

Electronic Supporting Information

Pinning down the solid-state polymorphism of the ionic liquid [bmim][PF₆]

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Single-crystal X-ray diffraction

Data integration and global-cell refinement were performed using the program SAINT.¹ High-pressure data processing was performed according to the procedure by Dawson *et al.*² Unless otherwise specified the program SADABS³ was used to correct for absorption and systematic errors. For the high-pressure data, the program SHADE⁴ was additionally used. All structures were solved with direct methods using SHELXS.⁵ All non-H atoms were refined with anisotropic displacement parameters. All H-atoms were placed geometrically and allowed to ride on the parent atoms. $U_{\text{iso}}(\text{H})$ values were assigned in the range 1.2–1.5 times U_{eq} of the parent atom. Full-matrix least-squares structure refinement against F^2 was performed using SHELXL⁵ through the SHELXLE GUI.⁶

α -phase

Sample transfer to the diffractometer proved to be particularly difficult for this phase as any mechanical interference with the crystal at high enough temperatures where the crystal could be manipulated resulted in a phase transition. A suitable crystal for diffraction was hence grown on a secondary glass shard support placed on the Linkam stage and the shard was subsequently mounted on a Bruker SMART 6000 Apex II CCD diffractometer. Diffraction data were collected using Cu K α radiation of $\lambda = 1.54178 \text{ \AA}$ from a rotating anode at 100(2) and 193(2) K. The structure at 100 K was found to be ordered. At 193 K disorder could be modelled for the [PF₆]⁻ anion [0.44(2) : 0.56(2)] and for the atoms C8 and C9 of the butyl side chain [0.752(13) : 0.248(13)] using two-site split models. To ensure reasonable anion geometry, restraints on bond distances and angles as well as on anisotropic displacement parameters were used. Distance restraints were also used for the disordered atoms in the cation.

β -phase

Diffraction data were collected using a Bruker AXS SMART Apex II CCD diffractometer equipped with Mo K α sealed-tube radiation of $\lambda = 0.71073 \text{ \AA}$ for an *in situ* grown crystal contained in a capillary at 193(2) K. A similar diffractometer equipped with a Ag microsource (Incoatec) of $\lambda = 0.56085 \text{ \AA}$ was used for the 293(2) K high-pressure DAC experiment. Both low-temperature and high-pressure structures were found to be pseudomerohedral triclinic twins, with unit-cell constants emulating a monoclinic *C* metric cell and a [-1 1 0] twin direction; the twin law is expressed by the matrix (0 -1 0/ -1 0 0/ 0 0 -1). As expected, the lowest deviation from perfect monoclinic *C* symmetry was observed for the high-pressure structure collected at phase-boundary conditions and this is also

the structure exhibiting the highest degree of pseudosymmetry and perfect domain overlap. Further compression of the single crystal to *ca.* 0.35 GPa resulted in a unit cell with a higher degree of deviation from a perfect monoclinic *C* cell [triclinic unit-cell parameters: $a = 9.4360(15)$, $b = 9.4899(8)$, $c = 14.4658(8)$ Å, $\alpha = 98.944(5)$, $\beta = 98.754(9)$, $\gamma = 100.586(9)^\circ$]. Two orientation matrices were used to integrate the low-temperature data, for which the two twin components did not perfectly overlap; the program TWINABS⁷ was used to correct for absorption and systematic errors and a HKLF5 reflection file was used for the refinement of the low-temperature structure. The twin scale factors were 0.445(5) and 0.509(18) for the low-temperature and high-pressure crystals, respectively. The octahedral geometry of the F-atoms was enforced through the use of restraints whilst opposite F-atoms were constrained to have the same anisotropic displacement parameters. For the high-pressure structure, disordered C-atoms were refined with isotropic displacement parameters. Both [PF₆]⁻ anions were found to be disordered. A two-component disorder model was refined for each of these groups with occupancy factors refining to approximately 50:50 values at both low temperature and high pressure (occupancies were fixed to these values for the high-pressure refinement). Disorder was additionally found in the butyl side chain of the cations: at low temperature disorder was clearly identifiable for carbon C10 in one of two symmetry-independent molecules [0.68(4) : 0.32(4)]. At high pressure terminal methyl carbons were disordered in both molecules [site occupancies were fixed to 0.7 : 0.3 after initial refinement]. Distance, angle, as well as rigid-bond (DELU) and thermal similarity (SIMU) restraints were applied to ensure reasonable molecular geometries and ADPs and increase the data to parameter ratio, in particular for the high-pressure data. In addition, the independent molecules in the asymmetric unit were restrained to have similar geometries. The preference for using a heavily restrained anisotropic model over the use of an isotropic model with fewer parameters for crystals whose weak diffraction can be ascribed to large thermal motion has been discussed by Watkin.⁸

γ -phase

Diffraction data were collected on a single crystal grown on the Linkam stage and transferred to a Bruker AXS SMART Apex II CCD diffractometer with Mo K α sealed-tube radiation of $\lambda = 0.71073$ Å at 263(2) K. A minor but significant disordered component of the butyl side chain, atoms C8 and C9, could be successfully refined using a split-site model [0.921(8) : 0.079(8)]. The residual electron density was distributed around the anion but no disorder could be modelled satisfactorily; the resulting anisotropic displacement parameters are not unusually large for a 263 K structure.

Disorder of the [PF₆]⁻ anion in the solid state

Rotational disorder of the [PF₆]⁻ group is often observed in the solid state, as expected for a highly symmetric molecule. At 193 K the only crystalline phase which does not show evidence of anion disorder is that of γ , which incidentally is also the most dense phase at this temperature. In the α -phase the nature of the anion disorder is most likely to be dynamic, as exemplified by the ordering observed on cooling the single-crystal from 193 to 100 K. In the β -phase at 193 K, the two crystallographically

independent anions are both extensively disordered about axial F-P-F bonds (F101-P1-F103 and F204-P11-F206 for molecules 1 and 2, respectively); at low temperature the [PF₆]⁻ groups were found to be primarily disordered about an axis rotation, whilst at high pressure an additional significant tilt component was observed. A similar but less pronounced type of disorder is also observed in the slightly denser α -phase at 193 K (about the F2-P1-F5 axis). The trends in the anion disorder in the crystalline state are in agreement with the results of the spin-lattice rotational dynamics study of Endo *et al.*⁹

Table S1. Geometric parameters describing the planar or nearly planar centrosymmetric and pseudo-centrosymmetric dimeric arrangements of the cations in the three polymorphs of [bmim][PF₆].

		Centroid-centroid distance / Å	Dihedral angle between ring planes/ ^o	Interplanar ^c distance / Å	Offset / Å ^d
α -phase	"open" dimer 100 K	5.0554(9) ^a	0	3.5298(7)	3.619
	"open" dimer 193 K	5.0668(14)	0	3.6224(11)	3.543
β -phase	"open" dimer 193 K Cg1 Cg1 ^b	4.818(5)	0	3.715(4)	3.068
	"closed" dimer 193 K Cg1 Cg2	5.950(5)	6.2(5)	5.452(4)	-
	"open" dimer 193 K Cg2 Cg2	4.490(5)	0	3.832(4)	2.342
	"open" dimer 0.07 GPa Cg1 Cg1	4.762(12)	0	3.877(10)	2.765
	"closed" dimer 0.07 GPa Cg1 Cg2	6.082(12)	3.9(13)	5.542(10)	-
	"open" dimer 0.07 GPa Cg2 Cg2	4.732(10)	0	3.837(8)	2.770
γ -phase	"open" dimer 193 K	4.865(6)	0	3.4856(9)	3.394
	"closed" dimer 193 K	6.133(7)	0	4.3688(9)	4.304
	"open" dimer 263 K	4.857(2)	0	3.5357(15)	3.330
	"closed" dimer 263 K	6.152(2)	0	4.4425(15)	4.255

^a All standard deviations were calculated with the program PLATON¹⁰. Atoms N1, C2, N3, C4, C5 were chosen to define a ring, the derived centroid and the least-squares plane. ^b For the β -phase the aforementioned atoms define Cg1. Atoms N11, C12, N13, C14, C15 define Cg2. ^c The interplanar distance is defined as the perpendicular distance between the centroid of one ring onto the second ring plane. ^d The offset is defined as the distance between the centroid of one ring and the perpendicular projection of the centroid of the second ring onto the first ring plane.

Table S2. Coordination numbers for the cation and anion, as well as short H...F contacts in the three polymorphs of [bmim][PF₆].

		Cation C.N. ^a	Anion C.N.	H...F contacts < sum vdW		Total number of H...F contacts < sum vdW ^c
<i>α</i> - phase	100 K	7 Anions	7	Imid. ^b	H2, H4, H5	8
		4 Cations	Cations	Me-imid.	H6B, H6C	
			Butyl	H7A		
	193 K	7 Anions	7	Imid.	H2, H4, H5	
6 Cations		Cations	Me-imid.	H6B, H6C		
			Butyl	H7A, H7C		
<i>β</i> - phase	193 K Mol 1	7 Anions	1 Anion	Imid.	H2, H4, H5	8
		3 Cations	8	Me-imid.	H6A, H6B	
				Cations	Butyl	H7A, H7B, H8A, H8B
	193 K Mol 2	6 Anions	1 Anion	Imid.	H12, H14, H15	7
		2 Cations	8	Me-imid.	H16A, H16B, H16C	
				Cations	Butyl	H17B, H18A, H20A
0.07 GPa Mol 1	8 Anions	8	8	Imid.	H2, H4, H5	6
		4 Cations	Cations	Me-imid.	H6A, H6B	
				Butyl	H7A, H7B, H8A, H8C	
	0.07 GPa Mol 2	7 Anions	8	Imid.	H12, H14, H15	6
4 Cations		Cations	Me-imid.	H16A, H16C,		
			Butyl	H17A, H17B, H18A, H20A		
<i>γ</i> - phase	193 K	8 Anions	8	Imid.	H2, H4, H5	11
		4 Cations	Cations	Me-imid.	H6A, H6B	
				Butyl	H7B, H8A, H10A, H10C	
	263 K	8 Anions	8	Imid.	H2, H4, H5	9
5 Cations		Cations	Me-imid.	H6A,		
			Butyl	H7B, H7D, H10A, H10C, H10D		

^a C.N. = Coordination number, defined as the number of molecules with distances < sum of van der Waals (vdW) radii + 0.2 Å. Contacts were identified using the programs PLATON¹⁰ and MERCURY.¹¹ vdW radius for H = 1.20 Å, vdW radius for F = 1.47 Å. For the determination of C.N. all disorder components were considered. ^b H atoms are grouped according their chemical environment: Imidazolium (Imid.), Methyl-imidazolium (Me-imid.) and butyl (Butyl). ^c Total number of contacts: contacts involving disordered atoms were weighted according to site occupancies and rounded to the nearest integer, see Table S3 for details.

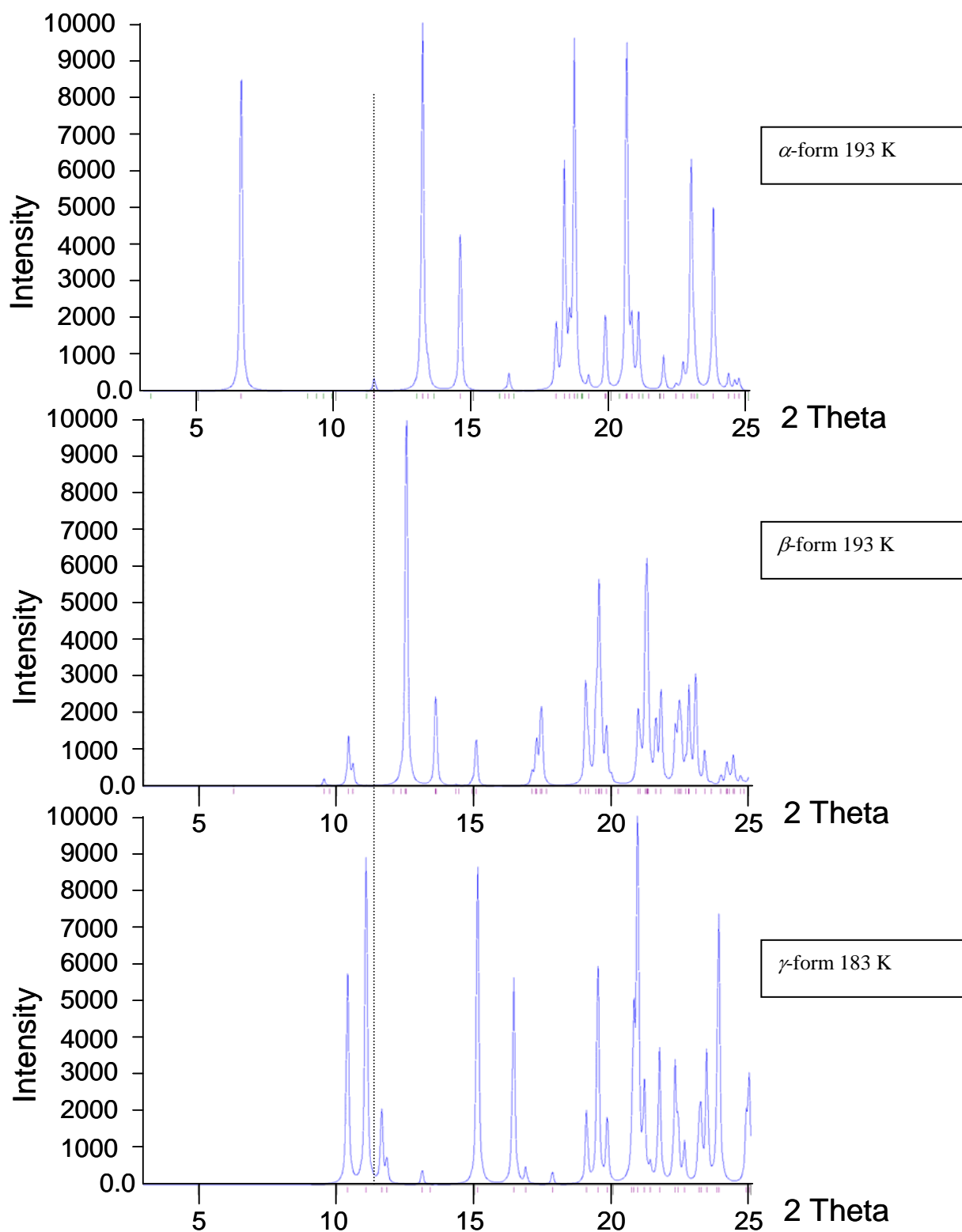
Table S3. Short contacts with H...F distances < sum of vdW radii. vdW radius for H = 1.20 Å, vdW radius for F = 1.47 Å. The programs Mercury¹¹ and Platon¹⁰ were used to check these values. The structure of the γ -form at 193 K was taken from MAZXOB01.

																Symmetry codes	
Alpha 100 K								Alpha 193 K									
	C	H	X	ARU	H...X/Ang	C...F/Ang	C - H...F/°		C	H	X	ARU	H...X/Ang	C...F/Ang	C - H...F/°		
1	C2	H2	F3	4555.02	2.61	3.4466(18)	146	0.5	C2	H2	F51	4555.02	2.32	3.062(6)	134	[6455]	=-1/2+x,y,1/2-
1	C2	H2	F5	4555.02	2.29	3.0412(17)	135	0.5	C2	H2	F5	4555.02	2.38	3.064(9)	128	[4555]	=-x,1/2+y,1/2-
1	C4	H4	F1	8565.02	2.47	3.4128(19)	170	0.5	C4	H4	F11	8565.02	2.49	3.436(5)	175	[8565]	=x,3/2-y,1/2+i
1	C4	H4	F5	8565.02	2.65	3.2448(18)	121	0.5	C4	H4	F1	8565.02	2.57	3.503(9)	167	[4545]	=-x,-1/2+y,1/2
1	C5	H5	F1	4545.02	2.54	3.2328(19)	130	0.5	C4	H4	F5	8565.02	2.55	3.207(9)	127	[6555]	=1/2+x,y,1/2-i
1	C6	H6B	F6	8565.02	2.51	3.463(2)	165	0.5	C5	H5	F11	4545.02	2.64	3.274(7)	125	[2475]	=-1/2-x,2-y,1/
1	C6	H6C	F5	6455.02	2.49	3.228(2)	132	0.5	C6	H6B	F61	8565.02	2.45	3.354(12)	154		
1	C7	H7A	F2	6555.02	2.63	3.274(2)	123	0.5	C6	H6C	F51	6455.02	2.52	3.247(7)	131		
8 Number of contacts considering site occupancy factors								0.5	C6	H6C	F5	6455.02	2.54	3.321(10)	137		
								0.375	C7	H7A	F21	6455.01	2.61	3.241(9)	122		
								0.125	C7	H7C	F21	6455.01	2.28	3.241(9)	162		
								0.125	C7	H7C	F2	6455.01	2.41	3.387(9)	169		
								5.125 Number of contacts considering site occupancy factors									
Gamma 193 K								Gamma 263 K									
	C	H	X	ARU	H...X/Ang	C...F/Ang	C - H...F/°		C	H	X	ARU	H...X/Ang	C...F/Ang	C - H...F/°		
1	C2	H2	F5		2.35	3.233(5)	152	1	C2	H2	F5		2.41	3.255(5)	152	[1555]	=x,y,z
1	C2	H2	F3	2766.02	2.6	3.192(4)	120	1	C2	H2	F3	2766.02	2.66	3.263(5)	123	[2766]	=2-x,1-y,1-z
1	C4	H4	F2	2756.02	2.45	3.38(5)	164	1	C4	H4	F2	2756.02	2.51	3.419(5)	165	[2756]	=2-x,-y,1-z
1	C5	H5	F2	1656.02	2.67	3.563(5)	155	1	C5	H5	F3	1656.02	2.65	3.461(4)	147	[1656]	=1+x,y,1+z
1	C5	H5	F3	1656.02	2.59	3.418(4)	145	1	C6	H6A	F4	2756.02	2.56	3.42(5)	149	[1655]	=1+x,y,z
1	C6	H6A	F4	2756.02	2.49	3.342(5)	148	0.92	C7	H7B	F6	1656.02	2.57	3.336(4)	136	[2767]	=2-x,1-y,2-z
1	C6	H6B	F1	1655.02	2.67	3.382(5)	131	0.08	C7	H7D	F6	1656.02	2.37	3.336(4)	173	[1556]	=x,y,1+z
1	C7	H7B	F6	1656.02	2.53	3.309(4)	138	0.92	C8A	H8A	F5	2767.02	2.66	3.632(5)	176	[2656]	=1-x,-y,1-z
1	C8	H8A	F5	2767.02	2.67	3.622(5)	175	0.92	C10	H10A	F3	1556.02	2.6	3.513(6)	159	[2765]	=2-x,1-y,z
1	C10	H10A	F3	1556.02	2.58	3.503(5)	162	0.92	C10	H10C	F2	2656.02	2.66	3.592(5)	165	[2765]	=2-x,1-y,z
1	C10	H10C	F2	2656.02	2.66	3.553(5)	155	0.08	C10	H10D	F3	2765.02	2.66	3.513(6)	149	[1665]	=1+x,1+y,z
11 Number of contacts considering site occupancy factors								8.76 Number of contacts considering site occupancy factors									

Table S3 (cont.). Short contacts with H...F distances < sum of vdW radii. vdW radius for H = 1.20 Å, vdW radius for F = 1.47 Å. The programs Mercury¹¹ and Platon¹⁰ were used to check these values.

Beta 193 K								Beta 0.07 Gpa								
Molecule 1	C	H	X	ARU	H...X/Ang	C...F/Ang	C - H...F/°	Molecule 1	C	H	X	ARU	H...X/Ang	C...F/Ang	C - H...F/°	
0.5	C2	H2	F103	1565.03	2.57	3.366(17)	142	0.5	C2	H2	F113	1565.03	2.24	3.08(3)	149	[1565] =x,1+y,z
0.5	C2	H2	F206	1565.04	2.3	3.018(18)	132	0.5	C2	H2	F206	1565.04	2.59	3.15(3)	120	[2665] =1-x,1-y,-z
0.5	C2	H2	F113	1565.03	2.37	3.13(19)	137	0.5	C4	H4	F205	2665.04	2.54	3.31(3)	140	[2565] =-x,1-y,-z
0.5	C2	H2	F216	1565.04	2.57	3.188(19)	123	0.5	C4	H4	F216	2665.04	2.34	3.16(3)	147	[1665] =1+x,1+y,z
0.5	C4	H4	F205	2665.04	2.45	3.26(2)	143	0.5	C5	H5	F203		2.56	3.33(4)	141	[1455] =-1+x,y,z
0.5	C4	H4	F215	2665.04	2.62	3.561(17)	171	0.5	C6	H6A	F205	2665.04	2.45	3.35(3)	155	[2666] =1-x,1-y,1-z
0.5	C5	H5	F203		2.45	3.308(19)	150	0.5	C6	H6C	F105	1565.03	2.38	3.13(4)	134	[2566] =-x,1-y,1-z
0.5	C6	H6A	F105	1565.03	2.47	3.246(19)	136	0.5	C7	H7A	F201	1565.04	2.35	3.21(3)	146	[2555] =-x,-y,-z
0.5	C6	H6B	F205	2665.04	2.65	3.51(2)	146	0.5	C7	H7B	F104	1665.03	2.6	3.45(3)	147	
0.5	C6	H6B	F115	2565.03	2.46	2.86(2)	104	0.5	C7	H7B	F111	1665.03	2.54	3.44(4)	155	
0.5	C7	H7A	F101	1665.03	2.5	3.44(2)	159	0.35	C8	H8A	F202		2.46	3.33(3)	151	
0.5	C7	H7A	F111	1665.03	2.38	3.35(2)	166	0.35	C8	H8A	F213		2.4	3.35(3)	176	
0.5	C7	H7B	F201	1565.04	2.28	3.21(2)	155	0.15	C8	H8C	F202		2.51	3.33(3)	144	
0.5	C8	H8A	F213		2.26	3.205(19)	160	0.15	C8	H8C	F213		2.55	3.35(3)	142	
0.5	C8	H8B	F106	1565.03	2.66	3.54(2)	148	6 Number of contacts considering site occupancy factors								
7.5 Number of contacts considering site occupancy factors																
Molecule 2	C	H	X	ARU	H...X/Ang	C...F/Ang	C - H...F/°	Molecule 2	C	H	X	ARU	H...X/Ang	C...F/Ang	C - H...F/°	
0.5	C12	H12	F101	1565.03	2.43	3.32(18)	156	0.5	C12	H12	F101	1565.03	2.51	3.26(3)	138	
0.5	C12	H12	F111	1565.03	2.3	3.193(19)	156	0.5	C12	H12	F111	1565.03	2.44	3.2(3)	139	
0.5	C12	H12	F204	1455.04	2.61	2.921(16)	99	0.5	C12	H12	F204	1455.04	2.24	2.74(3)	112	
0.5	C14	H14	F204	2666.04	2.57	3.335(19)	138	0.5	C12	H12	F214	1455.04	2.64	3.19(3)	118	
0.5	C14	H14	F214	2666.04	2.42	3.16(15)	135	0.5	C14	H14	F201	2666.04	2.62	3.43(3)	147	
0.5	C15	H15	F202		2.62	3.198(18)	120	0.5	C14	H14	F214	2666.04	2.56	3.37(3)	146	
0.5	C16	H16A	F102	1565.03	2.47	3.402(18)	159	0.5	C15	H15	F202		2.62	3.29(3)	129	
0.5	C16	H16A	F112	1565.03	2.51	3.31(2)	139	0.5	C16	H16A	F102	1565.03	2.66	3.42(4)	136	
0.5	C16	H16B	F201	2666.04	2.57	3.46(2)	152	0.5	C16	H16C	F114	2566.03	2.59	3.04(3)	109	
0.5	C16	H16C	F114	2566.03	2.5	2.97(2)	109	0.5	C17	H17A	F215	1455.04	2.38	3.29(4)	156	
0.5	C17	H17B	F104		2.62	3.564(18)	160	0.5	C17	H17B	F103		2.61	3.49(4)	150	
0.5	C18	H18A	F206		2.66	3.526(16)	146	0.5	C18	H18A	F213		2.43	3.38(4)	170	
0.5	C18	H18A	F213		2.66	3.627(17)	165	0.35	C20	H20A	F101		2.65	3.57(4)	162	
0.5	C20	H20A	F101	2555.03	2.57	3.55(2)	175	6.35 Number of contacts considering site occupancy factors								
7 Number of contacts considering site occupancy factors																

Figure S4. Powder patterns simulated using the experimentally-determined single-crystal structures as input. For the γ -form, MAZXOB01 was used. Dotted lines are used as a guide to the eye to facilitate comparison with Figs. 8, 9 and 10 in the paper for Triolo *et al.*¹² The program Mercury¹¹ was used to generate the simulated patterns. Input parameters were as following: $\lambda = 1.54056 \text{ \AA}$; 2θ range: $2-20^\circ$, 2θ Step: 0.02° . FWHM Peak shape: 0.1. Tick marks colour: magenta; systematic absences colour: green.



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