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Development and characterization of new families of organic alkaline salts for Charge Transfer Complexes in battery applications

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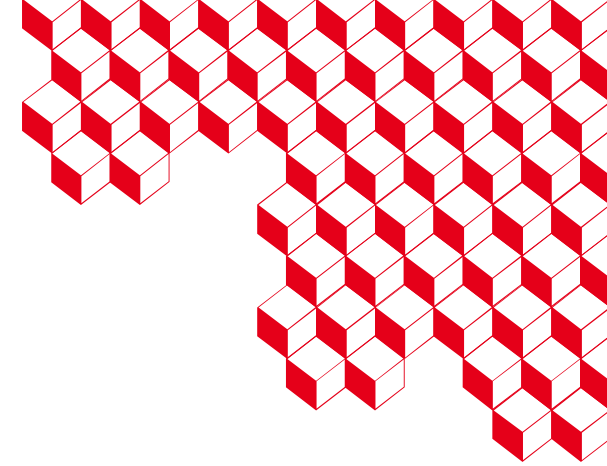
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Development and characterization of new families of organic alkaline salts for Charge Transfer Complexes in battery applications

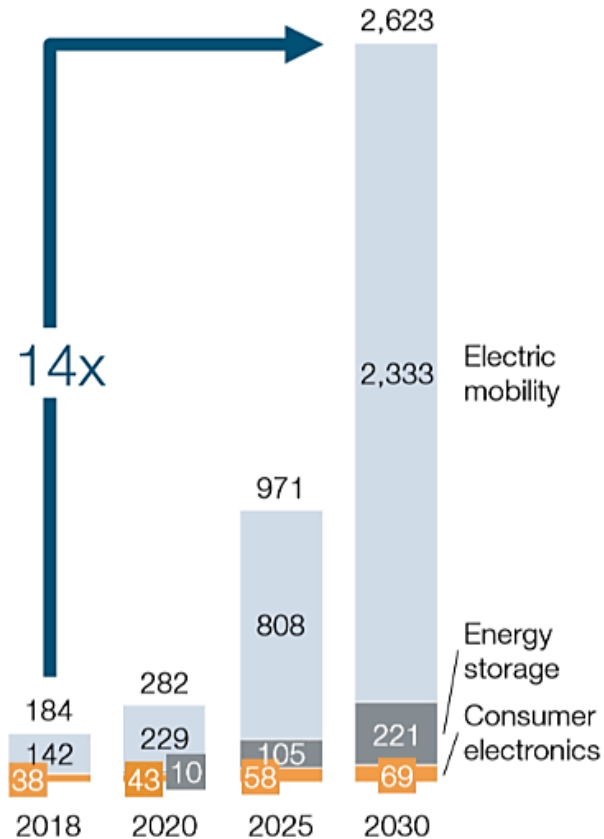
Commissariat à l'énergie atomique et aux énergies alternatives, Grenoble (France)

KUNERT Romain / TESSIER Noëline / BERNARD Laurent / PICARD Lionel





Some numbers



- Global need of batteries for electric mobility:
 - Approx. **30% annual increase** for electric transportation
 - **135 to 250 million** electric vehicles in 2030 (30 millions currently)

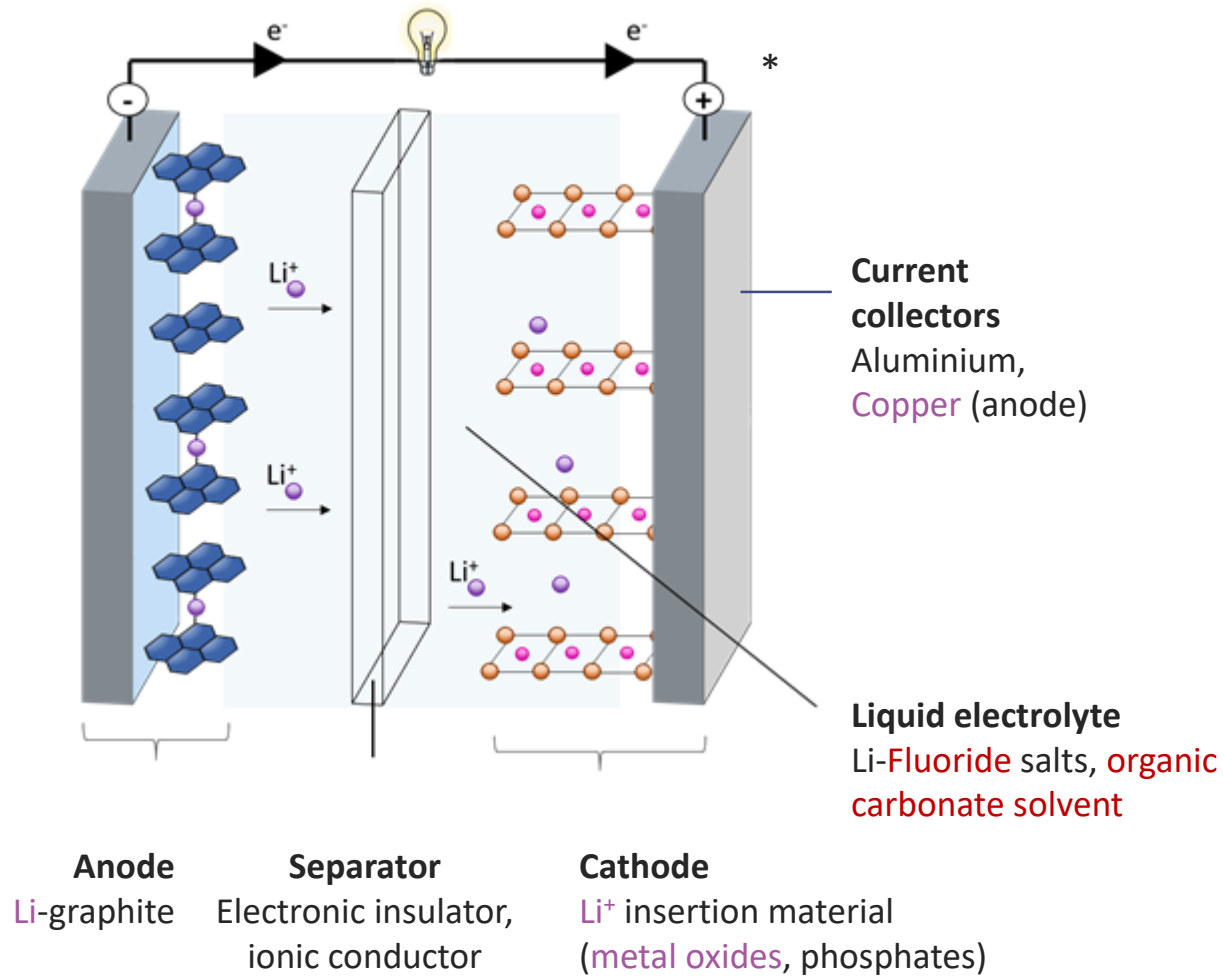


- global market of **58 billion USD** (2022)
- expected to reach **293 billion USD** by 2032**

*Prevision of battery needs throughout 2030 (GWh)**



Li-ion technology

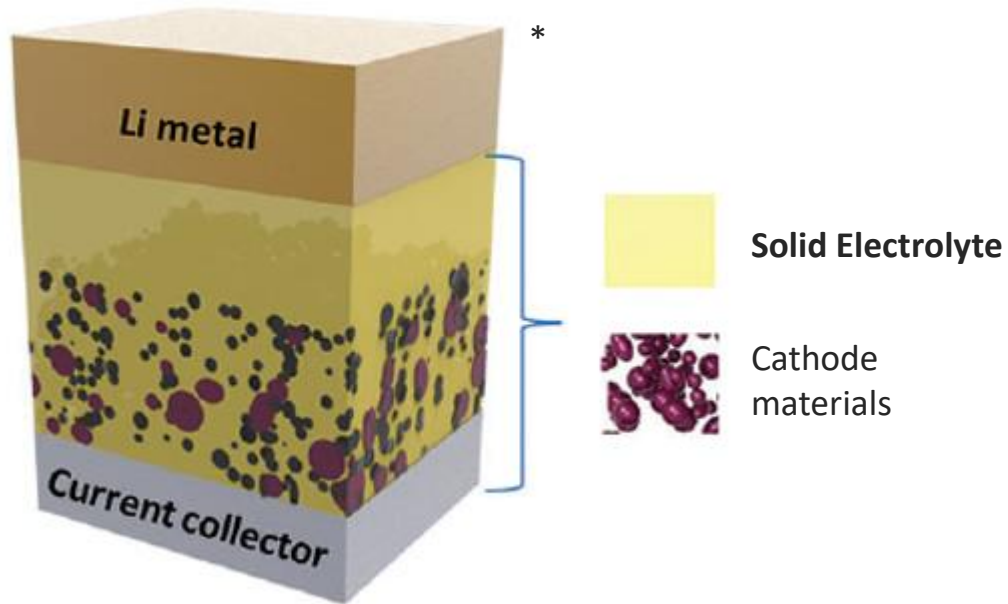


- Roadblocks to globalization:
 - ✓ Autonomy, wear and tear
 - ✗ Materials cost and **criticality**
 - Alternative Na/K technologies, LFP cathodes ...
 - ✗ **Safety hazards** (leakage, inflammable toxic electrolyte)



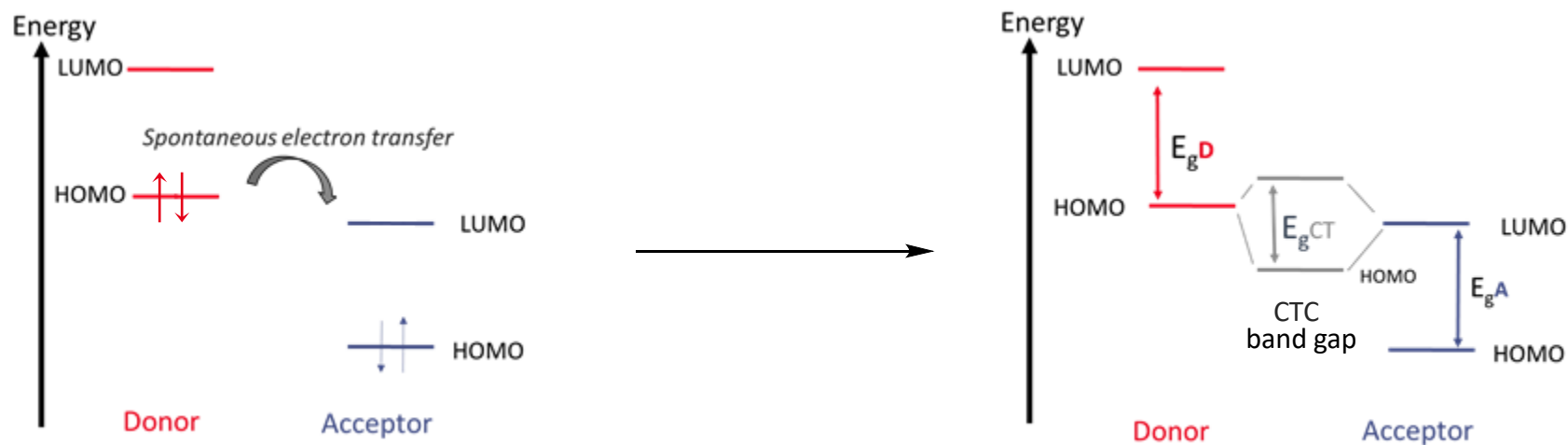
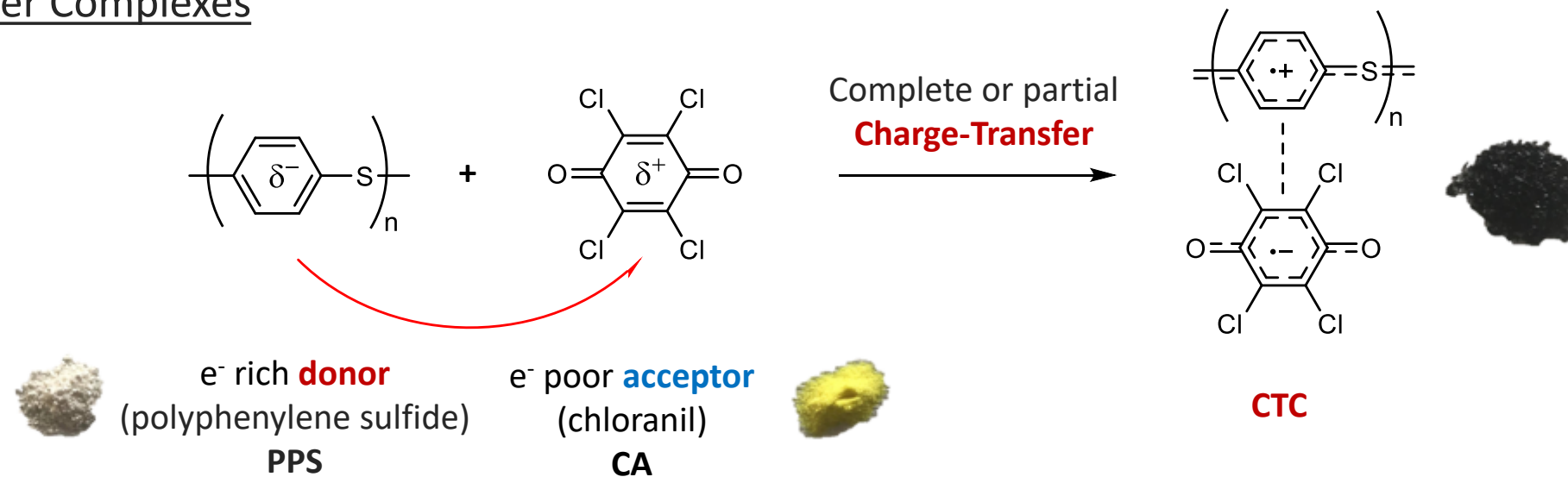


Solid-state batteries

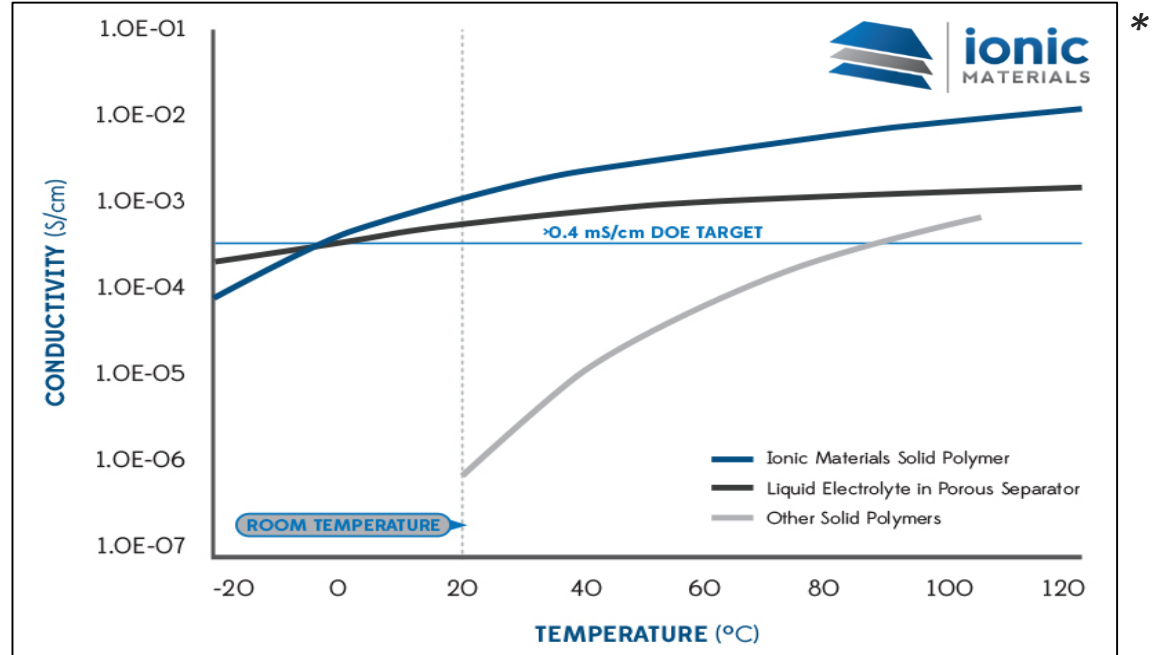
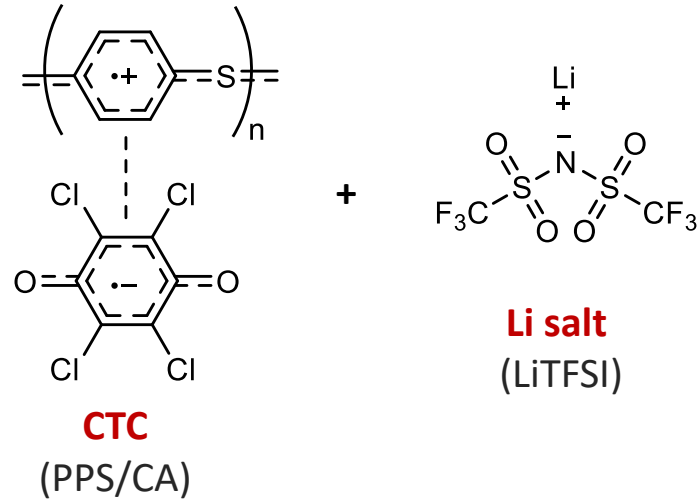


- ✓ Performances: Li metal anode (energy density)
- ✓ Enhanced safety: reduced flammability, dendrites growth
- Solid Electrolytes:
 - Inorganic: sulfurs, oxides
 - Composites: Polymer matrix + inorganic electrolyte
 - **Organic electrolytes**
- ✓ Tunable mechanical properties
- ✓ Cheaper and usually easier to process
- ✗ Limited electrochemical properties
 - Ionic conductivities ($\sigma_{PEO} = 10^{-6} \text{ S.cm}^{-1}$ at 25°C)
 - Li transference number ($t_{Li^+,PEO} = 0,2$)

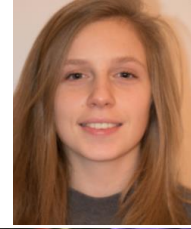
Charge-Transfer Complexes



Charge-Transfer Complexes (ionic materials)

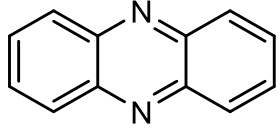


- ✓ Super-ionic conductivity ($\sigma > 10^{-3}$ S/cm at RT)
- ✓ Electrochemical stability
- ✗ No reproducibility
- ✗ Unclear conduction mechanism (interface polarity, segmental motion?)

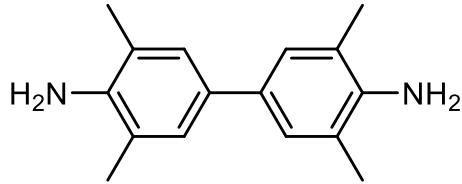


Alternative CTC electrolyte systems (N. Tessier)

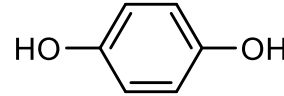
Donors



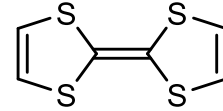
PNZ



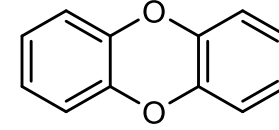
TMB



HQ

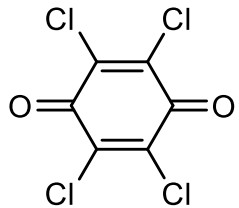


TTF

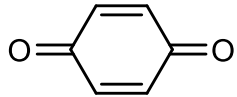


DD

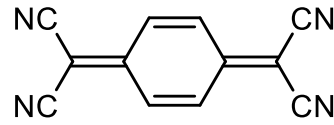
Acceptors



CA

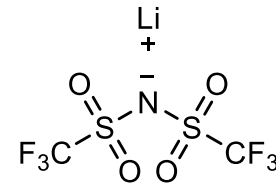


BQ



TCNQ

Li salt



LiTFSI

- Standardized preparation and characterization of CTC electrolytes:
 - Mixing in tetrahydrofuran solvent, evaporation then reduced pressure drying (80°C, 48 h)
 - Impedance + Wagner polarization method to determine electronic/ionic conductivity



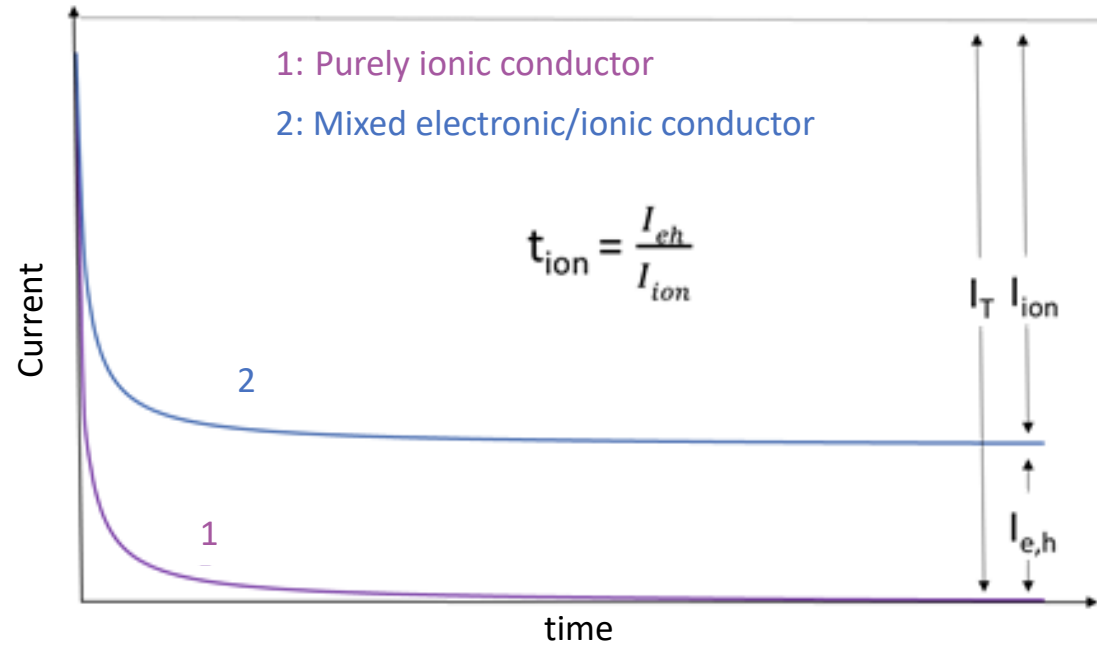
PNZ/TCNQ CTC



HQ/BQ/LiTFSI powders

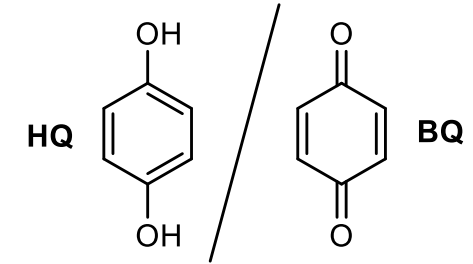


Alternative CTC electrolyte systems (N. Tessier)



➤ Selected HQ/BQ system

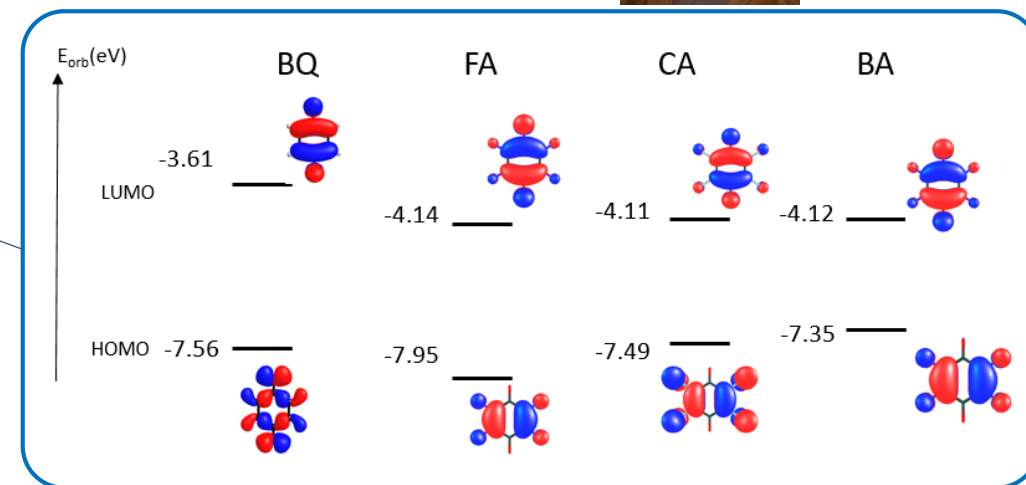
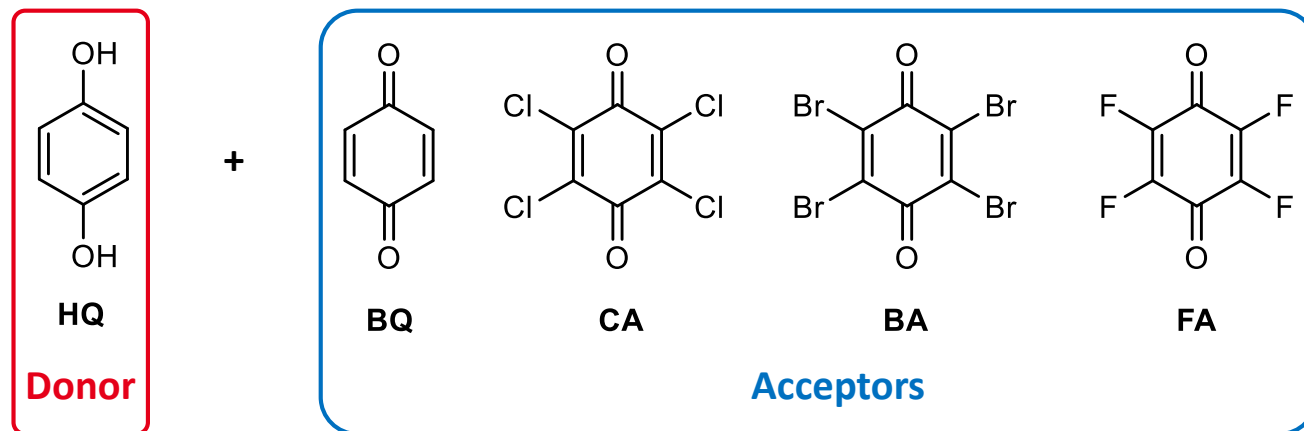
- Alternative Li salts
- Different formulations
- Different material processes



	HQ/BQ	TTF/CA	PNZ/TCNQ	TMB/TCNQ	TMB/CA	DD/TCNQ
Conductivity	Ionic	Mixed ?	Ionic	Ionic	Electronic	Electronic
Value at RT (S.cm ⁻¹)	5.6x10⁻⁶	1.4x10 ⁻⁷	2.9x10 ⁻⁸	1.6x10 ⁻⁸	1.7x10 ⁻⁷	2.4x10 ⁻⁸



Alternative CTC electrolyte systems (N. Tessier)



➤ HQ/BQ derivatives (LiTFSI Li salt)

- Benzoquinone derivatives with increasingly electrowithdrawing substituents
- Modification of CTC orbitals: impact on ionic conductivity ?
- Investigated in theoretical calculations: charge transfer degree, dipolar moment (μ_{dip}), CTC band gap (E_g)...

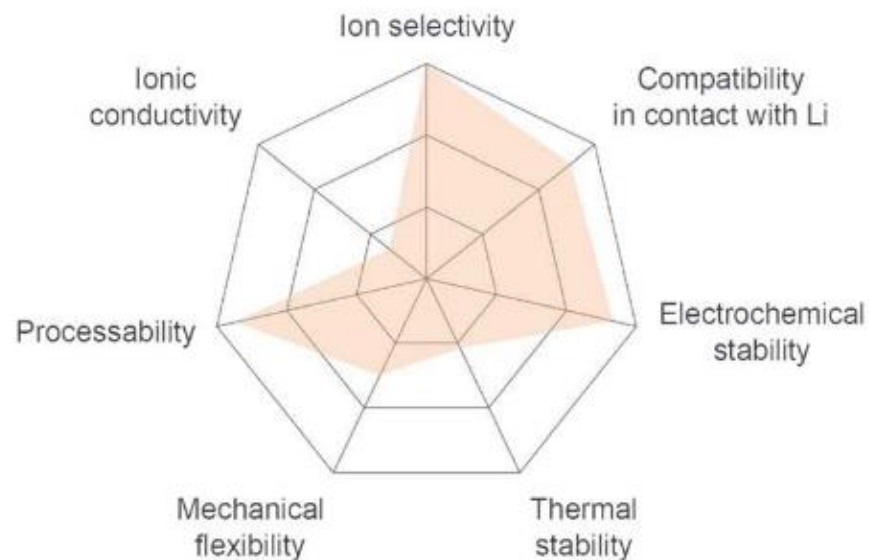
	HQ/BQ	HQ/CA	HQ/BA	HQ/FA
σ : RT (S.cm ⁻¹)	1.0x10 ⁻⁸	1.0x10 ⁻⁷	3.0x10 ⁻⁸	5.0x10 ⁻⁸
σ : 80°C (S.cm ⁻¹)	2.5x10 ⁻⁶	6.4x10 ⁻⁶	1.7x10 ⁻⁵	1.5x10 ⁻⁷

✗ No direct correlation

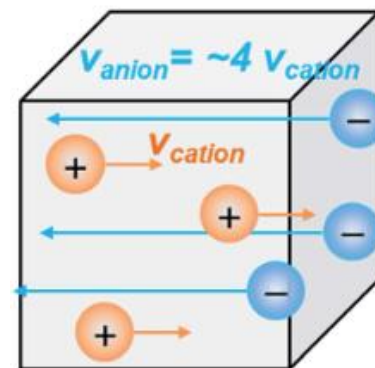
✗ Confirmed in DFT calculations

➤ Different parameters: morphology studies

Single-ion conducting polymers



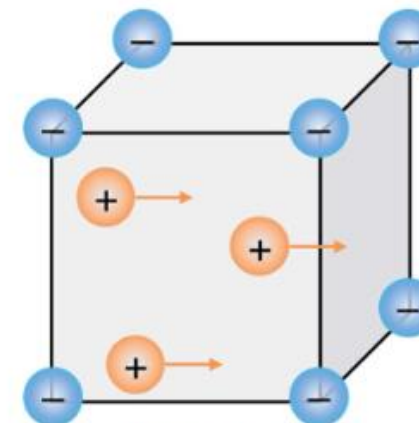
Binary-ion conductor



Mobile anions

- ✓ Low ionic selectivity ($t_{Li^+} \approx 0.2$)
- ✓ Low oxidation voltage (< 4 V)
- ✓ High cell polarization

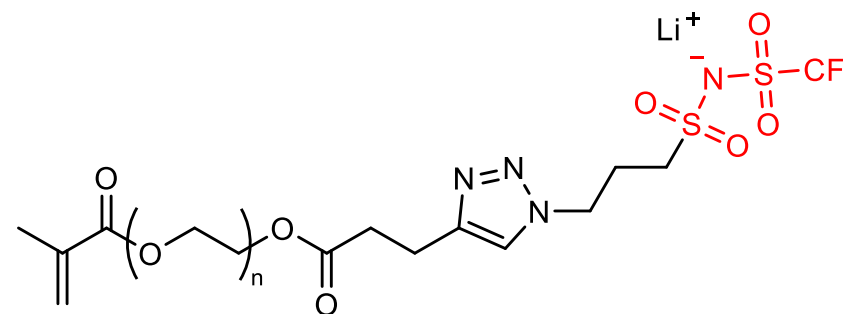
Single-ion conductor



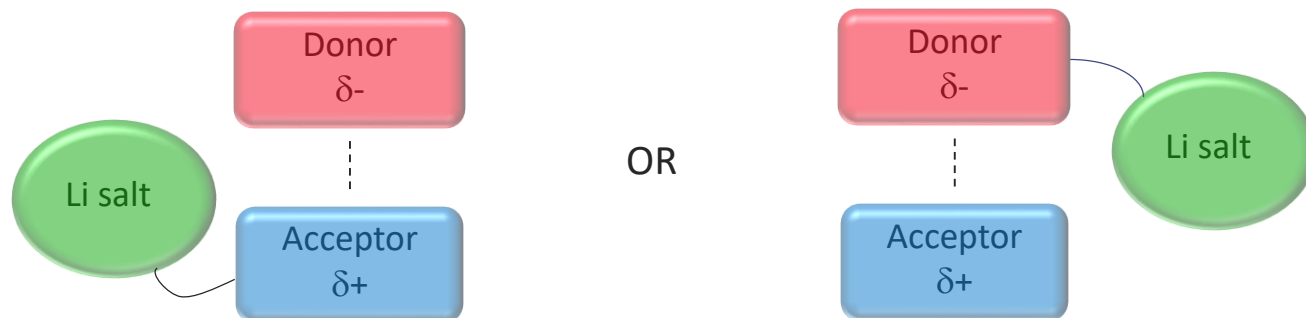
Immobile anions

- ✓ High ionic selectivity ($t_{Li^+} \approx 1$)
- ✓ High oxidation voltage (> 4 V)
- ✓ Resistance to dendrite growth

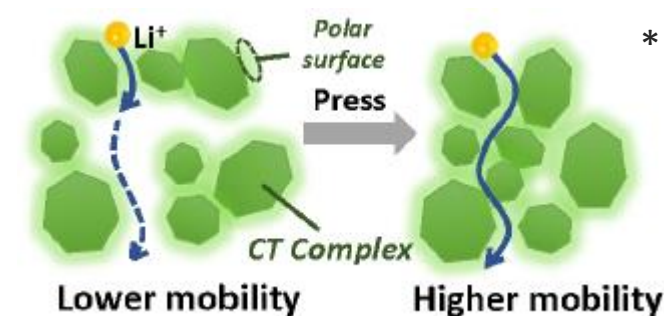
- Immobilized Li^+ anion partner
- ✗ Improvable ionic conductivities ($\sigma = 10^{-4}$ - 10^{-6} S/cm)



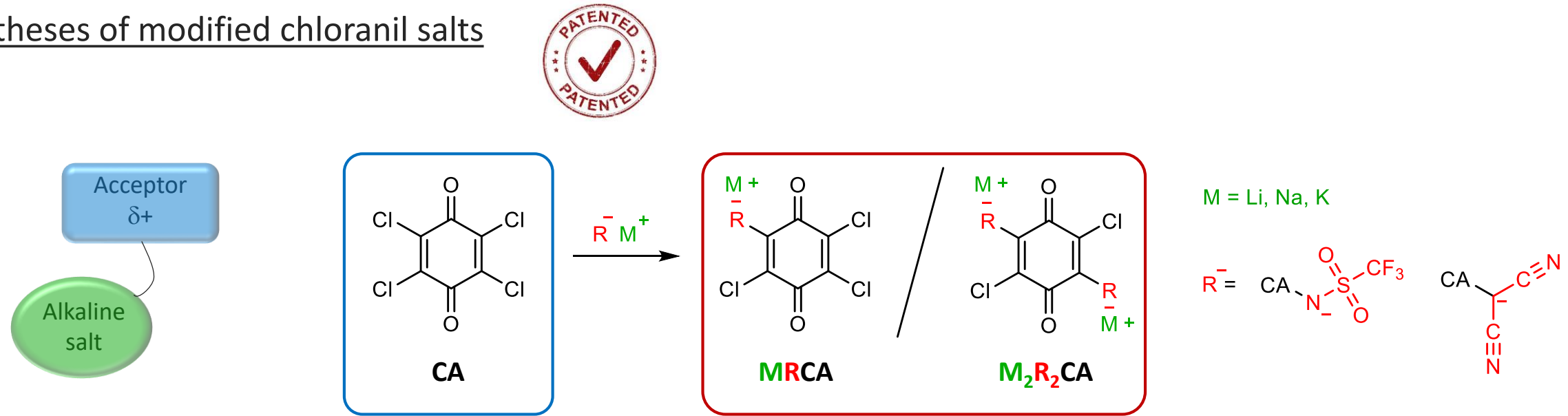
Single-ion CTCs



- Covalent grafting on **acceptor** or **donor** molecules of the CTC
- Expected high ionic selectivity ($t_{\text{Li}^+} \approx 1$) and electrochemical stability
- Investigation on the conduction mechanism of CTC electrolytes

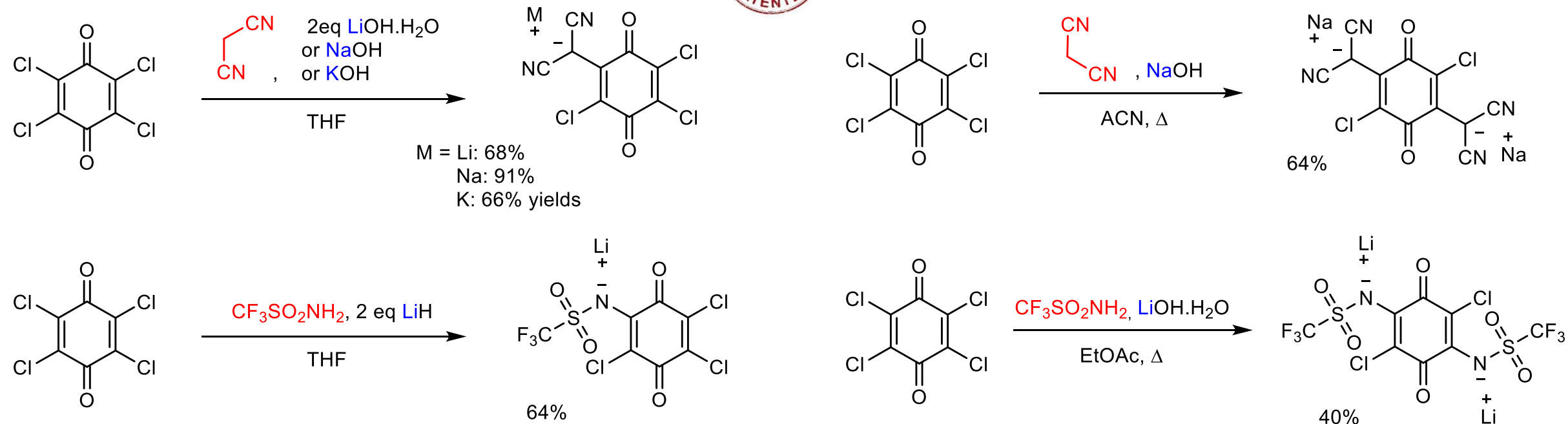


Syntheses of modified chloranil salts



- Ideal organic platform to implant **anions** (TFSI derivative or fluoride-free malononitrile)
- ✓ Adaptable one-pot syntheses
- ✓ Possibility to reach bis-lithiated salts (better energy density ?)
- ✓ Na^+/K^+ cations incorporation for Na/K battery technologies
- ✓ More convenient and versatile formulation and processing to form CTC electrolytes

Syntheses of modified chloral salt

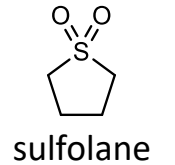
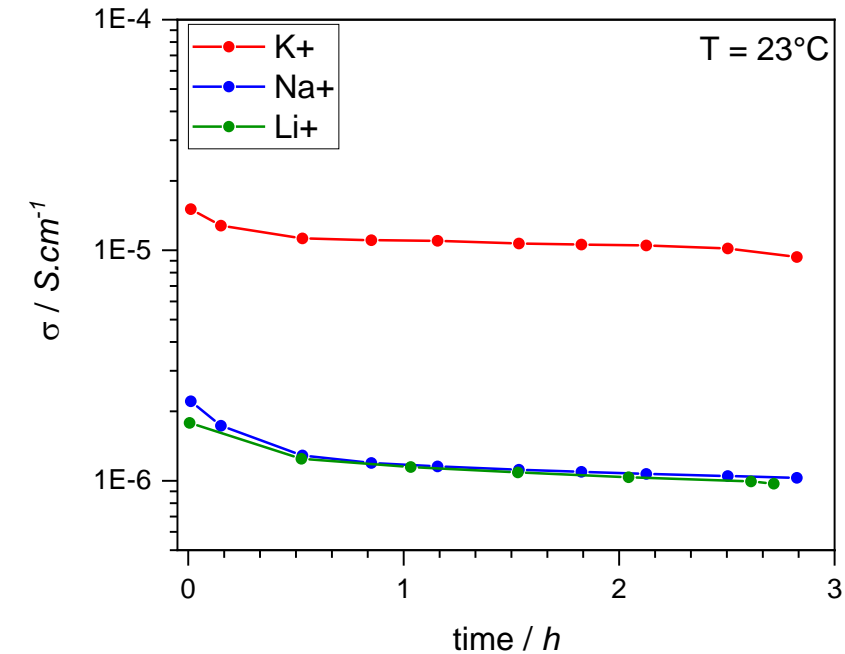
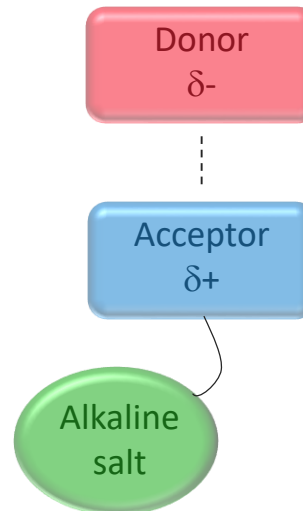
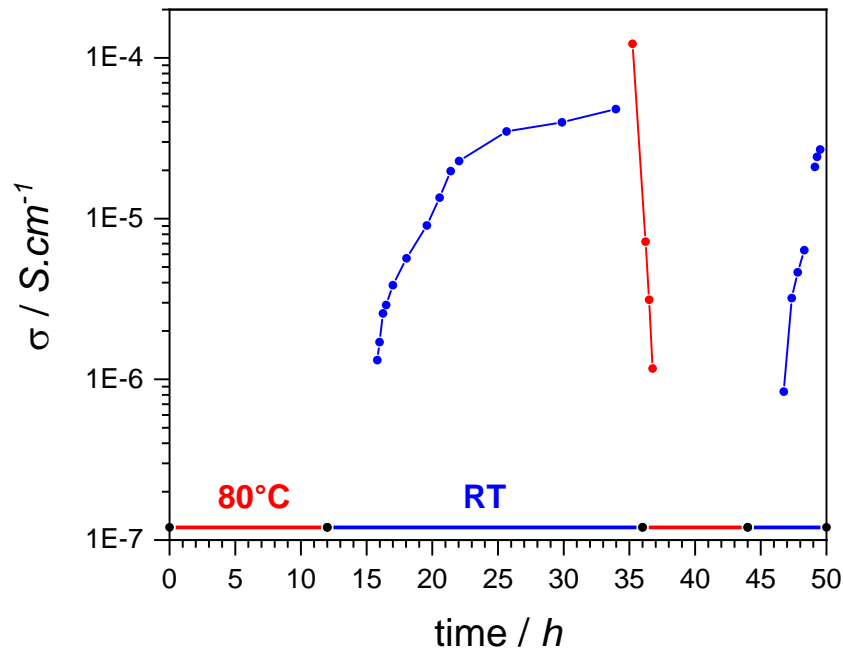


- Different alkaline bases (LiOH·H₂O, LiH), solvents, reagents introduction order.. allow for further optimization
- Purification through simple successive filtrations
- ✓ Products and purities verified through ⁷Li (Li salts), ¹³C, ¹⁹F (TFSI derivatives) NMR, ESI-MS(-) and FTIR spectroscopies



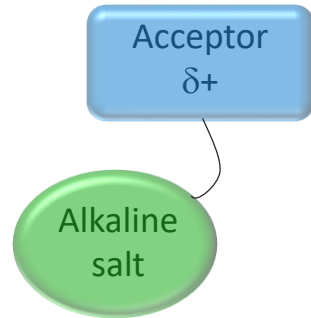
Impedance results (patent in preparation)

- Solid-state conductivities in polymer matrix
 - Reproducibility issues ($<10^{-8}$ to $5 \cdot 10^{-4}$ S.cm $^{-1}$)
 - Unclear behaviour under temperature
- Addition of sulfolane plasticizer (10 to 17% wt.)
 - Reproducible but limited conductivities
 - ✓ $\sigma > \mu\text{S.cm}^{-1}$ at RT for 3 alkaline ions (Li,Na,K)





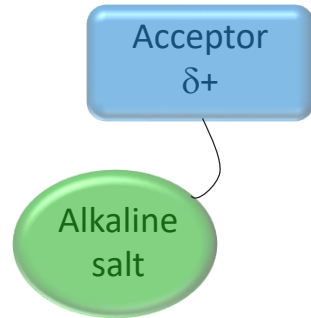
Conclusion: functionalized chloranil acceptor



- ✓ Promising results for improvement
- ✗ Many components for optimization/understanding
 - Taking 1 polymer:
 - 4 different salts for 1 metal cation (Li or Na or K)
 - Polymer/acceptor salt ratio
 - Different preparations possible (solvents / annealing...)
 - Impact of plasticizer

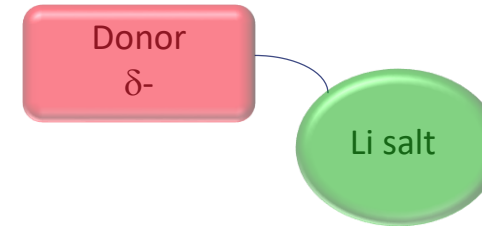


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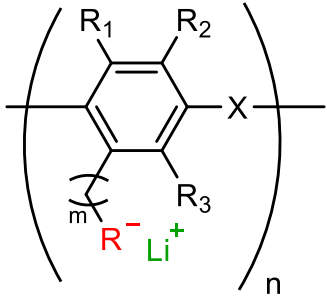
➤ Functionalized polyphenylene polymers



Focus on one polymer system
for deep characterization



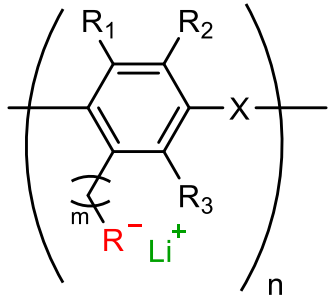
Functionalized polyphenylene polymer for single-ion CTCs (patent in preparation)



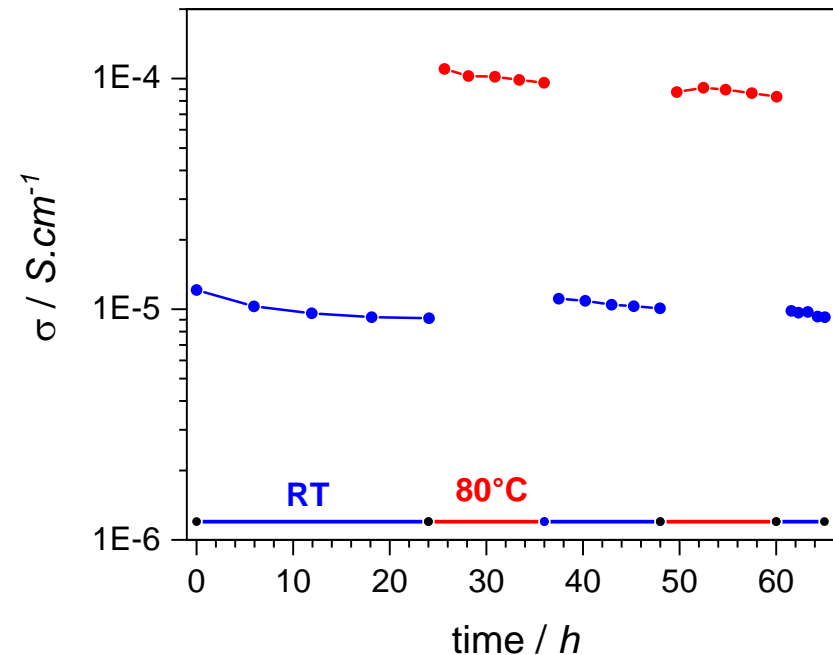
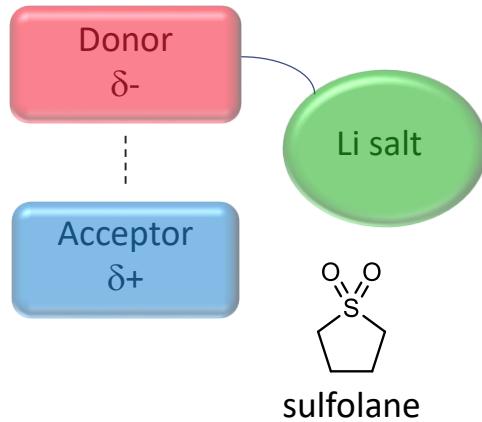
- Exact structures and syntheses to be protected in patent
- Characterized through NMR and FTIR spectroscopies
- ✗ Solubility issues: purification and processing difficulties
- Tested as single-ion polymers in CTC electrolytes with plasticizer



Functionalized polyphenylene polymer for single-ion CTCs (patent in preparation)



- Exact structures and syntheses to be protected in patent
- Characterized through NMR and FTIR spectroscopies
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- Tested as single-ion polymers in CTC electrolytes with plasticizer



- ✓ Reproducible results
- ✓ Decent conductivities:
 1.10^{-5} S.cm⁻¹ at RT, 9.10^{-5} S.cm⁻¹ at 80°C
- Further characterizations on-going



Conclusion and perspectives

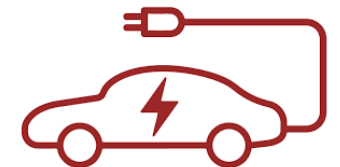
- ✓ Mixed but promising results for improvement in CTC solid-state electrolyte systems
- ✓ Development of a new family of alkaline salts to be expanded upon
- ✗ Remaining hardships to overcome (mechanical properties, conduction mechanism..)

➤ Perspectives of deeper CTC characterization and rationalization:

- solid-state NMR coupled to EPR spectroscopy
- DFT investigations
- $^6\text{Li}/^7\text{Li}$ isotopic labeling + TOF-SIMS spectrometry...



➤ Development of complete battery prototype with CTC single-ion electrolyte



THANK YOU!



Commissariat à l'énergie atomique et aux énergies alternatives
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