Electronic Supplementary Material (ESI) for CrystEngComm


# Supporting Information

## Engineering Homologous Molecular Organization in 2D and 3D.

## Cocrystallization of Aminoazines and Alkanecarboxylic Acids

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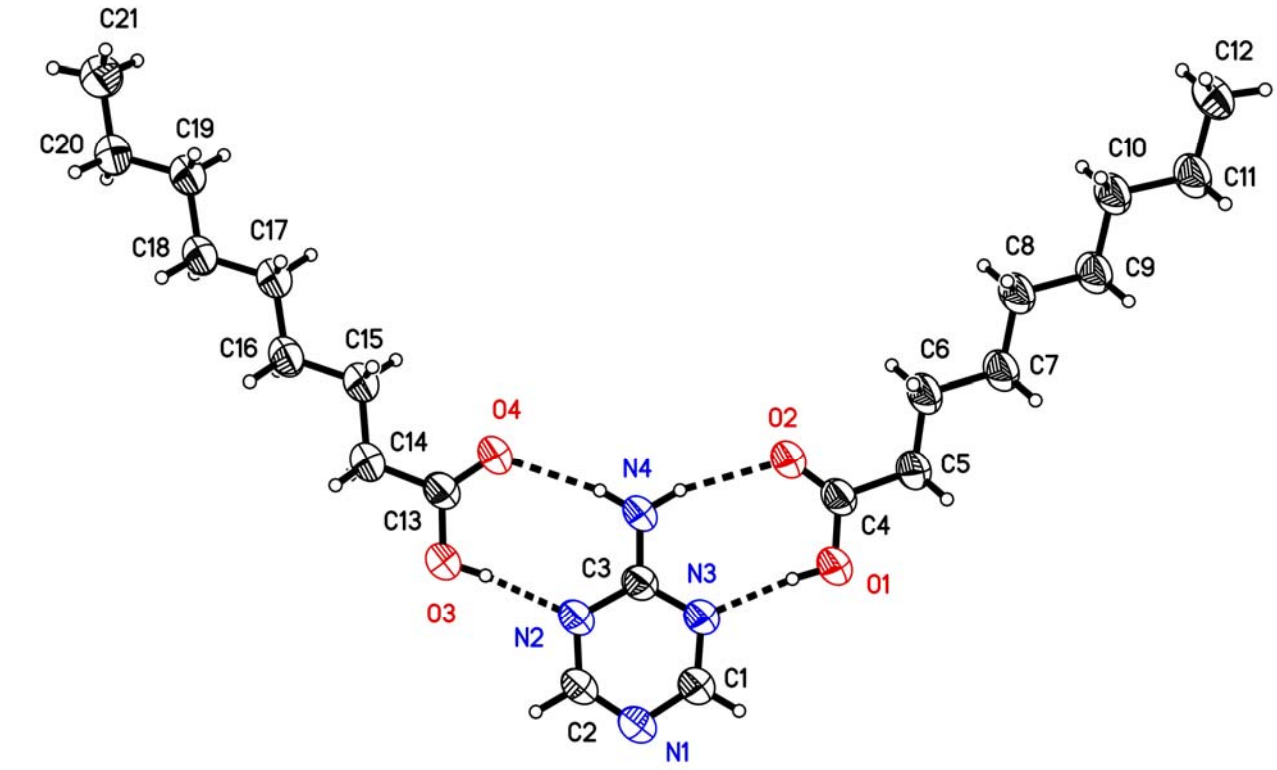


**Figure S1.** Thermal atomic displacement ellipsoid plot of the structure of the 1:2 cocrystals of 2-amino-1,3,5-triazine (**1**) with nonanoic acid. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

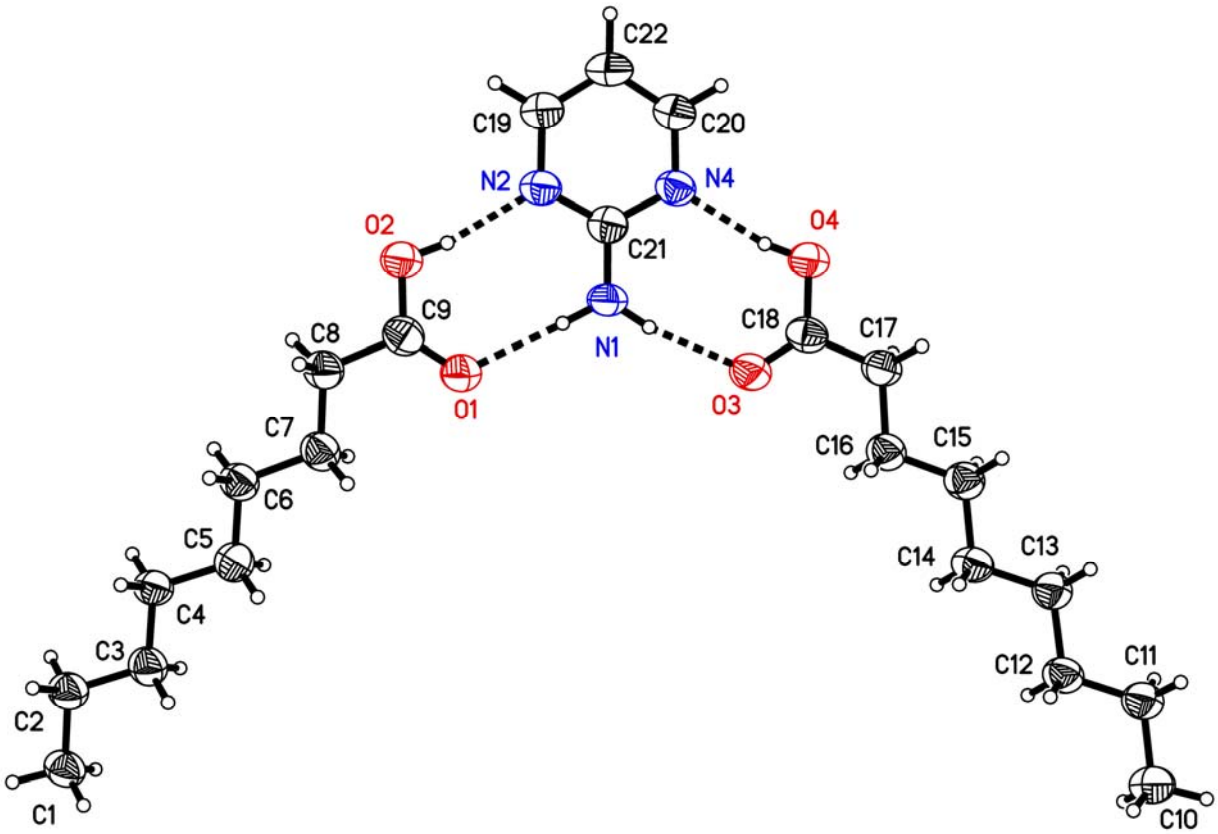


**Figure S2.** Thermal atomic displacement ellipsoid plot of the structure of the 1:2 cocrystals of 2-aminopyrimidine (**2**) with nonanoic acid. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

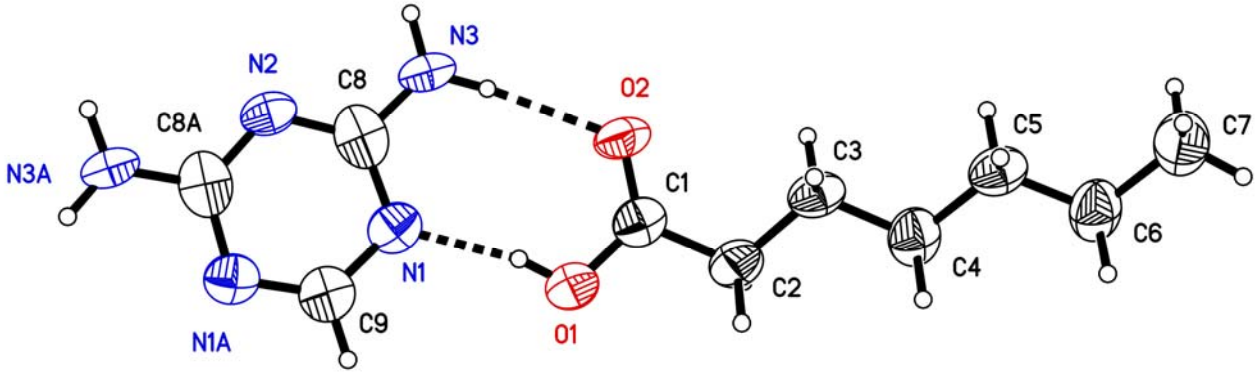


**Figure S3.** Thermal atomic displacement ellipsoid plot of the structure of the 1:2 cocrystals of 2,4-diamino-1,3,5-triazine (**3**) with heptanoic acid. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

**Homogeneity of Bulk Crystalline Samples**

In all structural studies, experimental powder X-ray diffraction patterns were recorded for each bulk crystalline sample and then compared with those calculated from single-crystal X-ray diffraction data. In all cases, these comparisons confirmed that the single-crystal specimens selected for structural analysis were representative of the bulk crystalline samples from which they were chosen. Experimental powder X-ray diffraction patterns were recorded using one of the following two instruments:

1) Bruker D8 Discover diffractometer with GADDS HTS, using graphite monochromatized Cu Kα radiation generated at 40 kV and 40 mA, working in reflection mode. The 2D general area detector was positioned at a distance of 15 cm from the powder sample, which was placed on a glass plate. This allowed simultaneous collection of data over an angular domain up to 35° in 2θ. Measurements were carried out 293 K in coupled scan mode (θ-θ geometry). Four separate images (diffraction arcs) were collected (scanning time: 5 min/image), and intensity along each arc was integrated to create the 1D powder pattern of intensity versus 2θ, over the angular range $10° < 2\theta < 105°$.

2) Single-crystal Bruker Microstar diffractometer mounted with an FR591 rotating anode generator, Helios optics, and a 2D Pt135 CCD detector, working in transmission mode. A small amount of ground sample was mounted in a fiber loop, and the diffraction patterns were recorded at 150 K by phi-scan over five different detector positions, merged, and integrated to give the 1D powder diffraction pattern

Structural data from single-crystal analyses were used to calculate theoretical powder X-ray diffraction patterns with the aid of Mercury software.[1] The diffraction pattern of the 1:2 cocrystals of 2,4-diamino-1,3,5-triazine (**3**) with heptanoic acid was subject to strong preferred orientation affecting *(h00)* reflections, so the calculated pattern was modeled using a March-Dollase function[2] as implemented in the powder diffraction module of Materials Studio.[3] Peak fitting and the refinement of lattice parameters were carried out using TOPAS software,[4] and Pawley fitting was applied to the powder X-ray diffraction patterns.

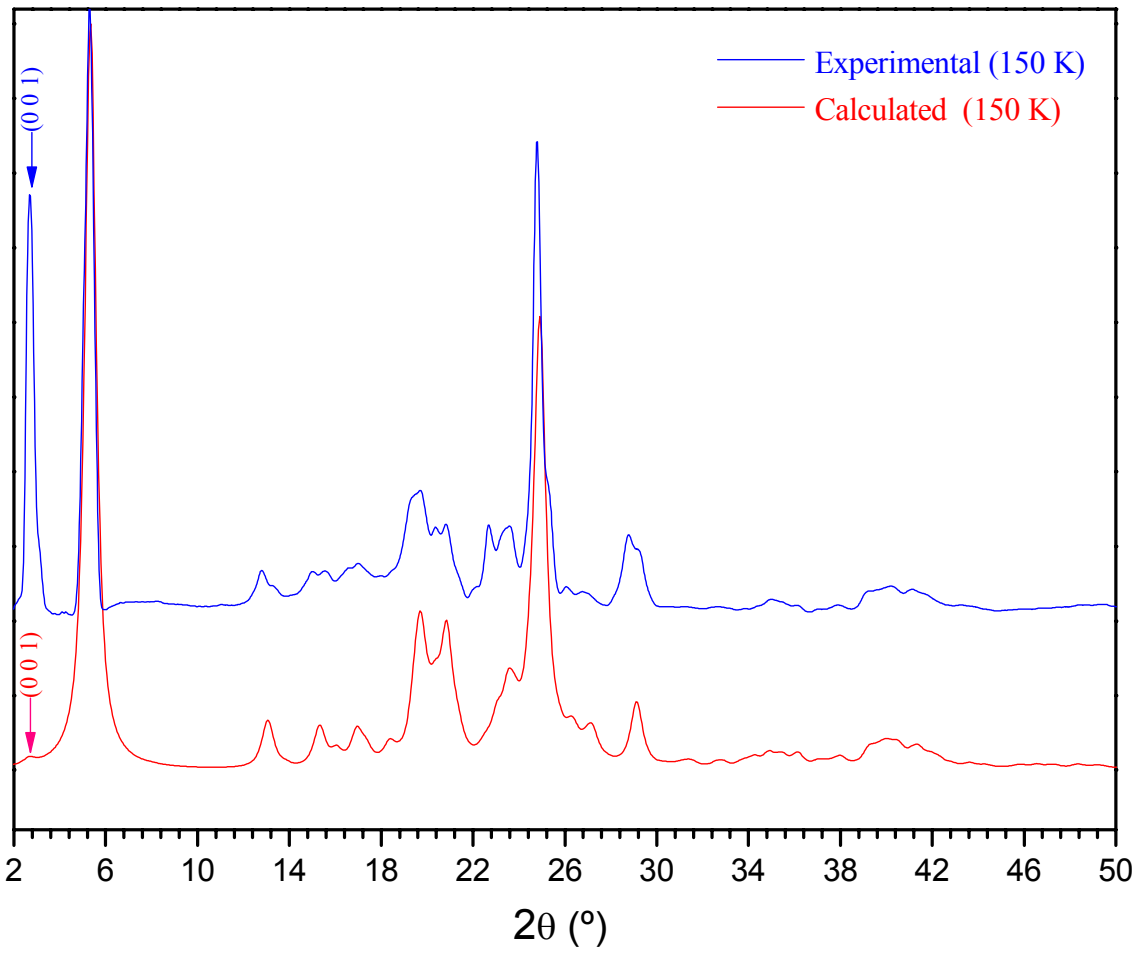


**Figure S4.** Comparison between experimental (collected using Bruker Microstar) and calculated powder X-ray diffraction patterns for the 1:2 cocrystals of 2-amino-1,3,5-triazine (**1**) with nonanoic acid. The two diffractograms are closely similar, confirming that the bulk crystalline sample consists of a single phase.

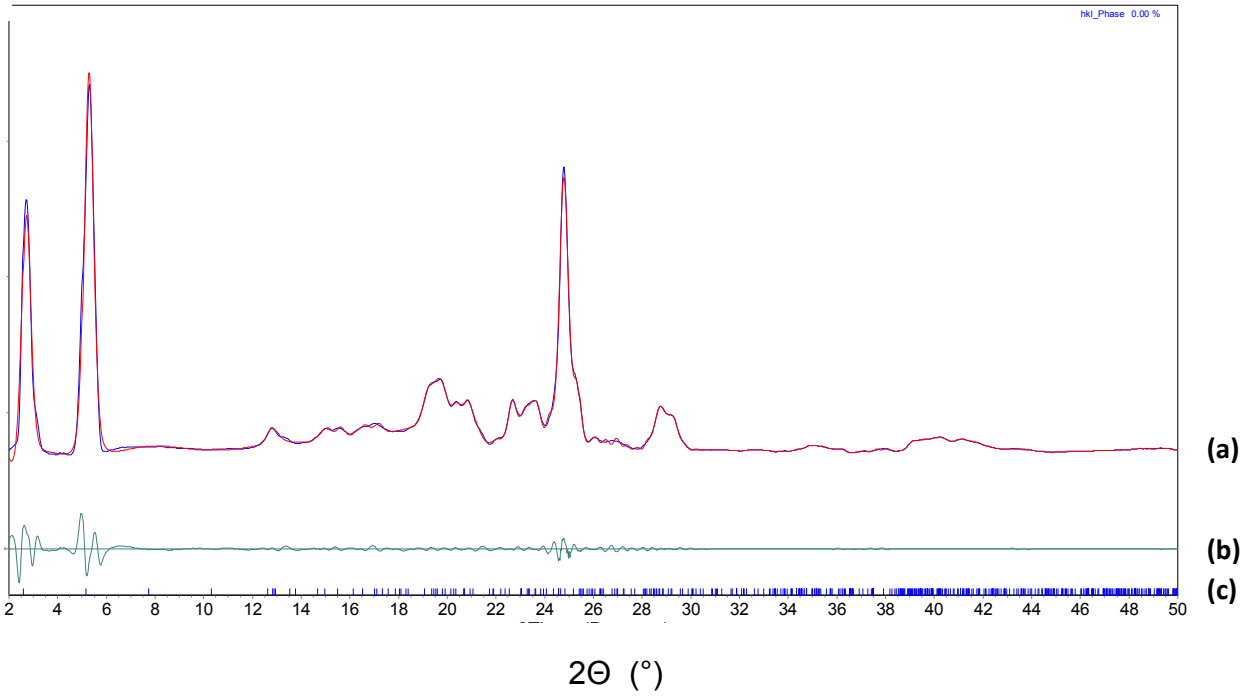


**Figure S5.** (a) Simulated powder X-ray diffraction pattern of the 1:2 cocrystals of 2-amino-1,3,5-triazine (**1**) with nonanoic acid (red curve), as determined by Pawley fitting of the experimental powder X-ray diffraction pattern (nearly superimposed blue curve). (b) Difference between experimental and calculated intensities. (c) Position of calculated reflections.

**Table S1.** Crystallographic Data for the 1:2 Cocrystals of 2-Amino-1,3,5-triazine (**1**) with Nonanoic Acid, as Determined by Pawley Fitting of Powder X-Ray Diffraction Data at 150 K.

| compound | **1** • 2 nonanoic acid |
|---|---|
| composition | $C_3H_4N_4 \cdot 2(C_9H_{18}O_2)$ |
| temperature (K) | 150 |
| crystal system | triclinic |
| space group | $P\bar{1}$ |
| *a* (Å) | 5.292(14) |
| *b* (Å) | 7.120(26) |
| *c* (Å) | 34.337(30) |
| *α* (º) | 90.86(25) |
| *β* (º) | 92.47(25) |
| *γ* (º) | 100.18(65) |
| *V* (Å$^3$) | 1271.8(65) |
| Z | 2 |

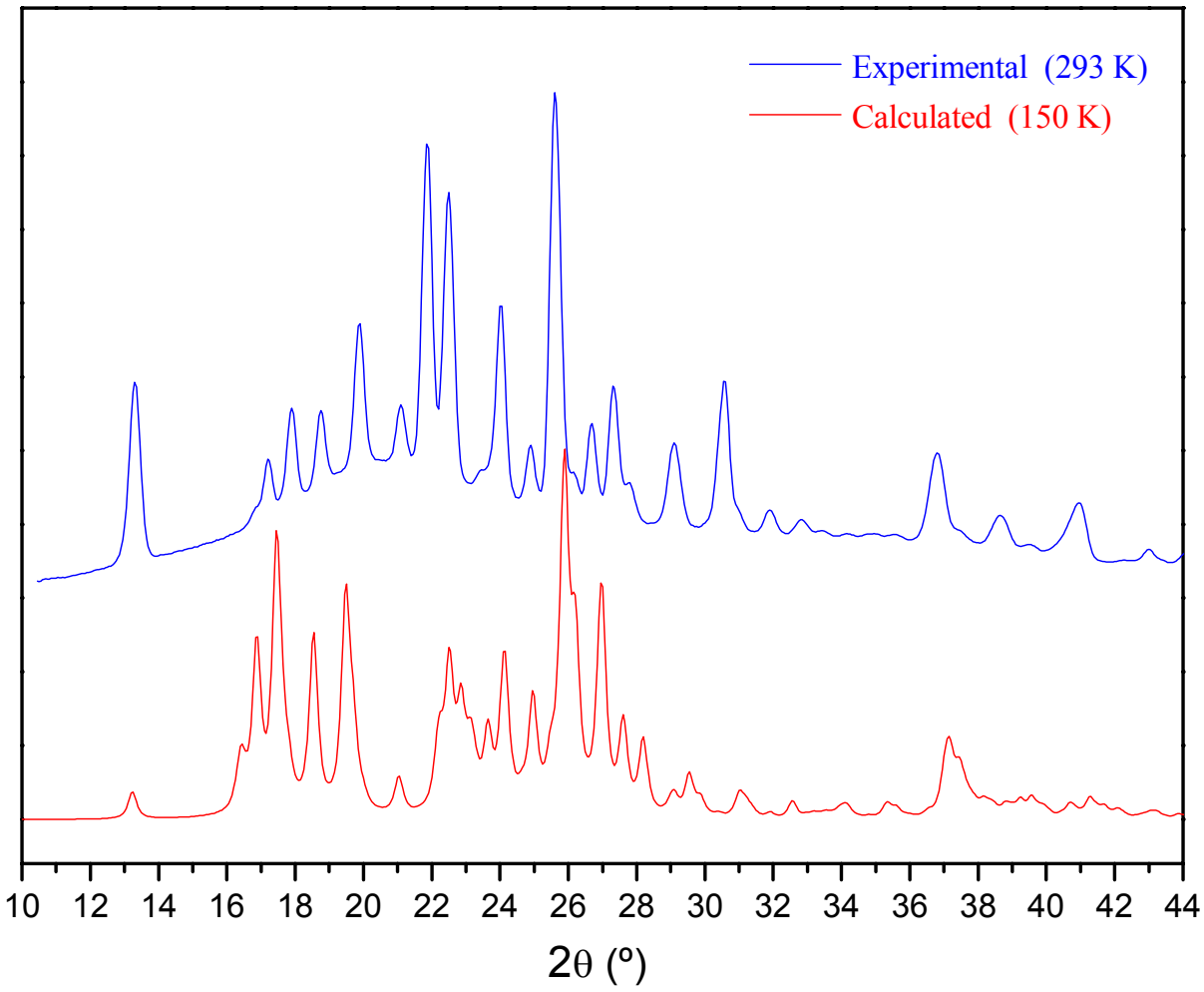


**Figure S6.** Comparison between experimental (collected using D8 Discover) and calculated powder X-ray diffraction patterns for the 1:2 cocrystals of 2-aminopyrimidine (**2**) with nonanoic acid. The *x*-axis of the experimental pattern was shifted to minimize the slight angular shift due to the effect of temperature. The two diffractograms are closely similar, confirming that the bulk crystalline sample consists of a single phase.

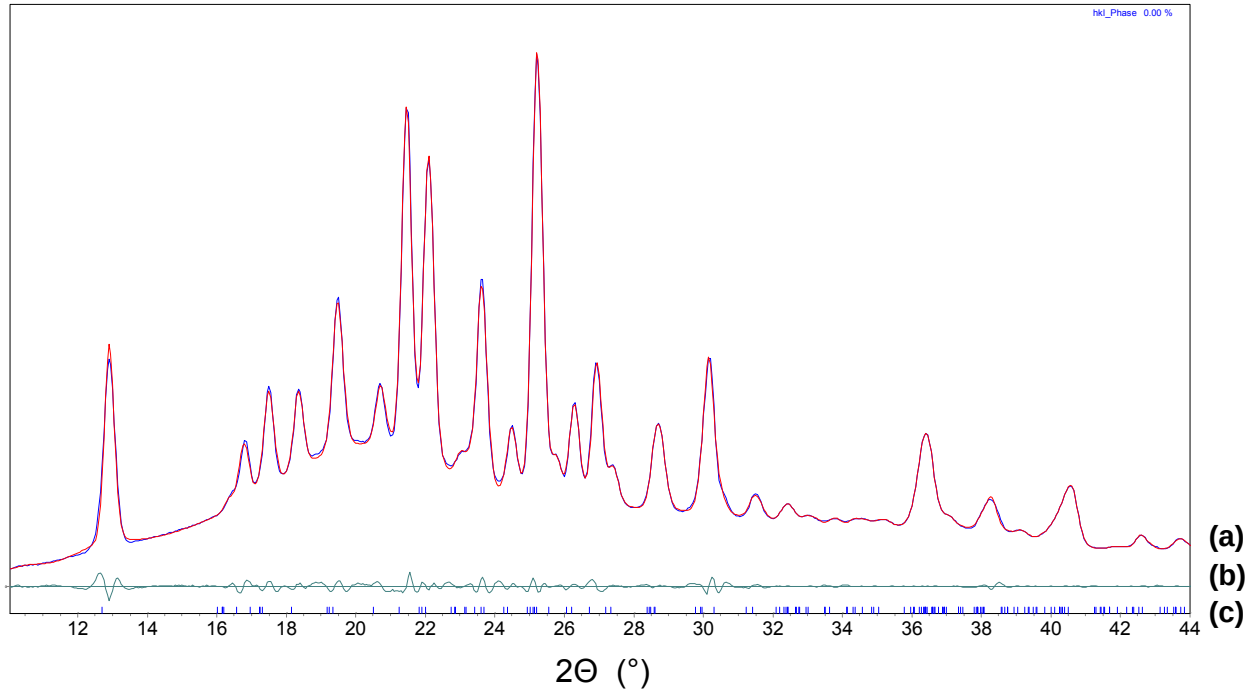


**Figure S7.** (a) Simulated powder X-ray diffraction pattern of the 1:2 cocrystals of 2-aminopyrimidine (**2**) with nonanoic acid (red curve) as determined by Pawley fitting of the experimental powder X-ray diffraction pattern (nearly superimposed blue curve). (b) Difference between experimental and calculated intensities. (c) Position of calculated reflections.

**Table S2.** Crystallographic Data for the 1:2 Cocrystals of 2-Aminopyrimidine (**2**) with Nonanoic Acid as Determined by Pawley Fitting of Powder X-Ray Diffraction Data at 293 K.

| compound | **2** • 2 nonanoic acid |
|---|---|
| composition | $C_4H_5N_3 \cdot 2(C_9H_{18}O_2)$ |
| temperature (K) | 293 |
| crystal system | monoclinic |
| space group | *P*c |
| *a* (Å) | 5.5201(43) |
| *b* (Å) | 5.5275(10) |
| *c* (Å) | 42.1094(77) |
| $\alpha$ (º) | 90 |
| $\beta$ (º) | 97.059(50) |
| $\gamma$ (º) | 90 |
| $V$ (Å$^3$) | 1275.1(10) |
| $Z$ | 2 |

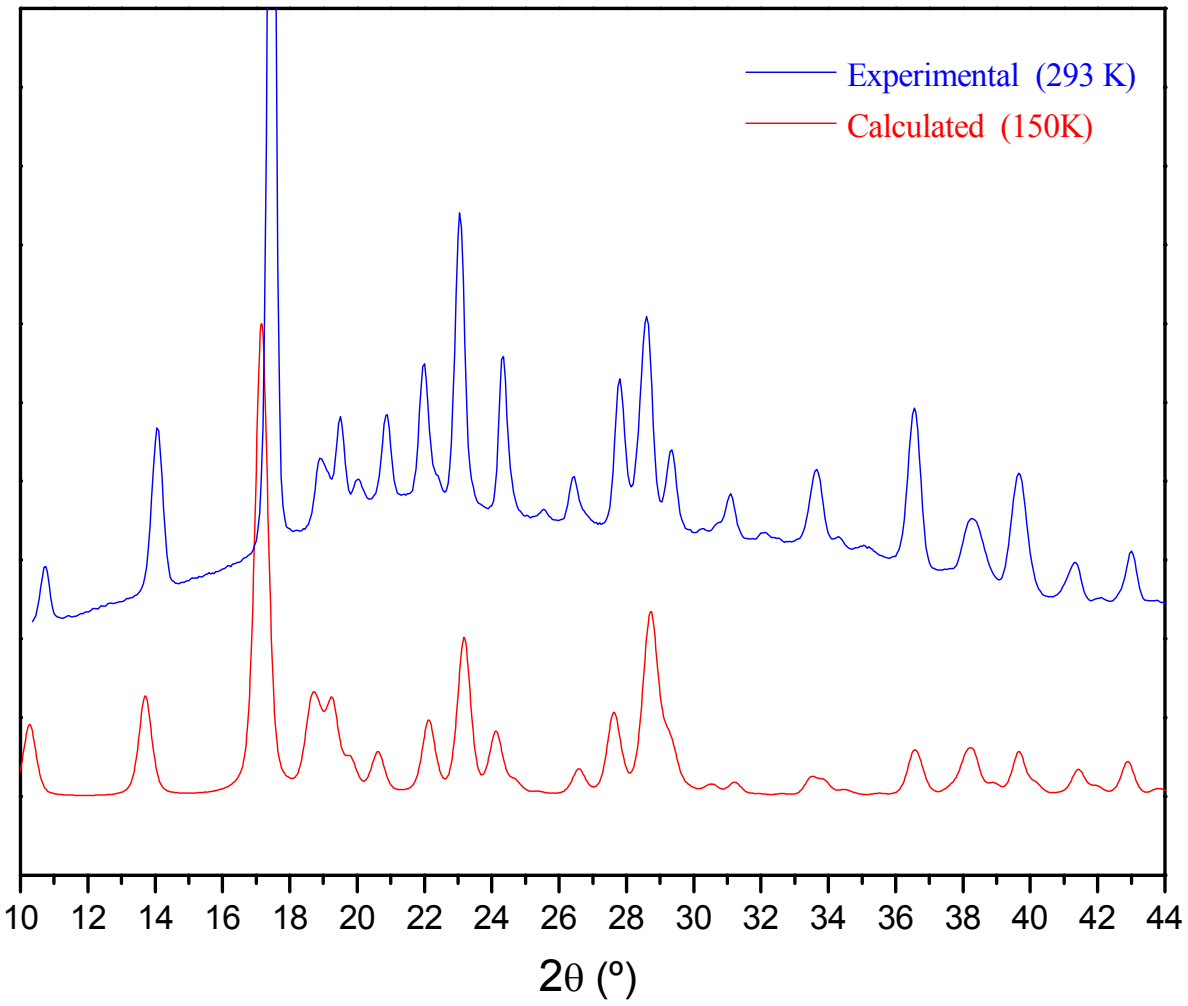


**Figure S8.** Comparison between experimental (collected using D8 Discover) and calculated powder X-ray diffraction patterns for the 1:2 cocrystals of 2,4-diamino-1,3,5-triazine (**3**) with heptanoic acid. The *x*-axis of the experimental pattern was shifted to minimize the slight angular shift due to the effect of temperature. The two diffractograms are closely similar, confirming that the bulk crystalline sample consists of a single phase.

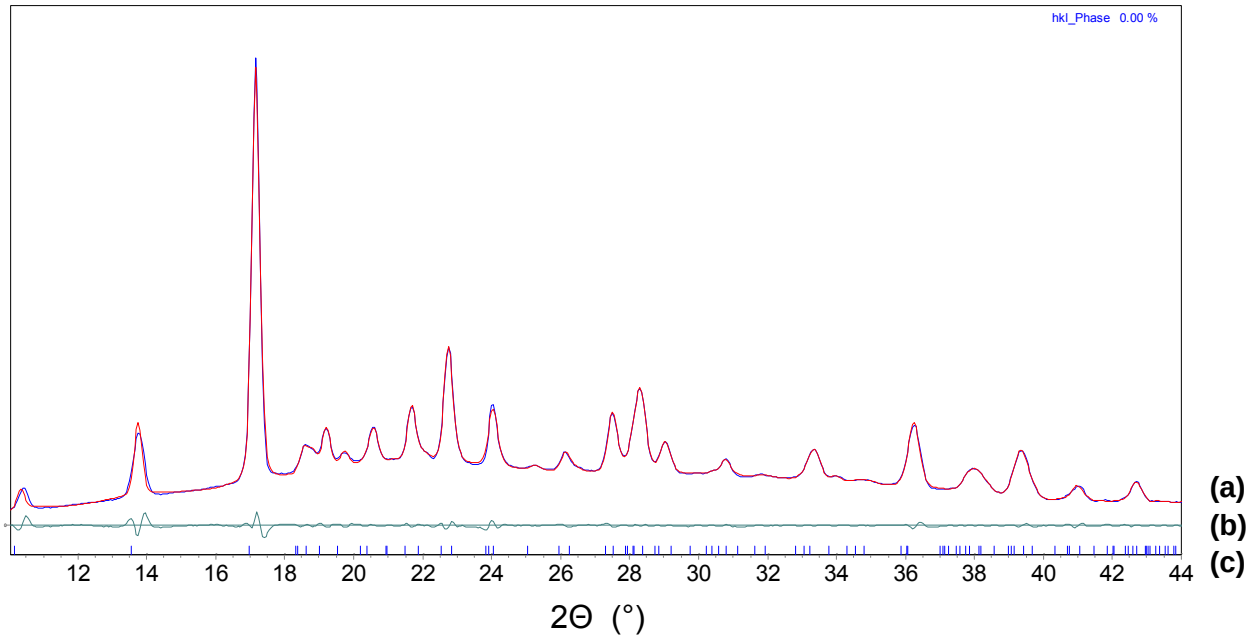


**Figure S9.** (a) Simulated powder X-ray diffraction pattern of the 1:2 cocrystals of 2,4-diamino-1,3,5-triazine (**3**) with heptanoic acid (red curve) as determined by Pawley fitting of the experimental powder X-ray diffraction pattern (nearly superimposed blue curve). (b) Difference between experimental and calculated intensities. (c) Position of calculated reflections.

**Table S3.** Crystallographic Data for the 1:2 Cocrystals of 2,4-Diamino-1,3,5-triazine (**3**) with Heptanoic acid as Determined by Pawley Fitting of Powder X-Ray Diffraction Data at 293 K.

| Compound | **3** • 2 heptanoic acid |
|---|---|
| composition | $C_3H_5N_5 \cdot 2(C_7H_{14}O_2)$ |
| temperature (K) | 293 |
| crystal system | orthorhombic |
| space group | $Pmn2_1$ |
| $a$ (Å) | 52.233(17) |
| $b$ (Å) | 4.8431(20) |
| $c$ (Å) | 4.2549(11) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 1076.37(62) |
| $Z$ | 2 |

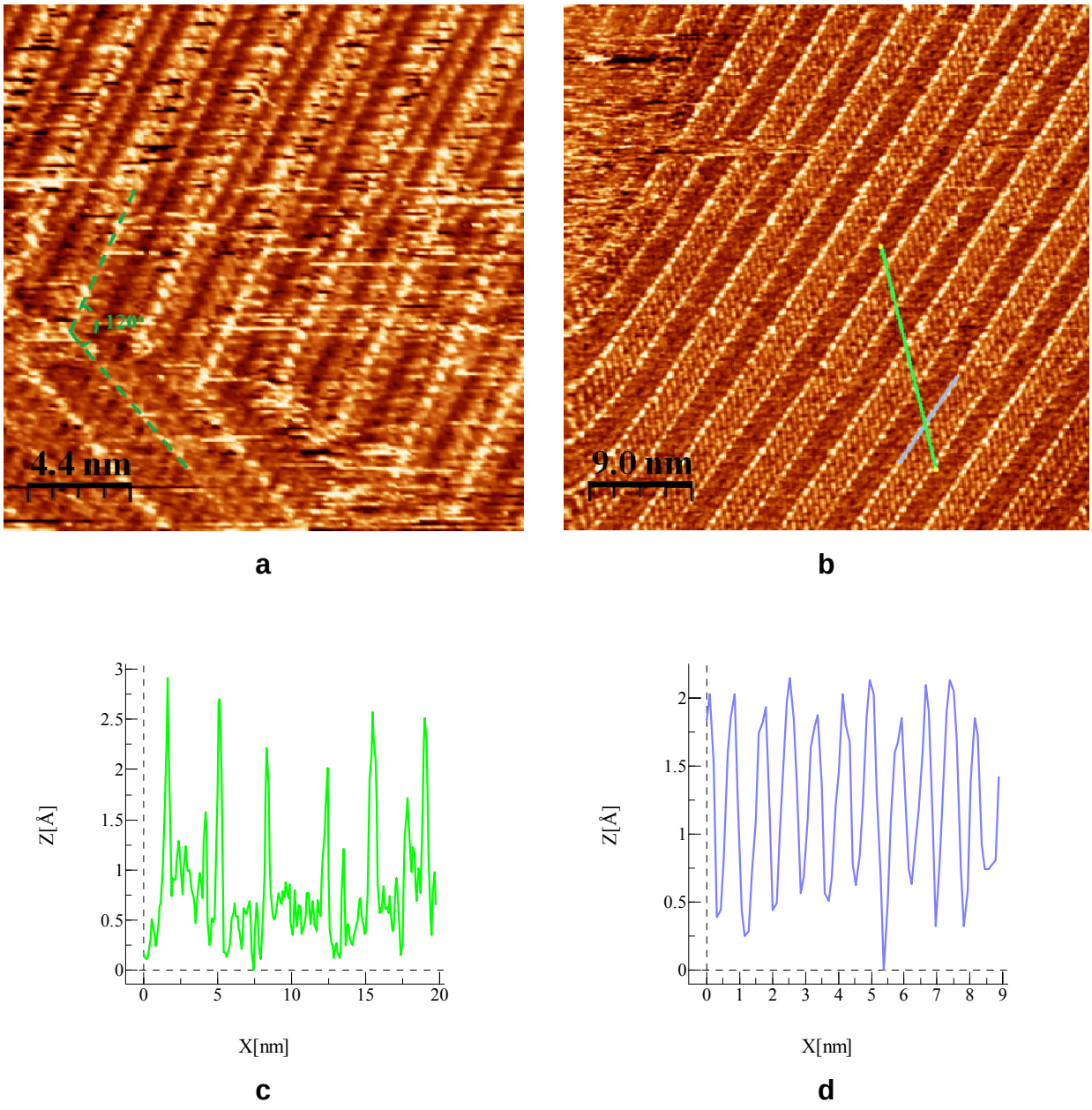


**Figure S10.** (a) Supplementary STM image of the 2D cocrystallization of 2-amino-1,3,5-triazine (**1**) and nonanoic acid on HOPG, showing the intersection of two domains (deposition from nonanoic acid, with $V_{bias}$ = -1.39 V and $I_{set}$ = 0.22 nA). (b) Large-scale STM image obtained under the same conditions. (c) Profile along the green axis shown in Figure S10b. (d) Profile along the blue axis shown in Figure S10b.

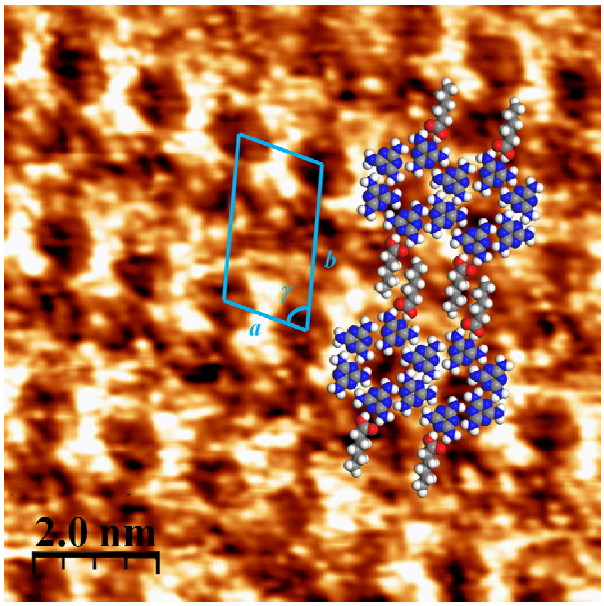


**Figure S11.** STM image of the 2D cocrystallization of melamine (**4**) and hexanoic acid on HOPG (deposition from hexanoic acid, with $V_{bias}$ = -1.40 V and $I_{set}$ = 0.25 nA). Superimposed on the image are a scale bar, the measured unit cell, and a model of the proposed assembly. The unit cell parameters are $a$ = 10.1 Å, $b$ = 22.8 Å, and $\gamma$ = 80°.

## References

1) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Cryst.* **2006**, *39*, 453-457.

2) Dollase, W. A. *J. Appl. Cryst.* **1986**, *19*, 267-272.

3) Accelrys, Inc., 10188 Telesis Court, Suite 100, San Diego, California 92121 USA.

4) Coelho, A. A. *TOPAS User Manual*, Version 3.1 ed.; Bruker-AXS GmbH: Karlsruhe, Germany, 2003.