Advanced Li-ion Batteries based on the Use of Renewable Organic Electrodes

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Abstract

The present project entitled Advanced Li-ion Batteries based on the use of renewable ORGanic electrodes "ALIBORG" aims towards the design of greener electrochemical storage devices by introducing the concepts of sustainability and renewability at the electrode materials level by using organics. The project started on September 1st, 2008, and the present document reports the major accomplishments of the research.

Prior to the GCEP project, we demonstrated over the 2006-2008 period some positive attributes of redox-active structures based on multiple adjacent carbonyl groups (e.g., "C_6O_6"-type structure − oxocarbons) such as an easier connection with green resources. Therefore, our research effort to promote "green" organic-based electrode materials was rather centered on this class of redox-active compounds, with the aim of grasping the relevant parameters that affect the redox potential of an organic electroactive material, its reactivity, its stability upon cycling, and so on. Thus, for the past few years, we have been revisiting selected organic structures based on carbonyl functionalities to create in parallel of computational methods (DFT calculations) a reliable experimental database of model chemical structures, in relation with their solid state electrochemical behaviour in order to identify stable and efficient redox-active organic structures reacting at both high and low potentials vs. Li. Our basic screening approach consisted in pursuing the evaluation of stabilized rings deriving from "C_6O_6"-type structure.

The first variation was the introduction of N-atom in the skeletal arrangement of the molecule to probe the potential modifications, since nitrogen (like carbonyl group) is an essential building block in natural substances. Numerous structures have been electrochemically evaluated. Our first selected family of heterocycles was based on 2,3,5,6-tetraketopiperazine unit ("C_6O_6"-type structure to "$C_4O_4N_2$"-type structure); carbons of such a tetraketopiperazine unit can originate from renewable resources since the typical synthesis approach consists in using oxalic acid derivatives. Working in a systematic way, a series of tetraketopiperazine molecules with quite different R groups as substituents (i.e., phenyl, allyl and propyl functions) have been synthesized and characterized. Such small molecules were found to rapidly solubilize in commonly used electrolytes. To bypass this issue, we prepared an oligomeric form of this structure: the strategy being to decrease the solubility by increasing the molecular mass. Thanks to this chemical trick, 2,3,5,6-tetraketopiperazine unit is then able to sustain a reversible capacity of 110 mAh g^{-1} at near 2.45 V vs. Li. Several other series of N-cyclic structures have been

evaluated such as 5-benzylidene hydantoin-type materials, lithiated salts of isatine or bulky pyrazine-based structures but very poor electrochemical properties were obtained due to their solubility, demonstrating (by the way) how the liquid/organic nature of the electrolyte can ruin the cyclability of a promising redox-active organic solid.

Learning from our different electrochemical investigations on various families of heterocycles, we succeeded in designing another polyketone with N-cyclic structure able to exhibit better electrochemical properties thanks to the integration of some criteria: (*i*) a restricted five-membered heterocycle to reduce the electrochemically dead matter (*ii*) connected to a single phenyl group in a planar structure to stabilize the as-produced radical in reduction, and (*iii*) including permanent negative charges (*i.e.*, organic multi-anion rather than neutral molecular structure). The latter aims to decrease the redox potential compared to that of the tetraketopiperazine as well as the solubility thanks to permanent negative charges. Thus, pyromellitic diimide dilithium salt was selected. Although never reported to date, such a lithiated salt was readily synthesized making its electrochemical evaluation in Li battery possible. This novel material reversibly inserts two Li per formula unit at a relatively low potential giving a stable capacity value of 200 mAh g^{-1} for an average potential around 1.8 V vs. Li. However, the redox potential of both the oligomeric form of 2,3,5,6-tetraketopiperazine unit or the pyromellitic diimide dilithium salt were too low (or too high) for a practical application as electrode material. The insight gained from this first series of compounds was that incorporation of two intracyclic nitrogen atoms induces a decrease in the redox potential and that negatively charged organic structures are more stable towards the electrolyte. So, the next part of the present research consisted in designing stable *lithiated organic structures* able to be reversibly oxidized in the 3 V region vs. Li (application as positive electrode materials). Following this direction, we performed a broad evaluation of several derivatives of the *p*-benzoquinone (*p*-Q) unit, and in particular lithiated salts, because it was known in molecular electrochemistry that the redox potential of *p*-Q can be widely tuned depending on the nature of the substituents.

To go further in the establishment of the key parameters that govern especially the electrochemical features of organics, DFT calculations were also performed. Identifying strategies of ideal functionalization and of crystalline-type structure to optimize the deintercalation properties of the organic matrices would thus enable to assist and guide the great experimental effort performed in this new research area. Within this context, a computational study was applied to the crystalline *para*-benzoquinone derivatives. The relative ability of several common and newer exchange-correlation functionals as well as the dispersion-corrected DFT method to account for both inter/intra-molecular structural features and electrochemical features was first addressed in systems influenced by different intermolecular interactions of various strengths.

Introduction

The threats of climate change and the issues of secure energy supply are among the fundamental challenges of the 21st century that push humanity to revise its current energy engineering. Mitigation options result in efficient vehicles, buildings and energy production systems, capture and storage of CO_2, and a reduced deforestation, but the top necessary action seems to switch to environmentally sound energy sources in particular for electricity generation advocating "renewable energies" (hydropower, photovoltaic, geothermal, biomass…). Thus, decarbonising the logistic chain of the electrical sector constitutes probably one of the basic steps towards a sustainable development. Along that line, developing advanced electrochemical storage systems for the sustainable use of electric energy is becoming a worldwide imperative. In

this context, Li-ion batteries (LIBs) appear today as a flagship technology with applications or potential applications in several sectors of high environmental interest (Electric vehicles/Power grid stabilization). However, the current technology itself could still fall short of both the sustainability and CO_2 footprint criteria because LIBs are nearly exclusively based on inorganic compounds, non-renewable and energy-greedy materials. Thus, in parallel with regular research on inorganic-based LIBs, a possible alternative consists in moving from inorganic to organic matter-based electrodes, which could be prepared i) from renewable resources (biomass) and ii) via eco-efficient processes (green chemistry concepts) making the concept of "greener and sustainable" Li-ion batteries possible. Figure 1 illustrates this concept proposed by our group in 2008.[1]
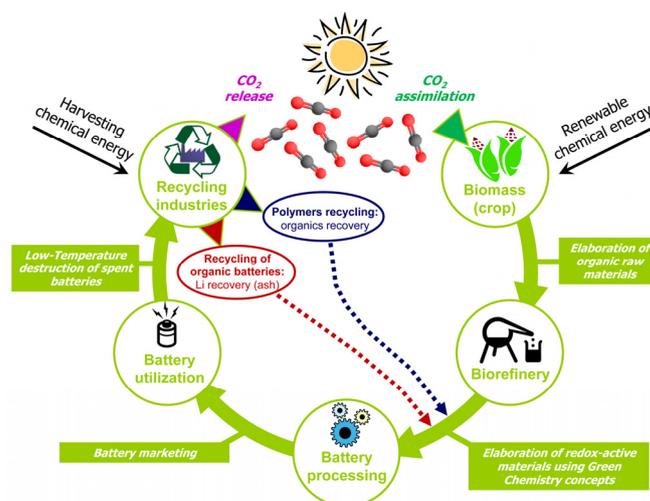
Figure 1: Illustration comparing a simplified cycle life of a "greener" Li-ion battery taking benefit of redox-active organic electrode materials deriving typically from biomass

To promote the emergence of "green" organic-based electrode materials, the present project aimed at grasping the relevant parameters that affect the redox potential of an organic electroactive material, its reactivity, its stability upon cycling, and so on. Having previously identified [1] the positive attribute of the six-membered oxocarbon "C_6O_6", a wide variety of single/multiple ring molecules containing chemically active C=O functions (in particular) with various heteroatoms or substituents had to be considered for this new project with the challenge to grasp an efficient redox-active system while chemically stable towards the electrolyte. Consequently, the main objectives of the ALIBORG project was to create a reliable experimental database of model chemical structures, in relation with their solid state electrochemical behavior in order to identify stable and efficient redox-active organic structures reacting at both high and low potentials vs. Li. Indeed, little is reported in the literature regarding organics. Looking back on historic developments of electrode materials for Li-based batteries and in comparison with inorganic compounds that benefit of decades of intensive years of research, the use of organics was just sporadically studied. Thus, we have been revisiting for the past few years step by step selected organic structures mainly based on carbonyl functionalities; in parallel of DFT calculations, it was a kind of trial/error approach since the field of organics involves too many combinations.

Our general approach consisted in pursuing with cyclic structure, still based on carbonyl units but containing nitrogen, and then probing possible changing in terms of electrochemical features. The first variation was the introduction of N-atom in the skeletal arrangement of the molecule, since nitrogen (like carbonyl group) is an essential building block in natural substances. The first selected family was that of polyketones with N-cyclic structure based on 2,3,5,6-tetraketopiperazine unit,[2] because this structure constituted a logical entry to pursue our previous evaluations on redox-active carbonyl functions involved in a six-atom ring structure such C_6O_6-type structure (Figure 2), and then probe the potential influence of intracyclic nitrogen atoms. It is worth noting that little data have been reported in the literature. Additionally, carbons of such a tetraketopiperazine unit can originate from renewable resources since the typical synthesis approach consists in using oxalic acid derivatives. Oxalates are very common products, widely spread in nature.


C_6O_6-type structure (oxocarbon)   2,3,5,6-tetraketopiperazine unit
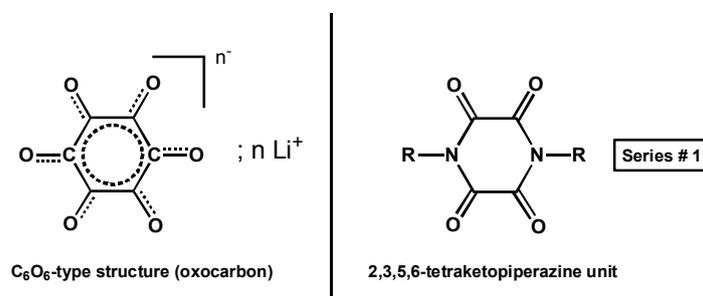
Figure 2: Comparison between C_6O_6-type structure and 2,3,5,6-tetraketopiperazine unit

The second selected series was a bit specific since the chosen N-cyclic structures, based on the pyrazine functionality, were free of carbonyl groups (Figure 3). The aim was to evaluate this particular redox system especially the stability of "bulky" aromatic redox systems towards the dissolution phenomenon (such aromatic structure favors pi-pi stacking).

Hexaazatrinaphtylene
(HATN)

Hexaazatriphenylene
hexacarbonitrile
(HAT(CN)$_6$)
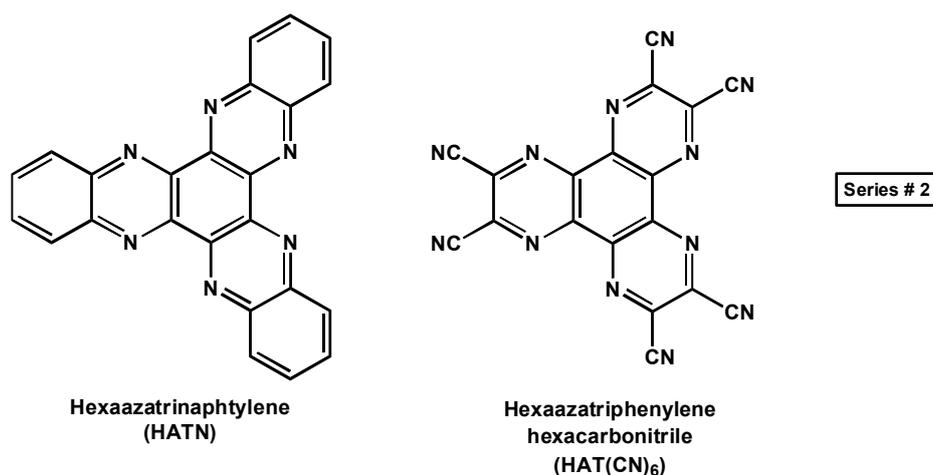
**Figure 3:**   Structures of HATN and HAT(CN)$_6$

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The third series of nitrogen-containing heterocycles was based on 5-benzylidene hydantoin-type products (Figure 4).
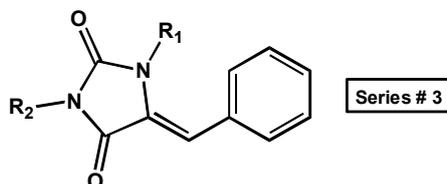
Figure 4:   5-Benzylidene hydantoin core

5-benzylidene hydantoins are common in nature as secondary metabolites of numerous marine species (sponge, tunicate, algae…). Furthermore, their attractiveness rested on their chemical synthesis, which allowed various modulations and gave us the opportunity to compare the electrochemical behavior of different hydantoin derivatives, bearing different substituents and having different heteroatoms.

We have then considered as the fourth series two lithiated salt of N-cyclic structure containing several adjacent carbonyl functionalities (Figure 5). Indeed, we knew that negatively charged moieties are more insoluble (i.e., more stable towards the liquid electrolyte).

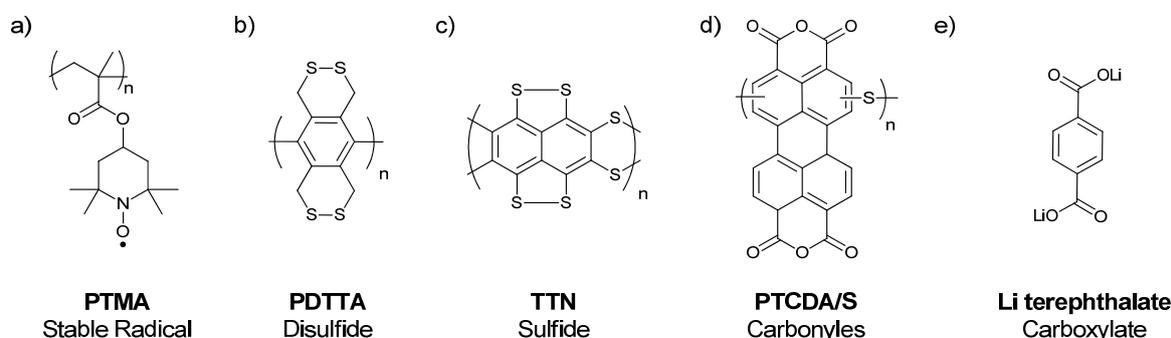**Isatine lithium salt**   **Pyromellitic diimide dilithium salt**
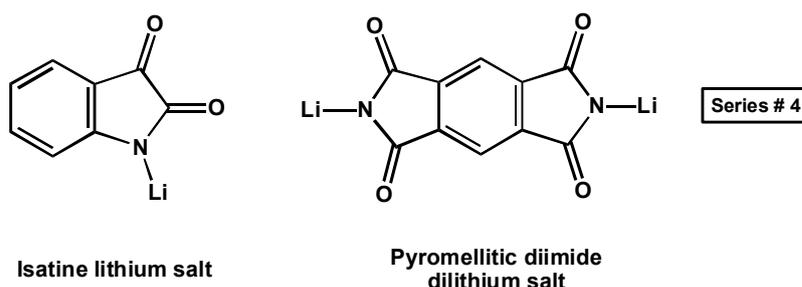
Figure 5:   Structures of Isatine and Pyromellitic diimide lithium salts

After this first investigation focused on N-cyclic structures, we have again centered our attention on the redox activity of quinone-type structures since such structures are intimately in connection with natural oxygen-containing compounds such as carbohydrates (renewable raw compounds). Actually, we had previously identified that tetrahydroxy-*p*-benzoquinone derivatives (THQLi$_4$) show a reversible capacity of near 200 mAh g^{-1} for an average potential of 1.8 V.[3] Using this basic backbone, we have focused our attention on substituting the hydroxyl groups of THQLi$_4$ for other groups. This strategy enabled us to identify two interesting compounds able to react at near 3V.

Background

Interestingly, the first commercial Li-ion batteries used a conducting polymer as a positive electrode [4] but research on organic systems has been limited because of poor performances, energy density-wise, coupled with the lower emphasis on producing lower-cost devices with smaller CO$_2$ footprints at that time. Looking back more precisely on historic

developments of electrode materials for Li-based batteries and in comparison with inorganic compounds that benefit of decades of intensive years of research, the use of organics was just sporadically studied and as cathodic materials only. However, the idea of using organics as electrode materials started 40 years ago when Williams et *al*.[5] proposed dichloroisocyanuric acid as a high energy density material for primary lithium battery. Around the 80's, different organic molecules were also rapidly evaluated but for secondary lithium battery applications.[6-8] Thereafter, rather redox-active organic polymers, more stable towards the electrolytes, were tested as electrode materials,[4] with some of them like polyaniline (PANI) being commercialized (PANI/LiAl cell [9]). Generally speaking, organic materials present some structural drawbacks such as relatively low thermal stability, low packing density and appreciable solubility in common organic electrolytes as compared to the inorganic cathode materials. Nevertheless, for the past few years we witnessed a renewed interest in organic electrodes materials with many different reports trying to harness any electroactive chemical function (Figure 6).

a) **PTMA** Stable Radical b) **PDTTA** Disulfide c) **TTN** Sulfide d) **PTCDA/S** Carbonyles e) **Li terephthalate** Carboxylate

Figure 6:   Examples of organic structure reported in the literature displaying specific electroactive chemical functions vs. Li

Recently a new class of polymers able to store electric energy has been disclosed and consists of a stable organic polymeric chain bearing stabilized nitroxyl radicals [10] like 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TEMPO) radicals (Figure 6a). Depending on the design, these materials can involve either cations (like Li^+) or anions insertion and give typically very high rate capability and good cyclability owing to the fast electrochemical reaction of the radicals. Nishide et *al*. have shown the possibility of building devices, capable of a charging/discharging cyclability of 10^4 times at 100 mA.[11] Limitations usually come with the poor electric conductivity of the radical polymers inducing quite high amounts of added carbon (~ 50% in mass) and relatively low specific capacity values due to the appreciable content of electrochemically "dead matter". Very recently the same authors reported on the possibility to build electrochemical storage devices based on organic materials only (without lithium cation) using such radical polymers.[12,13]

In the restricted family of redox-active hetero-atoms, sulphur is one of the few non-metal simple bodies displaying an amphoteric character making it electrochemically interesting. In organic structures, sulphur atoms could be linked onto a carbon backbone making, for instance, the use of redox-active disulfide bond possible like in PDTTA (Figure 6b).[14] To exploit sulphur properties at best (to make the most of sulphur properties) while trying to avoid its main drawbacks, recent works have taken benefit of the redox activity of the C−S−C (thioether bond)

(Poly(tetrathionaphtalene) (TTN), Figure 6c). TTN exhibits quite a good capacity retention (over 180 cycles) at an average potential of 3.8 V leading to a practical capacity of 122 mAh g^{-1}.[15] Note that the disulfide bonds were not reduced in TTN, which was used as a cathode material through an anion insertion mechanism.

Another highly interesting and common organic redox centre consists in the carbonyl group. When stabilized by conjugation, the redox system is most often reversible, be it in solution or in solid state. Quinone-type structures are the most common and before 2008, a few articles announced interesting electrochemical properties vs. Li for cathode materials like poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) (PDBM).[16] In recent years many groups exploited these properties. For example, we can report the carbonylated aromatic compounds 3,4,9,10-perylene-tetracarboxylicacid-dianhydride sulphide polymer (PTCDA/S) [17] with stable capacity retention of about 130 mAh g^{-1} for an average potential value of 2.5 V (Figure 7d). However, it is worth noting that the purpose of most of the research on organics was not to develop a "greener" battery and as a consequence reported organic structures derived from oil.

As a previous work in the laboratory about the search for a negative electrode for Li-ion batteries, lithium carboxylates showed promising properties. In particular, Li-terephthalate (Li$_2$C$_8$H$_4$O$_4$, Figure 6e) [18] has demonstrated quite good electrochemical performance *vs*. Li with a stable specific capacity retention at an average potential of 0.95 V.

In the specific area of organic electrodes for LIBs, one main challenge remains: the preparation of a classical positive electrode, i.e. a lithiated material able to react at high potential upon oxidation vs. Li. Very recently the Dahn's group proposed a lithiated 1,4,5,8-naphthalenetetraol formaldehyde polymer, able to cycle to 4.2 V.[19] Nevertheless this material was characterized by some severe limitations like a poor capacity (60 mAh g^{-1}), a limited capacity retention (10 cycles) and an important polarization of more than 1 V.
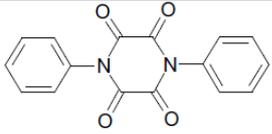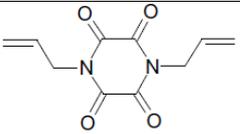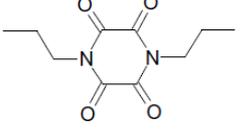
Results

In this final report, we will present main results obtained in the course of our electrochemical evaluations of several series of organics vs. Li with the aim to design efficient and "green" organic-based electrode materials.

PART A: Nitrogen Containing Molecules

### a) Tetraketopiperazines (series #1)

With the GCEP support starting from September 2008, we have first investigated the chemical synthesis and probed the electrochemical signature of a series of tetraketopiperazine derivatives (Figure 2) to pursue our previous evaluations of redox active carbonyl functions involved in a six-atom ring structure. We succeeded in synthesizing several 2,3,5,6-tetraketopiperazine derivatives characterized by quite different R groups (i.e., aromatic, unsaturated and alkyl functions). We have first synthesized N,N'-diphenyl-2,3,5,6-tetraketopiperazine (**PHP**) then N,N'-diallyl-2,3,5,6-tetraketopiperazine (**AP**) and N,N'-dipropyl-2,3,5,6-tetraketopiperazine (**PRP**). Table 1 recaps the corresponding molecular structures.

Structure	Name	Acronym
	N,N'-diphenyl-2,3,5,6-tetraketopiperazine	PHP
	N,N'-diallyl-2,3,5,6-tetraketopiperazine	AP
	N,N'-dipropyl-2,3,5,6-tetraketopiperazine	PRP

Table 1: Molecular structures and acronyms of 2,3,5,6-tetraketopiperazine derivatives electrochemically evaluated vs. Li

As expected, these tetraketopiperazine-based molecular structures display an efficient electrochemical activity characterized by a well defined plateau located in the 2.5 V region (a bit lower for **PHP**) coupled with a weak polarization value (Figure 7, as recap). Note that a deeper reduction beyond 1.5 V (not shown here) induces an irreversible step as previously observed by Owens et *al*. in aqueous media.[20] Interestingly, compared to $Li_2C_6O_6$ oxocarbon,[1] this electrochemical behaviour seems to indicate that introduction of two intracyclic nitrogen atoms or a lithiated ene-diolate functionality in the C_6-based polyketone cyclic structure induces a similar tuning of the redox potential. However, these small molecules suffer from both an incomplete electrochemical reaction (one electron per mol, only) and a very poor cyclability

owing to their solubility in organic media like commercial electrolytes. Increasing the molecular mass constituted a possible pathway to overcome the dissolution phenomenon in the electrolyte. Among these piperazine derivatives, the **AP** molecule appeared obviously as a good starting monomer for polymerization. Along that line, we decided to use an ADMET (Acyclic Diene Metathesis) polymerization approach, never reported using such monomers to date, taking into account the specificity of this reaction (i.e.; diene groups, compared to a radical polymerization that could affect carbonyl groups).
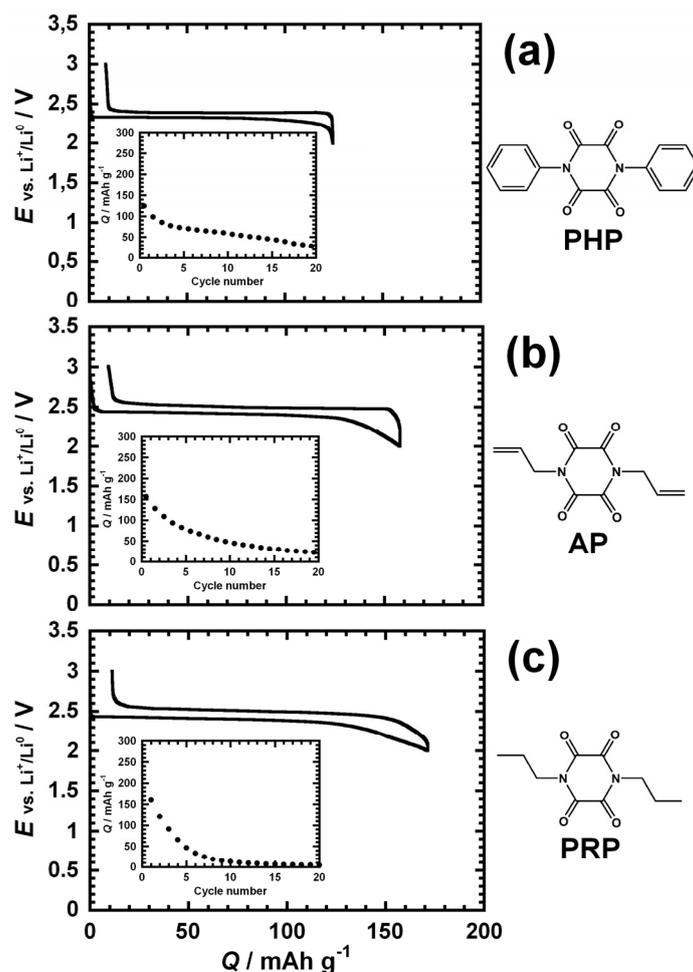
Figure 7: Typical electrochemical feature of **PHP**, **AP** and **PRP** using a Swagelok-type cell [Li metal disc as negative electrode, LiPF$_6$ 1 M in EC/DMC as electrolyte. Active material mixed with 50%(w/w) of carbon. Rate: 1 e^- exchanged in 10 h]

Scheme 1 shows the corresponding reaction. We tested three kinds of catalysts (Grubbs 1st and 2nd generations, Hoveyda-Grubbs 2nd generation, two different solvents (toluene or 1,2-dichloroethane (1,2-DCE)), and two different molar ratios (2% or 5% mol/mol catalyst/substrate). Several reaction temperatures were also checked (temperatures between 60 and 110°C) and the reaction time was 24 h. Finally, we have successfully obtained an oligomer for the first time.

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The optimum set of parameters is the use of Hoveyda-Grubbs 2nd Generation catalyst 5% mol/mol in toluene at 85°C.
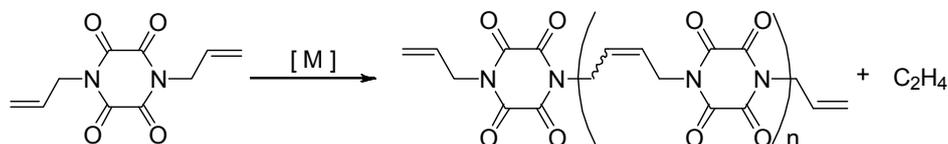
Scheme 1:   ADMET   polymerization   reaction   of   N,N'-diallyl-2,3,5,6-tetraketopiperazine

The degree of polymerization (DP) for the oligomer was 2.278, determined thanks to the ^{1}H-NMR study.[21] This means that we have a mixture of oligomers (dimers, and trimers,). The obtaining of such a polymer (denoted **p-AP**) enables us to get better electrochemical performances compared to the monomer; the solubility being clearly reduced. Basically, the general feature of the potential-capacity curve appears quite similar to the **AP** one with an average potential of 2.5 V and the uptake of one Li^+ per piperazine ring. However, this polymer derivative is now able to sustain the capacity upon cycling at relatively high rate (Figure 8).
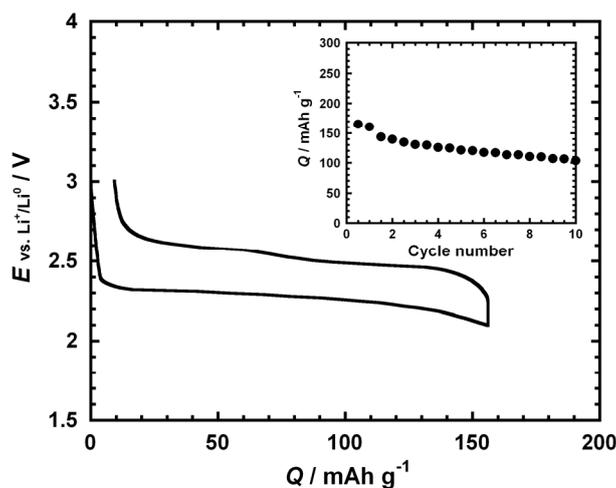

Figure 8: Typical electrochemical feature of p-AP using a Swagelok-type cell [Li metal disc as negative electrode, $LiPF_6$ 1 M in EC/DMC as electrolyte. Active material mixed with 50%(w/w) of carbon. Rate: 1 e^- exchanged in 2 h]

### b) Conjugated Pyrazines Rings (series #2)

In the direct continuity of our electrochemical studies of nitrogen containing molecules we have selected bulky molecules based on the pyrazine functionality to probe both this particular redox system and the stability of bulky aromatic systems towards the dissolution phenomenon. For this purpose we have prepared HATN [22-24] and HAT(CN)$_6$ [25,26], two derivatives having the benefit of concentrating three pyrazine rings by formula unit (Figure 3).

A straightforward synthesis of HATN has been previously described by Skujins and Webb [24] and consists of the condensation reaction of triquinoyl (cyclohexanehexone) and o-phenylenediamine. Triquinoyl belongs to the family of oxocarbons [27] as the oxidation product of rhodizonic acid and therefore has potentially the same green precursor issued from biomass: *myo*-inositol. Following the synthesis of Skujins and Webb we mixed o-phenylenediamine with triquinoyl in acetic acid, and the reaction product was isolated with 80% yield by a simple filtration after one hour at reflux (Scheme 2).
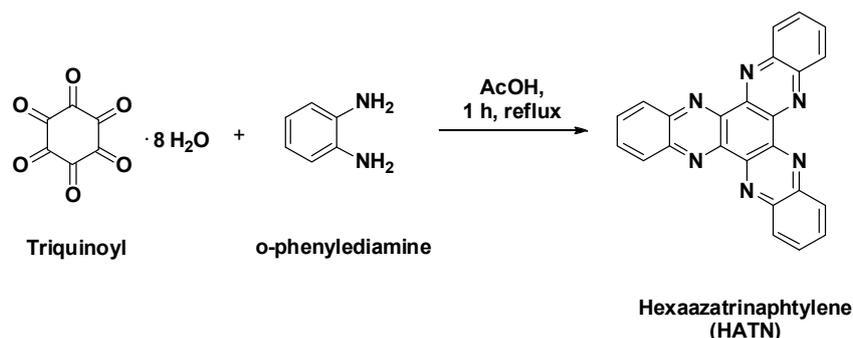

Scheme 2: Synthetic preparation of HATN

The same approach was followed for the synthesis of HAT(CN)$_6$. The condensation reaction of triquinoyl and diaminomaleonitrile has been described by Kanakajaran and Czarnik (Scheme 3). [25] After refluxing the mixture for two hours in acetic acid the compound was isolated by filtration in analytical pure form and with 90% yield.
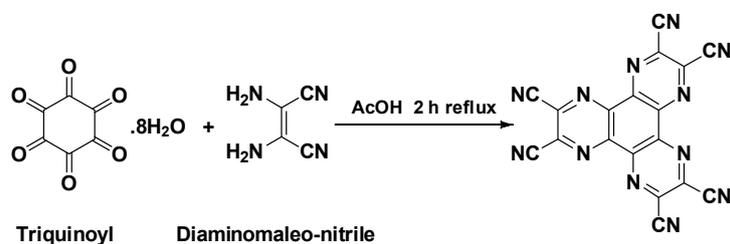
**Scheme 3**: Synthetic preparation of HAT(CN)$_6$

Our electrochemical data demonstrated that both compounds exhibited an efficient electrochemical activity vs. Li characterized by well-defined plateaus. However, reductions exceeding one electron per formula unit (not shown here) led to some irreversible steps requiring limiting the potential windows for the cycling studies. Thus, by using an appropriate potential range (Figure 9), the electrochemical insertion process appears almost reversible with a low polarization value (ΔE ~100-150 mV). Obviously the as-obtained specific capacity values are consequently low due to the numerous rings involved in such organic structures (i.e., high molecular mass for one exchanged electron only). Compared to HATN, the presence of nitriles (electron withdrawing groups) in the HAT(CN)$_6$ structure induces a rise of the first reduction plateau but restricted to 300 mV, which is a bit lower than expected taking into account the six CN groups. DFT calculations are under progress to grasp more explanations about this point.

Finally, these two "neutral" organic structures suffer also from a very poor cyclability (nil capacity in less than ten cycles) owing to a dissolution phenomenon. This solubility is even more important in the case of HAT(CN)$_6$. The point is that bulky aromatic molecules also seem to confirm this trend.
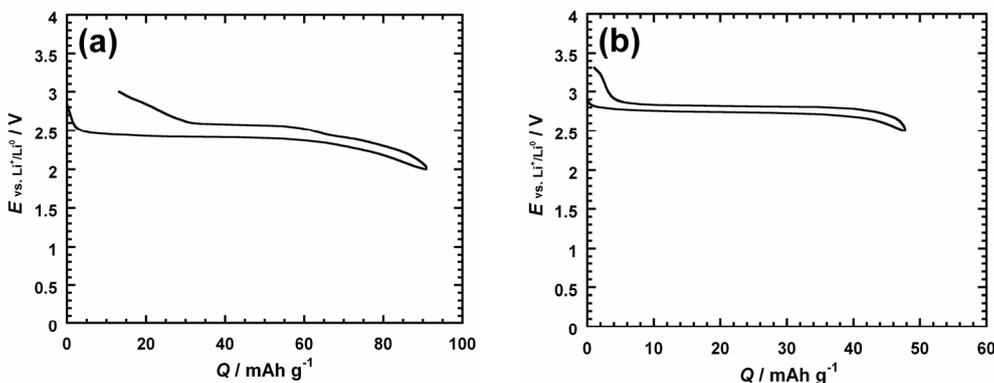
Figure 9: Typical electrochemical feature of (a) HATN and (b) HAT(CN)$_6$ using a Swagelok-type cell [Li metal disc as negative electrode, LiPF$_6$ 1 M in EC/DMC as electrolyte. Active material mixed with 50%(w/w) of carbon. Rate: 1 e^- exchanged in 2 h]

As an attempt to tackle this issue from a technological approach, we have tested the most stable molecule (HATN) towards a polymer-based electrolyte (i.e., PEO (PolyEthyleneOxide) membrane with LiClO$_4$ as salt); the solvation effect of POE chains being reduced in comparison with carbonate-based liquid electrolytes. Figure 10 shows the corresponding potential-capacity curve. Basically, the general feature appears almost similar compared to Figure 9a by showing a plateau located at 2.4 V but the most interesting point is that the capacity retention of HAT is clearly upgraded with this polymeric electrolyte showing a kind of saturation effect after 10 cycles leading to a stable capacity value of 40 mAh g^{-1} after 10 cycles (Figure 10b).
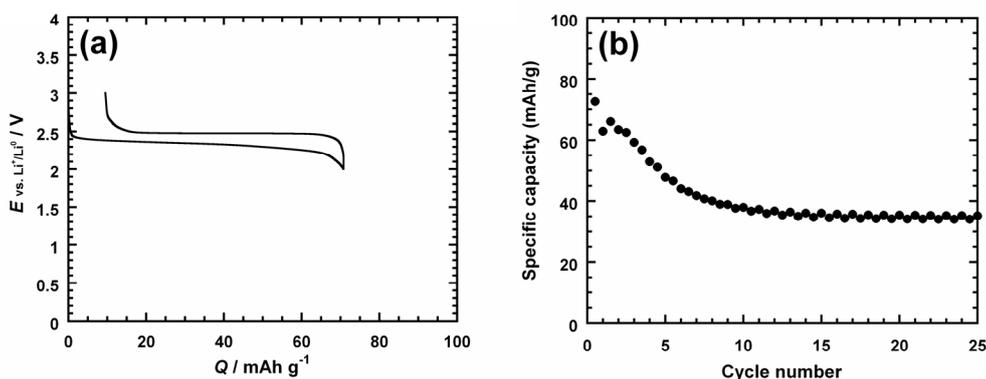
Figure 10: (a) Typical potential-composition curve of HATN and (b) HAT(CN)$_6$ using a POE membrane as solid electrolyte. (b) Corresponding capacity retention curve. [Li metal disc as negative electrode, T = 80°C, active material mixed with 50%(w/w) of carbon, rate: 1 e^- exchanged in 10 h.

These new examples of neutral organic compounds demonstrate again how the nature of the electrolyte can ruin the cyclability of promising redox-active organic solids. These data might raise the question about a new engineering of batteries assembly more compatible with molecular active materials.

c) Hydantoins (series #3)

To complete our knowledge on the electrochemical reactivity of nitrogen-containing heterocycles vs. Li, we have studied another series of molecular structures starting with 5-benzylidene hydantoin-type products (Figure 4). 5-benzylidene hydantoins are common in nature as secondary metabolites of numerous marine species (sponge, tunicate, algae…).[27] From a biosynthetic point of view, their *in vivo* formation is due to condensation-cyclization of urea and *L*-phenylalanine, simple and inexpensive materials. Furthermore, their attractiveness sits in their chemical synthesis, which allowed various modulations and gives us the opportunity to compare the electrochemical behaviour of different hydantoin derivatives, bearing different substituents and having different heteroatoms. Preliminary essays showed an interesting electrochemical activity with a plateau located at an average potential of 3 V. Unfortunately, fast solubilization in the electrolyte strongly limited this type of structure. The need for negative charges in the organic structure to decrease this solubility effect led us to investigate lithiated salts.

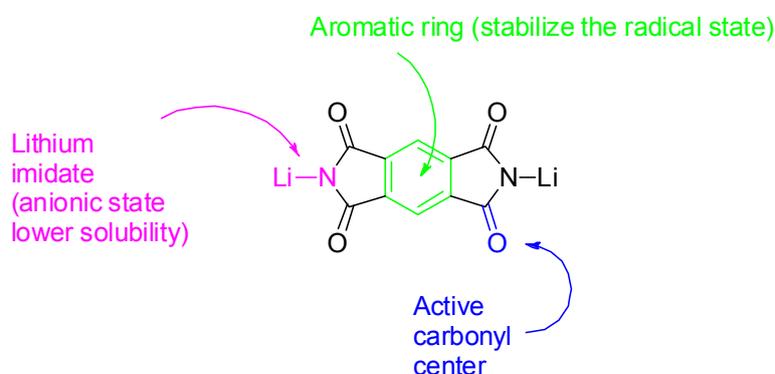### d) Isatine and Pyromellitic diimide lithium salts (series #4)

We first considered isatine lithium salt (Figure 5). Isatine is a heterocycle easily obtained by several oxidation steps of indicant, a natural compound extracted from *Indigofera tinctoria*, a common plant in tropical and temperate Asia, as well as parts of Africa.[28] For our part, we have succeeded in synthesizing isatine lithium salt by simply mixing isatine and lithium hydride in THF for several hours. After THF removal by a thermal treatment, the product was analytically pure (Scheme 4).

1) LiH (1 eq.), THF, RT, 22 h.
2) 190°C, 3 h.
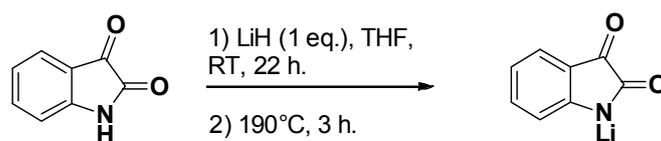
**Scheme 4:** Chemical synthesis route toward isatine lithium salt

This as-prepared isathine lithium salt was then tested vs. Li; however this salt is quite soluble in the electrolyte leading to a rapid capacity fading upon cycling indicating that a single charge is not enough. This behaviour led us to investigate dilithium salts. Taking now benefit of previous observations, we designed another polyketone with N-cyclic structure able to (potentially) exhibit better electrochemical properties thanks to the integration of some criteria: (i) a restricted five-membered heterocycle to decrease the electrochemically dead matter (ii) connected to a single phenyl group in a planar structure to stabilize the as-produced radical in reduction, and (iii) including permanent negative charges (i.e., organic anion rather than neutral

molecular structure). The latter aims to decrease the redox potential compared to the tetraketopiperazine one as well as the solubility issues as previously explained. Thus, pyromellitic diimide dilithium salt (Figure 11) appeared as a relevant candidate.

Figure 11: Pyromellitic diimide dilithium salt and illustration of the different benefits of its design

Pyromellitic diimide dilithium salt being not reported to the best of our knowledge, we first performed its synthesis. A convenient chemical approach consisted in direct lithiation of the commercial pyromellitic diimide with lithium hydride in DMF under inert atmosphere (Scheme 5).
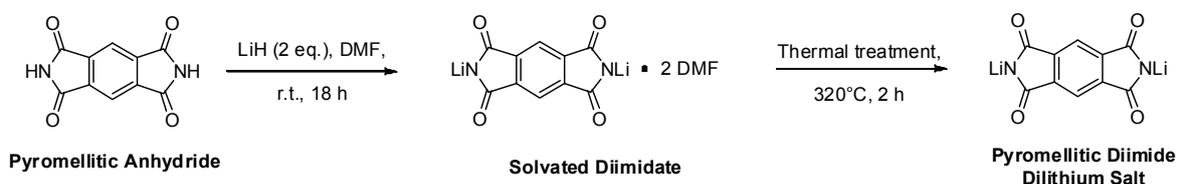

Scheme 5: Synthetic route to pyromellitic diimide dilithium salt

Both ^{1}H and ^{13}C NMR data are in agreement regarding the obtaining of pyromellitic diimide but with the presence of two extra DMF molecules. Further characterizations by thermal analyses coupled with mass spectrometry confirmed that the as-produced compound co-crystallizes with two DMF molecules per formula unit. Interestingly, this salt exhibits quite high thermal stability (mp (dec.) ~570°C), which makes total decomplexation and elimination of residual DMF possible by annealing the pale yellow powder at 330°C during 2 hours. Finally, pyromellitic diimidate was obtained as a brown powder in two steps with a good overall yield of 91%.

The electrochemical features of pyromellitic diimide dilithium salt have been obtained from Swagelok-type cells using a Li metal disc as a negative electrode and a glass-fibre separator soaked with a molar LiTFSI solution in DMC as electrolyte. Figure 12 shows the first discharge/charge curve for the material cycled vs. Li at a rate of one Li$^+$ exchanged in 20 h. As expected, this new organic lithiated salt displays an efficient reversible electrochemical activity characterized by a series of plateaus weakly polarized and occurring at more reducing potentials compared to both the neutral tetraketopiperazine structure or the neutral pyromellitic

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dianhydride.[6] The first discharge curve reveals the uptake of near 1.86 Li per formula unit ($\sim$220 mAh g^{-1}) and the removal of 1.66 on the subsequent charge leading to a practical reversible capacity above 200 mAh g^{-1} on dozens of cycles.
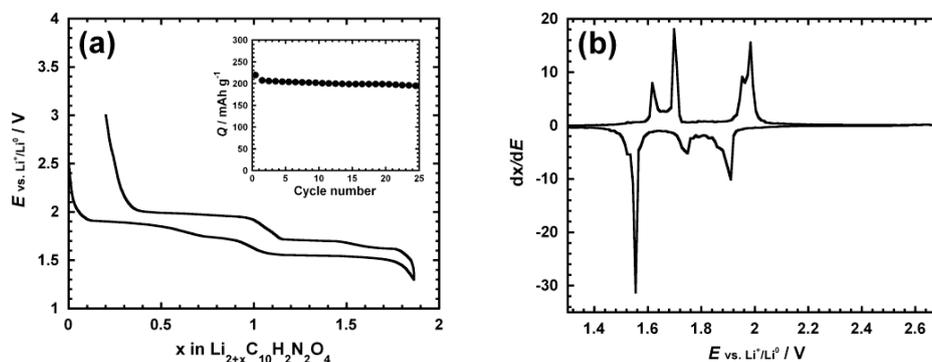
Figure 12:   (a) Typical electrochemical feature of a Li half cell using pyromellitic diimide dilithium salt galvanostatically cycled between 1.3 and 3 V at a rate of 1 Li^{+}/20 h in DMC/LiTFSI 1 M as electrolyte.   Inset: corresponding capacity retention curve. (b) Corresponding differential capacity vs. potential curve of the first cycle.

The several electrochemical steps can be more accurately visualized on a differential capacity vs. potential curve, which simulates the electrochemical features of a cyclic voltammetry (Figure 12b).   In parallel, we have also tested the electrochemical reduction of commercial pyromellitic diimide as blank experiment.   Interestingly, this acidic form displays an electrochemical activity, although very poor cyclability was observed due to its relatively fast dissolution in the tested electrolyte. However, the first discharge analysis reveals that switching from N-H bond to more ionic N-Li bond in the vicinity of the redox centres results in a noticeable potential drop. Note this effect was also observed between tetrahydroxybenzoquinone (THQ) and its related tetralithiated salt when reduced in Li battery.[29]

To conclude this investigation on N-cyclic structure, we have observed that the introduction of N-atom close to the C=O function decreases the redox potential. We have also point out that molecular (neutral) organic structures induce a very poor cyclability owing to a dissolution phenomenon (e.g., 2,3,5,6-tetraketopiperazine unit, 5-Benzylidene hydantoin unit). However, the point is that bulky aromatic molecules seem also confirm this trend. These results raise also the question of a new engineering of batteries assembly more compatible with molecular active materials.   Finally, beyond the "polymer" approach, we confirm that high charged lithiated organic structures lead to quite good solid state electrochemical performances because the dissolution issue within the liquid electrolyte is better controlled.

PART B: *para*-Benzoquinone Derivatives

Beyond our investigations focused on the effect of nitrogen atom on the electrochemical reactivity of heterocycles based on the C=O functions, we have also decided to directly probe the nature of the substituent (i.e., nature of the chemical bond) on the redox active "C_6O_6"-type structure. Thus we have centered our attention on a series of tetrahydroxy-*p*-benzoquinone derivatives (THQ) since previous electrochemical investigations on $Li_4C_6O_6$ (THQLi$_4$) had shown a reversible capacity of near 200 mAh g^{-1} for an average potential of 1.8 V.[3] This previous study led us to prepare during this GCEP project two lithiated salts able to react upon oxidation at high potential vs. Li.

Conclusions

To sum up, our research effort to promote "green" organic-based electrode materials was rather centred on the redox activity of quinone-type structures, with the aim to grasp the relevant parameters that affect the redox potential of an organic electroactive material, its reactivity, its stability upon cycling, and so on. Thus, we have been revisiting selected organic structures based on carbonyl functionalities to create a reliable experimental database of model chemical structures, in relation with their solid state electrochemical behaviour in order to identify stable and efficient redox-active organic structures reacting at both high and low potentials *vs*. Li$^+$/Li^0. In the course of this study, we have assessed several molecular arrangements and demonstrated how the liquid/organic nature of the electrolyte can ruin the cyclability of a promising redox-active organic solid. To bypass this issue, several approaches have been successfully tested such as increase the molecular mass or the anionic charge of the organics. In particular, we have succeeded in preparing two lithiated compounds able to react around 3 V during the oxidation process demonstrating some opportunities offer with organics at high potential. Nevertheless, searching for redox-active organic compounds stable/insoluble towards a liquid electrolyte induces to rule out numerous chemical structures of interest. A potential alternative could be seen in designing protective interphases (coating) by grafting the particle surface of a valuable organics, for instance. On the other hand, the redox flow system (where electroactive matter is typically soluble) appears also an interesting technology for stationary applications and soluble organics displaying high redox potentials could be used as well. Another interesting finding is that our data coupled with others coming from the literature enabled us to pinpoint two general families of organic architectures possessing (*i*) a quasi-systematic reversible electrochemical activity *vs*. Li and (*ii*) some possibilities to tune the properties of the related structure (redox potential, stability towards the electrolyte,...) by specific substitutions (Figure 13).

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1,4-benzoquinone system

1,4-benzenedicarbonyl (terephthaloyl) system
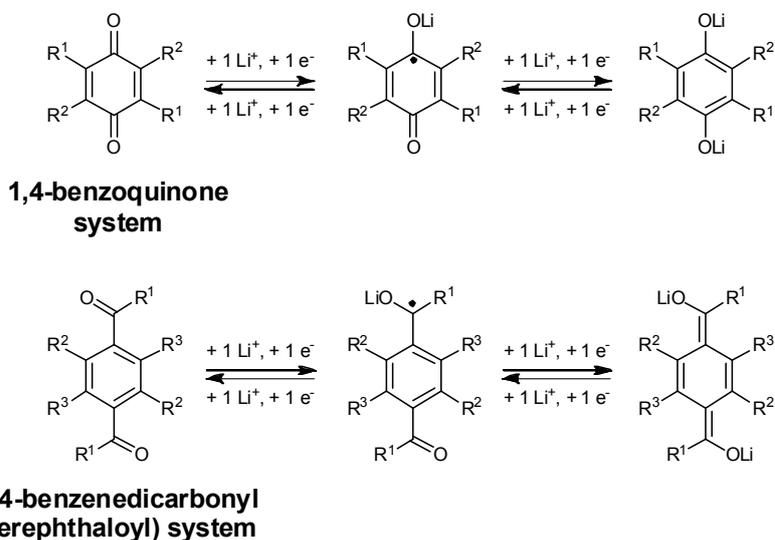
Figure 13: Identification of two key organic backbones (note that further poly-aromatic groups or conjugated system can be considered in place of the phenyl group).

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14. Four other papers in preparation: two articles dealing with the new high redox potential materials (i.e., DMQLi and DHTLi$_4$; the other two articles being focused on the DFT calculations.

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