Supplementary Material (ESI) for Soft Matter

Supplementary Information

Anion Tuning of the Rheology, Morphology and Gelation of a Low Molecular Weight Salt Hydrogelator

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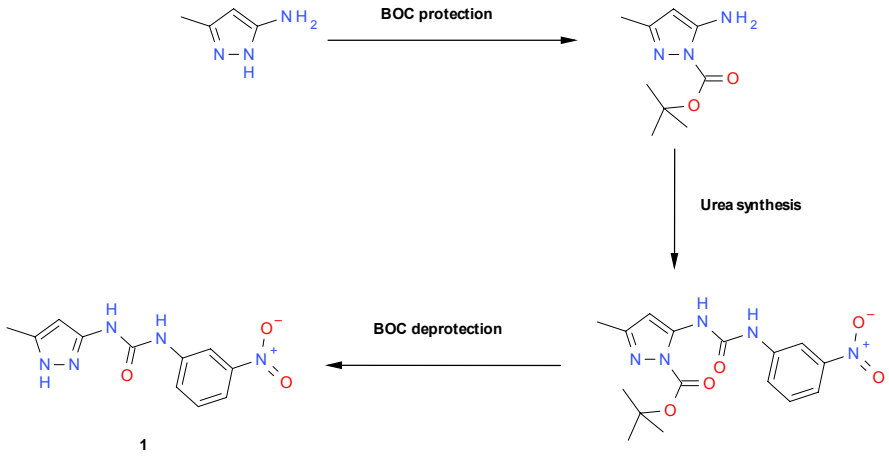
Synthesis



Synthesis of **1**

Gel characterisation

Gel formation was found to occur within the narrow general pH range of 1 − 2. Below pH 1 a solution was only observed. Above pH 2 crystallisation of pure **1** was observed.

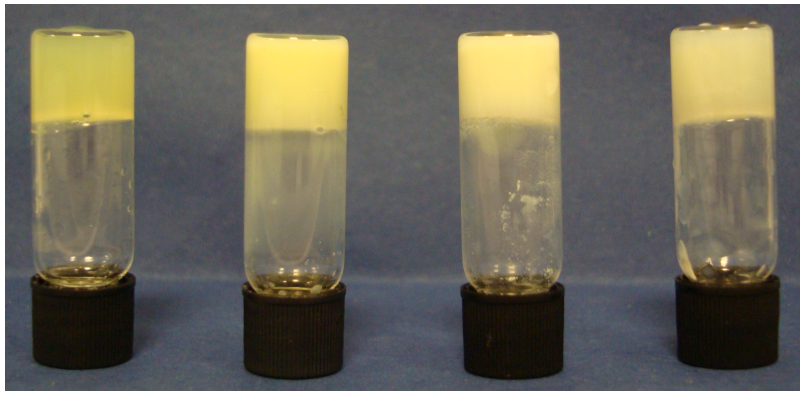


Fig. S1. Photograph of the gels of compound **1** at 1% by weight in water acidified with, from left to right, H_3PO_4; H_2SO_4; HPF_6 and HBF_4.

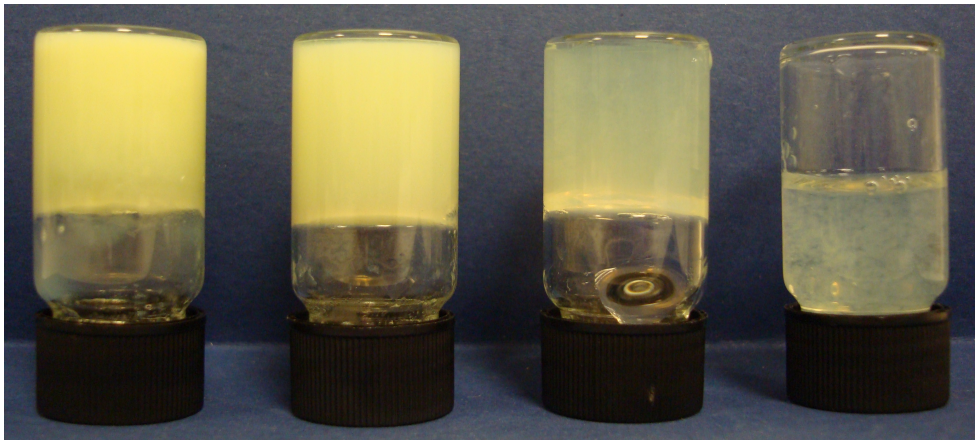


Fig. S2. Gels formed by compound **1** in water at pH 1.0 acidified with H_2SO_4. From left to right the concentrations are 1.3%, 0.6%, 0.15% and 0.1% by weight in 5 ml of solution. The 0.1% by weight solution only partially gels and therefore does not survive the inversion test.

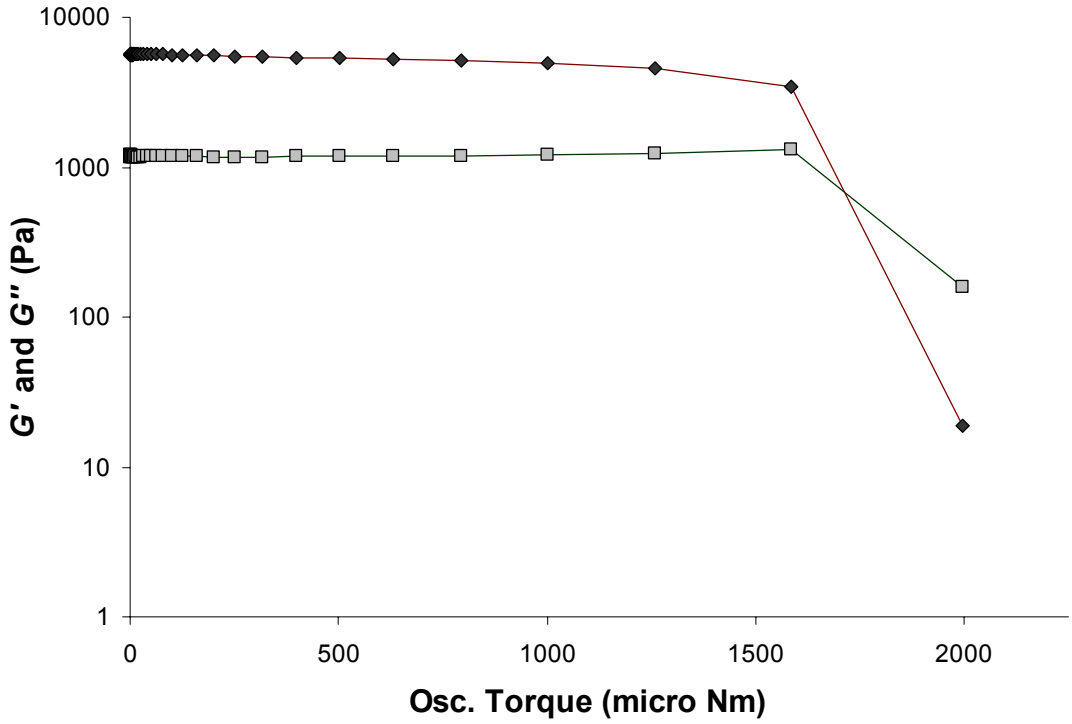


Fig. S3. Rheology of the gelation by **1** showing a stress sweep on a gel of **1** at 0.1% by weight in water acidified with H_2SO_4 to a pH of 1.0. The stress sweep shows the rigidity and strength of the gel which breaks at a relatively high shear strength. *G′* value (Dark grey filled ◇ with brown line) stays constant until the torque begins to become too strong and the struts start to break under the strain where upon *G′* becomes less than *G′′* (Light grey filled □ with green line). Lines are there to aid the eye. The *G′* and *G′′* axis is shown on a log scale.

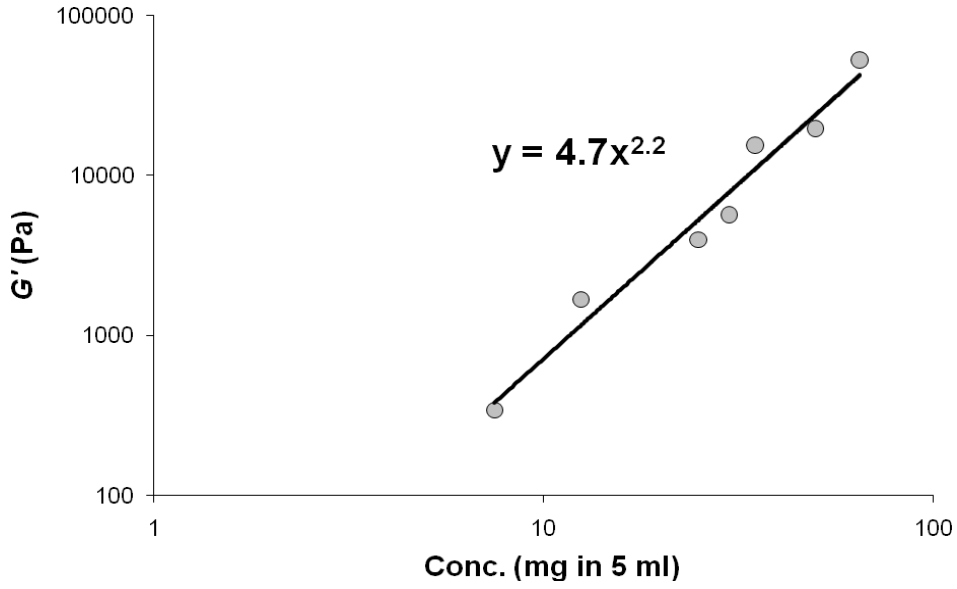


Fig. S4. Study in the variation in *G′* with change in concentration for gels of **1** in acidified water at pH 1.0 using H_2SO_4 (y = *G′* (Pa) and x = concentration in mg in 5 ml). $G' \propto [\text{conc}]^n$ relationship is confirmed with n = 2.2. Errors on data points, determined as standard deviations of ten measurements on a sample, are smaller than symbol size used. Both the *G′* axis and concentration axis are shown on a log scale.

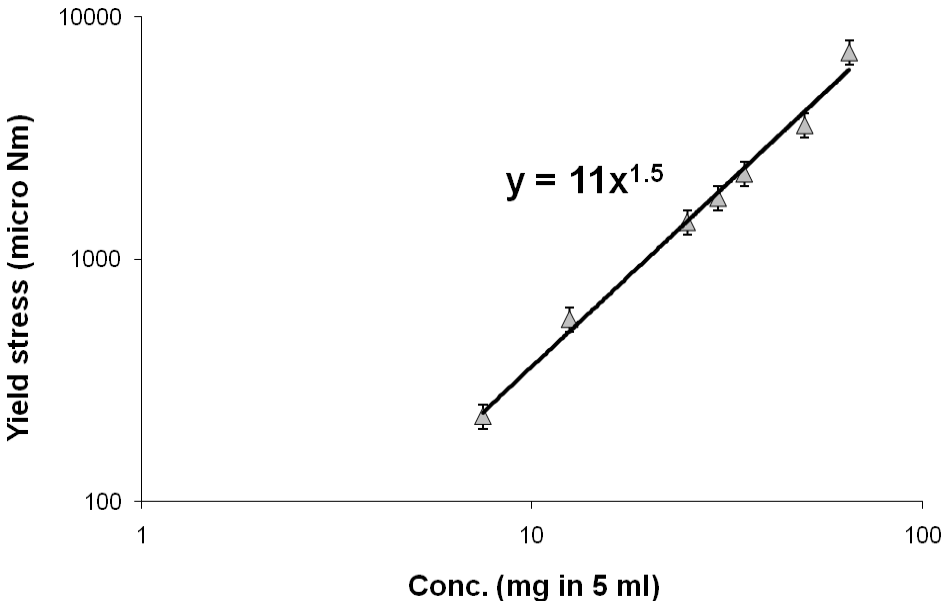


Fig. S5. Study in the variation in "yield stress" with change in concentration for gels of **1** in acidified water at pH 1.0 using H_2SO_4 (y = "Yield Stress" (micro Nm) and x = concentration in mg in 5ml). "Yield stress" $\propto$ [conc]^n relationship is confirmed with n = 1.5. Errors on plotted points are determined as the standard deviation for the point determined by taking the average of the measured points either side of the "yield stress" (see Fig. S3 for example). Both the "yield stress" axis and concentration axis are shown on a log scale.

Electron energy-loss spectroscopy (EELS) was run on the TEM samples to confirm that SO_4^{2-} or HSO_4^- were incorporated into the gel and that the gel was a salt (Fig. S6). As the samples were under high vacuum there was no liquid present so any sulfur found to be present was due to that in the gel struts as counter ion to the protonated **1**, although it could have been deposited from the evaporation of the solvent but the amount would be small and the signal weak. The EELS clearly shows a peak at 164 eV which can be assigned to the 2p shell electron peak of sulfur confirming the presence of sulphur and therefore SO_4^{2-} or HSO_4^-.[6] The other elements that were expected to be present in this gel, carbon, nitrogen and oxygen can also be identified at 284 eV, 401 eV and 532 eV, respectively.[6]

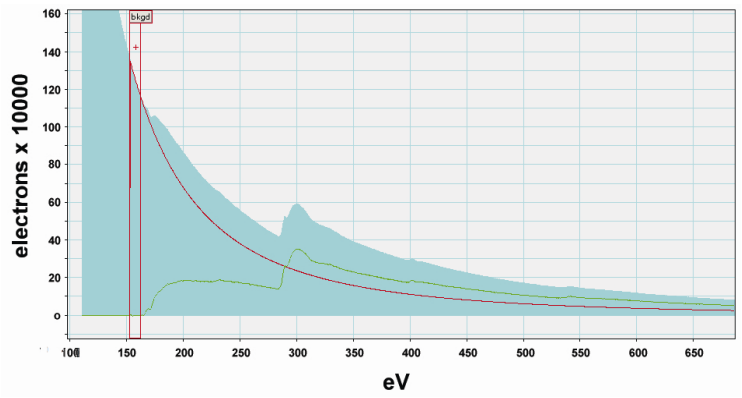


Fig. S6. EELS data from the gel sample of **1** in water acidified to pH 1.0 with H_2SO_4. The collected spectra (Filled blue area) is baseline corrected (Red line) to give the EELS data (Green line). This reveals peaks at 164 eV (S), 284 eV (C), 401 eV (N) and 532 eV (O).

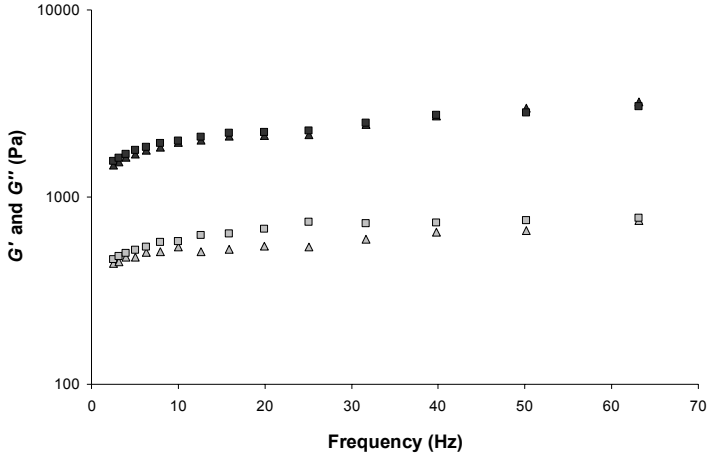


Fig. S7. Rheology by frequency sweep of the HBF_4 (△) and HPF_6 (□) acidified gels of **1**.

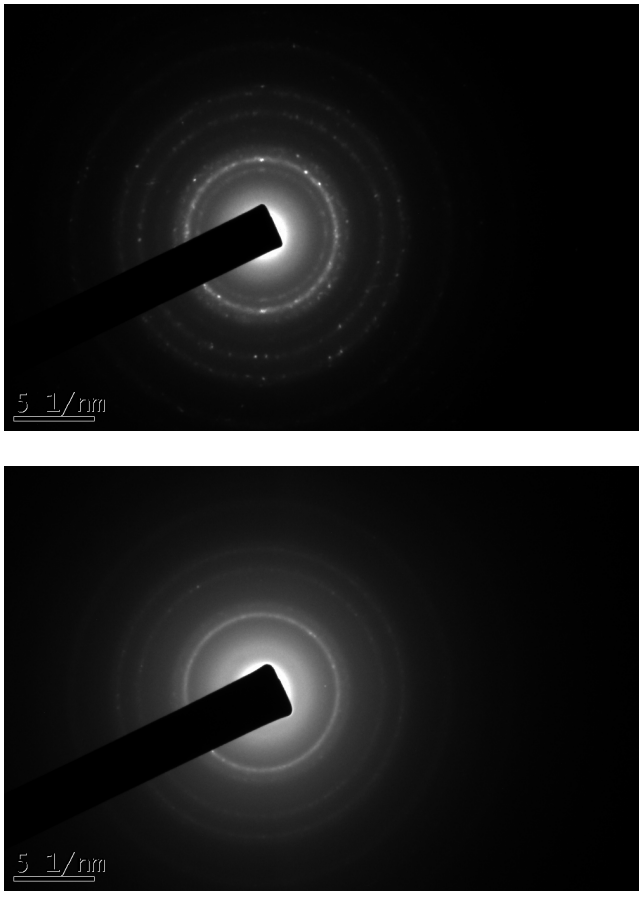


Fig. S8. Electron diffraction images of gels of **1** acidified with HBF_4 (top) and HPF_6 (bottom). Top diffraction *d*–spacing for the HBF_4 acidified gels are 2.46 Å; 2.11 Å; 1.86 Å; 1.55 Å; 1.32 Å and 1.12 Å. Bottom diffraction *d*–spacing for the HPF_6 acidified gels are 2.07 Å; 1.81 Å; 1.31 Å and 1.10 Å.

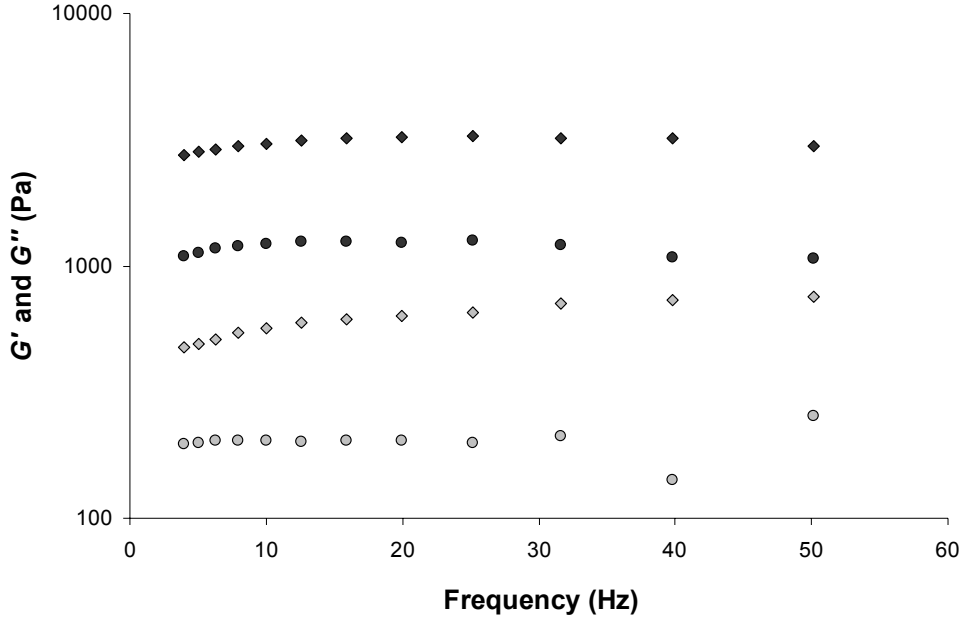


Fig. S9. Frequency sweep rheometry of **1** gels acidified with H_3PO_4 (○) and $MePO_3H_2$ (◇). Dark grey filled symbols are of *G′* and light grey filled symbols are of *G″*.

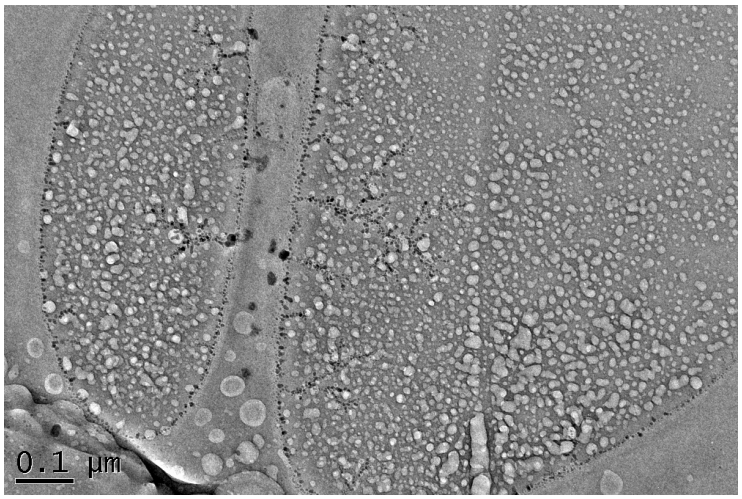


Fig. S10. TEM image of **1** gel acidified with H_3PO_4 at room temperature.

Crystallographic data

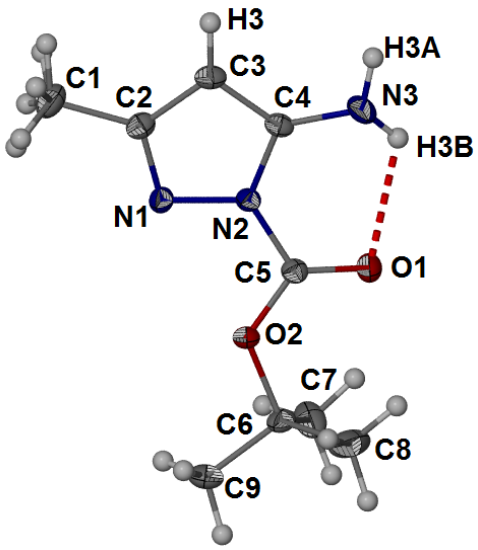


Fig. S11. ASU of the crystal structure of *tert*-butyl 5-amino-3-methyl-1*H*-pyrazole-1-carboxylate.

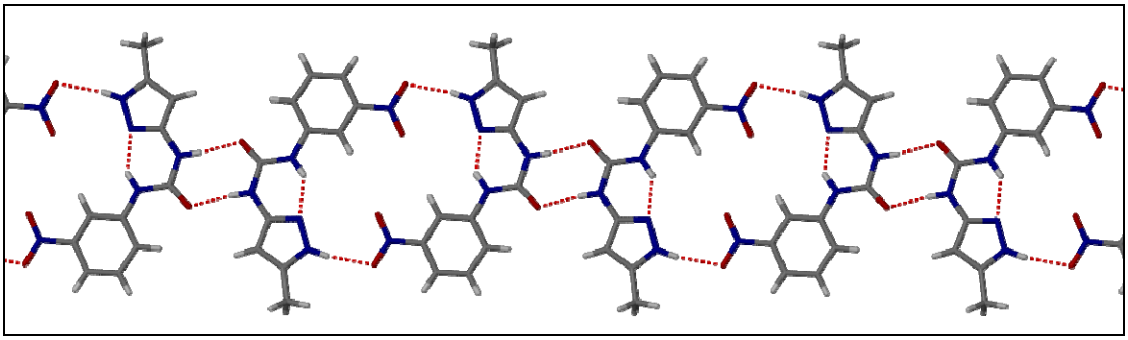


Fig. S12. Hydrogen bonding of the dimers of **1** to form a hydrogen bond chain. Selected hydrogen bonds: N3···O1^{i} = 2.8153(15) Å; ∠ N3–H3N···O1^{i} = 166.3^{o} and N1···O3^{ii} = 2.9703(16) Å; ∠ N1–H1N···O3^{ii} = 171.1^{o} (*i* = -x, 1-y, -z and *ii* = 1-x, -y-1, -z)

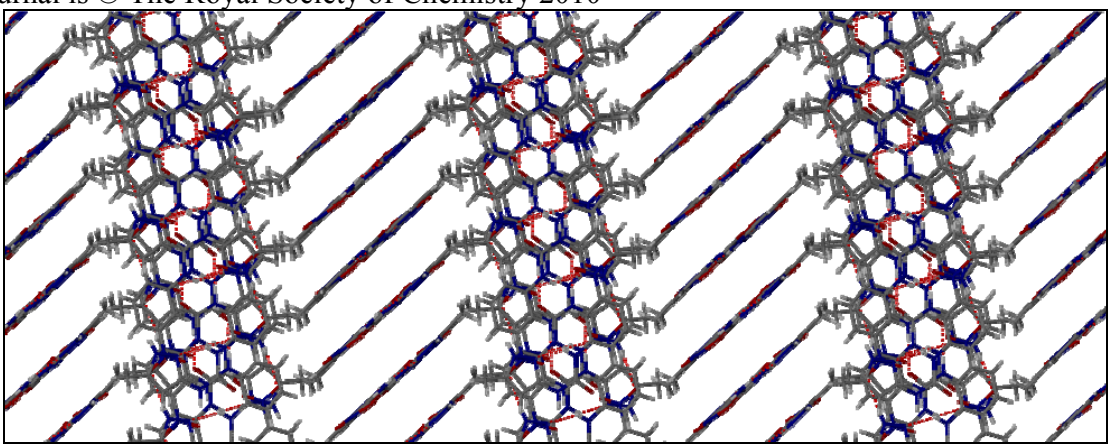


Fig. S13. Perpendicular inter-chain packing of **1**.

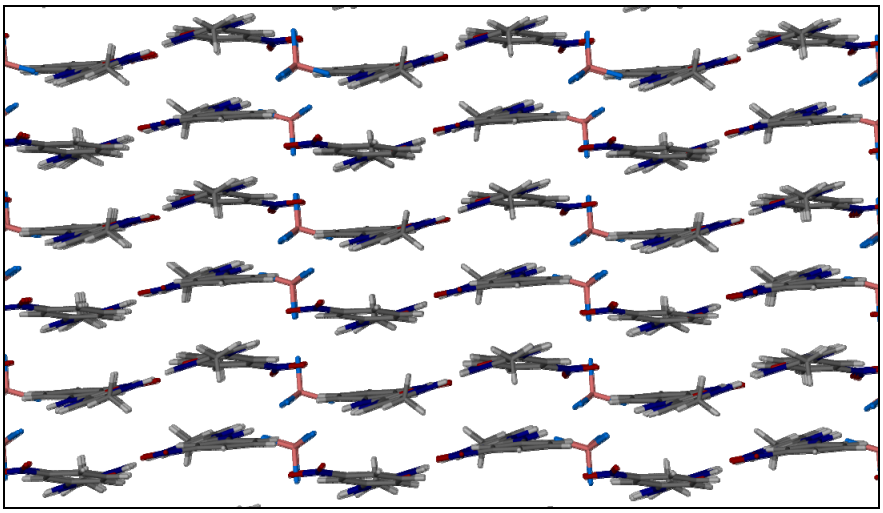


Fig. S14. Packing diagram of (**1H**$^+$)(BF_4^-)·**1** showing the stacking of 1D hydrogen bonded **1H**$^+$ **1** threads alternating with the layers of BF_4^-. Hydrogen bonds are not shown for clarity.

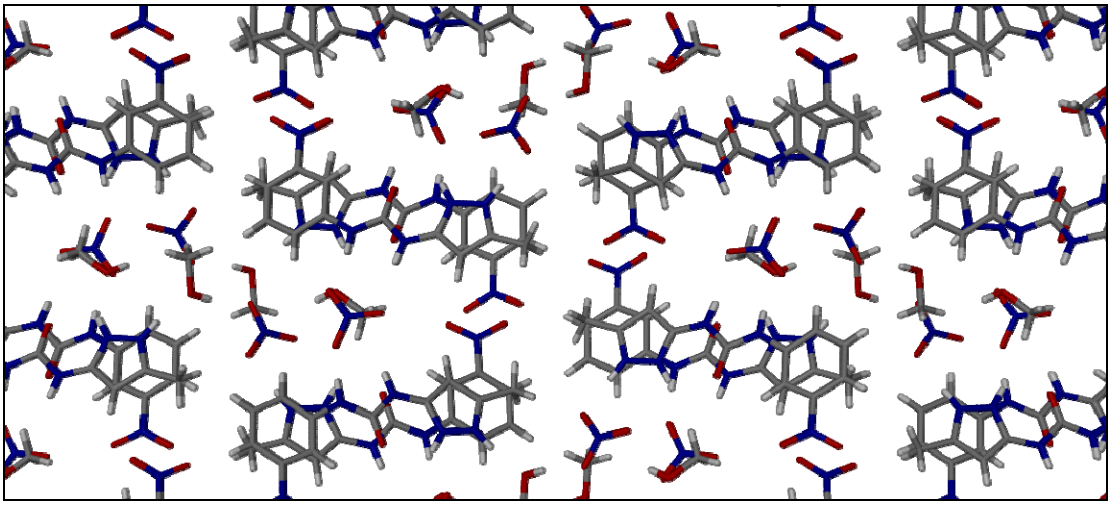


Fig. S15. Overall crystal packing of (**1H**$^+$)(NO_3^-)·MeOH. Hydrogen bonds are not shown for clarity.

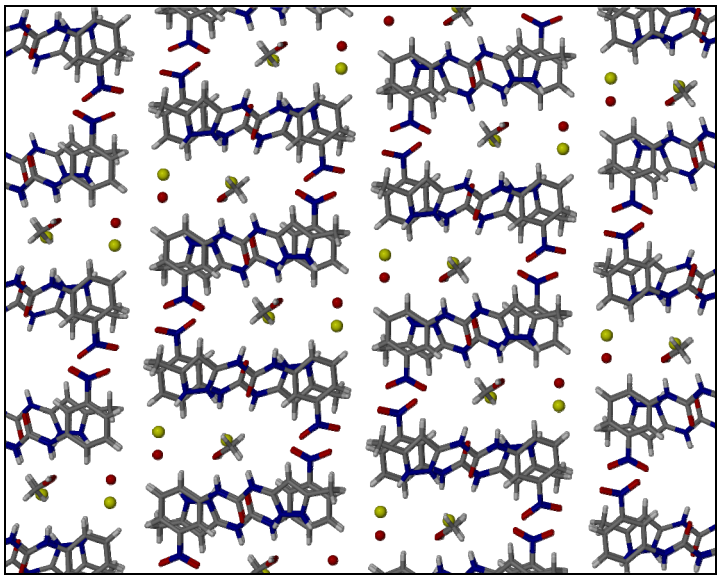


Fig. S16. Overall packing of 2(**1H**$^+$) 2Cl^- MeOH H_2O. Atoms are shown in capped stick representation except for the Cl^- and water oxygen which are shown as small spheres.

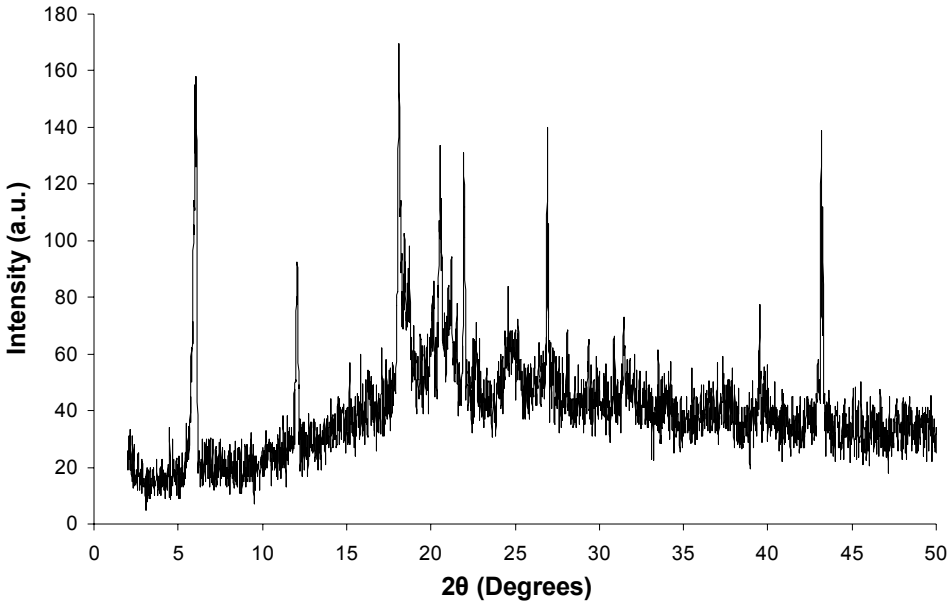


Fig. S17. PXRD pattern for dried **1** gel acidified with HPF_6. Selected *d*-spacings: 2.08 Å; 1.85 Å; 1.70 Å; 1.21 Å and 1.13 Å.

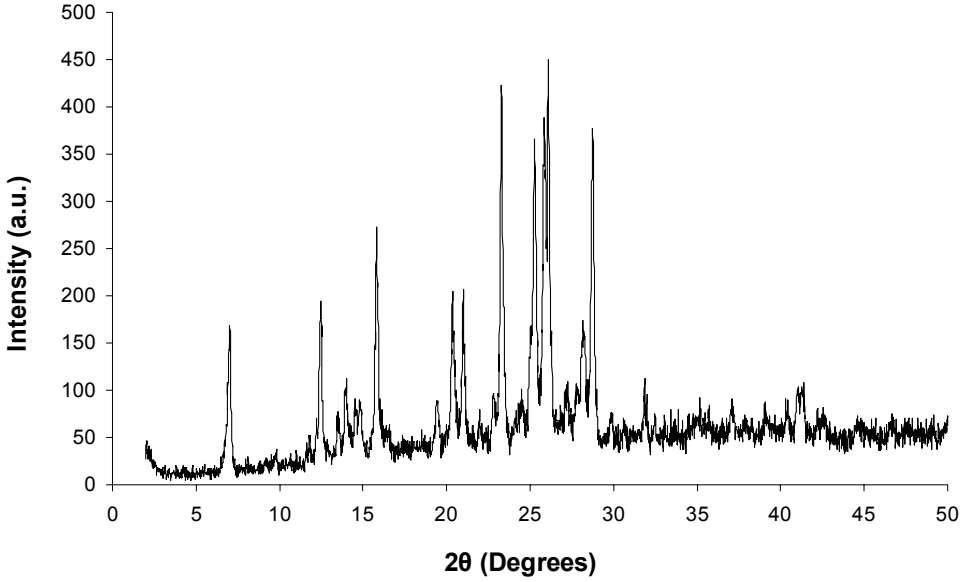


Fig. S18. PXRD pattern for dried **1** gels acidified with HBF_4. Selected *d*-spacings: 2.15 Å; 1.95 Å; 1.81 Å; 1.77 Å; 1.75 Å; 1.60 Å and 1.46 Å.

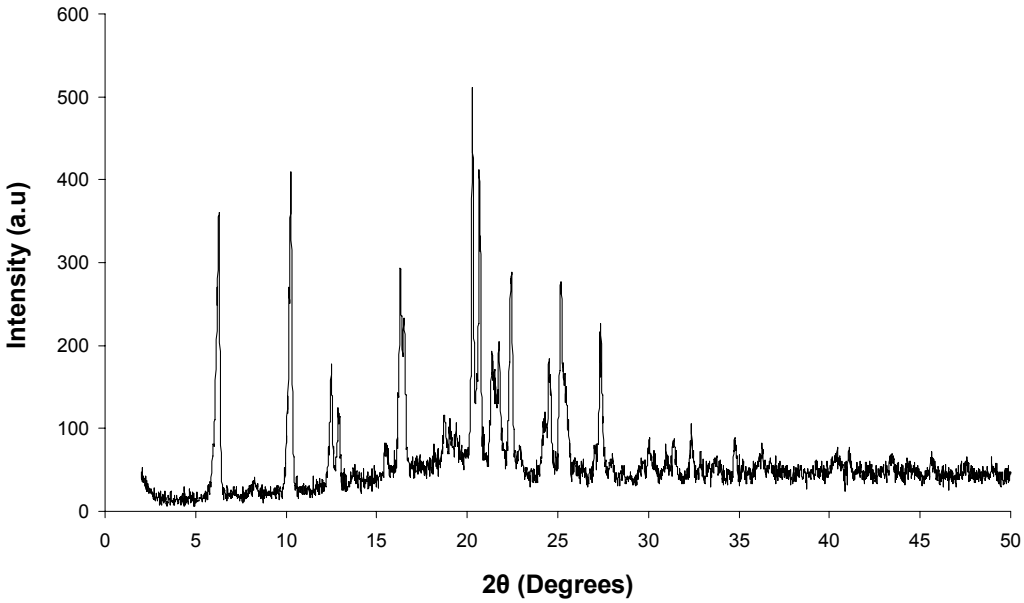


Fig. S19. PXRD pattern for dried **1** gel acidified with $MePO_3H_2$.

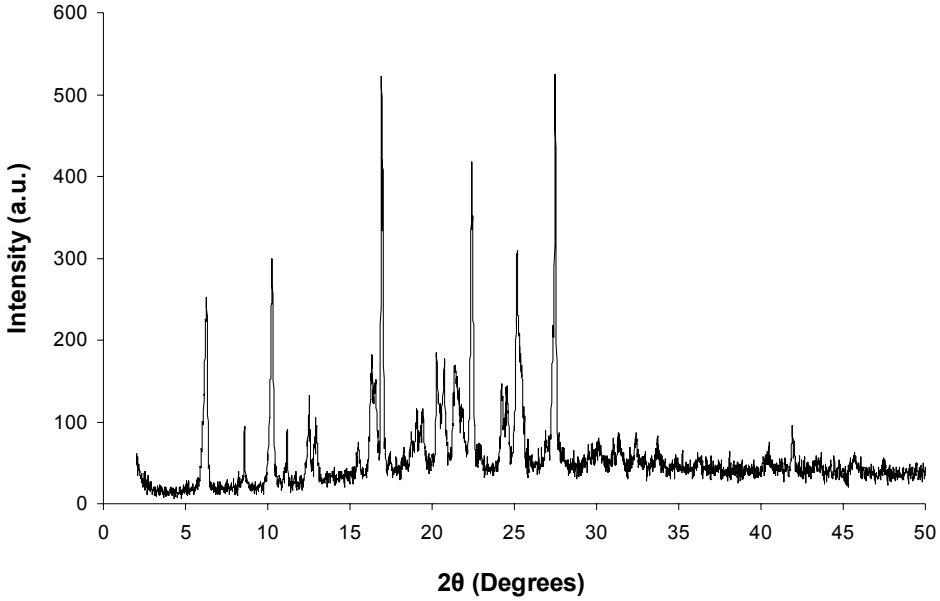


Fig. S20. PXRD pattern for dried **1** gels acidified with $EtPO_3H_2$.

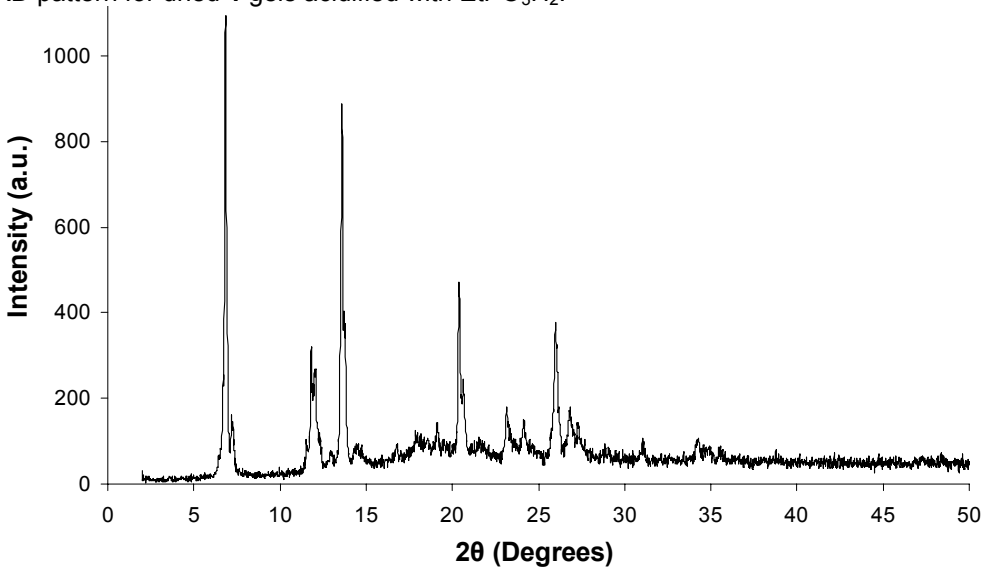


Fig. S21. PXRD pattern for dried **1** gel acidified with HNO_3.

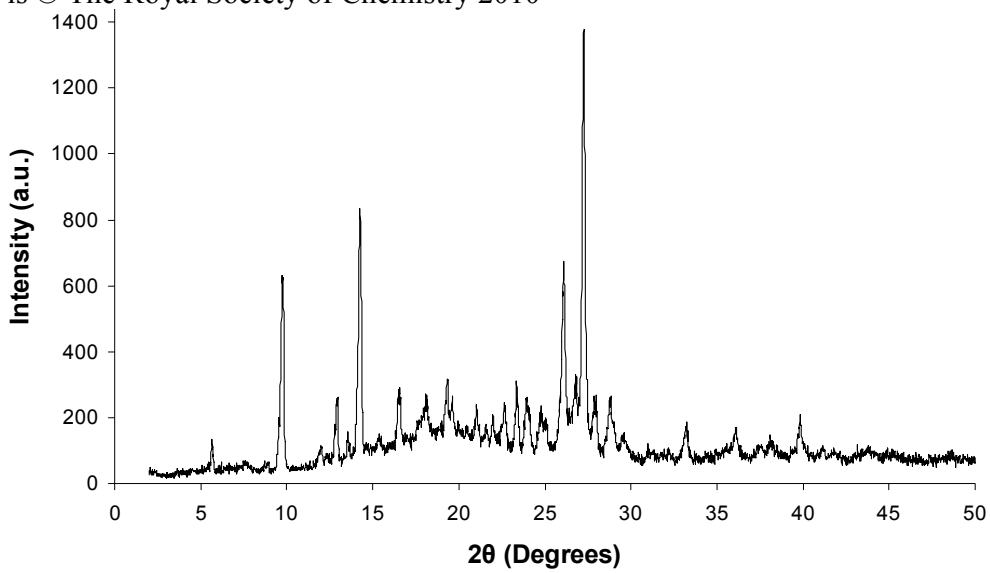


Fig. S22. PXRD pattern for dried **1** gel acidified with HCl.

Table S1. Hydrogen bond parameter details for hydrogen bonds within the structure of $(\mathbf{1H^+})_2(SO_4^{2-})\cdot 7H_2O$.

Water Donor or Acceptor[a]	Hydrogen bond Atoms[b]	Donor – Acceptor Distance (Å)	Hydrogen bond Angle (Degrees)
Acceptor	N7–H7N···O4	2.742(2)	145.9
Acceptor	N6–H6N···O7	2.6405(19)	175.6
Donor	O2–H2WA···O15	2.8887(19)	167.3
Donor	O1–H1WA···O14	2.6901(19)	160.5
Donor	O4–H4WA···O3	2.877(2)	150.3
Donor	O5–H5WB···O6	2.7185(18)	153.1
Donor	O4–H4WB···O5	2.828(2)	167.0
Acceptor	N4–H4N···O6	2.9226(18)	170.2
Acceptor	N3–H3N···O5	2.8797(18)	165.6
Donor	O3–H3WA···O12	3.069(2)	168.2
Acceptor	N2–H2N···O1^{i}	2.7514(19)	152.9
Donor	O1–H1WB···O4^{ii}	2.931(2)	170.1
Donor	O2–H2WB···O17^{iii}	2.8721(19)	174.3
Donor	O3–H3WB···O14^{iv}	3.134(2)	145.2
Donor	O5–H5WA···O15^{iv}	2.9319(19)	172.7
Donor	O6–H6WA···O16^{v}	2.8173(18)	170.3
Donor	O7–H7WB···O2^{v}	2.674(2)	165.4
Donor	O6–H6WB···O16^{vi}	2.7833(19)	177.1
Donor	O7—7WA···O16^{vi}	2.8333(19)	168.2
n/a	N2–H2N···O8	2.575(2)	118.4
n/a	C7–H7···O8	2.750(2)	121.5
n/a	N7–O7N···O11	2.663(2)	118.3
n/a	C18–H18···O11	2.836(2)	121.1
n/a	N9–H9N···O15	2.9459(18)	168.2
n/a	N8–H8N···O14	2.8184(19)	169.4
n/a	N1–H1N···O17^{vii}	2.7439(18)	171.9

[a] Denotes if the water molecule is a donor or acceptor of an hydrogen bond. [b] *ii* = 1-x, ½+y, ½-z; *iii* = -x, 3-y, 1-z; *iv* = -x, y-½, ½-z; *v* = x, $^5/_2$–y, z-½; *vi* = 1-x, y-½, ½-z, *vii* = x, y-1,z.

References

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