

Supporting Information

Tuning Layer to Pillared-layer Metal-Organic Framework for Adsorption and Separation of Light Hydrocarbons

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Experimental Section

Materials and Instrumentation: All reagents were purchased commercially and used without further purification. All syntheses were carried out in a 20 ml vial under autogenous pressure. All Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) with a step size of 0.05° . Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ under an air atmosphere. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System. Fluorescence spectra were measured with a HORIBA Jobin-Yvon FluoroMax-4 spectrometer.

Synthesis of $[\text{Zn}_3\text{L}_2(\text{DMPU})_2]$ (FIR-6)

H_3L (60 mg, 0.1 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (60 mg, 0.2 mmol) were dissolved in DMPU, which were placed in a small vial. The mixture was heated at $120 \text{ }^\circ\text{C}$ for 48 h and then cooled to room temperature. Yellow block crystals of the product were formed and collected by filtration and washed with DMF several times. (yield: 70% based on H_3L).

Synthesis of $[\text{Zn}_3\text{L}_2(\text{DMPU})(\text{bpp})] \cdot 10\text{DMPU}$ (FIR-7)

H_3L (60 mg, 0.1 mmol), bpp (20 mg, 0.1 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (60 mg, 0.2 mmol) were dissolved in DMPU, which were placed in a small vial. The mixture was heated at $120 \text{ }^\circ\text{C}$ for 48 h and then cooled to room temperature. Yellow block crystals of the product were formed and collected by filtration and washed with DMF several times. (yield: 65% based on H_3L).

Crystal data for FIR-6: space group $P-1$, triclinic, $a = 16.0621(4) \text{ \AA}$, $b = 20.7199(5) \text{ \AA}$, $c = 21.2873(5) \text{ \AA}$, $\alpha = 62.257(2)^\circ$, $\beta = 83.386(2)^\circ$, $\gamma = 82.529(2)^\circ$, $V = 6204.8(3) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $Z = 2$, 40380 reflections measured, 19396 independent reflections ($R_{\text{int}} = 0.0286$). The final $R1$ value was 0.0507 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1431 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 1.095. **Crystal data for FIR-7:** space group $C2/c$, monoclinic, $a = 21.9124(2) \text{ \AA}$, $b = 36.7010(3) \text{ \AA}$, $c = 38.7102(4) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 100.5990(10)^\circ$, $\gamma = 90.00^\circ$, $V = 30599.9(5) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $Z = 8$, 32294 reflections measured, 14260 independent reflections ($R_{\text{int}} = 0.0443$). The final $R1$ value was 0.0835 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.2478 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 1.102. The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program.

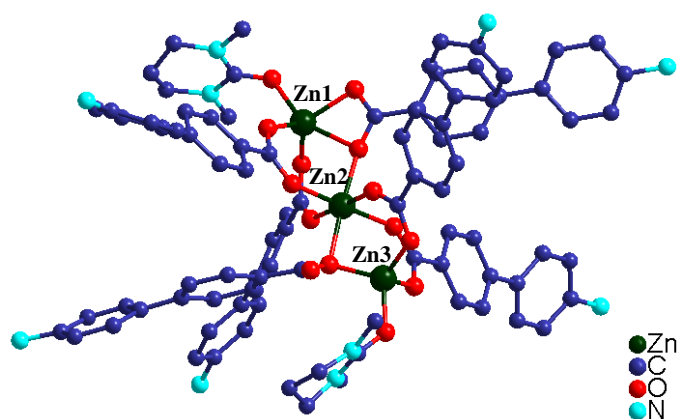


Figure S1. Coordination environment of Zn²⁺ atom in **FIR-6**.

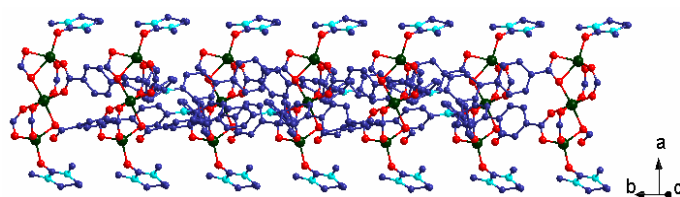


Figure S2. The 2D layer with terminal DMPU molecules extending outside in **FIR-6**.

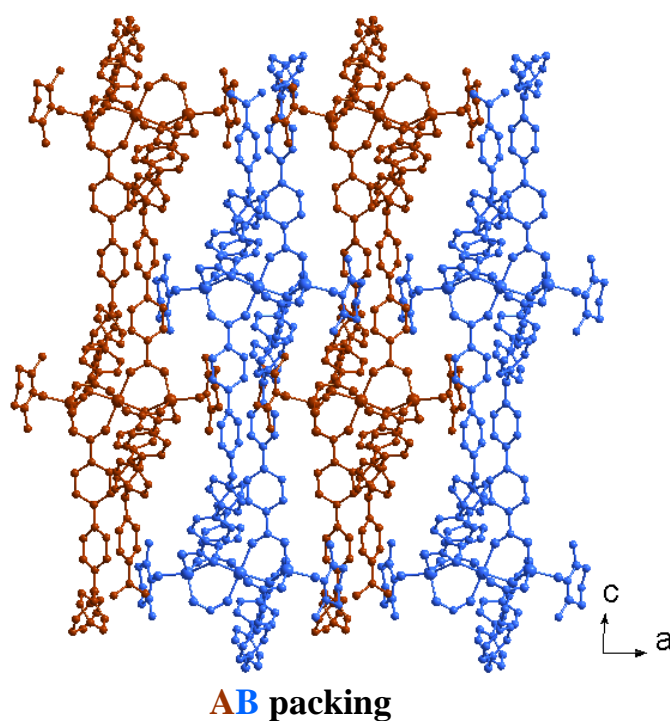


Figure S3. Packed layers of **FIR-6** in an AB fashion.

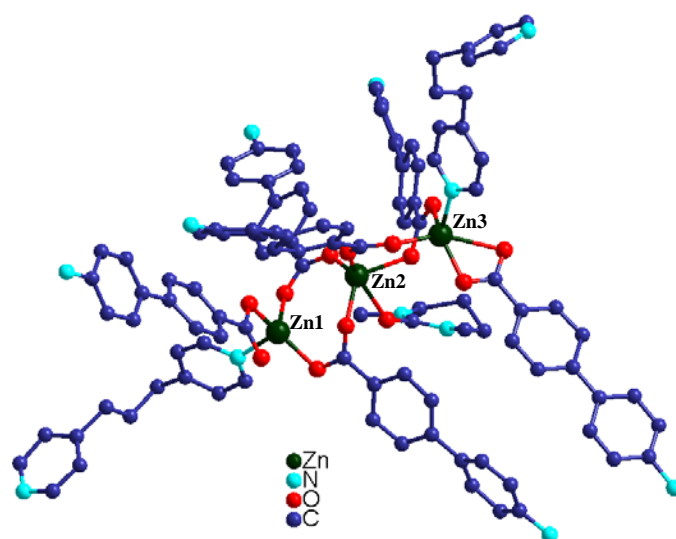


Figure S4. The asymmetric unit in **FIR-7**.

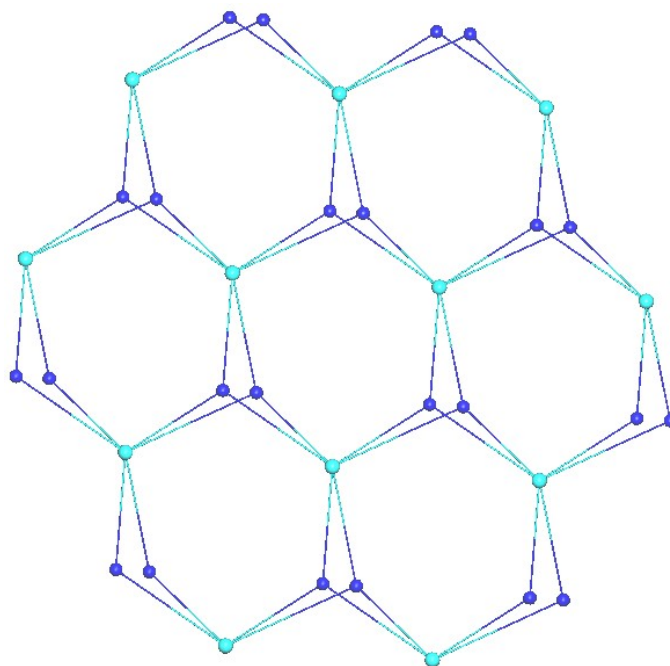


Figure S5. View of the (3,6)-connected NbSe_2 net of **FIR-7**.

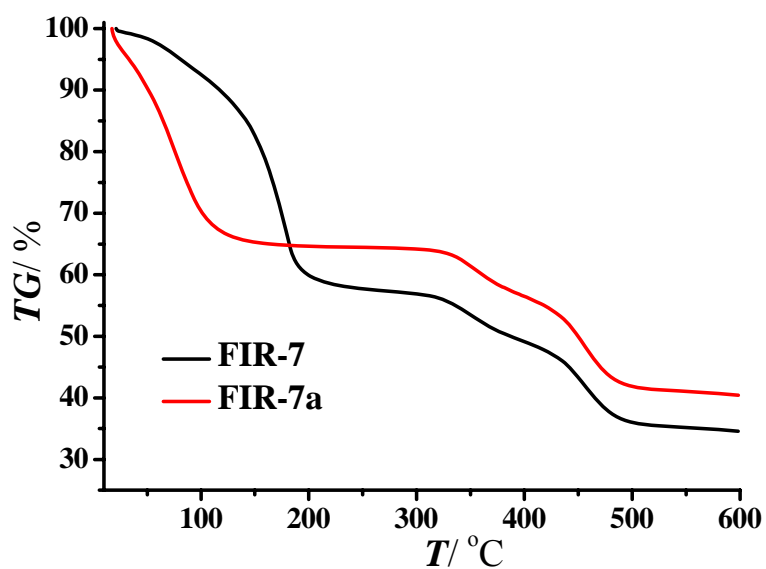


Figure S6. TGA curves of **FIR-7** and **FIR-7a**.

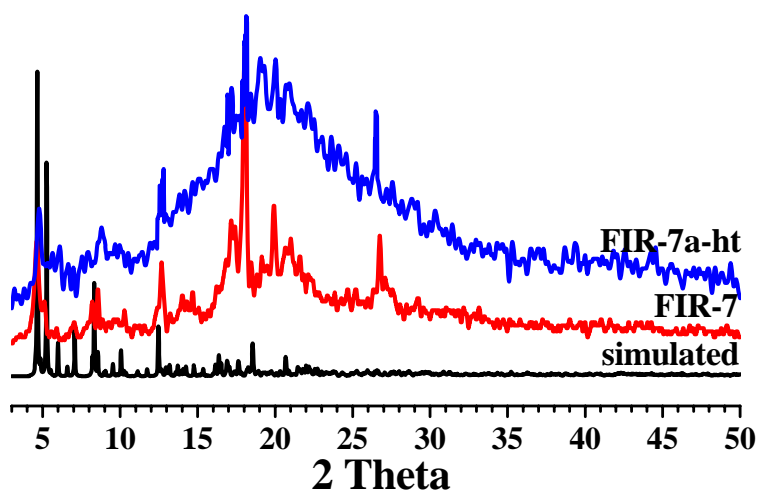


Figure S7. PXRD patterns of simulated from the single-crystal data of **FIR-7** (black); as-synthesized **FIR-7** (red); desolvated solid **FIR-7a-ht** (blue).

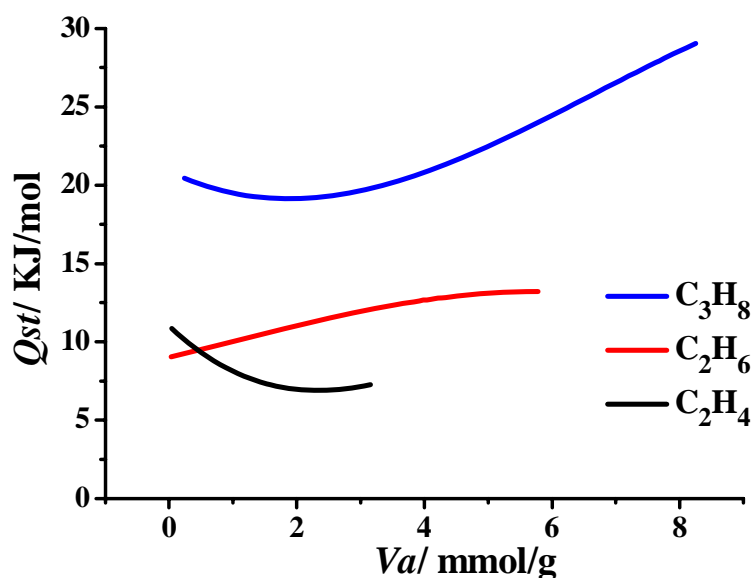


Figure S8. The isosteric heat of adsorption for C₃H₈, C₂H₆, and C₂H₄ in **FIR-7a-ht**.

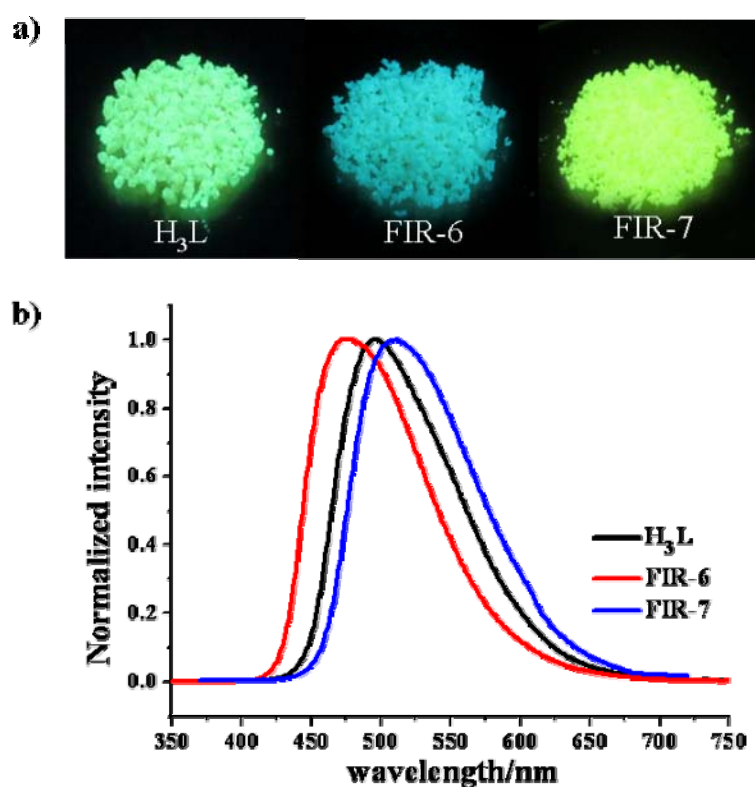


Figure S9. a) Luminescence photos of H₃L ligand, **FIR-6** and **FIR-7** under laboratory UV (365 nm) light; b) the solid-state emission spectra ($\lambda_{\text{ex}}=360$ nm) measured at room temperature of H₃L ligand, **FIR-6** and **FIR-7**.

The solid-state emission spectra of compounds **FIR-6** and **FIR-7** together with the H₃L ligand in this work have also been investigated at room temperature. It is shown that the free H₃L ligand displays the emission maxima at 494 nm which can be assigned to the $\pi \rightarrow \pi^*$ transition, whereas compound **FIR-6** and **FIR-7** have a pattern similar to that of the ligand

with a maximum absorption emission band at around 474 nm and 510 nm, respectively. In comparison with the strongest emission of H₃L, slight blue-shift of 20 nm occur in the maximum emission peaks in compounds **FIR-6** and slight red-shift of 6 nm occur in **FIR-7**. In this case, the ligand-based luminescence dominates and the blue-shifted or red-shifted emission can be assigned to the metal–ligand coordinative interactions.