Supplementary information

Molecular motion in the nanospace of MOFs upon gas adsorption investigated by in situ Raman spectroscopy

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General Procedures and Materials

General Procedures

The powder X-ray diffraction patterns (PXRD) measurements were carried out on a Rigaku MiniFlex600 using a Cu Kα radiation (λ = 1.5406 Å) with a scan rate of 10 degree/min at room temperature.

Simulated powder patterns from single-crystal X-ray diffraction data were generated using Mercury 1.4.1 software.

N_2 adsorption measurements at 77 K were performed with BELSORP-mini (MicrotracBEL corp.). A sample was heated at 120 °C under vacuum for 6 h prior to the measurements.

Materials

$Cu(HCOO)_2 \cdot 4H_2O$ and toluene were purchased from FUJIFILM Wako Pure Chemical Corp., 1,4-benzenedicarboxylic acid (H_2bdc) and 1,4-diazabicyclo[2.2.2]octane (dabco) were from Tokyo Chemical Industry, methanol (MeOH) was from Nacalai Tesque and formic acid was from Kanto Chemical Co., Inc..

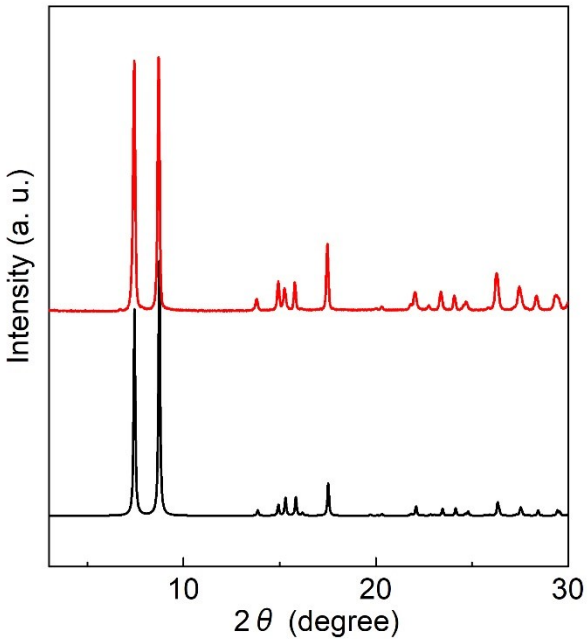

Fig. S1. PXRD patterns of MIL-140A (black: simulated, red: experimental)

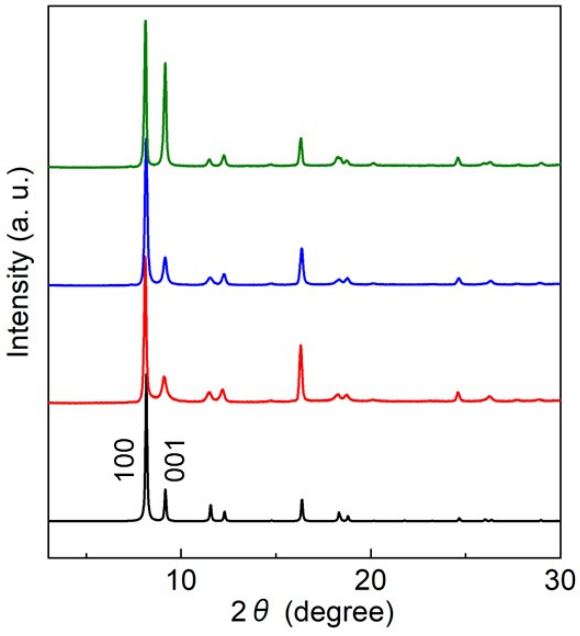

Fig. S2. PXRD patterns of Cu-JAST-1 (black: simulated, red: experimental), Cu-JAST-1D (blue: experimental) and Cu-JAST-5 (green: experimental)

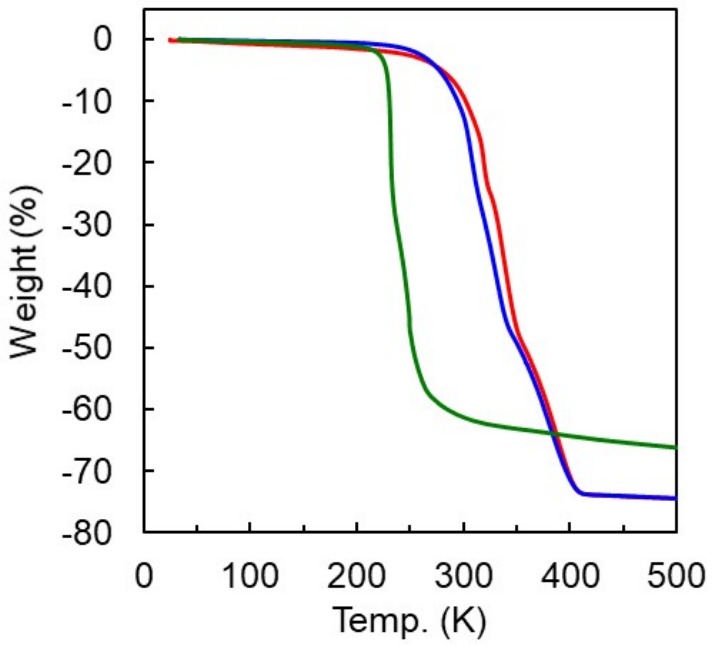

Fig. S3. Thermogravimetric analysis curves for Cu-JAST-1 (red), Cu-JAST-1D (blue) and Cu-JAST-5 (green)

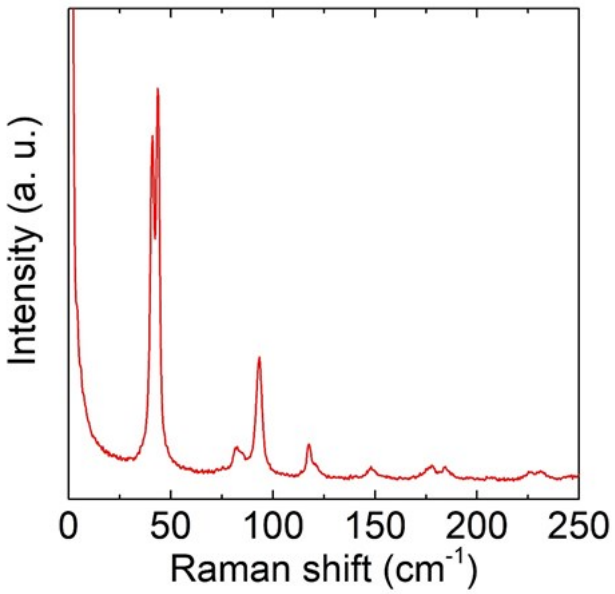

Fig. S4. Raman spectrum of MIL-140A.

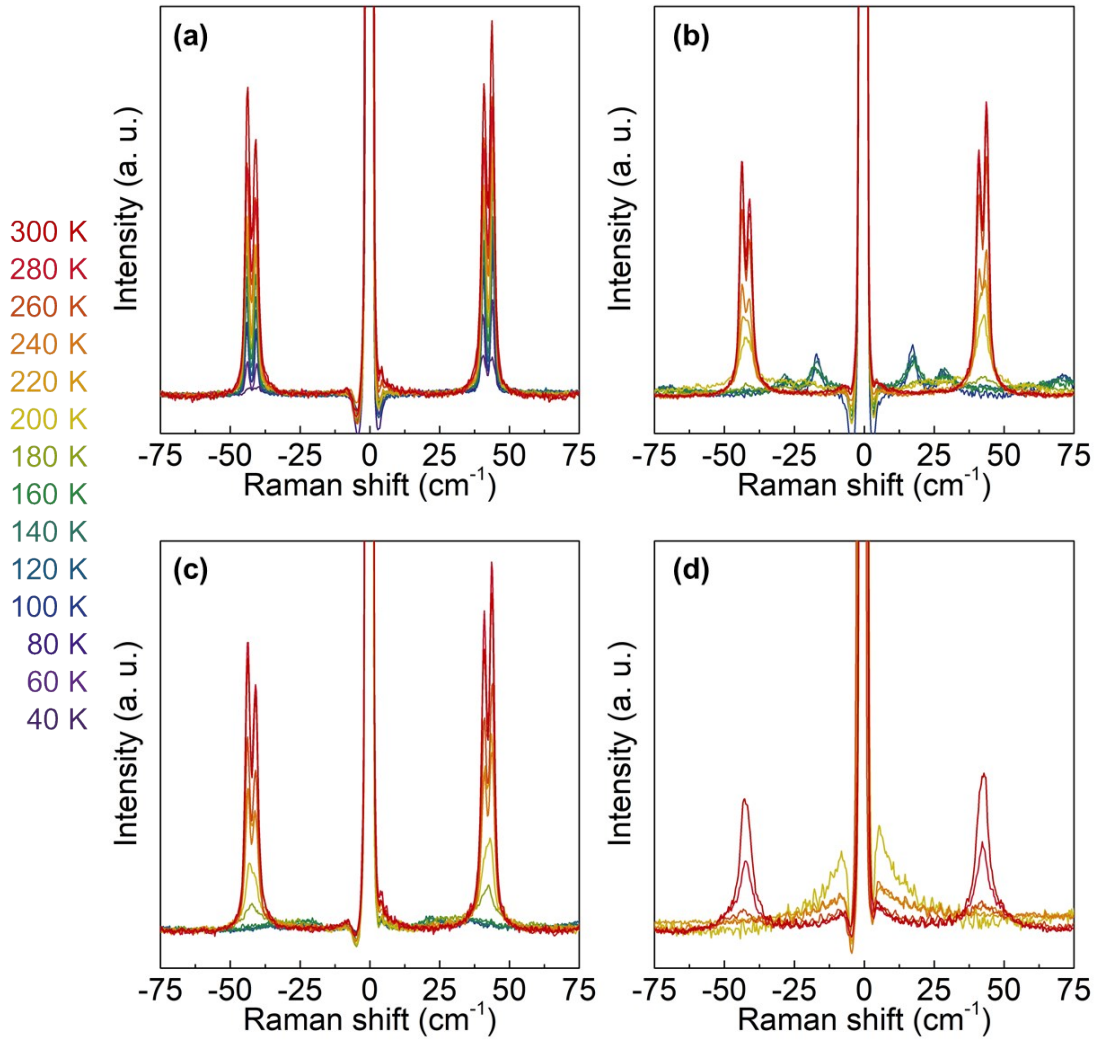

Figure S5. Temperature dependent Raman spectra of MIL-140 A of low frequency region under (a) He (b) Ar (c) N_2 (d) CO_2 at 100 K. The peak intensity was normalized using the peak at 800 cm^{-1} as the standard.

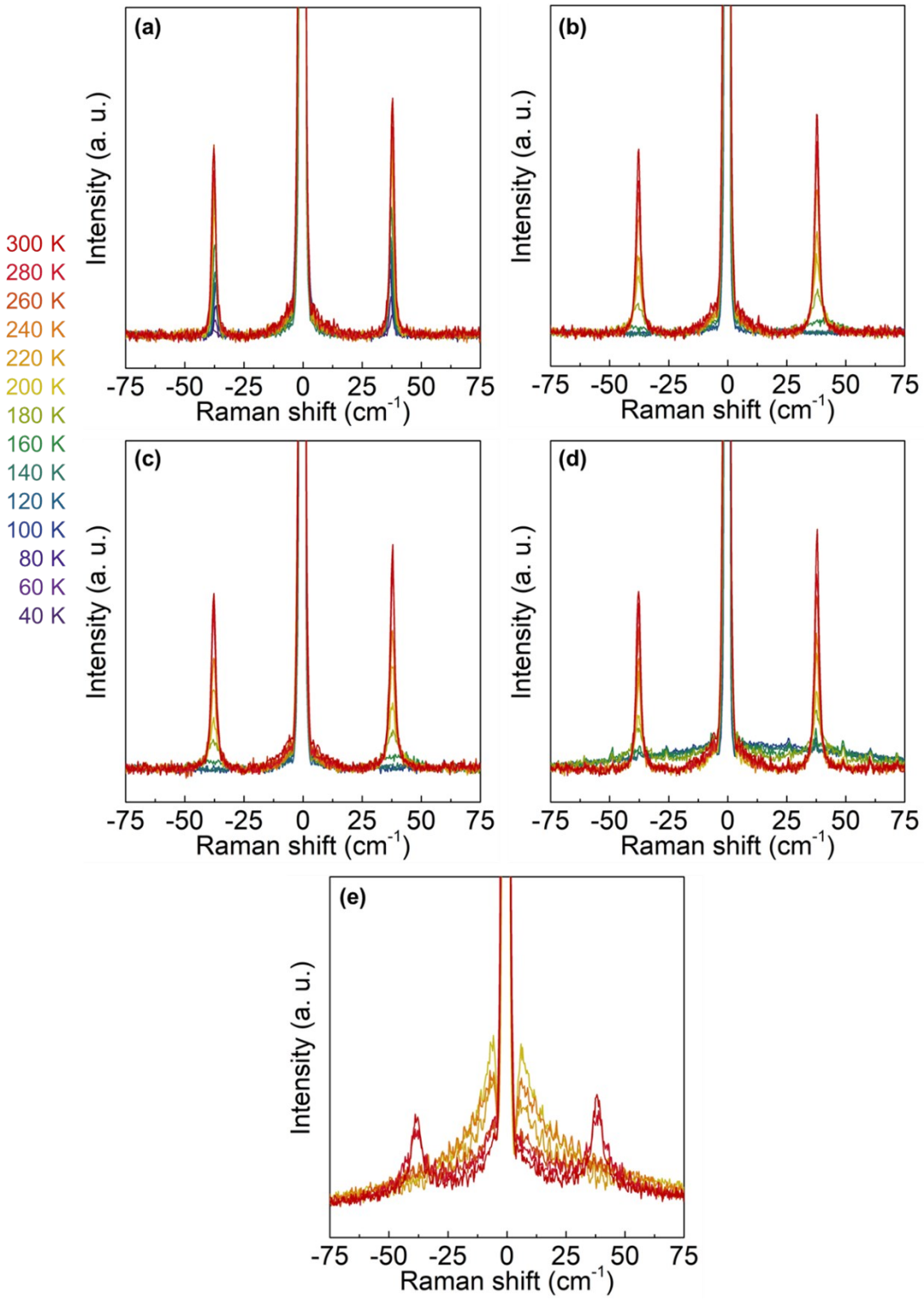

Figure S6. Temperature dependent Raman spectra of Cu-JAST-1 of low frequency region under (a) He (b) Ar (c) N_2 (d) O_2 (e) CO_2 at 100 KPa. The peak intensity was normalized using the peak at 450 cm^{-1} as the standard.

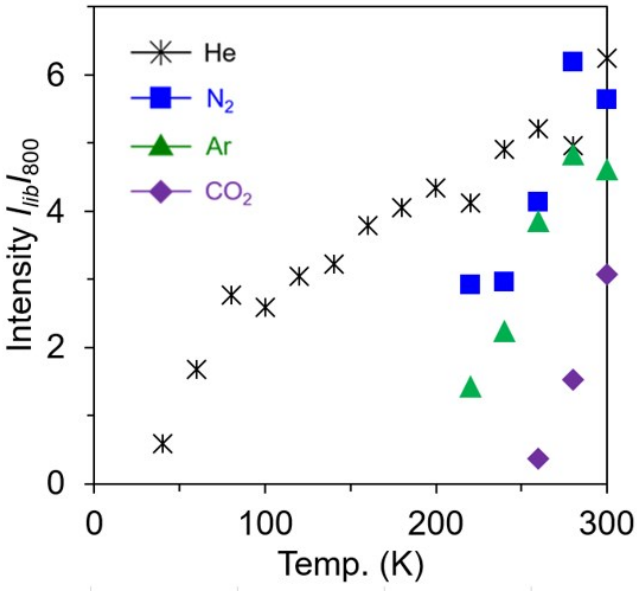

Fig. S7. Temperature dependent Raman peak intensity for the libration mode in MIL-140A

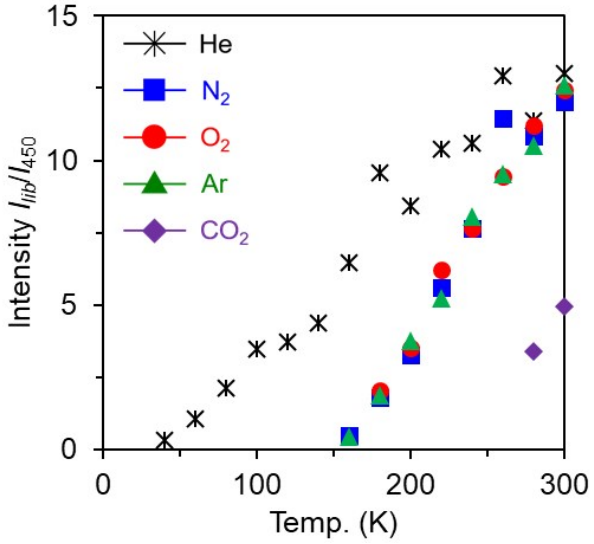

Fig. S8. Temperature dependent Raman peak intensity for the libration mode in Cu-JAST-1

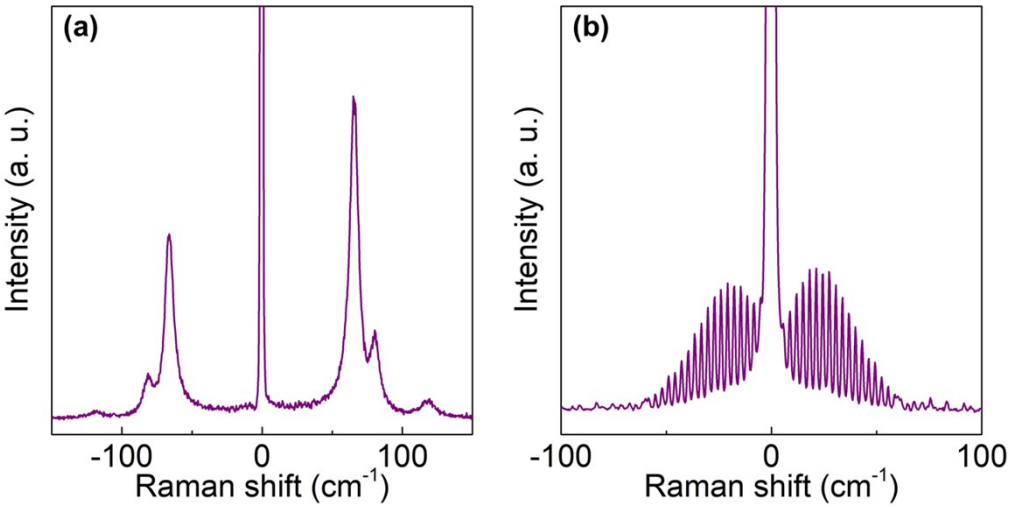

Fig. S9. Raman spectra for CO_2 in (a) solid and (b) gas phases.

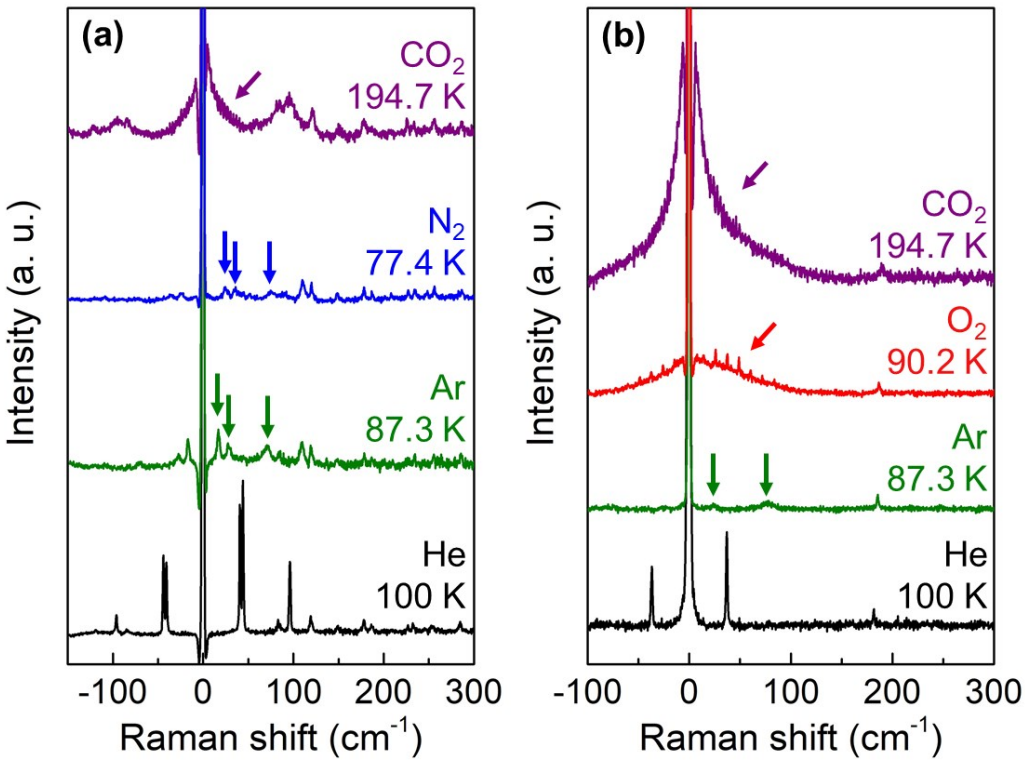

Fig. S10. Raman spectra of (a) MIL-140A and (b) Cu-JAST-1 under each gas at 100 kPa

Table S1. Experimental values of rotational constants for each gas.

	Reported	This work
N_2	1.998[S1]	1.987
O_2	1.438[S2]	1.436
CO_2	0.3915[S3]	0.3896

References

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S3. G. Herzberg and L. Herzberg, *J*. *Opt*. *Soc*. *Am*., 1953, **43**, 1037.