Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

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Materials and General methods

Ligands 1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene (TCPBBr)[1] 4-((pyridin-4-ylthio) methyl) pyridine (**Ls**)[2] were synthesized following the procedures reported. 4,4 -Azopyridine and 4,4'-bipyridine were purchased from J&K Chemical Company. 4-Mercaptopyridine was purchased from Tokyo chemical industry. Sodium hydroxide was purchased from Tianjing Baishi Chemical Company. All organic reagents were used without further purification. ^{1}H NMR spectra was collected on a Bruker AVANCE III 600 spectrometer using deuterated dimethyl sulfoxide ($(CD_3)_2SO$-d_6) and deuterated chloroform ($CDCl_3$). Laboratory powder X-ray diffraction patterns (PXRD) of all complexes were collected on a Rigaku D/Max 2200 PC diffractometer with Cu Kα radiation (λ = 1.5418 Å) and graphite monochromator from 5° to 30°, scanning rate of 5.0° per min. The surface areas of all synthesized samples and CO_2 adsorption experiments were estimated and measured by the Brunauer−Emmett−Teller (BET) method with a Micromeritics instrument (ASAP 2020). Energy-dispersive X-ray spectroscopic (EDX) analysis was characterized by a field emission scanning electron microscopy (SEM, Hitachi S–4800). Solid-state FT-IR spectra were measured on a Bruker Tensor 37 spectrophotometer using the KBr pellets technique. Elemental analyses (C, H, N, S) were performed on an Elementar Vario EL analyzer. The metal ions ratios were measured using ICP-AES (Agilent 7500). Thermogravimetric measurements were obtained with a Bruker TG/DTA 2000 SA, using a heating rate of 5 ^{o}C/min in dry atmosphere.

General treatment of solid samples used for component analysis

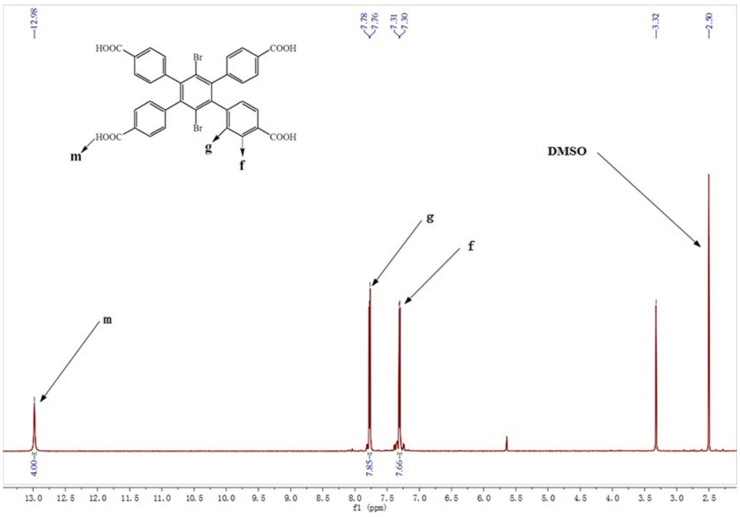
In this study, all solid samples used to ^{1}H NMR, FT-IR, elemental analysis and BET surface area measurement were pretreated as following standard procedure: The solids were soaked within methanol (8 mL) for 10 h, and then the solvent was removed and fresh methanol was used to continue the soaking. The repeated soaking was carried for five times to remove the residues such as reaction reagent DMF, organic ligands and metal salts absorbed on the surfaces or included within the pores of the solids. After the final wash, the powders were collected via centrifugation and were subjected to be heated at 100 ^{o}C under vacuo for 12 hours, yielding the desolvated solids for further analysis and experiments.

^{1}H NMR study on complexes MOF-A, MOF-B, MOF-A/S and MOF-B/S were carried out *via* the same procedure as following: about 5mg of each desolvated sample was dissolved in 0.6 ml d_6-DMSO and 2 drops of D_2SO_4. The suspension was subjected to sonication. Once a homogeneous solution was obtained, the sample was transferred to an NMR tube for ^1H NMR test.

EXPERIMENTAL SECTION

Synthesis of 1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene (TCPBBr)[1]

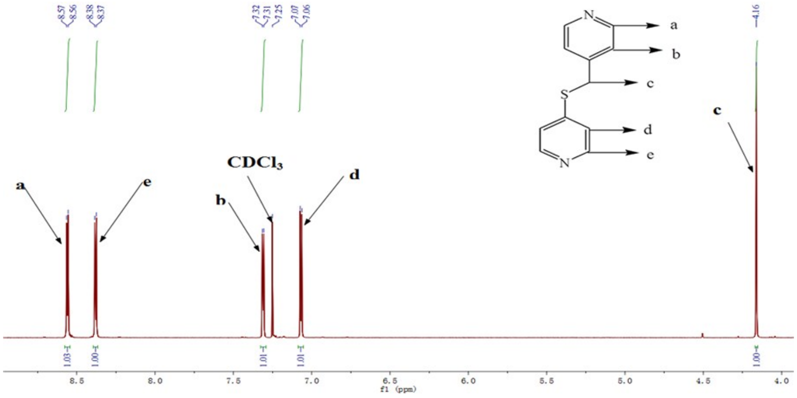
100 ml of p-tolylmagnesium bromide (1M in THF, 100 mmol) was added under nitrogen to a flask containing 5g of hexabromobenzene (9.07 mmol). The mixture was stirred at room temperature for 15 hours (gray suspension). Then, the reaction was placed on an ice-bath, to which a mixture of 7ml bromine and 60ml CCl_4 in an addition funnel was then added dropwise. The reaction was stirred at room temperature for 1.5 h and then poured on ice, which was followed by the addition of 50 ml of 6M HCl. Solid product was achieved, filtered and washed with methanol. Isolated yield: 2 g, 38 %. Then the solid product was placed in a 100 ml teflon lined vessel, to which 24 ml water and 6 ml HNO_3 were subsequently added. The vessel was sealed and heated at 180℃ for 24 hrs. The solid TCPBBr was collected by filtration and washed with THF/$CHCl_3$ (7:3). Yield: 1.5g. ^1H NMR (d_6-DMSO): δ=7.31 (d, 8H), δ=7.78(d, 8H), δ=12.98 (s, 4H) ppm. $C_{34}H_{20}Br_2O_8$ (715.80). ^1H NMR spectrum of TCPBBr in d_6-DMSO is shown as following:

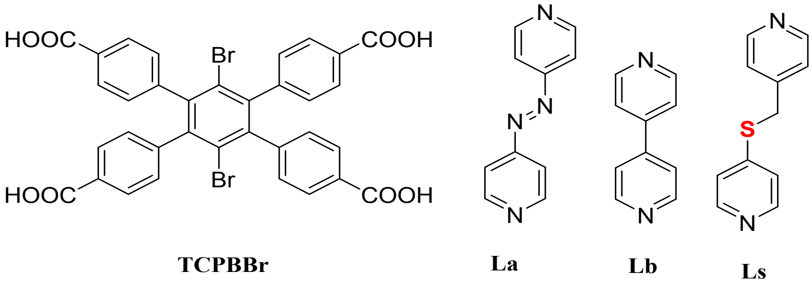


Synthesis of 4-((pyridin-4-ylthio) methyl) pyridine (Ls)[2]

4-(Chloromethyl) pyridine hydrochloride (984 mg, 6mmol), pyridine-4-thiol (666 mg, 6mmol), sodium hydroxide (800 mg, 20mmol) and 50ml anhydrous ethanol were added to 100 mL two-neck flask equipped with a magnetic stirring bar. The reaction mixture was refluxed at 80 °C under

N_2 for 20 h. After cooling down, the reaction mixture was filtered to remove the insoluble substance. After that, the solvents were removed with a rotary evaporator and the yellowish residue was washed extensively with water and dichloromethane. The organic layer was separated, dried with anhydrous magnesium sulfate, and concentrated in a vacuum. The crude product was purified by flash chromatography on silica gel, using a 56-mm inner diameter column containing 250 cm^3 of silica gel under a positive pressure of lab air, with ethyl acetate : methanol (4:1) as eluent to provide brown oily liquid product (738 mg, 61% yield). ^1H NMR (600M Hz, $CDCl_3$): δ = 8.57（d, 2 H）, δ = 8.38（d, 2H,）, δ = 7.32（d, 2 H,）, δ = 7.07（d, 2 H,）, δ = 4.16(s, 2 H,) ppm. $C_{11}H_{10}N_2S$ (202.29), as following shown:





Scheme 1. Ligands TCPBBr, **La**, **Lb** and **Ls** used in this study.

Synthesis of MOF-A and MOF-B

MOF-A was obtained following the reported procedure by heating TCPBBr (214.8mg, 0.3mmol), **La** (55.2mg, 0.3mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (178.2mg, 0.6mmol) in 30 mL of DMF with three drops of concentrated HCl.[1] This solution was divided equally between five 6-dram screw cap vials and heated to 80 °C for 5 days, at which time clear orange block crystals MOF-A has formed. MOF-A crystals were collected and washed with DMF, the solid was collected and further soaked within methanol (8 mL) for 10 h, and then the solvent was removed and fresh methanol was used to continue the soaking. The repeated soaking was carried for five times to remove the residues such as reaction reagent DMF, organic ligands and metal salts absorbed on the surfaces or included within the pores of the solids. After the final wash, the powders were collected via centrifugation and were subjected to be heated at 100 ^oC under vacuo for 12 hours, yielding the desolvated solid. The resulted solid was characterized via elemental analysis, powder X-ray diffraction, FT-IR spectra and BET surface areas measurement, and further used as parent material for following experiment. Elemental analysis: Found C (50.94%), H (2.32%), N (5.45%) [Calcd. C (51.30%), H (2.34%), N (5.45%)], inferring a formula $C_{44}H_{24}O_8N_4Br_2Zn_2$ corresponding to a Zn_2·TCPBBr·**La** component. MOF-B was obtained through a procedure similar to that for MOF-A by using **Lb** instead of **La** ligand, which is not verbose descripted here. MOF-B was also characterized *via* elemental analysis, FT-IR, PXRD, BET surface area measurements which are shown in the following context. Elemental analysis found: C (52.47%), H (2.51%), N (2.65%) [Calcd. C(52.87%), H (2.40%), N (2.80%)], inferring a formula $C_{44}H_{24}O_8N_2Br_2Zn_2$.

Solvent-assisted ligand exchange synthesis of MOF-A/S (Zn_2TCPBBr·0.4La·0.6Ls)

MOF-A/S was synthesized via solvent-assisted ligand exchange method with ligand **Ls** as an external exchange reactant. Reaction temperature exhibited no obvious effect on the ligand exchange ratio. However, reaction time, reactant concentration and solvent medium exhibited apparent influence on the solvent-assisted ligand exchange reaction of the dynamic exchange process. A high concentration of **Ls** and a long reaction time will increase the ligand exchange ratio. As **Ls** (57 mg, 0.28 mmol) and desolvated MOF-A (72 mg, 0.07 mmol) (based on the formula Zn_2TCPBBr·**La**) were added to 2mL DMF in a sealed glass tube with stirring at 25 ˚C, the progress of the linker exchange reaction was monitored by ^1H NMR. After 1 day, 3 days and 8 days, the solid samples in different reaction time were collected through centrifugation and washed with DMF (80ml), respectively. Each solid was collected and further immersed in 10 mL DMF with fluxing for 8 hour to remove **Ls** and **La** that may be enclosed within the pores of MOF. The treated solid was further soaked within methanol (8 mL) for 10 h, and then the solvent was removed and fresh methanol was used to continue the soaking. The repeated soaking was carried five times to remove the residues such as reaction reagent DMF, organic ligands and metal salts absorbed on the surfaces or included within the pores of the solids. After the final wash, the powders were collected via centrifugation and were subjected to be heated at 100 ^oC under vacuo for 12 hours. The collected solids were characterized via ^1H NMR spectra, FT-IR, surface area BET, PXRD, element analysis, and SEM and EDX measurements. ^1H NMR showed the sample of 8 days with 60% percent of the pillar **La** ligands replaced by **Ls** with a formula $Zn_2TCPBBr\cdot 0.4$**La**$\cdot 0.6$**Ls**, being consistent with the elemental analysis found: C (51.70%), H (2.40%), N (3.75%), S (1.80%) [Calcd. C (51.45%), H (2.43%), N (3.78%), S (1.85%), based on the $Zn_2TCPBBr\cdot 0.4$**La**$\cdot 0.6$**Ls** component and $C_{44.6}H_{25.2}O_8N_{2.8}S_{0.6}Br_2Zn_2$ formula]. Elevated temperature and more lengthened time exhibited no obvious influence on the final exchange ratio. The following photography show the solution color changed within glass tubes at reaction beginning, 1 day, 3 days and 8 days which are labeled as 1, 2, 3 and 4, respectively.

MOF-B/S complex was obtained by use of the similar approach as that for MOF-A/S, which is not verbosely descripted herein. **Ls** (57 mg, 0.28 mmol), desolvated MOF-B (70 mg, 0.07 mmol).

Heavy metal ion uptake study of MOF-A/S material

The Hg^{2+} uptake capacity of a MOF-A/S sample from a $HgCl_2$ methanolic solution from 10 ppm to 289 ppm was conducted and determined via a similar procedure as following. The desolvated MOF-A/S solid was allowed to soak undisturbedly in $HgCl_2$ methanolic solution at room temperature for 2 weeks. The mixture was then suction-filtered, and the Hg-loaded solid was washed with 3×10 mL of methanol to remove the Hg^{2+} absorbed on the solid surface, giving a Hg^{2+}-loaded product. For the $HgCl_2$ concentration of 289 ppm case, the resulted solid was subjected to elemental analysis which found: C (46.87%), H (2.13%) and N (3.66%), agreeing well with the calculated values of C (46.92%), H(2.21%) and N(3.44%) based on the

$Zn_2TCPBBr \cdot 0.4\mathbf{La} \cdot 0.6\mathbf{Ls} \cdot (HgCl_2)_{0.38}$ formula. In comparison, Hg^{2+}-uptake of the MOF-A material was also conducted following the same condition as that for MOF-A/S. Each solid sample was collected and further dissolved in HNO_3 aqua and subjected to the regular ICP (Agilent 7500 Ce, inductively coupled plasma) component analyses. The ICP measured and calculated data of the mercury uptake tests are listed in table S1.

Table S1. Hg^{2+} adsorption capacity of MOF-A/S and MOF-A in different $HgCl_2$ concentrations through ICP analyses.

	Initial Hg^{2+} concentration (C_0) (ppm)	After adsorption Hg^{2+}concentration (C_e) (ppm)	$[Zn^{2+}]/[Hg^{2+}]$ of Hg^{2+}-loaded sample (ng/ml)	Zn : Hg molar ratio	Hg^{2+}adsorption capacity (mg g^{-1}) (q_e)	Hg^{2+} removal Efficiency
MOF-A/S	10	0.286	128.437/9.236	42.8:1	9.236	96.99%
	20	0.793	127.427/18.45	21.251:1	18.45	95.87%
	40	1.976	122.521/32.043	11.765:1	32.043	94.19%
	60	5.754	129.405/59.476	6.695:1	59.476	91.17%
	80	8.89	127.279/75.05	5.218:1	75.05	89.5%
	100	31.493	128.136/75.658	5.211:1	75.658	70.6%
	200	122.684	128.518/76.052	5.20:1	76.052	38.26%
	289	207.493	133.913/78.601	5.258:1	78.831	27.53%
MOF-A	10	9.23	127.343/0.343	1142.3:1	0.343	3.58%
	40	37.804	125.592/1.432	269.86:1	1.432	3.64%
	80	77.52	128.663/1.135	348.8:1	1.135	1.44%
	200	195.818	128.047/2.511	156.91:1	2.511	1.26%
	289	286.194	130.265/2.072	193.44:1	2.072	0.72%

Water stability of MOF-A/S and its secondary adsorption of Hg^{2+} test

Hg^{2+}-loaded MOF-A/S sample was suspended in boiling water with stirring for 5 days, and the solid was collected and isolated *via* centrifugation, obtaining the Hg^{2+}-depleted sample which showed the main framework remained intact. ICP measurement of the solid sample washed *via* deionized water revealed the molar ratio of Zn : Hg = 383.038:1, and then was subjected to be immersed again within $HgCl_2$ solution (289 ppm) for 2 weeks. Table S2 shows the ICP measurements of the solids of Hg^{2+}-depleted MOF-A/S, MOF-A and reused MOF-A/S soaked in $HgCl_2$ (289 ppm).

Table S2. Zn^{2+} and Hg^{2+} components of Hg^{2+}-depleted MOF-A/S, MOF-A and reused MOF-A/S soaked in $HgCl_2$ (289 ppm).

Entry	Hg^{2+}-depleted MOF-A/S	Hg^{2+}-loaded second MOF-A/S	MOF-A soaked in $HgCl_2$
Initial Hg^{2+} concentration	Boiling H_2O	289 ppm	289 ppm
Zn (ng/ml)	128.471	126.324	129.437
Hg (ng/ml)	1.032	69.433	0.945
Zn : Hg molar ratio	383.038:1	5.598:1	421.447:1

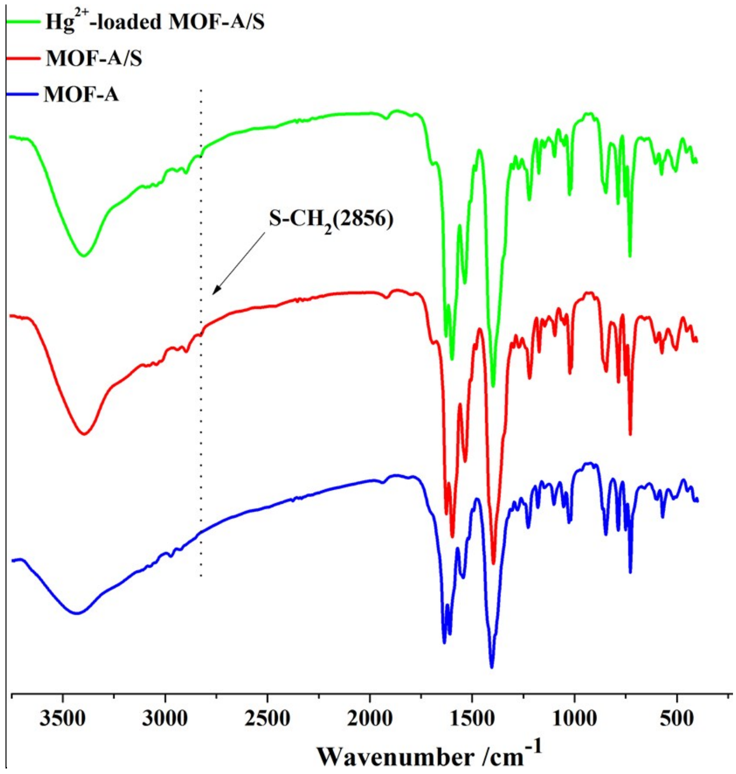
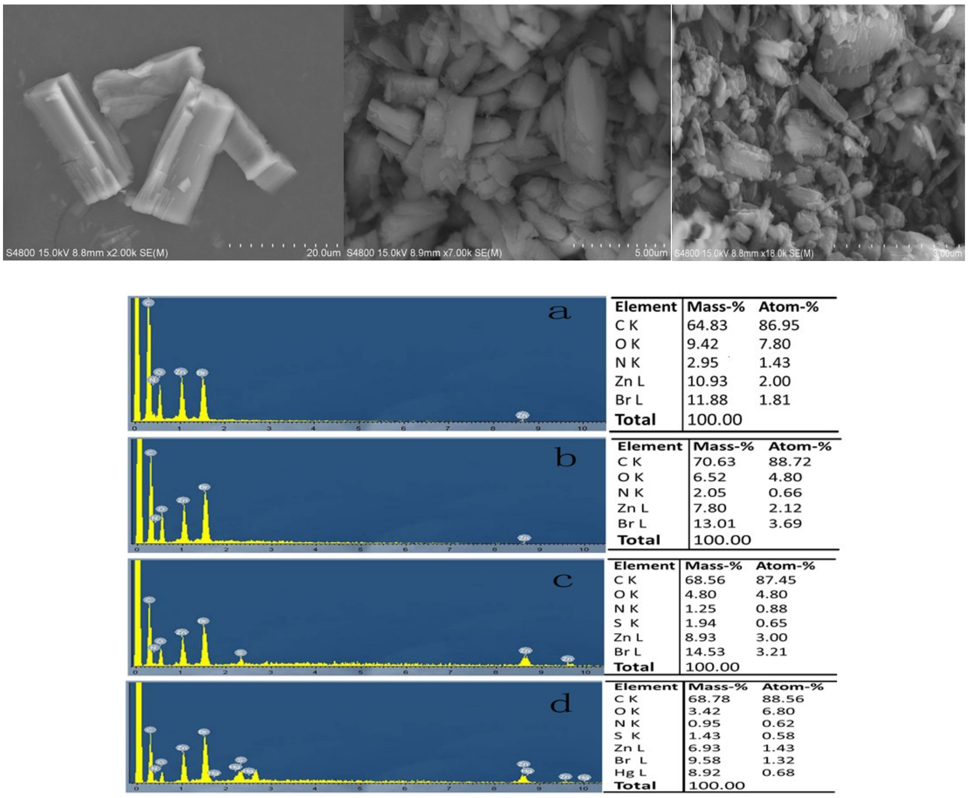


Figure S1. FT-IR spectra of MOF-A, MOF-A/S and Hg^{2+}-loaded MOF-A/S.



Element	Mass-%	Atom-%
C K	64.83	86.95
O K	9.42	7.80
N K	2.95	1.43
Zn L	10.93	2.00
Br L	11.88	1.81
Total	100.00	

Element	Mass-%	Atom-%
C K	70.63	88.72
O K	6.52	4.80
N K	2.05	0.66
Zn L	7.80	2.12
Br L	13.01	3.69
Total	100.00	

Element	Mass-%	Atom-%
C K	68.56	87.45
O K	4.80	4.80
N K	1.25	0.88
S K	1.94	0.65
Zn L	8.93	3.00
Br L	14.53	3.21
Total	100.00	

Element	Mass-%	Atom-%
C K	68.78	88.56
O K	3.42	6.80
N K	0.95	0.62
S K	1.43	0.58
Zn L	6.93	1.43
Br L	9.58	1.32
Hg L	8.92	0.68
Total	100.00	

Figure S2. SEM pictures (top) of MOF-A, MOF-A/S and Hg^{2+}-loaded MOF-A/S (from left to right), and EDX analyses (bottom) of MOF-based materials: a) MOF-A, b) Hg^{2+}-treated MOF-A, c) MOF-A/S and d) Hg^{2+}-loaded MOF-A/S.

Figure S3. Photography of MOF-A, MOF-A/S and Hg^{2+}-loaded MOF-A/S solid.

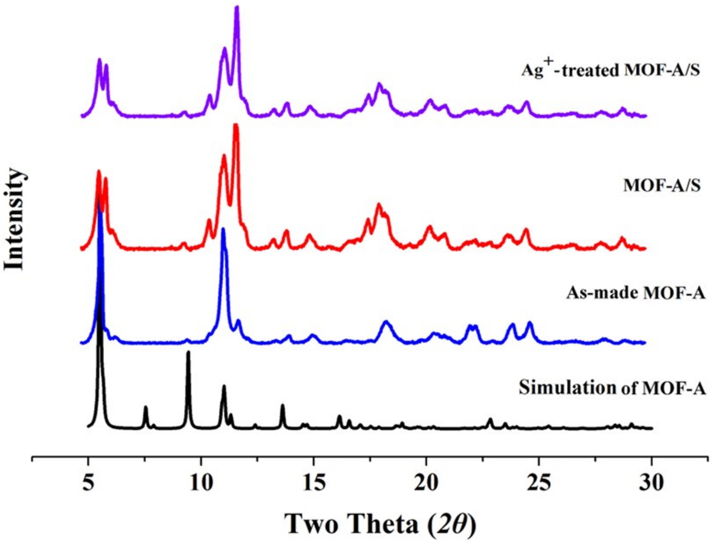


Figure S4. PXRD patterns of MOF-A, MOF-A/S and Ag$^+$-treated samples by soaking MOF-A/S within $AgBF_4$ DMF solution for 2 weeks.

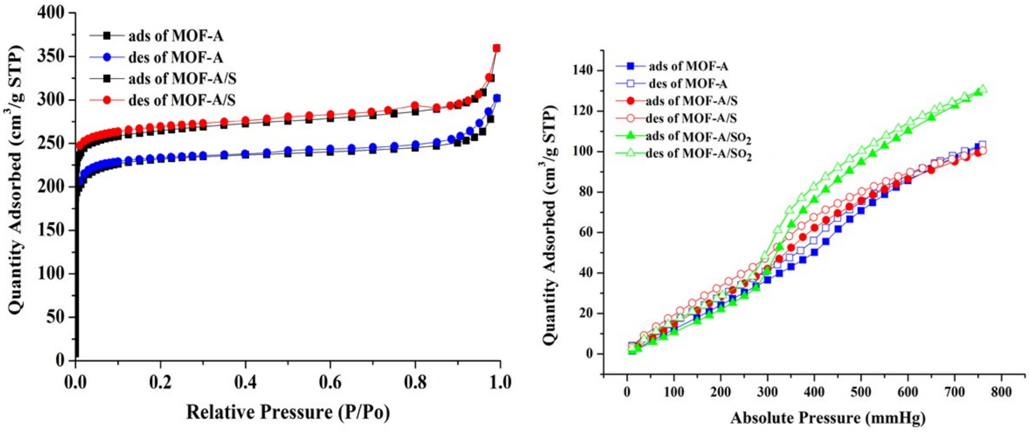


Figure S5. N_2 adsorption isotherm at 77 K of MOF-A and MOF-A/S (left) and CO_2 adsorption isotherm at 273 K of them together with that of MOF-A/SO_2 (right).

Table S3. BET surface area and pore volume measurements of MOF-A, MOF-A/S and MOF-A/SO_2 in comparison.

Entry	MOF-A	MOF-A/S	MOF-A/SO_2
BET Surface Area (m^2/g)	912.0684	1059.9935	890.2531
Pores Volume(cm^3/g)	0.313646	0.353227	0.292074
Langmuir Surface Area(m^2/g)	976.7648	1171.6541	948.4598

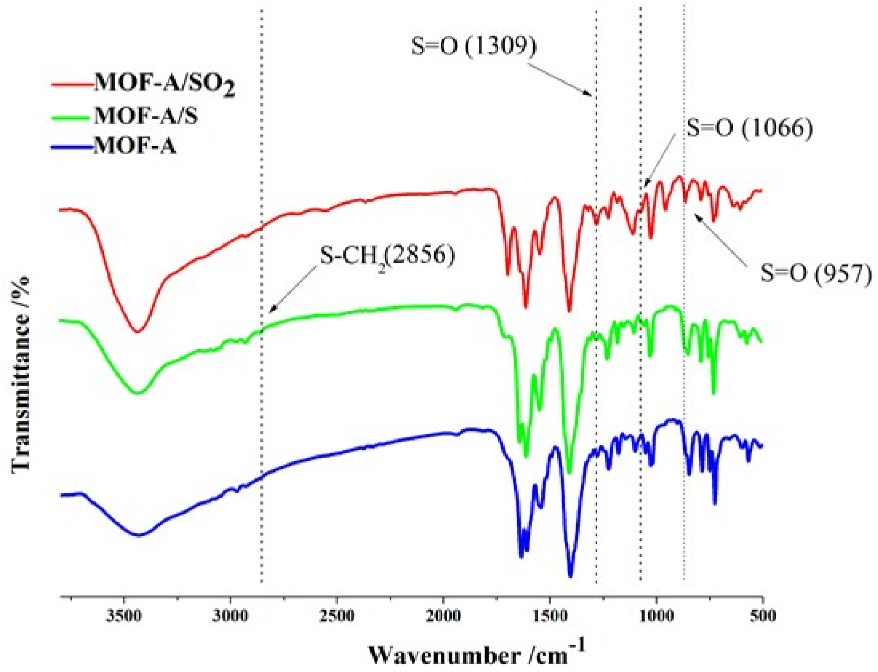


Figure S6 FT-IR spectra of MOF-A, MOF-A/S and MOF-A/SO$_2$.

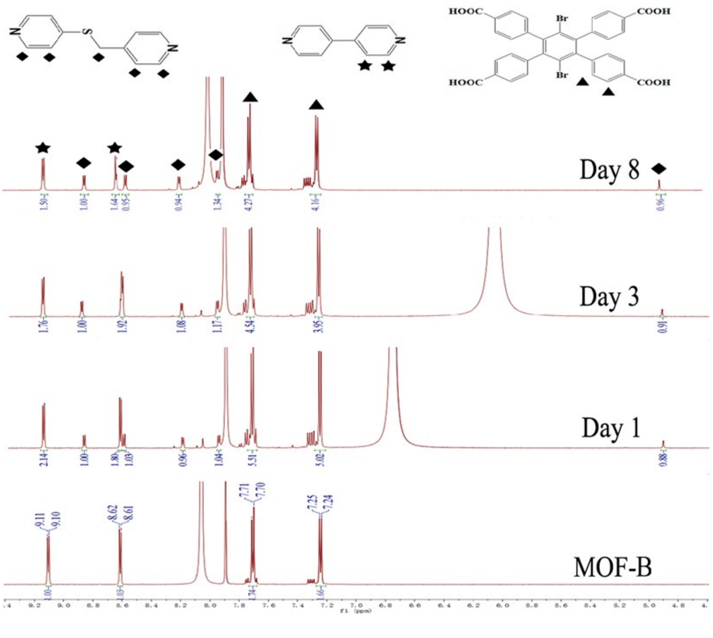


Figure S7 ^{1}H NMR spectroscopy (D_2SO_4/d_6-DMSO, 25℃): parent MOF-B material, reaction with **Ls** after 1 day (10% exchange), 3 day (30% exchange), 5 day (40% exchange), 8 day (50% exchange).

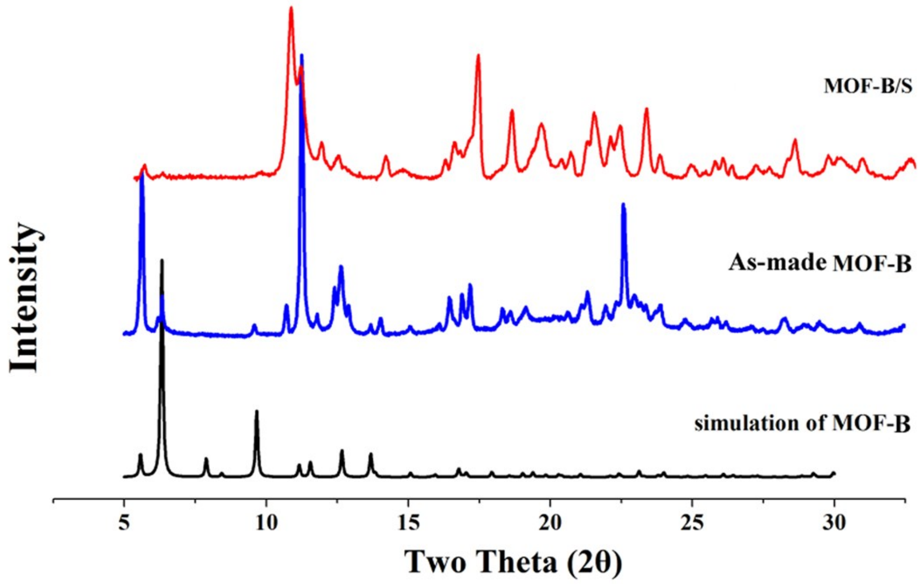


Figure S8. PXRD patterns of simulation mode of MOF-B, as-made MOF-B and MOF-B/S.

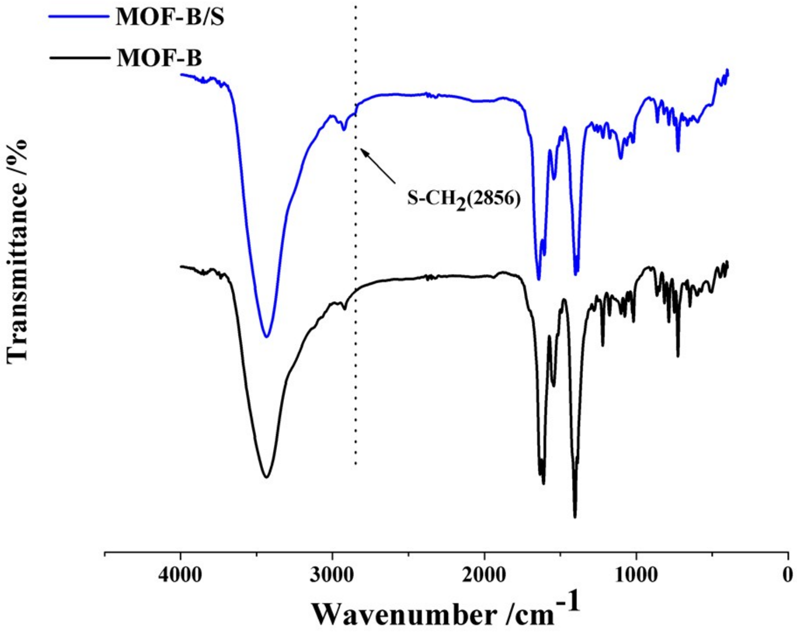


Figure S9. FT-IR spectra of MOF-B and MOF-B/S.

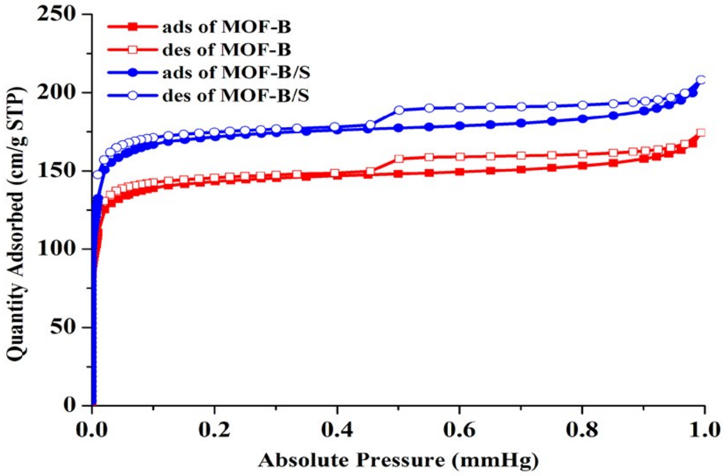


Figure S10. N_2 adsorption isotherm at 77 K of MOF-B and MOF-B/S.

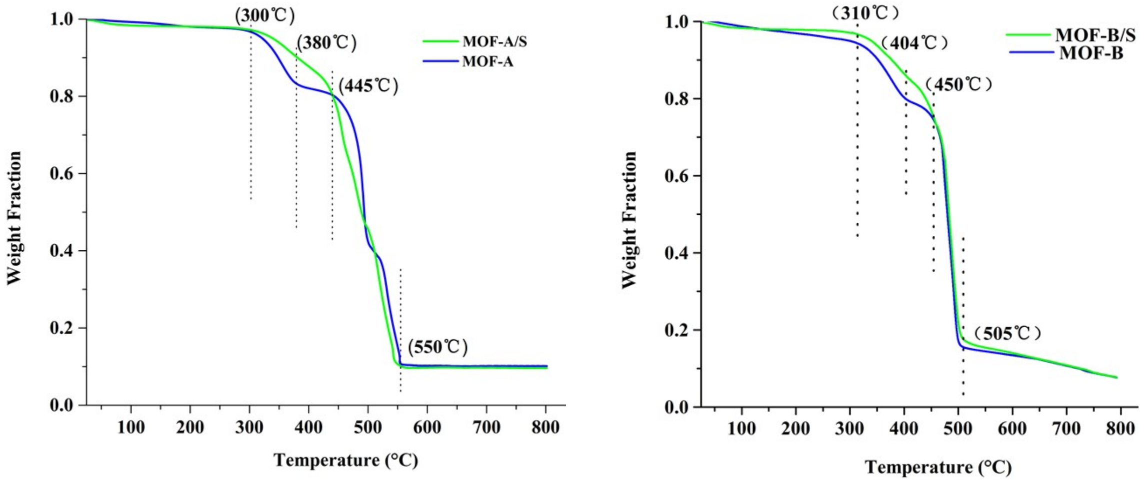


Figure S11. Thermogravimetric characterization curves of desolvated MOF-A, MOF-B, MOF-A/S and MOF-B/S.

Table S4. BET surface area and pore volume measurements of MOF-B and MOF-B/S.

Entry	MOF-B	MOF-B/S
BET Surface Area (m^2/g)	603.0902	724.2615
Pores Volume(cm^3/g)	0.269695	0.321997
Langmuir Surface Area(m^2/g)	598.7134	745.7331

Reference:

1. O. K. Farha, C. D. Malliakas, M. G. Kanatzidis, J. T. Hupp, *J. Am. Chem. Soc*. 2010,132, 950–952.

2. Wen-Hua Chen, Hao-Jie Yan, Hui Chen, Rui-Heng Liu, Ai-Min Li, Guo Wang, Chong-Qing Wan, *J. Solid State Chem.* 2017, 250, 24–31.