Application of a chiral metal-organic framework in enantioselective separation


[a] Westfälische Wilhelms-Universität, NRW Graduate School of Chemistry, Organisch-Chemisches Institut, Corrensstraße 40, 48149 Münster, Germany
[b] Department of Inorganic Chemistry, Dresden University of Technology, Bergstr. 66, 01062 Dresden, Germany
[c] Institute of Chemical Technology, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany
[d] Department of Bioanalytical Chemistry, Dresden University of Technology, Bergstr. 66, 01062 Dresden, Germany. Fax: +49 351 463 37188; Tel: +49 351 46332631; E-mail: eike.brunner@tu-dresden.de

Supporting Information

1. General Information
2. Synthesis of Chir-BDC derivatives
3. MOF synthesis
4. Crystal structure determination
5. Powder X-ray diffraction patterns
6. Adsorption experiments
7. Infrared spectroscopy
8. Thermogravimetric analysis
9. Liquid state NMR of MOFs
10. Solid state NMR
11. Column packing procedure and HPLC measurements
12. Further $^1$H and $^{13}$C NMR Spectra
1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Toluene was purified by distillation over CaH₂ prior to use. Triethylamine was distilled over CaH₂ and was transferred under argon. 2-bromo terephthalic acid was purchased from Acros. K₂CO₃ was dried by heating at 110 °C for 12 h and left to cool under argon and stored in the glove box. N,N-Diethylformamide (DEF) was distilled from phosphorus pentoxide and stored under argon. (S)-4-Isopropyl-2-oxazolidinone and (S)-4-benzyl-2-oxazolidinone were prepared by the literature procedures.¹

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short UV light or KMnO₄ staining solutions followed by heating. Flash chromatography was performed on Merck silica gel (40-63 mesh) by standard techniques eluting with solvents as indicated. All compounds were fully characterized.

¹H and ¹³C liquid-state NMR spectra were recorded on Bruker AV 300, or AV 400 MHz INOVA instruments in solvents as indicated. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δH = 7.26 ppm, δC = 77.16 ppm), (DMSO-d₆: δH = 2.50 ppm, δC = 39.52 ppm).

¹³C{¹H} cross-polarization (CP) MAS solid-state NMR spectra were measured with a mixing time of 5 ms on a Bruker Avance 300 spectrometer using a commercial double-resonance MAS NMR probe (4 mm outer rotor diameter). The temperature inside the rotor was calibrated using the well known temperature dependence of the ²⁰⁷Pb NMR signal of lead nitrate.

Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (n) of recorded IR-signals are quoted in cm⁻¹. ESI mass spectra were recorded on a Bruker Daltonics MicroTof. The SEM images were taken on a Cambridge CamScan 44 scanning electron microscope at an excitation voltage of U = 5 kV.

For the powder X-ray diffraction experiments a Bruker AXS D8 Advance or STOE STADI P diffractometer was used, Cu-Kα₁ (λ= 1.5406 Å). The N₂ and H₂ physisorption isotherms were measured up to 1 bar at 77 K using a Quantachrome Autosorb1C (or 3B) apparatus.

The chromatographic experiments were carried out on a Hewlett-Packard 1100 series HPLC with degasser, autosampler, temperable column compartment and a DAD. Additional a new Agilent 1200 series RID was used. The typical analysis conditions were: an isocratic flow of n-heptane at 0.5 ml min⁻¹, eluent / column temperature of 30 °C, detector temperature of 40 °C (RID) and detection at 254 nm wavelength (DAD). From the taken chromatograms the performance parameters selectivity α, the resolution Rs, the capacity factor k, the plate height H and the plate number N were calculated.

2. Synthesis of ChirBDC derivatives

Scheme 1. Synthesis of chiral auxiliary substituted BDC derivatives.

**Dimethyl 2-bromoterephthalate**

Following the known procedure\(^2\) a three necked 250 mL flask was charged with 2-bromoterephthalic acid (4.90 g, 20 mmol) and MeOH (168 mL). The reaction mixture was heated 70°C, and SOCl\(_2\) (30 mL, 400 mmol) was added dropwise and the reaction mixture was stirred for 30 minutes. After the addition of SOCl\(_2\) the reaction mixture was refluxed for 6 h. Then the reaction mixture cooled to r.t. MeOH was removed under reduced pressure. The reaction mixture was extracted with Et\(_2\)O (3 x 25 mL), the combined organic phases washed with 10% KOH (3 x 25 mL), followed by brine (3 x 25 mL), the combined organic phases were dried over MgSO\(_4\), and concentrated in vacuo. The residue was purified by column chromatography to give dimethyl 2-bromoterephthalate as a white solid (4.40 g, 83%).

![Scheme 1](image)

\( \text{Rf (EtOAc/pentane = 10/90): 0.48; } {^1}H \text{ NMR (300 MHz, CDCl}_3) \delta \text{ 8.31 (d, } J = 1.6 \text{ Hz, 1H), 8.00 (dd, } J = 8.1, 1.6 \text{ Hz, 1H), 7.81 (d, } J = 8.1 \text{ Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H). } {^{13}}C \text{ NMR (75 MHz, CDCl}_3) \delta \text{ 166.28, 165.14, 136.25, 135.34, 133.84, 131.16, 128.24, 121.59, 52.92, 52.84. ESI-MS: calculated } [\text{M+Na}]^+ \text{ for } C_{10}H_9BrO_4Na: 296.9556, \text{ found: 296.9561. ATR-FTIR (cm}^{-1}): \text{ 3073, 3023, 2964, 2851, 2362, 1742, 1724, 1557, 1480, 1434, 1374, 1284, 1242, 1191, 1112, 1041 953, 912, 853, 814, 744, 677, 661, 602.}

**(S)-Dimethyl 2-(4-benzyl-2-oxooxazolidin-3-yl)terephthalate**

Dimethyl 2-bromoterephthalate (4.00 g, 14.6 mmol), (S)-4-benzylazoxazolidi-2-one (2.85 g, 16.1 mmol), CuI (0.42 g, 2.20 mmol) and K\(_2\)CO\(_3\) (4.05 g, 29.3 mmol) were weighted under argon in to flame dried reaction vessel with a Teflon screw cap. Toluene (24 mL) and DMEDA (0.48 mL, 4.40 mmol) were added and the reaction mixture stirred at 110 °C for 36 hrs. The reaction mixture allowed to cool to room temperature and was filtered through a short silica column (eluent: EtOAc 150 mL). The solvents were removed under reduced pressure. The

---

residue was purified by column chromatography to give (S)-dimethyl 2-(4-benzyl-2-oxooxazolidin-3-yl)terephthalate as a yellowish foam solid (2.40 g, 44%).

\[ \text{R}_f (\text{EtOAc/pentane} = 50/50): 0.45; [\alpha]^2_{20} = + 75.8 \text{ (c = 0.027 in DCM); } ^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta \text{ 8.02 (d, } J = 1.6 \text{ Hz, 2H), 7.94 (t, } J = 1.0 \text{ Hz, 1H), 7.28 – 7.07 \text{ (m, 5H), 4.67 – 4.63 (m, 1H), 4.46 (t, } J = 8.5 \text{ Hz, 1H), 4.25 (dd, } J = 8.7, 6.6 \text{ Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.11 (dd, } J = 13.5, 4.7 \text{ Hz, 1H), 2.91 (dd, } J = 13.5, 9.8 \text{ Hz, 1H). } ^1\text{C NMR (75 MHz, CDCl}_3\text{)} \delta \text{ 165.77, 165.45, 156.81, 136.44, 135.49, 134.14, 132.59, 131.78, 129.30, 129.03, 128.99, 128.52, 127.25, 68.14, 59.48, 52.93, 52.82, 39.49. ESI-MS: calculated [M+Na]^+ for C\text{\textsubscript{20}}H\text{\textsubscript{19}}NO\text{\textsubscript{6}}Na: 392.1105, found: 392.1106. ATR-FTIR (cm\textsuperscript{-1}): 3028, 2953, 2846, 2362, 1755, 1720, 1572, 1496, 1435, 1399, 1287, 1251, 1216, 1112, 1085, 1038, 1008, 962, 913, 817, 754, 702, 663, 610.} 

(S)-Dimethyl 2-(4-isopropyl-2-oxooxazolidin-3-yl)terephthalate

Dimethyl 2-bromoterephthalate (3.00 g, 11.0 mmol), (S)-4-isopropyloxazolidin-2-one (1.56 g, 12.0 mmol), CuI (0.32 g, 1.65 mmol) and K\text{\textsubscript{2}}CO\text{\textsubscript{3}} (3.03 g, 22.0 mmol) were weighed under argon in to flame dried reaction vessel with a Teflon screw cap. Toluene (18 mL) and DMEDA (0.36 mL, 3.29 mmol) were added and the reaction mixture stirred at 110°C for 36 hrs. The reaction mixture allowed to cool to room temperature and was filtered through a short silica column (eluent: EtOAc 150 mL). The solvents were removed under reduced pressure. The residue was purified by column chromatography to give (S)-dimethyl 2-(4-isopropyl-2-oxooxazolidin-3-yl)terephthalate as a yellowish solid (1.05 g, 30%).

\[ \text{R}_f (\text{EtOAc/pentane} = 50/50): 0.60; [\alpha]^2_{20} = + 130.3 \text{ (c = 0.031 in DCM); } ^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta \text{ 8.01 (s, 2H), 7.91 (s, 1H), 4.54 – 4.47 (m, 1H), 4.37 – 4.24 (m, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 2.04 (m, 1H), 1.03 (d, } J = 6.8 \text{ Hz, 3H), 0.88 (d, } J = 7 \text{ Hz, 3H). } ^1\text{C NMR (75 MHz, CDCl}_3\text{)} \delta \text{ 165.81, 165.56, 157.30, 137.00, 134.01, 131.98, 131.94, 128.20, 128.11, 64.10, 62.46, 52.83, 52.79, 28.85, 18.34, 15.12. ESI-MS: calculated [M+Na]^+ for C\text{\textsubscript{16}}H\text{\textsubscript{19}}NO\text{\textsubscript{6}}Na: 344.1105, found: 344.1108. ATR-FTIR (cm\textsuperscript{-1}): 2990, 2957, 2360, 1724, 1610, 1574, 1492, 1426, 1401, 1375, 1327, 1302, 1259, 1239, 1214, 1148, 1105, 1055, 1027, 957, 900, 860, 816, 772, 754, 710, 659, 608.} 

(S)-2-(4-Benzyl-2-oxooxazolidin-3-yl)terephthalic acid

Following a procedure by Guichou et al. (S)-dimethyl 2-(4-benzyl-2-oxooxazolidin-3-yl)terephthalate (1.89 g, 5.12 mmol) was dissolved in THF (200 mL) and MeOH (200 mL). Aqueous NaOH (c = 1 mol L\textsuperscript{-1}, 4.32 g, 108 mmol) was added dropwise over a period of 20 minutes at room temperature and the mixture stirred at room temperature for 16 h. The
mixture was acidified with concentrated HCl to pH 5-6 and the organic solvents were removed under reduced pressure. The aqueous residue was diluted with H2O (100 mL) and the mixture was extracted with CHCl3/i-PrOH (5:1, 3 x 50 mL). The combined organic phases were dried over MgSO₄ and the solvents were removed under reduced pressure. The crude product was dissolved in acetone and the product was precipitated by dropwise addition of Pentane. The solids were collected by filtration and dried in vacuo. The product (S)-2-(4-benzyl-2-oxooxazolidin-3-yl)terephthalic acid was obtained as colorless solid (1.45 g, 82%).

\[ \alpha \]$_{20}^\circ$ = + 66.8 (c = 0.029 in DMSO); $^1$H NMR (300 MHz, CDCl₃) δ 13.39 (bs, 2H), 7.92 – 7.87 (m, 3H), 7.21 – 7.13 (m, 5H), 4.81 – 4.74 (m, 1H), 4.46 – 4.42 (m, 1H), 4.22 – 4.18 (m, 1H), 2.97 – 2.87 (m, 2H). $^{13}$C NMR (75 MHz, CDCl₃) δ 166.54, 166.02, 156.01, 136.25, 136.04, 134.24, 133.19, 131.16, 128.94, 128.41, 127.82, 126.51, 67.63, 58.49, 30.72. ESI-MS: calculated [M+Na]$^+$ for C18H15NO6Na: 364.0797, found: 364.0793. ATR-FTIR (cm$^{-1}$): 3098, 3061, 3021, 1737, 1702, 1603, 1571, 1497, 1479, 1417, 1291, 1220, 1196, 1179, 1121, 1082, 1037, 1004, 903, 868, 825, 755, 731, 703, 665, 607.

(S)-2-(4-Isopropyl-2-oxooxazolidin-3-yl)terephthalic acid

Following a procedure by Guichou et. al. (S)-dimethyl 2-(4-isopropyl-2-oxooxazolidin-3-yl)terephthalate (1.20 g, 3.73 mmol) was dissolved in THF (150 mL) and MeOH (150 mL). Aqueous NaOH (c = 1 mol L$^{-1}$, 3.04 g, 76 mmol) was added drop wise over a period of 20 minutes at room temperature and the mixture stirred at room temperature for 16 h. The mixture was acidified with concentrated HCl to pH 5-6 and the organic solvents were removed under reduced pressure. The aqueous residue was diluted with H2O (100 mL) and the mixture was extracted with CHCl3/i-PrOH (5:1, 3 x 50 mL). The combined organic phases were dried over MgSO₄ and the solvents were removed under reduced pressure. The crude product was dissolved in acetone and the product was precipitated by drop wise addition of Pentane. The solids were collected by filtration and dried in vacuum. The product (S)-2-(4-isopropyl-2-oxooxazolidin-3-yl)terephthalic acid was obtained as colorless solid (0.94 g, 86%).

\[ \alpha \]$_{20}^\circ$ = + 131.7 (c = 0.034 in DMSO); $^1$H NMR (300 MHz, CDCl₃) δ 13.43 (s, 2H), 7.99 – 7.52 (m, 3H), 4.53 – 4.34 (m, 2H), 4.27 (dd, J = 6.4, 4.5 Hz, 1H), 1.94 – 1.80 (m, 1H), 0.90 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.9 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl₃) δ 169.76, 167.30, 151.19, 151.19, 135.76, 132.15, 113.85, 112.78, 112.45, 61.02, 58.68, 28.54, 19.71, 17.48. ESI-MS: calculated [M+Na]$^+$ for C14H15NO6Na: 316.0797, found: 316.0792. ATR-FTIR (cm$^{-1}$): 2966, 2888, 2819, 2655, 1760, 1685, 1612, 1571, 1500, 1483, 1442, 1409, 1291, 1260, 1208, 1148, 1123, 1085, 1052, 971, 935, 904, 860, 781, 756, 691, 611.
3. MOFs synthesis

For the synthesis of oxazolidinone substituted UMCMs-1, the reaction conditions reported by Matzger et al. should be optimized. The ratio between the two linkers and the metal salt used in the reaction was crucial for the phase purity of the product. For the Bn-ChirUMCM-1 a ratio 1:1.56:6.2 of H$_3$BTB, Chir-H$_2$BDC and Zn(NO$_3$)$_2$(H$_2$O)$_4$ was used, and for iPr-ChirUMCM-1 the ratio 1:2.13:8.55, respectively. Also the reaction temperature was increased from 85 °C to 100 °C. The purity of synthesized compounds was proved via powder X-ray diffraction (PXRD) experiments (Figure S1).

Synthesis of Zn$_4$O(BTB)$_{4/3}$(iPr-ChirBDC)(DEF)$_{19}$(H$_2$O)$_6$ (1): H$_3$BTB (22.2 mg, 0.0506 mmol), iPr-ChirH$_2$BDC (31.7 mg, 0.108 mmol) and Zn(NO$_3$)$_2$(H$_2$O)$_4$ (113.3 mg, 0.433 mmol) were dissolved in DEF (4 ml). The solution was heated in a Pyrex® tube at 100 °C for 48 h. The resulting crystals were collected by filtration under argon, washed twice with DEF, and dried in an argon flow at room temperature. Yield: 274 mg (75.4%). Elemental analysis: calc (%): C 54.8, H 8.1, N 8.8, O 20.1, Zn 8.2; found (%): C 55.3±0.5, H 7.6±0.2, N 8.7±0.2, O 20.5±0.2, Zn 8.6±0.07.

Synthesis of Zn$_4$O(BTB)$_{4/3}$(Bn-ChirBDC)(DEF)$_{20}$(H$_2$O)$_8$ (2): H$_3$BTB (30.7 mg, 0.069 mmol), Bn-Chir-H$_2$BDC (37.1 mg, 0.108 mmol) and Zn(NO$_3$)$_2$(H$_2$O)$_4$ (113.3 mg, 0.433 mmol) were dissolved in DEF (4 ml). The solution was heated in a Pyrex® tube at 100 °C for 48 h. The resulting crystals were collected by filtration under argon, washed twice with DEF, and dried in an argon flow at room temperature. Yield: 384 mg (73.2 %). Elemental analysis: calc (%): C 54.9, H 8.1, N 8.7, O 20.4, Zn 7.77; found (%): C 54.5±0.5, H 8.0±0.2, N 8.8±0.2, O 20.1±0.2, Zn 7.68±0.04.

4. Crystal structure determination

The single crystals of 1 and 2 were sealed in a glass capillary with a small amount of solvent. The reflection intensities were measured at 20°C using synchrotron radiation on beamline BL14.2 of the Joint Berlin-MX Laboratory at BESSY-II (Berlin, Germany) with a MX-225 CCD detector (Rayonics, Illinois). The data images were integrated and scaled with the XDS software. The structures were solved using direct methods with the help of SHELXS-97 and refined by full-matrix least squares techniques using SHELXL-97. All non-hydrogen atoms, except disordered chiral substituents in BDC residue, were refined in anisotropic approximation. Several geometrical constraints were used to fix the geometry of the phenyl rings and carboxylic groups. Both structures show positional statistic disorder of chiral substituent in BDC moiety. Only the positions of nitrogen atoms could be localized from difference Fourier map. In the case of compound 1, the chiral substituent is disordered over two equally occupied positions, which are located at the same side of the phenyl ring. In the structure of compound 2 four positions for the nitrogen atom are found. All others atoms of the chiral substituents are highly disordered and could not be located from difference Fourier map. The Forcite geometry optimization tool (Material Studio 5.0) was used for modeling of
the chiral substituents in each disordered position. The calculated coordinates of the substituent atoms are omitted from refinement but included in the final *.cif files. The SQUEEZE/PLATON routine has been applied to modify the intensities, corresponding to the highly disordered chiral substituents and solvent molecules. The hydrogen atoms were positioned geometrically and refined using a riding model. The main experimental data are summarized in Table S1.

Table S1. Crystallographic data for iPr-ChirUMCM-1 and Bn-ChirUMCM-1.

<table>
<thead>
<tr>
<th></th>
<th>iPr-ChirUMCM-1 (1)</th>
<th>Bn-ChirUMCM-1 (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{50}H_{32}N_{15}O_{15}Zn_{4}</td>
<td>C_{54}H_{30}N_{15}O_{15}Zn_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1148.25</td>
<td>1194.27</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Hexagonal, P6(_3)</td>
<td>Hexagonal, P6(_3)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 41.459(6))</td>
<td>(a = 41.414(6))</td>
</tr>
<tr>
<td></td>
<td>(c = 17.561(4))</td>
<td>(c = 17.637(3))</td>
</tr>
<tr>
<td>Volume</td>
<td>26140(7)</td>
<td>26197(7)</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>6.0, 0.438</td>
<td>6.0, 0.454</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.016</td>
<td>1.015</td>
</tr>
<tr>
<td>F(000)</td>
<td>3474</td>
<td>3606</td>
</tr>
<tr>
<td>(\theta) Range</td>
<td>1.61 to 31.82</td>
<td>1.23 to 32.24</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-49 (\leq) h (\leq) 33</td>
<td>-19 (\leq) h (\leq) 49</td>
</tr>
<tr>
<td></td>
<td>-33 (\leq) k (\leq) 49</td>
<td>-49 (\leq) k (\leq) 49</td>
</tr>
<tr>
<td></td>
<td>-18 (\leq) l (\leq) 17</td>
<td>-16 (\leq) l (\leq) 19</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>80884 / 28147 ([R(int) = 0.0501])</td>
<td>83244 / 28628 ([R(int) = 0.0354])</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>28147 / 313 / 502</td>
<td>28628 / 308 / 682</td>
</tr>
<tr>
<td>Goof</td>
<td>1.042</td>
<td>0.942</td>
</tr>
<tr>
<td>Final R indices ([I&gt;2\sigma(I)])</td>
<td>(R_1 = 0.0427, wR_2 = 0.1142)</td>
<td>(R_1 = 0.0398, wR_2 = 0.1066)</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>(R_1 = 0.0532, wR_2 = 0.1181)</td>
<td>(R_1 = 0.0533, wR_2 = 0.1115)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.398 and -0.352</td>
<td>0.342 and -0.482</td>
</tr>
</tbody>
</table>

5. PXRD

![PXRD patterns of iPr-ChirUMCM-1 (1) (left) and Bn-ChirUMCM-1 (2) (right). a) Calculated for UMCM-1; b) as-synthesized; c) activated.](image1)

![PXRD patterns of Bn-ChirUMCM-1: a) calculated; b) as-synthesized material; c) after treatment with isopropanol.](image2)

6. Adsorption experiments

For physisorption measurements, the synthesized materials were washed with fresh DEF and in the next step DEF included in the MOF pores was exchanged with DCM. Prior the measurements, the materials were dried in vacuum at ambient temperature for 24h.

The multipoint BET surface area was calculated using the p/p\textsubscript{0} range from 6×10^{-3} to 1×10^{-1} for 1 and from 6×10^{-3} to 5×10^{-2} for 2. The pore volume was calculated at 0.9 p/p\textsubscript{0}.
7. Infrared spectroscopy (IR)

The IR spectra of 1 and 2 (Figure S4 and S5) show the specific vibrational bands in the typical region for symmetric vibrations of bridging mode coordinating carboxylate groups (1685 cm\(^{-1}\) (1); 1687 cm\(^{-1}\) (2)). The C-O vibration of the R-C=O\(_{NR2}\) group of the chiral substituent was obtained at 1762 cm\(^{-1}\) in both cases. For compound 2 vibration bands at 709 cm\(^{-1}\) and 748 cm\(^{-1}\) are detected. They can be assigned to the hydrogen atoms of the phenyl ring of the chiral oxazolidinone.

Figure S4. IR spectrum of: a) \textit{i}Pr-Chir-UMCM-1 (1), b) \textit{i}Pr-ChirH\textsubscript{2}BDC, c) H\textsubscript{3}BTB.

Figure S5. IR spectrum of: a) Bn-Chir-UMCM-1 (2), b) Bn-ChirH\textsubscript{2}BDC c) H\textsubscript{3}BTB.
8. Thermal analysis (TGA)

The thermo gravimetric analysis was performed on the argon flow dried samples of 1 and 2 in air atmosphere using a Netzsch STA 409 PC Luxx thermal analyzer. Both compounds are stable up to 300 °C. In the temperature range from 300 °C to 500 °C the network collapses with a weight loss of 71.6 % in the case of 1 and 66.6 % for 2. For 2 a small amount (7 %) of residual solvent is observed up to 300 °C. (Figures S6 and S7).

Figure S6. TGA of iPr-Chir-UMCM-1 (1).

Figure S7. TGA of Bn-Chir-UMCM-1 (2).
9. Liquid state NMR of MOFs

Unless otherwise specified, the NMR experiments were performed in DMSO-d_6. The synthesized and completely dried MOF samples were dissolved in aqueous NaOH (1 M) and the linkers were precipitated using diluted hydrochloric acid. In the case of Zn_4O(BTB)_4/3(Bn-ChirBDC) (2) the NMR experiment verifies the presence of an intact Bn-ChirBDC linker (Fig. S9). The BTB:Bn-ChirBDC ratio, determined by the integrated aromatic protons, is 20.0 : 3.0 (Fig. S11) and is consistent with the theoretical value of 20.0 : 3.0 (4/3 : 1). The NMR spectra of Zn_4O(BTB)_4/3(iPr-ChirBDC) (1) also show the typical peaks originated from the chiral oxazolidinone moiety (Figure S14). The aromatic protons of the BDC are observed only once proving that no chemical modification of iPr-Chir-BDC occurs during the synthesis or drying process. Surprisingly, the BTB : BDC aryl proton ratio was determined as 121.3 : 3.2 (Fig. S15). This value would correspond to a linker ratio of 7.6 : 1 indicating a leaching of linker during sample preparation. For the next experiment the dry iPr-ChirUMCM-1, DMSO-d_6, and DCI (37% in D_2O) were mixed directly in a NMR tube. After 3 hours the NMR measurements was performed. The spectra show an aromatic proton ratio of 20.1 : 3.0 corresponding to a BTB : iPr-ChirBDC ratio of 4/3 : 1 (Fig. S16 - S18).

Figure S8. NMR spectrum of Bn-ChirH_2BDC.
Figure S9. NMR spectrum of dissolved 2; crosses and circles indicate the H$_3$BTB and Bn-Chir-H$_2$BDC signals, respectively.

Figure S10. NMR spectrum of dissolved 2 in the range of 2.7-4.9 ppm showing the aliphatic protons of Bn-Chir-H$_2$BDC.
Figure S11. NMR spectrum of dissolved 2 in the range of 7.0-8.3 ppm showing the aromatic protons of Bn-Chir-H$_2$BDC and H$_3$BTB ligand.

Figure S12. NMR spectrum of iPr-Chir-H$_2$BDC.
Figure S13. NMR spectrum of dissolved 1; crosses and circles indicate the H$_3$BTB and iPr-Chir-H$_2$BDC signals, respectively.

Figure S14. NMR spectrum of dissolved 1 in the range of 0.7-4.9 ppm showing the aliphatic protons of iPr-Chir-H$_2$BDC.
Figure S15. NMR spectrum of dissolved 1 in the range of 7.5-8.4 ppm showing the aromatic protons of iPr-Chir-H$_2$BDC and H$_3$BTB ligand.

Figure S16. NMR spectrum of 1 in a DCl/D$_2$O/DMSO-$d_6$ mixture; crosses and circles indicate the H$_3$BTB and iPr-Chir-H$_2$BDC signals, respectively.
Figure S17. NMR spectrum of 1 in a DCl/D2O/DMSO-d6 mixture in the range of 0.1-4.4 ppm showing the aliphatic protons of iPr-Chir-H2BDC.

Figure S18. NMR spectrum of dissolved 1 in the range of 7.3-8.5 ppm showing the aromatic protons of iPr-Chir-H2BDC and H3BTB ligand.
10. Solid state NMR

Figure S19. $^{13}$C-$^1$H cross-polarization (CP) MAS NMR spectra of compounds 1 (iPr-ChirUMCM-1) and 2 (Bn-ChirUMCM-1) measured at room temperature (RT) and 247 K. For comparison the spectrum of unmodified UMCM-1 is also shown. Note the pronounced temperature-dependence of the spectra.
11. **Column packing procedure for HPLC measurements**

The columns (with 5 cm length and 2 mm inner diameter) for the experiments were obtained from Bischoff Chrom Leonberg, Germany. Before the packing the material was crushed under dry inert atmosphere in dichloromethane applying soft pressure. After crushing, the crystals are suspended in iso-propanol. The slurry is pressed with a maximum pressure of 200 bar and *n*-hexane as eluent into the empty column. By changing the solvent while pressing the slurry into the column, the crystals could dispose slowly to get a better packing.

After packing, the column was conditioned by flushing with *n*-heptane for 15 minutes at a flow of 0.5 ml min\(^{-1}\). Afterwards, an injection of a certain amount of interacting analyte and flushing for another 30 minutes with pure eluent followed.

![Figure S20. SEM image of the crushed Bn-ChirUMCM-1 crystals.](image)

![Figure S21. Chromatogram of 1-phenylethanol enantiomers using UMCM-1.](image)
Table S2. Comparison of chosen analytes on non-chiral UMCM-1 and chiral modified Bn-ChirUMCM-1 columns.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>UMCM-1 column $t_R$ / min</th>
<th>Bn-ChirUMCM-1 column $t_R$ / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4R)-benzyl-2-oxazolidinone</td>
<td>0.60$^1$</td>
<td>3.40</td>
</tr>
<tr>
<td>(4S)-benzyl-2-oxazolidinone</td>
<td>0.60$^1$</td>
<td>3.40</td>
</tr>
<tr>
<td>(4R)-phenyl-2-oxazolidinone</td>
<td>0.60$^1$</td>
<td>3.26</td>
</tr>
<tr>
<td>(4S)-phenyl-2-oxazolidinone</td>
<td>0.60$^1$</td>
<td>3.26</td>
</tr>
<tr>
<td>cis-(4R,5S)-diphenyl-2-oxazolidinone</td>
<td>0.60$^1$</td>
<td>3.33</td>
</tr>
<tr>
<td>cis-(4S,5R)-diphenyl-2-oxazolidinone</td>
<td>0.60$^1$</td>
<td>3.33</td>
</tr>
<tr>
<td>(1R)-2-butanol</td>
<td>n.m</td>
<td>3.28</td>
</tr>
<tr>
<td>(1S)-2-butanol</td>
<td>n.m</td>
<td>3.28</td>
</tr>
<tr>
<td>(1R)-phenylethanol</td>
<td>4.41</td>
<td>11.21</td>
</tr>
<tr>
<td>(1S)-phenylethanol</td>
<td>4.32</td>
<td>7.84</td>
</tr>
<tr>
<td>1-phenylethanamine</td>
<td>---$^2$</td>
<td>---$^2$</td>
</tr>
<tr>
<td>D,L-alanine</td>
<td>---$^2$</td>
<td>---$^2$</td>
</tr>
</tbody>
</table>

$^1$Hold-up time; $^2$Broad peak, no $t_R$ assignable, analyte remained on column; n. m. – not measured
12. Further $^1$H and $^{13}$C NMR Spectra

[Diagram of NMR spectra showing chemical shifts and peaks.]