Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for

Semiconducting Metal-Chalcogenide-Organic Framework with Square-Planar Tetra-Coordinated Sulfur

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EXPERIMENTAL SECTION

Materials. 1,3,5-benzenetricarboxylate (BTC, 99.99%), Manganese acetate ($Mn(CH_3COO)_2$, 99.9%), thiourea (99%), N, N-dimethylformamide (DMF) and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU). All analytical grade chemicals employed in this study were commercially available and used without further purification.

Synthesis. 1,3,5-benzenetricarboxylate (BTC) (121 mg), $Mn(CH_3COO)_2$ (65 mg), and thiourea (160 mg) were mixed with N,N-dimethylformamide (DMF, 2 mL) and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 3 mL) at 190 °C for 7 days in a 23-mL Teflon lined stainless autoclave and under vigorous stirring for 30 min. Then the vessel was sealed and heated at 190 ^oC for 7 days and then taken out from the oven. The autoclave was subsequently allowed to cool to room temperature and pale yellow cubic crystals were obtained. The crystals were washed by ethanol, and then dried in air. And the compound is stable under ambient conditions.

Single Crystal X-ray Diffraction (SCXRD). The single-crystal X-ray diffraction measurements were performed on Photon II CPAD diffractometer controlled using graphite-monchromated Mo-*Kα* (λ =0.71073 Å) radiation at 296 K. The structure was solved by direct method using SHELXS-2014 and the refinements against all reflections of the compound were performed using SHELXS-2014. The protonated organic amines and water molecules located in the void space of the framework cannot be identified owing to their serious disorder. As a result, the contribution of the disordered solvent molecules was subtracted from the reflection data by the SQUEEZE method as implanted in PLATON program.

Powder X-ray Diffraction (PXRD). PXRD data were collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-Kα (λ=1.54056 A) radiation operated at 30 kV and 10 mA.

The samples were ground into fine powders for several minutes before the test.

Elemental Analysis. Energy dispersive spectroscopy (EDS) analysis was obtained on energy dispersive spectroscopy (EDS) detector. The EDS measurement indicates that Mn : S is 6.5 : 1.8 and close to the ratio of Mn : S = 4 : 1. Elemental analysis (EA) of C, H, and N was performed on VARIDEL III elemental analyzer {Calcd. (wt%): C , 45.06; H, 4.47; N, 5.01. Found: C, 42.67; H, 4.97; N, 5.35}. The content deviation of C could be ascribed to the incomplete combustion of the samples.

Thermogravimetric Analysis (TGA). TGA measurement was performed with a Shimadzu TGA-50 system under nitrogen flow. The TG curve was performed by heating the sample from 20 to 800 °C with heating rate of 10 °C /min.

UV-Vis Absorption. Room-temperature solid-state UV-Vis diffusion reflectance spectra of crystal samples were measured on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer coupled with an integrating sphere by using $BaSO_4$ powder as the reflectance reference. The absorption spectra were calculated from reflectance spectra by using the Kubelka-Munk function: $F(R)=\alpha/S=(1-R)^2/2R$, where R, α, and S are the reflection, the absorption and the scattering coefficient, respectively.

Fourier Transform Infrared Absorption. Fourier transform-Infrared spectral analysis was performed on a Thermo Nicolet Avatar 6700 FT-IR spectrometer with cesium iodide optics allowing the instrument to observe from 600-4000 cm^{-1}.

Ion Exchange. The sample of **MCOF-89** (20 mg) was dipped in 20 mL methanol solution of $LiNO_3$ in glass vial, which was slowly shaken by hand for several seconds, then placed at room temperature. During the treatment, the $LiNO_3$ solution was refreshed every 12 hours. After a

certain time, the crystals were taken out of solution and washed with methanol to remove residual Li^+ ions adsorbed on the crystal surface. The products were then characterized by EA.

Gas Adsorption. N_2 and CO_2 sorption measurements of Li^+-exchanged sample were carried out on a Micromeritics ASAP 2020 Physisorption Analyzer. Prior to the measurement, the as-synthesized sample was dried in the vacuum oven for several hours and further dried by using "degas" process of the surface area analyzer for 12 hours at 30 ^oC.

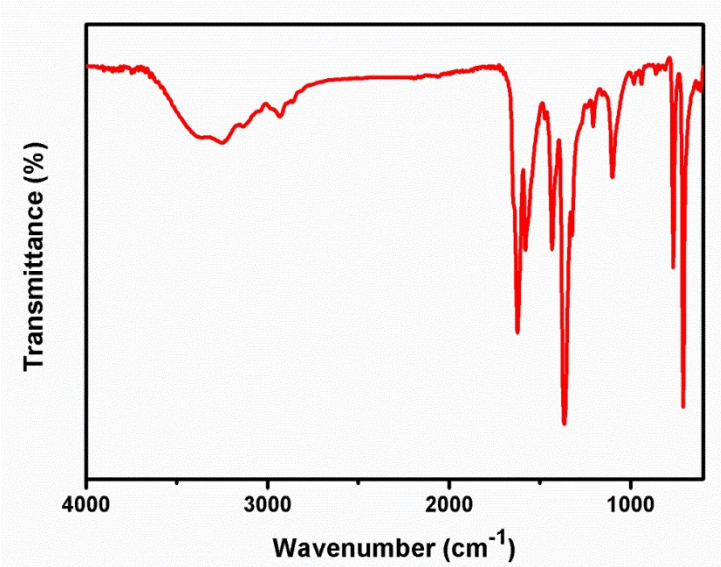

Figure S1. FT-IR spectrum of **MCOF-89.**

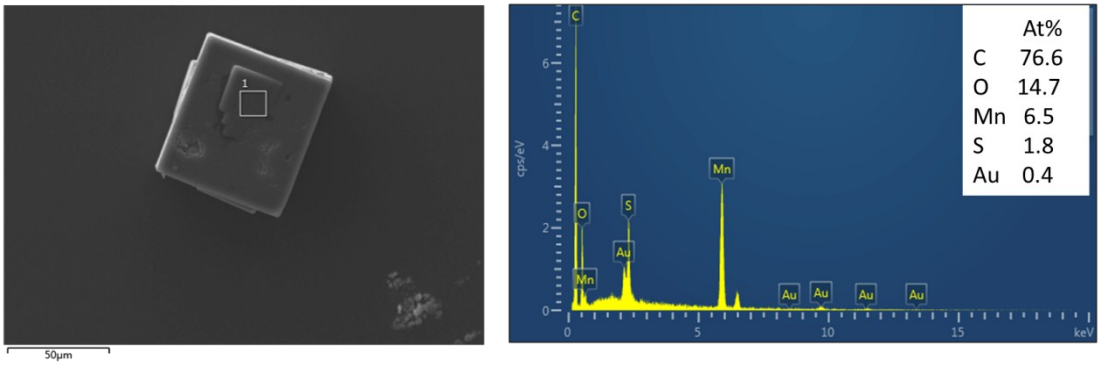

Figure S2. Left: SEM image of as-synthesized **MCOF-89** crystal. Right: energy X-ray dispersive spectroscopy (EDS) of **MCOF-89**.

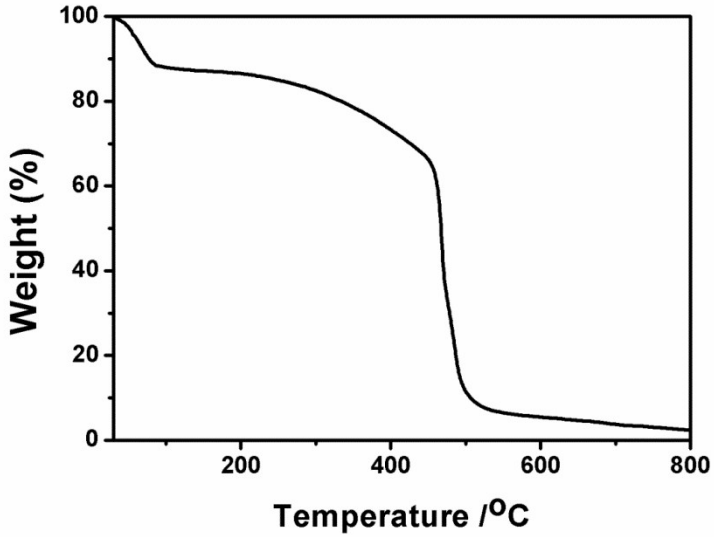

Figure S3. TGA curve of **MCOF-89**.

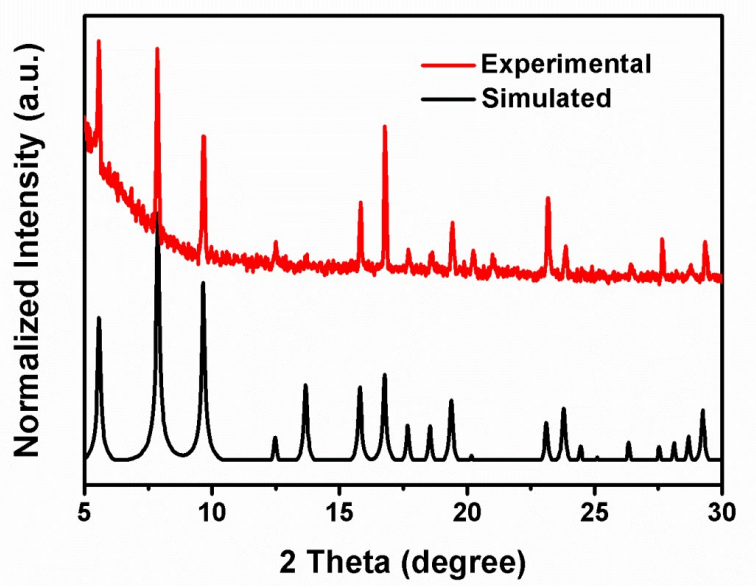

Figure S4. PXRD patterns of the simulated and as-synthesized **MCOF-89.**

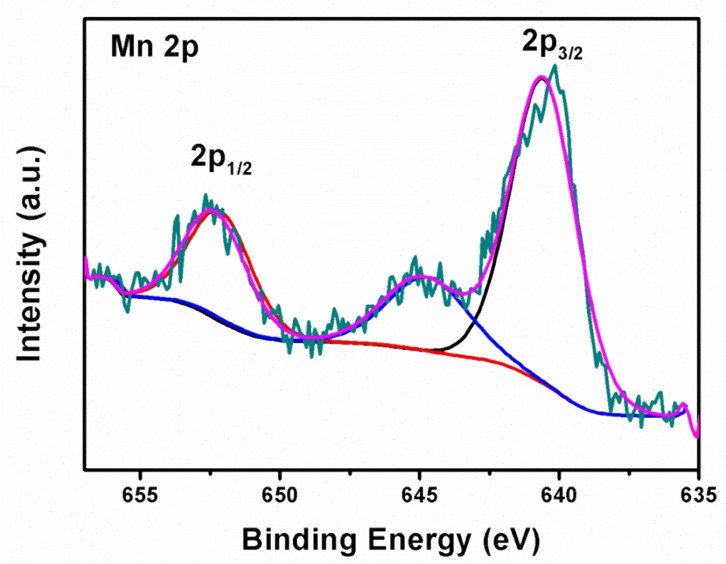

Figure S5. Peak fitting of the Mn2p XPS spectrum for **MCOF-89**.

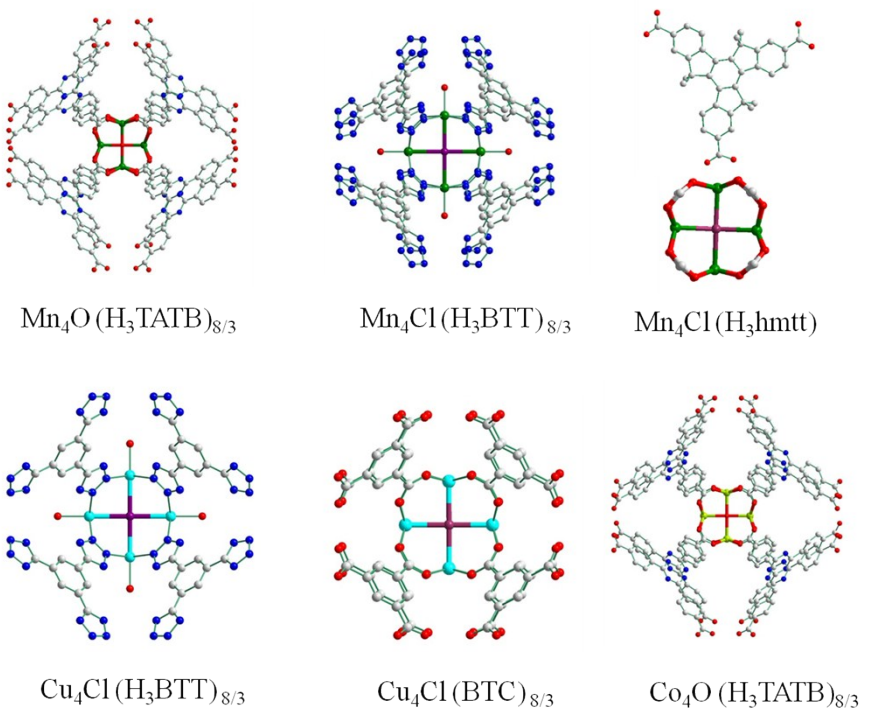

Figure S6. Several reported MOFs based on the similar inorganic M_4Cl (or M_4O) units connected by organic ligands containing three carboxylic acids.

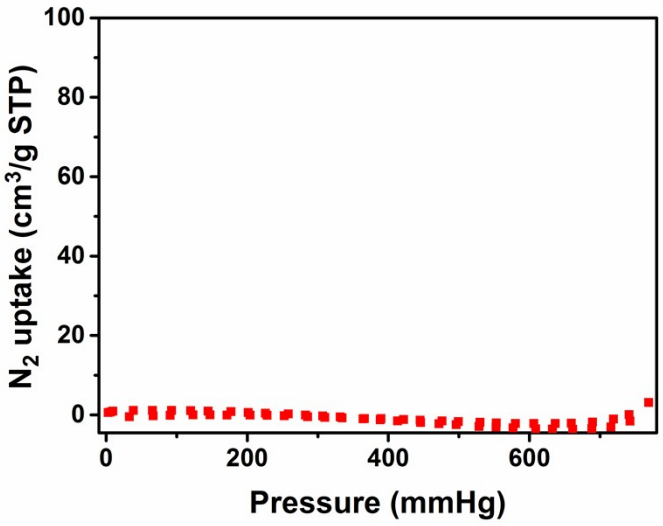

Figure S7. 77 K N_2 adsorption isotherm of pristine **MCOF-89**.

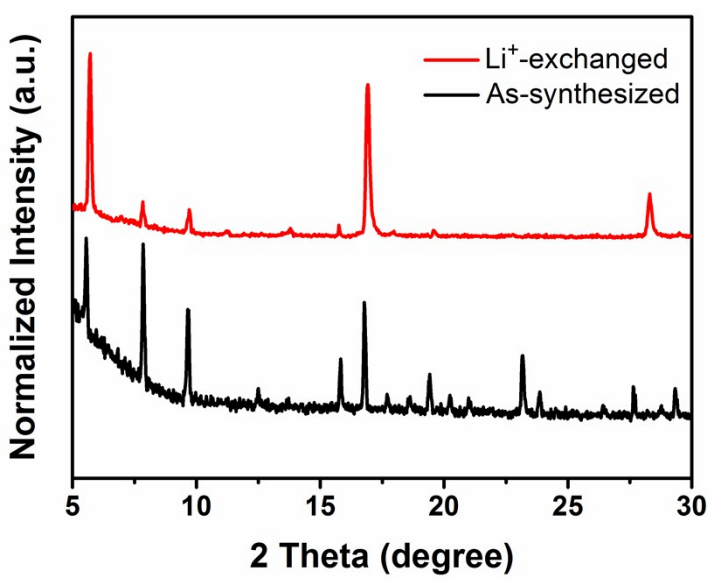

Figure S8. PXRD patterns of as-synthesized **MCOF-89** and Li^+-exchanged samples.

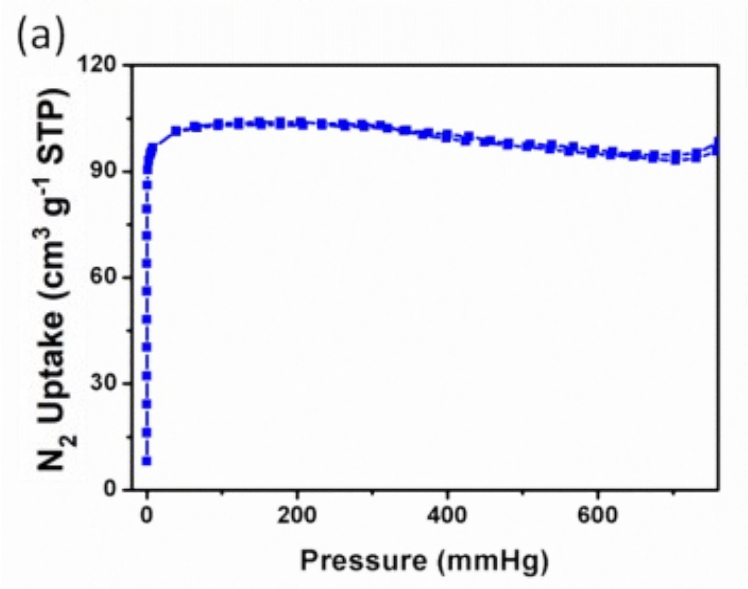

Figure S9. 77 K N_2 adsorption isotherm of 2 M Li^+-exchanged sample.

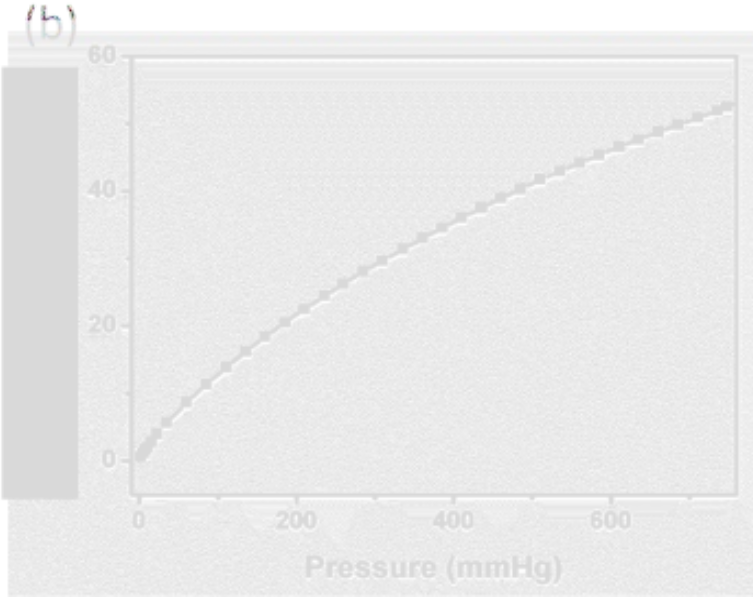

Figure S10. CO_2 adsorption isotherm of 2 M Li^+-exchanged sample at 273 K.

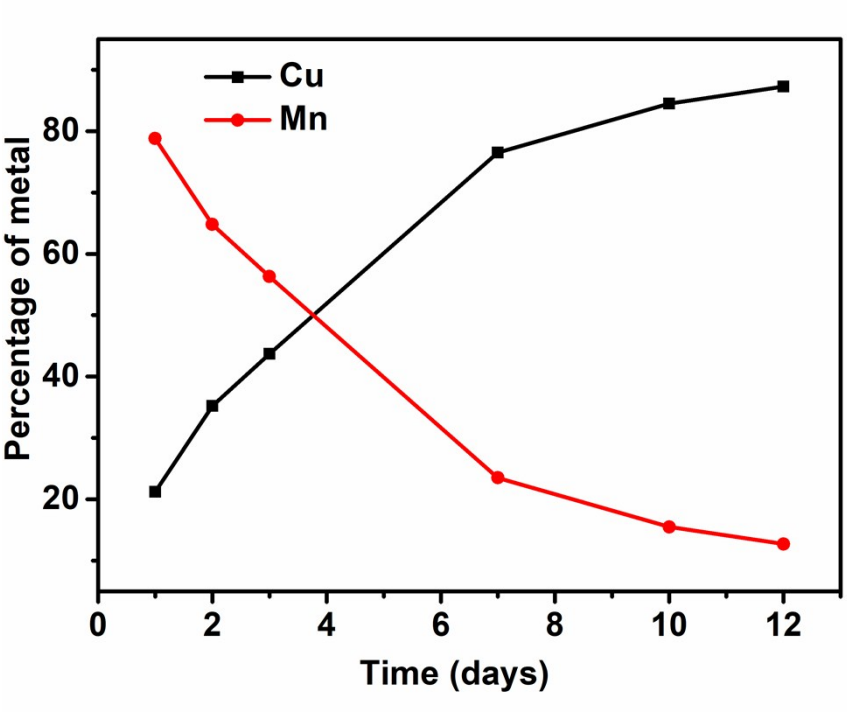

Figure S11. Kinetic profile of Cu^{2+} ion exchange of **MCOF-89**.

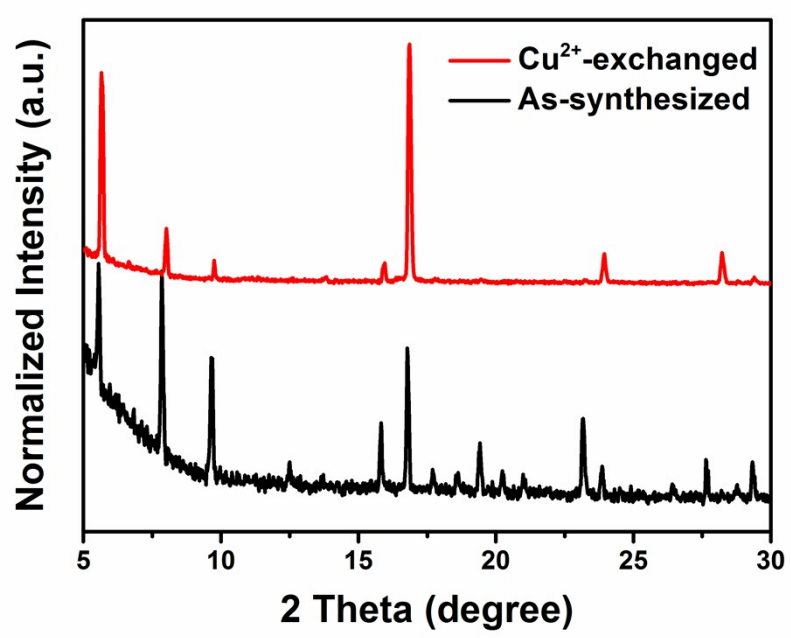

Figure S12. PXRD patterns of as-synthesized **MCOF-89** and Cu^{2+}-exchanged **MCOF-89**.

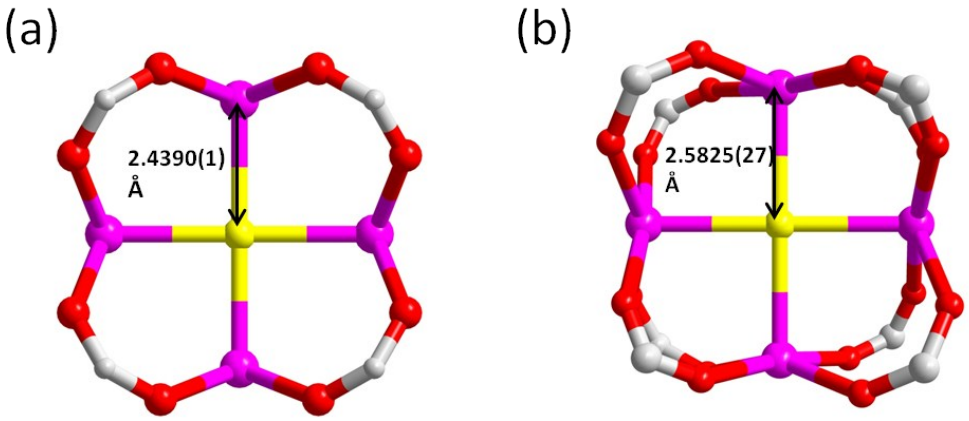

Figure S13. (a) The M-S bond lengths of pristine **MCOF-89;** and (b) the M-S bond lengths of Cu-exchanged **MCOF-89**.

Table S1. Crystal data and refinement results of **MCOF-89**.

	MCOF-89
Framework Formula	$C_{72}Mn_{12}O_{48}S_3$(no H?)
Formula weight	2388.18
Crystal morphology	cubic
Crystal system	cubic
Z	1
Space group	*Pm -3m*
T/K	296(2)
λ/ Å	0.71073
a/ Å	15.8573(6)
b/ Å	15.8573(6)
c/ Å	15.8573(6)
a/^{0}	90.00
β/^{0}	90.00
γ/^{0}	90.00
V(Å^3)	3987.4(5)
F(000)	3219
D(g cm^{-3})	0.995
μ (mm^{-1})	1.009
Collected reflections	11737
Independent reflections	741
GOF on F^2	1.019
R_1, wR_2 ($I > 2\sigma(I)$)	0.0347, 0.0980
R_1, wR_2 (all data)	0.0383, 0.1004

Table S2. C/H/N elemental analysis of Li^+ ion-exchanged **MCOF-89**.

Samples	C (%)	N (%)	H (%)	Exchange degree
Pristine **MCOF-89**	42.69	5.354	4.970	
0.1 M $LiNO_3$ exchanged	32.47	3.465	3.676	35.3%
0.5 M $LiNO_3$ exchanged	28.40	2.317	3.112	56.7%
1.0 M $LiNO_3$ exchanged	26.15	1.415	3.114	73.6%
1.5 M $LiNO_3$ exchanged	26.16	1.215	2.963	77.3%
2.0 M $LiNO_3$ exchanged	25.37	1.012	2.713	81.1%

Table S3. ICP-AES results of Cu^{2+} ion-exchanged samples after different exchange time.

Time	Mn : Cu	Formula	Exchange degree
1 days	3.15 : 0.85	$Cu_{0.85}Mn_{3.15}S$	21.2 %
2 days	2.59 : 1.41	$Cu_{1.41}Mn_{2.59}S$	35.2 %
3 days	2.25 : 1.75	$Cu_{1.75}Mn_{2.25}S$	43.7 %
7 days	0.94 : 3.06	$Cu_{3.06}Mn_{0.94}S$	76.5 %
10 days	0.62: 3.38	$Cu_{3.38}Mn_{0.62}S$	84.5%
12 days	0.51 : 3.49	$Cu_{3.49}Mn_{0.51}S$	87.3 %