Supplementary Material for:

New findings on crystal polymorphism of imepitoin

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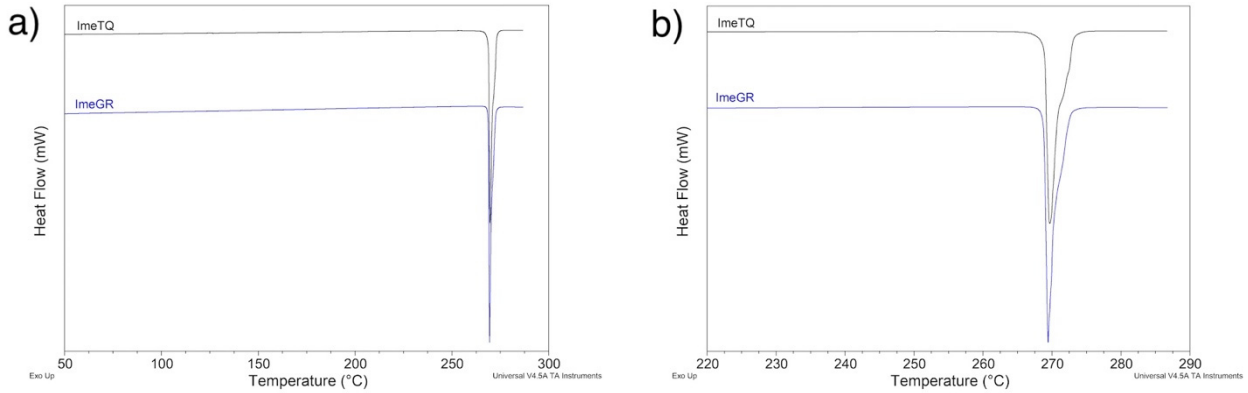


Figure S1- DSC curves of *ImeTQ* and *ImeGR* at 10 K min^{-1}: a) temperature scale from 50 °C to 300 °C; b) the same DSC curves with the temperature scale expanded (from 220 °C to 290 °C).

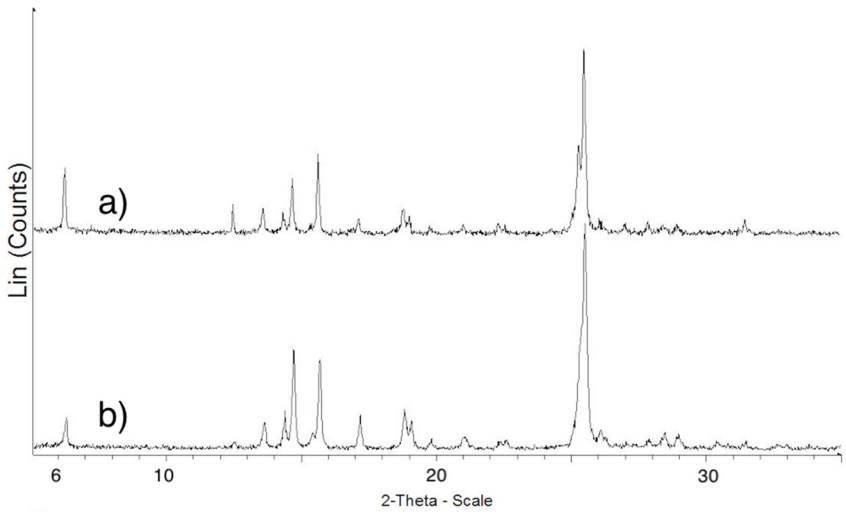
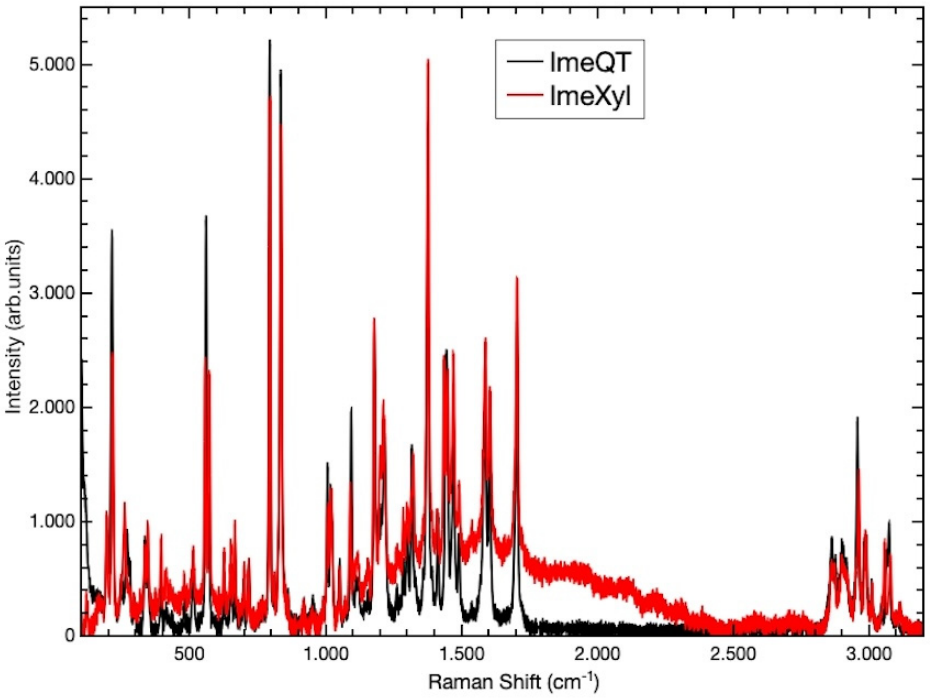
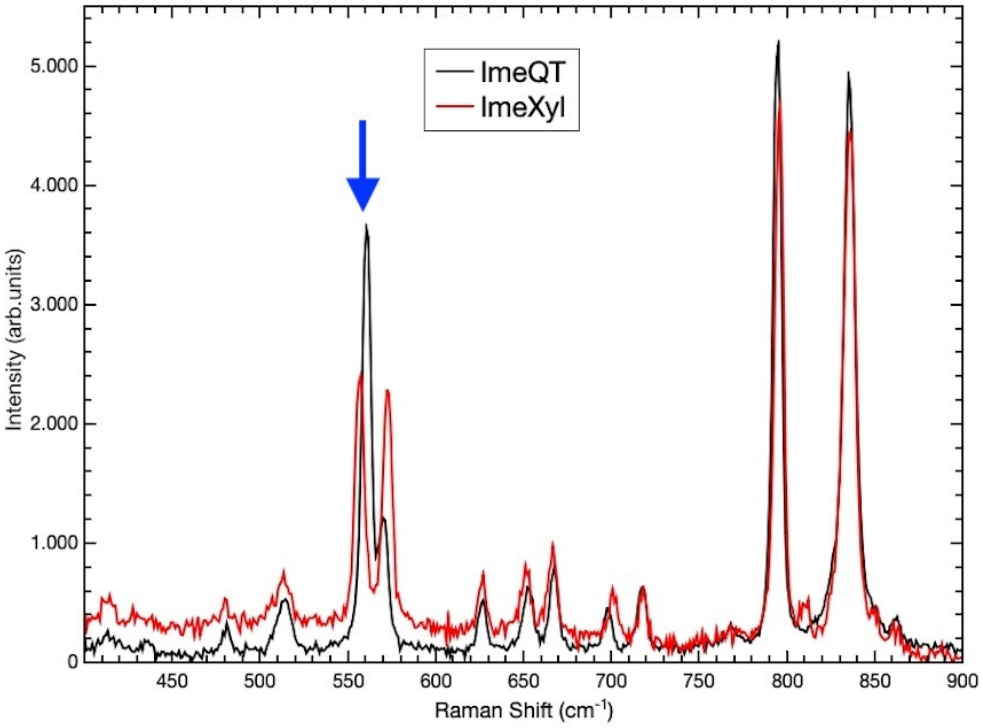


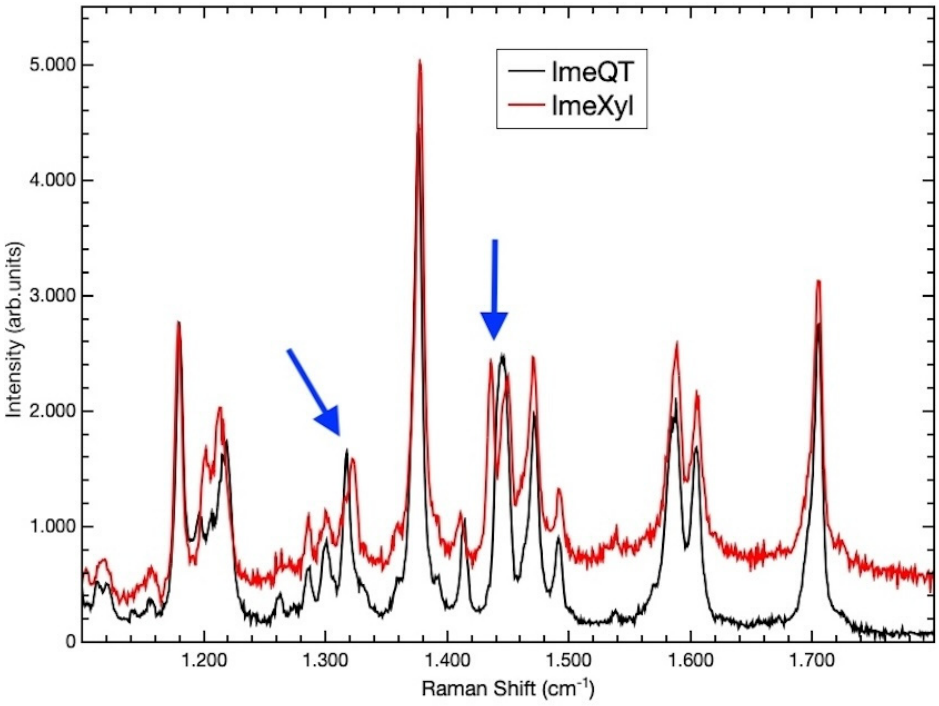
Figure S2 – XRPD patterns of *ImeTQ* (a) and *ImeGR* (b).


ImeQT
ImeXyl
Intensity (arb.units)
Raman Shift (cm-1)
0
1.000
2.000
3.000
4.000
5.000
500
1.000
1.500
2.000
2.500
3.000

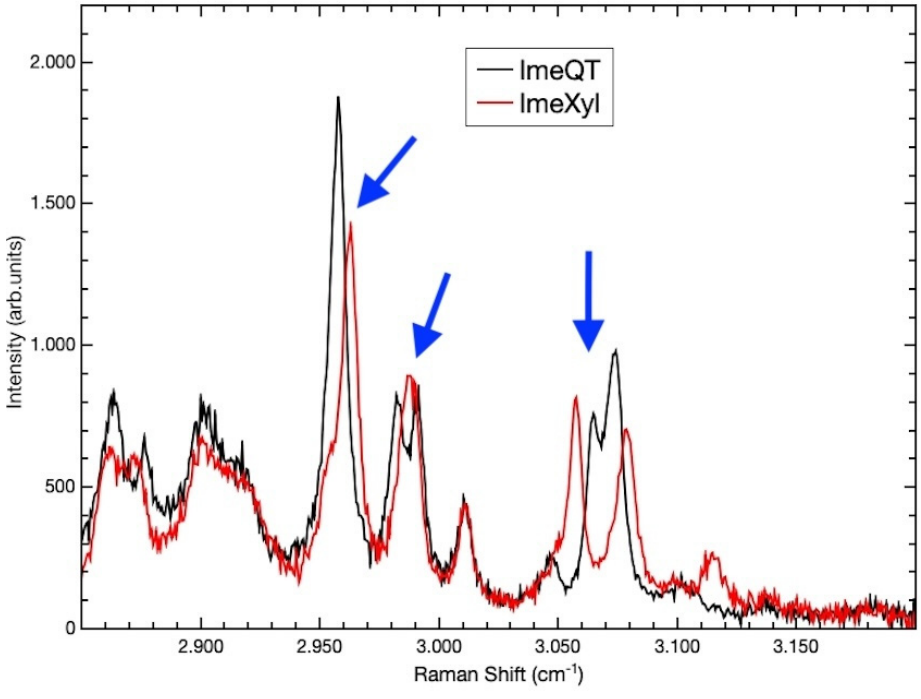
(**a**)


ImeQT
ImeXyl
Intensity (arb.units)
Raman Shift (cm-1)
0
1.000
2.000
3.000
4.000
5.000
450
500
550
600
650
700
750
800
850
900

(**b**)



(c)



(d)

Figure S3 - a) The whole Raman spectra for *ImeTQ* (black line) and *ImeXyl* (red line). The enlarged spectra in the energy regions; b) between 400 and 900 cm^{-1}, c) 1100-1800 cm^{-1} and d) 2850-3100 cm^{-1}. The arrows indicate the main observed spectral changes.

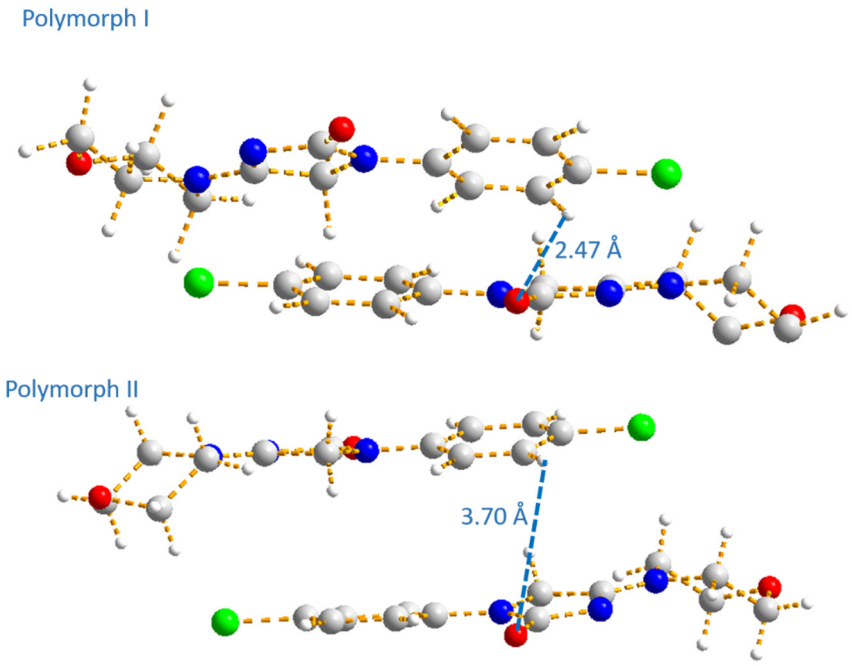


Figure S4 - H1···O1 distances in Polymorph I and Polymorph II.

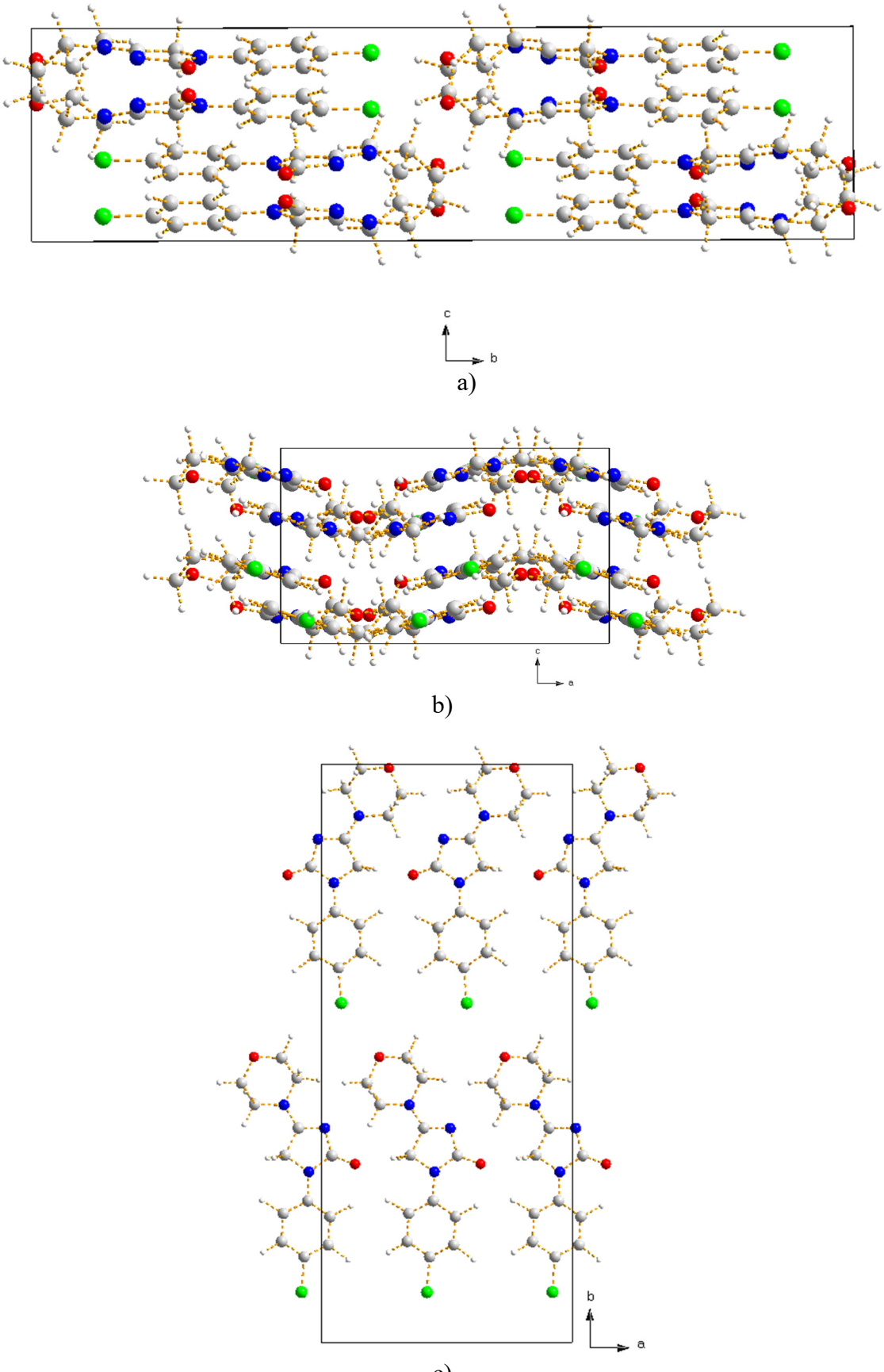


Figure S5 - Imepitoin polymorph I crystal structure viewed down a) *a*-, b) *b*- and c) *c*-axes.

Table S1 - X-ray Crystallographic Data Collection and Structure Refinement for imepitoin polymorph II.

Crystal data	**Imepitoin Polymorph II**
Chemical formula	$C_{13}H_{14}ClN_3O_2$
Formula weight (g/mol)	279.72
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature (K)	298
Cell parameters (Å,°)	a = 14.8687(6) b = 7.2434(2) c = 12.5592(4) β = 107.5586(8)
Volume (Å^3)	1289.61(8)
Z	4
Z′	1
Radiation type	Synchrotron radiation, λ = 0.35418 Å
Data collection	
Beamline	ID22@ESRF
Specimen mounting	borosilicate capillary
Data collection mode	transmission
2θ (°)	$2\theta_{min}$ = 0.00 $2\theta_{max}$ = 36.00
Structure solution	
Methods	Direct methods, simulated annealing (SA)
Parameters (SA)	6+2 DOF, 19 non-hydrogen atoms
Cost function (SA) Building the starting model (SA) Geometry optimization (SA)	R_{wp} = 17.251 ACD/ChemSketch [1] MOPAC2016 [2]
Refinement	
R_p	5.447
R_{wp}	8.104
R_{exp}	6.246
R_{Bragg}	6.576

χ^2	1.277
No. of data points	9750
No. of reflections	1169
Profile function	Pearson VII
Refinement parameters	
Lattice	4
Positional	57
ADP	3
Profile	10
Background	19
Zero error	1
Restraints	50
H-atom treatment	H-atom parameters constrained
Programs	
Indexing	*TOPAS4.2* [3]
Space group determination	EXPO [4]
Structure solution and refinement	EXPO [4]
Model building	Diamond (version3.0)

Table S2 – Comparison of H···A and C···A distances (Å) for the two polymorphic forms. The polymorph I data are taken from table 1 reported by Kaduk et al [5].

	Polymorph II		**Polymorph I**	
H-Bond	**H···A (Å)**	**C···A (Å)**	**H···A (Å)**	**C···A (Å)**
C8-H4···O1	2.34	3.24	2.13	3.20
C13-H14···O1	2.24*	2.87	2.18	2.90
C1-H1···O1	3.70	3.74	2.47	3.23
C12-H12···O1	2.78	3.71	2.66	3.69
C10-H8···O2	2.70	3.49	2.57	2.48
C11-H11···N3	2.41*	2.83*	2.38*	2.85*
C9-H6···Cl1	3.25	4.24	3.06	4.00

[1] ACD/ChemSketch, Advanced Chemistry Development, Inc.: Toronto, ON, Canada, 2003.
[2] MOPAC2016, Version 18.305L, in: J. J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA. http://OpenMOPAC.net/.
[3] *TOPAS4.2*; Bruker: Karlsruhe, Germany, 2009.
[4] Altomare, A.; Cuocci, C.; Giacovazzo, C.; Moliterni, A.; Rizzi, R.; Corriero, N.; Falcicchio, A. EXPO2013: a kit of tools for phasing crystal structures from powder data. *J. Appl. Cryst*. **2013**, *46*, 1231–1235.
[5] Kaduk, J.A.; Gindhart, A.M.; Gates-Rector, S.; Blanton, T.N. Crystal structure of imepitoin, $C_{13}H_{14}ClN_3O_2$. *Powder Diffr*. **2022**, *37*, 206-2010.