Monitoring the Activation of a Flexible Metal-Organic Framework Using Structurally Sensitive Spectroscopy Techniques

Yuan Chen¹ Jingming Zhang² Jing Li² Jenny Lockard^{1*}

¹Department of Chemistry, Rutgers University - Newark

Newark, NJ 07102

²Department of Chemistry and Chemical Biology, Rutgers University - New Brunswick,

Piscataway, NJ 08854

Supporting Information

I. Synthesis of [Co(Hoba)₂·2H₂O] (1)

 $Co(NO_3)_2 \cdot 6H_2O$ (0.4 mmol) and H_2 oba (0.8 mmol) were mixed in 10 mL of distilled water, and two drops of TEA was added in to the solution to adjust the pH value to ~7.00. The solution was then heated at 120 °C for 3 days, followed by cooling at a rate of 0.1 °C/min to room temperature. The pink plate-like crystals of **1** (0.1452 g, 0.24 mmol, 60 % yield based on cobalt) were collected.

II. Powder X-ray diffraction experiment

Powder X-ray diffraction patterns of all the samples were recorded on a Rigaku Ultima IV X-Ray diffractometer at room temperature using Cu K α radiation ($\lambda = 1.5406$ Å). Graphite monochromator was used and the generator power settings were at 40 kV and 44 mA. Data were collected between a 2 θ of 3-50° with a step size of 0.02° at a scanning speed of 4.0 deg/min.

III. Thermogravimetric Analysis

Thermogravimetric (TG) analysis was performed on a TA Q50 Thermogravimetric Analyzer with a temperature ramp of 10 °C/min from room temperature to 600 °C under nitrogen gas flow. The TG profile (Figure S1) shows a weight loss of 6.0 wt% for the as-synthesized sample (1) in the range of 110 °C to 160 °C upon heating. The weight loss can be assigned to the coordinated water molecules in 1 and matches very well with the theoretically calculated amount (5.9 %) based on the crystal structure. The water-free sample (1') is thermally stable up to 300 °C, followed by decomposition at higher temperatures.



Figure S1. Thermogravimetric analysis of a freshly prepared sample of **1** showing a good match of the observed weight loss with the calculated value.



IV. X-ray absorption spectroscopy

Figure S2. The progression of XAS spectra collected *in situ* upon heating the sample from $\sim 25^{\circ}$ C (black trace) to 150° C (red trace)



Figure S3. Model derived from crystal structure of **1** used in EXAFS fitting. Atom labels pertain to scattering paths listed in Table 1 with the following equivalencies: O6 = O2, C7=C21



V. Reference Raman Spectra

Figure S4. Raman spectra of Na₂oba (green), H_2 oba (magenta) and $D_2O@1$ (blue), 1 (black) and 1' (red)



Figure S5. Raman spectra of $D_2O@1$ (blue) and the activated form D2O @1' (red), showing disappearance of coordinated D_2O vibrational modes at 1082 and 788 cm⁻¹ upon activation. Note the presence of the water bending mode peak at ~1530 cm⁻¹ in the spectrum of the $D_2O@1$ sample that also disappears after vacuum/heat activation. We attribute this peak to the presence of coordinated H_2O molecules that derive from either the hexahydrate cobalt salt starting material and/or H/D exchange with labile protons in the framework (eg carboxylic acid groups). * denotes peaks from the KNO₃ standard (mixed with non-activated $D_2O@1$ sample only).

V. DFT Computational methods and theoretical vibrational frequency results

The geometry optimizations and theoretical vibrational modes of several reference molecules and were calculated using the Gaussian 09 program package¹ at the density functional theory (DFT) level with Beck's three parameter functional and Lee-Yang-Parr functional (B3LYP) method. 6-31G* basis set was used for all the calculations. Calculations were performed on the model systems whose optimized geometries are depicted in **Figure S5.** Mode descriptions were assessed based on animation of the atomic vector displacements using Chemcraft. A summary of the calculated frequencies for the most Raman active vibrational modes is provided in **Table S1** and does not include compensation for vibrational mode anharmonicities through the use of a scaling factor.²



Figure S6. Optimized geometries for model systems, a) 4,4'-oxybis(benzoic acid), b) 4,4'-oxybis(benzoate) c) coordination mode of 4,4'-oxybis(benzoate) to the Co metals.

Table S1. Experimental and Calculated Raman active vibrational mode frequencies with descriptions of dominant components of the corresponding vibrational mode assignments for the 4,4'-oxybis(benzoic acid) reference molecule

Experimental	Calc. Frequency	Vibrational assignment
Frequency		
303	298	Phenyl ring tilt
419	427	δ Phenyl ring
503	518	$\beta (CC_{Ph}C_{COOH}) + \gamma (CH)$
613	602	γ (OH)
621	628	γ (OH) + δ Phenyl ring
653	654	δ Phenyl ring
739	732	β (COC) + γ (CH) + δ Phenyl ring
781	784	β (COC) + δ Phenyl ring
819	828	v_{sym} (CO) _{ether} + β (COC) + δ Phenyl ring
840 br	846	$\gamma(CH)_{phenyl}$
1133	1190	β(CH)
1166	1221	β (CH) + γ (OH)
1203	1239	v_{sym} (CO) _{ether} + β (CH)
1290	-	v (HOH) _{carboxylic acid}
1317	1397	β (OH) + ν_{sym} (C-OH)
1593	1637	ν (CC) _{phenyl}
-	1654	v (CC) _{phenyl}
1613	1673	v (CC) _{phenyl}
1635br	1820	v _{sym} (C=O) _{carboxylic acid}

v - stretching; v_s - sym. stretching; v_{as} - asym.stretching; β - in-plane-bending; γ - out-of-plane bending;; δ - deformation; sh – shoulder; br – broad

Experimental Frequency	Calc. Frequency	Vibrational assignment
295	304	Phenyl ring tilt
634	661	δ Phenyl ring
656	-	$\nu (Na^+O^-)^a$
763	761	β (OCO) + γ (CH) + δ Phenyl ring
790	790	$\beta(COC) + \gamma(OCO) + \delta$ Phenyl ring
853	838	$\beta(OCO) + v_{sym} (CO)_{ether} + \delta$ Phenyl ring
864sh	844	$\gamma(CH)_{phenyl}$
1136	1126	$\nu(CC)_{carboxylate} + \beta(CH)$
1164	1175	β(CH)
1192	1205	v_{sym} (CO) _{ether} + β (CH)
1429	1364	v_{sym} (CO) _{carboxylate}
1502	-	v_{asym} (CO) _{carboxylate}
1593	1640	$\nu(CC)_{phenyl}$
1606	1653	$\nu(CC)_{phenyl}$

Table S2. Experimental and Calculated Raman active vibrational mode frequencies with descriptions of dominant components of the corresponding vibrational mode assignments for the 4,4'-oxybis(benzoate)dianion reference molecule

v - stretching; v_s - sym. stretching; v_{as} - asym.stretching; β - in-plane-bending; γ - out-of-plane bending;; δ - deformation; sh – shoulder; br - broad ^aExperimental data only; Na⁺ counter ions most likely situated near oxygens of carboxylate

groups

Calc.	Vibrational assignment	
Frequency		
320	Phenyl ring tilt	
405	Phenyl ring tilt	
426	δ Phenyl ring	
490	δ Phenyl ring + β (CC _{Ph} C _{COOH})	
507	β (CC _{Ph} C _{COOH})+ γ (OH) + δ Phenyl ring	
556	v_{asym} (CoO) + δ Phenyl ring+ γ (OH)	
564	v_{asym} (CoO) + δ Phenyl ring	
679	v_{sym} (CoO) + β (COC) _{ether} + γ (OH) + δ Phenyl ring	
718	$\gamma(OH) + \gamma(CH) + \beta(COC)_{ether}$	
745	$\beta(OCO)_{COOH} + \beta(COC)_{ether} + \gamma(CH)$	
818	$\beta(OCO) + \beta(COC)_{ether} + \delta$ Phenyl ring	
848	γ (CH) _{phenyl}	
881	$\beta(OCO)_{carboxylate} + v_{asym} (CO)_{ether} + \delta Phenyl ring$	
898	γ (CH) _{phenyl} + δ Phenyl breathing + β (COC) _{carboxylate} + β (OCO) _{carboxylate}	
1153	v_{sym} (CO) _{carboxylate} + δ Phenyl ring	
1189	$\nu (CO)_{ether} + \beta (CH)^{b}$	
1205	$\nu (CO)_{ether} + \beta (CH)^{a}$	
1223	$\nu(CO)_{ether} + \beta(COH) + \nu(CC)^{b}$	
1338	$\nu (CO)_{ether} + \beta (CH)^{a}$	
1469	ν (CC) _{carboxylate} + ν _{sym} (CO) _{carboxylate} + β (CH) ^a	
1571	ν (CC) _{carboxylate} + ν (CC) _{phenyl} + β (CH) ^a	
1650	v (CC) _{phenyl}	
1670	v (CC) _{phenyl}	
1833	v (C=O) _{carboxylic acid}	

Table S3. Calculated Raman active vibrational mode frequencies with descriptions of dominant components of the corresponding vibrational mode assignments for the model system with coordination of Hoba to the Co metal

v - stretching; v_s - sym. stretching; v_{as} - asym.stretching; β - in-plane-bending; γ - out-of-plane bending;; δ - deformation; sh – shoulder; br - broad ^a localized on phenyl group closest to Co(II) ^b localized on phenyl group attached to the carboxylic acid group

REFERENCES:

M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox; Gaussian Inc.: Wallingford, CT, 2010.
(2) Qiu, S.; Liu, L.; Jin, X.; Zhang, A.; Wu, K.; Wang, L. Spectro. Chim. Acta A 2010, 77, 572.