Supporting Information

Rational Design of BINOL-Based Diimidazolyl Ligands: Homochiral Channel-like Mono-Component Organic Frameworks by Hydrogen-Bond-Directed Self-Assembly

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I. General remarks

$^1$H NMR spectra were obtained with a Bruker AV-400 (400 MHz) or a Varian Inova-400 (400 MHz) spectrometer, while $^{13}$C NMR spectra were also recorded with a Bruker AV-400 (100 MHz), a Bruker AV-600 (150 MHz), a Varian Inova-400 (100 MHz) or a Varian Inova-600 (150 MHz) spectrometer. The $^1$H NMR chemical shifts were measured relative to tetramethylsilane, CDCl$_3$ or DMSO-$d_6$ as the internal reference, while the $^{13}$C NMR chemical shifts were recorded with CDCl$_3$ or DMSO-$d_6$ as the internal standard. Elemental analyses were performed with a CARLO ERBA1106 instrument or a Heraeus CHN-O-RAPID instrument. The ESI-TOF mass spectra were recorded with a Waters Q-Tof premier instrument. High-resolution FAB mass spectra was obtained using a JEOL JMS-SX/SX 102A instrument. The optical rotations were determined with a WZZ-2B polarimeter. Melting points were determined with XRC-1 and are uncorrected. Powder X-ray diffraction (PXRD) patterns were collected on a Philips X’PERT Pro MPDX powder diffractometer with Cu K$\alpha$ radiation (1.54056 Å). The tube voltage and amperage were set at 40 kV and 35 mA, respectively. The sample was scanned between 5° and 45° in 2$\theta$ with a step size of 0.03°. The simulated PXRD spectra from single-crystal structures was carried out using Mercury (version 1.4.2, 2002) and were compared to confirm the composition of the crystal with the experimental PXRD pattern.

Materials: $(R)$-1,1′-Bi-2-naphthol [(R)-4] (>99% ee) was purchased from Lian YunGang Chiral Chemicals (China) Co., Ltd. Pyridine was distilled before use, while the others were used without further purification. Solvents were dried by heating at reflux for at least 24h over CaH$_2$ (dichloromethane and DMSO) or sodium/benzophenone (tetrahydrofuran and diethyl ether) and were freshly distilled prior to use. Unless otherwise indicated, all syntheses and manipulations were carried out under a dry nitrogen atmosphere. $n$BuLi in Et$_2$O was prepared according to the
Compounds (R)-5, (R)-6 and (R)-7 were synthesized according to literature methods. Compound (R)-8 was synthesized by following literature procedures. Compounds (R)-10 and (R)-11 were prepared according to literature procedures.

II. Procedures for the preparation of chiral ligands (R)-1-3

i. Synthesis of chiral ligand (R)-1

\[
\text{(R)-4} \quad \text{OCH}_3 \quad \text{OCH}_3 \quad 1) \text{nBuLi, TMEDA, Et}_2\text{O, rt, 3 h} \\
\quad \text{OH} \quad \text{OH} \quad 2) \text{B(OCH}_3)_3, -78 \degree\text{C to rt, 8 h} \\
\quad \text{B(OH)}_2 \quad 3) 1\text{M HCl} \quad \text{(R)-5} \quad \text{OCH}_3 \quad \text{OCH}_3 \\
\text{Im, CuCl, CH}_3\text{OH, air} \quad \text{reflux, 3 h} \quad \text{(R)-6} \quad \text{B(OH)}_2 \quad \text{B(OH)}_2 \\
\text{(R)-7} \quad \text{N} \quad \text{N} \quad 1) \text{BBr}_3, \text{CH}_2\text{Cl}_2, 0 \degree\text{C, 24 h} \\
\quad \text{OH} \quad \text{OH} \quad 2) \text{H}_2\text{O, 0 \degree\text{C}} \quad 3) \text{NaHCO}_3 \quad \text{(R)-1} \quad \text{OH} \quad \text{OH} \\
\]

*Scheme S1* Synthesis of the 3,3'-diimidazolyl-substituted BINOL (R)-1.

(R)-3,3'-Bis(1H-imidazol-1-yl)-1,1'-bi-2-naphthol ((R)-1)

A flame-dried Schlenk flask was charged with (R)-7 (0.47 g, 1 mmol) and anhydrous CH\textsubscript{2}Cl\textsubscript{2} (20 mL) under N\textsubscript{2}. The solution was cooled to 0 °C, and then BBr\textsubscript{3} (1.0 M in CH\textsubscript{2}Cl\textsubscript{2}, 4 mL, 4 mmol) was added over a period of 30 min. The mixture was allowed to warm to room temperature and stirred for 24 h. Thereafter, water (5 mL) was carefully added at 0 °C to quench the reaction, followed by MeOH (5 mL) and solid NaHCO\textsubscript{3} to neutralize the mixture. The resulting mixture was stirred for a further 12 h at room temperature and then filtered through a pad of Celite. The filtrate was washed with saturated aqueous NaCl solution (10 mL). The organic layer was separated, and the aqueous phase was extracted with CH\textsubscript{2}Cl\textsubscript{2} (2×10 mL). The combined organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}.
and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel eluting with CH$_2$Cl$_2$/MeOH (12:1 to 10:1) to give (R)-1 (0.36 g, 85%) as a pale-yellow solid. M.p. > 300 ºC; [α]$^\text{D}$ = +30.2 (c = 0.51, DMSO); $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 6.93 (d, $J$ = 8.4 Hz, 2H), 7.11 (s, 2H), 7.27 (t, $J$ = 6.8 Hz, 2H), 7.36 (t, $J$ = 8.0 Hz, 2H), 7.62 (s, 2H), 7.97 (d, $J$ = 8.0 Hz, 2H), 8.07 (s, 2H), 8.13 (s, 2H) ppm; $^{13}$C NMR (150 MHz, DMSO-d$_6$): $\delta$ 116.4, 120.8, 121.5, 123.6, 124.1, 126.7, 127.8, 127.9, 128.1, 132.9, 135.0, 137.7, 148.4 ppm; HRMS (FAB): calcd for C$_{26}$H$_{19}$N$_4$O$_2$ [M+H]$^+$: 419.1508, found: 419.1505; Anal. Calcd. for C$_{26}$H$_{18}$N$_4$O$_2$: C, 74.63; H, 4.34; N, 13.39. Found: C, 74.38; H, 4.45; N, 13.20.

ii. Synthesis of chiral ligand (R)-2

![Scheme S2](image)

Scheme S2 Synthesis of the 5,5′-diimidazolyl-substituted BINOL (R)-2.

(R)-5,5′-Dibromo-2,2′-diacetoxy-1,1′-dina...
at room temperature. The organic layer was separated, washed with NaHSO₃ (15%, 2×100 mL) and brine (2×100 mL), and then dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (13:1) to give \((R)-9\) (3.33 g, 42%) as a white foam. M.p. 123-124 °C; \([\alpha]_{D}^{20} = +32.0 (c = 0.50, CH₂Cl₂); \) \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 1.89 (s, 6H), 7.08-7.15 (m, 4H), 7.52 (d, \(J = 8.8\) Hz, 2H), 7.76 (d, \(J = 7.2\) Hz, 2H), 8.45 (d, \(J = 9.2\) Hz, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta\) 20.5, 122.9, 123.2, 123.3, 125.9, 127.2, 129.1, 129.9, 130.0, 134.4, 147.4, 169.0 ppm; HRMS (ESI): calcd for C₂₄H₁₇Br₂O₄ [M+H]⁺: 528.9473, found: 528.9456.

\((R)-5,5'\) -Bis(1H-imidazol-1-yl)-1,1' -bi-2-naphthol ((\(R\))-2)

A flame-dried Schlenk flask was charged with CuI (457 mg, 2.4 mmol), \(N,N\)-dimethylglycine (495 mg, 4.8 mmol), K₂CO₃ (11.59 g, 84 mmol), \((R)-9\) (6.34 g, 12 mmol), imidazole (2.86 g, 42 mmol), and DMSO (18 mL) at room temperature under nitrogen. After being heated at 110 °C for 60 h, the mixture was evaporated under vacuum. Thereafter, the resulting residue was partitioned with 200 mL of CH₂Cl₂ and filtered through a pad of Celite. The filtrate was removed under reduced pressure to give the crude product. Aqueous KOH (3 M, 15 mL) was then added to the solution of the crude product in THF (80 mL) and methanol (40 mL). The resulting solution was refluxed for 24 h until the conversion of reactant was complete. The solution was then cooled to room temperature and neutralized by addition of saturated aqueous NH₄Cl solution. The resulting mixture was stirred for a further 2 h and volatiles were then removed in vacuo. The aqueous phase was extracted with CH₂Cl₂ (3×120 mL). The combined organic layers were dried over Na₂SO₄ and evaporated under vacuum. The resulting residue was purified by flash column chromatography on silica gel eluting with CH₂Cl₂/MeOH (13:1 to 8:1) to give \((R)-2\) (3.41 g, 68% (two steps)) as a pale-yellow solid. M.p.
$>300\, ^\circ\text{C}; \, [\alpha]^{20}_D = +39.0 \, (c = 0.50, \text{DMSO}); \, ^1\text{H} \text{NMR (400 MHz, DMSO-$d_6$): } \delta \, 7.09 \, (d, \, J = 7.6 \, \text{Hz}, \, 2\text{H}), \, 7.23 \, (s, \, 2\text{H}), \, 7.32-7.37 \, (m, \, 4\text{H}), \, 7.41 \, (d, \, J = 8.8 \, \text{Hz}, \, 2\text{H}), \, 7.47 \, (d, \, J = 9.2 \, \text{Hz}, \, 2\text{H}), \, 7.62 \, (s, \, 2\text{H}), \, 8.03 \, (s, \, 2\text{H}) \, \text{ppm}; \, ^{13}\text{C} \text{NMR (100 MHz, DMSO-$d_6$): } \delta \, 115.8, \, 120.0, \, 120.4, \, 122.2, \, 123.2, \, 123.8, \, 125.3, \, 125.8, \, 128.9, \, 134.2, \, 134.9, \, 138.6, \, 153.9 \, \text{ppm}; \, \text{HRMS (ESI): calcd for } C_{26}H_{19}N_4O_2 \, [M+H]^+: \, 419.1508, \, \text{found: } 419.1517; \, \text{Anal. Calcd. for } : \, \text{C}, \, 74.63; \, \text{H}, \, 4.34; \, \text{N}, \, 13.39. \, \text{Found: } \, \text{C}, \, 74.26; \, \text{H}, \, 4.36; \, \text{N}, \, 13.10.

iii. Synthesis of chiral ligand (R)-3

![Scheme S3 Synthesis of the 6,6′-diimidazolyl-substituted BINOL (R)-3.](image)

(R)-6,6′-Bis(1H-imidazol-1-yl)-2,2′-dimethoxymethoxy-1,1′-binaphthyl ((R)-12)

A flame-dried Schlenk flask was charged with CuI (381 mg, 2.0 mmol), N,N-dimethylglycine (412 mg, 4.0 mmol), K$_2$CO$_3$ (11.04 g, 80 mmol), (R)-11 (5.32 g, 10 mmol), imidazole (2.72 g, 40 mmol), and DMSO (15 mL) at room temperature under nitrogen. After being heated at 110 °C for 48 h, the mixture was concentrated under reduced pressure. The resulting residue was then partitioned between water (60 mL) and CH$_2$Cl$_2$ (120 mL). The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3×30 mL). The combined organic layers were dried over Na$_2$SO$_4$ and evaporated in vacuo. The crude product was purified by chromatography on a silica gel column.
eluting CH$_2$Cl$_2$/MeOH (20:1 to 15:1). (R)-12 was obtained in 84% yield (4.26 g) as a yellow solid. M.p. 77-78 ºC; [a]$_{D}^{20} = -5.0$ (c = 0.50, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.31 (s, 6H), 4.94 (dd, $J = 6.8$ Hz, 7.2 Hz, 4H), 7.14-7.22 (m, 6H), 7.60 (d, $J = 9.2$ Hz, 2H), 7.79 (d, $J = 2.0$ Hz, 2H), 7.86 (s, 2H), 7.92 (d, $J = 9.2$ Hz, 2H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 56.0, 95.0, 118.4, 118.5, 119.3, 120.6, 120.9, 127.4, 129.6, 129.8, 130.4, 132.8, 133.4, 135.8, 153.2 ppm; HRMS (ESI): calcd for C$_{30}$H$_{27}$N$_4$O$_4$ [M+H]$^+$: 507.2032, found: 507.2040.

(R)-6,6’-Bis(1H-imidazol-1-yl)-1,1’-bi-2-naphthol ((R)-3)

Aqueous HCl (6 M, 10 mL) was added to a solution of (R)-12 (3.04 g, 6.0 mmol) in THF (40 mL) and methanol (20 mL). The resulting solution was refluxed for 18 h until the conversion of (R)-12 was complete. The solution was then cooled to room temperature and neutralized by addition of saturated aqueous Na$_2$CO$_3$ solution. After the resulting mixture was stirred for a further 12 h and volatiles were removed under reduced pressure. The aqueous phase was extracted with CH$_2$Cl$_2$ (3×100 mL). The combined organic layers were dried over Na$_2$SO$_4$ and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel eluting with CH$_2$Cl$_2$/MeOH (18:1 to 10:1) to give (R)-3 (2.23 g, 89%) as a pale-yellow solid. M.p. >300 ºC; [a]$_{D}^{20} = +15.0$ (c = 0.50, DMSO); $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 7.06 (d, $J = 9.2$ Hz, 2H), 7.13 (s, 2H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.49 (dd, $J = 2.0$ Hz, 2.4 Hz, 2H), 7.74 (s, 2H), 7.95 (d, $J = 9.2$ Hz, 2H), 8.13 (d, $J = 2.4$ Hz, 2H), 8.24 (s, 2H), 9.47 (s, 2H) ppm; $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 115.8, 118.9, 119.0, 120.4, 120.6, 126.7, 128.6, 129.4, 130.1, 132.3, 133.2, 136.2, 154.0 ppm; HRMS (ESI): calcd for C$_{26}$H$_{19}$N$_4$O$_2$ [M+H]$^+$: 419.1508, found: 419.1510; Anal. Calcd. for : C, 74.63; H, 4.34; N, 13.39. Found: C, 74.32; H, 4.31; N, 13.12
III. General procedure for the preparation of organic crystals (R)-1-3

At elevated temperature, (R)-1-3 (50 mg) was dissolved in a DMF solution (2 mL) with constant stirring to give a light yellow solution. Then the mixture was filtered to remove a trace amount of undissolved substance. Colorless block crystals (R)-1-3 suitable for X-ray analysis were obtained by slow diffusion of 1,4-dioxane into the corresponding DMF solution at ambient temperature after several days (yields: 70-75%).

IV. Single-crystal X-ray diffraction determination and refinement

X-Ray single-crystal diffraction data for (R)-1-3 were collected on a Bruker SMART 1000 CCD areadetector diffractometer at 100 K with graphite monochromated Mo Kα radiation (\( \lambda = 0.71073 \) Å) with \( \omega \) scan mode. All the structures were solved by direct methods using the SHELXS program and refined by full-matrix least-squares methods with SHELXL. All non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on \( F^2 \). Hydrogen atoms were included in calculated positions and refined with constrained thermal parameters riding on their parent atoms. The guest molecules of (R)-3 could not be located in the difference map because of disorder. The crystal parameters, data collection and refinement results for the three compounds are summarized in Table S1.

<p>| Table S1 Crystallographic Data for Crystals (R)-1-3 |
|---------------------------------|---------|---------|---------|
| Chemical formula               | (R)-1   | (R)-2   | (R)-3   |
| C(<em>{26})H(</em>{18})N(<em>{4})O(</em>{2}) | C(<em>{33})H(</em>{33})N(<em>{5})O(</em>{5}) | C(<em>{26})H(</em>{18})N(<em>{4})O(</em>{2}) |
| Formula weight (M)             | 418.44  | 579.64  | 418.44  |
| Temperature (K)                | 297(2)  | 100(2)  | 297(2)  |
| Wavelength (Å)                 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system                 | Orthorhombic | Orthorhombic | Tetragonal |
| Space group                    | ( P \ 2 1 2 ) | ( P \ 2 1 2 \ 2 ) | ( P \ 4 3 ) |
| Crystal size (mm(^3))        | 0.75×0.50×0.17 | 0.44×0.42×0.38 | 0.60×0.58×0.48 |</p>
<table>
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<th>Value 2</th>
<th>Value 3</th>
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<td>9.2610(3)</td>
<td>11.950(2)</td>
</tr>
<tr>
<td>b (Å)</td>
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<td>16.4271(5)</td>
<td>11.950(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.3143(11)</td>
<td>19.8316(4)</td>
<td>21.080(6)</td>
</tr>
<tr>
<td>α (°)</td>
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<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
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<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
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<td>90</td>
<td>90</td>
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<tr>
<td>Volume (Å³)</td>
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<td>3017.01(15)</td>
<td>3010.3(12)</td>
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<tr>
<td>Z</td>
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<td>4</td>
<td>4</td>
</tr>
<tr>
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<td>1.276</td>
<td>0.923</td>
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<tr>
<td>µ (mm⁻¹)</td>
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<td>0.060</td>
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<td>13487</td>
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<td>5247</td>
<td>5400</td>
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<tr>
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<td>0.1045</td>
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<tr>
<td>F(000)</td>
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<td>1224</td>
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<tr>
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<tr>
<td>R1, wR2 [I &gt;2 σ (I)]</td>
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<td>0.0624, 0.1703</td>
<td>0.0770, 0.2107</td>
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<tr>
<td>R1, wR2 (all data)</td>
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<td>0.0694, 0.1774</td>
<td>0.0838, 0.2197</td>
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</table>

**Fig. S1** 2-D network layer of (R)-2 viewed along the b-axis. Color code: C, dark gray; N, blue; O, red; H atoms were omitted for clarity. DMF and 1,4-dioxane molecules were positioned in the network.
V. Powder X-ray diffraction analysis of (R)-1-3

Fig. S2 Comparison of powder X-ray diffraction patterns of (R)-1: the top and bottom patterns correspond to the simulated and experimental results, respectively.

Fig. S3 Comparison of powder X-ray diffraction patterns of (R)-2: the top and bottom patterns correspond to the simulated and experimental results, respectively.

Fig. S4 Comparison of powder X-ray diffraction patterns of (R)-3: the top and bottom patterns correspond to the simulated and experimental results, respectively.
VI. References


VII. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of (R)-1-3, 9 and 12
(R)-9

\[
\begin{align*}
\text{Br} & \quad \text{OAc} \\
\text{Br} & \quad \text{OAc}
\end{align*}
\]