Solution stoichiometry determines crystal stoichiometry in halogen-bonded supramolecular complexes†

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† Electronic Supplementary Information (ESI) available: Experimental procedures, IR and DSC characterization, CIFs for **3a,b**.
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Experimental Section

Reagents. Methylisonicotinate (MINC, **1**) was used as purchased from Aldrich (98% pure), without any further purification; 1,4-diiodotetrafluorobenzene (DITFB, **2**) was used as purchased from Apollo Scientific Ltd. (98% pure), without any further purification. HPLC grade solvents were used for the crystallization methods.

Supramolecular synthesis. 1:1 DITFB to MINC ratio compound (**3a**). 83 mg of DITFB and 28 mg of MINC (about 1:1 ratio) where dissolved in methanol: the solvent was allowed to slowly evaporate until dryness. At this point the product was obtained in crystalline form, suitable for single-crystal x-ray structure determination. The product was dried *in vacuo* overnight for further analysis. 1:2 DITFB to MINC ratio compound (**3b**). 80 mg of DITFB and 268 mg of MINC (about 1:20 ratio) where dissolved in methanol: the solvent was allowed to slowly evaporate from the resulting solution, until the product was obtained in crystalline form, suitable for single-crystal x-ray structure determination. The crystals were then mechanically separated, washed with water and dried *in vacuo* overnight for further analysis.

Crystallography, single-crystal diffraction. For both the products **3a,b** X-ray single-crystal data collection was performed on a BRUKER-NONIUS KAPPACCD diffractometer, geared with graphite-monochromated Mo Kα radiation (λ=0.71073 Å) and provided of an APEXII area detector and an OXFORD CRYOSTREAM cryogenic device. Data collection: COLLECT. Cell refinement and data reduction: EVALCCD. Absorption corrections: SADABS. Structure solution and refinement SHELXTL.

Crystallography, powder diffraction. X-ray powder diffraction data collection was performed on a Huber G670 imaging-plate Guinier camera, geared with pure line-focused Cu$K\alpha_1$ radiation (λ=1.5406 Å). The measurements were carried out in Guinier-type transmission geometry with 45° angle between the incident beam and the sample normal. The hand-ground samples were prepared on a paraffine-

coated Mylar foil of 3.5 μm thickness. Simulated powder patterns were calculated from the single-crystal diffraction data, using Diamond 3.0a[1].

General analysis. DSC measurements were carried out using 50 μl sealed aluminium sample pans with pinholes. The temperature calibration was carried out using three standard materials (*n*-decane, In, Zn) and the energy calibration using In standard. The samples were heated under nitrogen (flow rate of 50 ml/min) at the rate of 10°C/min from −50 C, up to the boiling point. IR measurements were performed on KBr tablets (DITFB) or on thin liquid film supported on NaCl (MINC), using a Perkin-Elmer System 2000 FT-IR.

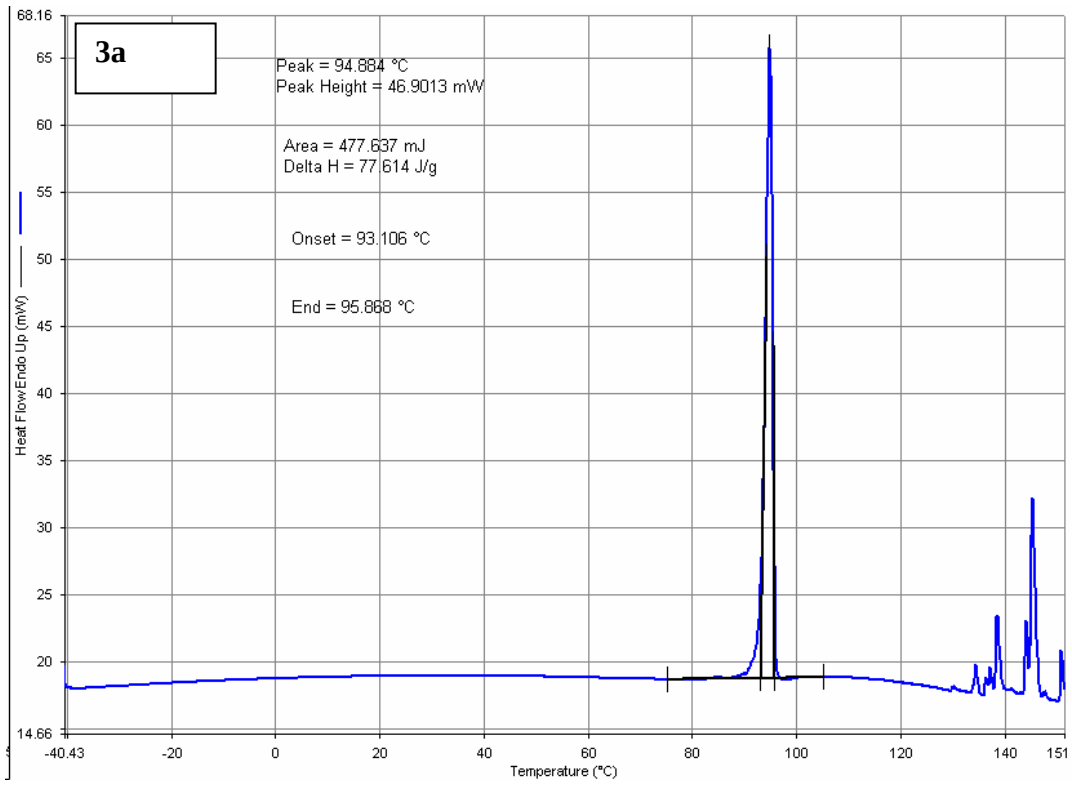
Crystal data and structure refinement for 3a.

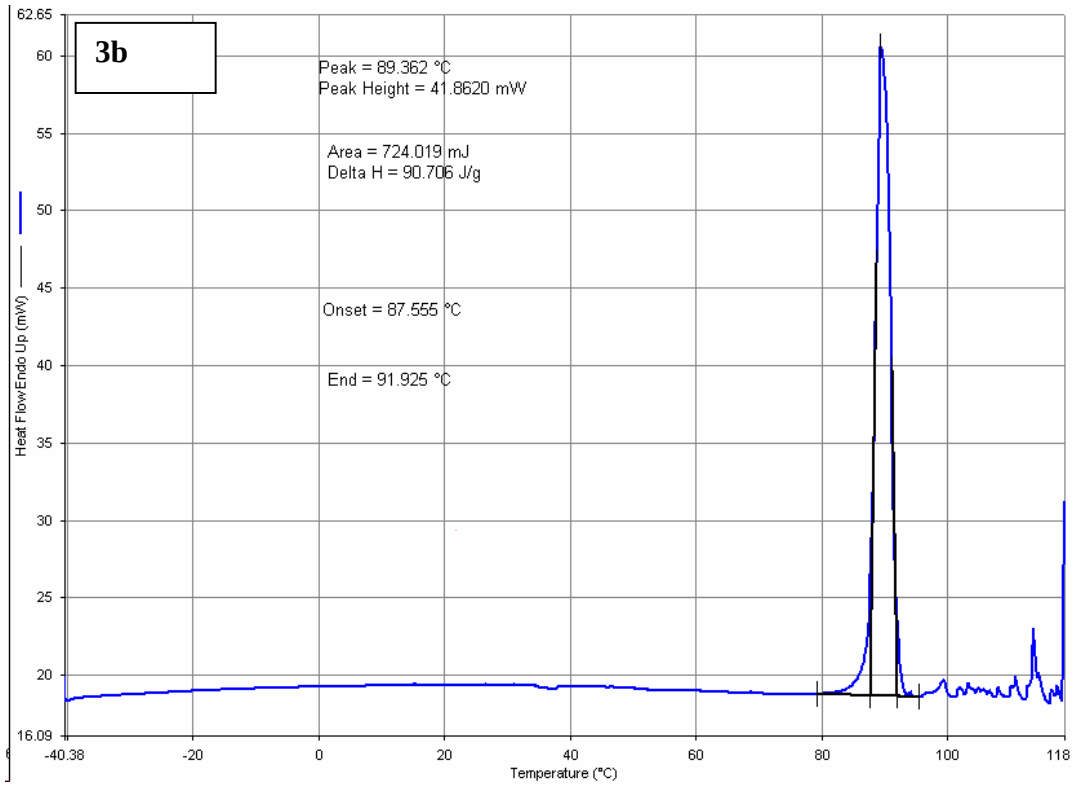
Chemical formula (moiety)	$C_6F_4I_2 \cdot C_7H_7O_2N$	
Chemical formula (total)	$C_{13}H_7F_4I_2NO_2$	
Formula weight	539.00	
Temperature	173(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 6.4055(13) Å	α = 78.22(3)°
	b = 9.589(2) Å	β = 86.37(3)°
	c = 13.479(5) Å	γ = 73.407(15)°
Cell volume	776.7(4) $Å^3$	
Z	2	
Calculated density	2.305 g/cm^3	
Absorption coefficient μ	4.095 mm^{-1}	
F(000)	500	
Crystal colour and size	colourless, 0.60 × 0.05 × 0.05 mm^3	
Reflections for cell refinement	2428 (θ range 2.5 to 27.5°)	
Data collection method	Nonius KappaCCD diffractometer	
	ϕ and ω scans	
θ range for data collection	3.3 to 27.6°	
Index ranges	h −8 to 7, k −12 to 12, l −17 to 17	
Completeness to θ = 27.6°	98.7 %	
Reflections collected	11047	
Independent reflections	3558 (R_{int} = 0.0284)	
Reflections with $F^2>2\sigma$	2970	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.1925 and 0.8214	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0121, 0.1306	
Data / restraints / parameters	3558 / 0 / 199	
Final R indices [$F^2>2\sigma$]	R1 = 0.0270, wR2 = 0.0415	
R indices (all data)	R1 = 0.0385, wR2 = 0.0459	
Goodness-of-fit on F^2	1.118	
Largest and mean shift/su	0.002 and 0.000	
Largest diff. peak and hole	0.46 and −0.60 e $Å^{-3}$	

Crystal data and structure refinement for 3b.

Chemical formula (moiety)	$2C_7H_7O_2N \cdot C_6F_4I_2$	
Chemical formula (total)	$C_{20}H_{14}F_4I_2N_2O_4$	
Formula weight	676.13	
Temperature	173(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 4.1581(4) Å	α = 91.102(11)°
	b = 10.7974(8) Å	β = 97.913(12)°
	c = 12.7958(19) Å	γ = 90.912(8)°
Cell volume	568.81(11) $Å^3$	
Z	1	
Calculated density	1.974 g/cm^3	
Absorption coefficient μ	2.826 mm^{-1}	
F(000)	322	
Crystal colour and size	colourless, 0.60 × 0.30 × 0.15 mm^3	
Reflections for cell refinement	2343 (θ range 2.5 to 27.5°)	
Data collection method	Nonius KappaCCD diffractometer	
	ϕ and ω scans	
θ range for data collection	5.2 to 27.6°	
Index ranges	h –4 to 5, k –13 to 13, l –15 to 16	
Completeness to θ = 27.6°	83.9 %	
Reflections collected	6768	
Independent reflections	2217 (R_{int} = 0.0279)	
Reflections with $F^2>2\sigma$	2038	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.2819 and 0.6765	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0000, 0.3199	
Data / restraints / parameters	2217 / 0 / 145	
Final R indices [$F^2>2\sigma$]	R1 = 0.0179, wR2 = 0.0384	
R indices (all data)	R1 = 0.0245, wR2 = 0.0427	
Goodness-of-fit on F^2	1.167	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.53 and –0.51 e $Å^{-3}$	

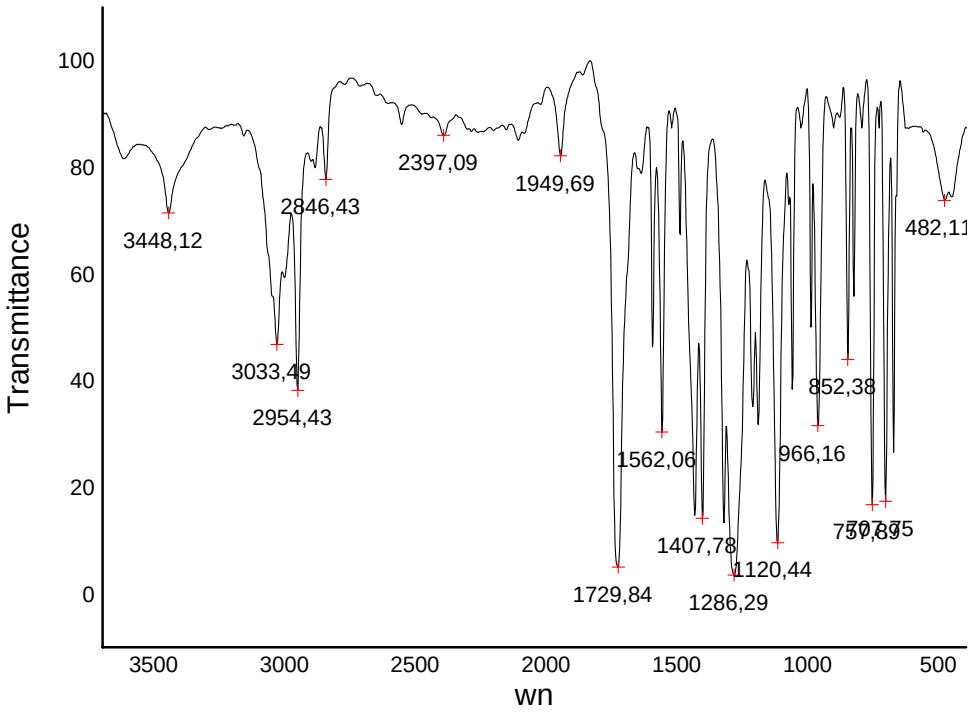
DSC data.


3a
Peak = 94.884 °C
Peak Height = 46.9013 mW
Area = 477.637 mJ
Delta H = 77.614 J/g
Onset = 93.106 °C
End = 95.868 °C
Heat Flow Endo Up (mW)
Temperature (°C)
68.16
65
60
55
50
45
40
35
30
25
20
14.66
-40.43
-20
0
20
40
60
80
100
120
140
151


3b
Peak = 89.362 °C
Peak Height = 41.8620 mW
Area = 724.019 mJ
Delta H = 90.706 J/g
Onset = 87.555 °C
End = 91.925 °C
Heat Flow Endo Up (mW)
Temperature (°C)
62.65
60
55
50
45
40
35
30
25
20
16.09
-40.38
-20
0
20
40
60
80
100
118

IR data.

1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2000
1500
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500
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2846,43
2397,09
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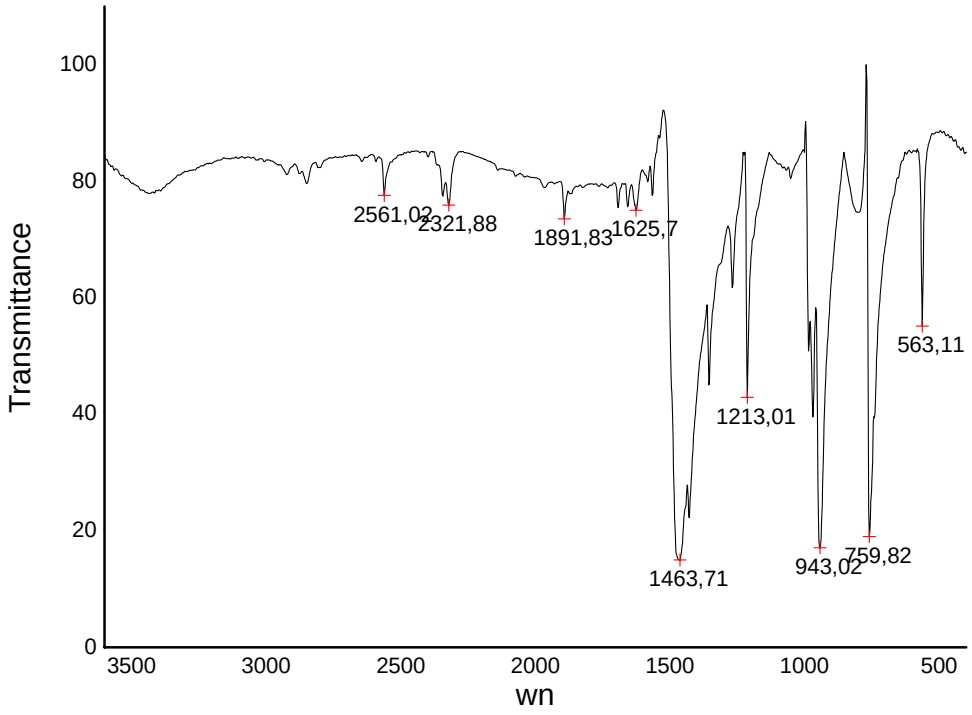
1729,84
1562,06
1407,78
1286,29
1120,44
966,16
852,38
482,11

2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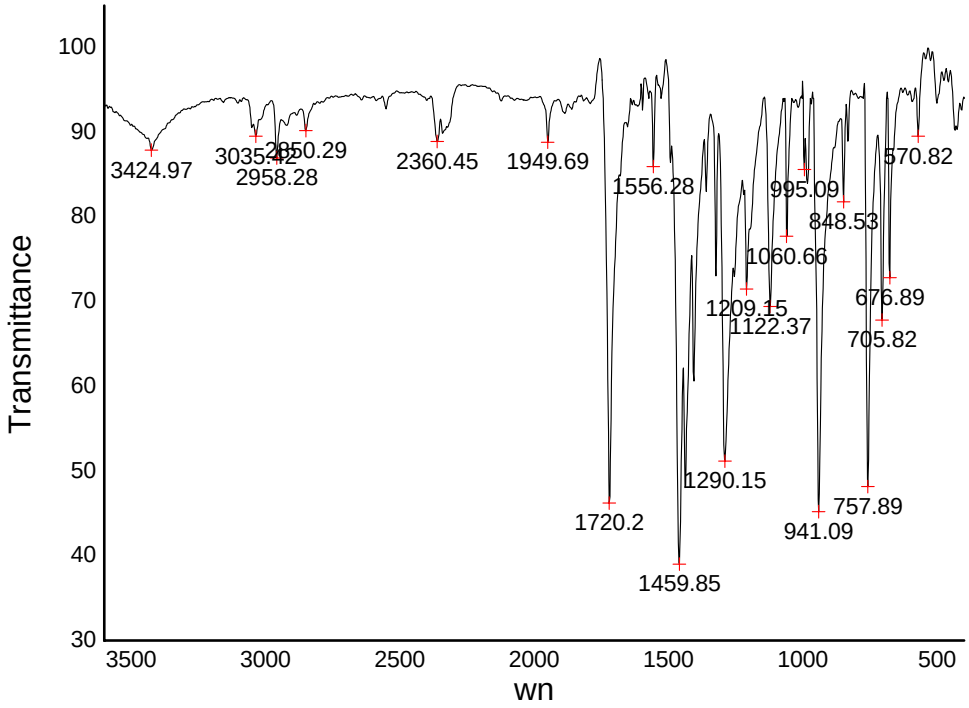
1625,7
1463,71
1213,01
943,02
759,82
563,11

3a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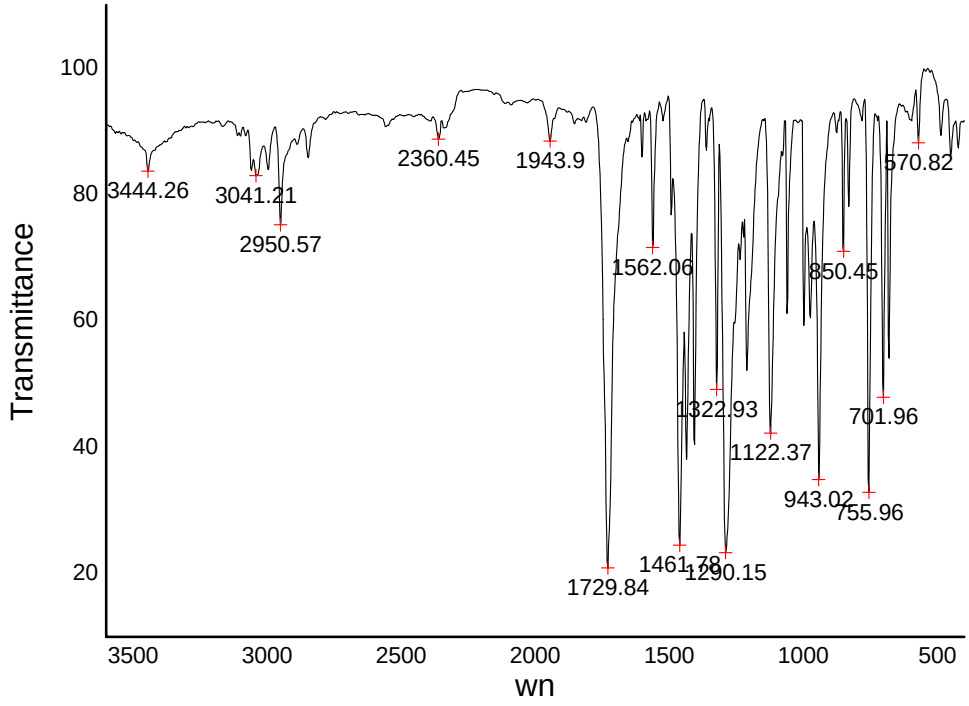
3035.42
2958.28
2850.29
2360.45
1949.69
1556.28
995.09
848.53
1060.66
1209.15
1122.37
676.89
705.82
570.82
1290.15
1720.2
1459.85
941.09
757.89

3b


Transmittance
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3500
3000
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2000
1500
1000
500
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2360.45
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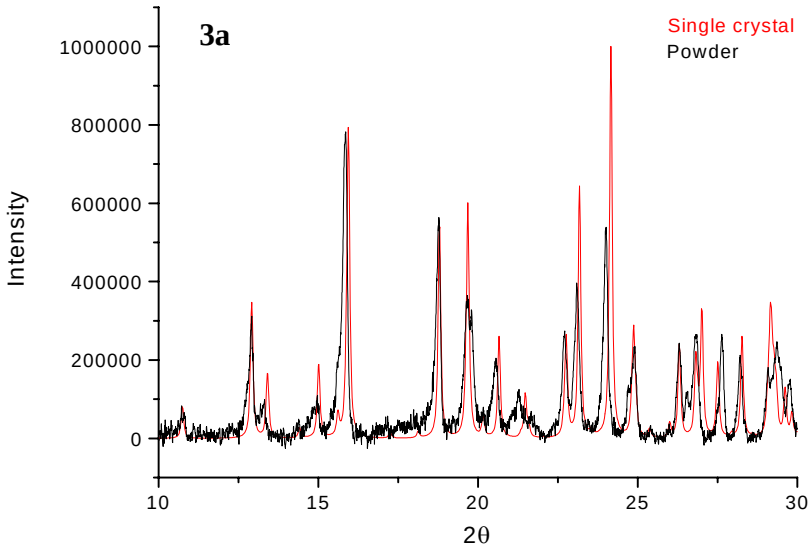
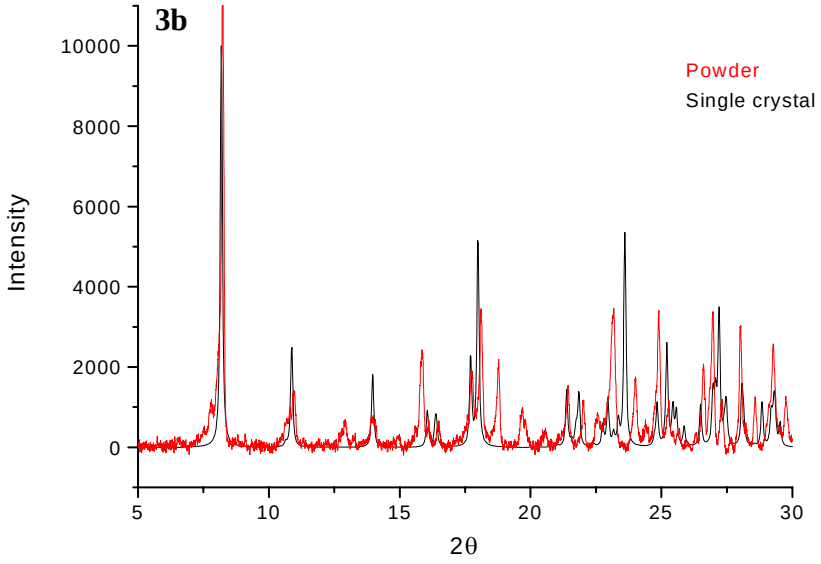
1562.06
850.45
570.82
1322.93
1122.37
701.96
943.02
755.96
1461.79
1290.15
1729.84

Powder X-ray diffraction data.





[1] Brandenburg, K. *DIAMOND 3.0a*; Crystal Impact GbR, Bonn, Germany.