Supplementary Information

LICSAR2: Lithium chloride, anhydrous (99% pure, used as received from Acros Organics, 0.5 g, 11.8 mmol) and sarcosine (98% pure, used as received from Aldrich, 3.15 g, 35.4 mmol) were dissolved in 2 ml of hot deionized water. It was maintained on the hot plate until crystals emerged from the solution. Colorless block crystals (1213 mg) were harvested from the hot solution.

LINBTN2: Lithium nitrate (98%, anhydrous, used as received from Fluka, 413.4 mg, 6.0 mmol) and betaine (99+% pure, used as received from Sigma, 1405.6 mg, 12.0 mmol) were dissolved in 2.0 mL of hot deionized water. It was maintained on the hot plate until crystals emerged from the hot solution. Colorless plates (357 mg) were collected from the hot solution.

LICDMG2: Lithium chloride (99%, anhydrous, used as received from Acros Organics, 0.5 g, 11.8 mmol) and N,N-dimethylglycine (used as received from Alfa Aesar, 2.44 g, 23.6 mmol) were dissolved in 3.0 ml of hot deionized water. It was maintained on the hot plate until crystals emerged from the hot solution. Colorless block crystals (1488 mg) were collected from the hot solution.

LIBDMG2: Lithium bromide (99%, anhydrous, used as received from Acros Organics, 0.5 g, 5.76 mmol) and N,N-dimethylglycine (used as received from Alfa Aesar, 1.19 g, 11.5 mmol) were dissolved in 2.0 ml of hot deionized water. It was maintained on the hot plate until crystals emerged from the hot solution. Colorless block crystals (696 mg) were collected from the hot solution.

LICPRO2: Lithium chloride (99%, anhydrous, used as received from Acros Organics, 0.50 g, 11.8 mmol) and L-proline (99+% pure, used as received from Acros Organics, 2.72 g, 23.6 mmol) were dissolved in 2.0 ml of hot deionized water. It was maintained on the hot plate until crystals emerged from the hot solution. Colorless block crystals (1266 mg) were harvested from the hot solution.

LIBPRO2: Lithium bromide (99+%, anhydrous, used as received from Acros Organics, 0.50 g, 5.76 mmol) and L-proline (99+% pure, used as received from Acros Organics, 1.33 g, 11.5 mmol) were dissolved in 2.0 ml of hot deionized water. It was maintained on the hot plate until crystals emerged from the hot solution. Colorless block crystals (861 mg) were collected from the hot solution.

LINPRO2: Lithium nitrate (98%, anhydrous, used as received from Fluka, 413.4 mg, 6.0 mmol) and L-proline (99+% pure, used as received from Acros Organics, 1381.2 mg, 12.0 mmol) were dissolved in 2 ml of hot deionized water. It was maintained on the hot plate until crystals emerged from the hot solution. Colorless plates (LINPRO2, ABW) were collected from the hot solution. These crystals were observed to convert to rhombohedral crystals (LINPRO2, dia, 603 mg) upon removal from the hot plate.
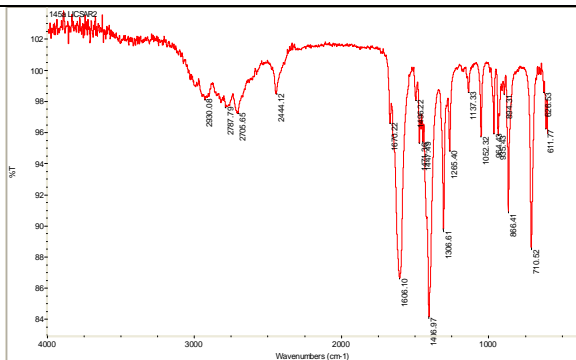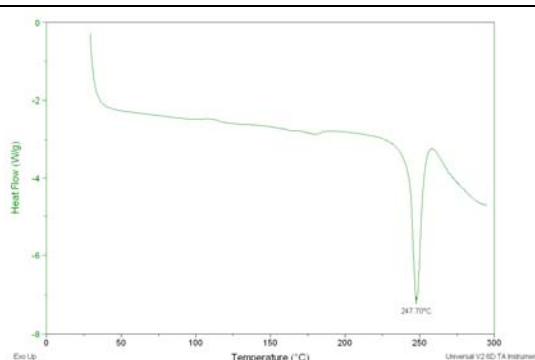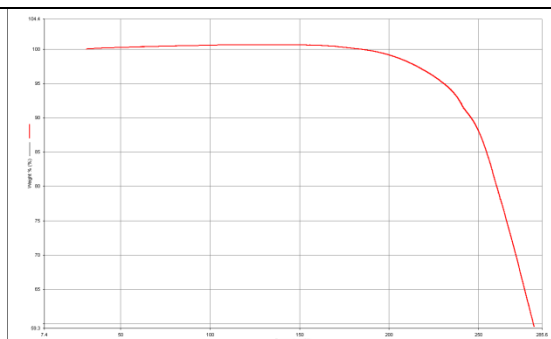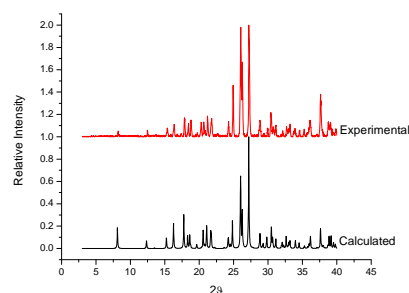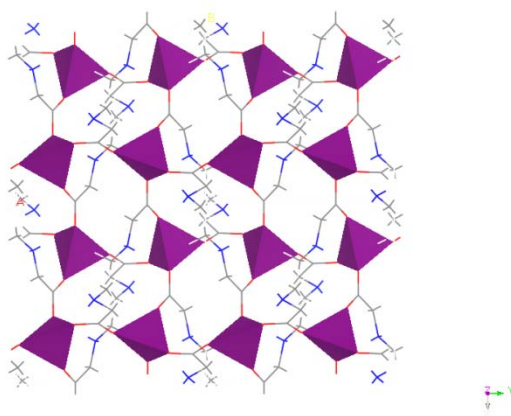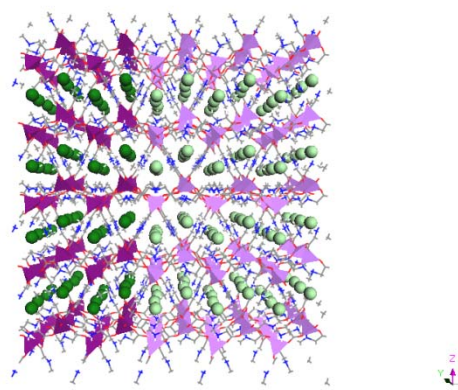
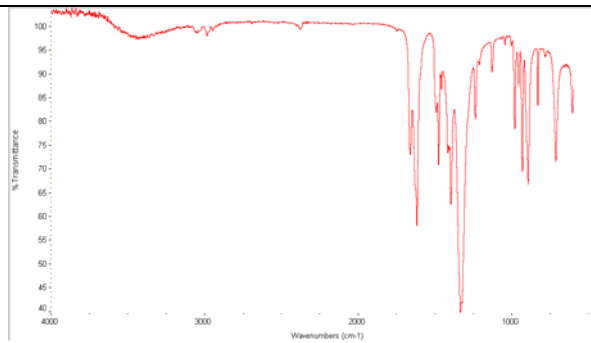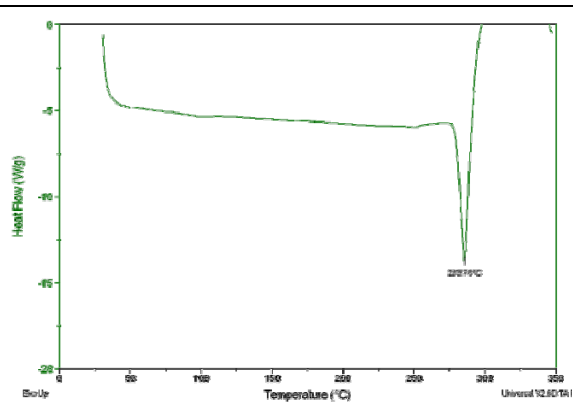| LICSAR2	
1a	1b
1c	1d
1e	1f

Each lithium cation is bridged by four carboxylates to form an undulating square grid (figure 1e), while the opposite ends of the amino acids point away (above and below) from the square grid to establish a bilayer packing arrangement (figure 1f). The chloride anions reside in proximity with the ammonium groups sustained by N-H···Cl [3.1011(1) Å, 3.1549(1) Å] interactions. The square cavities are ca. 5.0 Å by 6.0 Å.
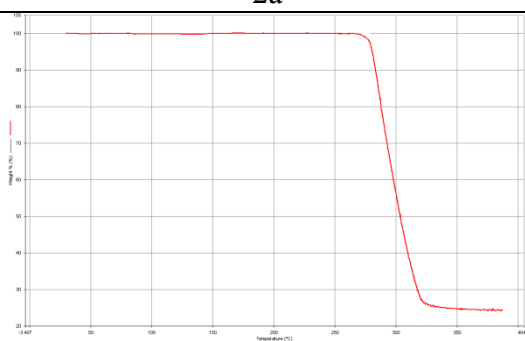
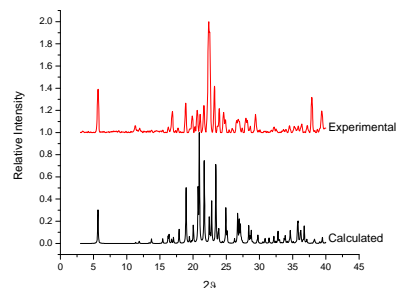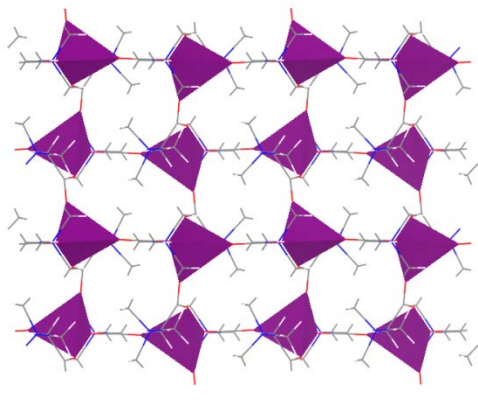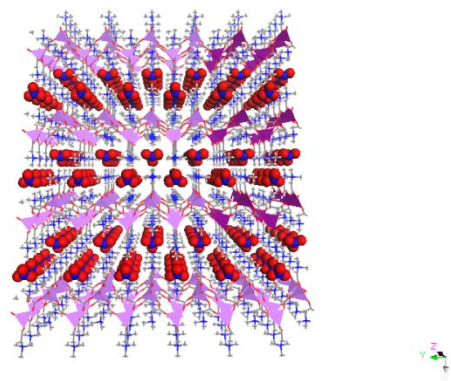| LINBTN2	
2a	2b
2c	2d
2e	2f

Each lithium cation is bridged by four carboxylates to form an undulating square grid (figure 2e), while the opposite ends of the amino acids point away (above and below) from the square grid to establish a bilayer packing arrangement (figure 2f). The nitrate anions reside in proximity with the ammonium groups sustained by C-H···O [3.154(2) Å to 3.606(2) Å] interactions. These square cavities are ca. 5.5 Å by 5.7 Å.
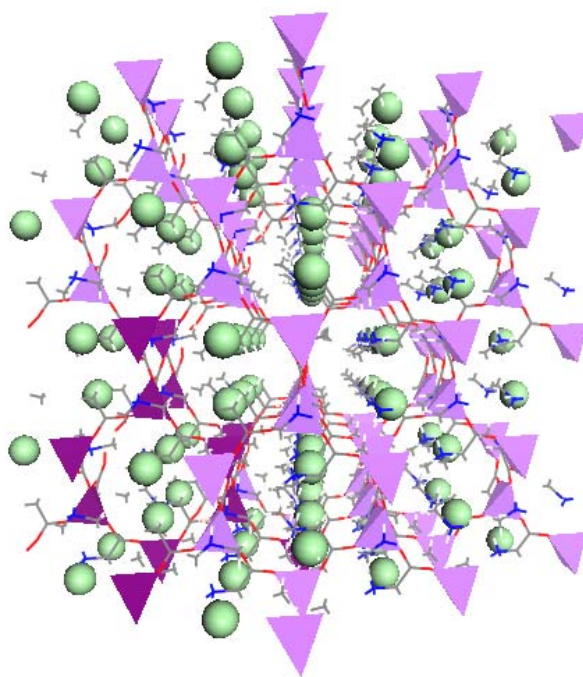
LICDMG2
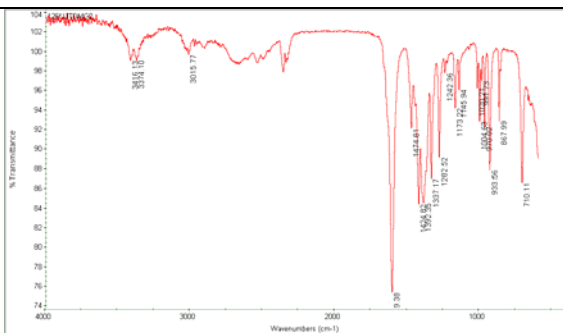
3a
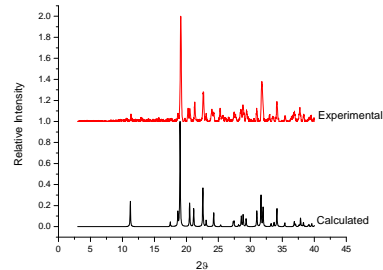
3b

3c

Each lithium cation is bridged by four carboxylates to form a cationic **dia** net with hexagonal channels exhibiting diameters ranging from 10.6 Å to 12.0 Å, populated by pairs of chloride anions (figure 3c). The framework is reinforced by hydrogen bonding between the carboxylate of one amino acid and the ammonium moiety of an adjacent amino acid [N-H···O, 2.742(2) Å]. The presence of pairs of chloride anions [C-H···Cl, 3.628(3) Å, 3.633(2) Å and 3.635(2) Å] in these hexagonal channels interacting with neighboring methyl groups renders interpenetration impossible.

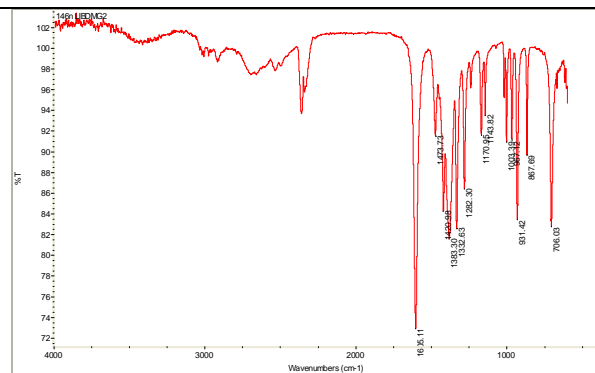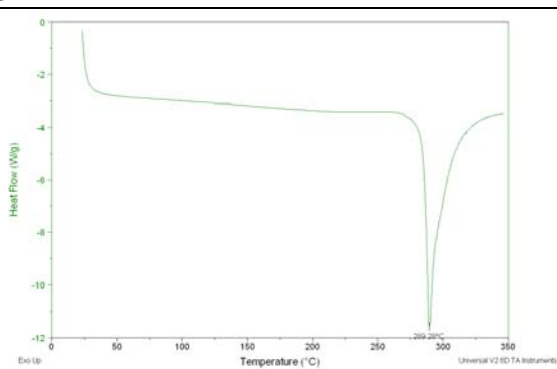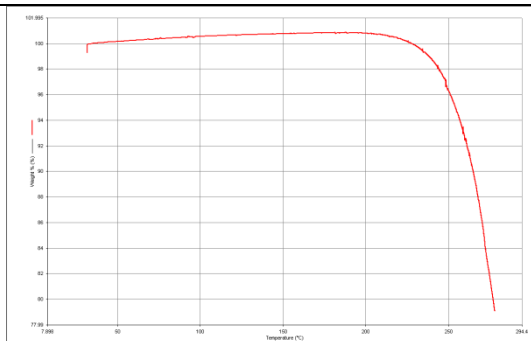| LIBDMG2	
4a	4b
4c	4d
4e	

Each lithium cation is bridged by four carboxylates to form a cationic **dia** net with hexagonal channels exhibiting diameters ranging from 10.7 Å to 12.1 Å, populated by pairs of bromide anions (figure 4e). The framework is reinforced by hydrogen bonding between the carboxylate of one amino acid and the ammonium of an adjacent amino acid [N-H···O, 2.747(2) Å]. The presence of pairs of bromide anions [C-H···Br, 3.716(3) Å, 3.731(2) Å and 3.772(2) Å] in these hexagonal channels interacting with neighboring methyl groups renders interpenetration impossible.
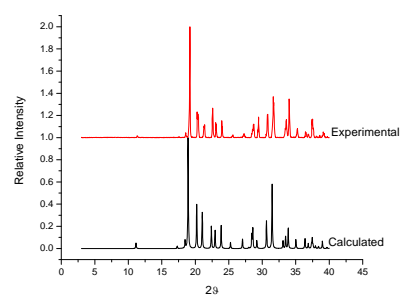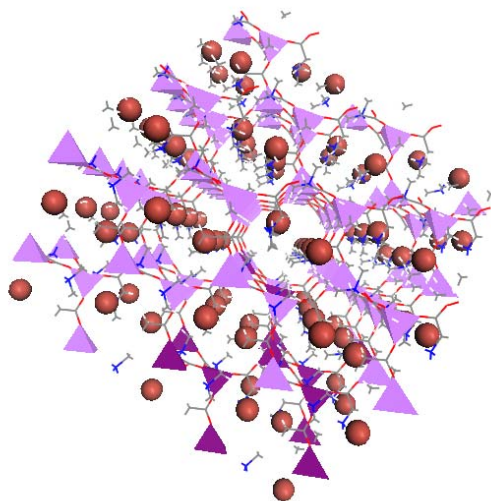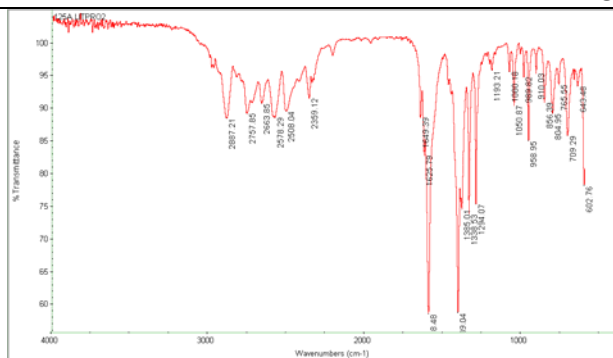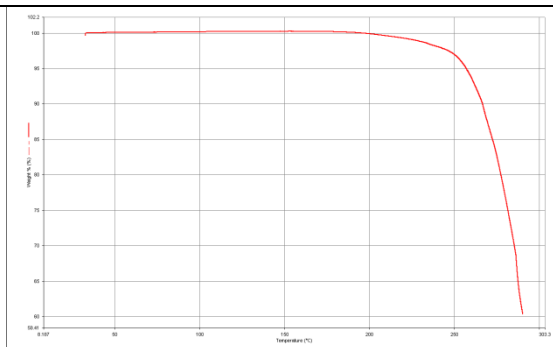
LICPRO2	
5a	5b
5c	5d
5e	

Each lithium cation is bridged by four carboxylates to form a cationic **dia** net with hexagonal channels exhibiting diameters ranging from 10.1 Å to 12.5 Å, populated by pairs of chloride anions (figure 5e). The framework is reinforced by hydrogen bonding between the carboxylate of one amino acid and the ammonium of an adjacent amino acid [N-H···O, 2.7404(15) Å]. The presence of pairs of chloride anions [N-H···Cl, 3.1322(12) Å] in these hexagonal channels interacting with neighboring ammonium groups renders interpenetration impossible.
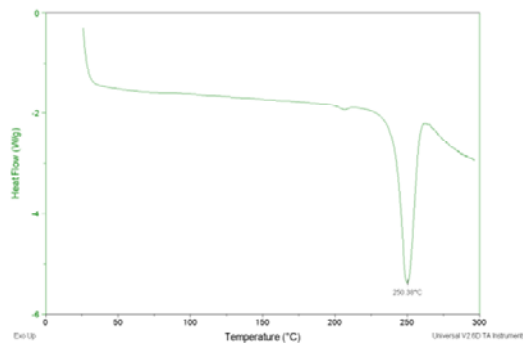
LIBPRO2

6a

6b
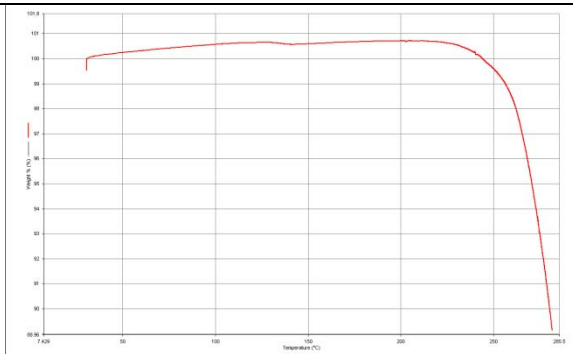
6c
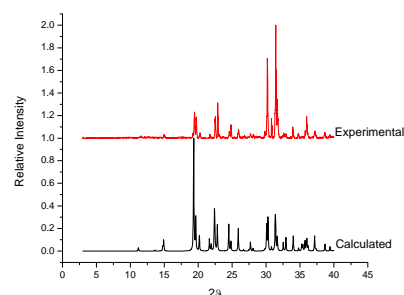
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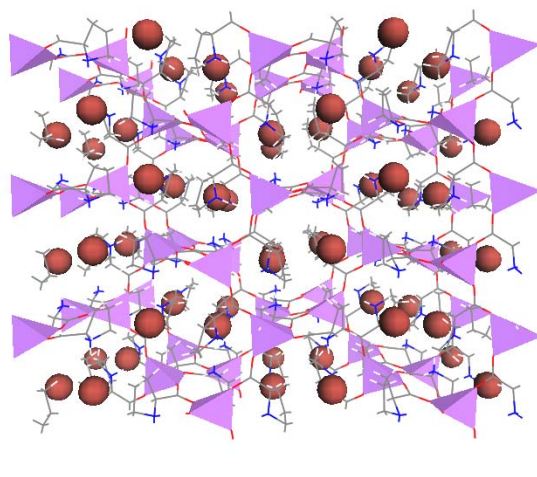
6e

Each lithium cation is bridged by four carboxylates to form a cationic **dia** net with hexagonal channels exhibiting diameters ranging from 10.2 Å to 12.6 Å, populated by pairs of bromide anions (figure 6e). The framework is reinforced by hydrogen bonding between the carboxylate of one amino acid and the ammonium of an adjacent amino acid [N-H···O, 2.737(2) Å]. The presence of pairs of bromide anions [N-H···Br: 3.2769(15) Å] in these hexagonal channels interacting with neighboring ammonium groups renders interpenetration impossible.
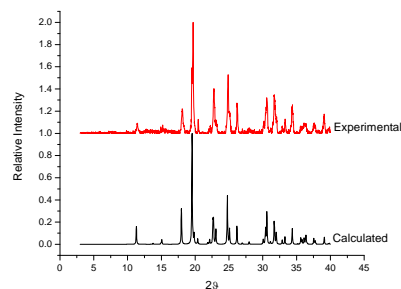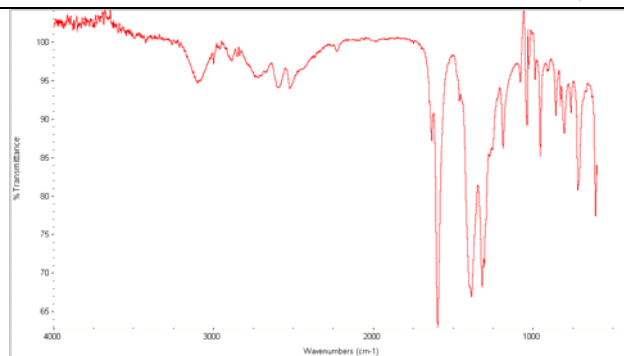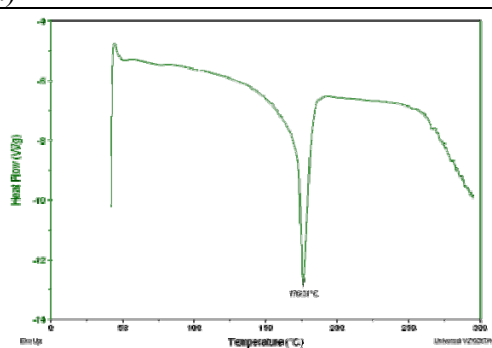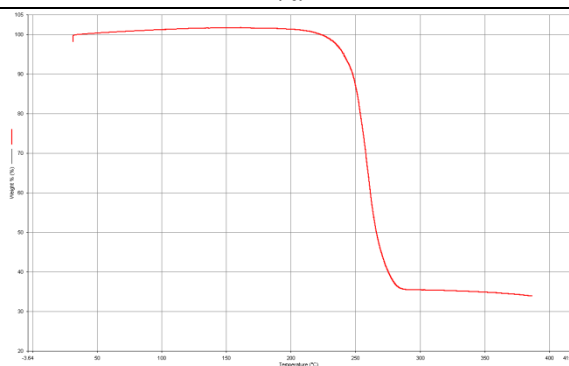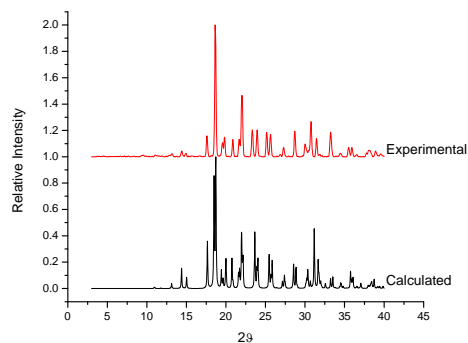
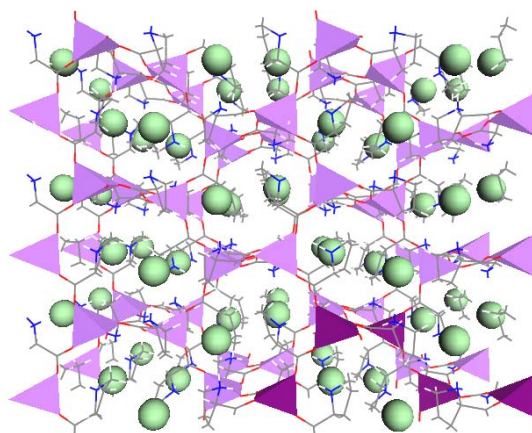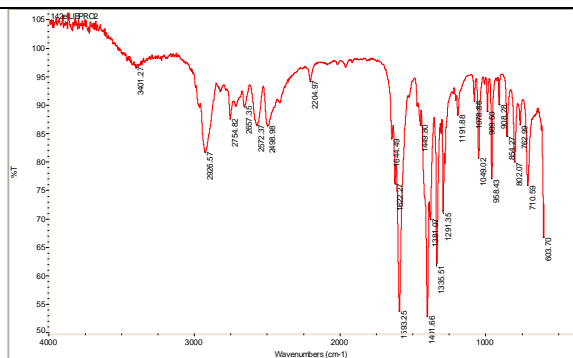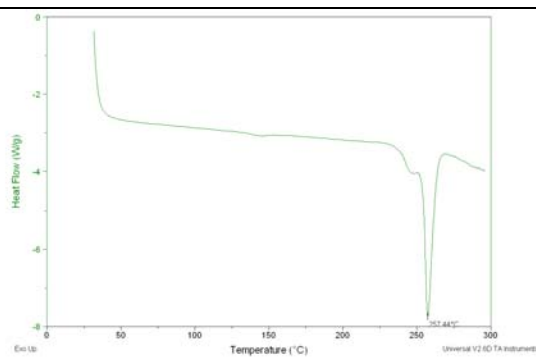| LINPRO2 (dia)	
7a	7b
7c	7d
7e	
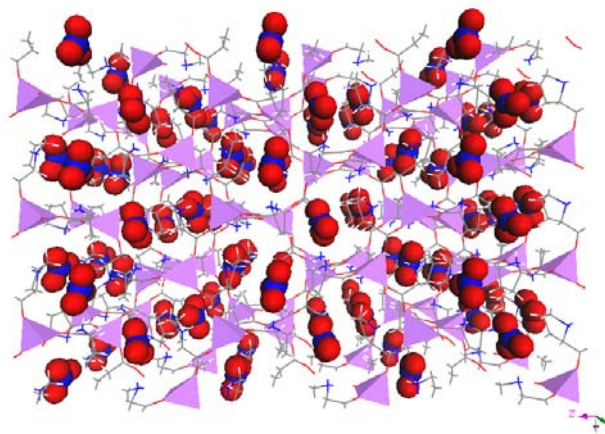
Each lithium cation is bridged by four carboxylates to form a cationic **dia** net with hexagonal channels exhibiting diameters ranging from 10.6 Å to 12.3 Å, populated by pairs of nitrate anions (figure 7e). The framework is reinforced by hydrogen bonding between the carboxylate of one amino acid and the ammonium of an adjacent amino acid [N-H···O, 2.751(5) Å, 2.762(5) Å]. The presence of pairs of nitrate anions [N-H···O, 2.741(6) Å, 2.870(6) Å, 3.046(6) Å] in these hexagonal channels interacting with neighboring ammonium groups renders interpenetration impossible.
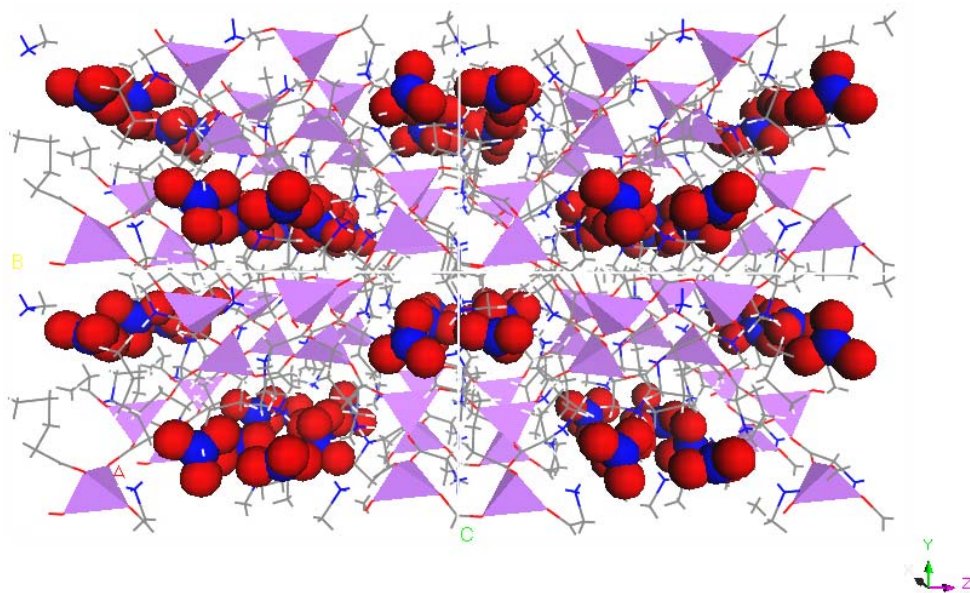
| LINPRO2 (ABW) |
|---|
| |
| 8a |
| A combination of 4- and 8-membered ring channels exist down the crystallographic a axis. When viewed down the crystallographic c axis, 6-membered ring channels are observed. Pairs of nitrate anions occupy the 8-membered ring channels, aided by N-H···O interactions [2.735(8) Å, 2.885(8) Å, 3.005(8) Å]. |

X-ray Crystallography

The X-ray diffraction data were collected using a Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in APEX2 [1] and WinGX v1.70.01 [4,5,6,7] programs packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions or found in the Fourier difference map and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.5Ueq(-CH3), Uiso(H) = 1.2Ueq(-CH2,-CH).

For LINPRO2 (*dia*) the model of the crystal structure was refined as a twin with 0.309(3) twin ratio. The twin operation was a two-fold axis along [110] direct space direction. Table 1 contains a summary of the crystallographic data.

[1] Bruker (2010). *APEX2*). Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker (2009). SAINT. Data Reduction Software. Bruker AXS Inc., Madison, Wisconsin, USA.

[3] Sheldrick, G. M. (2008). *SADABS. Program for Empirical Absorption*

Correction. University of Gottingen, Germany.

[4] Farrugia L.J. Appl. Cryst. (1999). 32, 837±838

[5] Sheldrick, G.M. (1997) SHELXL-97. Program for the Refinement of Crystal

[6] Sheldrick, G.M. (1990) Acta Cryst. A46, 467-473

[7] Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

Table 1. Table of crystallographic data

	LICSAR2	LINBTN2	LICDMG2	LIBDMG2
Formula	$C_6H_{14}ClLiN_2O_4$	$C_{10}H_{22}LiN_3O_7$	$C_8H_{18}ClLiN_2O_4$	$C_8H_{18}BrLiN_2O_4$
MW	220.58	303.25	248.63	293.09
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	Pbca	$P2_1$/c	Fdd2	Fdd2
***a* (Å)**	9.5197 (1)	16.0472 (16)	14.0427 (5)	14.0912 (2)
***b* (Å)**	9.9275 (1)	8.4767 (10)	14.6533 (5)	14.9035 (2)
***c* (Å)**	21.7783 (2)	10.8836 (11)	12.4822 (4)	12.5426 (2)
α (deg)	90	90	90	90
β (deg)	90	103.731 (6)	90	90
γ (deg)	90	90	90	90
***V* /Å^3**	2058.20 (4)	1438.2 (3)	2568.49 (15)	2634.05 (7)
***D_c*/mg m^{-3}**	1.424	1.401	1.286	1.478
Z	8	4	8	8
2θ range	4.06 to 67.95	2.83 to 66.56	5.62 to 68.02	5.58 to 66.35
Nref./Npara.	1838/145	2484/196	1080/76	1114/77
***T* /K**	100 (2)	100 (2)	100 (2)	100 (2)
R$_1$ [I>2sigma(I)]	0.0274	0.0408	0.0312	0.0178
***w*R$_2$**	0.0786	0.1134	0.0726	0.0464
GOF	1.031	1.023	0.994	1.089
Abs coef.	3.248	0.992	2.660	4.282
	LICPRO2	LIBPRO2	LINPRO2 (ABW)	LINPRO2 (*dia*)
Formula	$C_{10}H_{18}ClLiN_2O_4$	$C_{10}H_{18}BrLiN_2O_4$	$C_{10}H_{18}LiN_3O_7$	$C_{10}H_{18}LiN_3O_7$
MW	272.65	317.11	299.21	299.21
Crystal system	Tetragonal	Tetragonal	Orthorhombic	Orthorhombic
Space group	$P4_12_12$	$P4_12_12$	$P2_12_12_1$	$P2_12_12_1$
***a* (Å)**	9.0791 (1)	9.1703 (3)	11.0448 (3)	9.5219 (9)
***b* (Å)**	9.0791 (1)	9.1703 (3)	12.0393 (3)	9.5664 (9)
***c* (Å)**	15.4104 (2)	15.5694 (14)	20.2019 (5)	15.0812 (12)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
***V* /Å^3**	1270.28 (3)	1309.30 (14)	2686.28 (12)	1373.8 (2)
***D_c*/mg m^{-3}**	1.426	1.609	1.480	1.447
Z	4	4	8	4
2θ range	5.66 to 67.91	5.60 to 68.18	4.27 to 65.93	2.93 to 65.90
Nref./Npara.	1150/84	1182/83	4505/379	2347/191
***T* /K**	100 (2)	100 (2)	100 (2)	100 (2)
R$_1$ [I>2sigma(I)]	0.0229	0.0181	0.0314	0.0576
***w*R$_2$**	0.0662	0.0447	0.0799	0.1454
GOF	1.022	1.078	1.045	1.046
Abs coef.	2.745	4.362	1.061	1.038