

Supporting Information for

Hierarchical Assembly of Homochiral Porous Solids Using Coordination and Hydrogen Bonds

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Experimental Section

Materials and Methods. With the exception of 2,2'-dihydroxy-1,1'-binaphthalene-6,6'-dicarboxylic acid, all chemicals were purchased from Aldrich, and used without further purification. The IR spectra were recorded as KBr pellets on a Nicolet Magna-560 FT-IR spectrometer. X-ray powder diffraction data (XRPD) were recorded on a Rigaku MultiFlex diffractometer at 40 kV, 40 mA for CuK α ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of 0.05-0.2 deg/min. The calculated XRPD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. TGA experiments were carried out at a heating rate of 4 °C/min in air. The CD spectra were recorded as KBr pellets on a JASCO J-810 Circular Dichroism system.

Synthesis of 2,2'-dihydroxy-1,1'-binaphthalene-6,6'-dicarboxylic acid. 2.3 g (6.8 mmol) of 6,6'-dicyano-2,2'-dihydroxy-1,1'-binaphthalene was added to a mixture of 10 mL aqueous solution 6N NaOH and 15 mL of distilled water. The reaction mixture was heated to reflux for 12 hrs. Upon cooling to room temperature, the reaction mixture was neutralized with 20 mL of conc. HCl. The precipitate was suction filtered, and the solid was re-crystallized from MeOH and acetone to afford 2.5 g of pure white solid of 2,2'-dihydroxy-1,1'-binaphthalene-6,6'-dicarboxylic acid. (Yield: 99%). ¹H NMR (DMSO-d₆): δ 9.84 (s, 2H, -CO₂H), 8.50 (s, 2H, H₅) 8.07 (d, ³J_{H-H} = 8.7 Hz, 2H, H₃), 7.68 (dd, ³J_{H-H} = 8.8 Hz, ⁴J_{H-H} = 1.3 Hz, 2H, H₇), 7.43 (d, ³J_{H-H} =

8.9 Hz, 2H, H₄), 6.98 (d, 2H, ³J_{H-H} = 8.7 Hz, 2H, H₈).

Synthesis of [Mn(BDA)(DEF)₂(MeOH)]·Lu, 1. A mixture of Mn(NO₃)₂·6H₂O, (2.9 mg, 0.01 mmol) and H₂BDA (3.7 mg, 0.01 mmol) was placed in a small vial containing DEF (5 mL), H₂O (1 mL), MeOH (1 mL) and 2, 6-lutidine (1 mL). The vial was sealed, heated at 60 °C for 3 days, and allowed to cool to room temperature. The crystals suitable for X-ray diffraction were filtered off, washed with diethyl ether and dried in air. Yield: 32%. Anal. calc. for C₄₀H₄₇MnN₃O₉: C, 62.49; H, 6.16; N, 5.47%. Found: C, 61.56; H, 5.94; N, 5.34%. IR (cm⁻¹): 3427 (m), 2974 (w), 2925 (w), 1654 (s), 1640 (ms), 1560 (ms), 1540 (m), 1473 (ms), 1400 (s), 1384 (ms), 1340 (ms), 1285 (w), 1211 (w), 1124 (w), 956 (m), 887 (w), 819 (m), 791 (w), 770 (m), 633 (w).

Synthesis of [Co(BDA)(DEF)(H₂O)]·Lu·DEF, 2. A mixture of Co(NO₃)₂·6H₂O (2.9 mg, 0.01 mmol) and H₂BDA (3.7 mg, 0.01 mmol) was placed in a small vial containing DEF (5 mL), H₂O (1 mL), MeOH (1 mL) and 2, 6-lutidine (1 mL). The vial was sealed, heated at 60 °C for 3 days, and allowed to cool to room temperature. The crystals suitable for X-ray diffraction were filtered off, washed with diethyl ether and dried in air. Yield: 55%. Anal. calc. for C₃₉H₄₅CoN₃O₉: C, 61.74; H, 5.98; N, 5.54%. Found: C, 61.12; H, 5.77; N, 5.36%. IR (cm⁻¹): 3422 (m), 2977 (w), 2929 (w), 1653 (m), 1615 (m), 1570 (s), 1496 (m), 1473 (ms), 1407 (ms), 1384 (ms), 1323 (s), 1260 (w), 1223 (m), 1144 (w), 1091 (m), 1058 (w), 1021 (w), 893 (w), 816 (w), 799 (w), 771 (w), 640 (w).

Synthesis of [Cd(BDA)(Py)₃]·Py·H₂O, 3. A mixture of Cd(NO₃)₂·6H₂O, (3.5 mg, 0.01 mmol) and H₂BDA (3.7 mg, 0.01 mmol) was placed in a small vial containing DEF (5 mL), H₂O (0.5 mL), MeOH (0.5 mL) and Py (1 mL). The vial was sealed and put at room temperature for 4 days. The crystals suitable for X-ray diffraction were filtered off, washed with diethyl ether and dried in air. Yield: 65%. Anal. calc. for C₄₂H₃₄CdN₄O₇: C, 61.58; H, 4.18; N, 6.84%. Found: C, 60.79; H, 4.11; N, 6.50%. IR (cm⁻¹): 3447 (m), 2980 (w), 2927 (w), 1653 (ms), 1642 (m), 1623 (s), 1559 (s), 1507 (m), 1436 (ms), 1394 (ms), 1337 (ms), 1279 (w), 1242 (w), 1066 (w), 1038 (m), 882 (w), 815 (w), 796 (w), 701 (m), 668 (w).

Synthesis of [HNMe₃]₂[Cd₂Cl₂(BDA)₂]·6H₂O, 4. A mixture of CdCl₂·xH₂O, (1.8 mg, 0.01 mmol) and H₂BDA (7.5 mg, 0.02 mmol) was placed in a small vial containing DMF (5 mL), MeOH (1 mL) and N, N'-dimethylaniline (0.2 mL). The vial was sealed, heated at 50 °C for 2 days, and allowed to cool to room temperature. The crystals suitable for X-ray diffraction

were filtered off, washed with diethyl ether and dried in air. Yield: 41%. Anal. calc. for $C_{50}H_{56}Cd_2N_2O_{18}$: C, 47.33; H, 4.45; N, 2.21%. Found: C, 46.17; H, 4.39; N, 2.12. IR (cm^{-1}): 3424 (m), 2975 (w), 1655 (s), 1622 (ms), 1565 (w), 1541 (ms), 1475 (ms), 1421 (s), 1342 (ms), 1340 (ms), 1283 (m), 1245 (m), 1125 (w), 1104 (w), 890 (w), 817 (w), 792 (w), 768 (m), 640 (w).

Removal and Re-introduction of Guest Molecules.

Freshly ground samples of **3** (246 mg) and **4** (290 mg) were subjected to a 10^{-2} Torr vacuum at room temperature. After 50 h, the samples exhibited a weight loss of 31.2 mg for **3** and 26.1 mg for **4**, equivalent to the loss of one pyridine and one water molecules for **3** (calc. 29.3 mg), and six water molecules for **4** (calc. 24.7 mg), respectively. The PXRD patterns taken on the samples after removal of the guest molecules remain essentially identical to those of pristine compounds of **3** and **4** (Figures S8 and S9).

Guest molecules can also be readily reintroduced into the evacuated samples of both **3** and **4** via exposure to corresponding guest molecule vapors. When 150 mg of evacuated sample of **1** was exposed to the vapor of a mixture of water and pyridine (1:1 v/v) for one week, the samples experienced a weight gain of 21.2 mg. This weight gain matches the value expected for the re-introduction of one pyridine and one water molecules per formula unit (expected 20.3 mg). Similarly, when 165 mg of evacuated sample of **4** was exposed to water vapor for one week, the sample experienced a weight gain of 16.2 mg, which corresponds to the absorption of six water molecules per formula unit (expected 15.5 mg). The PXRD patterns taken on the samples after re-introduction of the guest molecules are essentially identical to those of pristine compounds of **3** and **4**.

In contrast, when similar evacuation experiments were performed on compounds **1** and **2**, no weight loss was observed until the samples were heated to 90 °C. After being subjected to a 10^{-2} Torr vacuum at 90 °C for 7 hours, freshly ground samples of **1** (185 mg) and **2** (210 mg) experienced a weight loss of 18.5 mg (25.7 mg expected for complete removal of Lu molecules) for Mn-Lu and 46.5 mg (57.8 mg expected for complete removal of included Lu and DEF molecules), respectively. PXRDs indicated that evacuated samples of **1** and **2** have become completely amorphous, probably as a result of the collapse of the 2D H-bonded framework structures.

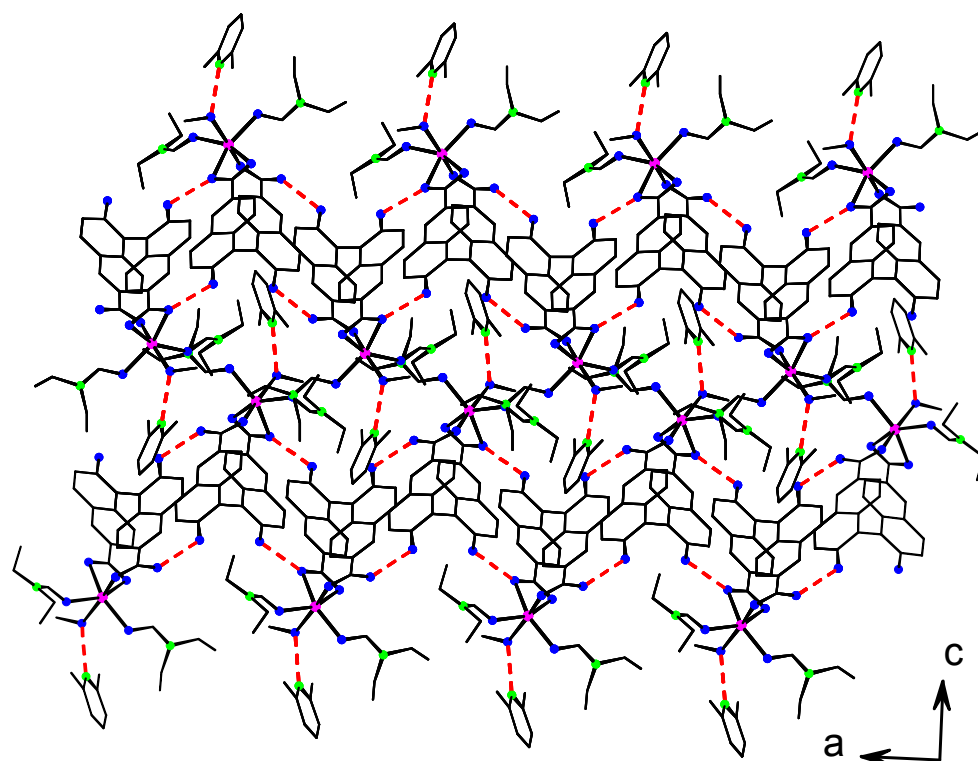


Fig S1. A view of the stacking of lamellae of **1** along the *c* axis. Lu molecules fill the void space between adjacent layers.

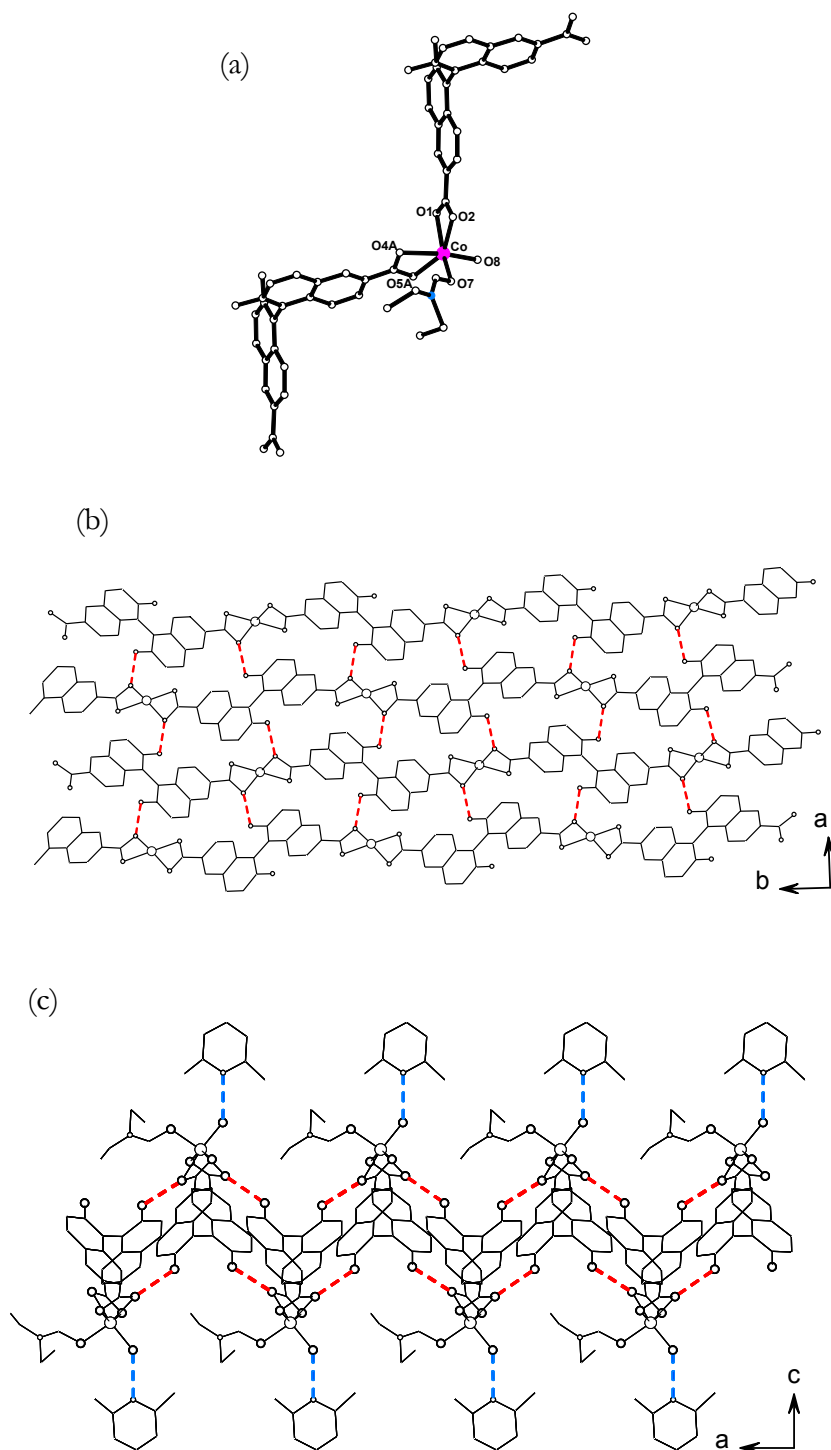


Fig S2. (a) Coordination environment of **2**. (b) A schematic showing 2D H-bonded network as viewed down the *c* axis. (c) A schematic showing the capping of 2D networks by Lu molecules via H-bonding with coordination methanol molecules.

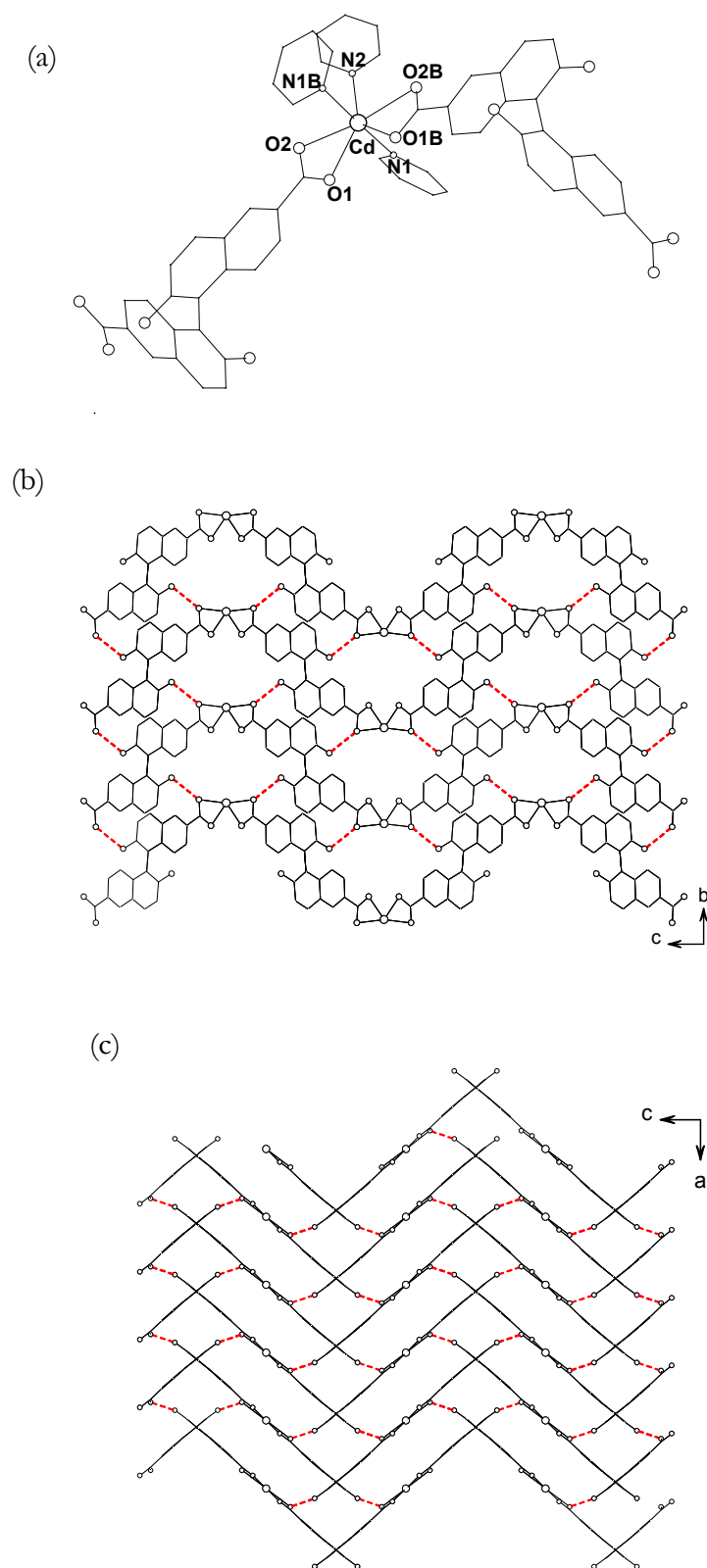


Fig S3. (a) Coordination environment of **3**. (b) A schematic showing 2D H-bonded network as viewed down the *a* axis. (c) A schematic showing 2D H-bonded network as viewed down the *b* axis.

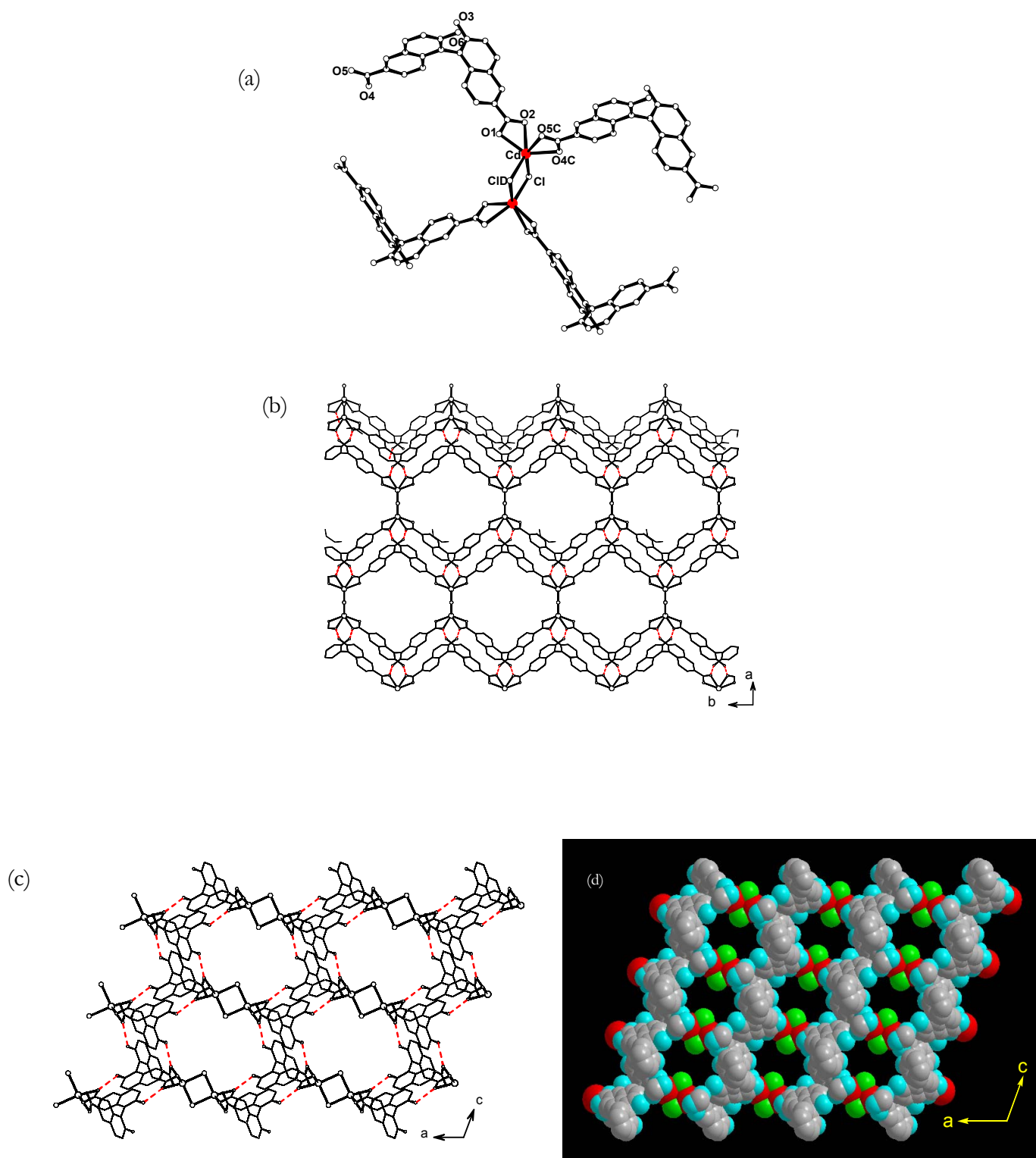


Fig S4. (a) Coordination environment of **4**. (b) A schematic showing 2D H-bonded network as viewed down the *c* axis. (c) A schematic showing 2D H-bonded network as viewed down the *b* axis. (d) Space-filling model of **4** as viewed down the *b* axis. Open channels have dimensions of $0.8 \times 0.6 \text{ nm}^2$.

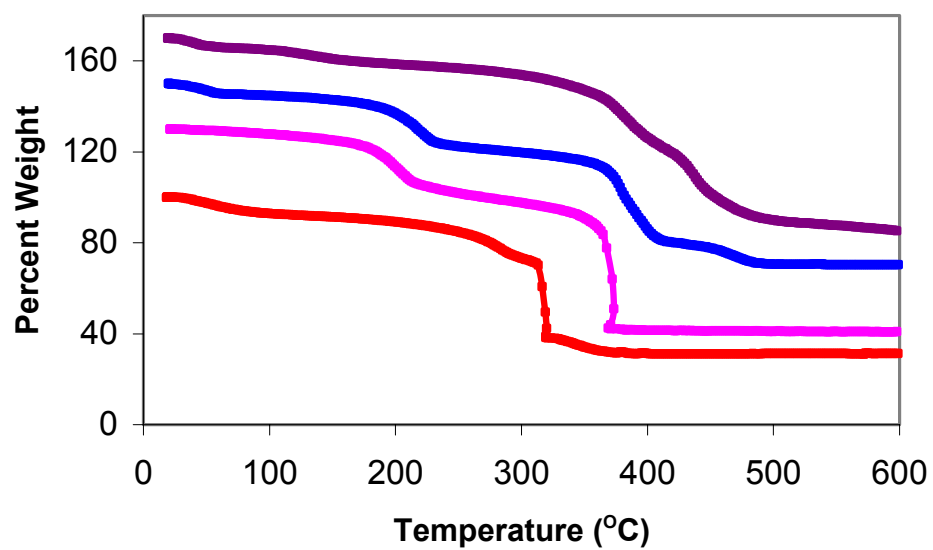


Fig S5. TGA curves of **1** – **4** (from bottom to top). For clarity, the curves for **2**-**4** have been shifted vertically.

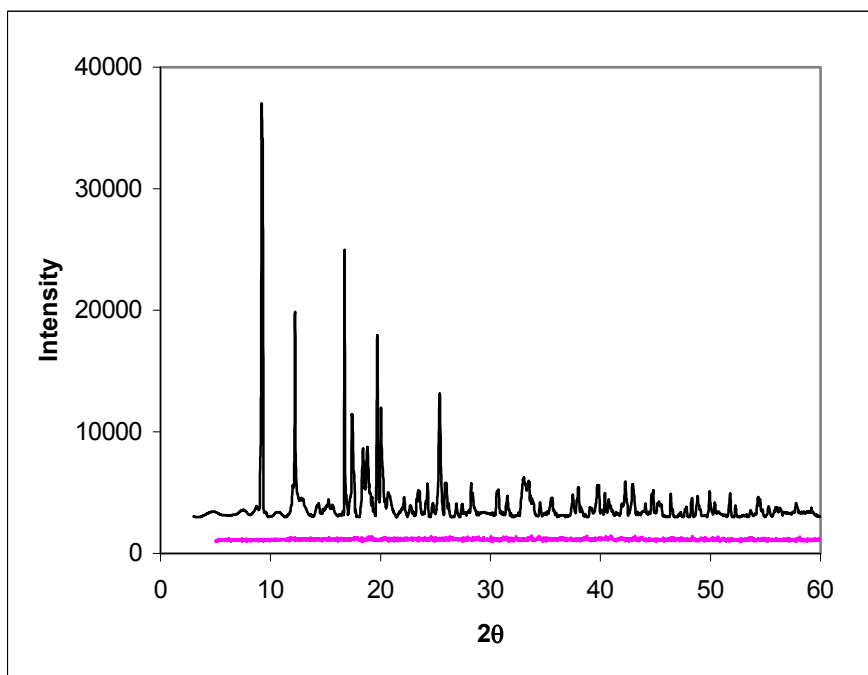


Figure S6. PXRD patterns of pristine solid of **1** (top) and of evacuated solid of **1** (bottom).

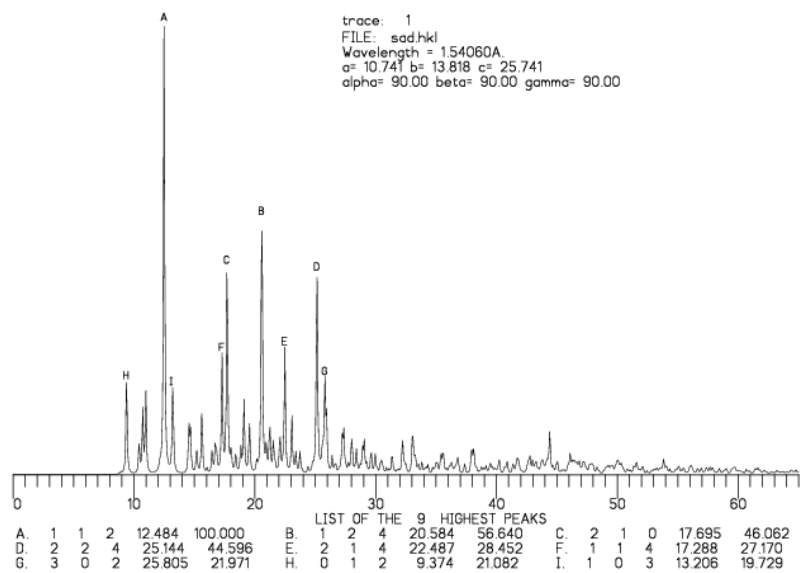


Figure S7. Simulated PXRD pattern for **1**.

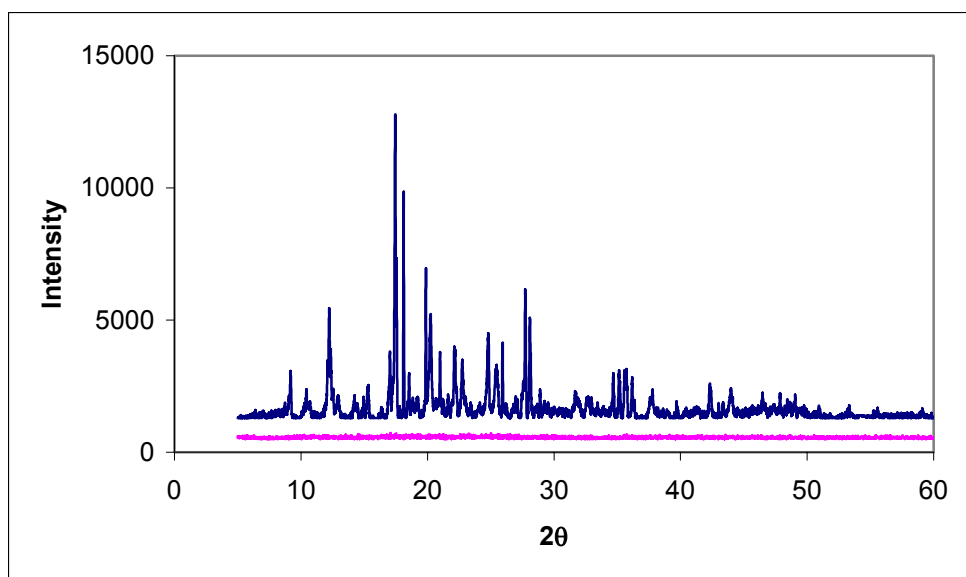


Figure S8. PXRD patterns of pristine solid of **2** (top) and of evacuated solid of **2** (bottom).

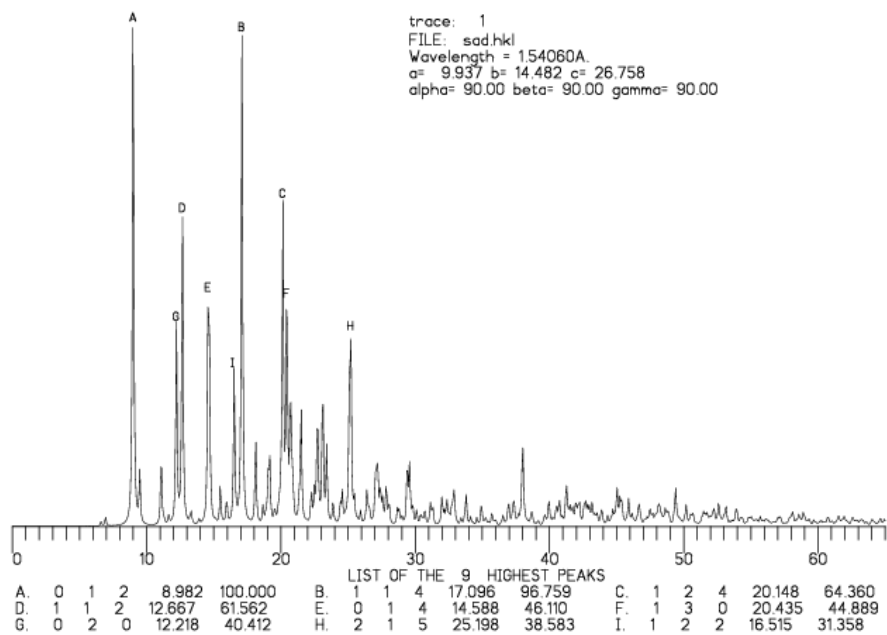


Figure S9. Simulated PXRD pattern for **2**.

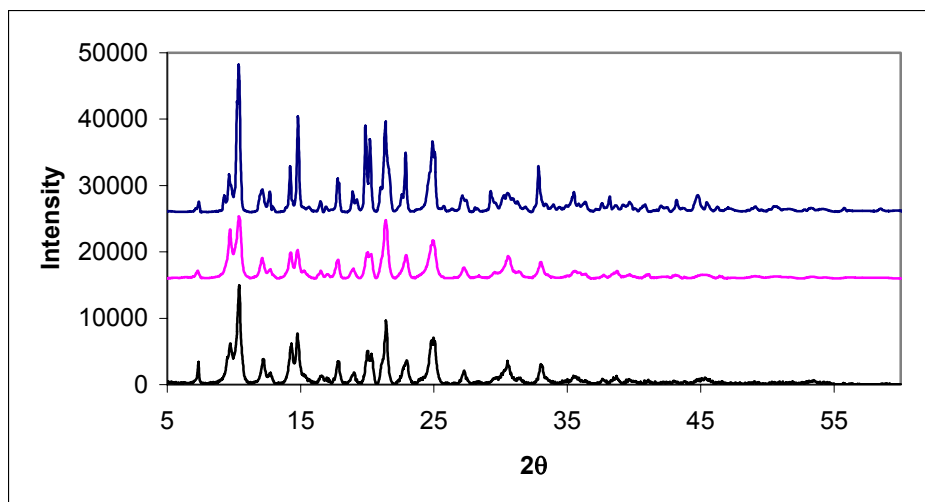


Figure S10. PXRD of **3** before (top) and after (middle) the removal of Py and water guest molecules, and after exposure of evacuated solid to Py and water vapors (bottom).

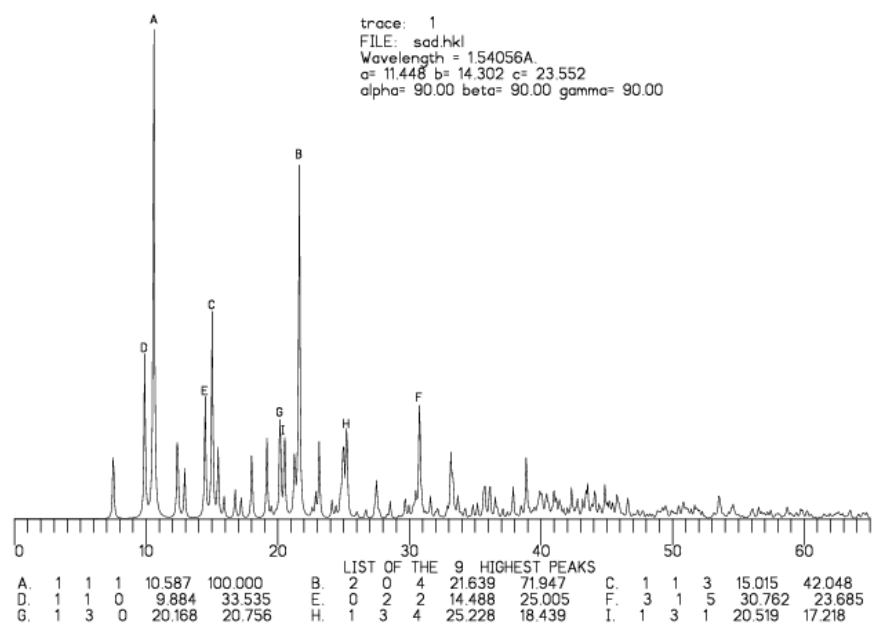


Figure S11. Simulated PXRD of **3**.

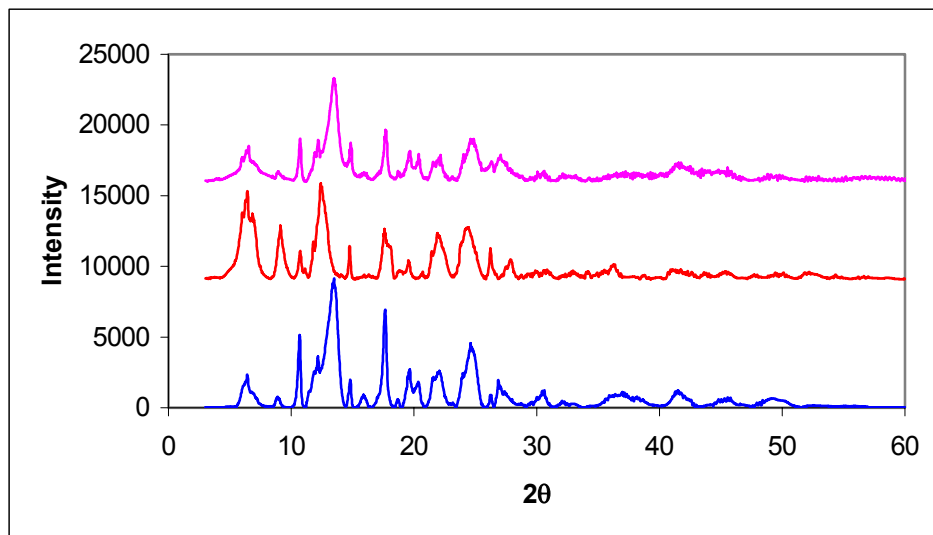


Figure S12. PXRD of **4** before (top) and after (middle) the removal of water guest molecules, and after exposure of evacuated solid to water vapor (bottom).

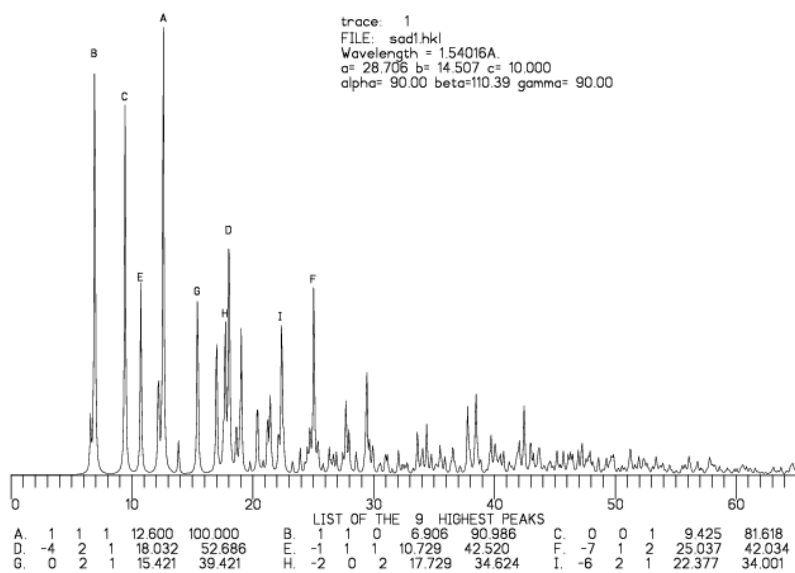


Figure S13. Simulated PXRD of **4**.

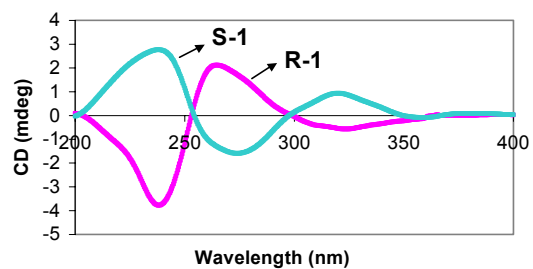


Figure S14. Solid-state CD spectra of (R)- and (S)-1

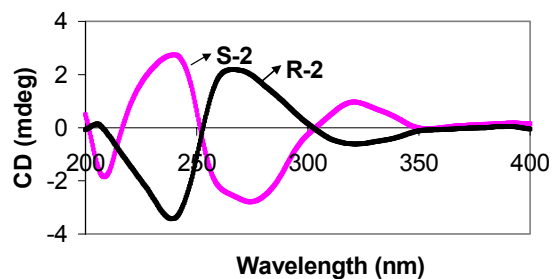


Figure S15. Solid-state CD spectra of (R)- and (S)-2

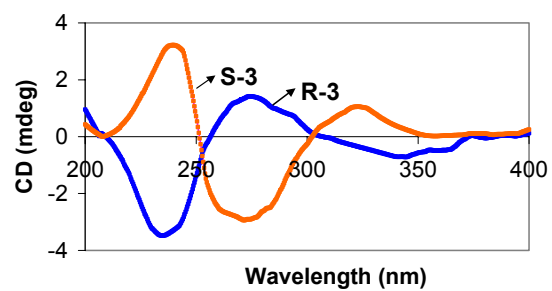


Figure S16. Solid-state CD spectra of (R)- and (S)-3

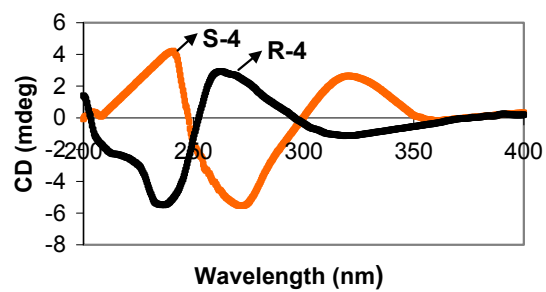


Figure S17. Solid-state CD spectra of (R)- and (S)-4