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Supporting Information

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Structure Calculation of an Elastic Hydrogel from Sonication of Rigid Small Molecule Components

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Molecular structures (melamine, uric acid and water) were optimised using density functional theory (at the PW91/dnp level of theory) within the program Dmol3 [Delley 1990]. The program Crystal Predictor [Karamertzanis and Pantelides 2005] was then used to generate trial crystal structures in 20 of the most common space groups for 1:1 **M:U** ($P2_1/c$, $P\bar{1}$, $C2/c$, $P2_1$, $P2_12_12_1$, $Pna2_1$, $Pbca$, $Pnma$, Cc, $P1$, $P2_12_12$, $Pca2_1$, $Pbcn$, $C2$, Pc, $P2_1/m$, $C2/m$, $P2/c$, $Pccn$ and $R\bar{3}$) and 10 of the most common space groups for 1:1:2 **M:U:H$_2$O** ($P2_1/c$, $P\bar{1}$, $C2/c$, $P2_1$, $P2_12_12_1$, $Pna2_1$, $Pbca$, $Pnma$, Cc and $P1$); the search algorithm generates then lattice energy minimises structures with quasi-random values for lattice parameters, molecular positions and molecular orientations using a low-discrepancy sequence and the positions of all molecules in the asymmetric unit were varied independently. 100,000 trial crystal structures were generated for 1:1 **M:U** and 270,000 for 1:1:2 **M:U:H$_2$O**.

Energy mimisations during this initial search were performed using a simple model for intermolecular energies: an *exp-6* model for repulsion-dispersion (with C, N, O parameters from Cox and Williams [Cox, Hsu and Williams 1981; Williams and Cox 1984] and polar hydrogen parameters from Coombes and coworkers [Coombes 1996]) and atomic charges fitted to reproduce the Dmol calculated molecular electrostatic potential. The best structures from this initial search were then refined in a two-step process similar to that proposed for crystal structure prediction of flexible molecules [Day, Motherwell and Jones 2007]. First, all crystal structures within 20 kJ/mol of the global minimum were reminimised allowing flexibility of the amine groups on melamine, while keeping the rest of the molecules rigid. Flexibility of the amine groups was treated using bond angle and torsion parameters from the CVFF force field [Dauber-Osguthorpe 1988], while N-H bondlengths were restrained at the density functional theory calculated values. The final step of the refinement was to perform a rigid molecule lattice energy minimisation of the resulting structures (each with its optimised melamine geometry) with a high quality model for intermolecular

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interactions, using the same *exp-6* parameters as the original search, but with electrostatic interactions modelled by a distributed multipole analysis of a density functional theory calculated wavefunction for each molecule. The distributed multipoles (up to hexadecapole on each atom) were calculated within the program CADPAC on a PW91/6-31G(*d,p*) wavefunction. Only one set of multipoles needed to be calculated for each of uric acid and water, whose geometries were identical in all crystal strucutres. However, a separate calculation had to be performed for melamine for each crystal structure, because of the different molecular geometry in each crystal structure. The energy of each crystal structure was then taken as a sum of the *exp-6* + distributed multipoles lattice energy and the strain energy of the melamine molecule (the CADPAC calculated energy of the geometry in the crystal structure relative to its gas phase optimised geometry). The final sets of crystal structures were then clustered based on geometry to remove duplicates.

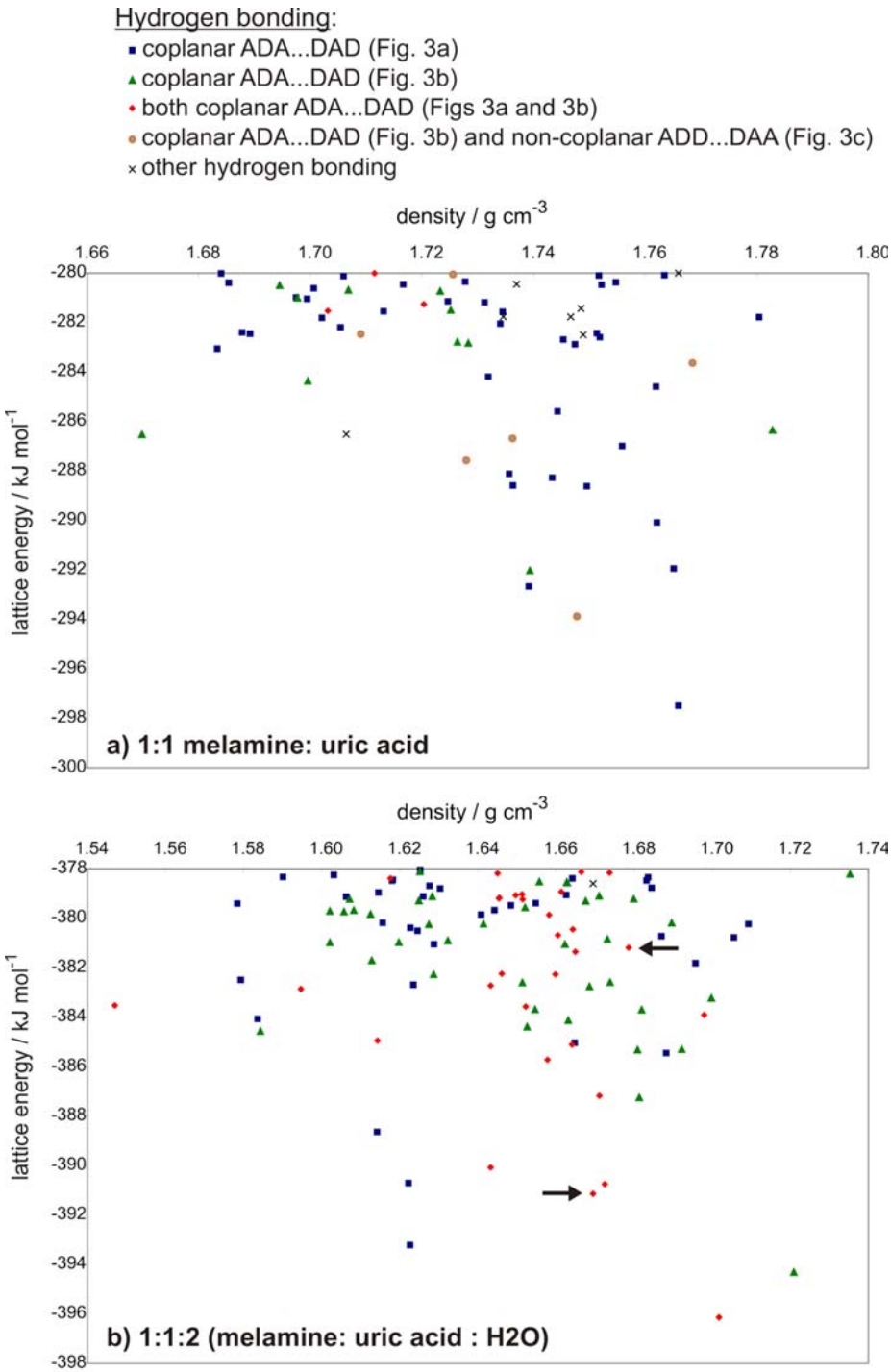

Figure S1. Lattice energy vs density plots of the low energy computer-generated crystal structures of a) 1:1 melamine : uric acid and b) 1:1:2 melamine : uric acid : H_2O. All structures have been classified by the presence of one or a combination of the hydrogen bond dimers in Fig. 3. The structures giving simulated PXRD patterns matching that from the dried gel are indicated with bold arrows.

Supporting References

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D. E. Williams and S. R. Cox, *Acta Cryst.* **B40**, 404 (1984).
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G. M. Day, W. D. S. Motherwell and W. Jones, *Physical Chemistry Chemical Physics* **9**, 1693 (2007).
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Computational.

The four **M**.**U** pair geometries were optimized with MP2 and the 6-31+G* basis set, using the *Gaussian*[1] program. The energies of the minimum energy structures were then determined from MP2/aug-cc-pVDZ single-point calculations, with the counterpoise correction method employed for basis-set superposition error (BSSE). Density functional theory (PBE1PBE hybrid functional) was also employed, and again geometry optimizations with the 6-31+G* basis and counterpoise corrected single-point energies with the aug-cc-pVDZ basis were performed. The geometries of the DFT optimized pairs and relative energy differences compare very favourably with the MP2 results. The same DFT method was therefore used to investigate the minimum energy structures of the $\mathbf{M}.\mathbf{U_3}$ and $\mathbf{M_3}.\mathbf{U}$ quartets.

Experimental Section

Preparation of the Gels. Weighed amounts of melamine and uric acid were combined and distilled water was added (15 mL) to give mixtures of 2 % (w/v). The suspensions were shook for 3 s and sonicated for 60 s. This was repeated 5 times. The mixtures were allowed to stand whereupon they gelled.

Rheological Characterisation. Rheological characterisation was performed using a controlled stress rheometer (TA Instruments AR2000) equipped with a double-gap concentric cylinder measuring system (cup dimensions: r_{inner} = 20.00 mm, r_{outer} = 22.36 mm; rotor dimensions: r_{inner} = 20.38 mm, r_{outer} = 21.96 mm; immersed height = 57.00 mm, gap distance = 3.00 mm) which was connected to a water bath for control of the sample temperature (±0.1 ºC). The gels were shook to form a liquid, drawn up into a syringe, and injected into the assembly gap. The sample was pre-sheared for 30 s at 10 rad/s and subsequently allowed to equilibrate for 10 min. G' and G" were obtained from oscillatory measurements at a frequency of 1 Hz. A stress sweep experiment was performed by increasing the amplitude from 0.03 to 125.00 Pa in 11 min. All measurements were performed at 20 ± 0.1 ºC.

Component Masses

Molar Ratio (M:U)	Melamine Mass / g	Uric Acid Mass / g
9:1	0.26	0.04

8:2	0.23	0.07
7:3	0.19	0.11
6:4	0.16	0.14
5:5	0.13	0.17
4:6	0.10	0.20
3:7	0.07	0.23
2:8	0.05	0.25
1:9	0.02	0.28

Rheological Properties of the Gels. The formation of hydrogels of uric acid and melamine is caused by their self-assembly into fibres to produce an entangled network that entraps the liquid. The strongest gel should result from the sample with the optimal ratio of the components and so to determine this and thus their probable ratio in the fibres of the gel, we subjected the samples to dynamic oscillatory measurements. The strengths of the gels were quantified in terms of a plateau elastic modulus, G^{∞}, and yield stress, σ^*, as a function of the molar ratio of both components. A typical run is shown in Figure S2. We calculated the plateau value, G^{∞} as the average value of the elastic modulus, G', before the gel began to yield and took σ^* as the first stress in which G'' > G'. Figure 2 shows the variation in G^{∞} as a function of the molar ratio and figure S3 shows the respective variation in σ^*. Both graphs show a maximum at a 1:1 molar ratio, therefore we conclude that the fibres are composed of melamine and uric acid in this ratio, in agreement with the x-ray powder diffraction experimental and simulated data.

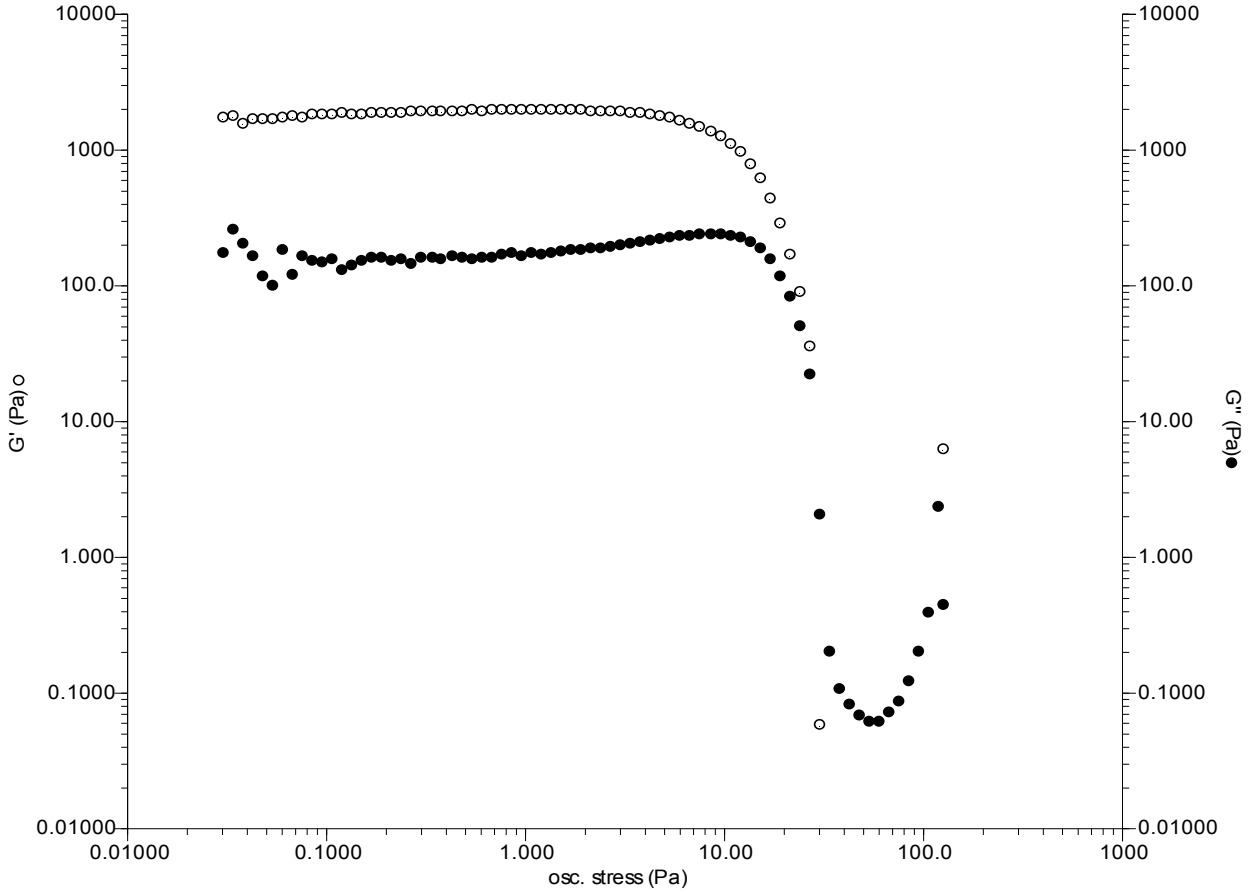


Figure S2: Variation of G' (●), and G'' (○) with Oscillatory Stress in a Melamine:Uric Acid mixture (1:1) at 2 % (w/v).

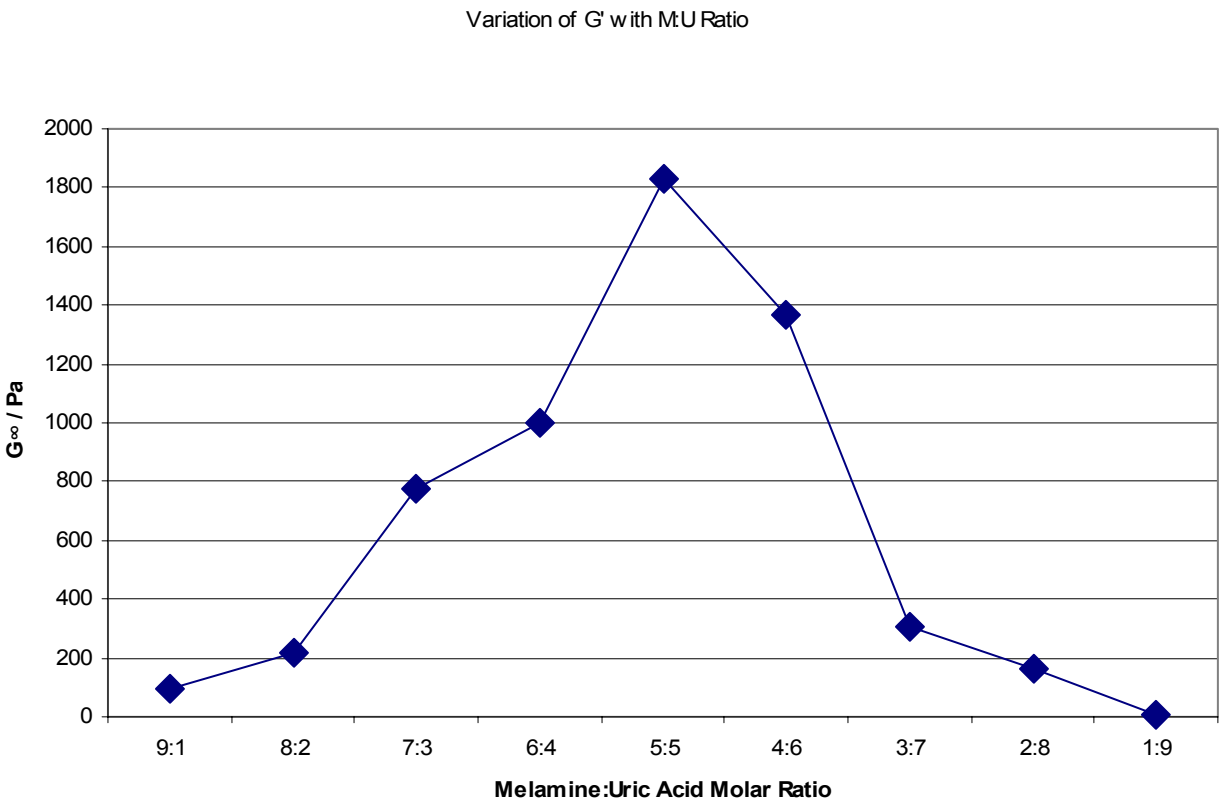


Figure S3: Variation of G^{∞} with Melamine:Uric Acid Molar Ratio

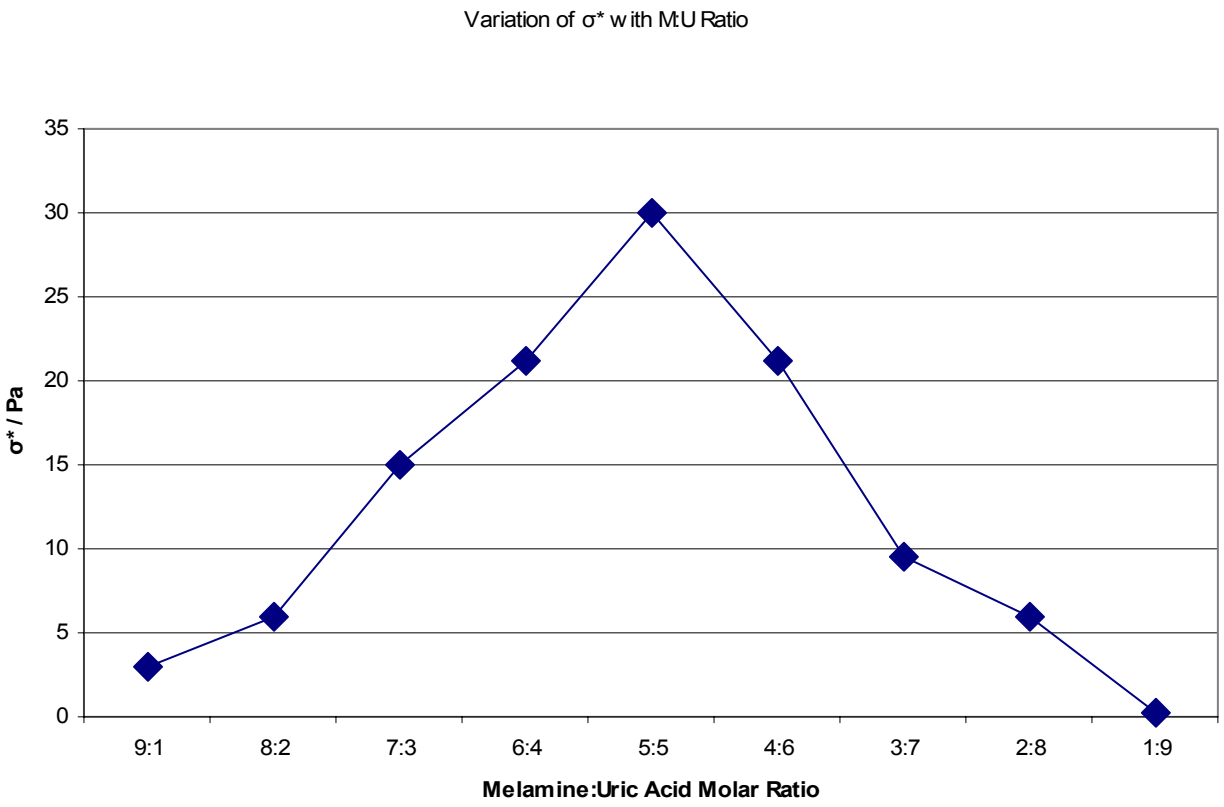


Figure S4: Variation of σ* with Melamine:Uric Acid Molar Ratio

Figure S5: PXRD pattern of a ground mixture of melamine and uric acid.

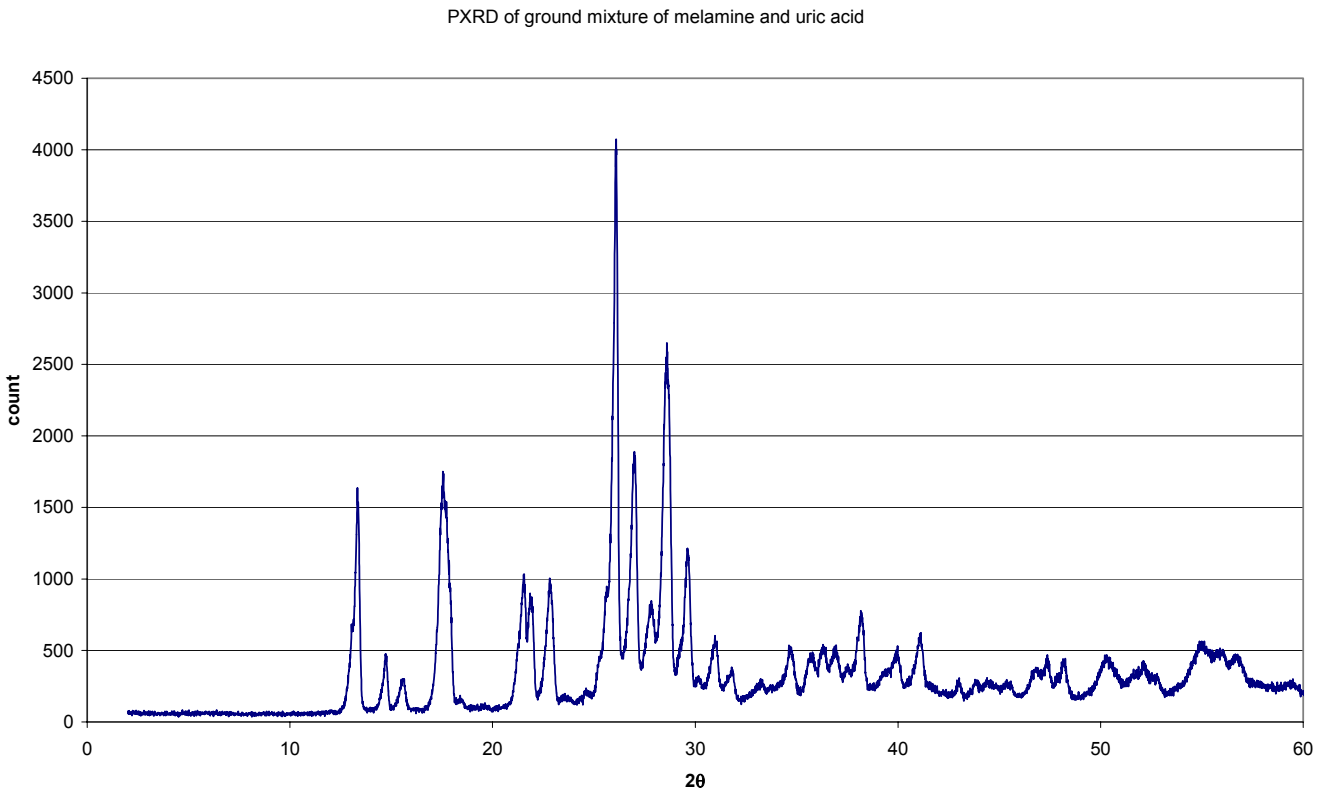
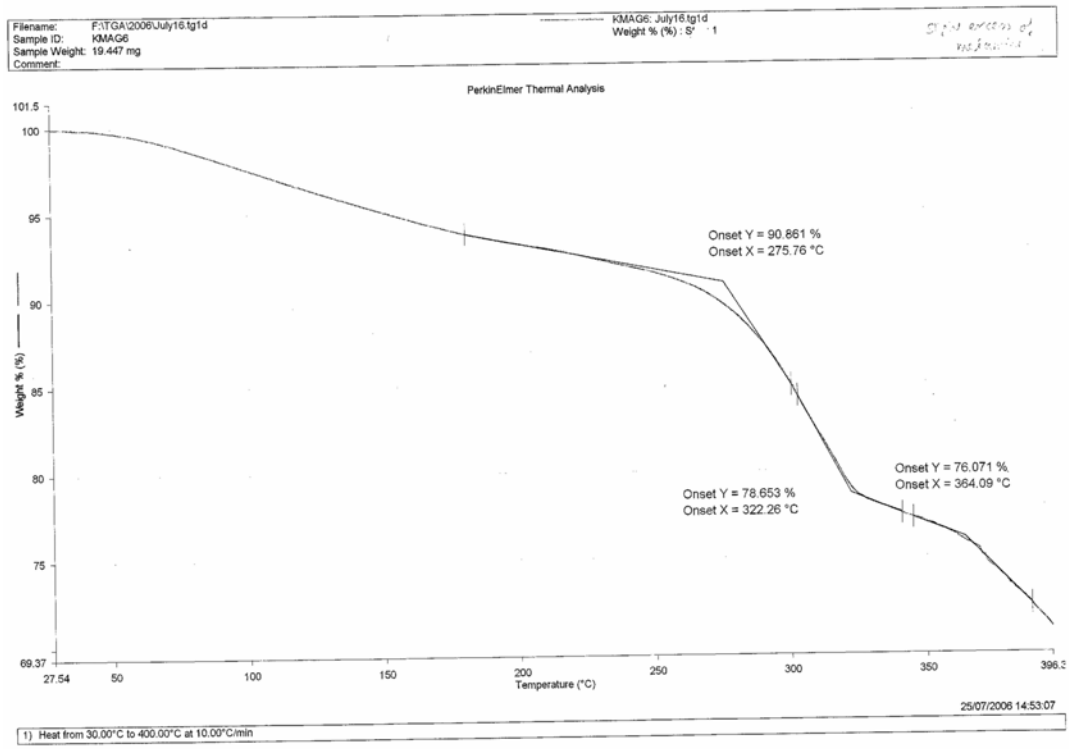
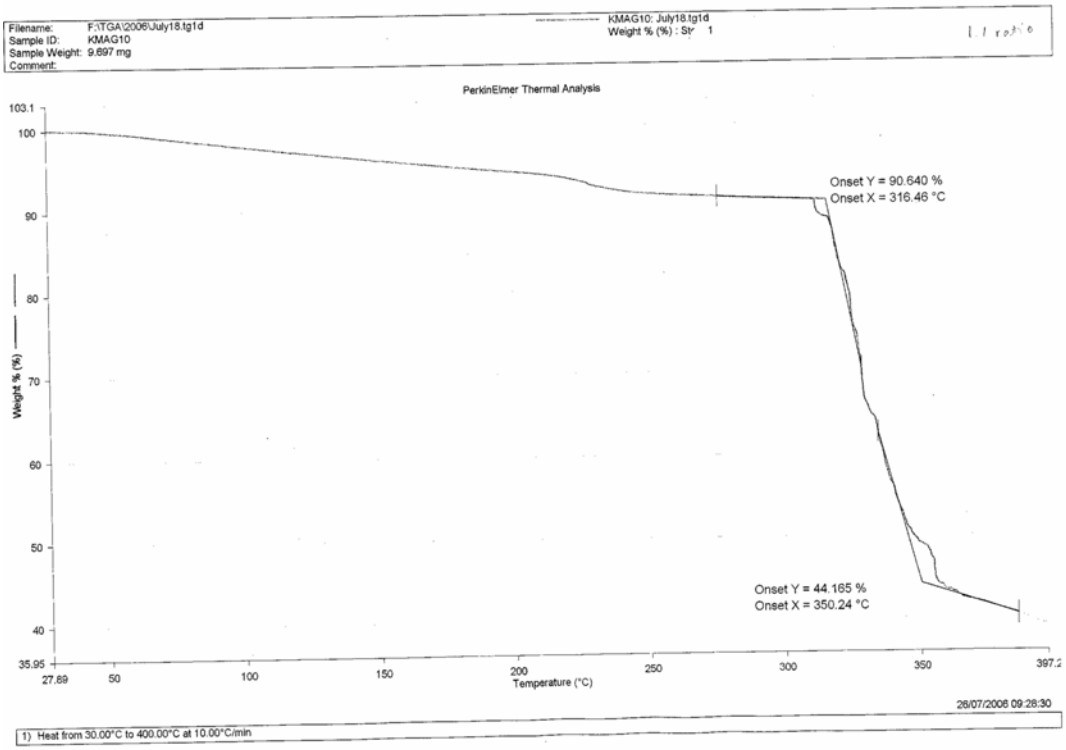


Figure S6: TGA Scans for xerogels

(a) Slight excess of melamine over uric acid



(b) 1 : 1 Melamine : uric acid



(c) Slight excess of uric acid over melamine

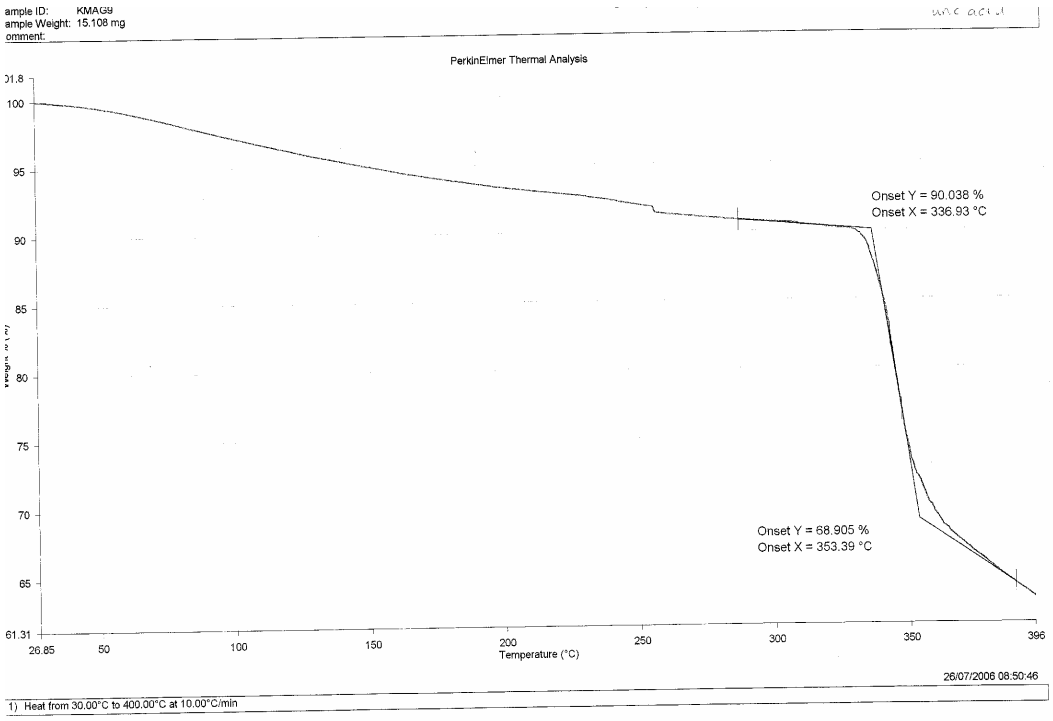
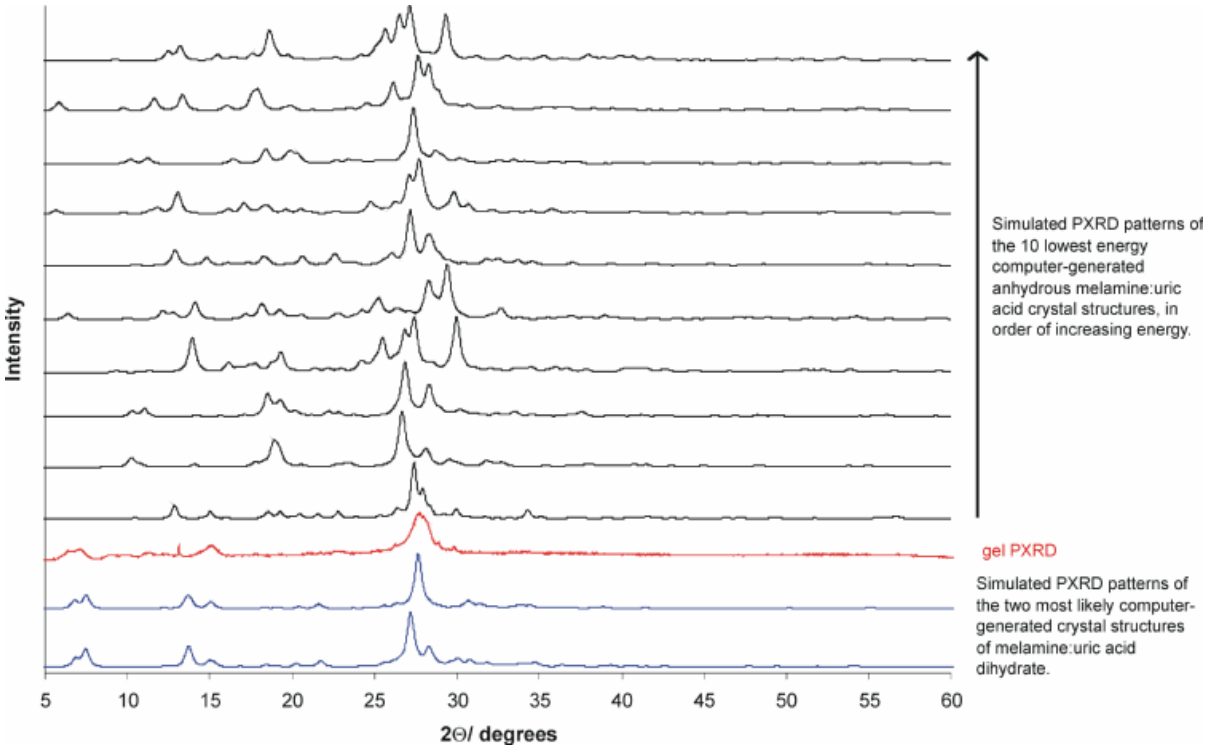


Figure S7: Simulated PXRD patterns for the 10 lowest energy anhydrous melamine: Uric acid 1:1 structures



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N2 N 0.640722 0.364173 0.387692
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H7 H 0.179140 0.327435 0.538315
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H8 H 1.453866 0.264779 0.135113
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