

Supporting information

Zeolitic Porous Lithium Organic Framework Constructed from Cubane Clusters

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Experimental details:

Synthesis of $\text{Li}_4(\text{OPy})_4$: The compound was synthesized by injection of 0.5 ml *t*-BuOLi (1.0 M solution in hexane) to a 20 ml glass vial containing well stirred methanol (5.0 g) solution of 4-hydroxypyridine (48.2 mg, 0.5 mmol). After stirring for 15 min, the glass vial was loosely sealed and placed in a 120 °C oven for about 24 hours, when the solvent was almost evaporated out and pure colorless crystals were obtained at the bottom of the vial. The yield was above 95% based on the metal. The phase purity was identified by the powder X-ray diffraction (Figure S2). This compound was also synthesized in the 2-propanol solution and *t*-BuLi could be also adopted as the lithium source. Although *t*-BuOLi is sensitive to the moisture in the atmosphere, the synthesis could be performed in the air when small amount of reagent was used. Compared to the *t*-BuLi, the reactivity of *t*-BuOLi is a lot gentler and easier to handle.

Measurements:

Powder X-ray diffraction: Powder X-ray diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 30kV and 30mA ($\text{CuK}\alpha$ radiation, $\lambda = 1.5418\text{\AA}$). The data collection was performed with a step size of 0.03° and counting time of 1s per step. The 2-theta angular range is from 5 to 40° .

Single crystal X-ray diffraction: Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$), operating in the ω and ϕ scan mode. The SADABS program was used for absorption correction. The structure was solved by direct methods followed by successive difference Fourier methods. All non-hydrogen atoms were refined anisotropically. Computations were performed using SHELXTL and final full-matrix refinements were against F^2 .

Thermal analysis: The simultaneous DSC-TGA thermal analysis was performed on TA Instruments SDT Q600 under the flowing nitrogen atmosphere. The flow rate of the nitrogen gas was controlled at about 100 milliliters per minute. The thermal treated samples were prepared by heating up the samples to the desired temperature at $20^\circ\text{C}/\text{min}$ under nitrogen flow. After holding the temperature for 30 minutes, the samples were allowed to slowly cool down to room temperature.

Gas sorption measurements: N_2 gas sorption experiments were carried out on a Micromeritics ASAP 2010 surface area and pore size analyzer. Prior to the measurement, the sample was dried by using the "degas" function of the surface area analyzer for 10 hours at 180°C . The N_2 , H_2 and CO_2 adsorption measurement were performed at 77K, 77K, and 273K, respectively.

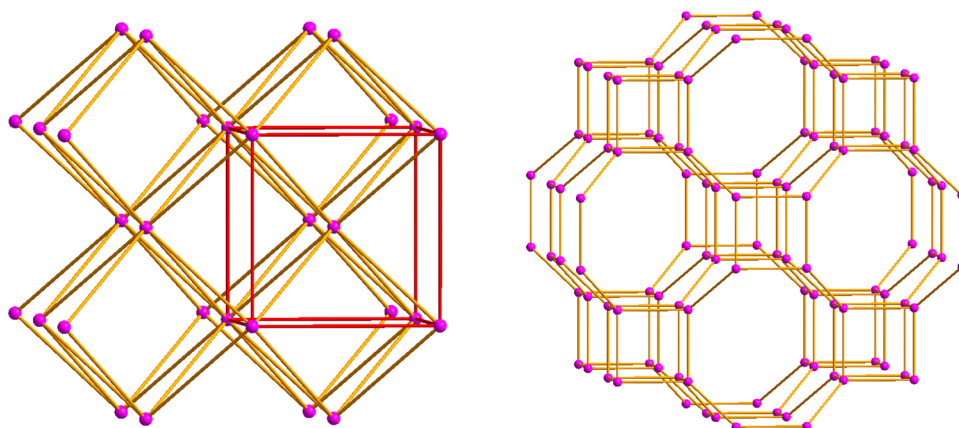


Figure S1 The topology of the compound can be described in two ways: a bcu net (Left) or an ACO net (Right). The purple nodes represent Li_4O_4 clusters (Left) and Li (or O) atoms (Right), respectively.

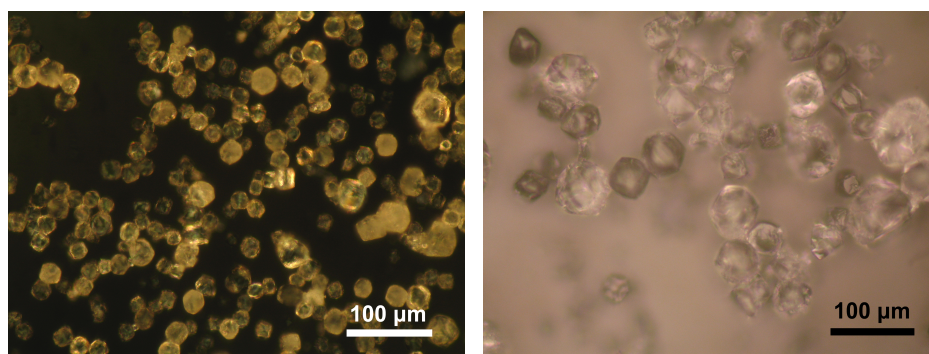


Figure S2. Dark field (left) and bright field (right) optical images of the as-synthesized crystals.

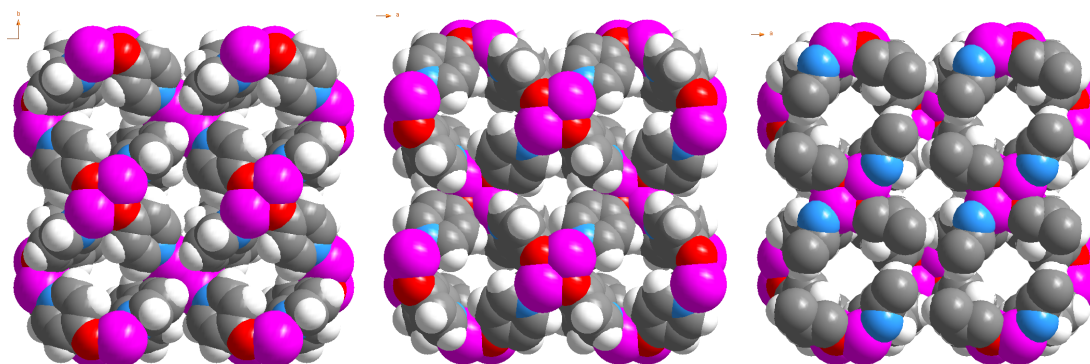


Figure S3. Space filling diagram of the pore channels along *Left* (100), *Middle* (010) and *Right* (001) directions (Li: purple, O: red, N: blue, C: grey and H: white).

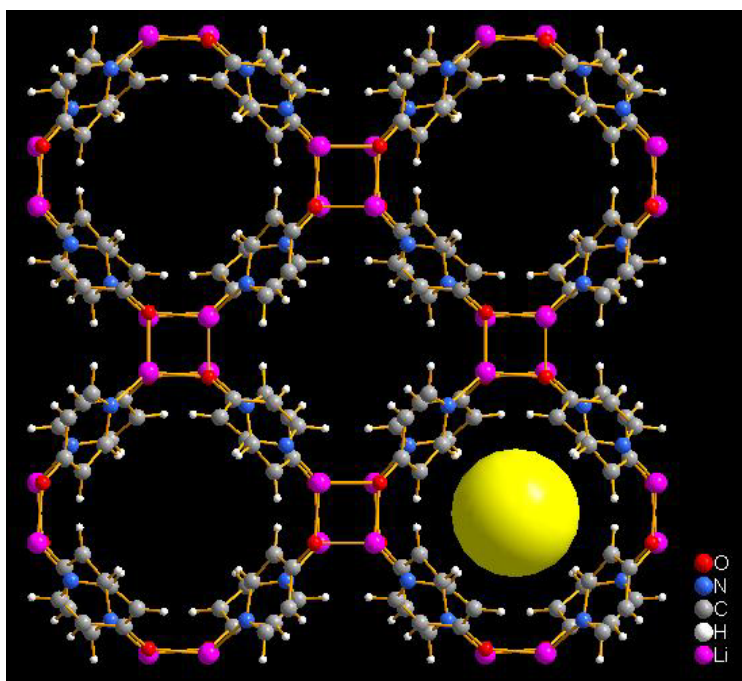


Figure S4. Diagram of the framework structure (Li: purple, O: red, N: blue, C: grey and H: white). The big yellow sphere represents the void space in the cage.

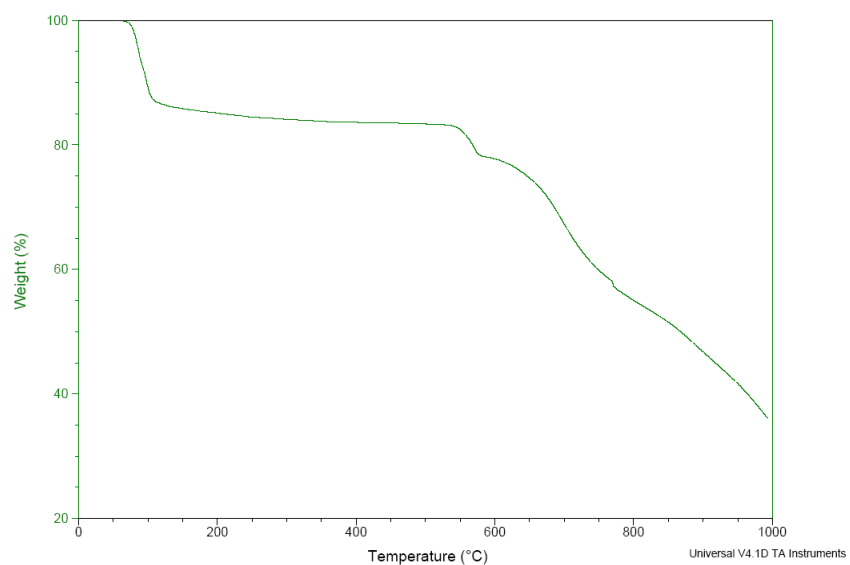


Figure S5. Thermogravimetric analysis (TGA) for $\text{Li}_4(\text{OPy})_4$.

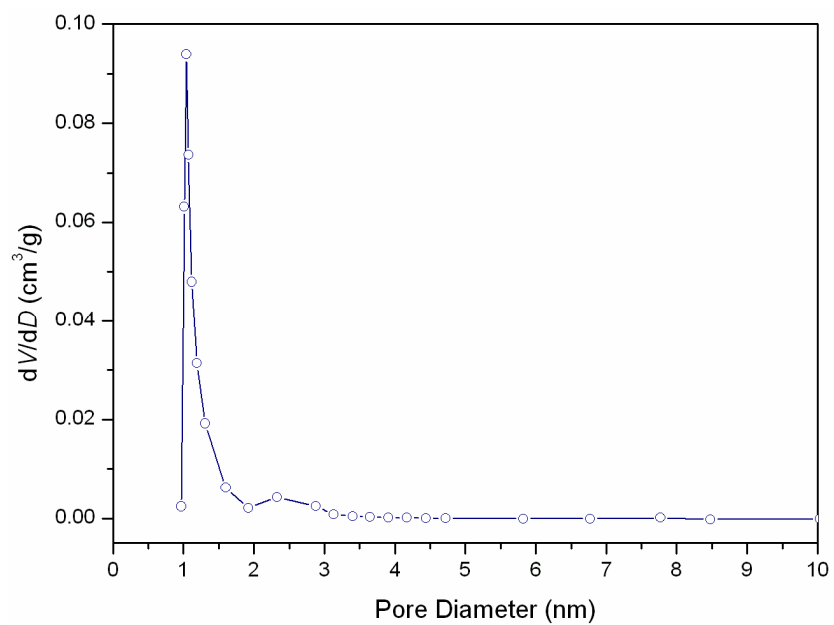


Figure S6. Pore size distribution analysis of $\text{Li}_4(\text{OPy})_4$.