Electronic Supplementary Information (ESI)

A series of isostructural mesoporous metal-organic frameworks obtained by ion-exchange induced single-crystal to single-crystal transformation

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Supporting information

S1– Materials and methods

H_3BTB was synthesized according to the reported procedure.[1] All other chemicals were purchased from commercial suppliers and used without further purification. FT-IR spectrum was performed on a Varian 670-IR spectrometer. Metal ion ratio was analyzed using ICP-AES on an ESCALAB2000 analyzer. Single-crystal X-ray diffraction data were collected at room temperature on an Oxford Diffraction Xcalibur 3 diffractometer equipped with a CCD camera using Mo Kα (λ = 0.71073 Å) radiation. Powder X-ray diffraction (PXRD) patterns were collected using a PANanalytical X'Pert PRO diffractometer equipped with a Pixel detector and using Cu Kα (λ = 1.5406 Å) radiation. All samples were ground with a little DMF prior to data collection and dispersed uniformly on zero-background Si plates.

S2 – Direct synthesis

SUMOF-1-Zn: a mixture of H_3BTB (85.0 mg, 0.2 mmol), bipyridine (24.0 mg, 0.15 mmol), and $Zn(NO_3)_2{\cdot}6H_2O$ (91.0 mg, 3.0 mmol) dissolved in DMF (10.0 mL) was tightly sealed in a vial and heated at 85° C for 2 days. Faint yellow crystals were isolated by decanting the mother liquid and washed with DMF. Yield > 60% (based on H_3BTB). The resulting crystals were immersed in fresh DMF. The phase purity of the product was confirmed by powder X-ray diffraction.

SUMOF-1-Co: this compound was prepared by a similar procedure as SUMOF-1-Zn, but using $Co(NO_3)_2{\cdot}6H_2O$ instead of $Zn(NO_3)_2{\cdot}6H_2O$. Yield > 30% (based on H_3BTB).

S3 – Single-crystal X-ray crystallography

Single crystal X-ray diffraction data were collected on an XCalibur3 diffractometer equipped with a CCD camera and using Mo Kα (λ=0.71073 Å) radiation at room temperature. Data reduction was done by CrysAlisPro program and multi-scan adsorption correction was applied. The structures were solved by direct methods. All non-hydrogen framework atoms were located from the difference Fourier map and refined anisotropically. All hydrogen framework atoms were added on a riding model. The final structures were refined by full-matrix least-squares techniques against F^2 using the SHELX programs.[2] Due to the high symmetry of the framework structures and large pore sizes, the guest molecules (DMF and H_2O) could not be located due to the disorder. Solvent-free diffraction intensities, produced by PLATON/SQUEEZE[3] to remove the scattering contribution from the highly disordered guest molecules, were used for the final structure refinement. Due to the large fractional pore volume in SUMOF-1, the intensity quality and resolution of the diffraction data were rather poor as indicated by the low I/σ, high R_{int} and low 2θ angles. These also resulted in relatively high R-values in the final refinements. Due to the similar atomic scattering factors for all metals, it was not possible to determine the occupancies of different metals by X-ray diffraction. The molar ratios of the metals determined by ICP-AES analysis were used in the refinement.

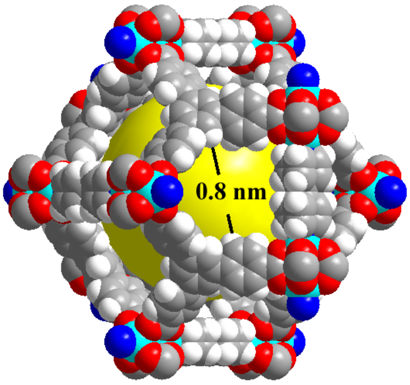


Fig. S1 Dodecahedral mesorporous cavity in space-filling mode. The yellow ball with a diameter of 2.1 nm indicates the available pore volume of the cavity. The cavity window has a free diameter of 0.8 nm. The 4,4'-bipyridine molecules are disordered.

Table S1. Crystal data and structure refinements for all SUMOF-1s.

Identification code	SUMOF-1-Zn	SUMOF-1-Co
Empirical formula	$C_{23}H_{14}NO_4Zn$	$C_{23}H_{14}NO_4Co$
Formula weight	433.72	427.28
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	cubic	cubic
Space group	*Pm*-3*n*	*Pm*-3*n*
a (Å)	27.6567(7)	27.6523(6)
Volume (Å^3)	21154.4(9)	21144.3(8)
Z	12	12
Density (calculated)	0.409 g/cm^3	0.403 g/cm^3
Absorption coefficient	0.356	0.252
F(000)	2652	2616
Crystal size (mm^3)	0.55 × 0.50 × 0.50	0.55 × 0.35 × 0.28
Crystal color	Faint yellow	brown
Theta range for data collection	$4.17° < \theta < 20.83°$	$4.30° < \theta < 24.40°$
Index ranges	$-20 \leq h \leq 27$, $-27 \leq k \leq 27$, $-27 \leq l \leq 27$	$-32 \leq h \leq 29$, $-32 \leq k \leq 26$, $-32 \leq l \leq 29$
Reflections collected	79277	116524
Unique reflections	1991 ($R_{(int)}$= 0.1535)	3090 ($R_{(int)}$= 0.1324)
Completeness to theta	0.988	0.992
Absorption correction	Multi-scan	Multi-scan
Min. and max. transmission	0.82378 and 1.00000	0.89927 and 1.00000
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1991 / 6 / 77	3090 / 6 / 77
Goodness-of-fit on F^2	1.076	1.064
Final R indices [I>2sigma(I)]	$R1 = 0.0983$, $wR2 = 0.2734$	$R1 = 0.0834$, $wR2 = 0.2195$
R indices (all data)	$R1 = 0.1183$, $wR2 = 0.2972$	$R1 = 0.1171$, $wR2 = 0.2487$
Largest diff. peak and hole	0.569 and -0.263 e·Å^3	0.646 and -0.357 e·Å^3

Identification code	SUMOF-1-Cu	SUMOF-1-(Co:2Zn)	SUMOF-1-(Ni:2Zn)
Empirical formula	$C_{23}H_{14}NO_4Cu$	$C_{23}Co_{0.35}H_{14}NO_4Zn_{0.65}$	$C_{23}Ni_{0.38}H_{14}NO_4Zn_{0.62}$
Formula weight	431.89	431.37	431.19
Temperature (K)	293	293	293
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	cubic	cubic	cubic
Space group	*Pm*-3*n*	*Pm*-3*n*	*Pm*-3*n*
a (Å)	27.4490(8)	27.6890(7)	27.529(4)
Volume ($Å^3$)	20681.4(10)	21228.5(9)	20862(5)
Z	12	12	12
Density (calculated)	0.416 g/cm^3	0.405 g/cm^3	0.405 g/cm^3
Absorption coefficient	0.325	0.319	0.328
F(000)	2640	2639	2643
Crystal size (mm^3)	0.50 × 0.35 × 0.28	0.56 × 0.49 × 0.46	0.50 × 0.40 × 0.38
Crystal color	blue	dark red	green
Theta range for data collection	$4.33° < \theta < 19.78°$	$4.16° < \theta < 23.25°$	$4.16° < \theta < 17.22°$
Index ranges	$-26 \le h \le 26$, $-26 \le k \le 24$, $-24 \le l \le 26$	$-19 \le h \le 30$, $-30 \le k \le 30$, $-30 \le l \le 30$	$-18 \le h \le 23$, $-23 \le k \le 20$, $-23 \le l \le 22$
Reflections collected	67474	103500	47799
Unique reflections	1679 ($R_{(int)}$= 0.1707)	2721 ($R_{(int)}$= 0.1510)	1164 ($R_{(int)}$= 0.1636)
Completeness to theta	0.986	0.992	0.981
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Min. and max. transmission	0.99188 and 1.00000	0.92917and 1.00000	0.93150 and 1.00000
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1679 / 4/ 77	2721 / 6 / 77	1164 / 7 / 77
Goodness-of-fit on F^2	1.099	1.097	1.110
Final R indices [I>2sigma(I)]	$R1 = 0.1234$, $wR2 = 0.3233$	$R1 = 0.1075$, $wR2 = 0.2752$	$R1 = 0.0955$, $wR2 = 0.2725$
R indices (all data)	$R1 = 0.1512$, $wR2 = 0.3540$	$R1 = 0.1369$, $wR2 = 0.3050$	$R1 = 0.1116$, $wR2 = 0.2936$
Largest diff. peak and hole	0.377 & -0.228 e·$Å^3$	0.894 & -0.451 e·$Å^3$	0.415 & -0.232 e·$Å^3$

S4 – Procedure for framework metal ion exchange

SUMOF-1-Cu: to obtain the Cu^{2+} exchanged framework of SUMOF-1, single crystals of the parent compound SUMOF-1-Zn were soaked in a DMF solution of $Cu(NO_3)_2·3H_2O$ (0.04 M) for 3 days. After decanting the solution, the Cu^{2+}-exchanged crystals were washed thoroughly with DMF and then soaked in fresh DMF. For ICP-AES analysis, the crystals were transferred to fresh DMF, kept there for 7 days to remove the excess metal salt within the pores, and dried at 100 °C overnight. ICP-AES analysis revealed that the framework Zn^{2+} ions were completely exchanged by Co^{2+}, resulting in SUMOF-1-Cu. The reverse ion exchange was also investigated by soaking the fully exchanged SUMOF-1-Cu in DMF solution of $Zn(NO_3)_2·6H_2O$ (0.04 M) for three month. ICP-AES analysis revealed 38% of the framework Cu^{2+} ions were exchanged by Zn^{2+}, resulting in **SUMOF-1-(Cu:2Zn)**.

For kinetic study of the metal ion exchange, crystals of SUMOF-1-Zn were soaked in 0.04 M DMF solution of $Cu(NO_3)_2·3H_2O$. A small amount of sample was taken out at regular intervals (see Table S1), washed thoroughly with DMF, kept in fresh DMF for 7 days and dried at 100 °C overnight prior to ICP-AES analysis.

SUMOF-1-(Co:2Zn): single crystals of SUMOF-1-Zn were immersed in DMF solution of $Co(NO3)_2·6H_2O$ (0.04 M) for 3 months, washed thoroughly with DMF, and then soaked in fresh DMF. For ICP-AES analysis, the crystals were transferred to fresh DMF, kept there for 7 days and dried at 100 °C overnight. ICP-AES analysis revealed that 35% of the framework Zn^{2+} ions were exchanged by Co^{2+}, resulting in SUMOF-1-(Co:2Zn). The reverse ion exchange was also investigated by soaking the resulting SUMOF-1-(Co:2Zn) in DMF solution of $Zn(NO_3)_2·6H_2O$ (0.04 M) for 7 days. ICP-AES analysis revealed that all framework Co^{2+} ions were completely exchanged by Zn^{2+}, indicating a complete reversible ion exchange.

SUMOF-1-(Ni:2Zn): single crystals of SUMOF-1-Zn were immersed in DMF solution of $Ni(NO_3)_2·6H_2O$ (0.04 M) for 3 months, washed thoroughly with DMF, and then soaked in fresh DMF. For ICP-AES analysis, the crystals were transferred to fresh DMF, kept there for 7 days and dried at 100 °C overnight. ICP-AES analysis revealed 38% of the framework Zn^{2+} ions were exchanged by Ni^{2+}, resulting in SUMOF-1-(Ni:2Zn). The reverse ion exchange was also investigated by soaking the resulting SUMOF-1-(Ni:2Zn) in DMF solution of $Zn(NO_3)_2·6H_2O$ (0.04 M) for 7 days. ICP-AES analysis revealed that all framework Ni^{2+} ions were exchanged by Zn^{2+}, indicating a complete reversible ion exchange.

Table S2. Metal ion ratio during the ion exchange process analyzed by ICP-AES.

Samples	**Time**	**Metal molar ratio (%)**	
		Zn	**Cu**
SUMOF-1-Zn soaked in DMF solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.04 M)	0 min	100	0
	5 min	89	11
	10 min	78	21
	30 min	60	40
	1 h	54	46
	6 h	40	60
	12 h	23	77
	2 d	6	94
	3 d	5	95
	90 d (yielding SUMOF-1-Cu)	1	99
SUMOF-1-Cu soaked in DMF solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.04 M)	90 d	38	62
		Zn	**Co**
SUMOF-1-Zn soaked in DMF solution of $Co(NO_3)_2{\cdot}6H_2O$ (0.04 M)	90 d (yielding SUMOF-1-(Co:2Zn))	65	35
SUMOF-1-(Co:2Zn) soaked in DMF solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.04 M)	7 d	100	0
		Zn	**Ni**
SUMOF-1-Zn soaked in DMF solution of $Ni(NO_3)_2{\cdot}6H_2O$ (0.04 M)	90 d (yielding SUMOF-1-(Ni:2Zn))	62	38
SUMOF-1-(Ni:2Zn) soaked in DMF solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.04 M)	7 d	100	0

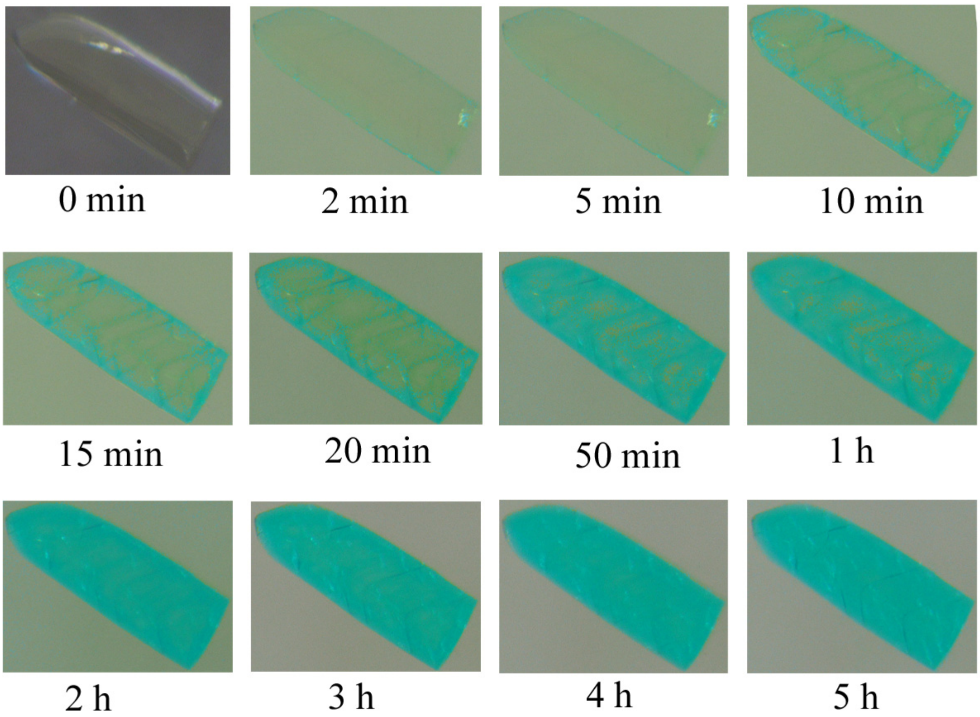
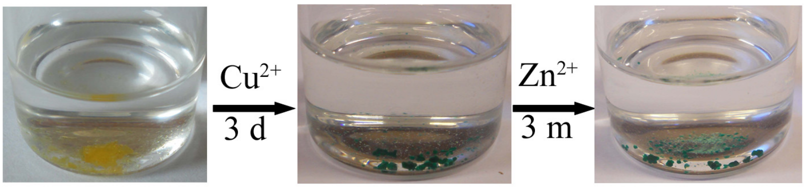
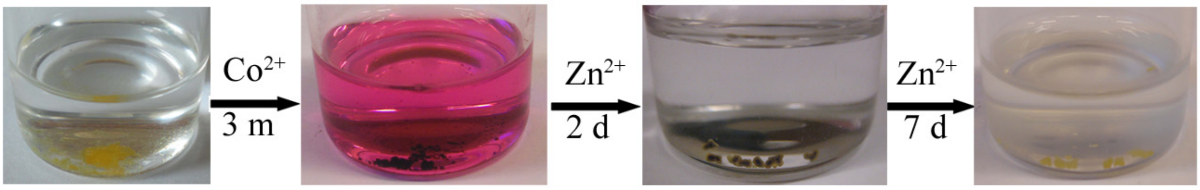


Fig. S2 Photographs of a SUMOF-1-Zn crystal (0.5 × 0.5 × 1.5 mm in size) soaked in DMF solution of $Cu(NO_3)_2{\cdot}3H_2O$ at different time periods, showing that the diffusion of Cu^{2+} ions into the crystal is isotropic. The cyan color is associated with the incorporation of Cu^{2+} ions into the crystal.



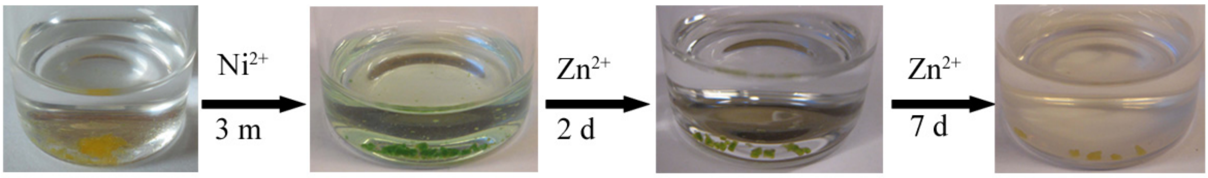
(a) **(b)** **(c)**

Fig. S3 Photographs of ion exchange process between Cu^{2+} and Zn^{2+}. (a) Yellow SUMOF-1-Zn crystals in DMF. (b) SUMOF-1-Cu crystals after soaking the SUMOF-1-Zn crystals in DMF solution of $Cu(NO_3)_2{\cdot}3H_2O$ for three days. The color of the crystals is changed from yellow to blue. (c) SUMOF-1-(Cu, 2Zn) crystals after soaking the SUMOF-1-Cu crystals in DMF solution of $Zn(NO_3)_2{\cdot}6H_2O$ for three months. The color of the crystals is changed from blue to light blue.



(a) **(b)** **(c)** **(d)**

Fig. S4 Photographs of ion exchange process between Co^{2+} and Zn^{2+}. (a) Yellow SUMOF-1-Zn crystals in DMF. (b) SUMOF-1-(Co:2Zn) crystals after soaking the SUMOF-1-Zn crystals in DMF solution of $Co(NO_3)_2{\cdot}6H_2O$ for three months. The color of the crystals is changed from yellow to dark brown. (c) and (d) SUMOF-1-(Co, 2Zn) crystals being soaked in DMF solution of $Zn(NO_3)_2{\cdot}6H_2O$ for two and seven days, respectively. The yellow color of the crystals is recovered, indicating that the ion exchange process is reversible.



(a) **(b)** **(c)** **(d)**

Fig. S5 Photographs of ion exchange process between Ni^{2+} and Zn^{2+}. a) Yellow SUMOF-1-Zn crystals in DMF. (b) SUMOF-1-(Ni:2Zn) crystals after soaking the SUMOF-1-Zn crystals in DMF solution of $Ni(NO_3)_2{\cdot}6H_2O$ for three months. The color of the crystals is changed from yellow to green. (c) and (d) SUMOF-1-(Ni, 2Zn) crystals being soaked in DMF solution of $Zn(NO_3)_2{\cdot}6H_2O$ for two and seven days, respectively. The yellow color of the crystals is recovered, indicating that the ion exchange process is reversible.

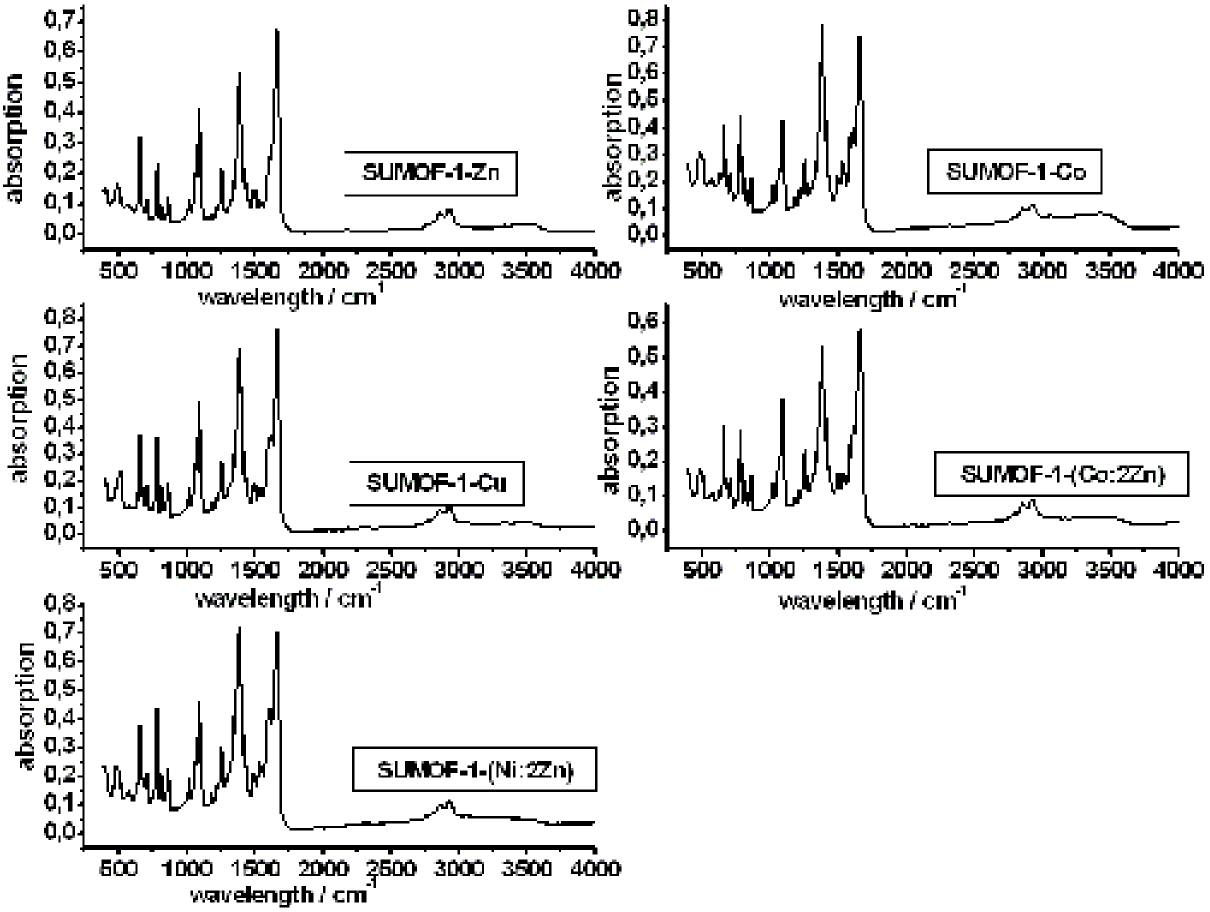


Fig. S6 FT-IR spectra of SUMOF-1-Zn, SUMOF-1-Co, SUMOF-1-Cu, SUMOF-1-(Co:2Zn), SUMOF-1-(Ni:2Zn). All the spectra are similar, indicating the same framework.

S5 – Thermal stability study

Thermogravimetric analysis (TGA) was performed in air flow from 30 °C to 600 °C with a heating rate of 10 °C/min using a high-resolution thermogravimetric analyzer (Perkin Elmer TGA 7). TGA analysis showed that the samples lost the solvents (> 60%) in the range of 30-200 °C and decomposed between 260 °C and 350 °C. Note that the final weight losses of SUMOF-1-Zn and SUMOF-1-(Ni : 2Zn) are much higher than the complete losses of the solvents and organic linkers, probably due to the partial losses of the metal clusters.

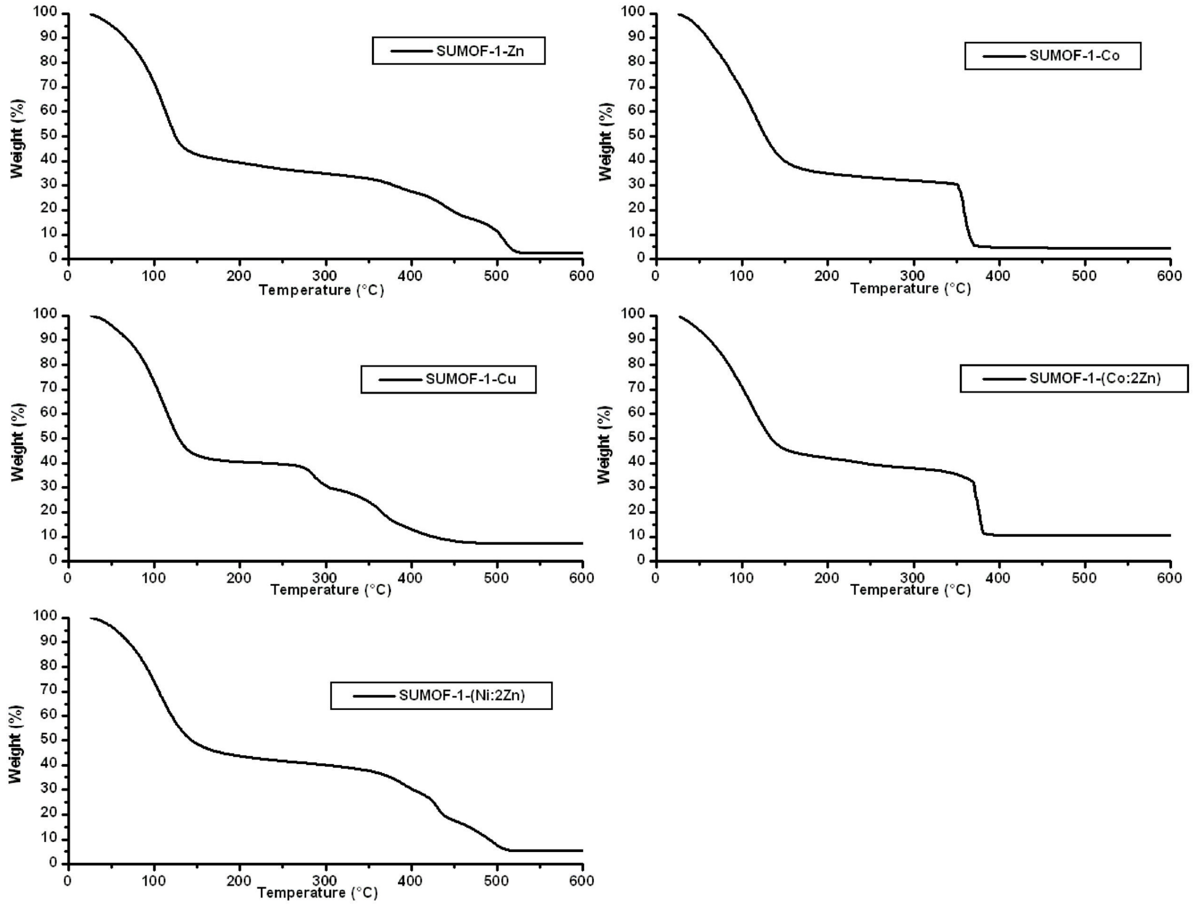


Fig. S7 TGA plots of SUMOF-1-Zn, SUMOF-1-Co, SUMOF-1-Cu, SUMOF-1-(Co:2Zn), and SUMOF-1-(Ni:2Zn).

References

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