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 (H₄dobpdc) was synthesized according to the literature procedure. ¹ ²

**Synthesis of [Zn(H₂dobpdc)(H₂O)₂]·0.2H₂O (1):** H₄dobpdc (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 ZnSO₄·7H₂O (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 precipitation. Yield: 0.45 g (64%). Elemental analysis (%) calcd for C₁₄H₁₂O₈Zn: C 44.58, H 3.31; found: C 44.38, H 3.35.

**Synthesis of M₂(dobpdc):**

[Mg₂(dobpdc)(DMF)₂]·1.6DMF·1.3H₂O [Mg₂(dobpdc)]: H₄dobpdc (86 mg, 0.36 mmol), Mg(NO₃)₂·6H₂O (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 °C 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 C₂₄₈H₃₃₈Mg₂N₃₆O₁₀₉: C 49.21, H 5.63, N 8.33; found: C 48.86, H 5.64, N 8.59.

[Zn₂(dobpdc)(DMF)₂]·1.6DMF·1.3H₂O [Zn₂(dobpdc)]: H₄dobpdc (86 mg, 0.36 mmol), Zn(NO₃)₂·6H₂O (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 °C 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 C₂₄₈H₃₃₈Zn₂N₃₆O₁₀₉: C 43.33, H 4.96, N 7.33; found: C 43.71, H 4.64, N 7.03.
Synthesis of bimetallic $[\text{Mg}_{1.08}\text{Zn}_{0.92}(\text{dobpdc})(\text{DMF})_2] \cdot 1.1\text{H}_2\text{O}$: H$_4$dobpdc (43 mg, 0.16 mmol), Mg(NO$_3$)$_2$·6H$_2$O (140 mg, 0.56 mmol), Zn(NO$_3$)$_2$·6H$_2$O (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 °C 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$_2$O$_{9.1}$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:

$[\text{Mg}_{1.02}\text{Zn}_{0.98}(\text{dobpdc})(\text{DMF})_2] \cdot \text{1DMF}_{0.5}\text{H}_2\text{O} \ [\text{Mg/Zn}(\text{dobpdc})]$: Polymer 1 (66.5 mg, 0.178 mmol), Mg(NO$_3$)$_2$·6H$_2$O (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 °C 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$_3$O$_{9.5}$: 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.

$[\text{Mg}_{1.2}\text{Zn}_{0.8}(\text{dobpdc})(\text{DMF})_2] \cdot 2.3\text{DMF} \cdot \text{1H}_2\text{O}$: 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$_4$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 $[\text{Mn/Zn}(\text{dobpdc})]$: This compound was prepared according to the synthetic procedure similar to Mg/Zn(dobpdc) except for the use of MnCl$_2$·4H$_2$O. The metal composition was checked by XPS.

Co/Zn phase $[\text{Co/Zn}(\text{dobpdc})]$: This compound was prepared according to the synthetic procedure similar to Mg/Zn(dobpdc) except for the use of Co(NO$_3$)$_2$·6H$_2$O. 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(NO₃)₂·6H₂O. The metal composition was checked by XPS.

Synthesis of mmen-M₂(dobpdc) and of mmen-Mg/Zn(dobpdc):

[Mg₂(dobpdc)(mmen)₁.₅₈(H₂O)₀.₄₂]·₂.₉₈H₂O [mmen-Mg₂(dobpdc)]: The solid Mg₂(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’-Dimethylethlyenediamine (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 C₂₀.₃₂H₃₁.₇₆Mg₂N₃.₁₆O₉.₄: 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.

[Zn₂(dobpdc)(mmen)₁.₅(H₂O)₀.₅]·₀.₇H₂O [mmen-Zn₂(dobpdc)]: This compound was prepared according to the synthetic procedure similar to mmen-Mg₂(dobpdc) except for the use of Zn₂(dobpdc). Yield: 183 mg (98.3%). Elemental analysis (%) calcd for C₂₀H₂₆₄Zn₂N₃O₇.₂: 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.

[Mg₁.₀₂Zn₀.₉₈(dobpdc)(mmen)₁.₇(H₂O)₀.₃]·₁.₂H₂O (mmen-Mg/Zn(dobpdc)]: This compound was prepared according to the synthetic procedure similar to mmen-Mg₂(dobpdc) except for the use of Mg/Zn(dobpdc) synthesized by polymer 1. Yield: 173 mg (98.1%). Elemental analysis (%) calcd for C₂₀.₈₂H₂₉.₄Mg₁.₀₂Zn₀.₉₈N₃.₄O₇.₅: 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 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\textsubscript{2} (99.999\%) and CO\textsubscript{2} (99.999\%) were used in the sorption experiments. The N\textsubscript{2} and CO\textsubscript{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\textsubscript{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.\textsuperscript{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\textsubscript{14}H\textsubscript{12}O\textsubscript{8}Zn, \( M_r = 373.61 \), \( T = 100(2) \) K, space group = \( P2_1/c \), \( a = 8.4040(17) \) Å, \( b = 5.2320(10) \) Å, \( c = 15.513(3) \) Å, \( \beta = 103.76(3)^\circ \), \( V = 662.5(2) \) Å\textsuperscript{3}, \( Z = 2 \), \( D_{calc} = 1.873 \) g cm\textsuperscript{-3}, \( \mu = 1.898 \) mm\textsuperscript{-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.
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 °C for 3 h.
**Figure S4.** Ratio of Mg/Zn as a function of Mg$^{2+}$/I 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.

<table>
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<tr>
<th>Reaction time</th>
<th>Mg (mmol L$^{-1}$)</th>
<th>Zn (mmol L$^{-1}$)</th>
<th>Mg/Zn</th>
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<tr>
<td>3 h</td>
<td>1806.8</td>
<td>2422.8</td>
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<td>4 h</td>
<td>1554.8</td>
<td>1500.1</td>
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<tr>
<td>12 h</td>
<td>1642.7</td>
<td>1096.6</td>
<td>1.50</td>
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Figure S5. XPS data of the phases prepared by a solvothermal reaction of 1 with 3.5 equiv of Mg²⁺ 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 function of reaction time. A 3.5 equiv of Mg$^{2+}$ was reacted with compound 1 at 130°C. The ratio was obtained using XPS data in Figure S5.
Figure S7. $^1$H NMR of (a) 1 and (b) H$_4$dobpdc (NMR solvent: DMF-$d_7$).
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 intermediate 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$_6$).
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.
Figure S12. (a) PXRD profiles of Mg/Zn(dobpdc), and Zn$^{2+}$/3.5Mg$^{2+}$/H$_4$dobpdc for the solvothermal reaction of Mg$^{2+}$ (3.5 equiv), Zn$^{2+}$ (1 equiv), and H$_4$dobpdc (1 equiv) in DMF/EtOH at 130 °C for 4 h. (b) IR spectra of the corresponding samples.
**Figure S13.** TEM-EDS images of Zn$^{2+}$/3.5Mg$^{2+}$/H$_4$dobpdc formed by the solvothermal reaction of Mg$^{2+}$ (3.5 equiv), Zn$^{2+}$ (1 equiv), and H$_4$dobpdc (1 equiv) in DMF/EtOH after 4 h

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<th>Area</th>
<th>Mg/Zn</th>
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<td>1</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>1.58</td>
</tr>
<tr>
<td>3</td>
<td>0.79</td>
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**Table S2.** ICP-AES results of Mg/Zn(dobpdc) and Zn$^{2+}$/3.5Mg$^{2+}$/H$_4$dobpdc.

<table>
<thead>
<tr>
<th></th>
<th>Reaction time</th>
<th>Mg (mmol L$^{-1}$)</th>
<th>Zn (mmol L$^{-1}$)</th>
<th>Mg/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/Zn(dobpdc)</td>
<td>4 h</td>
<td>1554.8</td>
<td>1500.1</td>
<td>1.04</td>
</tr>
<tr>
<td>Zn$^{2+}$/3.5Mg$^{2+}$/H$_4$dobpdc</td>
<td>4 h</td>
<td>2362.9</td>
<td>2004.6</td>
<td>1.18</td>
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**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 °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 °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 °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.
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.
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).
Figure S22. CO$_2$ isotherms of (a) Mg$_2$(dobpdc), (b) Mg/Zn(dobpdc), and (c) Zn$_2$(dobpdc) at three different temperatures.
**Figure S23.** \(\text{CO}_2\) 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.
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.
**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.
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 surface 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

