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Supporting Information

The Dark Side of Crystal Engineering: Creating Glasses from Small Symmetric Molecules that Form Multiple Hydrogen Bonds

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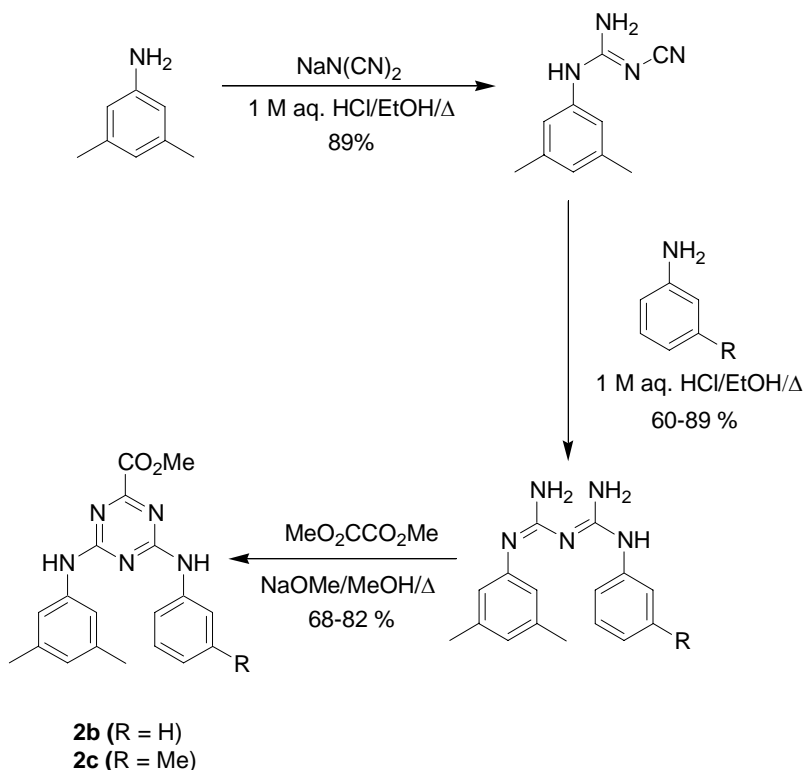
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Experimental Section

1,5-Dimethylbiguanide (**1**),¹ methyl 4,6-bis(dimethylamino)-1,3,5-triazine-2-carboxylate (**2a**),² methyl 4,6-bis(phenylamino)-1,3,5-triazine-2-carboxylate (**3a**),² methyl 4,6-bis[(4-methylphenyl)amino]-1,3,5-triazine-2-carboxylate (**3b**),² methyl 4,6-bis[(3-methylphenyl)amino]-1,3,5-triazine-2-carboxylate (**3c**),² methyl 4,6-bis[(2-methylphenyl)amino]-1,3,5-triazine-2-carboxylate (**3d**),² and 4,6-dichloro-2-methylamino-1,3,5-triazine³ were prepared according to published procedures. New compounds **2b-f** and **4a-c** were prepared by the routes summarized in Schemes 1-3 and described in detail below.

Scheme 1



Methyl 4-(mexylamino)-6-phenylamino-1,3,5-triazine-2-carboxylate (**2b**)

3,5-Dimethylaniline (6.23 mL, 6.06 g, 50.0 mmol) was added to aqueous HCl (50.0 mL, 1.00 M, 50.0 mmol) in a round-bottom flask equipped with a magnetic stirrer. The mixture was stirred for 15 min at room temperature, then sodium dicyanamide (4.45 g, 50.0 mmol) was added, and the mixture was heated at reflux for 2 h. The resulting mixture was cooled to room temperature, AcOEt was added, and the two phases were separated. The organic phase was recovered, dried over MgSO_4 , and filtered, and volatiles were removed by evaporation under reduced pressure. The crude product was triturated with hot hexane to yield mexyldicyandiamide (8.35 g, 44.4 mmol, 89%): mp 128 °C; IR (KBr) 3392, 3322, 3215, 3015, 2953, 2919, 2732, 2504, 2439, 2173, 1658, 1602, 1552, 1467, 1382, 1328, 1300, 1269, 1238, 1178, 1102, 1037, 891, 881, 839, 709, 682, 589, 534 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H), 6.88 (s, 1H), 6.87 (s, 2H), 5.91 (s, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 140.0, 135.6, 129.0, 122.2, 118.4, 21.4; HRMS (ESI) calcd for

$\text{C}_{10}\text{H}_{13}\text{N}_4$ *m/e* 189.1135, found 189.1143. Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{N}_4$: C, 63.81; H, 6.43; N, 29.77. Found: C, 63.75; H, 6.65; N, 29.36.

A mixture of aniline (0.243 mL, 0.248 g, 2.66 mmol), aqueous HCl (2.66 mL, 1.00 M, 2.66 mmol), and EtOH (10 mL) was stirred at room temperature for 15 min, then mexyldicyandiamide (0.500 g, 2.66 mmol) was added and the mixture was heated at reflux overnight. Volatiles were removed by evaporation *in vacuo*, then the crude product was recrystallized from hot water and washed with CH_2Cl_2 to give 1-mexyl-5-phenylbiguanide hydrochloride (0.755 g, 2.38 mmol, 89%): mp 210 °C; IR (KBr) 3428, 3308, 3178, 3120, 2994, 2945, 2912, 2605, 1635, 1615, 1602, 1582, 1523, 1494, 1447, 1377, 1300, 1249, 1178, 1088, 1036, 901, 871, 849, 759, 741, 718, 684, 627, 555, 521, 501, 473 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.69 (s, 1H), 9.66 (s, 1H), 7.42 (s, 2H), 7.32 (m, 6H), 7.10 (m, 1H), 6.88 (s, 2H), 6.75 (s, 1H), 2.20 (s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 157.3, 156.6, 138.2, 138.1, 137.6, 129.0, 126.3, 124.5, 122.0, 119.9, 21.1; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{N}_5$ *m/e* 282.1713, found 282.1709. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{ClN}_5$: C, 60.47; H, 6.34; N, 22.04. Found: C, 60.06; H, 6.35; N, 21.97.

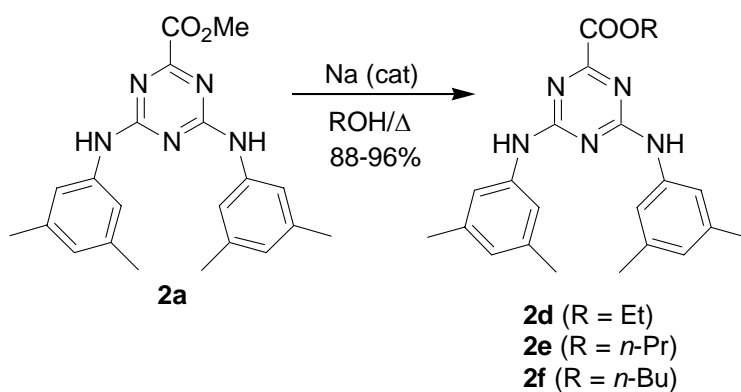
Methanolic NaOMe (25%, 0.440 mL, 1.92 mmol) was added to a mixture of 1-mexyl-5-phenylbiguanide hydrochloride (0.466 g, 1.47 mmol) in MeOH (30 mL), and the resulting mixture was stirred for 15 min at room temperature. Dimethyl oxalate (0.521 g, 4.41 mmol) was added and the mixture was heated at reflux overnight. The mixture was then cooled to room temperature, H_2O and AcOEt were added, and the two phases were separated. The organic phase was recovered and dried over MgSO_4 , and volatiles were removed by evaporation under reduced pressure. The crude product was then passed through a short pad of silica using 1:1 AcOEt/hexane as eluent. Evaporation of the solvent then yielded methyl 4-(mexylamino)-6-phenylamino-1,3,5-triazine-2-carboxylate (**2b**; 0.421 g, 1.20 mmol, 82%): T_g 51 °C; IR (KBr) 3267, 3186, 3104, 3012, 2949, 2918, 2851, 1749, 1703, 1604, 1577, 1521, 1442, 1350, 1297, 1263, 1217, 1169, 1100, 1042, 1005, 976, 911, 842, 826, 788, 754, 687, 647, 619, 541, 504 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $^3J = 7.6$ Hz, 2H), 7.54 (bs, 1H), 7.47 (bs, 1H), 7.36 (t, $^3J = 7.6$ Hz, 2H), 7.19 (s, 2H), 7.15 (t, $^3J = 7.6$ Hz, 1H), 6.80 (s, 1H), 4.02 (s, 3H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 164.5, 163.5, 163.3, 138.6, 137.4, 137.1, 128.9, 126.1, 124.3, 121.2, 118.6, 53.4, 21.3; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{N}_5\text{O}_2$ *m/e* 350.1612, found 350.1614. Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{N}_5\text{O}_2$: C, 65.32; H, 5.48; N, 20.04. Found: C, 64.96; H, 5.51; N, 19.92.

Methyl 4-(mexylamino)-6-[(3-methylphenyl)amino]-1,3,5-triazine-2-carboxylate (**2c**)

1-Mexyl-5-(3-methylphenyl)biguanide hydrochloride was prepared by a method analogous to the one used to make 1-mexyl-5-phenylbiguanide hydrochloride. The reaction of 3-methylaniline (0.569 mL, 0.569 g, 5.31 mmol) with mexyldicyandiamide (1.00 g, 5.31 mmol) yielded 1-mexyl-5-(3-methylphenyl)biguanide hydrochloride (1.06 g, 3.19 mmol, 60%): mp 212 °C; IR (KBr) 3308, 3189, 3131, 3005, 2917, 1633, 1602, 1519, 1489, 1454, 1376, 1319, 1260, 1182, 1092, 842, 775, 719, 682, 501 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.67 (s, 1H), 9.65 (s, 1H), 7.38 (s, 2H), 7.34 (s, 2H), 7.20 (t, $^3J = 8.0$ Hz, 1H), 7.10 (m, 2H), 6.92 (d, $^3J = 7.4$ Hz, 2H), 6.89 (s, 2H), 6.75 (s, 1H), 2.25 (s, 3H), 2.20 (s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 156.6, 156.3, 137.7, 137.6, 137.5, 137.4, 128.2, 125.5, 124.5, 121.9, 119.2, 118.5, 20.7, 20.6; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{22}\text{N}_5$ *m/e* 296.1870, found 296.1875. Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{ClN}_5$: C, 61.53; H, 6.68; N, 21.10. Found: C, 61.65; H, 6.94; N, 21.30.

Triazine **2c** was prepared from 1-mexyl-5-(3-methylphenyl)biguanide hydrochloride using the same method used to make triazine **2b**. Yield: 68%; T_g 38 °C; IR (KBr) 3266, 3181, 3104, 3013, 2950, 2918, 2851, 1749, 1702, 1583, 1525, 1489, 1428, 1345, 1300, 1256, 1220, 1164, 1104, 1044, 1000, 976, 893, 842, 827, 787, 728, 685, 648, 620, 540 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (bs, 1H), 7.57 (bs, 1H), 7.52 (d, $^3J = 8.0$ Hz, 1H), 7.24 (t, $^3J = 8.0$ Hz, 1H), 7.17 (m, 3H), 6.96 (d, $^3J = 8.0$ Hz, 1H), 6.79 (s, 1H), 3.97 (s, 3H), 2.32 (s, 3H), 2.29 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3 , 283 K) δ 164.6, 164.5, 163.7, 163.3, 138.8, 138.6, 137.5, 137.3, 128.8, 126.2, 125.3, 121.9, 118.9, 118.7, 53.5, 21.5, 21.4; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{N}_5\text{O}_2$ m/e 364.1768, found 364.1779. Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{N}_5\text{O}_2$: C, 66.10; H, 5.82; N, 19.27. Found, C, 65.86; H, 5.94; N, 19.00.

Scheme 2



Ethyl 4,6-bis(mexylamino)-1,3,5-triazine-2-carboxylate (**2d**)

Ethanollic NaOEt was prepared by dissolving a small piece of sodium in EtOH (30 mL) in a round-bottom flask at room temperature. Compound **2a** (0.500 g, 1.32 mmol) was added, and the mixture was heated at reflux overnight. Volatiles were removed by evaporation under reduced pressure, and H_2O and AcOEt were then added. The two phases were separated, and the organic phase was separated, dried over MgSO_4 , and filtered. Solvent was removed by evaporation under reduced pressure, and the residue was thoroughly dried *in vacuo* for at least 2 days. The resulting glassy solid was ethyl 4,6-bis(mexylamino)-1,3,5-triazine-2-carboxylate (**2d**; 0.477 g, 1.22 mmol, 92%) of high enough purity to be used without further purification: T_g 62 °C; IR (KBr) 3271, 3186, 3102, 2977, 2917, 2857, 1746, 1613, 1586, 1524, 1432, 1368, 1336, 1301, 1260, 1213, 1162, 1104, 1053, 1021, 992, 965, 887, 865, 841, 791, 757, 684, 645, 539 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (bs, 2H), 7.14 (s, 4H), 6.79 (s, 2H), 4.49 (q, $^3J = 7.1$ Hz, 2H), 2.27 (s, 12H), 1.45 (t, $^3J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 163.7, 163.2, 138.5, 137.3, 126.1, 119.0, 62.7, 21.2, 14.0; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{26}\text{N}_5\text{O}_2$ m/e 392.2081, found 392.2084. Anal. Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_5\text{O}_2$: C, 67.50; H, 6.44; N, 17.89. Found, C, 67.26; H, 6.58; N, 18.12.

Esters **2e** and **2f** were synthesized by the same method of transesterification using the corresponding alcohols as solvents.

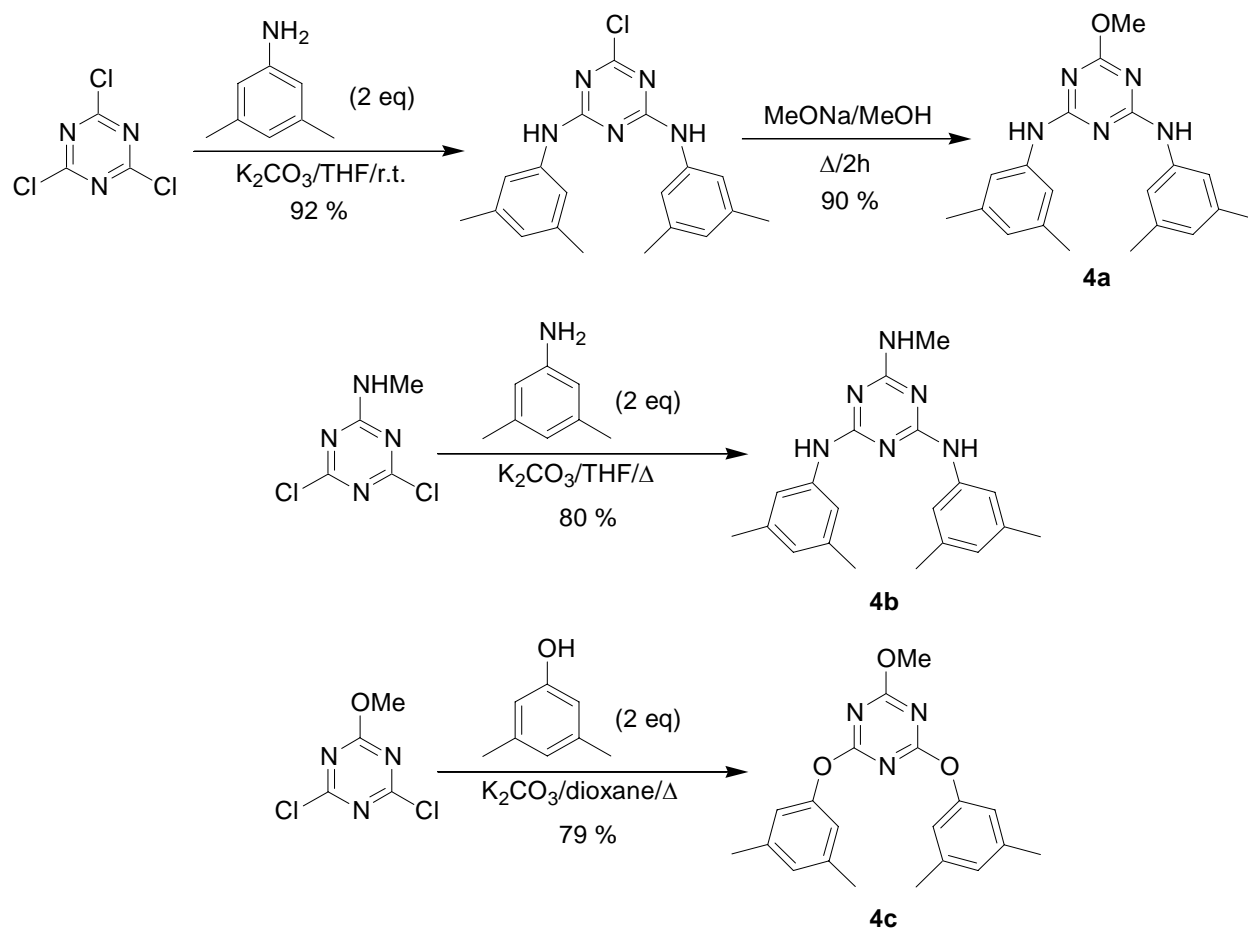
Propyl 4,6-bis(mexylamino)-1,3,5-triazine-2-carboxylate (2e)

Yield: 96%; T_g 58 °C; IR (KBr) 3269, 3186, 3107, 3005, 2966, 2918, 1746, 1613, 1587, 1558, 1524, 1432, 1385, 1335, 1260, 1211, 1169, 1104, 1055, 996, 920, 886, 841, 791, 755, 684, 645, 539 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (bs, 2H), 7.14 (s, 4H), 6.78 (s, 2H), 4.37 (q, $^3J = 6.9$ Hz, 2H), 2.27 (s, 12H), 1.84 (sext, $^3J = 6.9$ Hz, 2H), 1.02 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3 , 283 K) δ 164.7, 163.8, 163.5, 138.5, 137.5, 126.2, 119.3, 68.3, 21.8, 21.5, 10.2; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{28}\text{N}_5\text{O}_2$ m/e 406.2238, found 406.2241. Anal. Calcd for $\text{C}_{23}\text{H}_{27}\text{N}_5\text{O}_2$: C, 68.13; H, 6.71; N, 17.27. Found: C, 68.30; H, 6.91; N, 17.48.

Butyl 4,6-bis(mexylamino)-1,3,5-triazine-2-carboxylate (2f)

Yield: 88%; T_g 54 °C; IR (KBr) 3252, 3097, 3012, 2959, 2916, 2871, 1753, 1737, 1592, 1574, 1528, 1454, 1433, 1383, 1341, 1301, 1262, 1211, 1163, 1104, 1055, 995, 969, 917, 896, 861, 839, 794, 764, 726, 676, 654, 642, 544 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (bs, 2H), 7.14 (s, 4H), 6.78 (s, 2H), 4.43 (q, $^3J = 7$ Hz, 2H), 2.27 (s, 12H), 1.81 (quint, $^3J = 7$ Hz, 2H), 1.47 (m, 2H), 0.98 (t, $^3J = 7$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3 , 283 K) δ 164.7, 163.7, 163.6, 138.7, 137.4, 126.3, 119.1, 66.8, 30.5, 21.5, 19.1, 13.9; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{30}\text{N}_5\text{O}_2$ m/e 420.2394, found 420.2388. Anal. Calcd for $\text{C}_{24}\text{H}_{29}\text{N}_5\text{O}_2$: C, 68.71; H, 6.97; N, 16.69. Found: C, 68.59; H, 7.08; N, 16.72.

Scheme 3



2-Methoxy-4,6-bis(mexylamino)-1,3,5-triazine (4a)

To a solution of cyanuric chloride (5.00 g, 27.1 mmol) in acetone (100 mL) in a round-bottom flask at 0 °C, 3,5-dimethylaniline (6.77 mL, 6.58 g, 54.3 mmol) was slowly added. K_2CO_3 (3.75 g, 27.1 mmol) was then added, and the mixture was stirred for 2 h at room temperature. H_2O was added, and the resulting precipitate was separated by filtration and washed thoroughly with H_2O and hexane to yield 2-chloro-4,6-bis(mexylamino)-1,3,5-triazine (8.80 g, 24.9 mmol, 92%), which proved to be pure enough to be used without further purification: mp 186 °C; IR (KBr) 3259, 3185, 3139, 3096, 3015, 2955, 2916, 2853, 2474, 2343, 1710, 1622, 1604, 1592, 1577, 1525, 1441, 1386, 1305, 1275, 1248, 1230, 1167, 1047, 988, 957, 943, 885, 866, 842, 802, 755, 728, 681, 656, 641, 565, 543 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.63 (bs, 2H), 7.12 (s, 4H), 6.79 (s, 2H), 2.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 (br), 164.2, 138.6, 136.9, 126.4, 119.2, 21.3; HRMS (ESI) calcd for $C_{19}H_{21}ClN_5$ m/e 354.1480, found 354.1487. Anal. Calcd for $C_{19}H_{20}ClN_5$: C, 64.49; H, 5.70; N, 19.79. Found: C, 64.82; H, 5.72; N, 20.07.

A methanolic solution of sodium methoxide (25 wt%, 0.30 mL, 1.3 mmol) was diluted with methanol (10 mL) in a round-bottom flask. 2-Chloro-4,6-bis(mexylamino)-1,3,5-triazine (0.354 g, 1.00 mmol) was added, and the mixture was heated at reflux for 2 h. Volatiles were removed by

evaporation *in vacuo*, and then H₂O and AcOEt were added. The two phases were separated, and the organic phase was dried over MgSO₄ and filtered. Removal of solvent by evaporation under reduced pressure left a residue of pure 2-methoxy-4,6-bis(mexylamino)-1,3,5-triazine (**4a**; 0.316 g, 0.904 mmol, 90%): *T_g* 54 °C; IR (KBr) 3377, 3273, 3132, 3010, 2950, 2917, 2851, 1615, 1591, 1564, 1517, 1456, 1384, 1347, 1184, 1118, 1100, 1035, 993, 928, 884, 840, 811, 685, 644, 609, 539 cm⁻¹; ¹H NMR (400 MHz, benzene-*d*₆) δ 8.67 (bs, 2H), 7.34 (bs, 4H), 6.68 (s, 2H), 3.82 (s, 3H), 2.25 (s, 12H); ¹³C NMR (100 MHz, benzene-*d*₆) δ 170.4, 166.2, 139.1, 138.1, 125.4, 119.6, 53.8, 21.5; HRMS (ESI) calcd for C₂₀H₂₄N₅O *m/e* 350.1975, found 350.1976. Anal. Calcd for C₂₀H₂₃N₅O: C, 68.74; H, 6.63; N, 20.04. Found: C, 68.58; H, 6.75; N, 20.02.

2-Methylamino-4,6-bis(mexylamino)-1,3,5-triazine (**4b**)

To a stirred solution of 4,6-dichloro-2-methylamino-1,3,5-triazine³ (0.456 g, 2.55 mmol) in THF (30 mL) in a round-bottom flask were added successively 3,5-dimethylaniline (0.637 mL, 0.619 g, 5.11 mmol) and K₂CO₃ (0.352 g, 2.55 mmol), and the resulting mixture was heated at reflux overnight. The mixture was allowed to cool to room temperature, AcOEt and H₂O were added, and the two phases were separated. The organic phase was extracted with aqueous K₂CO₃ and then with brine. The organic phase was subsequently dried over MgSO₄, and volatiles were removed by evaporation under reduced pressure. The residue was triturated with AcOEt/hexane to remove any unreacted 3,5-dimethylaniline, yielding pure 2-methylamino-4,6-bis(mexylamino)-1,3,5-triazine (**4b**; 0.713 g, 2.05 mmol, 80%): *T_g* 94 °C; IR (KBr) 3401, 3274, 3148, 3013, 2945, 2916, 1587, 1555, 1515, 1426, 1355, 1318, 1180, 1092, 1034, 908, 882, 838, 808, 732, 686, 640, 538 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (bs, 4H), 7.01 (s, 2H), 6.69 (s, 2H), 5.19 (bs, 1H), 2.98 (d, ³*J* = 5.0 Hz, 3H), 2.28 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 164.3, 164.1, 138.8, 138.6, 138.2, 124.8, 124.5, 118.5, 118.1, 27.4, 21.3; HRMS (ESI) calcd for C₂₀H₂₅N₆ *m/e* 349.2135, found 349.2137. Anal. Calcd for C₂₀H₂₄N₆: C, 68.94; H, 6.94; N, 24.12. Found, C, 68.62; H, 7.25; N, 24.25.

2-Methoxy-4,6-bis(mexyloxy)-1,3,5-triazine (**4c**)

To a solution of 4,6-dichloro-2-methoxy-1,3,5-triazine (0.500 g, 2.78 mmol) in dioxane (10 mL) were added 3,5-dimethylphenol (0.679 g, 5.56 mmol) and K₂CO₃ (0.768 g, 5.56 mmol), and the mixture was heated at reflux for 48 h. Volatiles were removed by evaporation under reduced pressure, and then H₂O and AcOEt were added. The two phases were separated, and the organic phase was dried over MgSO₄ and filtered. Evaporation of solvent under reduced pressure left a residue that was triturated with hot hexane to give pure 2-methoxy-4,6-bis(mexyloxy)-1,3,5-triazine (**4c**; 0.771 g, 2.19 mmol, 79%): mp 125 °C; IR (KBr) 3017, 2955, 2919, 2863, 1620, 1598, 1567, 1503, 1470, 1452, 1431, 1360, 1285, 1199, 1153, 1114, 1091, 1036, 998, 949, 929, 901, 893, 868, 848, 813, 703, 683, 656, 634, 616, 543, 522, 508 cm⁻¹; ¹H NMR (400 MHz, benzene-*d*₆) δ 6.73 (s, 4H), 6.58 (s, 2H), 3.55 (s, 3H), 2.00 (s, 12H); ¹³C NMR (100 MHz, benzene-*d*₆) δ 174.7, 174.3, 152.5, 139.2, 127.6, 119.6, 55.1, 21.1; HRMS (ESI) calcd for C₂₀H₂₂N₃O₃ *m/e* 352.1656, found 352.1651. Anal. Calcd for C₂₀H₂₁N₃O₃: C, 68.36; H, 6.02; N, 11.96. Found: C, 68.47; H, 5.83; N, 11.99.

Measurement of *T_g* by Modulated Differential Scanning Calorimetry (mDSC). Measurements were made with a TA Instruments Q1000 calorimeter, using a 60 sec period and heating/cooling

rates of 5 °C/min from 20 °C to 200 °C. Three cycles of heating and cooling were recorded. Essentially identical thermograms were obtained when slower heating/cooling rates were used.

Crystal Structure of Methyl 4,6-Bis(dimethylamino)-1,3,5-triazine-2-carboxylate (2a). Single crystals of compound **2a** suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution in CHCl₃. Data were collected using a Nonius Kappa CCD diffractometer at the University of Toronto. Compound **2a** crystallized in the monoclinic space group C2/c with cell lattice parameters $a = 24.7394(1)$ Å, $b = 13.3588(6)$ Å, $c = 19.2393(5)$ Å, and $\beta = 114.790(2)^\circ$. One included molecule of CHCl₃ was located, whereas disordered molecules of included H₂O were accounted for by using the Bypass/Squeeze method⁴ implemented in Platon.⁵ Platon found a remaining solvent void of 1109 Å³ filled with 93 electron of diffuse scattering. Refinement on F² of 3656 observed reflections over a total of 6596 unique reflections led to residual factors $R_1 = 0.0701$, $wR_2 = 0.1973$, and GoF = 1.035.

FT-IR Spectra. Infrared spectra were recorded using a Perkin-Elmer Spectrum One spectrometer. Pellets containing compound **2a** in KBr were prepared from the amorphous solid generated by heating and from single crystals grown from CHCl₃. A solution of compound **2a** in CH₂Cl₂ was also prepared, and its spectrum was recorded using cells with NaCl windows.

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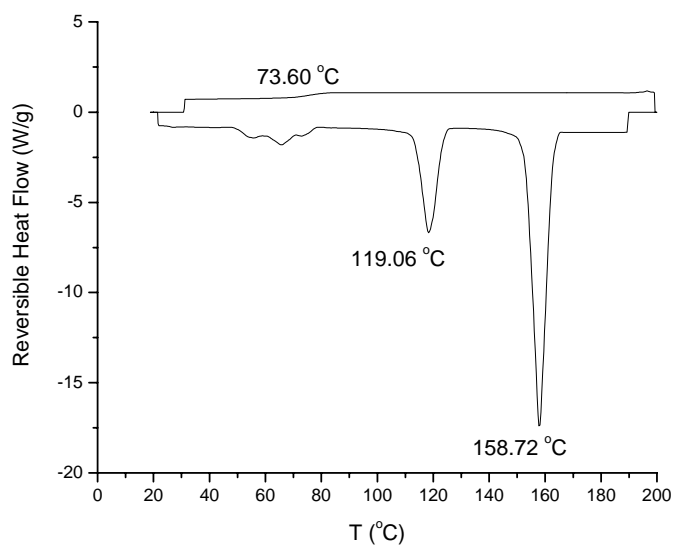
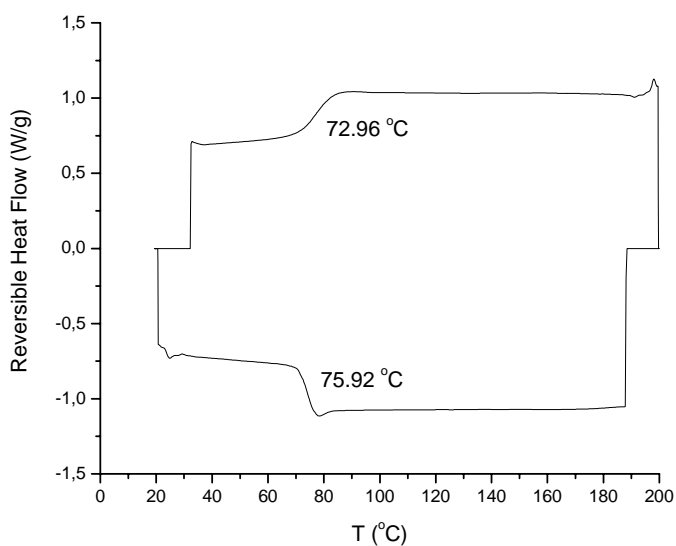
**a****b**

Figure S1. Representative thermograms obtained by modulated differential scanning calorimetry (mDSC) of single crystals of compound **2a** crystallized from CHCl_3 . a) First heating/cooling cycle. b) Second heating/cooling cycle. Glass transition temperatures and melting points are indicated in

each case. For the sake of simplicity, only the reversible heat flow signal is shown. In the initial heating cycle (Figure S1a), small exotherms near 60 °C are presumably due to loss of included CHCl_3 , another (near 119 °C) appears to correspond to loss of included H_2O , and a third (near 159 °C) is also attributed to loss of guests. Further heating/cooling cycles show only the presence of a glassy phase, as shown in Figure S1b. The initial behavior of crystalline compound **2a** is abnormal because it is an inclusion compound of CHCl_3 and H_2O , as shown by X-ray crystallography, and it therefore undergoes transitions related to loss of the guests.

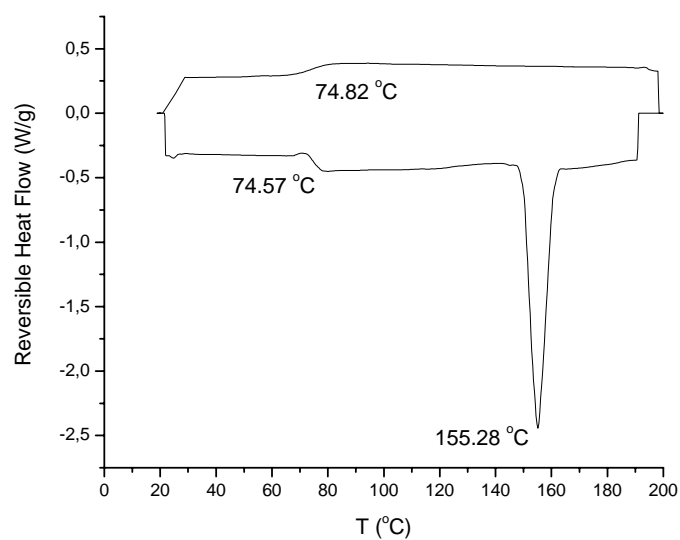
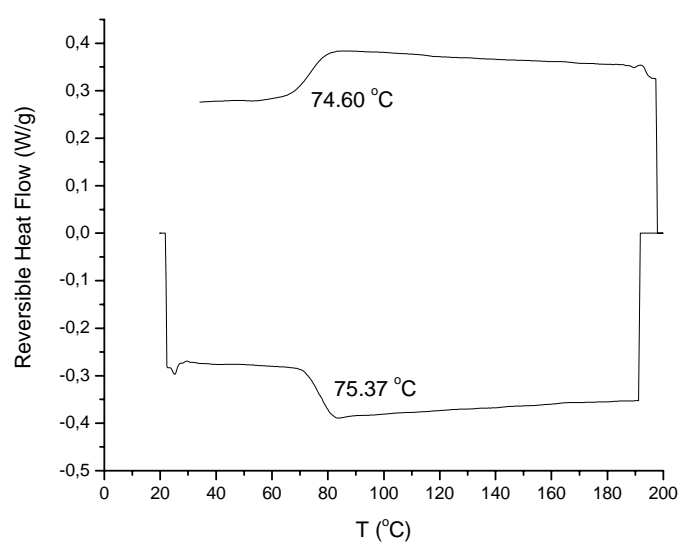
**a****b**

Figure S2. Representative thermograms obtained by modulated differential scanning calorimetry (mDSC) of amorphous **2a**. a) First heating/cooling cycle. b) Second heating/cooling cycle. Glass transition temperatures and melting points are indicated in each case. For the sake of simplicity,

only the reversible heat flow signal is shown. The solid sample used in the initial heating cycle was shown to be amorphous by X-ray powder diffraction and polarized optical microscopy. The exotherm at 155 °C in Figure S2a appears only in the initial cycle of heating and is presumably related to the loss of trapped guests.

CRYSTAL AND MOLECULAR STRUCTURE OF
C₂₂ H₂₆ Cl₃ N₅ O₃ COMPOUND (JW1027)

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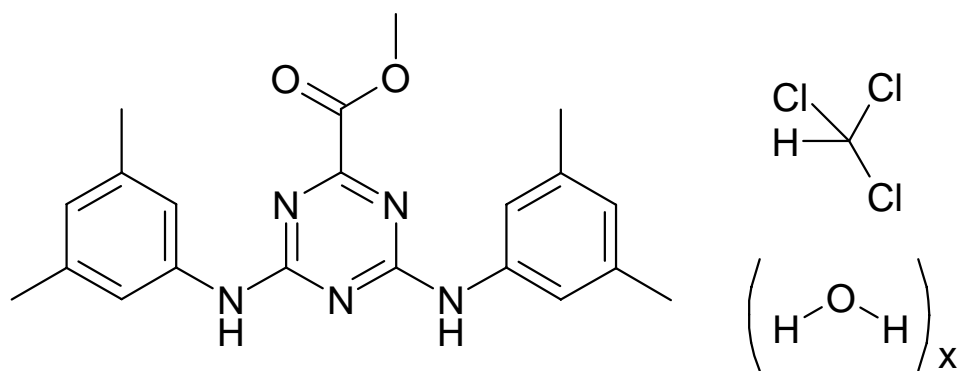


Table S1. Crystal data and structure refinement for C₂₂ H₂₄ Cl₃ N₅ O₂.

Identification code	JW1027
Empirical formula	C ₂₂ H ₂₄ Cl ₃ N ₅ O ₂
Formula weight	496.81
Temperature	225(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 24.7394(1) \text{ Å}$ $\alpha = 90^\circ$ $b = 13.3588(6) \text{ Å}$ $\beta = 114.790(2)^\circ$ $c = 19.2393(5) \text{ Å}$ $\gamma = 90^\circ$
Volume	5772.5(3) Å ³
Z	8
Density (calculated)	1.143 g/cm ³
Absorption coefficient	0.342 mm ⁻¹
F(000)	2064
Crystal size	0.50 x 0.40 x 0.25 mm
Theta range for data collection	2.61 to 27.55°
Index ranges	$-32 \leq h \leq 32, -17 \leq k \leq 17, -22 \leq \ell \leq 24$
Reflections collected	16419
Independent reflections	6596 [$R_{\text{int}} = 0.062$]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9930 and 0.7260
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6596 / 0 / 295
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0701, wR_2 = 0.1973$
R indices (all data)	$R_1 = 0.1247, wR_2 = 0.2238$

Extinction coefficient	0.0019(5)
Largest diff. peak and hole	0.444 and -0.454 e/Å ³

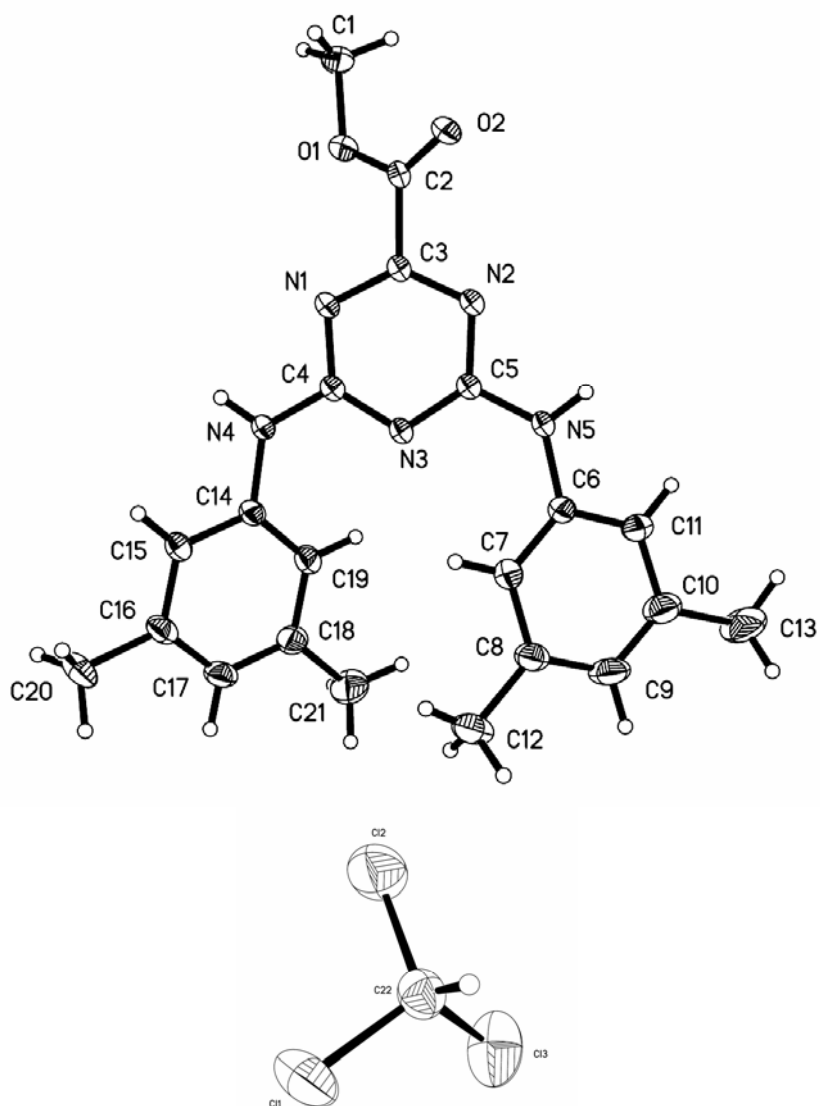


Figure S3 ORTEP view of the C₂₂ H₂₄ Cl₃ N₅ O₂ compound with the numbering scheme adopted. Ellipsoids are drawn at 30% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

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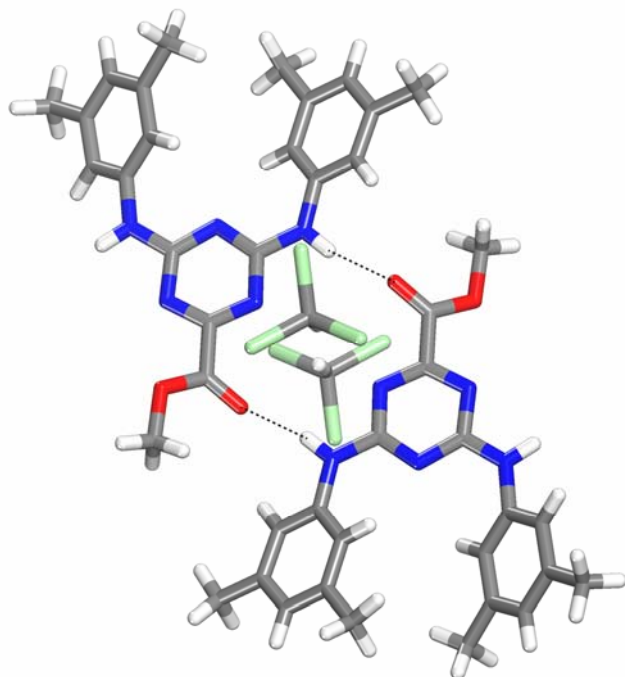


Figure S4. View of the crystal structure of methyl 4,6-bis(dimethylamino)-1,3,5-triazine-2-carboxylate (**2a**), showing two included molecules of CHCl_3 . The hydrogen atoms of the CHCl_3 molecules point into a small cavity between two hydrogen-bonded molecules of compound **2a**. No notable interactions are present between molecules of compound **2a** and CHCl_3 (the shortest N-H distance between the triazine rings and the hydrogen atoms of CHCl_3 is 2.937 Å). Hydrogen bonds are represented as dotted lines. Carbon atoms are shown in gray, hydrogen atoms in white, chlorine atoms in light green, nitrogen atoms in blue, and oxygen atoms in red.

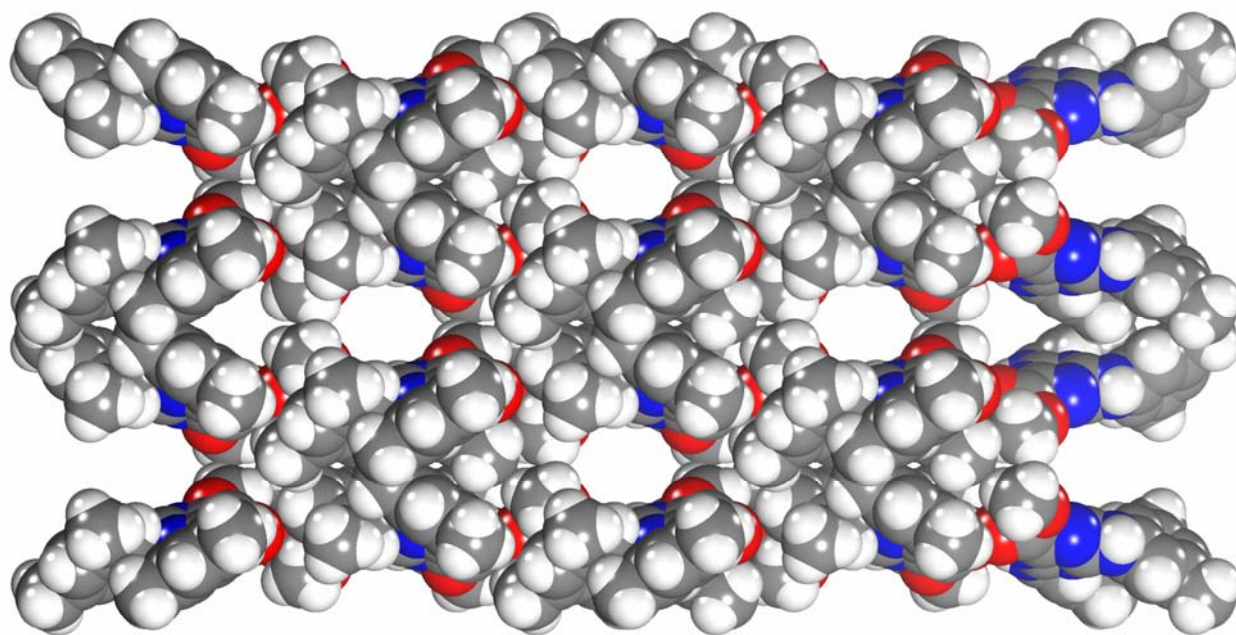
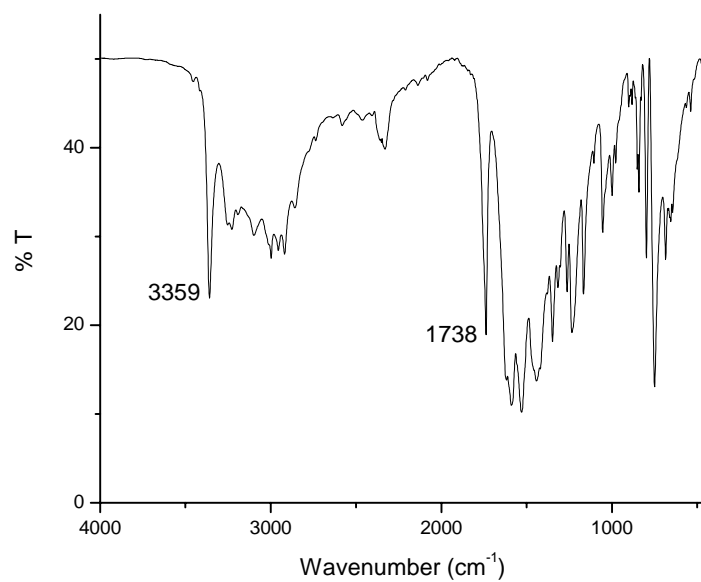
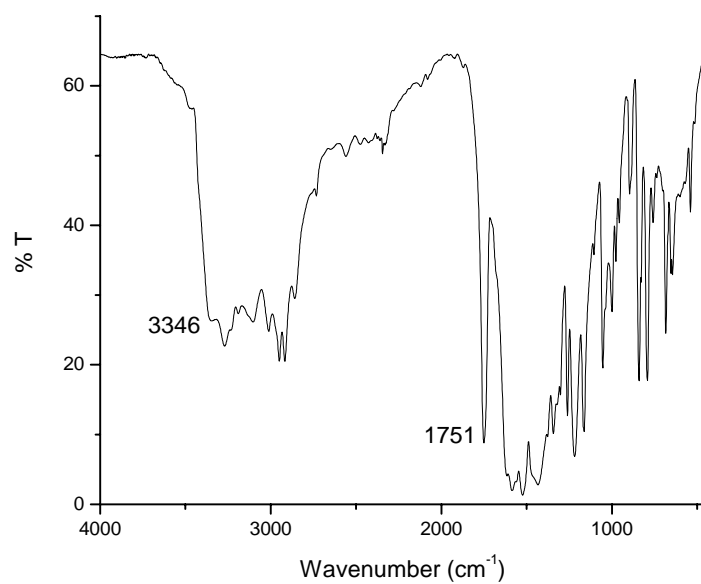


Figure S5. View along the c axis of a $2 \times 4 \times 1$ array of unit cells in the crystal structure of compound **2a**. Guest molecules have been omitted for clarity, revealing the presence of small channels along the c axis occupied by disordered water molecules. Carbon atoms are shown in gray, hydrogen atoms in white, nitrogen atoms in blue, and oxygen atoms in red.

**a****b**

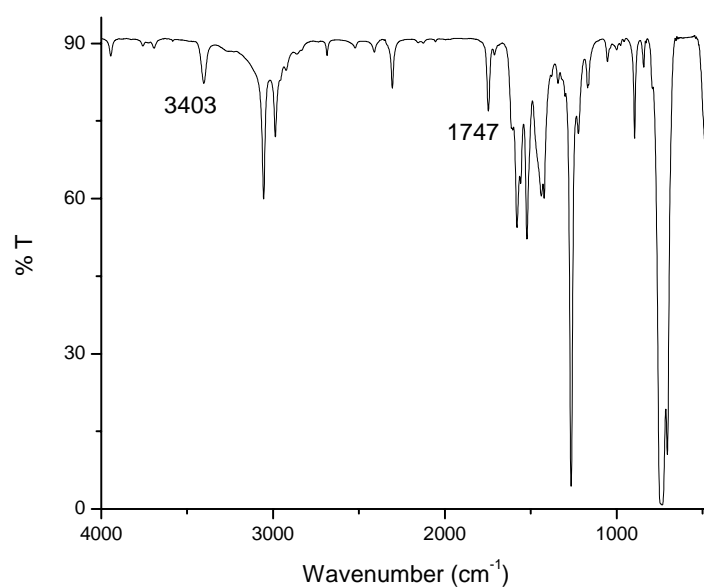
**c**

Figure S6. FT-IR spectra of compound **2a** in a) the crystalline state, b) the amorphous state, and c) in solution in CH_2Cl_2 . Wavenumbers are indicated for peaks corresponding to N-H and C=O stretching.