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

Koichi Tanaka*, Toshihide Muraoka#, Yasuhiro Otubo#, Hiroki Takahashi$ and Atsushi Ohnishi4

aDepartment of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan. E-mail: ktanaka@kansai-u.ac.jp

bGraduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

cCPI Company, Daicel Corporation., Aboshi, Himeji, Hyogo 671-1283, Japan.

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-methylbenzyldrol 40, 4-methylbenzyldrol 41, 4-chrolobenzhydrol 44 and 1-hydroxyinden 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\textsuperscript{4}. 4-Benzoyloxy-2-azetidinone \textsuperscript{48} and 2-azabicyclo[2.2.1]hept-5-en-3-one \textsuperscript{55} were purchased from Tokyo Kasei Kogyo co., ltd. Mandelamide \textsuperscript{56} was purchased from Wako Pure chemical Industries, ltd. 4-Phenylazetidin-2-one \textsuperscript{49}, 4-(2-chlorophenyl)-azetidin-2-one \textsuperscript{50}, 4-(3-chlorophenyl)-azetidin-2-one \textsuperscript{51}, 4-(4-chlorophenyl)-azetidin-2-one \textsuperscript{52}, 4-(4-fluorophenyl)-azetidin-2-one \textsuperscript{53}, 4-(4-bromophenyl)-azetidin-2-one \textsuperscript{54} were prepared using previously reported method. Benzoin \textsuperscript{57}, 4,4'-dimethylbenzoin \textsuperscript{58}, anisoin \textsuperscript{59}, 2-chloro-2-phenylacetophenone \textsuperscript{60}, benzoin methyl ether \textsuperscript{61}, 2,2'-thenoin \textsuperscript{62}, flavanone \textsuperscript{63} and trans-stilbene oxide \textsuperscript{68} were purchased from Tokyo Kasei Kogyo co., ltd. 7-Methoxyflavanone \textsuperscript{64}, 7-chloroflavanone \textsuperscript{65}, 4'-methoxyflavanone \textsuperscript{66} and 4'-chloroflavanone \textsuperscript{67} were prepared using previously reported method.\textsuperscript{6}

**Synthesis of (R)-CuMOF-1**

(R)-CuMOF-1\textsuperscript{7} 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(NO\textsubscript{3})\textsubscript{2}•6H\textsubscript{2}O (20 mg, 0.067 mmol) and (R)-1,1'-binaphthyl-2,2'-dihydroxy-6,6'-dicarboxylic acid (H\textsubscript{2}BDA) \textsuperscript{11} (50 mg, 0.134 mmol) in a glass-tube was heated at 80°C for 24 h. Colorless prisms were collected by filtration to yield (R)-ZnMOF-1, [Zn(BDA)(NMF)\textsubscript{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\textsuperscript{-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,N-dimethylacetoamide (DMA, 2.0 mL) and H\textsubscript{2}O (2.0 mL) containing Cu(NO\textsubscript{3})\textsubscript{2}•3H\textsubscript{2}O, (1.2 mg, 0.005 mmol) and (R)-1,1'-binaphthyl-2,2'-dimethoxy-6,6'-dicarboxylic acid (H\textsubscript{2}BDMA) \textsuperscript{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, \([\text{Cu(BDMA)}]_{2}\text{DMA}\) (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).

\[(S)\text{-ZnMOF-1}\]

\[(R)\text{-ZnMOF-1}\]

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

\[(S)\text{-ZnMOF-1}\]

\[(R)\text{-ZnMOF-1}\]

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.
Synthesis of (R)-CuMOF-1-silica composite
(R)-CuMOF-1-silica composites were prepared according to the previously reported method.\textsuperscript{7}

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

A mixture of \( (R)-1 \) (50 mg, 0.134 mmol), \( \text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (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.

Synthesis of (R)-CuMOF-2-silica composite
A mixture of \((R)-2\) (50 mg, 0.124 mmol), \(\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}\) (54 mg, 0.223 mmol) and Daisogel (SP-120-7P)(150 mg) in DEF (1.5 mL) and \(\text{H}_2\text{O}\) (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.

![SEM image of (R)-CuMOF-2-silica composite.](image)

**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 \(\text{K}_a\) radiation of Cu (\(\lambda = 1.5418 \text{ Å}\)). A scanning range of 20 values from 2° to 60° at a scan rate of 1°/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 N$_2$ adsorption isotherms and was calculated by Brunauer-Emmeet-Teller (BET method).

**Table S1. BET surface area**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R)-CuMOF-1</td>
<td>17.2</td>
</tr>
<tr>
<td>Silica-(R)-CuMOF-1</td>
<td>236.2</td>
</tr>
<tr>
<td>(R)-CuMOF-2</td>
<td>27.4</td>
</tr>
<tr>
<td>Silica-(R)-CuMOF-2</td>
<td>280.2</td>
</tr>
<tr>
<td>(R)-ZnMOF-1</td>
<td>7.6</td>
</tr>
<tr>
<td>Silica-(R)-ZnMOF-1</td>
<td>228.2</td>
</tr>
<tr>
<td>Silica gel</td>
<td>241.2</td>
</tr>
</tbody>
</table>
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 MoKα radiation ($\lambda = 0.71073$ Å); $\omega$ 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 SIR97 and refined on $F^2$ with all data using SHELXL2014. 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 XG2009. 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: $C_{30}H_{32}N_4O_{10}Zn$, $M = 673.96$, $a = 9.845(3)$ Å, $b = 22.697(6)$ Å, $c = 15.055(4)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 3364.1(16)$ Å$^3$, $T = 100(2)$ K, space group $C2221$, $Z = 4$, $\mu$(MoKα) = 0.788 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: $C_{28}H_{26}CuNO_8$, $M = 568.04$, $a = 27.62(6)$ Å, $b = 13.15(3)$ Å, $c = 7.699(15)$ Å, $\alpha = 90^\circ$, $\beta = 92.16(3)^\circ$, $\gamma = 90^\circ$, $V = 2794(10)$ Å$^3$, $T = 100(2)$ K, space group $C2$, $Z = 4$, $\mu$(MoKα) = 0.830 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