Engineering Entanglement: Controlling the Formation of Polycatenanes and Polyrotaxanes Using π-Interactions

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Supporting Information

Syntheses of H_2LeuNDI, H_2LeuPDI and Compounds 1, 2 and 3

All reagents were purchased from standard commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were collected using a Bruker Avance 400 spectrometer operating at 400 and 100 MHz, respectively, with signals referenced to the residual solvent signals. ESI mass spectra were collected using a Micromass Platform II instrument. ATR-IR spectra were collected using a Agilent Cary 630 spectrometer. Elemental analyses were performed at the Campbell Analytical Laboratories, University of Otago, New Zealand. Thermogravimetric data were collected using a Mettler Toledo STARe TGA/DSC 1 instrument in the range 30 - 400 ºC with samples heated at a rate of 5 ºC/min in air.

H_2LeuNDI: Naphthalene-1,4,5,8-tetracarboxylic dianhydride (0.500 g, 1.86 mmol) and L-Leucine (0.733 g, 5.59 mmol) were dissolved in DMF (20 mL) and stirred at 80-90°C overnight, giving a brown solution. The solution was added to water (80 mL) and the product was extracted with diethyl ether (2 x 100 mL) which was subsequently washed with water (2 x 200 mL), dried over magnesium sulfate and the solvent was removed under reduced pressure to give the product as a brown solid. Yield 1.87 g (94 %). m.p. 199-202 ^{0}C. ATR-IR, υ / cm^{-1} : 2935w, 2957w, 2872w, 1708s, 1667s, 1583m, 1452m, 1335s , 1248s, 1194s, 1005m, 770s. δ_H (400 MHz, d_6-DMSO): δ 0.87 (d, J=6.4 Hz, 6H, CH_3), 0.94 (d, J=6.4 Hz, 6H, CH_3), 1.57 (m, 2H, $C\underline{H}(CH_3)_2$), 2.01 (m, 2H, CH_2), 2.12 (m, 2H, CH_2), 5.59 (dd, J=8.8 Hz, 2H, *CH), 8.75 (s, 4H, ArH). δ_C (100 MHz, d_6-DMSO): 21.92, 22.88, 24.84, 37.58, 51.85, 125.99, 126.36, 131.20, 162.37, 170.87. MS (ESI$^-$): *m/z* = 494.2 ([M-H]$^-$, 18), 449.2 ([M-CO_2-H]$^-$, 80%). Elemental analysis calculated for $C_{26}H_{26}N_2O_8 \cdot H_2O$, C, 60.93; H, 5.51; N, 5.47 %. Found, C, 60.76; H, 5.41; N, 5.55 %.

H_2LeuPDI: Perylene-3,4,9,10-tetracarboxylic dianhydride (0.500 g, 1.28 mmol) was dissolved in DMSO (50 mL) and heated to 100 ^{0}C in a reflux apparatus. L-leucine (0.5 g, 3.83 mmol) was dissolved in 2 M KOH (2.5 mL) and added dropwise to the DMSO solution, at which stage the red solution darkened. The solution was left for 3 hours at 100 ^{0}C before cooling to room temperature with the formation of a precipitate which was recovered by filtration and recrystallised from hot water and acetone to yield the dipotassium salt, K_2LeuPDI. The salt was dissolved in hot water and transformed to the diacid by the addition of conc. HCl yielding a precipitate which was recovered by filtration and washed extensively with water before being dried *in vacuo*. Yield 0.584 g, 74 %. mp 345-347 ^{0}C. ATR-IR υ / cm^{-1}: 1957w, 5874w, 1698s, 1655s, 1592s, 1577, 1344s, 1343s, 1243m, 808s, 752s. δ_H (400 MHz, d_6-DMSO): 1.00 (d, *J*=6.4 Hz, 6H, CH_3), 1.04 (d, *J*=6.4 Hz, 6H, CH_3), 1.68 (m, 2H, $C\underline{H}(CH_3)_2$), 2.12 (m, 4H, CH_2), 5.56 (dd, *J*=8.8, 4.9 Hz, 2H, C*H), 8.21 (m, 8H, ArH), 12.87 (s, 2H, CO_2H). δ_C (100 MHz, d_6-DMSO): δ 22.0, 22.9, 25.0, 37.9, 51.4, 121.1, 122.5, 123.7, 127.3, 130.1, 132.4, 161.7, 171.2. MS (ESI^-): *m/z* = 530 ($[M-2CO_2-H]^-$, 100), 573 ($[M-CO_2H-H]^-$, 40) 618 ($[M-H]^-$, 13%). Elemental analysis calculated for $C_{36}H_{30}N_2O_8\cdot 2H_2O$, C, 66.05; H, 5.23; N, 4.28 %. Found, C, 66.29; H, 4.90; N, 4.30 %.

***Poly*-{[Cd_2(LeuNDI)$_2$(DMA)$_4$]·DMA} (1):** H_2LeuNDI (10 mg, 20.2 μmol) and $Cd(NO_3)_2\cdot 4H_2O$ (12.3 mg, 39.9 μmol) were dissolved in dimethylacetamide (3 mL) and heated at 120 ^{0}C in a sealed vial for 72 hours during which time an orange crystalline product formed. Isolated yield 0.8 mg (3 %). ATR-IR, υ/cm^{-1}: 2954m, 2874w, 1579s, 1400s, 1331s, 1249m, 1194m, 1020m, 786s. Elemental analysis calculated for [Cd_2(LeuNDI)$_2$(DMA)$_4$]·3DMA·5H_2O ($C_{80}H_{121}Cd_2N_{11}O_{28}$), C, 50.32; H, 6.39; N, 8.07 %. Found, C, 50.43; H, 6.25; N, 8.33 %. TGA: On-set, 70 °C; mass loss = 35.7 % (calculated 36.7 % for 7 DMA and 5 H_2O per Cd_2). TGA and microanalysis suggests a higher, yet mutually consistent, degree of solvation than the crystal structure, presumably due to surface solvent or hydration on standing. Bulk phase purity confirmed by PXRD (*vide infra*).

***Poly*-{[Cd_2(LeuNDI)$_2$(bipy)(DMF)$_3$(H_2O)]·DMF·H_2O} (2):** H_2LeuNDI (15 mg, 30.4 μmol), 4,4-bpyridine (2.4 mg, 15.2 μmol) and $Cd(NO_3)_2\cdot 4H_2O$ (19 mg, 61.6 μmol) were added to dimethylformamide (3 mL) with sonication to dissolve. The solution was placed in a sealed vial at 120^{0}C for four days to yield a light orange crystalline product. Isolated yield 10.3 mg (41 %). ATR-IR, υ/cm^{-1}: 3071w, 2950w, 2870w, 2114w, 1708m, 1646s, 1579s, 1451m, 1378m, 1331s, 1248s, 1194m, 1102m, 991m, 862w, 821w, 786m. Elemental analysis calculated for [Cd_2(LeuNDI)$_2$(bipy)(DMF)$_3$(H_2O)]·DMF·H_2O ($C_{74}H_{88}Cd_2N_{10}O_{22}$), C, 52.43; H, 5.29; N, 8.26 %. Found, C, 52.18; H, 4.96; N, 8.06 %. TGA: On-set, 77 °C; mass loss = 19.3 % (calculated 19.1 % for 4DMF and 2H_2O per Cd_2). Bulk phase purity was confirmed by PXRD (*vide infra*).

***Poly*-{[Cd_2(LeuPDI)$_2$(H_2O)$_4$]·3DMF} (3):** H_2LeuPDI (10 mg, 16.2 μmol) and $Cd(NO_3)_2\cdot 4H_2O$ (9.9 mg, 32.1 μmol) were added to dimethylformamide (3 mL) with sonication to dissolve. The solution was placed in a sealed vial at 110 ^{0}C for four days to yield a red crystalline material. Isolated yield 5 mg (20 %). ATR-IR, υ/cm^{-1}: 3484w, 2952w, 2870w, 2117w, 1696, 1648m, 1570s, 1402m, 1337s, 1251m, 1181m, 1106m, 851m, 812m. Elemental analysis calculated for [Cd_2(LeuPDI)$_2$(H_2O)$_4$]·H_2O·3DMF ($C_{81}H_{96}Cd_2N_7O_{24}$), C, 55.05; H, 4.96; N, 5.55 %. Found, C, 54.81; H, 4.81; N, 5.79 %. TGA: On-set, 50 °C; mass loss = 17.2 % (calculated 17.5 % for 3DMF and 5H_2O per Cd_2). Results from SQUEEZE (see below) suggest a solvent contribution of 3DMF, in reasonable agreement with TGA/microanalysis, with additional water in the analyses believed to come from a small degree of hydration upon standing in air. Bulk phase purity was confirmed by PXRD (*vide infra*).

Crystallographic Information

Data for all structures was collected using the MX1 and MX2 beamlines at the Australian Synchrotron operating at 17.4 KeV (0.7107 Å). Data collection temperatures were maintained at 100 K using an open-flow N_2 cryostream. Data indexing and integration was conducted using the XDS package. All structures were solved by direct methods using SHELXS-2013 and refined by least-squares cycles using SHELXL-2013 or SHELXL-97 with the program Olex2 as a graphical interface. All non-hydrogen atoms were refined using an anisotropic model except where noted in individual structure refinement details given below. All hydrogen atoms were placed in idealised X-ray positions and refined using riding models. Full crystallographic refinement parameters are given below alongside special refinement details for each of the structures.

Compound	**1**	**2**	**3**
Composition	Poly-{[Cd_2(LeuNDI)$_2$(DMA)$_4$]·DMA}	*Poly-*{[Cd_2(LeuNDI)$_2$(bipy)(DMF)$_3$(H_2O)]·DMF·H_2O}	*Poly-*{[Cd_2(LeuPDI)$_2$(H_2O)$_4$]·3DMF }
Empirical formula	$C_{72}H_{93}Cd_2N_9O_{21}$	$C_{74}H_{88}Cd_2N_{10}O_{22}$	$C_{81}H_{94}Cd_2N_7O_{23}$
M	1645.35	1694.34	1758.43
Crystal system	Triclinic	Monoclinic	Hexagonal
Space group	*P*1	*C*2	$P6_122$
a / Å	10.239(2)	45.995(9)	19.928(3)
b / Å	13.283(3)	15.366(3)	19.928(3)
c / Å	15.851(3)	32.009(6)	78.862(16)
α / º	73.28(3)	90	90
β / º	79.44(3)	134.07(3)	90
γ / º	80.24(3)	90	120
V / Å^3	2014.1(7)	16255(6)	27122(8)
Z	1	4	12
μ / mm^{-1}	0.601	0.597	0.541
No. reflections (R_{int})	69001 (0.0565)	93495 (0.0800)	113556 (0.1084)
Unique reflections	23372	25655	10626
Obs. reflections (I>2σI)	18858	19898	9176
Theta range	1.36-31.53	0.89 – 24.14	1.29-21.70
R_1 (I>2σI / all reflections)	0.0575 / 0.0735	0.0920 / 0.1075	0.0765 / 0.0832
wR2 (all reflections)	0.1732	0.2704	0.2175
GooF	1.075	1.032	1.030
Flack parameter	0.04(2)	0.09(3)	0.06(4)

Poly-{[$Cd_2(LeuNDI)_2(DMA)_4$]·DMA}

The structure contains two partial occupancy DMA sites within the macrocycle motif which are modelled to be 50 % occupancy. Both coordinated and uncoordinated DMA molecules showed some signs of disorder that could not be modelled, necessitating the use of distance restraints in some instances. Several of the terminal CH_3 groups of the isobutyl chains required distances restraints to preserve the geometry of the group; all were refined using an anisotropic model. TGA and microanalysis suggests a slightly higher degree of solvation than that determined crystallographically (see synthetic section). This may to be due to the DMA occupancies being higher than those modelled (there is evidence of a second disorder position for each which could not be fully elucidated) and the possibility of unresolved water in small spaces between the chains, although no significant electron density is present suggesting the water is disordered if this is the case. It may also be due to surface solvent for the classical analytical methods and hydration on standing out of the mother liquor.

Poly-{[$Cd_2(LeuNDI)_2(bipy)(DMF)_3(H_2O)$]·DMF·$H_2O$}

Due to unresolvable disorder and a slightly low diffraction limit of the sample, the DMF ligands and isobutyl groups of the LeuNDI ligands were not well resolved. Both of the two unique chains in the structure were refined with three full occupancy DMF ligands and a full occupancy aqua ligand (hydrogen atoms not modelled). One DMF molecule (refined as a rigid body) and two water molecules per ASU (i.e. ½ DMF and 1 H_2O per Cd_2) were located in the lattice. Microanalysis and TGA suggests the presence of both H_2O and DMF in the sample (2 and 4 per Cd_2 unit in total, respectively).

All bar one of the DMF ligands and six of the eight isobutyl groups were refined using an isotropic model. Six of the isobutyl groups and one DMF were readily locatable from the Fourier difference map and were refined using distance restraints where necessary. The remaining isobutyl and DMF groups were less easily distinguished and were modelled as rigid bodies using input coordinates from a non-disordered structure. Four terminal CH_3 carbon atoms of isobutyl chains were refined with their u_{iso} values riding on the tertiary carbon atom to which they are bonded.

The data was processed using the SQUEEZE [i] routine due to the presence of unresolvable electron density, suggesting a volume of significant voids of 1280 $Å^3$ containing 174 e^- which equates to 43.5 e^- per ASU. This value suggests an additional DMF per ASU (42 e^-) bringing the total DMF to one per Cd_2 unit. The TGA and microanalysis results are in reasonable agreement with this formulation. Several smaller voids were also located (~ 20 $Å^3$) that contained no significant electron density.

Poly-{[$Cd_2(LeuPDI)_2(H_2O)_4$]·3DMF}

Due to the low diffraction limit of the crystalline sample, using the strongest synchrotron radiation available to us, the coordinated solvent could not be well resolved. The solvent is modelled as only O atoms given that only the immediately coordinating atoms could be located. Microanalysis and TGA suggests the presence of both H_2O and DMF in the sample (5 and 3 per Cd_2, respectively), although it cannot categorically be stated which species are coordinating and which are in the lattice. Due to large volumes on unresolvable electron density, the data was processed using the SQUEEZE routine, suggesting a void volume of

9876 Å^3 containing 1445 e$^-$ which suggests 3DMF molecules per Cd_2 unit (total = 1512 e$^-$). It is assumed that the additional water seen in TGA/microanalysis may be due to hydration upon standing in air. The solvent contribution of 3DMF per Cd_2 and non-located H_2O hydrogen atoms have been incorporated into the crystal data of the refined structure.

Given the low resolution, several restraints were applied to the refinement model. The four leucine ^{i}Bu groups in the structure were refined using an isotropic model with distance restraints to maintain bond lengths and geometry. In two instances, terminal carbon atoms were refined with their u_{iso} values riding on that of the tertiary carbon to which they are bonded. One end of one of the PDI groups shows signs of disorder, appearing to results from side-to-side movement within the catenane motif, which could not be modelled. Bond distances within the five atoms of the diimide functionality were restrained. Large displacement parameters remain that are a good description of the apparent disorder. The disorder appears to involve Cd2 and associated coordinating atoms which could also not be resolved. No restraints have been applied to the metals, coordinating groups or other parts of the PDI ligands. The structure and connectivity are unambiguous.

Powder X-Ray Diffraction (PXRD)

PXRD data was obtained on all structures to confirm bulk purity. Data was collected at room temperature using a Bruker D8 instrument equipped with Cu-Kα radiation (1.54 Å). Patterns were calculated from the 100 K single crystal X-ray data using Mercury. In all cases, analysis of the bulk samples show them to compose of a single crystalline product that agrees with that calculated from the crystal structures with minor differences arising from collection temperatures and the effects of preferred orientation.

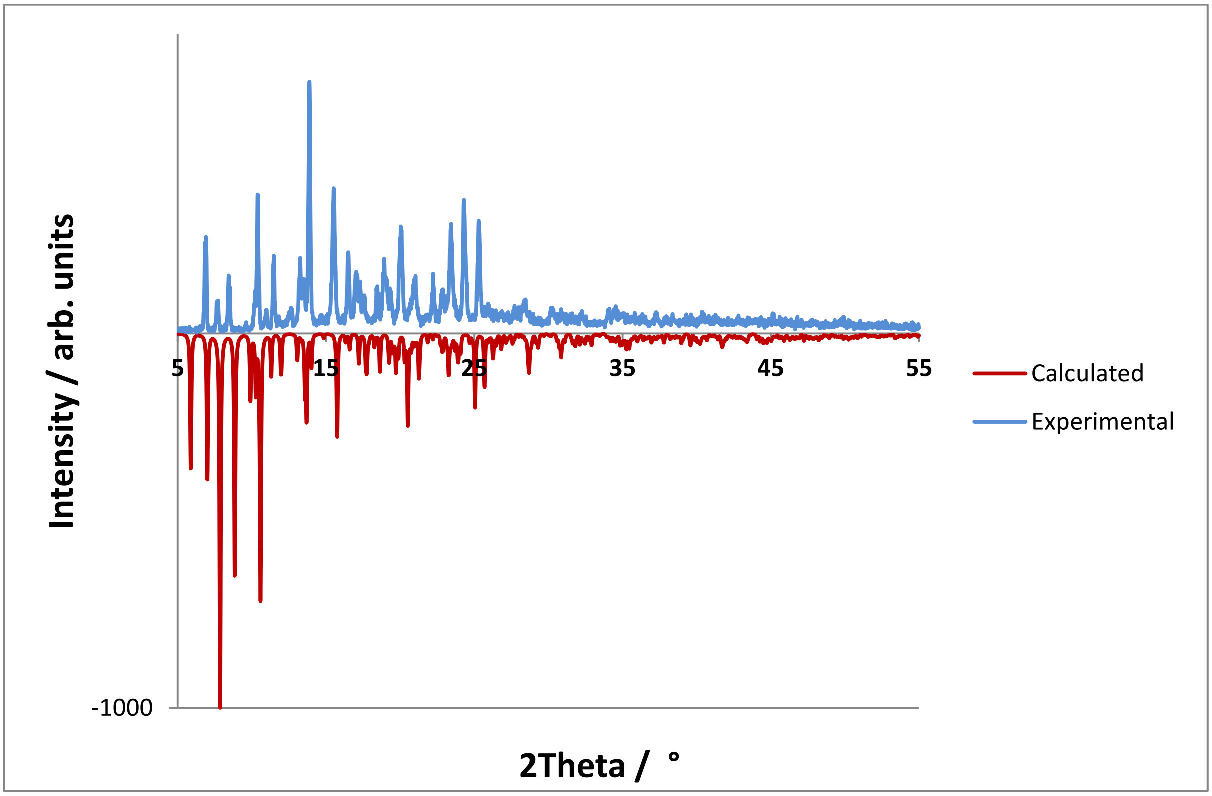

Figure S1: *Comparison of experimental and calculated PXRD patterns for* ***1****. Note, calculated peak at ~ 2θ = 6 is cut-off by the sample holder in the experimental pattern.*

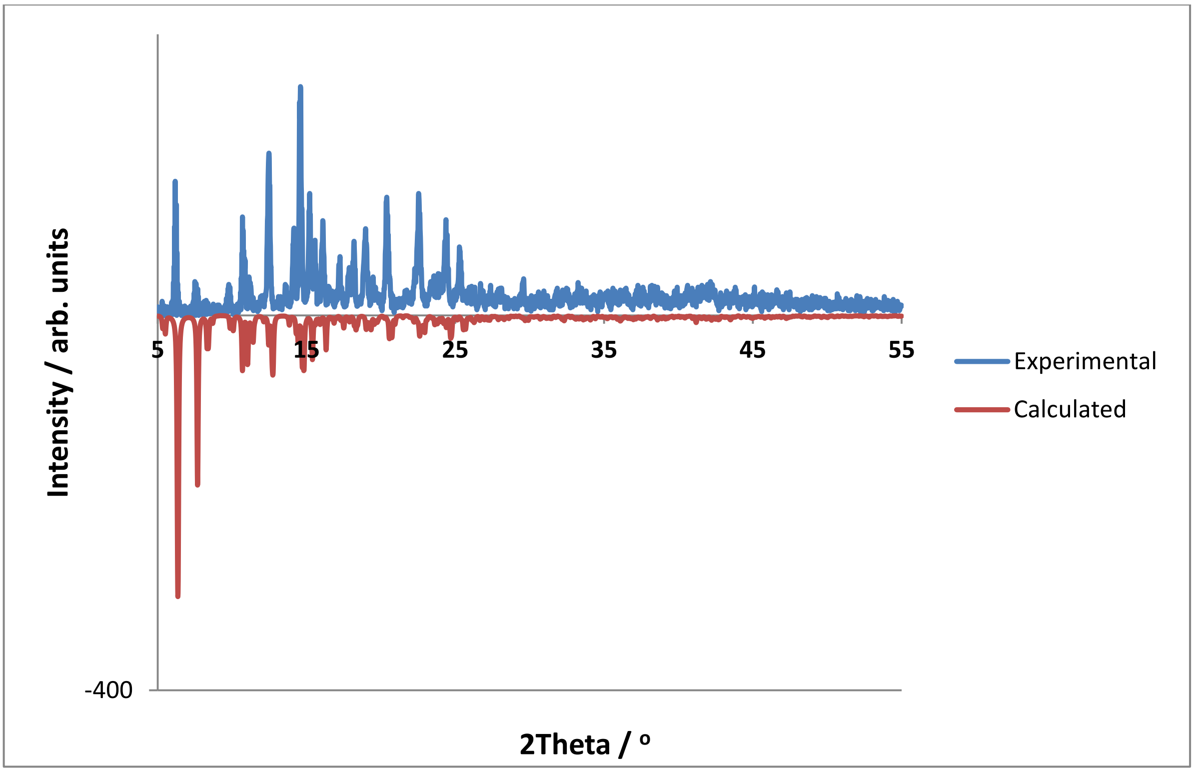

Figure S2: *Comparison of experimental and calculated PXRD patterns for* ***2****.*

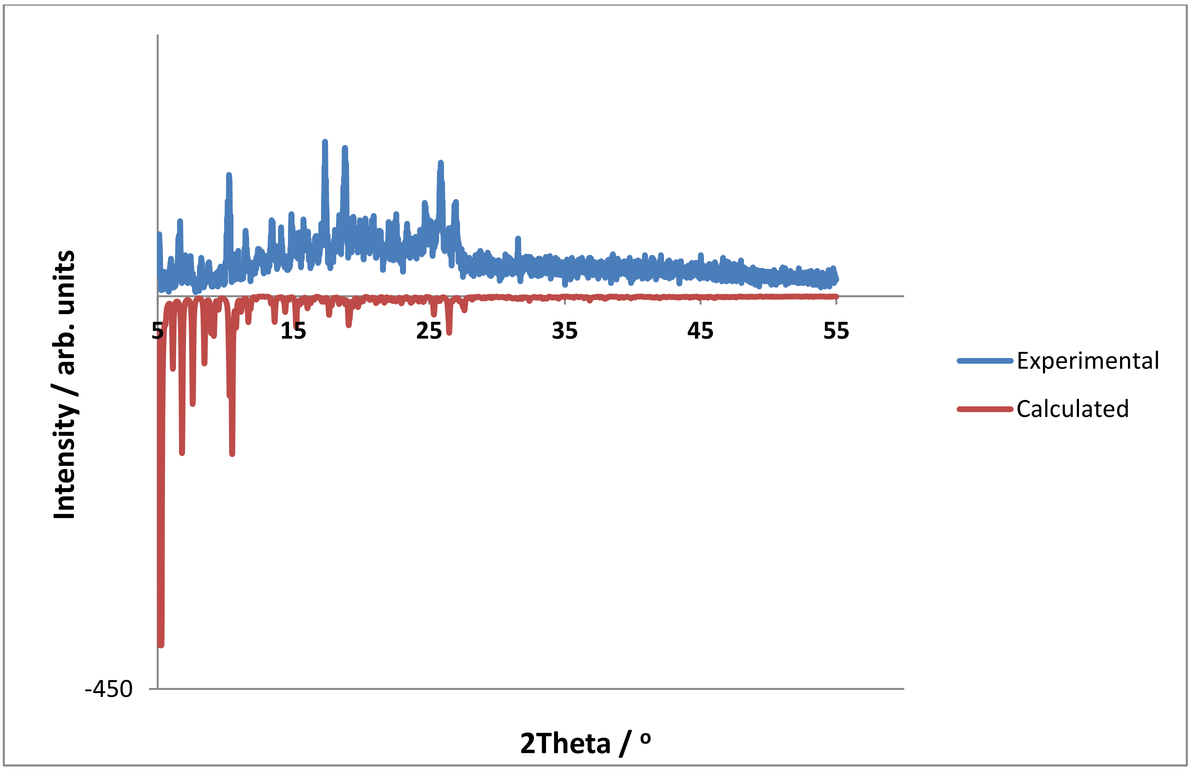

Figure S3: *Comparison of experimental and calculated PXRD patterns for* ***3****. Calculated peak at 2θ=5.2 is truncated for clarity. Sample rapidly lost crystallinity, leading to some amorphous signal.*

Thermogravimetric Analysis

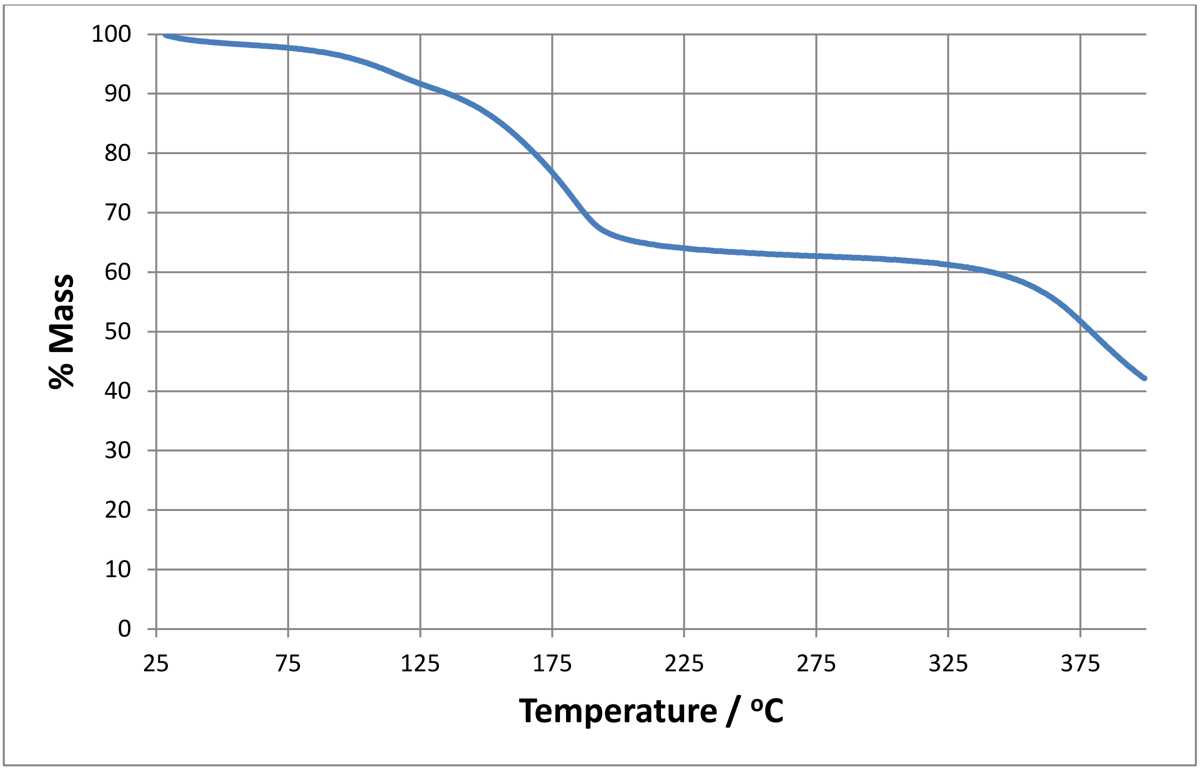

Figure S4: *Thermogravimetric analysis plot of* ***1****.*

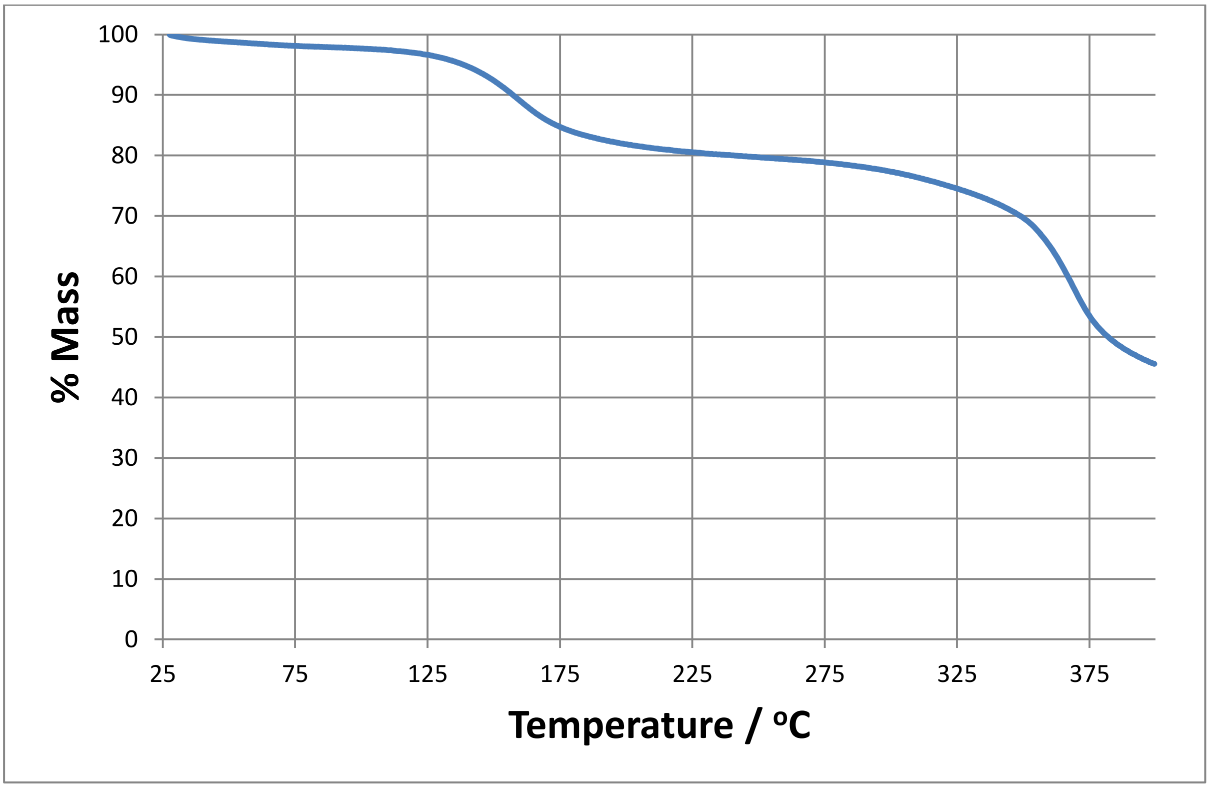

Figure S5: *Thermogravimetric analysis plot of* ***2****.*

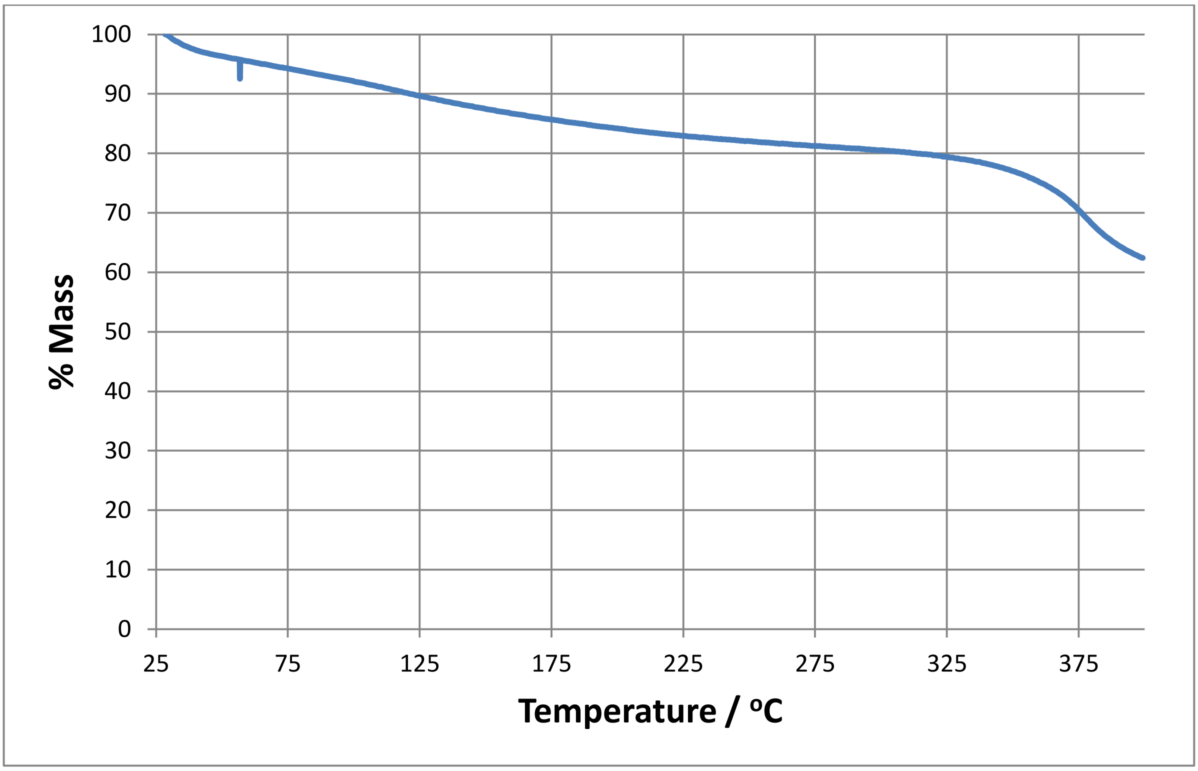

***Figure S6:** Thermogravimetric analysis plot of **3**.*

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[i] A.L. Spek, Acta Cryst. 2009, D65, 148-155