

Supporting Information for HPLC Enantioseparation on Homochiral MOF–Silica Composite as a Novel Chiral Stationary Phase

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Materials

(*R*)-1,1'-binaphthyl-2,2'-dihydroxy-6,6'-dicarboxylic acid **1** was prepared using previously reported method.¹ (*R*)-1,1'-binaphthyl-2,2'-dimethoxy-6,6'-dicarboxylic acid **2** was prepared using previously reported method.² Phenyl methyl sulfoxide **3** and phenyl vinyl sulfoxide **5** were purchased from Tokyo Kasei Kogyo co., ltd. Phenyl ethyl sulfoxide **4**, 2-methylphenyl methyl sulfoxide **6**, 4-methylphenyl methyl sulfoxide **7**, 2-methoxyphenyl methyl sulfoxide **8**, 4-methoxyphenyl methyl sulfoxide **9**, 2-nitrophenyl methyl sulfoxide **10**, 4-hydroxyphenyl methyl sulfoxide **11**, 2-chlorophenyl methyl sulfoxide **12**, 3-chlorophenyl methyl sulfoxide **13**, 4-chlorophenyl methyl sulfoxide **14**, 2-bromophenyl methyl sulfoxide **15**, 3-bromophenyl methyl sulfoxide **16**, 4-bromophenyl methyl sulfoxide **17**, benzyl methyl sulfoxide **18**, benzyl phenyl sulfoxide **19**, 2-naphthyl methyl sulfoxide **20**, cyclohexyl methyl sulfoxide **21**, *n*-butyl methyl sulfoxide **22**, *t*-butyl methyl sulfoxide **23**, *n*-octyl methyl sulfoxide **24** and 4-hydroxybutyl methyl sulfoxide **25** were prepared as reported.³ 1-phenylethyl alcohol **26**, 1-phenylethyl alcohol **26**, 1-phenyl-1-propanol **27**, 1-phenyl-1-butanol **28**, 1-phenyl-1-hexanol **29**, 1-(*p*-methylphenyl)ethanol **30**, 4-bromo- α -methylbenzyl alcohol **33**, 4-fluoro- α -methylbenzyl alcohol **35**, 2-chloro- α -methylbenzyl alcohol **36**, 3-chloro- α -methylbenzyl alcohol **37**, 4-chloro- α -methylbenzyl alcohol **38**, 1-phenylethane-1,2-diol **39**, 2-methylbenzhydrol **40**, 4-methylbenzhydrol **41**, 4-chlorobenzhydrol **44** and 1-hydroxyindan **45** were purchased from Tokyo Kasei Kogyo co., ltd. 1-(*p*-methoxyphenyl)ethanol **32**, 1-(*m*-fluorophenyl)ethanol **34**, *m*-chlorobenzhydrol **43** were purchased from Wako Pure chemical Industries, ltd. *o*-Chlorobenzhydrol **42** was purchased from Aldrich. 1-(*p*-Ethylphenyl)ethanol **31** and 11H-benzo[b]fluoren-11-ol **46** were prepared by NaBH₄ reduction of *p*-ethylacetophenone and 11H-benzo[b]

fluoren-11-one, respectively. α -[(Phenylamino)methyl]-benzeneethanol was prepared using previously reported method.⁴ 4-Benzoyloxy-2-azetidinone **48** and 2-azabicyclo[2.2.1]hept-5-en-3-one **55** were purchased from Tokyo Kasei Kogyo co., ltd. Mandelamide **56** was purchased from Wako Pure chemical Industries, ltd. 4-Phenylazetidin-2-one **49**, 4-(2-chlorophenyl)-azetidin-2-one **50**, 4-(3-chlorophenyl)-azetidin-2-one **51**, 4-(4-chlorophenyl)-azetidin-2-one **52**, 4-(4-fluorophenyl)-azetidin-2-one **53**, 4-(4-bromophenyl)-azetidin-2-one **54** were prepared using previously reported method.⁵ Benzoin **57**, 4,4'-dimethylbenzoin **58**, anisoin **59**, 2-chloro-2-phenylacetophenone **60**, benzoin methyl ether **61**, 2,2'-thenoin **62**, flavanone **63** and *trans*-stilbene oxide **68** were purchased from Tokyo Kasei Kogyo co., ltd. 7-Methoxyflavanone **64**, 7-chloroflavanone **65**, 4'-methoxyflavanone **66** and 4'-chloroflavanone **67** were prepared using previously reported method.⁶

Synthesis of (*R*)-CuMOF-1

(*R*)-CuMOF-1⁷ was prepared and characterized according to the previously reported method.

Synthesis of (*R*)-ZnMOF-1

A solution of *N*-methylformamide (NMF, 5 mL) and EtOH (1.5 mL) containing Zn(NO₃)₂•6H₂O (20 mg, 0.067 mmol) and (*R*)-1,1'-binaphthyl-2,2'-dihydroxy-6,6'-dicarboxylic acid (H₂BDA) **1**¹ (50 mg, 0.134 mmol) in a glass-tube was heated at 80°C for 24h. Colorless prisms were collected by filtration to yield (*R*)-ZnMOF-1, [Zn(BDA)(NMF)₂]•2NMF (46 mg). Similarly, (*S*)-ZnMOF-1 was prepared using (*S*)-**1**. The product was characterized by infrared and circular dichroism (CD) spectroscopy, thermogravimetric and X-ray analysis. IR (KBr pellet, cm⁻¹): 1656, 1623, 1541, 1475, 1410, 1336, 1244, 991, 954, 895, 819, 789. The enantiomeric nature of (*R*)- and (*S*)-ZnMOF-1 in the solid state was demonstrated by the solid-state CD spectra, which were almost mirrorimages of each other (Figure S1).

Synthesis of (*R*)-CuMOF-2

A solution of *N,N*-dimethylacetoamide (DMA, 2.0 mL) and H₂O (2.0 mL) containing Cu(NO₃)₂•3H₂O, (1.2 mg, 0.005 mmol) and (*R*)-1,1'-binaphthyl-2,2'-dimethoxy-6,6'-dicarboxylic acid (H₂BDMA) **2**² (2 mg, 0.005 mmol) in a

glass-tube was heated at 60°C for 48 h. Green prisms were collected by filtration to yield (*R*)-CuMOF-2, [Cu(BDMA)]•2DMA (2 mg). Similarly, (*S*)-CuMOF-2 was prepared using (*S*)-2. The product was characterized by infrared and circular dichroism (CD) spectroscopy, thermogravimetric and X-ray analysis. IR (KBr pellet, cm⁻¹): 1647, 1620, 1475, 1398, 1324, 1243, 1089, 1033, 788. The enantiomeric nature of (*R*)- and (*S*)-CuMOF-2 in the solid state was demonstrated by the solid-state CD spectra, which were almost mirrorimages of each other (Figure S2).

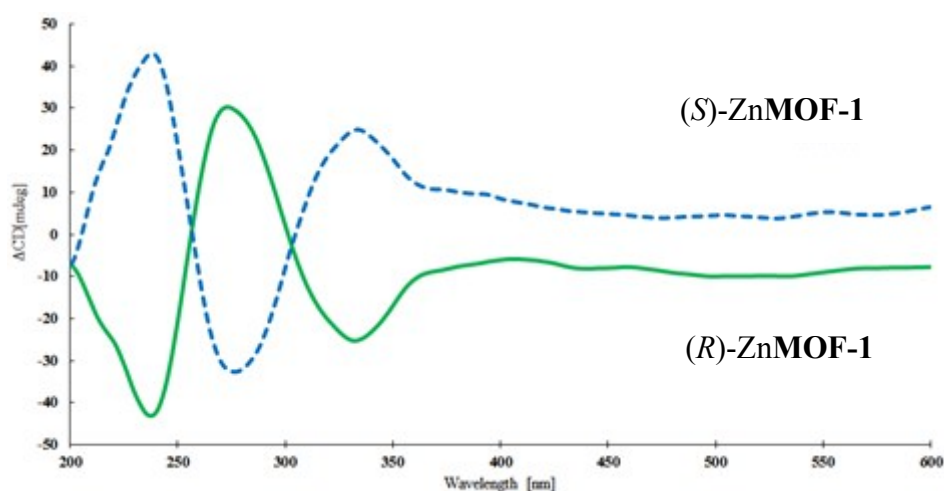


Figure S1. CD spectra for (*S*)-(blue) and (*R*)-ZnMOF-1 (green) in KBr.

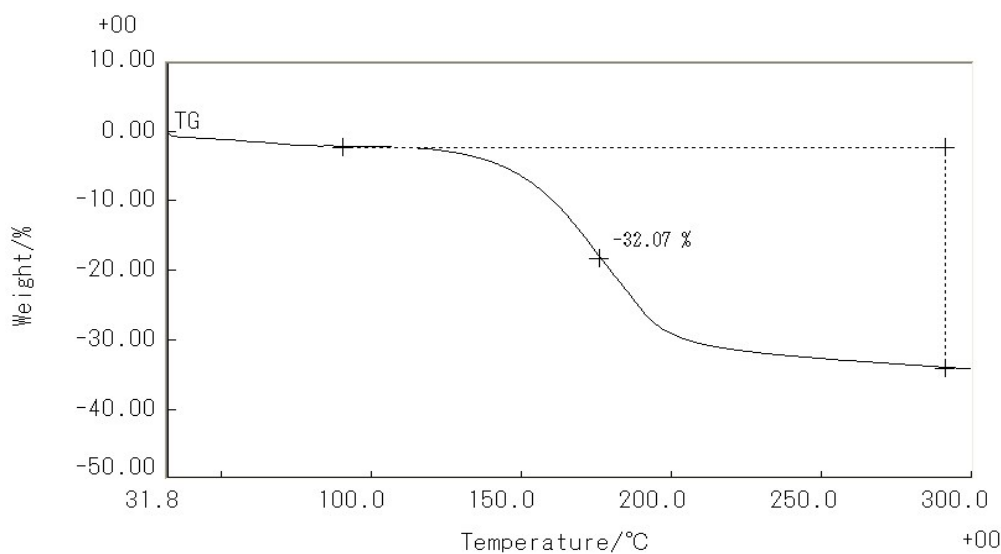


Figure S2. TGA curve of (*R*)-ZnMOF-1.

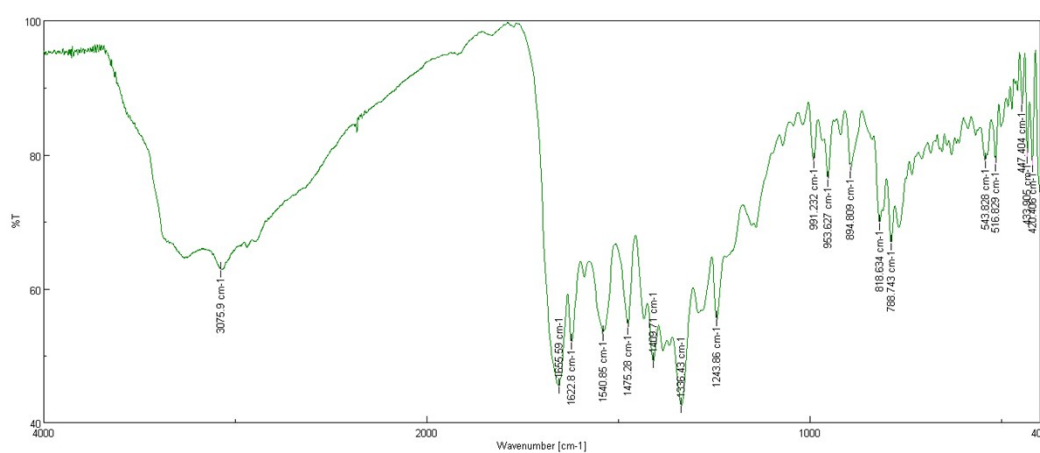


Figure S3. IR spectrum of (*R*)-ZnMOF-1.

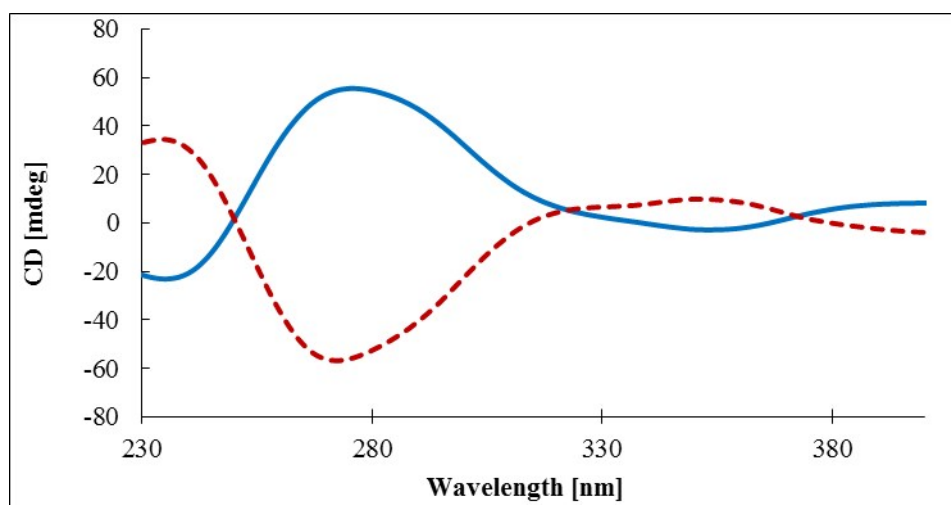


Figure S4. CD spectra for (*R*)- (blue) and (*S*)-CuMOF-2 (red) in KBr.

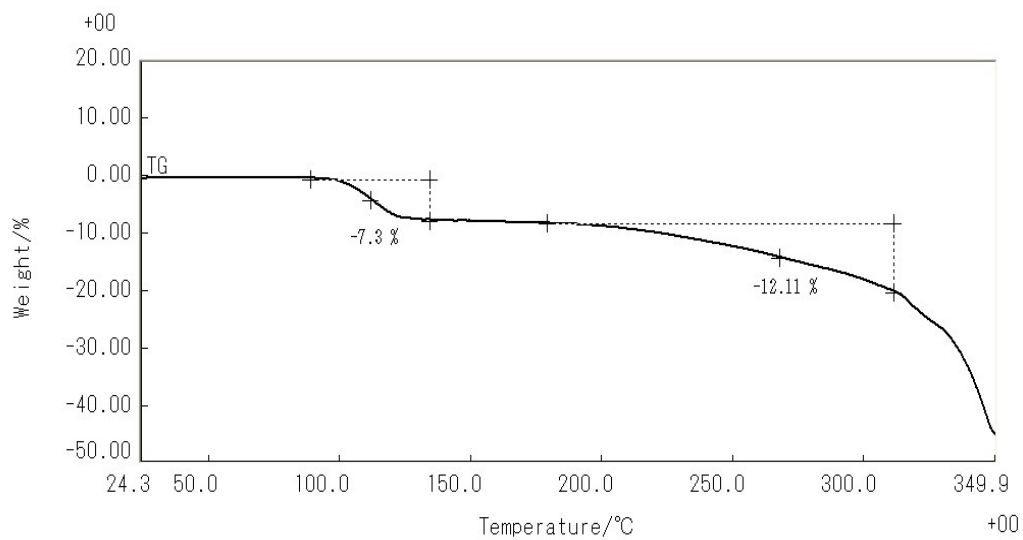


Figure S5. TGA curve of (R)-CuMOF-2.

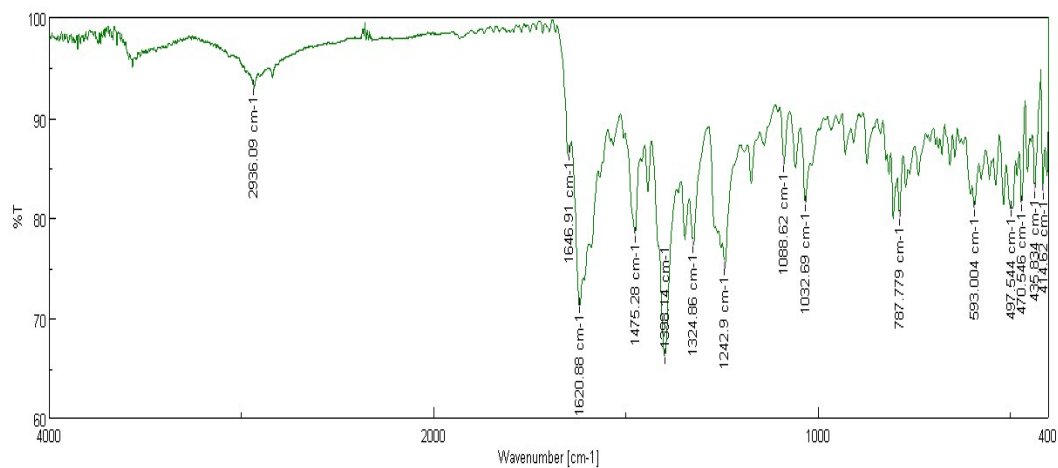


Figure S6. IR spectrum of (R)-CuMOF-2.

Synthesis of (R)-CuMOF-1-silica composite

(*R*)-CuMOF-1-silica composites were prepared according to the previously reported method.⁷

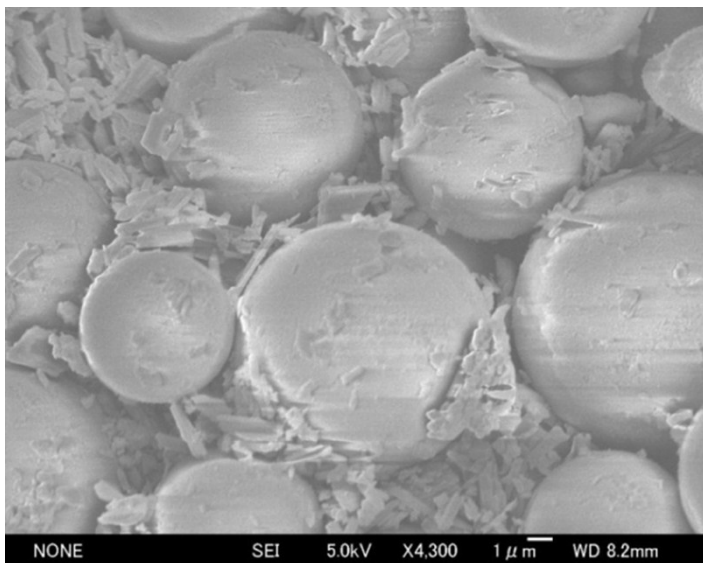


Figure S7. SEM image of (*R*)-ZnMOF-1-silica composite.

Synthesis of (*R*)-ZnMOF-1-silica composite

A mixture of (*R*)-1 (50 mg, 0.134 mmol), Zn(NO₃)₂•6H₂O (20 mg, 0.067 mmol) and Daisogel (SP-120-7P)(150 mg) in NMF (5 mL) and EtOH (1.5 mL) was stirred and heated at 80°C for 24 h. The resulting green precipitate was filtered and washed with DMF and MeOH, and dried *in vacuo* at 80°C. The yield is 210 mg.

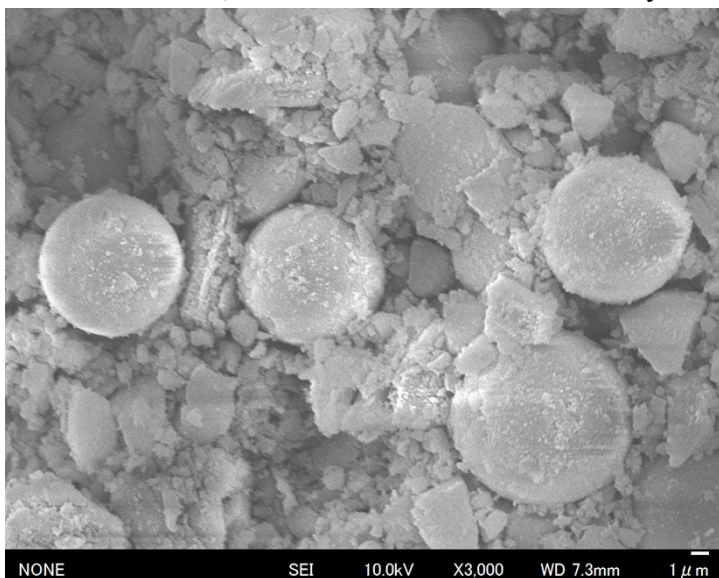


Figure S8. SEM image of (*R*)-ZnMOF-1-silica composite.

Synthesis of (*R*)-CuMOF-2-silica composite

A mixture of (*R*)-**2** (50 mg, 0.124 mmol), Cu(NO₃)₂•3H₂O (54 mg, 0.223 mmol) and Daisogel (SP-120-7P)(150 mg) in DEF (1.5 mL) and H₂O (0.5mL) was stirred and heated at 80°C for 18 h. The resulting green precipitate was filtered and washed with DMF and MeOH, and dried *in vacuo* at 80°C. The yield is 198 mg.

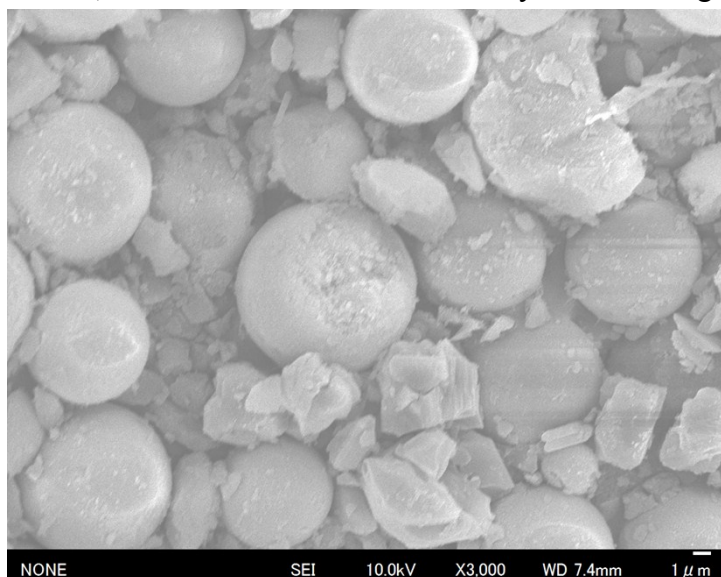


Figure S9. SEM image of (*R*)-CuMOF-**2**-silica composite.

Experimental for Powder X-ray Diffraction (PXRD)

X-ray powder diffraction measurements were recorded on a Rigaku RINT2100 diffractometer equipped with a Cu X-ray source operating at 40kV and 40mA and a secondary graphite monochromator allowing to select the K α radiation of Cu ($\lambda = 1.5418 \text{ \AA}$). A scanning range of 2θ values from 2° to 60° at a scan rate of $1^\circ/\text{min}$ was applied and the intensity of diffracted X-rays being collected at intervals of 0.01° .

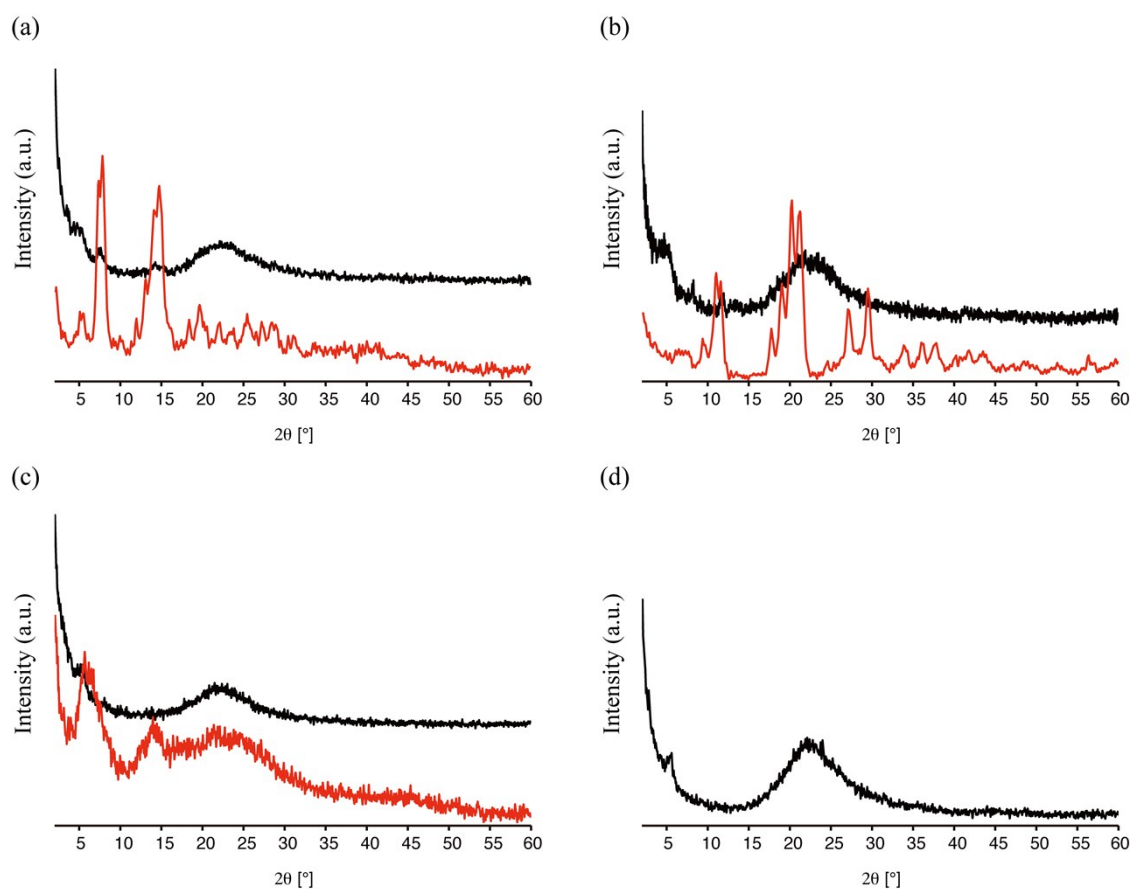


Figure S10. Powder X-ray diffraction patterns of (a) (*R*)-CuMOF-1 (red) and Silica-(*R*)-CuMOF-1 (black), (b) (*R*)-CuMOF-2 (red) and Silica-(*R*)-CuMOF-2 (black), (c) (*R*)-ZnMOF-1 (red) and Silica-(*R*)-ZnMOF-1 (black), and (d) Silica gel.

Experimental for BET surface area

Nitrogen adsorption measurements were performed on a Germini VII 2390p Analyzer at 77K using the volumetric method. The specific surface area was obtained from N₂ adsorption isotherms and was calculated by Brunauer-Emmett-Teller (BET method).

Table S1. BET surface area

Compound	Surface area (m ² /g)
(<i>R</i>)-CuMOF-1	17.2
Silica-(<i>R</i>)-CuMOF-1	236.2
(<i>R</i>)-CuMOF-2	27.4
Silica-(<i>R</i>)-CuMOF-2	280.2
(<i>R</i>)-ZnMOF-1	7.6
Silica-(<i>R</i>)-ZnMOF-1	228.2
Silica gel	241.2

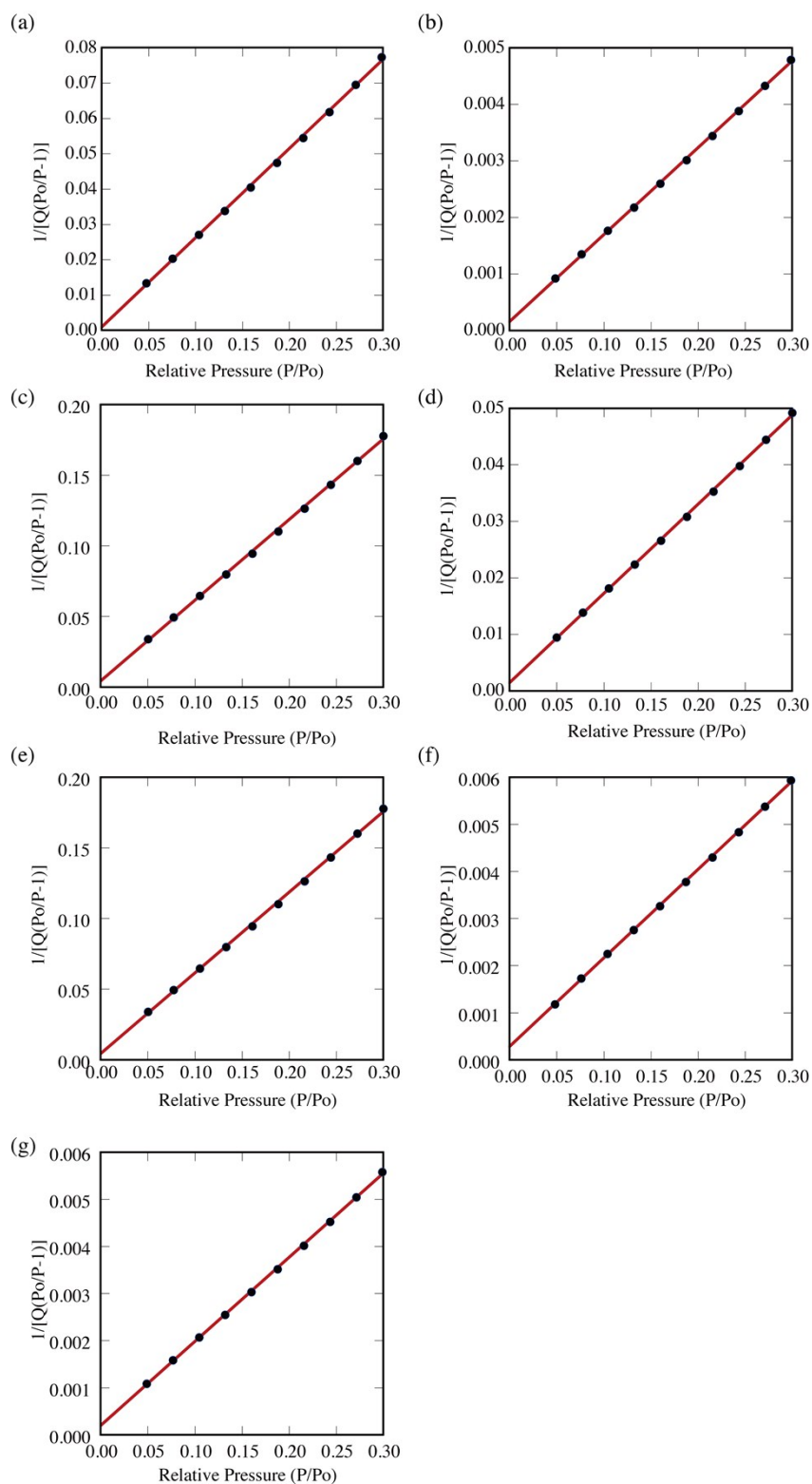


Figure S11. BET surface area plots of (a) R -CuMOF-1, (b) Silica- R -CuMOF-1, (c) R -CuMOF-2, (d) Silica- R -CuMOF-2, (e) R -ZnMOF-1, (f) Silica- R -ZnMOF-1, and (g) Silica gel

Single Crystal X-Ray Diffraction

X-ray diffraction data were collected on a Rigaku Saturn724+ CCD area detector diffractometer mounted on a $1/4 \chi$ goniometer [graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$); ω scans] with a Rigaku low-temperature equipment. Full data sets were measured at 100 K for (R)-ZnMOF-1 and (R)-CuMOF-2. All the structures were solved by direct methods using SIR97⁸ and refined on F^2 with all data using SHELXL2014.⁹ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically or using the riding model. All calculations were carried out using Yadokari XG2009¹⁰. Crystallographic data for the structures of (R)-ZnMOF-1 and (R)-CuMOF-2 reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1427406 and 1427405. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail deposit@ccdc.cam.ac.uk).

Crystal data for (R)-ZnMOF-1: C₃₀H₃₂N₄O₁₀Zn, $M = 673.96$, $a = 9.845(3) \text{ \AA}$, $b = 22.697(6) \text{ \AA}$, $c = 15.055(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 3364.1(16) \text{ \AA}^3$, $T = 100(2) \text{ K}$, space group $C2221$, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.788 \text{ mm}^{-1}$, 20470 reflections measured, 3848 independent reflections ($R_{int} = 0.0634$). The final R_I and $wR(F^2)$ values were 0.0280 ($I > 2\sigma(I)$) and 0.0541 ($I > 2\sigma(I)$), respectively. The final R_I and $wR(F^2)$ values were 0.0333 (all data) and 0.0551 (all data), respectively. The goodness of fit on F^2 was 0.865. Flack parameter = 0.008(7).

Crystal data for (R)-CuMOF-2: C₂₈H₂₆CuNO₈, $M = 568.04$, $a = 27.62(6) \text{ \AA}$, $b = 13.15(3) \text{ \AA}$, $c = 7.699(15) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 92.16(3)^\circ$, $\gamma = 90^\circ$, $V = 2794(10) \text{ \AA}^3$, $T = 100(2) \text{ K}$, space group $C2$, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.830 \text{ mm}^{-1}$, 10364 reflections measured, 5977 independent reflections ($R_{int} = 0.0717$). The final R_I and $wR(F^2)$ values were 0.0838 ($I > 2\sigma(I)$) and 0.2004 ($I > 2\sigma(I)$), respectively. The final R_I and $wR(F^2)$ values were 0.1377 (all data) and 0.2591 (all data), respectively. The goodness of fit on F^2 was 0.992. Flack parameter = 0.01(2).

References

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