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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 ($Y(NO_3)_3 \cdot xH_2O$) (Sigma Aldrich, 99.8% trace metal basis), 2,6-naphthalene dicarboxylic acid (H_2NDC) (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, $[Y_2NDC_3(C_3H_7NO)_2]$: $Y(NO_3)_3 \cdot xH_2O$ (38.30 mg, 0.1 mmol) was dissolved in 1:1 mixture of DMF/DI water (4 mL). H_2NDC (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_2NDC solution . The reaction mixture was sealed and placed in the thermal oven at 80ºC 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, $[Y_2NDC_3(C_3H_7NO)_4]\cdot 2H_2O$: $Y(NO_3)_3 \cdot xH_2O$ (38.30 mg, 0.1 mmol) was dissolved in DMF (3 mL). H_2NDC (12.21 mg, 0.05 mmol) was dissolved in DMF (3 mL). The yttrium nitrate solution was slowly added into the H_2NDC solution. The reaction mixture was sealed and placed in the thermal oven at 80ºC 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[1]. Absorption correction was performed by using the program PLATON[2]. The structure was solved by ShelXT[3] using Intrinsic Phasing and refined by ShelXL[4]. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added to their geometrically ideal positions.

Y7-MOF, $[Y_2NDC_3(C_3H_7NO)_2]$: $C_{42}H_{32}N_2O_{14}Y_2$, crystal dimensions 0.41 × 0.22 × 0.13 μm^3, Monoclinic *P2$_1$/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 ^{3}, T = -173 ℃ (Reported CCDC deposit number: 1878168)

Y9-MOF, $[Y_2NDC_3(C_3H_7NO)_4]\cdot 2H_2O$: $C_{48}H_{46}N_4O_{19}Y_2$, crystal dimensions 0.30 × 0.25 × 0.20 μm^3, triclinic *P-1*, 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 ^{3}, T = -173 ℃ (Reported CCDC deposit number: 1878170)

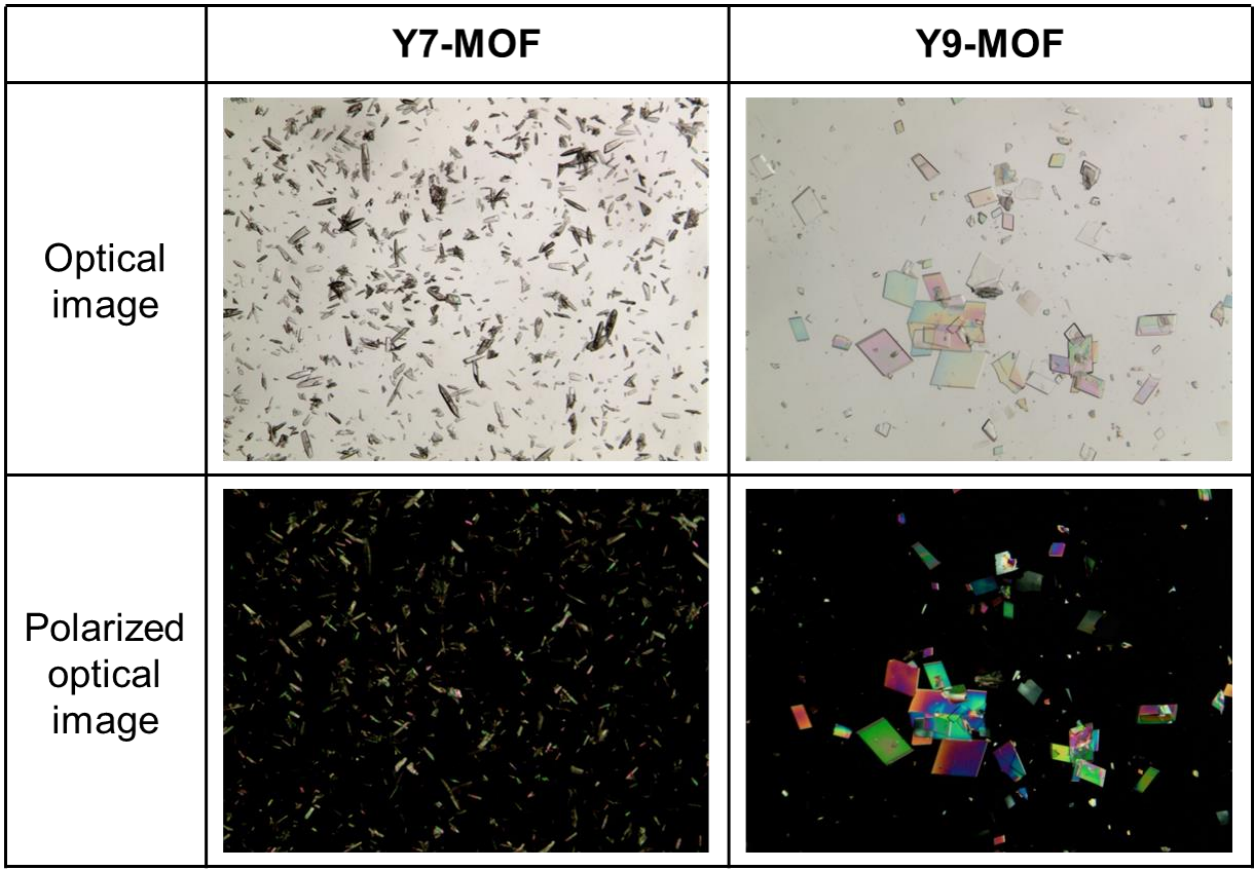


Fig S1. Optical (top row) and polarized (bottom row) microscope images of yttrium-based MOFs

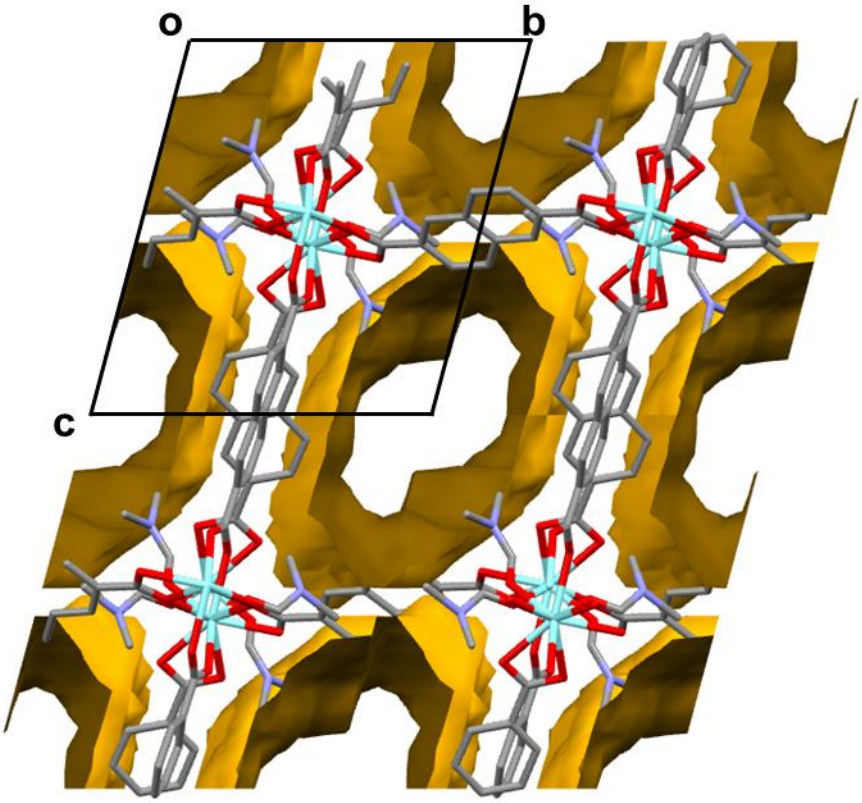


Fig S2. Void space of **Y9-MOF**: 40.8 % (706.76Å^3).

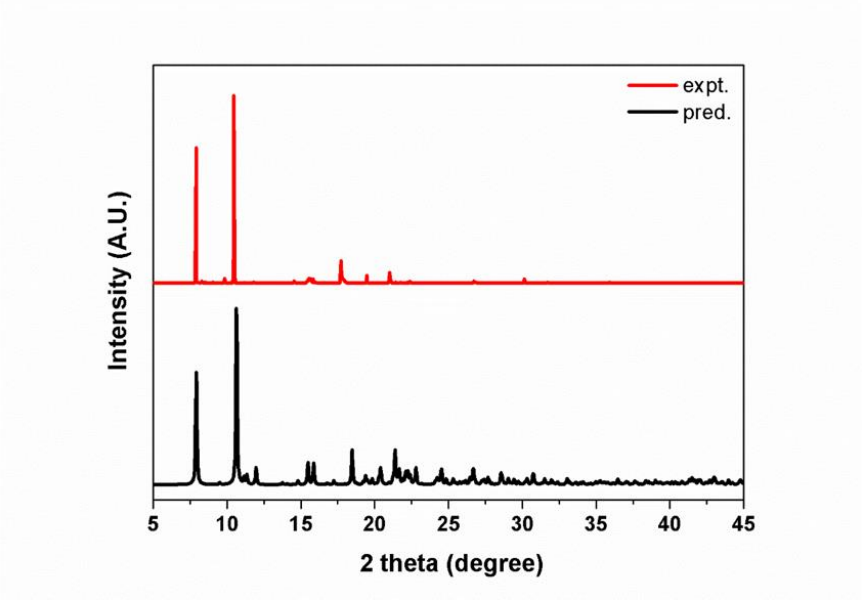


Fig S3. Comparison of the experimental (red) and predicted (black) PXRD patterns of **Y7-MOF**.

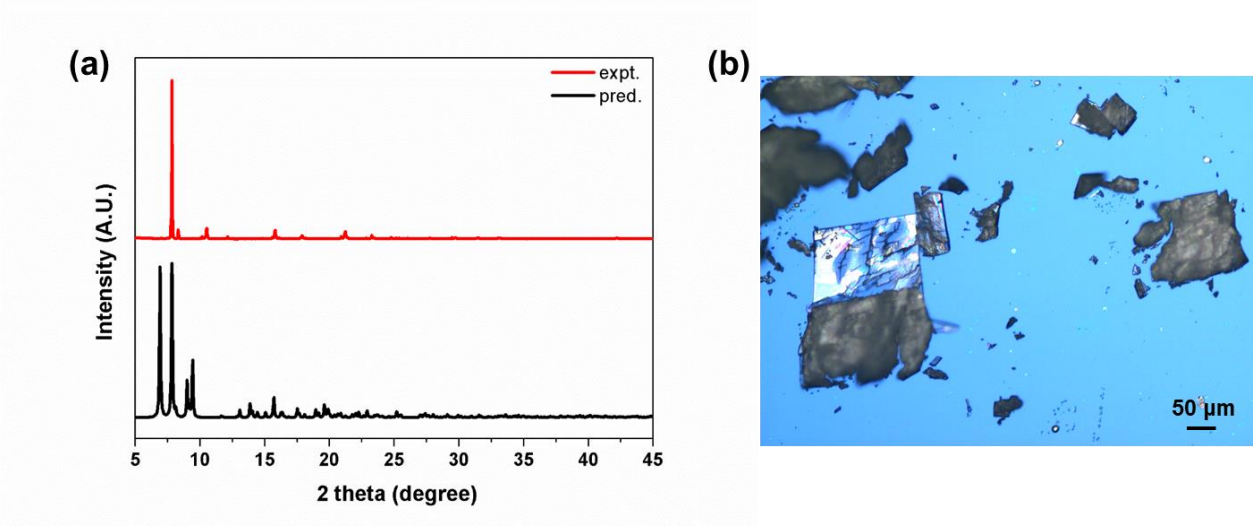


Fig S4. (a) Comparison of the experimental (red) and predicted (black) PXRD patterns of **Y9-MOF**. The result shows instability of **Y9-MOF** under ambient atmosphere. (b) Optical microscope image of **Y9-MOF** after measuring PXRD. This clearly indicates the structural collapse of **Y9-MOF** during measurement.

$Y(NO_3)_3$	H_2NDC	DMF	DI water (mL)	Network
38.30 mg, 0.1 mmol	12.21 mg, 0.05 mmol	4 mL	2	**Y7-MOF**
			1	
			0.5	
			0.1	**Y9-MOF**
			0.01	
			-	

Table S1. Reaction condition to evaluate the effect of the amount of water.

$Y(NO_3)_3$	H_2NDC	DMF	DI water (mL)	Network
0.1 mmol	0.05 mmol	4 mL	2	**Y7-MOF**
			1	
			0.5	

Y7-MOF	Amount of added water		
	2 mL	1 mL	0.5 mL
Optical image			
Polarized optical image			

Fig S5. Optical (top row) and polarized (bottom row) microscope images of **Y7-MOF**s. 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.

$Y(NO_3)_3$	H_2NDC	DMF	DI water (mL)	Network
0.1 mmol	0.05 mmol	4 mL	0.1	**Y9-MOF**
			0.01	
			-	

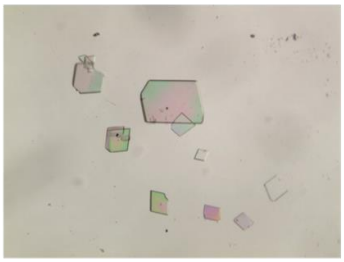
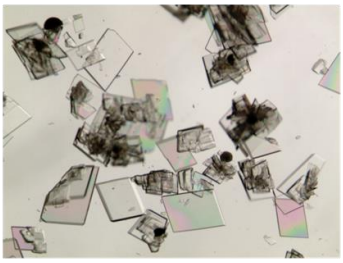
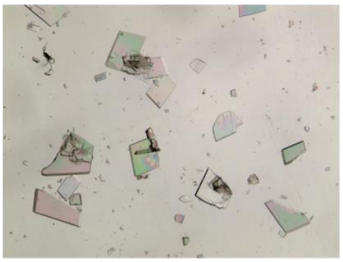
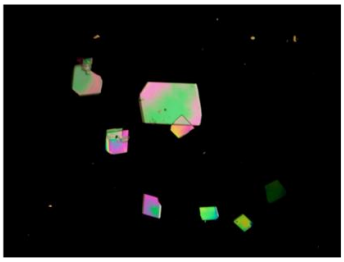
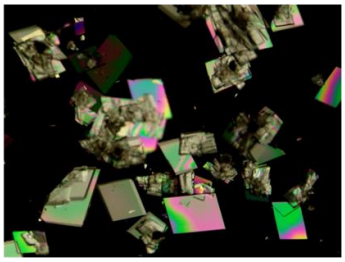
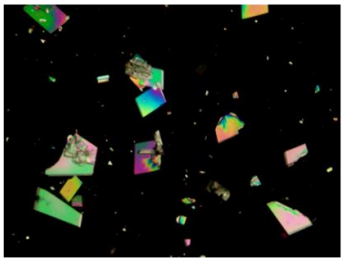
Y9-MOF	Amount of added water		
	0.1 mL	0.01 mL	0 mL
Optical image			
Polarized optical image			

Fig S6. Optical (top row) and polarized (bottom row) microscope images of **Y9-MOF**s. 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.

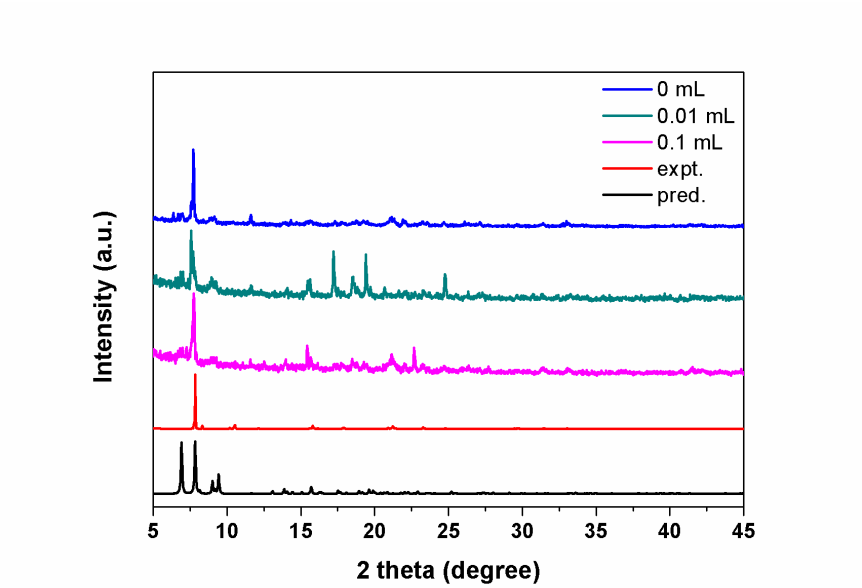


Fig S7. Comparison of the PXRD patterns of **Y9-MOFs**. Predicted: black, experimental: red, 0.1 mL water is added: magenta, 0.01 mL water is added: dark cyan, and water is not added: blue. This results clealy indicate the structural collapse of **Y9-MOF** during measurement.

$Y(NO_3)_3$	NDC^{2-}	Network
0.1 mmol	0.2 mmol	**Y7-MOF**
	0.02 mmol	**Y9-MOF**
	0.01 mmol	

Table S2. Reaction condition to evaluate the effect of NDC^{2-} concentration.

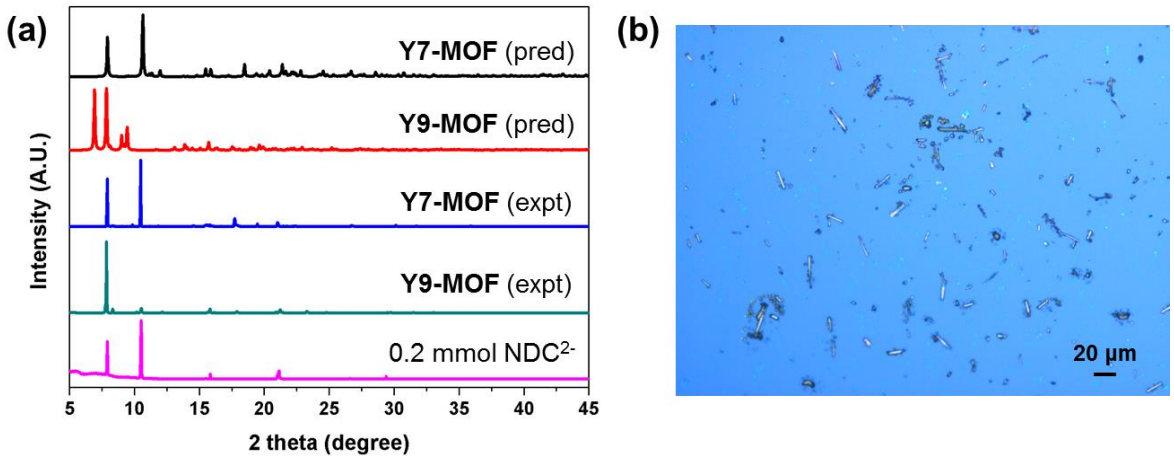


Fig S8. (a) Comparison of the experimental and predicted PXRD patterns with **Y7-MOF**, **Y9-MOF** and the crystals obtained with 0.2 mmol NDC^{2-}. This result clearly shows that when 0.2 mmol NDC^{2-} is used, the PXRD pattern matches with **Y7-MOF**. (b) The size of crystals obtained with 0.2 mmol NDC^{2-}. Due to its very small size, it was not possible for SC-XRD measurement.

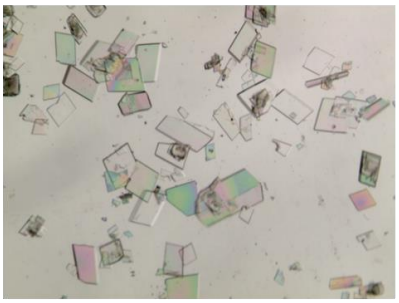
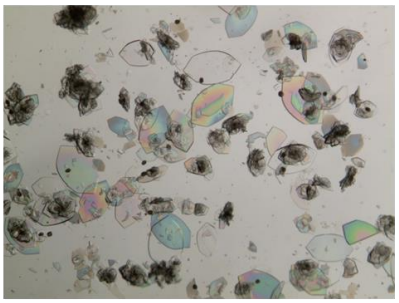
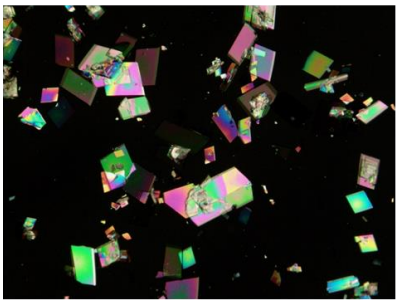
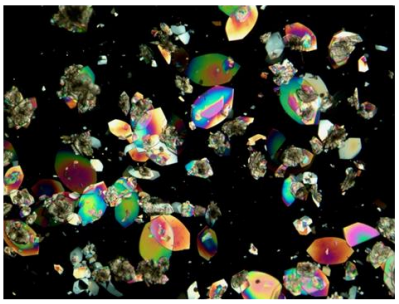
Y9-MOF	Amount of NDC^{2-}	
	0.02 mmol	0.01 mmol
Optical image		
Polarized optical image		

Fig S9. Optical (top row) and polarized (bottom row) microscope images of **Y9-MOF**s. 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.

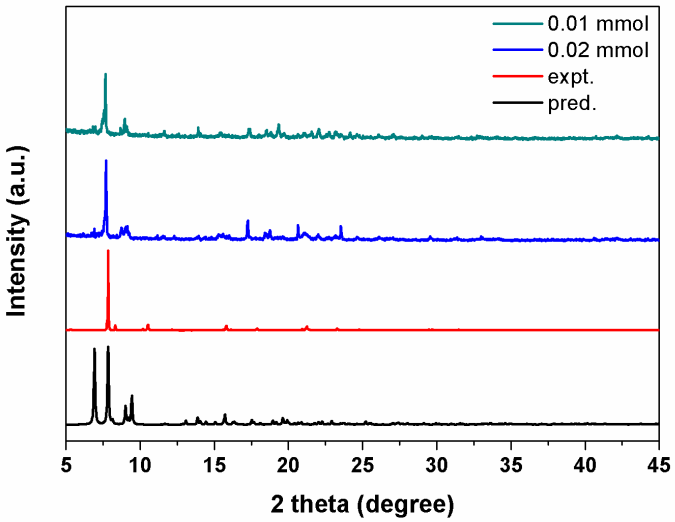


Fig S10. Comparison of the PXRD patterns of **Y9-MOFs**. Predicted: black, experimental: red, 0.02 mmol NDC2- is used: blue, 0.01 mmol NDC2- is used: dark cyan. This results clealy indicate the structural collapse of **Y9-MOF** during measurement.

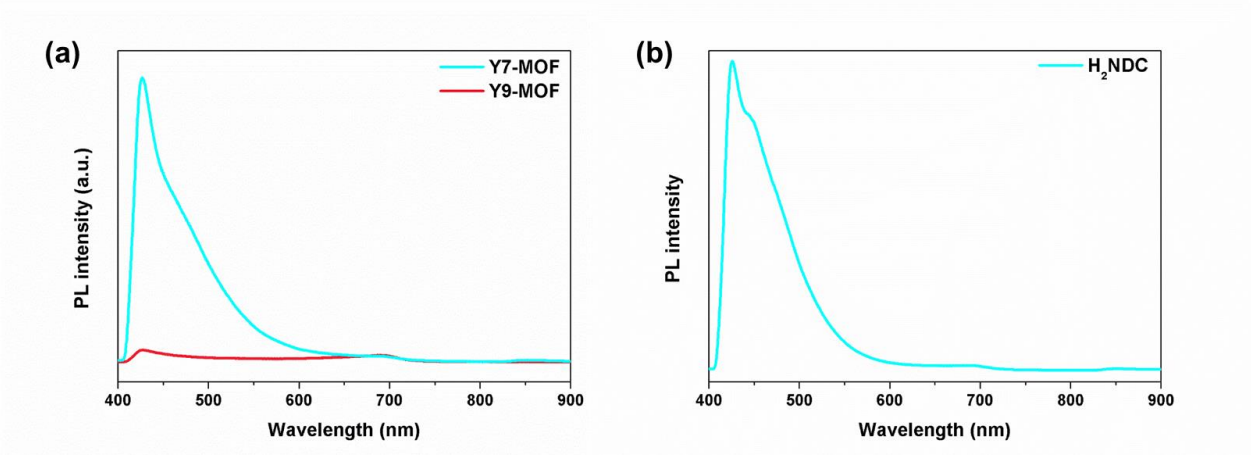


Fig S11. Photoluminescence spectra of (a) **Y7-MOF** (cyan) and **Y9-MOF** (red), (b) H_2NDC (cyan).

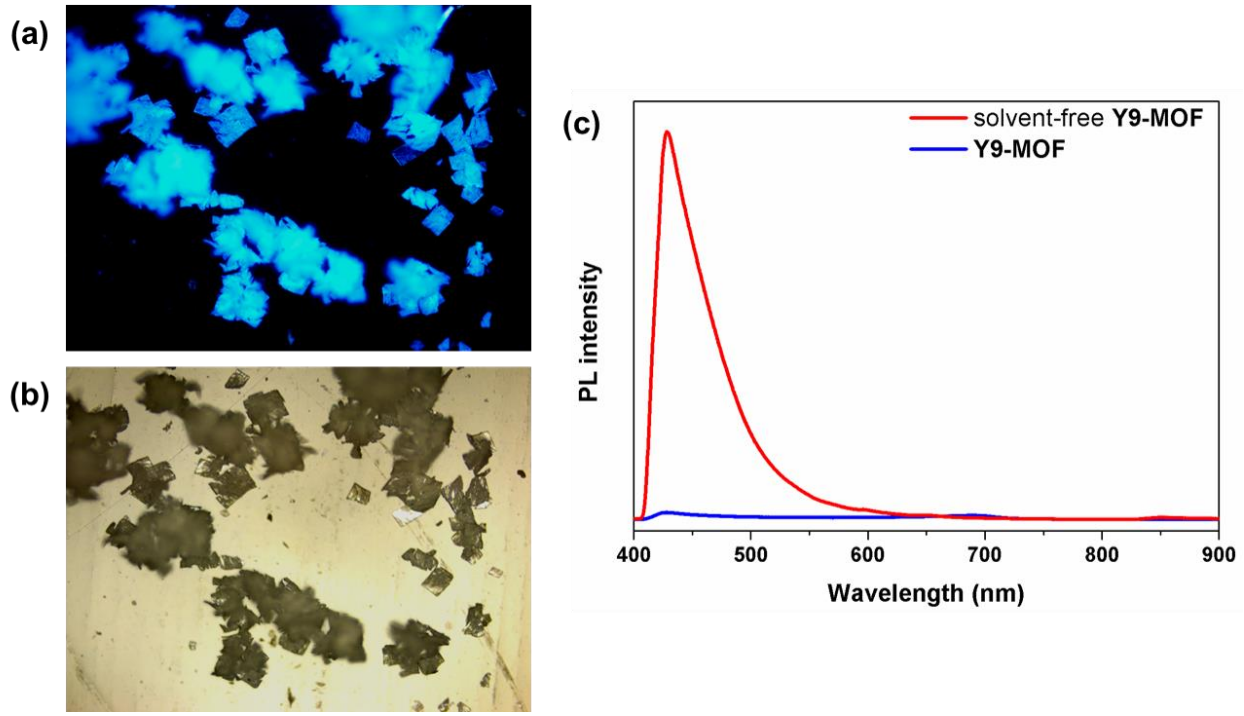


Fig S12. (a) PL, and (b) optical microscope images of solvent-free **Y9-MOF**. (c) PL spectra of **Y9-MOF** (blue) and solvent-free **Y9-MOF** (red).

References

1) Otwinowski Z.; Minor, W. Methods Enzymol., Processing of X-ray Diffraction Data Collected in Oscillation Mode 1997, 276, 307-326.

2) Spek, A. L. Acta Crystallogr. D, 2009, 65, 148-155.

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

4) Sheldrick, G. M. Acta Crystallogr. A, 2008, A64, 112-122.