Supplementary Information

Efficient approach to modulate the coordination number of yttrium ion for diverse network formation

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1: General experimental information

Yttrium nitrate hydrate (Y(NO$_3$)$_3$:xH$_2$O) (Sigma Aldrich, 99.8% trace metal basis), 2,6-naphthalene dicarboxylic acid (H$_2$NDC) (TCI, >98.0% (GC)), N,N-dimethylformamide (Samchun, 99.0%) were purchased from commercial sources and used without further purification and deionized water (Milli-Q System, Millipore, Billerica, MA, USA) was used. All crystallization processes were conducted in a thermal oven (OF-11E, JEIOTECH, Korea). The photoluminescence (PL) images and spectra were obtained using a fluorescence microscope (Olympus microscope) and spectrometer (SpectraPro, Prineton Instruments) equipped with a filter set (Exciter BP 330 – 380 nm; beam splitter 400 nm; Emitter LP 410 nm, Semrock). Powder X-ray diffraction data was obtained from synchrotron X-ray source (PAL 5D beamline) with 1.23992 Å. Note that the two theta values were rescaled to the conventional wavelength (Cu Kα= 1.54057 Å) for a better comparison with reference data.

2: Syntheses

**Synthesis of Y7-MOF, [Y$_2$NDC$_3$(C$_3$H$_7$NO)$_2$]:** Y(NO$_3$)$_3$:xH$_2$O (38.30 mg, 0.1 mmol) was dissolved in 1:1 mixture of DMF/DI water (4 mL). H$_2$NDC (12.21 mg, 0.05 mmol) was dissolved in DMF (2 mL). The yttrium nitrate solution was slowly added into a 20 mL scintillation vial that contains the H$_2$NDC solution. The reaction mixture was sealed and placed in the thermal oven at 80°C for 48 hours, after which colorless stubby rod crystals were found on the bottom of the vial (16.2 mg, 85.4%).

**Synthesis of Y9-MOF, [Y$_2$NDC$_3$(C$_3$H$_7$NO)$_4$]-2H$_2$O:** Y(NO$_3$)$_3$:xH$_2$O (38.30 mg, 0.1 mmol) was dissolved in DMF (3 mL). H$_2$NDC (12.21 mg, 0.05 mmol) was dissolved in DMF (3 mL). The yttrium nitrate solution was slowly added into the H$_2$NDC solution. The reaction mixture was sealed and placed in the thermal oven at 80°C for 48 hours, after which colorless rectangular, plate shaped crystals were found on the bottom of the vial (9.4 mg, 37%).
3: Single crystal X-ray structure determination

The X-ray diffraction data for Y7-MOF and Y9-MOF were recorded on an ADSC Q210 CCD area detector with a synchrotron radiation (λ = 0.65000 Å) at 2D beamline in Pohang Accelerator Laboratory (PAL). The diffraction images were processed by using HKL3000. Absorption correction was performed by using the program PLATON. The structure was solved by ShelXT using Intrinsic Phasing and refined by ShelXL. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added to their geometrically ideal positions.

Y7-MOF, [Y\textsubscript{2}NDC\textsubscript{3}(C\textsubscript{3}H\textsubscript{7}NO)\textsubscript{2}]: C\textsubscript{42}H\textsubscript{32}N\textsubscript{2}O\textsubscript{14}Y\textsubscript{2}, crystal dimensions 0.41 × 0.22 × 0.13 μm\textsuperscript{3}, Monoclinic P\textsubscript{2}\textsubscript{1}/c, a = 22.7429(9) Å, b = 8.9462(3) Å, c = 18.9147(8) Å, α= 90 °, β = 101.149(3) °, γ = 90 °, V = 377.5.8 Å\textsuperscript{3}, T = -173 °C (Reported CCDC deposit number: 1878168)

Y9-MOF, [Y\textsubscript{2}NDC\textsubscript{3}(C\textsubscript{3}H\textsubscript{7}NO)\textsubscript{4}]-2H\textsubscript{2}O: C\textsubscript{48}H\textsubscript{46}N\textsubscript{4}O\textsubscript{19}Y\textsubscript{2}, crystal dimensions 0.30 × 0.25 × 0.20 μm\textsuperscript{3}, triclinic P\textsubscript{-}I, a = 11.655(2) Å, b = 12.214(2) Å, c = 13.356(3) Å, α= 101.56(3) °, β = 98.59(3) °, γ = 107.22(3) °, V = 1734.3(7) Å\textsuperscript{3}, T = -173 °C (Reported CCDC deposit number: 1878170)
Fig S1. Optical (top row) and polarized (bottom row) microscope images of yttrium-based MOFs
Fig S2. Void space of Y9-MOF: 40.8 % (706.76Å$^3$).
**Fig S3.** Comparison of the experimental (red) and predicted (black) PXRD patterns of **Y7-MOF**.
Fig S4. (a) Comparison of the experimental (red) and predicted (black) PXRD patterns of Y9-MOF. The result shows instability of Y9-MOF under ambient atmosphere. (b) Optical microscope image of Y9-MOF after measuring PXRD. This clearly indicates the structural collapse of Y9-MOF during measurement.
<table>
<thead>
<tr>
<th>Y(NO$_3$)$_3$</th>
<th>H$_2$NDC</th>
<th>DMF</th>
<th>DI water (mL)</th>
<th>Network</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.30 mg, 0.1 mmol</td>
<td>12.21 mg, 0.05 mmol</td>
<td>4 mL</td>
<td>2</td>
<td>Y7-MOF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
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<td>0.1</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>0.01</td>
<td>Y9-MOF</td>
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</table>

*Table S1.* Reaction condition to evaluate the effect of the amount of water.
Fig S5. Optical (top row) and polarized (bottom row) microscope images of Y7-MOFs. When 2 mL water is added in the solution, small crystals are formed. When 0.5 mL water is added, crystals with relatively bad crystallinity are formed.
Fig S6. Optical (top row) and polarized (bottom row) microscope images of Y9-MOFs. When 0.1 mL water is added in the solution, small amounts of crystals are formed. When water is not added, imperfect crystals are formed.
Fig S7. Comparison of the PXRD patterns of Y9-MOFs. Predicted: black, experimental: red, 0.1 mL water is added: magenta, 0.01 mL water is added: dark cyan, and water is not added: blue. This results clearly indicate the structural collapse of Y9-MOF during measurement.
Table S2. Reaction condition to evaluate the effect of NDC\(^{2-}\) concentration.

<table>
<thead>
<tr>
<th>Y(NO(_3))(_3)</th>
<th>NDC(^{2-})</th>
<th>Network</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mmol</td>
<td>0.2 mmol</td>
<td>Y7-MOF</td>
</tr>
<tr>
<td></td>
<td>0.02 mmol</td>
<td>Y9-MOF</td>
</tr>
<tr>
<td></td>
<td>0.01 mmol</td>
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</tbody>
</table>
Fig S8. (a) Comparison of the experimental and predicted PXRD patterns with Y7-MOF, Y9-MOF and the crystals obtained with 0.2 mmol NDC²⁻. This result clearly shows that when 0.2 mmol NDC²⁻ is used, the PXRD pattern matches with Y7-MOF. (b) The size of crystals obtained with 0.2 mmol NDC²⁻. Due to its very small size, it was not possible for SC-XRD measurement.
Fig S9. Optical (top row) and polarized (bottom row) microscope images of Y9-MOFs. When 0.02 mmol of NDC$^{2-}$ is used for precursor, clear rectangular shaped crystals are formed. However, when 0.01 mmol of NDC$^{2-}$ is used for precursor, imperfect crystals are formed.
Fig S10. Comparison of the PXRD patterns of Y9-MOFs. Predicted: black, experimental: red, 0.02 mmol NDC2- is used: blue, 0.01 mmol NDC2- is used: dark cyan. This results clearly indicate the structural collapse of Y9-MOF during measurement.
Fig S11. Photoluminescence spectra of (a) Y7-MOF (cyan) and Y9-MOF (red), (b) H$_2$NDC (cyan).
Fig S12. (a) PL, and (b) optical microscope images of solvent-free Y9-MOF. (c) PL spectra of Y9-MOF (blue) and solvent-free Y9-MOF (red).
References


3) Sheldrick, G. M. University of Göttingen, Germany, 1996.