Boric Acid Cocrystals in Guar Gelation

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SUPPLEMENTARY INFORMATION

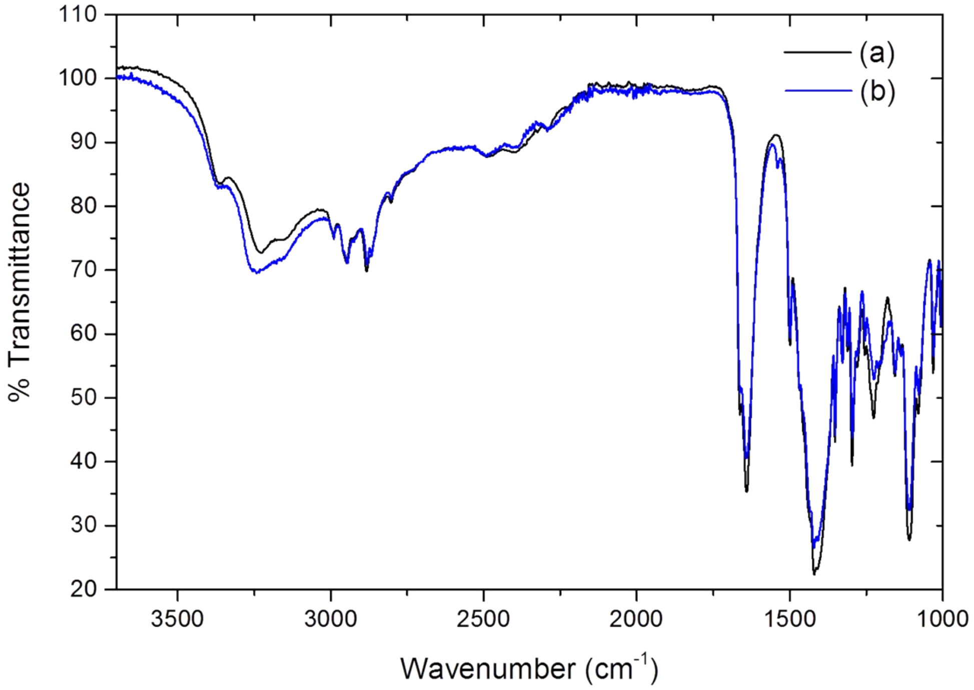

Figure S1: Solid-state IR spectra for (a) single crystals of **1**·2B$(OH)_3$ grown from ethanol and (b) mechanochemically prepared crystalline solid.

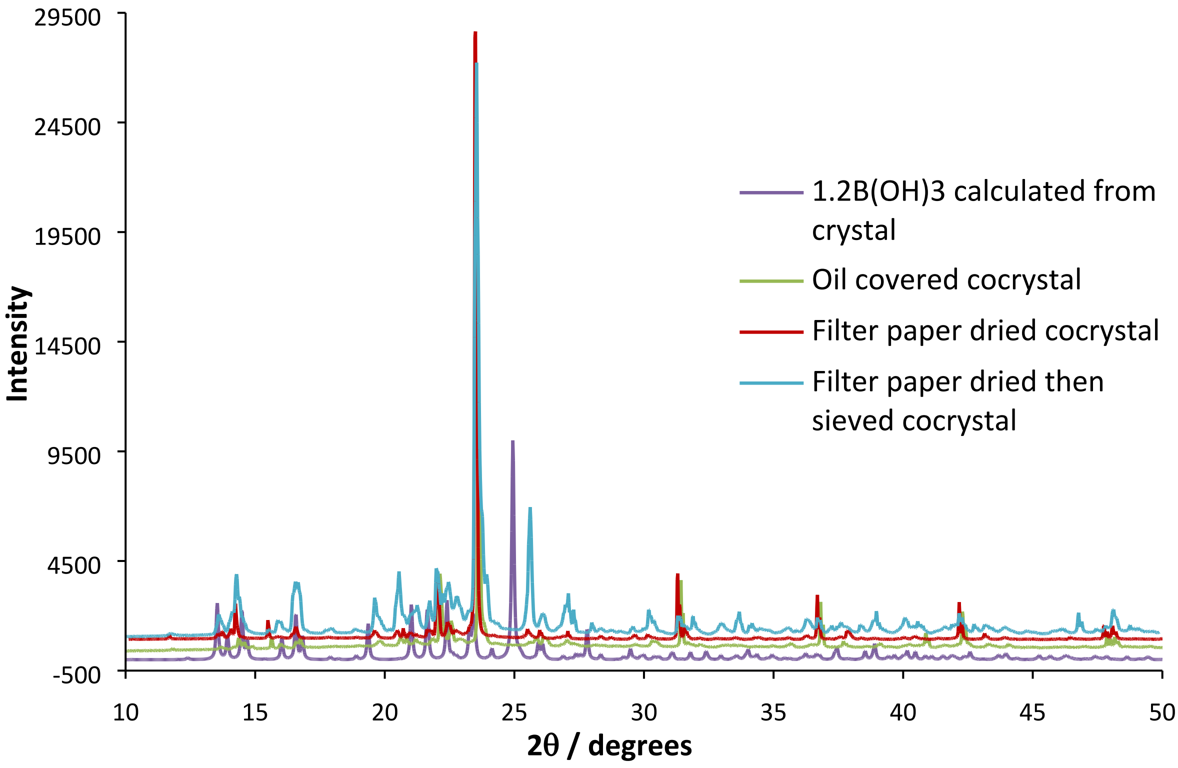

Figure S2. XRPD patterns for **1**·2B(OH)$_3$ under various conditions and the pattern calculated from the single crystal structure.

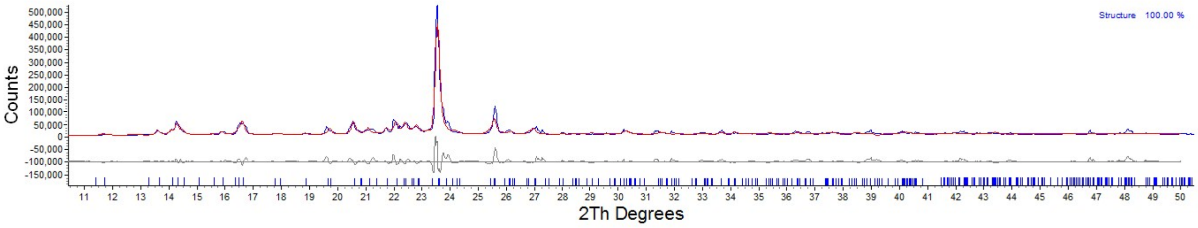

Figure S3. Room temperature Rietveld fit (red) incorporating preferred orientation for the XRPD pattern for **1**·2B(OH)$_3$ (blue – sample has been dried and sieved). The unit cell by XRPD *a* = 6.9800, *b* = 8.4318, *c* = 17.4944 Å, α = 77.958°, β = 80.603°, γ = 68.869° is consistent with the solid form at 120 K studied by single crystal X-ray crystallography and DSC indicates no phase change between 120 K and the melting of the sample at 60 °C.

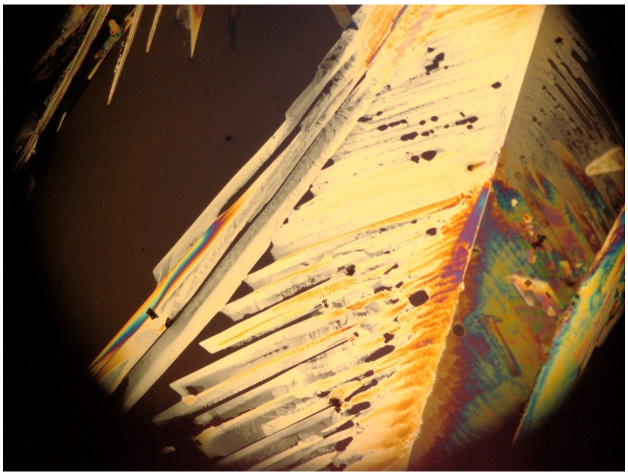

Figure S4. Polarised optical microscope image of crystals of **1**·2B$(OH)_3$ showing the blade-like morphology.

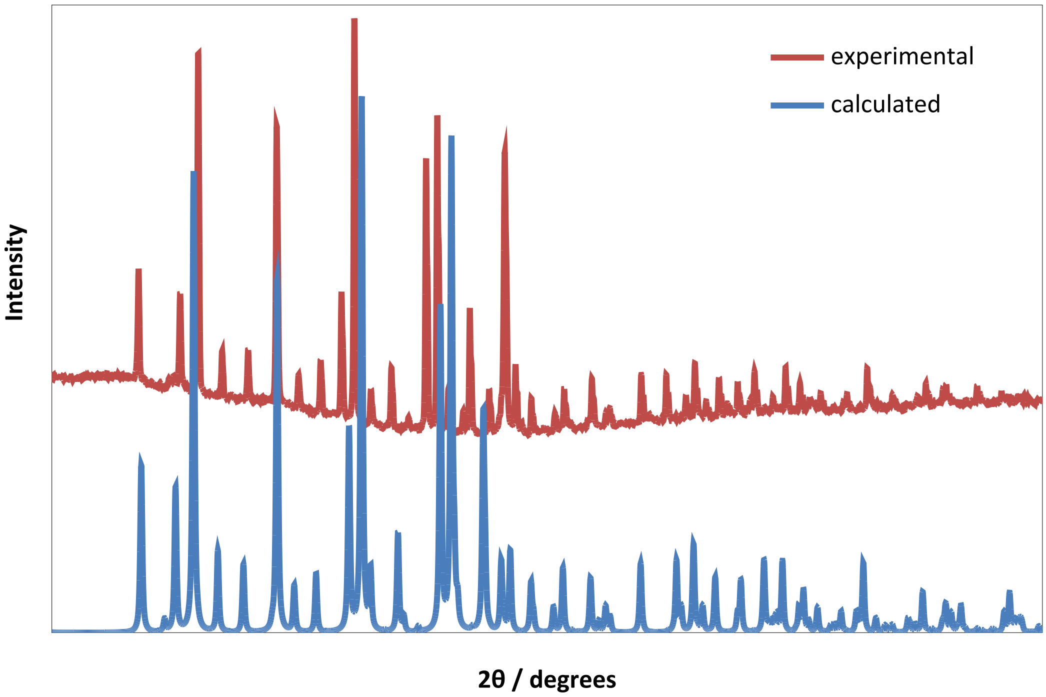

Figure S5. Experimental XRPD pattern of **2**·B$(OH)_3$ at room temperature and the XRPD pattern calculated from the low temperature single crystal X-ray data.

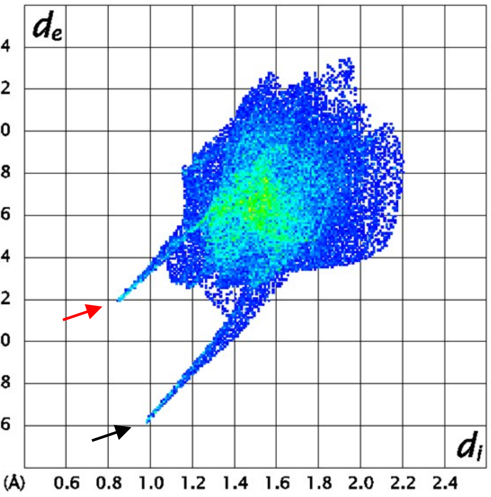

Figure S6. Hirshfeld surface fingerprint plot for the molecule of **2** in **2**·B(OH)$_3$. The sharp peaks on the left represent hydrogen bond NH···O donor (red arrow) and OH···O acceptor interactions (black arrow). The small diffuse blue region between the two hydrogen bonding peaks is indicative of a cyclic hydrogen bonding motif.

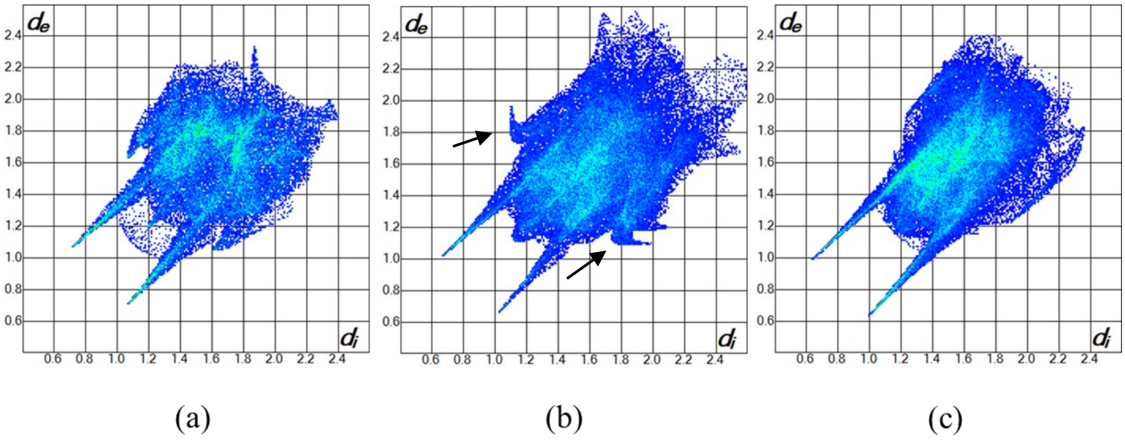
(a) (b) (c)

Figure S7. Hirshfeld surface fingerprint plots for (a) 4-hydroxyphenylboronic acid, (b) (ε-caprolactam)$_2$·4-hydroxyphenylboronic acid and (c) **1**·2B(OH)$_3$. Prominent 'wings' in 'b' (arrows) represent CH···π interactions.

Commercial 4-hydroxyphenylboronic acid (purchased from TCI) contained good quality single crystals, and the single crystal X-ray structural analysis was undertaken for completeness. The asymmetric unit of this boronic acid contains two independent molecules (*Z*′ = 2) with hydrogen bonding interactions between the hydroxyl moieties (O(3)···O(4) 2.836(2) Å), as seen in Fig. S8. The boronic acid units form conventional 8-membered hydrogen bonded rings while the hydroxyl groups form a 1D hydrogen bonded chain. The *Z*′ > 1 structure is common for monoalcohols[1] and is consistent with the increased tendency for molecule with a parent structure with high *Z*′ to form co-crystals.[2]

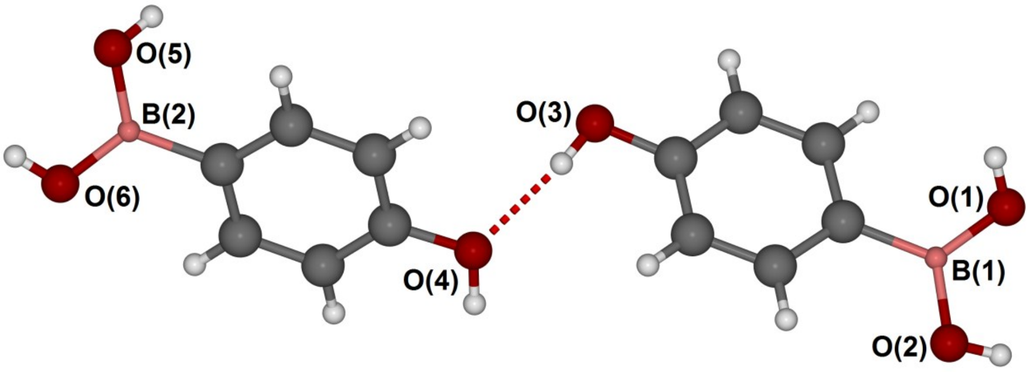

Figure S8. Asymmetric unit of 4-hydroxyphenylboronic acid.

The BOH groups of neighbouring molecules are held by hydrogen bonding interactions in a *syn-anti* conformation, resulting in an overall tape arrangement, Fig. S9.

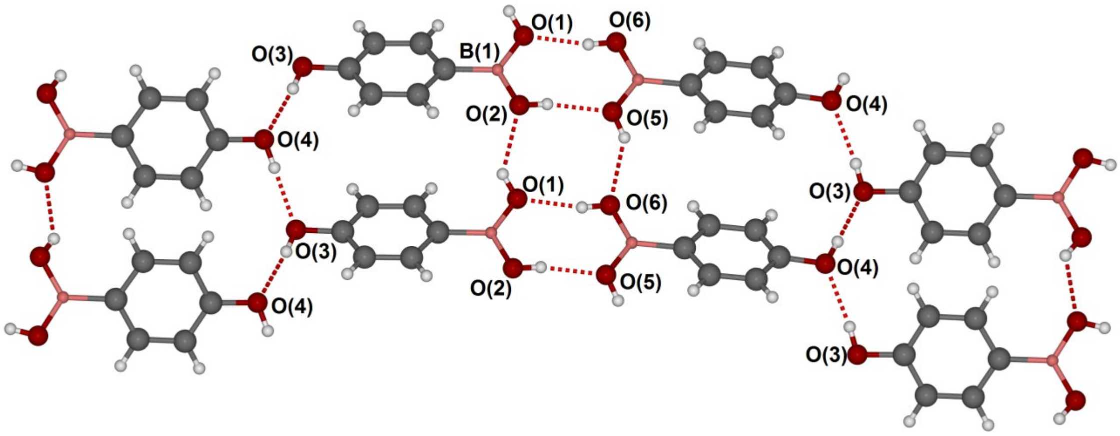

Figure S9. Crystallographic packing in 4-hydroxyphenylboronic acid. Hydrogen bonding distances (Å) (D···A): O(1)···O(2) 2.784(2), O(1)···O(6) 2.746(2), O(2)···O(5) 2.757(2), O(3)···O(4) 2.836(2), O(4)···O(3) 2.815(2), O(5)···O(6) 2.781(2) Å.

Crystal data for 4-hydroxyphenylboronic acid, $M = 137.93$, colourless trapezoid, 0.4094 × 0.1855 × 0.1143 mm^3, monoclinic, space group P2$_1$/c (No. 14), $a = 14.3765(4)$ Å, $b = 5.04525(19)$ Å, $c = 17.3563(7)$ Å, $\alpha = 90$ °, $\beta = 90.695(3)$ °, $\gamma = 90$ °, $V = 1258.81(8)$ Å^3, $Z = 8$, $D_c = 1.457$ g/cm^3, $F_{000} = 574.000$, Xcalibur, Sapphire3, MoKα radiation, $\lambda = 0.71073$ Å, $T = 120$K, $2\theta_{max} = 52.0^{o}$, 15899 reflections collected, 2475 unique ($R_{int} = 0.0445$). Final $GooF = 1.088$, $R1 = 0.0438$, $wR2 = 0.1088$, R indices based on 2036 reflections with I >2σ(I) (refinement on F^2), 193 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.113$ mm^{-1}.

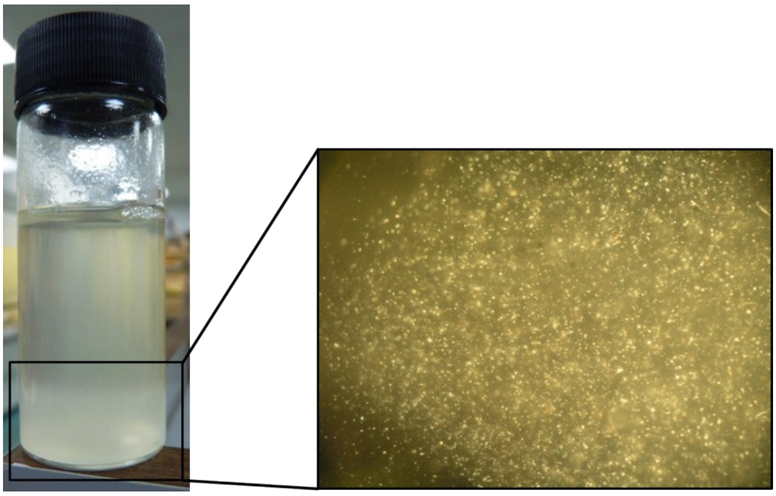

Figure S10. Sample vial showing biphasic **1**·2B(OH)$_3$-guar mixture prepared on a molar equivalent boron basis of the co-crystal after 3 days standing. Pop-out image shows the polarised optical micrograph of the crystalline material produced in the lower layer.

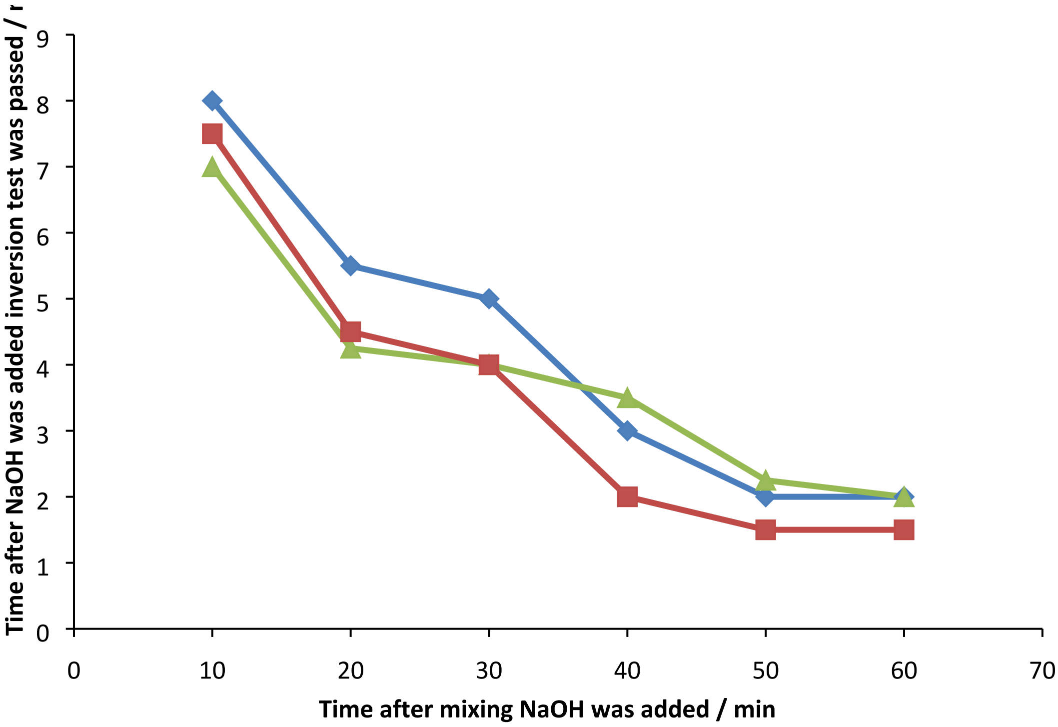

Figure S11. Average gelation time over two experiments of samples containing boric acid (◆), **1**·2B(OH)$_3$ (□) or **2**·B(OH)$_3$ (■) with varying times before addition of NaOH.

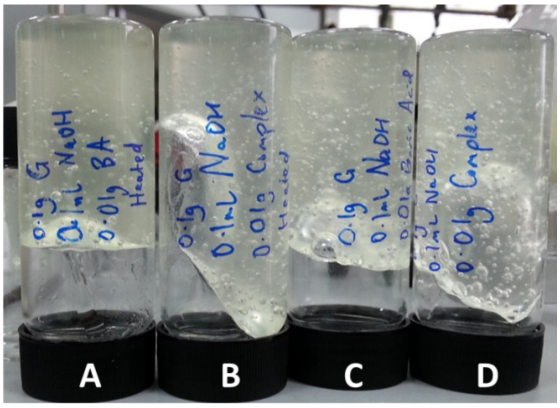

Figure S12. Cross-linked guar gels upon vial inversion. Samples A and B are heated, C and D gelled at room temperature. Initially the boric acid cross-linked gels A and C are more viscous than those cross-linked with the same mass of the co-crystal **1**·2B$(OH)_3$, however on standing the mixtures reach similar viscosity.

References

1. C. P. Brock and L. L. Duncan, *Chem. Mater.*, 1994, **6**, 1307.
2. K. M. Anderson, M. R. Probert, C. N. Whiteley, A. M. Rowland, A. E. Goeta and J. W. Steed, *Cryst. Growth. Des.*, 2009, **9**, 1082.