Electronic Supplementary Information†

Crystallization

Sublimed crystals **1**s: The purified host compound **1** after column chromatography (ref. 4) was taken in a sublimation apparatus at 0.2 Torr and heated to 150 °C for 2 h. Plate and needle shaped crystals suitable for single crystal X-ray diffraction deposited on the cold finger (ice-water circulation). Unit cells of a few good crystals were checked to find out the polymorphic form.

Melt crystals **1**m: Compound **1** was heated to 190 °C in a thick-walled test-tube (oil-bath heating). The test-tube was taken out of the oil bath and its outer surface was washed with *n*-hexane to rapidly cool the melt fluid. Singe crystals of block and plate morphology were obtained. Unit cells of a few good crystals were checked to find out the polymorphic form.

Table S1 Unit cell checking (at 100 K) on different single crystals from melt crystallization and sublimed batches.

Melt phase batches, **1**m

Crystal No.	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	Crystal size (mm^3)
1	9.6278	20.9561	28.0324	5655.85	0.09 x 0.28 x 0.34
2	9.636	20.9802	28.0423	5655.72	0.23 x 0.28 x 0.17
3	9.6263	20.9539	28.039	5669.21	0.22 x 0.18 x 0.16
4	9.8248	20.9166	28.6473	5885.29	0.20 x 0.09 x 0.18
5	9.629	20.942	28.048	5655.01	0.12 x 0.14 x 0.12
6	9.632	20.943	28.046	5654.88	0.16 x 0.14 x 0.09

Sublimation batches, **1**s

Crystal No.	*a* (Å)	*b* (Å)	*c* (Å)	α (º)	β (º)	γ (º)	*V* (Å^3)	Crystal size (mm^3)
1 298 K	6.3011	10.9056	11.4685	101.779	103.04	103.009	718.89	0.26 x 0.11 x 0.08
2	6.2267	10.8477	11.3352	101.609	103.425	103.113	698.76	0.13 x 0.20 x 0.22
3	6.2346	10.8767	11.3498	101.6263	103.3257	103.1919	702.445	0.08 x 0.06 x 0.26
4	6.2700	10.8850	11.3842	101.5923	103.3421	103.1402	704.982	0.04 x 0.06 x 0.21

Additional figures

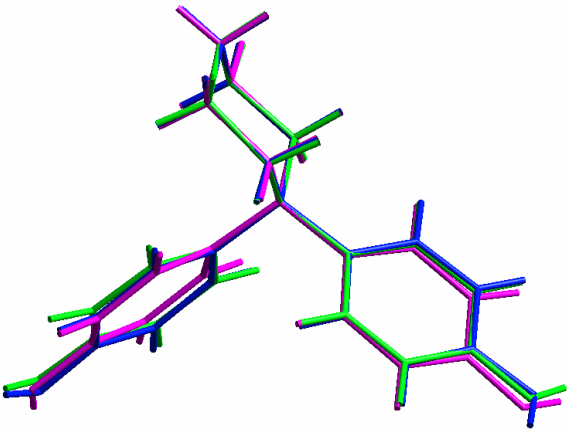


Fig. S1 Molecular overlay of **1**. **1**s = magenta, A (**1**m) = blue, B (**1**m) = green. OH groups are *syn* in conformer **1**s and A (**1**m) and *anti* in B (**1**m).

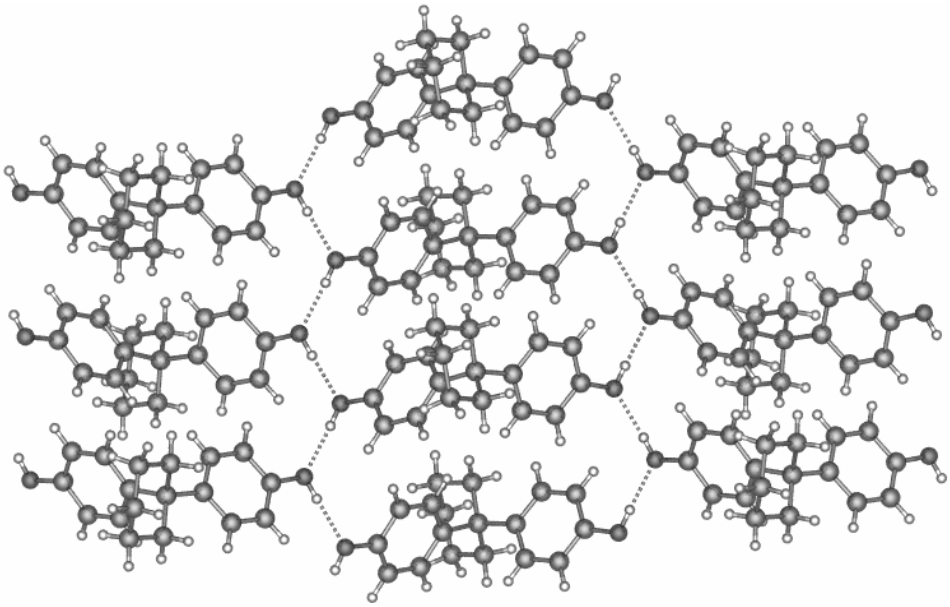


Fig. S2 Cooperative O–H···O bonds along [100] in the ladder network of B molecules in orthorhombic polymorph **1**m. Symmetry-independent A molecules are not shown for clarity.

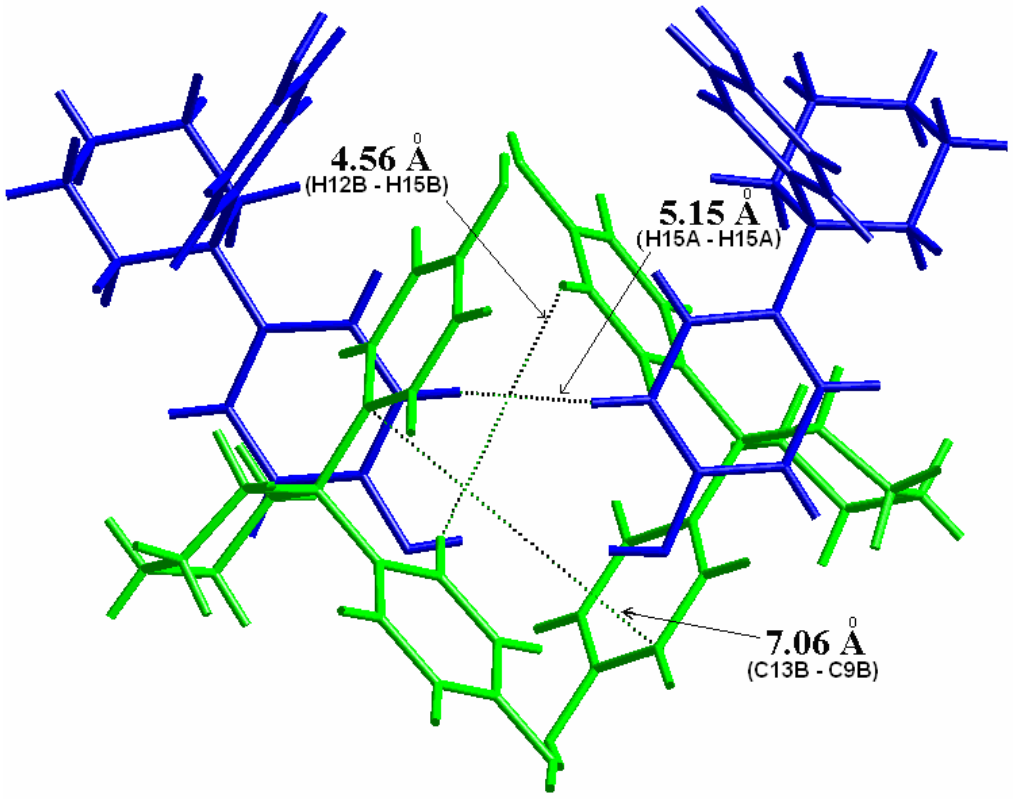
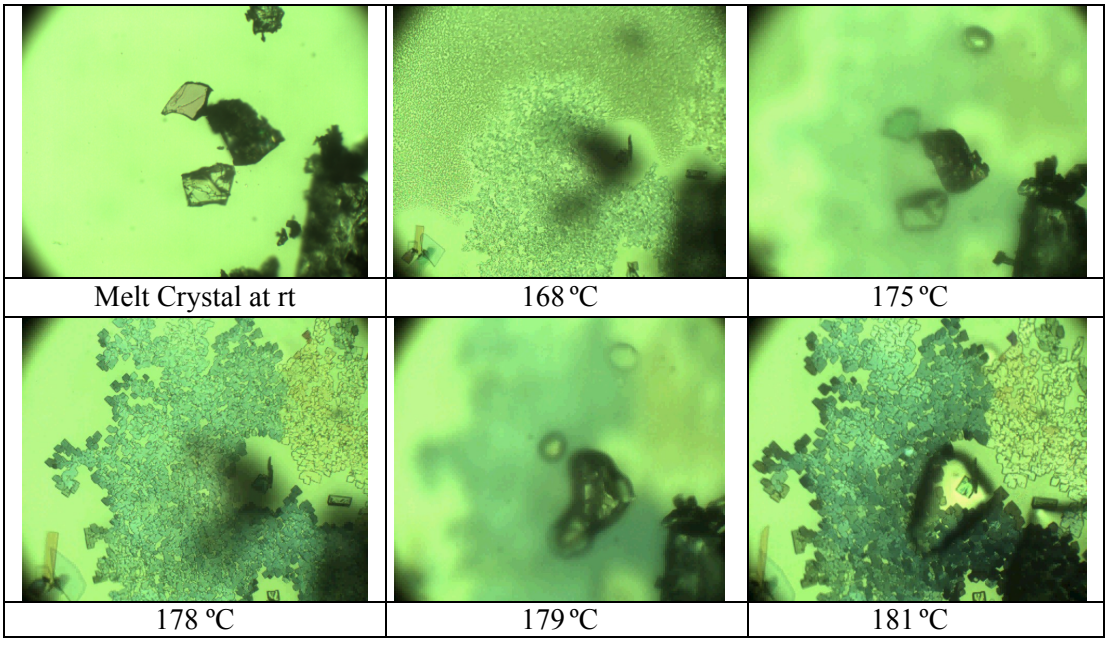
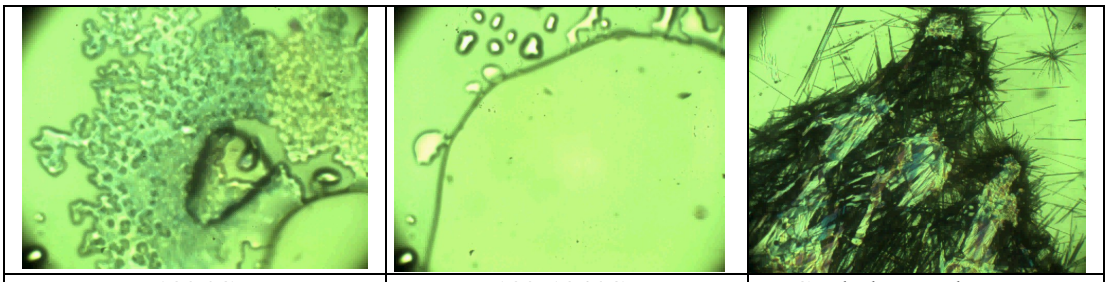


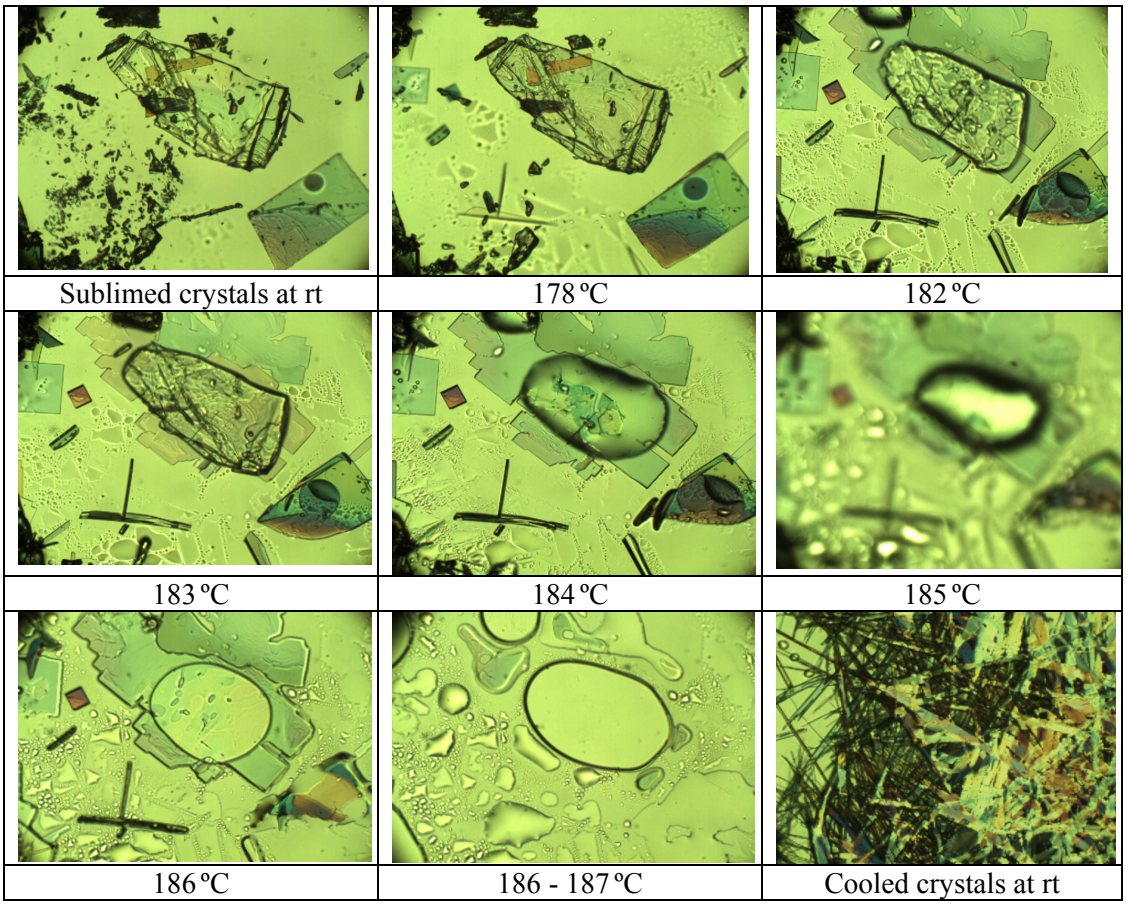
Fig. S3 The available pore dimensions in **1**m are 3.66 Å (= 7.06 – 3.40 Å), 2.26 Å (= 4.66 – 2.40 Å) and 2.75 Å (= 5.15 – 2.40 Å). Symmetry independent A (blue) and B (green) molecules are color-coded.





182 ºC	183-184 ºC	Cooled crystals at rt

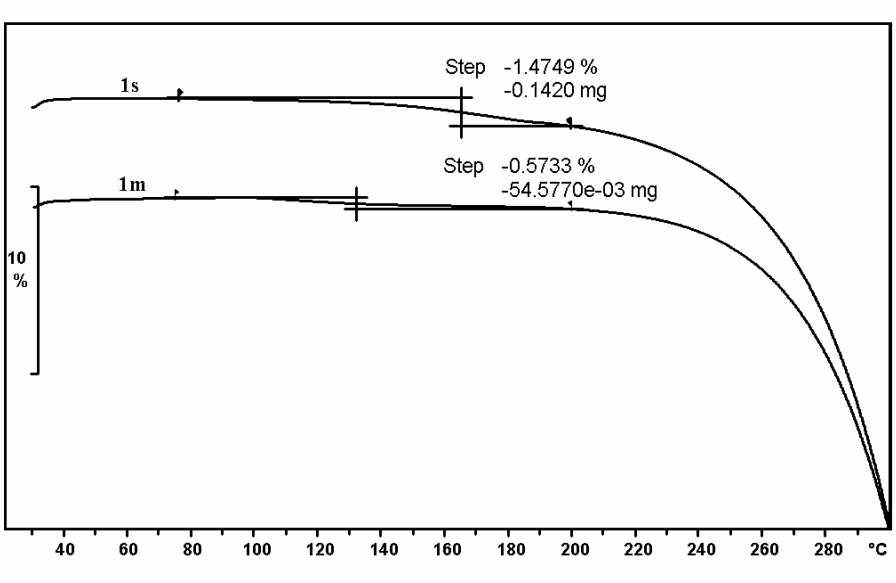
(a)



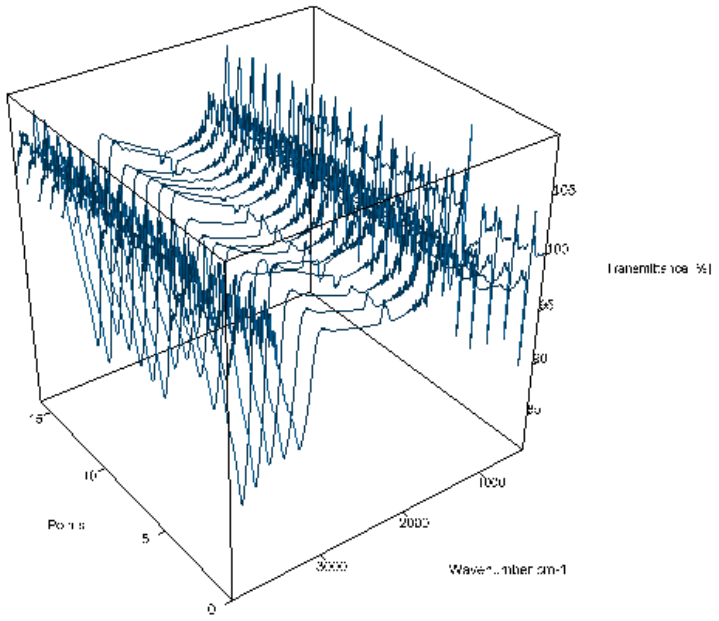
Sublimed crystals at rt	178 ºC	182 ºC
183 ºC	184 ºC	185 ºC
186 ºC	186 - 187 ºC	Cooled crystals at rt

(b)

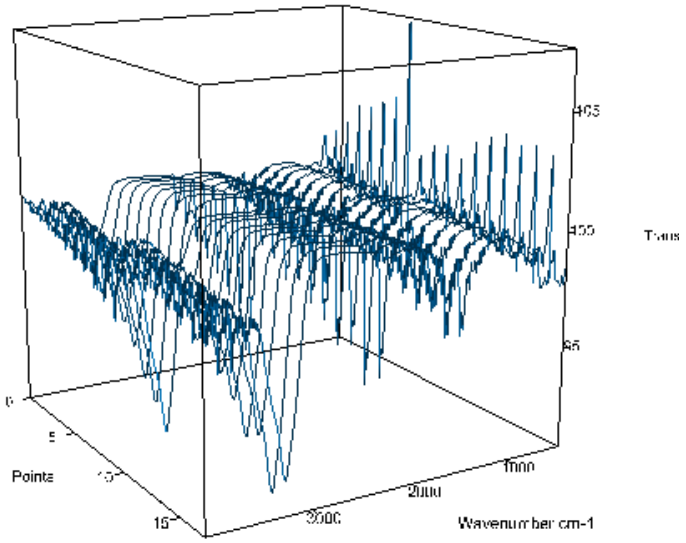
Fig. S4 HSM snaps at different temperatures. (a) The block morphology crystal of **1**m transforms to needle-like fibers of **1**s after a heat–cool cycle. (b) The plate morphology of **1**s becomes needle-like after heat–cool cycle but there is no change in the crystalline form. The sublimation content (droplet size) is larger in **1**s compared to **1**m.


Step -1.4749 %
-0.1420 mg
1s
Step -0.5733 %
-54.5770e-03 mg
1m
10
%
40 60 80 100 120 140 160 180 200 220 240 260 280 °C

(a)



(b)



(c)

Fig. S5 Thermal gravimetric analysis and infrared spectroscopy of the evolved vapor. (a) TGA, (a) IR of **1**s, and (b) IR of **1**m polymorph. 8-12 mg of the sample was heated at 10 ºC/min and dry N_2 gas purged at 100 mL/min. The evolved vapor from TGA was passed through a heated transfer line at 100 ºC and IR recorded using DlaTGS detector. The up peaks in the spectrum are due to incomplete cancellation of background air. TG–IR was recently used by us[1] to characterize the sublimation phenomenon in polymorphs. Sublimation is known to occur even when there is marginal to nil weight loss in TGA,[2] as observed in (a).

1 S. Roy, S. Aitipamula and A. Nangia, *Cryst. Growth Des.*, 2005, **5**, 2268.
2 M. M. J. Lowes, M. R. Caira, A. P. Lötter and J. G. van der Watt, *J. Pharm. Sci.*, 1987, **76**, 744.

Cambridge Structural Database searches

CSD version 5.27, ConQuest 1.8, May 2006 update was used in all searches and crystal structures were visualized in Mercury 1.4.1. Organic crystal structures with the All Text phrase 'melt' and 'sublimation' were retrieved in separate searches. The saved hits were manually sorted to include those structures where 'from the melt' or 'sublimation' was mentioned in the Crystal Data field. The lower *R*-factor structure was retained for duplicate refcodes. *Z*' frequency for structures in the three categories were calculated as percentage of the total hits. The overall numbers in Table 1 (of paper) are taken to represent 'slow evaporation of solvent', the most common method of crystallization.

Table S2 Host–guest structures of **1** (31 hits, one duplicate is removed)

GANBUS	GANCAZ	GEFRIS	GEFROY	GEFRUE	GEFSAL
GIVYOZ	GIVZAM	GIVZEQ	HADJUS	JIDPUH	JIDRAP
NEZLUZ	NEZMAG	NONMIM	NONMOS	OFENUI	OFEPAQ
OFEPEU	OFEPIY	OFEPOE	OFEQIZ	OFEPUK	OFEQAR
OFEQEV	QENNIG	TABXUP	WAPTAI	ZEHFAT	ZEHDUL
LAPLIY					

Table S3 Crystals obtained by sublimation (334 hits, duplicate refcodes are removed)

ALEBOI	ALOCAF	ALOCEJ	ANTCEN17	ASEPUJ	ASOROP
AXEKUJ	AYIMUQ	AYOHIF	AYOHOL	AYOJAZ	AYOJED
AZOBAS	BAPJEH01	BATCAA	BATDIJ	BAVLOZ	BAXHOY
BAXHUE	BERGIP	BETHAZ01	BEWYUY01	BEZLUO	BEZPOM
BUZBAZ	BEZQAZ	BIPHDS01	BIBPEH	COWRIP	CUZDIK
CEJYUL	CEZQIH	CICYES01	CORRUW	COVMAB01	CUKBAL
CTCYME	DOQYUD	DITHAN01	DADLOK	DAVLIV	DCHLAN01
DEWGOB	DICNIM01	DICNUY01	EYISIO	ETYNBZ01	EBOBON
EBUKOB	EBUKUH	EBULAO	ECAKEY	EHAVUE	QAWVIU
ELASIT	ELATUG	EQOMUS	FUGJEW	FOMHAR	FACXOX
FADDUK	FAQFAF	FEGBID	FEHROA	FIBKUW02	FIMWOO
FIRLAU	FOHHOA	FOJTUU	FOJVAC	GOGXAB	GOGXOP
GIXXIU	GIYHUR01	GODTEY	HULSEM	HUYBUY	HAGBIB
HAKYOI	HANDIK	HEXWIQ01	HIPTOP	HIRREF	HIXMOQ
HIZYUK	HMHOCN01	HOFGEO	HOKHEU	HOYMEN	HUHVUB
IVETOS	IVETUY	IBOMUH	IBONAO	IBONES	IBONIW
IDEWUJ	IDUWEJ	IFULUQ	IFULUQ01	IFULUQ02	IFULUQ03
IHITOI	IHITUO	IKUWOA	IMIJUJ	IMIKAQ	IMIXAD
IRUYID	ITIJIE	ITOLEN02	IXASEF	JISPUW	JATFUF02
JURQUI	KACRUC01	KAPNAQ	KEDNEM	KABTAJ	KABTEN
KABVEP	KACRUC	LURMUG	LUKLIM	LUTDEJ	LAFMAH
LEQJIA	LURNER01	LIBJOV01	LODZIN	LOKJAW	LOKJEA
LOQLEI	LURNOB	MUMFOP	MAFSUL01	MALDEJ	MALDIN
MAPGIU	MASCOY	MEYNAF	MIHFAK	MIHFEO	MILMOJ
MIWGEE	MIWGII	MIWGOO	MIWGUU	MIWHAB	MIWHEF
MORYEX	MUBZOY	MUBZUE	MUDCAP	NUNKUC	NACLOT
NACMEK	NAPOIM01	NECNIS	NECZUQ	NEDNEP	NEKZEI
NELBAH	NEPGCL01	NIGZUY	NIHBAH	NIMREG	NIWXOG01
NOLDIB	NOLFUP	NOLFUP01	NOLJON	NOSQUH01	QAVWEQ
OMOPAH	OBIZEE	OFUWAN	OGEMOC	OGIREB	OHIXUY
OHIYAF	PUYWUB	PAGRIZ	PALXEG	PALXIK	PALXOQ
PANCOX	PAZKUW	PENCEN03	PFPHSE01	PIPROV	POVDOT
POYXAC	POYXEG	PUBHEZ	PUCMIJ	PUCMIJ01	PUHMOU
PUTGIU	PUVNEZ	PUYHOG	QUDWUH	QACYIC	QAHZIJ
QAHZOP	QAZQAJ	QEGJUH	QUPMUJ	QEZROC01	QICPOH
QIGBEN04	QIQXIX	QIQXUJ	QIQYAQ	QIXWAV	QIYJUD
QOQSIY	QOTGOV02	SUWMIG02	SUWMIG03	SABZAX	SAGMOD
SALNAU	SANGIY	SAQZOY	SEDNAQ	SERQUB01	SOBFEU
SUWGEW	TIFFAP	TDCHCH02	TAGNEV	TAGNIZ	UMASIK
UMASEG	UGUYOK	UHAPIC	UHENEA	UHUZUS	UKUPAR
UKUPEV	UKUPIZ	ULOJUA	ULOKAH	ULOKEL	ULOKIP
ULOKOV	ULOKUB	ULOLAI	UMAROP	UMARUV	UMASAC
VARYIW02	QAVWAM	VAPJAY	VAQLIJ	VARYIW01	WUVKON
WUXNIM	WAGBOW	WAGBUC	WAGCAJ	WAGCEN	WAGCIR
WAJVUZ	WAJXOV	WIWWEE	WOHDAY	WOJNAK	WONYIH

WONYON	WONYUT	WOQPAT	WOSWAC	WUBCOL	WUDKAH
WUSRUX	XUGVIE	XUNPEB	XADCUA	XAJPII	XAKZIS
XATDOL	XAXTEV	XEFSOQ	XEFTAD01	XEHTEJ	XEJNUV
XIQFUY	XODFAX	XOPNIZ	XOPWEE	XOPYAC	XORQOK01
XOYDUK	YULNUO03	YEFCES	RAZKEJ	ZZZIYE05	ZZZIYE06
ZZZMUC05	ZZZVPO03	CORANN11	IFULUQ04	QIKNUT02	QIZHIQ01
RAPKID	RAQSIM	RARSIN	RARSOT	SATDUN	TASXUH
WASHAA	WASHEE	XARHEE	XARHOO	CARJAG01	DAZZEK
HAWRAZ	HAWRAZ01	JEFPIU	JEFPOA	JEFRIW	KEBWUK01
KEDPUF	MAVQAC	MAVQUW	MAVRAD	MAYJEC	MAYJIG
PINCOL02	QAWVOA	SAYZIC	YEFCAO		

Table S4 Crystals obtained from the melt (83 hits, duplicate refcodes are removed)

AJATEK	AMBACO06	AMECIE	AMECOK	BENCLN05	BINPIX
BOMKUJ	BPHENO02	CONCUD	CABWIM	CBMZPN11	CEWKAQ01
CLPHOL12	CODHEI	COBJIM	DCLANT01	DANLOU	EBEKIG01
GAJLAF	GUZVIG	GUZWIH	EGULOH	FEPVEC	FEPVOM
IZAJAU	IJUWIT	IJUWEP	HABFOG	HABLIG	HISRUW
HOYMAJ	IDOREY	IJEQUJ	KANGEM	KANGOW	LIWPIQ
MEXZOE	MEXZUK	MNPHOL02	MUQLOZ	NABZAS	OKAZIJ
OLOPUA	POCWAF02	POTJAJ	LOJJOJ	QQQAXJ01	SAQXOX
TAJCUD	TAJCUD01	TAJDAK	TAJDOX	UJOSER	UNEWUF02
VAMPEF	VAMPIJ	VOQLOC	VOQLUI	WOBSAH	WOLXOK03
WUSNIH	XIDXEN	XIDXIR	XINFAB01	XINFEF01	XINYEY
XINYIC	DANWAR	QAQSUX	WANMUU	WANMUU01	YAWPIW
DAYDUD	LAWKOK	LAWYUE	LAZREK	LAZRIO	LAZROU
LAZRUA	MAZXOB01	PAWNUX	PEFTIE02	JASBIO	