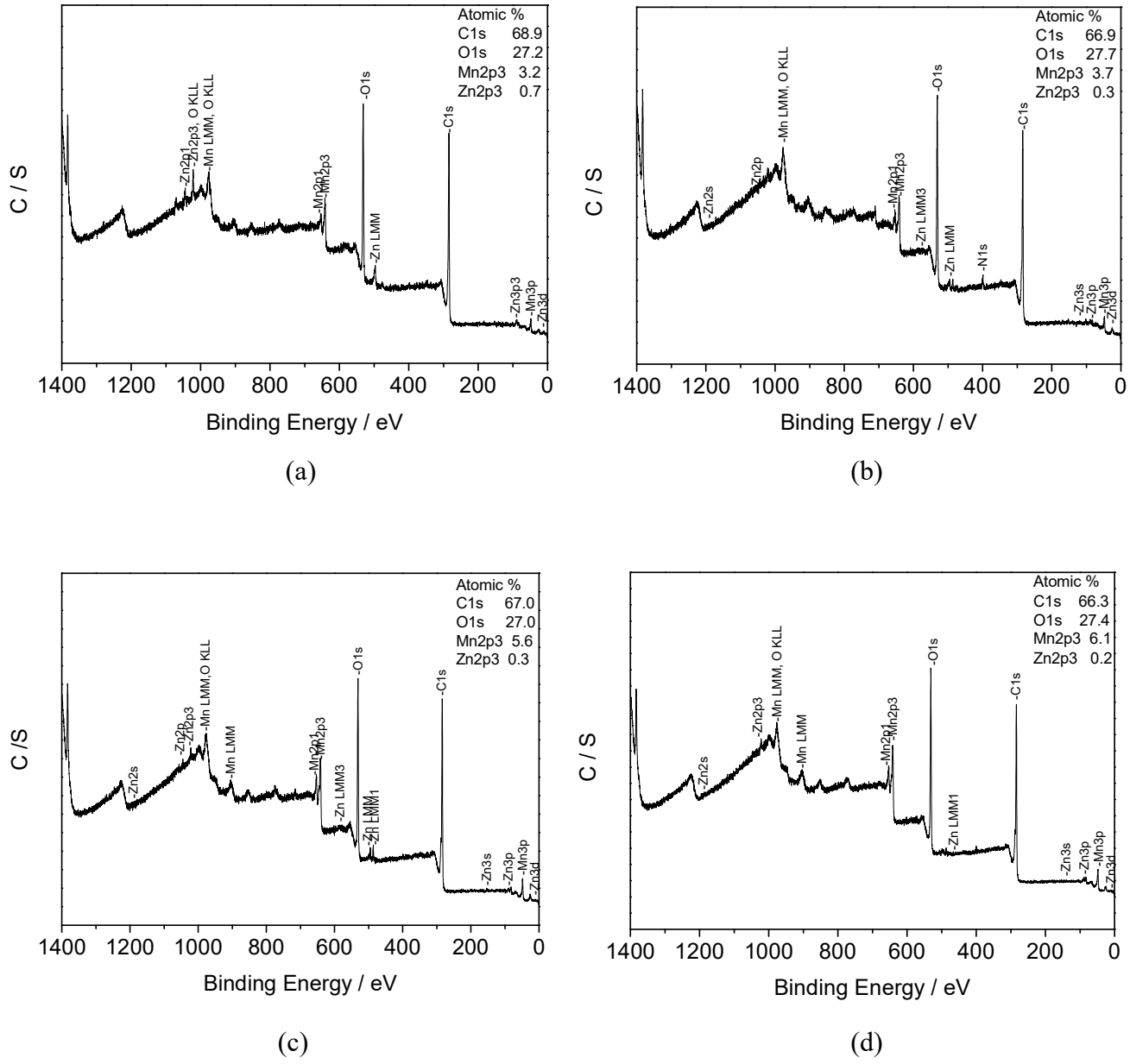


Figure S14. XPS data of the phases prepared in Mn:Zn ratio of (a) 1:1, (b) 2:1, (c) 3:1, and (d) 3.5:1. The solvothermal reaction of **1** with Mn^{2+} in DMF/EtOH was carried out at 130 ^{o}C for 3 h.

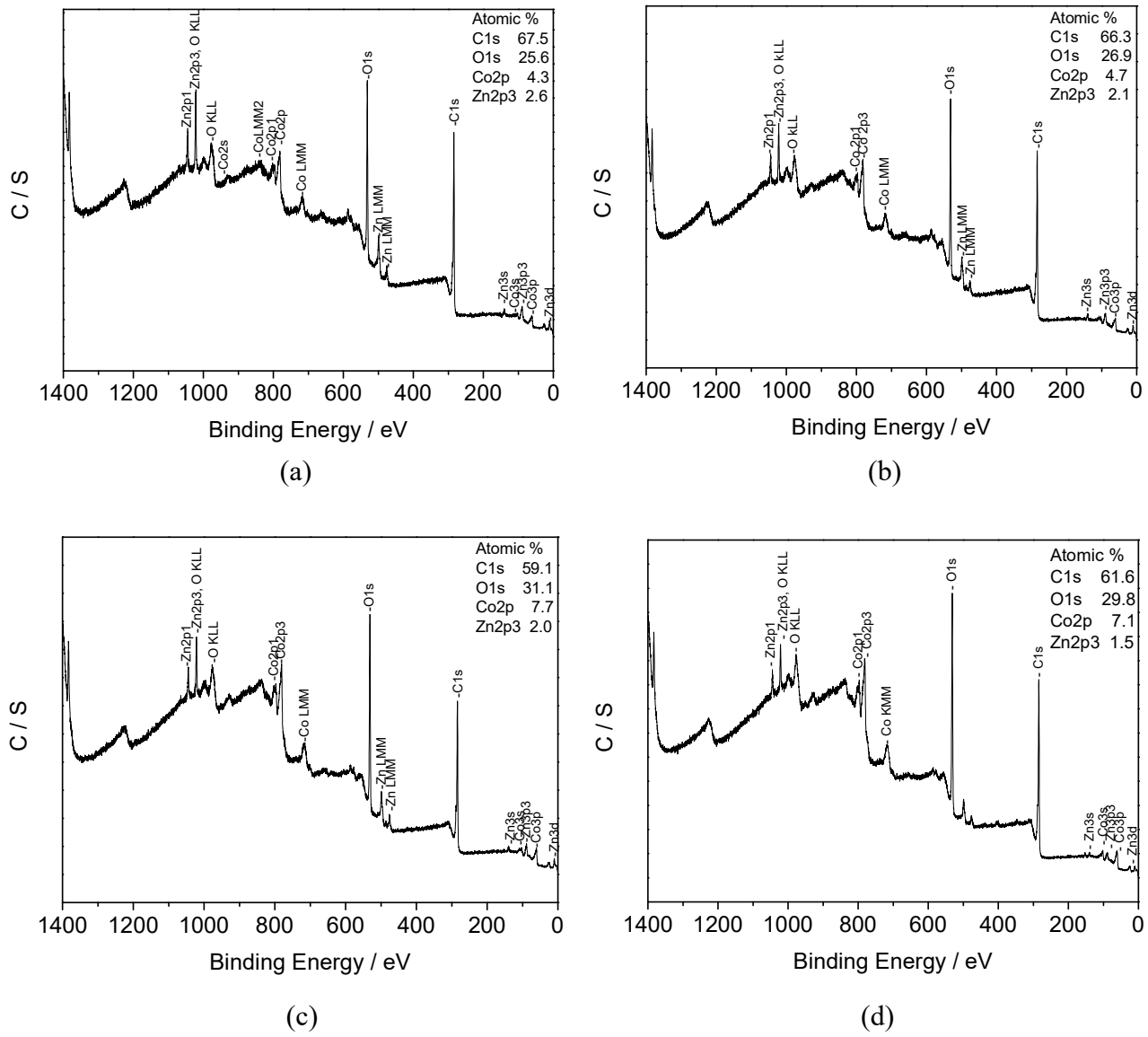


Figure S15. XPS data of the phases prepared in Co:Zn ratio of (a) 1:1, (b) 2:1, (c) 3:1, and (d) 3.5:1. The solvothermal reaction of **1** with Co^{2+} in DMF/EtOH was carried out at 130 ^{o}C for 3 h.

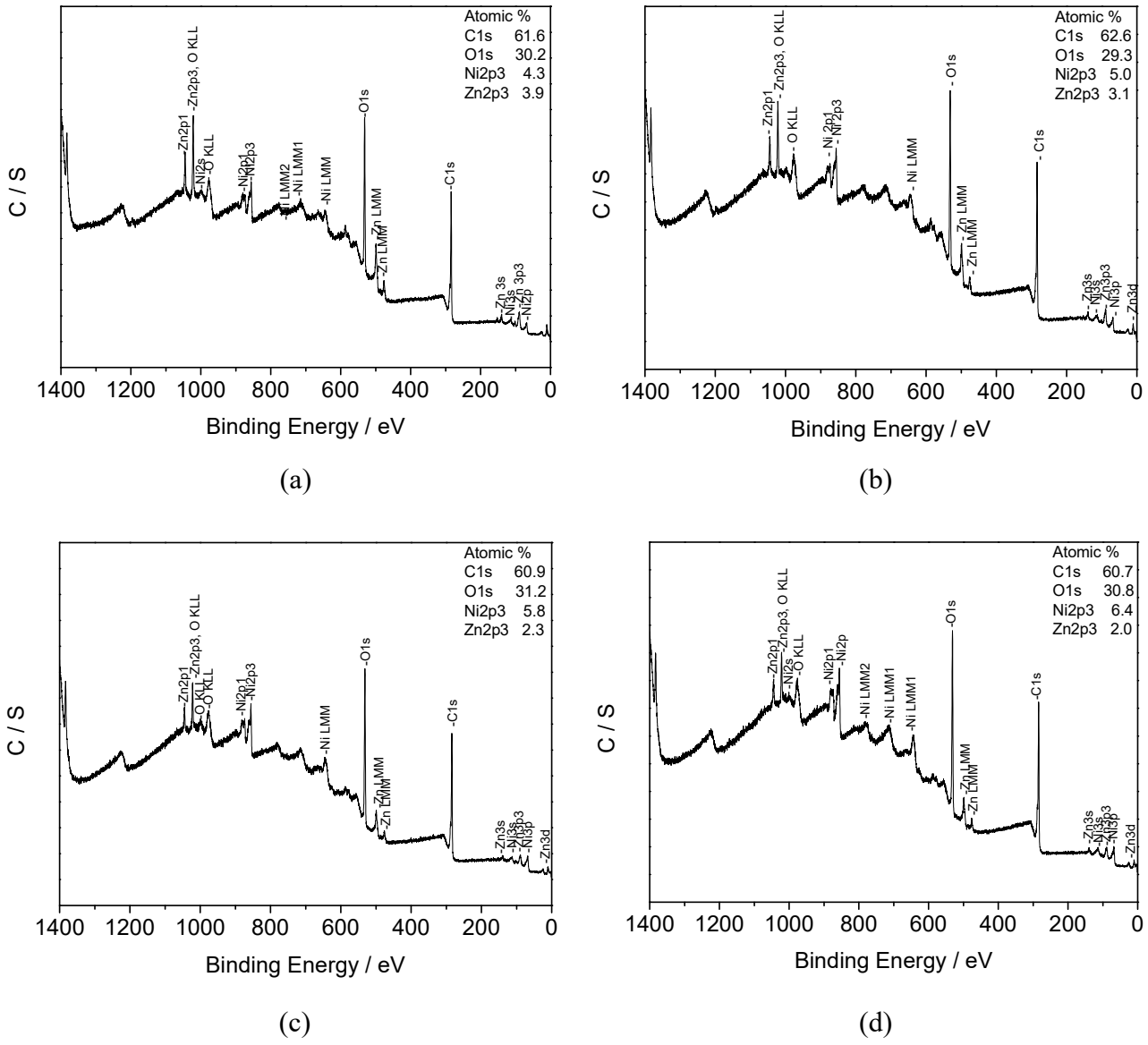


Figure S16. XPS data of the phases prepared in Ni:Zn ratio of (a) 1:1, (b) 2:1, (c) 3:1, and (d) 3.5:1. The solvothermal reaction of **1** with Ni^{2+} in DMF/EtOH was carried out at 130 ^{o}C for 3 h.

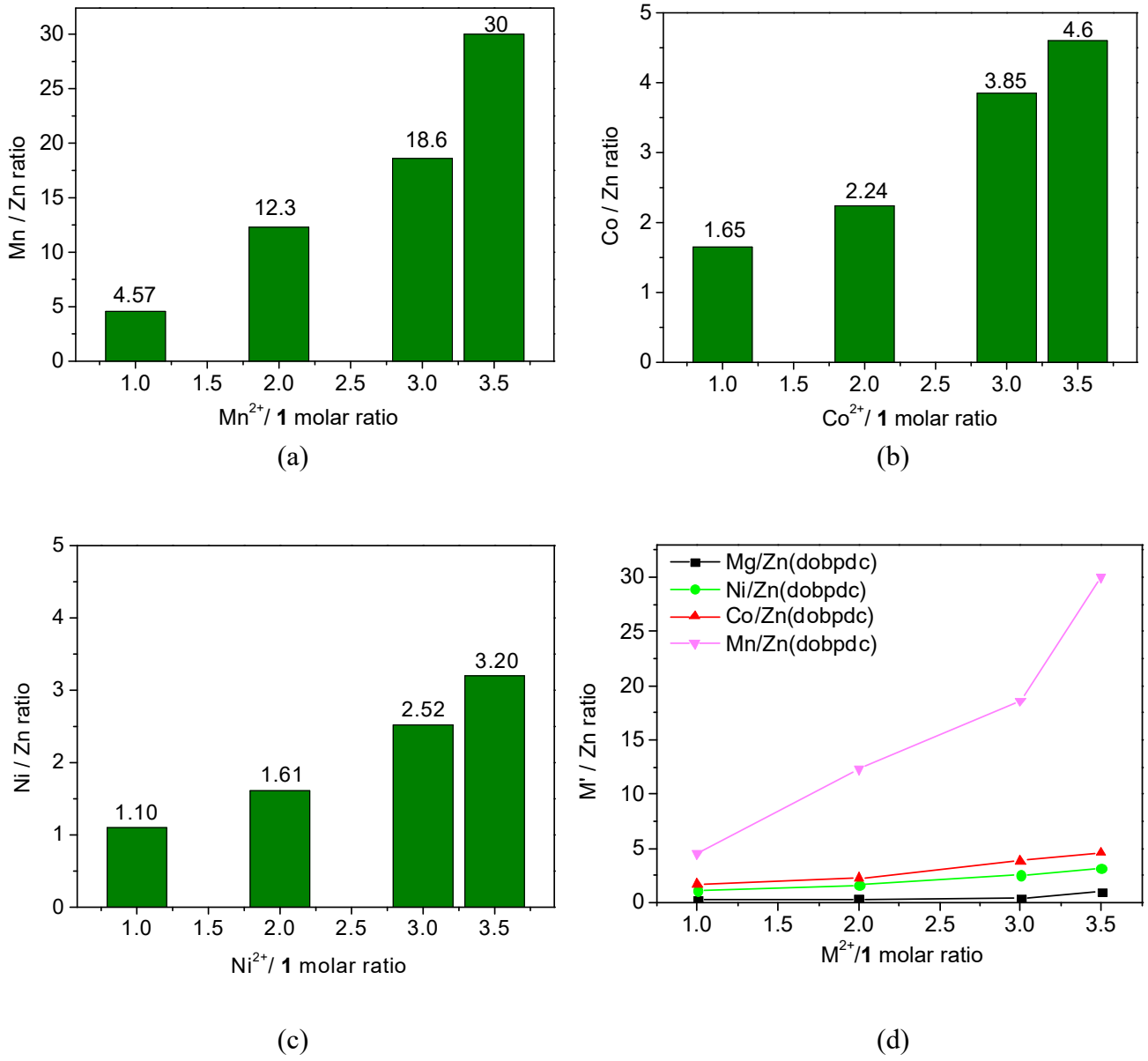


Figure S17. Ratio of M‘/Zn as a function of M^{2+}/**1** molar ratio: M‘ = Mn (a), Co (b), and Ni (c). (d) Plots of M‘/Zn ratio for the corresponding bimetallic frameworks. The compositional ratio was obtained by XPS data.

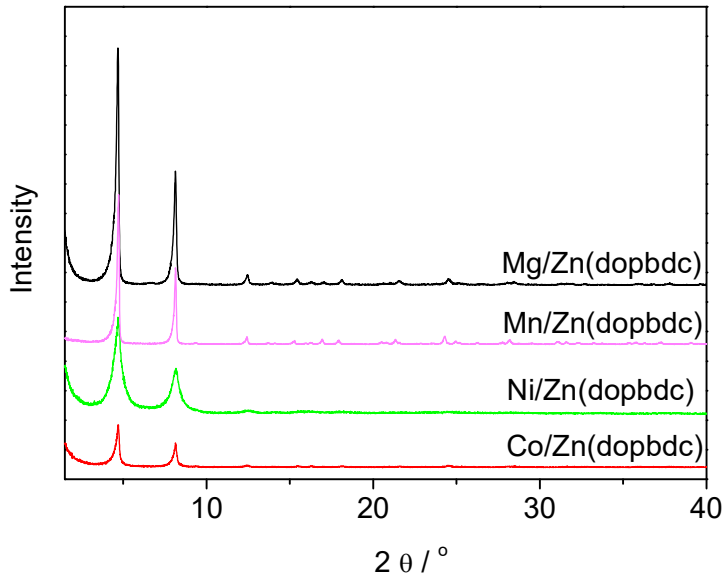
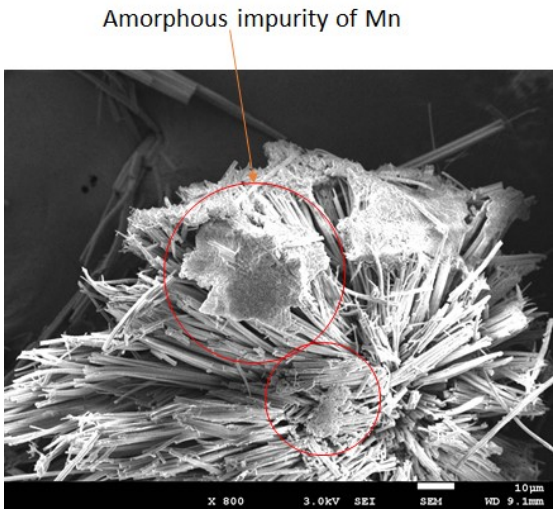
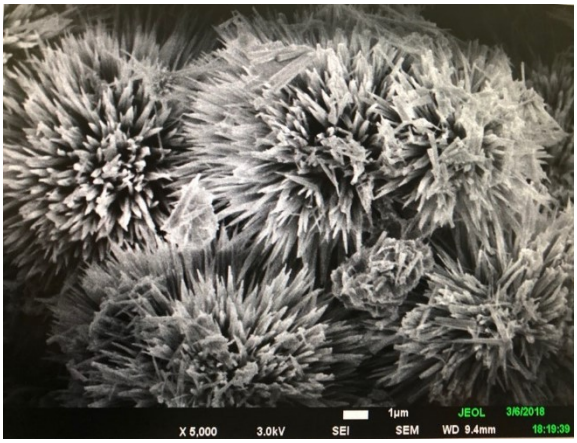


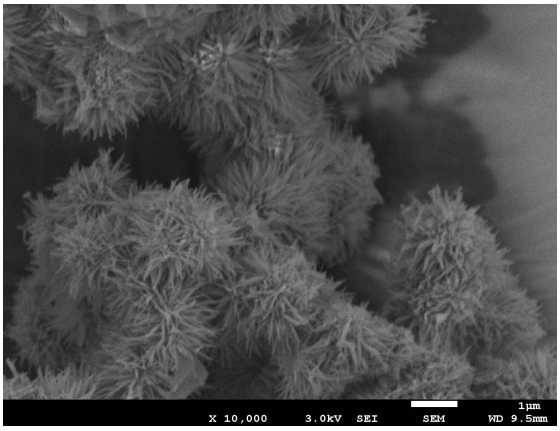
Figure S18. PXRD profiles of bimetallic frameworks prepared by the solvothermal reaction of **1** with 3.5 equiv of M^{2+} ions at 130 °C and 3 h.



(a)

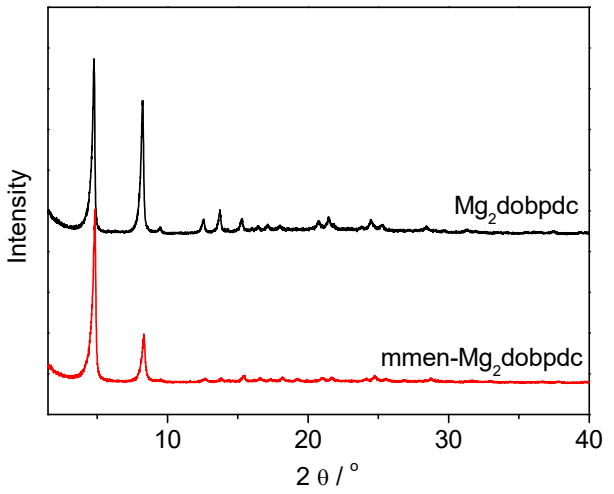


(b)

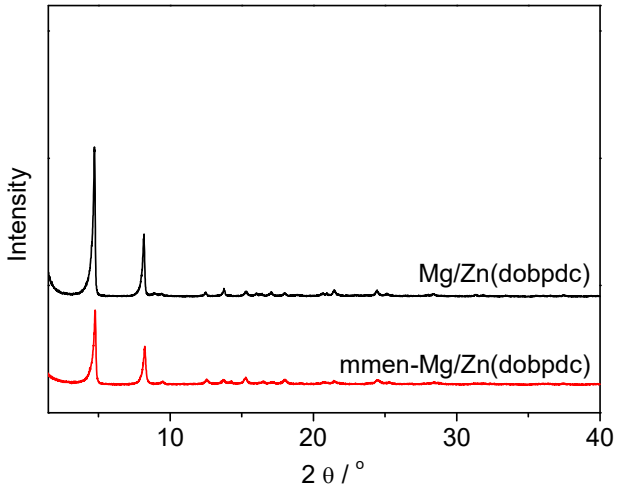


(c)

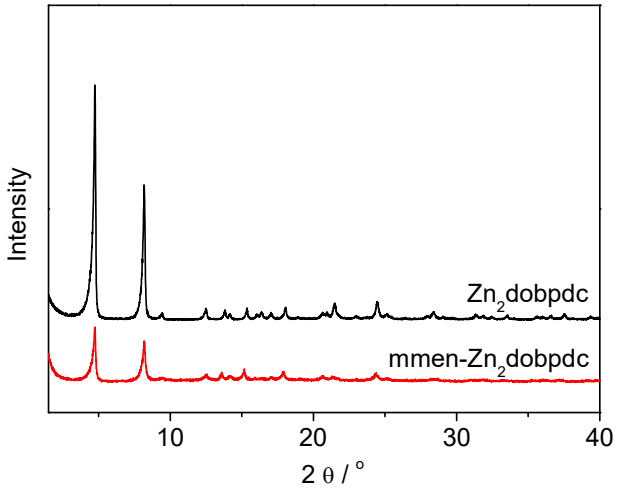
Figure S19. SEM images of (a) Mn/Zn(dobpdc), (b) Co/Zn(dobpdc), and (c) Ni/Zn(dobpdc). For the Mn-based bimetallic framework, amorphous impurities of Mn were present on the surface of crystals.



(a)



(b)



(c)

Figure S20. PXRD profiles of (a) Mg_2(dobpdc) and mmen-Mg_2(dobpdc), (b) Mg/Zn(dobpdc) and mmen-Mg/Zn(dobpdc), and (c) Zn_2(dobpdc) and mmen-Zn_2(dobpdc).

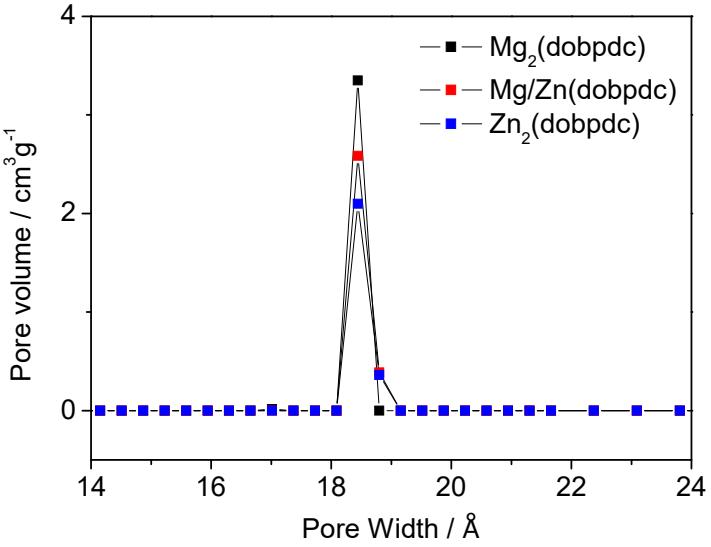
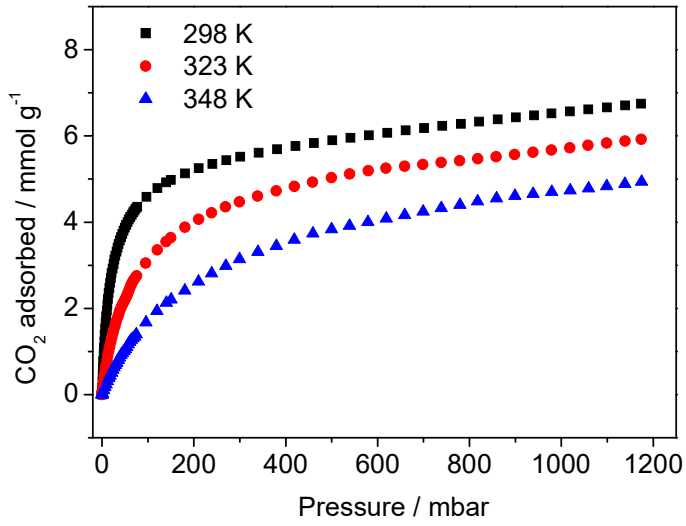
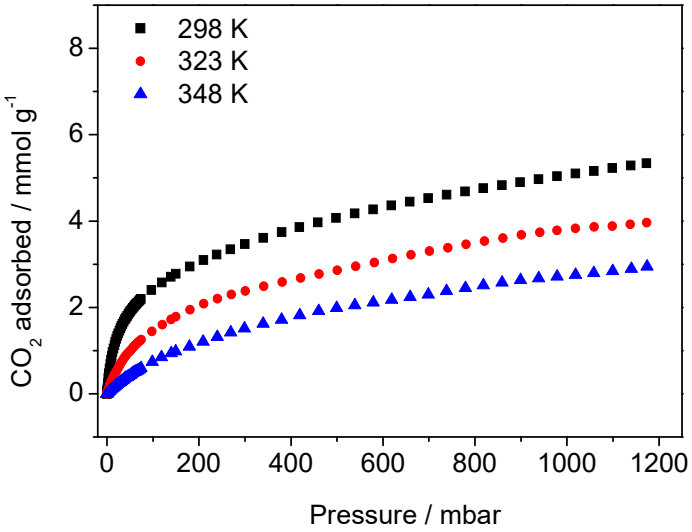


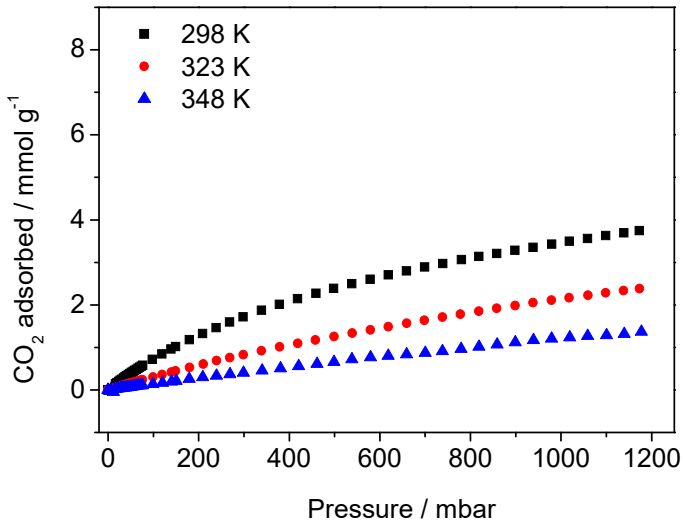
Figure S21. Pore size distribution images of Mg_2(dobpdc), Zn_2(dobpdc), and Mg/Zn(dobpdc).



(a)

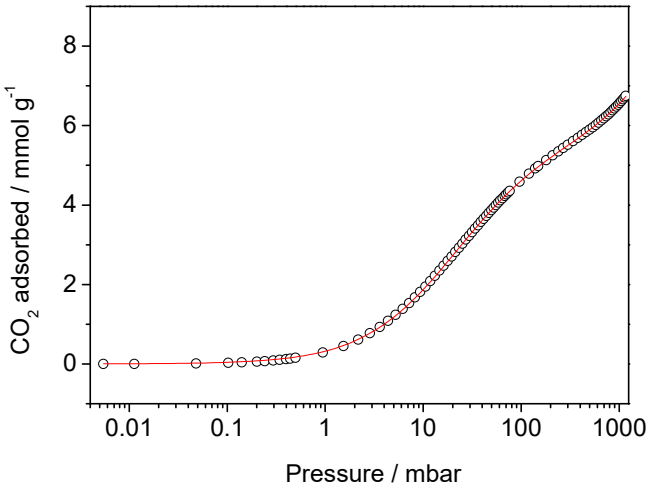


(b)

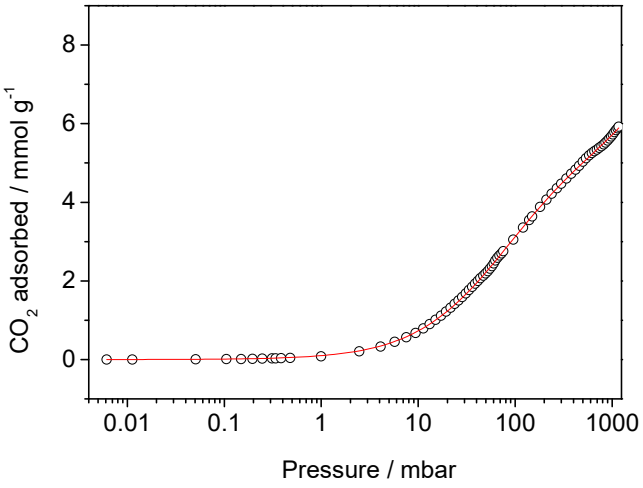


(c)

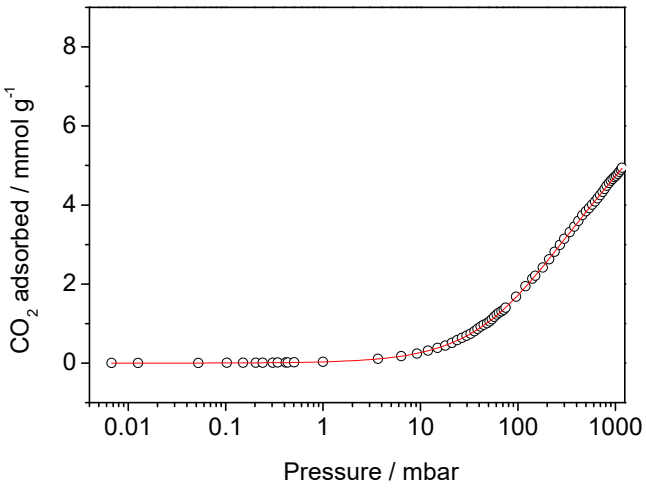
Figure. S22. CO_2 isotherms of (a) Mg_2(dobpdc), (b) Mg/Zn(dobpdc), and (c) Zn_2(dobpdc) at three different temperatures.



(a)

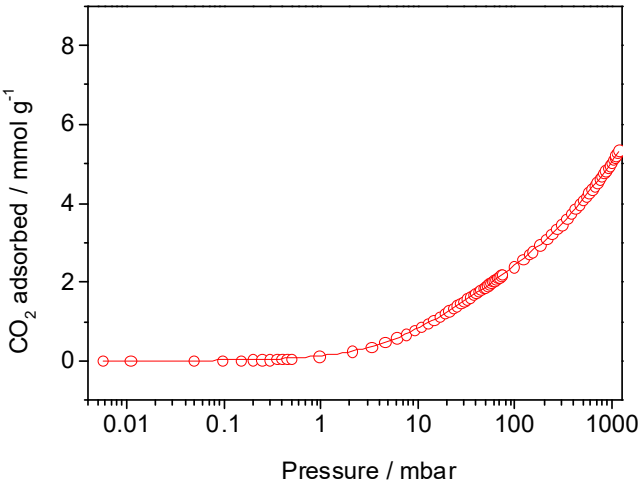


(b)

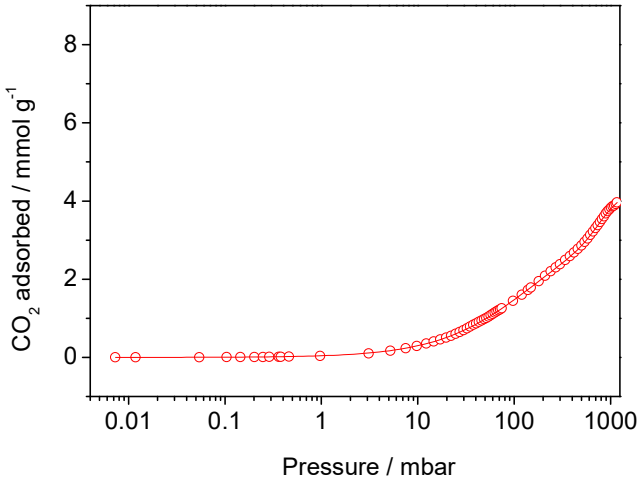


(c)

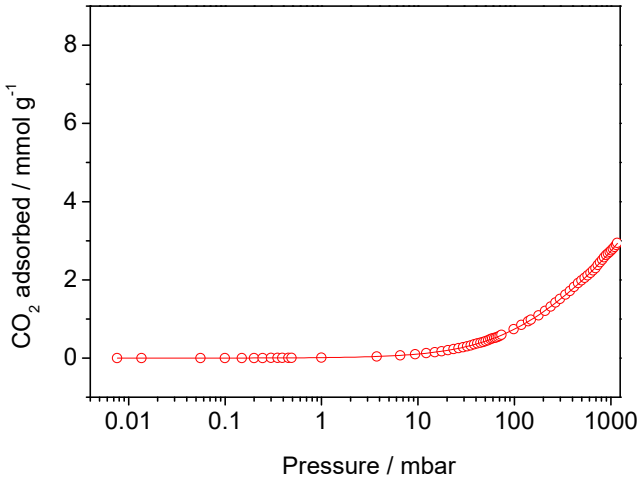
Figure S23. CO_2 adsorption isotherms of Mg_2(dobpdc) at (a) 298 K, (b) 323 K, and (c) 348 K, fitted by a dual-site Langmuir-Freundlich equation.



(a)

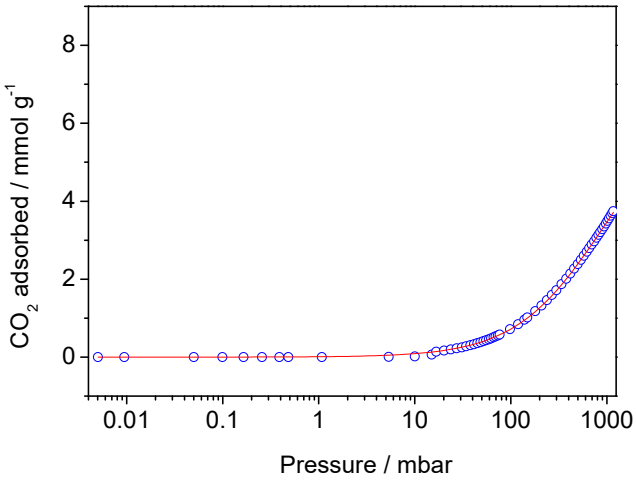


(b)

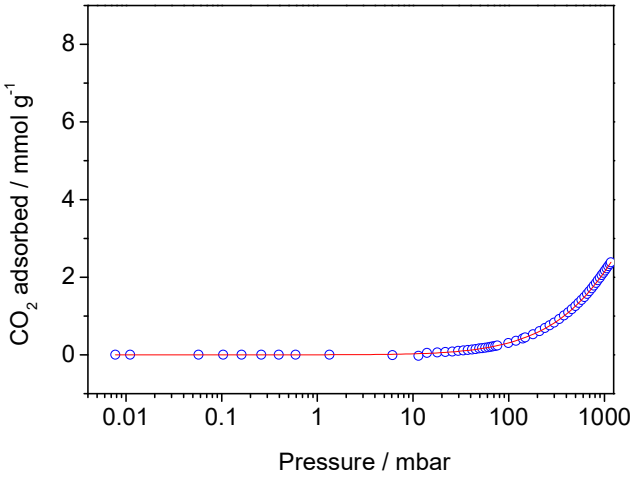


(c)

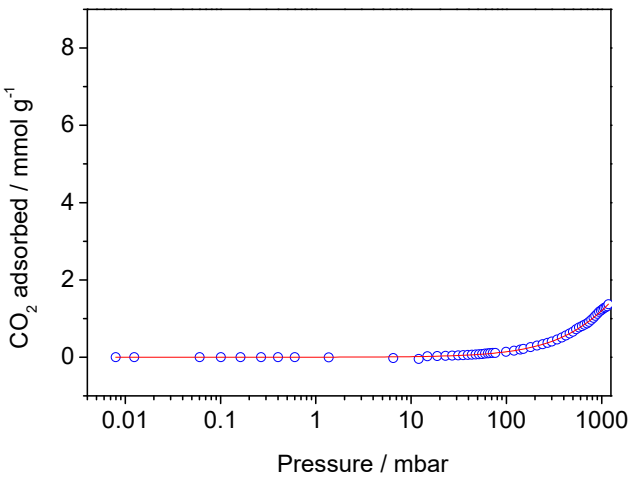
Figure S24. CO_2 adsorption isotherms of Mg/Zn(dobpdc) at (a) 298 K, (b) 323 K, and (c) 348 K, fitted by a dual-site Langmuir-Freundlich equation.



(a)

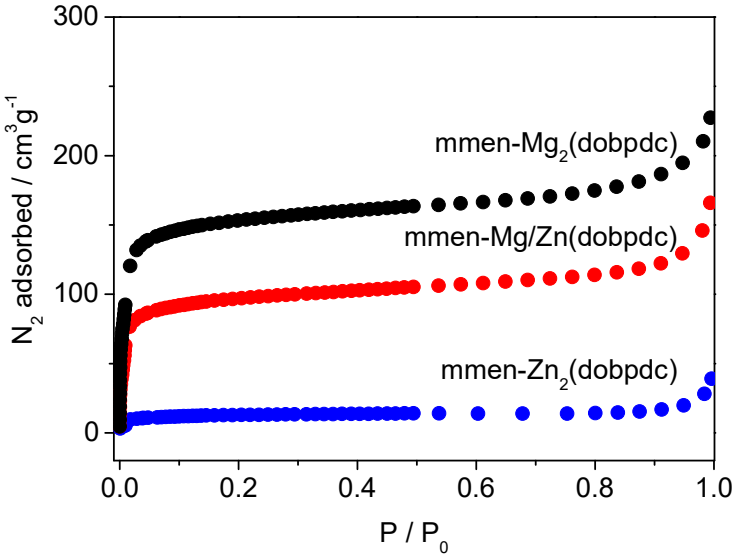


(b)

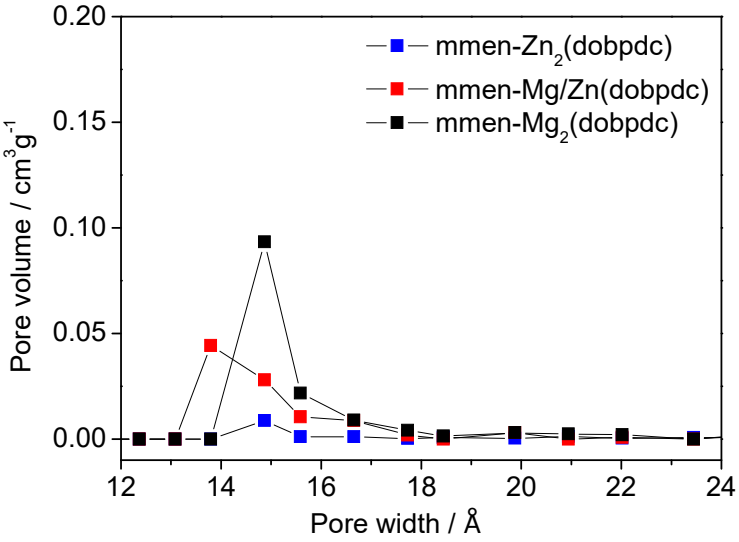


(c)

Figure S25. CO_2 adsorption isotherms of Zn_2(dobpdc) at (a) 298 K, (b) 323 K, and (c) 348 K, fitted by a dual-site Langmuir-Freundlich equation.



(a)



(b)

Figure S26. (a) N_2 isotherms of Mg_2(dobpdc), Mg/Zn(dobpdc), and Zn_2(dobpdc) at 77 K. (b) Pore size distribution of the corresponding samples estimated by DFT calculations. The BET suface areas corresponded to 604 m^2 g^{-1} for mmen-Mg_2(dobpdc), 378 m^2 g^{-1} for mmen-Mg/Zn(dobpdc), and 49 m^2 g^{-1} for mmen-Zn_2(dobpdc). These results could be associated with mmen loading, defect, and formula weight.

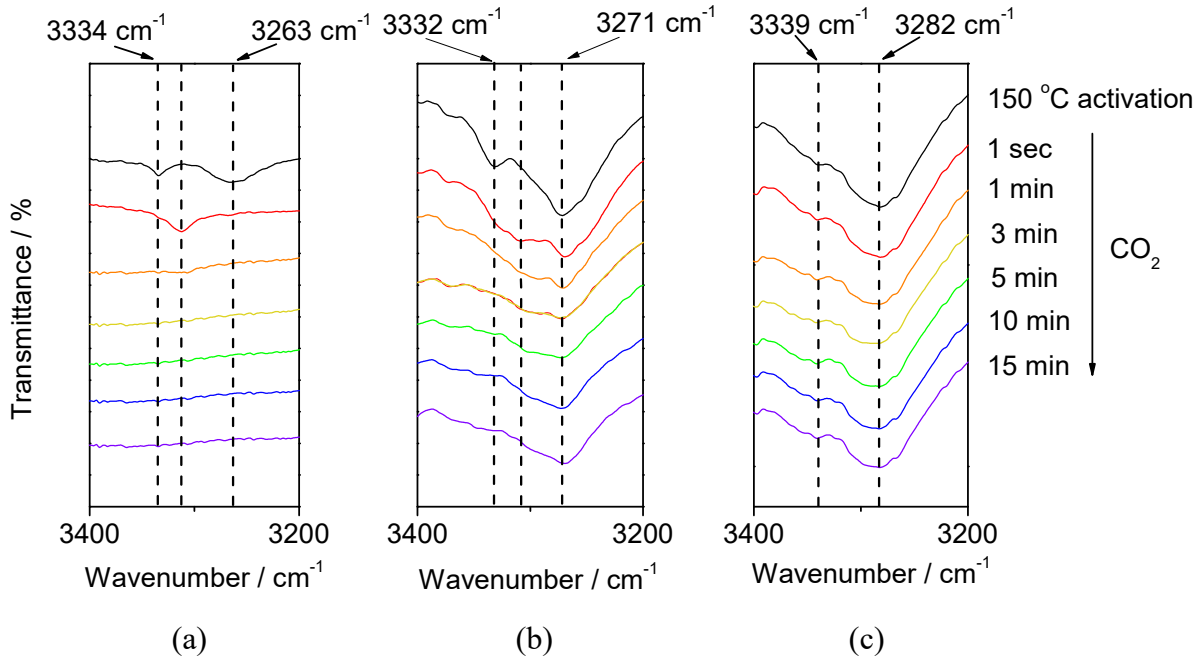


Figure S27. *In situ* IR spectroscopic data of (a) mmen-Mg_2(dobpdc), (b) mmen-Mg/Zn(dobpdc), and (c) mmen-Zn_2(dobpdc). During the measurements, the cell was isolated from the external environment by using an airtight IR cell (with KBr windows) and an oil bubbler.

References

(1) McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R., Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal-organic framework mmen-Mg2(dobpdc). *J. Am. Chem. Soc.* **2012,** *134* (16), 7056-65.
(2) Lee, W. R.; Hwang, S. Y.; Ryu, D. W.; Lim, K. S.; Han, S. S.; Moon, D. H.; Choi, J. K.; Hong, C. S., Diamine-functionalized metal–organic framework: exceptionally high CO 2 capacities from ambient air and flue gas, ultrafast CO 2 uptake rate, and adsorption mechanism. *Energy Environ. Sci.* **2014,** *7* (2), 744-751.
(3) Sheldrick, G. M., *SHELXTL,Version6.12, Bruker Analytical X-raySystems,Inc.,Madison,* **2000**.