Electronic Supplementary Material (ESI) for CrystEngComm.

Tuning Sorption Properties *via* Activative Treatments in A Metastable Zn-1,3,5-Benzenetricarboxylate Framework with Dodecahedral and Cubic Cages

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Experimental Section

1. Material and Methods.

All reagents and solvents were used as received from commercial suppliers without further purification. The elemental analyses were performed with Perkin–Elmer 240 CHN analyzers. Thermogravimetric analyses (TGA) were measured using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 10 ^{o}C/min. Powder X-ray diffraction (PXRD) patterns were recorded by a Rigaku Ultima IV diffractometer operated at 40 kV and 44 mA with a scan rate of 5 degree/min. A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms.

2. Synthesis of $[Zn_{22}(btc)_{12}(H_2O)_{22}(NO_3)_8]\cdot x$guest (1)

$Zn(NO_3)_2\cdot 6H_2O$ (293 mg, 1 mmol) and H_3btc (210 mg, 1 mmol) were added to a screw cap vials, then 1 mL DEF and 3 mL EtOH were added to the mixture. The content was sonicated for 30 min and then heated at 100 ^{o}C for 3 day, giving colourless X-ray-quality crystals with the yield of 63% based on Zn.

X-ray Crystallographic Study: The diffraction data for compounds were collected on an Oxford Xcalibur diffractometer equipped with a graphite–monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. Crystal data for **1**: $C_{108}H_{36}O_{94}Zn_{22}$, M = 4275.94, cubic, a = 20.4421(2) Å, V = 8542.33(14) Å ^{3}, T = 293(2) K, space group *Pm-3m*, Z = 2, 1485 reflections measured, 1091 independent reflections (R_{int} = 0.0811). The final R_1 value was 0.0656 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.2236 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 1.120.

3. Typical freeze-drying procedure

After decanting all the mother liquid, freshly prepared crystals of **1** were washed with EtOH three times over a 8 hours period, and then washed with benzene several times and soaked in benzene overnight before loading into a sample cell. About 1 mL of benzene was left in the sample cell, and the sample cell was then frozen at 0 ^{o}C for 8 hours. After three freeze-thaw cycles, the sample cell was placed in an ice/H_2O bath and evacuated under a dynamic vacuum for 12 hours. The ice/H_2O bath was removed and the sample was kept under vacuum at room temperature for another 8 hours. The resulting freeze-dried **1b** was used to perform gas uptake measurements.

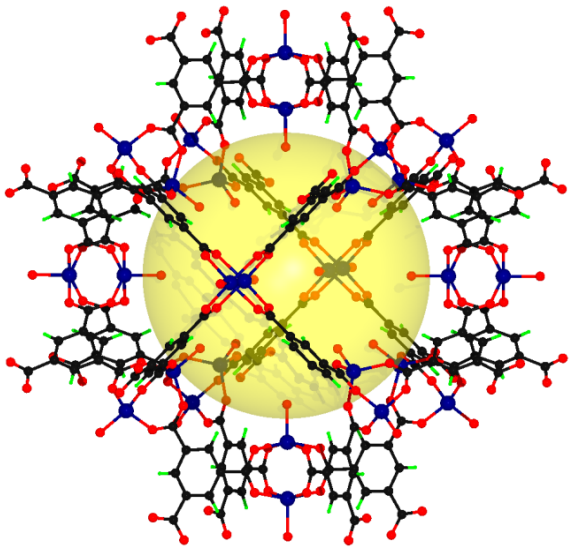

Figure S1. The large cage considered as rhombic dodecahedron in **1**.

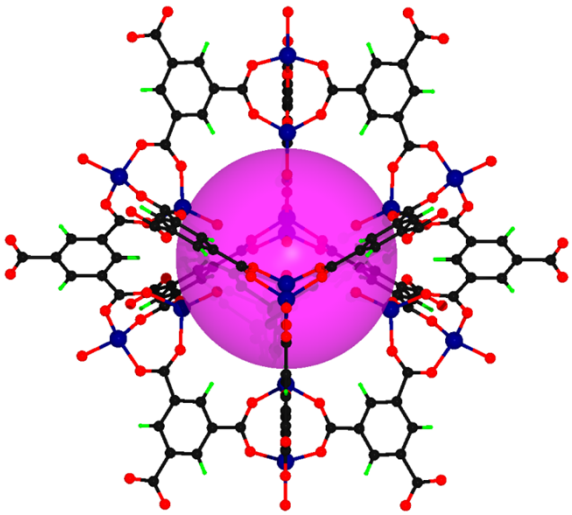

Figure S2. The small cage considered as cube in **1**.

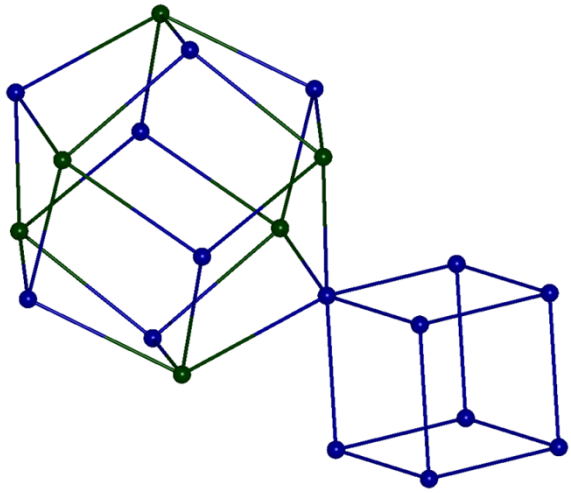

Figure S3. Linkage between rhombic dodecahedron and cube through shared vertexes

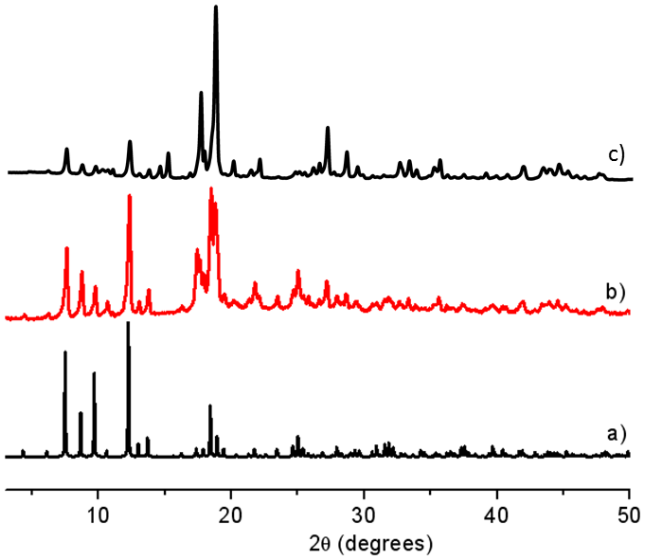

Figure S4. The PXRD patterns for the simulated one (a), as-synthesized **1** (b) and vacuum-dried sample **1a** (c).

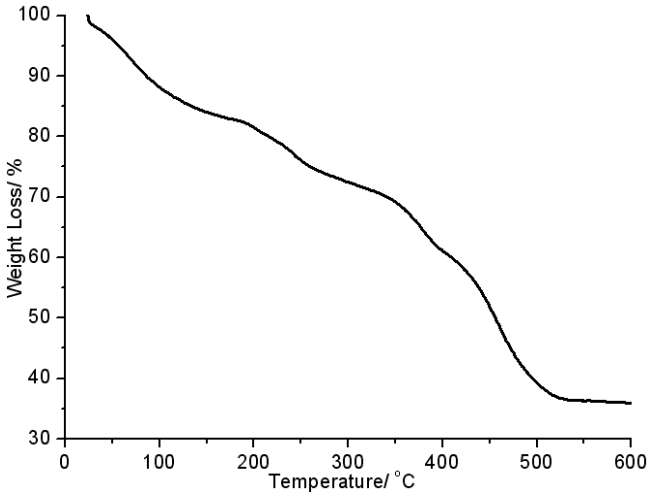

Figure S5. The TGA curve of **1**.

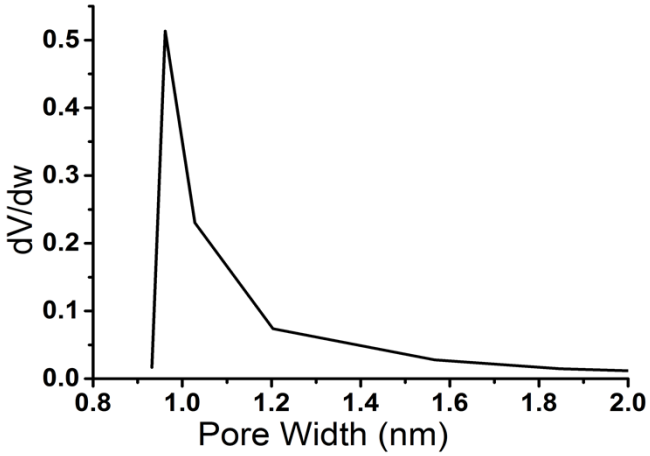

Figure S6. The Horvath-Kawazoe pore distribution plots for **1c**.

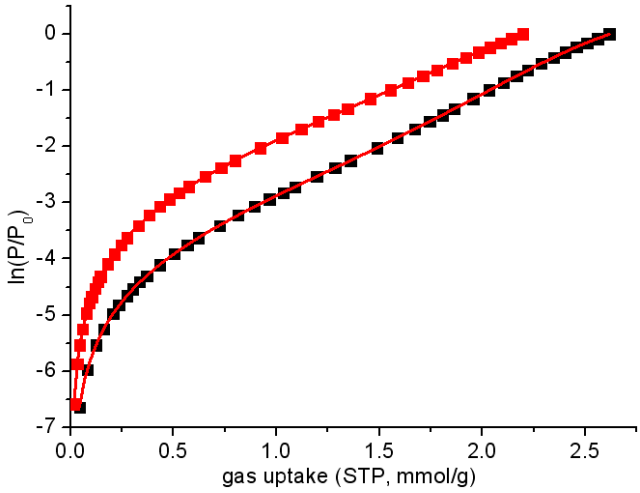

Figure S7. CO_2 adsorption isotherms for **1c** fitting by virial method.

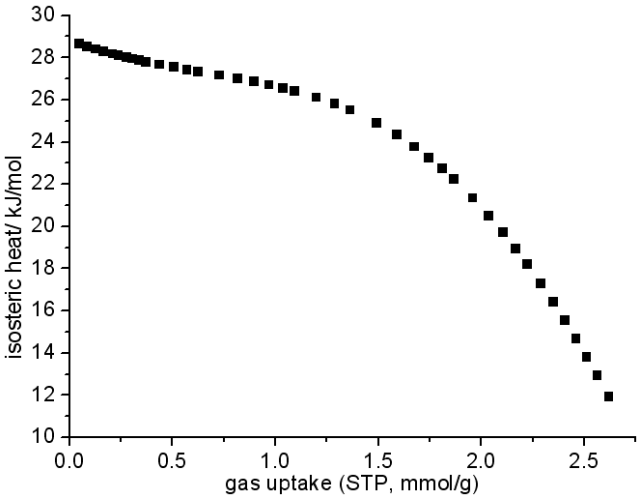

Figure S8. The isosteric heats of CO_2 adsorption for **1c**.

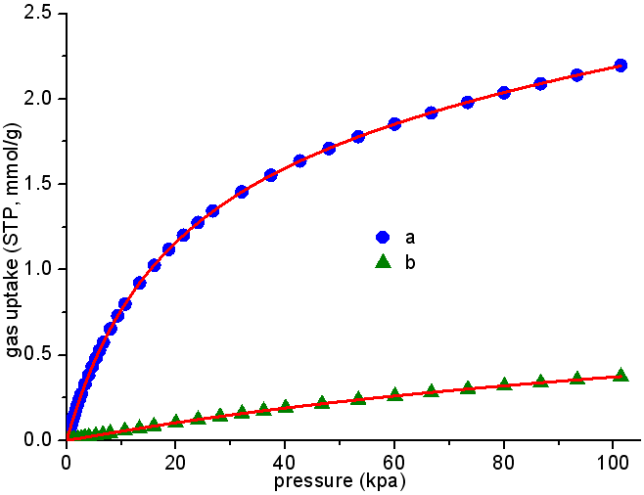

Figure S9. Adsorption isotherms for CO_2 (a) and CH_4 (b) in **1d** at 298 K. Solid lines through the experimental data are fits to the DSLF model.