# Li ion chemosensors for the detection of liquid electrolyte leakage

Ricardo da Costa Barata
Georgios Karaiskakis
Natalia Lebedeva

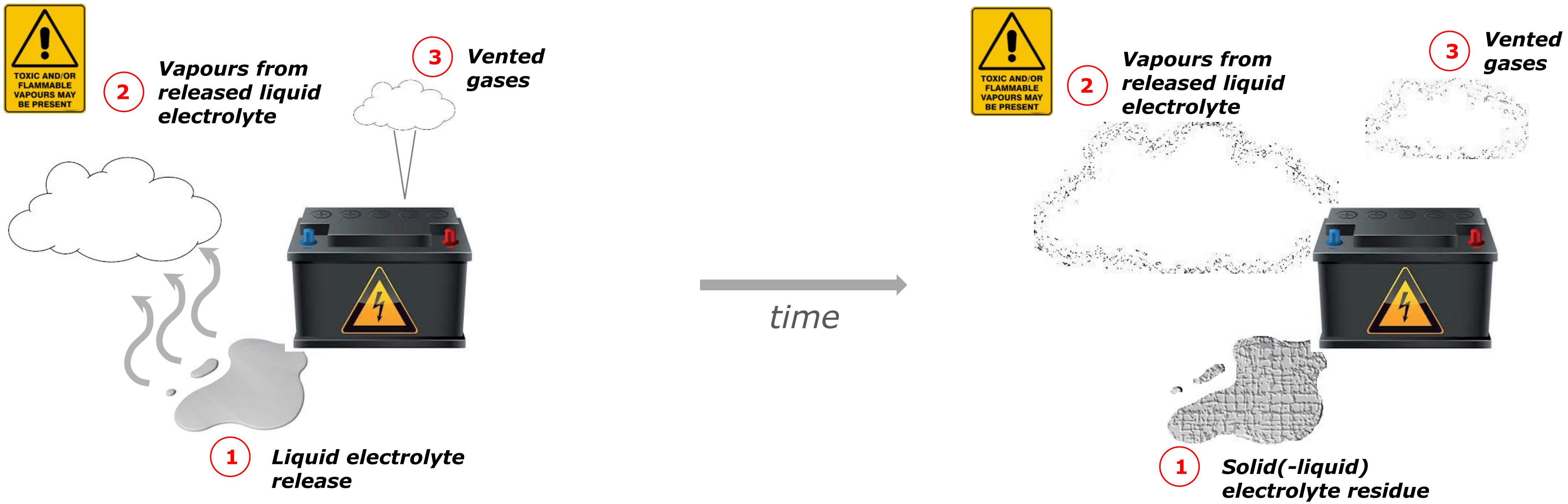
# Li ion chemosensors for the detection of liquid electrolyte leakage

Motivation

Chemosensors - Literature Review

Future Work

# Introduction



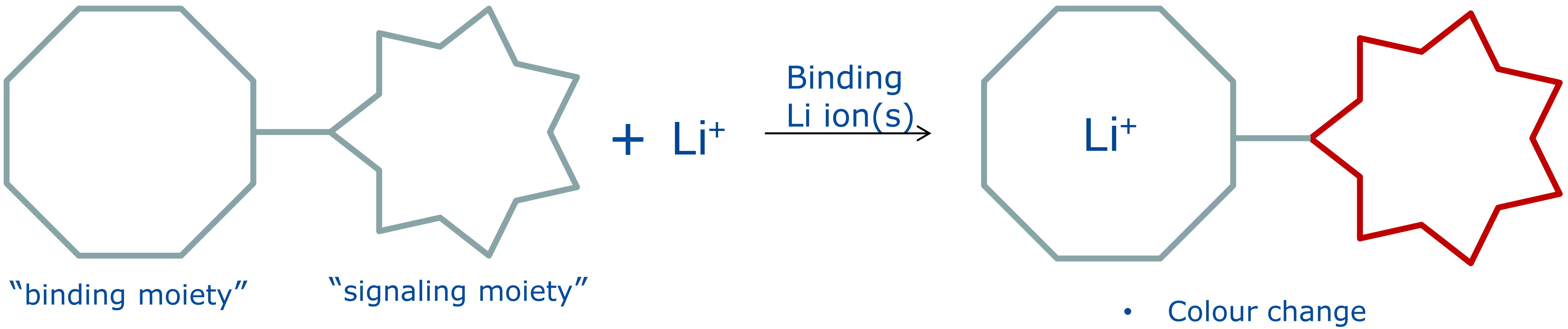

## *Possible approaches for detection of electrolyte release*

1 Detection of Li-ion presence

2 + 3 Gas detection

# Li-ion chemosensor

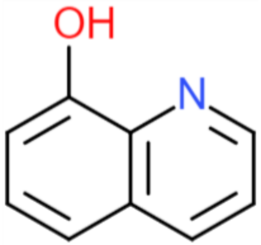
**Chemosensor** – molecule able to simultaneously bind and signal the presence of other species[a].




- Colour change
- Fluorescence change

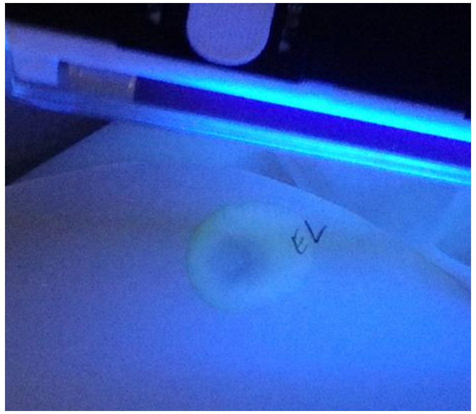
[a] F. Pina et al, *Chemosensors displaying pH controlled multistage fluorescence emission*, J. Photochem. Photobiol. A, 126 (1999), 65-69

# Experimental Results: 8-Hydroxyquinoline




## Proof of concept:

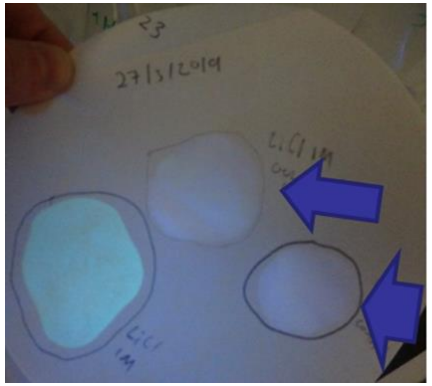
- use of 8-HQ can help detecting Li-ion battery electrolyte release
- a coating based on 8-HQ treated filter paper was demonstrated



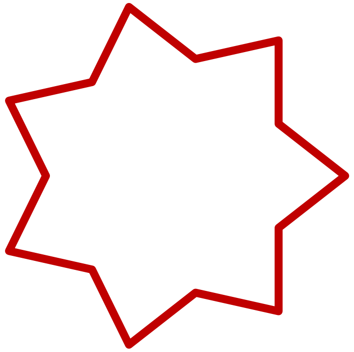
## Drawbacks:

- ✗ Not Li ion specific
- ✗ Coolants are fluorescent
- ✗ Low sensitivity, under experimental conditions
- ✗ Fluorescence quenched by water

**EXPERIMENTAL CONDITIONS**
Detector: human eye.
UV Source: handheld dispersive lamp.
Sample holder: coating around the pack.



# Li-ion chemosensor – Classification



"signaling moiety"

**Chelation Induced ENHANCED LUMINESCENCE**

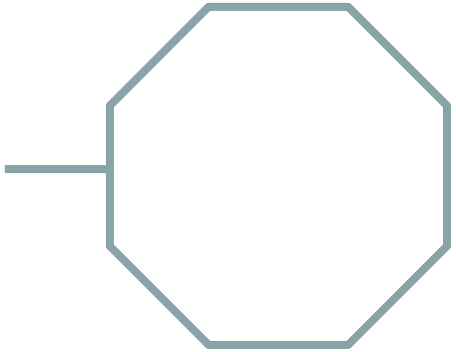
**Chelation Induced LUMINESCENCE QUENCHING**

**Chelation Induced ABSORBANCE CHANGE**

| Ideal Chemosensor |
| --- |
| Change of colour in the visible range. |

E. Villemin, O. Raccurt, *Optical lithium sensors*, Coord Chem Rev, 435 (2021), 213801

# Li-ion chemosensors - Classification




- CHELATING sensors
- PODAND-based sensors
- CROWN-containing$^{*}$ sensors
- CRYPTAND-based sensors
- CALIXARENE-based sensors

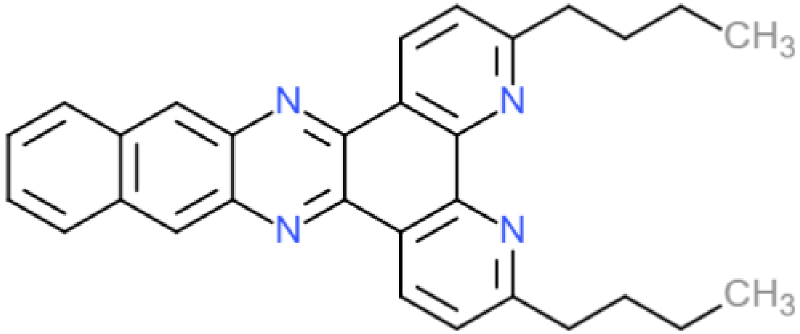
* - includes not only crown polyethers but all planar cyclic compounds

| **Ideal Chemosensor** |
| --- |
| Selectively binds to $Li^+$ |


B. Valeur, I. Leray, *Design Principles of fluorescent molecular sensors for cation recognition,* Coord. Chem. Rev., 205 (2000), 3-40

# Li-ion chemosensor – Chelating Sensors

## Chelant 1




Selectivity for $Li^+$ over $Na^+$ and $K^+$.

Fluorescence dependant on polarity of solvent (increasing polarity):

- Benzene **531** nm
- Tetrahydrofuran **538** nm
- Ethanol **553** nm
- Methanol **562** nm

$Li^+$ binding induces fluorescence red shift.

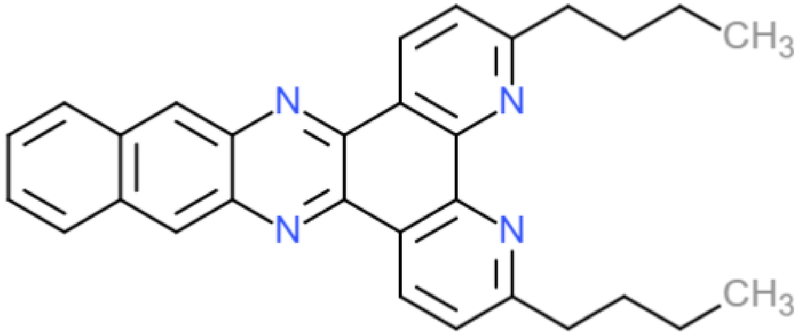
Fluorescence quenched by increasing $Li^+$ concentration in Ethanol.

Fluorescence increased by increasing $Li^+$ concentration in Tetrahydrofuran.

S. Obare, C. Murphy, *A Two-Color Fluorescent Lithium Ion Sensor*, Inorg. Chem., 2001, 40, 6080-6082

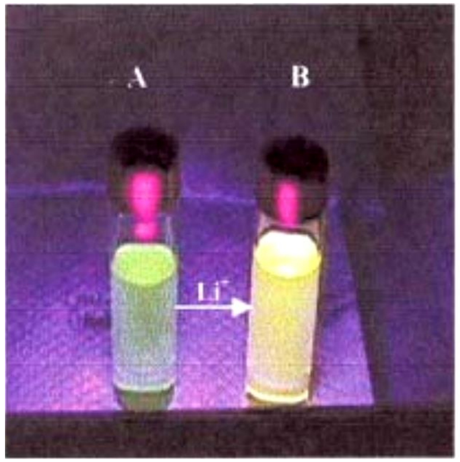
# Li-ion chemosensor – Chelating Sensors

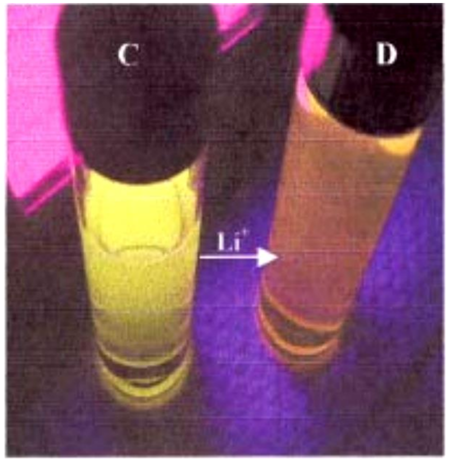
## Chelant 1




From green (A) to yellow (B) in non-polar solvents. (from 0 to 1.05M)

From yellow (C) to orange (D) in polar solvents. (from 0 to 26mM)

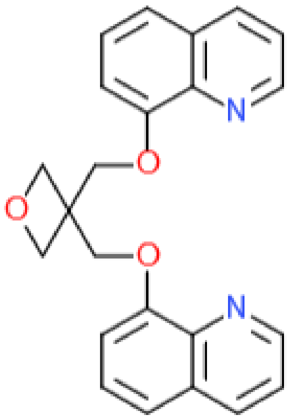



| Ideal Chemosensor | Chelant 1 |
|---|---|
| Li-ion selective | ☑ |
| Change of colour in visible range | ☒ |
| High sensitivity under experimental conditions | ? Fluorescence titration |
| Not solvent or pH sensitive | ☒ |
| Commercially available | ☒ |

# Li-ion chemosensor – Podand-based Sensors

## Podand 1




Emission maximum change by addition of 10 mM $LiClO_4$:

- in dioxane* - **378** nm (UV) to **391** nm (Vis)
- in MeCN - **385** nm to **392** nm
- in $CH_3Cl$* - **382** nm to **378** nm (UV)

** - lithium salt partly insoluble*

Selectivity for $Li^+$ over $Na^+$, $K^+$ and $Ba^{2+}$.

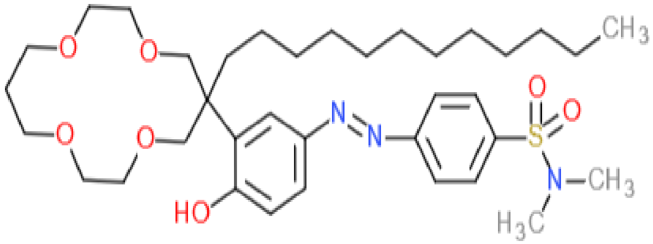
Fluorescence quenched by $Ag^+$ and $Cu^{2+}$, and with high ratio (>100) of $Mg^{2+}$:ligand.

| Ideal Chemosensor | Podand 1 |
|---|---|
| Li-ion selective | ✗ Better than 8-HQ, but not selective |
| Change of colour in visible range | ✗ |
| High sensitivity under experimental conditions | ? Spectrofluoro-metry |
| Not solvent or pH sensitive | ✗ |
| Commercially available | ✗ |

K. Hiratani et al, *Fluorescence Behaviours of 3,3-Bis(8-Quinolyloxymethyl) oxetane: Effects of Solvents, Carrier-concentration and Metal Ions on the Fluorescence Intensity*, Bull. Chem. Soc. Jpn., 1990, 63, 1349-1353

# Li-ion chemosensor – Crown-containing Sensors

## Crown-Ether 1




Selectivity for $Li^+$ over $Na^+$, $K^+$, $Cs^+$ and $Rb^+$.

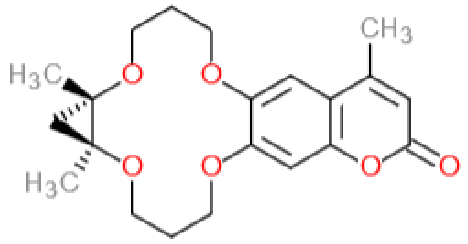
$Li^+$ binding induces red shift, changing the colour of the solution from yellow to orange.

| Ideal Chemosensor | Crown-ether 1 |
|---|---|
| Li-ion selective | ☑ |
| Change of colour in visible range | ☑ |
| High sensitivity under experimental conditions | ? |
| Not solvent or pH sensitive | ☒ |
| Commercially available | ☒ |

K. Kimura, M. Tanaka, S. Kitazawa, T. Shono, *Highly lithium-selective crown ether dyes for extraction photometry*, Chem. Lett., 1985, 8, 1239-1240.

# Li-ion chemosensor – Crown-containing Sensors

## CROWN-ETHER 2




In a $H_2O$/MeOH (99:1) system the main fluorescence peak at λ= **426** nm takes a blue shift to λ= **380** nm.

Fluorescence quenched with increasing $Li^+$ concentration.

Quantitative determination of $Li^+$ in a wide range of concentrations ($10^{-5}$ M to $10^{-1}$ M).

Other alkaline ($Na^+$, $K^+$) and alkaline-earth metal ($Ca^{2+}$, $Mg^{2+}$) cations were shown not to interfere with the detection.

| Ideal Chemosensor | Crown-ether 2 |
|---|---|
| Li-ion selective | ☑ |
| Change of colour in visible range | ☒ |
| High sensitivity under experimental conditions | ? |
| Not solvent or pH sensitive | ☑ |
| Commercially available | ☒ |

D. Citterio et al, *pH-Independent Fluorescent Chemosensor for Highly Selective Lithium Ion Sensing*, Analytical Chemistry, 2007, 79, 1237-1242

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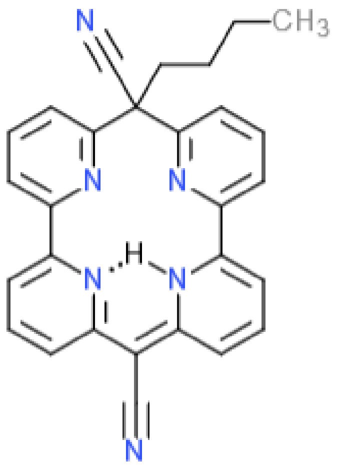
# Li-ion chemosensor – Crown-containing Sensors

## HETEROCYCLE 1




Selectivity of $Li^+$ in the presence of other alkali ($Na^+$, $K^+$) and alkaline-earth ($Mg^{2+}$, $Ca^{2+}$)

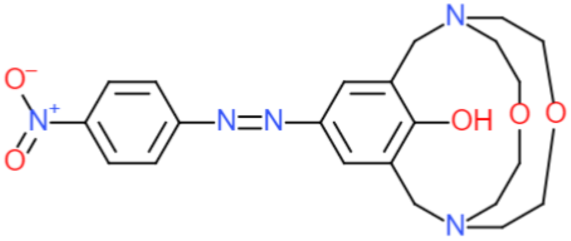
$Li^+$ binding induces blue shift, changing the colour of the solution from **red** to colourless.

| Ideal Chemosensor | Heterocycle 1 |
|---|---|
| Li-ion selective | ☑ |
| Change of colour in visible range | ☑ |
| High sensitivity under experimental conditions | ? Membranes |
| Not solvent or pH sensitive | ? No pH study with labile H. |
| Commercially available | ☒ |

S. Tsuchiya et al, *Highly Efficient Separation of Lithium Chloride from Seawater*, Journal of American Chemical Society, 2002, 124, 4936-4937.

# Li-ion chemosensor – Cryptand-based Sensors

## CRYPTAND 1



Presents different colours depending on its state of binding.

pH dependent:

- The protonated phenol, metal free Abs $\lambda_{max}$ = **494 nm**
- The deprotonated phenol, metal free Abs $\lambda_{max}$ = 575 nm
- Deprotonated phenol bound to $Na^+$ Abs $\lambda_{max}$ = 575 nm
- Deprotonated phenol bound to $K^+$ Abs $\lambda_{max}$ = 572.5 nm
- Deprotonated phenol bound to Li-ion Abs $\lambda_{max}$ = **517 nm**

| Ideal Chemosensor | Cryptand 1 |
|---|---|
| Li-ion selective | ☑ |
| Change of colour in visible range | ☑ |
| High sensitivity under experimental conditions | ? |
| Not solvent or pH sensitive | ☒ |
| Commercially available | ☒ |

E. Chapoteau, *First Practical Colorimetric Assay of Lithium in Serum*, Clin. Chem., 1992, 38 (9), 1654-1657

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# Li-ion chemosensor – Calixarene-based Sensors

## CALIXARENE-1

PyAzoC4-IM does not show a high selectivity towards $Li^{+}$ vs $Na^{+}$ when free.

By creating a layer of the sensor on quartz and a after a 'priming' procedure involving washing with 0,1M HCl:

- Increased selectivity towards $Li^{+}$, compared to $Na^{+}$, $K^{+}$, $Mg^{2+}$, $Ca^{2+}$, $Fe^{2+}$ and $Mn^{2+}$.
- Shows a change of colour when exposed to a 1 mM Li-ion solution in MeCN .
- No further change above 4,7 mM Li-ion

| Ideal Chemosensor | Calixarene-1 |
|---|---|
| Li-ion selective | ☑ |
| Change of colour in visible range | ☑ |
| High sensitivity under experimental conditions | ? Primed in silicon |
| Not solvent or pH sensitive | ☑ |
| Commercially available | ☒ |

A. Gulino et al , *A Viable Route for Lithium Ion Detection*, Eur. J. Inorg. Chem., 2014, 442–449

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# Li-ion chemosensor – Other architectures

## LMOF-321

Luminescent Metal-Organic Framework (LMOF), named LMOF-321.

Fluorescence $\lambda_{max}$ approx. 480 nm.

Fluorescence quenched in the presence of Li-ion over the competing Alkaline or Alkaline Earth metals.

$Li^{+}$ concentration from 0 to 88 mM.

| Ideal Chemosensor | LMOF-321 |
|---|---|
| Li-ion selective | ☑ |
| Change of colour in visible range | ☒ |
| High sensitivity under experimental conditions | ? |
| Not solvent or pH sensitive | ☑ |
| Commercially available | ☒ |

N. Rudd et al, *Luminescent Metal−Organic Framework for Lithium Harvesting Applications*, ACS Sustainable Chem. Eng. 2019, 7, 6561−6568

# Evolution of motivation for Li ion sensing

**1998**

- *"The major interest for $Li^+$ analysis arises from the effective prophylactic and therapeutic action of $Li^+$ in various affective disorders..."*
  P. Bühlmann et al *Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 2. Ionophores for Potentiometric and Optical Sensors*, Chem. Rev. 98 **(1998)** 1593-1687

**2000**

- *"…it is important to control the serum levels of lithium in patients under treatment for manic depression…"*
  B. Valeur, I. Leray, Design Principles of fluorescent molecular sensors for cation recognition, Coord. Chem. Rev., 205 **(2000)** 3-40

**2017**

- *"Lithium salts… have been widely and effectively used in the treatment of bipolar disorders… The expanding use of **lithium ion batteries**, in particular, is likely to bring more **environmental exposure through leaching of landfill**."*
  M Kamenica et al, Lithium Ion Sensors, Sensors, 17 **(2017)** 2430

**2021**

- ***"Battery failure** may causes fire and sometimes explosions… So, the **detection and quantification of active lithium** is a primordial key to understand the lithium plating mechanisms…"*
  E. Villemin, O. Raccurt, *Optical lithium sensors*, Coord Chem Rev, 435 **(2021)** 213801

# Summary

| Ideal Chemosensor | 8-HQ (Chelant type) | Chelant 1 | Podand 1 | Crown-ether 1 | Crown-ether 2 | Heterocycle 1 | Cryptand 1 | Calixarene 1 | LMOF-321 |
|---|---|---|---|---|---|---|---|---|---|
| Li-ion selective | ☒ | ☑ | ☒<br>Better than 8-HQ, but not selective | ☑ | ☑ | ☑ | ☑ | ☑ | ☑ |
| Change of colour in visible range | ☒ | ☒<br>Changes to Fluorescence | ☒<br>Increased Fluorescence | ☑ | ☒<br>Decreased Fluorescence | ☑ | ☑ | ☑ | ☒ |
| High sensitivity under experimental conditions | ☒ | ?<br>Fluorescence titration | ?<br>Spectrofluoro-metry | ? | ? | ?<br>Membranes | ? | ?<br>Primed in silicon | ? |
| Not solvent or pH sensitive | ☒ | ☒ | ☒ | ☒ | ☑ | ?<br>No pH study with labile H. | ☒ | ☑ | ☑ |
| Commercially available* | ☑ | ☒ | ☒ | ☒ | ☒ | ☒ | ☒ | ☒ | ☒ |

* - to the best of our knowledge

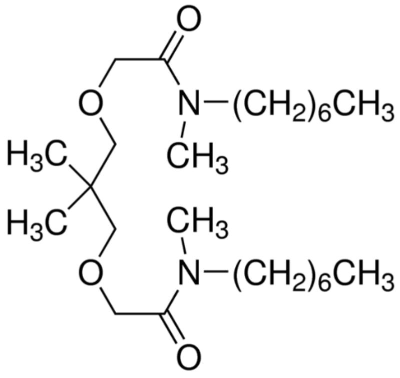
# Future Work

| Ideal Chemosensor | 8-HQ (Chelant type) | Crown-ether 2 | Heterocycle 1 | Calixarene 1 | LMOF-321 |
|---|---|---|---|---|---|
| Li-ion selective | ☒ | ☑ | ☑ | ☑ | ☑ |
| Change of colour in visible range | ☒ | ☒ Decreased Fluorescence | ☑ | ☑ | ☒ |
| High sensitivity under experimental conditions | ☒ | ? | ? Membranes | ? Primed in silicon | ? |
| Not solvent or pH sensitive | ☒ | ☑ | ? No pH study with labile H. | ☑ | ☑ |
| Commercially available | ☑ | ☒ | ☒ | ☒ | ☒ |

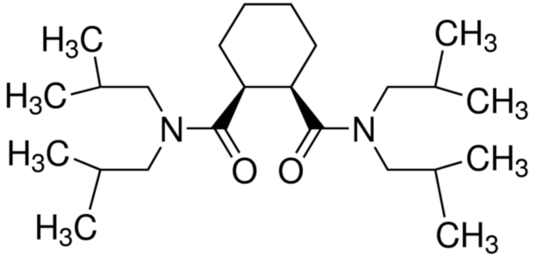
LABORATORY TESTING ?

How critical for going forward?

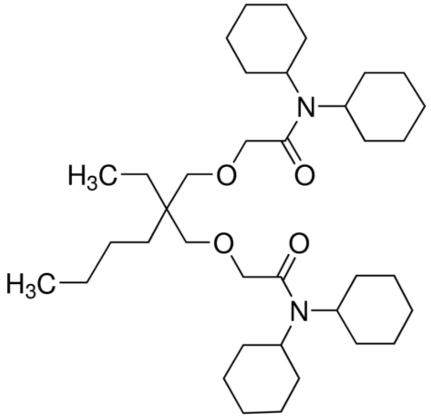
# Commercially Available Li ionophores



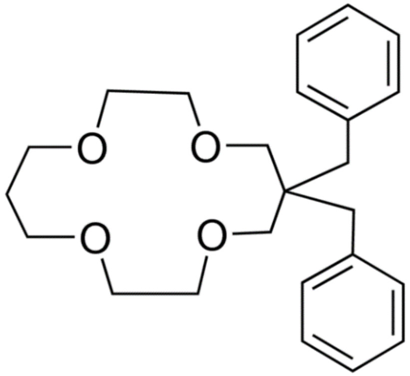
LITHIUM IONOPHORE I



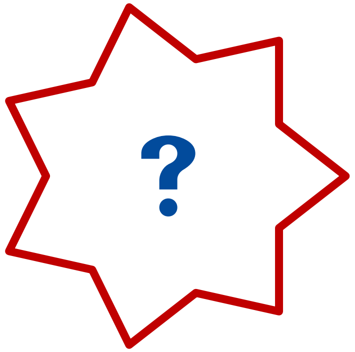
LITHIUM IONOPHORE II



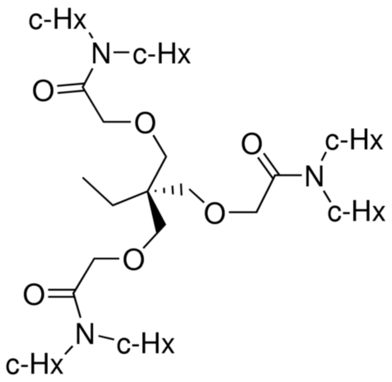
LITHIUM IONOPHORE IV



LITHIUM IONOPHORE VI




“signaling moieties?”



LITHIUM IONOPHORE VIII

# Conclusions and Outlook

☑ JRC work provided a proof of concept for a coating with a chemosensor (8-hydroxyquinoline) to help identify liquid release of electrolyte from Li-ion batteries during testing.

☒ use of 8-HQ can’t differentiate electrolyte release from other liquids.

Present JRC work outlines possible alternative chemosensors that could allow to differentiate electrolyte release from other releases.

- ☐ JRC will further explore commercially available ionophores to ascertain their suitability for detection of Li ions presence.
- ☐ JRC will explore collaboration with a partner that can synthesize and provide the identified chemosensor molecules for laboratory testing.

# Thank you



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