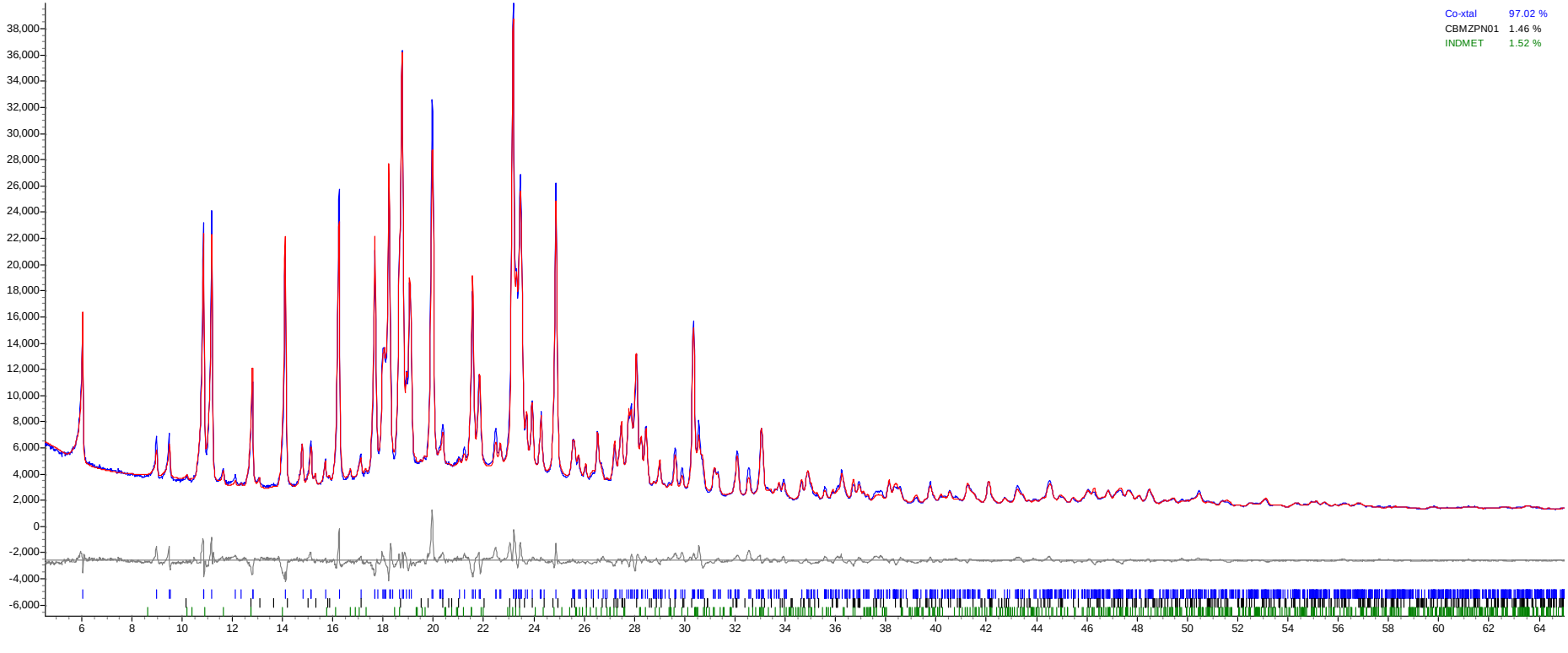
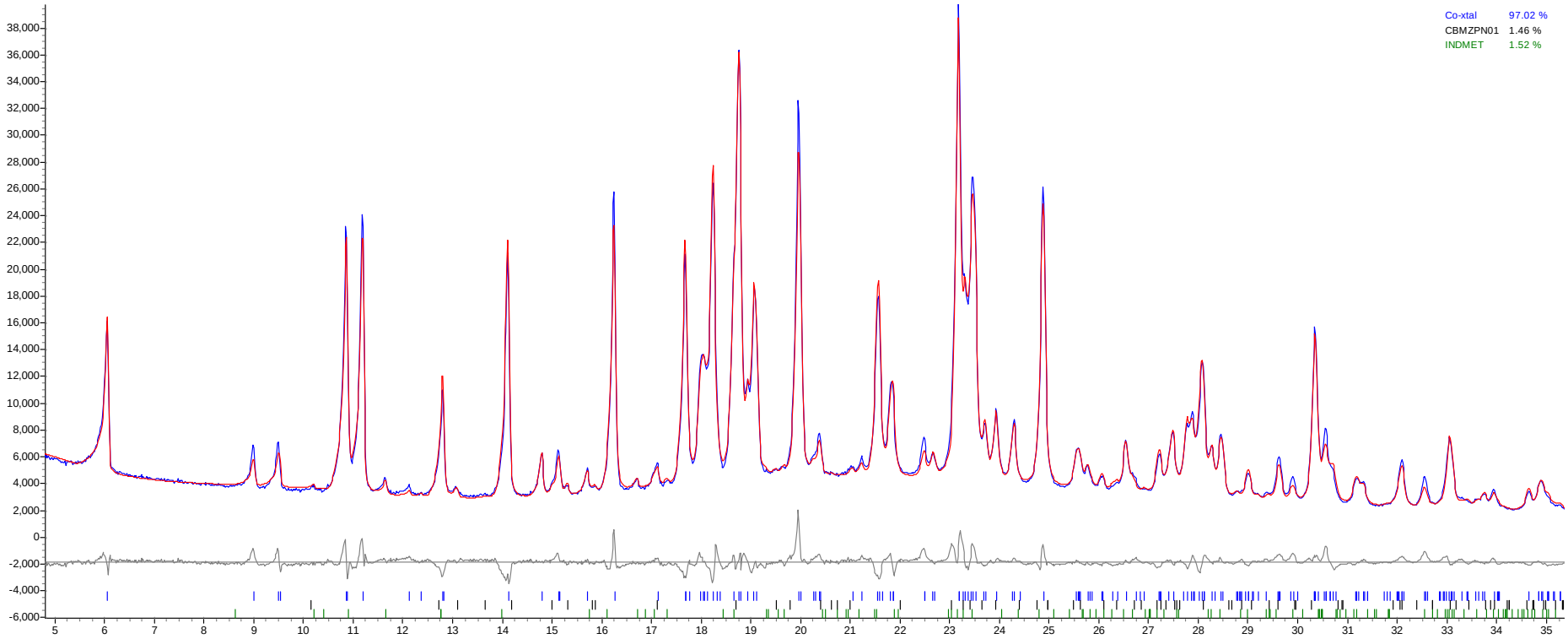
Electronic Supplementary Information

Profile plot of three phase Rietveld fit to the CBZ:IND diffraction data - full range

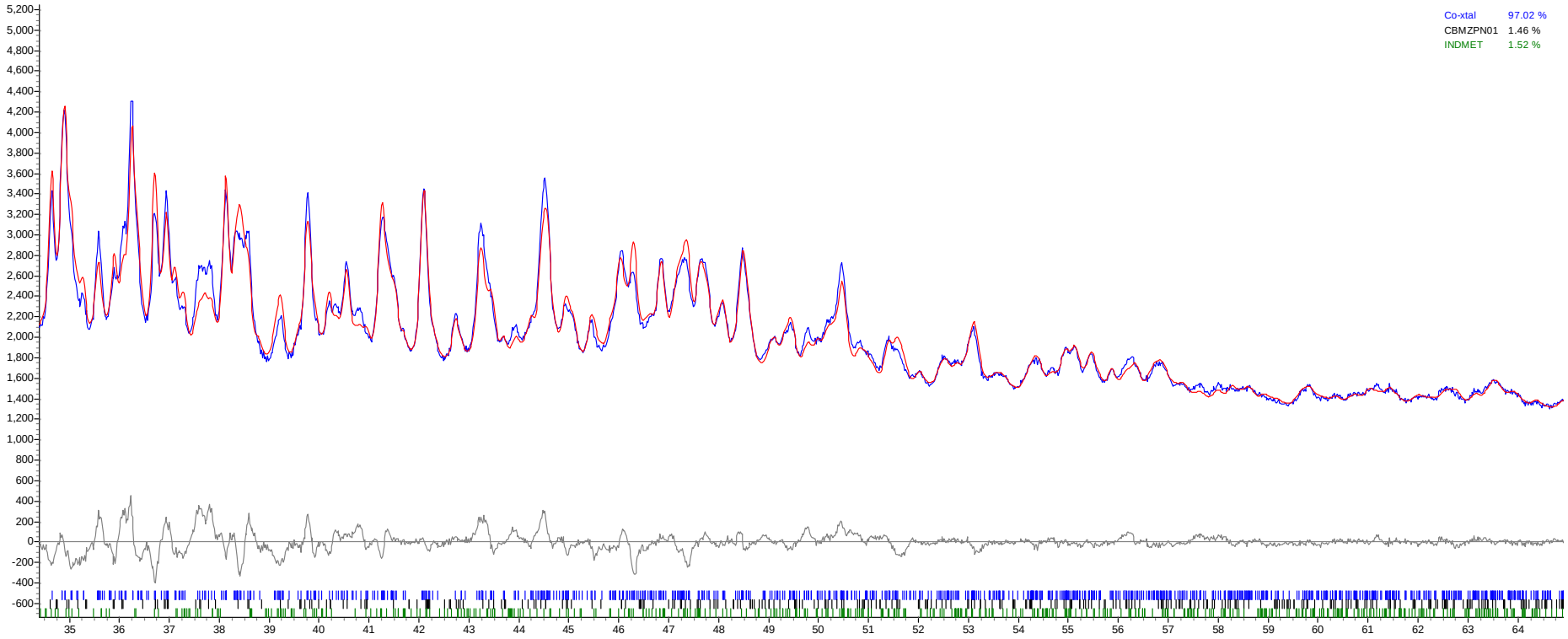


Profile plot of three phase Rietveld fit to the CBZ:IND diffraction data - low angle range



Electronic Supplementary Material (ESI) for CrystEngComm

Profile plot of three phase Rietveld fit to the CBZ:IND diffraction data - high angle range



Solid state calculations

The DASH crystal structure of $C_{15}H_{12}N_2O$:$C_{19}H_{16}ClNO_4$ was optimized in the program MOPAC2009, [1] running on a PC equipped with 2.4GHz Intel Core2 Quad CPU and 4Gb memory, using PM6 parameterization.[2,3]

The input cluster of molecules (a packed unit cell of the experimental crystal structure, with H-atoms normalized, 284 atoms total) was created in Mercury[4] and the first atom in the resultant Cartesian coordinate listing was placed at the origin (all other atom positions adjusted accordingly). Translation vectors were applied[5] and the crystal structure geometry optimized using the eigenvector following routine, without the use of symmetry, allowing (*x*,*y*,*z*) of all 284 atoms, plus the lattice parameters, to optimize. The calculation was set to terminate when the gradient norm reached a value < 5 kcal mol^{-1} $Å^{-1}$ (the default) and ran to completion in 210 minutes [enthalpy of formation in the solid state, ΔH_f (solid) = -129.4 kcal mol^{-1}]. The output file was visualized using Mercury and showed a good correspondence with the experimental crystal structure, as evidenced by:

(i) small lattice parameter differences (Exp. – PM6): Δa = 0.215, Δb = -0.070, Δc = 0.318 Å; $\Delta\alpha$ = 0.03 , $\Delta\beta$ = 0.81, $\Delta\gamma$ = -0.34°; ΔV = +132.58 $Å^3$ ≈ -4.5%;

(ii) RMSD = 0.255 Å for a 15 molecule overlay of the experimental and PM6 crystal structures.

References

[1] J. J. P. Stewart, MOPAC2009, Stewart Computational Chemistry, Colorado Springs, CO, USA, http://OpenMOPAC.net.

[2] J. J. P. Stewart, Optimization of parameters for semiempirical methods V: modification of NDDO approximations and application to 70 elements, *J. Mol. Model*. **13**, 1173-1213, 2007.

[3] J. J. P. Stewart, Application of the PM6 method to modeling the solid state, *J. Mol. Model*. **14**, 499-535, 2008.

[4] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures, *J. Appl. Cryst.*, **41**, 466-470, 2008.

[5] C. Giacovazzo et al., Transformation from triclinic to orthonormal axes in Fundamentals of Crystallography 2nd ed., Oxford University Press, p74 – 76, 2002.

Differential scanning calorimetry (DSC) Thermal analyses were performed using a Jade DSC (Perkin Elmer, USA), calibrated for T and H using indium. Samples were weighed (3-5mg), crimped in non-hermetic aluminium pan and scanned at 10 ^{o}C/min from 25 ^{o}C to 300^{o}C under continuously purged dry nitrogen (flow = 20ml/min). The instrument was equipped with a refrigerated cooling system. Data were collected and analysed using Pyris software.

Thermogravimetric analysis (TGA) The change in % of weight upon heating of the samples was performed using STA 6000 thermogravimetric analyser (Perkin Elmer, USA). Samples (~ 12mg) were placed onto a TGA crucible pan and scanned at 10^{o}C/min from 25^{o}C to 300^{o}C under continuously purged dry nitrogen (flow rate of 20ml/min). Data were collected and analysed using Pyris software.

Results Thermal analysis data showed an onset of melting at ~ 144^{o}C and enthalpy (ΔH) of ~ 95 J/g for CBZ:IND (1:1) co-crystals using DSC; no noticeable weight loss was observed before melting to support any hydrate mass equivalent loss upon heating using TGA.

DSC and TGA of CBZ, IND and CBZ-IND (1:1) co-crystal