Crystal engineering urea organic acid hydrogen bonded networks with solvent inclusion properties

Lucy K. Saunders[a,b] , Harriott Nowell[b], Paul R. Raithby[a], Chick C. Wilson[a]

a Department of Chemistry, University of Bath, Bath, BA2 7AY, UK.

b Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, UK.

E-mail: C.C.Wilson@bath.ac.uk

SUPPLEMENTARY INFORMATION

Contents

m/z, MS3 = 27 m/z, MS4 = 29 m/z, water peak MS5 = 18 m/z and (c) **IM3**: acetonitrile peaks MS1 = 41 m/z, MS2 = 39 m/z, MS3 = 28 m/z, MS4 = 14 m/z.

Figure S10 The TG-MS analysis for (a) **IM4**: acetone peaks MS1 = 43 m/z, MS2 = 58 m/z, MS3 = 15 m/z, MS4 = 42 m/z, water peaks MS5 = 18 m/z, (b) **IM5**: THF peaks MS1 = 42 m/z, MS2 = 41 m/z, MS3 = 71 m/z, MS4 = 43 m/z, water peak MS5 18 m/z and (c) **IM6**: ethyl acetate peaks MS1 = 43 m/z, MS2 = 61 m/z, MS3 = 45 m/z, MS4 = 70 m/z.

Figure S11 The TG-MS analysis for (a) **IM7**: THF peaks MS1 = 42, MS2 = 41, MS3 = 71, MS4 = 43, methanol peaks and MS5 = 31, MS6 = 32, MS7 = 29, MS8 = 15, (b) **CIM1**: water peaks MS1 = 18 m/z, MS2 =17 m/z and MS3 = 16 m/z and (c) **CIM2**: acetone peaks MS1 = 43 m/z, MS2 = 58 m/z, MS3 = 15 m/z, MS4 = 42 m/z, water peaks MS5 = 18 m/z.

Table S12 Mass loss data for TG analysis of **IM1** to **IM7**, **CIM1** and **CIM2**.

Table S13 The corresponding energies of the desolvation endotherm for **IM1** – **IM7**, **CIM1** and **CIM2**.

Figure S14 PXRD patterns for (a) **IM1**, (b) **IM2**, (c) **IM3** and (d) **IM4** at 25 ^{o}C on samples at 25 ^{o}C and preheated to 145 ^{o}C.

Figure S15 PXRD patterns for (a) **IM5**, (b) **IM6**, (c) **IM7** and (d) **CIM2** at 25 ^{o}C on samples at 25 ^{o}C and preheated to 145 ^{o}C (**CIM2** preheated to 150 ^{o}C).

Figure S16 PXRD patterns for (a) **NS2** at 25 ^{o}C and on a sample preheated to 150 ^{o}C and (b) **CIM1** at 25 ^{o}C and on a sample preheated to 145 ^{o} C and 189 ^{o}C.

Figure S17 PXRD patterns of (a) **NS1** and (b) **NS2**: (i) the simulated powder pattern of the material, (ii) each material pre-vapour diffusion and post vapour diffusion with (iii) methanol, (iv) ethanol, (v) acetonitrile, (vi) acetone, (vii) THF and (viii) ethyl acetate at -18 ^{o}C.

Figure S18 A comparison of PXRD patterns of (i) **NS1** pre vapour diffusion with (ii) the acetone solvent vapour diffusion product and (iii) the simulated powder pattern for **CIM2**. The boxes highlight similarities in the patterns.

Figure S19 A comparison of PXRD patterns of (i) **NS2** pre vapour diffusion with (ii) the acetone solvent vapour diffusion product and (ii) the simulated powder pattern for **CIM2**. The boxes highlight similarities in the patterns.

Table S1 Hydrogen atom refinement details for all IMs.

IM	Hydrogen atom refinement details
IM1	Treated by a mixture of independent and constrained refinements, located from Fourier difference maps or in calculated positions. The methyl hydrogen atoms of the two methanol solvent molecules were positioned geometrically using HFIX 137. The alcohol hydrogen atoms of the two methanol solvent molecules were refined with isotropic displacement parameters set to -1.5. Two of the 5-nitroisophthalic acid molecules were refined with one of the hydroxyl hydrogen atom isotropic displacement parameters set to -1.5. One of the *N*-phenylurea molecules had a primary N—H hydrogen atom refined with an isotropic displacement parameter set to -1.5.
IM2	Treated by constrained refinements in calculated positions. The hydroxyl hydrogen atoms on the 5-nitroisophthalic acid molecules were fixed geometrically using HFIX 83. The primary amine hydrogen atoms of the *N*-phenylurea molecules were fixed geometrically using HFIX 93. The aromatic hydrogen atoms of the *N*-phenylurea and 5-nitroisophthalic acid molecules were fixed geometrically using HFIX 43. The secondary amine hydrogen atoms of the *N*-phenylurea molecule were fixed geometrically using HFIX 43.
IM3	Located from Fourier difference map and refined freely.
IM4	Treated by a mixture of independent and constrained refinements, located from Fourier difference maps or in calculated positions. The N—H distances of the secondary amine groups in the *N*-phenylurea molecules were constrained to 0.86 Å. In the water solvent molecule, the O—H distances were constrained to 0.82 Å and the HOH angle constrained using DANG 1.319 Å between the two water hydrogen atoms. All 5-nitroisophthalic acid molecule hydroxyl hydrogen atoms were positioned geometrically using HFIX 83. The aromatic hydrogen atoms in the *N*-phenylurea and 5-nitroisophthalic acid molecules were positioned geometrically using HFIX 43. The methyl hydrogen atoms (both methyl groups) of the acetone solvent molecule were positioned geometrically using HFIX 137. The hydrogen atoms in the primary amine groups of the *N*-phenylurea molecule were positioned geometrically using HFIX 93.
IM5	Located from Fourier difference map and refined freely.
IM6	Located from Fourier difference map and refined freely.
IM7	Treated by a mixture of independent and constrained refinements, located from Fourier difference maps or in calculated positions. Aromatic hydrogen atoms of the 5-nitroisophthalic acid and *N*-phenylurea molecules were positioned geometrically using HFIX 43.
CIM1	Treated by a mixture of independent and constrained refinements, located from Fourier difference maps or in calculated positions. The water solvent hydrogen atoms were located in Fourier difference maps and refined with an O—H distance constrained to 0.82 Å. The *N*-phenylurea and 5-nitroisophthalic acid aromatic and secondary amine hydrogen atoms were positioned geometrically using HFIX 43. The primary amine hydrogen atoms were positioned geometrically using HFIX 93.
CIM2	Located from Fourier difference map and refined freely.
NS1	Located from Fourier difference map and refined freely.
NS2	Located from Fourier difference map and refined freely.

Table S2 Structural variation in the molecular components across the IMs; including the angle between the urea and phenyl moiety planes in *N*-phenylurea (co-planarity) and the 5-nitroisophthalic acid carboxylic acid group torsion angle to the benzene ring (torsion angle 1 and torsion angle 2)

IM	Co-planarity		Torsion angle		
	N-phenylurea	Angle (°)	5-nitroisophthalic acid	Torsion angle 1 (°)	Torsion angle 2 (°)
IM1	1 2 3 4 5 6 7	2.93 2.73 20.40 10.13 12.56 8.02 8.58	1 2 3 4	-0.6(3) -3.5(4) 1.9(4) 0.8(3)	-2.6(4) -1.2(4) 3.3(3) 2.6(3)
IM2	1 2 3	7.13 11.58 3.42	1 2	-0.2(8) -0.1(9)	-1(1) 2(1)
IM3	1 2 3	3.83 9.45 28.37	1 2	4.0(2) -4.2(2)	-1.9(2) -3.9(2)
IM4	1 2 3	5.05 3.34 5.85	1 2	3.3(8) -2.4(8)	-11.6(9) 8.4(9)
IM5	1 2 3	0.35 3.57 35.41	1 2	6.0(3) 8.3(3)	-1.3(3) 5.7(3)
IM6	1 2 3 4	6.54 6.93 13.67 7.12	1 2	-4.2(3) 0.2(3)	0.4(3) 0.3(3)
IM7	1	13.85	1	1.0(3)	4.5(3)
CIM1	1 2	4.40 33.68	1 2	1.0(5) 4.0(5)	-2.1(5) -3.2(5)
CIM2	1	8.08	1	1.5(1)	-3.4(1)
NS1	1 2	31.66 16.78	1	6.9(3)	4.4(3)
NS2	1 2	17.83 14.65	1 2	-4.4(3) 16..3(3)	12.1(3) 1.8(3)

Table S3 Hydrogen bond details of those involved in network formation in **IM1** to **IM2**.

IM	D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)	Sym op
IM1	N(14)-H(26)...O(8)#3	0.87(3)	2.20(3)	3.044(3)	161(2)	#3 -x,-y+1,-z
	O(7)-H(102)...O(14)#3	1.05(4)	1.45(4)	2.500(2)	175(3)	#3 -x,-y+1,-z
	N(3)-H(42)...O(32)#2	0.96(3)	1.93(3)	2.877(3)	170(3)	#2 x+1,y,z
	O(31)-H(79)...O(26)#1	1.04(4)	1.61(4)	2.632(2)	170(3)	#1 x-1,y,z
	N(1)-H(51)...O(5)#4	0.88(3)	2.13(3)	2.984(3)	161(2)	#4 -x+1,-y+1,-z+1
	O(6)-H(80)...O(25)#4	0.91(4)	1.62(4)	2.520(3)	168(3)	#4 -x+1,-y+1,-z+1
	N(9)-H(73)...O(4)#3	0.92(3)	1.97(3)	2.882(3)	174(2)	#3 -x,-y+1,-z
	O(3)-H(81)...O(21)#3	0.96(3)	1.61(4)	2.555(2)	165(3)	#3 -x,-y+1,-z
	N(11)-H(77)...O(18)#1	0.93(3)	1.93(3)	2.850(3)	169(3)	#1 x-1,y,z
	O(17)-H(83)...O(13)#2	1.06(3)	1.55(4)	2.595(2)	169(3)	#2 x+1,y,z
	N(7)-H(101)...O(11)	0.95(3)	1.96(3)	2.902(3)	173(3)	
	O(12)-H(82)...O(23)	1.02(3)	1.56(3)	2.559(2)	166(3)	
	N(13)-H(28)...O(20)	0.86(2)	2.07(2)	2.899(3)	162.0(19)	
	N(14)-H(27)...O(20)	0.89(3)	2.35(3)	3.085(3)	140(2)	
	N(2)-H(53)...O(28)	0.87(2)	2.11(2)	2.927(3)	158(2)	
	N(1)-H(52)...O(28)	0.93(3)	2.25(3)	3.042(3)	142(2)	
	N(3)-H(41)...O(29)	0.90(2)	2.18(3)	3.064(3)	169(2)	
	N(4)-H(56)...O(30)	0.87(2)	2.30(2)	3.157(3)	172(2)	
	N(6)-H(16)...O(10)#2	0.88(3)	2.40(3)	3.273(3)	177(2)	#2 x+1,y,z
	N(7)-H(17)...O(9)#2	0.88(3)	2.10(3)	2.980(3)	176(2)	#2 x+1,y,z
	N(9)-H(72)...O(1)#5	0.96(3)	2.05(3)	3.006(3)	179(2)	#5 -x+1,-y+1,-z
	N(8)-H(74)...O(2)#5	0.83(3)	2.44(3)	3.265(3)	171(3)	#5 -x+1,-y+1,-z
	N(11)-H(14)...O(16)	0.86(2)	2.13(3)	2.986(3)	171(2)	
	N(10)-H(12)...O(15)	0.87(2)	2.33(2)	3.179(3)	164(2)	
IM2	O(1)-H(3)...O(14)#4	0.82	1.73	2.534(6)	166	#4 -x+1,-y,-z+1
	N(6)-H(20)...O(2)#4	0.86	2.18	2.961(7)	150	#4 -x+1,-y,-z+1
	O(6)-H(1)...O(13)	0.82	1.71	2.514(6)	164	
	N(4)-H(11)...O(5)	0.86	2.23	3.061(7)	161	
	O(10)-H(6)...O(15)#2	0.82	1.81	2.580(6)	156	#2 -x+1,-y+1,-z
	N(8)-H(27)...O(9)#2	0.86	2.06	2.904(6)	165	#2 -x+1,-y+1,-z
	N(4)-H(12)...O(7)#5	0.86	2.39	3.150(7)	146	#5 x,y+1,z
	N(3)-H(13)...O(7)#5	0.86	2.08	2.923(7)	165	#5 x,y+1,z
	N(5)-H(19)...O(3)#7	0.86	2.55	3.384(7)	164	#7 -x+1,-y+1,-z+1
	N(6)-H(21)...O(4)#7	0.86	2.20	3.043(7)	167	#7 -x+1,-y+1,-z+1
	N(7)-H(29)...O(11)#3	0.86	2.54	3.371(7)	162	#3 -x+1,-y,-z
	N(8)-H(28)...O(12)#3	0.86	2.18	3.020(7)	166	#3 -x+1,-y,-z

Table S4 Hydrogen bond details of those involved in network formation in **IM3** and **IM4**.

IM	D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)	Sym op
IM3	O(6)-H(21)...O(1)#1	0.92(3)	1.64(3)	2.5566(15)	174(2)	#1 -x,-y+2,-z
	N(3)-H(14)...O(10)#1	0.87(2)	2.00(2)	2.8559(17)	166.5(19)	#1 -x,-y+2,-z
	O(3)-H(20)...O(4)	0.94(3)	1.59(3)	2.5256(15)	169(2)	
	N(7)-H(4)...O(9)	0.89(2)	2.10(2)	2.9706(17)	167.9(18)	
	O(8)-H(23)...O(5)#3	0.93(2)	1.63(3)	2.5538(15)	171(2)	#3 -x+2,-y+1,-z+1
	N(6)-H(12)...O(11)#3	0.84(2)	2.06(2)	2.8939(19)	170(2)	#3 -x+2,-y+1,-z+1
	N(1)-H(6)...O(2)	0.88(2)	2.22(2)	3.0254(16)	152.1(18)	
	N(7)-H(5)...O(2)	0.92(2)	2.07(2)	2.9087(17)	151.9(18)	
	N(6)-H(13)...O(14)#4	0.84(2)	2.13(2)	2.9580(18)	171(2)	#4 -x+2,-y+2,-z+1
	N(5)-H(27)...O(12)#4	0.82(2)	2.48(2)	3.2791(17)	164(2)	#4 -x+2,-y+2,-z+1
	N(2)-H(16)...O(13)#2	0.84(2)	2.38(2)	3.2152(17)	171.4(18)	#2 -x,-y+1,-z
	N(3)-H(15)...O(15)#2	0.85(2)	2.14(2)	2.9873(18)	177(2)	#2 -x,-y+1,-z
IM4	O(7)-H(42)...O(5)#2	0.82	1.76	2.572(5)	168	#2 x,y,z-1
	N(4)-H(4A)...O(10)#1	0.86	2.04	2.862(6)	158	#1 x,y,z+1
	O(1)-H(1)...O(4)	0.82	1.70	2.506(6)	166	
	N(10)-H(10A)...O(12)	0.86	2.13	2.966(7)	163	
	O(3)-H(60)...O(11)#1	0.82	1.76	2.576(5)	171	#1 x,y,z+1
	N(3)-H(3A)...O(14)#2	0.86	2.07	2.894(5)	161	#2 x,y,z-1
	N(7)-H(52)...O(13)#5	0.857(19)	2.09(3)	2.914(6)	162(5)	#5 x-1,y,z
	N(10)-H(10B)...O(13)#5	0.86	2.37	3.113(6)	145	#5 x-1,y,z
	N(3)-H(3B)...O(9)#3	0.86	2.18	3.038(6)	173	#3 x+1,y,z-1
	N(2)-H(51)...O(6)#3	0.865(19)	2.44(2)	3.280(6)	164(4)	#3 x+1,y,z-1
	N(4)-H(4B)...O(8)#4	0.86	2.16	3.021(6)	174	#4 x-1,y,z+1
	N(6)-H(50)...O(15)#4	0.80(6)	2.45(6)	3.236(7)	164(6)	#4 x-1,y,z+1

Table S5 Hydrogen bond details of those involved in network formation in **IM5** to **IM7**.

IM	D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)	Sym op
IM5	O(4)-H(43)...O(13)#2	0.98(5)	1.56(4)	2.5333(19)	170(4)	#2 -x,-y+1,-z
	N(7)-H(39)...O(3)#2	0.84(3)	2.21(3)	3.022(2)	164(2)	#2 -x,-y+1,-z
	O(6)-H(41)...O(15)#7	1.00(3)	1.51(3)	2.5115(19)	174(3)	#7 x-1,y-1,z
	N(3)-H(8)...O(5)#4	0.85(3)	2.09(3)	2.918(2)	168(2)	#4 x+1,y+1,z
	O(7)-H(4)...O(14)#6	0.83(3)	1.78(3)	2.6112(19)	175(3)	#6 -x+2,-y,-z+1
	N(5)-H(14)...O(10)#6	0.84(3)	2.07(3)	2.900(2)	169(2)	#6 -x+2,-y,-z+1
	N(7)-H(38)...O(11)#1	0.89(3)	2.38(3)	3.153(2)	146(2)	#1 x-1,y,z
	N(8)-H(37)...O(11)#1	0.87(3)	2.10(3)	2.942(2)	161(2)	#1 x-1,y,z
	N(4)-H(6)...O(1)#3	0.92(3)	2.47(3)	3.363(2)	164(2)	#3 x,y+1,z
	N(3)-H(7)...O(2)#3	0.84(3)	2.15(3)	2.964(2)	161(2)	#3 x,y+1,z
	N(5)-H(15)...O(8)#5	0.88(3)	2.17(3)	3.034(2)	170(3)	#5 -x+1,-y,-z+1
	N(6)-H(16)...O(9)#5	0.88(3)	2.40(3)	3.270(2)	172(2)	#5 -x+1,-y,-z+1
IM6	O(4)-H(33)...O(8)#2	0.98(4)	1.56(4)	2.5288(19)	169(4)	#2 -x+1,-y+1,-z+1
	N(8)-H(13)...O(3)#2	0.88(3)	2.06(3)	2.927(2)	169(2)	#2 -x+1,-y+1,-z+1
	O(5)-H(42)...O(7)	1.07(3)	1.47(3)	2.525(2)	169(3)	
	N(4)-H(1)...O(6)	0.87(3)	2.07(3)	2.929(2)	168(2)	
	O(9)-H(20)...O(11)	1.00(3)	1.57(3)	2.574(2)	176(3)	
	N(5)-H(18)...O(10)	0.89(3)	2.01(3)	2.871(2)	163(2)	
	N(7)-H(29)...O(15)#1	0.87(3)	2.13(3)	2.928(2)	152(2)	#1 x,y+1,z
	N(8)-H(14)...O(15)#1	0.87(2)	2.14(2)	2.927(2)	150(2)	#1 x,y+1,z
	N(6)-H(21)...O(1)#3	0.85(3)	2.50(3)	3.342(2)	168(2)	#3 x,y-1,z-1
	N(5)-H(19)...O(2)#3	0.85(3)	2.16(3)	3.001(2)	176(3)	#3 x,y-1,z
	N(4)-H(1)...O(6)	0.87(3)	2.07(3)	2.929(2)	168(2)	
	N(3)-H(3)...O(12)	0.82(3)	2.46(3)	3.257(2)	164(2)	
IM7	O(2)-H(5)...O(7)#3	0.94(5)	1.60(5)	2.534(2)	169(4)	#3 -x+1,-y+1,-z+1
	N(3)-H(7)...O(1)#3	0.85(3)	2.17(3)	3.007(3)	167(3)	#3 -x+1,-y+1,-z+1
	N(3)-H(6)...O(4)#2	0.83(3)	2.25(3)	3.045(3)	159(3)	#2 -x+1,-y+1,-z+1
	N(2)-H(8)...O(4)#2	0.96(4)	2.23(4)	3.143(2)	158(3)	#2 -x+1,-y+1,-z+1
	O(6)-H(1)...O(5)#4	0.96(6)	1.70(7)	2.623(2)	160(6)	#4 -x+2,-y+1,-z+1

Table S6 Hydrogen bond details of those involved in network formation in **CIM1** and **CIM2**.

IM	D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)	Sym op
CIM1	O(13)-H(13)...O(1)#3	0.82	1.72	2.516(4)	163	#3 -x+1,-y+1,-z
	N(5)-H(5A)...O(12)#3	0.86	2.12	2.954(4)	163	#3 -x+1,-y+1,-z
	N(4)-H(4A)...O(3)	0.86	2.14	2.955(4)	157	
	N(5)-H(5B)...O(3)	0.86	2.20	2.977(4)	150	
	N(2)-H(2A)...O(6)#5	0.86	2.29	3.137(4)	168	#5 -x+1,-y+1,-z+1
	N(3)-H(3B)...O(7)#5	0.86	2.11	2.962(4)	169	#5 -x+1,-y+1,-z+1
CIM2	O(1)-H(3)...O(7)#1	0.97(2)	1.54(2)	2.5057(11)	171.2(18)	#1 -x,-y+2,-z+2
	N(3)-H(9)...O(2)#1	0.861(15)	2.115(15)	2.9600(13)	166.7(13)	#1 -x,-y+2,-z+2
	N(3)-H(8)...O(3)#2	0.855(16)	2.325(16)	3.0673(13)	145.5(13)	#2 x-1,-y+3/2,z+1/2
	N(2)-H(7)...O(3)#2	0.865(15)	2.072(15)	2.9058(12)	161.6(13)	#2 x-1,-y+3/2,z+1/2

Table S7 Hydrogen bond details of those involved in the host-guest interactions in **IM4** to **IM7**, **CIM1** and **CIM2**.

IM	D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)	Sym op
IM1	O(27)-H(78)...O(100)#4	0.88(4)	1.72(4)	2.603(3)	172(3)	#4 -x+1,-y+1,-z+1
	O(100)-H(106)...O(26)#1	0.92(5)	1.99(5)	2.801(3)	146(4)	#1 x-1,y,z
	N(16)-H(48)...O(101)	0.85(3)	2.08(3)	2.918(3)	167(3)	
	O(101)-H(107)...O(8)#2	1.09(4)	1.70(4)	2.783(3)	172(4)	#2 x+1,y,z
	O(19)-H(100)...O(22)	0.98(4)	1.58(4)	2.561(3)	177(4)	
	O(27)-H(78)...O(100)#4	0.88(4)	1.72(4)	2.603(3)	172(3)	#4 -x+1,-y+1,-z+1
IM2	O(8)-H(10)...O(16)#1	0.82	1.79	2.611(9)	176	#1 x-1,y-1,z
IM3	O(7)-H(22)...N(9)	0.92(2)	1.85(2)	2.762(2)	174(2)	
IM4	O(2)-H(2)...O(17)	0.82	1.81	2.626(7)	175	
	O(17)-H(54)...O(100)	0.814(19)	2.02(3)	2.795(10)	158(5)	
	O(17)-H(53)...O(10)#6	0.809(19)	2.24(5)	2.859(8)	133(6)	#6 -x+1,-y+1,-z
IM5	O(12)-H(5)...O(17)	0.82(3)	1.78(3)	2.594(2)	176(3)	
	O(17)-H(23)...O(16)	0.86(5)	1.96(5)	2.805(3)	167(4)	
	O(17)-H(22)...O(14)	0.84(5)	2.07(5)	2.867(2)	160(4)	
IM6	O(14)-H(32)...O(16)#4	0.89(3)	1.75(3)	2.630(2)	168(3)	#4 x,y-1,z
CIM1	O(2)-H(2B)...O(16)	0.82	1.74	2.555(4)	176	
	O(16)-H(100)...O(10)	0.85(7)	1.95(7)	2.783(4)	169(6)	
	O(11)-H(105)...O(15)	0.82	1.88	2.690(4)	171.3	
	O(15)-H(103)...O(8)#2	0.84(2)	2.02(3)	2.840(4)	167(6)	#2 x,y-1,z
	O(15)-H(102)...O(14)#1	0.83(2)	1.93(4)	2.691(4)	151(7)	#1 x-1,y,z
CIM2	O(4)-H(1)...O(8)	0.88(2)	1.77(2)	2.6433(12)	175.8(19)	
	N(3)-H(8)...O(8)#2	0.855(16)	2.453(15)	3.0691(13)	129.6(12)	#2 x-1,-y+3/2,z+1/2

Table S8 Hydrogen bond details of those involved in network formation in **NS1** and **NS2**.

IM	D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)	Sym op
NS1	O(6)-H(21)...O(1)#5	0.96(3)	1.66(3)	2.610(2)	170(2)	#5 x-1,y+1,z
	N(3)-H(14)...O(5)#2	0.93(3)	1.98(3)	2.889(3)	168(2)	#2 x+1,y-1,z
	O(4)-H(1)...O(2)#4	1.02(3)	1.53(3)	2.5232(18)	164(2)	#4 x,y+1,z
	N(4)-H(12)...O(3)#3	0.94(3)	2.25(3)	3.135(2)	156(2)	#3 x,y-1,z
	N(4)-H(11)...O(3)#1	0.86(2)	2.43(2)	3.045(2)	129(2)	#1 -x+2,-y+1,-z
	N(5)-H(10)...O(3)#1	0.87(2)	2.37(2)	3.113(2)	143.4(18)	#1 -x+2,-y+1,-z
	N(2)-H(15)...O(7)	0.86(2)	2.30(3)	3.151(2)	171(2)	
	N(3)-H(13)...O(8)	0.88(3)	2.21(3)	3.084(3)	174(2)	
NS2	O(8)-H(24)...O(1)#4	1.04(5)	1.44(5)	2.479(2)	173(4)	#4 x,y+1,z
	N(4)-H(21)...O(7)#3	0.88(3)	2.22(3)	3.068(3)	163(3)	#3 x,y-1,z
	O(13)-H(100)...O(2)#2	0.90(4)	1.61(4)	2.481(2)	163(3)	#2 -x+2,-y+2,-z+1
	N(2)-H(15)...O(14)#2	0.87(3)	2.15(3)	3.010(3)	170(3)	#2 -x+2,-y+2,-z+1
	N(1)-H(16)...O(12)#1	0.89(3)	2.30(3)	3.127(3)	155(3)	#1 -x+2,-y+1,-z+1
	N(2)-H(14)...O(12)#1	0.87(3)	2.34(3)	3.121(3)	150(3)	#1 -x+2,-y+1,-z+1
	N(3)-H(17)...O(4)	0.86(3)	2.28(3)	3.082(3)	155(3)	
	N(4)-H(22)...O(4)	0.89(4)	2.47(4)	3.157(3)	134(3)	
	O(6)-H(23)...O(14)#3	0.98(4)	1.68(4)	2.655(2)	175(4)	#3 x,y-1,z
	O(10)-H(1)...O(7)	0.95(4)	1.74(4)	2.661(2)	163(3)	

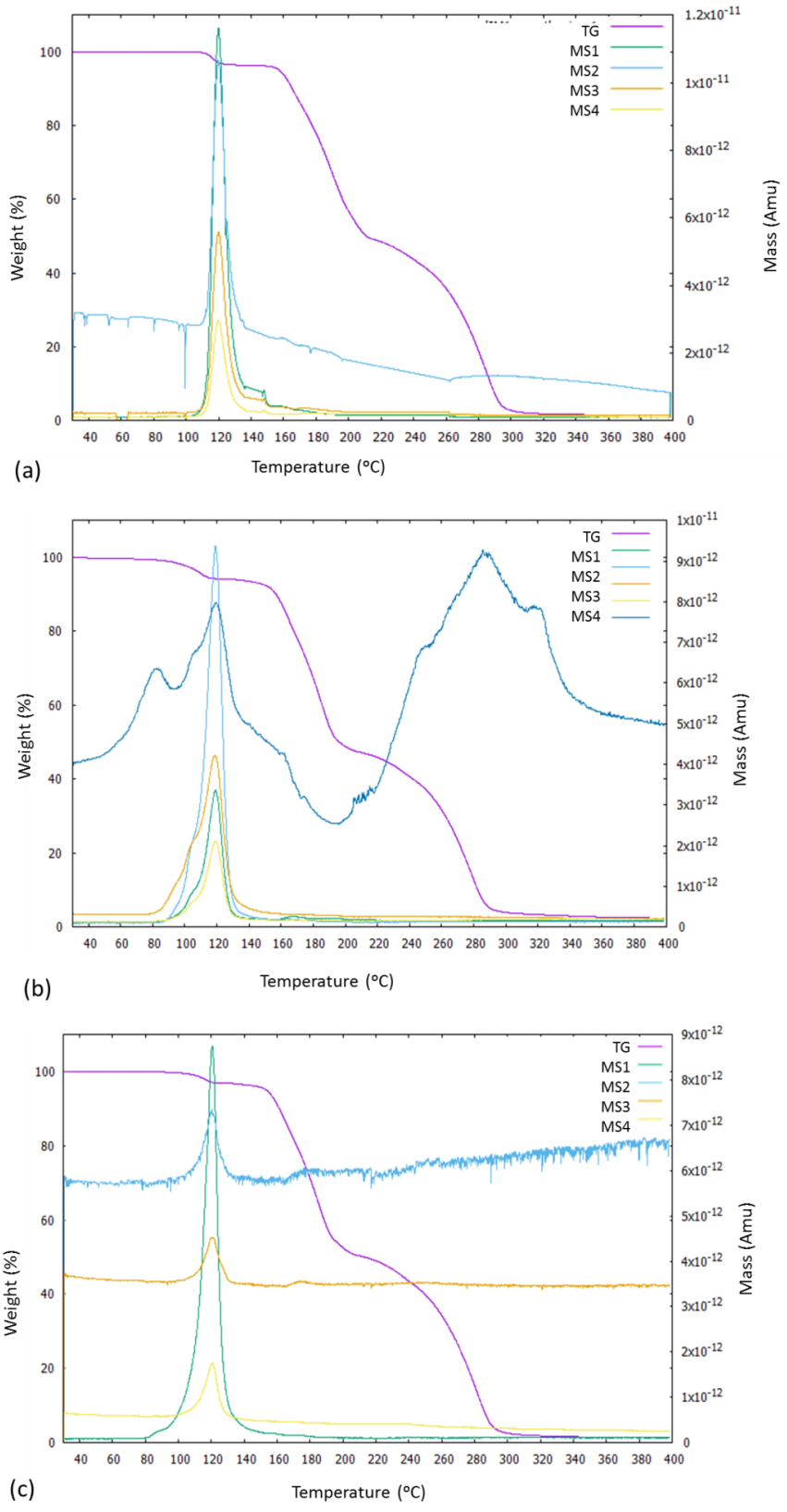


Figure S9 The TG-MS analysis for (a) **IM1**: methanol peaks MS1 = 31 m/z, MS2 = 32 m/z, MS3 = 29 m/z, MS4 = 15 m/z, (b) **IM2**: ethanol peaks MS1 = 31 m/z, MS2 = 45 m/z, MS3 = 27 m/z, MS4 = 29 m/z, water peak MS5 = 18 m/z and (c) **IM3**: acetonitrile peaks MS1 = 41 m/z, MS2 = 39 m/z, MS3 = 28 m/z, MS4 = 14 m/z.

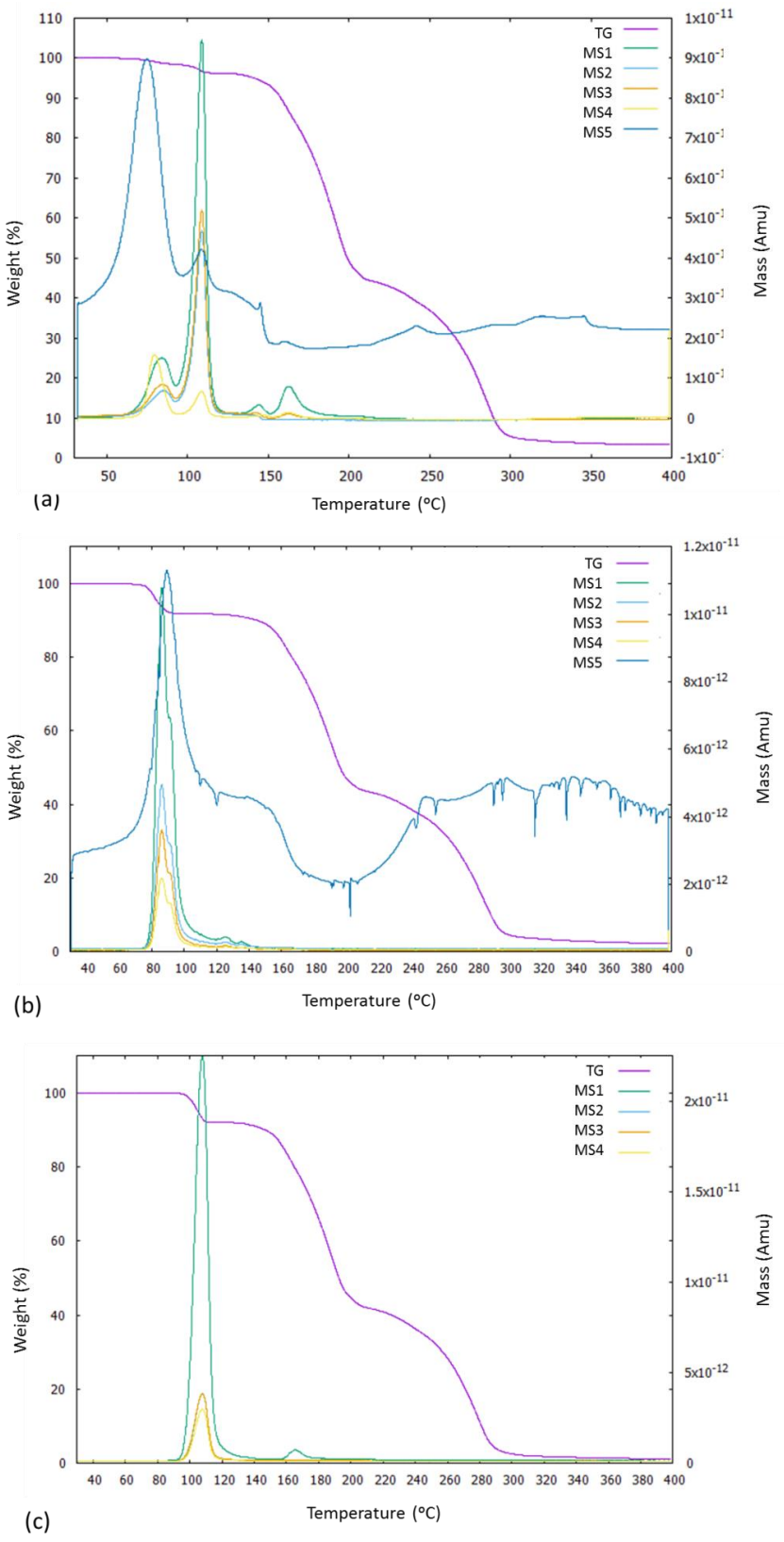


Figure S10 The TG-MS analysis for (a) **IM4**: acetone peaks MS1 = 43 m/z, MS2 = 58 m/z, MS3 = 15 m/z, MS4 = 42 m/z, water peaks MS5 = 18 m/z, (b) **IM5**: THF peaks MS1 = 42 m/z, MS2 = 41 m/z, MS3 = 71 m/z, MS4 = 43 m/z, water peak MS5 18 m/z and (c) **IM6**: ethyl acetate peaks MS1 = 43 m/z, MS2 = 61 m/z, MS3 = 45 m/z, MS4 = 70 m/z.

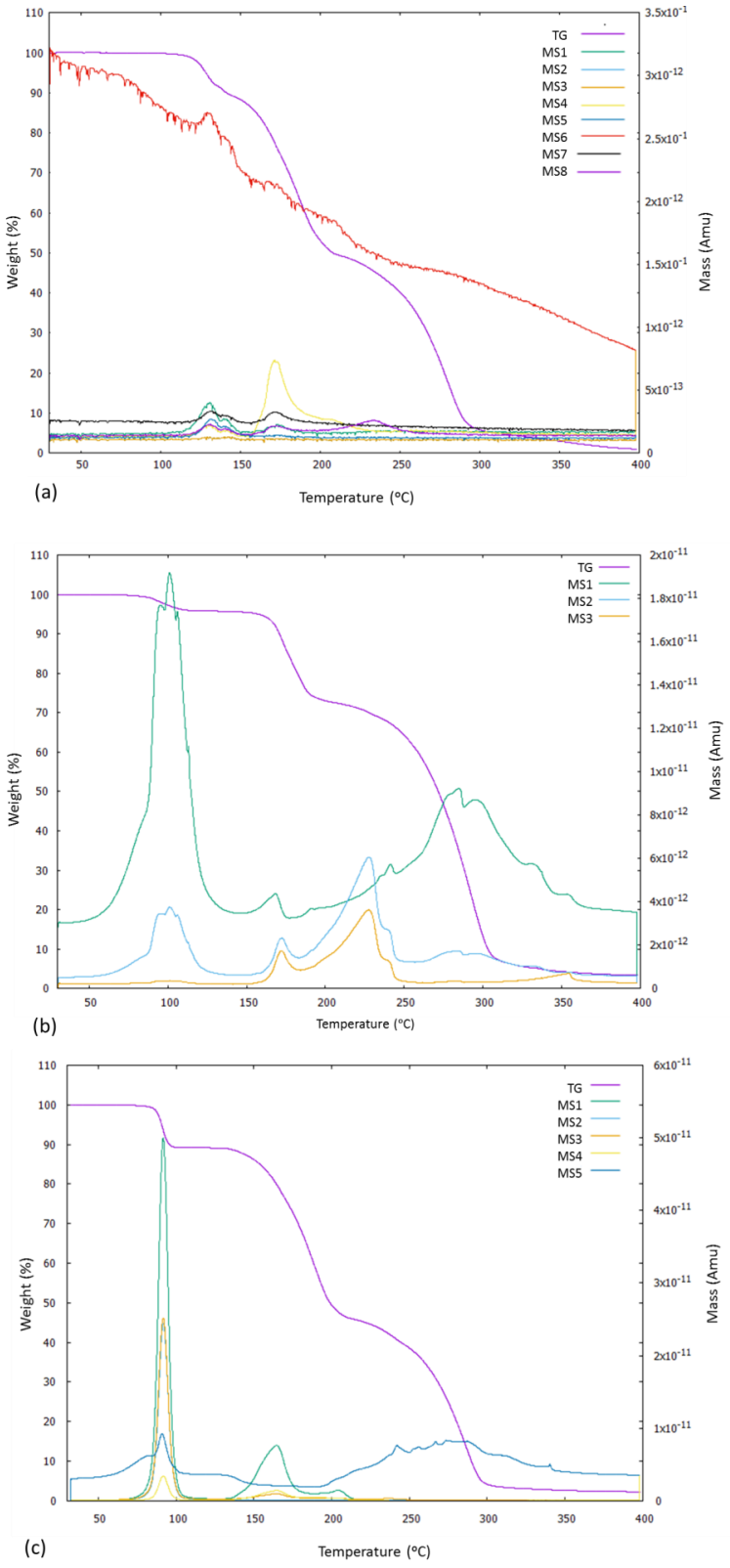


Figure S11 The TG-MS analysis for (a) **IM7**: THF peaks MS1 = 42, MS2 = 41, MS3 = 71, MS4 = 43, methanol peaks MS5 = 31, MS6 = 32, MS7 = 29, MS8 = 15, (b) **CIM1**: water peaks MS1 = 18 m/z, MS2 =17 m/z and MS3 = 16 m/z and (c) **CIM2**: acetone peaks MS1 = 43 m/z, MS2 = 58 m/z, MS3 = 15 m/z, MS4 = 42 m/z, water peaks MS5 = 18 m/z.

Table S12 Mass loss data for TG analysis of **IM1** to **IM7**, **CIM1** and **CIM2**.

IM	Step 1: solvent		Step 2: *N*-phenylurea		Step 3: 5-nitroisophthalic acid	
	Expected loss (%)	Observed loss (%)	Expected loss (%)	Observed loss (%)	Expected loss (%)	Observed loss (%)
IM1	3.4	3.4	45.3	47.6	51.1	46.2
IM2	7.2	5.2	45.6	46.2	47.1	43.2
IM3	4.7	3.2	46.9	46.0	48.4	48.0
IM4	8.4	1.7, 2.0	45.0	51.7	46.6	39.2
IM5	9.8	8.1	44.4	46.5	45.9	40.9
IM6	9.6	7.9	44.4	50.4	45.9	40.1
IM7	13.0	10.9	34.0	39.6	52.8	45.2
CIM1	4.9	4.2	37.3	22.8	57.8	68.9
CIM2	14.3	10.7	33.6	43.7	52.0	43.0

Table S13 The corresponding energies of the desolvation endotherm for **IM1** – **IM7**, **CIM1** and **CIM2**.

IM	Onset temperature (°C)	Energy (J/g)
IM1	103.3	33.8
IM2	86.9, 112.8	26.0, 1.7
IM3	106.6	79.4
IM4	80.8, 99.8	17.3, 21.8
IM5	76.0, 89.5	68.7
IM6	95.8	38.8
IM7	143.4	81.8
CIM1	96.6	0.2
CIM2	83.2	104.5

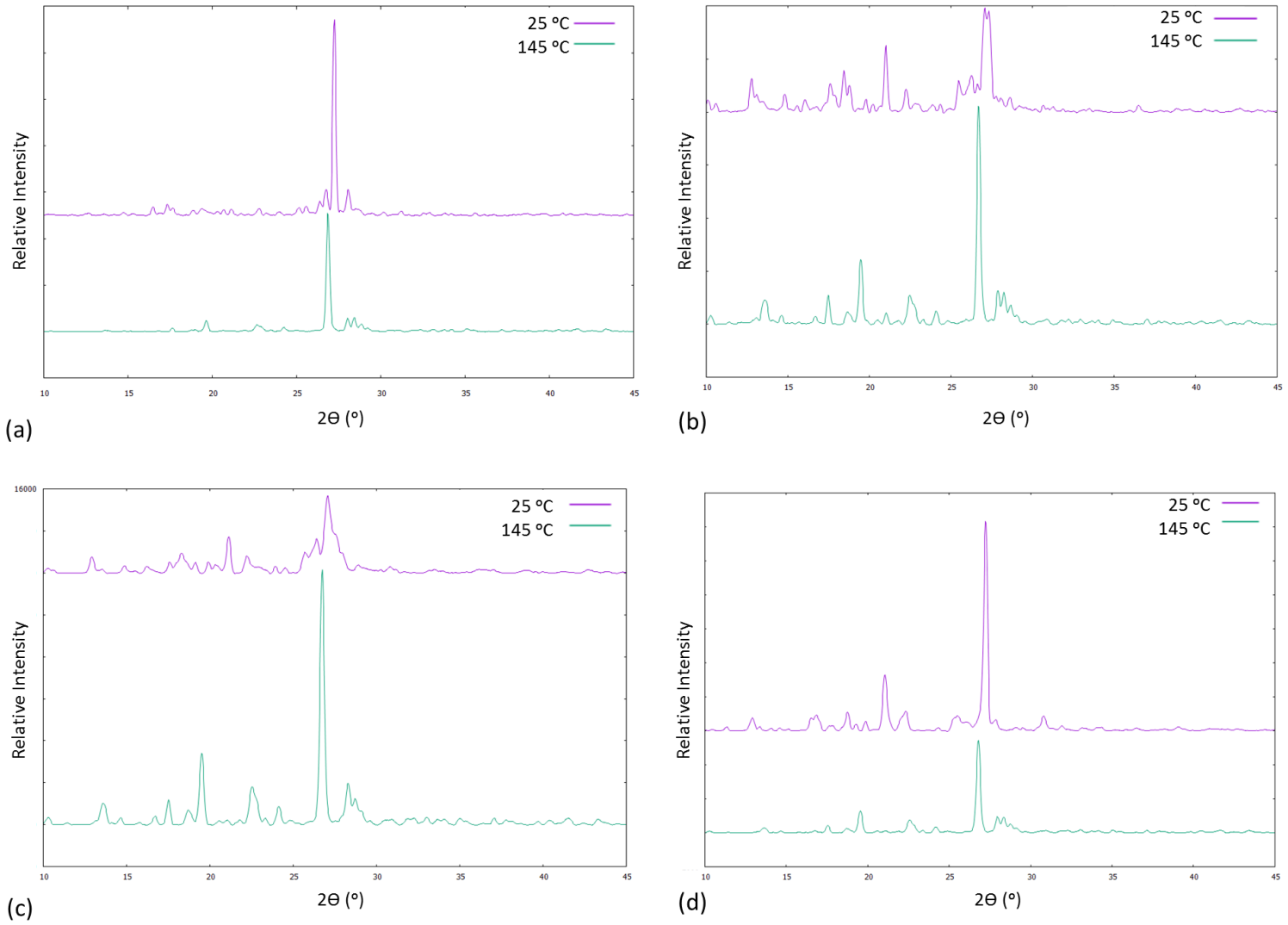


Figure S14 PXRD patterns for (a) **IM1**, (b) **IM2**, (c) **IM3** and (d) **IM4** at 25 °C on samples at 25 °C and preheated to 145 °C.

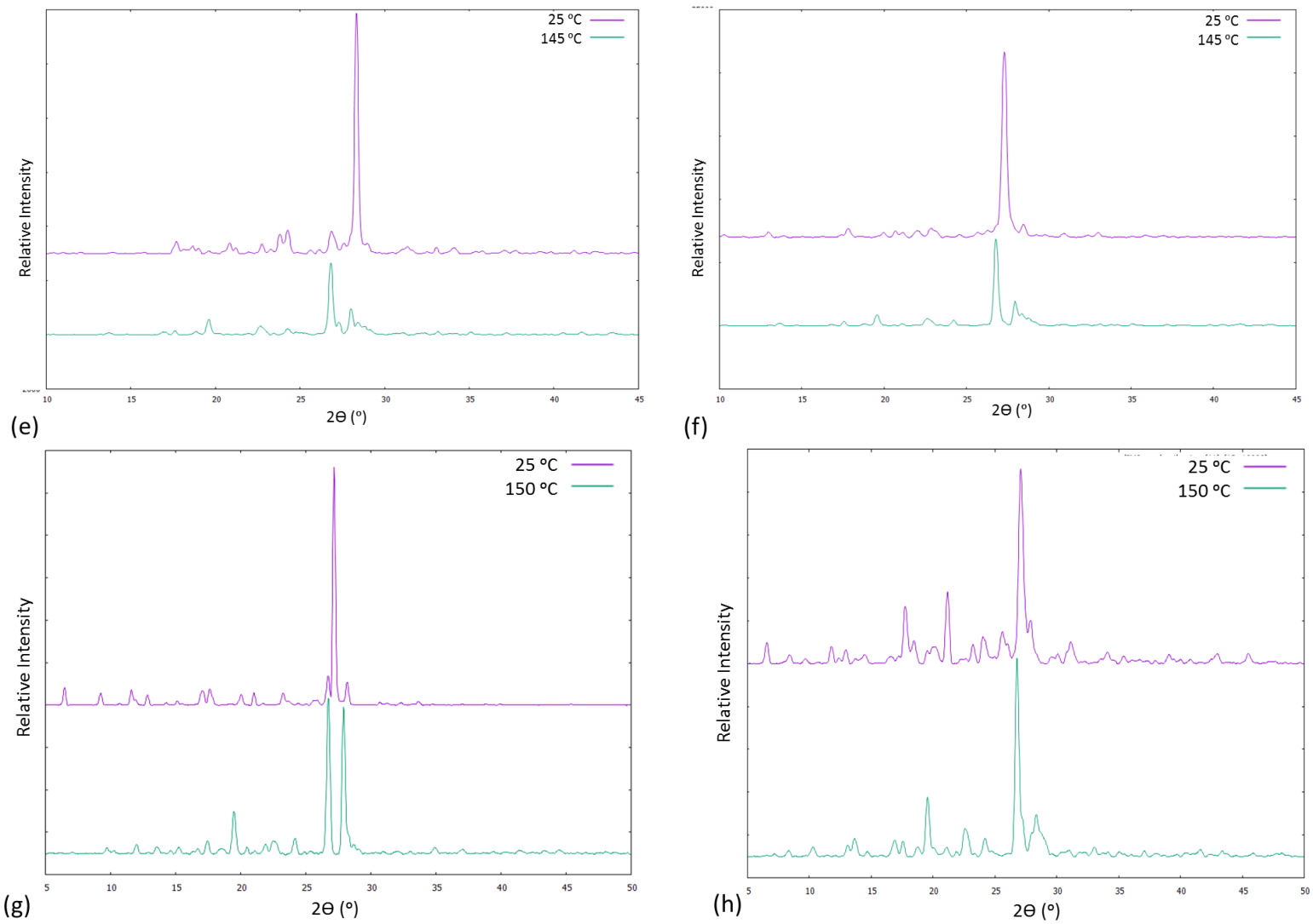


Figure S15 PXRD patterns for (a) **IM5**, (b) **IM6**, (c) **IM7** and (d) **CIM2** at 25 °C on samples at 25 °C and preheated to 145 °C (**CIM2** pre-heated to 150 °C).

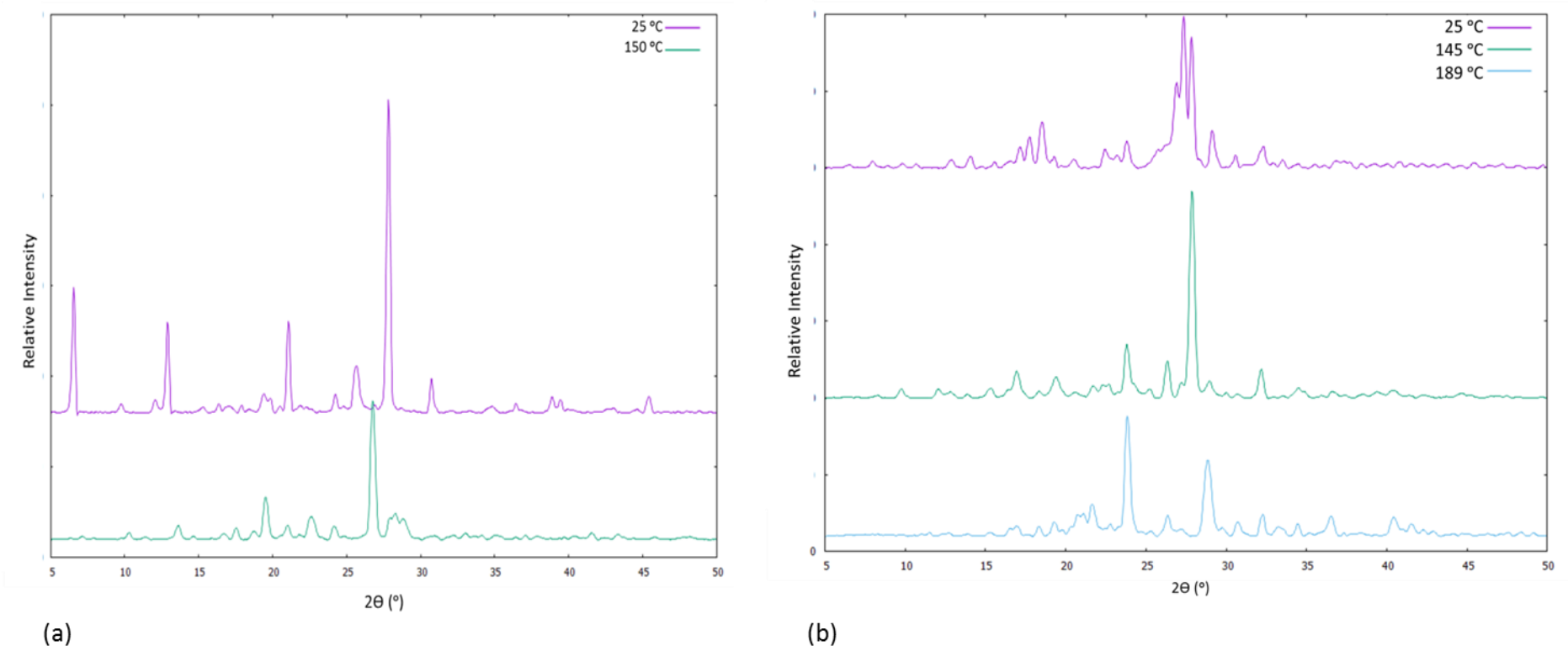
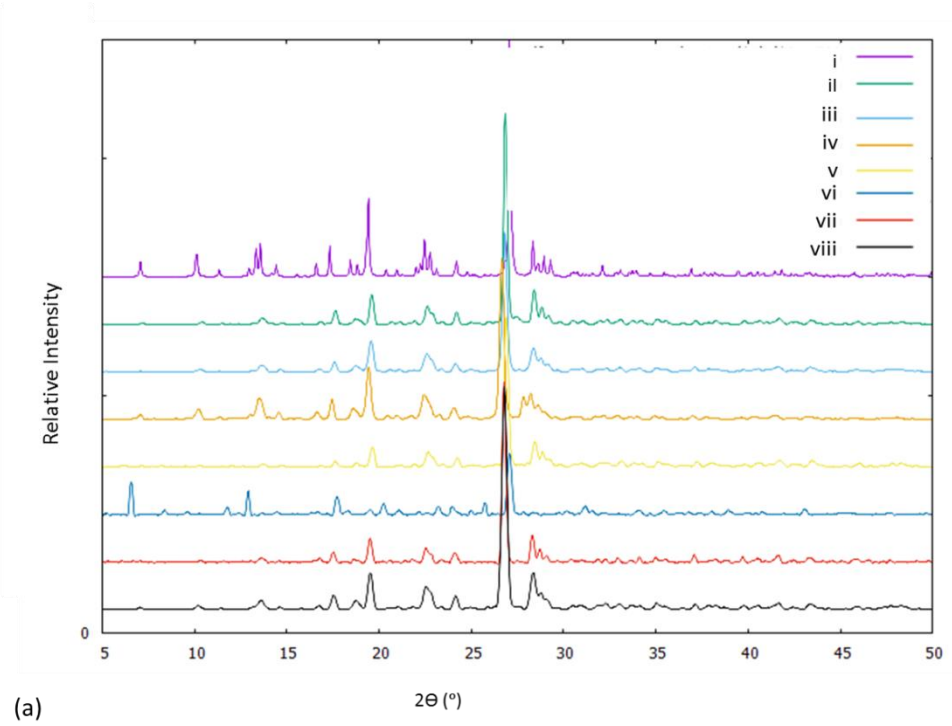


Figure S16 – PXRD patterns for (a) **NS2** at 25 °C and on a sample preheated to 150 °C and (b) **CIM1** at 25 °C, on a sample preheated to 145 ° C and 189 °C.



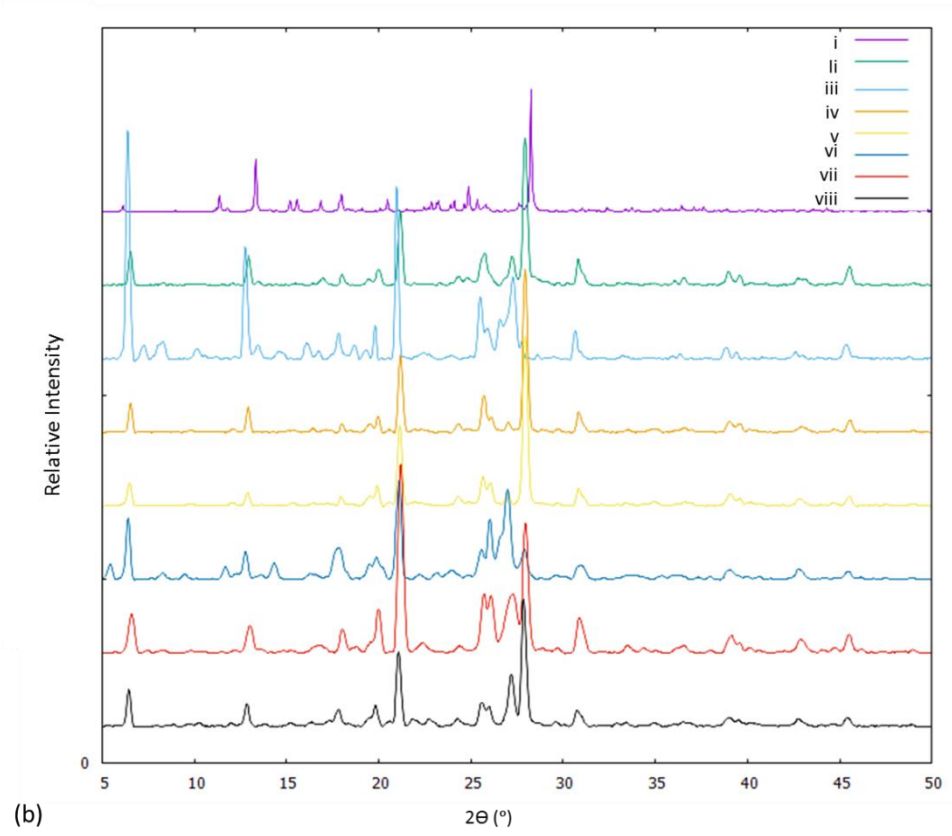


Figure S17 PXRD patterns of (a) **NS1** and (b) **NS2**: (i) the simulated powder pattern of the material, (ii) each material pre-vapour diffusion and post vapour diffusion with (iii) methanol, (iv) ethanol, (v) acetonitrile, (vi) acetone, (vii) THF and (viii) ethyl acetate at -18 °C.

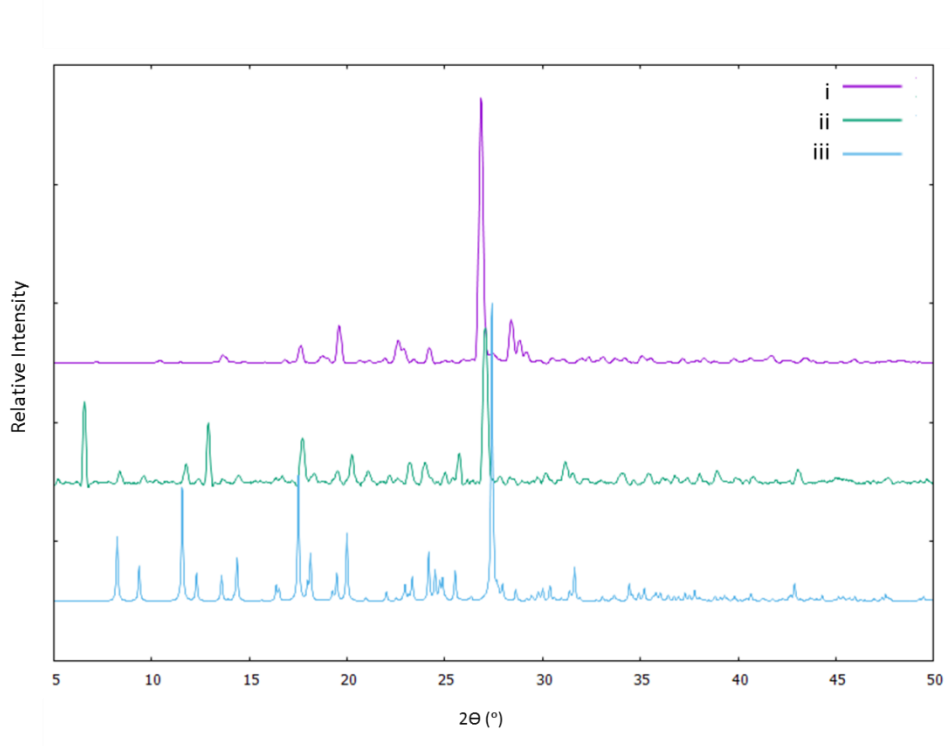


Figure S18 A comparison of PXRD patterns of (i) **NS1** pre vapour diffusion, (ii) post vapour diffusion with acetone solvent and (iii) the simulated powder pattern for **CIM2**.

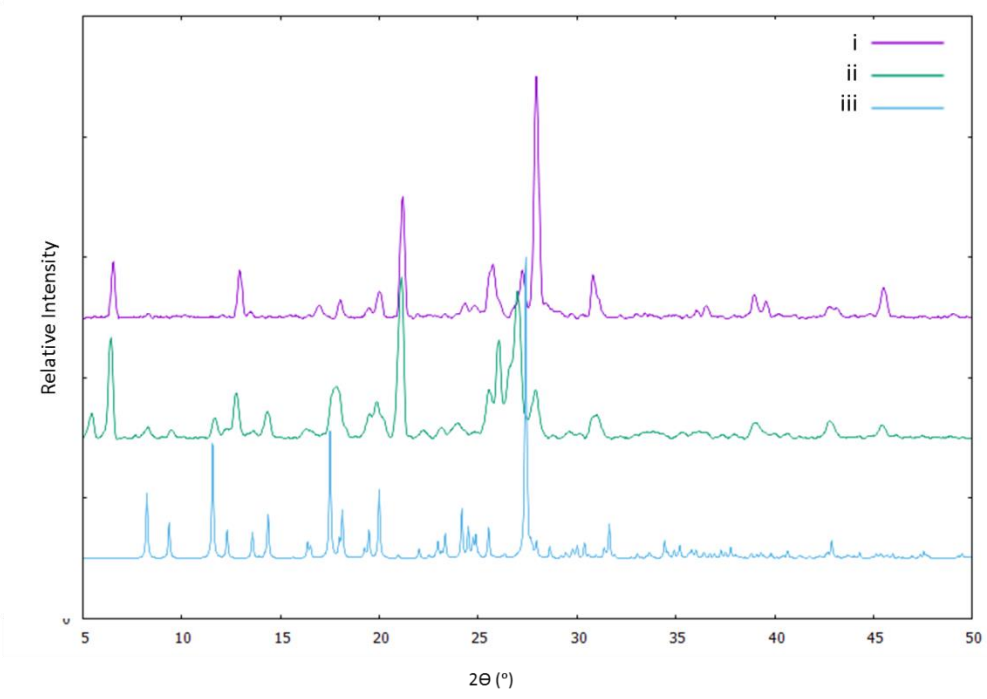


Figure S19 A comparison of PXRD patterns of (i) **NS2** pre vapour diffusion, (ii) post vapour diffusion with acetone solvent and (ii) the simulated powder pattern for **CIM2**.