Supplementary information

Homochiral crystallisation of helical coordination chains bridged by achiral ligands: can it be controlled by the ligand structure?

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Experimental Section

*Synthesis of 2-[5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl]pyridine (L1)*

In a round-bottom two-neck 250-ml flask equipped with a magnetic stirrer, a condenser and a CaCl$_2$ tube, the nicotinic acid (20 g, 162 mmol) was added, and SOCl$_2$ (24.5 ml, 336 mmol) was added slowly from a dropping funnel under N$_2$ atmosphere. After the resulting solution was refluxed for 4 hrs, dried toluene (30 ml) was added. After the toluene was evaporated to dry under reduced pressure, compound A was obtained in a quantitative yield. $^1$H NMR (DMSO-$d_6$): 9.95 (b, 1 H), 9.4 (d, 1 H), 9.0 (dd, 1 H), 8.65 (dt, 1 H), 7.75 (dd, 1 H) ppm.

In a round bottom two-neck 250-ml flask equipped with a magnetic stirrer, a condenser and a CaCl$_2$ tube, the compound A (1.37 g, 7.7 mmol) was stirred at 0 °C in dried pyridine (30 ml) under N$_2$ atmosphere. A solution of picolinic acid hydrazine (1.05 g, 7.7 mmol) in dried pyridine (30 ml) was added through a dropping funnel. After stirring for 1 hr at room temperature, the mixture was refluxed for 2 hrs. The excess pyridine was evaporated to dry under reduced pressure. Compound B was directly used for the following cyclisation without further purification. Compound B (1.21 g, 5 mmol) was mixed with POCl$_3$ (30 ml), and the mixture was refluxed for 2 hrs to afford a clear yellow solution. The excess POCl$_3$ was removed to give a pale-yellow slurry.
under reduced pressure. Ice-water (ca. 100 ml) was added and the solid formed after standing was collected by filtration, then washed with a large volume of water, dilute aqueous Na$_2$CO$_3$ solution and water, subsequently. A pale-yellow needle-like crystals of L1 was yielded by recrystallization using ethanol, 0.67 g, yield 60%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 9.4$ (dd, 1H), 8.8 (t, 2H), 8.5 (m, 1H), 8.3 (d, 1H), 7.9 (q, 1H), 7.5 ppm (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 164.4, 163.6, 152.9, 150.5, 148.4, 143.4, 137.5, 134.6, 126.3, 123.9, 123.6, 120.4 ppm. IR (KBr, cm$^{-1}$): $\nu$ 3066.4(s), 2995.8(w), 1955.69w), 1785.9(w), 1642.8(w), 1593.7(s), 1548.6(w), 1478.3(m), 1453.9(d), 1410.1(s), 1367.2(w), 133.6(m), 1280.4(s), 1247.3(m), 1190.1(m), 1150.8(w), 1120.0(m), 1086.8(s), 1040.9(w), 1021.8(m), 988.1(m), 965.1(m), 897.7(w), 819.3(s), 796.9(s), 725.1(s), 700.1(s), 617.7(s), 530(w), 508.1(w). ESI-MS (ESITOF, N$_2$): $m/z$ 225 (M + 1). Anal. Calcd for C$_{12}$H$_8$N$_4$O: C, 64.28; H, 3.60; N, 24.99. Found: C, 64.45; H, 3.59; N, 25.08.

**Synthesis of 2-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine (L2).**

![Chemical structure of L2](image)

L2 was synthesized by a similar method for L1, using picolinic acid and isonicotinic acid hydrazine in place of nicotinic acid and picolinic acid hydrazine, respectively. The yield was 61%.
$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.8$ (t, 3H), 8.3 (m, 1H), 8.1 (dd, 2H), 7.9 (t, 1H), 7.5 ppm (t, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 164.7$, 163.9, 151.1, 150.6, 143.3, 137.5, 130.9, 126.4, 123.8, 120.8 ppm. IR (KBr, cm$^{-1}$): $\nu$ 3046.2 (m), 2992.6 (w), 1946 (w), 1694.6 (w), 1604.5 (w), 1588.9 (w), 1507.9 (m), 1544 (s), 1480.8 (s), 1450.1 (s), 1410.5 (s), 1322.3 (m), 1274.8 (w), 1248.7 (w), 1218.8 (w), 1157.6 (w), 1119.3 (w), 1089.8 (m), 1040.9 (w) 989.8 (m), 966.4 (m), 828.8 (s), 797.9 (s), 741.8 (m), 716.8 (s), 691.5 (w), 618.3 (w), 533.3 (w), 512.9 (w), 488.2 (w). ESI-MS (ESI-TOF, N$_2$): $m/z$ 225 (M + 1). Anal. Calcd for C$_{12}$H$_8$N$_4$O: C, 64.28; H, 3.60; N, 24.99. Found: C, 63.98; H, 3.59; N, 24.88.

**Synthesis of [CdI$_2$(L1)$_\infty$]**: To a methanol solution (30 ml) containing CdI$_2$ (0.037 g, 0.1 mmol) was added slowly a methanol solution (30 ml) of L1 (0.022 g, 0.1 mmol). The mixture was stirred at 70 °C for 30 minutes. After cooling to room temperature, the resulting solution was filtered. Pale-yellow single crystals suitable for X-ray analysis were obtained by very slow evaporation for two weeks. The yield was 18 mg (ca. 87%). Elemental analysis calcd (%) for C$_{12}$H$_8$CdI$_2$N$_4$O: C, 24.41, H, 1.37, N, 9.49; found: C, 24.30, H, 1.36, N, 9.52.

**Synthesis of [CdI$_2$(L2)$_\infty$]**: The process is similar to the above where L1 (0.1 mmol) was displaced by L2 (0.1 mmol) (yield ca. 81%). Elemental analysis calcd (%) for C$_{12}$H$_8$CdI$_2$N$_4$O: C, 24.41, H, 1.37, N, 9.49; found: C, 24.49, H, 1.38, N, 9.45.

**Synthesis of [{CdI$_2$(L2)(H$_2$O)}$_2$DMF]$_\infty$**: The procedures are identical to those of [CdI$_2$(L2)$_\infty$] except that the solvent DMF (2 ml) was used to replace methanol (yield ca. 85%). Elemental analysis calcd (%) for C$_{18}$H$_{24}$CdI$_2$N$_6$O$_4$: C, 25.65, H, 3.21, N, 11.14; found: C, 25.72, H, 3.20, N, 11.18.
Figure S1. Neighbouring chains for 1. Blue chain stands for (M) left-handed helix. Purple one does for (P) right-handed helix.

Figure S2. Neighbouring chains for 2.

Figure S3. Neighbouring two chains for 3.
Figure S4. Interchain π–π stacking interactions and C–H···I hydrogen bonds between the chains in 3.