Supporting Information

Metal-Organic Framework Architecture with Polyhedron-in-Polyhedron and Further Polyhedral Assembly

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Figure S1. The crystal structure of 1.

Figure S2. Cu 2p spectra of 1 shown that the main component peak at higher BE (↑ 934.01 eV) is assigned to Cu$^{2+}$ ions. Observation of the satellite (939.68-943.62 eV) structure also is consistent with a copper oxidation state of +2.
**Figure S3.** The TG plots of 1, ethanol-exchanged sample 1 and CH$_2$Cl$_2$-exchanged sample 1.

**Figure S4.** Powder XRD patterns: (a) simulated one, (b) after removal of the guests, (c) ethanol-exchanged one, (d) dichloromethane-exchanged one.
**Figure S5.** H₂ adsorption isotherms of 1: (a) H₂ at 77K; (b)H₂ at 87 K.

**Figure S6.** CO₂ adsorption isotherms for 1 fitting by virial method.
Figure S7. The isosteric heat of CO\textsubscript{2} adsorption for 1 estimated by the virial equation.

Adsorption selectivity of CO\textsubscript{2}/N\textsubscript{2} calculation:
The CO\textsubscript{2} and H\textsubscript{2} sorption data for 1 measured up to 1 bar at different temperature were fitted by the virial equation (Figure S5, S6, S7).

\[
\ln(\textit{P}) = \ln(\textit{Va}) + (a_0 + a_1 \textit{Va} + a_2 \textit{Va}^2 + a_3 \textit{Va}^3)/\textit{T} + (b_0 + b_1 \textit{Va}) \quad (1)
\]

Where \textit{P} is pressure, \textit{Va} is amount adsorbed, \textit{T} is temperature, and \textit{a}_0, \textit{a}_1, \textit{a}_2, \textit{a}_3 and \textit{b}_0, \textit{b}_1 are temperature independent empirical parameters.

References:
Figure S8. The FT-IR spectrum of 1.