Supplementary information

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

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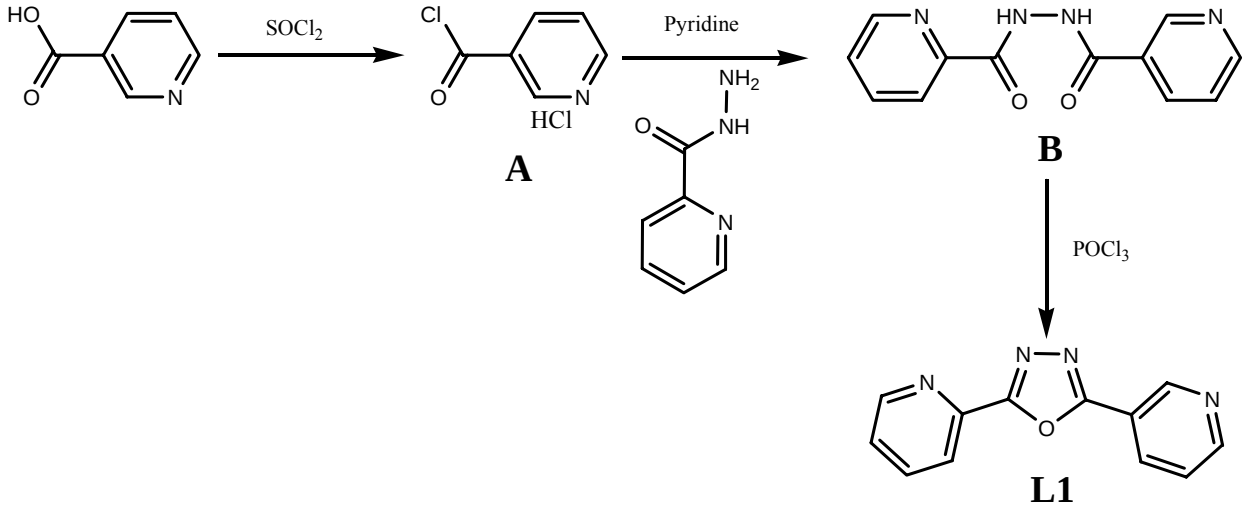
Experimental Section

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

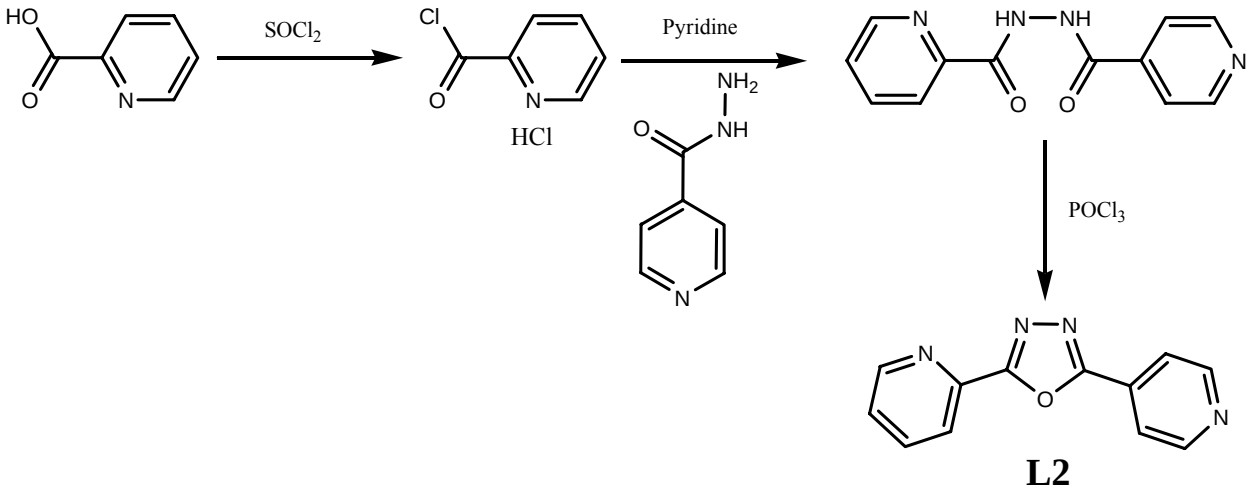


In a round-bottom two-neck 250-ml flask equipped with a magnetic stirrer, a condenser and a $CaCl_2$ tube, the nicotinic acid (20 g, 162 mmol) was added, and $SOCl_2$ (24.5 ml, 336 mmol) was added slowly from a dropping funnel under N_2 atmosphere. After the resulting solution was refluxed for 4 hrs, 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_2CO_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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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}): *v* 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 $C_{12}H_8N_4O$: 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).**



L2

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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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}): *v* 3046.2(m), 2992.6(w), 1946(w), 1694.6(w), 1604.5(w), 1588.9(w), 1567.9(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 (ESITOF, N_2): *m*/*z* 225 (M + 1). Anal. Calcd for $C_{12}H_8N_4O$: C, 64.28; H, 3.60; N, 24.99. Found: C, 63.98; H, 3.59; N, 24.88.

Synthesis of $[CdI_2(\mathbf{L1})]_\infty$: 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 $C_{12}H_8CdI_2N_4O$: C, 24.41, H, 1.37, N, 9.49; found: C, 24.30, H, 1.36, N, 9.52.

Synthesis of $[CdI_2(\mathbf{L2})]_\infty$: 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 $C_{12}H_8CdI_2N_4O$: C, 24.41, H, 1.37, N, 9.49; found: C, 24.49, H, 1.38, N, 9.45.

Synthesis of $\{[CdI_2(\mathbf{L2})(H_2O)]\cdot 2DMF\}_\infty$: The procedures are identical to those of $[CdI_2(\mathbf{L2})]_\infty$ except that the solvent DMF (2 ml) was used to replace methanol (yield *ca.* 85%). Elemental analysis calcd (%) for $C_{18}H_{24}CdI_2N_6O_4$: C, 25.65, H, 3.21, N, 11.14; found: C, 25.72, H, 3.20, N, 11.18.

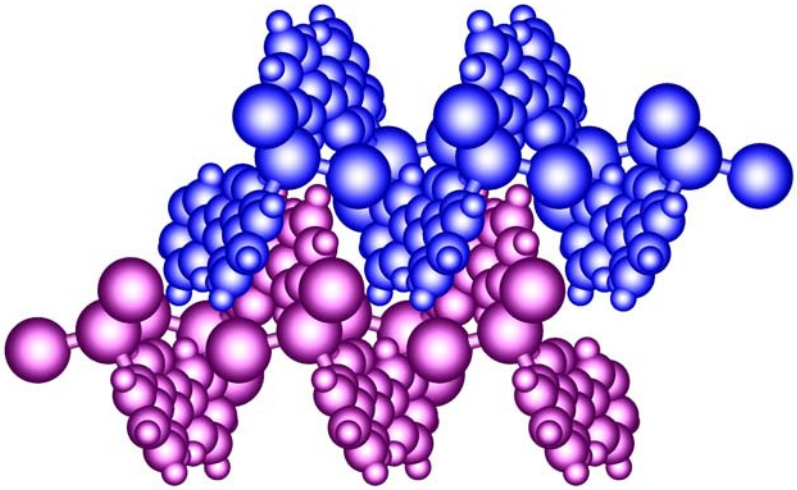


Figure S1. Neighbouring chains for **1**. Blue chain stands for (*M*) left-handed helix. Purple one does for (*P*) right-handed helix.

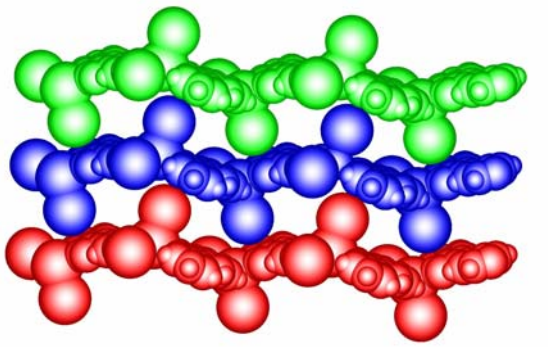


Figure S2. Neighbouring chains for **2**.

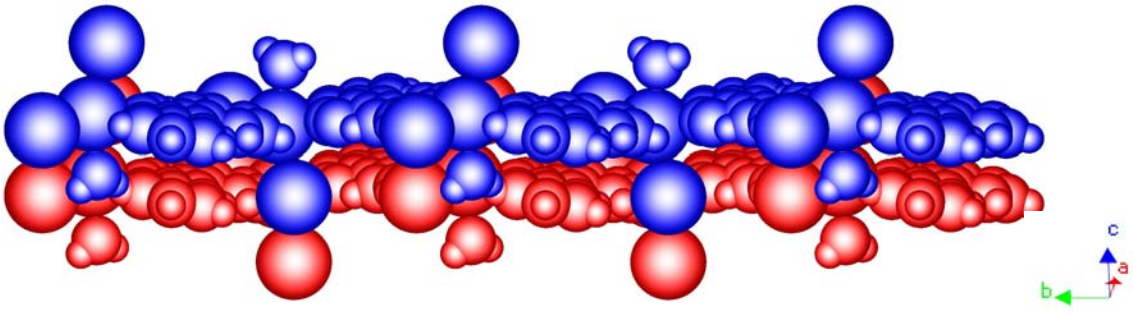


Figure S3. Neighbouring two chains for **3**.

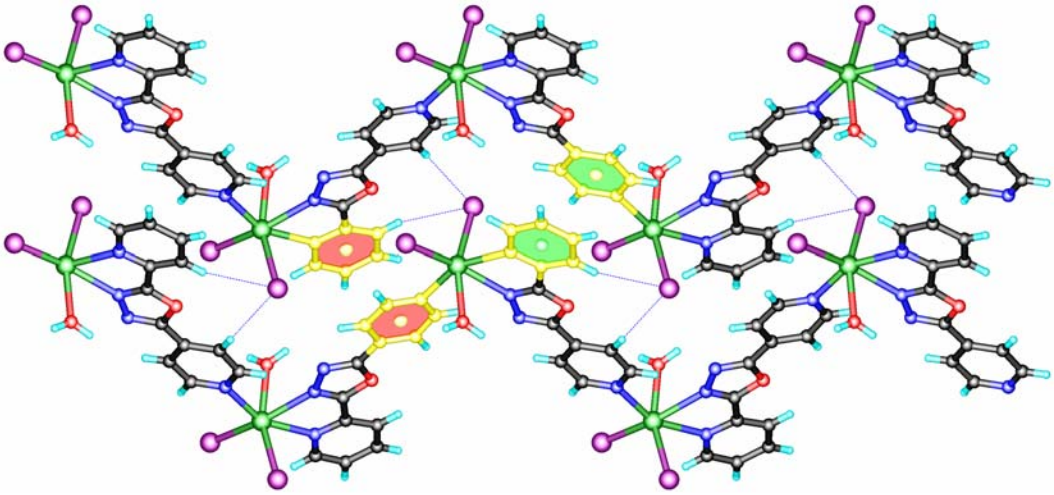


Figure S4. Interchain π–π stacking interactions and C−H···I hydrogen bonds between the chains in **3**.