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 Kα radiation (λ = 1.54056 Å) 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 °C/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 [Zn$_3$L$_2$(DMPU)$_2$] (FIR-6)
H$_3$L (60 mg, 0.1 mmol) and Zn(NO$_3$)$_2$·6H$_2$O (60 mg, 0.2 mmol) were dissolved in DMPU, which were placed in a small vial. The mixture was heated at 120 °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$_3$L).

Synthesis of [Zn$_3$L$_2$(DMPU)(bpp)]·10DMPU (FIR-7)
H$_3$L (60 mg, 0.1 mmol), bpp (20 mg, 0.1 mmol) and Zn(NO$_3$)$_2$·6H$_2$O (60 mg, 0.2 mmol) were dissolved in DMPU, which were placed in a small vial. The mixture was heated at 120 °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$_3$L).

Crystal data for FIR-6: space group $P$-1, triclinic, $a = 16.0621(4)$ Å, $b = 20.7199(5)$ Å, $c = 21.2873(5)$ Å, $\alpha = 62.257(2)^\circ$, $\beta = 83.386(2)^\circ$, $\gamma = 82.529(2)^\circ$, $V = 6204.8(3)$ Å$^3$, $T = 293(2)$ K, $Z = 2$, 40380 reflections measured, 19396 independent reflections ($R_{int} = 0.0286$). The final $R_1$ 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, $a = 21.9124(2)$ Å, $b = 36.7010(3)$ Å, $c = 38.7102(4)$ Å, $\alpha = 90.00^\circ$, $\beta = 100.5990(10)^\circ$, $\gamma = 90.00^\circ$, $V = 30599.9(5)$ Å$^3$, $T = 293(2)$ K, $Z = 8$, 32294 reflections measured, 14260 independent reflections ($R_{int} = 0.0443$). The final $R_1$ 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 Zn$^{2+}$ 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**<sub>2</sub> 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 (λex=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.