Tuning the Flexibility of Interpenetrated Frameworks by Small Difference in Fluorene Moiety

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Materials and general procedures

All the starting materials were of reagent grade and were used as purchased. **LMOF-202** and **LMOF-201** were prepared in a similar method to the literature. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima IV diffractometer with Cu-Kα radiation. Thermal gravimetric analyses were recorded on a Rigaku Thermo plus TGA 8120 apparatus in the temperature range 25 to 500 °C under nitrogen atmosphere at a heating rate of 5 °C/min.

Synthesis and crystallographic data

Synthesis of single crystals of **LMOF-202** and **LMOF-201**: A mixture of H_2FDC (0.051 g, 0.2 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.059 g, 0.2 mmol), bpy (0.031 g, 0.2 mmol) and DMF (10 mL) was sealed in a 20 mL Teflon-lined reactor and heated at 80 °C for 2 days. Pale yellow crystals of **LMOF-202** were obtained in a yield of 50%. Anal. Calcd (%) for evacuated sample of **LMOF-202** ($C_{40}H_{24}N_2O_8Zn_2$): C, 60.70; H, 3.06; N 3.54. Found: C, 60.45; H, 2.87; N, 3.27. FT-IR (KBr pellet, cm^{-1}): 1647 s, 1476 m, 1393 vs, 1224 m, 1086 m, 779 s, 717 m, 665 m, 457 s.

The *SQUEEZE* command in *PLATON* was used in the structure refinement for **LMOF-202**. Crystal data for **LMOF-202**. $C_{40}H_{24}N_2O_8Zn_2$, M = 791.35, monoclinic, $C2/c$, a = 33.678(7), b = 22.527(5), c = 19.523(4) Å, β = 123.92(3)°, V = 12296(6) $Å^3$, Z = 8, T = 103 K, μ = 8.13 cm^{-1}, 39203 reflections measured, 10771 unique (R_{int} = 0.038), R_1 = 0.0628 ($I > 2\sigma(I)$), wR_2 = 0.2137 (all reflections), GOF = 1.052.

LMOF-201 was prepared following a similar procedure to that for the preparation of **LMOF-202** except H_2OFDC was used. Pale yellow crystals of **LMOF-201** were obtained in a yield of 45%. Anal. Calcd (%) for $C_{40}H_{20}N_2O_{10}Zn_2$: C, 58.63; H, 2.46; N, 3.42. Found: C, 58.42; H, 2.35; N, 3.20. FT-IR (KBr pellet, cm^{-1}): 1714 s, 1665 s,

1388 vs, 1254 s, 1091 s, 822 m, 769 s, 680 s, 458 s.

Crystal data for **LMOF-201**. $C_{40}H_{20}N_2O_{10}Zn_2$, M = 819.32, monoclinic, $P2_1/c$, a = 13.848(3), b = 22.187(4), c = 19.784(4) Å, β = 102.60(3)°, V = 5932(2) Å^3, Z = 4, T = 103 K, μ = 8.47 cm^{-1}, 37600 reflections measured, 10355 unique (R_{int} = 0.027), R_1 = 0.0499 ($I > 2\sigma(I)$), wR_2 = 0.1474 (all reflections), GOF = 1.08.

Adsorption measurement

Before measurement, the solvent-exchanged sample (about 120 mg) was prepared by immersing the as-synthesized samples in methanol to remove nonvolatile solvents. The completely activated sample was obtained by heating the solvent-exchanged sample at 120 °C under reduced pressure (<10^{-2} Pa) for more than 20 h.

Gas adsorption isotherms were obtained using a Belsorp-max adsorption instrument from BEL Japan Inc. using the volumetric technique. The coincident PXRD/adsorption measurements were carried out using a Rigaku UltimaIV with Cu$K\alpha$ radiation connected with BELSORP-18 volumetric adsorption equipment (Bel Japan Inc.). Those apparatuses were synchronized with each other and each PXRD pattern was obtained at each equilibrium point of the sorption isotherms.

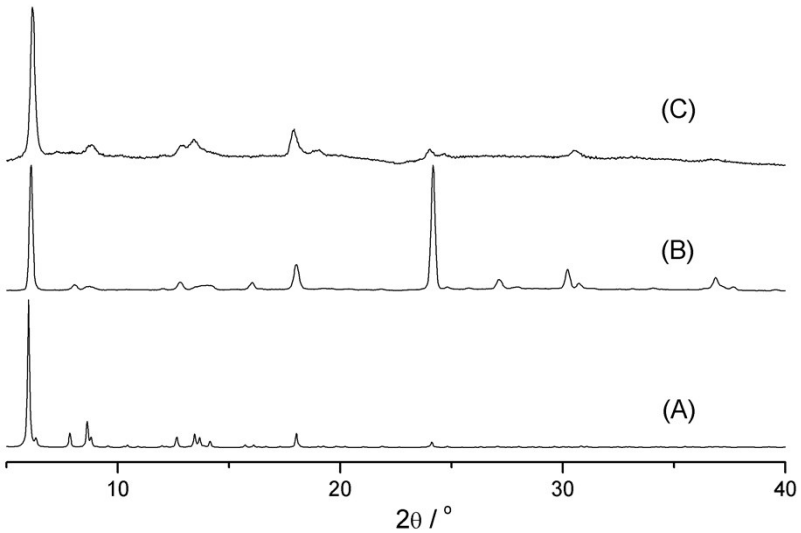

Fig. S1 PXRD patterns of (A) simulated from single-crystal structure of **LMOF-202**, (B) the as-synthesized **LMOF-202**, and (C) drying of **LMOF-202** in vacuum at 393 K.

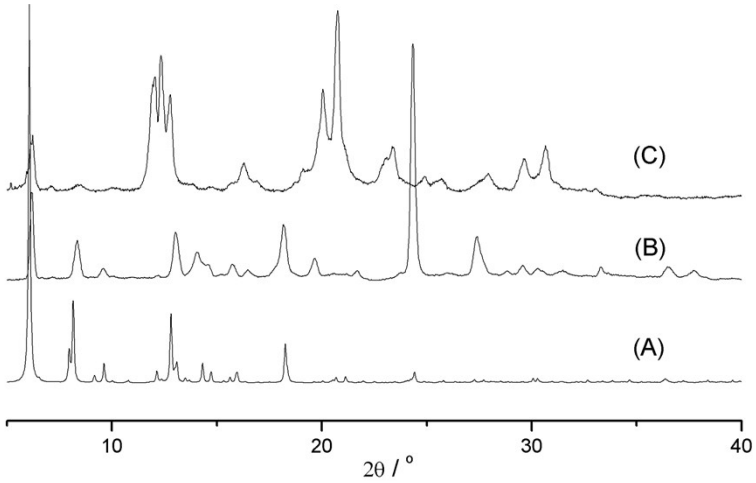

Fig. S2 PXRD patterns of (A) simulated from single-crystal structure of **LMOF-201**, (B) the as-synthesized **LMOF-201**, and (C) drying of **LMOF-201** in vacuum at 393 K.

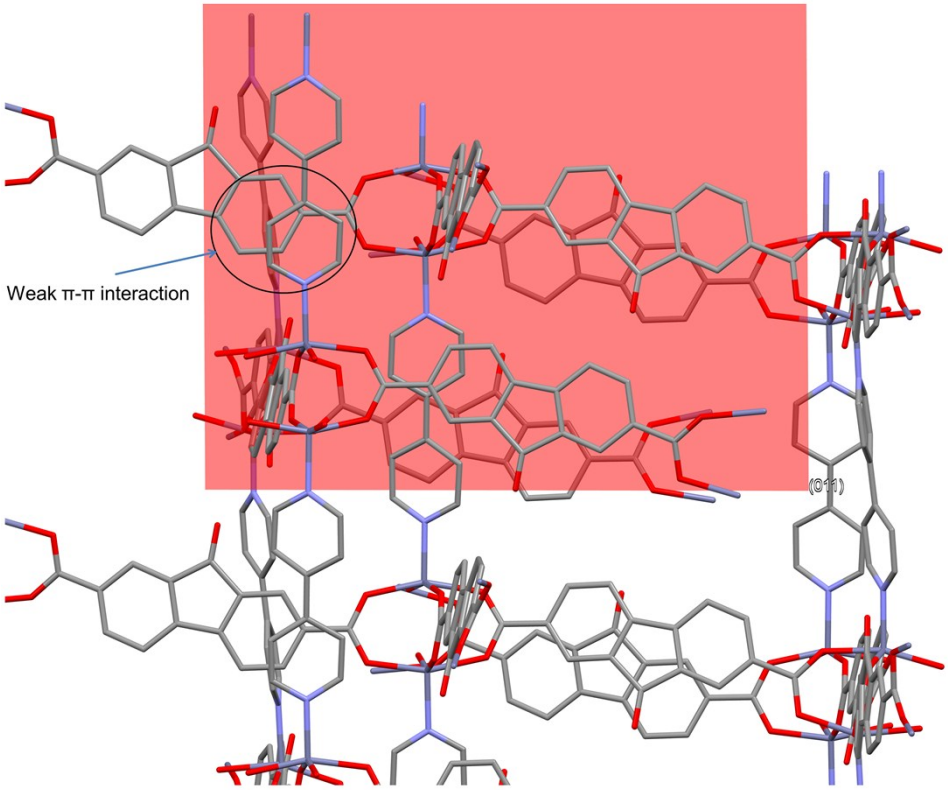

Fig. S3 Part of the frameworks for **LMOF-201**. The fluorenonyl and pyridyl group are nearly parallel to the (011) plane (in red).

Supporting results and discussions

Nitrogen adsorption

Fig. S4 shows the adsorption isotherm of N_2 at 77 K for **LMOF-202**. The isotherm shows a steep uptake at the low relative pressure followed by the plateau region. This is typically the type-I adsorption behavior, thus indicating that **LMOF-202** maintains permanent micro-porosity, which is in consistent with that observed in PXRD patterns.

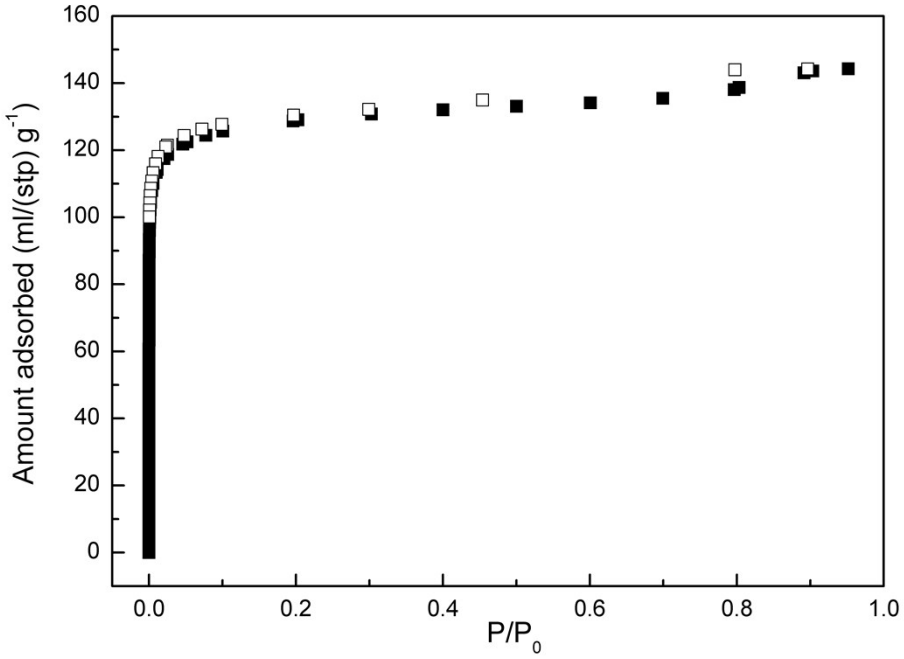

Fig. S4 Adsorption and desorption isotherm of N_2 at 77 K on **LMOF-202**.

LMOF-201 shows completely contrasting sorption behavior. It only exhibits particle surface adsorption for N_2 at 77 K (Fig. S5), which may be derived from framework contraction or diffusion problem at low temperature.

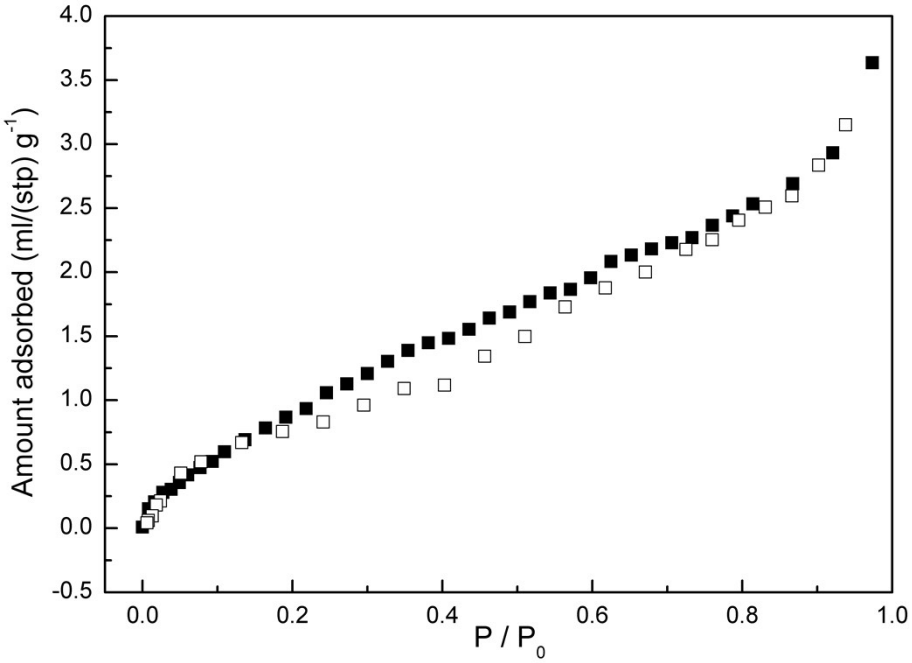

Fig. S5 Adsorption and desorption isotherm of N_2 at 77 K on **LMOF-201**.

Thermogravimetric Analysis

Thermogravimetric analysis of **LMOF-202** and **LMOF-201** show the release of guest molecules with increasing temperature up to 130 °C to give guest-free framework. The weight losses are 34% and 30% for **LMOF-202** and **LMOF-201**, respectively. The presences of platform between 130-200 °C indicate that the guest-free phase is stable (Fig. S6, S7).

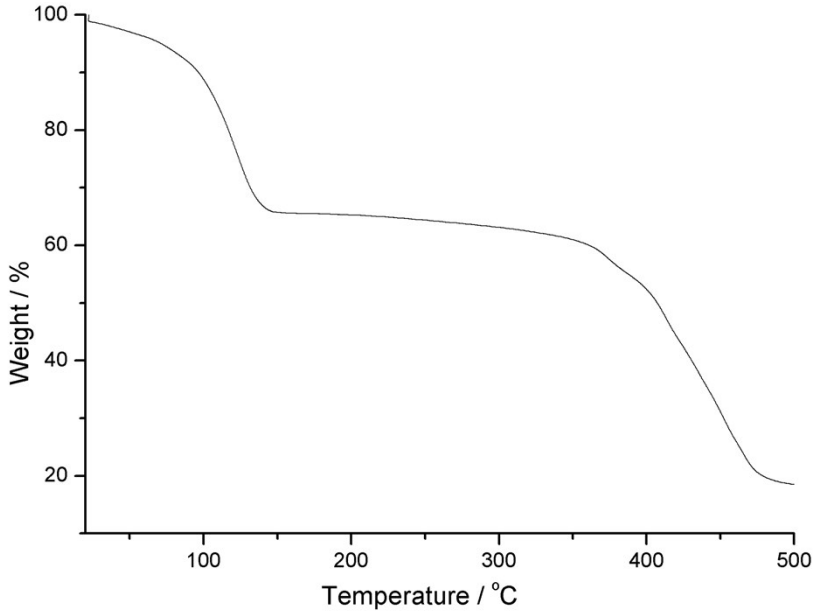

Fig. S6 Thermogravimetric curve of **LMOF-202** under N_2.

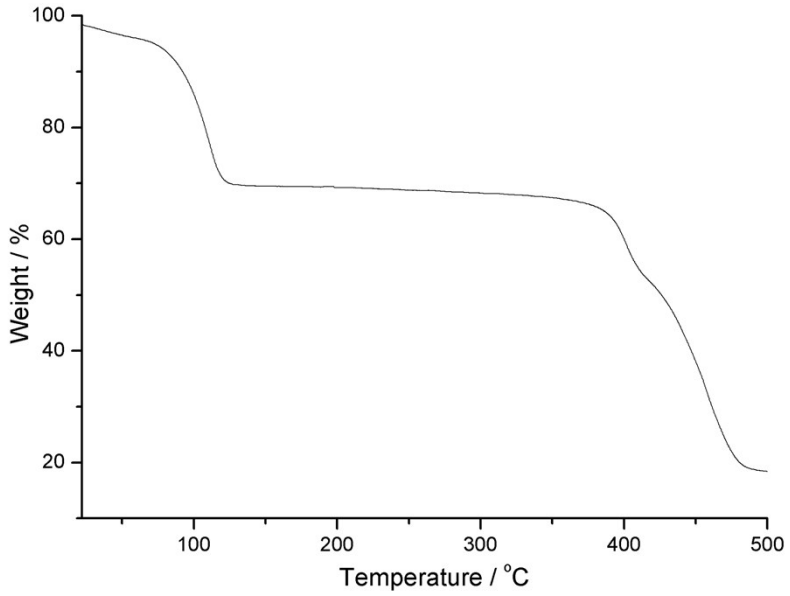

Fig. S7 Thermogravimetric curve of **LMOF-201** under N_2.