

## Supporting Information

### **A *p*-Phenylenediamine Oligomer-Mediated Li–O<sub>2</sub> Battery with an Extremely Low Charge Potential of 3.1 V**

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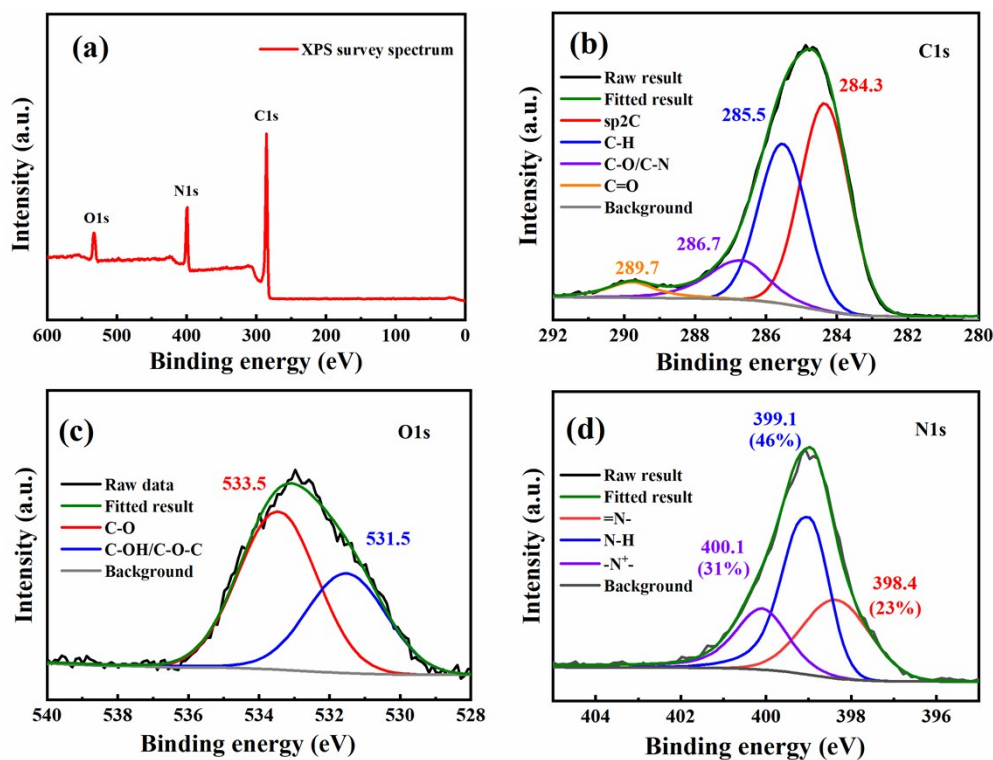
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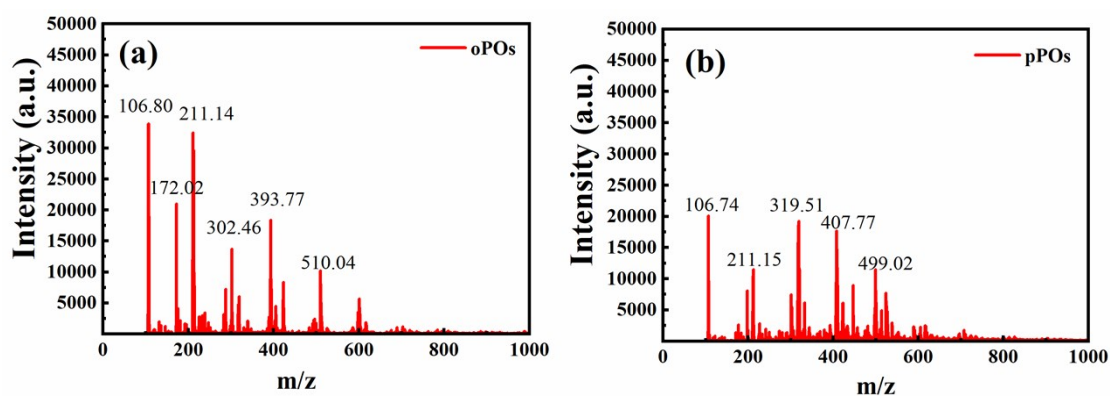
**Table S1. Comparison of the charge potential and overpotential of Li–O<sub>2</sub> batteries with the addition of various RMs.**

NO.	Redox mediator	Charging voltage (V)	Overpotential (V)	Reference
1	LiI	3.5	0.8	1
2	LiBr	3.5	0.8	2
3	MoCl <sub>5</sub>	3.6	0.9	3
4	TDPA	3.5	0.8	4
5	TTF	3.43	0.8	5
6	DBBQ	3.75	1.0	6
7	TEMPO	3.6	0.7	7
8	AZADO	3.6	0.9	8
9	Vitamin K	3.5	0.8	9
<b>10</b>	<b>pPO</b>	<b>3.1</b>	<b>0.4</b>	<b>This work</b>

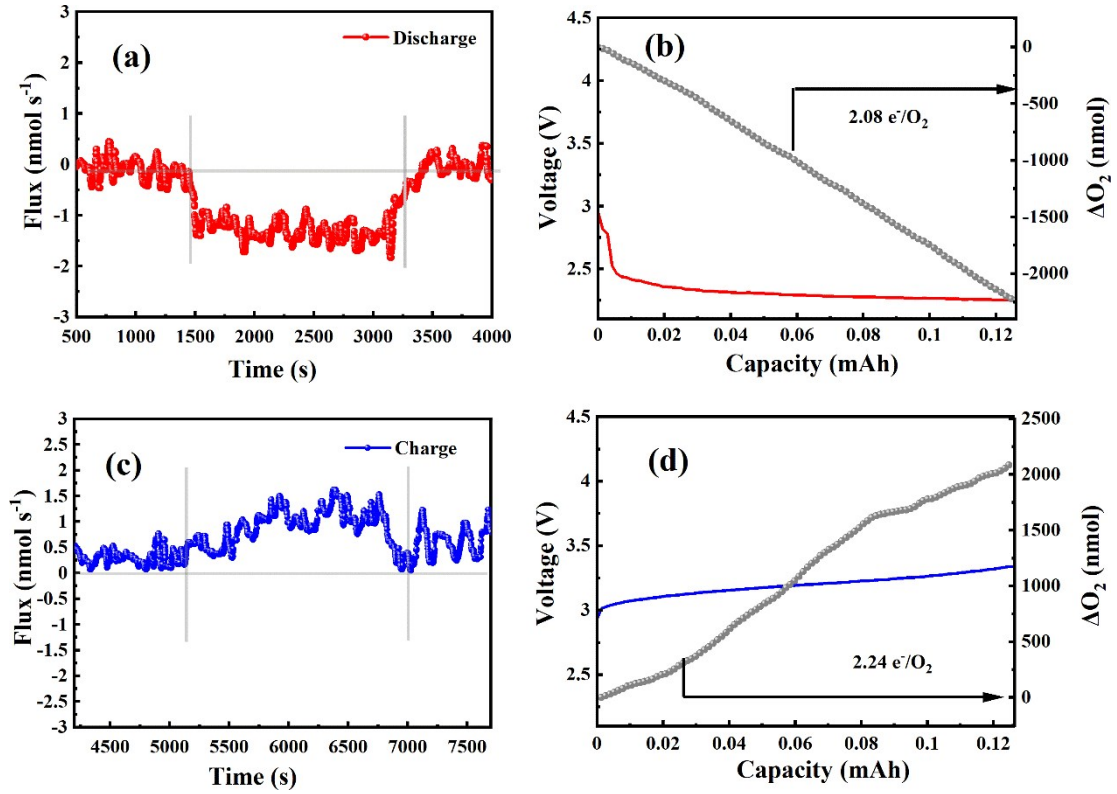
**Table 1:** shows the charge potential and overpotential of typical RM-mediated Li–O<sub>2</sub> batteries reported in the literature. In contrast, the Li–O<sub>2</sub> battery mediated by pPO shows the lowest charge potential.



**Fig. S1** Characterization of the molecular structure of pPO. X-ray photoelectron spectroscopy of pPO indicates the existence of various functional groups. **a** XPS total spectrum, and **b** C 1s, **c** O 1s and **d** N 1s XPS spectra.



**Fig. S2:** TOF-MS of oPO and pPO show that the main components of the phenylenediamine oligomers are dimers and trimers. **a** TOF mass spectrum of oPO. **b** TOF mass spectrum of mPO.



**Fig. S3:** The DEMS data indicate that the number of transferred electrons in the discharge and charge process is  $2.22 e^-/O_2$  and  $2.60 e^-/O_2$ . **a, b** Oxygen absorption during the discharge process and the corresponding discharge curve. **c, d** Oxygen evolution during the charging process and the corresponding charge curve.

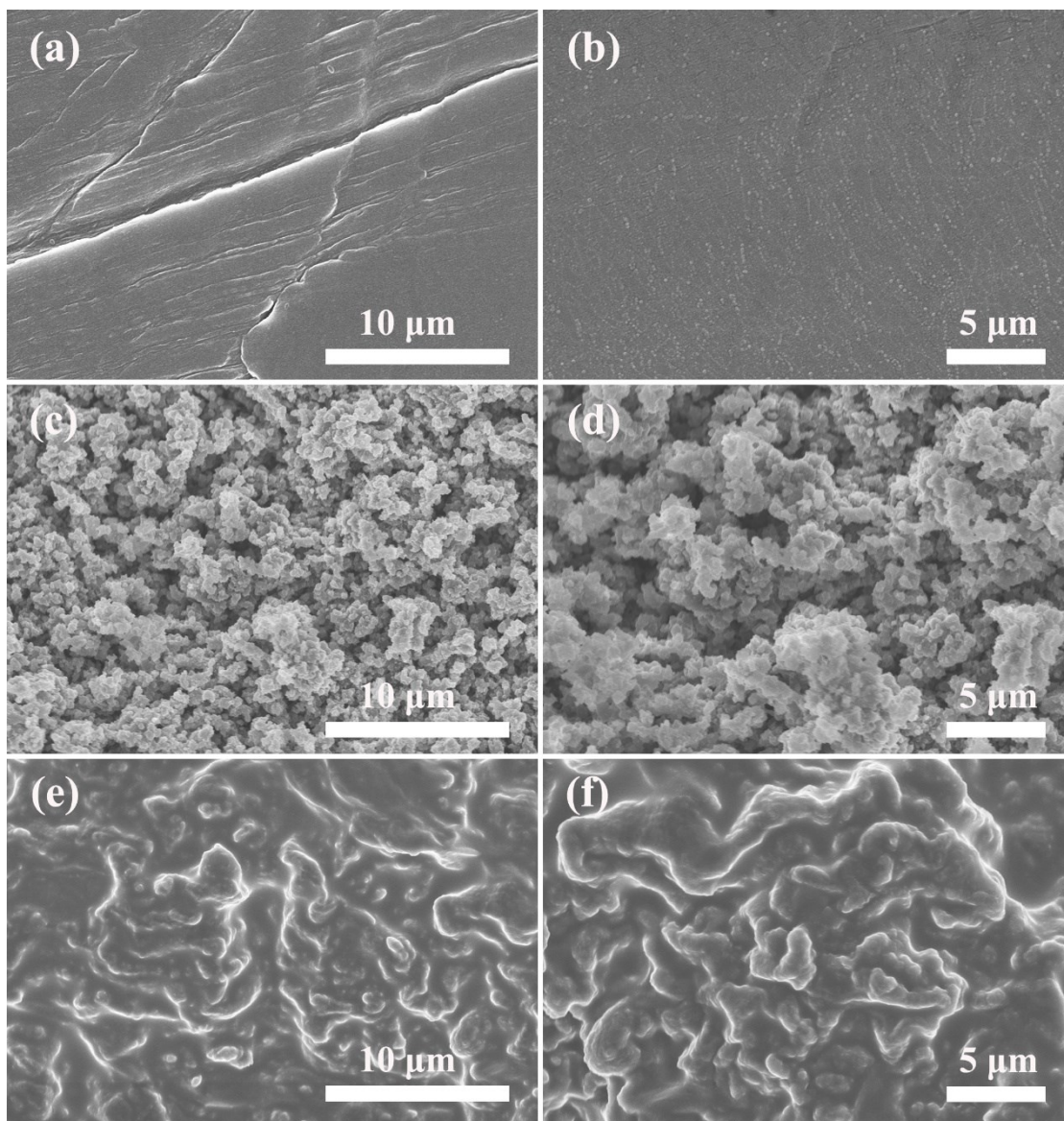
**Table 2: DEMS data of Li-O<sub>2</sub> cells with and without pPO.**

	$\Delta Q (e^-)$	$\Delta O_2 (nmol)$	$n (e^-/O_2)$
Discharge	$4.66 \times 10^{-6}$	2287.31	2.03
Charge	$4.66 \times 10^{-6}$	2083.53	2.24

$\Delta O_2$ : The amount of substance that releases oxygen;

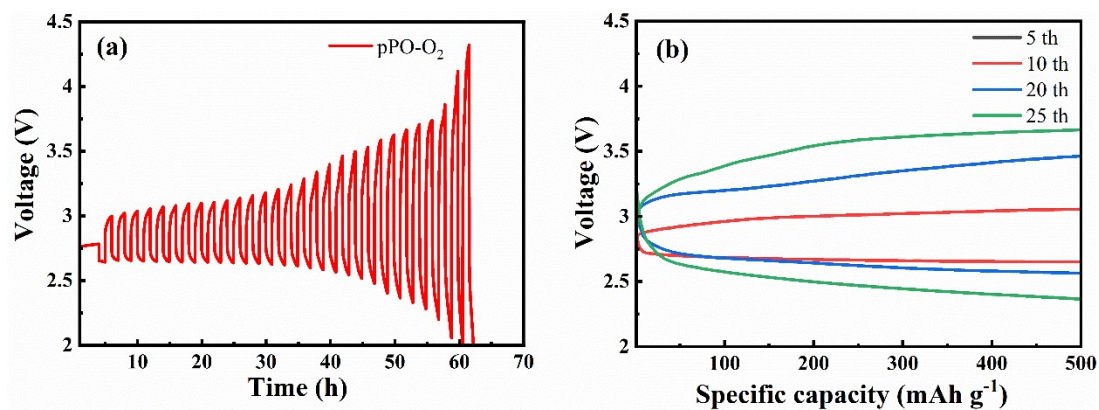
$\Delta Q$ : Total number of electrons;

$n$ : Number of electrons transferred,  $n = \Delta Q / \Delta O_2$ .

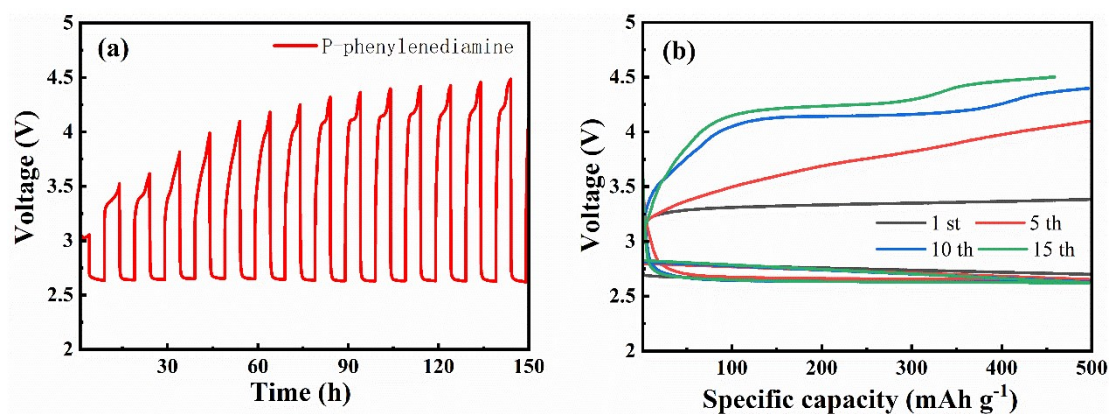


**Fig. S4:** SEM images of a lithium foil showing that pPO protects the foil, which can prevent its pulverization and failure. Lithium foil was cycled 120h at 200 mA g<sup>-1</sup> current density in a battery, and then taken out and dried to observe with an electron microscope. **a, b** Before the cycle and after 120 h; **c, d** TEGDME without pPO; **e, f** TEGDME containing pPO.

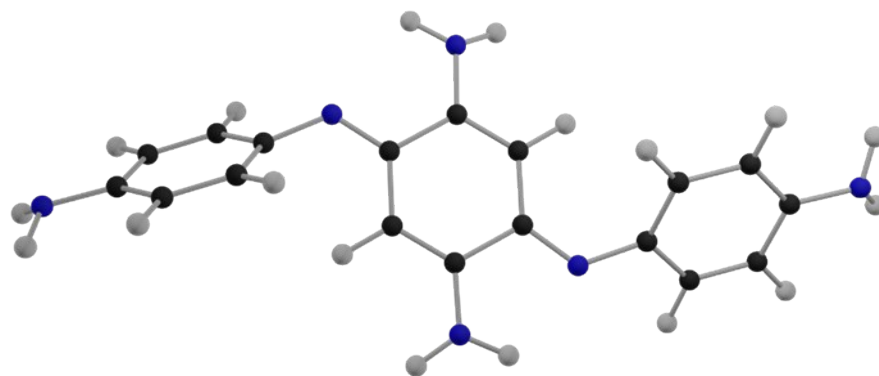




**Fig. S5:** The cycle performance of lithium oxygen battery with pPO added in oxygen atmosphere. **a** Voltage–time plot. **b** Charge–discharge curves of different cycles (5th, 10th, 20th, 25th).



**Fig. S6:** The cycle performance of lithium oxygen battery with P-phenylenediamine added in oxygen atmosphere. **a** Voltage–time plot. **b** Charge–discharge curves of different cycles (1st, 5th, 10th, 15th).



**Fig. S7:** Molecular structure of pPO after optimization.

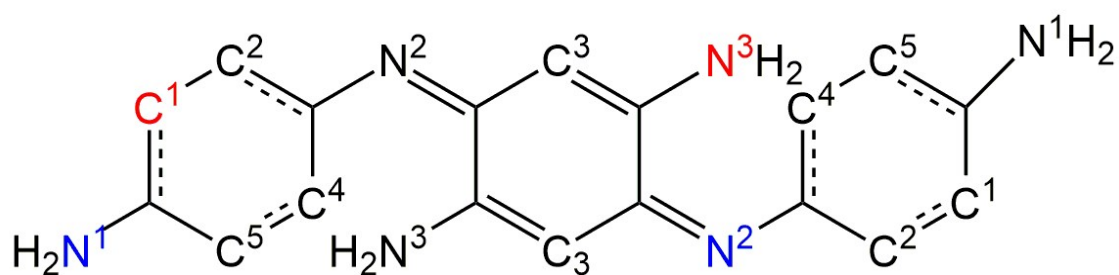
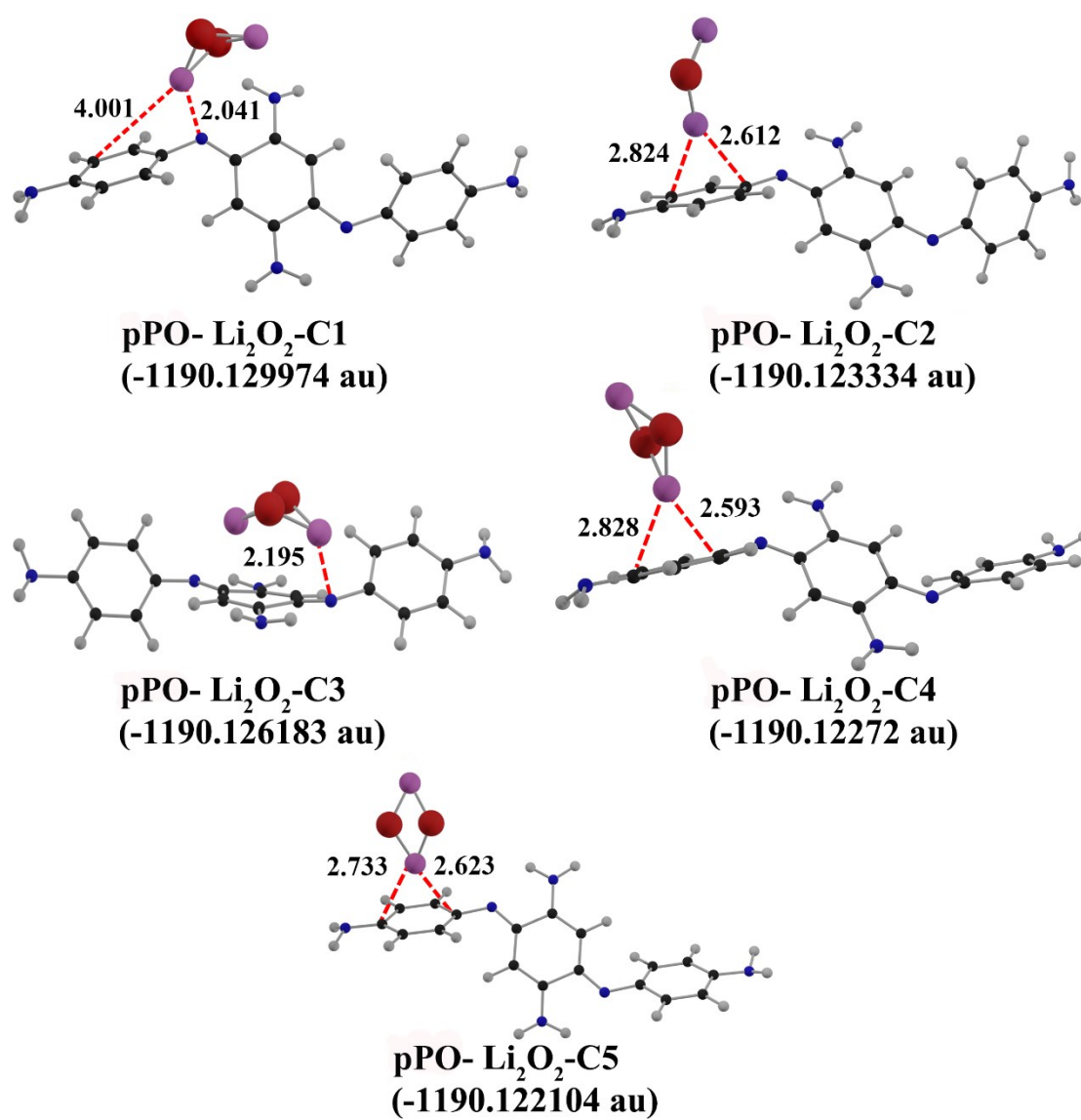


Fig. S8: The lithium adsorption sites in pPO.



**Fig. S9:** The structure of the complex after optimization with C as the adsorption site. The total Gibbs free energy of the complex after solvent correction is shown in parentheses.



**Table 3:** Comparison of bond energy and free energy of reaction with Li<sub>2</sub>O<sub>2</sub> at different reaction sites

Adsorption Site (*)		Å	Gibbs free energy (kcal mol <sup>-1</sup> )
pPO	N-O band	1.996	-7.2
TEMPO	O-O band	1.937	-5.2

Cartesian coordinates of the calculated species

Li<sub>2</sub>O<sub>2</sub>

0 1

Li	-0.70477000	1.37462700	0.00154300
O	-0.70477000	-0.36110500	-0.00057900
O	0.70477000	0.36110500	-0.00057900
Li	0.70477000	-1.37462700	0.00154300

pPO

0 1

C	-4.11455400	0.39404000	0.83999300
C	-5.40301100	0.91925200	0.83034600
C	-6.41603400	0.35162900	0.04118300
C	-6.08643500	-0.76133700	-0.74535800
C	-4.79156100	-1.27365500	-0.75387400
C	-3.78042100	-0.71134000	0.03966200
H	-3.35995600	0.83729300	1.48206400
H	-5.63367400	1.77373700	1.46345100
H	-6.85019700	-1.22755300	-1.36446300
H	-4.56014300	-2.12576400	-1.38992000
N	-7.73427000	0.84170100	0.09154600

H	-7.79581700	1.82298300	0.33799600
H	-8.27016400	0.65925700	-0.74939800
C	-1.27087900	-0.60713000	0.04681500
C	-0.11639900	-1.35518700	0.35851900
C	-1.13510500	0.73823600	-0.31111500
C	1.13510700	-0.73823000	0.31109900
C	0.11640100	1.35519300	-0.35853500
H	-2.01925900	1.30770800	-0.58244000
H	2.01926100	-1.30770200	0.58242400
C	3.78042200	0.71134200	-0.03966600
C	4.11456000	-0.39403400	-0.84000100
C	4.79155400	1.27364800	0.75388500
C	5.40301500	-0.91925000	-0.83034300
H	3.35996700	-0.83727900	-1.48208300
C	6.08642700	0.76132500	0.74538100
H	4.56013200	2.12575400	1.38993500
C	6.41603100	-0.35163600	-0.04116400
H	5.63368300	-1.77373200	-1.46345100
H	6.85018400	1.22753500	1.36449800
N	7.73426500	-0.84171300	-0.09151600
H	8.27015200	-0.65927400	0.74943400
H	7.79581300	-1.82299300	-0.33797100
N	0.27036900	2.73052800	-0.65981600
H	1.03666600	2.88353000	-1.31255800
H	-0.57972100	3.14047400	-1.03351100
N	-0.27036700	-2.73052300	0.65980000
H	0.57972400	-3.14046900	1.03349100
H	-1.03666000	-2.88352400	1.31254600
N	2.50347500	1.30099500	-0.08078500
N	-2.50347200	-1.30098800	0.08076900

C	1.27088100	0.60713600	-0.04683100
pPO- Li <sub>2</sub> O <sub>2</sub> -N1			
0 1			
C	3.81825072	-1.00488789	1.67039243
C	5.06151972	-1.08169289	1.04913043
C	5.20426972	-0.74147589	-0.29879357
C	4.07690272	-0.30909689	-1.00433457
C	2.83409372	-0.22083189	-0.38415657
C	2.68027672	-0.56860489	0.96994643
H	3.72769772	-1.28686989	2.71656743
H	5.92436472	-1.41870989	1.61861743
H	4.16971172	-0.02989089	-2.05133857
H	1.97552572	0.12529111	-0.94813157
N	6.49624772	-0.76370289	-0.92782957
H	7.10369572	-1.46782389	-0.51634957
H	6.42685572	-0.95771589	-1.92363257
C	0.17957272	-0.54192289	1.01317043
C	-0.82415528	0.36383911	1.40322143
C	-0.11468728	-1.52660789	0.05951243
C	-2.10378928	0.24934011	0.84029643
C	-1.37212728	-1.62424389	-0.52451257
H	0.66968372	-2.21672289	-0.24021357
H	-2.88972128	0.91879611	1.17257843
C	-4.78876228	-0.10059689	-0.52655057
C	-4.74012528	1.29387911	-0.68090357
C	-6.03438828	-0.68933389	-0.26594757
C	-5.89000028	2.06683011	-0.55483057
H	-3.79582328	1.77323511	-0.91617157

C	-7.18922128	0.08095511	-0.16555157
H	-6.09853728	-1.76695489	-0.13667857
C	-7.13805728	1.47687711	-0.29751657
H	-5.82430628	3.14485811	-0.68127957
H	-8.14225428	-0.40558089	0.02723843
N	-8.30554228	2.25210011	-0.24248657
H	-9.05443428	1.83837511	0.29729843
H	-8.15368128	3.21393511	0.03136143
N	-1.71762928	-2.63503889	-1.46234757
H	-2.08714328	-2.23581189	-2.32259857
H	-0.92697528	-3.22745789	-1.68961157
N	-0.55216228	1.30926911	2.40088043
H	0.42983972	1.56064911	2.42932143
H	-1.14742428	2.12652611	2.36501543
N	-3.64905828	-0.90918289	-0.70758057
N	1.45941372	-0.43125789	1.63707543
C	-2.39201228	-0.72832889	-0.11469357
Li	7.36071228	0.89625989	-0.74999643
O	8.77306028	1.80302589	-0.19965543
O	8.08572428	2.30774689	-1.52717943
Li	8.76551628	3.50892089	-0.48517943

pPO- Li<sub>2</sub>O<sub>2</sub>-N<sub>2</sub>

0 1

C	-4.52257400	0.12283800	-0.74922900
C	-5.72820200	-0.55687900	-0.59956300
C	-5.87650300	-1.54972000	0.38224800
C	-4.77286800	-1.83658200	1.20482500
C	-3.56546500	-1.16577700	1.04563100
C	-3.41110700	-0.17540600	0.05820400

H	-4.42188500	0.88184400	-1.52146900
H	-6.56736900	-0.31136500	-1.24575500
H	-4.86997800	-2.58655000	1.98626200
H	-2.73179300	-1.39534800	1.70157500
N	-7.10470000	-2.18641200	0.58238600
H	-7.71197300	-2.20478500	-0.22562900
H	-7.04769800	-3.09356000	1.02486200
C	-1.05738900	0.11759300	-0.23607600
C	0.11208600	1.06131100	-0.24423800
C	-0.78384100	-1.27265000	-0.44398300
C	1.39103300	0.53732700	-0.21587100
C	0.49494500	-1.76729400	-0.49305800
H	-1.62511700	-1.94945300	-0.53867500
H	2.22986400	1.22438300	-0.21037100
C	4.05279700	-0.85678700	-0.09532300
C	4.28135000	0.08758500	0.92749300
C	5.17196900	-1.29315900	-0.83189200
C	5.55524500	0.58507900	1.17669500
H	3.45553400	0.40533800	1.55479100
C	6.43973900	-0.77679300	-0.60458500
H	5.01660800	-2.04108700	-1.60340100
C	6.65664600	0.17614700	0.40645200
H	5.70468100	1.29528400	1.98683600
H	7.27999800	-1.12464500	-1.20098300
N	7.94407200	0.64475300	0.68730300
H	8.58864100	0.60503100	-0.09071400
H	7.97633300	1.54405100	1.14841900
N	0.79684400	-3.07254900	-0.66107400
H	1.78457600	-3.28719100	-0.72884400
H	0.09311400	-3.74904100	-0.90180900

N	-0.11232300	2.38991600	-0.23843100
H	-1.00138000	2.89982800	-0.50133100
H	0.71261200	2.97250100	-0.22151200
N	2.82737800	-1.46913000	-0.35663900
N	-2.25172000	0.62933200	-0.05934800
C	1.67051000	-0.85901100	-0.31495700
Li	-2.96771200	2.47115700	0.22626300
O	-2.31272000	3.81932200	-0.80790500
O	-2.78363600	4.19202100	0.63327100
Li	-2.84595200	5.46408000	-0.53666700

pPO- Li<sub>2</sub>O<sub>2</sub>-N3

0 1

C	4.09662800	0.52590500	-0.77606300
C	5.40561800	0.99459900	-0.73507700
C	6.39400000	0.31819200	-0.00165600
C	6.02951400	-0.86464500	0.66552800
C	4.72911100	-1.34539900	0.59912900
C	3.72124900	-0.65006800	-0.09607800
H	3.36075200	1.05568200	-1.37169900
H	5.67174200	1.89262500	-1.28805400
H	6.78164500	-1.41731800	1.22363300
H	4.46092600	-2.26870400	1.10324200
N	7.71979900	0.76445400	0.00112100
H	7.83421600	1.75366200	-0.17428100
H	8.26540900	0.46544400	0.79816000
C	1.33254100	-0.56922900	-0.06294200
C	0.10288800	-1.38549900	-0.31473300
C	1.14239800	0.81683200	0.26479300
C	-1.14240200	-0.81681900	-0.26481800



C	-0.10289100	1.38551200	0.31470800
H	2.01594700	1.41694500	0.49197100
H	-2.01595100	-1.41693200	-0.49199400
C	-3.72125000	0.65007200	0.09607400
C	-4.09661400	-0.52590300	0.77606600
C	-4.72912400	1.34539400	-0.59912400
C	-5.40560200	-0.99460500	0.73509500
H	-3.36072700	-1.05567400	1.37169400
C	-6.02952400	0.86463100	-0.66550700
H	-4.46095000	2.26869900	-1.10324300
C	-6.39399500	-0.31820600	0.00168400
H	-5.67171300	-1.89263200	1.28807700
H	-6.78166500	1.41729800	-1.22360600
N	-7.71979200	-0.76447700	-0.00107800
H	-8.26541300	-0.46547300	-0.79811200
H	-7.83420100	-1.75368600	0.17432700
N	-0.33120600	2.69145200	0.60192300
H	-1.30275900	2.95041900	0.71560700
H	0.40166500	3.27652000	0.96500000
N	0.33120200	-2.69143800	-0.60194700
H	-0.40166900	-3.27651000	-0.96501800
H	1.30275500	-2.95040600	-0.71563300
N	-2.45185200	1.23234900	0.15815700
N	2.45184800	-1.23233800	-0.15817800
C	-1.33254500	0.56924300	0.06291300
Li	0.40866150	4.77861611	-3.81009926
O	-0.44164850	3.85361834	-2.61255089
O	1.01595597	4.34955361	-2.24129935
Li	0.16402051	3.42813394	-1.04214889

pPO- Li<sub>2</sub>O<sub>2</sub>-Cl

0 1

C	3.87711127	-0.59002916	1.76545592
C	5.12038027	-0.66683416	1.14419392
C	5.26313027	-0.32661716	-0.20373008
C	4.13576327	0.10576184	-0.90927108
C	2.89295427	0.19402684	-0.28909308
C	2.73913727	-0.15374616	1.06500992
H	3.78655827	-0.87201116	2.81163092
H	5.98322527	-1.00385116	1.71368092
H	4.22857227	0.38496784	-1.95627508
H	2.03438627	0.54014984	-0.85306808
N	6.55510827	-0.34884416	-0.83276608
H	7.16255627	-1.05296516	-0.42128608
H	6.48571627	-0.54285716	-1.82856908
C	0.23843327	-0.12706416	1.10823392
C	-0.76529473	0.77869784	1.49828492
C	-0.05582673	-1.11174916	0.15457592
C	-2.04492873	0.66419884	0.93535992
C	-1.31326673	-1.20938516	-0.42944908
H	0.72854427	-1.80186416	-0.14515008
H	-2.83086073	1.33365484	1.26764192
C	-4.72990173	0.31426184	-0.43148708
C	-4.68126473	1.70873784	-0.58584008
C	-5.97552773	-0.27447516	-0.17088408
C	-5.83113973	2.48168884	-0.45976708
H	-3.73696273	2.18809384	-0.82110808
C	-7.13036073	0.49581384	-0.07048808
H	-6.03967673	-1.35209616	-0.04161508

C	-7.07919673	1.89173584	-0.20245308
H	-5.76544573	3.55971684	-0.58621608
H	-8.08339373	0.00927784	0.12230192
N	-8.24668173	2.66695884	-0.14742308
H	-8.99557373	2.25323384	0.39236192
H	-8.09482073	3.62879384	0.12642492
N	-1.65876873	-2.22018016	-1.36728408
H	-2.02828273	-1.82095316	-2.22753508
H	-0.86811473	-2.81259916	-1.59454808
N	-0.49330173	1.72412784	2.49594392
H	0.48870027	1.97550784	2.52438492
H	-1.08856373	2.54138484	2.46007892
N	-3.59019773	-0.49432416	-0.61251708
N	1.51827427	-0.01639916	1.73213892
C	-2.33315173	-0.31347016	-0.01963008
Li	5.37518671	1.12908290	1.55572231
O	5.95284425	2.58144289	2.37839410
O	5.29192985	2.79082679	0.96105696
Li	5.03763234	4.02970937	2.14054960

pPO-Li<sub>2</sub>O<sub>2</sub> -C2

0 1

C	3.87711127	-0.59002916	1.76545592
C	5.12038027	-0.66683416	1.14419392
C	5.26313027	-0.32661716	-0.20373008
C	4.13576327	0.10576184	-0.90927108
C	2.89295427	0.19402684	-0.28909308
C	2.73913727	-0.15374616	1.06500992
H	3.78655827	-0.87201116	2.81163092

H	5.98322527	-1.00385116	1.71368092
H	4.22857227	0.38496784	-1.95627508
H	2.03438627	0.54014984	-0.85306808
N	6.55510827	-0.34884416	-0.83276608
H	7.16255627	-1.05296516	-0.42128608
H	6.48571627	-0.54285716	-1.82856908
C	0.23843327	-0.12706416	1.10823392
C	-0.76529473	0.77869784	1.49828492
C	-0.05582673	-1.11174916	0.15457592
C	-2.04492873	0.66419884	0.93535992
C	-1.31326673	-1.20938516	-0.42944908
H	0.72854427	-1.80186416	-0.14515008
H	-2.83086073	1.33365484	1.26764192
C	-4.72990173	0.31426184	-0.43148708
C	-4.68126473	1.70873784	-0.58584008
C	-5.97552773	-0.27447516	-0.17088408
C	-5.83113973	2.48168884	-0.45976708
H	-3.73696273	2.18809384	-0.82110808
C	-7.13036073	0.49581384	-0.07048808
H	-6.03967673	-1.35209616	-0.04161508
C	-7.07919673	1.89173584	-0.20245308
H	-5.76544573	3.55971684	-0.58621608
H	-8.08339373	0.00927784	0.12230192
N	-8.24668173	2.66695884	-0.14742308
H	-8.99557373	2.25323384	0.39236192
H	-8.09482073	3.62879384	0.12642492
N	-1.65876873	-2.22018016	-1.36728408
H	-2.02828273	-1.82095316	-2.22753508
H	-0.86811473	-2.81259916	-1.59454808
N	-0.49330173	1.72412784	2.49594392

H	0.48870027	1.97550784	2.52438492
H	-1.08856373	2.54138484	2.46007892
N	-3.59019773	-0.49432416	-0.61251708
N	1.51827427	-0.01639916	1.73213892
C	-2.33315173	-0.31347016	-0.01963008
Li	3.92856260	1.18685816	1.61671239
O	4.50622014	2.63921815	2.43938418
O	3.84530574	2.84860205	1.02204704
Li	3.59100823	4.08748463	2.20153968

pPO- Li<sub>2</sub>O<sub>2</sub>-C3

0 1			
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.39012202
C	1.20527540	0.00000000	2.11311078
C	2.41217975	0.03684533	1.39070301
C	2.40903354	0.07000841	0.00363497
C	1.20666526	0.01650871	-0.72732653
H	-0.94570361	0.02922580	-0.53149659
H	-0.94542775	0.01136223	1.92724084
H	3.35697270	0.05841987	1.92797716
H	3.34459994	0.11879332	-0.54453437
N	1.20510051	0.03988323	3.50712597
H	0.37361899	-0.32647053	3.94966888
H	2.04833876	-0.30081279	3.94795692
C	0.57479935	-0.62724238	-2.93846684
C	0.73674787	-0.29594436	-4.38495238
C	-0.28630373	-1.74642629	-2.61353578
C	0.17293997	-1.09138863	-5.34910347
C	-0.95111372	-2.46238414	-3.58351884

H	-0.44581887	-1.98320860	-1.56786947
H	0.34013895	-0.86566701	-6.39600534
C	-0.65410849	-3.35590257	-7.14104381
C	0.69255802	-3.22105523	-7.55438770
C	-1.57931965	-3.85731658	-8.07790844
C	1.07805127	-3.56653377	-8.84739873
H	1.44178399	-2.89802611	-6.83327457
C	-1.19991586	-4.16287113	-9.37691995
H	-2.61022525	-3.98976857	-7.76448386
C	0.13959903	-4.02626876	-9.78878510
H	2.12277014	-3.47153341	-9.13574000
H	-1.94021514	-4.53308250	-10.08197080
N	0.53596433	-4.40526868	-11.06991296
H	-0.19091426	-4.39275868	-11.77180740
H	1.39251103	-3.98407384	-11.40189025
N	-1.85099798	-3.44301138	-3.32639388
H	-2.05109470	-4.04578975	-4.11657839
H	-1.92175653	-3.82476553	-2.39632621
N	1.45378569	0.83094688	-4.64848158
H	1.86054571	0.93875355	-5.56451645
H	1.97689984	1.18173055	-3.85400855
N	-1.08659243	-3.16632956	-5.82742166
N	1.28494871	0.09715099	-2.12025244
C	-0.62278123	-2.24326585	-5.02724830
Li	1.89475186	-4.99355743	-5.72907199
O	2.10411001	-4.78768474	-4.00084574
O	2.60866715	-3.61998023	-4.91121613
Li	1.51876079	-3.18202518	-3.59348069

pPO- Li<sub>2</sub>O<sub>2</sub>-C4



0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.39097402
C	1.20350196	0.00000000	2.11479361
C	2.40971852	0.03133432	1.39288801
C	2.40609621	0.06033771	0.00518240
C	1.20576119	0.01483393	-0.72946653
H	-0.94539233	0.02556994	-0.53154390
H	-0.94596056	0.01127363	1.92771211
H	3.35456209	0.05218405	1.93090807
H	3.34194907	0.10185857	-0.54345288
N	1.20233865	0.04683395	3.51290151
H	0.37133065	-0.32982794	3.94872384
H	2.04186353	-0.30997063	3.94908599
C	0.55377261	-0.58632508	-2.94916867
C	0.71508180	-0.20796944	-4.38881039
C	-0.36075162	-1.65389915	-2.65140916
C	-0.00813756	-0.83688457	-5.36761331
C	-1.08397073	-2.28281405	-3.63021114
H	-0.46223632	-1.97271350	-1.62044283
H	0.09334832	-0.51807182	-6.39857958
C	-1.57463030	-2.50562896	-7.28955553
C	-0.36885961	-2.49079623	-8.01900840
C	-2.77495617	-2.55113771	-8.02421852
C	-0.36884411	-2.49080348	-9.40998280
H	0.57652621	-2.51636058	-7.48745236
C	-2.77856137	-2.52214159	-9.41192387
H	-3.71081539	-2.59265616	-7.47559377
C	-1.57233684	-2.49080958	-10.13381514

H	0.57712350	-2.50207771	-9.94670885
H	-3.72339936	-2.54299508	-9.94995519
N	-1.57115726	-2.53765024	-11.53192375
H	-2.41067740	-2.18084883	-11.96812045
H	-0.74014468	-2.16098844	-11.96773879
N	-1.97094699	-3.28220485	-3.39656480
H	-2.34972382	-3.73162962	-4.22024477
H	-2.01642931	-3.73345639	-2.49905003
N	1.60205763	0.79141978	-4.62245730
H	1.64754657	1.24266868	-5.51997325
H	1.98083405	1.24084671	-3.79877773
N	-1.65910969	-2.59380075	-5.89694609
N	1.29022441	0.10301491	-2.12207693
C	-0.92266493	-1.90445596	-5.06985358
Li	1.60873054	-6.63105008	-7.81014753
O	1.62400032	-5.08241231	-7.05068050
O	1.68066770	-5.08621003	-8.61814542
Li	0.92614848	-3.65796116	-7.82367060

pPO- Li<sub>2</sub>O<sub>2</sub>-C5

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.39097402
C	1.20350196	0.00000000	2.11479361
C	2.40971852	0.03133432	1.39288801
C	2.40609621	0.06033771	0.00518240
C	1.20576119	0.01483393	-0.72946653
H	-0.94539233	0.02556994	-0.53154390
H	-0.94596056	0.01127363	1.92771211

H	3.35456209	0.05218405	1.93090807
H	3.34194907	0.10185857	-0.54345288
N	1.20233865	0.04683395	3.51290151
H	0.37133065	-0.32982794	3.94872384
H	2.04186353	-0.30997063	3.94908599
C	0.55377261	-0.58632508	-2.94916867
C	0.71508180	-0.20796944	-4.38881039
C	-0.36075162	-1.65389915	-2.65140916
C	-0.00813756	-0.83688457	-5.36761331
C	-1.08397073	-2.28281405	-3.63021114
H	-0.46223632	-1.97271350	-1.62044283
H	0.09334832	-0.51807182	-6.39857958
C	-1.57463030	-2.50562896	-7.28955553
C	-0.36885961	-2.49079623	-8.01900840
C	-2.77495617	-2.55113771	-8.02421852
C	-0.36884411	-2.49080348	-9.40998280
H	0.57652621	-2.51636058	-7.48745236
C	-2.77856137	-2.52214159	-9.41192387
H	-3.71081539	-2.59265616	-7.47559377
C	-1.57233684	-2.49080958	-10.13381514
H	0.57712350	-2.50207771	-9.94670885
H	-3.72339936	-2.54299508	-9.94995519
N	-1.57115726	-2.53765024	-11.53192375
H	-2.41067740	-2.18084883	-11.96812045
H	-0.74014468	-2.16098844	-11.96773879
N	-1.97094699	-3.28220485	-3.39656480
H	-2.34972382	-3.73162962	-4.22024477
H	-2.01642931	-3.73345639	-2.49905003
N	1.60205763	0.79141978	-4.62245730
H	1.64754657	1.24266868	-5.51997325

H	1.98083405	1.24084671	-3.79877773
N	-1.65910969	-2.59380075	-5.89694609
N	1.29022441	0.10301491	-2.12207693
C	-0.92266493	-1.90445596	-5.06985358
Li	1.53207970	-6.99676103	-9.57117207
O	1.54734949	-5.44812325	-8.81170503
O	1.60401687	-5.45192098	-10.37916995
Li	0.84949764	-4.02367211	-9.58469513

TEMPO

0 2

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.54000000
H	1.00880579	0.00000000	1.89666635
H	-0.50440312	0.87365131	1.89666635
H	-0.50440269	-0.87365135	1.89666686
C	0.72650209	1.25709334	-0.51333327
H	0.22232115	2.13096073	-0.15688221
H	1.73523143	1.25679249	-0.15645089
H	0.72673090	1.25696140	-1.58333324
C	-1.90068475	-0.87602799	-1.20778686
C	-3.11235035	-1.43340318	-0.43785220
H	-3.68193478	-0.62265979	-0.03391068
H	-3.72613813	-2.00378510	-1.10330619
H	-2.77084931	-2.06103168	0.35861469
C	-2.38551018	-0.17708689	-2.49154137
H	-3.00268729	-0.84810636	-3.05165321
H	-2.94992971	0.69408122	-2.23193258
H	-1.54077257	0.10839218	-3.08299726
C	0.76133457	-1.09710113	-0.40244318

H	1.09922913	-1.58210009	0.48946672
H	1.60251026	-0.70940349	-0.93818006
C	0.19165047	-2.08436193	-1.20696016
H	0.27671358	-3.00666132	-0.67121013
H	0.78078791	-2.13428077	-2.09877023
C	-1.13926866	-1.97389862	-1.60945272
H	-1.13924911	-1.97524942	-2.67945187
H	-1.64369391	-2.84708985	-1.25169269
N	-1.33134298	0.11079543	-0.40307170
O	-2.13348946	1.26727980	0.02119816

TEMPO- Li<sub>2</sub>O<sub>2</sub>

0 2

C	-1.32567390	-0.06971609	-0.08070707
C	-1.75644390	-0.18285209	1.39733993
H	-2.79540190	0.14688891	1.51165393
H	-1.68334790	-1.22525309	1.71989893
H	-1.13598590	0.42777591	2.06017393
C	-2.33486690	-0.82602409	-0.96043007
H	-2.41990690	-1.86721409	-0.64436007
H	-3.31808590	-0.34800009	-0.88620807
H	-2.02093590	-0.81038309	-2.00957407
C	1.33710310	-0.06970809	-0.08070407
C	1.76787110	-0.18285009	1.39733993
H	1.69477910	-1.22525209	1.71989593
H	2.80682710	0.14689891	1.51166193
H	1.14740510	0.42777091	2.06017393
C	2.34629710	-0.82601009	-0.96043507
H	3.32951810	-0.34799309	-0.88620307

H	2.43133110	-1.86720509	-0.64437807
H	2.03236810	-0.81035409	-2.00957907
C	-1.24163890	1.40150991	-0.53707307
H	-2.15577490	1.91260191	-0.21059107
H	-1.24140890	1.43116591	-1.63545507
C	0.00570210	2.12972291	-0.03246107
H	0.00569910	2.19004991	1.06322993
H	0.00570910	3.16422591	-0.39696207
C	1.25305310	1.40151191	-0.53706707
H	1.25281910	1.43116691	-1.63545007
H	2.16718110	1.91262091	-0.21058907
N	0.00571510	-0.74340709	-0.25780907
O	0.00571710	-2.02013709	-0.10689407
Li	0.21645438	-0.75270764	-2.18630653
O	1.15032607	-0.77044035	-3.69394081
O	-0.39720359	-0.84452040	-3.88464801
Li	0.59557225	-1.73018770	-5.02019623



## REFERENCES

1. H.-D. Lim, H. Song, J. Kim, H. Gwon, Y. Bae, K.-Y. Park, J. Hong, H. Kim, T. Kim, Y. H. Kim, X. Lepró, R. Ovalle-Robles, R. H. Baughman and K. Kang, *Angew. Chem., Int. Ed.*, 2014, **53**, 3926-3931.
2. W.-J. Kwak, D. Hirshberg, D. Sharon, M. Afri, A. A. Frimer, H.-G. Jung, D. Aurbach and Y.-K. Sun, *Energy Environ. Sci.*, 2016, **9**, 2334-2345.
3. X.-G. Wang, Z. Zhang, Q. Zhang, C. Wang, X. Zhang, Z. Xie and Z. Zhou, *J. Mater. Chem. A*, 2019, **7**, 14239-14243.
4. D. Kundu, R. Black, B. Adams and L. F. Nazar, *ACS Central Science*, 2015, **1**, 510-515.
5. Y. Chen, S. A. Freunberger, Z. Peng, O. Fontaine and P. G. Bruce, *Nat. Chem.*, 2013, **5**, 489-494.
6. X. Gao, Y. Chen, L. Johnson and Peter G. Bruce, *Nat. Mater.*, 2016, **15**, 882-888.
7. J. Zhang, B. Sun, Y. Zhao, A. Tkacheva, Z. Liu, K. Yan, X. Guo, A. M. McDonagh, D. Shanmukaraj, C. Wang, T. Rojo, M. Armand, Z. Peng and G. Wang, *Nat. Commun.*, 2019, **10**, 602.
8. B. J. Bergner, C. Hofmann, A. Schürmann, D. Schröder, K. Peppler, P. R. Schreiner and J. Janek, *Phys. Chem. Chem. Phys.*, 2015, **17**, 31769-31779.
9. Y. Ko, H. Park, J. Kim, H.-D. Lim, B. Lee, G. Kwon, S. Lee, Y. Bae, S. K. Park and K. Kang, *Adv. Funct. Mater.*, 2019, **29**.