Supplementary Material (ESI) for Chemical Communications

Novel Homochiral H-bonded Proline Based Metal Organic Frameworks

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Figure S1: Comparison of simulated and experimental powder X-ray diffraction patterns for Framework **1**.

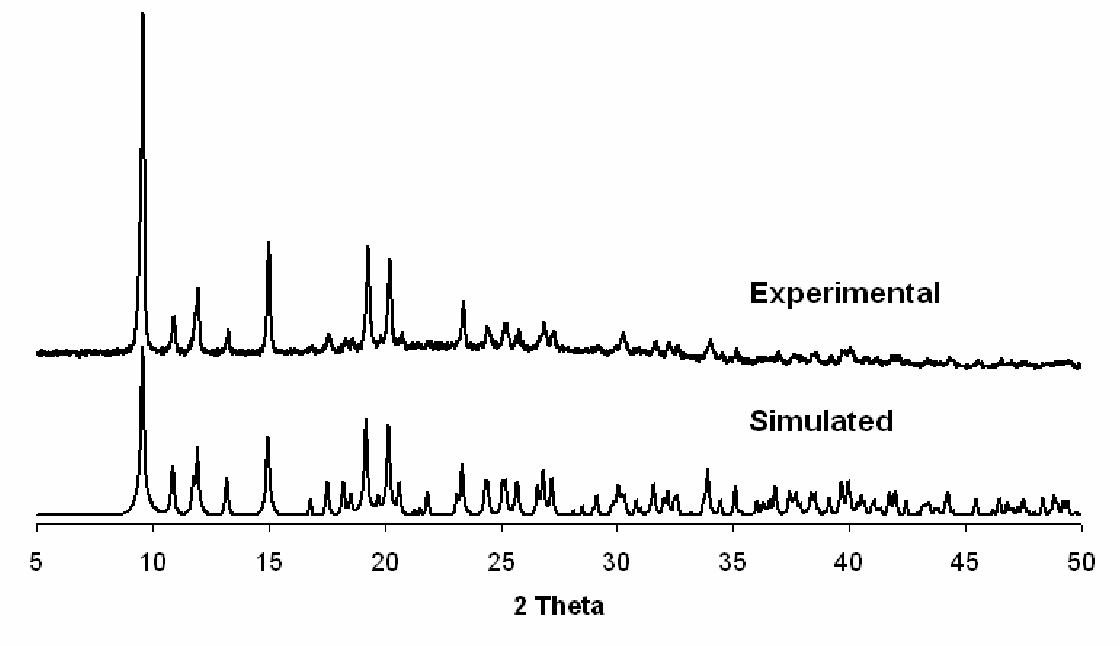


Figure S2: Powder X-ray diffraction patterns for Framework **1** synthesised by solvothermal and H-Cell diffusion methods

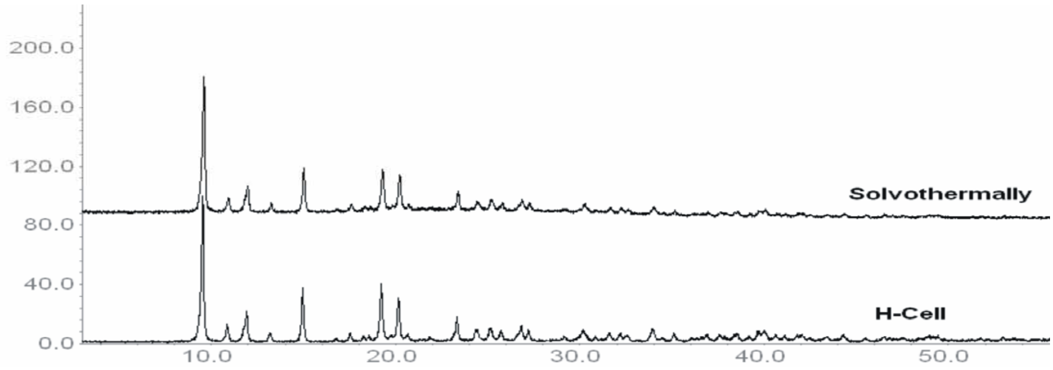


Figure S3: The efficient interlayer ABAB packing in framework **1**, left ball and stick view (20% van der Waals radii), right space filling diagram (100% van der Waals radii). Hydrogens and proximal Bipy molecules omitted for clarity.

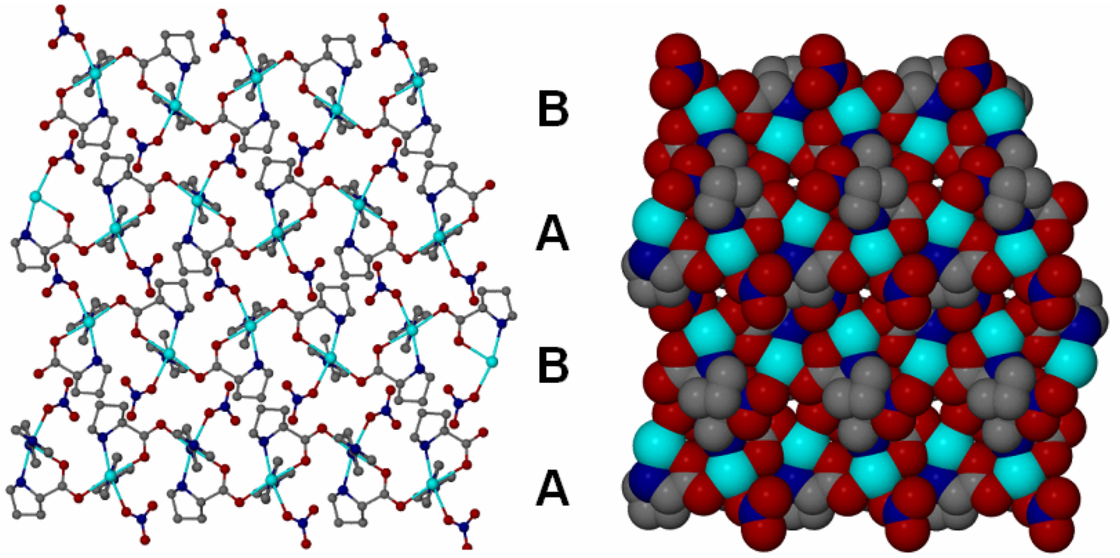


Figure S4: TGA for Framework **1** run under N_2, showing no solvent loss before framework decomposition at T ≈ 200°C.

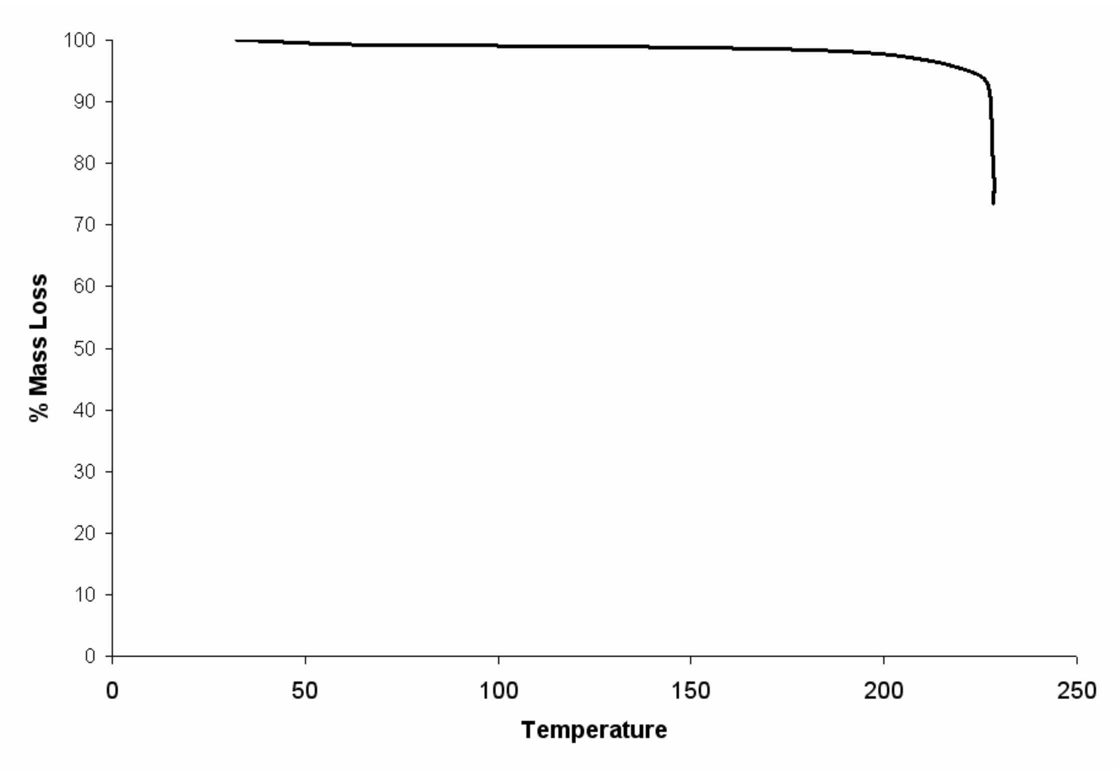


Figure S5: Powder X-Ray Diffraction patterns for Framework **2** synthesised solvothermally and by H-Cell diffusion.

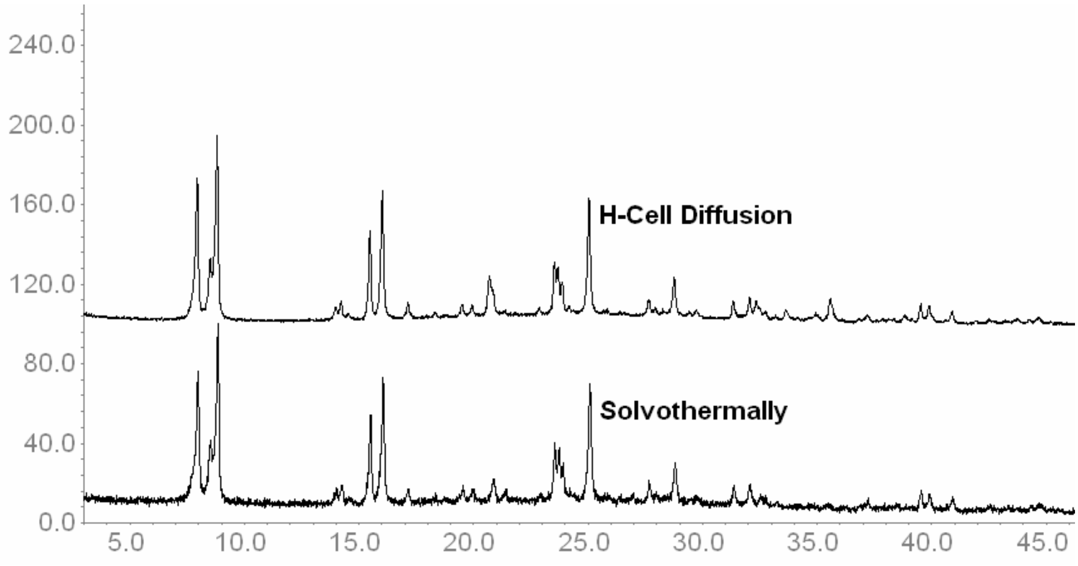


Figure S6: SEM image of Framework **2**, demonstrating the observed homogeneous platelet morphology.

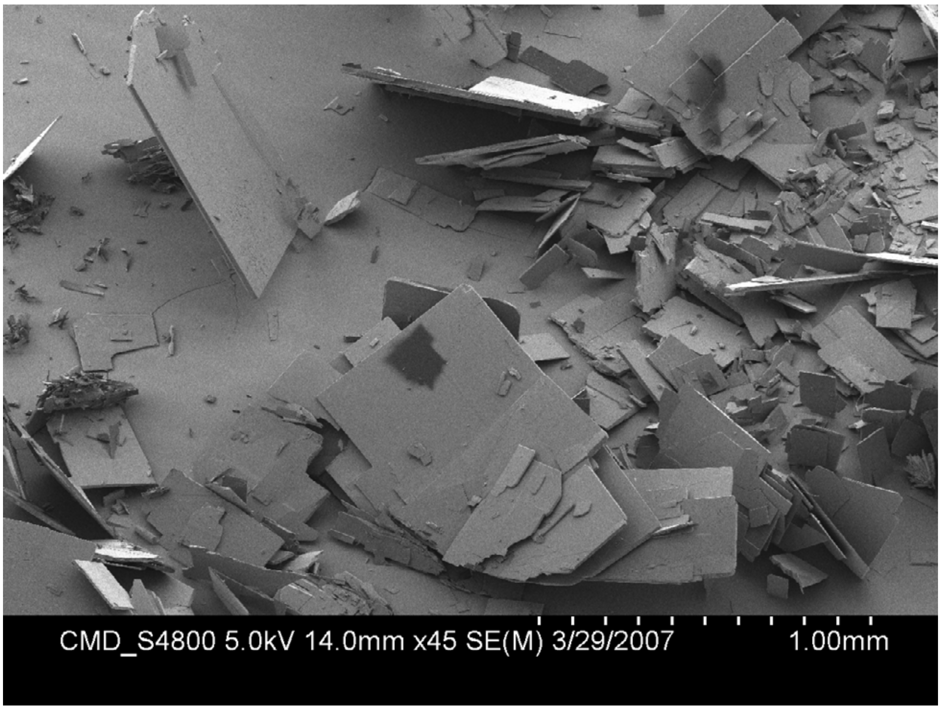


Figure S7: TGA (under a N_2 atmosphere) of Framework **2**, displaying a mass loss between 30°C and 120°C of 4.2% corresponding to 100% of the hydrogen bonded H_2O molecules.

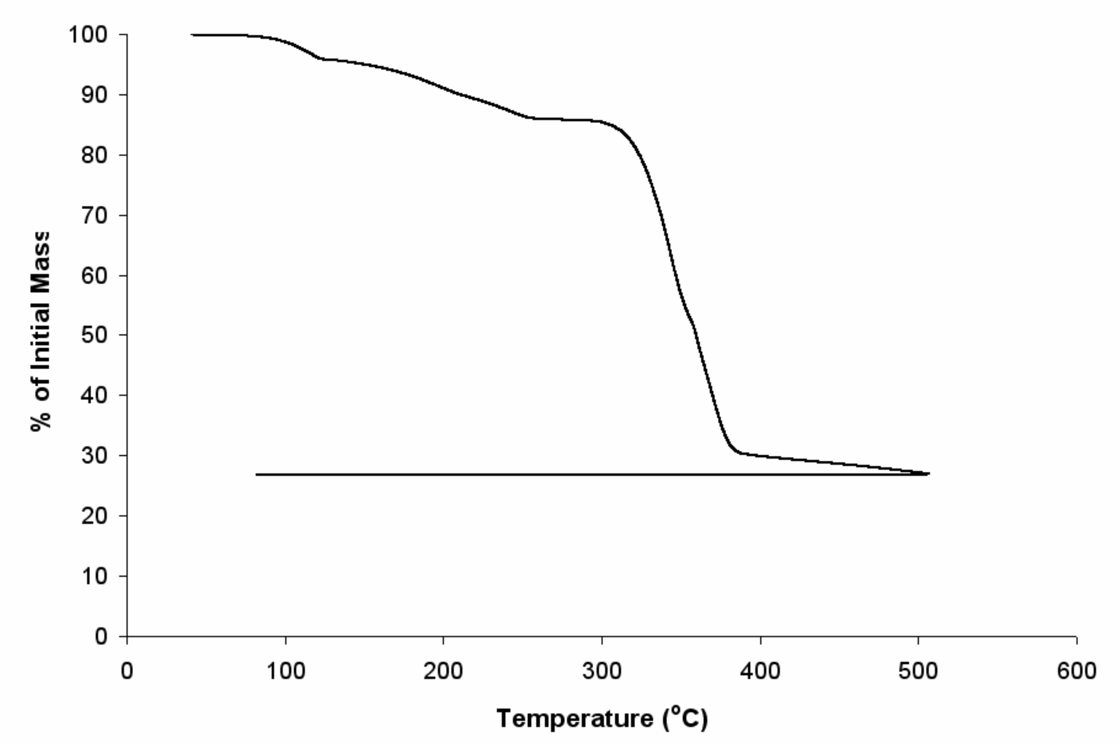
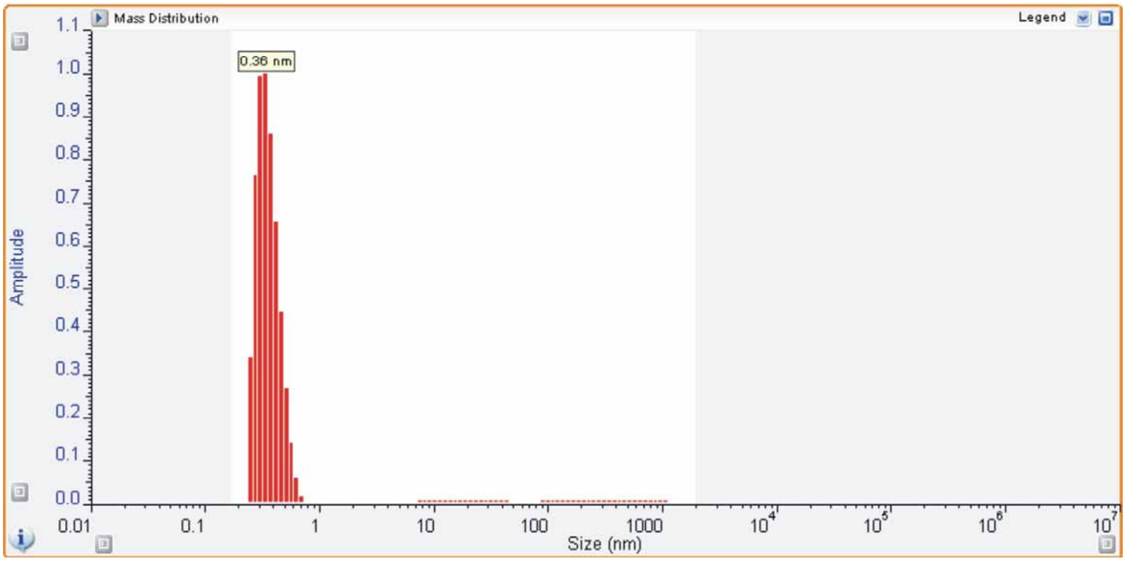


Figure S8: Dynamic Light Scattering of a saturated H_2O solution of framework **2**.



Structure Report for Framework 1 at 100(1) K

Crystal data for **1**: $C_{15}H_{16}CdN_4O_5$, $M = 444.72$, colourless platelet, 0.06 × 0.05 × 0.02 mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 9.5774(12)$, $b = 11.8132(15)$, $c = 14.7182(18)$ Å, $V = 1665.2(4)$ Å^3, $Z = 4$, $D_c = 1.774$ g/cm^3, $F_{000} = 888$, Bruker D8 diffractometer, synchrotron radiation, $\lambda = 0.78480$ Å, $T = 100(2)$K, $2\theta_{max} = 66.3°$, 14605 reflections collected, 4458 unique ($R_{int} = 0.0874$). Final $GooF = 0.984$, $R1 = 0.0464$, $wR2 = 0.0872$, R indices based on 4064 reflections with I >2sigma(I) (refinement on F^2), 230 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.346$ mm^{-1}. Absolute structure parameter = -0.06(3) (Flack, H. D. *Acta Cryst.* **1983**, *A39*, 876-881).

Data collection

A (colourless prism) having approximate dimensions of 0.06 mm x 0.05 mm x 0.02 mm was mounted onto a thin needle with (vacuum grease).
X-ray data were collected at Daresbury Synchrotron Radiation Source, Station 16.2MX on Bruker D8 diffractometer with an APEX II CCD detector with Si 111 monochromated radiation ($\lambda = 0.7848$ Å). The data were collected using ω-scans in the θ range 3.60 to 33.17° with a scan width of 0.3° in ω.

The final cell constants obtained from least-squares refinement on reflections from the integration corresponded to a primitive orthorhombic cell with dimensions:

$a =$ 9.5774(12)
$b =$ 11.8132(15)
$c =$ 14.7182(18)
$V =$ 1665.2(4)

For $Z = 4$ and *F.W.* = 444.72 (corresponding to the formula $CdC_{15}H_{16}N_4O_5$), the calculated density is 1.774 g/cm^3.

The reflection conditions $h00$: $h = 2n$
$0k0$: $k = 2n$
$00l$: $l = 2n$
indicated that the crystal belongs to the space group $P\,2_1\,2_1\,2_1$.

Data reduction, structure solution and refinement

The frames were integrated using the APEXII software using a narrow-frame integration algorithm. The integration of the data using the orthorhombic unit cell yielded a total of 14605 reflections to a maximum θ angle of 33° (0.717 Å resolution), of which 4458 were symmetry independent (completeness = 95.2%, $R_{int} = 8.74\%$). Analysis of the data showed negligible decay during data collection. A semi-empirical absorption correction based on multiply measured reflections was carried out with SADABS. The structure was solved by direct methods and refined using SHELX.

The H atom belonging to the proline amine group was located from difference maps and its position and isotropic temperature factor refined without restraints. All other H-atoms were placed in geometrically optimized positions and the bond distances and angles idealized during each cycle of refinement (phenyl C-H = 0.95 Å and secondary C-H = 0.99 Å) with the H-atom Uiso values set at 1.2 times the equivalent isotropic temperature factor of the carbon atoms to which they were attached.

After complete refinement, the highest residual peak and deepest hole in the difference map corresponded to 1.07, -1.11 e Å^{-3} respectively (located at the Cd atom). The absolute structure parameter (-0.06(3)) derived from the final refinement indicated that the absolute structure assigned to the structure was correct.

Structure Report for Compound 2 at 150(2) K

Crystal data for **2**: $Zn_1B_1F_5N_3O_3C_{15}H_{19}$, *M* = 460.51, colourless needle, 0.10 × 0.05 × 0.04 mm^3, monoclinic, space group $P2_1$ (No. 4), *a* = 11.3839(5), *b* = 7.4364 (3), *c* = 12.1179(5)Å β = 116.057(1)°, *V* = 921.57(4) Å^3, *Z* = 2, D_c = 1.660 g/cm^3, F_{000} = 468, Bruker D8 diffractometer, synchrotron radiation, λ = 0.6911 Å, *T* = 150(2)K, $2\theta_{max}$ = 71.8°, 7743 reflections collected, 4809 unique (R_{int} = 0.0578). Final *GooF* = 1.086, *R1* = 0.0676, *wR2* = 0.1852, *R* indices based on 4809 reflections with I >2sigma(I) (refinement on F^2), 256 parameters, 124 restraints. Lp and absorption corrections applied, μ = 1.403 mm^{-1}. Absolute structure parameter = -0.02(2) (Flack, H. D. *Acta Cryst.* **1983**, *A39*, 876-881).

Data collection

A colourless needle having approximate dimensions of 0.10 mm x 0.05 mm x 0.04 mm was mounted onto a thin glass fibre with (vacuum grease).
X-ray data were collected at Daresbury Synchrotron Radiation Source, Station 16.2MX on Bruker D8 diffractometer with an APEX II CCD detector with Si 111 monochromated radiation (λ = 0.6911 Å). The data were collected using ω-scans in the θ range 3.62 to 35.86° with a scan width of 0.3° in ω.

The final cell constants obtained from least-squares refinement on 3105 reflections from the integration corresponded to a primitive monoclinic cell with dimensions:

a = 11.3839(5)
b = 7.4365(3)
c = 12.1179(5)
β = 116.057(1)
V = 921.57(1)

For $Z = 2$ and $F.W. = 460.51$ (corresponding to the formula $ZnC_{15}H_{19}N_3O_3BF_5$), the calculated density is 1.660 g/cm^3.

The reflection condition $0k0$: $k = 2n$ indicated that the crystal belongs to the space group $P2_1$.

Data reduction, structure solution and refinement

The frames were integrated using the APEXII software using a narrow-frame integration algorithm. The integration of the data using the monoclinic unit cell yielded a total of 7743 reflections to a maximum θ angle of 33° (0.59 Å resolution), of which 4809 were symmetry independent (completeness = 91.5%, R_{int} = 5.78%). Analysis of the data showed negligible decay during data collection. A semi-empirical absorption correction based on multiply measured reflections was carried out with SADABS. The structure was solved by direct methods and refined using SHELX.

The proline ligand and the BF4- anion were disordered and both were modelled using two disorder components. The site occupancy factors were refined, and very close to ½. The site occupancies for each disorder component were fixed at 0.500 during the last cycles of refinement. The B-F and F…F distances were restrained to be equal, and the two proline components restrained to be equal using the SAME command in shelx.

The H atoms belonging to the water molecule of crystallization was located from difference maps, and verified by calculating distances and angles to closest hydrogen bond acceptor atoms. Their positions were refined using DFIX restraints in SHELX and their isotropic temperature factor refined without restraints. All other H-atoms were placed in geometrically optimized positions and the bond distances and angles idealized during each cycle of refinement with the H-atom Uiso values set at 1.2 times the equivalent isotropic temperature factor of the atoms to which they were attached.

All the non-hydrogen atoms except the disordered atoms of the proline group were refined anisotropically.

After complete refinement, the highest residual peak, corresponding to 1.524 Å^{-3}, was located approximately between the disordered BF4- anion and proline, a likely artifact of the disorder, while the deepest hole (-0.918 e Å^{-3}) was located at the Zn atom.

The absolute structure parameter (-0.02(2)) derived from the final refinement indicated that the absolute structure assigned to the structure was correct.

References:
Bruker (2004), APEXII. Bruker AXS inc. Madison, Wisconsin, USA
Bruker (2004), SADABS. Bruker AXS inc. Madison, Wisconsin, USA
Sheldrick, G. M. (1997). SHELX97, University of Göttingen, Germany.