Vapor-assisted Preparing Mn/Fe/Co/Zn-Cu Bimetallic Metal-organic Frameworks base on Octahedron Micron Crystal PCN-6'

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Supporting Information

Materials: All reagents and materials were obtained commercially and were used as received without any further purification. $Cu(NO_3)_2{\cdot}2.5H_2O$, $ZnCl_2$ and 4,4′,4″-*s*-triazine-2,4,6-triyl-tribenzoate (TATB, 97%) were purchased from Alfa Aesar, $CoCl_2$, $MnCl_2$ and $FeCl_2$ were purchased from Aladdin, N,N-dimethylformamide (DMF) and hydrochloric acid (38%) was purchased from Sinopharm Chemical Reagent Co. Ltd.

Synthesis of PCN-6': PCN-6' was first reported by Ma et al[1]. However, we slightly adjusted the synthesis conditions and used hydrochloric acid instand of oxalate. In a typical run, mixture of H_3TATB (500 mg) and $Cu(NO_3)_2{\cdot}2.5H_2O$ (1500 mg) were added to a mixing solution of 1 mol/L hydrochloric acid (4.5 mL) and DMF (70.5 mL), then the final solution was sealed in a glass bottles (250 mL) and heated to 80°C and kept for 48 hours. After the glass bottle cooled to room temperature, blue crystals was obtained. The final product was obtained by filtering and washing with DMF for 2 times.

Table S1. Crystal data for PCN-6'

	PCN-6'[a]	**PCN-6'[b]**
Chemical formula	$C_{32}H_{16}Cu_2N_4O_{10}$	$C_{32}H_{20}Cu_2N_4O_{10}$
Formula weight, g mol^{-1}	743.59	747.60
Space group	*Fm-3m*	*Fm-3m*
Temperature, K	250(2)	150(10)
a, Å	46.636(5)	46.4744(15)
b, Å	46.636(5)	46.4744(15)
c, Å	46.636(5)	46.4744(15)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^3	101432(20)	100378(10)
Z	24	24

ρ_{calc}, g cm^{-3}	0.292	0.297
μ, mm^{-1}	0.415	0.420
R_1[b], wR_2[c], %	6.5, 16.05	8.5, 29.04
GOF (F^2)	1.153	1.052

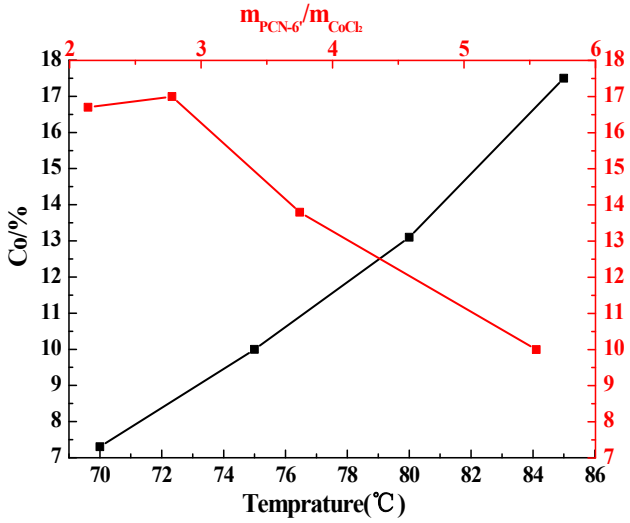
[a]Data from ref. S1.

[b]Data from this work

Steam-assisted Synthesis of PCN-6'(M): As-synthesized PCN-6' (100 mg) with $CoCl_2$ (36 mg) / $MnCl_2$ (27 mg) / $FeCl_2$ (8.7 mg) / $ZnCl_2$ (26 mg) was mixed and grinded in a glove box, the mixed samples was transferred into a weighing bottle (25 mm × 25 mm). Then, 1.5 mL DMF and a support stand (height approximate 3 cm) was added into a Teflon reactor. The weighing bottle was putted on the support stand steadily, the Teflon reactor was sealed and heated to 75°C/80°C/75°C/75°C and kept at this temperature for 48 hours. After cooled to room temperature, the sample was obtained by filtering and washing with DMF for 5-6 times.

Solvent-assisted Synthesis of PCN-6'(M): $CoCl_2$ (18 mg) / $MnCl_2$ (12 mg) was dissolved in 2mL of DMF, then, the solution was added to the PCN-6'(51 mg) in mother liquor in a glass reaction container and was heated to 75°C/80°C in an oven and kept at this temperature for 48 hours. After cooled to room temperature, the sample was obtained by filtering and washing with DMF for 5-6 times.

Determination of Optimal Exchange Conditions (take PCN-6'(Co) as an example): In order to obtain the best reponse conditions, we changed the exchange temperature and the mass ratio of PCN-6'/$CoCl_2$. The exchange temperature was 70°C, 75°C, 80°C, 85°C, respectively and the mass ratio of PCN-6'/$CoCl_2$ was 5.56, 3.75, 2.78, 2.14, respectively. The result show that the amount of metal salt has less effect on the exchange ratio, compared to reaction temperature. With the increase of temperature, the metal exchange ratio increased slowly. However, the XRD diffraction intensity and the BET surface area of obtianed bimetallic materials are reduced. To avoid significant crystallinity destruction, the optimal exchange conditions are obtained by combining the results of XRD, BET and EDS analysis. The optimal exchange conditions are same for other bimetallic MOFs.



The effect of temperature and amount of $CoCl_2$ added on Co exchange ratio in PCN-6'(Co)

Characterization:

PXRD was performed on a D8-Advance Bruker AXS diffractometer with CuKα radiation (λ= 1.54178 Å) operating at 298 K was employed (Göbel mirror; θ–2θ scan; 2θ = 3–30°; step size = 0.0102 (2θ); scan speed = 10 second/step; position sensitive detector; α-Al_2O_3 as external standard. TG data were collected on a thermal analyzer (STA 449 F5, NETZSCH, Germany). For this analysis, the atmosphere was comprised of N_2 at a flow rate of 100 mL/min and a heating rate of 5 °C/min was used. SEM analysis was conducted on an Hitachi SU8010 SEM operating at 1.0–3.0 kV at various accelerating voltages between 1 and 20 kV. The content of Cu, Co, Fe, Mn, Zn in the samples were determined using the EPA 200.8 method of acid digestion followed by measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, iCAP 7000 series, Thermo Scientific). The sorption isotherms for CO_2, H_2 and N_2 were tested using a volumetric gas sorption analyzer (ASAP-2460, micromeritics, USA) with ultra-high purity gases (99.999%).

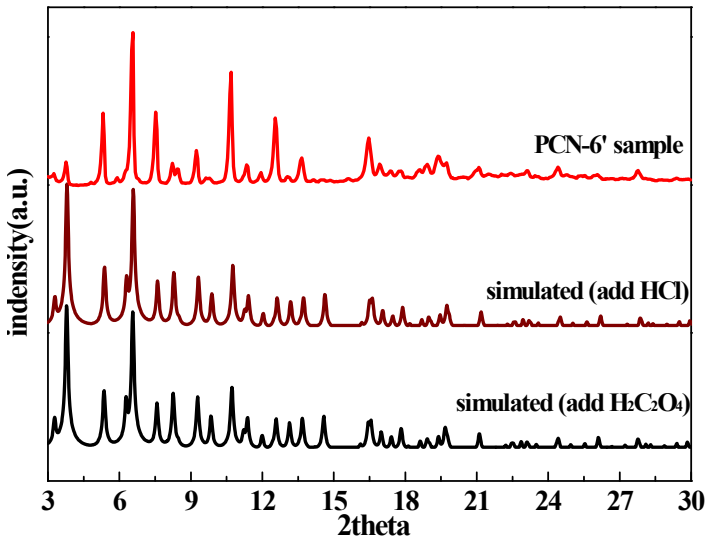


Figure S1 Powder X-ray diffraction patterns of PCN-6'

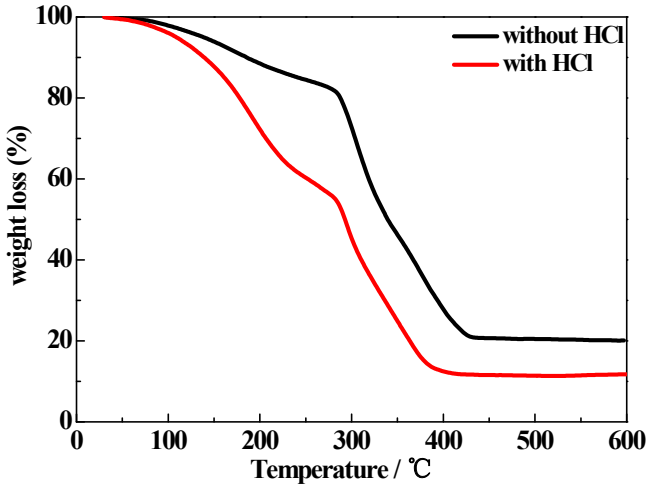


Figure S2 TG for with HCl and without HCl during the synthesis parent material

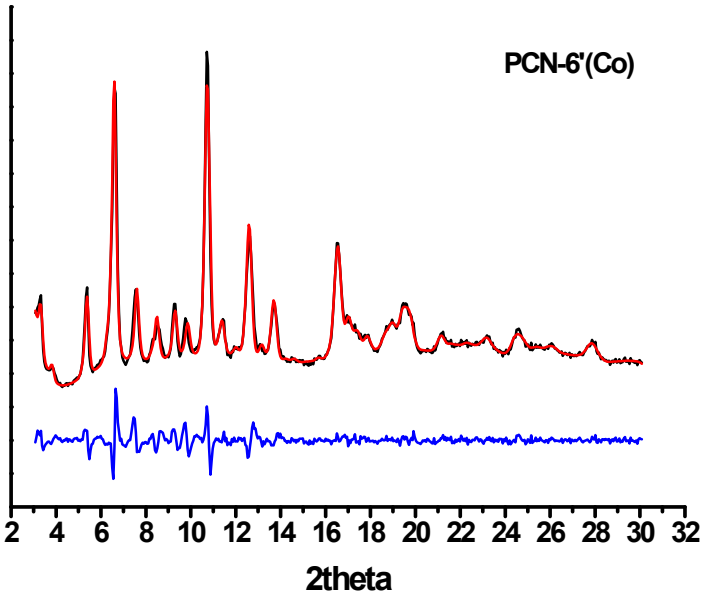


Figure S3 Observed (black), LeBail fit (red) and difference (blue) curves of the powder X-ray data of PCN-6'(Co).

Agreement factors		
Rp = 3.350	Rwp = 4.914	
Cell parameter		
a = 46.69348	b = 46.69348	c = 46.69348
α = 90.000	β = 90.000	γ = 90.000

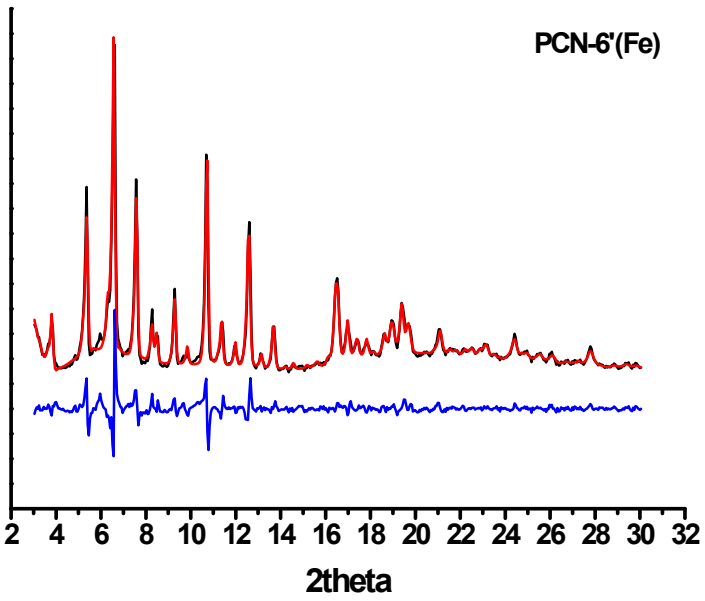


Figure S4 Observed (black), LeBail fit (red) and difference (blue) curves of the powder X-ray data of PCN-6'(Fe).

Agreement factors		
Rp = 5.282	Rwp = 7.818	
Cell parameter		
a = 46.75913	b = 46.75913	c = 46.75913
α = 90.000	β = 90.000	γ = 90.000

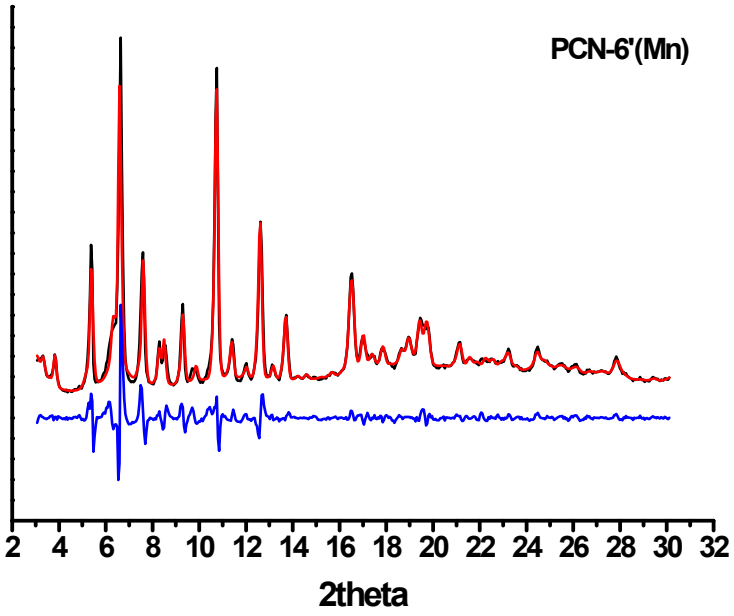


Figure S5 Observed (black), LeBail fit (red) and difference (blue) curves of the powder X-ray data of PCN-6'(Mn).

Agreement factors		
Rp = 6.092	Rwp = 9.873	
Cell parameter		
a = 46.67831	b = 46.67831	c = 46.67831
α = 90.000	β = 90.000	γ = 90.000

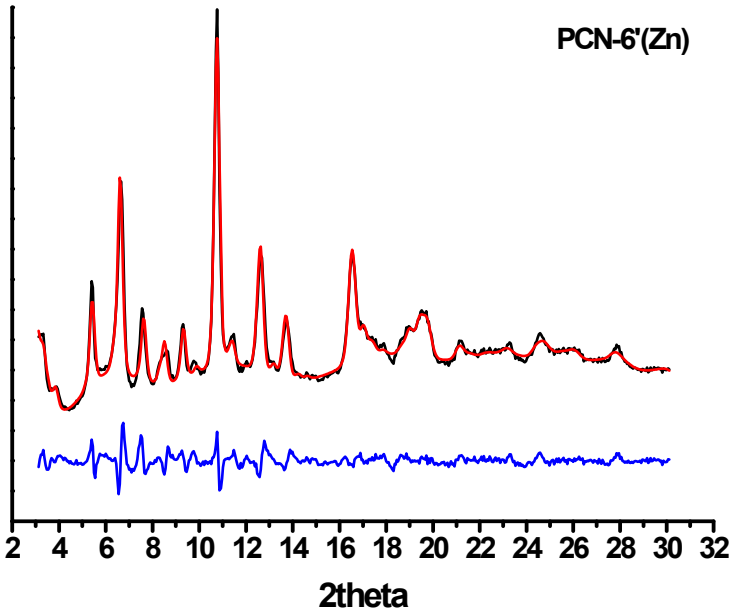


Figure S6 Observed (black), LeBail fit (red) and difference (blue) curves of the powder X-ray data of PCN-6'(Zn).

Agreement factors		
Rp = 3.579	Rwp = 4.966	
Cell parameter		
a = 46.54043	b = 46.54043	c = 46.54043
α = 90.000	β = 90.000	γ = 90.000

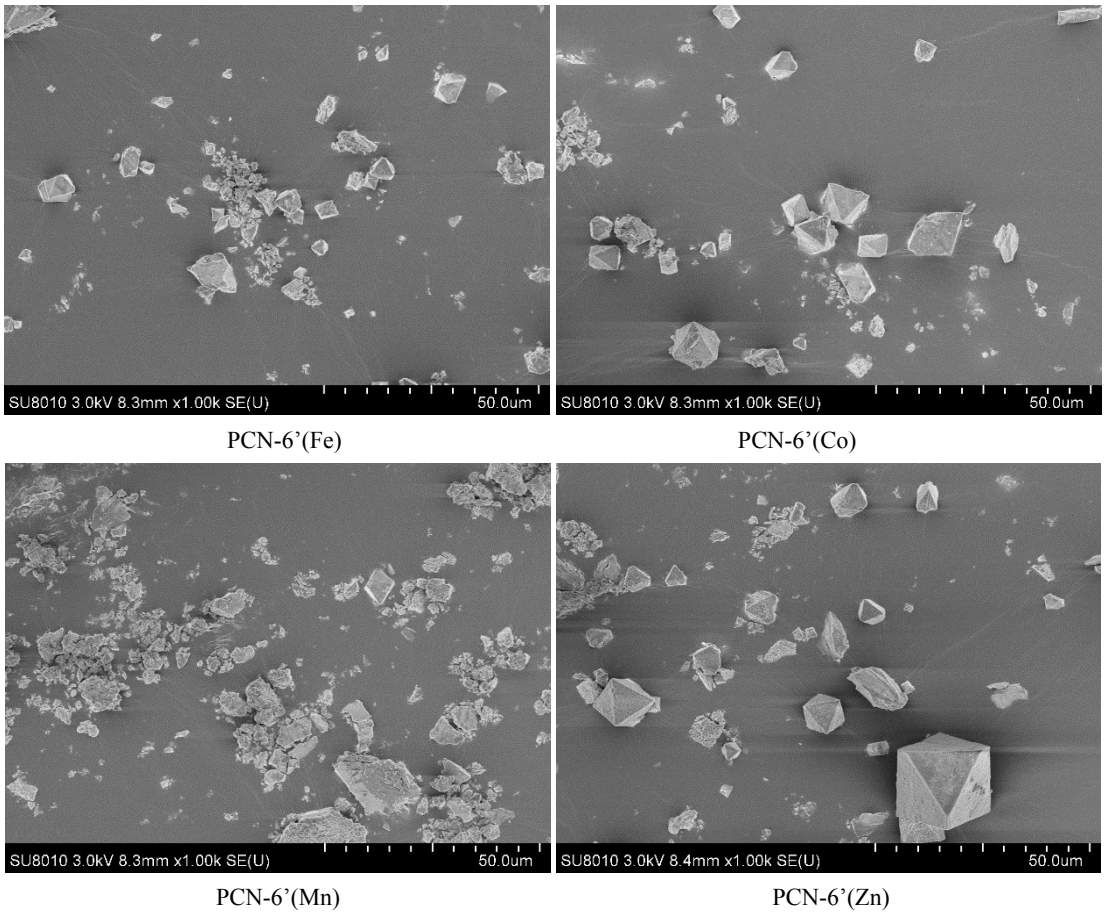


Figure S7 SEM of PCN-6'(Fe), PCN-6'(Co), PCN-6'(Mn) and PCN-6'(Zn)

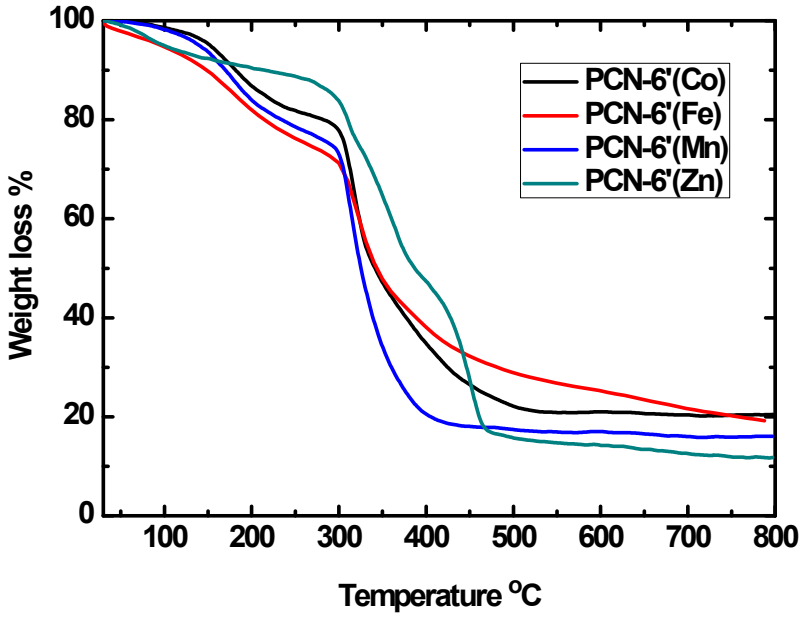


Figure S8. The TGA of PCN-6'(M) samples

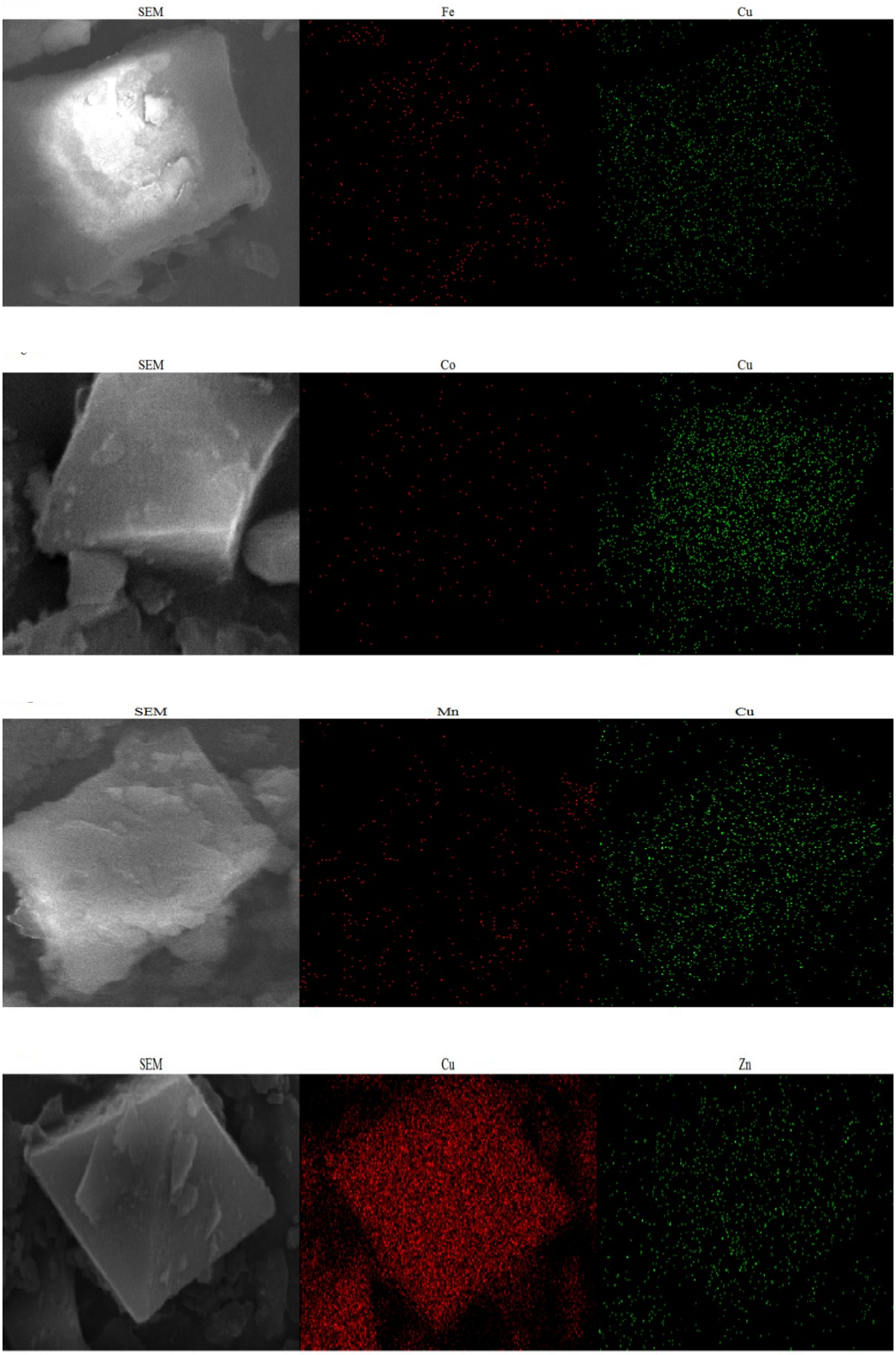


Figure S9 Elemental mapping of PCN-6’(M) (Top to bottom: PCN-6’(Fe), PCN-6’(Co), PCN-6’(Mn), PCN-6’(Zn))

Gas Adsorption Measurements: All the as-synthesized crystalline samples were immersed in CH_3OH for 2h, and the extract was discarded. Fresh CH_3OH was subsequently added, the sample was then treated with CH_2Cl_2 in a similar manner to remove methanol solvates. After the removal of CH_2Cl_2 by decanting the samples were dried in a glove box. Before the measurement, the sample were outgassed at 150 °C under vacuum for 2h.

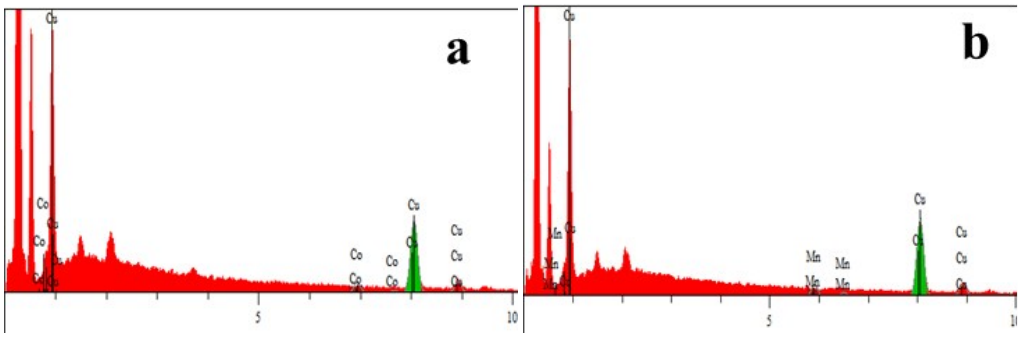


Figure S10 EDS spectra of PCN-6'(Co)(a) and PCN-6'(Mn)(b) by solvent-assisted.

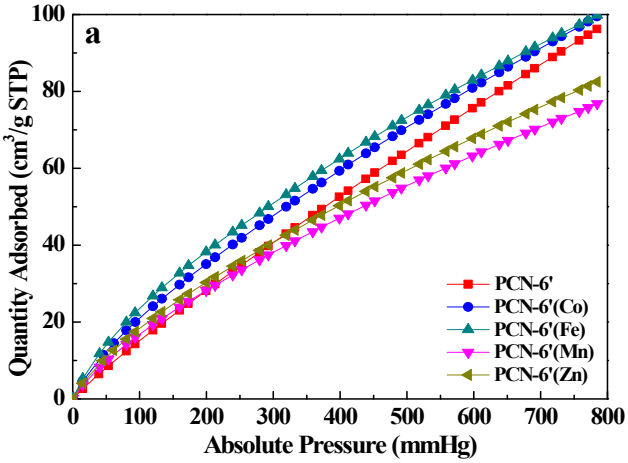


Figure S11 CO_2 sorption isothermsat at 298K of PCN-6' and PCN-6'(M)

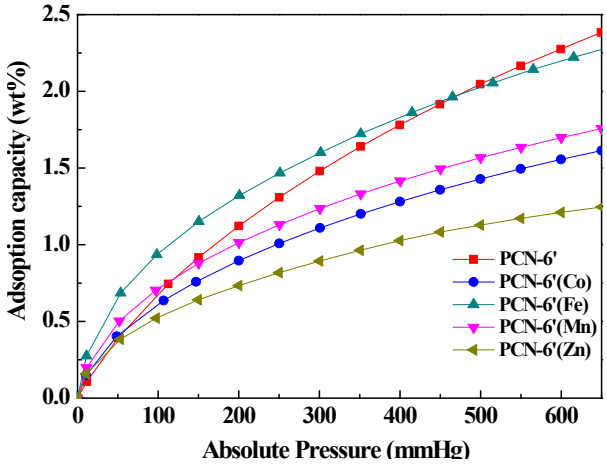


Figure S12 H_2 adsorption isotherm at 77K of PCN-6' and PCN-6'(M)

References

[S1] Shengqian Ma,Daofeng Sun,Michael Ambrogio,Jacqueline A. Fillinger,Sean Parkin,and Hong-Cai Zhou. Framework-Catenation Isomerism in Metal-Organic Frameworks and ItsImpact on Hydrogen Uptake. *J. AM. CHEM. SOC.* 2007, 129, 1858-1859.