Atomic/molecular layer deposition and electrochemical performance of dilithium 2-aminoterephthalate

Electronic Supplementary Information (ESI)

Calculating Densities

The critical angle is a direct indicator for the density of the film. To calculate the density we must approximate the empirical formula of the compound. This is done by assuming that each of the carboxylic acid react with 1 equivalent of Li(thd). Also it is assumed that film is composed of only the active material, which will cause some error. However, within a series of a same compound the densities should be relatively comparable. In addition the critical angle is often defined as: the angle of incidence above which total internal reflection occurs, which would mean the mid point between the intensity maximum and intensity minimum of the intensity drop. However, in reality we can't see the intensity minimum of the drop, since it is under the reflection caused by the silicon substrate. Nevertheless, as long as the critical angle is taken same way for every sample, the calculated densities can be compared within a series. For example calculating the density for $Li_2C_8H_5O_4N$ with 400 ALD/MLD cycles, the density becomes:

$$A(\mathrm{Li_2C_8H_5O_4N}) = \frac{(6.94\cdot 2 + 12.011\cdot 8 + 1.008\cdot 5 + 15.999\cdot 4 + 14.007)\,\frac{\mathrm{g}}{\mathrm{mol}}}{20}$$

$$A = 9.65\,\frac{\mathrm{g}}{\mathrm{mol}}$$

$$Z = \frac{3\cdot 2 + 6\cdot 8 + 1\cdot 5 + 8\cdot 4 + 7}{20} = 4.9$$

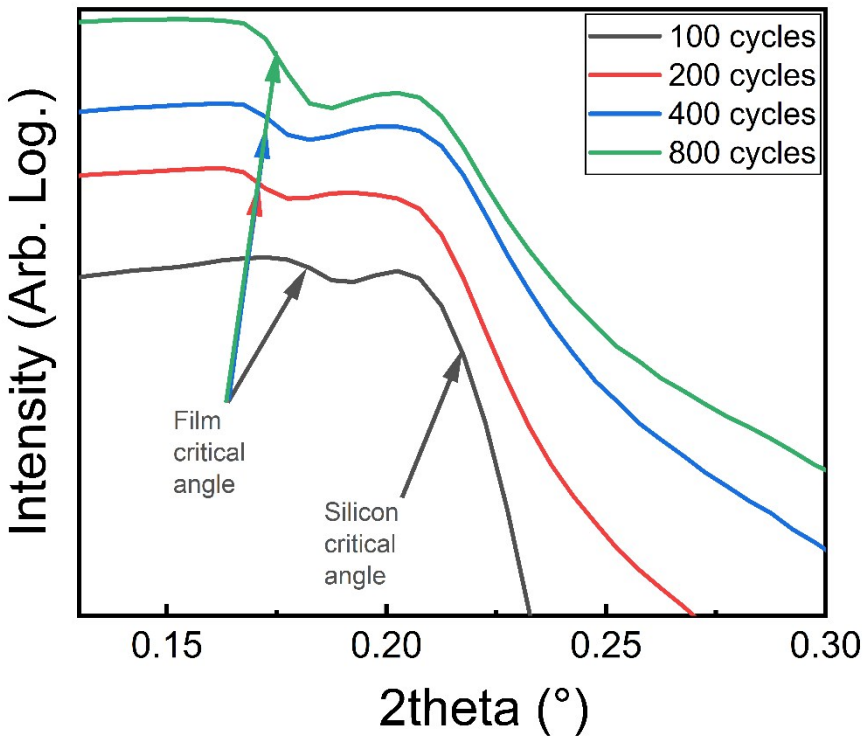
$$\rho_e = \frac{\theta_c^2 \pi}{\lambda^2 r_e} = \frac{0.003063^2 \cdot \pi}{(1.54\cdot 10^{-10}\,\mathrm{m})^2 \cdot 2.82\cdot 10^{-15}\,\mathrm{m}} = 4.41\cdot 10^{29}\,\mathrm{m}^3$$

$$\rho_m = \frac{\rho_e \cdot A}{N_A \cdot Z} = \frac{4.41\cdot 10^{29}\,\mathrm{m}\cdot 9.65\,\frac{\mathrm{g}}{\mathrm{mol}}}{6.022\cdot 10^{23}\,\mathrm{mol}^{-1}\cdot 4.9} = 1.44\,\frac{\mathrm{g}}{\mathrm{cm}^3}$$

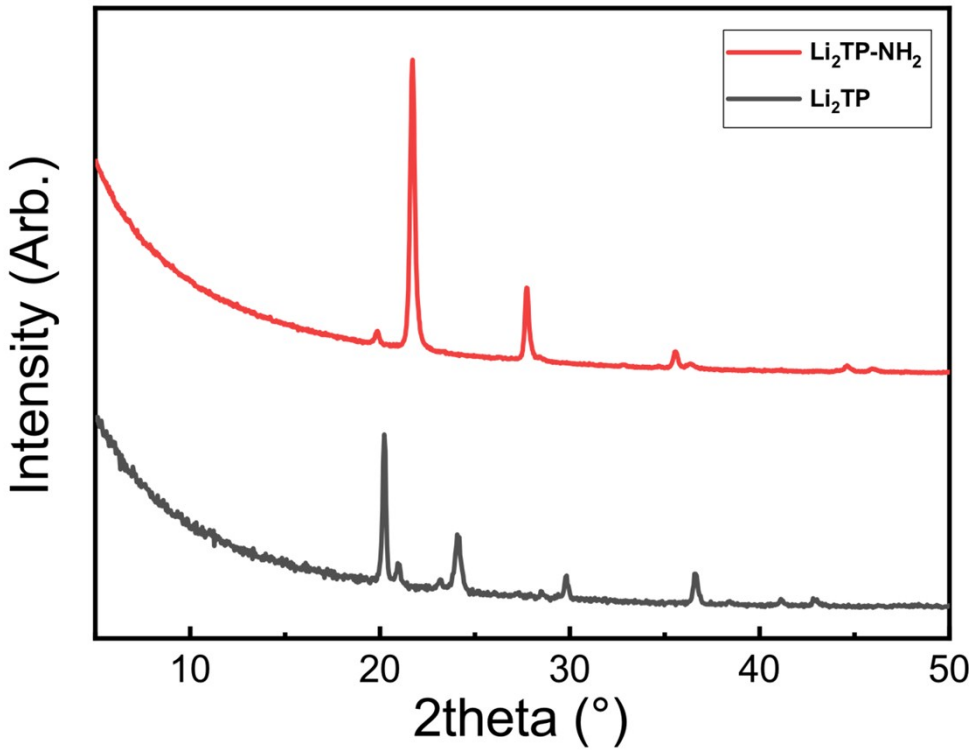
Where, A is the average molar mass, Z is the average atomic number, θ_c is critical angle in radians, λ is the X-ray wavelength of the equipment, r_e is the classical electron radius, N_A is the Avogadro's constant, ρ_e is mean electron density, and ρ_m is the mass density. All calculated densities can be found from Table 1.

Table S1. All calculated densities for the thin film samples. Three significant digits are given to highlight the difference between the samples.

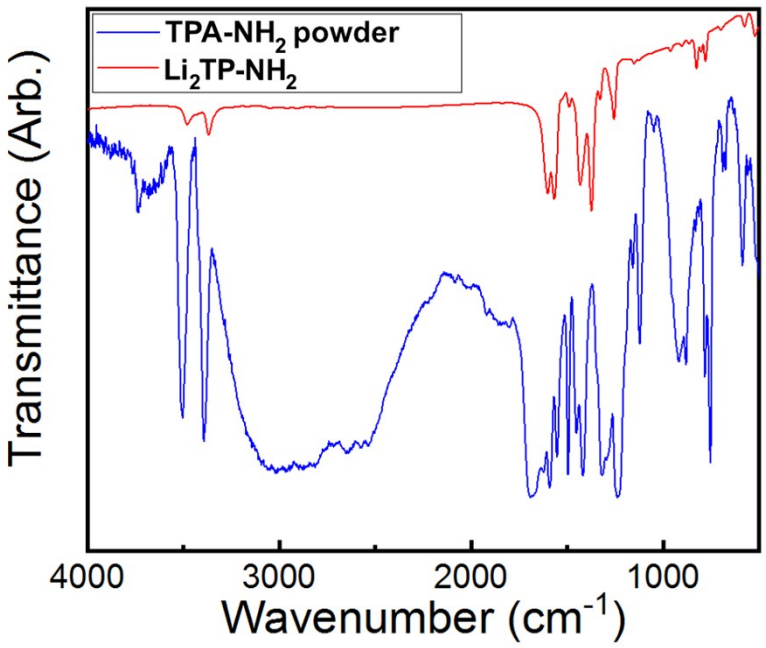
Sample	**Density (g/cm^3)**
$Li_2TP\text{-}NH_2$ – 100 ALD/MLD cycles	1.59
$Li_2TP\text{-}NH_2$ – 200 ALD/MLD cycles	1.40
$Li_2TP\text{-}NH_2$ – 400 ALD/MLD cycles	1.44



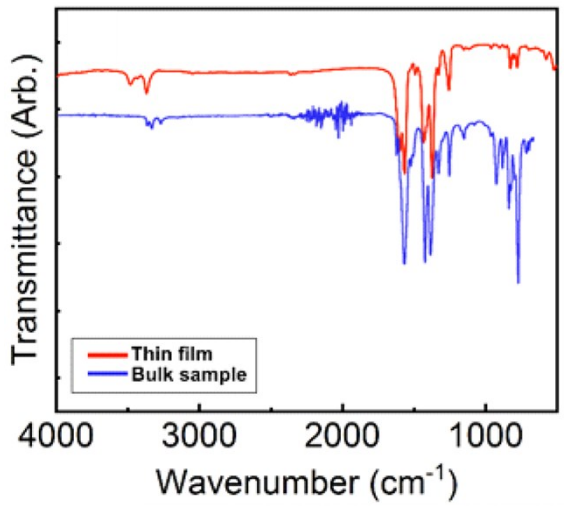
S1. Change in critical angle with respect to the amount of ALD/MLD cycles in the process of $Li_2TP\text{-}NH_2$



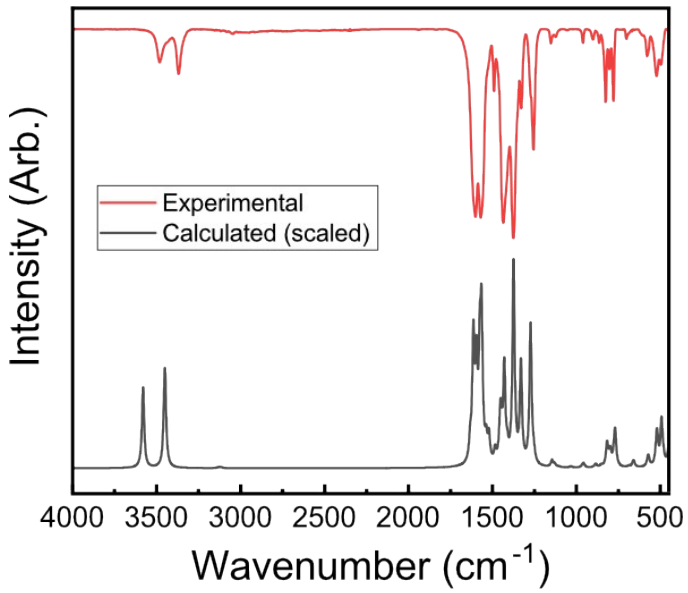
S2. Measured GIXRD patterns of the Li_2TP and $Li_2TP\text{-}NH_2$.



S3. Comparison between the 2-aminoterephtalic acid precursor and the $Li_2TP\text{-}NH_2$ film.



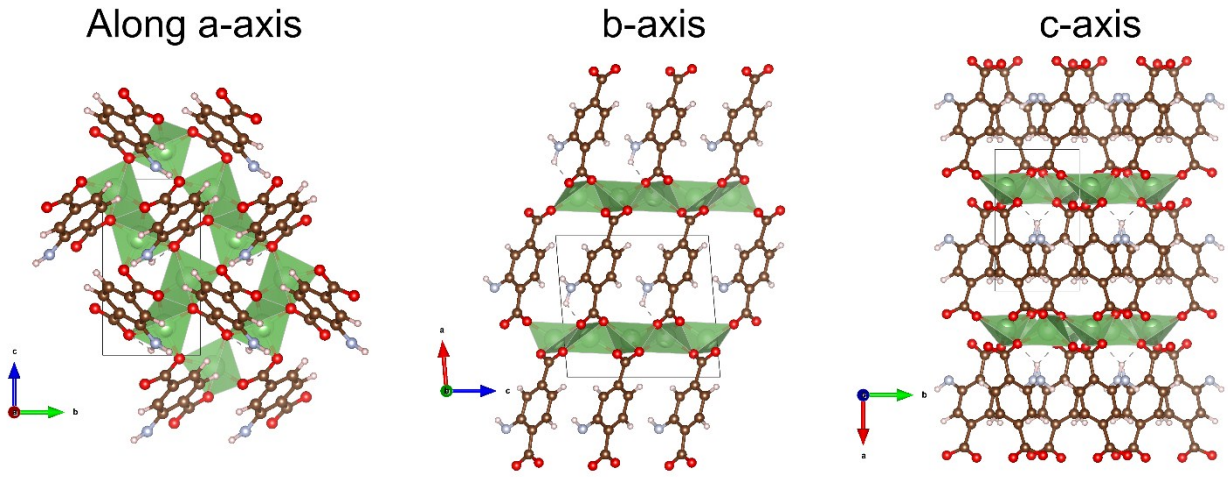
S4. Comparison of $Li_2TP\text{-}NH_2$ spectra measured from a thin film sample (red) and from a previous reports of the bulk form (blue), the latter spectra is measured with ATR-FTIR.[1]



S5. Comparison between calculated (DFT-PBE0) and the experimental FTIR spectra of $Li_2TP\text{-}NH_2$. The wavenumbers of the calculated spectra have been scaled with a factor of 0.965.

Table S2. Interpretation of the FTIR spectrum of $Li_2TP\text{-}NH_2$. A scale factor of 0.965 was applied to the calculated harmonic frequencies to make them better match the experimental data. The letters used: υs and υas symmetric–asymmetric stretching, β; in-plane bending, γ; out-of-plane bending, ρ; scissoring, r; rocking, τ; torsion. The benzene vibrations are named according to Wilson's number system.[2]

Experimental peak (cm^{-1})	Calculated peak(s) (cm^{-1})	Interpretation
3483	3580	$\upsilon_{as}NH_2$
3369	3449	$\upsilon_{s}NH_2$
~3000	3117	Benzene C-H, overtones, and combination bands
1670	1612, 1594	Quadrant benzene stretch 8a and 8b, in combination with ρNH_2
1568	1572, 1565	υ_{as}C=O coupled with ring vibrations
1490	1483	Benzene 19a, υC-C_{ring}
1433	1449, 1429	Benzene 19b, υC-C_{ring}
1372	1373	υ_{s}C=O coupled with ring vibrations
1329	1330	Benzene 14, υC-C_{ring}
1256	1271	υC-N, and υC-C_{ring}
1151	1144	9a and 9b benzene vibrations, βCH
960	955	γCH
900	883	γCH
863	847	γCH
826	815	Ring breathing, related to 802 cm^{-1}
802	797	Ring breathing, related to 826 cm^{-1}
779	769	γCOO and γCH
679	657	NH_2 wagging
579	570	β(CCC)
523	521	υLi-O, related to 497 cm^{-1}
497	492	υLi-O, related to 523 cm^{-1}



S6. Predicted crystal structure of $Li_2TP\text{-}NH_2$ a long with a, b, and c-axis visualized with VESTA.

Computational supporting information

USPEX and Quantum Espresso input files for the structure prediction of $Li_2TP\text{-}NH_2$

General input file INPUT.txt

```
******************************************
*      TYPE OF RUN AND SYSTEM            *
******************************************
USPEX : calculationMethod (USPEX, VCNEB, META)
310   : calculationType (dimension: 0-3; molecule: 0/1; varcomp: 0/1)
1     : optType (optimise by: 1=enthalpy, 2=volume, 3=hardness,...)
1     : AutoFrac

% atomType
H Li C O N
% EndAtomType

% numSpecies
2 4
% EndNumSpecies

% symmetries
2-230
% EndSymmetries

******************************************
*               POPULATION               *
******************************************
30    : populationSize
40    : numGenerations
10    : stopCrit
0     : reoptOld
******************************************
*          VARIATION OPERATORS           *
******************************************
0.50  : fracGene
0.20  : fracRand
0.10  : fracAtomsMut
0.10  : fracRotMut
0.10  : fracLatMut
0.00  : fracPerm
**************************************
*             CONSTRAINTS              *
```

```
****************************************
% IonDistances
0.5 0.5 0.5 0.5 0.5
0.0 1.0 1.0 1.0 1.0
0.0 0.0 1.0 1.0 1.0
0.0 0.0 0.0 1.0 1.0
0.0 0.0 0.0 0.0 1.0
% EndDistances

% MolCenters
2.5 1.0
0.0 1.0
% EndMol
****************************************
*   DETAILS OF AB INITIO CALCULATIONS   *
****************************************
% abinitioCode
8 8 8
% EndAbinit

% KresolStart
0.14 0.12 0.10
% Kresolend

% commandExecutable
srun pw.x -input qe.in > output
% EndExecutable

20   : numParallelCalcs
1    : whichCluster
0.0  : ExternalPressure
```

MOL_1

```
TPA-NH2
Number of atoms: 18
   O   -0.0348   0.7683  -3.9245   0  0  0  1
   C   -0.0124  -0.2406  -3.1450   1  0  0  1
   C    0.0108   0.0267  -1.6517   2  1  0  1
   O   -0.0167  -1.4558  -3.5298   2  1  3  0
   C   -0.0282   1.3331  -1.1469   3  2  1  0
   C    0.0783  -1.0272  -0.7244   3  2  5  0
   C   -0.0084   1.5742   0.2337   5  3  2  0
   H   -0.0724   2.1710  -1.8392   5  3  7  0
   C    0.0688  -0.7989   0.6657   6  3  2  0
   H    0.1452  -2.0455  -1.1015   6  3  9  0
   H   -0.0406   2.5999   0.5954   7  5  3  0
   C    0.0425   0.5194   1.1663   7  5 11  0
   N    0.2447  -1.9123   1.5269   9  6 12  0
   C    0.0020   0.8343   2.6552  12  7  9  0
   H   -0.3588  -2.6752   1.2521  13  9  6  0
   H    0.0380  -1.5839   2.4910  13  9 15  0
   O   -0.1865  -0.1399   3.4641  14 12  7  0
   O    0.1285   2.0525   3.0125  14 12 17  0
```

MOL_2

```
Li
Number of atoms: 1
   Li   0.0000  0.0000   0.0000    0  0  0  1
```

```
qEspresso_options_1&CONTROL
  calculation  = 'vc-relax'
  restart_mode = 'from_scratch'
  prefix       = 'uspex'
```

```
  wf_collect   = .false.
  disk_io = 'none'
  etot_conv_thr=1.0D-3
  forc_conv_thr=1.0D-2
  nstep = 25
/
&SYSTEM
  ibrav     = 0
  nat       = AAAA
  ntyp      = BBBB
  ecutwfc   = 40
  ecutrho   = 200
  nosym     = .true.
  occupations = 'smearing'
  smearing = 'gaussian'
  degauss = 0.02
/
&ELECTRONS
  conv_thr = 5.D-04
  mixing_beta = 0.7
  electron_maxstep = 100
/
&IONS
/
&CELL
  cell_factor = 2.0
/
ATOMIC_SPECIES
  H  1.00794 h_pbe_v1.4.uspp.F.UPF
  Li 6.941   li_pbe_v1.4.uspp.F.UPF
  C  12.0107 c_pbe_v1.2.uspp.F.UPF
  O  15.9994 o_pbe_v1.2.uspp.F.UPF
  N  14.0067 n_pbe_v1.2.uspp.F.UPF
```

qEspresso_options_2

```
&CONTROL
  calculation  = 'vc-relax'
  restart_mode = 'from_scratch'
  prefix       = 'uspex'
  wf_collect   = .false.
  disk_io = 'none'
  etot_conv_thr=1.0D-3
  forc_conv_thr=1.0D-2
  nstep = 30
/
&SYSTEM
  ibrav     = 0
  nat       = AAAA
  ntyp      = BBBB
  ecutwfc   = 40
  ecutrho   = 200
  nosym     = .true.
  occupations = 'smearing'
  smearing = 'gaussian'
  degauss = 0.01
/
&ELECTRONS
  conv_thr    = 1.D-05
  mixing_beta = 0.7
  electron_maxstep = 100
/
&IONS
/
&CELL
  cell_factor = 2.0
/
ATOMIC_SPECIES
  H  1.00794 h_pbe_v1.4.uspp.F.UPF
  Li 6.941   li_pbe_v1.4.uspp.F.UPF
  C  12.0107 c_pbe_v1.2.uspp.F.UPF
  O  15.9994 o_pbe_v1.2.uspp.F.UPF
```

```
  N  14.0067 n_pbe_v1.2.uspp.F.UPF
```

qEspresso_options_3

```
&CONTROL
  calculation  = 'vc-relax'
  restart_mode = 'from_scratch'
  prefix       = 'uspex'
  wf_collect   = .false.
  disk_io = 'none'
  etot_conv_thr=1.0D-4
  forc_conv_thr=1.0D-3
  nstep = 30
/
&SYSTEM
  ibrav     = 0
  nat       = AAAA
  ntyp      = BBBB
  ecutwfc   = 40
  ecutrho   = 200
  !nosym     = .true.
/
&ELECTRONS
  conv_thr    = 1.D-06
  mixing_beta = 0.7
  electron_maxstep = 100
/
&IONS
/
&CELL
  cell_factor = 2.0
/
ATOMIC_SPECIES
  H  1.00794 h_pbe_v1.4.uspp.F.UPF
  Li 6.941   li_pbe_v1.4.uspp.F.UPF
  C  12.0107 c_pbe_v1.2.uspp.F.UPF
  O  15.9994 o_pbe_v1.2.uspp.F.UPF
  N  14.0067 n_pbe_v1.2.uspp.F.UPF
```

Lowest-energy structures optimized at the DFT-PBE0/TZVP level of theory

Table S3. Relative energies of the lowest-energy structures (DFT-PBE0/TZVP). Structure **A** is the structure discussed in the main paper.

Structure	Relative energy (kJ/mol)
A	0.0
B	5.4
C	4.5
D	4.6
E	5.3

Structures in CIF format

Structure A

```
data_findsym-output
_audit_creation_method FINDSYM
```

```
_symmetry_space_group_name_H-M "P 1 c 1"
_symmetry_Int_Tables_number 7

_cell_length_a    8.47919
_cell_length_b    5.06878
_cell_length_c    9.15898
_cell_angle_alpha 90.00000
_cell_angle_beta  94.77340
_cell_angle_gamma 90.00000

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
1 x,y,z
2 x,-y,z+1/2

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
O1  O    2 a 0.17844  0.78321  -0.01586 1.00000
O2  O    2 a 0.16238  0.43179  0.83909  1.00000
O3  O    2 a 0.37245  0.73053  0.61812  1.00000
O4  O    2 a 0.39337  0.07740  0.76662  1.00000
N1  N    2 a 0.63125  0.45772  0.57159  1.00000
C1  C    2 a 0.10655  0.64072  0.88740  1.00000
C2  C    2 a -0.05808 0.71942  0.83040  1.00000
C3  C    2 a 0.86737  -0.06126 0.88789  1.00000
C4  C    2 a 0.86139  0.56453  0.72543  1.00000
C5  C    2 a 0.71129  -0.01122 0.84158  1.00000
C6  C    2 a 0.70218  0.61465  0.67589  1.00000
C7  C    2 a 0.62411  0.82693  0.74046  1.00000
C8  C    2 a 0.45286  0.88239  0.70651  1.00000
Li1 Li   2 a 0.26780  0.86955  0.43625  1.00000
Li2 Li   2 a 0.27885  0.63008  0.16690  1.00000
H1  H    2 a -0.06906 0.06287  -0.03107 1.00000
H2  H    2 a -0.07959 0.39504  0.68278  1.00000
H3  H    2 a 0.65088  0.15528  0.88560  1.00000
H4  H    2 a 0.69455  0.32081  0.52240  1.00000
H5  H    2 a 0.52051  0.50189  0.53131  1.00000
```

Structure B

```
data_findsym-output
_audit_creation_method FINDSYM

_symmetry_space_group_name_H-M "P 1 21 1"
_symmetry_Int_Tables_number 4

_cell_length_a    8.55004
_cell_length_b    5.05061
_cell_length_c    9.16772
_cell_angle_alpha 90.00000
_cell_angle_beta  96.73474
_cell_angle_gamma 90.00000

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
1 x,y,z
2 -x,y+1/2,-z

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
```

```
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
O1  O    2 a 0.61028  0.43485  0.06512 1.00000
O2  O    2 a 0.63203  0.07940  0.20903 1.00000
O3  O    2 a 0.42553  0.38925  0.42876 1.00000
O4  O    2 a 0.40017  0.72506  0.27220 1.00000
N1  N    2 a 0.17823  0.08609  0.46055 1.00000
C1  C    2 a 0.68807  0.28235  0.15490 1.00000
C2  C    2 a 0.85927  0.34361  0.19859 1.00000
C3  C    2 a -0.06799 0.55538  0.13527 1.00000
C4  C    2 a -0.05547 0.18721  0.30335 1.00000
C5  C    2 a 0.08913  0.60451  0.17947 1.00000
C6  C    2 a 0.10371  0.23965  0.35281 1.00000
C7  C    2 a 0.17766  0.45286  0.28691 1.00000
C8  C    2 a 0.34471  0.52766  0.33118 1.00000
Li1 Li   2 a 0.50243  0.02952  0.37345 1.00000
Li2 Li   2 a 0.51729  0.78465  0.10690 1.00000
H1  H    2 a 0.86581  0.67814  0.05322 1.00000
H2  H    2 a 0.88694  0.02027  0.34881 1.00000
H3  H    2 a 0.14801  0.76821  0.13265 1.00000
H4  H    2 a 0.11395  -0.03460 0.51748 1.00000
H5  H    2 a 0.28398  0.14612  0.50906 1.00000
```

Structure C

```
data_findsym-output
_audit_creation_method FINDSYM

_symmetry_space_group_name_H-M "P 1 21 1"
_symmetry_Int_Tables_number 4

_cell_length_a    8.19566
_cell_length_b    5.27252
_cell_length_c    9.44641
_cell_angle_alpha 90.00000
_cell_angle_beta  98.05366
_cell_angle_gamma 90.00000

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
1 x,y,z
2 -x,y+1/2,-z

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
O1  O    2 a 0.62571  0.11481  0.55711  1.00000
O2  O    2 a 0.67820  0.75037  0.67281  1.00000
O3  O    2 a 0.41002  0.33752  -0.00412 1.00000
O4  O    2 a 0.45714  0.42419  0.77626  1.00000
N1  N    2 a 0.22753  0.88949  -0.01684 1.00000
C1  C    2 a 0.71681  -0.02861 0.64019  1.00000
C2  C    2 a 0.88530  0.06626  0.70088  1.00000
C3  C    2 a -0.04812 0.27620  0.64033  1.00000
C4  C    2 a -0.02069 -0.06393 0.81196  1.00000
C5  C    2 a 0.11142  0.35068  0.69082  1.00000
C6  C    2 a 0.13770  0.01574  0.86737  1.00000
C7  C    2 a 0.20427  0.22721  0.80492  1.00000
C8  C    2 a 0.36981  0.33359  0.86297  1.00000
Li1 Li   2 a 0.64192  0.62767  0.85716  1.00000
Li2 Li   2 a 0.53236  0.46412  0.59284  1.00000
```

```
H1  H    2 a 0.87988  0.37805  0.55373  1.00000
H2  H    2 a -0.06910 0.76445  0.85379  1.00000
H3  H    2 a 0.16626  0.51106  0.64336  1.00000
H4  H    2 a 0.17337  0.72679  0.00904  1.00000
H5  H    2 a 0.34762  0.85375  -0.02922 1.00000
```

Structure D

```
data_findsym-output
_audit_creation_method FINDSYM

_symmetry_space_group_name_H-M "P 1 21 1"
_symmetry_Int_Tables_number 4

_cell_length_a    8.20426
_cell_length_b    5.26912
_cell_length_c    9.44825
_cell_angle_alpha 90.00000
_cell_angle_beta  98.16461
_cell_angle_gamma 90.00000

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
1 x,y,z
2 -x,y+1/2,-z

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
O1  O    2 a 0.12569  0.58297  0.55690  1.00000
O2  O    2 a 0.17816  0.21883  0.67322  1.00000
O3  O    2 a -0.08977 0.80608  -0.00427 1.00000
O4  O    2 a -0.04288 0.89167  0.77605  1.00000
N1  N    2 a 0.72766  0.35800  -0.01678 1.00000
C1  C    2 a 0.21680  0.43972  0.64023  1.00000
C2  C    2 a 0.38527  0.53476  0.70080  1.00000
C3  C    2 a 0.45168  0.74482  0.64024  1.00000
C4  C    2 a 0.47940  0.40455  0.81192  1.00000
C5  C    2 a 0.61119  0.81929  0.69073  1.00000
C6  C    2 a 0.63775  0.48425  0.86733  1.00000
C7  C    2 a 0.70420  0.69570  0.80483  1.00000
C8  C    2 a 0.86984  0.80176  0.86279  1.00000
Li1 Li   2 a 0.14136  0.09602  0.85744  1.00000
Li2 Li   2 a 0.03272  -0.06819 0.59280  1.00000
H1  H    2 a 0.37962  0.84679  0.55362  1.00000
H2  H    2 a 0.43108  0.23283  0.85369  1.00000
H3  H    2 a 0.66585  -0.02020 0.64329  1.00000
H4  H    2 a 0.67343  0.19548  0.00927  1.00000
H5  H    2 a 0.84751  0.32175  -0.02921 1.00000
```

Structure E

```
data_findsym-output
_audit_creation_method FINDSYM

_symmetry_space_group_name_H-M "P 1 21 1"
_symmetry_Int_Tables_number 4

_cell_length_a    8.52890
_cell_length_b    5.05859
_cell_length_c    9.16187
_cell_angle_alpha 90.00000
```

```
_cell_angle_beta  96.34309
_cell_angle_gamma 90.00000

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
1 x,y,z
2 -x,y+1/2,-z

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
O1  O    2 a 0.61125  0.18206  0.56423  1.00000
O2  O    2 a 0.63198  0.82659  0.70769  1.00000
O3  O    2 a 0.42535  0.13543  -0.07077 1.00000
O4  O    2 a 0.40147  0.47098  0.77285  1.00000
N1  N    2 a 0.17705  0.83268  -0.03976 1.00000
C1  C    2 a 0.68855  0.02949  0.65383  1.00000
C2  C    2 a 0.85985  0.09043  0.69778  1.00000
C3  C    2 a -0.06658 0.30212  0.63490  1.00000
C4  C    2 a -0.05570 -0.06616 0.80249  1.00000
C5  C    2 a 0.09056  0.35094  0.67947  1.00000
C6  C    2 a 0.10344  -0.01402 0.85233  1.00000
C7  C    2 a 0.17827  0.19897  0.78678  1.00000
C8  C    2 a 0.34530  0.27377  0.83156  1.00000
Li1 Li   2 a 0.48212  0.03189  0.39367  1.00000
Li2 Li   2 a 0.49706  0.27610  0.12650  1.00000
H1  H    2 a 0.86788  0.42508  0.55293  1.00000
H2  H    2 a 0.88602  0.76722  0.84778  1.00000
H3  H    2 a 0.15007  0.51475  0.63317  1.00000
H4  H    2 a 0.11212  0.71163  0.01677  1.00000
H5  H    2 a 0.28254  0.89275  0.00910  1.00000
```

References

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2 P. Larkin, *Infrared and Raman Spectroscopy*, Elsevier, 2011, vol. 9.