Supporting Information

CFA-7: An interpenetrated metal-organic framework of the MFU-4 family

Phillip Schmieder, [a] Maciej Grzywa,[a] Dmytro Denysenko,[a] Manuel Hambach [a] and Dirk Volkmer*,[a]

[a] Institute of Physics, Chair of Solid State and Material Science, Augsburg University, D-86135 Augsburg, Germany. E-mail: dirk.volkmer@physik.uni-augsburg.de; Fax: (+)49 (0)821 598-5955

Contents

1. XRPD data of CFA-7 and its derivatives

Le Bail fits of **CFA-7-Iodide** and **Co-CFA-7**

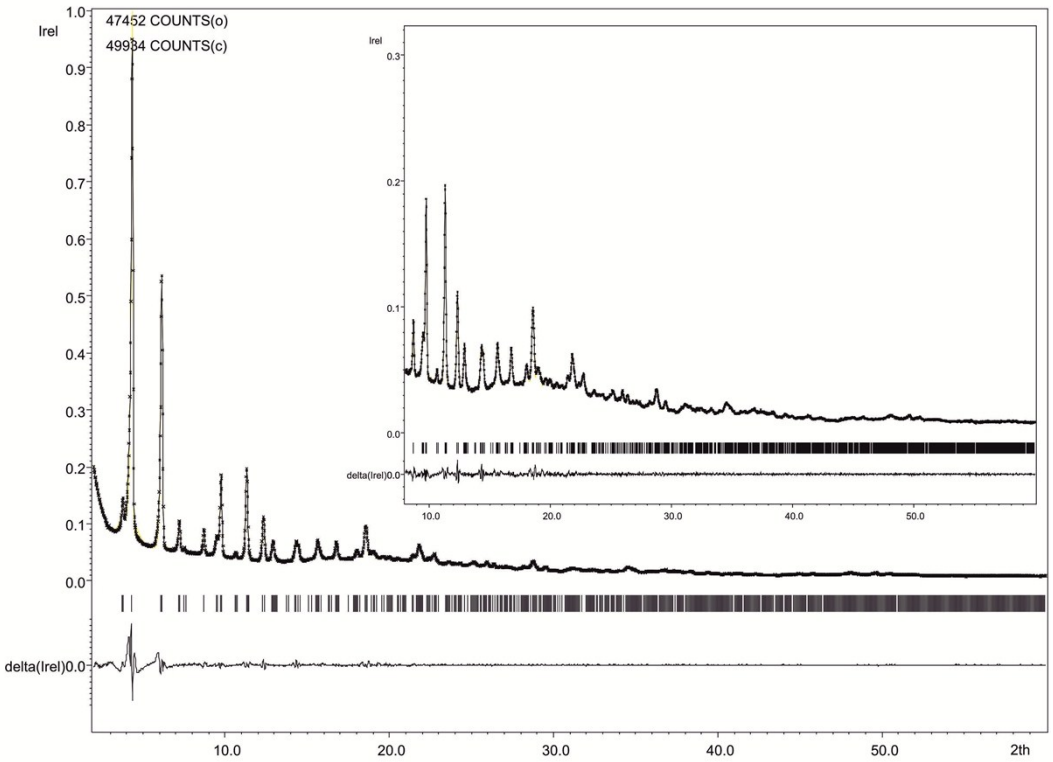

Fig. S 1 Le Bail fit of the XRPD pattern of **CFA-7-Iodide**. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom. Rp = 3.44 %, wRp = 5.25 %.

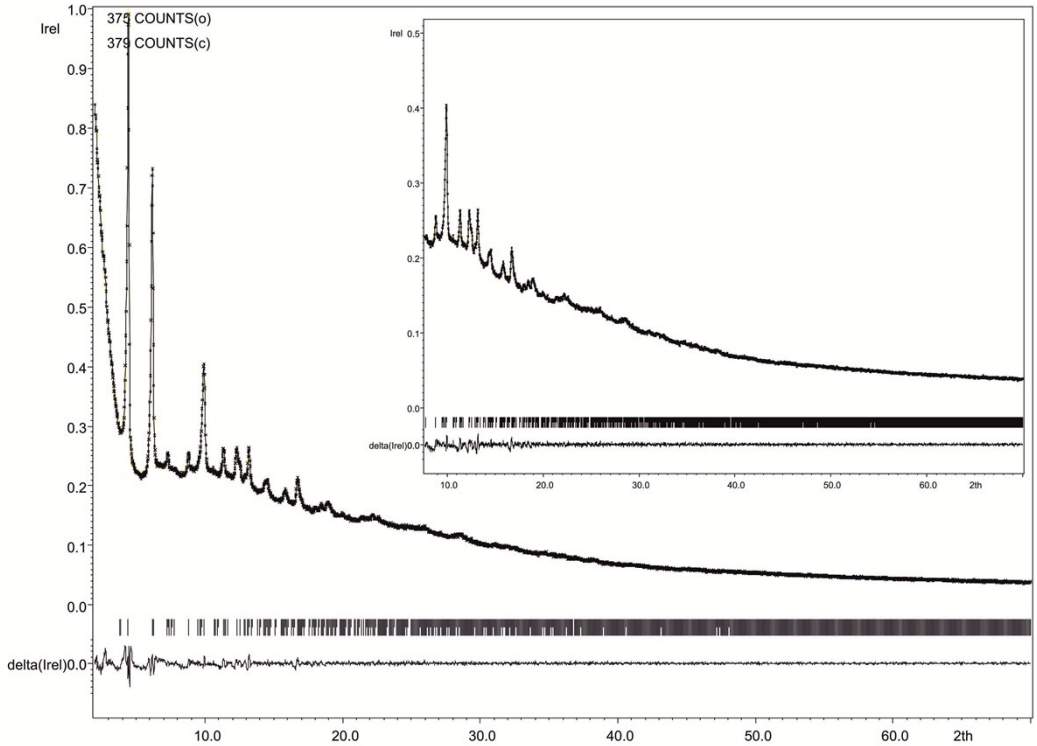

Fig. S 2 Le Bail fit of the XRPD pattern of **Co-CFA-7**. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom. Rp = 1.40 %, wRp = 1.91 %.

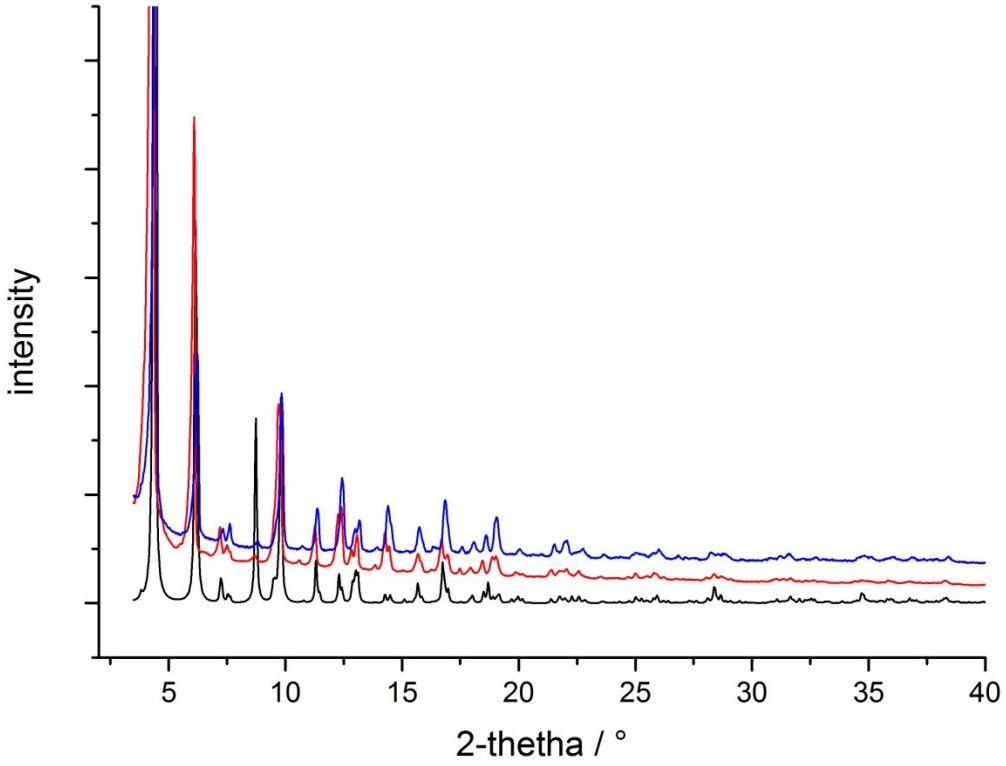

Fig. S 3 XRPD patterns of **CFA-7** (black: calculated pattern based on single crystal data of **CFA-7**; red: **CFA-7** sample as pseudo-cubic crystals; blue: **CFA-7** sample as hexagonal crystals).

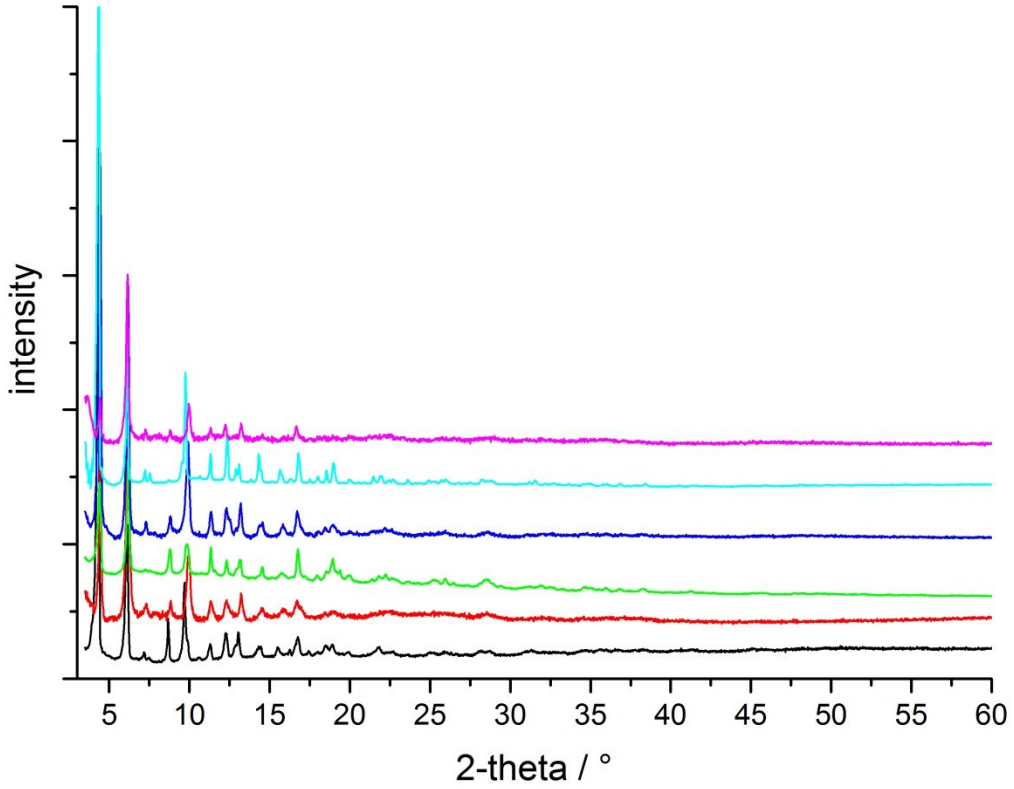

Fig. S 4 XRPD pattern of metal exchanged **CFA-7** samples (black: **CFA-7**; red: postsynthetic metal exchange with $CuCl_2$ (wf); green: postsynthetic metal exchange with $Cu(ClO_4)_2 \cdot 6\ H_2O$; blue: postsynthetic metal exchange with $CoCl_2 \cdot 6\ H_2O$; cyan: postsynthetic metal exchange with $NiCl_2$ (wf); pink: postsynthetic metal exchange with $MnCl_2 \cdot 2\ H_2O$).

2. IR spectroscopy

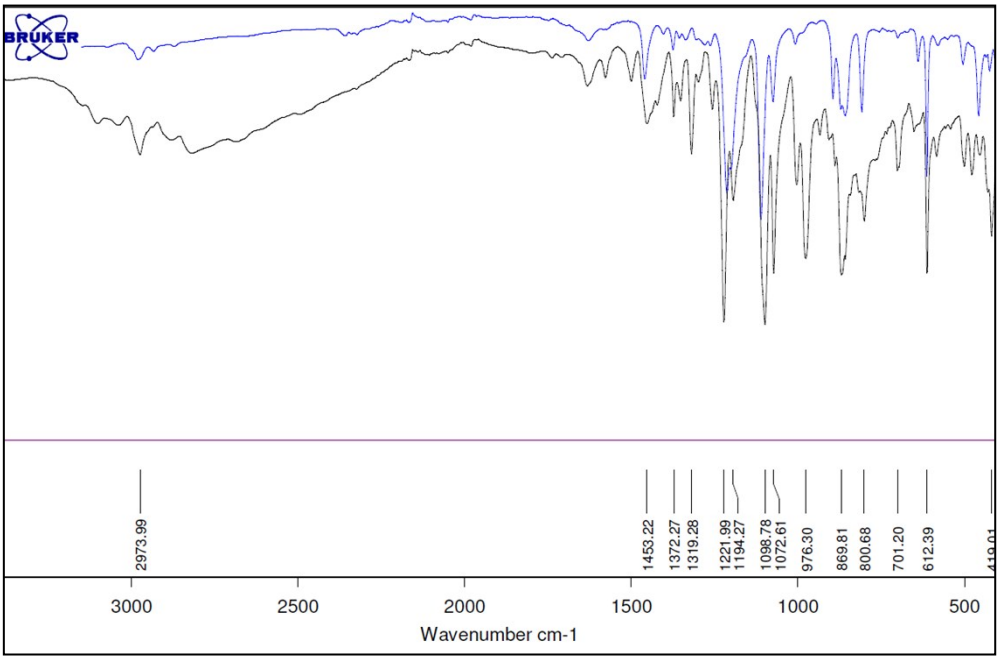

Fig. S 5 IR spectra of **CFA-7** (black) and of the organic linker H_2-tqpt (blue).

3. Gas sorption measurements

The isosteric heats of adsorption were calculated from the measured isotherms (Fig. S 7-9) using the Clausius-Clapeyron equation (**I**). The slopes of linear plots ln P versus 1/RT for different loadings (Fig. S 10-12) give the adsorption enthalpies, according to the equation (**II**).

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

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

MOF	BET surface area [$m^2\ g^{-1}$]	Langmuir Surface area [$m^2\ g^{-1}$]	total pore volume [$cm^3\ g^{-1}$]	micropore pore volume [$cm^3\ g^{-1}$]
Zn	1718	1939	0.70	0.61
Co	1689	1914	0.77	0.59
Ni	1529	1729	0.64	0.54
Cu	1693	1945	0.84	0.58

Table S1 Porosity data of **CFA-7** derivatives.

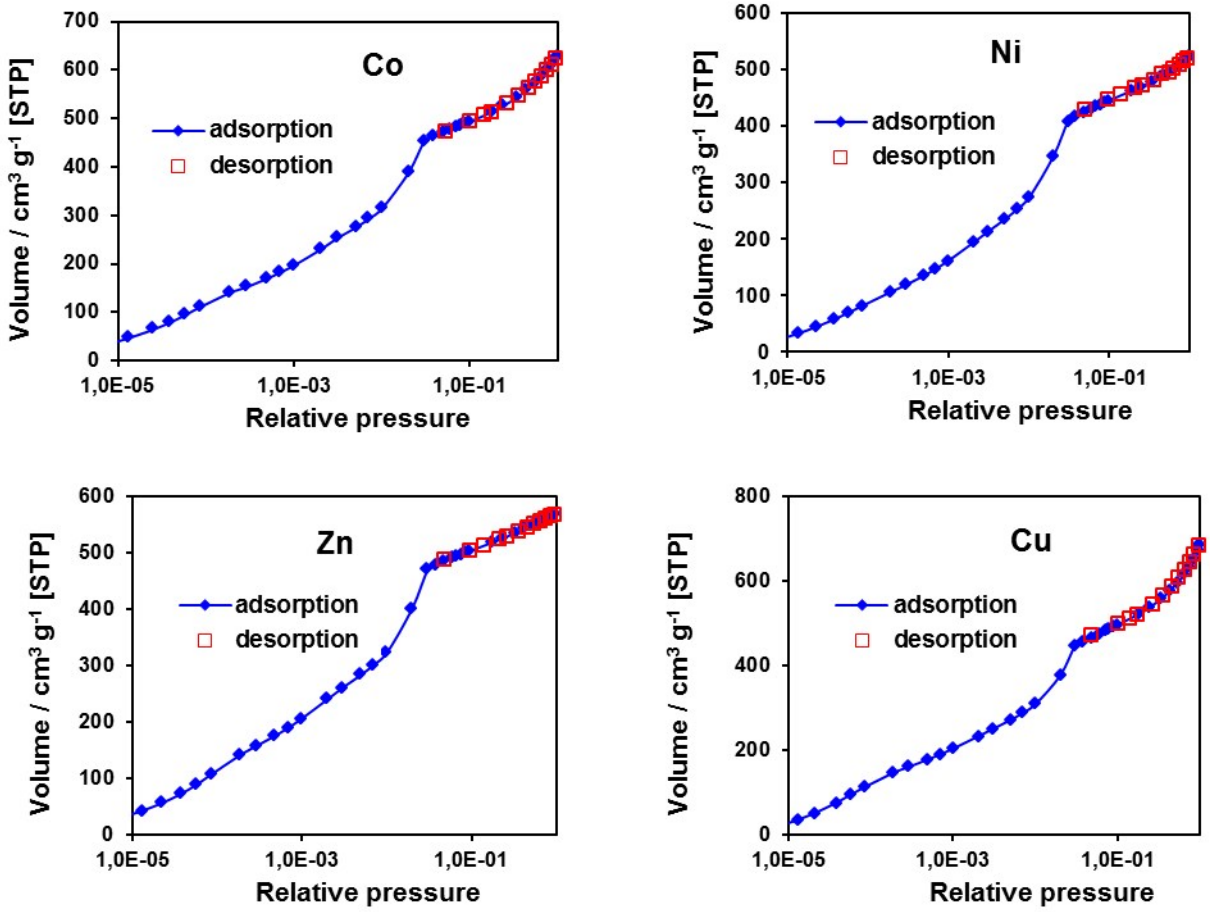

Figure S 6 Argon adsorption/desorption isotherm at 77.3 K for **CFA-7** derivatives.

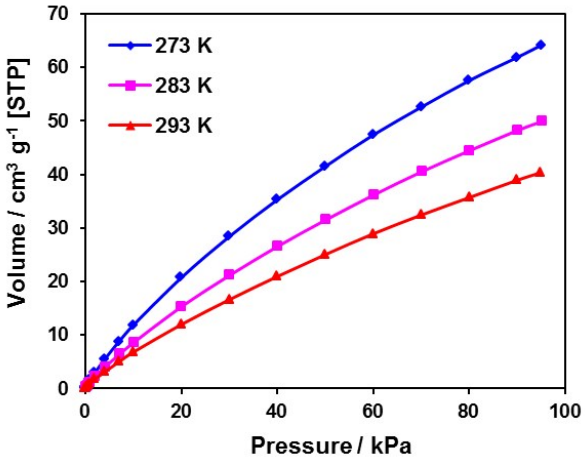

Figure S 7 CO_2 adsorption isotherms for **CFA-7** at different temperatures for the determination of the isosteric heat of adsorption.

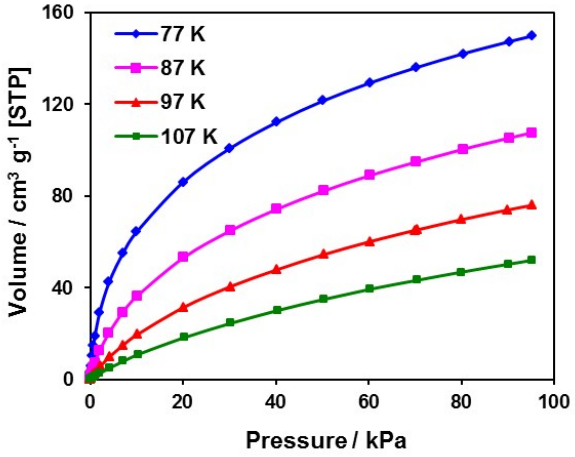

Figure S 8 H_2 adsorption isotherms for **CFA-7** at different temperatures for the determination of the isosteric heat of adsorption.

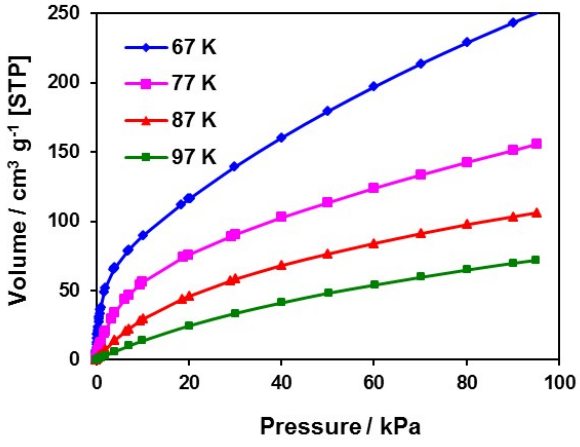

Figure S 9 H_2 adsorption isotherms for MFU-4*l* at different temperatures for the determination of the isosteric heat of adsorption.

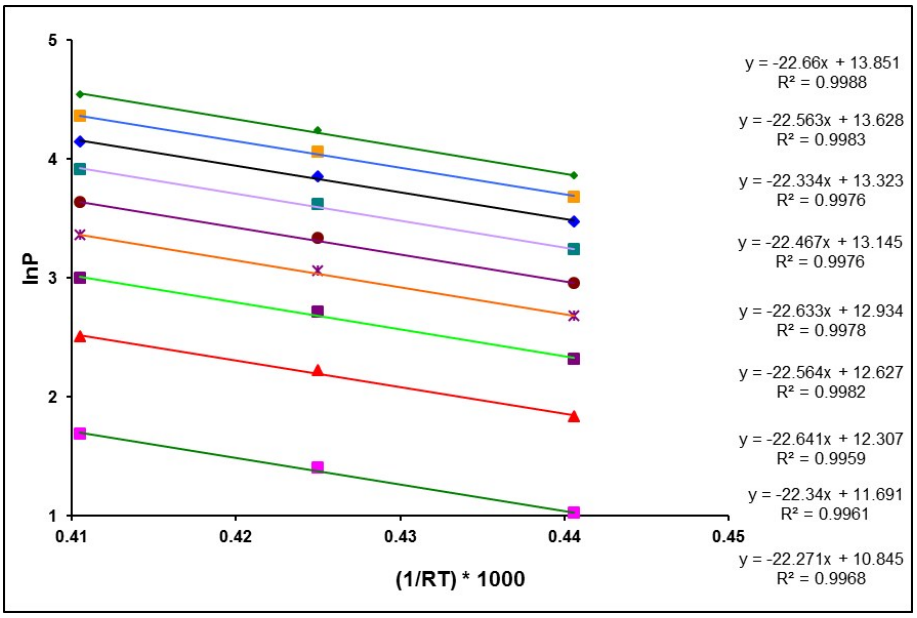

Figure S 10 ln P versus 1/RT plots for different loadings for CO_2 adsorption on **CFA-7**.

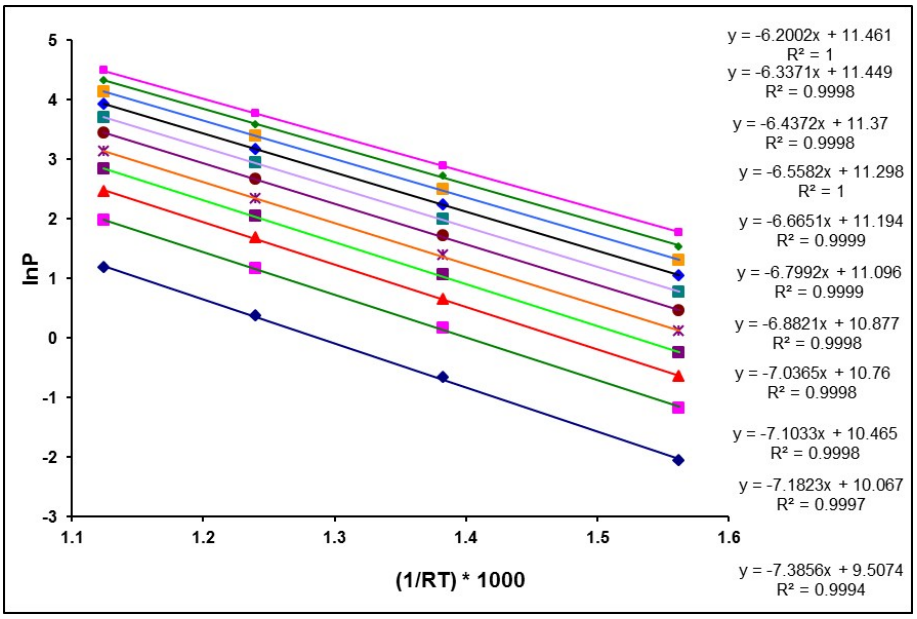

Figure S 11 ln P versus 1/RT plots for different loadings for H_2 adsorption on **CFA-7**.

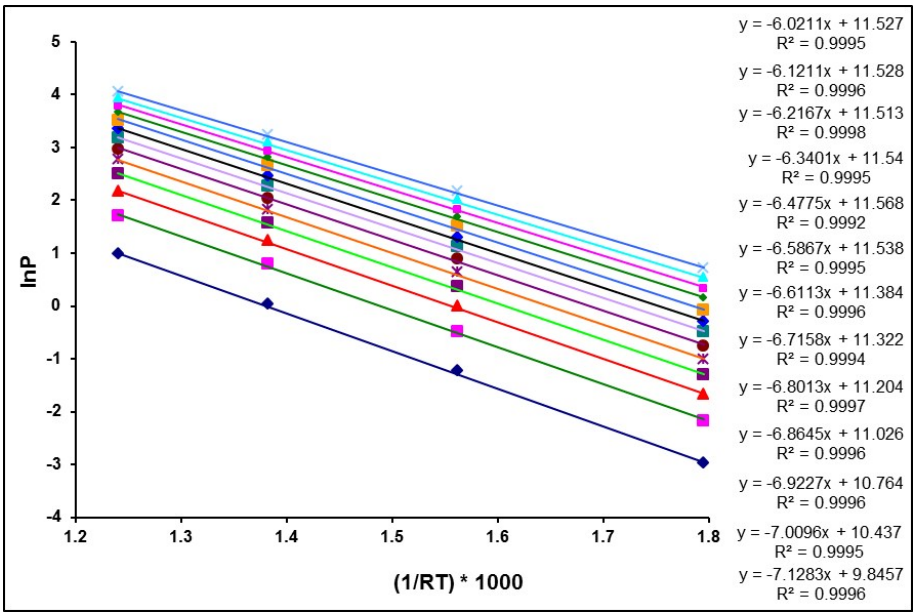

Figure S 12 ln P versus 1/RT plots for different loadings for H_2 adsorption on MFU-4*l*.

4. NMR spectroscopy

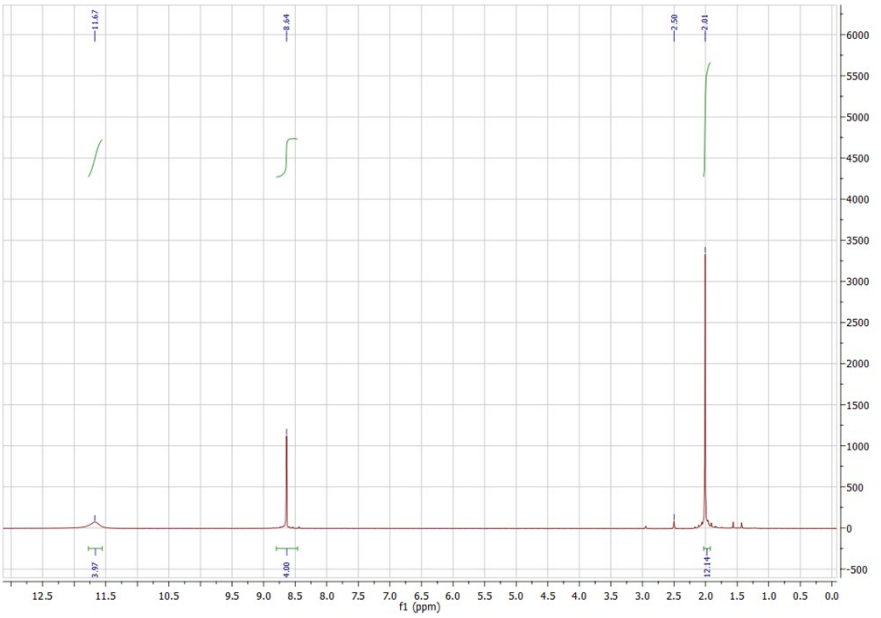

Figure S 13 ^{1}H-NMR of **H_2-tqpt** in deuterated DMSO/TFA mixture.

Note: organic ligand is two-times protonated from the trifluoroacetic acid.

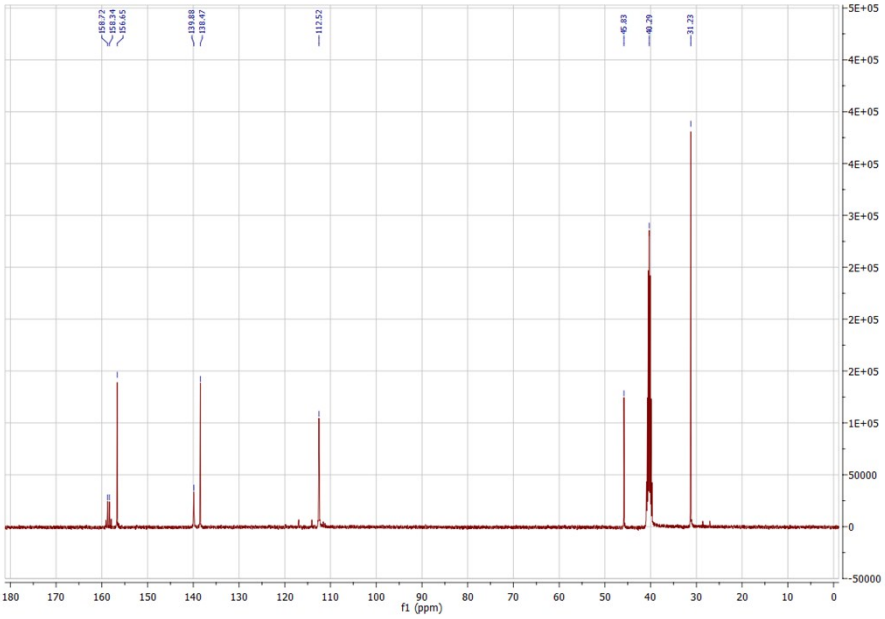

Figure S 14 ^{13}C-NMR of **H_2-tqpt** in deuterated DMSO/TFA mixture.

Note: organic ligand is two-times protonated from the trifluoroacetic acid.

5. Selected bond lengths [Å] and angles [°] for **CFA-7 · $Cl_{0.89}$ 29.25DMF**

Table S 2. Selected bond lengths [Å] and angles [°] for **CFA-7** · $Cl_{0.89}$ 29.25**DMF**

Zn(1)-N(4)	2.150(10)
Zn(1)-N(4)#1	2.150(10)
Zn(1)-N(4)#2	2.151(11)
Zn(1)-N(2)#1	2.209(9)
Zn(1)-N(2)	2.209(9)
Zn(1)-N(2)#2	2.209(10)
Zn(2)-N(3)	2.021(8)
Zn(2)-N(1)#3	2.039(6)
Zn(2)-N(1)	2.039(6)
Zn(2)-Cl(1)	2.070(6)
Zn(3)-O(1)#1	2.06(2)
Zn(3)-O(1)#2	2.06(2)
Zn(3)-O(1)	2.06(2)
Zn(3)-N(5)#2	2.134(13)
Zn(3)-N(5)#1	2.134(13)
Zn(3)-N(5)	2.135(13)
Zn(4)-N(8)	2.010(6)
Zn(4)-N(8)#4	2.010(6)
Zn(4)-N(10)	2.042(10)
Zn(4)-Cl(2)	2.121(4)
Zn(5)-N(11)#5	2.157(9)
Zn(5)-N(11)	2.157(10)
Zn(5)-N(11)#6	2.157(9)
Zn(5)-N(9)	2.190(9)
Zn(5)-N(9)#5	2.191(9)
Zn(5)-N(9)#6	2.191(9)
Zn(6)-Cl(3)	1.958(18)
Zn(6)-O(2)#5	2.094(12)
Zn(6)-O(2)	2.094(12)
Zn(6)-O(2)#6	2.094(12)
Zn(6)-N(12)#5	2.107(10)
Zn(6)-N(12)	2.107(10)
Zn(6)-N(12)#6	2.107(10)
N(4)-Zn(1)-N(4)#1	91.1(4)
N(4)-Zn(1)-N(4)#2	91.1(4)

N(4)#1-Zn(1)-N(4)#2	91.1(4)
N(4)-Zn(1)-N(2)#1	178.4(4)
N(4)#1-Zn(1)-N(2)#1	90.1(3)
N(4)#2-Zn(1)-N(2)#1	90.1(3)
N(4)-Zn(1)-N(2)	90.1(3)
N(4)#1-Zn(1)-N(2)	90.1(3)
N(4)#2-Zn(1)-N(2)	178.4(4)
N(2)#1-Zn(1)-N(2)	88.7(4)
N(4)-Zn(1)-N(2)#2	90.1(3)
N(4)#1-Zn(1)-N(2)#2	178.4(4)
N(4)#2-Zn(1)-N(2)#2	90.1(3)
N(2)#1-Zn(1)-N(2)#2	88.7(4)
N(2)-Zn(1)-N(2)#2	88.7(4)
N(3)-Zn(2)-N(1)#3	97.1(2)
N(3)-Zn(2)-N(1)	97.1(2)
N(1)#3-Zn(2)-N(1)	96.6(4)
N(3)-Zn(2)-Cl(1)	119.3(3)
N(1)#3-Zn(2)-Cl(1)	120.7(2)
N(1)-Zn(2)-Cl(1)	120.7(2)
O(1)#1-Zn(3)-O(1)#2	93.8(8)
O(1)#1-Zn(3)-O(1)	93.8(7)
O(1)#2-Zn(3)-O(1)	93.8(8)
O(1)#1-Zn(3)-N(5)#2	177.1(6)
O(1)#2-Zn(3)-N(5)#2	88.2(5)
O(1)-Zn(3)-N(5)#2	88.2(5)
O(1)#1-Zn(3)-N(5)#1	88.2(4)
O(1)#2-Zn(3)-N(5)#1	88.2(5)
O(1)-Zn(3)-N(5)#1	177.1(7)
N(5)#2-Zn(3)-N(5)#1	89.7(5)
O(1)#1-Zn(3)-N(5)	88.2(5)
O(1)#2-Zn(3)-N(5)	177.0(7)
O(1)-Zn(3)-N(5)	88.2(5)
N(5)#2-Zn(3)-N(5)	89.7(5)
N(5)#1-Zn(3)-N(5)	89.7(5)
N(8)-Zn(4)-N(8)#4	95.4(4)
N(8)-Zn(4)-N(10)	96.9(3)
N(8)#4-Zn(4)-N(10)	96.9(3)
N(8)-Zn(4)-Cl(2)	119.0(2)
N(8)#4-Zn(4)-Cl(2)	119.0(2)

N(10)-Zn(4)-Cl(2)	123.7(3)
N(11)#5-Zn(5)-N(11)	89.1(4)
N(11)#5-Zn(5)-N(11)#6	89.1(4)
N(11)-Zn(5)-N(11)#6	89.1(4)
N(11)#5-Zn(5)-N(9)	90.7(2)
N(11)-Zn(5)-N(9)	90.7(2)
N(11)#6-Zn(5)-N(9)	179.8(4)
N(11)#5-Zn(5)-N(9)#5	90.7(2)
N(11)-Zn(5)-N(9)#5	179.8(4)
N(11)#6-Zn(5)-N(9)#5	90.7(2)
N(9)-Zn(5)-N(9)#5	89.4(3)
N(11)#5-Zn(5)-N(9)#6	179.8(4)
N(11)-Zn(5)-N(9)#6	90.7(2)
N(11)#6-Zn(5)-N(9)#6	90.7(2)
N(9)-Zn(5)-N(9)#6	89.4(3)
N(9)#5-Zn(5)-N(9)#6	89.4(3)
Cl(3)-Zn(6)-O(2)#5	49.4(6)
Cl(3)-Zn(6)-O(2)	49.4(6)
O(2)#5-Zn(6)-O(2)	82.2(9)
Cl(3)-Zn(6)-O(2)#6	49.4(6)
O(2)#5-Zn(6)-O(2)#6	82.2(9)
O(2)-Zn(6)-O(2)#6	82.2(9)
Cl(3)-Zn(6)-N(12)#5	123.6(3)
O(2)#5-Zn(6)-N(12)#5	92.5(5)
O(2)-Zn(6)-N(12)#5	173.0(7)
O(2)#6-Zn(6)-N(12)#5	92.5(5)
Cl(3)-Zn(6)-N(12)	123.6(3)
O(2)#5-Zn(6)-N(12)	92.5(5)
O(2)-Zn(6)-N(12)	92.5(5)
O(2)#6-Zn(6)-N(12)	173.0(7)
N(12)#5-Zn(6)-N(12)	92.3(4)
Cl(3)-Zn(6)-N(12)#6	123.6(3)
O(2)#5-Zn(6)-N(12)#6	173.0(7)
O(2)-Zn(6)-N(12)#6	92.5(5)
O(2)#6-Zn(6)-N(12)#6	92.5(5)
N(12)#5-Zn(6)-N(12)#6	92.3(4)
N(12)-Zn(6)-N(12)#6	92.3(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y,-x+1,z #2 -y+1,x-y+1,z #3 -y+1,-x+1,z

#4 x,x-y,z #5 -y,x-y,z #6 -x+y,-x,z #7 -x+y,y,z

6. Asymmetric unit of **CFA-7**

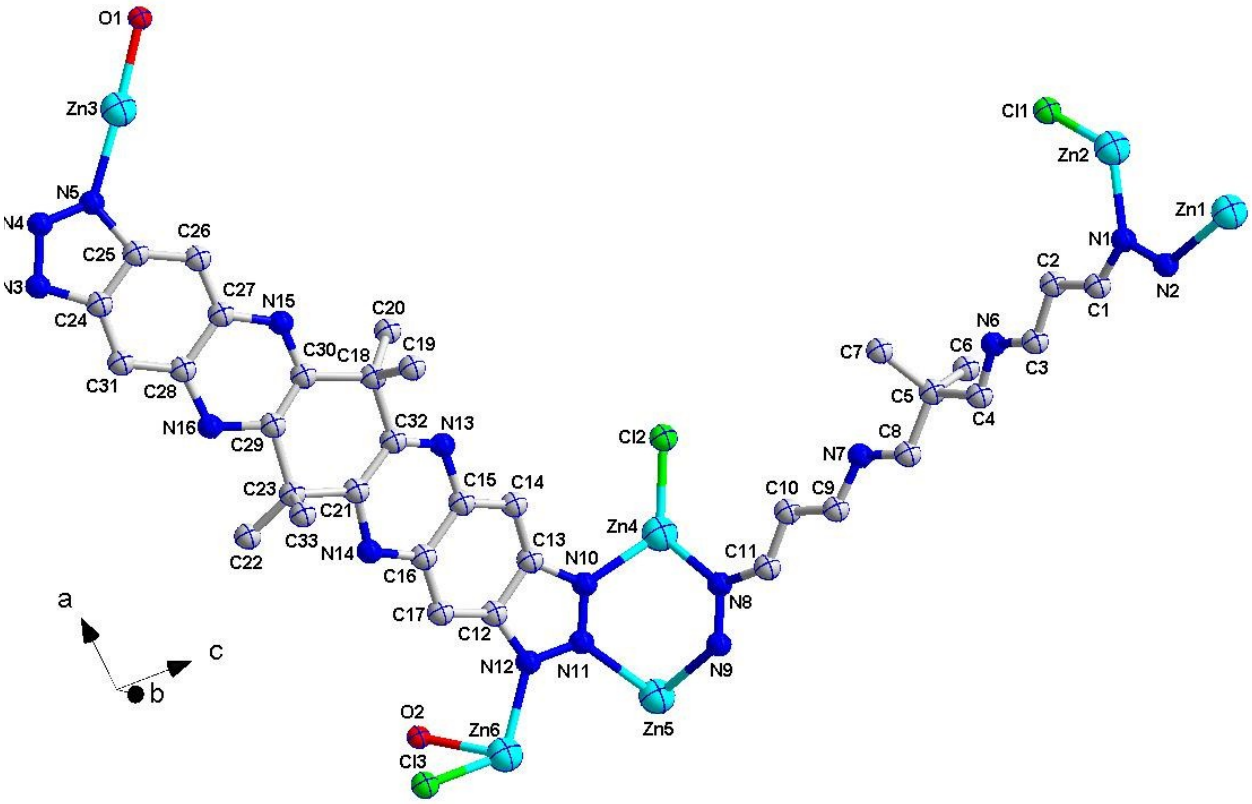

Fig. S 15 Asymmetric unit of **CFA-7** (atoms displayed as 50 % probability ellipsoids, C: grey, N: blue, Cl: green, O: red, Zn: cyan; H atoms omitted for clarity).

7. UV/Vis and IR measurements of **CFA-7** derivatives

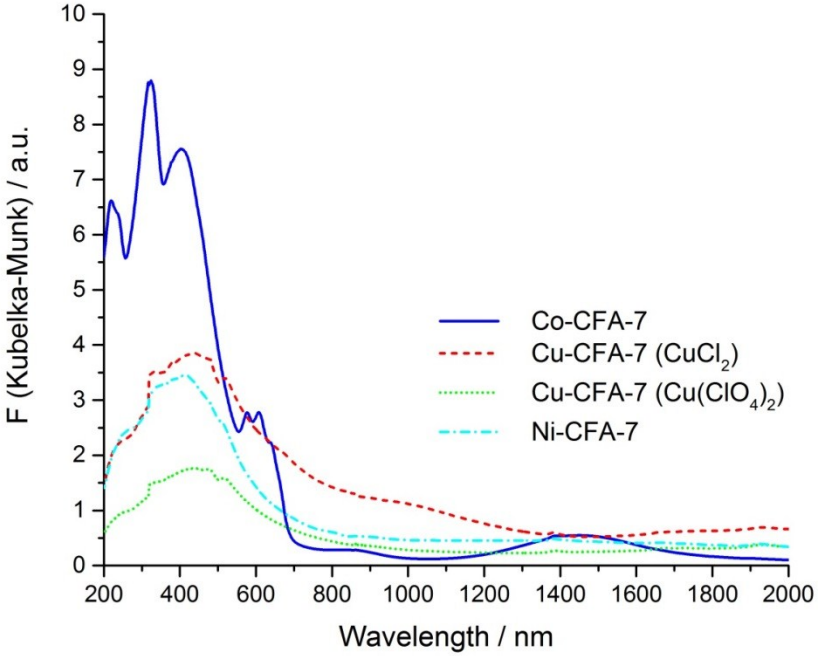

Fig. S 16 Diffuse reflectance UV-vis-NIR spectra of metal exchanged **CFA-7** derivatives.

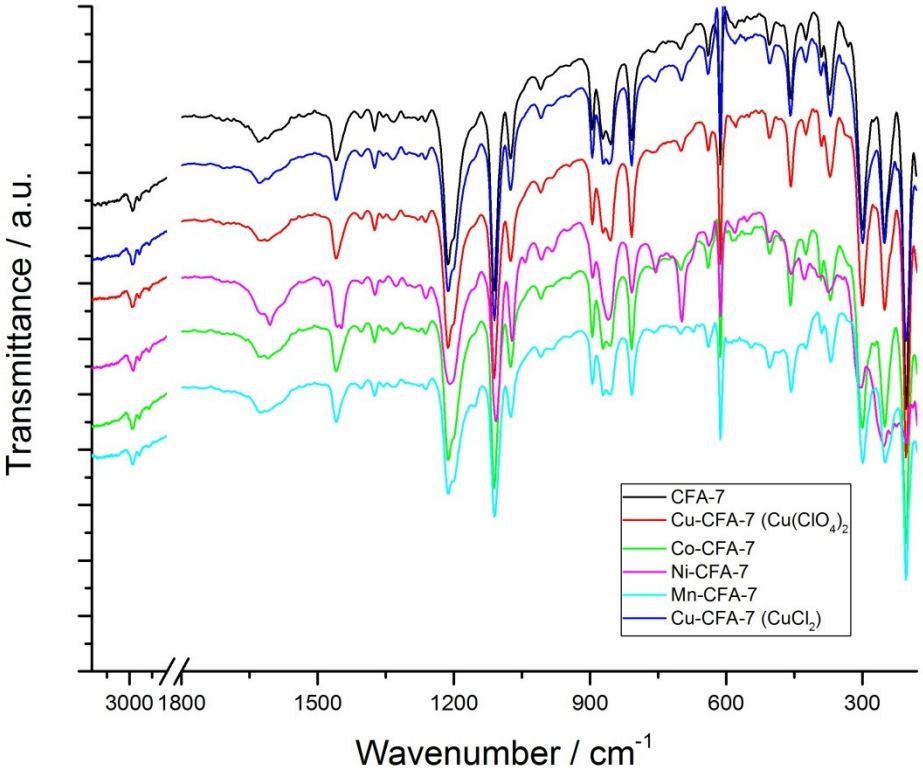

Fig. S 17 IR spectra of metal exchanged **CFA-7** derivatives.