Inclined 1D→2D Polycatenation of Chiral Chains with Large π-Surfaces

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Supporting Information

Synthetic Details

Synthesis of H_2AlaNDI: A suspension of 1,4,5,8-naphthalenetetraaceticdianhydride (1.023 g, 3.81 mmol) and L-alanine (1.011 g, 11.35 mmol) in DMF (11 mL) was heated to, and held between, 85-90°C for 24 hours. During this time, all solids were taken into solution. The reaction was quenched by pouring the hot solution onto approximately 400 mL of crushed ice, and allowed to stand until all of the ice had melted. H_2AlaNDI was collected by vacuum filtration as a fawn coloured powder (866 mg, 2.11 mmol, 55% yield). ^{1}H NMR (d_6-DMSO) δ 1.55 (d, J = 7.2 Hz, 6H, -CH_3), 5.56 (quartet, J = 6.8 Hz, 2H, CH-CH_3), 8.67 (s, 4H, aromatic CH) ppm. ^{13}C NMR δ (d_6-DMSO) δ 14.56 (CH_3), 49.26 (-$CHCH_3$), 126.31, 131.14, 162.22, 171.31 ppm.

Synthesis of [Cd(AlaNDI)(DMF)$_2$] (1): A solution of $CdCl_2 \cdot 2.5H_2O$ (23 mg, 103.0 μmol) and H_2AlaNDI (35 mg, 85.2 μmol) in DMF (4 mL) was heated to 120°C for two days. During this time, yellow block crystals of [Cd(AlaNDI)(DMF)$_2$] (8 mg, 13.5 μmol, 16% yield) formed in the hot solution. Microanalysis found; C, 43.83; H, 3.74; N, 7.55 %. Calc. for [Cd(Ala-NDI)]·$2H_2O$·1.5DMF; C, 44.16; H, 4.01; N, 7.36 %. Bulk PXRD is consistent with calculated pattern from single crystal data (see below).

The microanalysis results suggest that there is partial exchange of DMF with water when the bulk sample is left to stand in air and also that there is some non-coordinated water present within the structure. The presence of water is consistent with crystallographic results using SQUEEZE and microanalysis (see below). No evidence of water exchange was observed in the crystal structure although there are small pores that contain resolvable electron density (most likely water, see below). The extent of hydration determined by microanalysis and TGA differ slightly (by one water molecule per Cd), most likely arising from differences in the time for which the sample was exposed to air. Phase purity of the compound is unambiguous from PXRD results (see below).

X-Ray Crystallography

Data for poly-[Cd(Ala-NDI)$(DMF)_2$] were collected using the MX1 beamline at the Australian Synchrotron, Victoria, Australia. The wavelength was set at 0.7107 Å (17.4 keV) and data collection temperatures were maintained at 100 K using an open-flow N_2 cryostream. Data collection was conducted using the BluIce package.[1] Indexing and integration was conducted using the program XDS.[2]

The structure was solved by direct methods using SHELXS [3] and refined by alternating least-squares cycles using SHELXL [3] with X-Seed as a graphical interface.[4] All non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms attached to carbon were placed in idealised positions and refined using a riding model. One of the coordinated DMF molecules is disordered over two positions. The occupancies of these positions were refined against each other to give a 70:30 occupancy ratio. One of the methyl carbon atoms of the lower occupancy molecule was refined using an ISOR restraint. No other restraints were used.

The data was processed using the SQUEEZE routine of Platon.[5] This located two small solvent accessible voids in the unit cell (299 $Å^3$) each with 37 e^-. This calculates to be approximately four water molecules or one dimethylformamide molecule. Microanalysis suggests that there is some water present in the analysed sample, although more than is suggested by SQUEEZE (this is likely due to some displacement of DMF by H_2O in transit or simply hydration of the sample).

Powder X-Ray Diffraction

PXRD samples were runs as mulls in Vaseline using a Bruker D8 Focus instrument equipped with Cu-Kα radiation (λ = 1.54 Å) at room temperature. Simulated patterns were calculated from the low temperature single-crystal data using the program Mercury. Allowing for subtle differences due to changes in temperature between calculated (100 K) and experimental (298 K) the patterns are in good agreement. There is significant preferred orientation in the experiment.

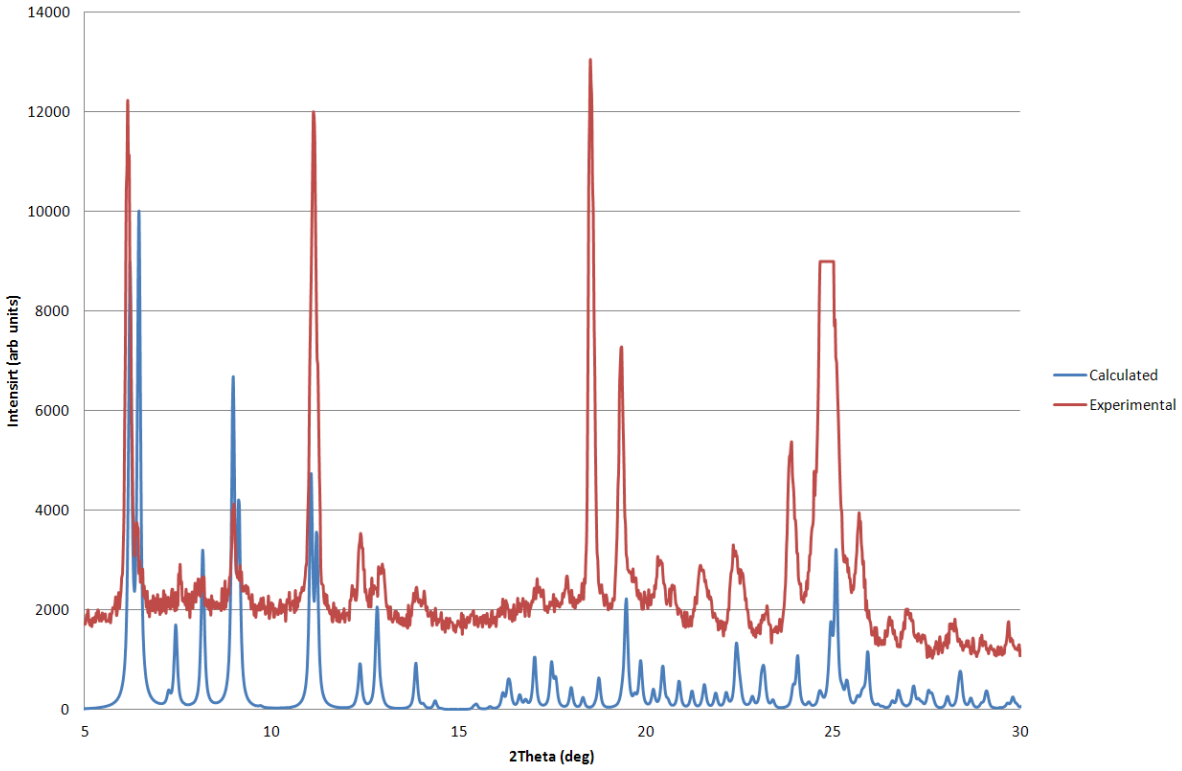

Figure S1: Comparison of calculated (100 K) and experimental (298 K) powder patterns for poly-[Cd(AlaNDI)(DMF)$_2$]. The large peak at ~25° (a result of preferred orientation) has been truncated for clarity.

Thermogravimetric Analysis (TGA)

TGA data were collected using a Mettler Toledo instrument in the range 25 - 400 °C with a scan rate of 10 °C min^{-1}. Weight loss occurs in the range 80-200 °C with the onset of decomposition at ~ 370 °C. The solvent mass loss is 18 % of the starting mass. This calculates (as below) to be either 1.5 DMF molecules or one DMF and two H_2O molecules per metal, the latter of which is consistent with microanalysis results and partial displacement of DMF ligands by water. The small (~ 3%), slow weight loss after 200 °C may represent a small degree of decomposition before the onset of major decomposition at 370 °C.

Mass of polymer = 522.

Loss of 18 % = mass of 115 per Cd is lost.

DMF = 71, H_2O = 18. Therefore 1.5 DMF = 106. DMF + $2H_2O$ = 107.

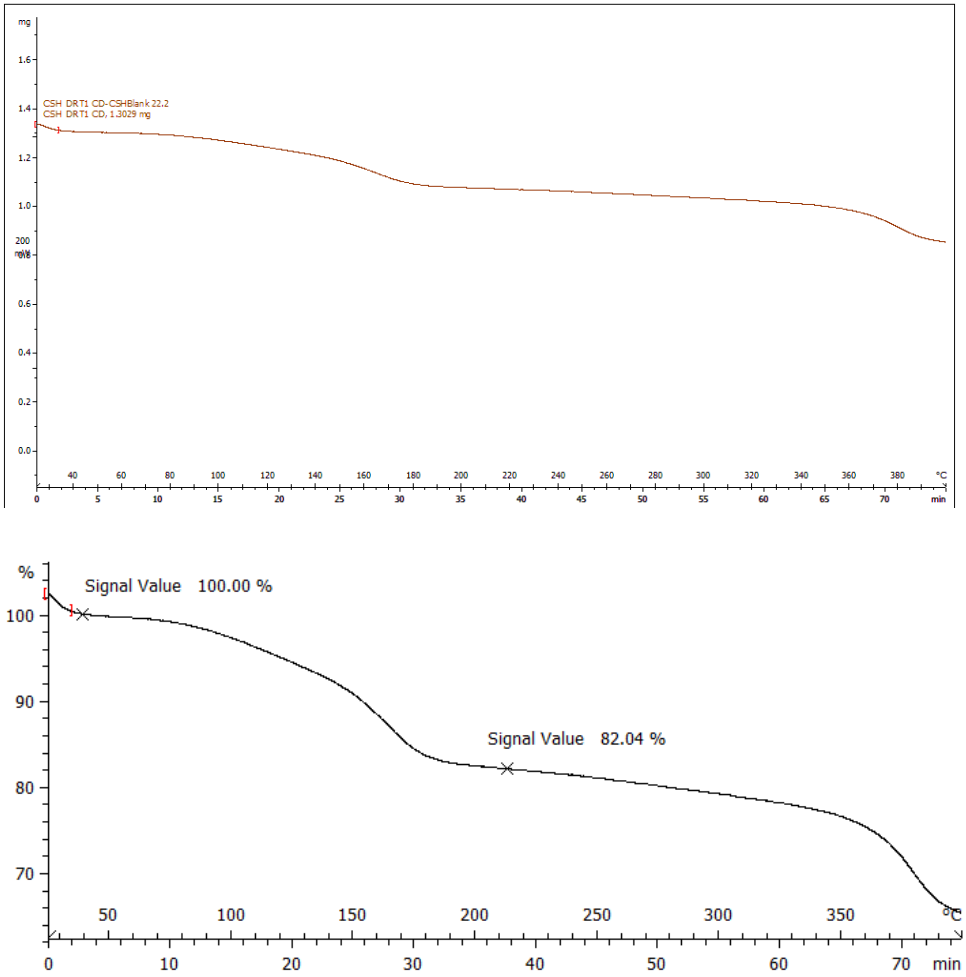

Figure S2: TGA plots for a bulk sample of poly-[Cd(AlaNDI)$(DMF)_2$].

References

[1] T.M. McPhillips, S.E. McPhillips, H.J. Chiu, A.E. Cohen, A.M. Deacon, P.J. Ellis, E. Garman, A. Gonzalez, N.K. Sauter, R.P. Phizackerley, S.M. Soltis, P. Kuhn, *J. Synchrotron Rad.* **2002**, *9*, 401-406.

[2] W. Kabsch, *Acta Crystallogr.* **2010**, *D66*, 125-132.

[3] G.M. Sheldrick, *Acta Crystallogr*. **2008**, *D64*, 112-122.

[4] L.J. Barbour, *J. Supramol. Chem.* **2001**, *1*, 189-191.

[5] A.L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7-13.