

# LITHIUM BASED RED COLORANTS IN ENVIRONMENTALLY FRIENDLY PYROTECHNICAL ILLUMINANTS

WP19-1287

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**Ludwig-Maximilian University of Munich**

**Project Outbrief**  
**08/26/2022**



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<b>14. ABSTRACT</b> The technical objectives of this project are listed below: <ul style="list-style-type: none"> <li>• Syntheses of new lithium salts with high nitrogen contents and positive oxygen balances for use as red pyrotechnic colorants, which do not require any toxic reagents or solvents, are prepared in only a few reaction steps and are highly scalable</li> <li>• Full characterization including sensitivity testing and toxicity assessment</li> <li>• Development of strontium-free and chlorine-free illuminant formulations with high color performance and luminosity, employing unknown as well as known or commercially available lithium compounds</li> <li>• Prototyping of cluster and parachute flares</li> </ul>					
<b>15. SUBJECT TERMS</b> New Fluorine-Free, Green Surfactant Mixtures, AFFF					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  UNCLASS	<b>18. NUMBER OF PAGES</b>  65	<b>19a. NAME OF RESPONSIBLE PERSON</b> Thomas Klapoetke
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# Project Team

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## Dr. Jared D. Moretti

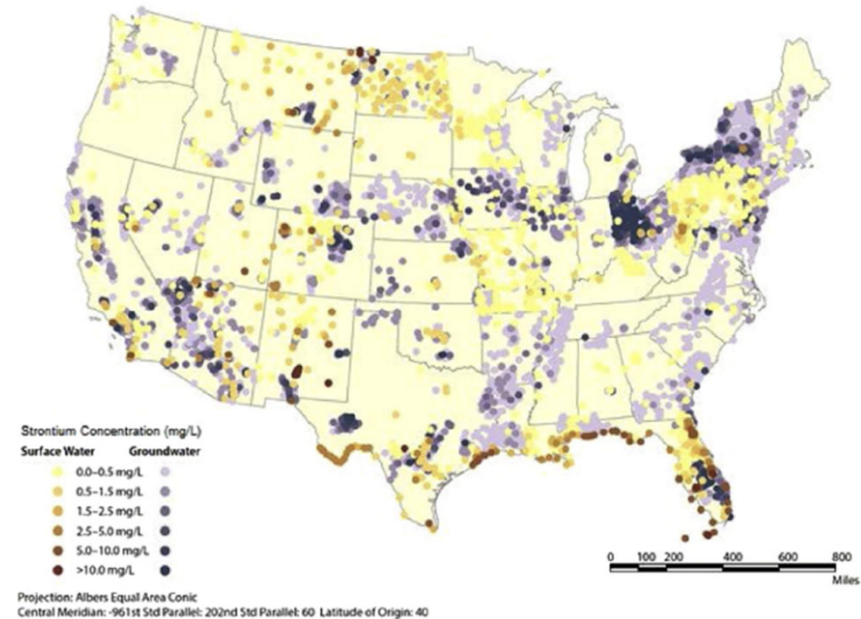
U.S. Army Armament Research, Development and Engineering Center (*DEVCOM*),  
*Pyrotechnics Technology and Prototyping Division*  
Specialist in the evaluation of performance metrics at the component or prototype level

## Dr. Anthony P. Shaw

U.S. Army Armament Research, Development and Engineering Center (*DEVCOM*),  
*Pyrotechnics Technology Division*  
Specialist in the development of environmentally benign pyrotechnics for military applications

# Background

- Initiation of the project was in May 2019 and the project was completed on May 20, 2022.
- Statement of need: removing toxic or potential harmful components from pyrotechnical mixtures
- Chlorine- and strontium-free pyrotechnical mixtures



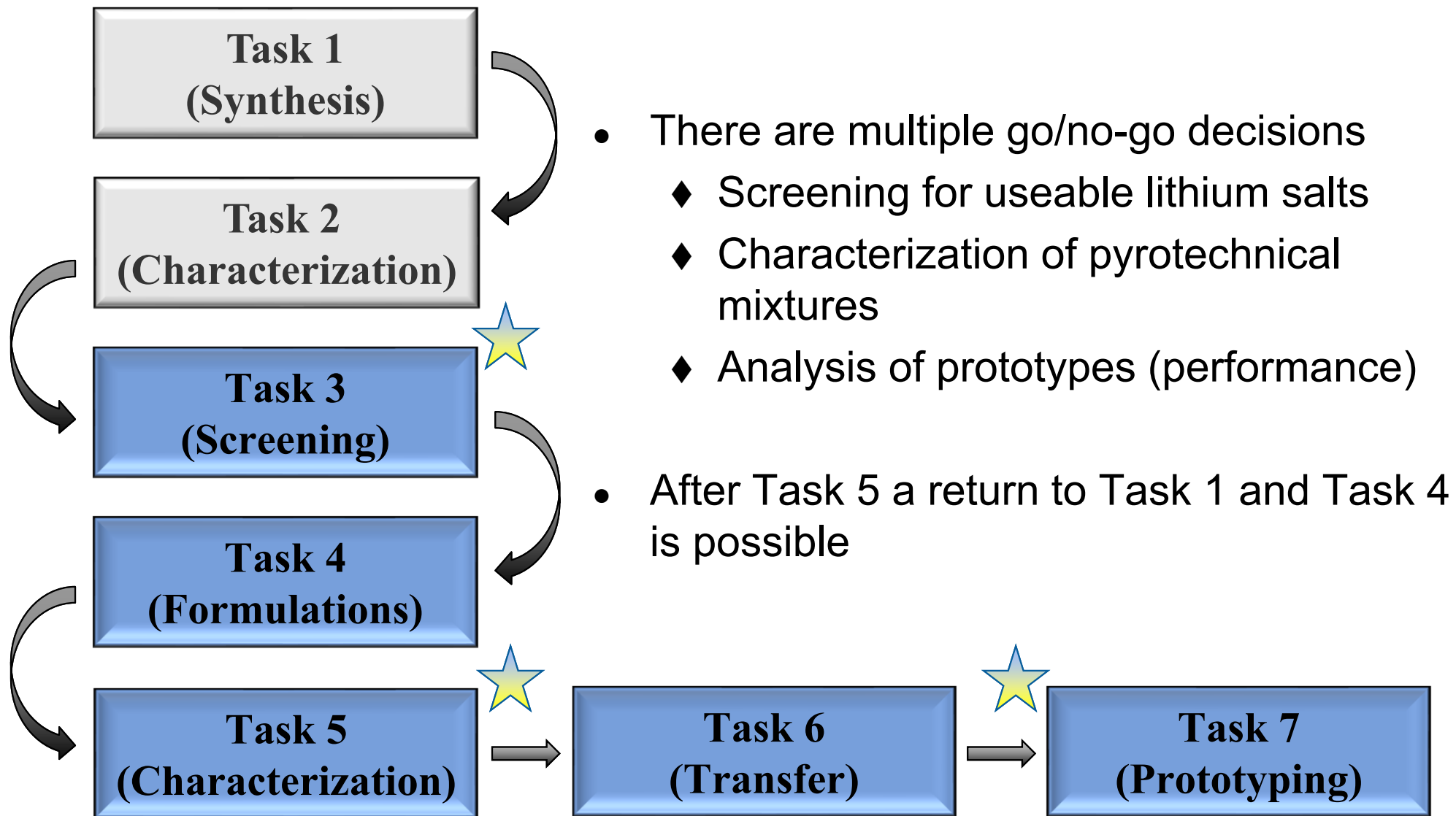
Strontium occurrence in surface and ground waters in the U.S.<sup>[1]</sup>

[1] A. J. O'Donnell et al., *Water Res.* **2016**, *103*, 319–333.

# Technical Objectives

- Syntheses of new lithium salts with high nitrogen contents and positive oxygen balances for use as red pyrotechnic colorants, which do not require any toxic reagents or solvents, are prepared in only a few reaction steps and are highly scalable
- Full characterization including sensitivity testing and toxicity assessment
- Development of strontium-free and chlorine-free illuminant formulations with high color performance and luminosity, employing unknown as well as known or commercially available lithium compounds
- Prototyping of cluster and parachute flares

# Technical Approach



# Results

## Synthesis & Characterization

- Synthesis of nitrogen-rich lithium salts
  - ◆ Ensures low flame temperature<sup>[1]</sup>
  - ◆ Increases light output<sup>[2]</sup>
  - ◆ Promotes efficient combustion<sup>[3]</sup>
- Comparison of mono- and multivalent salts
- Stability, hygroscopicity, sensitivity, toxicity and performance as go/no-go decisions

# Results

## Synthesis & Characterization

- NMR and IR: Product identification and purity determination
- X-ray diffraction: Crystal structure determination
- DTA: Investigation of decomposition temperatures
- Sensitivity measurements (friction, impact, electrostatic discharge)

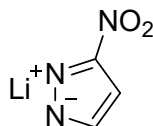


# Results

## Synthesis & Characterization

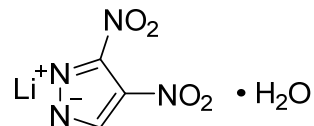
- Lithium salts based on pyrazole

Lithium 3-nitropyrazolate

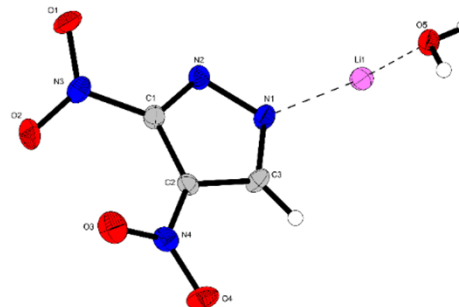


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Lithium 3,4-dinitropyrazolate monohydrate



2

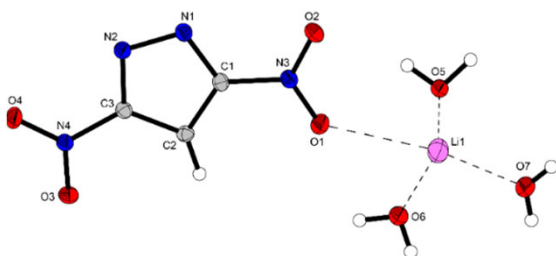
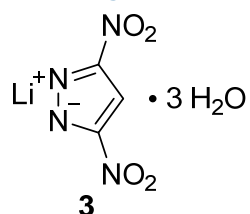


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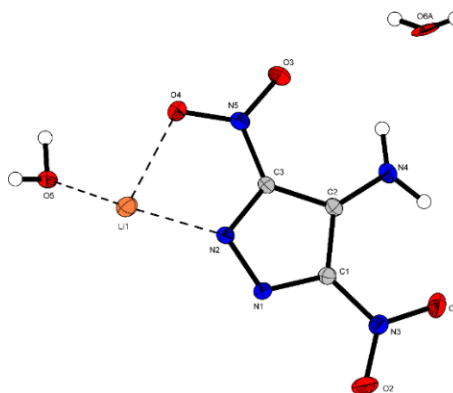
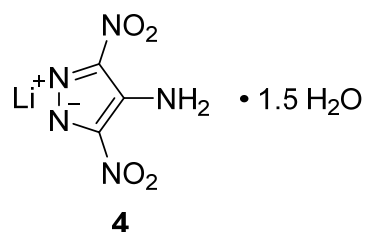
## Synthesis & Characterization

- Lithium salts based on pyrazole

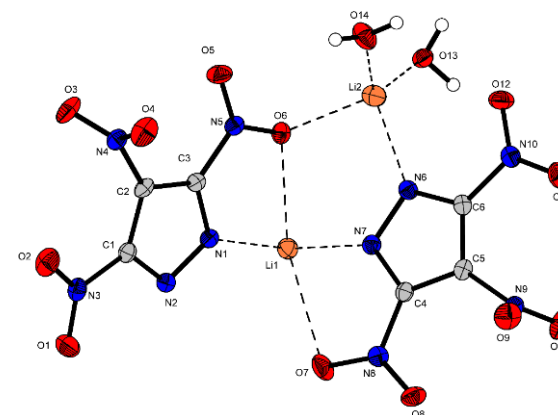
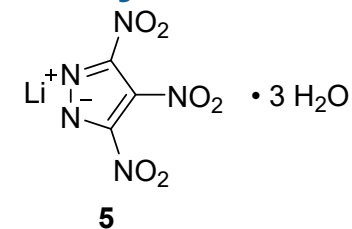
### Lithium 3,5-dinitropyrazolate trihydrate



### Lithium 4-amino-3,5-dinitropyrazolate sesquihydrate



### Lithium 3,4,5-trinitropyrazolate trihydrate

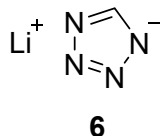


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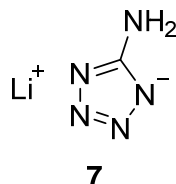
## Synthesis & Characterization

- Investigation of literature-known and new lithium salts
- Tetrazole based salts

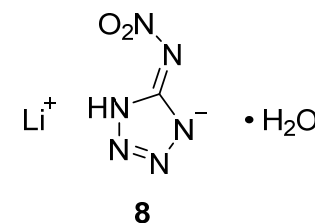
**Lithium tetrazolate**



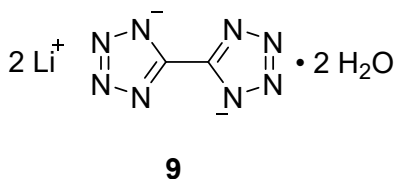
**Lithium 5-aminotetrazolate**



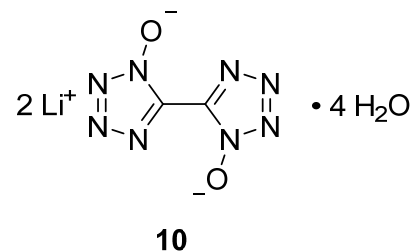
**Lithium 5-nitriminotetrazolate monohydrate**



**Dilithium 5,5'-bistetrazole dihydrate**



**Dilithium 5,5'-bis(tetrazole-1-oxide) tetrahydrate**

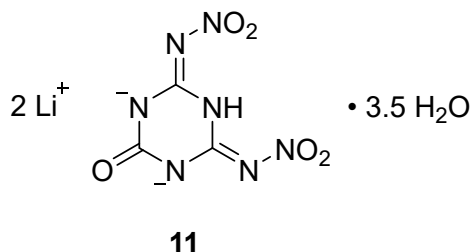


# Results

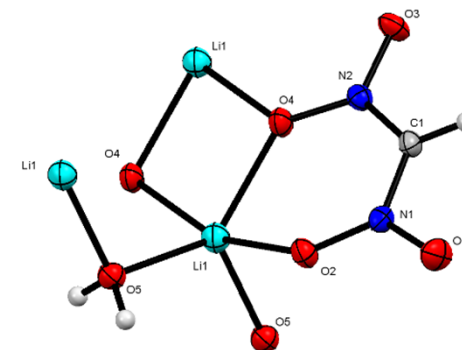
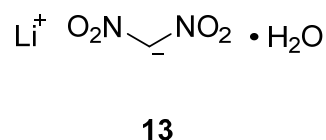
## Synthesis & Characterization

- Other interesting lithium salts

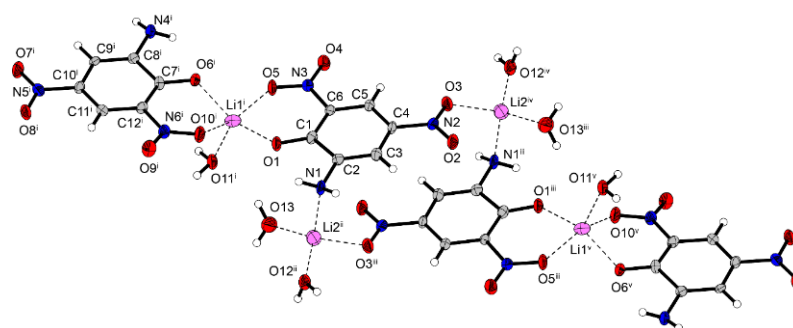
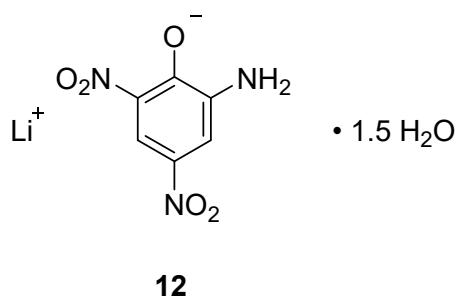
### Dilithium 4,6-bis(nitrimino-1,3,5-triazinan)-2-one • 3.5 H<sub>2</sub>O



### Lithium dinitromethanide monohydrate



### Lithium picramate sesquihydrate

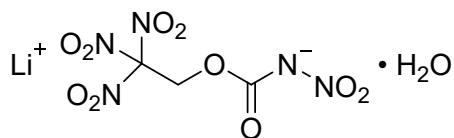


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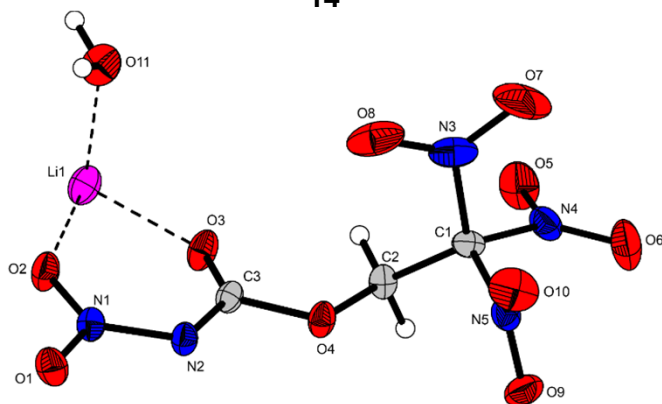
## Synthesis & Characterization

- Lithium salts based on nitrocarbammates

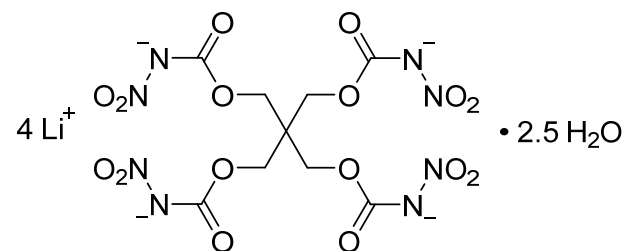
### Lithium 2,2,2-trinitroethyl nitrocarbamate monohydrate



14



### Tetralithium pentaerythritol tetranitrocarbamate • 2.5 H<sub>2</sub>O



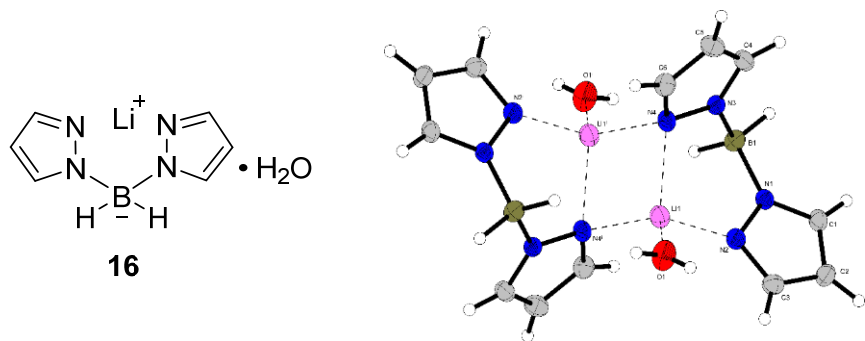
15

# Results

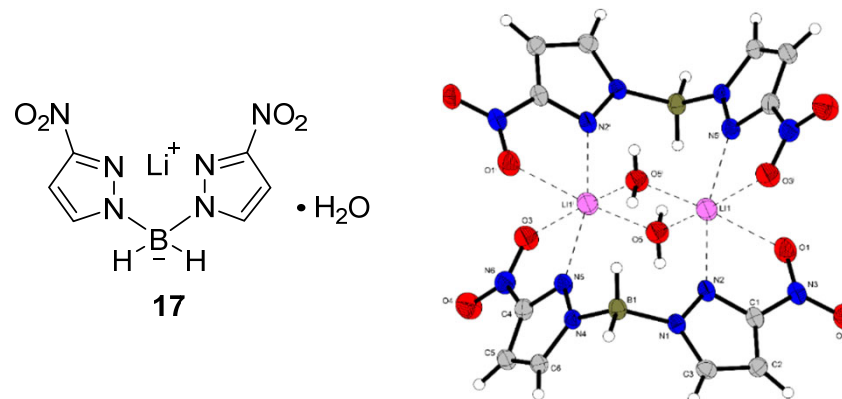
## Synthesis & Characterization

- Lithium salts based on borate

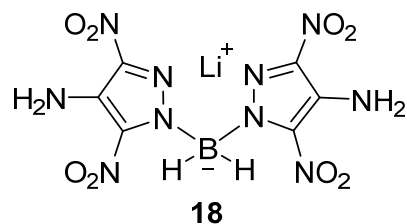
Lithium dihydrobis(pyrazol-1-yl)borate monohydrate



Lithium dihydrobis(3-nitropyrazol-1-yl)borate monohydrate



Lithium dihydrobis(4-amino-3,5-dinitropyrazol-1-yl)borate

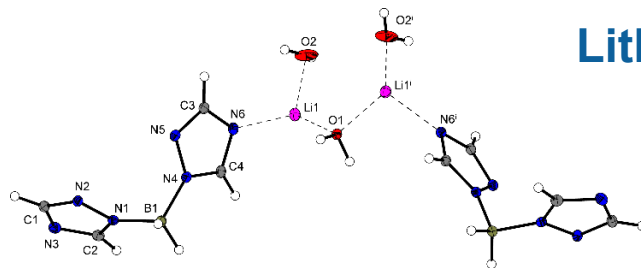
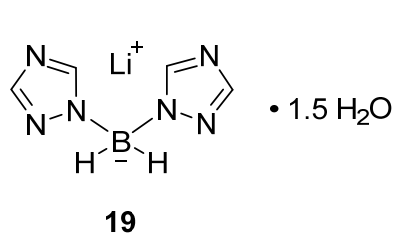


# Results

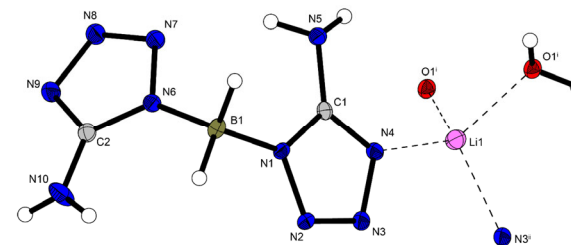
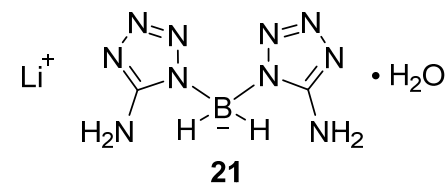
## Synthesis & Characterization

- Lithium salts based on borate

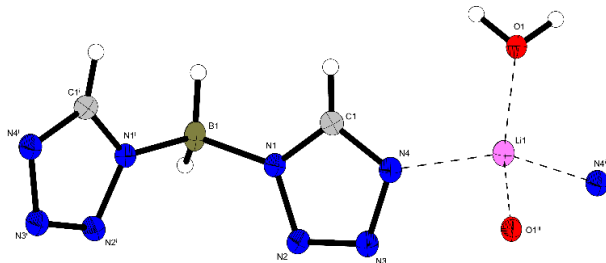
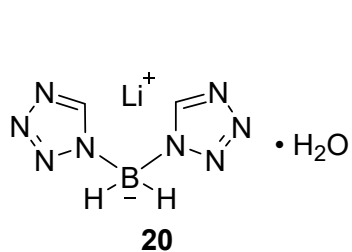
### Lithium dihydrobis(1,2,4-triazol-1-yl)borate sesquihydrate



### Lithium dihydrobis(5-aminotetrazol-1-yl)borate monohydrate



### Lithium dihydrobis(tetrazol-1-yl)borate monohydrate



# Results

## Synthesis & Characterization

### Overview of all synthesized lithium salts

Salt	Decomposition temperature [°C]	Impact sensitivity [J]	Friction sensitivity [N]	Go/No-go
1	332	Could not be determined due to hygroscopic character of the compound		
2	232	5	240	sensitive
3	284	6	192	sensitive
4	168	> 40	360	Low decomposition temperature
5	250	No measurements were conducted due to the hygroscopic character of the salt		
6	380	> 40	360	stable
7	196 (m.p.)	> 40	360	stable
8	240	4	160	sensitive
9	444	> 40	> 360	stable
10	327	> 40	> 360	stable
11	220	Could not be analyzed		
12	295	> 40	> 360	stable
13	Spontaneous decomposition made it impossible to characterize the compound completely			
14	120	10	80	sensitive
15	This compound could not be obtained completely pure, therefore no analysis was performed			
16	Target salt showed hygroscopic character, therefore no complete analysis could be performed			
17	200	2	144	hygroscopic
18	Directly after reaction the product partially hydrolyzed to boric acid			
19	317	> 40	> 360	stable
20	213	10	> 360	sensitive
21	280	> 40	> 360	stable

# Results

## Pyrotechnical formulations

- Drop-in formulations to test if a red color impression is given

Formulation	Sr(NO <sub>3</sub> ) <sub>2</sub> [wt%]	Mg 50/100 [wt%]	NH <sub>4</sub> NO <sub>3</sub> [wt%]	CH <sub>3</sub> N <sub>5</sub> [wt%]	4 [wt%]	7 [wt%]	19 [wt%]	21 [wt%]	Epon/Versamid [wt%]
AD-1	48	33	-	12	-	-	-	-	7
AD-2	-	12	48	-	-	-	33	-	7
AD-3	-	12	48	-	-	-	-	30	10
AD-4	-	12	48	-	30	-	-	-	10
AD-5	-	12	48	-	-	30	-	-	10

→ Red color impression was given

# Results

## Pyrotechnical formulations

- Modified system, due to hygroscopicity:
  - ◆  $\text{NH}_4\text{NO}_3 \rightarrow \text{KNO}_3$
  - ◆ Epoxide binder Epon/Versamid  $\rightarrow$  Nitrocellulose

Formulation	$\text{KNO}_3$ [wt%]	Mg 50/100 [wt%]	6 [wt%]	7 [wt%]	9 [wt%]	10 [wt%]	4 [wt%]	19 [wt%]	21 [wt%]	Nitrocellulose [wt%]
AD-6	48	12	33	-	-	-	-	-	-	7
AD-7	48	12	-	33	-	-	-	-	-	7
AD-8	48	12	-	-	33	-	-	-	-	7
AD-9	48	12	-	-	-	33	-	-	-	7
AD-10	48	12	-	-	-	-	33	-	-	7
AD-11	48	12	-	-	-	-	-	33	-	7
AD-12	48	12	-	-	-	-	-	-	33	7

# Results

## Pyrotechnical formulations

- Results described in the following table:

Formulation	$\Omega_{\text{CO}_2}$ [%]	BT [s]	$\lambda_d$ [nm]	$\Sigma$ [%]	LI [cd]
AD-6	- 8.48	6.7	597	41	3302
AD-7	- 8.52	6.2	600	48	3360
AD-8	- 2.48	3	601	40	3846
AD-9	- 3.73	15	581-596	-	-
AD-10	4.96	4.1	617	28	4114
AD-11	- 37.24	1.8	622	36	8308
AD-12	- 10.8	1.3	614	33	8675

# Results

## Pyrotechnical formulations

- Combustion pictures of several pyrotechnical mixtures



→ Changing the oxidizer and the binder improved the combustion behavior / hygroscopicity problem

# Results

## Pyrotechnical formulations

- To improve the values of spectral purity and dominant wavelength we increased the amount of colorant

Formulation	KNO <sub>3</sub> [wt%]	Mg 50/100 [wt%]	6 [wt%]	7 [wt%]	9 [wt%]	4 [wt%]	21 [wt%]	Nitrocellulose [wt%]
AD-13	30	12	51	-	-	-	-	7
AD-14	20	12	61	-	-	-	-	7
AD-15	10	12	71	-	-	-	-	7
AD-16	30	12	-	51	-	-	-	7
AD-17	20	12	-	61	-	-	-	7
AD-18	10	12	-	71	-	-	-	7
AD-19	30	12	-	-	51	-	-	7
AD-20	20	12	-	-	61	-	-	7
AD-21	10	12	-	-	71	-	-	7
AD-22	30	12	-	-	-	51	-	7
AD-23	20	12	-	-	-	61	-	7
AD-24	10	12	-	-	-	71	-	7
AD-25	30	12	-	-	-	-	51	7
AD-26	20	12	-	-	-	-	61	7
AD-27	10	12	-	-	-	-	71	7

# Results

## Pyrotechnical formulations

Formulation	$\Omega_{\text{CO}_2}$ [%]	BT [s]	$\lambda_d$ [nm]	$\Sigma$ [%]	LI [cd]
AD-13	- 25.08	4.2	597	66	1945
AD-14	- 34.30	6.9	596	87	847
AD-15	- 43.51	9.5	567	40	160
AD-16	- 25.13	4	598	62	1945
AD-17	- 34.36	6.9	597	76	852
AD-18	- 43.58	23.6	590	77	50
AD-19	- 15.80	4	595	67	1515
AD-20	- 23.10	8	592	64	1048
AD-21	- 30.59	9	591	98	900
AD-22	- 4.30	5.1	602	48	1138
AD-23	- 9.44	7.8	601	48	1535
AD-24	- 14.58	10.9	597	85	983
AD-25	- 28.65	2.5	610	41	5100
AD-26	- 38.57	4.1	602	58	1910
AD-27	- 48.48	6.5	599	70	1350

# Results

## Pyrotechnical formulations

- Combustion pictures of several pyrotechnical mixtures



→ Increasing the lithium content increases the spectral purity, but decreases the luminous intensity

# Results

## Pyrotechnical formulations

- To improve the luminous intensity, we increased the amount of fuel (magnesium)

Formulation	KNO <sub>3</sub> [wt%]	Mg 50/100 [wt%]	6 [wt%]	7 [wt%]	9 [wt%]	4 [wt%]	21 [wt%]	Nitrocellulose [wt%]
AD-28	40	20	33	-	-	-	-	7
AD-29	30	30	33	-	-	-	-	7
AD-30	40	20	-	33	-	-	-	7
AD-31	30	30	-	33	-	-	-	7
AD-32	40	20	-	-	33	-	-	7
AD-33	30	30	-	-	33	-	-	7
AD-34	40	20	-	-	-	33	-	7
AD-35	30	30	-	-	-	33	-	7
AD-36	40	20	-	-	-	-	33	7
AD-37	30	30	-	-	-	-	33	7

# Results

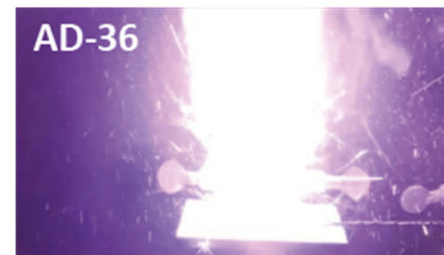
## Pyrotechnical formulations

Formulation	$\Omega_{\text{CO}_2}$ [%]	BT [s]	$\lambda_d$ [nm]	$\Sigma$ [%]	LI [cd]
AD-28	- 16.91	-	-	-	-
AD-29	- 27.45	-	-	-	-
AD-30	- 16.95	3.2	601	37	-
AD-31	- 27.49	1.5	599	44	14400
AD-32	- 10.91	1.7	602	38	14100
AD-33	- 21.45	2.2	603	34	14350
AD-34	- 3.47	2.7	615	27	14100
AD-35	- 14.01	2	606	28	14650
AD-36	-19.23	1.5	610	32	14500
AD-37	- 29.76	1.5	608	23	14600

# Results

## Pyrotechnical formulations

- Combustion pictures of several pyrotechnical mixtures



→ Mixtures containing lithium tetrazolate were not stable  
 Increasing the magnesium content → increases luminous intensity / decreases spectral purity

# Results

## Pyrotechnical formulations

- Influence of the grain size of the fuel was investigated

Formulation	KNO <sub>3</sub> [wt%]	Mg > 50 [wt%]	Mg 100/200 [wt%]	Mg 200/373 [wt%]	Mg < 373 [wt%]	7 [wt%]	9 [wt%]	4 [wt%]	Nitrocellulose [wt%]
AD-38	48	12	-	-	-	33	-	-	7
AD-39	48	-	12	-	-	33	-	-	7
AD-40	48	-	-	12	-	33	-	-	7
AD-41	48	-	-	-	12	33	-	-	7
AD-42	48	12	-	-	-	-	33	-	7
AD-43	48	-	12	-	-	-	33	-	7
AD-44	48	-	-	12	-	-	33	-	7
AD-45	48	-	-	-	12	-	33	-	7
AD-46	48	12	-	-	-	-	-	33	7
AD-47	48	-	12	-	-	-	-	33	7
AD-48	48	-	-	12	-	-	-	33	7
AD-49	48	-	-	-	12	-	-	33	7

# Results

## Pyrotechnical formulations

Formulation	$\Omega_{CO_2}$ [%]	BT [s]	$\lambda_d$ [nm]	$\Sigma$ [%]	LI [cd]
AD-38	- 8.52	6	599	37	1493
AD-39	- 8.31	10.9	598	56	1873
AD-40	- 8.31	7.6	596	78	774
AD-41	- 8.52	6.3	596	95	305
AD-42	- 2.47	6.4	605	39	2735
AD-43	- 14.22	4.1	602	54	1675
AD-44	- 2.48	1.7	601	57	2440
AD-45	- 2.48	1.5	598	78	647
AD-46	4.96	5.5	605	38	3280
AD-47	- 2.48	2.5	608	38	3625
AD-48	4.96	1.9	599	64	1510
AD-49	4.96	2.2	589	-	204

# Results

## Pyrotechnical formulations

- Combustion pictures of several pyrotechnical mixtures



- Smaller grain size leads to an inconsistent burnup
- Larger grain size shows magnesium particles as white/bright sparks

# Results

## Pyrotechnical formulations

- Investigation of different fuel (aluminum)
  - Magnesium burns hotter than aluminum → better color purity for aluminum expected

Formulation	KNO <sub>3</sub> [wt%]	Al 50/100 [wt%]	Al 100/150 [wt%]	7 [wt%]	9 [wt%]	4 [wt%]	Nitrocellulose [wt%]
AD-50	48	12	-	33	-	-	7
AD-51	48	-	12	33	-	-	7
AD-52	48	12	-	-	33	-	7
AD-53	48	-	12	-	33	-	7
AD-54	48	12	-	-	-	33	7
AD-55	48	-	12	-	-	33	7

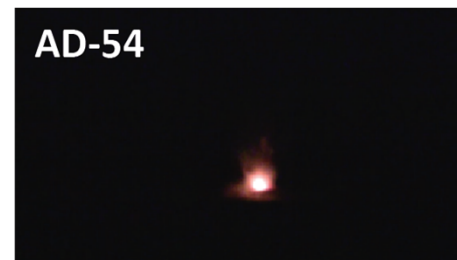
# Results

## Pyrotechnical formulations

- Results of the mixtures containing aluminum

Formulation	$\Omega_{\text{CO}_2}$ [%]	BT [s]	$\lambda_d$ [nm]	$\Sigma$ [%]	LI [cd]
AD-50	- 14.47	8.5	565	38	53
AD-51	- 14.47	9.7	590	94	62
AD-52	- 5.26	10.2	566	38	10
AD-53	- 5.26	6.5	598	76	340
AD-54	2.18	10.9	564	37	4
AD-55	2.18	11.1	587	76	189

→ Aluminum deteriorated all parameters



# Results

## Pyrotechnical formulations

- Modification of the mixtures with different additives (hexamine and 5-aminotetrazole)

Formulation	KNO <sub>3</sub> [wt%]	Mg 50/100 [wt%]	7 [wt%]	9 [wt%]	4 [wt%]	5-AT [wt%]	Hexamine [wt%]	Nitrocellulose [wt%]
AD-56	40	12	33	-	-	-	8	7
AD-57	33	12	33	-	-	-	15	7
AD-58	40	12	33	-	-	8	-	7
AD-59	33	12	33	-	-	15	-	7
AD-60	40	12	37	-	-	-	4	7
AD-61	40	12	33	-	-	4	4	7
AD-62	40	12	-	33	-	-	8	7
AD-63	33	12	-	33	-	-	15	7
AD-64	40	12	-	33	-	8	-	7
AD-65	33	12	-	33	-	15	-	7
AD-66	40	12	-	37	-	-	4	7
AD-67	40	12	-	33	-	4	4	7
AD-68	40	12	-	-	33	-	8	7
AD-69	33	12	-	-	33	-	15	7
AD-70	40	12	-	-	33	8	-	7
AD-71	33	12	-	-	33	15	-	7
AD-72	40	12	-	-	37	-	4	7
AD-73	40	12	-	-	33	4	4	7

# Results

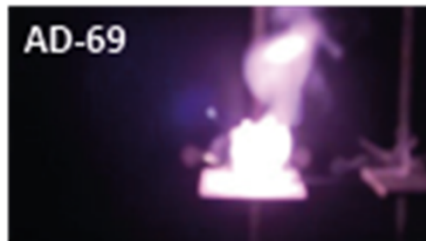
## Pyrotechnical formulations

Formulation	$\Omega_{\text{CO}_2}$ [%]	BT [s]	$\lambda_d$ [nm]	$\Sigma$ [%]	LI [cd]
AD-56	- 28.04	7.0	604	46	1095
AD-57	- 44.91	4.6	604	48	1045
AD-58	- 16.95	5.1	598	37	1102
AD-59	- 21.74	6.7	598	61	1845
AD-60	- 24.12	7.7	603	43	1183
AD-61	- 22.3	7.6	605	47	1070
AD-62	- 22	5.7	604	46	1780
AD-63	- 97.04	6.5	600	55	477
AD-64	- 10.9	4.7	593	73	418
AD-65	- 18.30	8.8	596	33	510
AD-66	- 22	3.9	598	57	2190
AD-67	- 14.22	4.1	602	54	1675
AD-68	- 14.56	8.4	595	39	12
AD-69	- 141.73	7.5	599	57	676
AD-70	- 3.47	7.8	604	48	1045
AD-71	- 10.85	5.4	607	28	2370
AD-72	- 6.85	6.7	603	49	1179
AD-73	- 9.01	8.2	603	58	1215

# Results

## Pyrotechnical formulations

- Combustion pictures of several pyrotechnical mixtures



→ Additives worsened the luminous intensity and the burning behavior

# Results

## Pyrotechnical formulations

- Thermal measurement of the pyrotechnical mixtures

Formulation	KNO <sub>3</sub> [wt%]	Mg 50/100 [wt%]	Nitrocellulose [wt%]	7 [wt%]	9 [wt%]	4 [wt%]	19 [wt%]	21 [wt%]
AD-7	48	12	7	33	-	-	-	-
AD-32	40	20	7	-	33	-	-	-
AD-34	40	20	7	-	-	33	-	-
AD-11	40	20	7	-	-	-	33	-
AD-36	48	12	7	-	-	-	-	33

# Results

## Pyrotechnical formulations

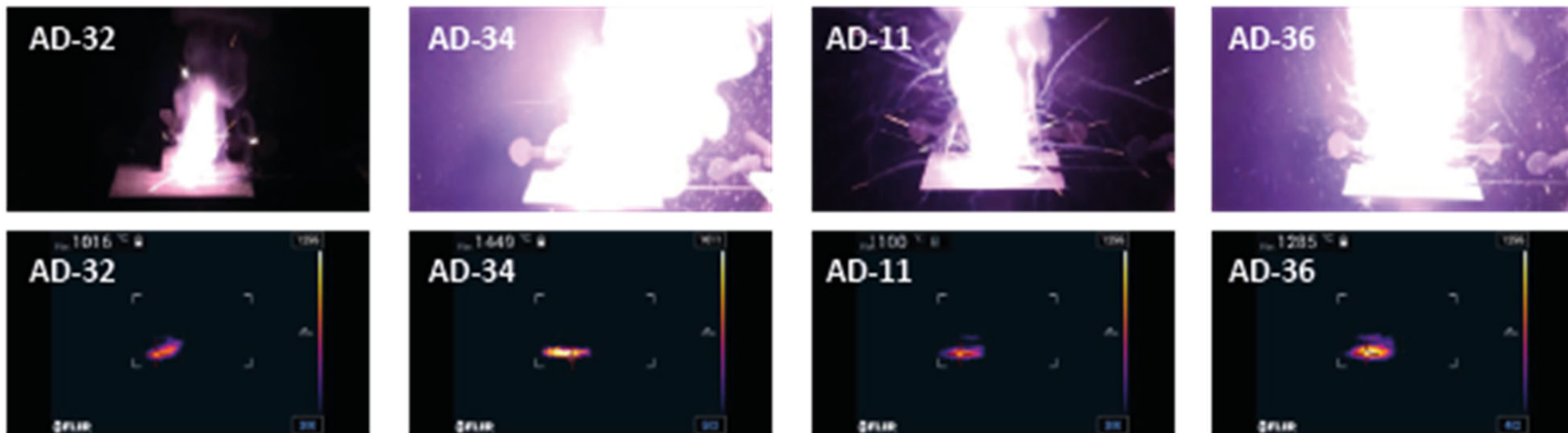
- Results of the thermal measurements:

Formulation	$\lambda_d$ [nm]	$\Sigma$ [%]	LI [cd]	BT [s]	T [°C]
AD-7	600	48	3360	6	-
AD-32	602	38	14100	1.7	1016
AD-34	615	27	14100	2.7	1449
AD-11	622	36	8308	1.8	1100
AD-36	610	32	14500	1.5	1285

# Results

## Pyrotechnical formulations

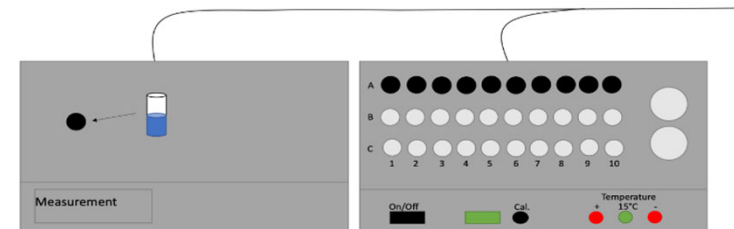
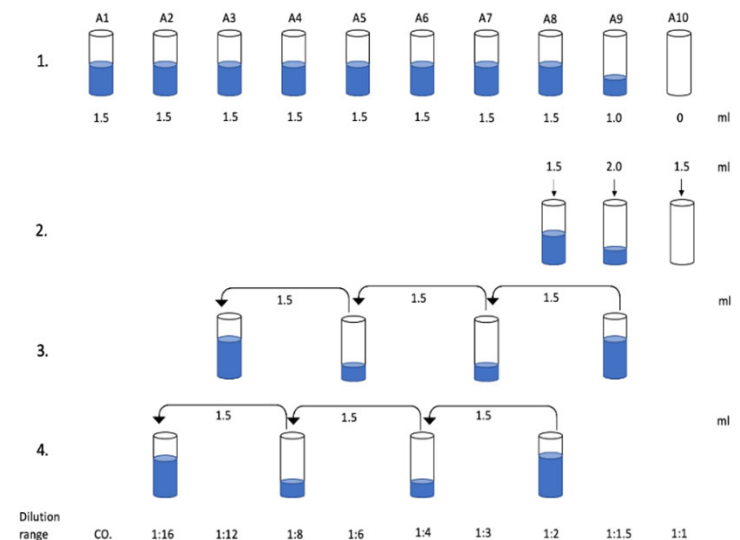
- The thermal pictures were taken by a FLIR thermal camera



→ high combustion temperature is caused by magnesium

# Results Screening

- Toxicity measurements were performed (luminescent bacteria inhibition test) with *Aliivibrio fischeri* bacteria
- Only a few preselected salts were tested, namely
  - Lithium 4-amino-3,5-dinitropyrazolate sesquihydrate (**4**)
  - Lithium 5-aminotetrazolate (**7**)
  - Dilithium 5,5`-bistetrazolate dihydrate (**9**)
  - Lithium dihydrobis(1,2,4-triazol-1-yl)borate sesquihydrate (**19**)
  - Lithium dihydrobis(4-aminotetrazol-1-yl)borate monohydrate (**21**)



# Results Screening

- Results of the toxicity measurements:
  - ◆ EC<sub>50</sub> was calculated after 15 and 30 min of incubation
  - ◆ Categorization:
 

< 0.10 g/L	very toxic (++)
0.10 g/L – 1.0 g/L	toxic (+)
> 1.0 g/L	non toxic (-)

	4	9	7	19	21
EC <sub>50</sub> (15 min) [g/L]	0.41	3.991	5.129	3.87	-
EC <sub>50</sub> (30 min) [g/L]	0.41	1.577	5.685	4.75	-
Toxicity level	+	-	-	-	++

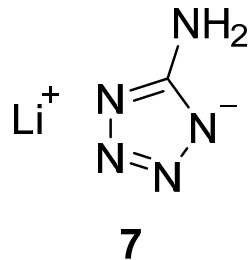
- For **21** no measurement was possible because all bacteria were inhibited

# Results Transfer

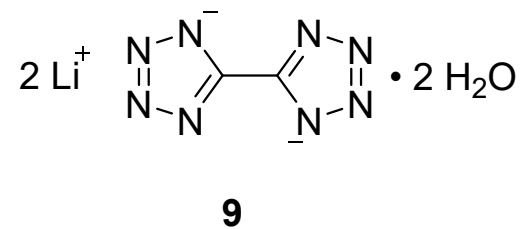
- After the selection process, two lithium salts, which showed the best ageing behavior, stability, toxicity values and performance were shipped to *DEVCOM*

→ *Based on performance, stability and toxicity, the following two salts were chosen*

## Lithium 5-aminotetrazolate



## Dilithium 5,5'-bistetrazole dihydrate



# Results

## Prototyping

- Initial testing (DSC, DTA) by *DEVCOM* confirmed that the transferred lithium salts did not undergo changes
  - Thermal tests showed no change for the drying process
- ***Both salts are suitable for prototyping***

# Results Prototyping

- Formulations I – II are baseline mixtures
  - ◆ Control: conventional red-burning illuminant composition based on strontium nitrate
  - ◆ Formulation I – II: lithium carbonate is the colorant donor
- Formulations III – VI are mixtures with the lithium salts from LMU

Ingredient	Illuminant Composition Percentages by Weight						
	Control	I	II	III	IV	V	VI
Sr(NO <sub>3</sub> ) <sub>2</sub>	48.4						
KNO <sub>3</sub>		39	39	30	48	30	48
Li <sub>2</sub> CO <sub>3</sub>		33	13.4				
5-AT			19.6				
7				33	33		
9						33	33
Mg 50/100		21	21	30	12	30	12
Mg 30/50	30.5						
PVC	14.1						
4:1 Epoxy	7						
NC		7	7	7	7	7	7

# Results

## Prototyping

- Solid materials were sieved and dried for 18 h at 60 ° C
- Binder solutions:
  - 80:20 Epon 813/Versamid 140 was weighed in a steel Hobart mixing bowl and vigorously mixed by hand with a wooden tongue depressor for 1 min
  - Nitrocellulose 8.1% w/w solution in acetone required no manual mixing
- Magnesium powder was added, blended with B-blade at 40 rpm for 10 min
- Other ingredients were added, blended with B-blade at 40 rpm for 20 min
- Dried in a ceramic evaporating dish over night at 60 ° C
- Expect the control mixture, other mixtures were re-wetted, manually kneading to near dryness
- Sieved through US standard 6-mesh and dried again over night
- Followed by pressing on the next day

# Results Prototyping

- Pictures of the prepared formulations at *DEVCOM*



# Results

## Prototyping

- **Cluster flares:**

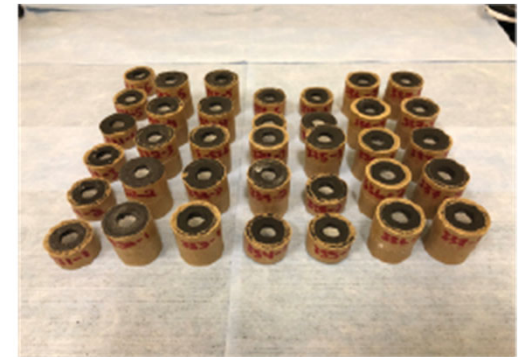
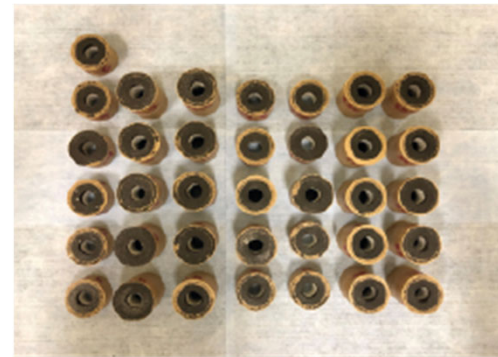
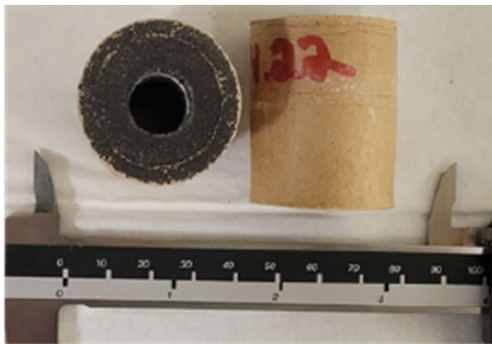
(perforated core (ID = 0.44") was assembled by adding the following energetic materials sequentially to a kraft paper tube (ID= 1.13", wall thickness = 0.11") inside a stainless steel tooling: 1.0 g black powder (MIL-P-223B, Class 7), 2.5 g igniter, and 16.0 g illuminant composition. Here the igniter was a thermite composition consisting of the following ingredients as a percent by weight: 33.0%  $\text{KNO}_3$ , 24.5% silicon powder, 20.8% black iron oxide, 12.3% aluminum powder, 3.8% charcoal, and 5.6% NC. The three powder layers were pressed in one increment at 10,000 lb. dead load with a 10-second dwell.

- **Parachute flares**

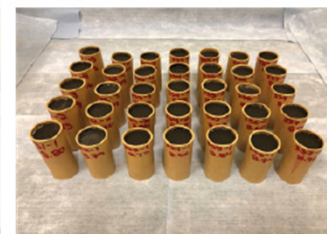
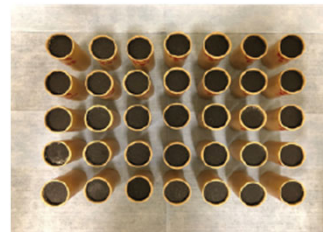
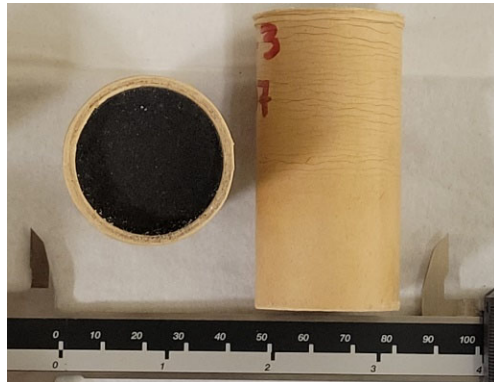
Each parachute flare with solid core was assembled by adding the following energetic materials sequentially to a kraft paper tube (ID= 1.23", wall thickness = 0.05") inside a stainless steel tooling: 1.0 g black powder (MIL-P-223B, Class 7), 2.5 g igniter from above cluster section, and 50.0 g illuminant composition. The three powder layers were also pressed in one increment at 10,000 lb. dead load with a 10-second dwell.

# Results Prototyping

- Pictures of the prepared cluster flares:



- Pictures of the prepared parachute flares:



# Results

## Prototyping

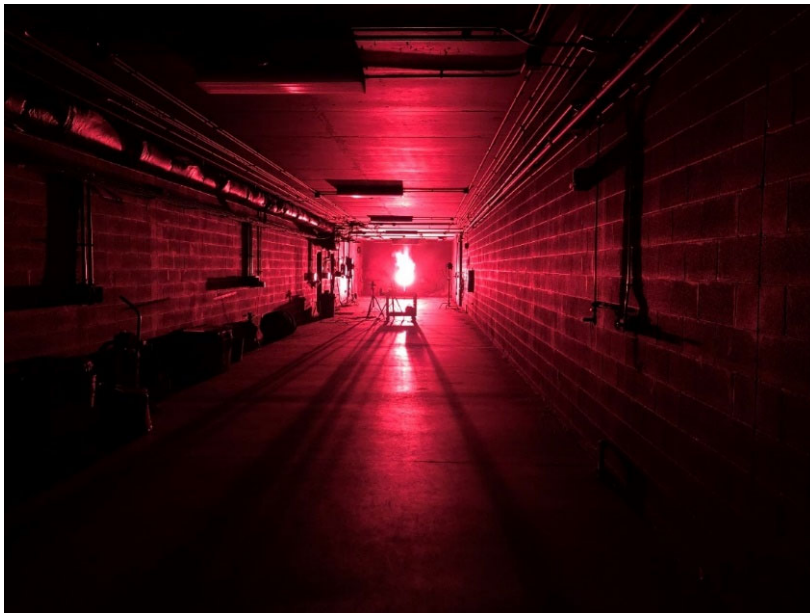
Cluster Identification	Pellet Density	Burn Time	Luminous Intensity	Dominant Wavelength	Spectral Purity
	(g/cc)	(s)	(cd)	(nm)	(%)
Control - 1	1.87	10.27	19,196	611.3	86.8
Control - 2	1.96	10.31	16,934	612.0	88.0
Control - 3	1.83	9.95	18,534	611.8	87.9
Control - 4	1.85	9.80	19,723	611.9	88.0
Control - 5	1.82	9.82	16,413	611.7	87.5
I - 1	1.37	6.40	4,134	597.7	31.2
I - 2	1.55	6.70	3,862	597.7	34.5
I - 3	1.46	6.04	4,602	598.7	34.1
I - 4	1.49	6.40	3,941	598.6	31.7
I - 5	1.45	6.63	3,851	599.3	31.0
II - 1	1.41	8.75	1,672	601.9	45.8
II - 2	1.38	8.46	1,752	600.8	46.3
II - 3	1.40	8.39	1,742	601.4	46.0
II - 4	1.46	8.49	1,699	601.3	46.9
II - 5	1.44	8.57	1,602	601.4	45.8
III - 1	1.40	4.87	3,761	595.3	61.5
III - 2	1.46	5.02	4,311	595.7	61.3
III - 3	1.54	5.25	4,027	595.7	60.4
III - 4	1.55	4.96	4,684	595.6	60.9
III - 5	1.42	4.78	3,916	596.1	60.5
IV - 1	1.39	5.08	608	596.5	58.7
IV - 2	1.54	5.55	620	596.0	59.4
IV - 3	1.50	5.14	613	596.7	59.2
IV - 4	1.55	5.51	578	596.7	59.8
IV - 5	1.52	5.65	592	596.8	58.2
V - 1	1.36	5.40	2,985	596.1	54.2
V - 2	1.34	5.69	2,758	596.8	54.9
V - 3	1.35	5.41	3,098	596.1	53.8
V - 4	1.36	5.28	3,021	596.4	53.6
V - 5	1.37	5.30	3,027	596.3	54.9
VI - 1	1.45	4.24	1,282	601.3	52.3
VI - 2	1.41	4.05	1,201	598.2	51.3
VI - 3	1.44	4.18	1,196	597.3	51.2
VI - 4	1.40	4.12	1,201	597.8	50.8
VI - 5	1.48	4.06	1,194	597.9	50.4

Parachute Identification	Pellet Density	Burn Time	Luminous Intensity	Dominant Wavelength	Spectral Purity
	(g/cc)	(s)	(cd)	(nm)	(%)
Control - 1	1.94	33.06	16,994	611.4	79.5
Control - 2	1.92	32.91	21,001	611.6	78.6
Control - 3	1.88	33.15	18,961	612.5	80.2
Control - 4	1.90	33.44	15,544	612.8	81.6
I - 1	1.43	28.23	1,180	604.1	29.1
I - 2	1.41	28.63	938	604.2	28.3
I - 3	1.43	27.83	1,031	600.1	27.2
I - 4	1.47	28.95	982	604.7	30.9
I - 5	1.45	29.45	1,138	600.6	26.3
II - 1	1.47	37.35	944	612.3	36.4
II - 2	1.52	38.74	659	614.0	38.6
II - 3	1.48	37.33	840	611.1	38.8
II - 4	1.46	38.64	760	611.5	37.2
II - 5	1.45	36.92	996	608.8	38.0
III - 1	1.49	21.39	3,684	598.5	48.0
III - 2	1.49	21.65	3,212	597.8	52.0
III - 3	1.46	21.44	3,639	598.0	49.3
III - 4	1.47	21.52	3,543	597.7	51.1
III - 5	1.47	21.60	3,708	597.7	51.0
IV - 1	1.52	24.64	482	No data*	
IV - 2	1.51	25.19	451	No data*	
IV - 3	1.51	24.90	488	605.1	58.8
IV - 4	1.51	24.82	509	600.0	54.2
IV - 5	1.50	25.10	513	599.9	53.2
V - 1	1.43	25.42	2,513	597.1	50.3
V - 2	1.44	25.59	2,372	599.0	47.7
V - 3	1.40	24.77	2,561	599.2	48.2
V - 4	1.43	26.15	2,470	598.6	50.4
V - 5	1.42	25.82	2,530	599.0	49.2
VI - 1	1.40	22.03	811	602.0	45.4
VI - 2	1.43	21.40	814	603.9	42.0
VI - 3	1.41	22.64	736	602.4	46.3
VI - 4	1.47	21.62	799	602.9	43.9
VI - 5	1.49	21.10	655	605.0	41.5

# Results

## Prototyping

- All formulations show poorer values due to the presence of additional burnup material (paper tube)
- Poor spectral purity leads to a washed out color impression (pinkish)



# Technology Transfer

- Poster presentation at the SERDP/ESTCP Symposium in December 2019
- Attendance at the SERDP/ESTCP Symposium in 2020
- Attendance at the SERDP/ESTCP Symposium in 2021
- Poster presentation at the NTREM Conference in April 2022

# Key Points

- In this work multiple new lithium salts have been synthesized and completely characterized
- With a selected numbers of lithium salts, new pyrotechnical mixtures were prepared
  - ◆ These mixtures burned with a red color impression
- Mixtures did not match all desired values
  - ◆ Contrariness of luminous intensity and flame purity (antagonists)
- However, the prototype flares burned with a pinkish color
  - ◆ Reason: low spectral purity
  - ◆ Lithium suffers from oxophilicity which degrades the optical performance

# Future Research

- Continued funding in this research is warranted, however there should be a different approach on the topic
  - ◆ The implementation of lithium salts is difficult with the current state of the art
- Future research should focus on coating of pyrotechnical mixtures
  - ◆ Example:  $\text{LiNO}_3$ , can be used if it shows no hygroscopicity
  - ◆ This would also expand the possible range/options

# BACKUP SLIDES

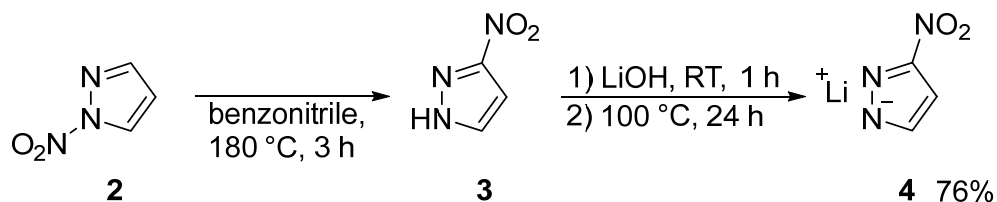
# Publications

- The Lithium Salts of Bis(azoxy)borates as Strontium- and Chlorine-free Red Pyrotechnic Colorants  
Alicia M. W. Dufter, Thomas M. Klapötke, Magdalena Rusan, and Jörg Stierstorfer  
*Z. Anorg. Allg. Chem.* **2020**, 646, 580–585.
- Comparison of Functionalized Lithium Dihydrobis(azoxy)borates with Their Corresponding Azolates as Environmentally Friendly Red Pyrotechnic Coloring Agents.  
Alicia M. W. Dufter, Thomas M. Klapötke, Magdalena Rusan, Alexander Schweiger and Jörg Stierstorfer  
*ChemPlusChem.* **2020**, 85, 2044–2050.
- Lithium Nitropyrazolates as Potential Red Pyrotechnic Colorants.  
A. M. W. Dufter-Münster, Alexander G. Harter, Thomas M. Klapötke, Elena Reinhardt, Julia Römer and Jörg Stierstorfer  
*Eur. J. Inorg. Chem.* **2022**, in press.

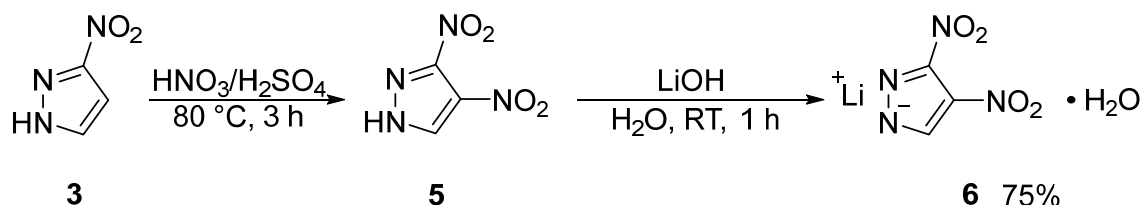
# Supporting Material

- Synthesis scheme of the lithium salts

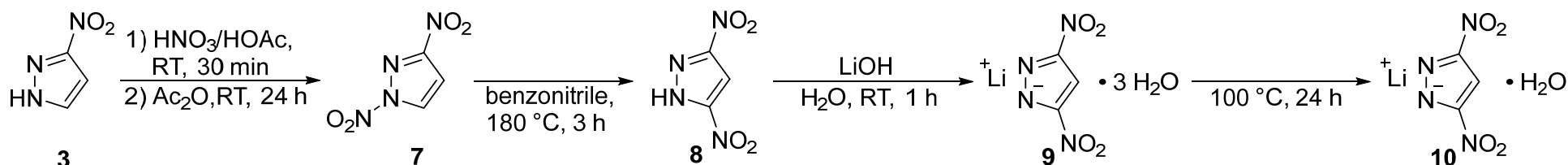
## Lithium 3-nitropyrazolate



## Lithium 3,4-dinitropyrazolate monohydrate



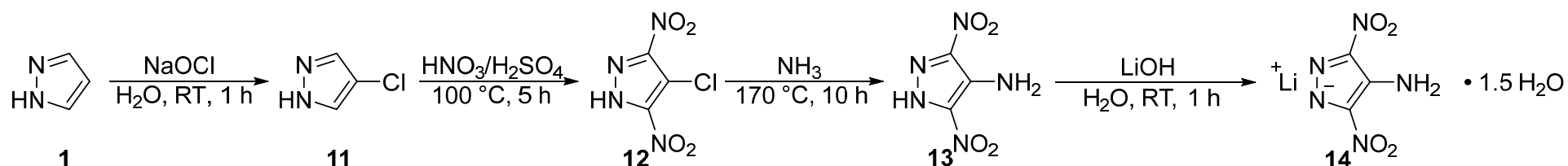
## Lithium 3,5-dinitropyrazolate monohydrate



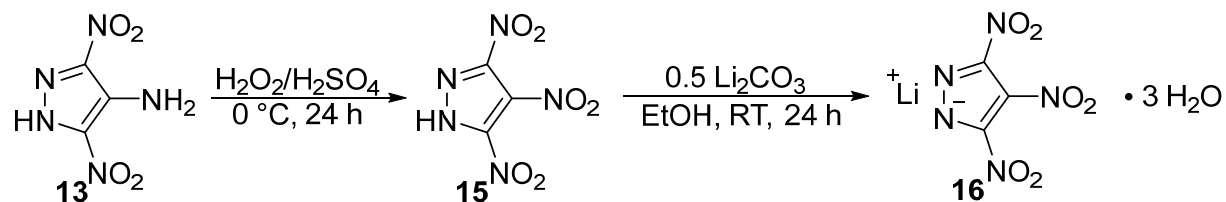
# Supporting Material

- Synthesis scheme of the lithium salts

## Lithium 4-amino-3,5-dinitropyrazolate sesquihydrate



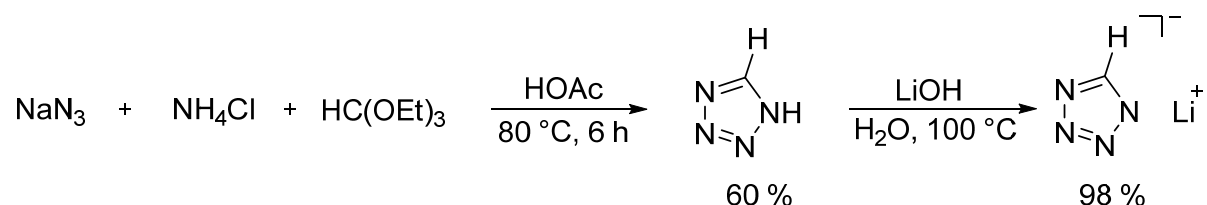
## Lithium 3,4,5-trinitropyrazolate trihydrate



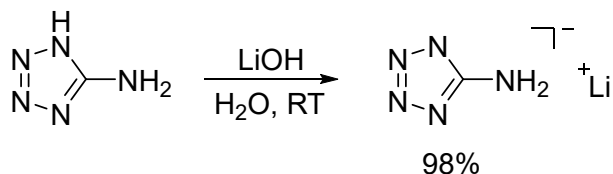
# Supporting Material

- Synthesis scheme of the lithium salts

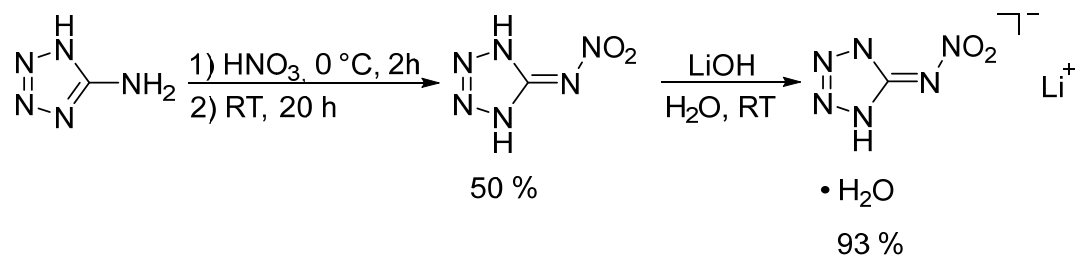
## Lithium tetrazolate



## Lithium 5-aminotetrazolate



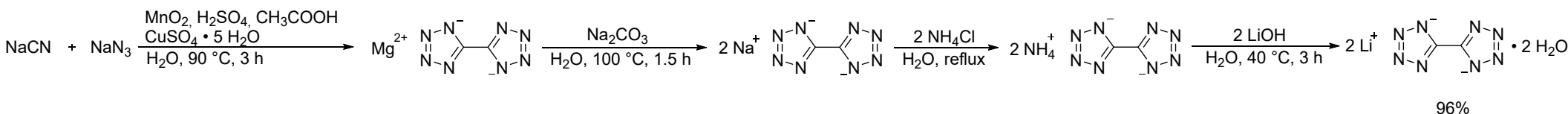
## Lithium 5-nitriminotetrazolate • H<sub>2</sub>O



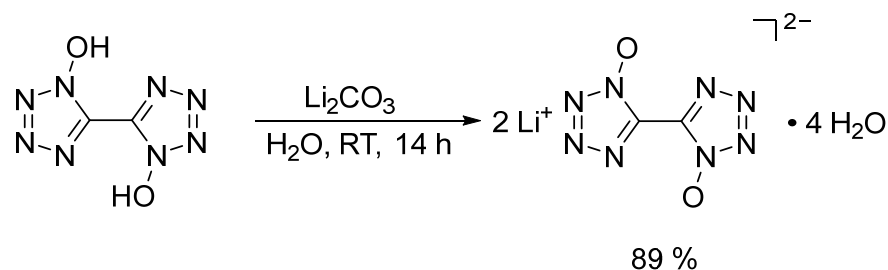
# Supporting Material

- Synthesis scheme of the lithium salts

## Dilithium 5,5'-bistetrazole • 2 H<sub>2</sub>O



## Dilithium 5,5'-bis(tetrazole-1-oxide) • 4 H<sub>2</sub>O

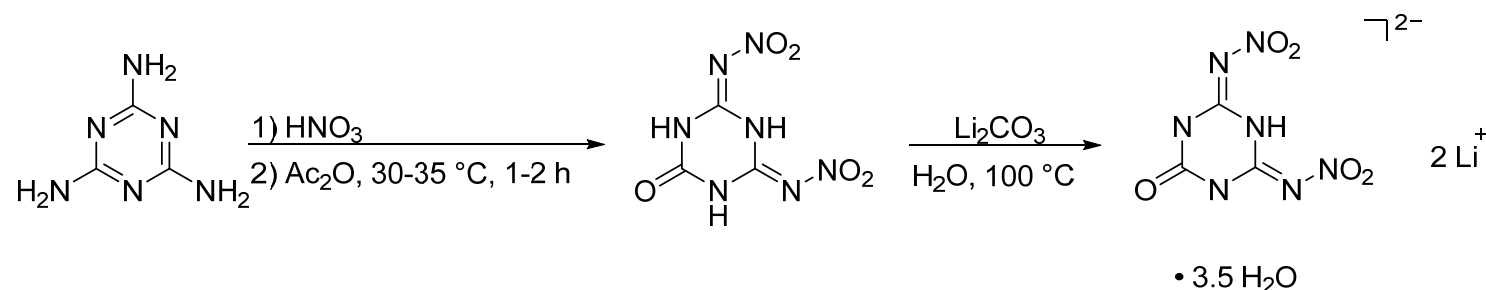


[1] D. E. Chavez et al., *J. Pyrotech.* **1999**, *10*, 17–36. [2] L. H. Finger et al., *Z. Anorg. Allg. Chem.* **2013**, *639*, 1140–1152. [3] N. Fischer et al., *Chem. Eur. J.* **2012**, *18*, 4051–4062. [4] N. Fischer et al., *Propellants Explos. Pyrotech.* **2013**, *38*, 448–459. [5] E. Oliveri-Mandala, T. Passalacqua, *Gazz. Chim. Ital.* **1914**, *43(II)*, 465–475.

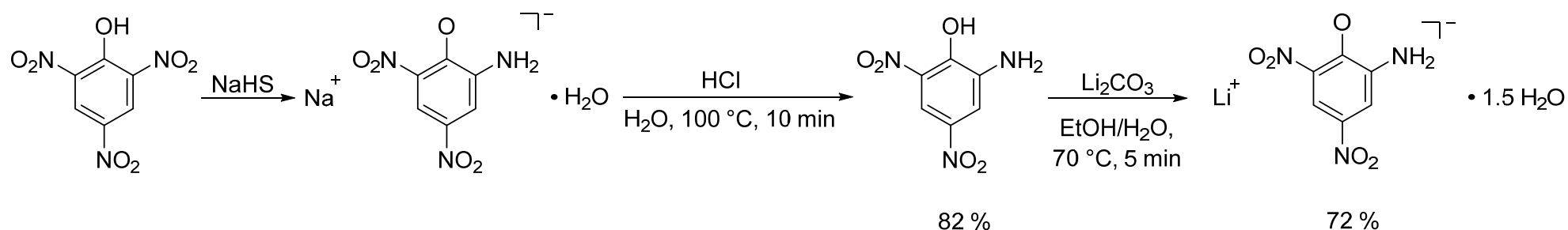
# Supporting Material

- Synthesis scheme of the lithium salts

## Dilithium 4,6-bis(nitrimino-1,3,5-triazinan)-2-one • 3.5 H<sub>2</sub>O



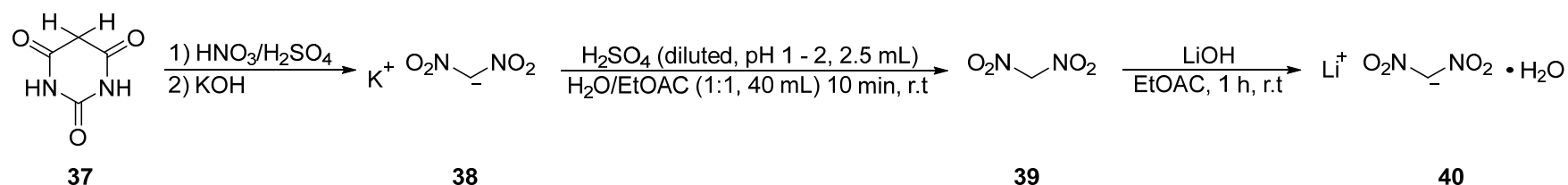
## Lithium picramate • 1.5 H<sub>2</sub>O



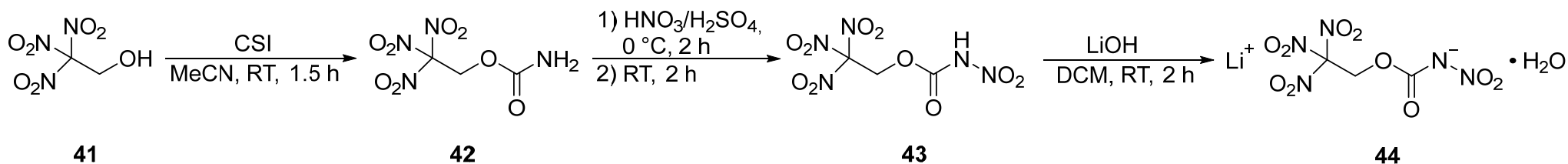
# Supporting Material

- Synthesis scheme of the lithium salts

## Lithium dinitromethanide • H<sub>2</sub>O



## Lithium 2,2,2-trinitroethyl nitrocarbamate • H<sub>2</sub>O

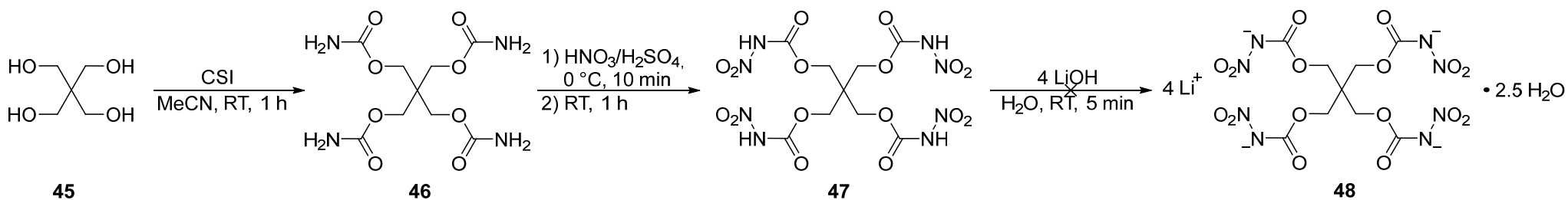


[1] A. Langlet, N. V. Latypov, U. Wellmar, U. Bemm, P. Goede, *J. Org. Chem.* **2002**, *67*, 7833–7838. [2] N. Latypov, U. Wellmar, A. Langlet, Method of Preparing Salts of Dinitromethane, 2002, US6340780B1. [3] Q. J. Axthammer, B. Krumm, T. M. Klapötke, *J. Org. Chem.* **2015**, *80*, 6329–6335. [4] Q. J. Axthammer, T. M. Klapötke, B. Krumm, R. Moll, Sebastian F. Rest, Z. *Anorg. Allg. Chem.* **2014**, *640*, 76–83.

# Supporting Material

- Synthesis scheme of the lithium salts

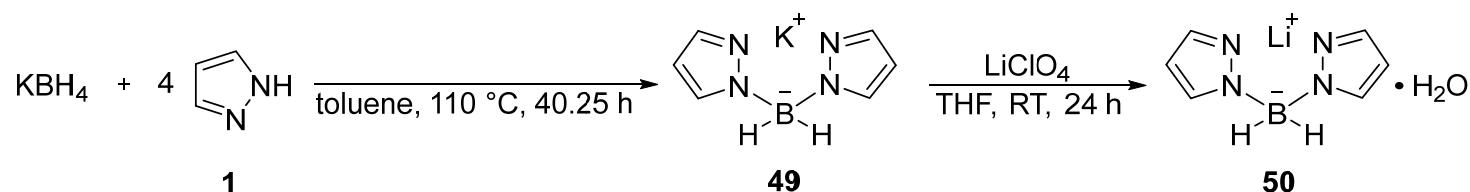
## Tetralithium pentaerythritol tetranitrocarbamate • 2.5 H<sub>2</sub>O



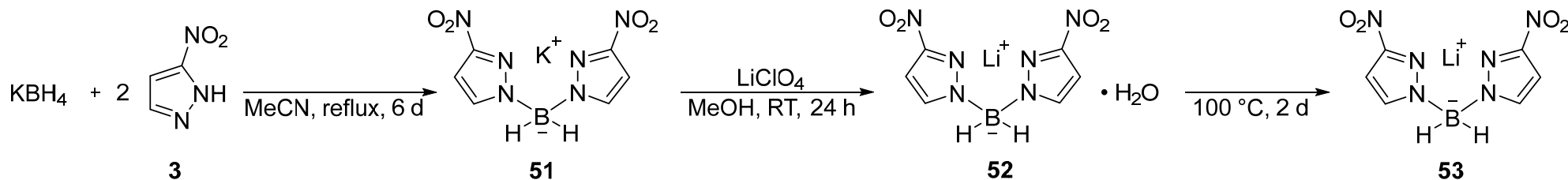
# Supporting Material

- Synthesis scheme of the lithium salts

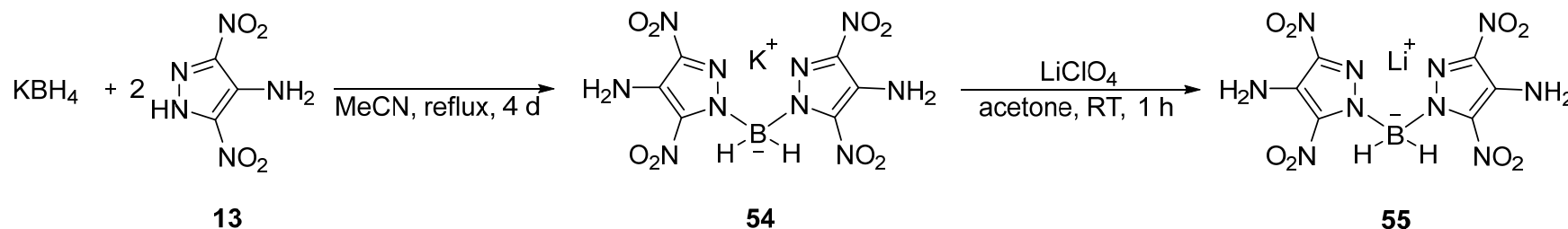
## Lithium dihydrobis(pyrazol-1-yl)borate monohydrate



## Lithium dihydrobis(3-nitropyrazol-1-yl)borate



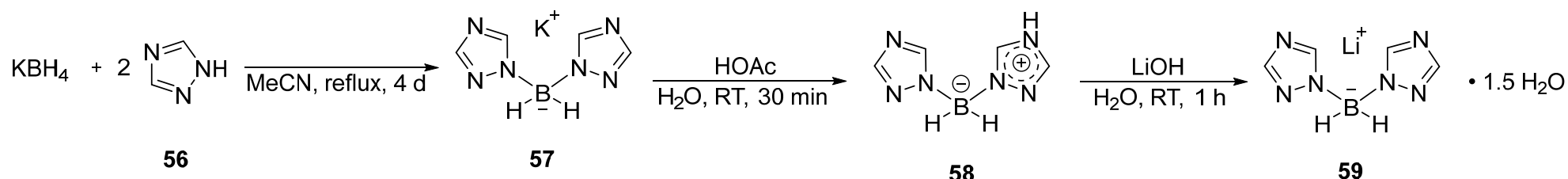
## Lithium dihydrobis(4-amino-3,5-dinitropyrazol-1-yl)borate



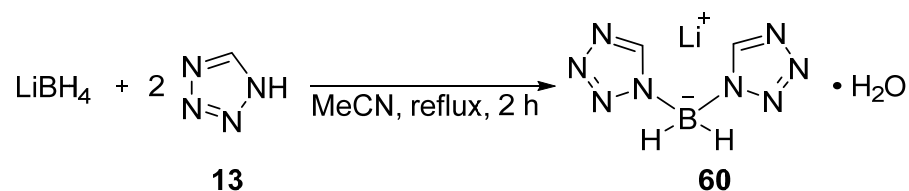
# Supporting Material

- Synthesis scheme of the lithium salts

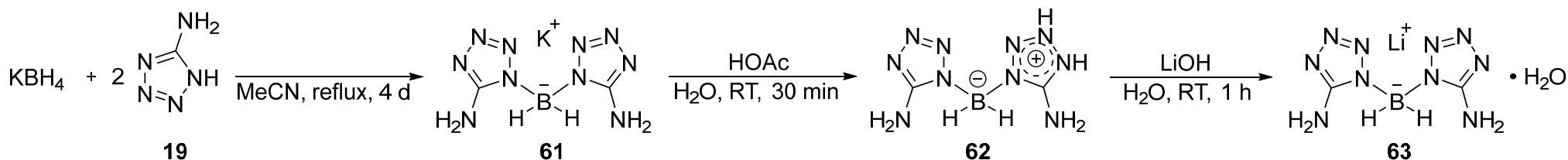
## Lithium dihydrobis(1,2,4-triazol-1-yl)borate sesquihydrate



## Lithium dihydrobis(tetrazol-1-yl)borate monohydrate



## Lithium dihydrobis(5-aminotetrazol-1-yl)borate monohydrate



# Supporting Material

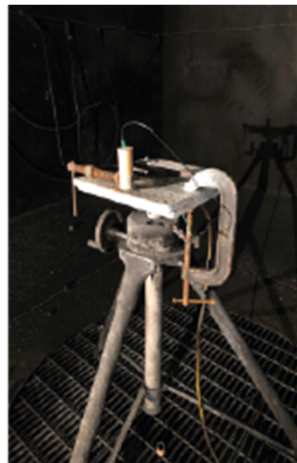
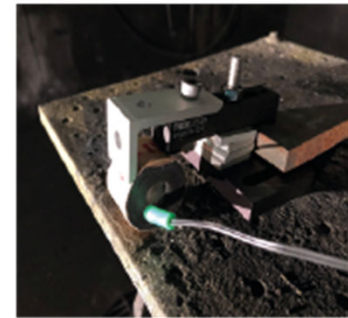
- Pyrotechnical measurement setup at *Ludwig-Maximilian University Munich*



# Supporting Material

- Pyrotechnical measurement setup at *DEVCOM*

Measurement setup of the cluster flares



Measurement setup of the parachute flares

# WP19-1287: LITHIUM BASED RED COLORANTS IN ENVIRONMENTALLY FRIENDLY PYROTECHNICAL ILLUMINANTS

## Performers:

- Prof. Dr. Thomas M. Klapötke (LMU)

## Technology Focus

- Synthesis and characterization of new lithium salts
- Screening of literature-known as well as unknown lithium compounds for red light production in “drop-in” formulations
- Formulation and optimization of the most promising candidates
- Prototyping

## Research Objectives

- Focus on nitrogen-rich, nitro-substituted and multivalent counterions
- Use of neutral compounds which are commercially available or accessible by easily scaled-up, few-step syntheses without requiring toxic reagents or solvents
- Study of the influence of the particle size and amounts of magnesium on the light intensity

## Project Progress and Results

- Preparation, analysis and determination of emissive properties of new lithium materials with high nitrogen contents and nitro groups
- Testing multiple lithium salts, different fuels/additives on laboratory scale
- Prototype flares were produced with the most stable, non-toxic and best performing salts
- Strontium could not be replaced by lithium according to the current state of the art

## Technology Transition

- Future research should focus on coating lithium species to address the problem of hygroscopicity
- This would increase the choice of cost-effective materials

