Supporting Information

Enhanced Fluorescence by Increasing Dimensionality: A Novel Three-Dimensional Luminescent Metal-Organic Framework with Rigidified Ligands

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Materials and characterizations. All reagents used were purchased from Alfa Aesar, Sigma Aldrich or other commercial vendors and used without further purification. Powder X-ray diffraction (PXRD) patterns were performed on a Bruker D8 Advance diffractometer. Data were collected between 5^o and 40^o of 2θ with a scan speed of 10.0 deg/min. Thermogravimetric analysis (TGA) data were recorded on a TGA550 (TA Instruments) Analyzer with a temperature ramping rate of 10 °C/min from RT to 600 °C under nitrogen atmosphere. Photoluminescence measurement was conducted with an Edinburgh FLS1000 unit and internal quantum yield was evaluated by a HAMAMATSU PHOTONICS K.K. analyzer. Single-crystal X-ray diffraction data were collected at 190 K on a Bruker APEX-II CCD diffractometer using GaKα radiation tuned to $\lambda = 1.34139$ Å. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL package.

Crystal structure of LMOF-321: Space group *P-1*, a = 11.8105(2) Å, b = 11.8159(2) Å, c = 14.7854(3) Å, α = 81.763(1), β = 69.718(1), γ = 73.452(1), V = 1852.96(6) $Å^3$, Z = 2, CCDC No: 1984426.

Synthesis of LMOF-321: 30 mg $ZnCl_2$, 20 mg H_4tcpe, and 10 mg pyrazine were dissolved in 5 mL DMF and 1 mL DI water in a 20-mL glass vial. The solution was sonicated for 10 minutes and then heated at 85 °C for 2 day. Block shaped colorless crystals were harvested.

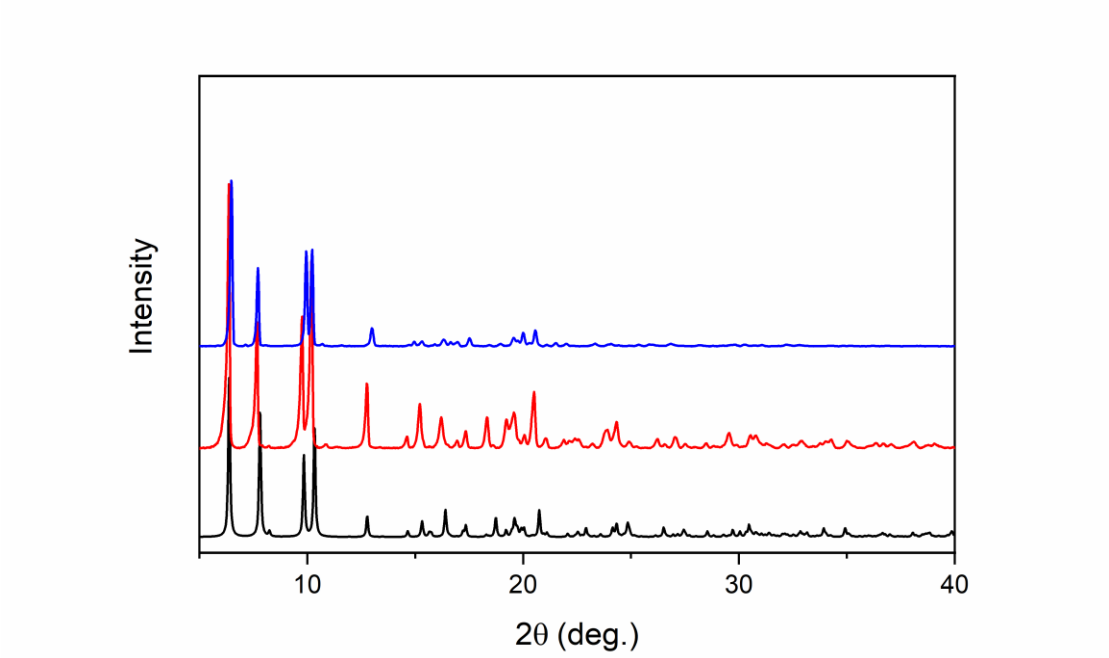

Figure S1. PXRD patterns of LMOF-321. Black: simulated, red: as-synthesized, blue: after heating at 200 ºC.

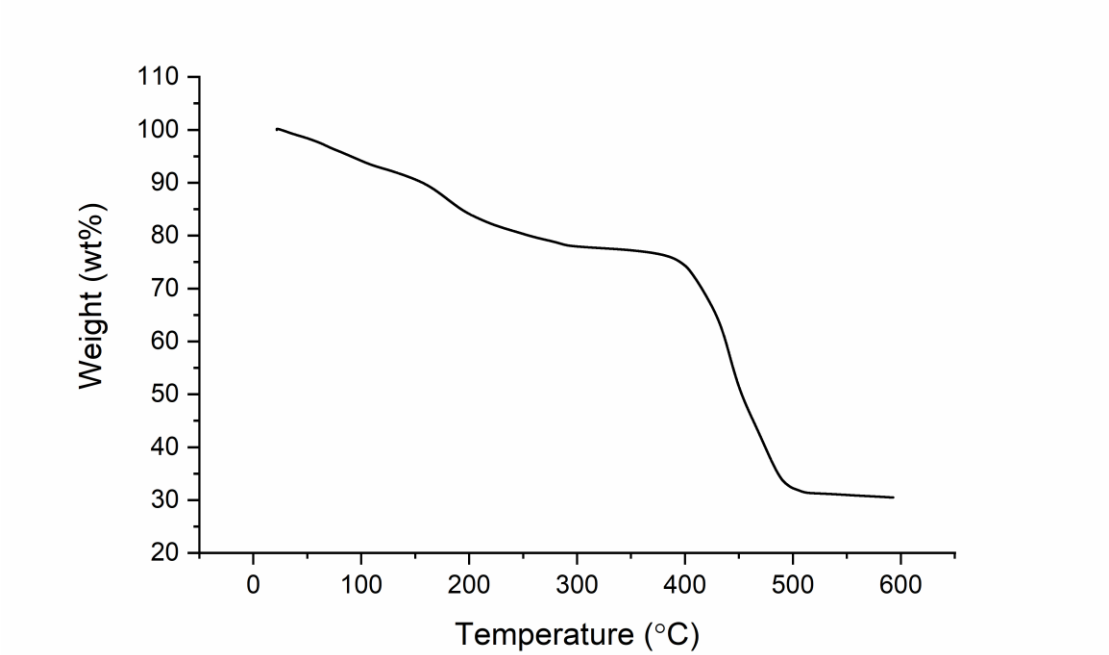

Figure S2. TGA curve of LMOF-321.

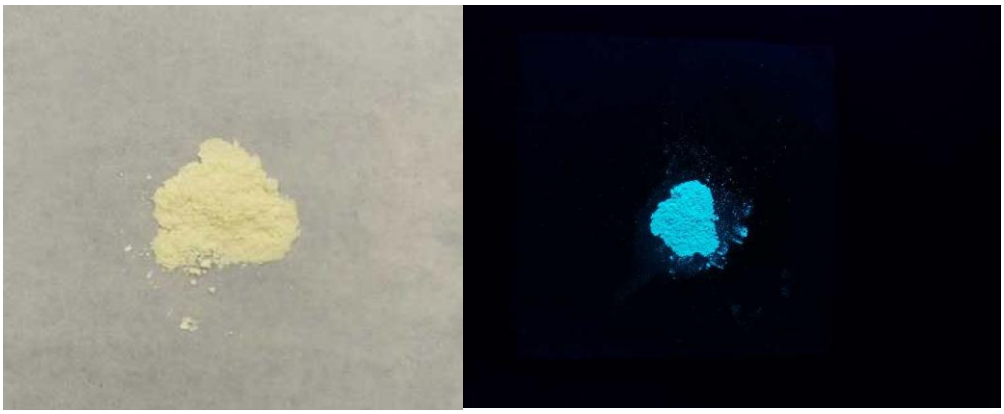

Fig. S3. Sample image of LMOF-321 under daylight (left) and under 360 nm UV excitation (right).

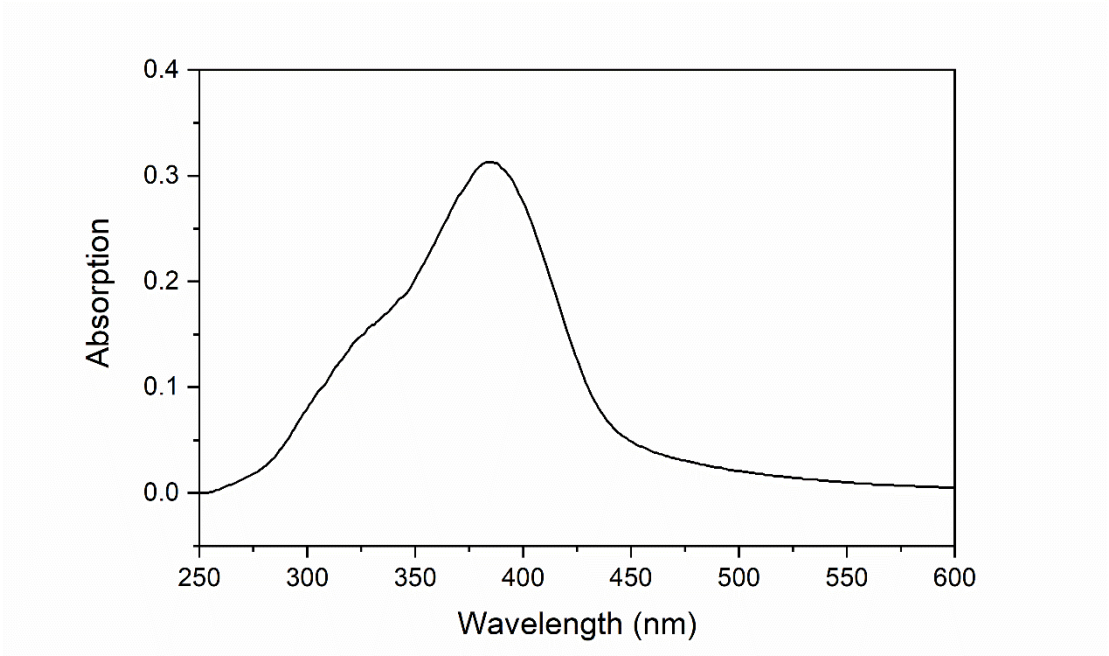

Fig. S4. UV-Vis spectra for LMOF-321 (black) and LMOF-322 (red).

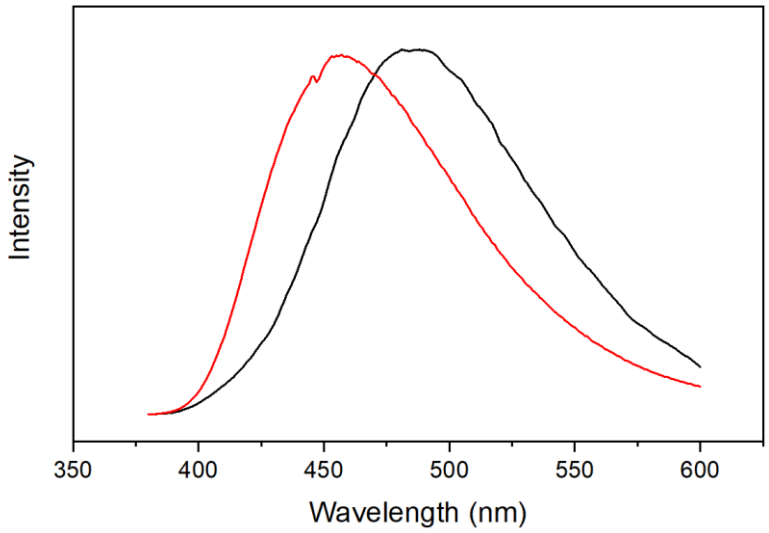

Fig. S5.

Photoluminescence emission spectra of LMOF-321. Blanc and red curves represent data for the pristine samples and samples after heating at 100 ºC.

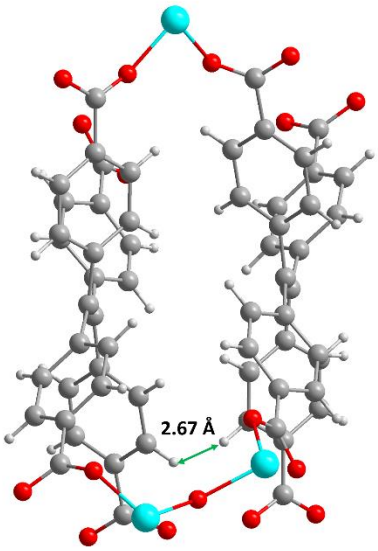

Fig. S6. Shortest H···H distances of the nearest phenyl rings in methanol exchanged LMOF-321.

Table S1. Crystal data and structure refinement for LMOF-321.

Identification code	LMOF-321	
Empirical formula	$C_{36}H_{34}N_2O_{13}Zn_3$	
Formula weight	898.76	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8105(2) Å	α= 81.7630(10)°.
	b = 11.8159(2) Å	β= 69.7180(10)°.
	c = 14.7854(3) Å	γ = 73.4520(10)°.
Volume	1852.96(6) $Å^3$	
Z	2	
Density (calculated)	1.611 Mg/m^3	
Absorption coefficient	2.852 mm^{-1}	
F(000)	916	
Theta range for data collection	3.91 to 72.46°.	
Reflections collected	7200	
Completeness to theta = 53.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3667 and 0.2745	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7200 / 265 / 550	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.1038	
R indices (all data)	R1 = 0.0372, wR2 = 0.1065	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.076 and -0.489 $e.Å^{-3}$	