Pressure-induced isostructural phase transition of a metal-organic framework $Co_2(4,4'\text{-bpy})_3(NO_3)_4.xH_2O$

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Experimental section

Reagents and preparation of complexes

4,4'-bipyridine is purchased from TCI (shanghai) and used without further purification. Acetone, anhydrous ethanol, $Co(NO_3)_2.6H_2O$ is analytical reagents, which is purchased from Beijing Chemical Plant(China). It is used without further purification.

$Co_2(4,4'\text{-bpy})_3(NO_3)_4.xH_2O$ is synthesized according to the literature[1].Under ambient conditions, it crystallizes into a orthorhombic structure with the *Ccca* space group , a=12.267(7), b=19.025(7), c=17.412(4)A, V=4063(2)A^3.

Equipments and characterization

The high-pressure cell used in this experiment is based on symmetric diamond anvil cell (DAC) having two diamonds with 500 μm culet size[2,3]. The pure desolvated samples were loaded into the DAC without any fluid PTM to rule out the possible guest-host interactions.

The sample with a small ruby chip (~10 μm) is loaded in a 200 μm hole drilled in a 250 μm thick T301 gasket pre-indented to 80 μm thickness. The pressure calibration is done using ruby fluorescence[4]. The Raman spectra are recorded using a Renishaw in Via Raman Microscopic instrument. Laser excitation at 514.5nm is obtained with a Spectra Physics 160M argon ion laser. A Leica microscope with *50 objective lenses enables measurements with backscattering geometry. The laser power is 3.6 mw and the typical accumulation time for each spectrum is 30 s. Frequency calibration of the Raman spectrum is realized using the characteristic 520 cm^{-1} line of silicon. All

measurements were performed under room temperature.

The Angle dispersive X-ray diffraction (ADXRD) measurements are conducted without any PTM at the High Pressure Collaborative Access Team's (HPCAT's) 16 BMD beam line facility of the Advanced Photon Source (APS) at Argonne National Laboratory. The 0.41222 Å beam with a diameter of 10 μm is utilized for pattern collection. The typical acquisition time was set to 300 s. The image-plate area detector (Mar345) is adopted to collect diffraction data. Then the collected 2-D images are first integrated and analyzed using the FIT2D program to gain plots of intensity versus 2θ. The XRD patterns are then indexed and refined by using the reflex module combined in the Materials Studio program (Accelrys Inc.). All experiments are carried out at room temperature.

Table S1. Frequency of CB-MOF and 4,4'-bipyridine and their frequency-pressure slope.

Frequency at ambient pressure(cm^{-1})		△v(cm^{-1})	dv/dP($cm^{-1}p^{-1}$)		Assignments
Co-MOFs	4,4'biphydine		Co-MOF	4,4'biphydine	
660	657	3	0.77	1.13	C-H out of plane vibration 6a(A1)
1022	998	24	2.48	3.29	Ring breathing vibration 1(A_1)
1228	1216	12	3.53	7.10	C-C stretching vibration 9a(A_1)
1302	1295	7	3.76	5.62	Inter-ring C-C stretching vibration3(B_2)
1519	1510	9	2.92	3.00	C-H wagging vibration 19a(A_1)
1621	1605	16	3.21	3.52	C-C stretching vibration 8a(A_1)

Based on [5] in Wilson notation with symmetries based on C_{20} point.

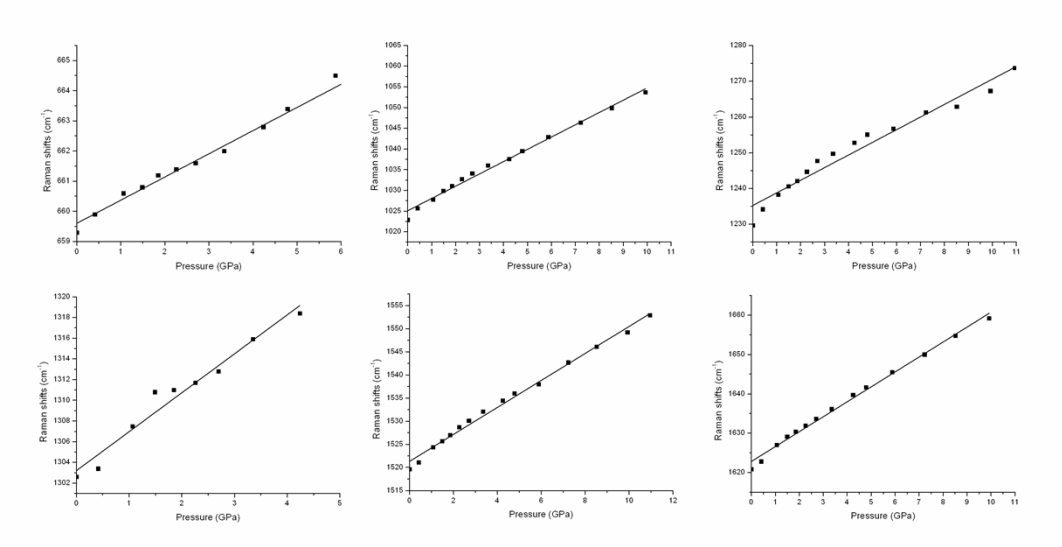

Figure S1. Frequency-pressure relationship of $Co_2(4,4'\text{-bpy})_3(NO_3)_4.xH_2O$

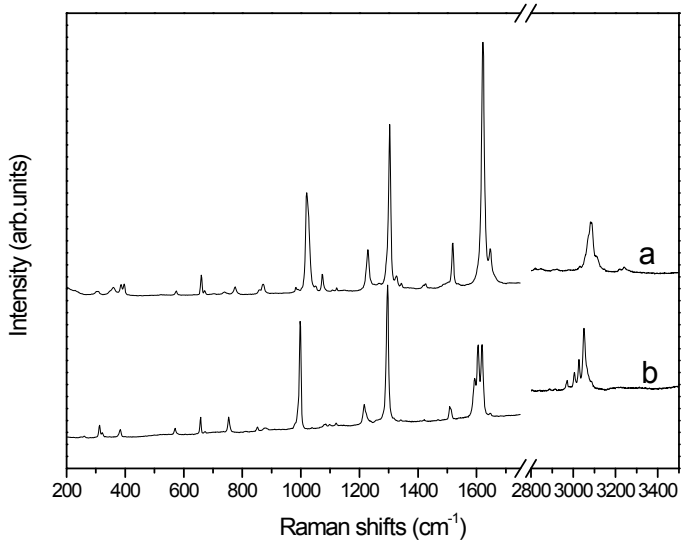

Figure S2. Raman spectra of $Co_2(4,4'\text{-bpy})_3(NO_3)_4.xH_2O$ (a) and 4,4'-biphydine (b)

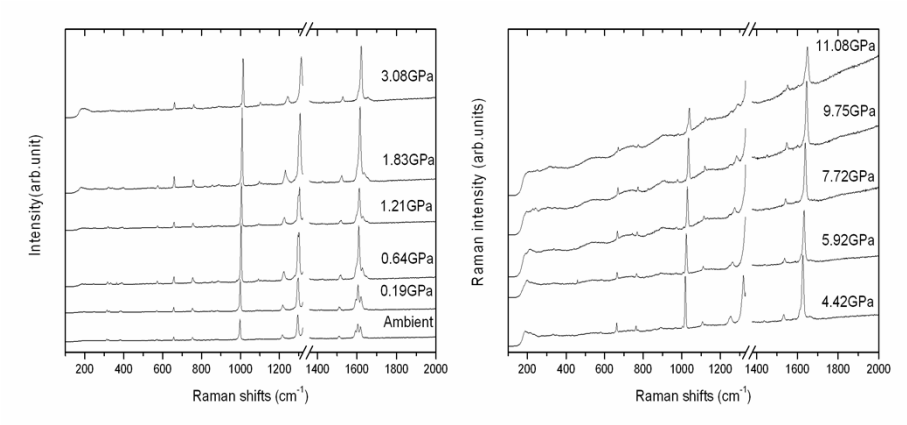

Figure S3. High pressure Raman spectra of 4,4'-bipyridine

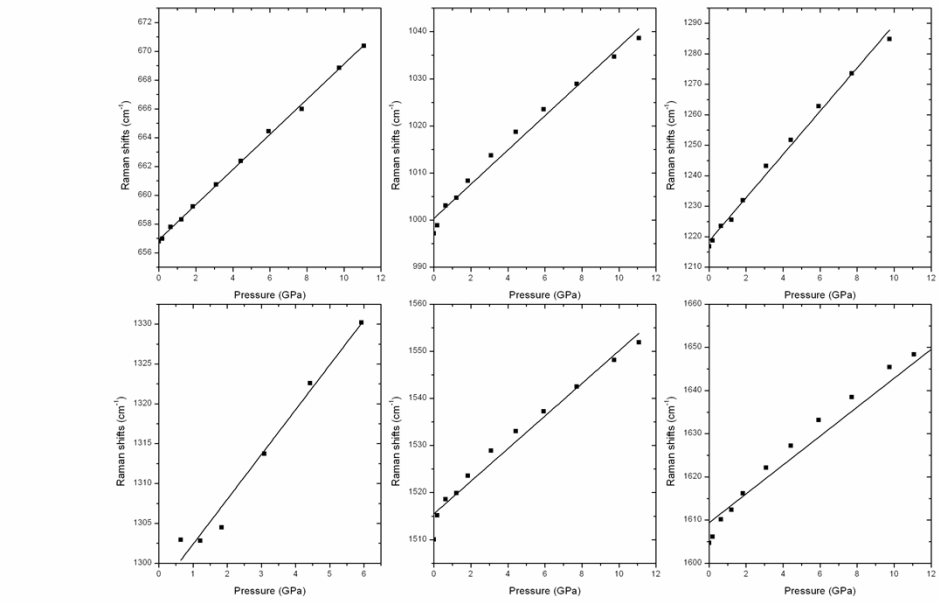

Figure S4. Frequency-pressure relationship of 4,4'-bipyridine

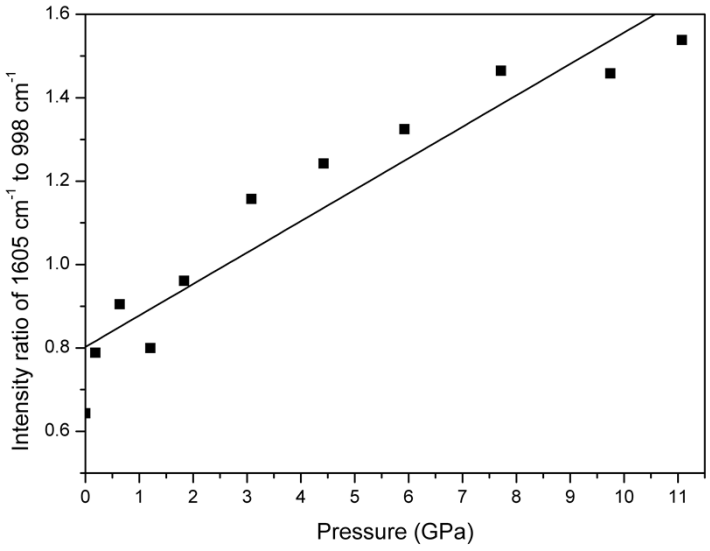

Figure S5. High pressure intensity ratio of 1605 cm-1 to 998 cm-1 of 4,4'-bipyridine crystal

Table S2. The indexed and refined structural parameters of CB-MOF at high pressure. The R_p and R_{wp} factors values are also given.

Pressure (GPa)	Cell parameters					
	a(Å)	b(Å)	c(Å)	V(Å^3)	R_p	R_{wp}
0.30	11.840	19.433	17.469	4019	1.12%	1.78%
0.82	11.790	19.430	17.422	3992	1.53%	2.84%
1.32	11.783	19.425	17.337	3968	1.68%	2.98%
2.38	11.709	19.369	17.299	3923	1.20%	1.83%
3.51	11.697	19.290	17.143	3862	0.99%	1.66%
4.69	11.622	19.227	16.997	3798	1.15%	1.81%
6.20	11.590	19.157	16.832	3737	0.79%	1.27%
8.90	11.443	19.165	16.764	3676	0.78%	1.21%
11.66	11.127	19.321	16.845	3621	0.78%	1.10%

Reference

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2. W. A. Bassett, *High pressure research*. 2009, **29,** 163-186

3. A. Jayaraman, *Reviews of Modern physics.* 1983, **55**, 65-108

4. H. K. Mao, J. Xu, P. M. Bell, *J. Geophys. Res*. 1986, **91**, 4673–4676.

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