Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Solvent-Directed Control over the Topology of Entanglement in Square Lattice (sql) Coordination Networks

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Experimental

General

All reagents and solvents were purchased from Sigma Aldrich or TCI and used as received.

Powder X-ray diffraction (PXRD) data were measured on Empyrean diffractometer (PANalytical, Philips) using CuKα source. Data were collected from 4 to 40° 2θ with a step size of 0.02° and a scan rate of 0.1° min^{-1}.

Thermogravimetric Analyses (TGA) were performed on a TA Instrument Q50 TG from ambient temperature to 500 °C under a 60 mL min^{-1} flow of N_2, at a scan rate of 20 °C min^{-1}.

Fourier Transform Infrared (FTIR) spectra were collected on a Perkin Elmer Spectrum 100 spectrometer with Universal ATR accessory between the range of 4000-650 cm^{-1}.

Crystal structures of compounds **1**, **3** and **6** were determined by single crystal X-ray diffraction (SCXRD). Measurements were performed at 100(2) K or 298(2) K with either Mo*Kα* (λ = 0.71073 Å) or Cu*Kα* (λ = 1.5418 Å) radiation and Bruker D8 Quest fixed-chi diffractometer equipped with Photon II or Photon 100 detector, and the nitrogen-flow Oxford Cryosystem attachment. Unit-cell determination, data reduction and absorption correction (multi-scan method) were conducted using the Bruker APEX3 suite with implemented SADABS software.[1] OLEX2 software containing ShelX package was used for structure solution and refinement.[2] All structures were solved by intrinsic phasing methods with program ShelXT-2014 and were refined with program ShelXL-2014 using the least-squares method.[3,4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at idealized positions based on the molecular geometry and assigned isotropic thermal parameters depending on the equivalent displacement parameters of their carriers. Detailed crystallographic information for all structures are listed in Table S1. All crystal structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1877136-1877138).

Synthesis

N,N'-(1,4-phenylenebis(methan-1-yl-1-ylidene))bis(4-(1H-imidazol-1-yl)aniline (**L**) ligand was made following a previously published method.[5]

Single crystals:

Compound 1: A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (15 mg, 0.05 mmol) and N,N'-(1,4-phenylenebis(methan-1-yl-1-ylidene))bis(4-(1H-imidazol-1-yl)aniline (**L**) (42 mg, 0.1 mmol) were dissolved in 5 mL (4:1 v/v) mixture of DMF/MeOH. The vial was sealed and heated at 120 ºC for two days. The reaction system was cooled to room temperature at a rate of 10 ºC per hour. The precipitate was filtered, washed with small amounts of methanol and dried in air. Single crystals suitable for single-crystal X-ray diffraction were obtained; yield: 67%.

Compound 3: A mixture of $Ni(NO_3)_2{\cdot}6H_2O$ (15 mg, 0.05 mmol) and N,N'-(1,4-phenylenebis(methan-1-yl-1-ylidene))bis(4-(1H-imidazol-1-yl)aniline (**L**) (42 mg, 0.1 mmol) were dissolved in 5 mL (4:1 v/v) mixture of nitrobenzene/MeOH. The vial was sealed and heated at 120 ºC for two days. The reaction system was cooled to room temperature at a rate of 10 ºC per hour. The precipitate was filtered, washed with small amounts of methanol and dried in air. Single crystals suitable for single-crystal X-ray diffraction were obtained; yield: 57%.

Compound 6: A mixture of zinc *p*-toluenesulfonate hydrate (20 mg, 0.05 mmol) and N,N'-(1,4-phenylenebis(methan-1-yl-1-ylidene))bis(4-(1H-imidazol-1-yl)aniline (**L**) (42 mg, 0.1 mmol) were dissolved in 5 mL (4:1 v/v) mixture of NB/MeOH. The vial was sealed and heated at 120 ºC for two days. The reaction system was cooled to room temperature at a rate of 10 ºC per hour. The precipitate was filtered, washed with small amounts of methanol and dried in air. Single crystals suitable for single-crystal X-ray diffraction were obtained; yield: 74%.

Powdered samples:

Compound 2: A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (15 mg, 0.05 mmol) and N,N'-(1,4-phenylenebis(methan-1-yl-1-ylidene))bis(4-(1H-imidazol-1-yl)aniline (**L**) (42 mg, 0.1 mmol) were dissolved in 5 mL (4:1 v/v) mixture of DMF/MeOH. The vial was sealed and heated at 120 ºC for two days. The reaction system was cooled to room temperature at a rate of 10 ºC per hour. The precipitate was filtered, washed with small amounts of methanol and dried in air; yield: 65%.

Compound 4: A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (15 mg, 0.05 mmol) and N,N'-(1,4-phenylenebis(methan-1-yl-1-ylidene))bis(4-(1H-imidazol-1-yl)aniline (**L**) (42 mg, 0.1 mmol) were dissolved in 5 mL (4:1 v/v) mixture of NB/MeOH. The vial was sealed and heated at 120 ºC for two days. The reaction system was cooled to room temperature at a rate of 10 ºC per hour. The precipitate was filtered, washed with small amounts of methanol and dried in air; yield: 52%.

Compound 5: A mixture of $Cu(NO_3)_2 \cdot 6H_2O$ (15 mg, 0.05 mmol) and N,N'-(1,4-phenylenebis(methan-1-yl-1-ylidene))bis(4-(1H-imidazol-1-yl)aniline (**L**) (42 mg, 0.1 mmol) were dissolved in 5 mL (4:1 v/v) mixture of NB/MeOH. The vial was sealed and heated at 120 ºC for two days. The reaction system was cooled to room temperature at a rate of 10 ºC per hour. The precipitate was filtered, washed with small amounts of methanol and dried in air; yield: 54%.

Crystallographic Data

Table S1. Crystal data and refinement details

Compound	**1**	**3**	**6**
Formula	$C_{104}H_{80}N_{28}Co_2O_{12}\cdot H_2O$	$C_{52}H_{40}N_{14}NiO_6\cdot C_6H_5NO_2$	$C_{66}H_{54}N_{12}O_6S_2Zn$
M(g·mol^{-1})	2049.83	1138.80	1240.70
T(K)	100(2)	297.73	100(2)
λ(Å)	1.54178	0.71073	1.54178
Crystal System	Orthorhombic	Monoclinic	Monoclinic
Space Group	$Pbcn$	$P2_1$	$P2_1/n$
Z/Z'	4/0.5	2/1	4/1
Unit-cell parameters (Å/°): a b c α β γ	22.0586(9) 9.5030(4) 44.7513(18) 90 90 90	12.9679(6) 15.1211(8) 14.4514(7) 90 111.8980(10) 90	17.908(5) 14.810(4) 23.713(7) 90 111.389(10) 90
Unit-cell volume V (Å^3)	9380.9(7)	2629.3(2)	5856(3)
ρ_{cal} (g·cm^{-3})	1.451	1.438	1.407
μ (mm^{-1})	3.454	0.443	1.783
Measured/independent Reflections	33926/6863	62049/12051	66752/11491
R_{int}	0.0548	0.1358	0.0360
Observed Reflections [I>2σ(I)]	5560	6970	10360
R_1^a, wR_2^b [I>2σ(I)]	0.0752, 0.1651	0.0721, 0.1241	0.0321, 0.0831
R_1, wR_2 (all data)	0.0933, 0.1732	0.1446, 0.1471	0.0363, 0.0866
Goodness-of-fit on F^2	1.146	1.013	1.030

Characterisation of Compounds

Compound (1).

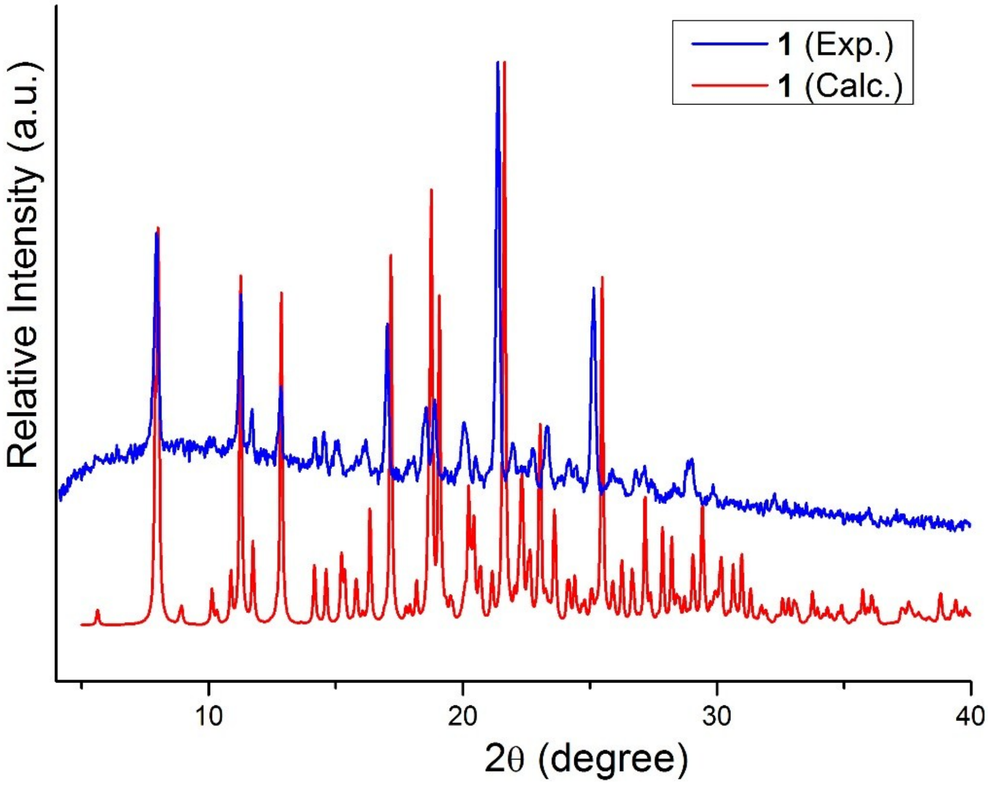

Figure S1. Calculated PXRD generated from single crystal structure of **1** (red) compared with **1** as-synthesised (blue).

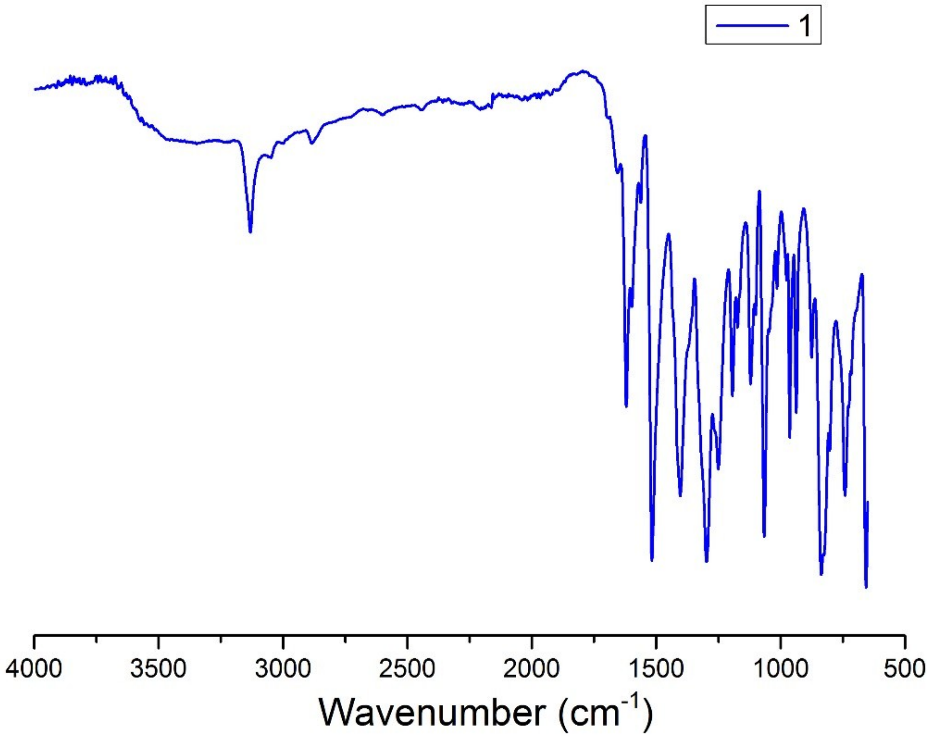

Figure S2. The FTIR spectra of **1.**

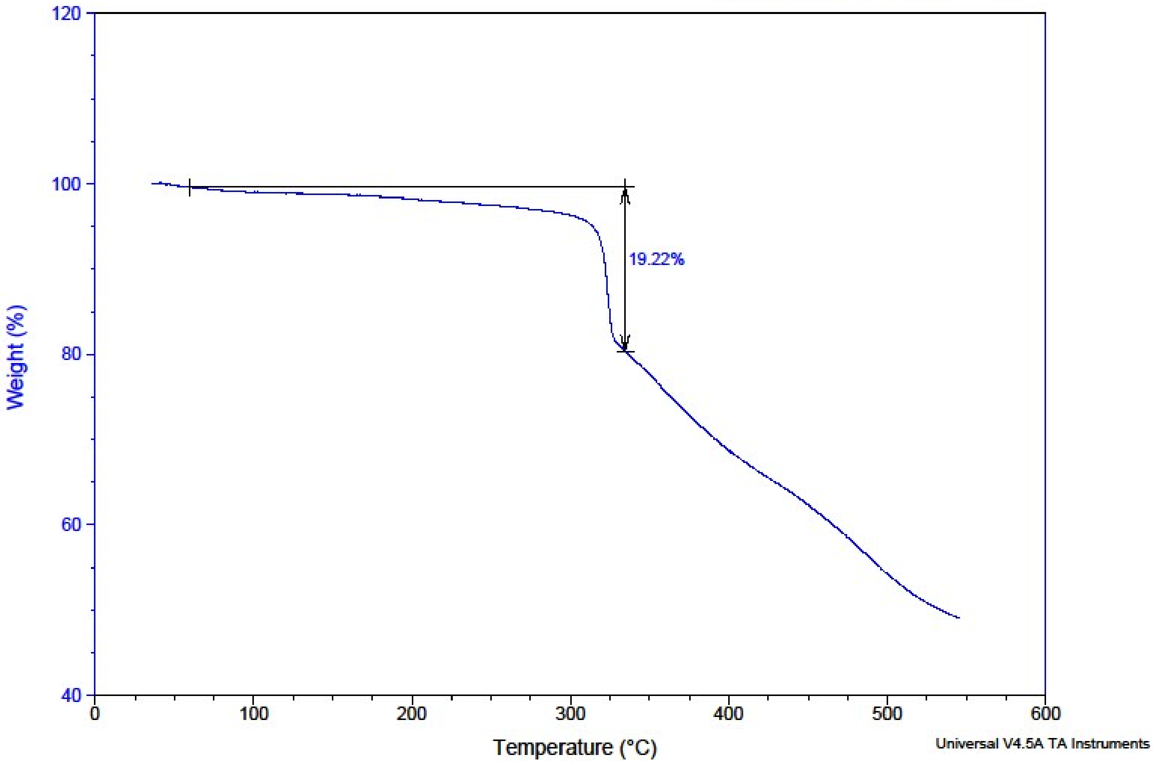

Figure S3. TGA profile for **1** as-synthesised.

Compound (2).

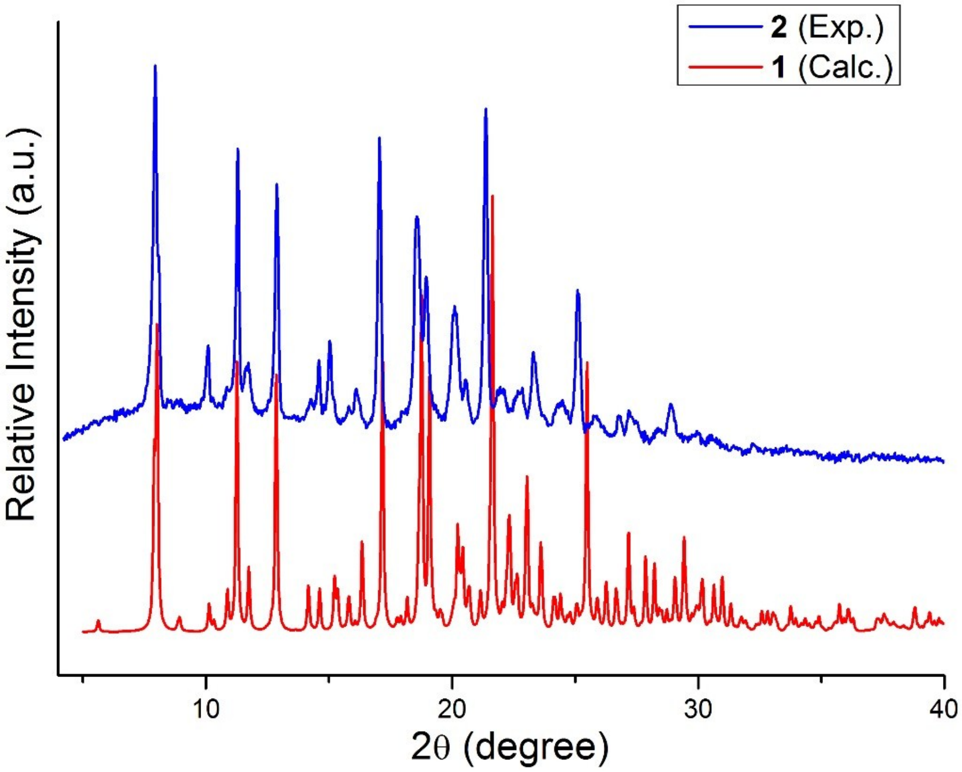

Figure S4. Calculated PXRD generated from single crystal structure of **1** (red) compared with **2** as-synthesised (blue).

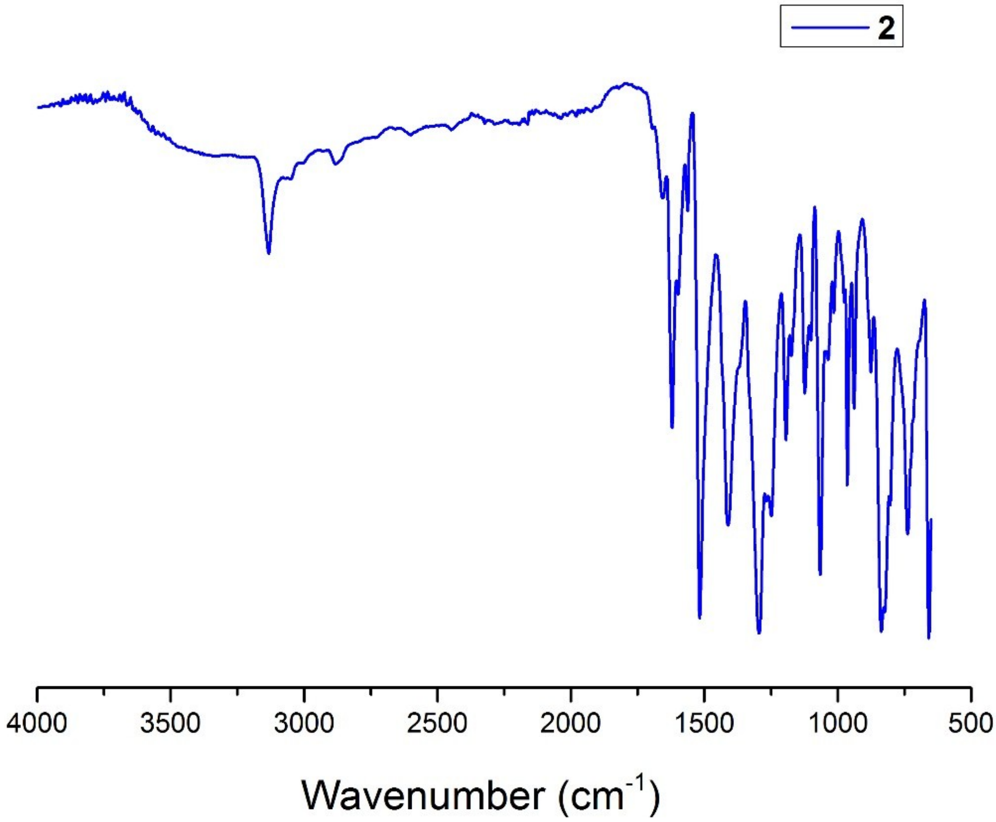

Figure S5. The FTIR spectra of **2**.

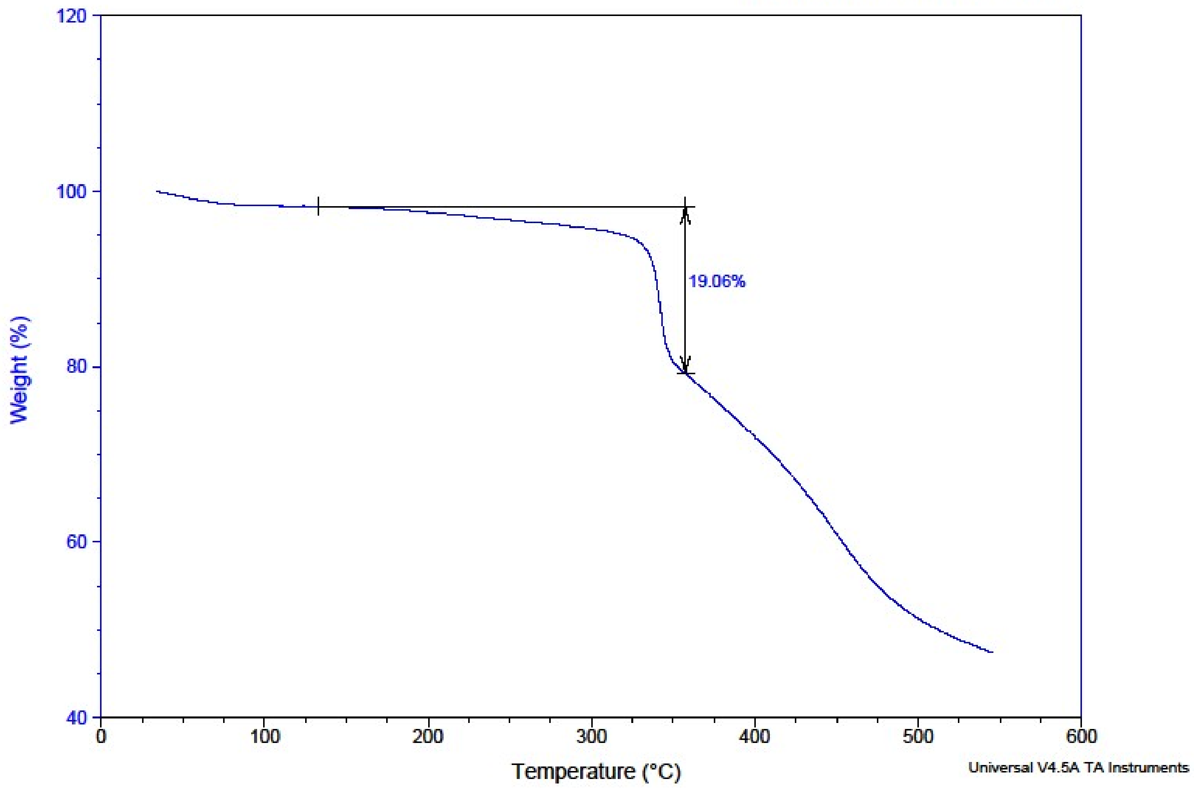

Figure S6. TGA profile for **2** as-synthesised.

Compound (3).

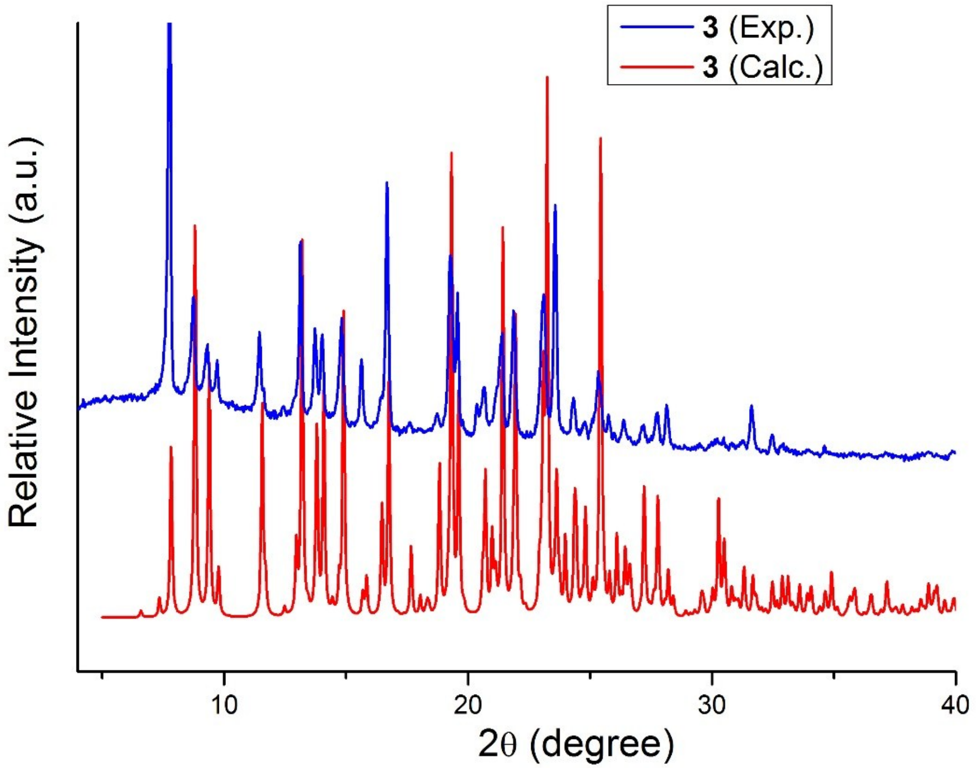

Figure S7. Calculated PXRD generated from single crystal structure of **3** (red) compared with **3** as-synthesised (blue).

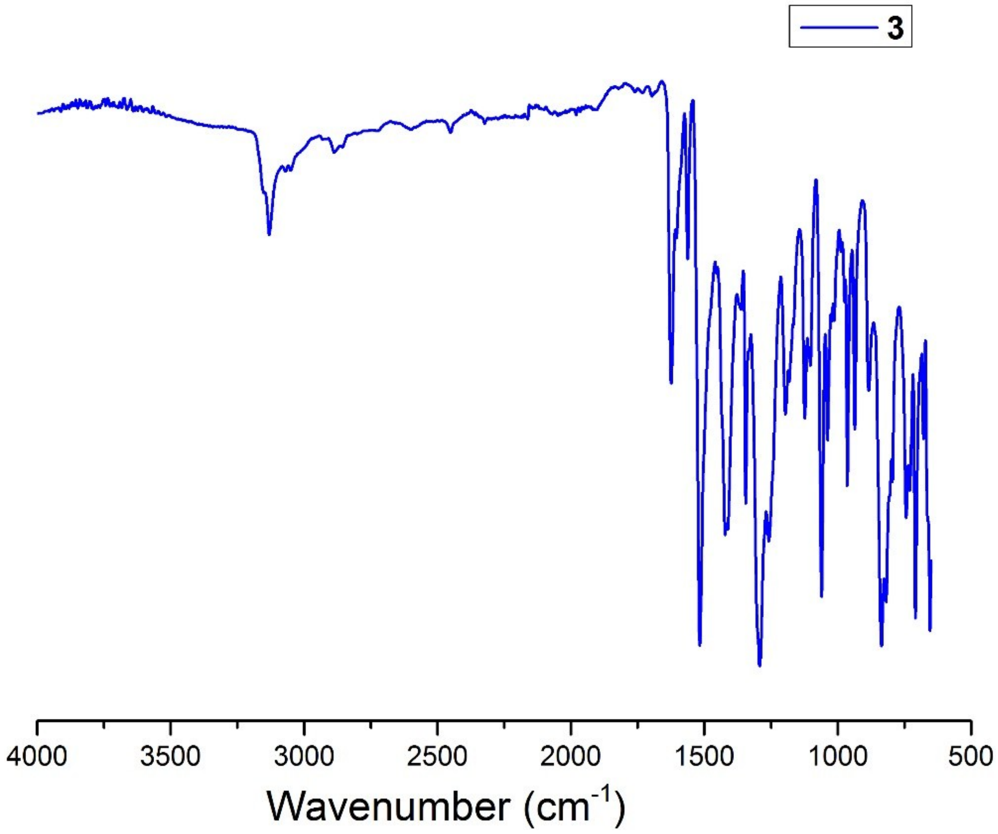

Figure S8. FTIR spectra of **3** as-synthesised.

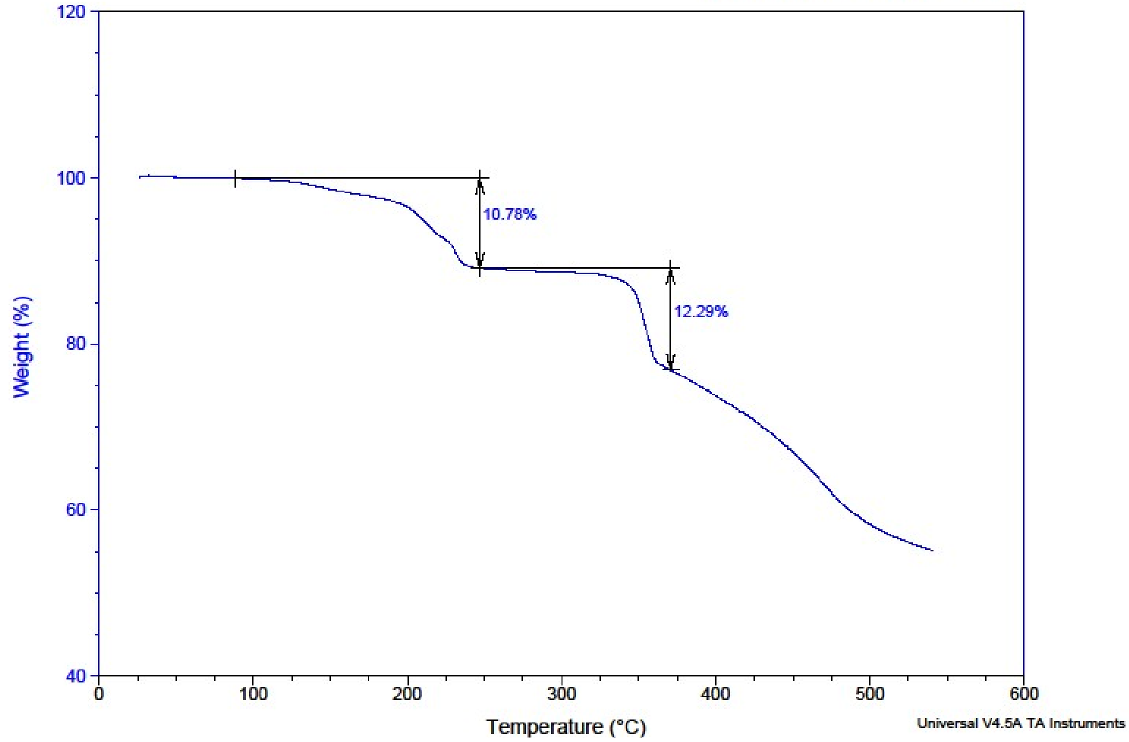

Figure S9. TGA profile for **3** as-synthesised.

Compound (4).

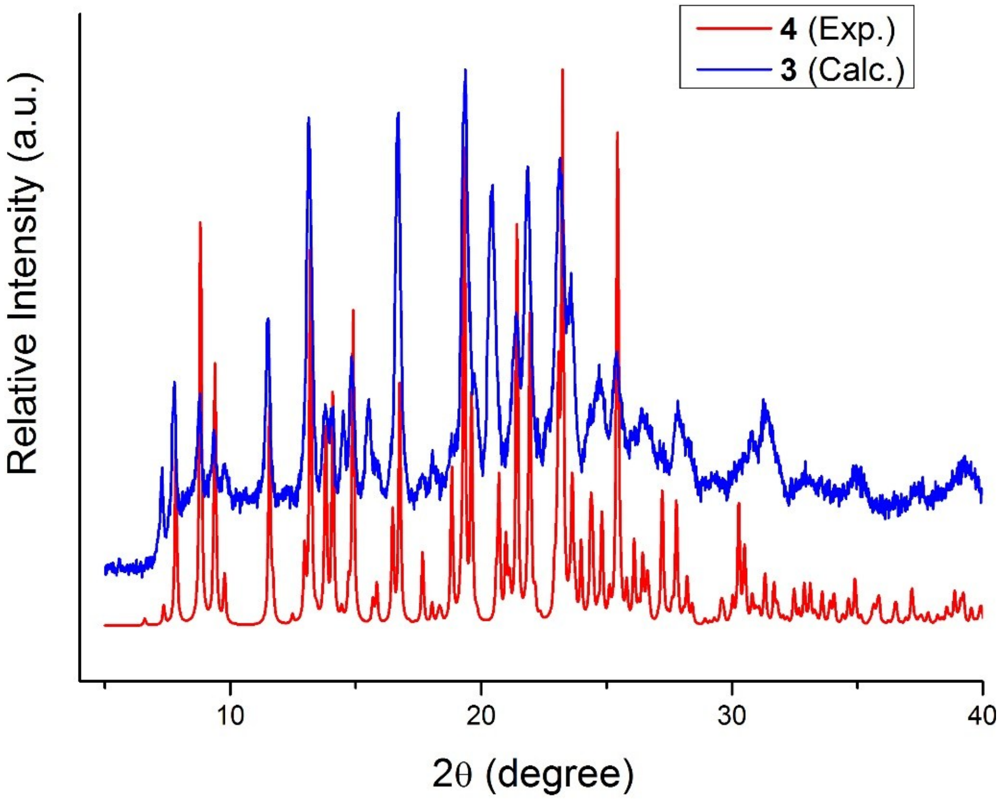

Figure S10. Calculated PXRD generated from single crystal structure of **3** (red) compared with **4** as-synthesised (blue).

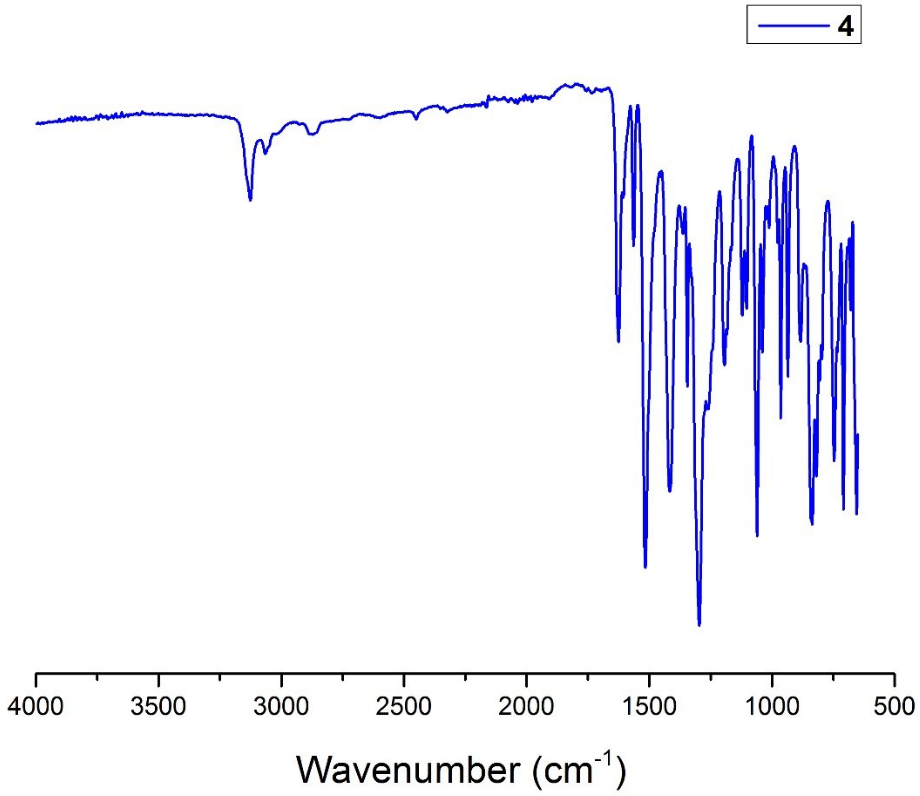

Figure S11. FTIR spectra of **4** as-synthesised.

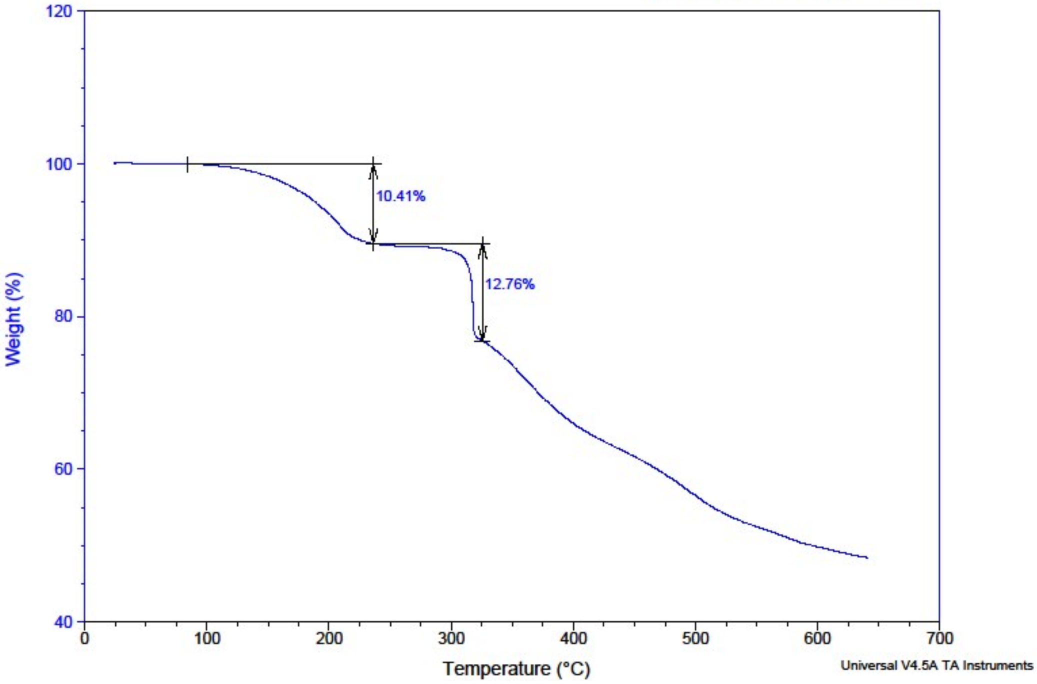

Figure S12. TGA profile for **4** as-synthesised.

Compound (5).

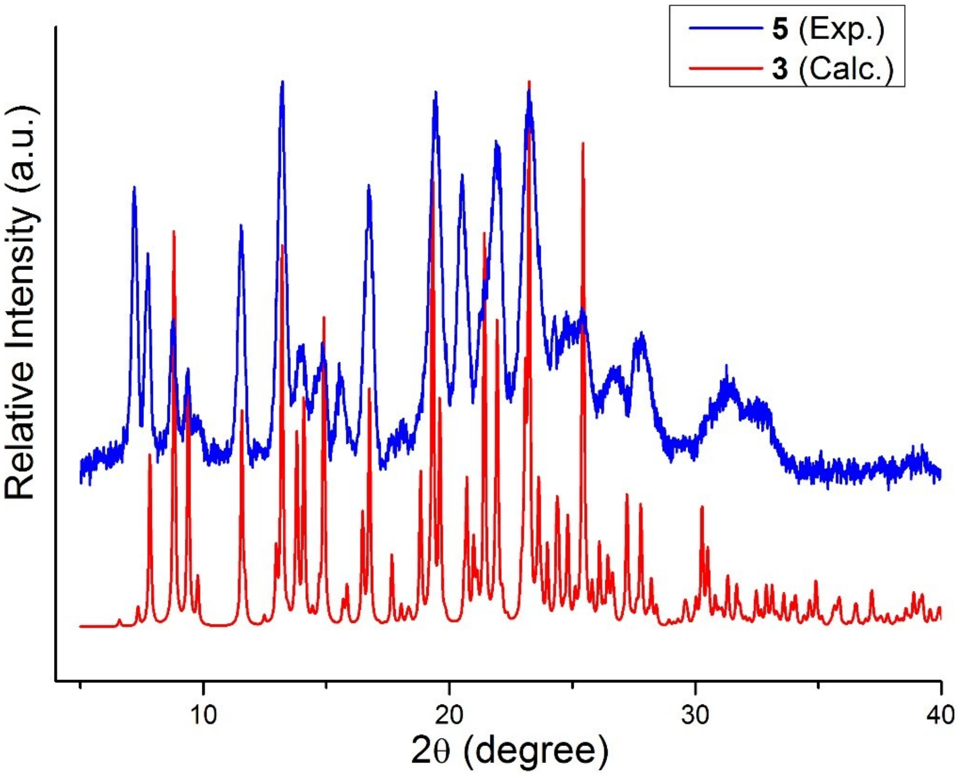

Figure S13. Calculated PXRD generated from single crystal structure of **3** (red) compared with **5** as-synthesised (blue).

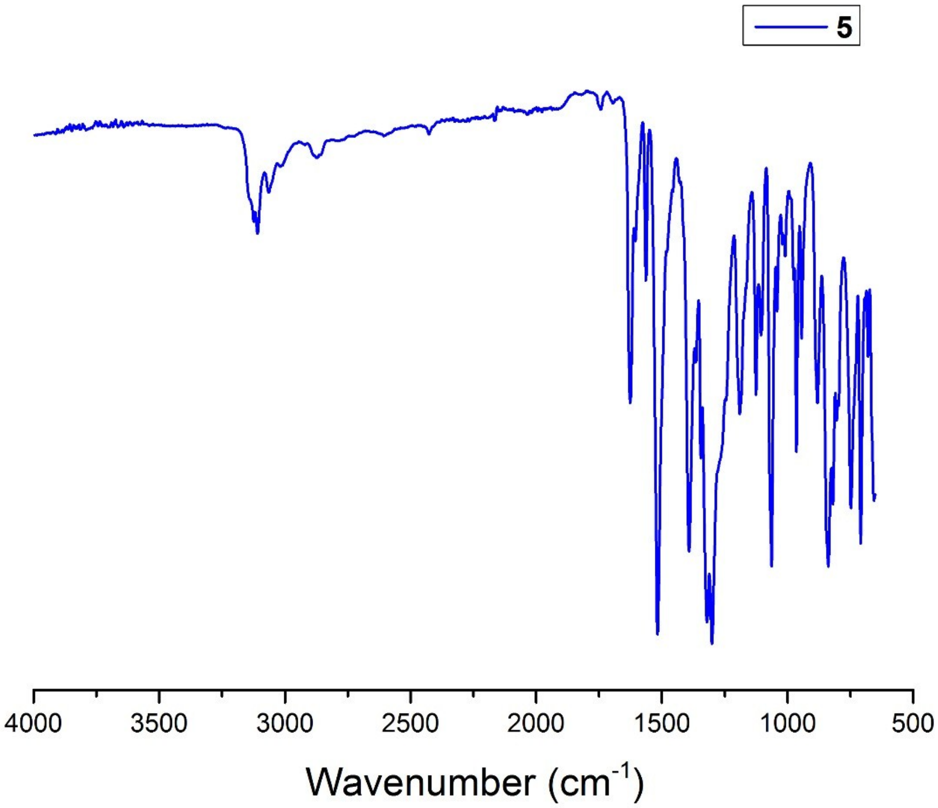

Figure S14. FTIR spectra of **5** as-synthesised.

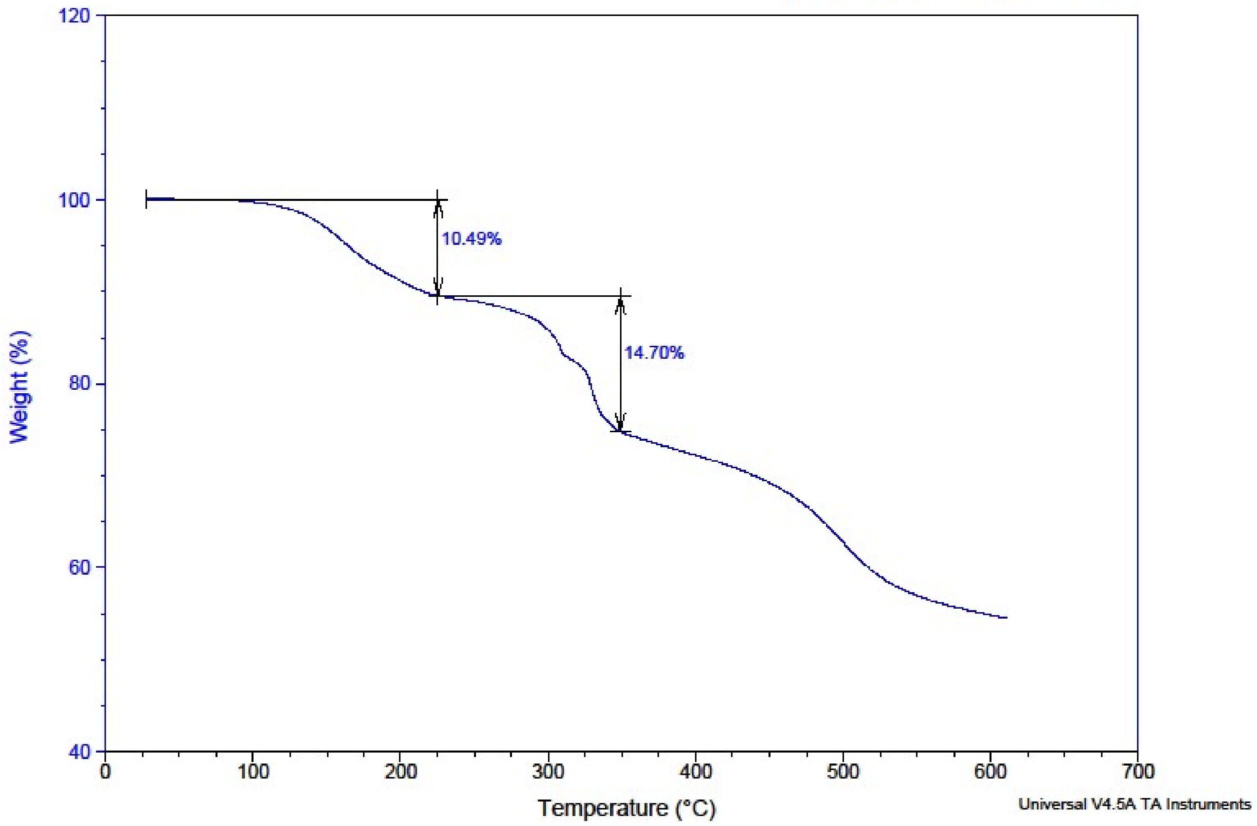

Figure S15. TGA profile for **5** as-synthesised.

Compound (6).

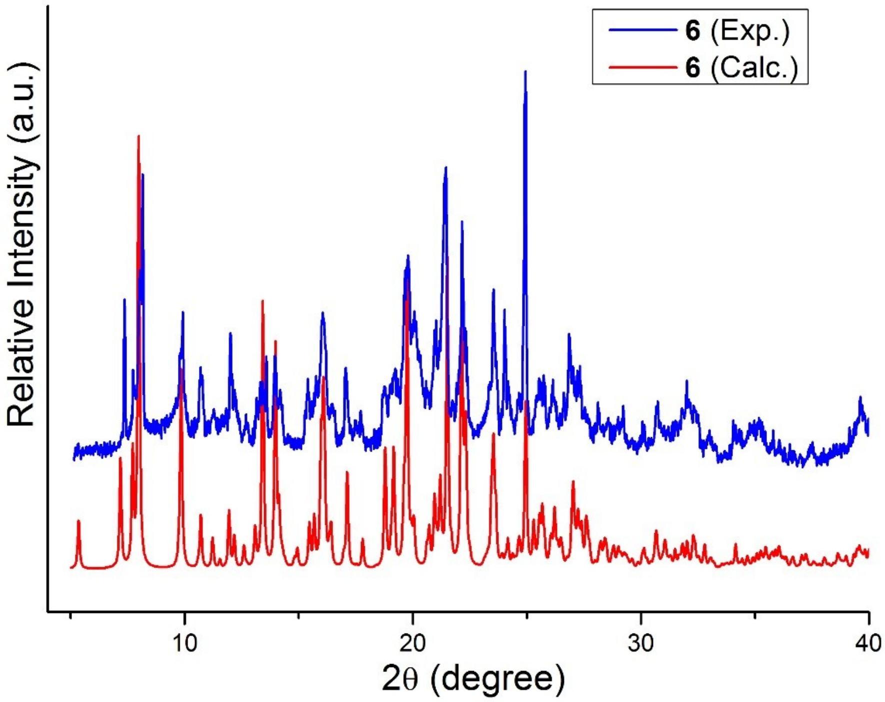

Figure S16. Calculated PXRD generated from single crystal structure of **6** (red) compared with **6** as-synthesised (blue).

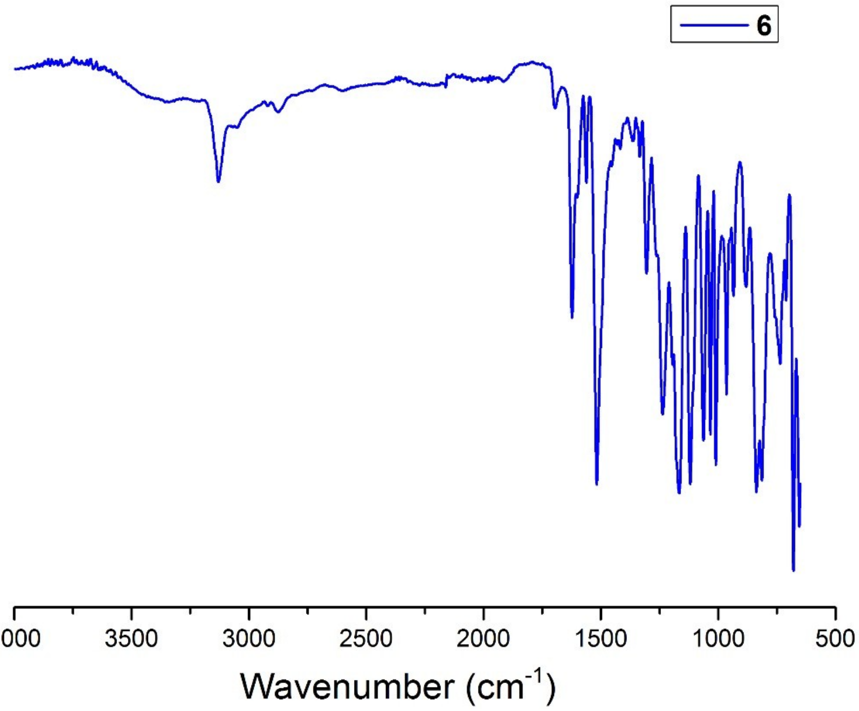

Figure S17. FTIR spectra of **6** as-synthesised.

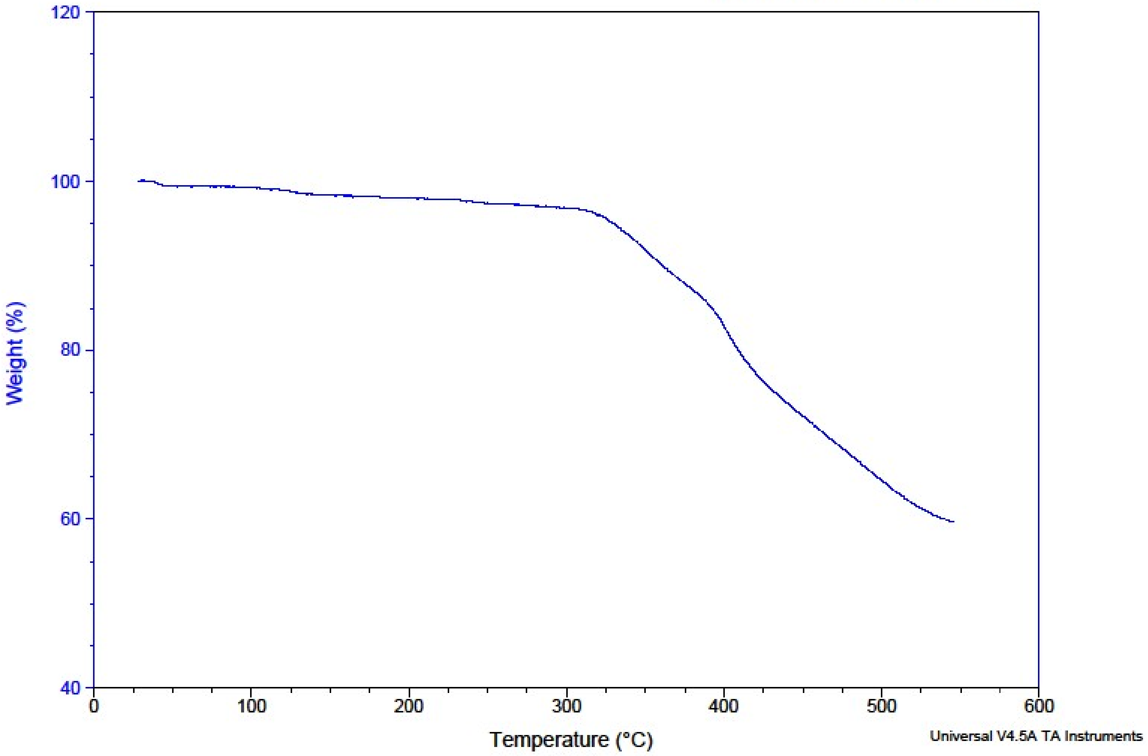

Figure S18. TGA profile for **6** as-synthesised.

References:

1. G. M. Sheldrick, (2008). *SADABS. Program for Empirical Absorption Correction*. University of Gottingen, Germany
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3. G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3-8.
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5. R. Sanii, A. Bajpai, E. Patyk-Kaźmierczak and M. J. Zaworotko, *Sustainable Chem. Eng.*, 2018, **6**, 14589-14598.
6. E. V. Alexandrov, V. A. Blatov and D. M. Proserpio, *CrystEngComm,* 2017, **19**, 1993-2006.