

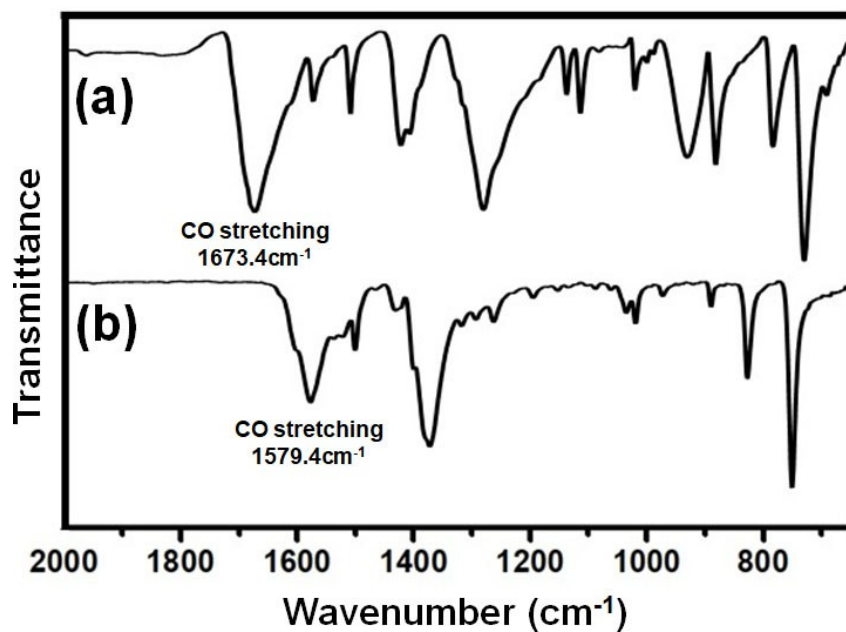
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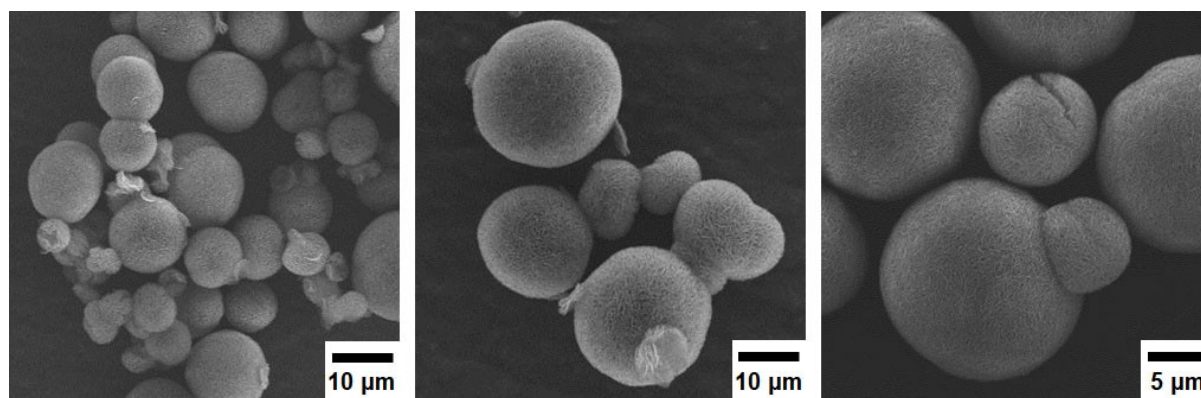
Supporting information for article:

Competitive formation between 2D and 3D metal-organic frameworks (MOFs): insights on the selective formation and lamination of 2D MOF

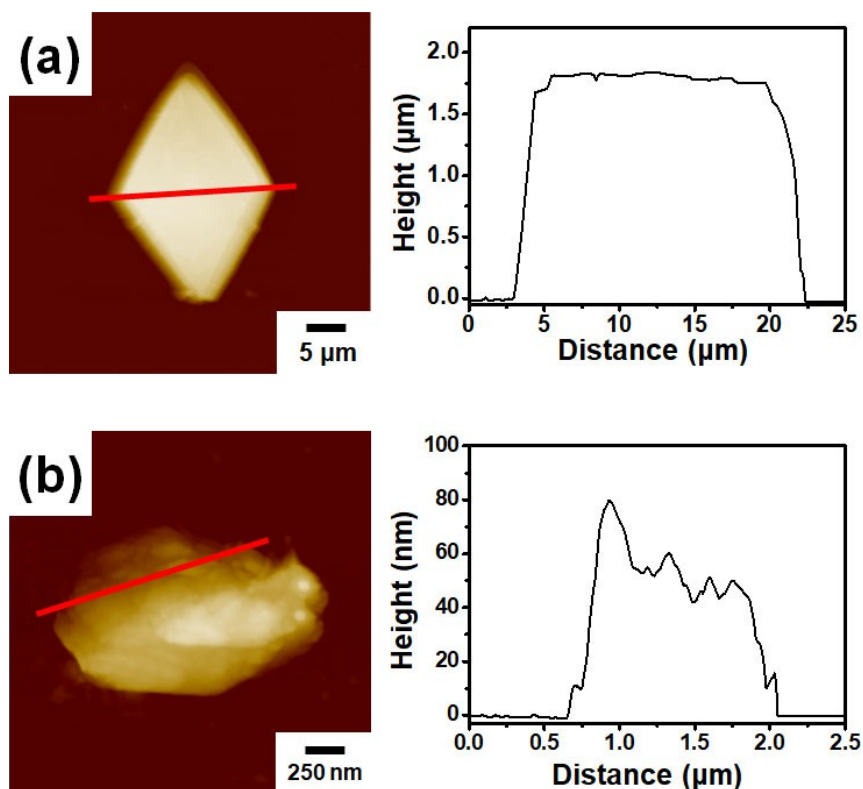
Sojin Oh, Jeehyun Park and Moonhyun Oh



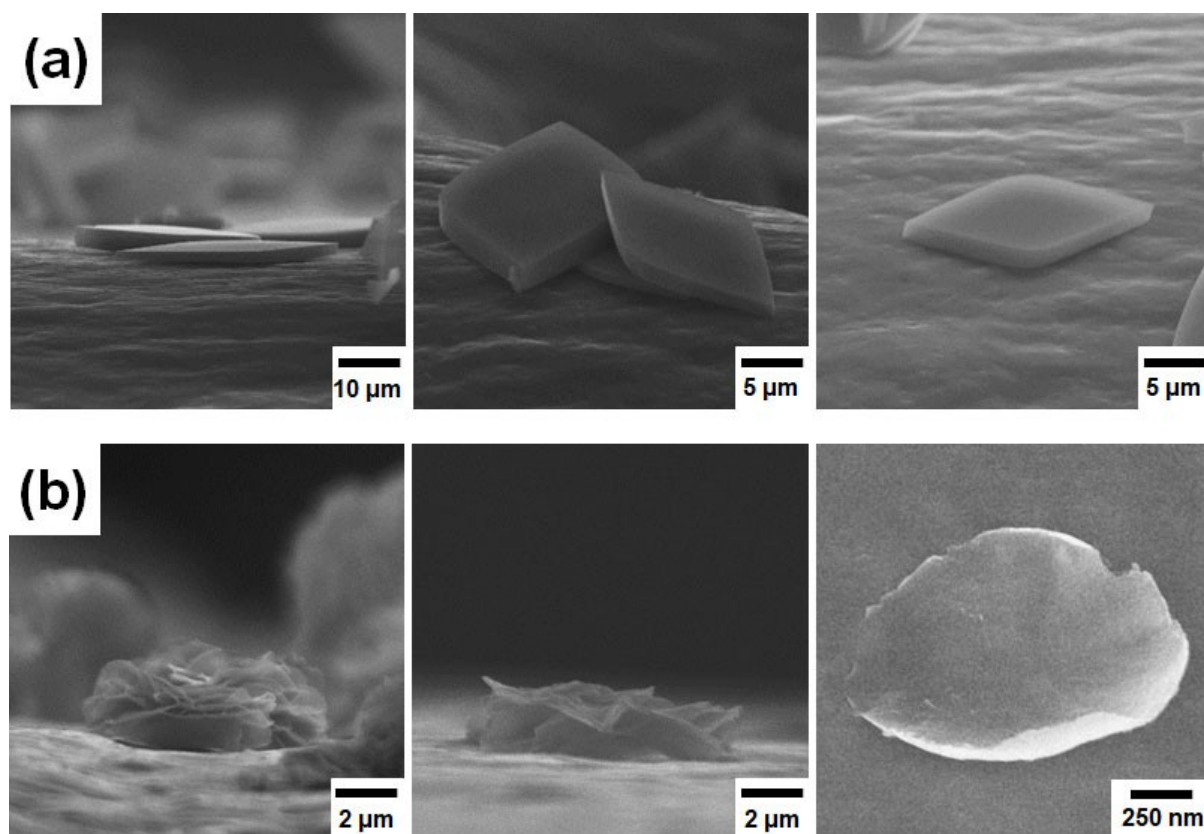
1 IR spectra of (a) H₂BDC and (b) 2D-L-MOF.



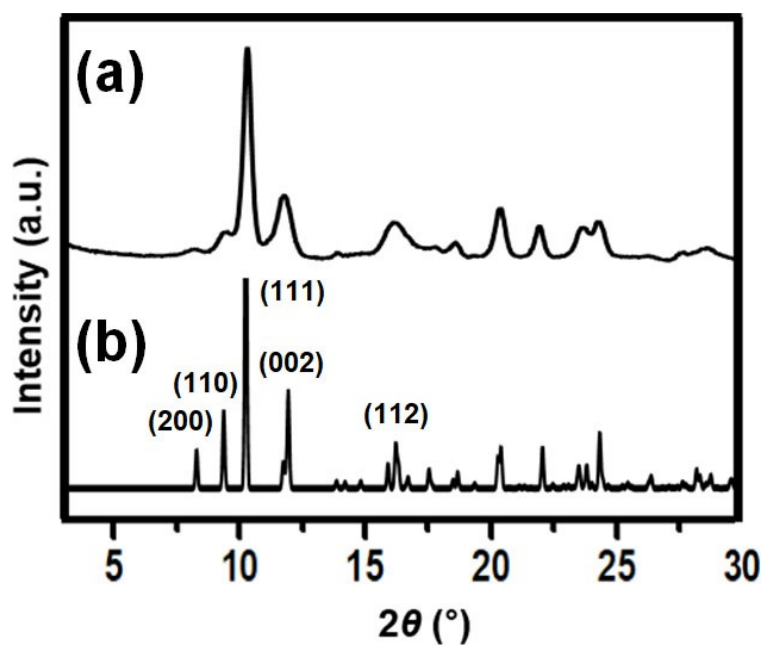
2 SEM images showing MOF product obtained from the solvothermal reaction of Zn(NO₃)₂ (0.54 mmol) and H₂BDC (1.62 mmol) in the presence of PVP without an ultrasonic dispersion process.



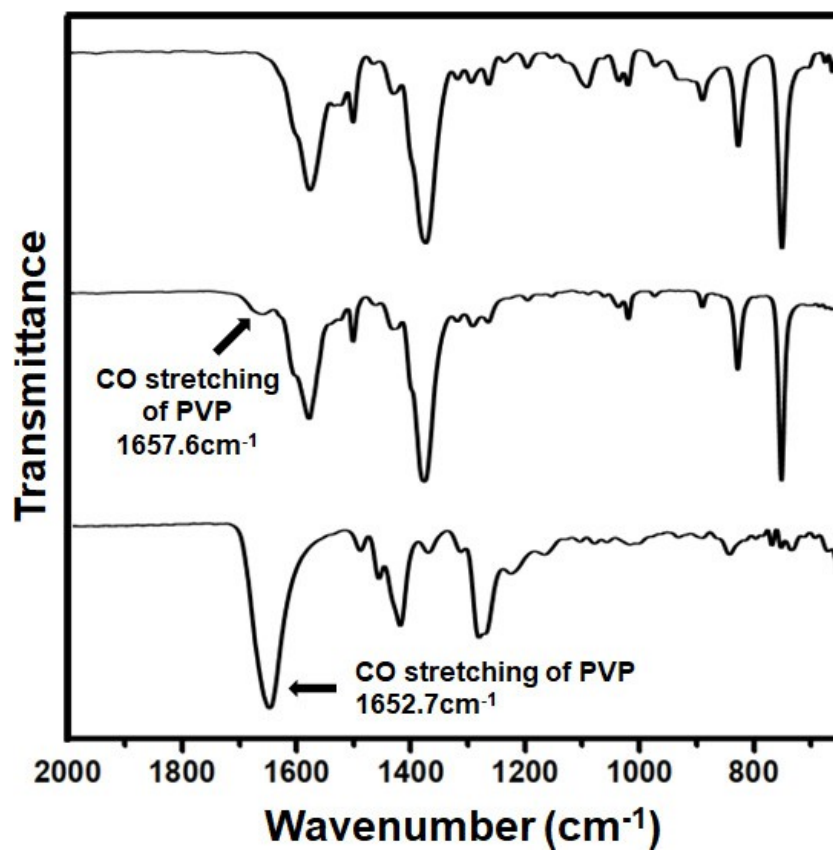
3 AFM images of (a) the rhombus **2D-L-MOF** particles obtained from the solvothermal ultrasonic reaction of $\text{Zn}(\text{NO}_3)_2$ (0.54 mmol) and H_2BDC (1.62 mmol); however, an ultrasonic dispersion process was stopped immediately after the initial seed formation and (b) the **2D-L-MOF** disks obtained from the solvothermal ultrasonic reaction of $\text{Zn}(\text{NO}_3)_2$ (0.54 mmol) and H_2BDC (1.62 mmol) in the presence of PVP. A single layer of **2D-L-MOF** was calculated to be *ca.* 1.06 nm based upon its single crystal structure. However, the thickness of laminated **2D-L-MOF** and the precise information on the number of layers could not obtain due to its waved-morphology. There are *ca.* ten layers of **2D-L-MOF** in a thin area presenting at the outside of particle shown in (b).



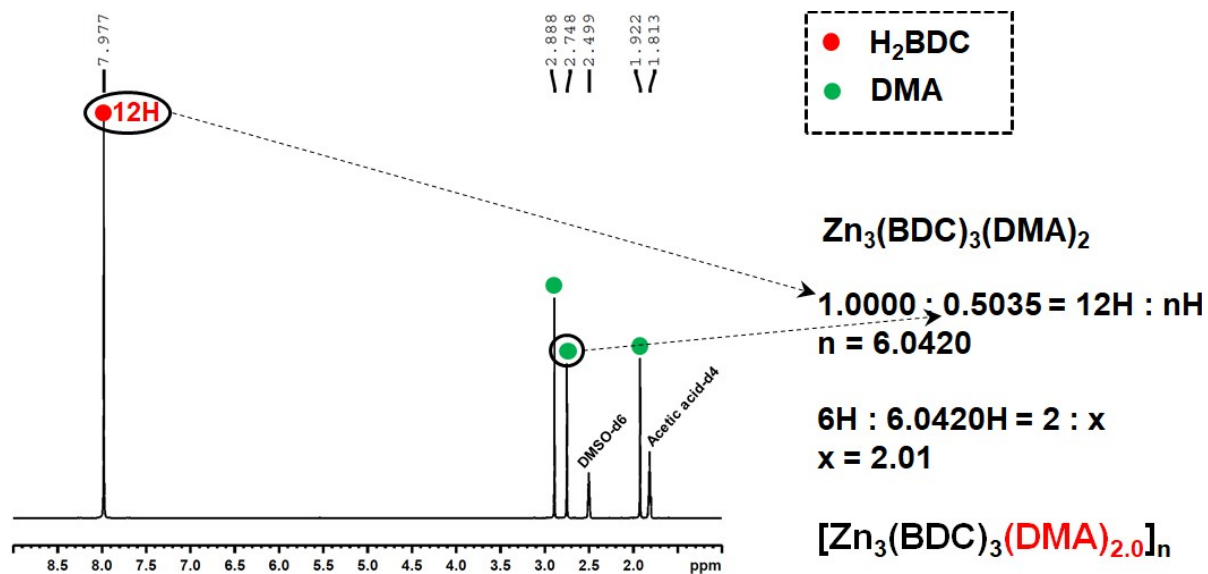
4 SEM images of samples measured at the side view. (a) The rhombus **2D-L-MOF** particles obtained from the solvothermal ultrasonic reaction of $\text{Zn}(\text{NO}_3)_2$ (0.54 mmol) and H_2BDC (1.62 mmol); however, an ultrasonic dispersion process was stopped immediately after the initial seed formation and (b) the **2D-L-MOF** disks obtained from the solvothermal ultrasonic reaction of $\text{Zn}(\text{NO}_3)_2$ (0.54 mmol) and H_2BDC (1.62 mmol) in the presence of PVP. In special, SEM images in (b) revealed its waved-morphology.



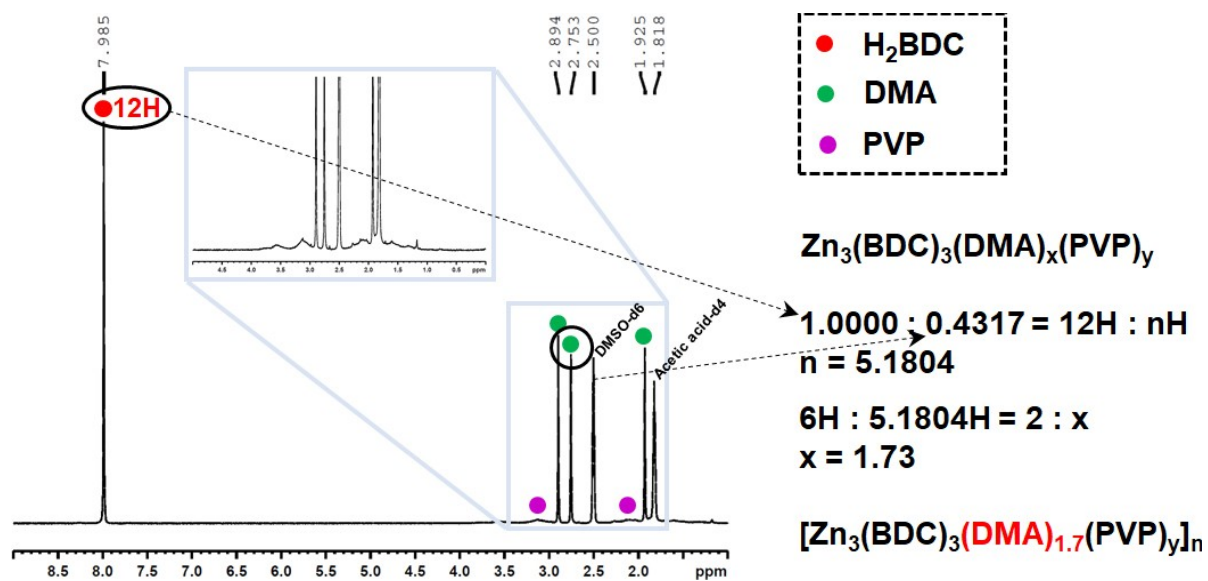
5 (a) PXR D pattern of the laminated **2D-L-MOF** disks obtained from the solvothermal ultrasonic reaction of $\text{Zn}(\text{NO}_3)_2$ and H_2BDC in the presence of PVP. (b) Simulated PXR D pattern of **2D-L-MOF**.



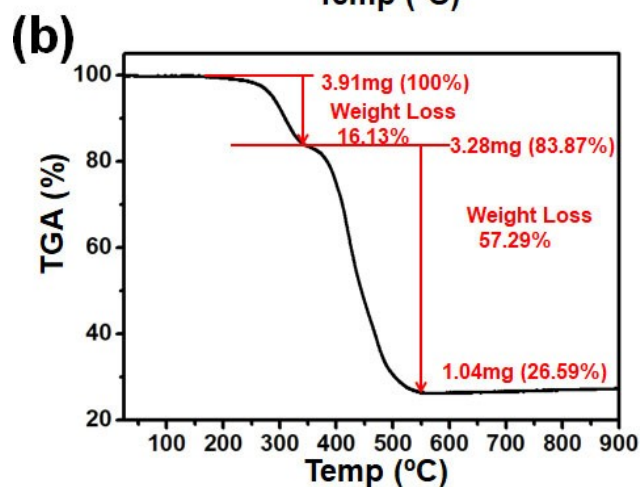
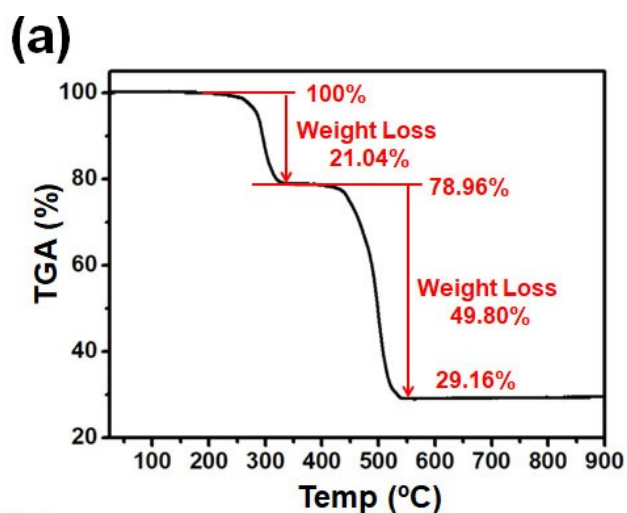
6 IR spectrum of the laminated **2D-L-MOF** disks (middle) obtained from the solvothermal ultrasonic reactions of $\text{Zn}(\text{NO}_3)_2$ and H_2BDC in the presence of PVP. For comparison, IR spectra of the bulk **2D-L-MOF** rhombus particles (top) and PVP (bottom) are included.



7 ¹H NMR spectrum of the bulk **2D-L-MOF** rhombus particles obtained from the solvothermal ultrasonic reaction of Zn²⁺ and H₂BDC. The number of DMA molecules within the bulk **2D-L-MOF** was calculated at ca. 2.0 per unit composition [Zn₃(BDC)₃(DMA)_{2.0}]_n based upon ¹H NMR spectrum.



8 ^1H NMR spectrum of the laminated **2D-L-MOF** disks obtained from the solvothermal ultrasonic reaction of Zn^{2+} and H_2BDC in the presence of PVP. The number of DMA molecules within the laminated **2D-L-MOF** was calculated at ca. 1.7 per unit composition $[\text{Zn}_3(\text{BDC})_3(\text{DMA})_{1.7}(\text{PVP})_y]_n$ based upon ^1H NMR spectrum.



$$1.04\text{mg} \div 244.14\text{g/mol} = 0.0043\text{mmol}$$

And thus, a sum of 0.0043mmol of $\text{Zn}_3(\text{BDC})_3$ and Xmg of PVP is 3.28mg

$$0.0043\text{mmol} \times 688.55\text{g/mol} + \text{PVP} = 3.28\text{mg}$$

$$\text{PVP} = 0.319\text{mg}$$

And finally, a sum of 0.0043mmol of $\text{Zn}_3(\text{BDC})_3(\text{DMA})_2$ and 0.319mg of PVP is 3.91mg

$$0.0043\text{mmol} \times X \text{ g/mol} + 0.319\text{mg} = 3.91\text{mg}$$

$$X = 835.12\text{g/mol}, \text{ and so } 1.68 \text{ mmol of DMA}$$

$$\text{Formula} = \text{Zn}_3(\text{BDC})_3(\text{DMA})_{1.68}$$

9 TGA curves of (a) the bulk **2D-L-MOF** rhombus particles and (b) the laminated **2D-L-MOF** disks. The amounts of DMA and PVP incorporated within the laminated **2D-L-MOF** were calculated based upon TGA curve.