

<Electronic Supplementary Information>

# Construction of right-handed-, left-handed- and racemic helical coordination polymers. Enantioselective recognition via chiral helical crystals

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## Experimental

**Materials and physical measurements.** CuCl<sub>2</sub> was purchased from Strem Co., and used as received. Elemental microanalyses (C, H, N) were performed on crystalline samples by KBSI Pusan Center using a Vario-EL III analyzer. Thermal analyses were performed under N<sub>2</sub> at a scan rate of 10 °C/min using a Labsys TGA-DSC 1600. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer using samples prepared as nujol mulls and KBr pellets. Cyclic voltammograms (CVs) were recorded using a potentiostat/galvanostat, Kosentech model KST-P2. from +0.80 to -0.10 V vs Ag/AgCl in a 0.01 M PBS of pH 7.0.

**Synthesis of bis(4-pyridyl)methylvinylsilane (L).** *n*-Butyllithium (35 mmol, 2.5 M solution in *n*-hexane) was added dropwise to a solution of 4-bromopyridine (33 mmol) in dry diethyl ether (60 mL) under nitrogen gas at -78 °C, at which temperature the resulting mixture was stirred for 1.5 h. At 0 °C, dichloromethylvinylsilane (16 mmol) was slowly

added to the yellow suspension and stirred for 12 h. Distilled water (50 mL) was added into the reaction solution, and the organic solution layer was separated. The organic solution was washed with water, and then was dried over  $\text{MgSO}_4$ . The crude product was purified by column chromatography on silica gel with ethyl acetate. The solvent was evaporated to obtain a viscous liquid in a 63% yield. Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{Si}$ : C, 68.98; H, 6.23; N, 12.38. Found: C, 69.10; H, 6.20; N, 12.44.  $^1\text{H}$  NMR ( $\text{Me}_2\text{SO}-d_6$ ,  $\text{SiMe}_4$ ,  $\delta$ ): 8.59 (d,  $J = 5.7$  Hz, 4H), 7.47 (d,  $J = 5.7$  Hz, 4H), 6.55 (dd,  $J = 14.4$  Hz,  $J = 20.4$  Hz, 1H), 6.30 (dd,  $J = 3.6$  Hz,  $J = 12.0$  Hz, 1H), 5.88 (dd,  $J = 3.3$  Hz,  $J = 20.4$  Hz, 1H), 0.70 (s, 3H). IR (KBr,  $\text{cm}^{-1}$ ): 636 (s), 787 (s), 1124 (s), 1402 (s), 1583 (s).

**Synthesis of  $[\text{CuCl}_2(\text{L})(\text{HCONMe}_2)]$ :** A methanol solution (5 mL) of  $\text{CuCl}_2$  (67 mg, 0.5 mmol) was mixed with an ethanol solution (5 mL) of L (113 mg, 0.5 mmol), and the resulting solid was filtered and dried in vacuum. Diethyl ether was vapor-diffused into the *N,N*-dimethylformamide ( $\text{HCONMe}_2$ ) solution of the crude product to obtain single crystals (consisting of racemic helices) suitable for X-ray crystallography. The single crystals were obtained in 3 days in an 80% yield. Anal. Calcd for  $\text{C}_{16}\text{H}_{21}\text{Cl}_2\text{CuN}_3\text{OSi}$ : C, 44.29; H, 4.88; N, 9.68. Found: C, 44.20; H, 4.78; N, 9.60. IR (nujol mull,  $\text{cm}^{-1}$ ): 1686 (s,  $\nu(\text{CO})$  of  $\text{HCONMe}_2$ ), 1645(s), 1124(s), 800(s), 553(s).

**Synthesis of  $[\text{CuCl}_2(\text{L})(\text{Me}_2\text{SO})]\cdot\text{Me}_2\text{SO}$ :** A methanol solution (5 mL) of  $\text{CuCl}_2$  (67 mg, 0.5 mmol) was mixed with an ethanol solution (5 mL) of L (113 mg, 0.5 mmol), and the resulting solid was filtered and dried in vacuum. Acetone was vapor-diffused into the dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ) solution of the crude product to obtain two kinds of single crystals (consisting of *P* and *M* helices) suitable for X-ray crystallography. Single crystals were obtained in 4 days in an 83% yield. Anal. Calcd for  $\text{C}_{17}\text{H}_{26}\text{Cl}_2\text{CuN}_2\text{O}_2\text{S}_2\text{Si}$ : C, 39.49; H, 5.07; N, 5.42. Found: C, 40.10; H, 5.01; N, 5.33. IR (nujol mull,  $\text{cm}^{-1}$ ): 1599 (m), 1411(s), 1012(s), 791(s), 723(s).

**Crystallographic structure determinations.** All X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a CCD detector at ambient temperature. The 36 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. Absorption effects were corrected by the multi-scan method. The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97).<sup>1</sup> The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model. For [CuCl<sub>2</sub>(L)(HCONMe<sub>2</sub>)], the vinyl groups and the methyl groups attached to silicon atom were disordered. Also, solvent molecules in the voids were highly disordered and were impossible to refine using conventional discrete-atom models. Therefore, the residual electron density was treated as diffuse contributions using the SQUEEZE of the PLATON software and located a series of voids (see below).<sup>2</sup>

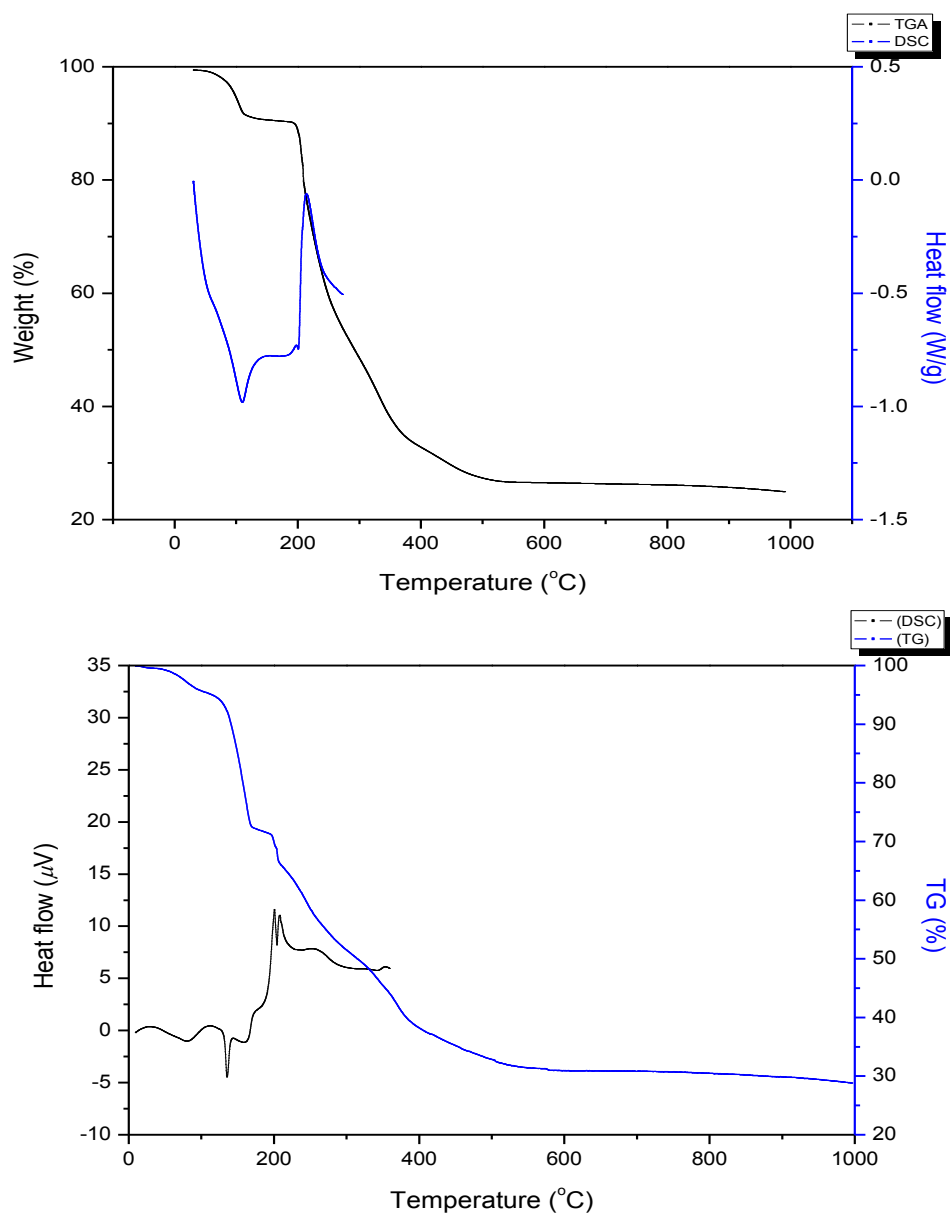
_platon_squeeze_void_nr	_platon_squeeze_void_average_x	_platon_squeeze_void_average_y	_platon_squeeze_void_average_z	_platon_squeeze_void_volume	_platon_squeeze_void_count_electrons	_platon_squeeze_void_content
1	0.114	0.114	0.114	423	28 ''	
2	0.114	-0.114	0.386	423	28 ''	
3	0.386	-0.114	0.614	423	28 ''	
4	0.386	0.114	0.886	423	28 ''	
5	0.636	0.136	0.364	423	28 ''	
6	0.864	0.136	0.636	423	28 ''	
7	0.364	0.364	0.364	423	28 ''	
8	0.136	0.364	0.636	423	28 ''	
9	0.886	0.385	0.114	423	28 ''	
10	0.614	0.386	0.886	423	28 ''	
11	0.886	0.614	0.386	423	28 ''	
12	0.614	0.614	0.614	423	28 ''	
13	0.364	0.635	0.136	423	28 ''	

14	0.136	0.635	0.864	423	28 ''
15	0.636	0.864	0.136	423	28 ''
16	0.864	0.864	0.864	423	28 ''

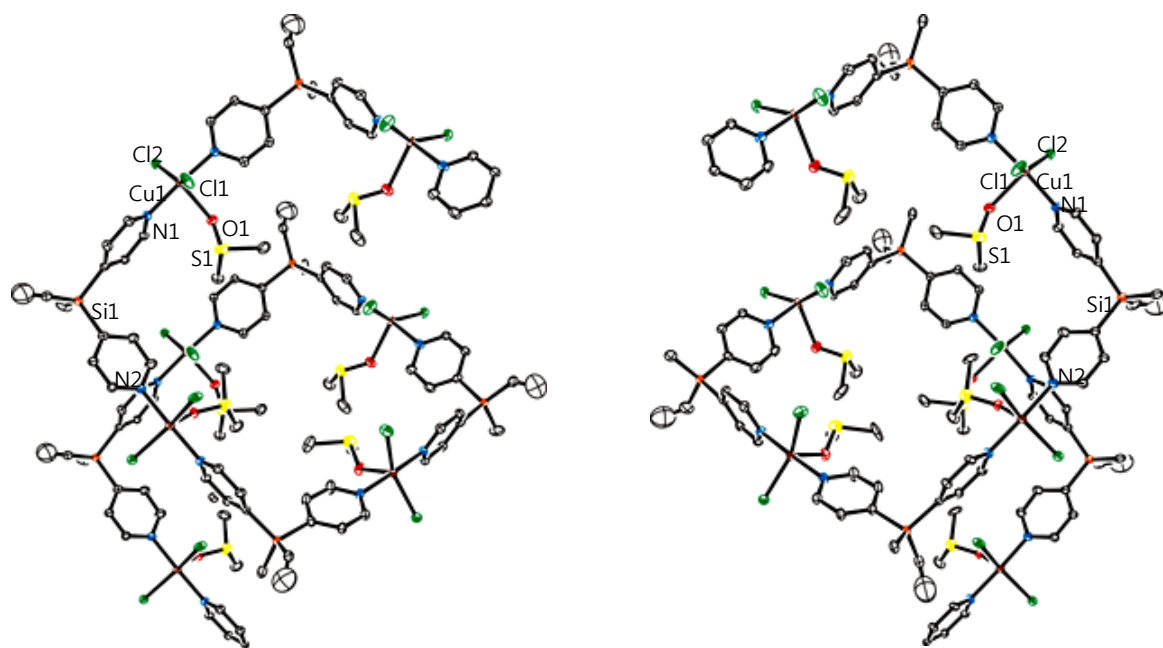
Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-830424, 830425, and 830426 for racemic, *P*, and *M* helices, respectively). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). The crystal parameters and procedural information regarding the data collection and structure refinement are given in Table S1, and relevant bond lengths and angles are listed in Table S2.

## References

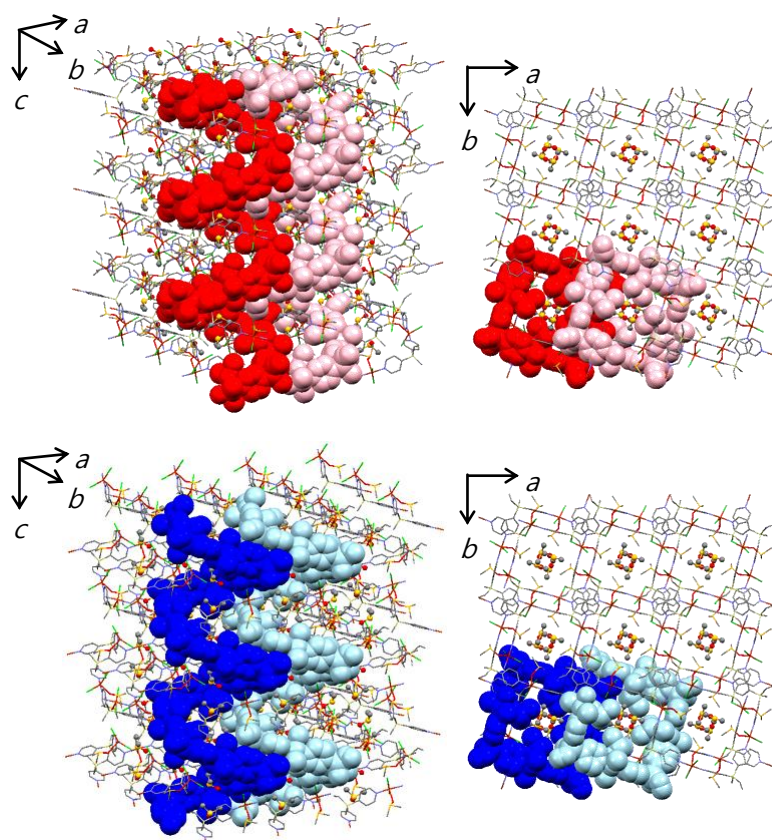
- 1 Sheldrick, G. M. SHELXS-97: A Program for Structure Determination; University of Göttingen, Germany, 1997; Sheldrick, G. M. SHELXL-97: A Program for Structure Refinement; University of Göttingen, Germany, 1997.
- 2 Spek, A. L. *J. Appl. Crystallogr.*, 2003, **36**, 7.



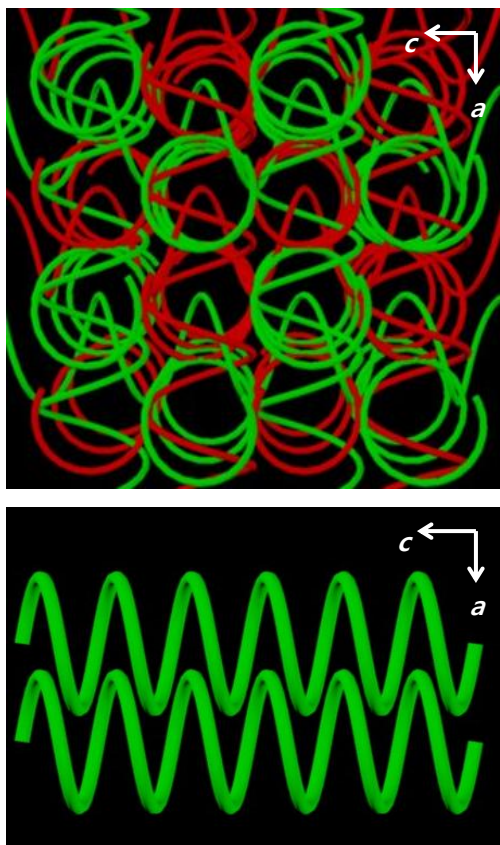
**Fig. S1** TGA and DSC analyses of [CuCl<sub>2</sub>(L)(HCONMe<sub>2</sub>)] (top) and [CuCl<sub>2</sub>(L)(Me<sub>2</sub>SO)]·Me<sub>2</sub>SO (bottom).



**Fig. S2** ORTEP drawings of *M*-[CuCl<sub>2</sub>(L)(Me<sub>2</sub>SO)]·Me<sub>2</sub>SO (left) and *P*-[CuCl<sub>2</sub>(L)(Me<sub>2</sub>SO)]·Me<sub>2</sub>SO (right).



**Fig. S3** Packing diagrams of *P*- $[\text{CuCl}_2(\text{L})(\text{Me}_2\text{SO})]\cdot\text{Me}_2\text{SO}$  (top) and *M*- $[\text{CuCl}_2(\text{L})(\text{Me}_2\text{SO})]\cdot\text{Me}_2\text{SO}$  (bottom).



**Fig. S4** Schematic representation of racemic crystal (top) and *P* crystal (bottom).



**Table S1** Crystallographic data for [CuCl<sub>2</sub>(L)(HCONMe<sub>2</sub>)] (racemic), *P*-[CuCl<sub>2</sub>(L)(Me<sub>2</sub>SO)]·0.5Me<sub>2</sub>SO (right-handed), and *M*-[CuCl<sub>2</sub>(L)(Me<sub>2</sub>SO)]·Me<sub>2</sub>SO (left-handed).

	Racemic	<i>P</i> (right-handed)	<i>M</i> (left-handed)
formula	C <sub>32</sub> H <sub>41</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>2</sub> Si <sub>2</sub>	C <sub>16</sub> H <sub>23</sub> Cl <sub>2</sub> CuN <sub>2</sub> O <sub>1.5</sub> S <sub>1.5</sub> Si	C <sub>17</sub> H <sub>26</sub> Cl <sub>2</sub> CuN <sub>2</sub> O <sub>2</sub> S <sub>2</sub> Si
weight	866.77	477.98	517.05
crystal system	Cubic	Tetragonal	Tetragonal
space group	<i>I</i> <sub>4</sub> <sup>3</sup> / <i>d</i>	<i>P</i> 4 <sub>1</sub>	<i>P</i> 4 <sub>3</sub>
<i>a</i> , Å	30.848(4)	11.9782(4)	12.0129(2)
<i>b</i> , Å	30.848(4)	11.9782(4)	12.0129(2)
<i>c</i> , Å	30.848(4)	15.789(1)	15.8085(3)
<i>V</i> , Å <sup>3</sup>	29354(6)	2265.4(2)	2281.32(7)
<i>Z</i>	24	4	4
<i>d</i> <sub>cal</sub> , Mg m <sup>-3</sup>	1.177	1.401	1.505
<i>μ</i> , mm <sup>-1</sup>	1.167	1.400	1.442
<i>R</i> { <i>I</i> > 2σ( <i>I</i> )}	<sup>a</sup> <i>R</i> <sub>1</sub> = 0.0454 <sup>b</sup> <i>wR</i> <sub>2</sub> = 0.1053	<i>R</i> <sub>1</sub> = 0.0491 <i>wR</i> <sub>2</sub> = 0.1221	<i>R</i> <sub>1</sub> = 0.0500 <i>wR</i> <sub>2</sub> = 0.1308
flack <i>χ</i> parameter	0.00(2)	0.01(2)	0.00(2)

<sup>a</sup>*R*<sub>1</sub> = ∑||*F*<sub>c</sub>| - |*F*<sub>o</sub>||/∑|*F*<sub>o</sub>|. <sup>b</sup>*wR*<sub>2</sub> = ∑*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>/∑*wF*<sub>o</sub><sup>4</sup>)<sup>1/2</sup>

**Table S2** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $[\text{CuCl}_2(\text{L})(\text{HCONMe}_2)]$  (racemic), *P*- $[\text{CuCl}_2(\text{L})(\text{Me}_2\text{SO})]\cdot\text{Me}_2\text{SO}$  (right-handed), and *M*- $[\text{CuCl}_2(\text{L})(\text{Me}_2\text{SO})]\cdot\text{Me}_2\text{SO}$  (left-handed).

Racemic		<i>P</i> (right-handed)		<i>M</i> (left-handed)	
Cu1–N1	2.028(4)	Cu1–N1	2.023(6)	Cu1–N1	2.018(4)
Cu1–N2	2.041(4)	Cu1–N2 <sup>#2</sup>	2.026(6)	Cu1–N2 <sup>#3</sup>	2.031(4)
Cu1–Cl1	2.290(1)	Cu1–Cl1	2.280(2)	Cu1–Cl1	2.285(2)
Cu1–Cl2	2.314(1)	Cu1–Cl2	2.274(3)	Cu1–Cl2	2.273(2)
Cu1–O1	2.195(3)	Cu1–O1	2.331(5)	Cu1–O1	2.307(4)
N1–Cu1–N2	168.7(2)	N1–Cu1–N2 <sup>#2</sup>	174.8(3)	N1–Cu1–N2 <sup>#3</sup>	176.1(2)
C3–Si1–C3 <sup>#1</sup>	104.5(3)	C5–Si1–C9	106.2(3)	C5–Si1–C9	106.5(2)
C8–Si2–C8 <sup>#1</sup>	102.9(3)				

<sup>#1</sup> $x, -y+2, -z+3/2$  <sup>#2</sup> $x, -y, z-1/4$ , <sup>#</sup>  $x-1, -y+2, z+1/4$