Supporting Information

Transition from Isotropic Positive to Negative Thermal Expansion by Local Zr_6O_8 Node Distortion in MOF-801

Rui Ma, [a] Zhanning Liu, [b,] * Liang Chen, [a] Qiang Li, [a] Kun Lin, [a] Xin Chen, [a] Jinxia Deng, [a] Koji Ohara, [c] and Xianran Xing [a,] *

[a] Beijing Advanced Innovation Center for Materials Genome Engineering, Institute of Solid State Chemistry, University of Science and Technology Beijing, Beijing 100083, China

[b] School of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao, 266590, China

[c] Diffraction and Scattering Division, Center for Synchrotron Radiation Research, Japan Synchrotron Radiation Research Institute, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

Supplementary Figures and Tables

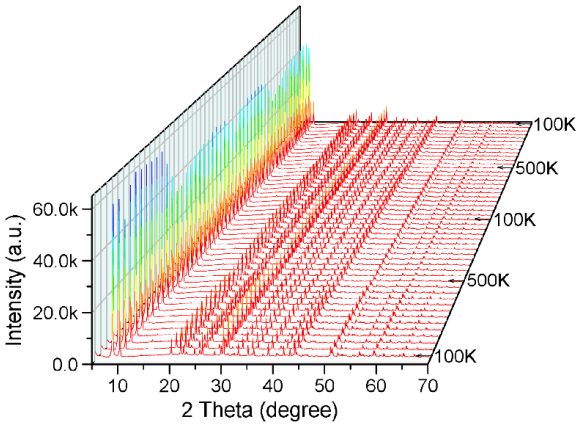

Figure S1. Cyclic temperature-dependent X-ray diffraction patterns were collected from 100 K to 500 K in MOF-801, containing cycles of both heating and cooling.

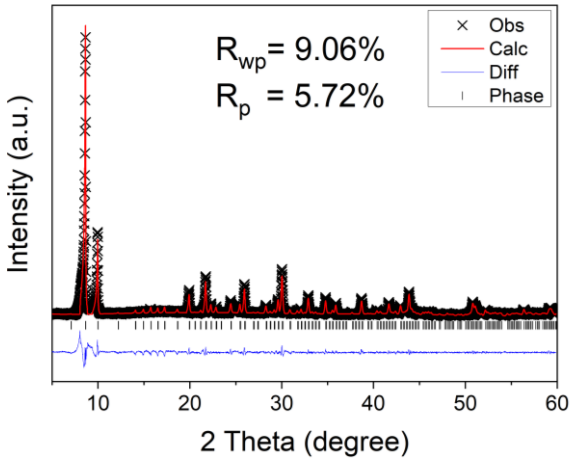

Figure S2. Rietveld refinement pattern of MOF-801 at 300K.

Table S1. The coefficients of some representative NTE MOFs.

Compound	CTE	Temperature range (K)	Reference
MOF-5	α_a = -13.1 MK^{-1}	100~500	[1]
$Cu_3(BTC)_2$	α_a = -4.1 MK^{-1}	80~500	[2]
TCNQ@$Cu_3(BTC)_2$	α_a = -2.8 MK^{-1}	100~300	[3]
MOF-14	α_a = -4 ~ -13.1MK^{-1}	3~400	[4]
MIL-68(In)	α_a = −5.6 MK^{-1} α_b = −2.7 MK^{-1} α_c = −4.0 MK^{-1}	125~600	[5]
Ca-sq	α_a = −4.7 MK^{-1} α_b = −0.1 MK^{-1}	100~450	[6]
Cd-sq	α_a = −14.3 MK^{-1} α_c = +14.8 MK^{-1}	100~350	[7]
Cd(trz)	α_a = −12.2 ~ −3.5 MK^{-1} α_c = +10.4 ~ +18.2 MK^{-1}	100~550	[8]
MOF-808-SO_4	α_a = −39.7 MK^{-1}	25~250	[9]
UiO-66(Hf)	α_a = −32.3 MK^{-1}	433~613	[10]
$[Zr_6O_4(OH)_4(edba)_6]$	α_a = −11.0 MK^{-1}	127~434	[11]
NU-1000-formate	α_a = −30.0 MK^{-1}	at 443	[12]
MOF-801	α_a = −31.6 MK^{-1}	375~500	This work

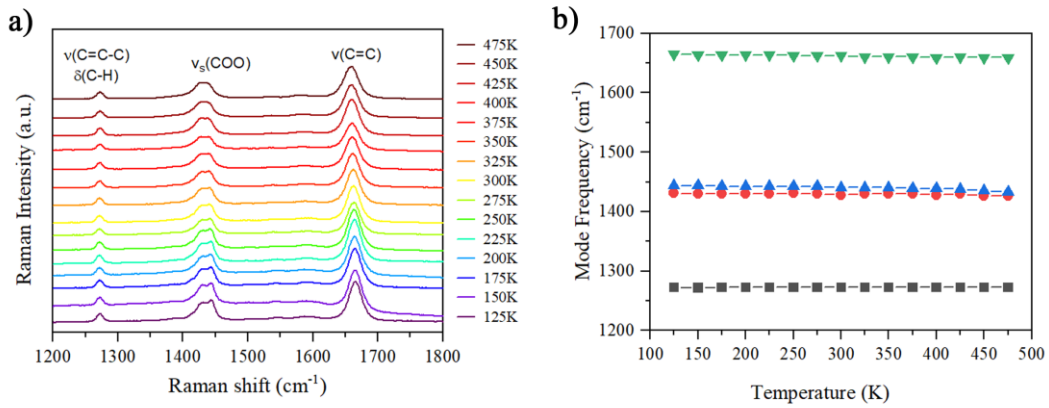

Figure S3. a) The zoomed part of *in situ* variable temperature Raman spectra of MOF-801 and b) the corresponding peak center.

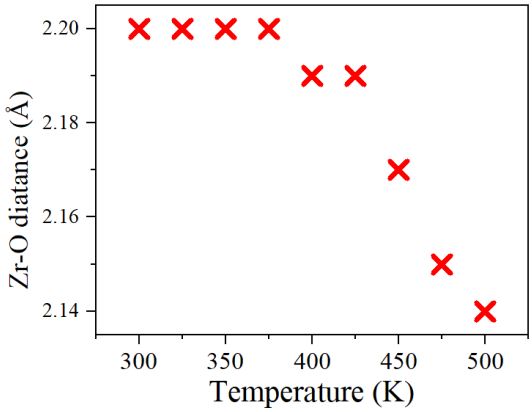

Figure S4. The change of Zr-O distance extracted from variable temperature PDF patterns.

References:

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