

Supporting information

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Title: Solvent and anion facilitated conformational changes in benzylamine substituted
thiazolamine

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Crystal Structure determination by X-ray crystallography: Single crystal X-ray diffraction data for **La**, **Lb**, **1**, **2**, and **3** were collected on a Oxford SuperNova diffractometer. SMART was used for data collection and also for indexing the reflections and determining the unit cell parameters. Cell refinement was performed using SAINT software. The structures were solved by direct methods and refined by full-matrix least squares calculations using SHELXTL. All the non-hydrogen atoms were refined in the anisotropic approximation against F^2 of all reflections. The hydrogen atoms attached to the heteroatom were located in the difference Fourier synthesis maps and refined with isotropic displacement coefficients. Crystal parameters are summarized in Table 1S.

Table 1S: Crystallographic Parameters of the Polymorphs **La**, **Lb** and **1-3**.

Compound No.	La	Lb	1	2	3
Formule	C ₁₆ H ₁₈ N ₄ S ₂	C ₁₆ H ₁₈ N ₄ S ₂	C ₁₆ H ₂₄ Br ₂ N ₄ O ₂ S ₂	C ₁₆ H ₂₀ N ₆ O ₆ S ₂	C ₁₆ H ₃₀ N ₄ O ₁₆ P ₄ S ₂
Mol. wt.	330.46	330.46	528.31	456.50	722.44
Crystal system	Monoclinic	monoclinic	Triclinic	monoclinic	monoclinic
Space group	C 2/c	C 2/c	P-1	P 21/n	P 21/c
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
a (Å)	19.017(2)	16.2875(16)	7.5072(6)	7.0178(17)	8.0722(8)
b (Å)	5.1090(5)	9.6657(10)	8.4305(7)	16.125(4)	19.8911(19)
c (Å)	17.805(2)	13.4747(13)	9.1386(7)	9.208(2)	9.3871(9)
α (°)	90.00	90.00	73.216(4)	90.00	90.00
β (°)	99.507(12)	127.121(8)	85.375(5)	104.814(15)	98.293(4)
γ (°)	90.00	90.00	74.943(5)	90.00	90.00

V (Å ³)	1706.2(3)	1691.5(3)	534.72(7)	1007.4(4)	1491.5(3)
Z	4	4	1	2	2
Density/Mgm ⁻³	1.287	1.298	1.641	1.505	1.609
Abs. Coeff. /mm ⁻¹	0.314	0.316	4.003	0.312	0.470
Abs. Correction	multi-scan	multi-scan	multi-scan	multi-scan	none
F(000)	696	696	266	476	748
Total reflections	1522	1518	1900	1812	2691
Reflections, $I > 2\sigma(I)$	1217	1273	1593	1298	2473
Max. $\theta/^\circ$	25.24	25.23	25.24	25.24	25.24
Ranges (h, k, l)	-20 ≤ h ≤ 22 -6 ≤ k ≤ 6 -19 ≤ l ≤ 20	-19 ≤ h ≤ 19 -11 ≤ k ≤ 11 -14 ≤ l ≤ 16	-9 ≤ h ≤ 9 -6 ≤ k ≤ 10 -10 ≤ l ≤ 10	-7 ≤ h ≤ 8 -19 ≤ k ≤ 19 -10 ≤ l ≤ 11	-9 ≤ h ≤ 8 -23 ≤ k ≤ 23 -11 ≤ l ≤ 11
Complete to 2 θ (%)	98.4	99.0	98.4	99.7	99.3
Data/restrain/parameter	1522/0/101	1518/0/101	1900/2/127	1812/0/137	2691/15/211
Goof(F2)	1.062	1.089	1.083	1.058	1.024
R indices [$I > 2\sigma(I)$]	0.0659	0.0380	0.0303	0.0678	0.0298
R indices (all data)	0.0765	0.0451	0.0386	0.0906	0.0331

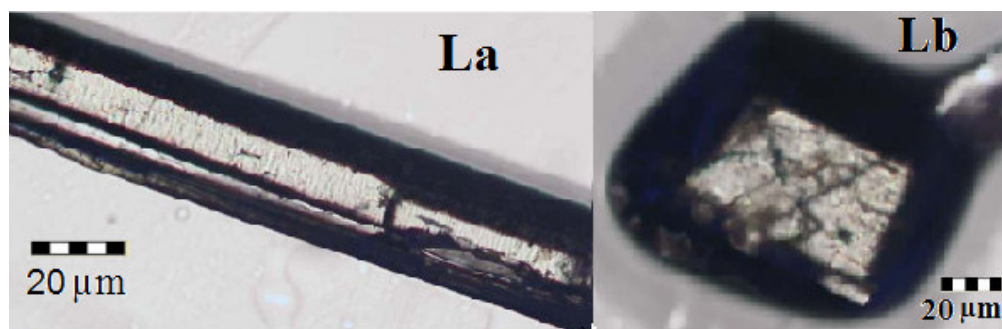


Figure S1: Crystal morphologies of **La** and **Lb**

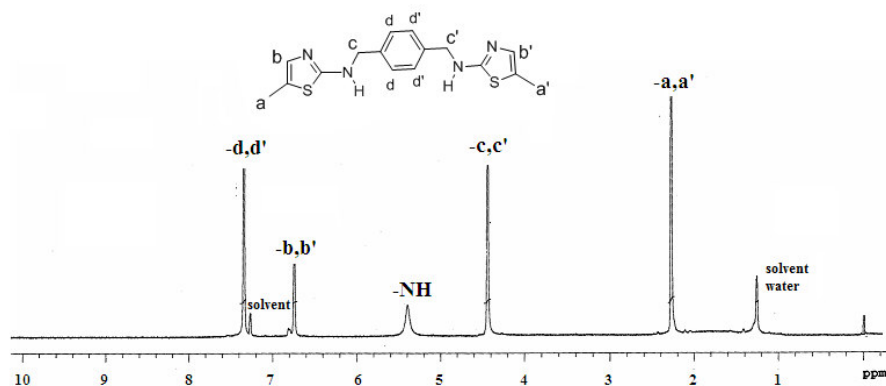


Figure S2: ¹H-NMR (CDCl₃) spectrum of **L**.

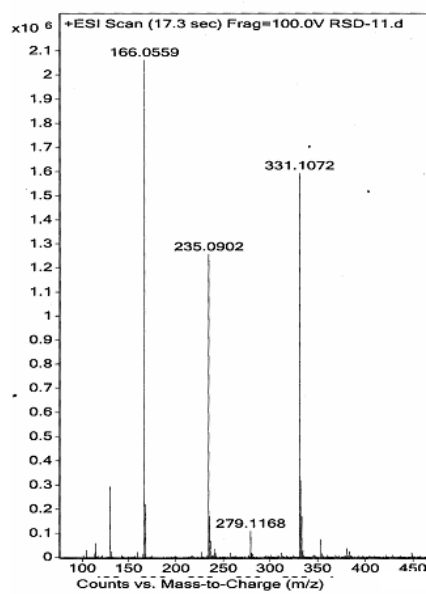


Figure S3: ESI mass spectrum of L.

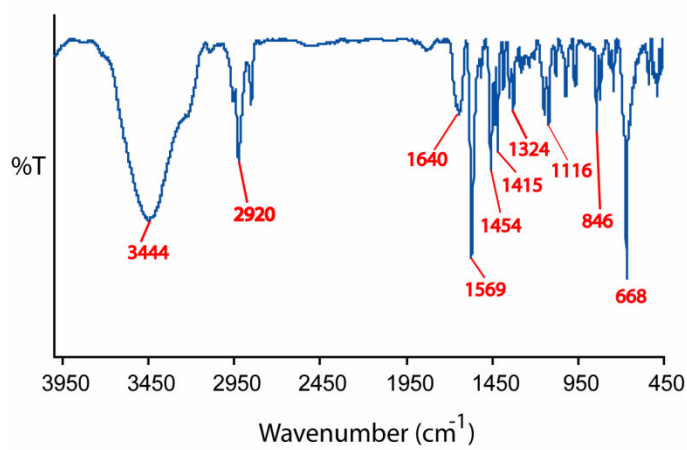
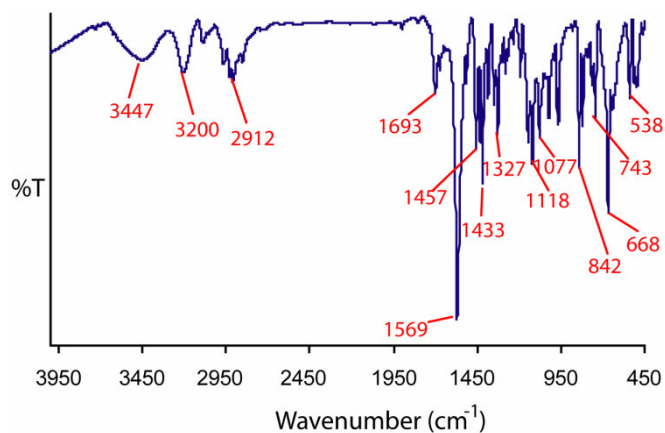
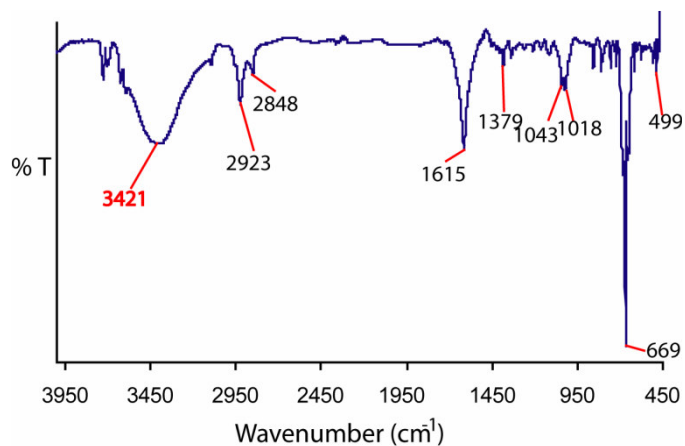
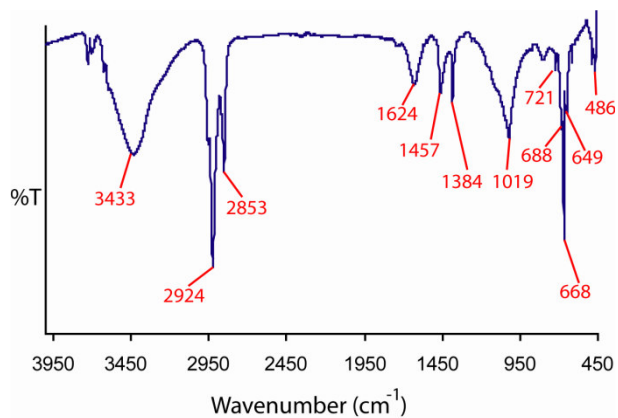


Figure S4: IR (KBr) spectrum of La.

Figure S5: IR (KBr) spectrum of **Lb**.Figure S6: IR (KBr) spectrum of salt **1**.Figure S7: IR (KBr) spectrum of salt **2**.

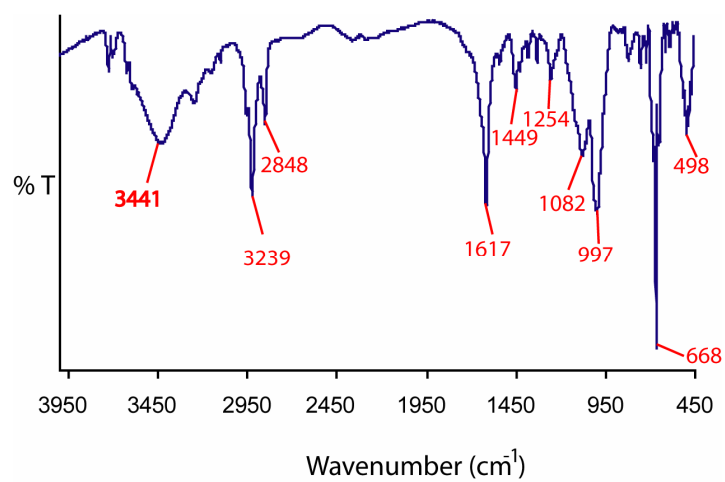
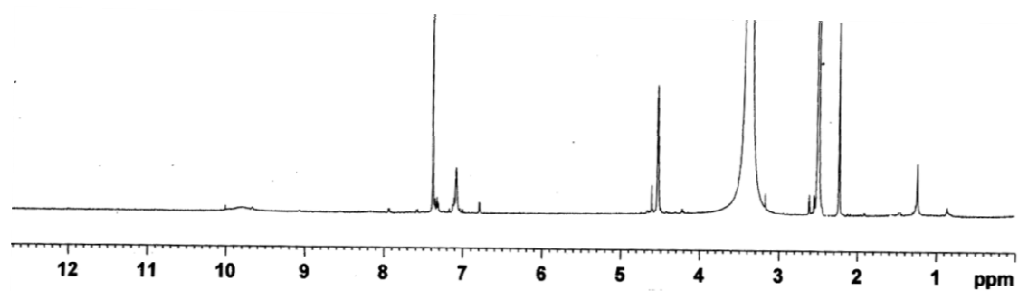
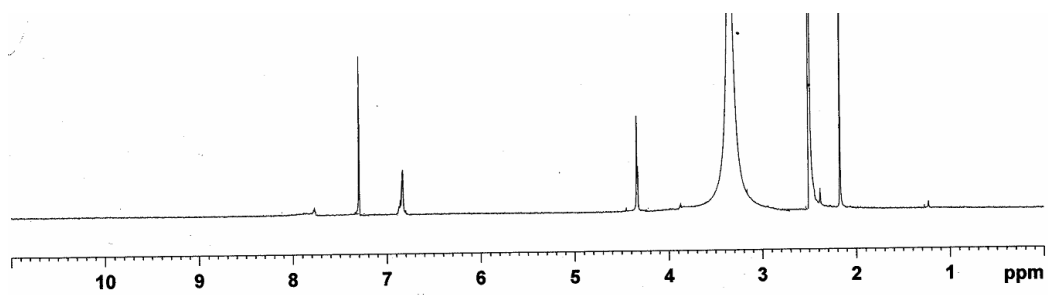


Figure S8: IR (KBr) spectrum of salt 3.

Figure S9: $^1\text{H-NMR}$ (DMSO- d_6) spectrum of salt 1.Figure S10: $^1\text{H-NMR}$ (DMSO- d_6) spectrum of salt 2.

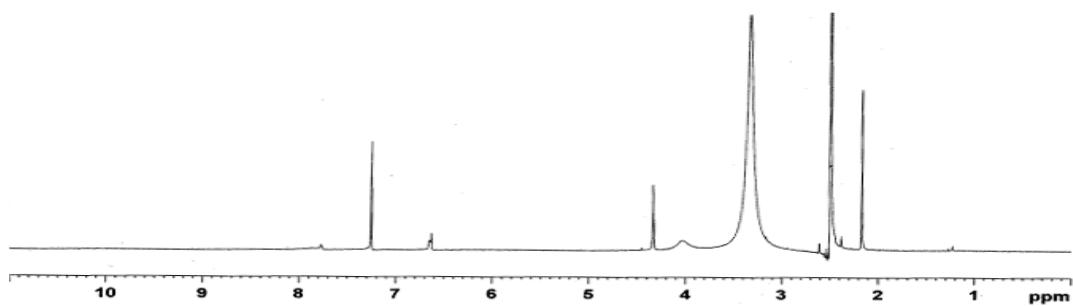


Figure S11: $^1\text{H-NMR}$ (DMSO-d_6) spectrum of salt **3**.

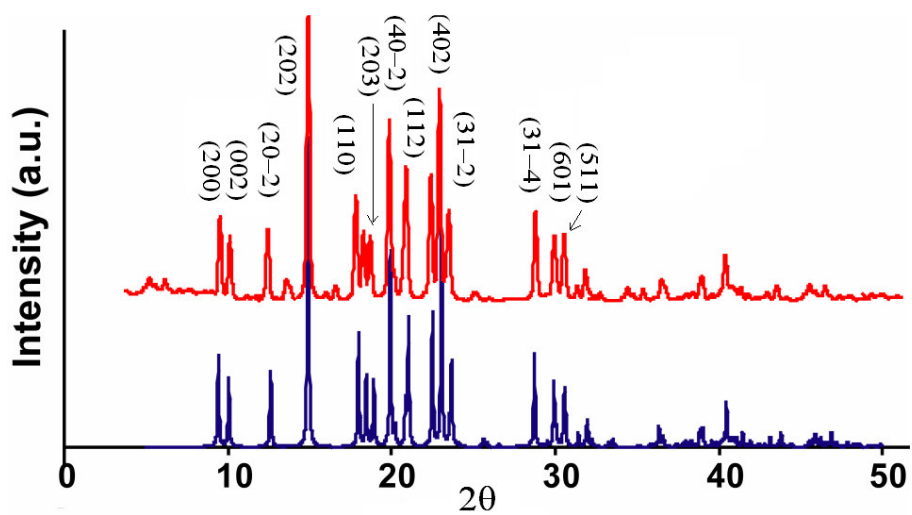


Figure S12: PXRD patterns of **La** (red = experimental, blue = generated from CIF).

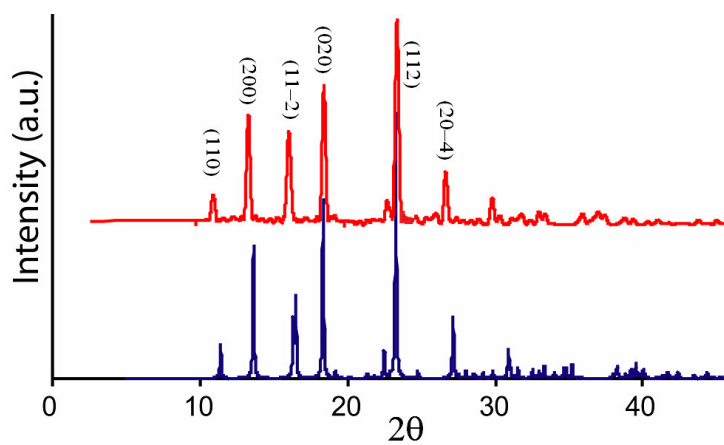


Figure S13: PXRD patterns of **Lb** (red = experimental, blue = generated from CIF).

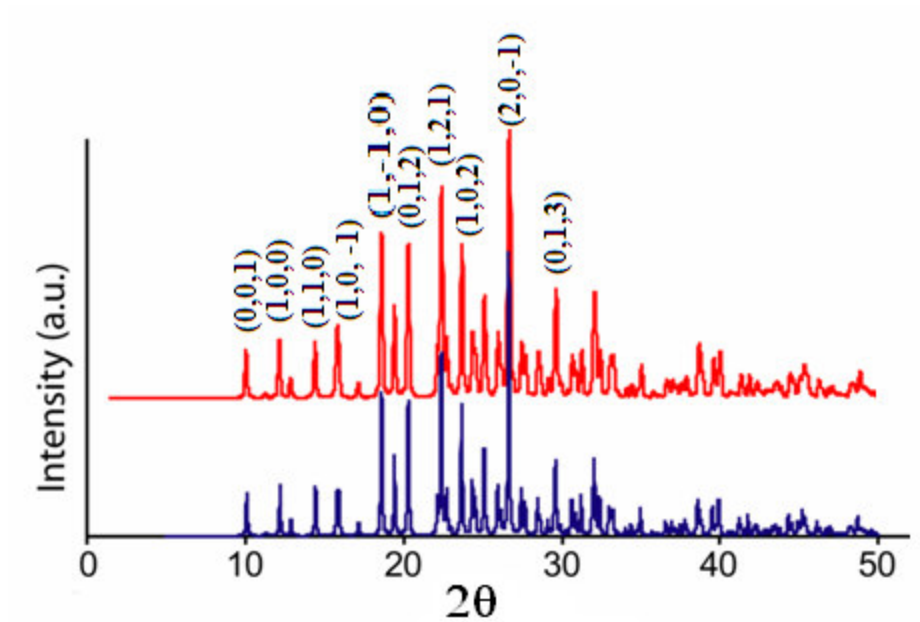


Figure S14: PXRD patterns of **1** (red = experimental, blue = generated from CIF).

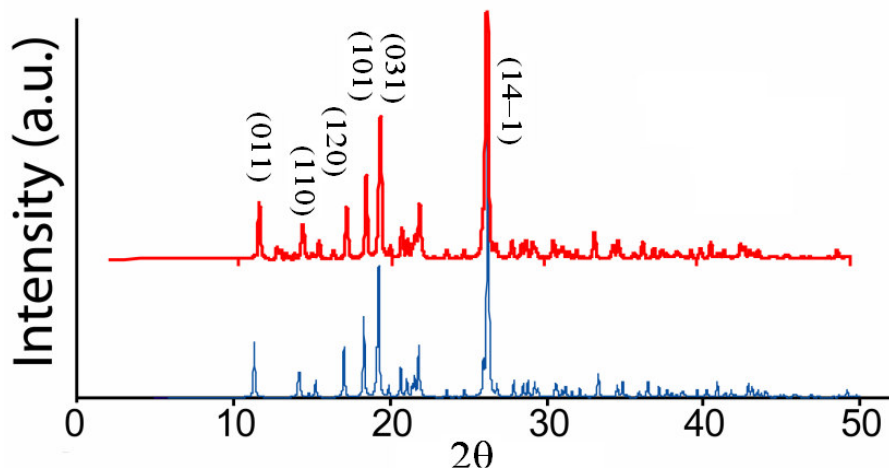


Figure S15: PXRD patterns of **2** (red = experimental, blue = generated from CIF).

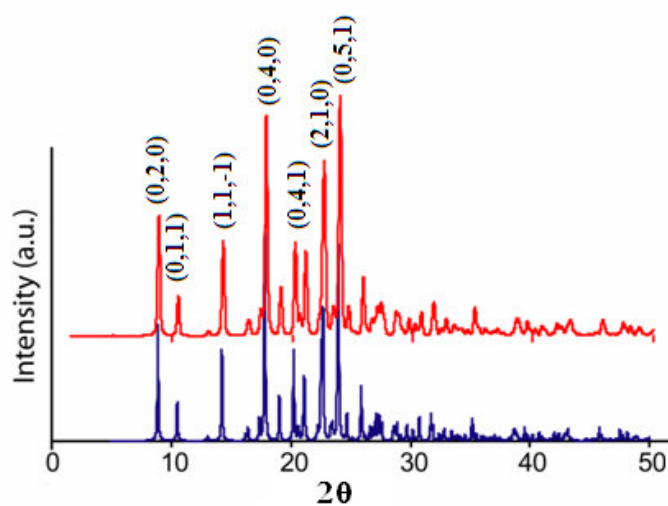


Figure S16: PXRD patterns of **3** (red = experimental, blue = generated from CIF).

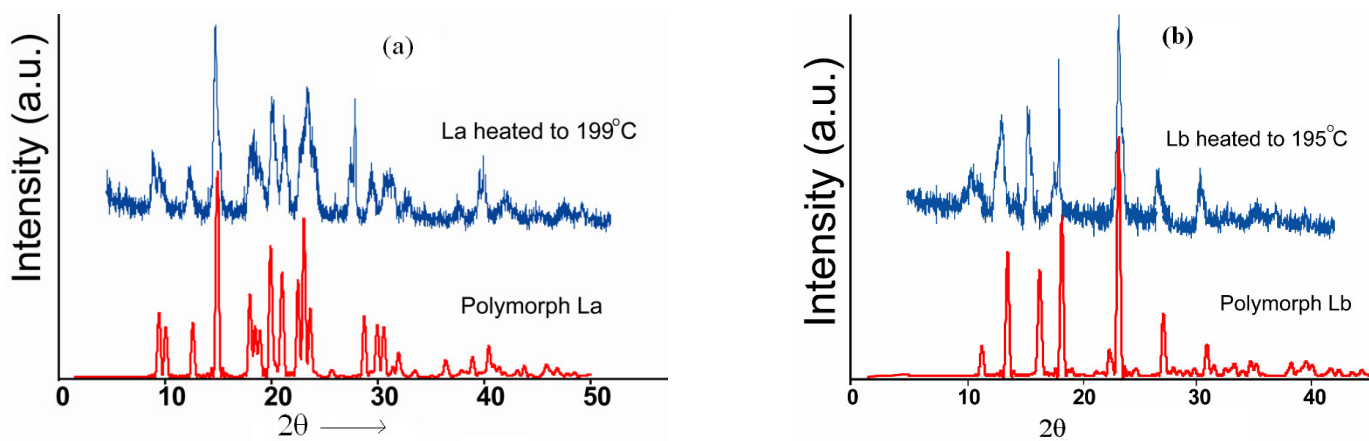


Figure S17: PXRD patterns of (a) **L_a** and (b) **L_b** at different temperatures.

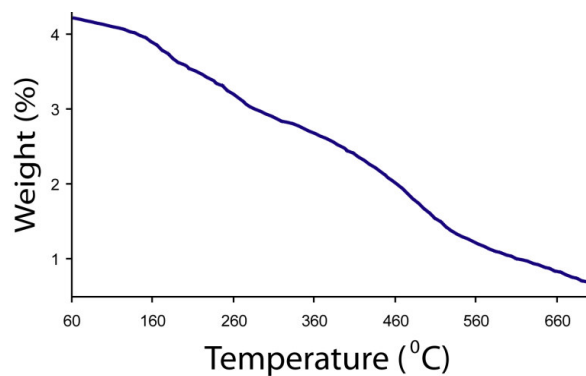


Figure S18: Thermogram of **3** (heating rate 5 °C/min).

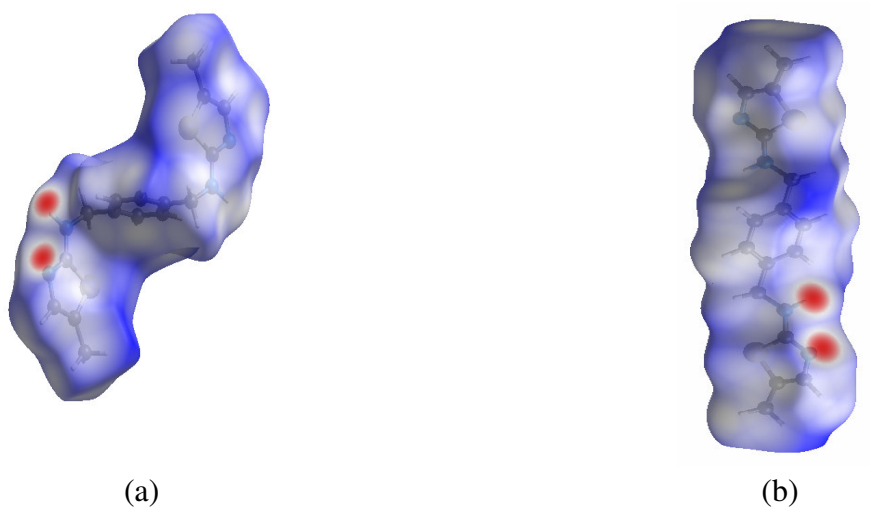
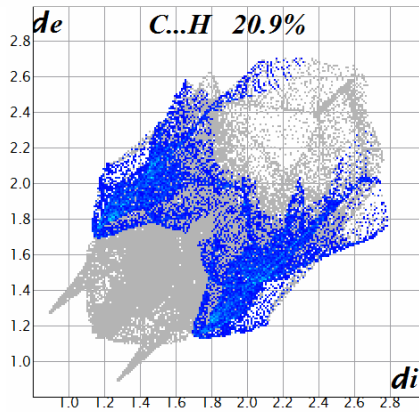
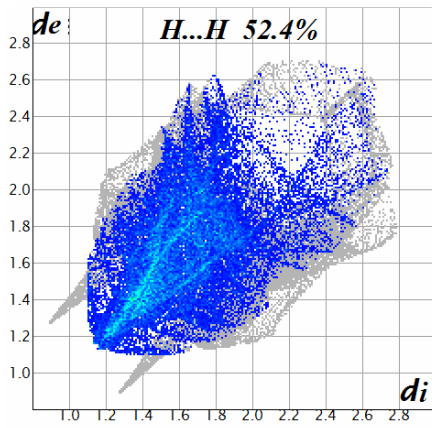
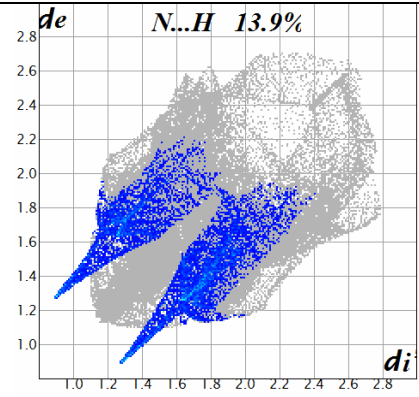
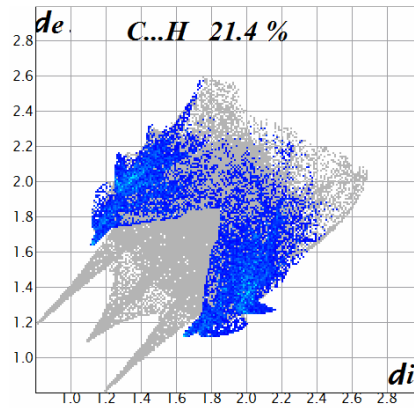
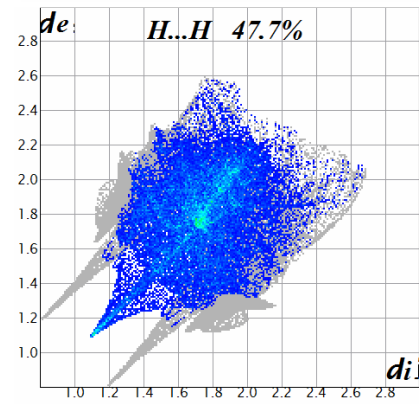
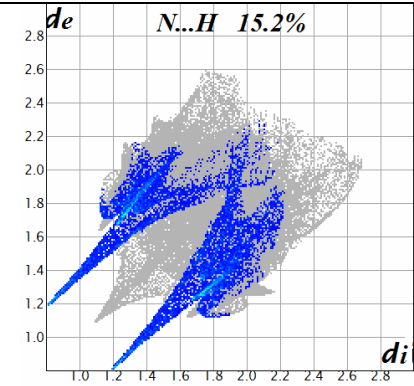


Figure S19: Hirshfeld surface of (a) polymorph **La** and (b) polymorph **Lb**.

Interactions in La



Interactions in Lb



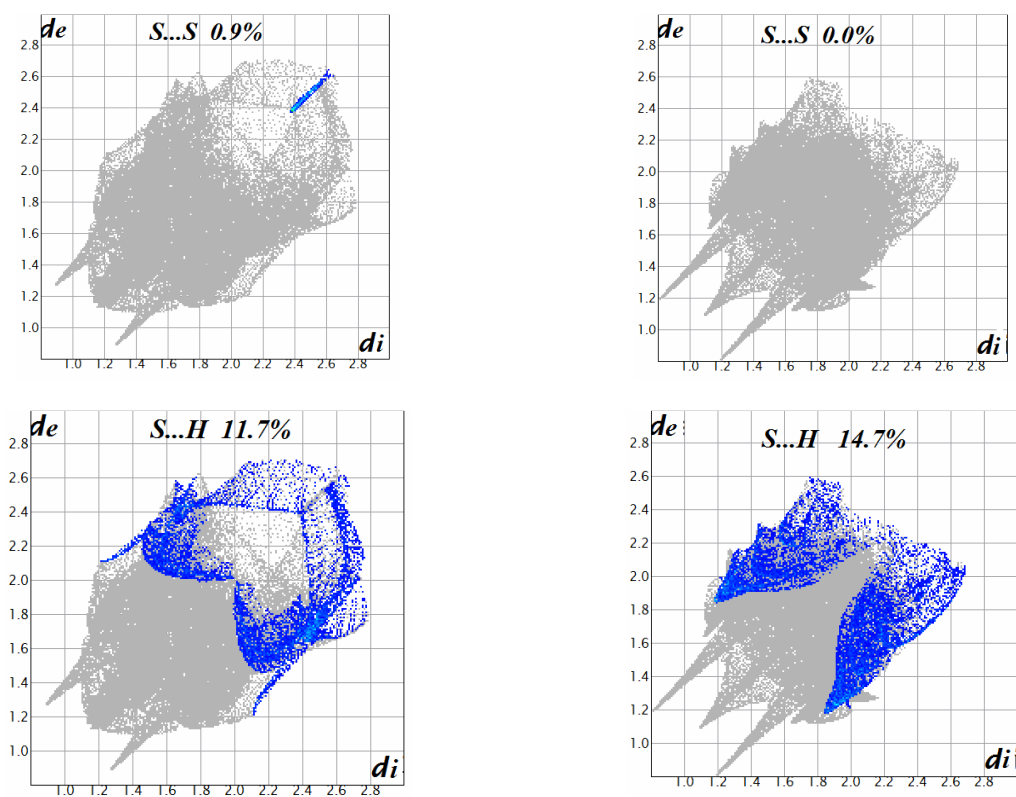
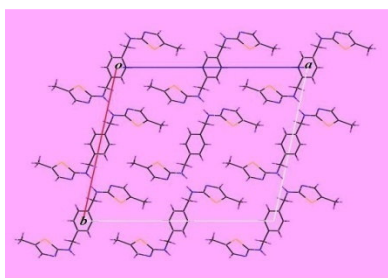
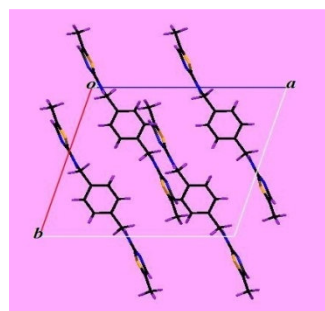


Figure S20: Fingerprint plots for polymorphs **L_a** and **L_b**, broken down into contributions from specific pairs of atom types.

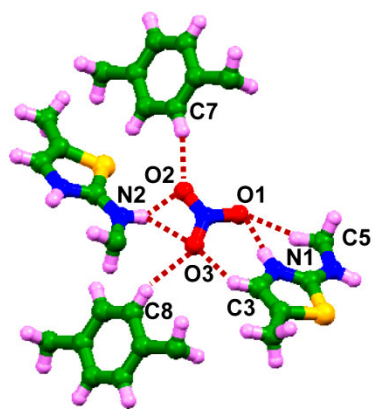


(a)

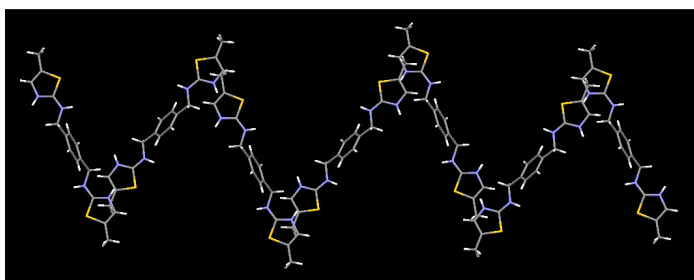


(b)

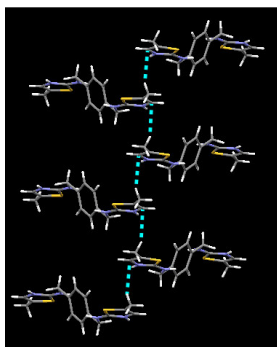
Figure S21: Crystal packing pattern along the *ab* crystallographic plane of (a) polymorph **L_a** and (b) polymorph **L_b**.



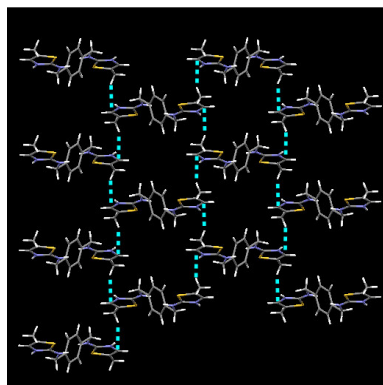
(a)



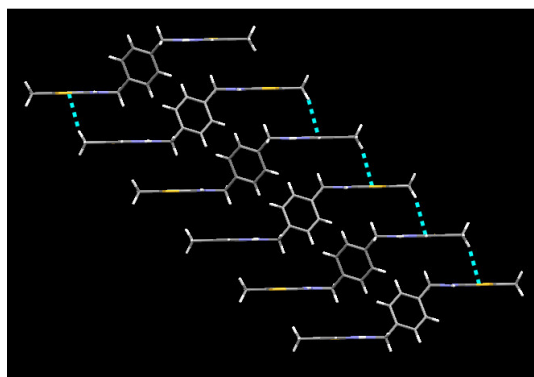
(b)



(c)



(d)



(e)

Figure S22: (a) Environment of nitrate ion in salt **2**. Different assemblies of $[\text{H}_2\text{L}]^{2+}$ within the crystal lattice of salt **2**: (b) zig-zag type, (c) ladder type, (d) 1D sheet-like, and (e) staircase type.

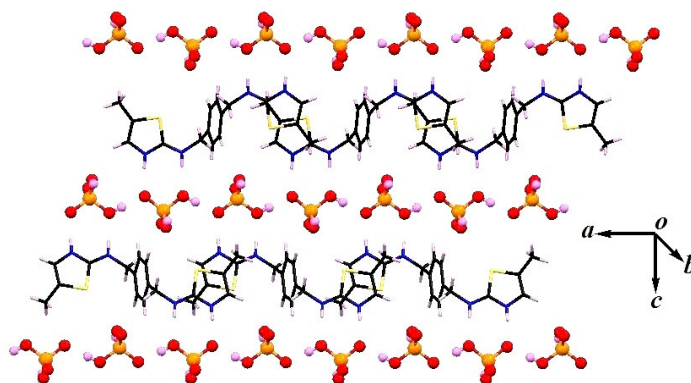


Figure S23: Packing diagram of salt **3** showing alternating layers of $[\text{H}_2\text{L}]^{2+}$ cations and H_2PO_4^- anions.

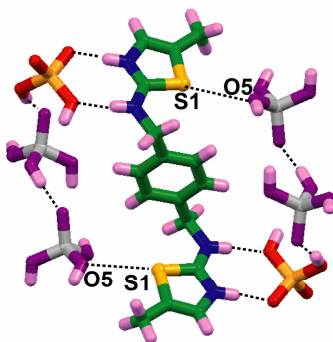
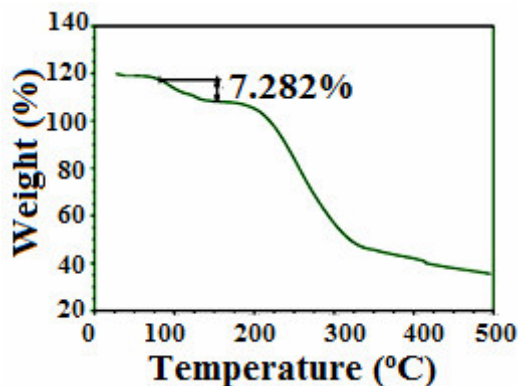


Figure S24: phosphoric acid molecules and biphosphate anions around $[\text{H}_2\text{L}]^{2+}$ in salt **3**.

Figure S25: TGA plot of **1** (heating rate 5 °C/min).**Table 2S:** Hydrogen-bond parameters in **L_a**, **L_b**, **1**, **2**, and **3**.

Compound No.	D-H...A	$d_{D-H}(\text{\AA})$	$d_{H...A}(\text{\AA})$	$d_{D...A}(\text{\AA})$	$\angle D-H...A(^{\circ})$
La	N(2)-H(2)···N(1) [1/2-x,1/2-y,1-z]	0.86	2.28	3.011(5)	142(2)
Lb	N(2)-H(2)···N(1) [1-x,1-y,-z]	0.86	2.14	2.939(2)	154(2)
Salt 1	N(1)-H(1)···O(1)	0.86	1.87	2.717(4)	170
	O(1)-H(1P)···Br(1)	0.86(3)	2.44(3)	3.297(3)	176(4)
	O(1)-H(1Q)···Br(1)	0.87(6)	2.41(5)	3.260(3)	165(7)
	N(2)-H(2)···Br(1)	0.86	2.51	3.364(3)	172
Salt 2	N(1)-H(1)···O(1)	0.86	1.94	2.790(5)	172
	N(1)-H(1)···O(3)	0.86	2.57	3.122(5)	123
	N(2)-H(2)···O(2) [1/2-x,1/2+y,1/2-z]	0.86	2.28	3.060(5)	150
	N(2)-H(2)···O(3) [1/2-x,1/2+y,1/2-z]	0.86	2.23	3.018(5)	152
	C(5)-H(5B)···O(1)	0.97	2.41	3.304(6)	153
	C(7)-H(7)···O(2) [1/2+x,1/2-y,1/2+z]	0.93	2.48	3.391(6)	167
	Intra C(5)-H(5B)···N(1)	0.97	2.60	2.962(6)	102
	C(8)-H(8)···O(3)	0.93	2.674	3.572	162
Salt 3	C(3)-H(3)···O(3)	0.93	2.714	3.212	115
	N(1)-H(1)···O(4)	0.86	1.91	2.760(3)	167
	N(2)-H(2)···O(3)	0.86	1.96	2.817(3)	178
	O(2)-H(2P)···O(6) [-1+x,y,z]	0.85(19)	1.78(2)	2.615(2)	170(3)
	O(3)-H(3P)···O(4) [x,1/2-y,-1/2+z]	0.86(2)	1.62(2)	2.480(2)	177(4)
	O(5)-H(5Q)···O(1)	0.85(2)	1.76(2)	2.605(2)	174(3)
	O(7)-H(7P)···O(6) [x,1/2-y,-1/2+z]	0.85(2)	1.76(2)	2.601(2)	174(3)
	O(8)-H(8P)···O(1) [x,1/2-y,-1/2+z]	0.86(2)	1.71(2)	2.565(2)	177(3)
	C(3)-H(3)···O(2) [x,1/2-y,1/2+z]	0.93	2.53	3.330(3)	145

