Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for
Highly efficient chromatographic resolution of sulfoxides using a new homochiral MOF–silica composite

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Materials

Phenyl methyl sulfoxide **2** and phenyl vinyl sulfoxide **12** were purchased from Tokyo Kasei Kogyo co., ltd. Phenyl ethyl sulfoxide **3**, 2-methylphenyl methyl sulfoxide **4**, 4-methylphenyl methyl sulfoxide **5**, 2-methoxyphenyl methyl sulfoxide **6**, 4-methoxyphenyl methyl sulfoxide **7**, 2-chlorophenyl methyl sulfoxide **8**, 3-chlorophenyl methyl sulfoxide **9**, 4-chlorophenyl methyl sulfoxide **10**, 4-nitrophenyl methyl sulfoxide **11**, benzyl methyl sulfoxide **13**, benzyl phenyl sulfoxide **14**, 2-naphthyl methyl sulfoxide **15**, cyclohexyl methyl sulfoxide **16** and *n*-butyl methyl sulfoxide **17** were prepared as reported.[1]

***Synthesis of (R)-MOF, $Cu_2(BDA)_2$*:** The (*R*)-MOF was prepared by slightly modified method of the previously reported by W. Lin.[2] A DMF solution (1.5 mL) containing $Cu(NO_3)_2 \cdot 3H_2O$, (54 mg, 0.223 mmol) and (*R*)-(+)-H_2BDA (50 mg, 0.134 mmol) in a glass-tube was heated at 80°C for 18 h. Green needles were collected, washed with DMF, and MeOH, and dried *in vacuo* to yield (*R*)-MOF**,** $Cu_2(BDA)_2$ (53 mg). The CD spectra and PXRD pattern were identical with those previously reported by W. Lin.[2]

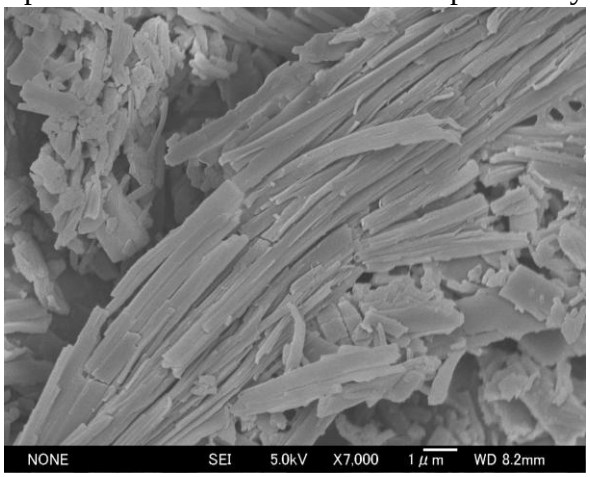


Figure S1. SEM image of (*R*)-MOF.

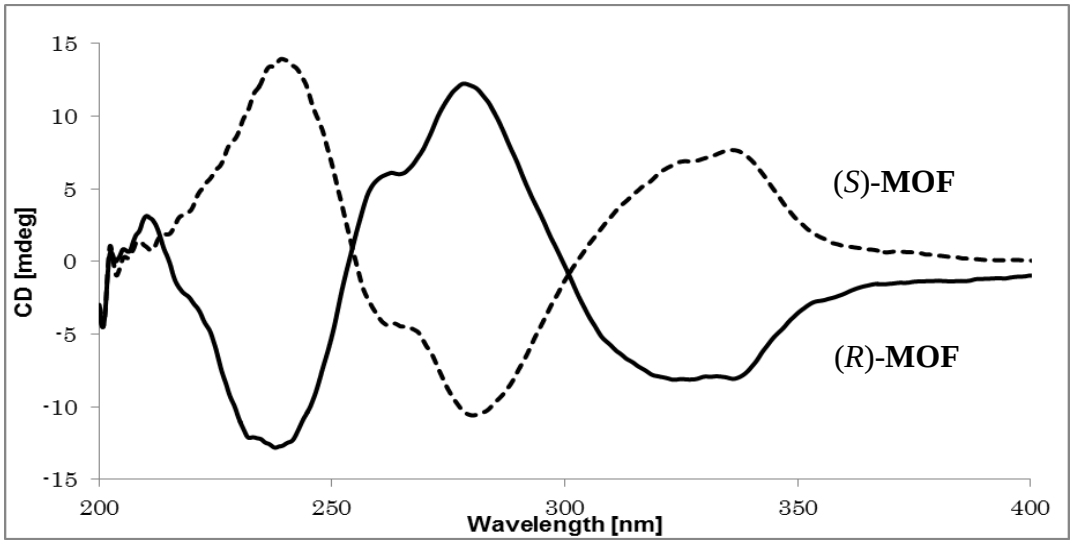


Figure S2. CD spectra for (*R*)-(blue) and (*S*)-MOF (green) in KBr.

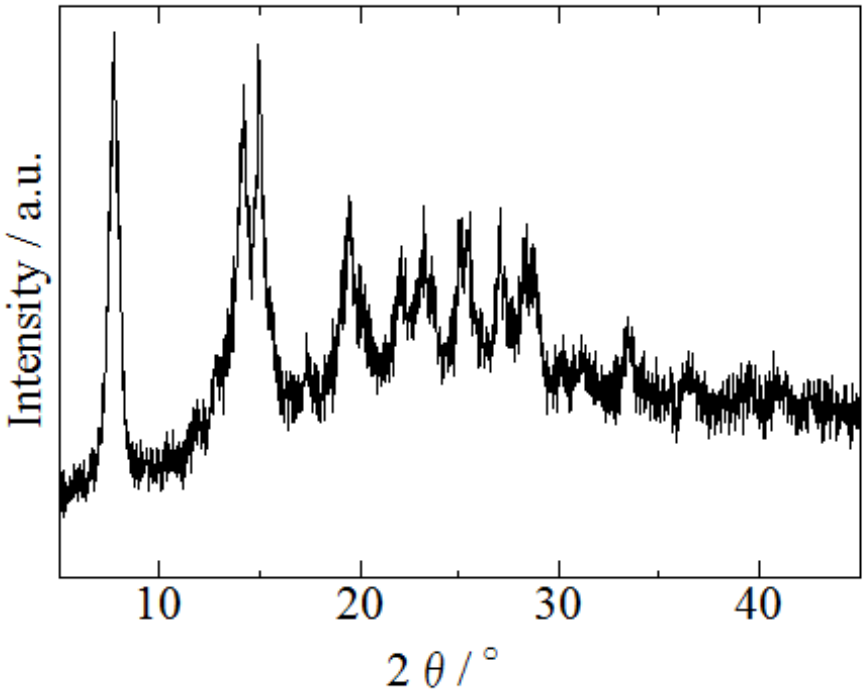


Figure S3. PXRD of (*R*)-MOF.

Synthesis of (R)-MOF-silica composite: A mixture of (*R*)-(+)-H_2BDA (50 mg, 0.13 mmol), $Cu(NO_3)_2$•$3H_2O$ (54 mg, 0.223 mmol) and Daisogel (SP-120-7P)(150 mg) in

DMF (1.5 mL) and H_2O (0.3mL) was stirred and heated at 80°C for 8 h. The resulting green precipitate was filtered and washed with DMF and MeOH, and dried *in vacuo* at 80°C. The yield is 175 mg.

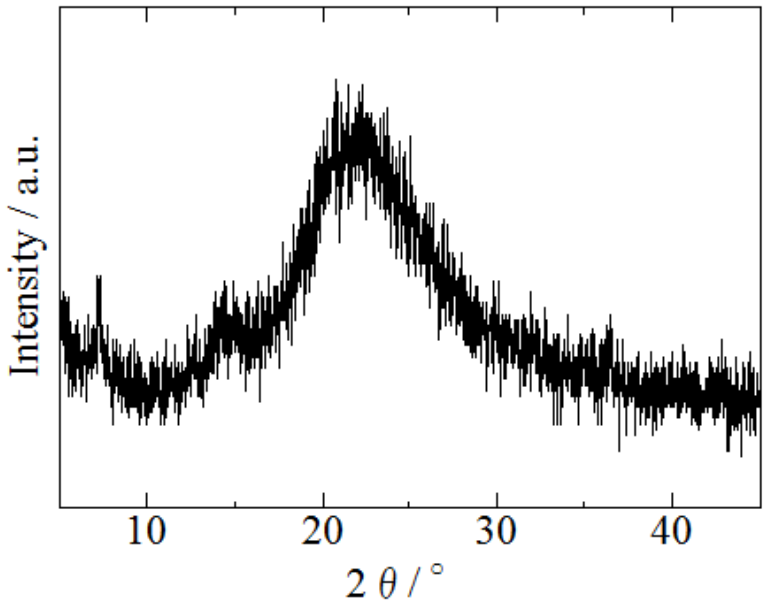


Figure S4. PXRD of (*R*)-MOF-silica composite.

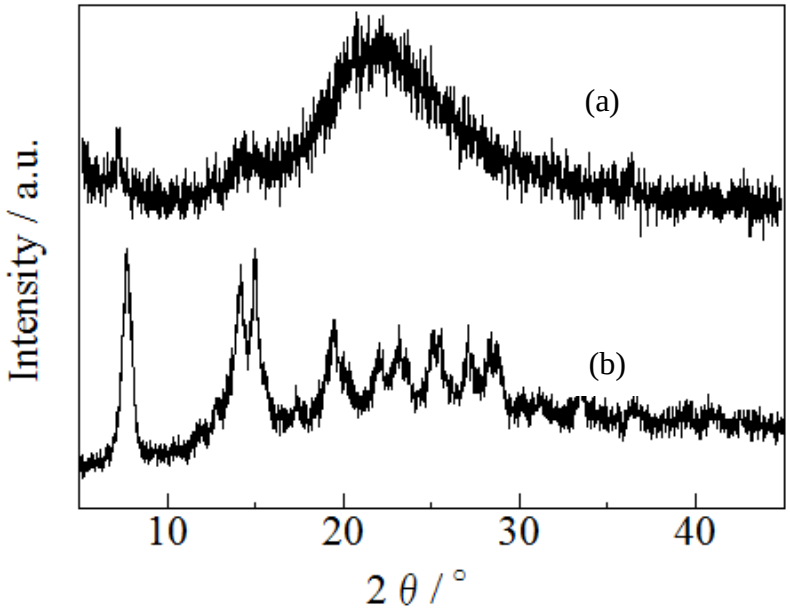
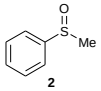
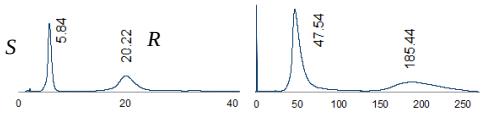
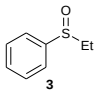
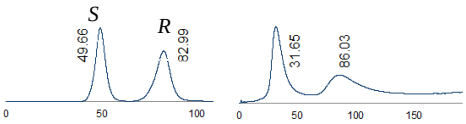
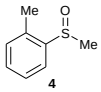
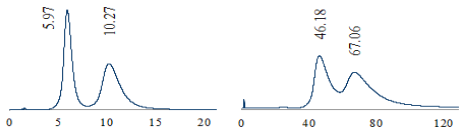
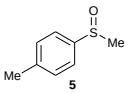
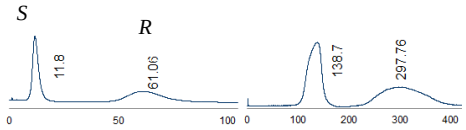
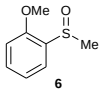
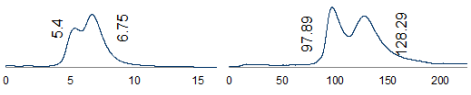
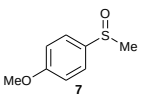
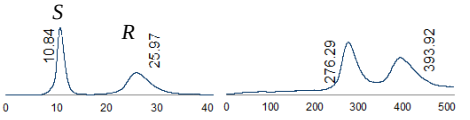
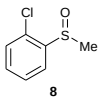
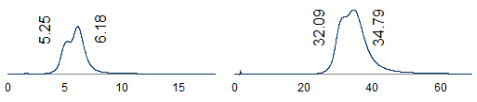
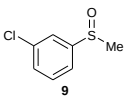
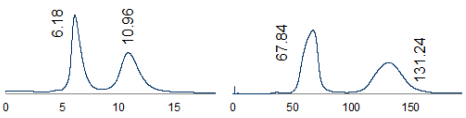
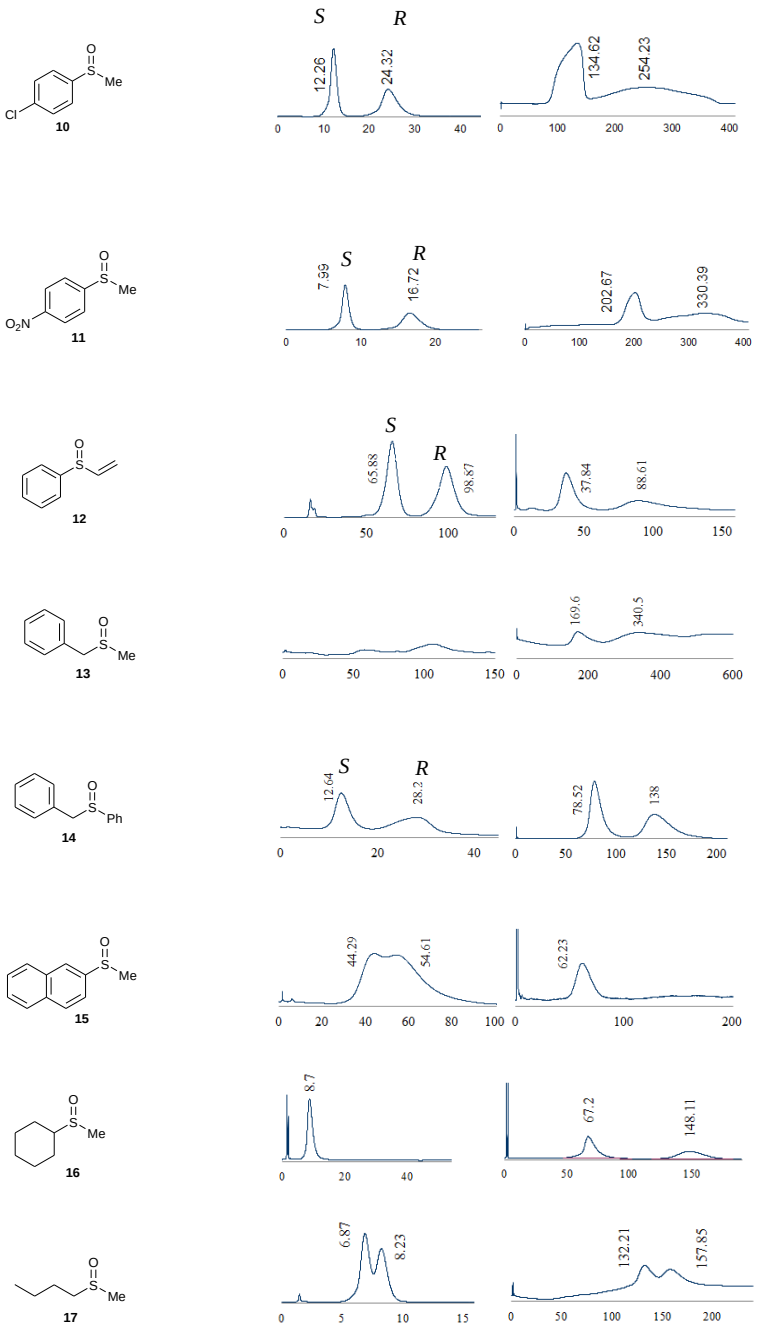


Figure S5. Comparison of PXRD patterns of (*R*)-MOF (a) and (*R*)-MOF-silica composite (b).

Enantioselective chromatographic separation procedure: The suspension of (*R*)-MOF-silica composite **1** (2.0 g) in hexane/*i*-PrOH (90:10) was slurry-packed into a stainless steel column (15 cm long x 4.6 mm i.d.). Chromatography was performed on a JASCO HPLC instrument at 25°C. Each of sulfoxides was dissolved in hexane/EtOH = 50/50 (Eluent I) and hexane/*i*-PrOH = 90/10 (Eluent II) (usually 1.0 mg mL^{-1}). The absolute configurations of the chiral sulfoxides were established by comparison of the HPLC chromatograms with the patterns described in previous report.[3]

Table S1 Chromatograms for the resolution of sulfoxides.[a]

Sulfoxide	Eluent I[b]	Eluent II[c]
 **2**		
 **3**		
 **4**		
 **5**		
 **6**		
 **7**		
 **8**		
 **9**		



[a] Flow rate : 1.0 mL min^{-1}; detection: UV 254 nm

[b] Hexane/EtOH = 50/50

[c] Hexane/*i*-PrOH = 90/10

Enantioselective sorption experiments: A racemic phenyl methyl sulfoxide **2** (70 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (2 mL), and the evacuated (*R*)-MOF (heated at 80°C for 8 h *in vacuo* before use, 100 mg, 0.23 mmol) was added to the solution. The CH_2Cl_2 solution was stirred for 16 h at room temperature. The crystalline material was subsequently isolated by filtration. After the adsorbed sulfoxide was extracted with MeOH (3 x 5 mL), the solvent was removed *in vacuo*. The enantiomeric excess was measured by HPLC[2] (Chiralcel OD; flow rate, 0.5 mL min^{-1}; detection, 254 nm; hexane/*i*-PrOH 9:1) as shown in Fig. S6.

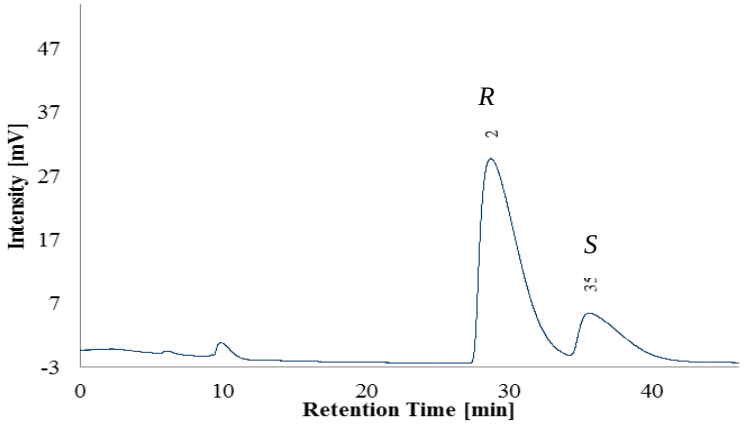


Figure S6. Chromatogram of phenyl methyl sulfoxide adsorbed in (*R*)-MOF.

References

1. F. Shi, M. K. Tse, H. M. Kaiser, M. Beller, *Adv. Synth. Catl.*, **2007**, *349*, 2425-2430.
2.Y. Cui, H. L. Ngo, P. S. White, W. Lin, *Chem. Commun.*, **2003**, 994-998.
3. J. Legros, C. Bolm, *Chem. Eur. J.*, **2005**, *11*, 1086-1092.