

## **Supporting Information**

### **CFA-4 - a fluorinated metal-organic framework with exchangeable interchannel cations**

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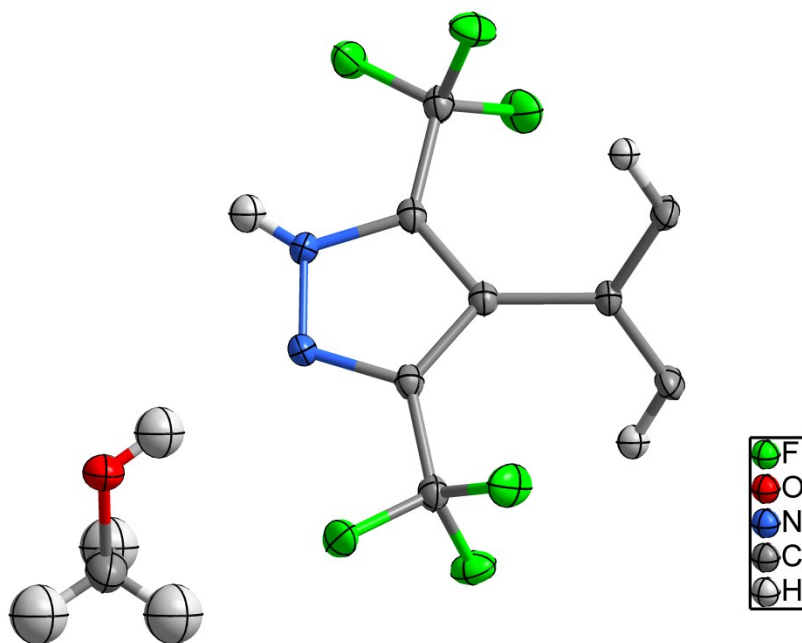
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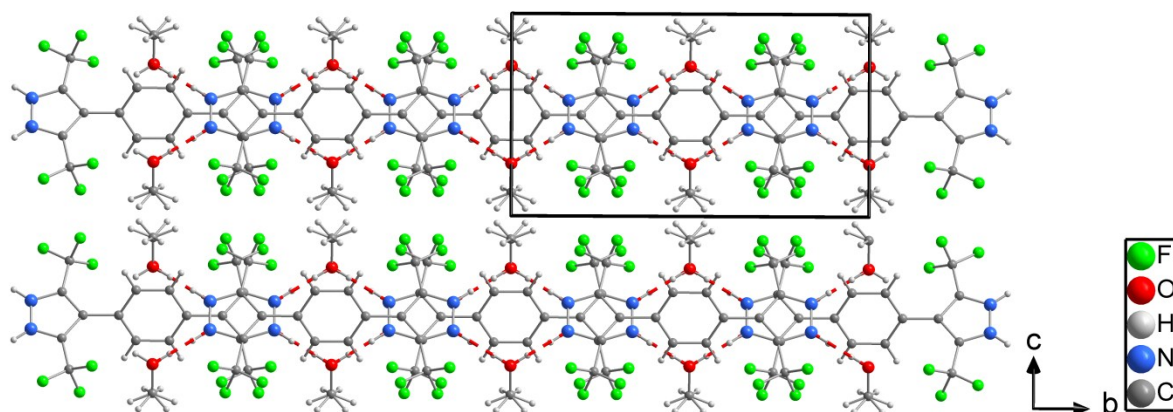
## 1. Single Crystal Structure Analysis of 1,4-bis(3,5-bis(trifluoromethyl)-1H-pyrazole-4-yl)benzene ·2MeOH (C<sub>16</sub>H<sub>6</sub>F<sub>12</sub>N<sub>4</sub> ·2CH<sub>3</sub>OH).

1·2MeOH crystallizes in the monoclinic crystal system within the space group *C2/m* (no. 12). The asymmetric unit consists of one nitrogen, six carbon, three fluoride, one oxygen and six hydrogen atoms accounting for 1/3 of H<sub>2</sub>-tfpb and one MeOH molecule. An Ortep-style plot of the asymmetric unit of 1·2MeOH is shown in Fig. S1. While the (CF<sub>3</sub>)<sub>2</sub>-pyrazole rings of the H<sub>2</sub>-tfpb molecule are almost parallel to the (100) plane, the phenyl ring is inclined with respect to the (CF<sub>3</sub>)<sub>2</sub>-pyrazole rings. The two equatorial planes created by atoms belonging to the (CF<sub>3</sub>)<sub>2</sub>-pyrazole rings and atoms of the phenyl ring enclose an angle of 57.44(5)°. The O1 and C6 atoms of MeOH are placed on a crystallographic mirror plane (4i in Wyckoff notation).



**Fig. S1** Ortep-style plot of the asymmetric unit of 1·2MeOH. Thermal ellipsoids probability: 50 %.

Compound **1** exhibits layered packing motif. Looking along the *a*-direction, the layers created by H<sub>2</sub>-tfpb molecules are separated by solvent molecules. The whole structure is stabilized by hydrogen bridges formed between MeOH molecules and nitrogen atoms of H<sub>2</sub>-tfpb. List of the hydrogen bonds for 1·2MeOH is presented in Table S1. The packing diagram of 1·2MeOH along the *a*-direction is shown in Fig. S2.



**Fig. S2** Packing diagram of **1·2MeOH** with hydrogen bonds shown as intercepted red lines. Hydrogen atoms from  $H_2$ -tfpb molecules are shown with 50% occupation. (In the crystal structure of **1·2MeOH** the acidic NH-protons of the  $H_2$ -tfpb molecule have been placed in calculated positions ( $d(NH) = 0.88 \text{ \AA}$ ). Owing to lattice symmetry both nitrogen atoms of each pyrazole ring and oxygen atoms of MeOH molecules appear to be protonated at 50% probability).

**Table S1** Hydrogen bonds for **1·2MeOH**

Donor---Hydrogen...Acceptor	Don--Hyd [ $\text{\AA}$ ]	Hyd--Acc [ $\text{\AA}$ ]	Don--Acc [ $\text{\AA}$ ]	D--H----A
O1---H1...N1»1	0.84	1.95	2.782	173.7°
N1---H1A...O1	0.88	1.92	2.782	165.1°
O1---H1»1...N1	0.84	1.95	2.782	173.7°
N1»1---H1A»1...O1	0.88	1.92	2.782	165.1°
O1»2---H1»2...N1»4	0.84	1.95	2.782	173.7°
N1»2---H1A»2...O1»2	0.88	1.92	2.782	165.1°
O1»3---H1»3...N1»7	0.84	1.95	2.782	173.7°
N1»3---H1A»3...O1»3	0.88	1.92	2.782	165.1°
O1»2---H1»4...N1»2	0.84	1.95	2.782	173.7°
N1»4---H1A»4...O1»2	0.88	1.92	2.782	165.1°
N1»5---H1A»5...O1»5	0.88	1.92	2.782	165.1°
N1»6---H1A»6...O1»6	0.88	1.92	2.782	165.1°
O1»3---H1»7...N1»3	0.84	1.95	2.782	173.7°
N1»7---H1A»7...O1»3	0.88	1.92	2.782	165.1°

## Topology analysis for Cu(I)[CFA-4]

### Topology for Sc1

Atom Sc1 links by bridge ligands and has

Common vertex with		R(A-A)		
V 1	0.3333 0.6667 0.5828 (0 0 0)	7.624A	1	
Ti 1	0.6667 0.3333 0.7500 (0 0 0)	7.679A	1	

### Topology for Sc2

Atom Sc2 links by bridge ligands and has

Common vertex with		R(A-A)		
V 1	-0.3333 0.3333 0.4172 (0 1 1)	7.702A	1	
V 1	0.3333 0.6667 0.5828 (0 0 0)	7.702A	1	

### Topology for Ti1

Atom Ti1 links by bridge ligands and has

Common vertex with		R(A-A)		
Sc 1	1.0002 0.4916 0.6651 (1 1 0)	7.679A	1	
Sc 1	1.0002 0.5086 0.8349 (1 0 1)	7.679A	1	
Sc 1	0.4914 0.4916 0.8349 (1 1 1)	7.679A	1	
Sc 1	0.5084 -0.0002 0.8349 (0 0 1)	7.679A	1	
Sc 1	0.4914 -0.0002 0.6651 (1 0 0)	7.679A	1	
Sc 1	0.5084 0.5086 0.6651 (0 0 0)	7.679A	1	

### Topology for V1

Atom V1 links by bridge ligands and has

Common vertex with		R(A-A)		
Sc 1	0.4914 0.9998 0.6651 (1 1 0)	7.624A	1	
Sc 1	0.5084 0.5086 0.6651 (0 0 0)	7.624A	1	
Sc 1	0.0002 0.4916 0.6651 (0 1 0)	7.624A	1	
Sc 2	0.4569 1.0000 0.5000 (0 1 0)	7.702A	1	
Sc 2	0.5431 0.5431 0.5000 (1 1 0)	7.702A	1	
Sc 2	0.0000 0.4569 0.5000 (0 0 0)	7.702A	1	

### Structural group analysis

Structural group No 1

Structure consists of 3D framework with V2TiSc9

### Coordination sequences

Sc1: 1 2 3 4 5 6 7 8 9 10  
Num 2 10 10 46 30 120 54 210 94 330  
Cum 3 13 23 69 99 219 273 483 577 907

Sc2: 1 2 3 4 5 6 7 8 9 10  
Num 2 10 10 46 30 120 54 210 94 330  
Cum 3 13 23 69 99 219 273 483 577 907

Ti1: 1 2 3 4 5 6 7 8 9 10  
Num 6 6 30 20 90 42 162 74 282 114  
Cum 7 13 43 63 153 195 357 431 713 827

V1: 1 2 3 4 5 6 7 8 9 10  
Num 6 6 30 20 90 42 162 74 282 114  
Cum 7 13 43 63 153 195 357 431 713 827

TD10=887

Vertex symbols for selected sublattice

-----  
Sc1 Point symbol: {8}  
Sc1 Point symbol with loops: {4}  
Extended point symbol: [8(4)]  
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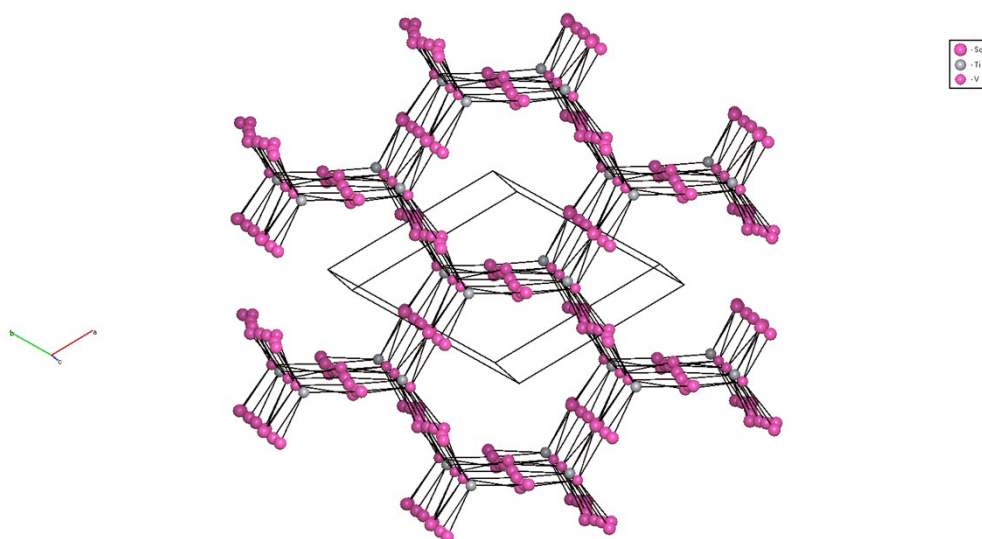
Sc2 Point symbol: {8}  
Sc2 Point symbol with loops: {4}  
Extended point symbol: [8(4)]  
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Ti1 Point symbol: {8<sup>9</sup>.12<sup>6</sup>}  
Ti1 Point symbol with loops: {4<sup>9</sup>.6<sup>6</sup>}  
Extended point symbol: [8.8.8.8.8.8(2).8(2).8(2).12(8).12(8).12(8).12(8).12(8).12(8)]  
-----

V1 Point symbol: {8<sup>9</sup>.12<sup>6</sup>}  
V1 Point symbol with loops: {4<sup>9</sup>.6<sup>6</sup>}  
Extended point symbol: [8.8.8.8.8.8(2).8(2).8(2).12(8).12(8).12(8).12(8).12(8).12(8)]  
-----

Point symbol for net: {8<sup>9</sup>.12<sup>6</sup>} {8}3  
Point symbol for net with loops: {4<sup>9</sup>.6<sup>6</sup>} {4}3  
2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net

New topology



**Fig. S3** Topological representation of **Cu(I)[CFA-4]**.

## 2. NMR spectra of 1,4-bis(3,5-bis(trifluoromethyl)-1*H*-pyrazole-4-yl)benzene (H<sub>2</sub>-tfpb)

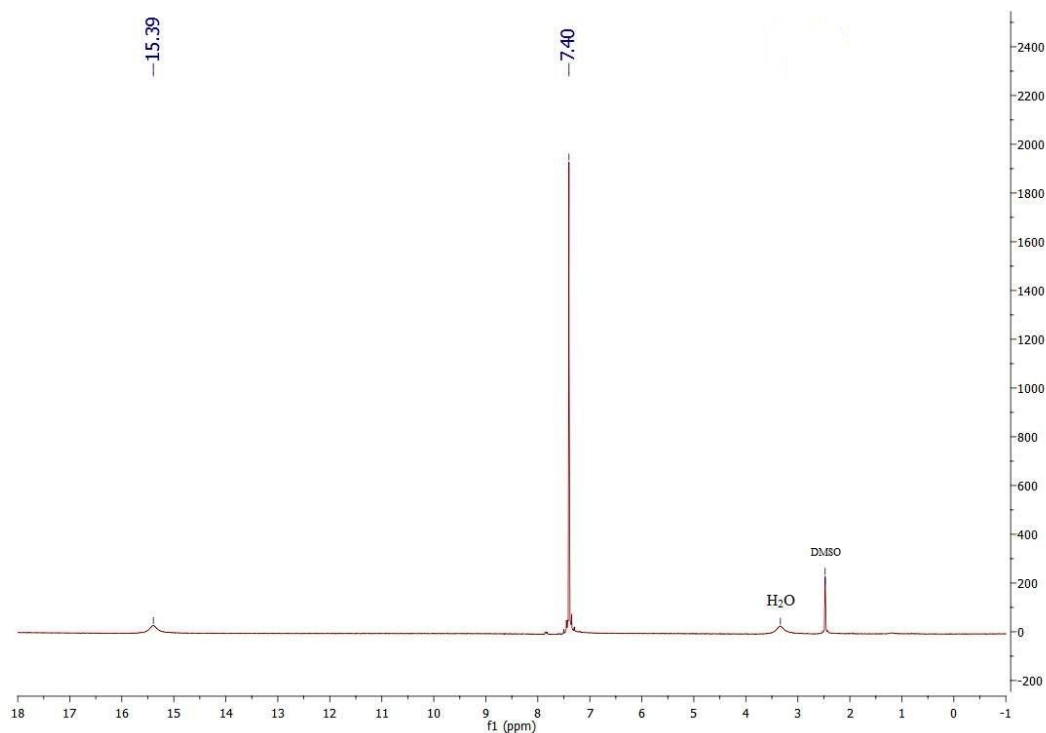


Fig. S4 <sup>1</sup>H-NMR spectrum of H<sub>2</sub>-tfpb in DMSO-d<sub>6</sub>.

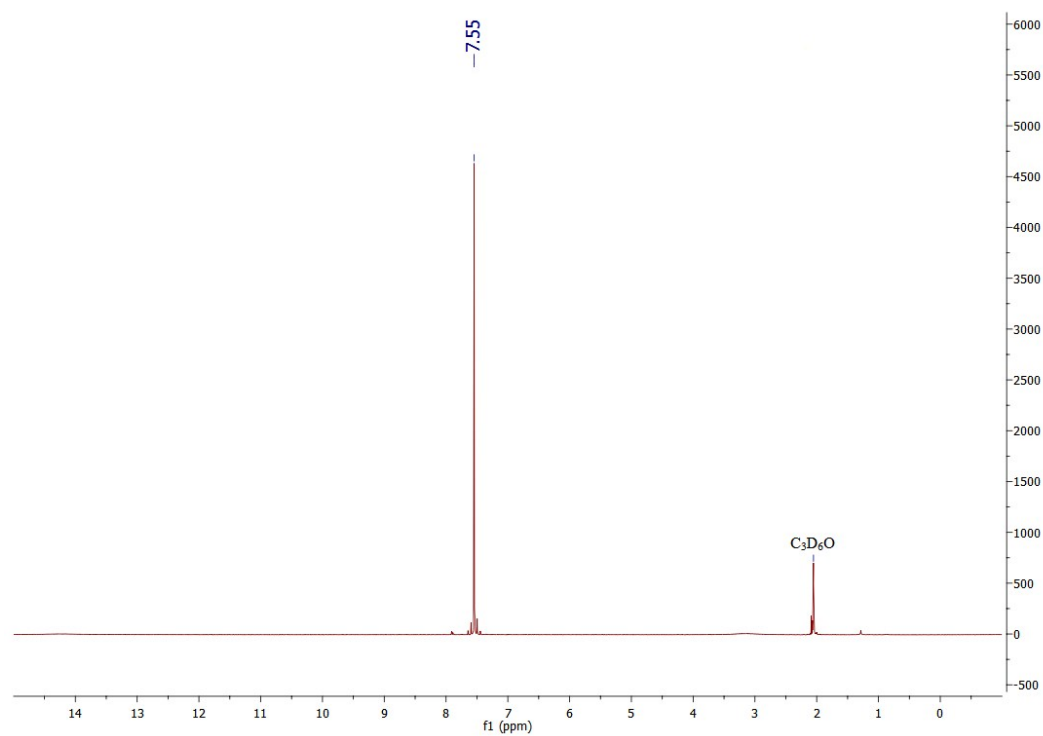
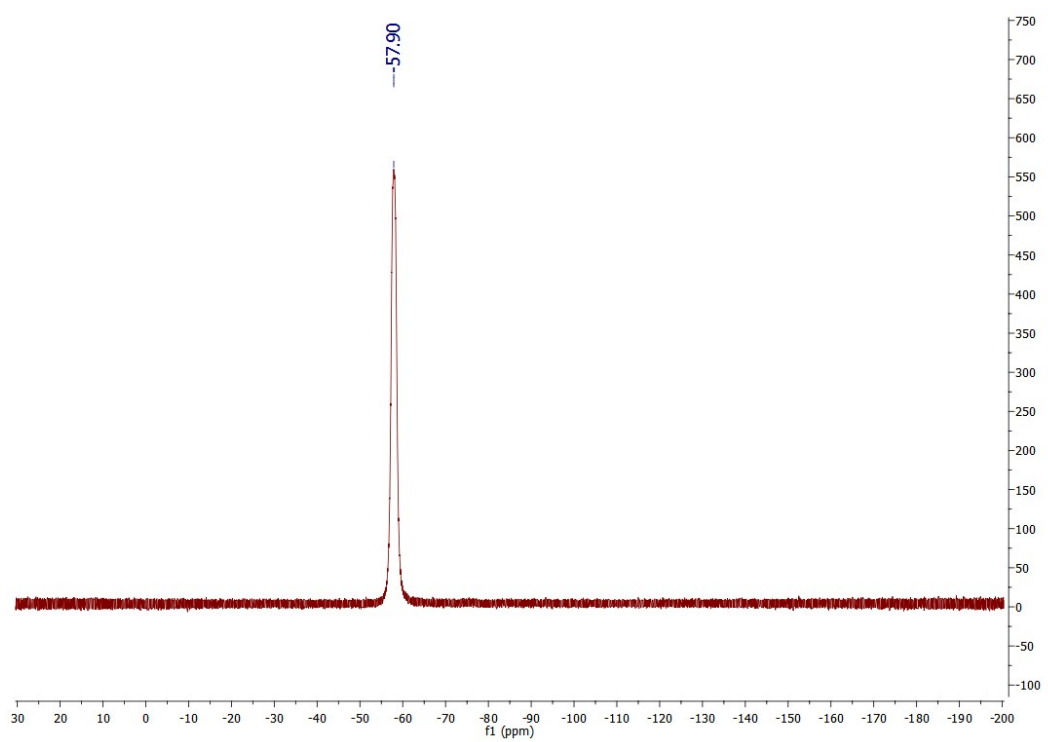


Fig. S5 <sup>1</sup>H-NMR spectrum of H<sub>2</sub>-tfpb in acetone-d<sub>6</sub>.



**Fig. S6**  $^{19}\text{F}$ -NMR spectrum of  $\text{H}_2\text{-tfpb}$  in  $\text{DMSO-d}_6$ .

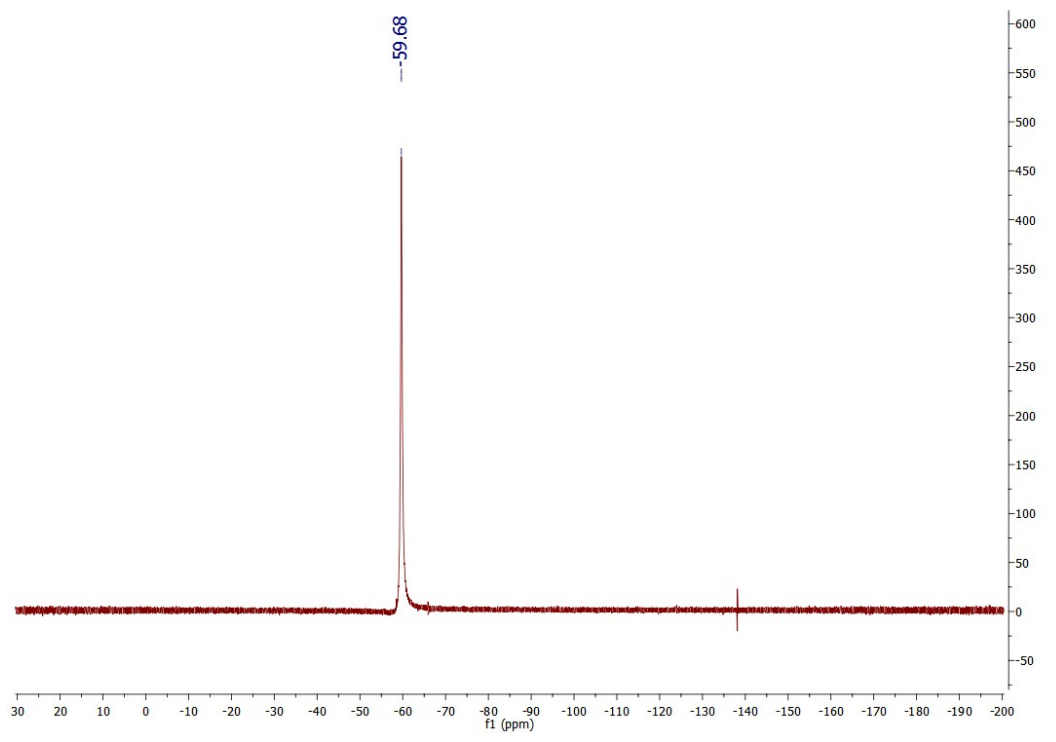


Fig. S7  $^{19}\text{F}$ -NMR spectrum of  $\text{H}_2$ -tfpb in acetone- $\text{d}_6$ .

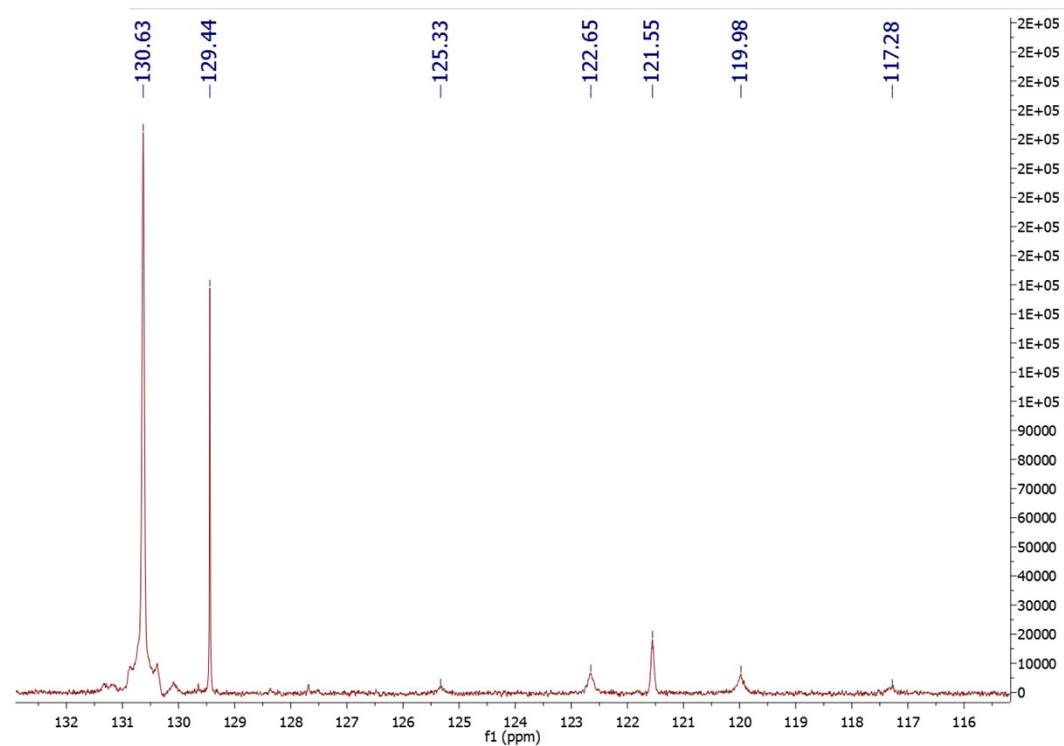
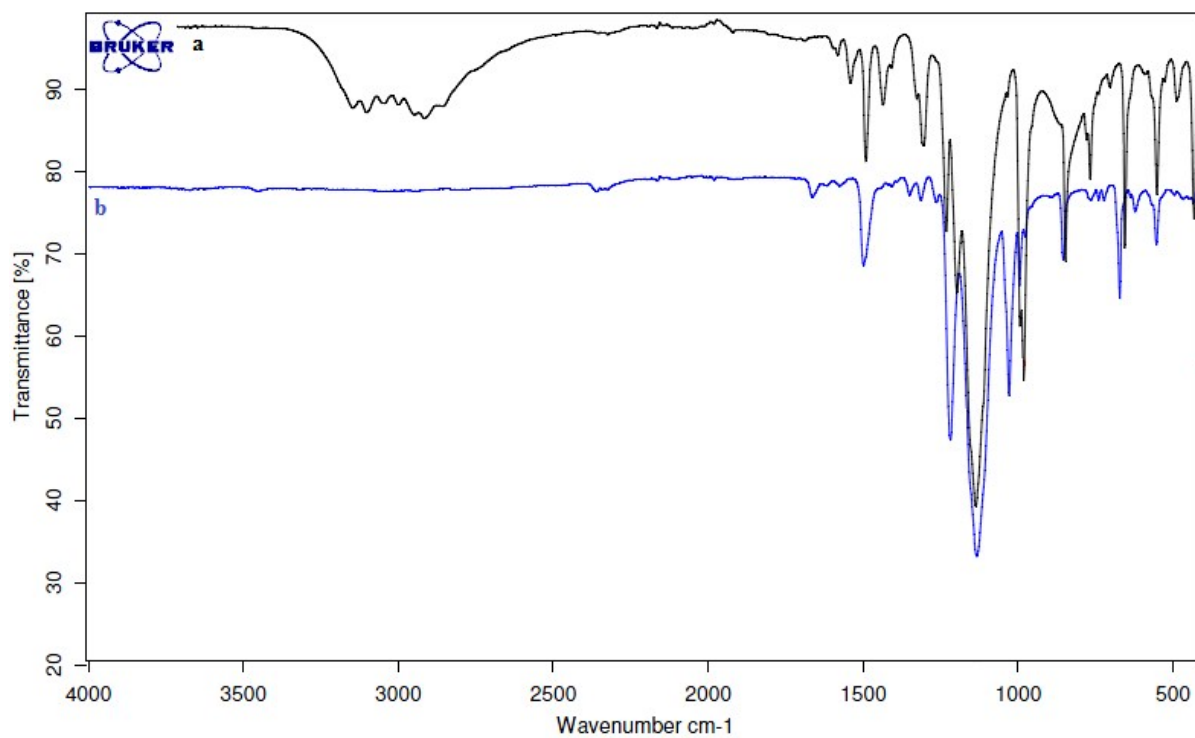


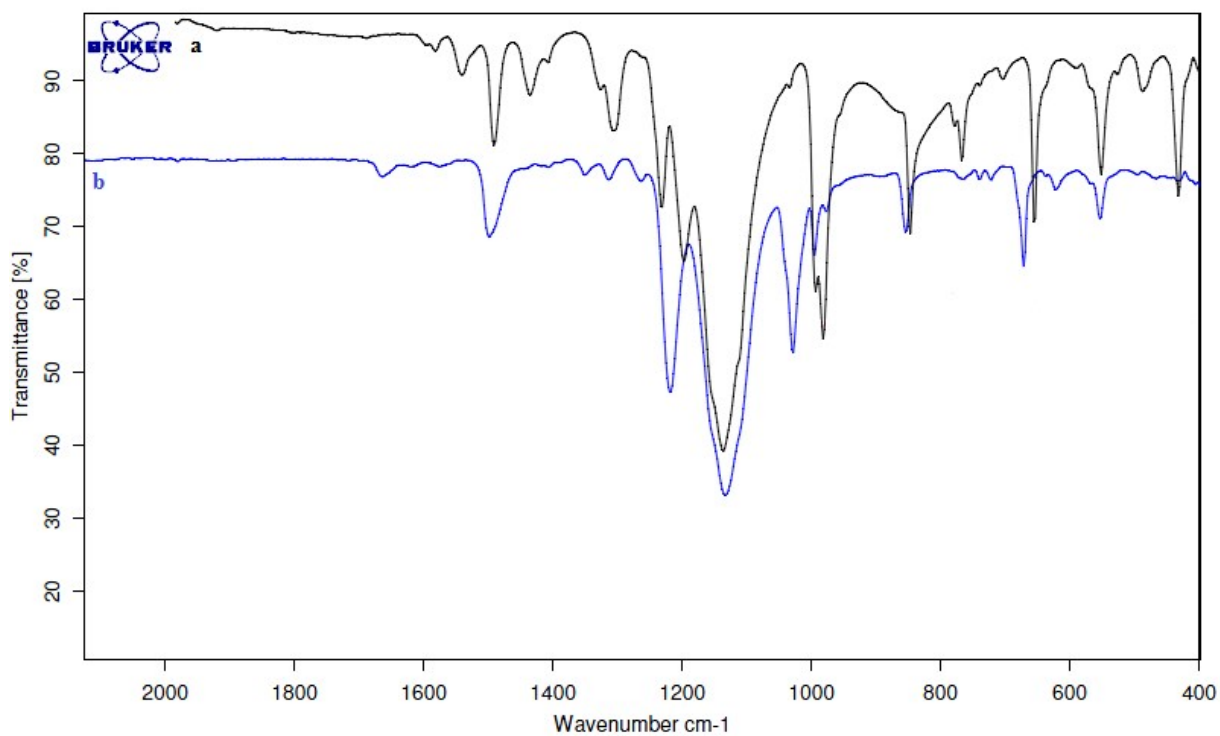
Fig. S8  $^{13}\text{C}$ -NMR spectrum of  $\text{H}_2$ -tfpb in acetone- $\text{d}_6$ .



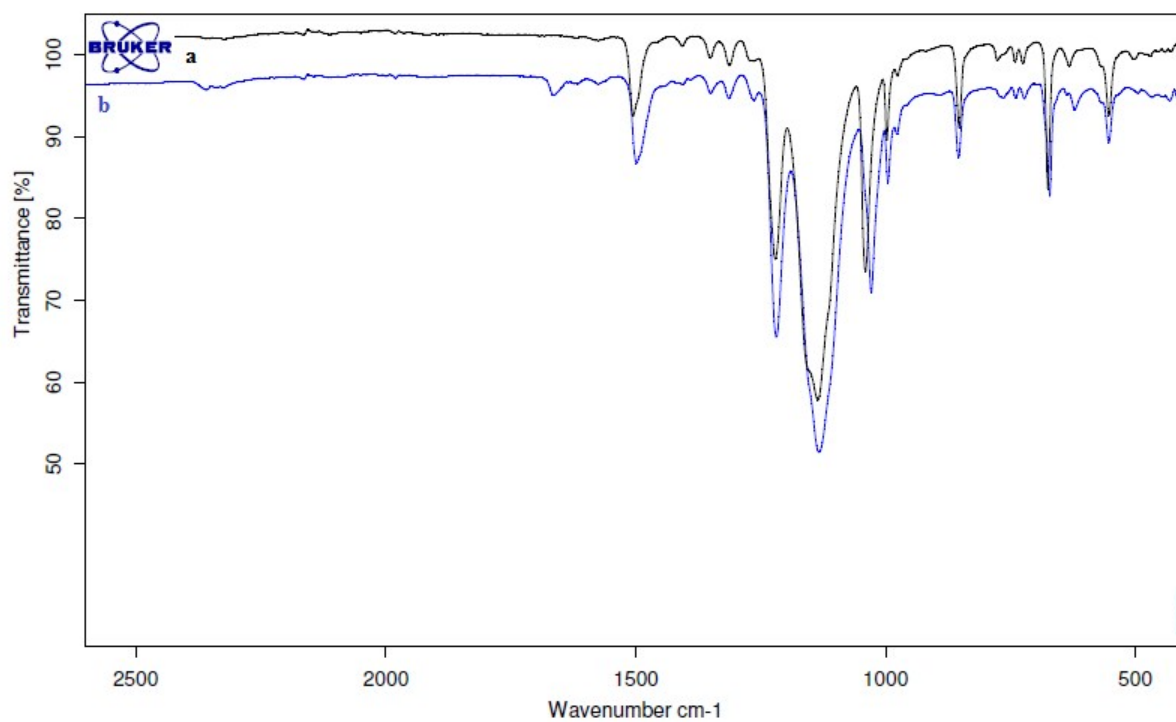
### 3. IR- Spectra



**Fig. S9** Full-range IR spectra of a) H<sub>2</sub>-tfpb; b) Cu(I)[CFA-4].

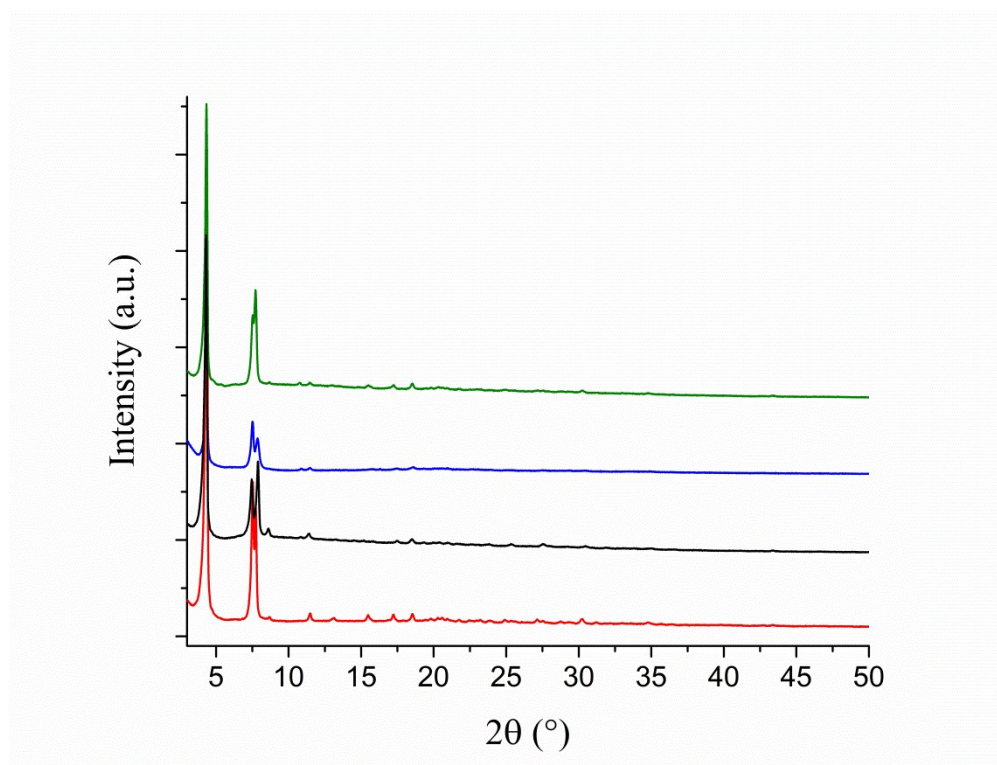


**Fig. S10** IR spectra in the range 2000-400 cm<sup>-1</sup> of a) H<sub>2</sub>-tfpb; b) Cu(I)[CFA-4].

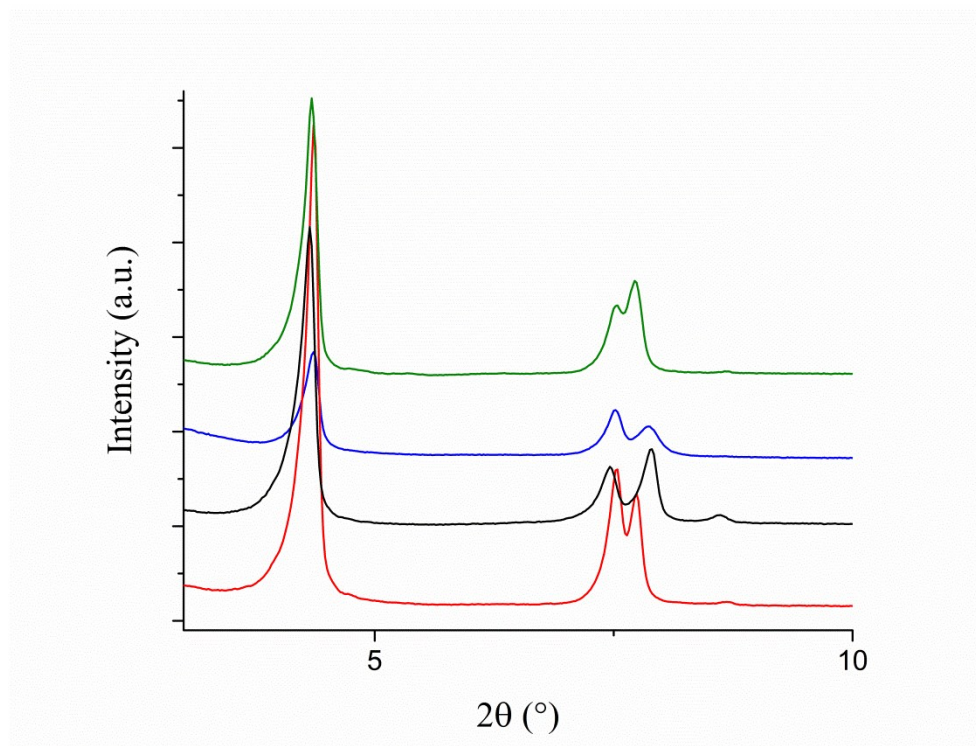


**Fig. S11** IR spectra of **Cu(I)[CFA-4]**: a) after drying at 300°C; b) fresh sample.

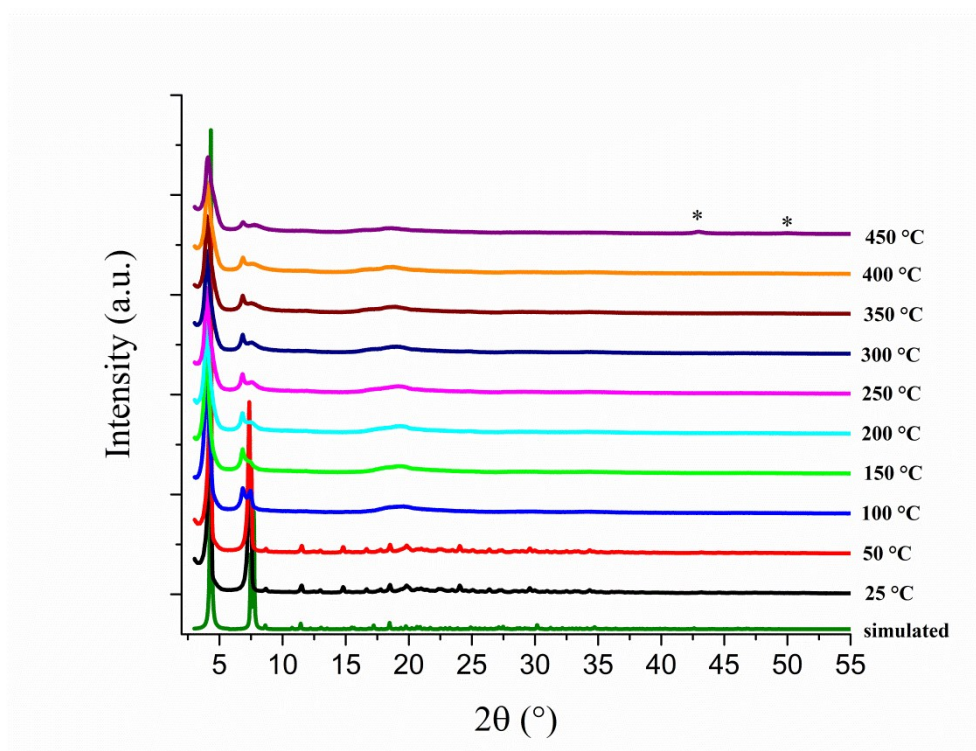
#### 4. X-Ray Powder Diffraction Pattern



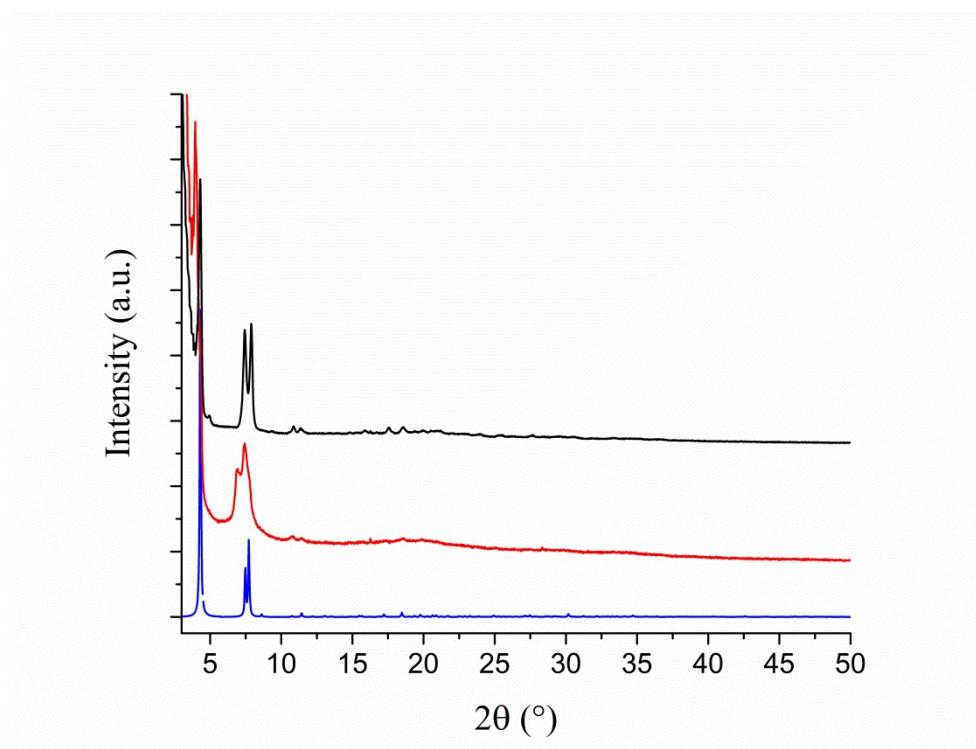
**Fig. S12** XRPD patterns of **Cu(I)[CFA-4]** (blue curve), **K[CFA-4]** (red curve), **Ca(0.5)[CFA-4]** (green curve) and **Cs[CFA-4]** (black curve).



**Fig. S13** XRPD patterns in the range 3-10° 2θ of **Cu(I)[CFA-4]** (blue curve), **K[CFA-4]** (red curve), **Ca(0.5)[CFA-4]** (green curve) and **Cs[CFA-4]** (black curve).

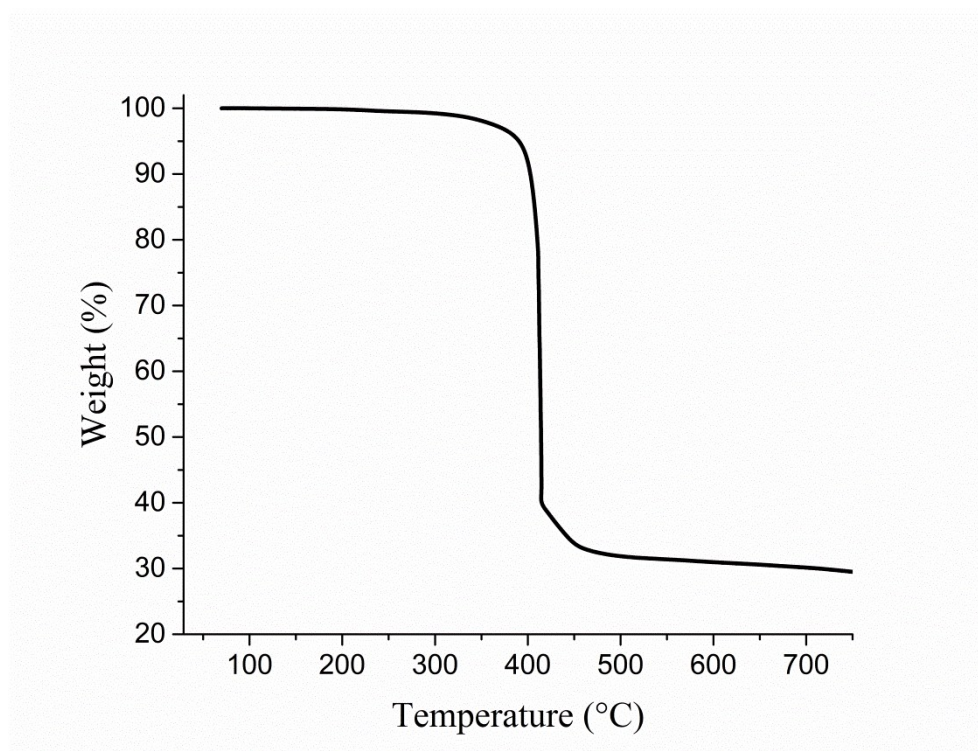


**Fig. S14** VTXRPD plots of  $\text{Cu(I)[Cu}_5(\text{tfpb})_3\text{]} \cdot x\text{CH}_3\text{CN}$  in the range of 25-450°C. The first XRPD pattern is simulated based on the single crystal X-ray data. \*peaks belong to Cu phase (PDF no. 4-836).



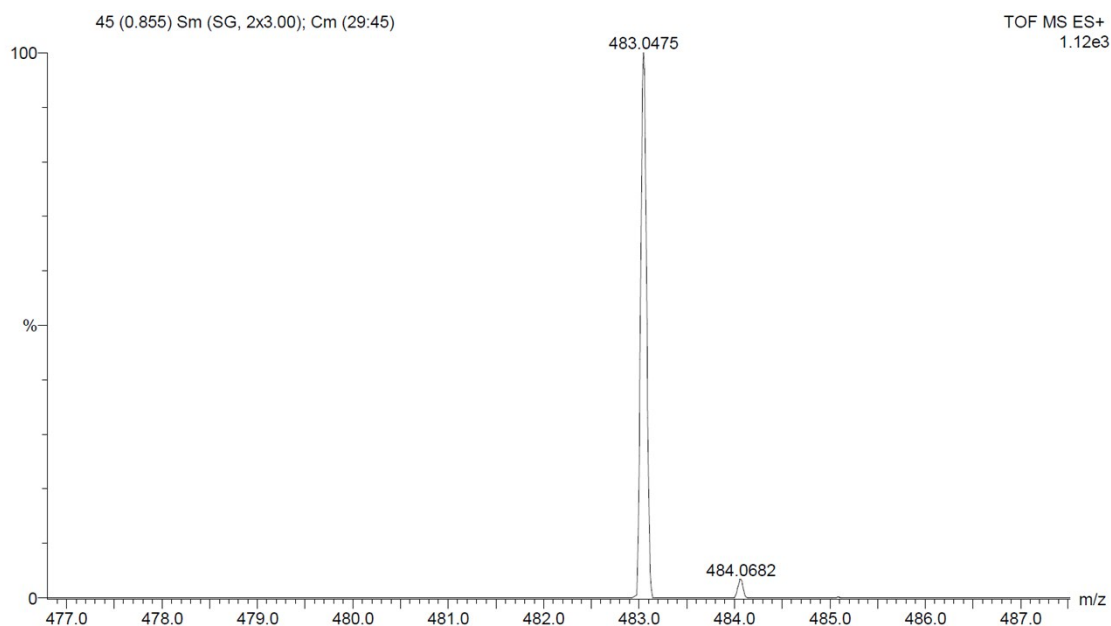
**Fig. S15** XRPD patterns of simulated  $\text{Cu(I)[CFA-4]}$  (blue curve), oxidised  $\text{Cu(I)[CFA-4]}$  (red curve) and reduced  $\text{Cu(I)[CFA-4]}$  (black curve).

## 5. TGA curve



**Fig. S16** Temperature dependent weight loss of **K[CFA-4]** under air.

## 6. Mass spectra



**Fig. S17** Mass spectra of H<sub>2</sub>-tfpb (TOF MS ESI+).

**Table S2** Elemental Composition Report of H<sub>2</sub>-tfpb.

Mass	Calc. Mass	mDa	PPM	DBE	Formula
483.0475	483.0478	-0.3	-0.5	-1.5	C8 H8 N4 F17
	483.0479	-0.4	-0.8	9.5	C16 H7 N4 F12
	483.0480	-0.5	-0.9	2.0	C13 H9 N F16
	483.0481	-0.6	-1.2	20.5	C24 H6 N4 F7
	483.0481	-0.6	-1.3	13.0	C21 H8 N F11
	483.0482	-0.7	-1.5	31.5	C32 H5 N4 F2
	483.0483	-0.8	-1.6	24.0	C29 H7 N F6
	483.0484	-0.9	-1.9	35.0	C37 H6 N F
	483.0422	5.3	11.1	31.5	C35 H6 F3
	483.0420	5.5	11.4	20.5	C27 H7 F8
	483.0420	5.5	11.5	28.0	C30 H5 N3 F4
	483.0419	5.6	11.6	35.5	C33 H3 N6
	483.0418	5.7	11.7	9.5	C19 H8 F13
	483.0418	5.7	11.8	17.0	C22 H6 N3 F9
	483.0418	5.7	11.9	24.5	C25 H4 N6 F5
	483.0417	5.8	12.0	-1.5	C11 H9 F18
	483.0416	5.9	12.1	6.0	C14 H7 N3 F14
	483.0416	5.9	12.2	13.5	C17 H5 N6 F10
	483.0414	6.1	12.5	2.5	C9 H6 N6 F15
	483.0540	-6.5	-13.5	2.0	C10 H8 N5 F15
	483.0542	-6.7	-13.8	13.0	C18 H7 N5 F10
	483.0542	-6.7	-13.9	5.5	C15 H9 N2 F14
	483.0543	-6.8	-14.2	24.0	C26 H6 N5 F5
	483.0544	-6.9	-14.2	16.5	C23 H8 N2 F9
	483.0545	-7.0	-14.5	35.0	C34 H5 N5
	483.0545	-7.0	-14.6	27.5	C31 H7 N2 F4
	483.0359	11.6	24.1	35.5	C36 H4 N2 F

Mass	Calc. Mass	mDa	PPM	DBE	Formula
483.0357	11.8	24.4	24.4	24.5	C28 H5 N2 F6
483.0357	11.8	24.5	24.5	32.0	C31 H3 N5 F2
483.0355	12.0	24.8	24.8	13.5	C20 H6 N2 F11
483.0355	12.0	24.9	24.9	21.0	C23 H4 N5 F7
483.0354	12.1	25.1	25.1	2.5	C12 H7 N2 F16
483.0353	12.2	25.2	25.2	10.0	C15 H5 N5 F12
483.0352	12.3	25.5	25.5	-1.0	C7 H6 N5 F17
483.0603	-12.8	-26.5	-26.5	5.5	C12 H8 N6 F13
483.0604	-12.9	-26.8	-26.8	16.5	C20 H7 N6 F8
483.0605	-13.0	-26.9	-26.9	9.0	C17 H9 N3 F12
483.0605	-13.0	-27.0	-27.0	1.5	C14 H11 F16
483.0606	-13.1	-27.1	-27.1	27.5	C28 H6 N6 F3
483.0606	-13.1	-27.2	-27.2	20.0	C25 H8 N3 F7
483.0607	-13.2	-27.3	-27.3	12.5	C22 H10 F11
483.0608	-13.3	-27.5	-27.5	31.0	C33 H7 N3 F2
483.0608	-13.3	-27.6	-27.6	23.5	C30 H9 F6
483.0610	-13.5	-28.0	-28.0	34.5	C38 H8 F
483.0296	17.9	37.1	37.1	32.0	C34 H4 N F3
483.0294	18.1	37.4	37.4	21.0	C26 H5 N F8
483.0294	18.1	37.5	37.5	28.5	C29 H3 N4 F4
483.0293	18.2	37.7	37.7	10.0	C18 H6 N F13
483.0292	18.3	37.8	37.8	17.5	C21 H4 N4 F9
483.0291	18.4	38.1	38.1	-1.0	C10 H7 N F18

## 7. EDX Data

**Table S3** Cu/metal ratios for different M[CFA-4] samples, calculated from the data shown in Fig. S18-S20.

Sample	Copper/metal ratio
K[CFA-4]	5.12/1
Ca(0.5)[CFA-4]	10.76/1
Cs[CFA-4]	6.45/1

Elem	wt %	At %	K-Ratio	Z	A	F
F K	30.04	57.38	0.1485	1.0734	0.4589	1.0034
K K	7.50	6.96	0.0686	1.0447	0.8700	1.0068
CuK	62.46	35.66	0.5911	0.9450	1.0014	1.0000
Total	100.00	100.00				

Element	Net Inte.	Backgrd	Inte. Error	P/B
F K	849.09	3.10	0.34	273.90
K K	325.87	0.12	0.55	2715.58
CuK	687.29	0.96	0.38	715.93

**Fig. S18** EDX data for K[CFA-4].

Elem	wt %	At %	K-Ratio	Z	A	F
F K	27.47	55.09	0.1436	1.0792	0.4825	1.0040
CaK	4.02	3.82	0.0396	1.0743	0.9051	1.0127
CuK	68.52	41.09	0.6530	0.9513	1.0019	1.0000
Total	100.00	100.00				

Element	Net Inte.	Backgrd	Inte. Error	P/B
F K	749.31	1.86	0.37	402.85
CaK	154.21	0.52	0.81	296.56
CuK	686.65	0.64	0.38	1072.89

**Fig. S19** EDX data for Ca(0.5)[CFA-4].

Elem	wt %	At %	K-Ratio	Z	A	F
CsL	24.50	13.43	0.2291	0.9017	1.0150	1.0215
CuK	75.50	86.57	0.7606	1.0339	0.9743	1.0000
Total	100.00	100.00				

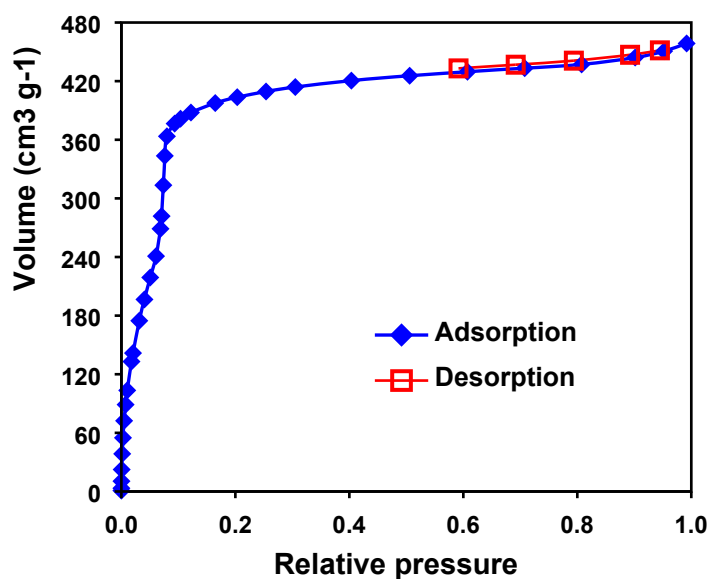
  

Element	Net Inte.	Backgrd	Inte. Error	P/B
CsL	208.04	0.26	0.69	800.15
CuK	569.22	0.64	0.42	889.41

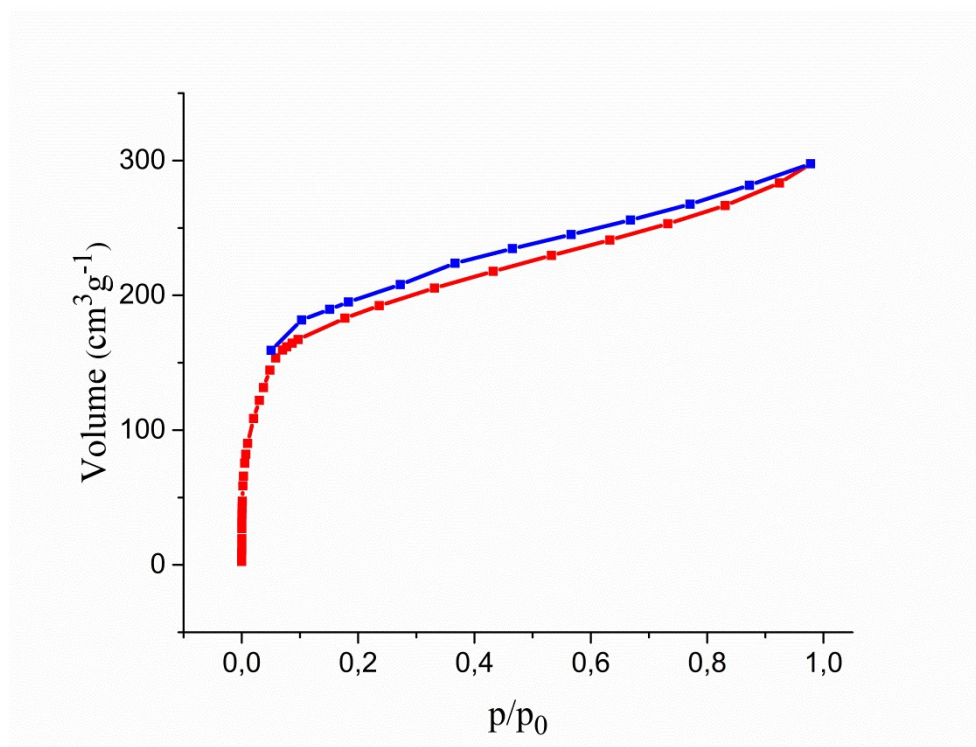
**Fig. S20** EDX data for Cs[CFA-4].



## 8. Gas sorption measurements



**Fig. S21** Argon adsorption (blue) and desorption (red) isotherms at 87 K for **Cu(I)[CFA-4]** sample heated at 100 °C in vacuum.



**Fig. S22** Argon adsorption (red) and desorption (blue) isotherms at 77 K for **Cu(I)[CFA-4]** sample heated at 350 °C in vacuum.

The isosteric heats of adsorption were calculated from the measured isotherms (Figs. S23-25) using the Clausius-Clapeyron equation (I). The slopes of linear plots  $\ln P$  versus  $1/RT$  for different loadings (Fig. S26-28) give the adsorption enthalpies, according to the equation (II).

$$Q_{st} = -R \left( \frac{\partial(\ln P)}{\partial(1/T)} \right)_{\theta} \quad (\text{I}), \theta - \text{surface coverage}$$

$$\ln P = -\frac{Q_{st}}{R} \left( \frac{1}{T} \right) + C \quad (\text{II}), C - \text{integration constant}$$

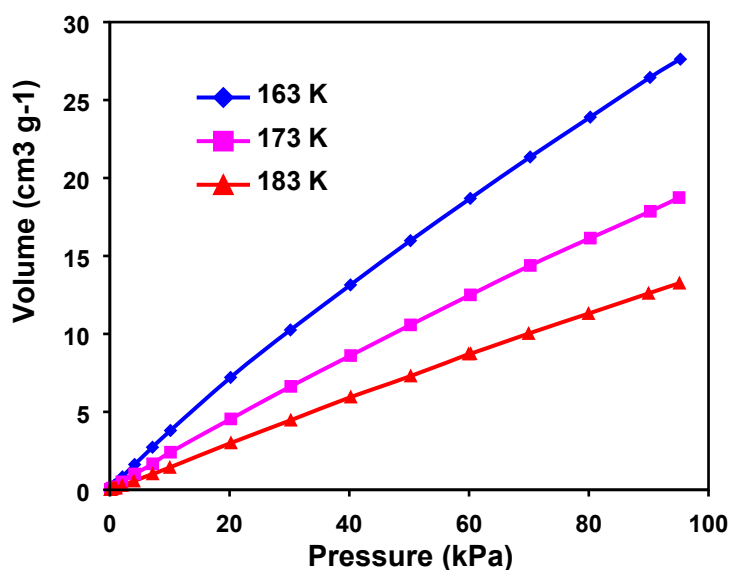
The isosteric heat of  $O_2$  adsorption at zero limit surface coverage (initial heat of adsorption) has been determined using Henry's constants  $K_H$ , obtained as a slope from the linear ranges of isotherms at low pressure (Table S4 and Fig. S29). In this range the dependence of amount adsorbed ( $n$ ) on pressure can be expressed with Henry's law (III). The initial isosteric heat of adsorption is obtained similarly using the Clausius-Clapeyron equation (IV) (Fig. S30).

$$n = K_H \cdot P \quad (\text{III})$$

$$\lim_{n \rightarrow 0} (Q_{st}) = Q_{st}^0 = R \left( \frac{\partial(\ln K_H)}{\partial(1/T)} \right) \quad (\text{IV})$$

**Table S4.** Henry's constants for  $O_2$  adsorption on CFA-4 ( $\text{cm}^3 \text{g}^{-1} \text{kPa}^{-1}$ )

T [K]	163	173	183
$K_H$	0.3971	0.2365	0.1534



**Fig. S23**  $O_2$  adsorption isotherms for Cu(I)[CFA-4] at different temperatures.

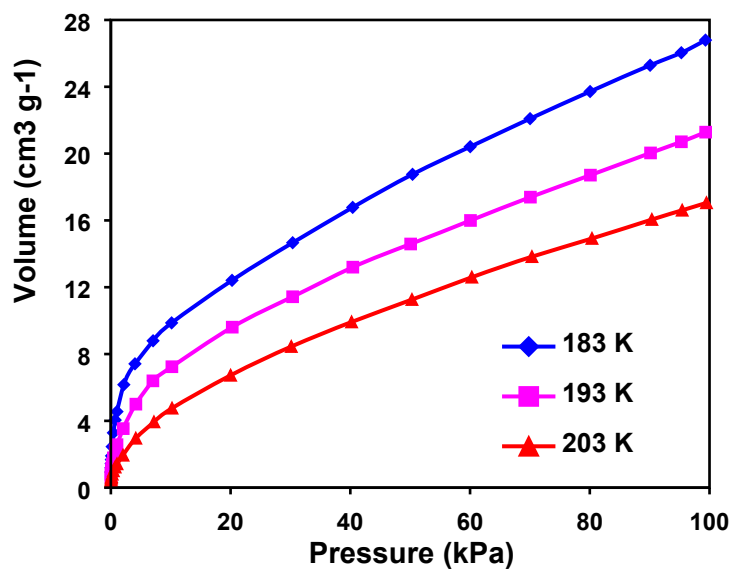


Fig. S24 CO adsorption isotherms for Cu(I)[CFA-4] at different temperatures.

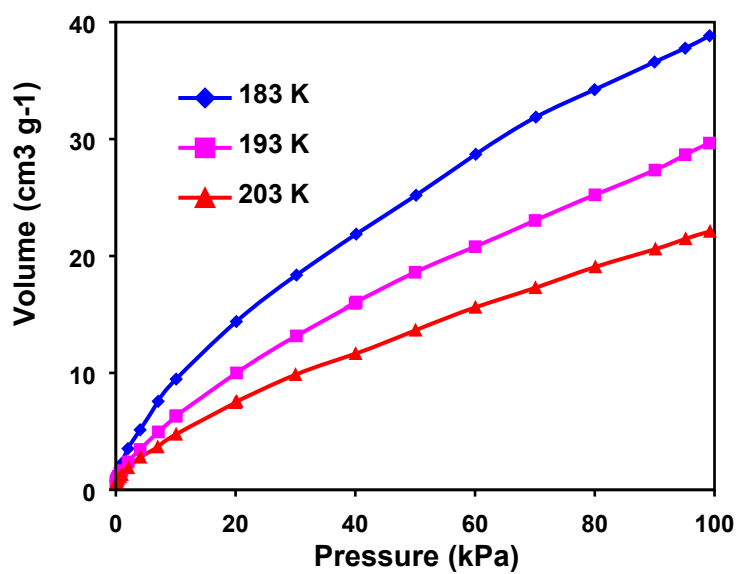


Fig. S25 CO adsorption isotherms for K[CFA-4] at different temperatures.

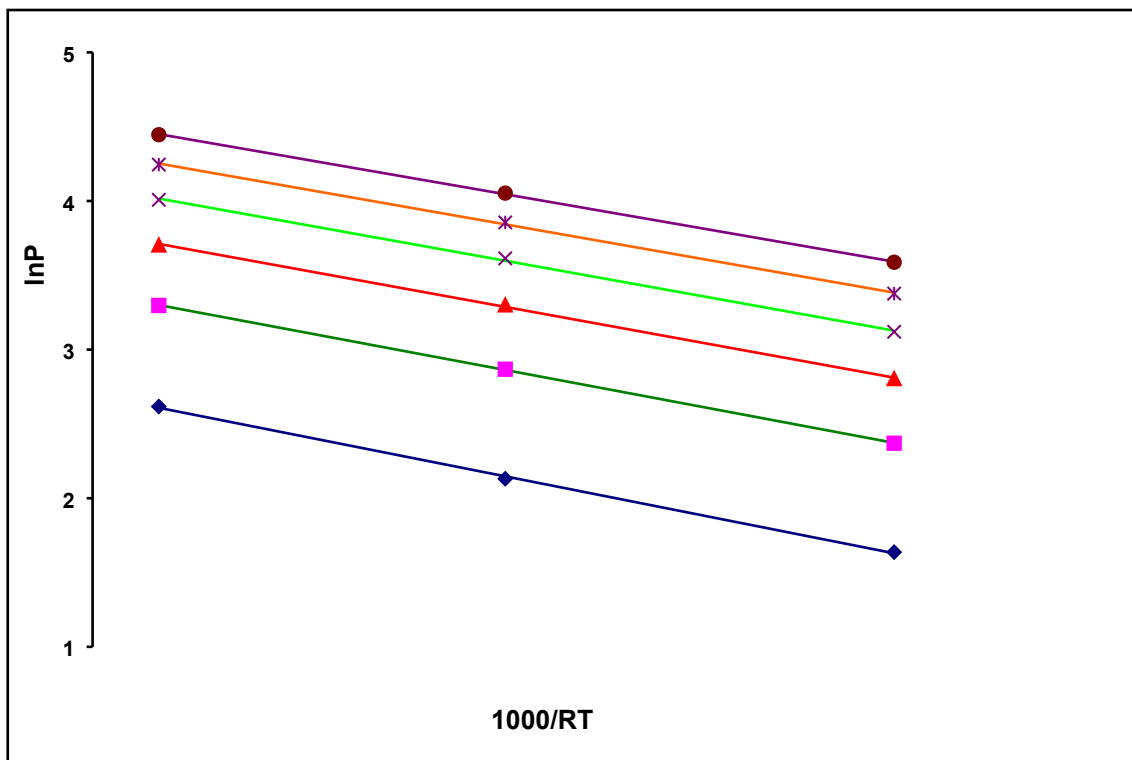


Fig. S26  $\ln P$  versus  $1/RT$  plots for different loadings for  $O_2$  adsorption on  $Cu(I)[CFA-4]$ .

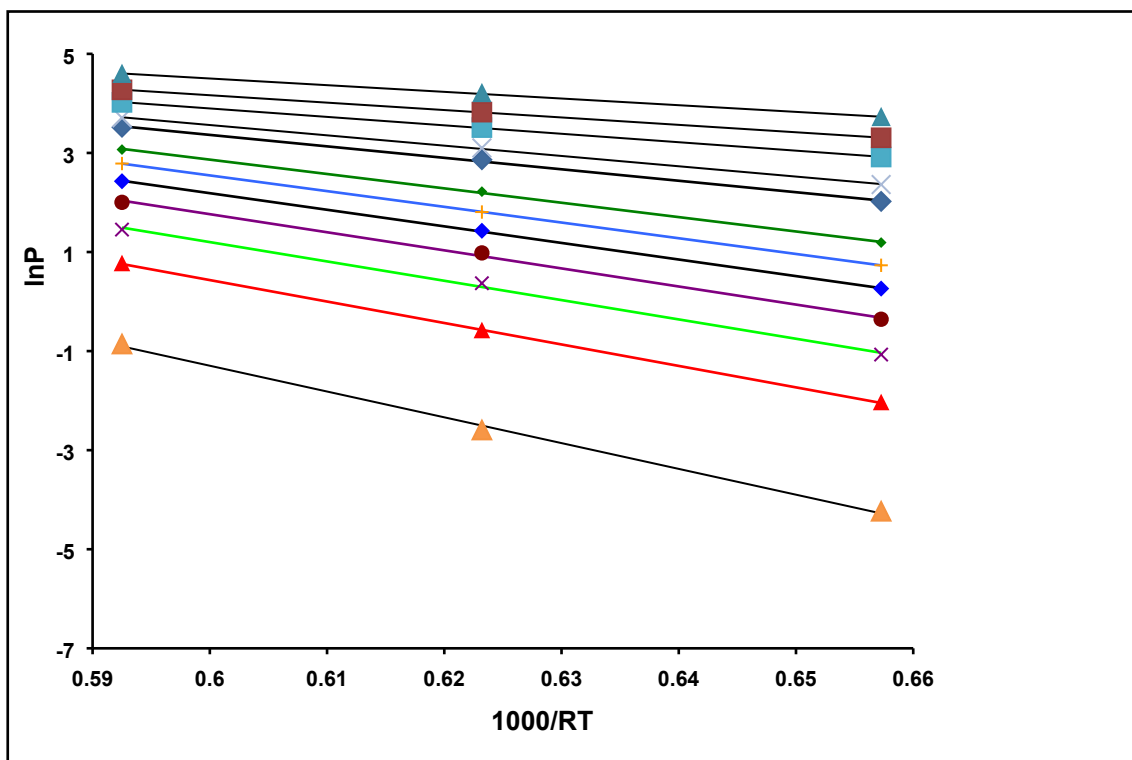


Fig. S27  $\ln P$  versus  $1/RT$  plots for different loadings for  $CO$  adsorption on  $Cu(I)[CFA-4]$ .

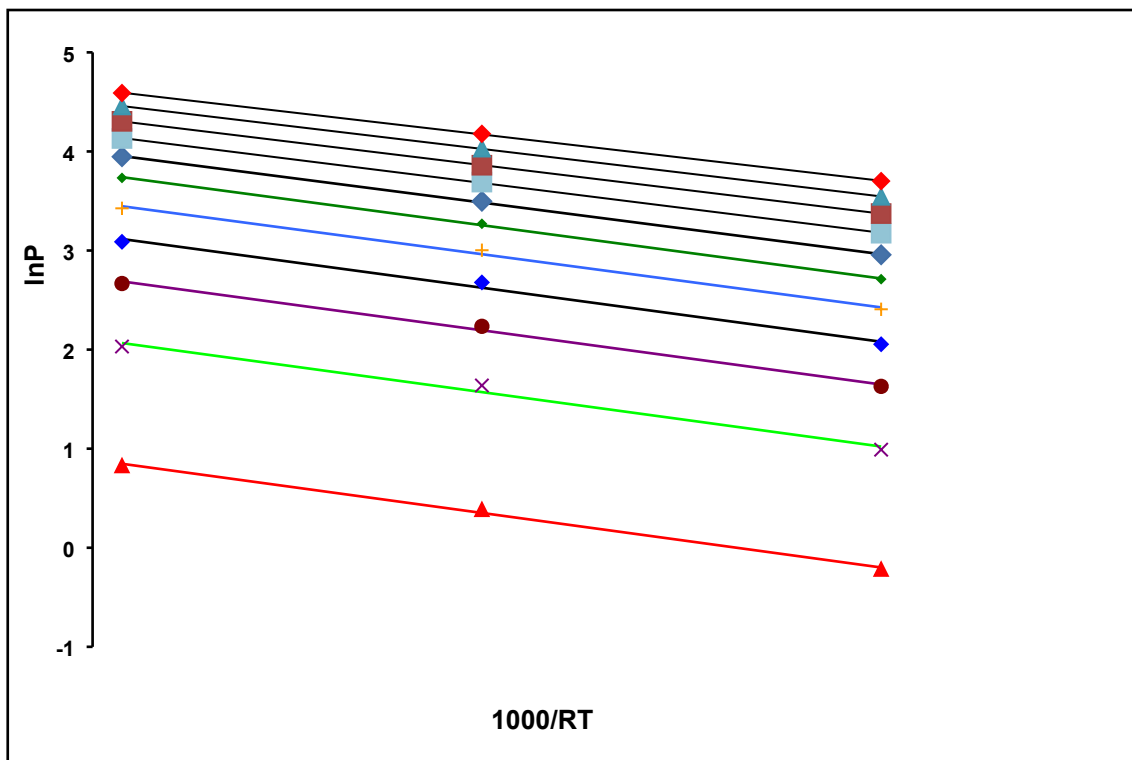


Fig. S28  $\ln P$  versus  $1/RT$  plots for different loadings for CO adsorption on  $K[CFA-4]$ .

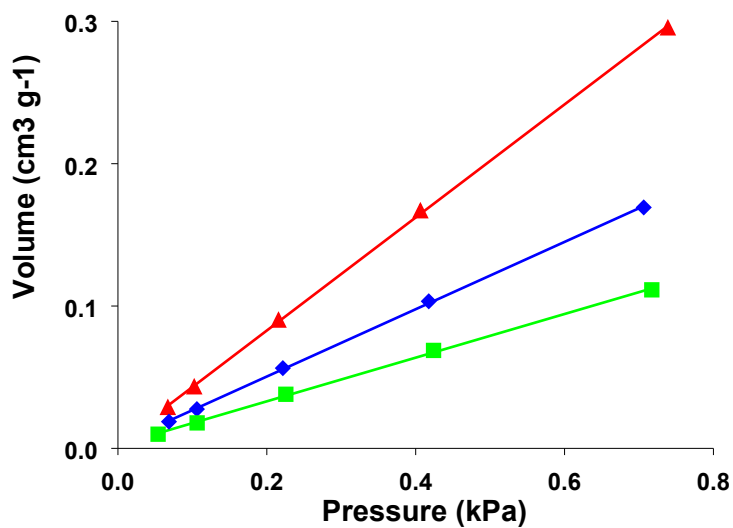


Fig. S29 Determination of Henry's constants for  $O_2$  adsorption on  $Cu(I)[CFA-4]$ .

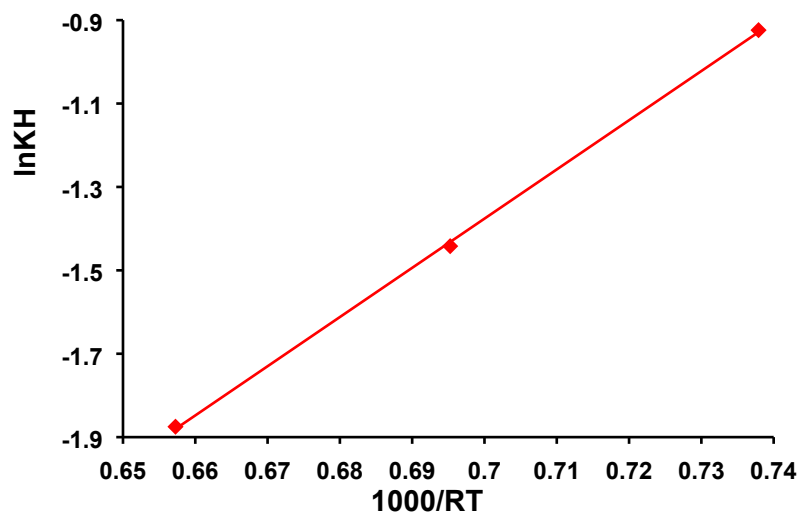
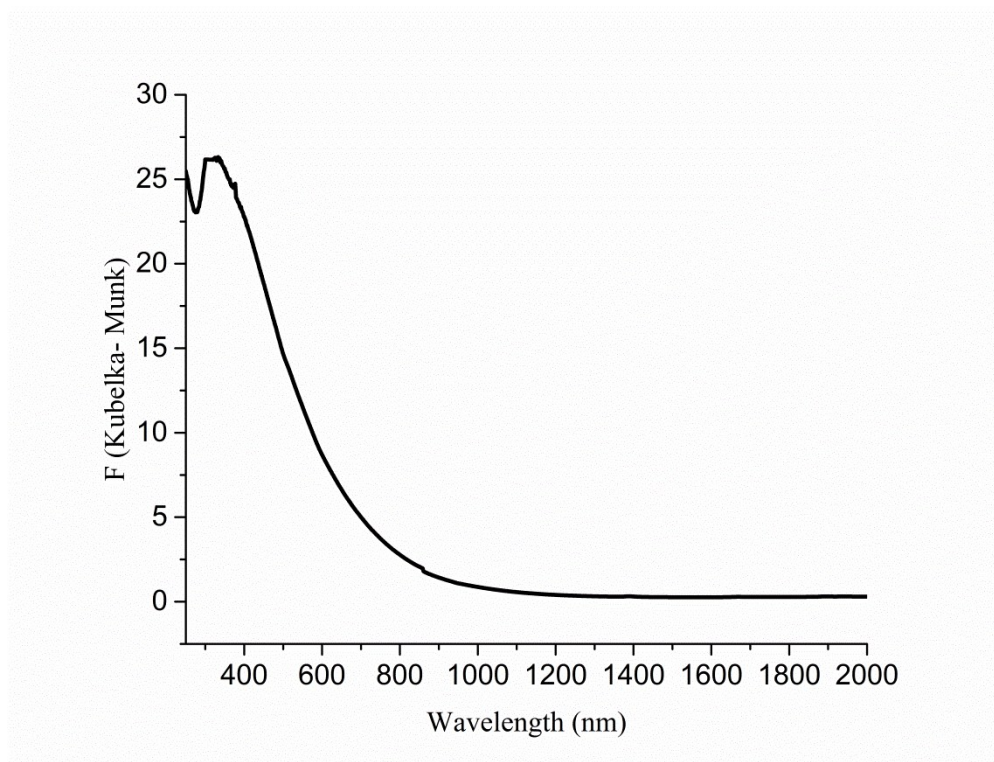


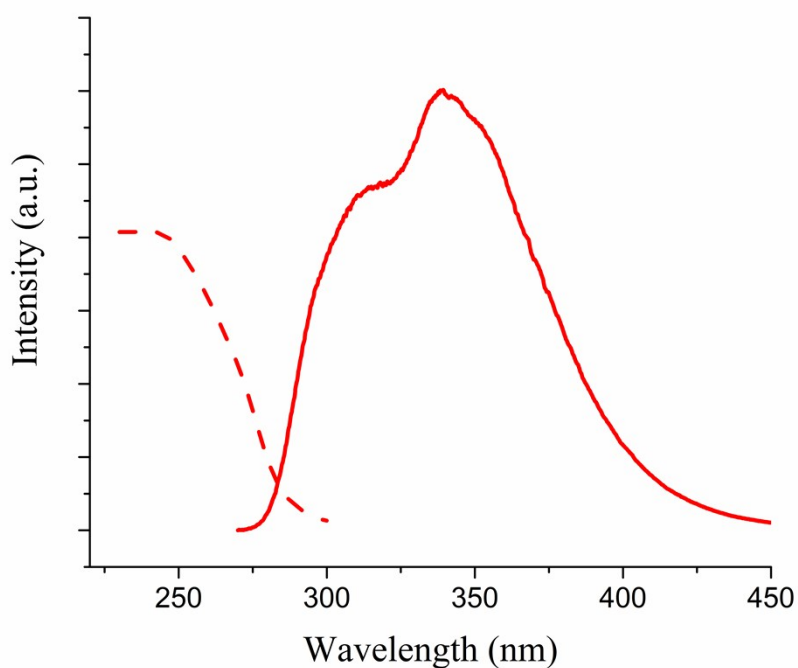
Fig. S30  $\ln K_H$  versus  $1/RT$  plot for  $O_2$  adsorption on  $Cu(I)[CFA-4]$ .

## 9. UV-Vis spectrum

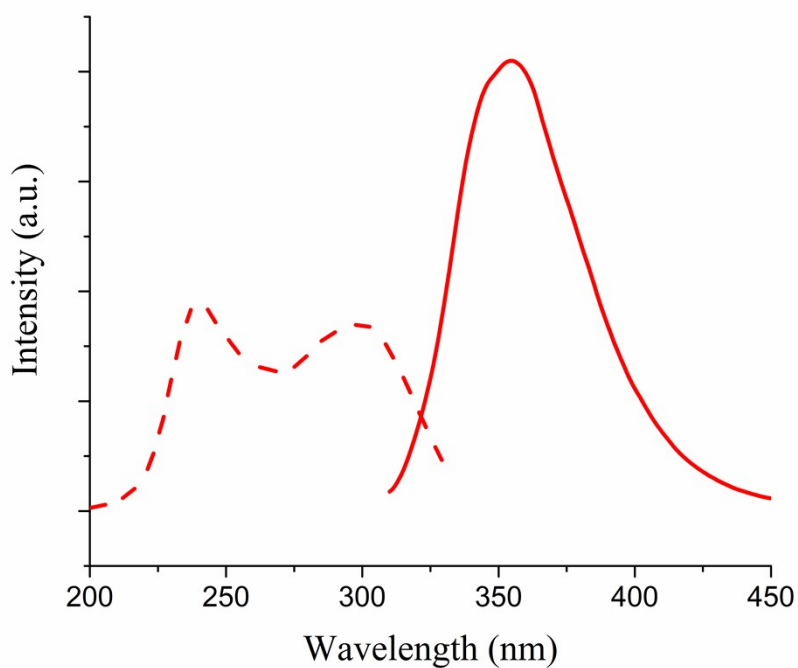


**Fig. S31** UV-Vis spectrum of **Cu(I)[CFA-4]**.

## 10. Photoluminescence spectra

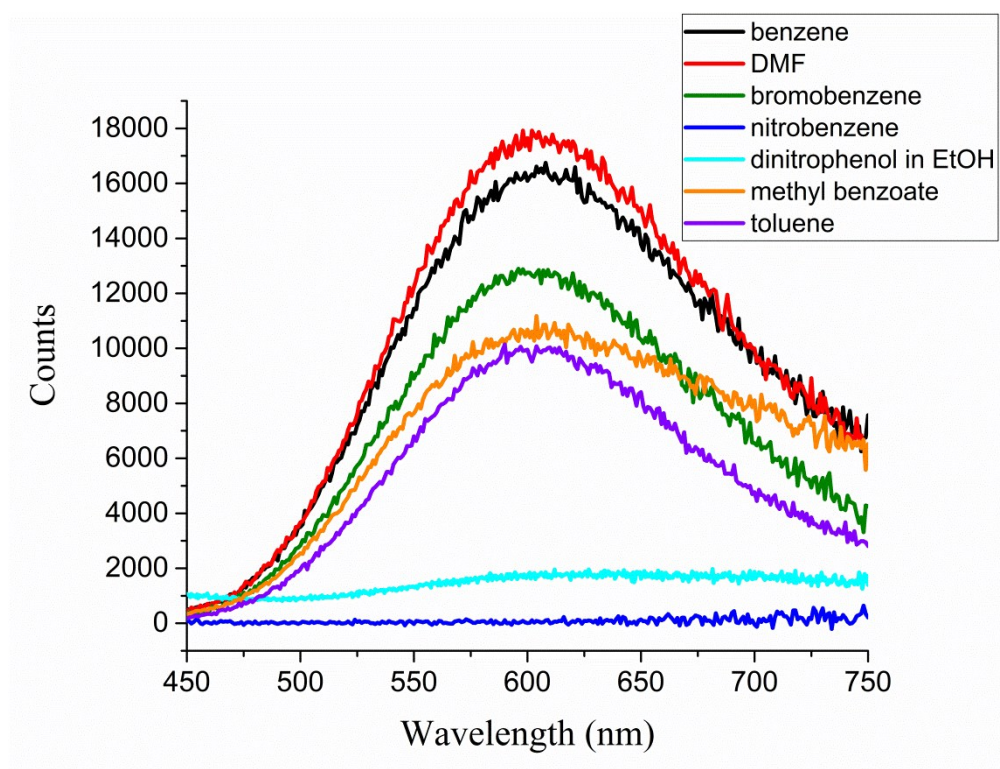


**Fig. S32** Photoluminescence spectra of **1** at room temperature. Dashed line: excitation spectrum ( $\lambda_{\text{em}} = 312$  nm); Continuous line: emission spectrum ( $\lambda_{\text{ex}} = 245$  nm).



**Fig. S33** Solid-state photoluminescence spectra for **1** at room temperature. Dashed line: excitation spectrum ( $\lambda_{\text{em}} = 350$  nm); Continuous line: emission spectrum ( $\lambda_{\text{ex}} = 290$  nm).





**Fig. S34** Photoluminescence spectra of **Cu(I)[CFA-4]** at room temperature with different solvents (excitation wavelength 320 nm).