

Bimetallic metal organic frameworks with precisely positioned metal centers for efficient H₂ storage

Daeok Kim,^a Kyung Seob Song,^c Onur Buyukcakil,^a Taner Yildirim,^{b*} Ali Coskun^{c*}

^a. Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guesong Dong, Daejeon, 305-701, Republic of Korea.

^b. NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, USA, E-mail: taner@nist.gov

^c. Department of Chemistry, University of Fribourg, Fribourg 1700, Switzerland. E-mail: ali.coskun@unifr.ch

Electronic Supplementary Information (ESI)



Materials: $\text{Pd}_3(\text{AcO})_6$ was purchased from Alfa Aesar and used after recrystallization to remove $\text{Pd}(0)$ impurity. $\text{Cu}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, 98%), Benzene-1,3,5-tricarboxylic acid (BTC, Aldrich, 99%), 1,3,5-Tris(4-carboxyphenyl)benzene (BTB, Aldrich, 98%), anhydrous methanol, anhydrous DMF and glacial acetic acid were purchased and used without further purification.

The synthesis of $\text{PdCu}(\text{AcO})_4\text{H}_2\text{O}$ was achieved through a modified literature report.^{S1} $\text{Cu}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ (0.444 mmol) was dissolved in 3 mL of glacial acetic acid containing 1.3 wt% H_2O , and was magnetically stirred at 80 °C until the solution became transparent. $\text{Pd}_3(\text{AcO})_6$ (0.1 g, 0.148 mmol based on the Pd_3 unit) was added to the mixture and sonicated at 80 °C for 5 min. The mixture was then refluxed at 85 °C until the solution became transparent, which took about 3 h. The hot solution was naturally cooled down to room temperature then kept in a refrigerator at 6 °C for 3 days. The precipitated crystals of $\text{PdCu}(\text{AcO})_4\text{H}_2\text{O}$ were separated by decantation, washed with cool acetic acid and dried in Ar flow at room temperature.

PdCuBTC synthesis: BTC (42.3 mg, 0.2 mmol) was suspended in the solvent mixture of EtOH/ H_2O (737/630 mg) and sonicated for 1 min. To this suspension, $\text{PdCu}(\text{AcO})_4\text{H}_2\text{O}$ (54.4 mg, 0.127 mmol) dissolved in 165.8 μL of DMF was added. The resulting mixture was stirred for 1 day and the product was centrifuged and washed with a copious amount of acetone.

PdCuBTB synthesis: BTB (87.7 mg, 0.2 mmol) was suspended in the mixture of EtOH/ H_2O (737/630 mg) and sonicated for 1 min. To this suspension, $\text{PdCu}(\text{AcO})_4\text{H}_2\text{O}$ (54.4 mg, 0.127 mmol) dissolved in 165.8 μL of DMF was added. The resulting mixture was stirred for 3 days and the product was centrifuged and washed with a copious amount of acetone.

The activation of MOFs was achieved by evacuating the samples under reduced pressure first at room temperature for 1 day and then at 50 °C for 1 day.

Characterization: Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping analyses were conducted using Magellan400 (FEI). For the measurements, the samples were placed on carbon tapes and then coated with osmium (Os). FT-IR spectra were measured using Bruker Alpha with 64 scan-times and 4 cm^{-1} of resolution. PXRD analysis was conducted using a SmartLab (Rigaku) with CuK radiation ($\lambda = 1.5406 \text{ \AA}$) at a generator voltage of 40 kV and generator current of 200 mA. Ar isotherms were measured using a 3Flex physisorption analyzer (Micromeritics, USA) at 87 K. To analyze the pore properties from the obtained isotherms, Nonlocal Density Functional Theory (NLDFT) adopting carbon slit pore model was employed. Gas sorption measurements were performed on a carefully calibrated, high accuracy Sieverts apparatus under computer control. XPS analysis was conducted by using multipurpose XPS (Sigma Probe, Thermo VG Scientific, X-ray source: monochromatic Al K(alpha)). Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis was conducted using Agilent ICP-OES 5110. Prior to the ICP-AES analysis, the samples were digested by microwave-assisted boiling in aqua regia.

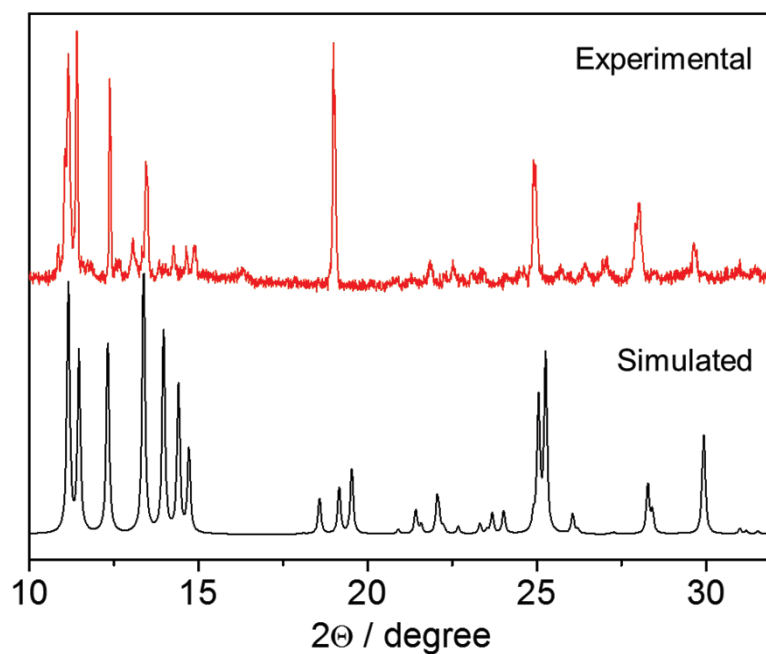


Figure S1. Powder X-ray diffraction pattern of $\text{PdCu}(\text{AcO})_4\text{H}_2\text{O}$.

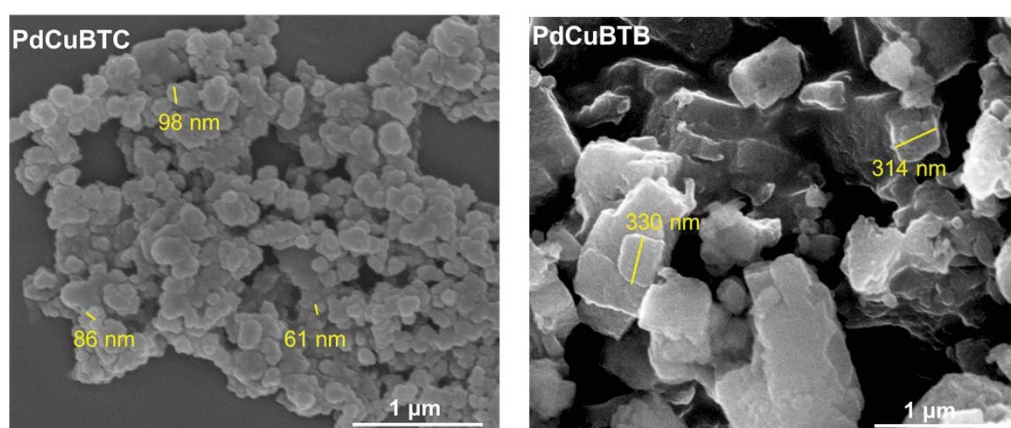


Figure S2. SEM images of PdCuBTC (left) and PdCuBTB (Right).

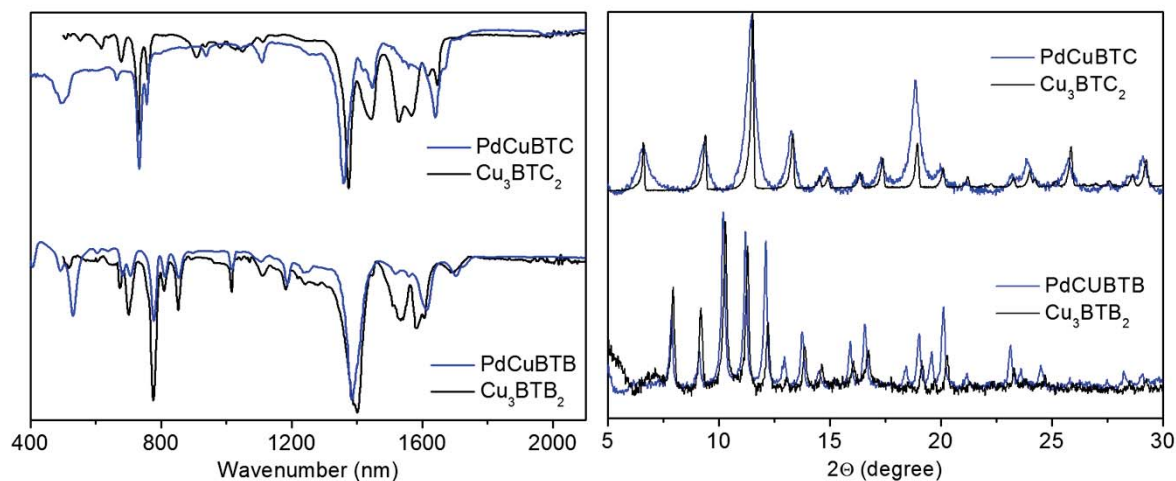


Figure S3. FT-IR (left) and XRD (right) spectra of PdCuBTC, Cu₃BTC₂, PdCuBTB and Cu₃BTB₂.

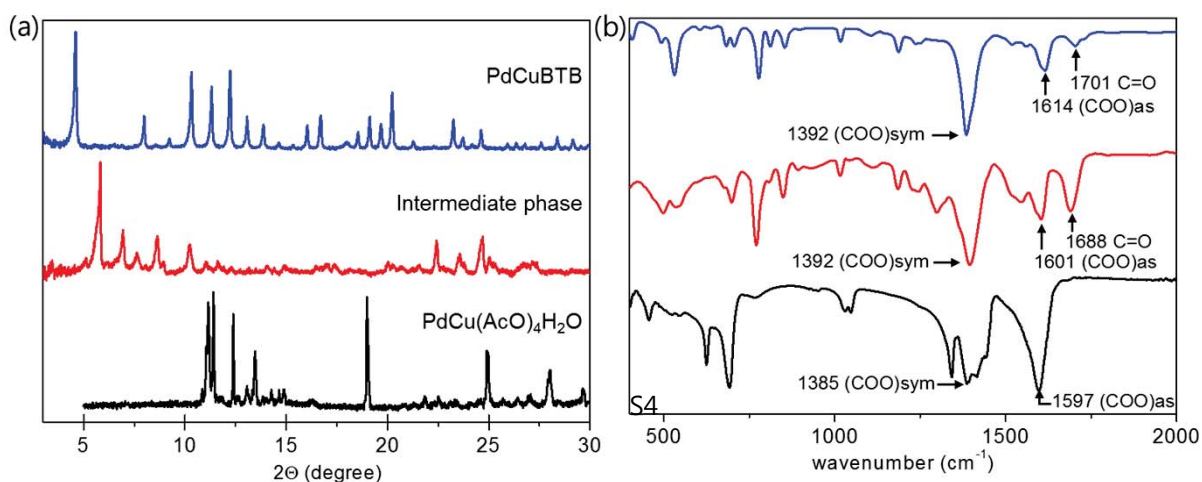
Table S1. ICP-AES analysis of PdCuBTC and PdCuBTB.

	Cu (mg/Kg)	Pd (mg/Kg)	Cu (mmol/kg)	Pd (mmol/kg)	Cu/Pd molar ratio
PdCuBTC	143716.034	205045.199	2.2616	1.9267	(0.54:0.46)
PdCuBTB	76801	105500	1.2085	0.99136	(0.55:0.45)

Table S2. EDS analysis of PdCuBTC and PdCuBTB.

PdCuBTC						
Element	Wt%	At%	K-Ratio	Z	A	F
CuL	41.52	54.32	0.2611	1.067	0.589	1
PdL	58.48	45.68	0.5389	0.946	0.974	1

PdCuBTB						
Element	Wt%	At%	K-Ratio	Z	A	F
CuL	39.03	51.74	0.2413	1.0704	0.5774	1.0004
PdL	60.97	48.26	0.5646	0.9489	0.9758	1



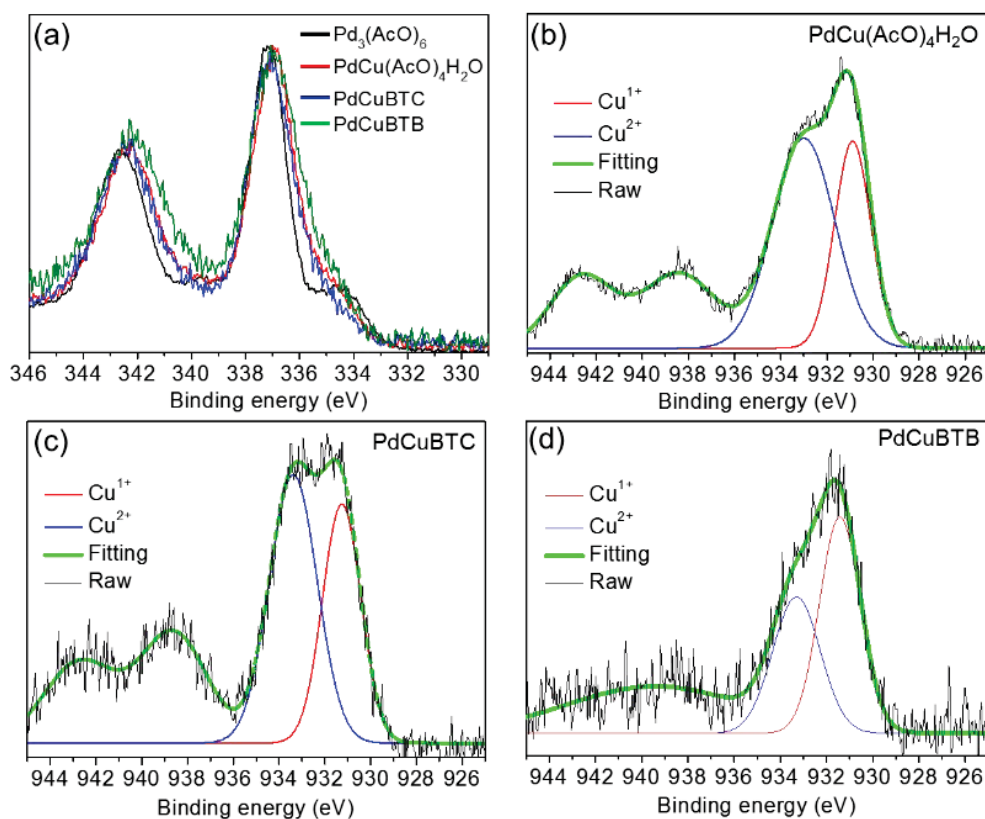


Figure S4. (a) XPS and (b) FT-IR spectra of $\text{PdCu}(\text{AcO})_4\text{H}_2\text{O}$, intermediate phase formed during the synthesis and PdCuBTB .

Sample name	Molar fraction (%)	
	Pd^{2+}	Cu ($\text{Cu}^{1+} : \text{Cu}^{2+}$)
$\text{PdCu}(\text{AcO})_4\text{H}_2\text{O}$	50.3	49.7 (36.6 : 63.4)
PdCuBTC	50.1	49.9 (27.1 : 72.9)
PdCuBTB	53.5	46.5 (57.6 : 42.4)

Figure S5. (a) Pd_{3d} and (b-d) Cu_{2p} XPS spectra of Pd and/or Cu complexes along with the oxidation states of Pd and Cu in $\text{PdCu}(\text{AcO})_4\text{H}_2\text{O}$, PdCuBTC and PdCuBTB .

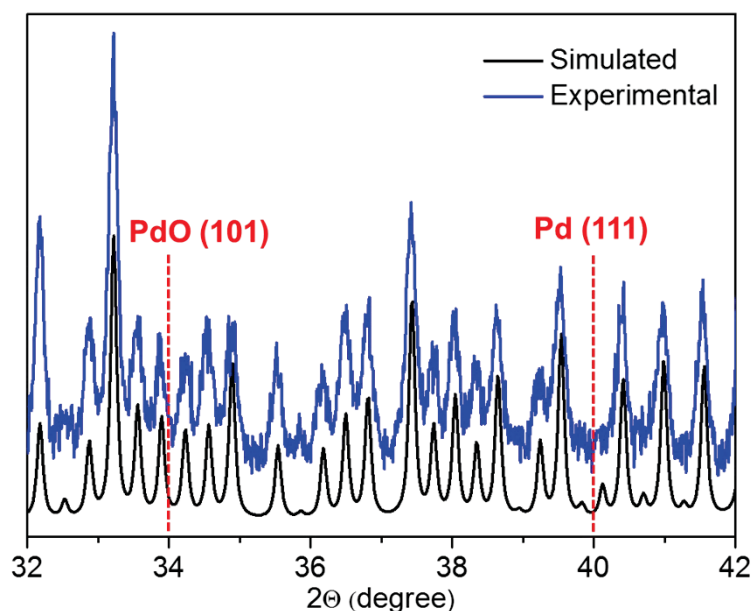


Figure S6. Experimental and simulated XRD patterns of PdCuBTB. Red dotted lines indicate the location of diffractions from PdO and Pd nanoparticles.

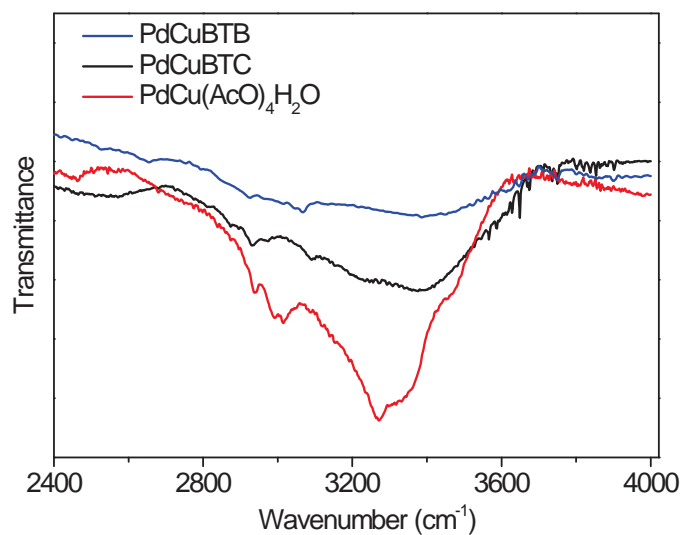


Figure S7. FTIR spectra of PdCu(AcO)₄H₂O complex and activated PdCu MOFs

Gas Sorption and Isostatic Heat of Adsorption, Q_{st} , Measurements:

Gas sorption measurements were performed on a carefully calibrated, high accuracy, Sieverts apparatus under computer control. Instrument and measurement-protocol details have been published elsewhere

(see the supporting information (SI) in Ref. S2). All gases were of Research or Scientific grade, with a minimum purity of 99.999%.

Our isotherm data at a series of temperatures (i.e. 67 K, 77 K, and 87 K) enable us to extract the heat of adsorption Q_{st} as a function of the adsorbed amount. Q_{st} is calculated using the “isosteric method” where a series of isotherms are measured at a wide range of temperatures. These isotherms are then parameterized by cubic-spline which does not require any fitting and allows us to interpolate the isotherm at a constant loading. Then, the Q_{st} is obtained from the $\ln(P)$ versus $1/T$ plots. As an alternative to cubic-spline interpolation, we also obtain Q_{st} by fitting the isotherm data using the following form of

$$\ln(p) = \ln(v) + \frac{1}{T} \sum_{i=0}^m a_i v^i + \sum_{i=0}^n b_i v^i$$

a virial equation:

where v , p , and T are the amount adsorbed, pressure, and temperature, respectively and a_i and b_i are empirical parameters. The first four constants (i.e. a_0 , b_0 , a_1 , and b_1) are obtained by linearizing the isotherms ($1/n$ versus $\ln p$) and then we increase the number of parameters gradually (two at a time) until the improvement in the fit is not significant. Usually 10 or 12 parameters are found to be enough to obtain a good fit to the isotherms. After the isotherms are fitted, by applying Clausius-Clapeyron equation, the heat of adsorption is obtained as

$$Q_{st} = -R \sum_{i=0}^m a_i v^i$$

where R is the universal gas constant. The details can be found in Ref. S3.

. All fitting parameters for H_2 , are summarized and plots of the adsorption isotherms with the corresponding dual-site Langmuir-Freundlich fits are shown in Figure S7.

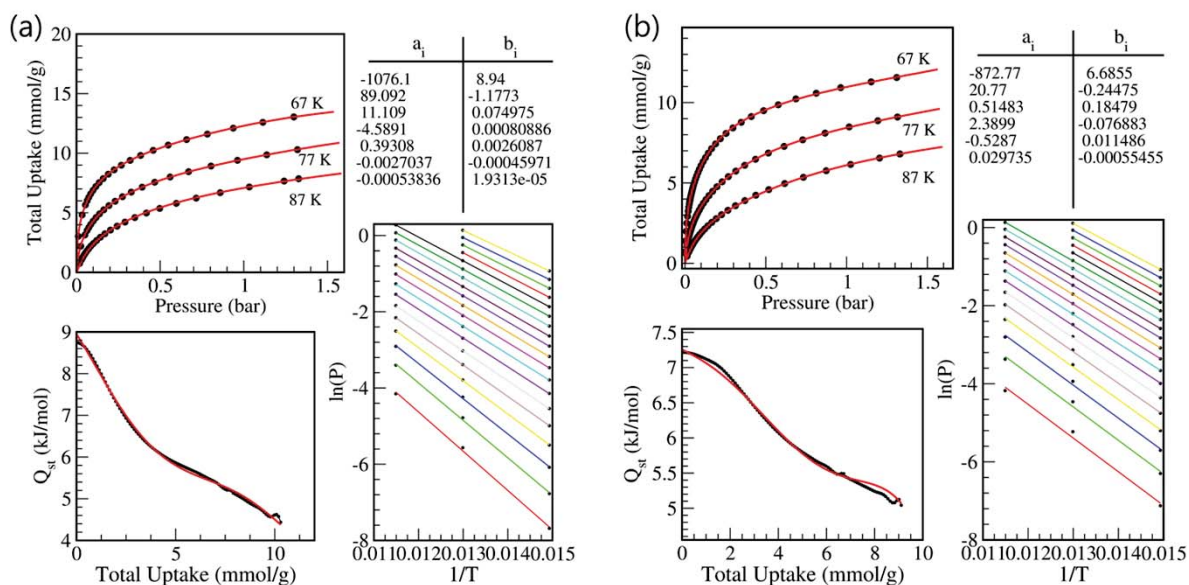


Figure S8. H_2 adsorption isotherms for (a) PdCuBTB and (b) PdCuBTC at 67, 77 and 87 K along with the corresponding dual-site Langmuir fits and resulting parameters.

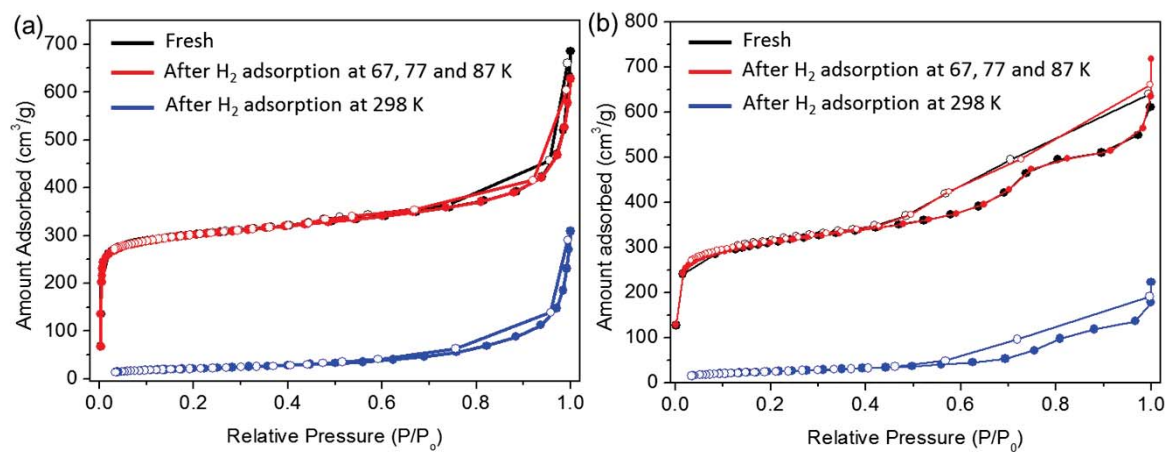


Figure S9. N_2 adsorption change of (a) PdCuBTC and (b) PdCuBTB after H_2 adsorption measurement at 67, 77, 87 and 298 K.

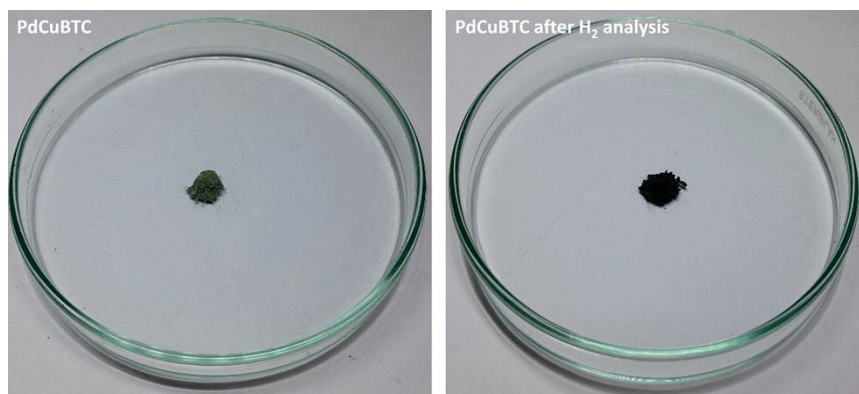


Figure S10. Picture of PdCuBTC (left) and PdCuBTC After H_2 anlysis (Right).

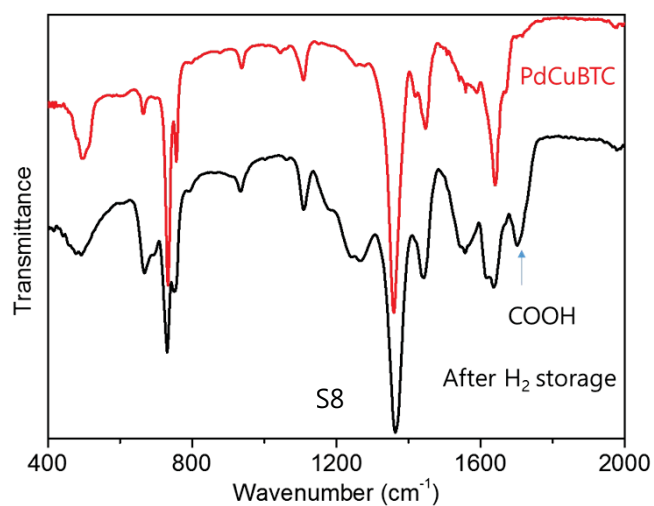


Figure S11. FT-IR of PdCuBTC before and after H₂ storage at 298 K.

References

- [S1] N. S. Akhmadullina, N. V. Cherkashina, N. Y. Kozitsyna, I. P. Stolarov, Elena V. Perova, A. E. Gekhman, S. E. Nefedov, M. N. Vargaftik and I. I. Moiseev, *Inorg. Chim. Acta*, 2009, **362**, 1943–1951.
- [S2] I. Eryazici, J. T. Hupp, O. K. Farha, and T. Yildirim, *J. Am. Chem. Soc.*, **2013**, **135**, 11887–11894.
- [S3] Jagiello et al., *J. Chem. Eng. Data*, 1995; **40**; 1288-92 and Jagiello et al, *Langmuir* 1996, **12**, 2837-42.