Selective Molecular-Gating Adsorption in a Novel Copper-Based Metal-Organic Framework

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Table S5. Crystallographic parameters of **1**(**MeOH**) and **1**(**EtOH**).

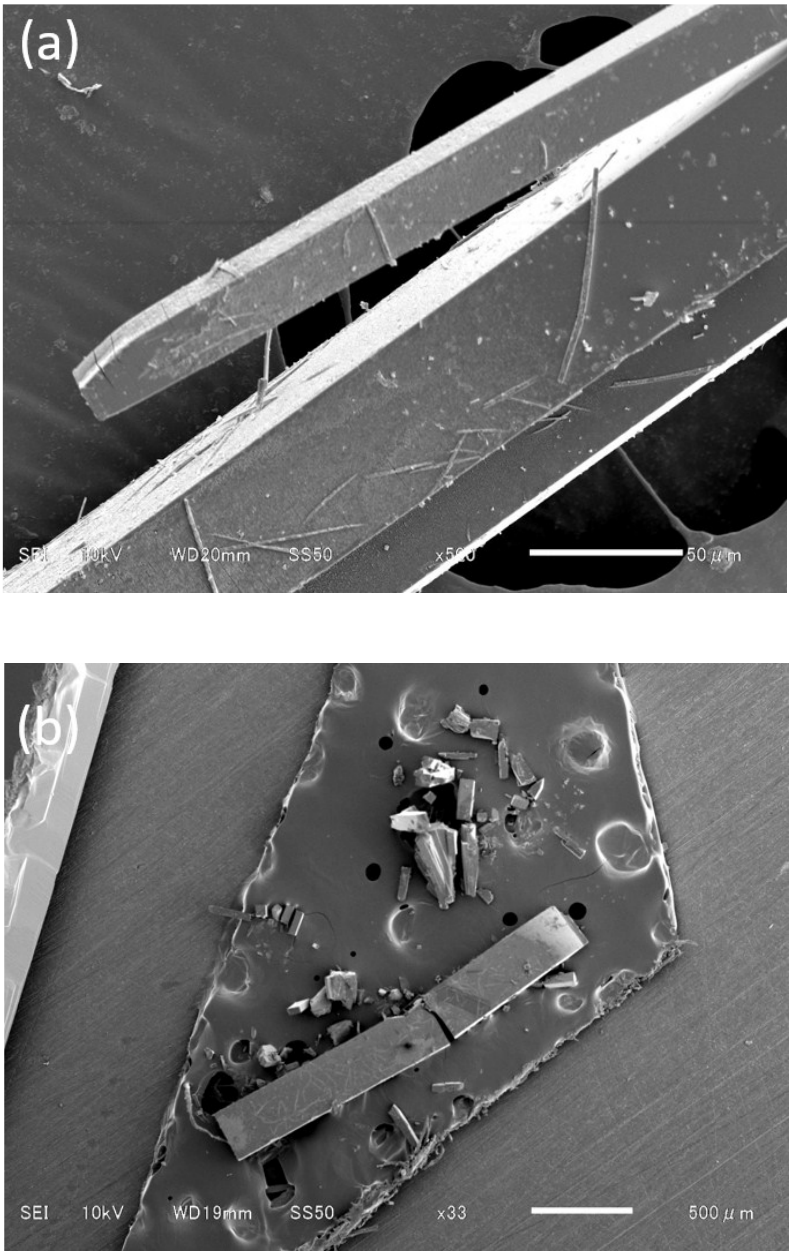


Figure S1. SEM images of (a) **1** and of (b) the sample after solvent exchange from acetonitrile to water put on a carbon tape.

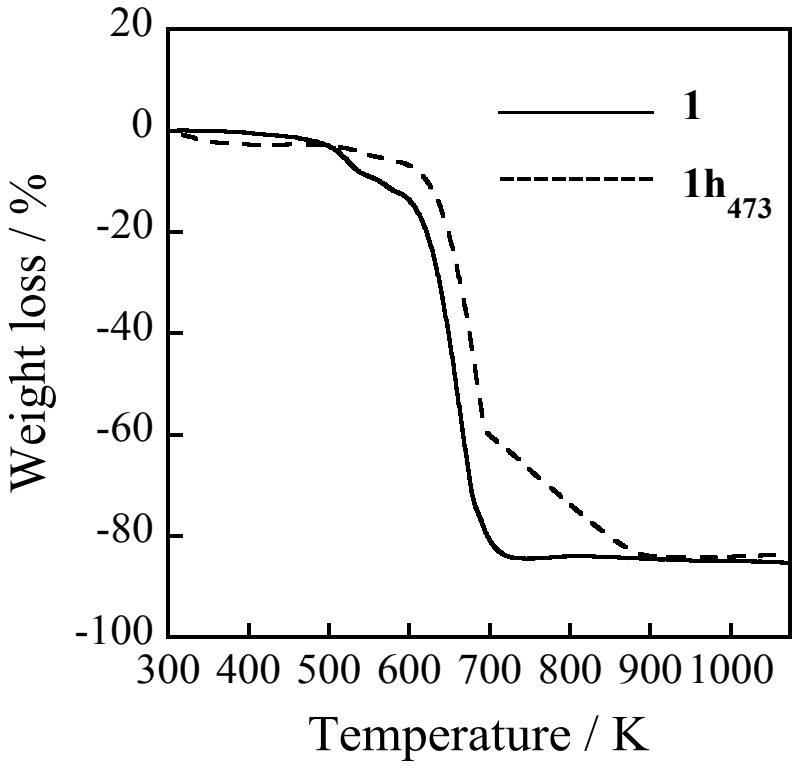


Figure S2. TG curves of **1** (solid) and **1h$_{473}$** (dotted) from room temperature to 1073 K measured under N_2 flow of 150 mL/min.

Table S1. CHN elemental analysis of **1** and **1h$_{473}$**.

		C / wt%	H / wt%	N / wt%
1	Obs.	47.48	2.84	19.29
	Calcd.[a]	47.69	3.00	19.46
1h$_{473}$	Obs.	44.47	2.68	17.42
	Calcd.[b]	44.42	2.76	17.27

[a] The values were calculated for $C_{40}H_{30}B_2F_8Cu_2N_{14}$ (Estimated chemical formula of $[Cu_2(tpt)_2(CH_3CN)_2]\cdot 2(BF_4)$)

[b] The values were calculated for $C_{36}H_{26.6}B_2F_8Cu_2N_{12}O_{2.6}$ (Estimated chemical formula of $[Cu_2(tpt)_2(BF_4)_2]\cdot 4/3H_2O$)

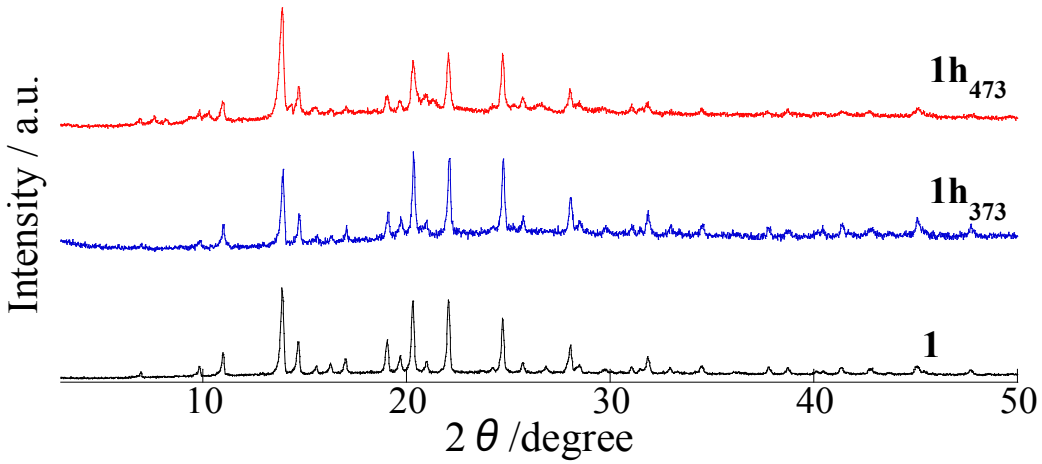


Figure S3. XRD patterns of **1**, **1h**$_{373}$, and **1h**$_{473}$ at room temperature in air. The wavelength is 1.5418 Å.

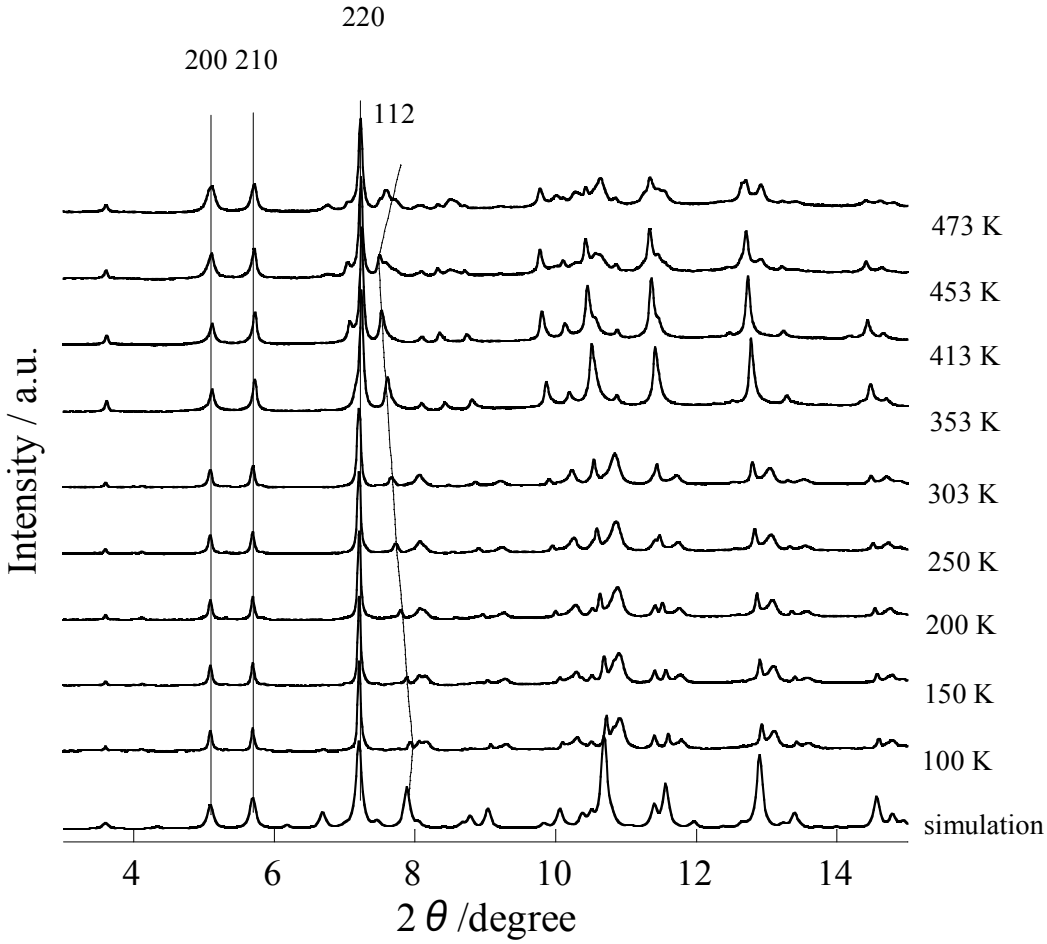


Figure S4. Synchrotron XRD patterns of **1** in a temperature range of 100 K-473 K under vacuum and simulated XRD pattern of **1** in the range of 3-15 (2θ/degree). In the heating process from 353 K to 473 K, the synchrotron

X-ray wavelength is 0.79942 Å, and in the cooling process from 303 K to 100 K, the wavelength is 0.79917 Å.

Table S2. Thermal expansion coefficients of some MOFs and Prussian blue complexes.

Materials	α_a / 10^{-6} K^{-1}	α_b / 10^{-6} K^{-1}	α_c / 10^{-6} K^{-1}	α_V / 10^{-6} K^{-1}	Reference
HKUST-1	−4.1	−4.1	−4.1	−11	1
MOF-5	−8	−8	−8	-24	2
$[Zn(L_1)_2(OH)_2]$[a]	−21	−21	127	89	3
H-MOF	177	−21	15	8	4
$In[Ag(CN)_2]_3$	105	105	−84	-	5
$Ag_3[Co(CN)_6]$	130 ~ 150	130 ~ 150	−130 ~ −120	-	6
$[Cu(OTf)_2(bpy)_2]$	−21	−21	79	38	7
ZIF-7III	65 ~ 181	−124 ~ −110	95 ~ 141	47 ~ 197	8
ZIF-9III	128 ~ 255	−150 ~ −135	110 ~ 160	82 ~ 278	8
$[Cu(BF_4)(tpt)_2]$[b]	0.5	0.5	216	217	This work

$\alpha_a = (a_{T1} - a_{T0})/(a_{To}\cdot(T_1 - T_0))$, $\alpha_b = (b_{T1} - b_{T0})/(b_{To}\cdot(T_1 - T_0))$, $\alpha_c = (c_{T1} - c_{T0})/(c_{To}\cdot(T_1 - T_0))$

$\alpha_V = (V_{T1} - V_{T0})/(V_{To}\cdot(T_1 - T_0))$

a. L_1 = 4-(1H-naphtho[2,3-di]imidazol-1-yl)benzoate, b. tpt = 2,4,6-tri(4-pyridyl)-1,3,5-triazine

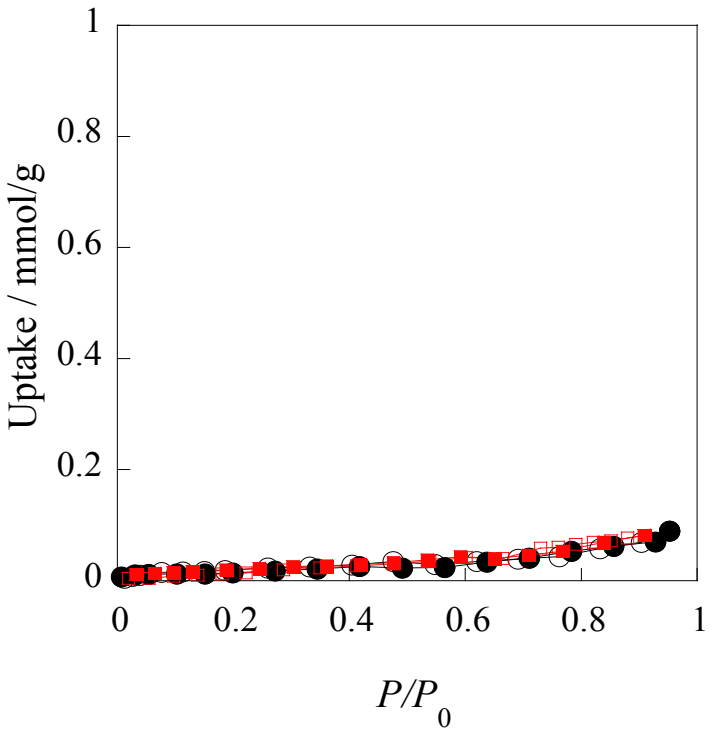


Figure S5. Adsorption isotherms of Ar (black circle) and O_2 (red square) at 77 K on **1a**. Filled and open symbols represent adsorption and desorption, respectively.

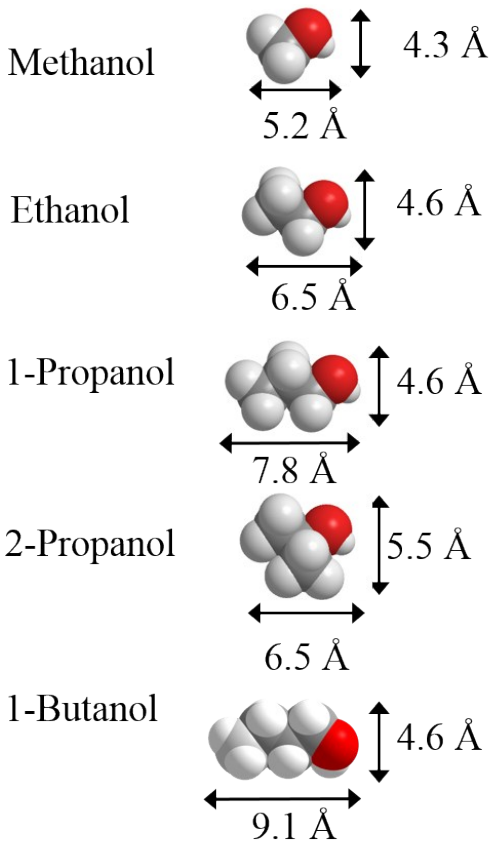
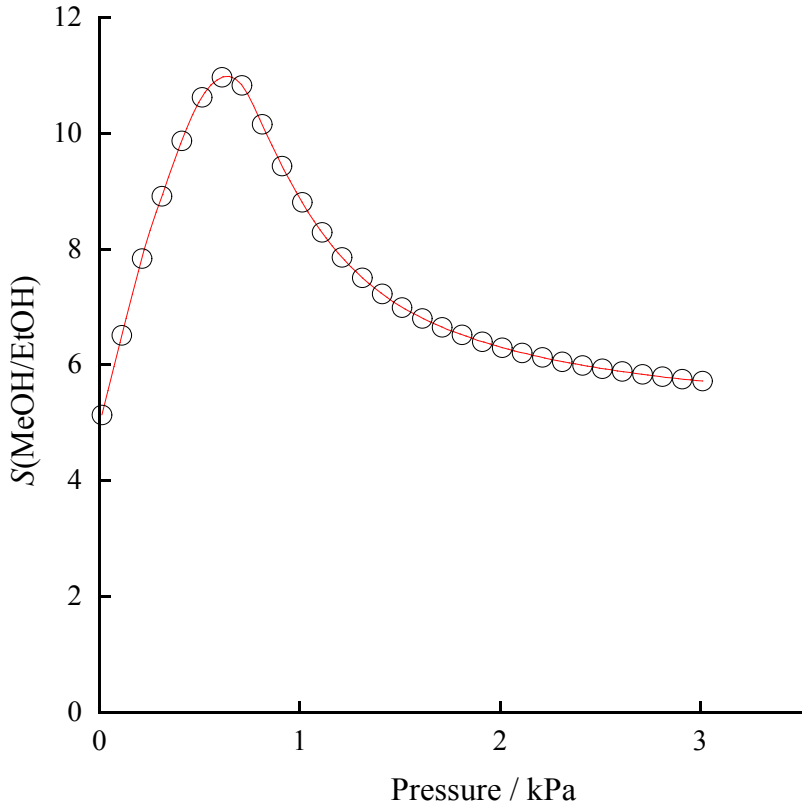
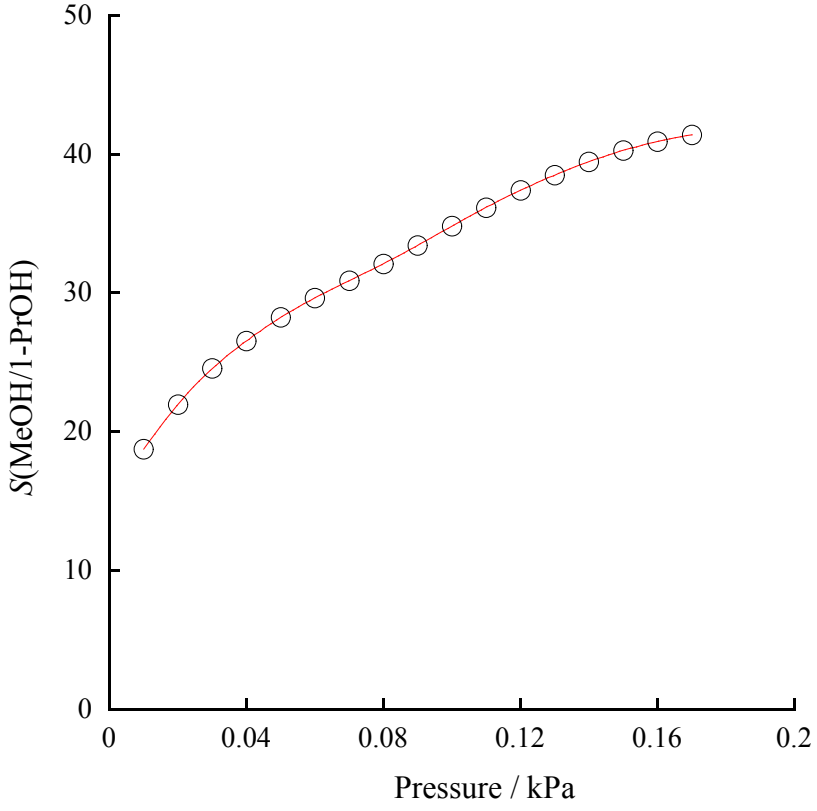


Figure S6. Molecular sizes of small alcohols.

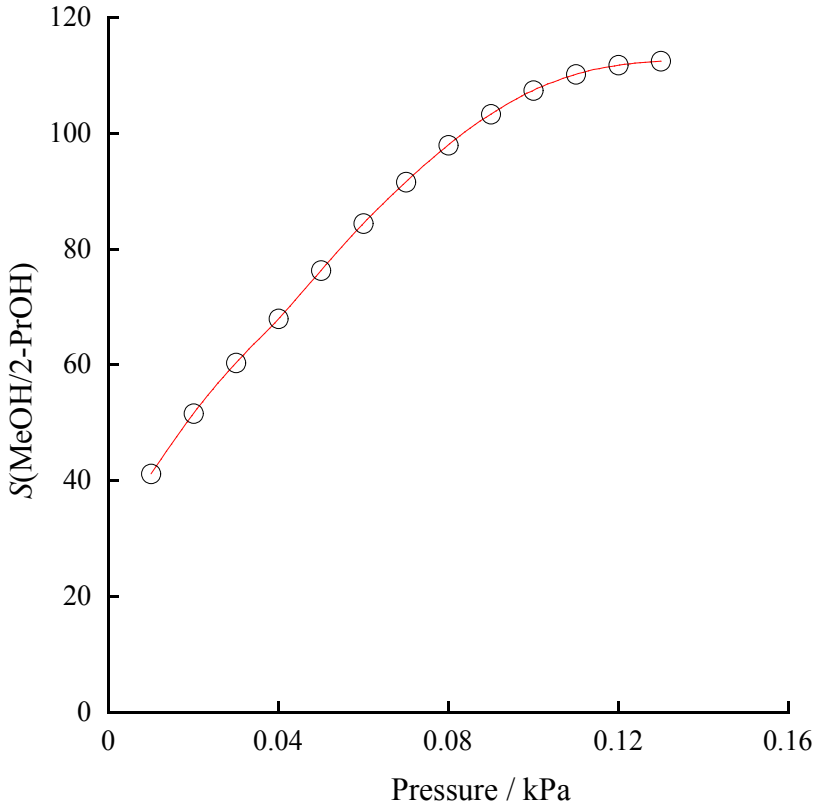
(a)


12
10
8
6
4
2
0
S(MeOH/EtOH)
0
1
2
3
Pressure / kPa

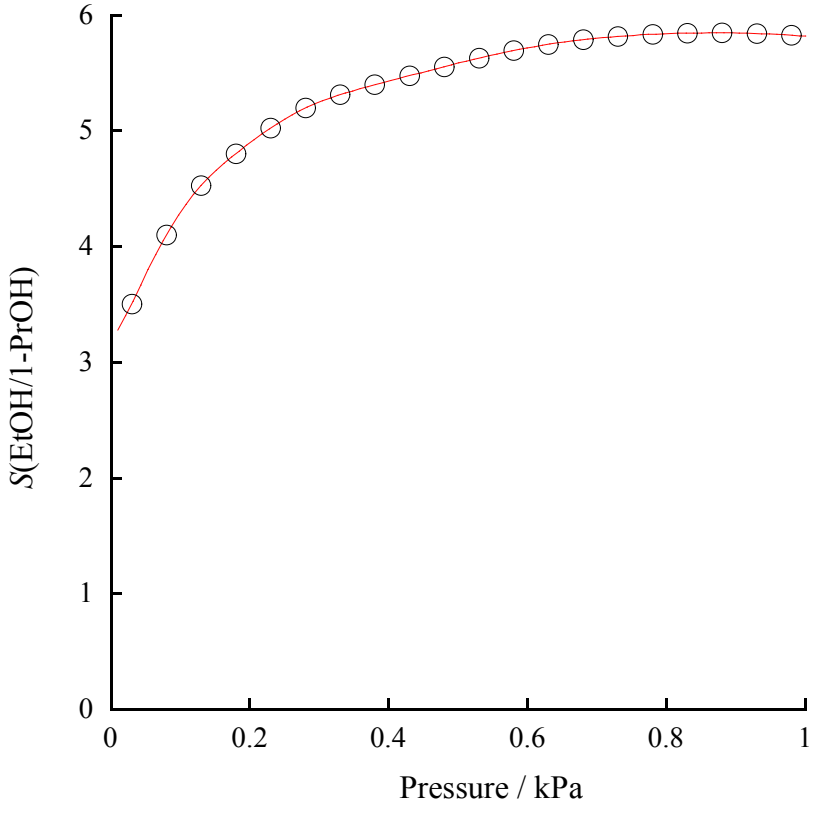
(b)


50
40
30
20
10
0
S(MeOH/1-PrOH)
0
0.04
0.08
0.12
0.16
0.2
Pressure / kPa

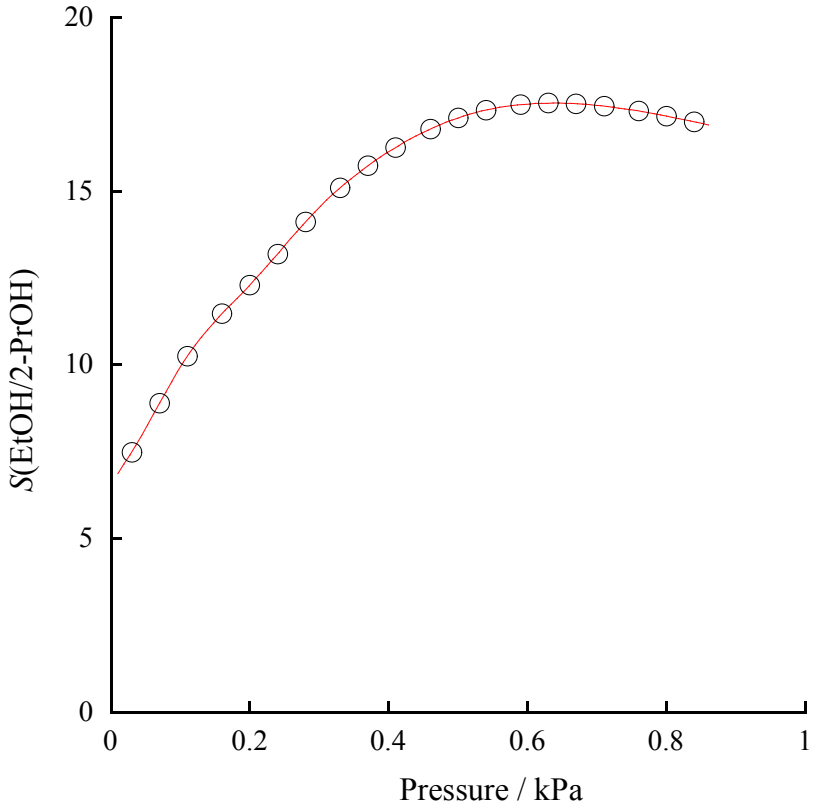
(c)


120
100
80
60
40
20
0
S(MeOH/2-PrOH)
0
0.04
0.08
0.12
0.16
Pressure / kPa

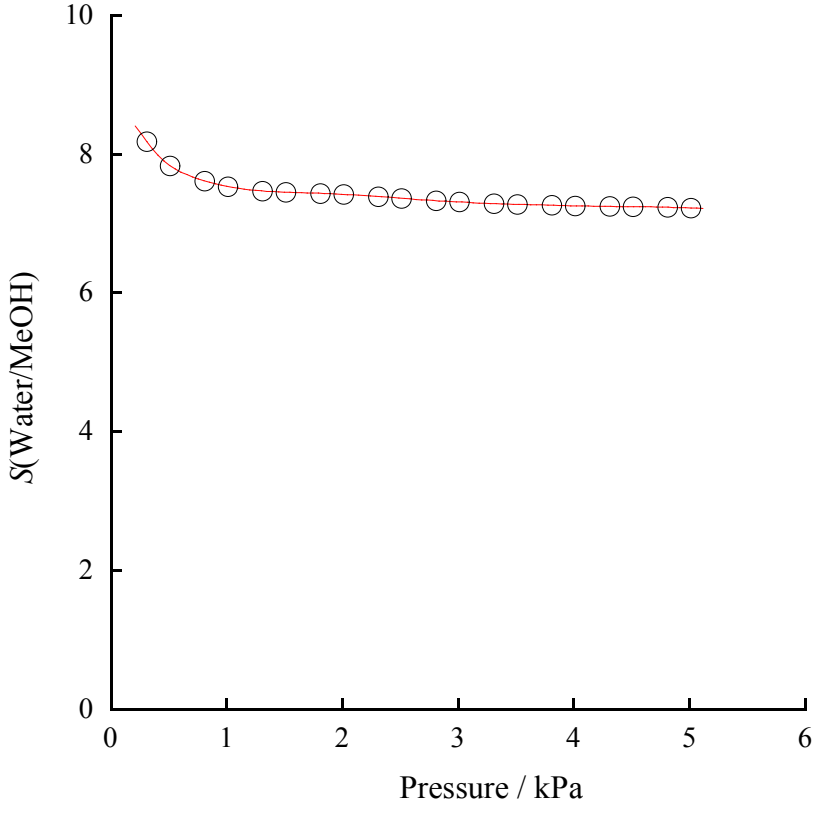
(d)


6
5
4
3
2
1
0
S(EtOH/1-PrOH)
0
0.2
0.4
0.6
0.8
1
Pressure / kPa

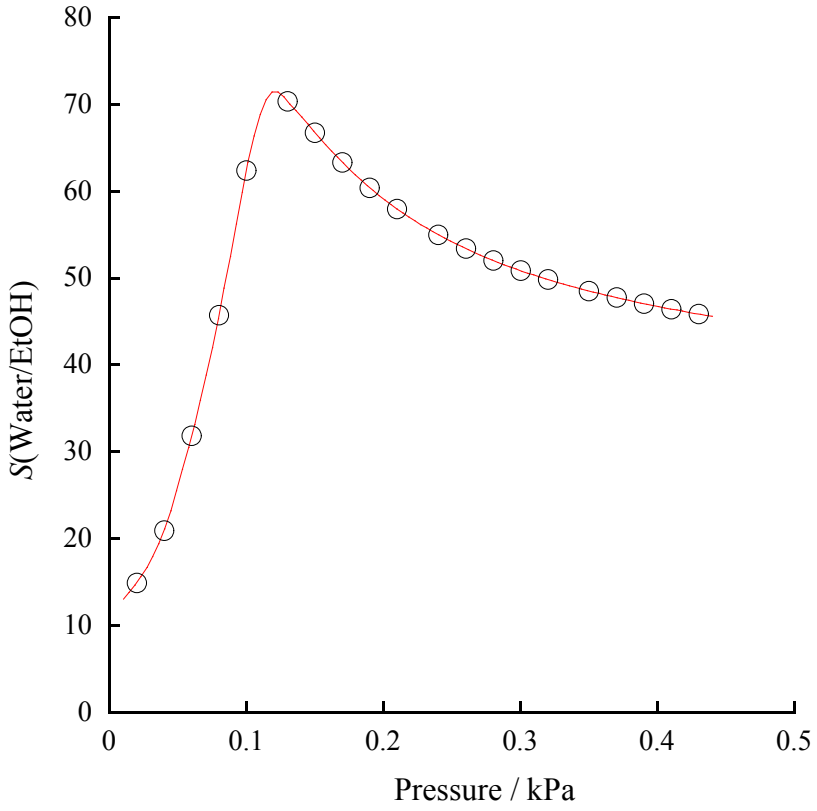
(e)


20
15
10
5
0
S(EtOH/2-PrOH)
0
0.2
0.4
0.6
0.8
1
Pressure / kPa

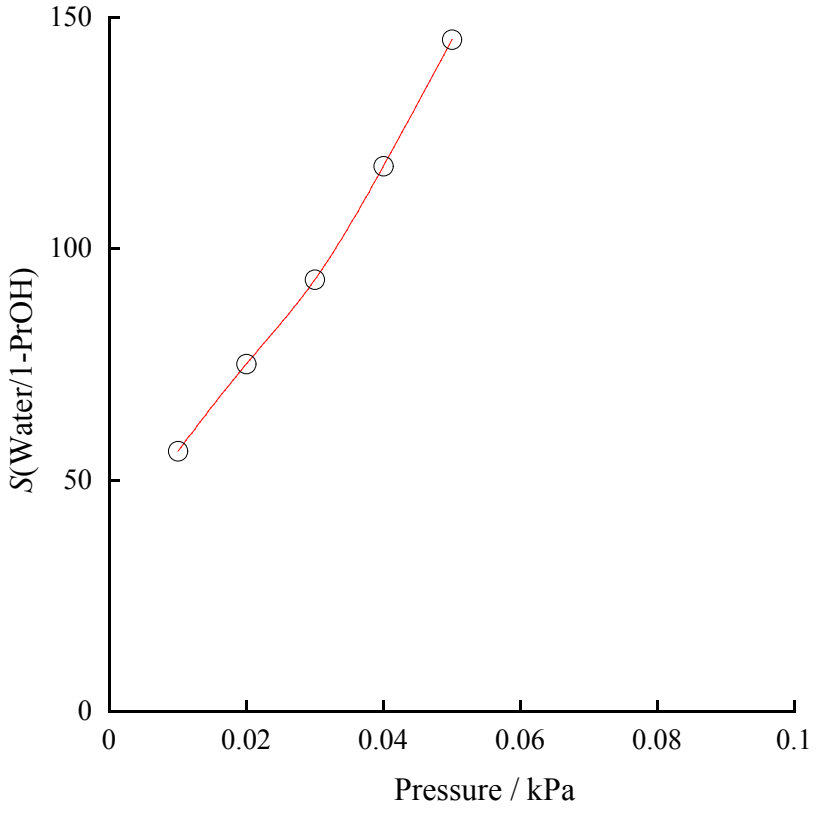
(f)


10
8
6
4
2
0
S(Water/MeOH)
0
1
2
3
4
5
6
Pressure / kPa

(g)


80
70
60
50
40
30
20
10
0
S(Water/EtOH)
0
0.1
0.2
0.3
0.4
0.5
Pressure / kPa

(h)


150
100
50
0
S(Water/1-PrOH)
0
0.02
0.04
0.06
0.08
0.1
Pressure / kPa

(i)

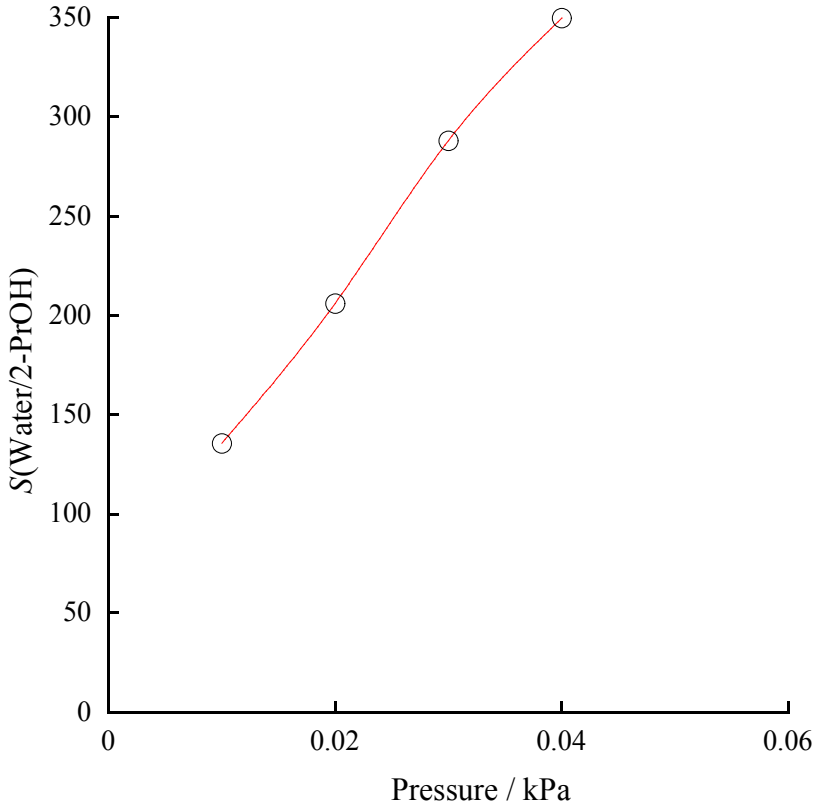


Figure S7. Vapor adsorption selectivity of (a) *S*(methanol/ethanol), (b) *S*(methanol/1-propanol), (c) *S*(methanol/2-propanol), (d) *S*(ethanol/1-propanol), (e) *S*(ethanol/2-propanol), (f) *S*(water/methanol), (g) *S*(water/ethanol), (h) *S*(water/1-propanol), (i) *S*(water/2-propanol) estimated by IAST.

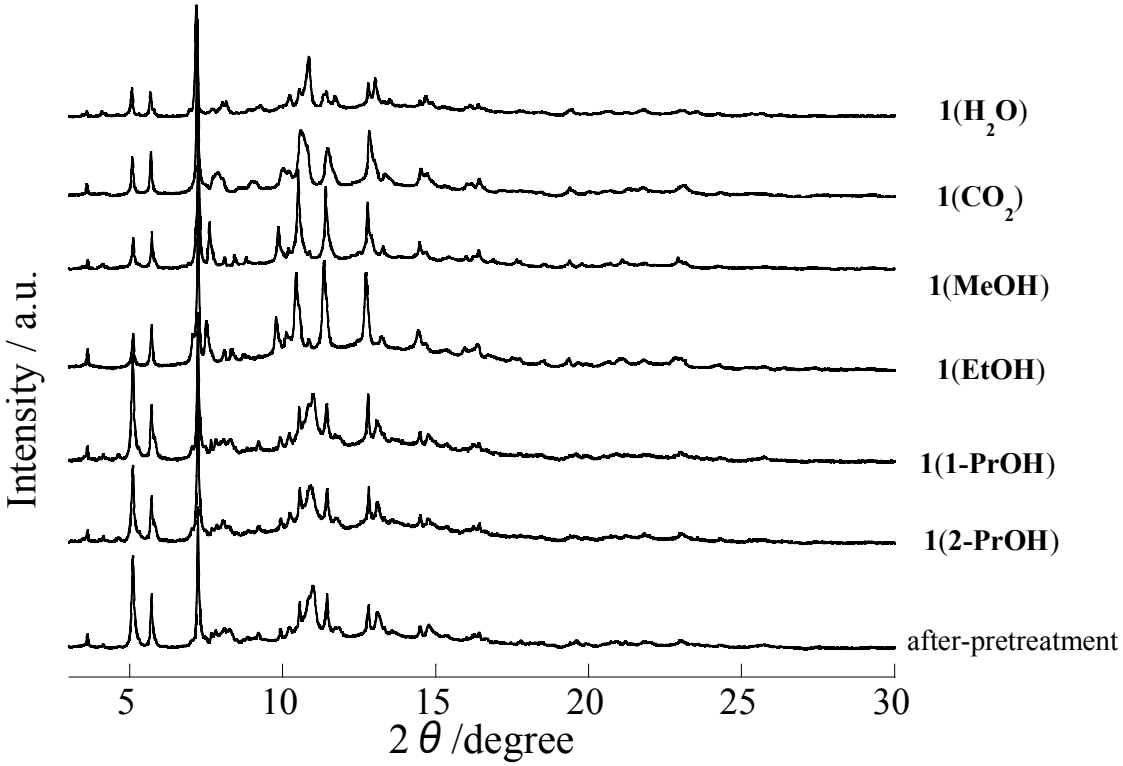
Table S3. Highest selectivities of some equimolar two-components mixed gases estimated by IAST. The values in parentheses are expected concentration percentages by one adsorption/separation process.

S(methanol/ethanol)	*S*(methanol/1-prolanol)	*S*(methanol/2-propanol)
11 (91.6 %)	41.4 (97.6 %)	112 (99.1 %)
S(ethanol/1-propanol)	*S*(ethanol/2-propanol)	*S*(H_2O/methanol)
5.8 (85.4 %)	17.5 (94.6 %)	8.4 (89.3 %)
S(H_2O/ethanol)	*S*(H_2O /1-propanol)	*S*(H_2O /2-propanol)
71.5 (98.6 %)	145 (99.3 %)	350 (99.7 %)

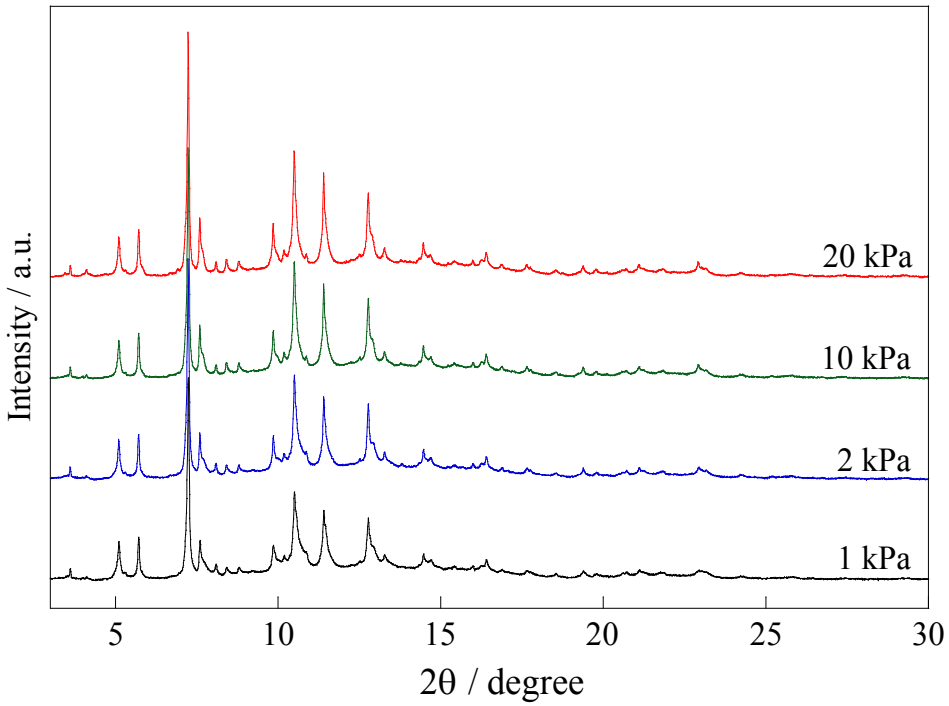
Table S4. Results of liquid phase ternary alcohol mixture adsorption.

Alcohol mixture	Initial relative amount against 1-butanol	Relative amount against 1-butanol after adsorption	Selectivity
Methanol 0.5 ml	0.13	0.092	~ 3.5 ($S_{MeOH/EtOH}$)
Ethanol 0.5 ml	0.087	0.080	
1-Butanol 9 ml	1	1	
Methanol 0.5 ml	0.13	0.11	~ 61 ($S_{MeOH/1\text{-}PrOH}$)
1-Propanol 0.5 ml	0.068	0.068	
1-Butanol 9 ml	1	1	
Methanol 0.5 ml	0.13	0.090	~ 80 ($S_{MeOH/2\text{-}PrOH}$)
2-Propanol 0.5 ml	0.066	0.066	
1-Butanol 9 ml	1	1	
Ethanol 0.5 ml	0.087	0.085	~ 5.7 ($S_{EtOH/1\text{-}PrOH}$)
1-Propanol 0.5 ml	0.068	0.068	
1-Butanol 9 ml	1	1	

(a)


Intensity / a.u.
1(H2O)
1(CO2)
1(MeOH)
1(EtOH)
1(1-PrOH)
1(2-PrOH)
after-pretreatment
5
10
15
20
25
30
2θ /degree

(b)


Intensity / a.u.
20 kPa
10 kPa
2 kPa
1 kPa
5
10
15
20
25
30
2θ / degree

(c)

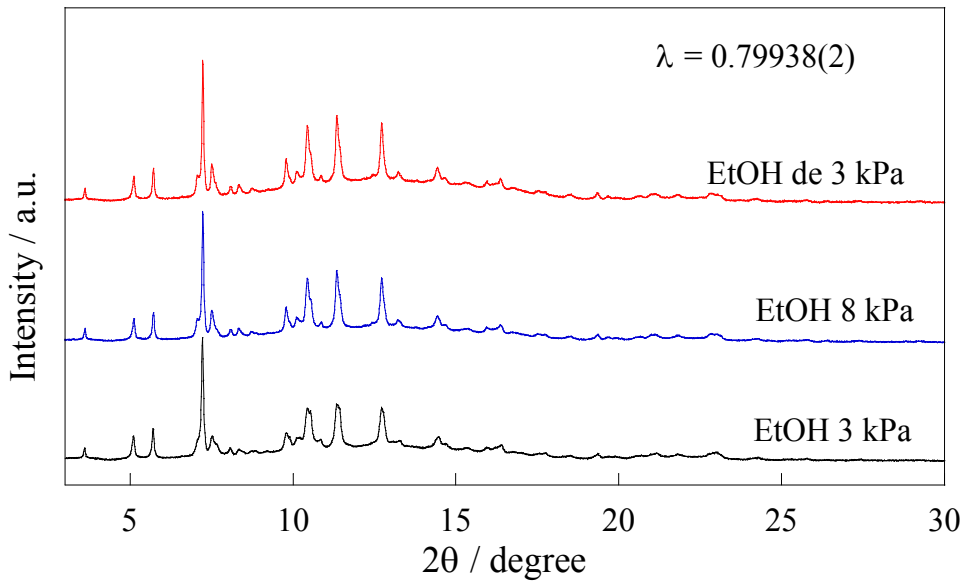


Figure S8. (a) In situ synchrotron XRD patterns of the MOF after the activation treatment (**1a**), **1**(**H_2O**), **1**(**CO_2**), **1**(**MeOH**), **1**(**EtOH**), **1**(**1-PrOH**), and **1**(**2-PrOH**). The wavelength was modified to be 0.79917 Å because **1**(**EtOH**) and **1**(**CO_2**) were measured with different wavelength (0.79942 Å). (b) In situ XRD patterns of **1**(**MeOH**) with several methanol gas loadings (λ = 0.79917 Å), and (c) in situ XRD patterns of **1**(**EtOH**) with several ethanol gas loadings (λ = 0.79938 Å). The XRD patterns were measured at 303 K except that with CO_2 gas (273 K).

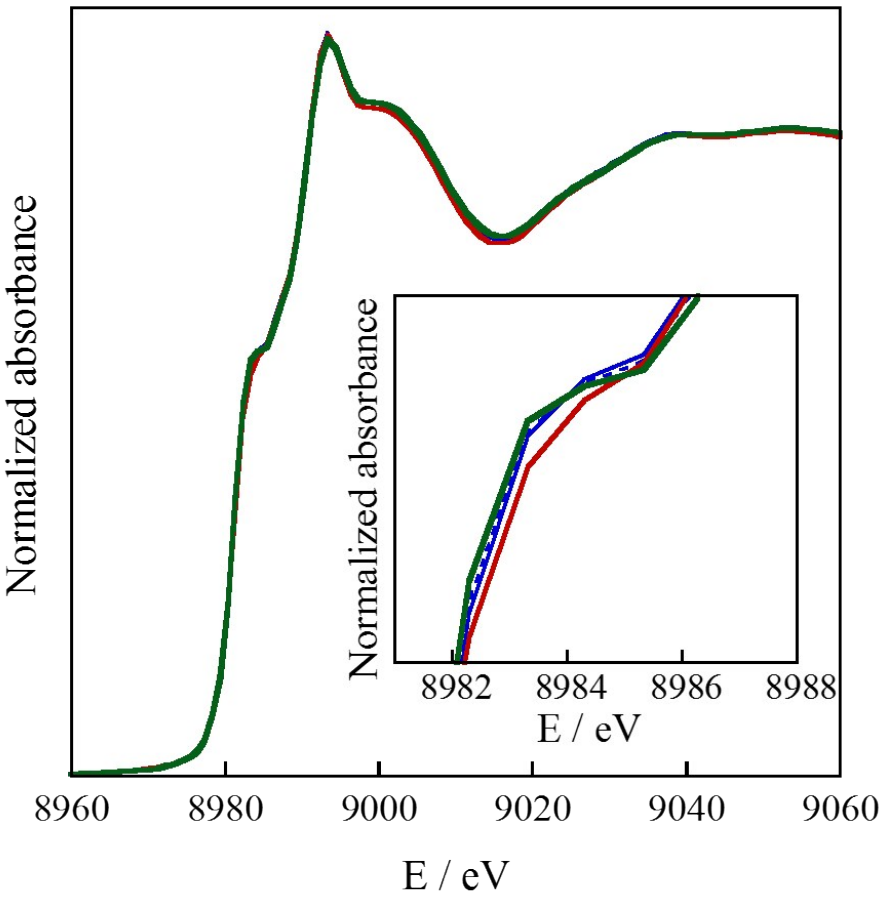


Figure S9. Local structure investigation around Cu(I) ion through vapor adsorption. Normalized Cu *K*-edge spectra of **1a** (green), **1**(**EtOH**) (brown), **1**(**1-PrOH**) (blue), and **1**(**2-PrOH**) (dotted blue). Inserted figure is enlarged one around 8983 eV.

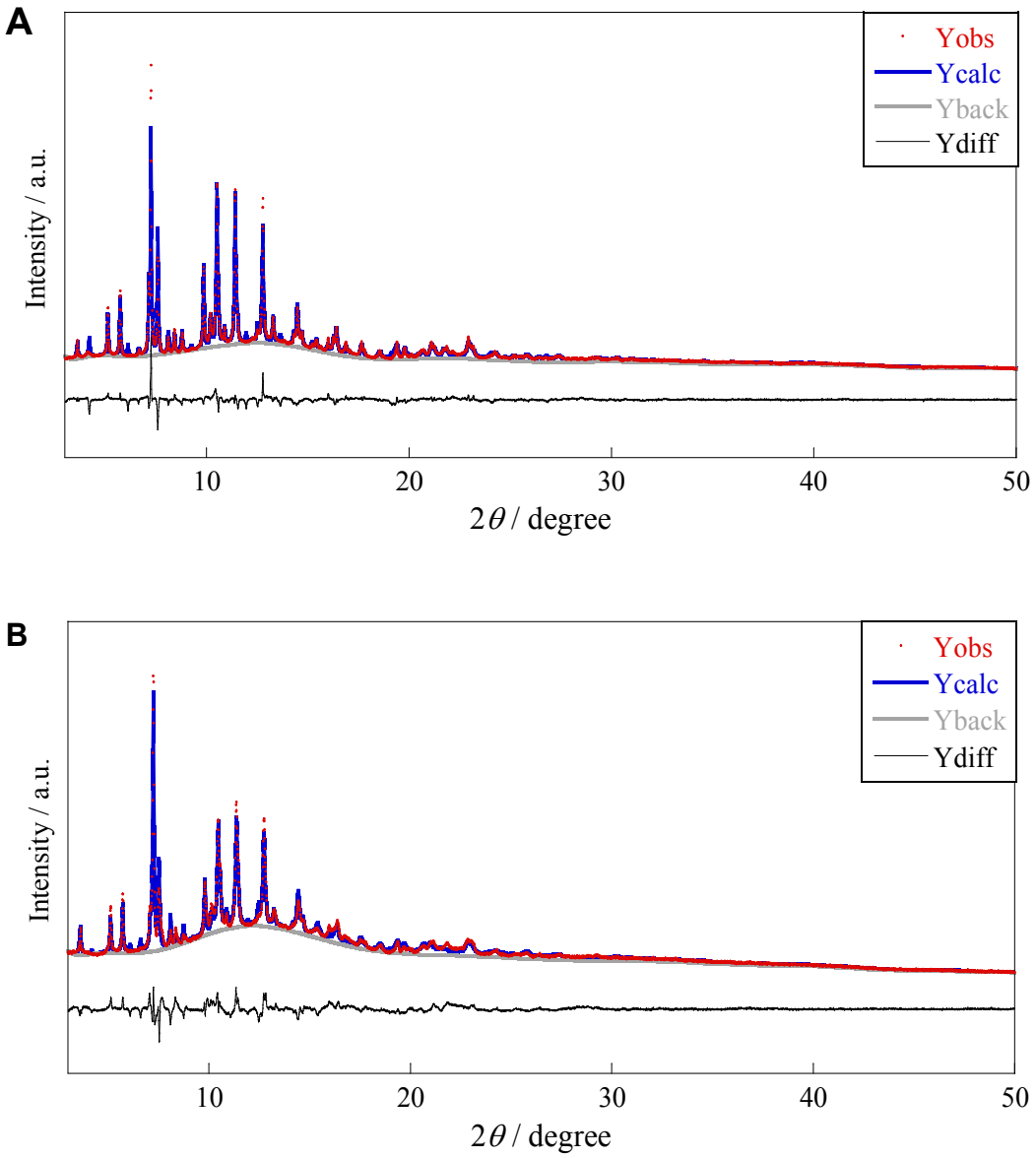


Figure S10. Final Rietveld fitting results of in situ synchrotron XRD patterns on (A) **1**(**MeOH**) (R_p = 2.1 %, R_{wp} = 3.5 %) and (B) **1**(**EtOH**) (R_p = 2.5 %, R_{wp} = 3.7 %). Synchrotron X-ray wavelength used is 0.79942(2) Å.

Table S5. Crystallographic parameters of **1**(**MeOH**) and **1**(**EtOH**).

	1(**MeOH**)	**1**(**EtOH**)
Crystal system	Tetragonal	Tetragonal
Space group	$P2_1c$	$P2_1c$
a / Å	17.8698(6)	17.8866(10)
c / Å	13.7392(10)	13.8782(20)
V / Å^3	4387.3(3)	4440.0(6)
Z	4	4
T / K	303	303
λ / Å	0.79942	0.79942
R_p	0.0021	0.0025
R_{wp}	0.035	0.037
R_F	0.050	0.083

Referemces

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