Electronic Supplementary Information

Breathing Effects of CO_2 Adsorption on Flexible 3D Lanthanide Metal-Organic Frameworks

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1. Synthesis

All the reagents and solvents were purchased from commercial sources and used without further purification. Solvothermal reactions were carried out in digestion bomb reactors. Exact amounts of $La(NO_3)_3 \cdot 6H_2O$ (1.8 mmol) and 1,3,5-Tris(4- carboxyphenyl)benzene acid (0.6 mmmol) were dissolved in 30 mL dimethylformamide (DMF). The mixture solution was heated at 95 °C for 48 hours. Then the colorless crystal $[La(BTB)(H_2O) \cdot 3DMF]_n$ (**1**) was obtained.

2. TGA

Thermogravimetric analyses were carried out with a NETZSCH STA 449 F1 Jupiter® TGA-DSC at a heating rate of 10 °C/min under helium atmosphere with 20 mL/min flow rate. The examined temperature range was 30 – 750°C. The as-synthesized sample (**1**) was exposed to air for 1 day before testing. The solvent-exchanged sample (**1'**) was exposed to air for less than 6 hours before testing, while the activated sample (**1"**) was exposed to air for less than 30 min.

3. Powder X-Ray Thermodiffraction

Powder X-ray thermodiffraction experiments were carried out at an X'Pert Pro work station equipped with high-speed RTMS detector and TTK-450 temperature/environment control chamber provided by PANalytical Company over a temperature range of 25 – 350°C. While heating, each scan was performed every 20°C until 200°C, and then scanning was intensified to every 10°C until reaching the maximum temperature of 350°C. After the temperature was maintained at 350°C for 30 minutes, scanning commenced for decreasing temperature and was recorded every 50°C until arriving at room temperature.

4. **Single-crystal X-ray crystallography**: Single-crystal XRD data of compound **1** was collected on a Rigaku Mercury CCD area-detector single crystal diffraction system with CuKα radiation (α = 1.54178 Å). The structure was solved by the Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined with anisotropic temperature parameters.

Compound	**1**
Chemical Formula	$C_{36}H_{38}N_3O_{10}La$
Formula weight	811.61
Crystal system	hexagonal
Space group	$P6_522$
a (Å)	16.5428(4)
b (Å)	16.5428(4)
c (Å)	24.3988(15)
α(°)	90.00
β(°)	90.00
γ(°)	120.00
V (Å^3)	5782.5(4)
D_c (g/cm^3)	1.017
Abso. coef. (mm^{-1})	8.806
Z	6
T (K)	296(2)
Wavelength (Å)	1.54178
F(000)	1740
Goodness-of-fit on F2	1.080
R_1 indices [$I>2.0\sigma(I)$]	0.0550
wR_2 indices[$I>2.0\sigma(I)$]	0.1508
R_1 indices (all data)	0.0565
wR_2 indices (all data)	0.1522

$$R_1 = \Sigma(|Fo| - |Fc|) \Sigma |Fo| \quad wR_2 = [\Sigma w(Fo^2 - Fc^2)^2 / \Sigma w(Fo^2)^2]^{1/2}$$

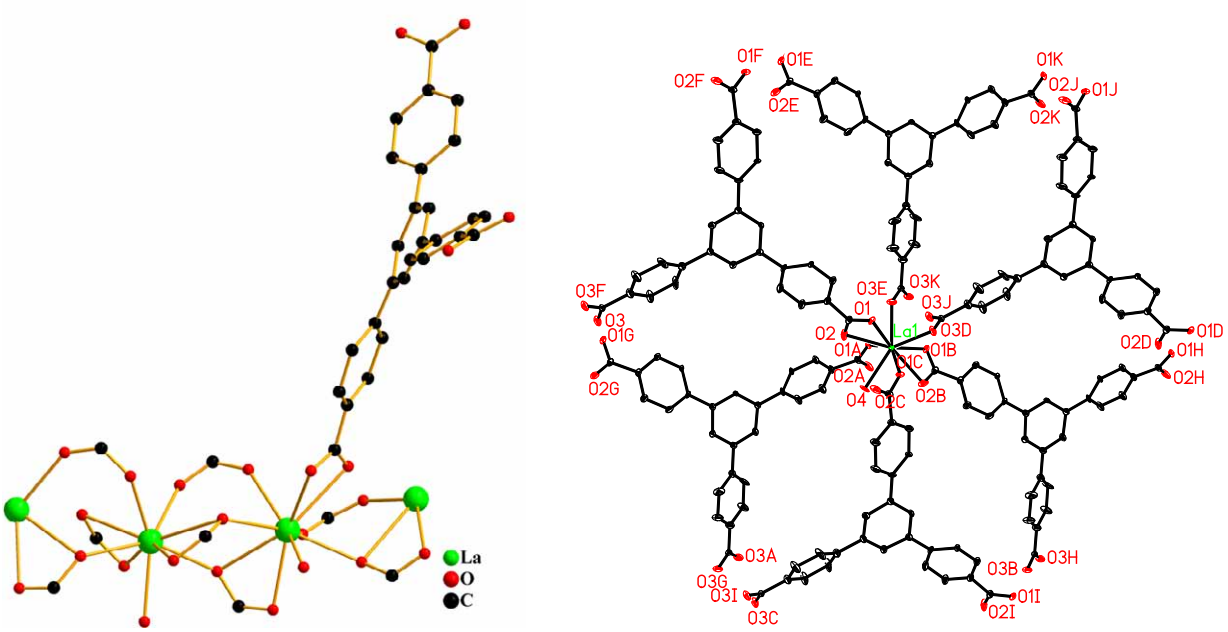
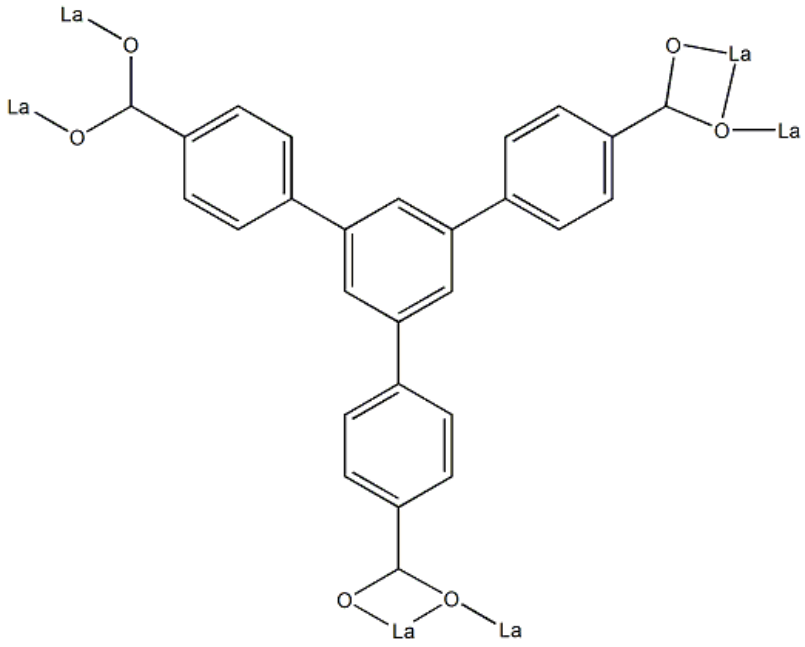


Figure S1. Coordination Environment of La atom



Scheme S1. Connecting mode of BTB ligand

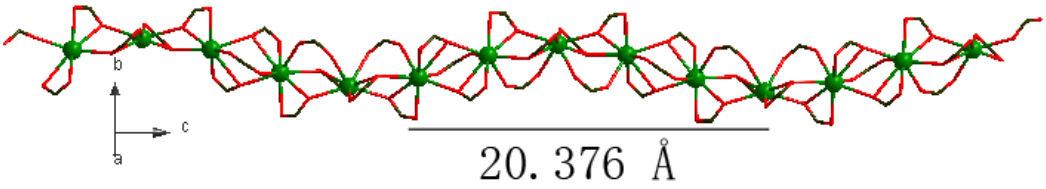


Figure S2. Inorganic helical chain composed of La and O

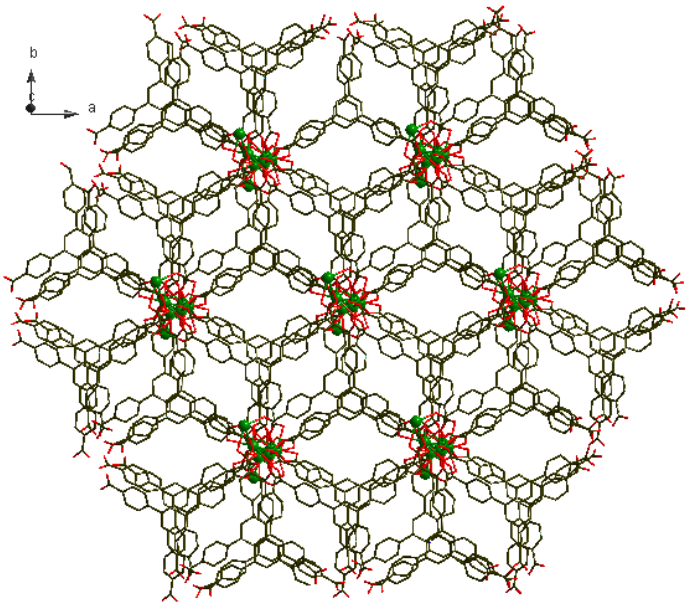


Figure S3. 3D framework in compound **1** along c axis

6. Elemental analysis and FTIR pattern: Elemental analyses were carried out on an Elementar Vario EL III analyzer. Infrared (IR) spectrum was recorded with PerkinElmer Spectrum One as KBr pellets in the range 4000-400cm^{-1}. Anal.Calcd for $C_{36}H_{38}N_3O_{10}La$: C, 53.28; H, 4.72; N, 5.18. Found: C, 53.26; H, 4.74; N, 5.19. IR(KBr pellet/cm^{-1}): 3431(s), 1663(vs), 1582(vs), 1526(s), 1254(m), 1095(m), 1016(m), 859(s), 784(vs), 706(m), 670(m), 553(w).

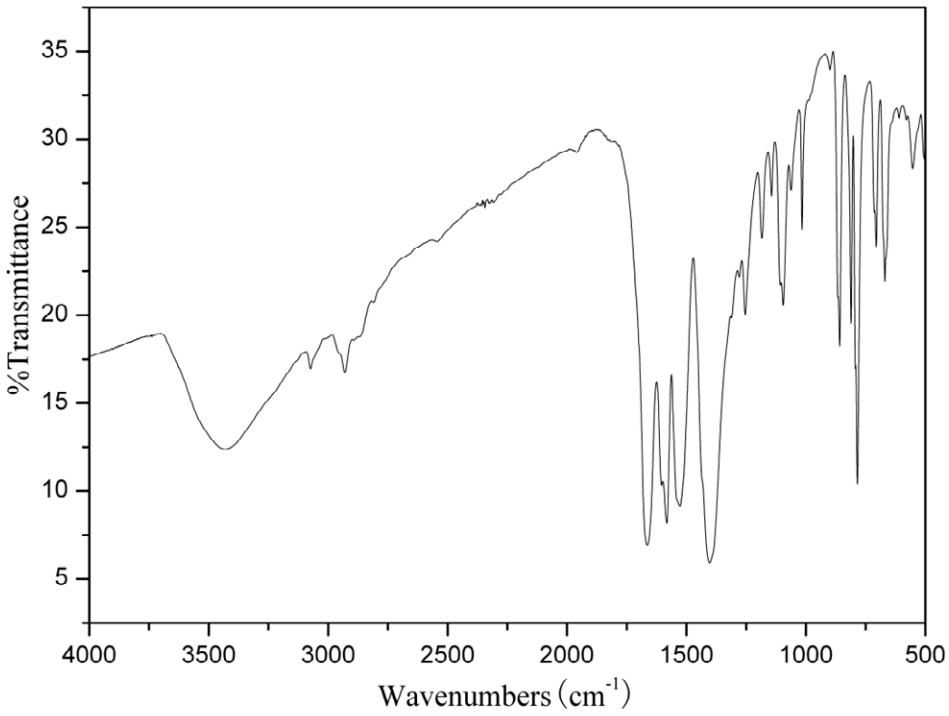


Figure S6. FTIR Spectrum of Compound **1**.